# PEER 6 - Waste Form & Disposal Room Data Qualification Peer Review

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CAO-96-1189

Date



# CAO PLAN Carlsbad Area Office

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Title: WASTE FORM AND DISPOSAL ROOM PEER REVIEW (WF&DRPR) PLAN

(Assistant Manager, Office of Regulatory Compliance, Carlsbad Area Office)

# 1. INTRODUCTION

This Waste Form and Disposal Room Peer Review (WF&DRPR) Plan describes the peer review and documentation the Waste Isolation Pilot Plant (WIPP) Project will use to ensure that the data used in the models describing waste form and disposal room for disposal room closure and chemistry in the performance assessment (PA) are qualified for use in the demonstration of compliance.

# 1.1 BACKGROUND

In accordance with the regulatory requirements specified in 40 CFR Part 191 and implemented in accordance with the criteria specified in 40 CFR Part 194, section 194.22 (b), "Any compliance application shall include information which demonstrates that data and information collected prior to the implementation of the quality assurance program required pursuant to paragraph (a) (1) of this section (194.22) have been qualified in accordance with an alternate methodology, approved by the administrator or the administrator's authorized representative, that employs one or more of the following methods: peer review, conducted in a manner that is compatible with NUREG-1297, "Peer Review for High-Level Nuclear Waste Repositories"; corroborating data; confirmatory testing; or a quality assurance program that is equivalent in effect to ASME NQA-1-1989 edition, ASME NQA-2a-" 1990 addenda, part 2.7, to ASME NQA-3-1989 edition (excluding Section 2.1 (b) and (c) and Section 17.1)." The DOE has generally opted to employ the peer review methodology to qualify existing data that it cannot demonstrate was collected in accordance with a quality assurance program that was equivalent to the quality assurance defined above. Accordingly, a peer review will be conducted to confirm the adequacy and completeness of data utilized to define parameter values as applied in conceptual models and scenarios that have been determined to be significant to waste containment. To facilitate review of the data, the data gualification peer reviews have been divided into the following three associated waste containment subsystems:

- Natural barriers (Salado and non-Salado flow and transport);
- Engineered systems (rock mechanics and shaft/borehole seals); and



Waste form and the disposal room.

Sandia National Laboratories (SNL) is responsible for the selection and development of conceptual models that reasonably define the WIPP containment system, and for the identification and development of mathematical models, numerical models, and computer codes utilized to assess the performance of the WIPP containment for the statutory confinement period. SNL is responsible for

identifying data for which it cannot provide assurance that the information was collected under a qualified quality assurance program accordance with NUREG-1297. Therefore, to meet the regulatory requirements cited above, this peer (as defined above). These data will then be reviewed under a peer review process conducted in review on waste form and disposal room for disposal room closure and chemistry will assess the qualification of data used in PA for the WIPP.

### 1.2 PURPOSE

The purpose of this WIPP peer review plan is to define the peer review process that will be conducted to *determine if (Rev. 1)* existing unqualified waste form and the disposal room subsystems data and information *are qualified to be (Rev. 1)* used in the demonstration of compliance. As stated above, the DOE has determined the peer review process to be the most appropriate method to demonstrate that all waste form and disposal room subsystems are qualified for use in the demonstration of compliance. These peer reviews will be conducted in accordance with the requirements of NUREG-1297 that state, "A peer review is a documented, critical review performed by peers who possess qualifications at least equal to those of the individuals who conducted the original work. These individuals must be independent of the work being reviewed; independence from the work reviewed means that the peer, a) was not involved as a participant, supervisor, technical reviewer or advisor in the work being reviewed."

### 1.3 SCOPE

This WF&DRPR Plan describes the peer review process that the DOE Carlsbad Area Office (CAO) will utilize for the review of those existing data and information that form the basis for determining the parameter values of the conceptual models that form the waste form and disposal room subsystems. The peer review will be an in-depth critique of assumptions, alternate interpretations, methodology, and acceptance criteria employed, and of the conclusions drawn in the original work. This WF&DRPR Plan defines the approach, methods, criteria, schedules, deliverables, and resources required for conducting the WF&DRPR to confirm: 1) the adequacy and completeness of the data; and 2) the data and information are qualified for use in the demonstration of compliance. See Attachment A for a description of the data to be reviewed and its intended use in PA.

The conceptual models and codes to be used in the PA of the waste form and disposal room subsystem include:

Waste Form and Disposal Room - Disposal Room Closure and Chemistry

#### Model

Gas Generation Chemical Conditions Dissolved Actinide Source Term Colloidal Actinides Source Term M

Code

BRAGFLO NUTS NUTS NUTS

Existing unqualified data and information which was utilized to establish the parameter values will form the basis of this WF&DRPR.

#### 2. PEER REVIEW PLANNING AND IMPLEMENTATION

### 2.1 APPROACH

The DOE-CAO has prepared the "Office of Regulatory Compliance (ORC) Team Procedure for Peer

Review" (TP 10.5) to document the approach for conducting the peer review process. The WF&DRPR Panel will conduct the peer review activities for the qualification of data in accordance with TP 10.5, this Plan and IDI 1.0.

Similarly, SNL has prepared a procedure to provide the data and information necessary to support peer review of the qualification of data. The SNL data packages to be provided to the WF&DRPR Panel will include: 1) identification of the applicable conceptual model parameter(s); 2) assignment of a parameter value or range of values; 3) description of the source of the data used to construct the parameter value or ranges of values; 4) a description of the process whereby the data was scaled up to parameter value(s); and 5) designation of data qualification status.

### 2.1.1 DATA USED IN THE DEMONSTRATION OF COMPLIANCE

The peer review of existing unqualified SNL data and information (see Attachment A) is to confirm and document its adequacy and completeness. The data and information qualification peer review will confine itself strictly to providing this confirmatory information.

### 2.1.2 COMPOSITION OF PEER REVIEW PANEL

The WF&DRPR Panel will be composed of a minimum of two individuals who meet requirements identified in TP 10.5. The duration of the WF&DRPR Panel review process is expected to last between three to six weeks. The WF&DRPR Panel may include up to two members of the Conceptual Model Peer Review Panel. The peer review selection team will appoint the remaining panel member(s) based on his/her technical expertise which will be equivalent to that required to perform the original work. Experience areas to be represented on this panel include actinide chemistry, corrosion chemistry, and colloid chemistry.



Through a formal orientation process, each panel member will become familiar with the WIPP containment system and the basis of the engineered systems models, data, parameters and information that describe the containment system. In addition, panel members will be provided with a basic description of how the models are represented in numerical models, algorithms, and codes. The peer reviewers will be familiarized with the parameter inputs to - the PA codes and the results of prior PAs, sensitivity analyses, and critical comments from previous reviews. Each peer reviewer will be selected, oriented, and trained in accordance with approved procedures.

### 2.1.3 LOGISTICS AND MANAGEMENT

When the WF&DRPR convenes to perform the peer review process, the intent is to have all the data packages accessible for review. However, not all information necessary to support peer review of the qualification of data for the engineered systems may be available at the beginning of the review. Therefore, it may be necessary to conduct the WF&DRPR in a phased manner, depending upon the availability of information.

### 2.2 METHODOLOGY

The WF&DRPR will follow the methodology provided in NUREG-1297 as augmented by the specific requirements contained in 40 CFR Part 194.22. The purpose for conducting a peer review of data associated with this WIPP subsystem is to ensure that those data that cannot be qualified by virtue of their collection under a QA program (equivalent in effect to ASME NQA-1-1989 edition, ASME NQA-2-1990 addenda, part 2.7, ASME NQA-3-1989 edition [excluding Section 2.1 (b) and <sup>ee</sup> and Section 17.1]) are qualified for use in the demonstration of compliance. To facilitate the conduct of the peer

review, a checklist containing potential areas of review is included in this plan as Attachment B. The basis of the peer review will be to determine the adequacy and completeness of specific unqualified data used to demonstrate compliance. Adequacy criteria are provided in Section 2.3.

