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BECHTEL
SAIC COMPANY LLC

Technical Work Plan for:
Thermodynamic Databases for Chemical Modeling

Prepared for:
U.S. Department of Energy
Office of Civilian Radioactive Waste Management
Office of Repository Development
1551 Hillshire Drive
Las Vegas, Nevada 89134-6321

Prepared by:
Bechtel SAIC Company, LLC
1180 Town Center Drive
Las Vegas, Nevada 89144

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Prepared by:

Carlos F. Jove Colon
Technical Work Plan Manager

09-07-06
Date

Concurrence by:

(N/A)
Kenneth Skipper
USGS TPO

Date

Approved by:

Ernest Hardin
Department Manager

9/7/06
Date

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CHANGE HISTORY

Revision Number	ICN Number	Date of Change	Description of Change
00	00	05/25/2006	Initial issue.
01	00	09/07/2006	Respond to DOE comments on Rev. 00.

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CONTENTS

TABLES

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ACRONYMS AND ABBREVIATIONS

CR	condition report
DOE	U.S. Department of Energy
DTN	data tracking number
FEPs	features, events, and processes
FY	fiscal year
IDPS	in-drift precipitates/salts
LA	license application
N/A	not applicable
OCRWM	Office of Civilian Radioactive Waste Management
ORNL	Oak Ridge National Laboratory
QA	quality assurance
QARD	*Quality Assurance Requirements and Description*
RPC	Records Processing Center
SNL	Sandia National Laboratories
TDMS	Technical Data Management System
THC	thermal-hydrologic-chemical
TSPA	total system performance assessment
TWP	technical work plan
YMP	Yucca Mountain Project

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1. WORK SCOPE

This technical work plan (TWP) describes work to be performed by the Near-Field Environment group in FY06 and FY07 to:

- Make necessary improvements to the existing Pitzer database (*data0.ypf.R1*) and the existing dilute-system database (*data0.ymp.R4*), generating new versions of these files, to support analysis/modeling for TSPA.
- Prepare an initial revision of the Pitzer database, correcting errors and providing additional refinements *In-Drift Precipitates/Salts Model* (ANL-EBS-MD-000045).
- Revise the two data qualification reports supporting these databases (ANL-WIS-GS-000001 and ANL-WIS-GS-000003).
- Address outstanding Condition Reports (CRs).

The two data qualification reports given above are *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]) and *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]). Each of these reports generates thermodynamic databases for use with the computer software package EQ3/6. The Pitzer database, *data0.ypf.R1* (Output DTN: SN0504T0502404.011), is intended for use with EQ3/6 options that implement the Pitzer approach for calculation of activity coefficients of aqueous species to model concentrated electrolyte solutions. The dilute-systems database, *data0.ymp.R4* (Output DTN: SN0410T0510404.002), is intended to be used with the "B-dot" equation for computing activity coefficients in relatively dilute electrolyte solutions.

Several changes to the Pitzer database are needed in the short term for use in revision of *In-Drift Precipitates/Salts Model* (BSC 2004 [DIRS 169863]). These changes will address errors and implement enhancements specific to application of the database in the in-drift precipitates/salts (IDPS) model. The database changes will be documented in the revised IDPS model report, and the revised database (i.e., *data0.ypf.R2*) will be output from that report. Later in 2007, revision of the Pitzer database qualification report (ANL-WIS-GS-000001) will describe these and additional database changes, and a new version of the database will be issued then. The additional changes to the database in FY07 will include results from evaluation of experimental data acquired at Oak Ridge National Laboratory (ORNL) in FY05.

The activities described in this TWP address the following CRs, which deal with errors and potential problems with thermodynamic parameters: 6489, 6731, 6752, 7542, 7721, and 7756. In addition, other opportunities for improvement to thermodynamic data used for TSPA are identified in this work plan. These CRs and related changes constitute the entire scope of revisions to the databases and reports identified above.

Background

The IDPS model is limited to representing inorganic salt systems that can occur in the repository host rock environment, and the evaporative concentration of those systems. The most recent

Pitzer database file used in the IDPS model report is entitled *data0.ypf.R0*. The Pitzer database qualified by *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]) is more recent, and includes more data for actinides, transition metals, and certain other species. The planned revision of the IDPS model report (as discussed above and described in TWP-MGR-PA-000038) will produce an updated Pitzer database based on *data0.ypf.R1*, for application in the IDPS model (restricted to the inorganic salt systems that occur in the repository host rock environment) and also for other problems involving transition metals and actinides. In other words, the next version of the Pitzer database (i.e., *data0.ypf.R2*) will be an iteration on the full Pitzer database, and changes from the previously qualified full Pitzer database will be documented in the IDPS model report revision. Finally, additional refinements and extensions in the full Pitzer database are planned in a later revision to be completed in FY07 (to be called *data0.ypf.R3*), supported by revision of the Pitzer database qualification report (ANL-EBS-MD-000001), and an impact evaluation at that time will determine the impacts, if any, on the IDPS model.

This TWP has been prepared in accordance with LP-2.29Q-BSC, *Planning for Science Activities*. The work described in this TWP supports the LA. The data qualification reports will be prepared in accordance with LP-SIII.2Q-BSC, *Qualification of Unqualified Data*, and LP-SIII.9Q-BSC, *Scientific Analysis*.

1.1 OBJECTIVES

The objective of the work scope covered by this TWP is to correct and improve the Yucca Mountain Project (YMP) thermodynamic databases, to update their documentation, and to ensure reasonable consistency among them. In addition, the work scope will continue to generate database revisions, which are organized and named so as to be transparent to internal and external users and reviewers.

Regarding consistency among databases, it is noted that aqueous speciation and mineral solubility data for a given system may differ according to how solubility was determined, and the method used for subsequent retrieval of thermodynamic parameter values from measured data.

Of particular concern are the details of the determination of "infinite dilution" constants, which involve the use of specific methods for activity coefficient corrections. That is, equilibrium constants developed for a given system for one set of conditions may not be consistent with constants developed for other conditions, depending on the species considered in the chemical reactions and the methods used in the reported studies. Hence, there will be some differences (for example in *log K* values) between the Pitzer and "B-dot" database parameters for the same reactions or species.

Another objective of the work scope covered by this TWP is to complete the evaluation of experimental data produced at Oak Ridge National Laboratory (ORNL) in FY05. These data are expected to decrease the uncertainty associated with use of the Pitzer activity model for the system $Ca(NO_3)_2$-KNO_3-$NaNO_3$-H_2O at elevated temperatures (see Section 1.2.3). The ORNL data analysis activity, which may include the qualification of data as per LP-SIII.2Q-BSC and corresponding changes to the Pitzer data qualification report, both planned for FY07, are longer-term activities that will support revision of *Analysis of Dust Deliquescence for FEP*