## 2.3 ADEQUACY CRITERIA

Adequacy of data associated with the conceptual models that nominally comprise the waste form and disposal room subsystem will be based on the peer review panel's determination that these data meet commonly accepted technical and scientific standards. Criteria utilized to make this determination include:

- Adequacy of requirements and criteria;
- Validity of assumptions;
- Alternate interpretations as appropriate;
- Uncertainty of results and consequences if wrong;
- Appropriateness and limitations of methodology and procedures;
- Adequacy of application;
- Accuracy of calculations; and
- Validity of conclusions.

In evaluating the existing data, the peer review panel shall also consider the following:

- The sources of the parameters and data, e.g., professional judgment, published source material, field tests, laboratory experiments, etc.;
- The processes used to produce the parameters from data are appropriate for the intended use; and
- The assumptions, calculations, extrapolations, interpretations, methods, and conclusions pertinent to the data are appropriate for the development of parameters used as input to the WIPP PA and are traceable.

### 2.4 SCHEDULE

The PR Manager, working closely with SNL, has developed a preliminary schedule that provides the necessary information on an "as available" basis. Flexibility is required by all supporting organizations, (i.e., DOE-CAO, SNL, the PR Manager, staff and panel members) to accommodate the peer review schedule and any changes made due to uncertainty in the timing of data availability. Attachment C contains a schedule of WF&DRPR activities and milestones in accordance with the Peer Review Management Plan. This schedule will serve as the baseline schedule from which requested schedule deviations will be evaluated and approved, if appropriate. Revisions to the baseline schedule will not require revision to this plan but will be attached to the plan by reference.

### 2.5 DELIVERABLES

A final report for the WF&DRPR will be submitted to DOE-CAO. A list of mandatory topics and suggested outline for the final WF&DRPR report is provided in Attachment D. This outline may be utilized to guide the review of each data package to ensure adequate review of the data packages.

### 3. QUALITY ASSURANCE

The WF&DRPR process will be conducted in a controlled manner and in compliance with TP 10.5.

#### 4. RECORDS MANAGEMENT

Records and documents generated as a result of peer review activities defined in this peer review plan are identified in the CAO Team Procedure, TP 10.5. WF&DRPR records will be assembled and maintained in accordance with the Peer Review Management Plan and the Informatics Desk Instruction, IDI-1.0. Upon completion of the peer review process, a complete set of WF&DRPR records will be delivered to CAO. Ultimately, peer review records will be dispositioned in accordance with DOE-CAO records management requirements.

### 5. DOCUMENT CONTROL

All plans, procedures, and other documents which require document control will be handled in accordance with applicable DOE-CAO controlled document procedures (MP 4.4).



# ATTACHMENT A

# PEER REVIEW PANEL DATA PACKAGE DESCRIPTIONS

DATA

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INTENDED USE

Actinide Solubility

Waste Form & Disposal Room Chemistry



.

# ATTACHMENT B

# SUGGESTED METHODS CHECKLIST

TUDY/EXPERIMENT IDENTIFICATION	COMMENTS
.0 Scientific Technical Items	comments.
.1 Were the technical objectives clearly stated in	
documents accompanying the data?	
2 Are all the stated objectives addressed by the data?	
3 Was there any test-to-test interference and/or was	
the impact of test-to-test interference on results	
adequately evaluated?	
4 Were the tests performed in accordance with:	
a) nationally recognized standards?	·····
b) modified recognized standards or specially	
prepared test procedures?	•
c) modified recognized standards or specially prepared test procedures?	
d) If so, are they documented in sufficient detail to be	· · · · · · · · · · · · · · · · · · ·
repeatable?	
e) Were they justified, evaluated, and approved by a	
cognizant individual/organization?	
5 Were the test procedures correctly implemented?	·····
6 Were testing irregularities and interruptions described?	· · · · · · · · · · · · · · · · · · ·
7 Was documentation of corrective actions sufficiently	
detailed?	
8 Were data reduction processes appropriate for the	
objectives of the test?	
9 Is the reduced data a true representation of all raw data	
acquired?	
10 Are the interpretations well supported by the data?	
11 Is the data quality adequate?	
a) Does the age of the data affect the results?	
b) Were the analytic methods used adequate?	
c) Were detection limits adequate?	· · · · · · · · · · · · · · · · · · ·
d) Is the range of uncertainty associated with each	
measurement adequate to satisfy the objectives of	
the test?	
e) Is the uncertainty associated with the cumulative	
data low enough to make a decision?	······································
f) Has invalid data been identified?	
g) Has valid data been characterized by providing	
qualitative or quantitative statements as to the validity and use?	
	·····
<ul> <li>h) is there a redundancy in measurements that provide checks of/on the data?</li> </ul>	
12 Were the number of data points taken enough to	
provide an adequate level of confidence in the results?	
13 Is there internal consistency between the sets of data	
for similar tests?	
14 Are the data complete?	·····
15 Can credible blocks be improved, or supported by:	
a) correlation with complementary or confirmatory	
data?	
b) additional work?	
16 Is any source of confirmatory data identified in	
database documents?	



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2.0	Summary of Conclusions	
2.1	Did the data meet adequacy of requirements and criteria?	
2.2	Did the data show validity of assumptions?	
2.3	Were there alternate interpretations of the data?	
2.4	Was there a discussion of uncertainty of results and consequences?	
2.5	Was there appropriateness and limitations of methodology and procedures?	
2.6	Was adequacy of application demonstrated for the data?	
2.7	Was the accuracy of calculations demonstrated?	
2.8	Was the validity of conclusions demonstrated?	
2.9	Were the sources of the parameters and data considered in evaluating the existing data?	
2.10	Were the processes used to produce the parameters from the data appropriate for the intended use?	
2.1	1 a) Were the assumptions, calculations, extrapolations, interpretations, methods, and conclusions pertinent to the data appropriate for the development of parameters used as input to the WIPP PA?	
	b) Were they traceable?	



# ATTACHMENT C

# WASTE FORM AND DISPOSAL ROOM PEER REVIEW SCHEDULE

	DBAET	EINAL
WF&DRPR Plan drafted	3/11	3/29
PR Panel Assigned	NA	4/29
WF&DR Data Package to PR Manager	4/22	4/29
Initiate WF&DRPR	NA	5/6
Complete WF&DRPR	NA	6/14
Submit WF&DRPR Report	6/14	6/28



# ATTACHMENT D

# PEER REVIEW REPORT OUTLINE

# **Executive Summary**

- 1. Introduction
- 2. Purpose
- 3. Description of Work Performed
- 4. Evaluation Work Performed
  - A. Adequacy of Requirements and Criteria
  - B. Validity of Assumptions
  - C. Alternate Interpretations
  - D. Uncertainty of Results and Consequences if Wrong
  - E. Appropriateness and Limitations of Methodology and Procedures
  - F. Adequacy of Application
  - G. Accuracy of Calculations
  - H. Validity of Conclusions
- 5. Conclusions
- 6. Dissenting Views
- 7. Summary
- 8. Signatures
- 9. Peer Review Members and Acceptability



# WASTE FORM AND DISPOSAL ROOM DATA QUALIFICATION

PEER REVIEW REPORT



# FINAL REPORT

# WASTE ISOLATION PILOT PLANT WASTE FORM AND DISPOSAL ROOM DATA QUALIFICATION PEER REVIEW REPORT

A PEER REVIEW CONDUCTED BY Duane Hrncir, Robert Knecht



for

U. S. Department of Energy Carlsbad Area Office Office of Regulatory Compliance

July 1996

### FOREWORD

The U.S. Environmental Protection Agency promulgated "Criteria for the Certification and Recertification of the Waste Isolation Pilot Plant's Compliance with the 40 CFR Part 191 Disposal Regulations Final Rule" in Code of Federal Regulations, Title 40, Part 194 (40 CFR Part 194) on February 9, 1996. The 40 CFR Part 194 regulation prescribes three specific peer reviews and also provides the opportunity for the Department of Energy to use peer reviews, conducted in accordance with NUREG 1297, as a means of qualifying data and information for use in the demonstration of compliance.

This report contains the results of a peer review of specific waste form and disposal room data used in the demonstration of Waste Isolation Pilot Plant (WIPP) compliance with 40 CFR Part 194. To ensure the independence of this review, the Department of Energy has directed the assignment of an independent contractor to administratively manage the peer review activities. Peer reviewers were selected based on their demonstrated independence from the work being reviewed and their technical expertise in the subject matter to be reviewed. The peer review panel, in aggregate, represents an appropriate spectrum of knowledge and experience in the subject matter reviewed.

This peer review was conducted in compliance with the quality assurance requirements as defined in 40 CFR Part 194.

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# ACRONYMS

- WIPP Waste Isolation Pilot Plant
- SNL Sandia National Laboratories
- PA performance assessment
- QA quality assurance



The Waste Form and Disposal Room Peer Review was conducted by two panel members (Panel) who examined the 26 parameters submitted to them for qualification by Sandia National Laboratories (SNL). The 26 parameters are listed in Table 1.1, together with the qualification status that resulted from this review.

In summary, the Panel was able to qualify all 26 of the parameters based on a thorough review of experimental data, literature reports, and confirmatory calculations.

ID number	Species	Brine	Status
WP037105	Am(III)	Salado	Qualified
WP037106	Am(III)	Castile	Qualified
WP037109	Pu(III)	Salado	Qualified
WP037108	Pu(III)	Castile	Qualified
WP037129	General An(III)	Salado	Qualified
WP037125	General An(III)	Castile	Qualified
WP037110	Pu(IV)	Salado	Qualified
WP037111	Pu(IV)	Castile	Qualified
WP037115	Th(IV)	Salado	Qualified
WP037112	U(IV)	Salado	Qualified
WP037130	General An(IV)	Salado	Qualified
WP037126	General An(IV)	Castile	Qualified
WP037131	General An(V)	Salado	Qualified
WP037127	General An(V)	Castile	Qualified
WP037113	U(VI)	Salado	Qualified
WP037114	U(VI)	Castile	Qualified
WP037132	General An(VI)	Salado	Qualified
WP037128	General An(VI)	Castile	Qualified

Table 1.1. Listing and Status of Reviewed Parameters

A. Inorganic Chemistry Controlled by Mg(OH)<sub>2</sub>/MgCO<sub>3</sub>

B. Organic Chemistry Controlled by Mg(OH)<sub>2</sub>/MgCO<sub>3</sub>

ID number	Species	Brine	Status
WP037116	General An(III)	Salado	Qualified
WP037121	General An(III)	Castile	Qualified
WP037117	General An(IV)	Salado	Qualified
WP037122	General An(IV)	Castile	Qualified
WP037118	General An(V)	Salado	Qualified
WP037123	General An(V)	Castile	Qualified
WP037120	General An(VI)	Salado	Qualified
WP037124	General An(VI)	Castile	Qualified

### 2.0 PURPOSE

The purpose of the Waste Form and Disposal Room Peer Review was to seek qualification of scientific data by performing a systematic review of unqualified parameters used in the models describing the waste form and disposal room subsystem in the Waste Isolation Pilot Plant (WIPP). This review is one of three recognized methods for providing assurance that scientific data collected are qualified for intended use. A peer review panel (Panel), consisting of two members, was convened to undertake the work, and the peer review was conducted in a manner compatible with NUREG-1297, Peer Review for High-Level Nuclear Waste Repositories. This report is a documented summary of the Panel's work and of the evaluation performed on selected parameters identified by Sandia National Laboratories (SNL). The report is intended primarily for use by the technical personnel at SNL/WIPP. It may also be included as supporting material in the WIPP Compliance Certification Application submitted to the Environmental Protection Agency.

The parameters evaluated consisted of information used as input to the WIPP performance assessment (PA), which in turn is to be incorporated in the demonstration of compliance. The Panel evaluated existing data and information that form the basis of the parameter values used in the mathematical expression of conceptual models for the waste form and disposal room subsystem. The parameters selected for evaluation had not previously been fully qualified for use in PA. The conceptual models used in the PA of the waste form and disposal room subsystem include components of 1) Gas Generation, 2) Chemical Conditions, 3) Dissolved Actinide Source Term, and 4) Colloidal Actinide Source Term.



### 3.0 DESCRIPTION OF WORK PERFORMED

The Waste Form and Disposal Room Peer Review Panel evaluated 26 parameters against the eight review criteria given in NUREG-1297. The parameters were solubilities of the actinides proposed to be at issue in the repository waste. The solvents were brines from the Salado and Castile formations.

The approach used by the Panel in its evaluation was to compare each calculated solubility parameter to those published in the peer-reviewed literature when such data were available. In order to make this comparison, the Panel had to consider compatibility of solvents, solution pH, and the absence of potentially ligating carbonate. The latter criterion is an imposed condition controlling the disposal room chemistry. When no literature value was available, the Panel used experimental data derived from several different laboratories. In using these data, the Panel was careful to evaluate the experimental approach, being certain that the methods used for data acquisition and interpretation were consistent with recognized standards.

No experimental data were available for some of the parameters. For these cases, the Panel examined the method of calculation used to derive the value. The experimental data used as input to the calculation were evaluated. The validity of the calculation result was critiqued relative to similar calculated values where experimental data were available.

During the course of its work, the Panel reviewed information packages provided by SNL for each parameter. In addition, technical reports, published literature, and internal documents were used to supplement the information in the parameter packages. Formal and informal discussions were held with SNL personnel in order to more fully understand the concepts and parameter derivation.



# 4.0 EVALUATION OF ACTINIDE SOLUBILITY PARAMETERS



Performance assessments for a nuclear waste repository require solubility data to determine ground water compositions. Concentrations of actinides (Th, U, Np, Pu, and Am) influence the performance of the WIPP repository. Chemical reactions that occur within the repository potentially produce or consume gases and also modify the brine chemistry. These reactions occur between influx brine, waste, backfill, and/or other materials used during the construction of the repository. Reactions modify the solution environment and affect the solubility of the gases and actinides in the brine.

Prediction of solution chemistry at various locations and under various conditions add to the understanding of actinide transport and support the calculations for WIPP performance assessment. As Brush (1990) noted

"Laboratory studies with nonradioactive simulated waste and, in some cases, radioactive simulated waste provide a unique opportunity to develop a mechanistic understanding of repository and radionuclide chemistry."

Two different solvents were considered, Salado brine and Castile brine. It is assumed that conditions in the disposal rooms will be such that the brine compositions will be in equilibrium with brucite,  $Mg(OH)_{2}$ , and magnesite,  $MgCO_{3}$ . Therefore, the calculated solubilities were derived using the condition that the brines are saturated with brucite and magnesite and that this saturation is maintained regardless of any chemistry that may affect the brines. The Castile Formation brine used in this analysis of actinide solubility is designated ERDA-HA-An-Mg; the Salado Formation brine is designated SPC-HA-An-Mg.

Investigators calculate solubility using an FMT code, based on a thermodynamic model. The code uses the Harvie-Moller-Weare (HMW) parameterization of the Pitzer activity coefficient model to calculate aqueous solution concentrations (solubility). Based on code calculations, these parameters (shown in Table 4.1) feed performance assessment models NUTS and GRIDFLOW.

# 4.1. Adequacy of Requirements and Criteria

The dissolved concentrations of the actinides in each of the brines given above were determined using equilibrium calculations constrained to fit the conditions anticipated in the disposal rooms. The calculations were targeted to fit an accuracy within one order of magnitude for the solubility predictions.

Material	Parameter	Median	High	Low
SOLMOD3	SOLSOM	4.5E-06	4.5E-07	4.5E-05
	SOLCOM	2.9E-06	2.9E-07	2.9E-05
	SOLSIM	3.8E-06	3.8E-07	3.8E-05
	SOLCIM	3.6E-07	3.6E-08	3.6E-06
SOLSIM	SOLAM3	3.8E-06	3.8E-07	3.8E-05
	SOLPU3	3.8E-06	3.8E-07	3.8E-05
SOLCIM	SOLAM3	3.6E-07	3.6E-08	3.6E-06
	SOLPU3	3.6E-07	3.6E-08	3.6E-06
SOLMOD4	SOLSOM	4.4E-06	4.4E-07	4.4E-05
	SOLCOM	5.7E-07	5.7E-08	5.7E-06
	SOLSIM	4.4E-06	4.4E-07	4.4E-05
	SOLCIM	6.0E-09	6.0E-10	6.0E-08
SOLSIM	SOLTH4	4.4E-06	4.4E-07	4.4E-05
	SOLU4	4.4E-06	4.4E-07	4.4E-05
	SOLPU4	4.4E-06	4.4E-07	4.4E-05
SOLCIM	SOLPU4	6.0E-09	6.0E-10	6.0E-08
SOLMOD5	SOLSOM	7.7E-06	7.7E-07	7.7E-05
	SOLCOM	7.4E-05	7.4E-06	7.4E-04
	SOLSIM	2.3E-06	2.3E-07	2.3E-05
	SOLCIM	2.2E-06	2.2E-07	2.2E-05
SOLMOD6	SOLSOM	1.0E-05	1.0E-06	1.0E-04
1	SOLCOM	7.0E-05	7.0E-06	7.0E-04
	SOLSIM	8.7E-06	8.7E-07	8.7E-05
	SOLCIM	8.8E-06	8.8E-07	8.8E-05
SOLSIM	SOLU6	8.7E-06	8.7E-07	8.7E-05
SOLCIM	SOLU6	8.8E-06	8.8E-07	8.8E-05

Table 4.1. Solubility Parameters for Disposal Room Dissolved Species Studies

The results of the calculations are given as a range that spans two orders of magnitude about the median. This approach is sound, and the solubilities that result from the equilibrium calculations are values that can be compared with those empirically determined and published in the literature.

No inorganic model exists for the calculation of An(VI) solubilities in the WIPP disposal room environment. The dissolved concentration of the +VI actinides in the brines are estimates based on an analysis of empirical solubility experiments in brines similar to those anticipated in the disposal rooms. The confidence in the estimate becomes a function of the quality of the experimental data. Migration of actinides to the accessible environments depends on their oxidation state and concentration in the brines. Hydrolysis affects the solubility, precipitation, and complexation of actinides in the brine solutions. Dissolved species concentrations also depend on solid phases to control solubility. The goal of the dissolved species study is to calculate valence-specific solubility for actinides, which are used directly in WIPP repository brine models for performance assessment. Based on the decision to backfill the disposal room, the scope of the work is reduced to focus on the chemically invariant point defined by the backfill (MgO) material.

Dissolved species parameters characterize solubility for oxidation states III, IV, V, and VI in Castile and Salado brines, with and without organic ligands. To achieve this goal, several specific tasks were implemented to investigate specific systems as analogs for the four oxidation states. Specific objectives related to these tasks were:

- □ To examine the solubility of Am(III) and Pu(III) in simulated brines under low carbonate conditions.
- **To examine the solubility of U(VI) in simulated brines under low carbonate conditions.**
- $\square$  To examine the solubility of Th(IV) and U(IV) in carbonate solutions.
- $\Box$  To examine the solubility of Np(V) in K<sub>2</sub>CO<sub>3</sub> media.
- □ To document the complexation of ligands with actinides in NaCl media.
- □ To review model parameters that represent solubility data.



### 4.2. Validity of Assumptions

The controlling assumption in the calculations is that the chemistry of the disposal room will be dominated by the saturation of the brines by brucite and magnesite. This condition will effectively keep the pH of the brine solutions basic. Thus, the pH calculated for the Castile and Salado brines is 9.24 and 8.69, respectively. An additional consequence of brucite and magnesite saturation is that any carbonate generated as a result of microbially produced carbon dioxide will be consumed. The calculations ignored the possibility of the formation of actinide carbonato complexes. Were these complexes to form, the effective solubility for some of the actinides in the disposal room brines would be larger than those under consideration. This is reflected in a calculation where the constraint of equilibrium with the magnesium minerals is removed. The calculated An(III) solubility increases by two orders of magnitude.

Weiner (1996) defined organic ligand concentrations based on proposed inventory of waste materials and the brine volume of the repository area. Bynum, in a meeting with the reviewers, clarified that the brine volume equals 75% of the remaining void volume of the repository area.

The actinides anticipated to be present in the disposal rooms in the +III oxidation state are Am and Pu. The median solubility of Am(III) under brucite/magnesite saturation is 3.8E-06 in Salado brine and 3.6E-06 in Castile brine (WP037105 and WP037106, respectively). The median solubility of Pu(III) under brucite/magnesite saturation is 3.8E-06 in Salado brine and 3.6E-06 in Castile brine (WP037109 and WP037108, respectively). Since the only +III actinides anticipated to be present in the disposal room are Am and Pu, an analysis of the calculated values for these elements will also be applicable to the general +III oxidation state model (WP037129 and WP037125).

Uranium and plutonium are the radionuclides present in the waste that have a potentially significant +VI chemistry. However, it is assumed that because of the reducing atmosphere anticipated in the disposal rooms, Pu(VI) will be reduced to lower oxidation states. Therefore, U(VI) is the only species at issue.

Solubilities for the IV and V oxidation states were calculated from thermodynamic codes refined and qualified for the WIPP Project. These codes assume that equilibrium thermodynamics applies and that the data represent equilibrium conditions. Thermodynamic parameters were obtained from literature sources and experimental studies.

A majority of the supporting documentation presents experimental data which varies as a function of time. Authors discuss test periods which extend for days, weeks, and even months to approach equilibrium conditions. According to Brush (1990), concentrations of actinides are assumed to reach equilibrium values instantaneously. Rates of dissolution depend on the chemical and physical nature of the solid phase. Since the waste form is heterogeneous and difficult to characterize and the concentrations of actinides are dilute, a study of the dissolution kinetics becomes extremely complex and difficult. A more appropriate statement of the assumption may be that the kinetics are not significant in terms of the brine concentration with respect to the transport mechanisms and contact times. Transport mechanisms in the vicinity of the disposal areas are slow, on the order of meters per days. Contact time between the brine and solids is long. Rates of dissolution are, therefore, assumed not significant since the brine has sufficient time to approach equilibrium, and equilibrium thermodynamics applies.

Actinides [Am(III), Th(IV), and Np(V)] serve as prototypes to validate thermodynamic models for actinides in the III, IV, and V oxidation states. Studies of Pu(IV) solubility pose a problem since this

oxidation state tends to form colloids. Although Th(IV) is more soluble than Pu(IV), the data introduce less uncertainty. Thorium, therefore, is used an analog for Pu(IV) and U(IV). Neptunium provides a good analog for Pu(V).

# 4.3. Alternate Interpretations

Code calculations set the precedence for determination of solubility parameters. Experimental studies provide data to define input variables to the code. An alternate approach focuses on empirical studies in which various actinides are added to raw or simulated brines. Simulated brine solutions, exposed to actinide solids, would ultimately reach a steady state concentration of actinides representative of the disposal room environment. A disadvantage of this approach, recognized by Brush (1990), is the complexity of the system, which diminishes the ability to obtain input variables to the code. The extent of the test program may become so complicated that it could not be implemented in a timely or cost effective manner. Empirical tests, however, should be implemented to verify that the results of the code (solubility in the simulated brines) adequately represent experimental results.

The nature of the value, a solubility parameter derived from available empirical data, does not lend itself to alternate interpretations. The important question to ask is what is the level of confidence associated with the value. This directly relates to the quality of the experimental data available and is addressed in Section 4.5.

### 4.4. Uncertainties and Consequences

There are no stated uncertainties associated with the solubility parameter. Instead, what is quoted is a range of solubilities for a given actinide under a given set of brine chemistry. The range spans two orders of magnitude and is adequate to describe the concentrations likely to be found in the disposal room. The solubility limits identify "source terms" for potential releases of actinides to the accessible environment. A conservative approach is presented, specifically with respect to the ranges (uncertainty), primarily because of the lack of experimental data for the effects of ligands on the solubility limits. Although the ranges bound the median, parameters consistently overestimate experimental values.

# 4.5. Appropriateness and Limitations of Methodology and Procedures

It is assumed that the repository environment will readily reduce metals as a result of excessive amounts of elemental iron and soluble iron (II). Table 4.2 lists the expected actinides and their proposed oxidation states in the disposal room.

Oxidation	ш	IV	V	VI
	Am	Th	Np	U
	Pu	Pu		
		U		

# Table 4.2. Oxidation States and Representative Actinides for Disposal Room Dissolved Species Studies

Experimental studies, published in the literature, document in detail procedures used to perform solubility tests. Three studies, Nitsche et al. (1994), Erten et al. (1994) and Rai (1995), illustrate a conventional and detailed procedure for solubility tests. The procedure consists of five basic activities:

- 1. Prepare the solutions.
- 2. Set up the experimental apparatus.
- 3. Conduct the experiment.
- 4. Analyze the materials (liquids and solids).
- 5. Analyze the results.



The Analysis Plan (Novak 1996) describes a four-step procedure "to render thermodynamic data into a consistent model and parameter framework that can be used to calculate actinide solubilities." Implementation of this procedure may require knowledge or experience with the software required to process the data.

Thermodynamic parameters are used to produce values of total actinide dissolved concentrations as a function of brine composition and chemical properties. These variables are incorporated into the CHEMDAT database file. Dissolved species parameters, characterized in terms of major actinides listed in table II, are input variables to the WIPP Compliance Certification Application. Accuracy of these parameters is specified at one order of magnitude, although code results compare more favorably with experimental data in brines without organic ligands. Experimental studies in brines that contain organic ligands have not been completed.

The solubility parameters for the actinides are calculated using calculated brine compositions. It would have been better to have measured actual brine composition under the conditions employed for the calculation (e.g., a Salado brine in equilibrium with halite, anhydrite, brucite and magnesite) in order to have a more realistic picture of the actual solvent characteristics. However, it is felt that the overriding consideration in solubility is not so much exact elemental composition as it is total ionic strength. The differences are not significant to the outcome of the calculation. In fact, the approach used to gage the relevance of the calculated solubility parameter is to compare it with literature values, when available, or with other defendable experimentally determined values. These values were obtained in simulated brines. The compositions of the five brines used in the analysis are given in molarity in Table 4.3.

ERDA6-HA-An-Mg		ERDA6-HA-An-Mg Spc-HA-An-Mg Yamazaki et		Yamazaki et al. (1992)	Khalili et al. (1993)	Nitsche (1994)
н	97.6	96.8	111	111	111	
0	49.7	48.8	55.6	55.7	55.7	
Na	5.45	4.09	1.82	1.82	2.40	
K	.096	.92	.767	.768	.031	
Mg	.039	.444	1.44	1.44	.074	
Ca	.012	.029	.015	.015	.029	
Cl	5.25	5.82	5.39	5.39	2.48	
S	.168	.52	.044	.044	.075	
В	.062	.024	.02	.02	.004	
Br	.011	.012	.005	.005	.001	

Table 4.3. Brine Comparison

It is clear that there are no significant differences in these compositions that would be an issue in determining the appropriateness of the calculated solubility parameter, especially in light of the two order of magnitude range that is used.

The use of Nd(III) as a surrogate for +(III) actinides is a well-established and accepted protocol. Khalili et al. (1993) have reported on the solubility of Nd in a brine of relevance to the WIPP project. At pH = 8.4, they found the Nd(III) solubility to be 2.3(+0.1)E-06. This value compares very favorably to the median calculated value of 3.8E-06 for Am(III) in the SPC-HA-An-Mg brine at pH = 8.7. In ERDA6-HA-An-Mg the calculated Am(III) solubility at pH = 9.2 is 3.6E-07. Khalili, et al. (1993) do not have a measurement at this pH. However, at pH = 10.4 the [Nd(III)] is below the detection limit of 3E-08. The Am(III) calculated value is intermediate between the measured value at pH = 8.4 and that at pH = 10.4. The value for the Am(III) solubility in Castile Formation brine is very acceptable based upon this analysis.

Americium(III) is used as an analog for Pu(III) (Brush, 1990). The analysis detailed above can be used to justify the calculated values for Pu(III), 3.8E-06 in SPC-HA-An-Mg and 3.6E-07 in ERDA6-HA-An-Mg. There is one report dealing with the measured solubility of Pu(III) in a synthetic brine at pH = 7.1 (Nitsche et al., 1994). They report a value of 1.63(+.52)E-07. The solubility of actinides generally decreases as the pH is raised. Therefore, the calculated values are at the high end of what would be anticipated based on the Nitsche data. They are not so high as to be unreasonable, however. The Nd

data, which were acquired at pH conditions more closely resembling those anticipated on the disposal room, should be weighed more heavily.

The final two calculated solubility values for the +III oxidation state are those in which a nonspecified +III species is dissolved in ERDA6-HA-An-Mg and SPC-HA-An-Mg (3.6E-07 and 3.8E-06, respectively). Since the only two +III radionuclides at issue are Am and Pu, the analysis above also applies to these general cases. The only other +III species possible in the disposal room is Fe(III). However, at pH values greater than 8, all of the iron will be precipitated as the very insoluble hydroxide and should not be a consideration.

Because no model exists from which to calculate a solubility parameter for U(VI) in Salado and Castile brines controlled by magnesium mineralogy, the values used in the PA were developed from a compilation of literature data. This approach is fine as long as the literature data are determined in conditions similar to what is anticipated in the disposal rooms.

Pashalidis et al. (1993) determined U(VI) solubilities under conditions of high (100%) and low (0.03%) carbon dioxide. Their values ranged from 1E-03 to 1E-06, at a pH of 4 to 5 for the low carbon dioxide environment. Their data were collected in solutions of low ionic strength, 0.1m. This value is vastly different from that of the disposal room brines. The Salado brine has a calculated ionic strength of 6.29m and the Castile brine, 4.99m. Ionic strength is an important parameter controlling actinide solubility, and the difference between the Pashalidis conditions and those of the disposal rooms requires that these values not be considered in the development of the U(VI) solubilities. Choppin calculated a U(VI) solubility of 1E-06, based on an ionic strength of zero (Hobart et al., 1996). He assigns a high uncertainty to this value.

Yamazaki et al. (1992) measured the solubility of U(VI) in the synthetic brine given above. The ionic strength of this brine is 3.8m. At pH = 10.4 under low carbonate conditions, they report a U(VI) solubility of 2E-07. Uranium solubility in 5.2m NaCl solution was determined by workers at Lawrence Livermore National Laboratory. At pH = 9.75 they report a solubility of 2.75E-06. This value was obtained after 119 days (Palmer 1996). There is no indication from the available data that the reaction was at steady state. A group at Argonne has studied the solubility of U(VI) in Castile brine in the absence of carbonate at pH = 10 (Reed et al., 1996). They have determined a value of 7.94(+1.2)E-07 for the U(VI) solubility after 149 days. The values of U(VI) solubility being submitted to the PA are 8.7E-06 in Salado brine (WP037113) and 8.8E-06 in Castile brine (WP037114). Based on the values determined at Lawrence Livermore, and especially the data from the Argonne group, the numbers being submitted to the PA are valid. It follows that the values for the general +VI model of 8.7E-06 and 8.8E-06 (WP037132 and WP037128, respectively) are valid as well.

Thorium(IV) is chosen as the analog for the (IV) oxidation state actinides. As reported in The Chemical Thermodynamics of Actinide Elements and Compounds (1976), tetravalent thorium is the only stable ionic species in solution and at higher pH, dimer and polymer hydrolyzed species become increasingly important. Calculated concentrations of thorium in saturated brine solutions are several orders of magnitude more concentrated, as illustrated in Figure 1. Calculated thorium concentrations in synthetic brine solutions contacted with magnesium and calcium solids, however, correlate well with experimental data. Solubility parameters for the (IV) oxidation state correspond to values for the brine contacted with magnesium. Overall, (IV) oxidation state solubility parameters for neutralized brines (contacted with magnesium and calcium) compare with experimental data better than the uncertainty (order of magnitude), and represent a conservative value for performance assessment.





Thorium solubility exceeds uranium solubility by several orders of magnitude, and the predominate species is the  $Th(CO_3)_5^{-6}$ , consistent with the calculated data. Hydrolyzed species may play a greater role in the solubility under these conditions.

Neptunium(V) is chosen as the analog for the (V) oxidation state actinides. As described in The Chemical Thermodynamics of Actinide Elements and Compounds (1976), pentavalent neptunium occurs from the dissolution of and hydrolysis of crystals in acid solution. The (V) oxidation state, which exists as NpO<sub>2</sub><sup>+</sup>, forms stable carbanato complexes, reported by Ueno and Saito (1975). Concentrations vary between E-04 and E-06 for carbonate systems and decrease as the strength of the chloride solution increases. Calculated neptunium concentration in synthetic brine solutions, including solutions contacted with magnesium and calcium solids, correlate well with a representative suite of experimental data from Novak (1995), Ueno and Saito (1975), and Neck et al. (1994), illustrated in Figure 2. These data illustrate similarity of neptunium solubility for sodium systems. Novak (1995) reports data which include samples run in triplicate to demonstrate consistency and to estimate experimental error. These data indicate an experimental error of approximately 3%, reasonable for solubility studies. Calculated concentrations decrease with the addition of magnesium and calcium. Solubility parameters for the (V) oxidation state correspond to values for the brine contacted with magnesium. Overall, (V) oxidation state solubility parameters compare with experimental data better than the uncertainty (order of magnitude) and represent a conservative value for performance assessment.





A portion of the waste composition contains various organic ligands which influence the solubility of actinides. Since no experimental data are provided with respect to the effects of organic ligands on the

actinide solubility in brines, this review focuses on similarity between these procedures with those for actinide solubility in brines without ligands. Chemical potentials and interaction coefficients are determined from both extraction and solubility, illustrated by Novak and Roberts (1994). These experiments produce data that are added to the data base used to calculate solubility. A similar procedure is used to obtain thermodynamic data for interactions between actinides and organic ligands. These data are obtained from extraction studies. Procedures and data are reported in various monthly project documents produced by Choppin (Choppin 1994 through 1996). His students determine chemical potentials and interaction coefficients, which are used to calculate actinide solubilities in the presence of organic ligands. Since the procedures are equivalent with and without organic ligands, calculated solubilities will be any less accurate than solubility in brines without organic ligands. Experimental studies should be conducted in brines containing organic ligands in order to validate calculated solubilities under these conditions. Currently, studies are in progress to determine the effects of organic ligands on the solubility of actinides in brine solutions. Data from these experiments were not available for this review.

Calculated solubility falls within the ranges set for the solubility parameters for actinides in brine solutions without organic ligands. Similar conditions are expected for solubility in brines with organic ligands, although experimental data are not available to verify this expectation. Ranges are set on the basis that studies with organic ligands have not been completed. Methodologies used to determine input variables to thermodynamic codes calculate solubility parameters that slightly overestimate experimental parameters in simulated brine solutions without organic ligands. Researchers currently use similar methodologies to produce input variables for systems with organic ligands. These data should also simulate experimental parameters.

### 4.6. Adequacy of Application

Documentation of solubility studies, conducted under the QA program, track implementation of experimental tests and qualification of the codes used to process data and calculate solubility of actinides in brines.

Researchers conduct experimental studies for individual species in simulated solutions in order to determine input parameters to thermodynamic codes. These codes calculate solubility parameters for both single-species systems and multicomponent systems, such as the Salado and Castile brine systems. Overall results of calculations for the multicomponent systems correlate with experimental data,

supporting observations that interactions potentially play a lesser role under these dilute conditions. Data presented in Figure 2 illustrate a consistency of data for neptunium based on experimental studies reported by various authors. An order of magnitude range demonstrates a conservative approach based on the lack of data to verify the effects of organic ligands. This approach coincides with a methodology of updating current input values in order to improve (refine) these values, noted by Novak (1995).

Calculated values for solubility parameters continue to improve as additional information and data become available to improve values for chemical potential and interaction coefficients. Calculated values for both Salado and Castile brines in contact with magnesium minerals coincide with solubility parameters tabulated in Table 4.4 for An(IV) and An(V) species. Only a portion of available information has been included in this report to illustrate consistency and adequacy of the data. Additional experimental data enhance the accuracy of the data, as well as the confidence that the data represent brine conditions.

The calculated values for the solubility of +III radionuclides of interest to the WIPP disposal room agree very well with the experimental data available. The approach of using equilibrium calculations to determine these values seems quite justified.

The numbers being submitted to the PA for the U(VI) solubility are consistent with the values determined by experiments.

# 4.7. Accuracy of Calculations

There are no uncertainty limits given for the calculated solubilities. This is rather unusual; however, their omission does not seriously compromise the value of the results, given that the acceptable range spans two orders of magnitude.

The An(VI) values being submitted to the PA are not calculated but, rather, are estimates based on the available empirical data. There is a paucity of U(VI) solubility data in high ionic strength solutions. Only three pieces of data were available to judge the confidence of the PA values, Yamazaki et al. (1992), the Lawrence Livermore experiments, and the Argonne work. More data upon which to evaluate the numbers would have been preferred, but it does not appear to exist.

Input to thermodynamic codes is determined from regression of experimental data. The codes estimate the solubility parameters. Verification of the accuracy of these calculations is beyond the scope of this

peer review, as well as being limited by access to the codes. Accuracy, however, is indirectly illustrated in the comparison presented in Figures 1 and 2.

Material	Parameter	Median	SPC	ERDA6
SOLMOD3	SOLSOM	4.5E-06		
	SOLCOM	2.9E-06		
	SOLSIM	3.8E-06		
	SOLCIM	3.6E-07		
SOLSIM	SOLAM3	3.8E-06		
	SOLPUS	3.8E-06		
SOLCIM	SOLAM3	3.6E-07		
	SOLPU3	3.6E-07		
SOLMOD4	SOLSOM	4.4E-06	5.03E-06	
	SOLCOM	5.7E-07		6.50E-06
	SOLSIM	4.4E-06	4.98E-6	
	SOLCIM	6.0E-09		6.78E-09
SOLSIM	SOLPU4	4.4E-06	4.98E-6	
	SOLU4	4.4E-06	4.98E-6	
	SOLTH4	4.4E-06	4.98E-6	
SOLCIM	SOLPU4	6.0E-09		6.78E-09
SOLMOD5	SOLSOM	7.7E-06	8.75E-06	
	SOLCOM	7.4E-05		8.40E-05
	SOLSIM	2.3E-06	2.64E-06	
	SOLCIM	2.2E-06		2.53E-06
SOLMOD6	SOLSOM	1.0E-05		
	SOLCOM	7.0E-05		
	SOLSIM	8.7E-06		
	SOLCIM	8.8E-06		
SOLSIM	SOLU6	8.7E-06		
SOLCIM	SOLU6	8.8E-06		

Table 4.4. Comparison of Solubility Parameters and Brine Calculations



### 4.8. Validity of Conclusions

Experimental data consistently fall below values defined for the solubility parameters. Several examples (both records and literature) illustrate the importance of interaction coefficients to adequately represent the solubility data. This program produced thermodynamic data to enhance calculated values and frequently demonstrated that the procedure produced data which confidently simulated experimental

conditions. These observations strengthened expectations that data to be obtained for the effects of organic ligands will also verify calculated values.

It is the opinion of the Panel that the values represented by the following reference numbers are valid and justifiable based on comparison with available experimental data and literature reports.

WP037110	WP037131	WP037130	WP037126	WP037127	WP037115
WP037111	WP037112	WP037105	WP037106	WP037108	WP037109
WP037113	WP037114	WP037125	WP037128	WP037132	WP037129

The following reference numbers are for solubility values in the presence of organic ligands. There are not sufficient experimental data available to justify these values based on comparison of published numbers. However, these calculated values were derived using the same procedures as those above. Since these calculations produced valid numbers for solubility ranges in the absence of organic ligands, we have no reason to doubt that the calculated solubilities in the presence of organics are outside the range of those found under disposal room conditions. The stability constants being input to the calculation are being determined by Choppin, a researcher known for producing quality experimental results. The Panel's opinion is that the solubility parameters represented by the following reference numbers are valid for use in the PA.

WP037122	WP037116	WP037120	WP037121	WP037124	WP03118
WP037117	WP037123				

### 4.9. Dissenting Views

None.

## 5.0 CONCLUSIONS

The Panel carefully reviewed each of the 26 parameters submitted for peer review. The details of the review and the individual conclusions for each parameter are presented in Section 4. In summary, the Panel agrees with the 26 values (listed below) being submitted to the WIPP PA for actinide solubility under repository conditions.

- Inorganic Chemistry
  - Am(III) in Salado and Castile brines
  - Pu(III) in Salado and Castile brines
  - General An(III) in Salado and Castile brines
  - Th(IV) in Salado brine
  - U(IV) in Salado brine
  - Pu(IV) in Salado and Castile brines
  - General An(IV) in Salado and Castile brines
  - General An(V) in Salado and Castile brines
  - U(VI) in Salado and Castile brines
  - General An(VI) in Salado and Castile brines
- Organic Chemistry
  - General An(III) in Salado and Castile brines
  - General An(IV) in Salado and Castile brines
  - General An(V) in Salado and Castile brines
  - General An(VI) in Salado and Castile brines

Determination of actinide solubilities in high ionic strength media is an experimentally difficult procedure. The Panel found the quality of the experimental data to be quite good and would like to commend the responsible scientists for a job well done.

# 6.0 SIGNATURES

I, by signature, acknowledge that I concur with the findings and conclusions within my area of assignment and expertise of this Waste Form and Disposal Room Peer Review Report.

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Duane Hrncir, Ph.D. WF&DR Panel Chairman

Robert Knecht, Ph.D. WF&DR Panel Member



Inorganic Chemistry

**Chemical Engineering** 

### 7.0 PEER REVIEW MEMBERS AND ACCEPTABILITY

Duane C. Hrncir, Panel Chairman, is an Associate Professor of Chemistry and former Head of the Chemistry Programs at the University of Texas at Dallas. He holds a Ph.D. in inorganic chemistry from Texas A&M University, an M.S. in inorganic chemistry from the University of Massachusetts at Amherst, and a B.S. in Chemistry from the University of Alabama. He has 24 years of experience in research involving the interactions of metals with organic molecules. This research includes the interactions of metals and organics with mineral surfaces and the controls these interactions have on speciation and transport in aquatic environments. His current area of research involves laboratory and field experiments to study the photoreduction of metal colloids in acidic and neutral surface waters and the control this process exerts over the biogeochemistry of the stream system. He is the author of 40 publications in peer-reviewed scientific journals and made numerous presentations at national and international scientific meetings.

Robert D. Knecht, Panel Member, is a Research Professor at the Colorado School of Mines. Dr. Knecht holds a Ph.D. and an M.S. in Chemical-Petroleum Refining Engineering from the Colorado School of Mines, as well as a Ph.D. in Metallurgical Engineering. His research interests include conventional recovery and separation technologies to treat environmental and municipal wastes. He has served as a consultant, providing technical and management assistance to the energy, minerals, and wastes industries. He has supervised a project management support team to assist the U.S. Geological Survey with management requirements for the Yucca Mountain Project. Additional consulting work includes the extraction of uranium from acidic solutions, the recovery of synthetic fuels from various feed stocks, and the design of a research program to simulate the leaching of heavy metals from spent catalyst feed stocks.



# 8.0 REFERENCES

## 8.1. Cited References

- Brush, L.H., 1990. Test Plan for Laboratory and Modeling Studies of Repository and Radionuclide Chemistry for the Waste Isolation Pilot Plant. SAND90-0266. Albuquerque, New Mexico: Sandia National Laboratory.
- Choppin, G. R. Monthly Progress Report for April 1996 to Dr. Robert Moore, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 1 May 1996.
- Choppin, G. R. Monthly Progress Report for March 1996 to Dr. Robert Moore, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 1 April 1996.
- Choppin, G. R. Monthly Progress Report for February 1996 to Dr. Robert Moore, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 1 March 1996.
- Choppin, G. R. Monthly Progress Report for January 1996 to Dr. Robert Moore, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 30 January 1996.
- Choppin, G. R. Monthly Progress Report for December 1995 to Dr. Robert Moore, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 30 December 1995.
- Choppin, G. R. Monthly Progress Report for November 1995 to Dr. Robert Moore, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 30 November 1995.
- Choppin, G. R. Monthly Progress Report for October 1995 to Dr. Robert Moore, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 31 October 1995.
- Choppin, G. R. Monthly Progress Report for September 1995 to Dr. Robert Moore, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 1 October 1995.
- Choppin, G. R. Monthly Progress Report for August 1995 to Dr. Robert Moore, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 25 August 1995



- Choppin, G. R. Monthly Progress Report for July 1995 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 4 August 1995.
- Choppin, G. R. Monthly Progress Report for June 1995 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 28 June 1995.
- Choppin, G. R. Monthly Progress Report for April 1995 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 28 April 1995.
- Choppin, G. R. Monthly Progress Report for March 1995 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 31 March 1995.
- Choppin, G. R. Monthly Progress Report for February 1995 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.4.1.1.5.1.2, Contract #AH-5590. 27 February 1995.

- Choppin, G. R. Monthly Progress Report for January 1995 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 31 January 1995.
- Choppin, G. R. Monthly Progress Report for December 1994 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 29 December 1994.
- Choppin, G. R. Monthly Progress Report for October 1994 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 31 October 1994.
- Choppin, G. R. Monthly Progress Report for September 1994 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 30 September 1994.
- Choppin, G. R. Monthly Progress Report for August 1994 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 31 August 1994.
- Choppin, G. R. Monthly Progress Report for July 1994 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 27 July 1994.
- Choppin, G. R. Monthly Progress Report for May 1994 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 31 May 1994.



- Choppin, G. R. Monthly Progress Report for April 1994 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 28 April 1994.
- Choppin, G. R. Monthly Progress Report for March 1994 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. March 1994.
- Choppin, G. R. Monthly Progress Report for February 1994 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. February 1994.
- Choppin, G. R. Monthly Progress Report for January 1994 to Dr. Craig F. Novak, Sandia National Laboratories, SWCF/RNC, SWF 1.1.1.1.4.1.1.5.1.2, Contract #AH-5590. 28 January 1994.
- Erten, H.N., A.K. Mohammed, and G.R. Choppin, 1994. "Variation of Stability Constants of Thorium and Uranium Oxalate Complexes with Ionic Strength." Radiochimica Acta, Vol 66/67: 123-128.
- Hobart, D.E., C.J. Bruton, F.J. Millero, I-M. Chou, K.M. Trauth, and D.R. Anderson, 1996. "Estimates of the Solubilities of Waste Element Radionuclides in Waste Isolation Pilot Plant Brines: A Report by the Expert Panel on the Source Term," SAND96-0098.
- Hobart, D.E. and R. Moore, 1996. "Analysis of (UVI) Solubility Data for WIPP Performance Assessment," Memorandum, March 28, 1996.
- Khalili, F.I., V. Symeopoulos, J-F. Chen, and G.R. Choppin, 1993. "Solubility of Nd in Brine," Radiochimica Acta, 66, pp. 51-54.
- Neck, V., J.I. Kim, and B. Kanellakopulos, 1994. "Thermodynamisches Verhalten von Neptunium (V) in Konzentrierten NaCl und NaClO4 Losungen," KfK5301, Institut fur Nukleare Entsorgungstechnik, Institut fur HeiBe Chemie, Kernforschungezentrum Karlsruhe.

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- Nitsche, H., K. Roberts, R. Xi, Y. Prussin, K. Becraft, I. Al Mahamid, H.B. Silber, S.A. Carpenter, R.C. Gatti, and C.F. Novak, 1994. "Long Term Plutonium Solubility and Speciation Studies in a Synthetic Brine." Radiochimica Acta, Vol 66/67: 3-8 (also SAND93-3846C).
- Novak, C.F., 1996. Analysis Plan: The Interpretation of Chemical Data to Obtain Thermodynamic Parameters, WIPP document, Sandia National Laboratories, Albuquerque, NM.
- Novak, C.F., 1995. "Revised Analysis of LBNL Data of the Solubility of Np(V) in K2CO3 Media," memorandum to I. Al Mahamid, 17 October 1995.
- Novak, C.F. and K.E. Roberts, 1994. Thermodynamic Modeling of Neptunium (V) Solubility in Na-CO3-HCO3-Cl-ClO4-H-OH-H2O Electrolytes. SAND94-0805C. Albuquerque, New Mexico: Sandia National Laboratories. Presented at the 1994 Scientific Basis for Nuclear Waste Management Symposium, 21-26 October 1994, Kyoto, Japan..
- Palmer, C.E.A, 1996. "Private Communication to Vann Bynum."
- Pashalidis, I., W. Runde, and J.I. Kim, 1993. AA Study of Solid-Liquid Phase Equilibria of Pu(VI) and U(VI) in Aqueous Carbonate Systems.," Radiochimica Acta, 66, p. 141.
- Rai, D., A.R. Felmy, D.A. Moore, and M.J. Mason, 1995. "The Solubility of Th(IV) and U(IV) Hydrous Oxides in Concentrated NaHCO3 and Na2CO3 Solutions." Mat. Res. Soc. Symp. Proc., Vol 353: pp. 1143-1150.
- Reed, D.T., D.G. Wygmans, and M.K. Richmann, 1996. "Stability of Pu(VI), Np(VI), and U(VI) in Simulated WIPP Brine," Argonne National Laboratory Interim Report.
- The Chemical Thermodynamics of Actinide Elements and Compounds, International Atomic Energy Agency, Vienna, Austria, 1976.
- Ueno, K. and A. Saito, 1975. "Solubility and Absorption Spectra of a Carbonato Complex of Pentavalent Neptunium," Radiochemical and Radioanalytical Letters, Vol 22, no 2, 127-133.
- Wang, Y., 1996. "Define Chemical Conditions for FMT Actinide Solubility Calculations." memorandum to M.D. Siegel, 18 March 1996.
- Weiner, R.F. 1996. "Dissolved Ligand Concentration." Memorandum to C.F. Novak. 27 March 1996.
- Yamazaki, H., B. Lagerman, V. Symeopoulos, and G.R. Choppin, 1992. "Solubility of Uranyl in Brine," High Level Radioactive Waste Management Proceedings of the Third International Conference, Las Vegas, NV, April 12-16, 1992.

### 8.2. Additional References

Geochimica et Cosmochimica Acta, Vol. 48 (1984), No. 4.

Geochimica et Cosmochimica Acta, Vol. 50 (1986), No. 12.

Geochimica et Cosmochimica Acta, Vol. 51 (1987), No. 5.



High Level Radioactive Waste Management, Proceedings of the Third International Conference.

Journal of Alloys and Compounds, Vol. 202 (1993).

Journal of Chemical and Engineering Data, Vol. 33 (1988), No. 3.

The Journal of Chemical Thermodynamics, Vol. 3 (1971).

The Journal of Physical Chemistry, Vol. 77 (1973), No. 19.

The Journal of Physical Chemistry, Vol. 96 (1992), No. 26.

Journal of Solution Chemistry, Vol. 6 (1977), No. 11.

Journal of Solution Chemistry, Vol. 20 (1991), No. 9.

Journal of Solution Chemistry, Vol. 21(1992), No. 5.

Journal of The Chemical Society: "Dalton Transactions," Royal Society of Chemistry, 1984.

Radiochemical and Radioanalytical Letters, Vol. 22 (1975), No. 1.

Radiochimica Acta, Vol. 52/53 (1991), Part I.

Radiochimica Acta, Vol. 55 (1991), No. 4.

Radiochimica Acta, Vol. 61 (1993), No. 3/4.

Radiochimicia Acta, Vol. 69 (1995), Issue 1.

Radiochimicia Acta, Vol. 69 (1995), Issue 3.

Choppin, G.R. and J.N. Mathur, 1990. "Hydrolysis of Actinyl (VI) Cations."

Drever, J.I., 1982. "The Geochemistry of Natural Waters."

- Fanghanel, T., V. Neck, and J.I. Kim, 1995. "Thermodynamics of Neptunium (V) in Concentrated Salt Solutions: II. Ion Interaction (Pitzer) Parameters for Np (V) Hydrolysis Species and Carbonate Complexes."
- Goldberg, R.N., 1979. "Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Bi-Univalent Compounds of Lead, Copper, Manganese, and Uranium." J. Phys. Chem. Ref. Data, Vol. 8, No. 4, pp 1005-1050.
- Grenthe, I. (Chairman), 1992. "Chemical Thermodynamics of Uranium," Nuclear Energy Agency Organisation for Economic Co-operation and Development.
- Harvie, C.E., N. Moller, and J.H. Weare, 1984. "The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O System to High Ionic Strengths at 25°C."



Martell, A.E. and R.M. Smith, 1977. Critical Stability Constants, Vol. 3: Other Organic Ligands".

- Nick, V., T. Fanghanel, G. Rudolph, and J.I. Kim, 1995. "Thermodynamic of Neptunium (V) in Concentrated Salt Solutions: Chloride Complexation and Ion Interaction (Pitzer) Parameters for the NpO<sub>2</sub><sup>+</sup> Ion."
- Pitzer, K.S., 1991. "Activity Coefficients in Electrolyte Solutions," 2nd Edition.
- Rai, D., A.R. Felmy, S.P. Juracich, and L. Rao, 1994. "Estimating the Hydrogen Ion Concentration in Concentrated NaCl and Na<sub>2</sub>SO<sub>4</sub> Electrolytes. "Sand 94-1949.

Robinson, R.A. and R.H. Stokes, 1959. "Electrolyte Solutions."

- Robinson, R.A. and R.H. Stokes, 1959. "Electrolyte Solutions: The Measurement and Interpretation of Conductance, Chemical Potential and Diffusion in Solutions of Simple Electrolytes," 2nd Ed.
- Silva, R.T. (Chairman), 1995. "Chemical Thermodynamics of Americium: Nuclear Energy Agency Organisation For Economic Co-Operation and Development."
- Sombert, C.G., 1991. "Scientific Basis for Nuclear Waste Management XV," Materials Research Society Symposium Proceedings, Vol. 257.
- Worley, T.J., 1992. "EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Theoretical Manual, User's Guide and Related Documentation Version 7.0."
- Worley, T.J. and S.A. Daveler, 1992. "EQ6, A Computer Program for Reaction Path Modeling of Aqueous Geochemical Systems: Theoretical Manual, Users Guide and Related Documentation, Version 7.0."



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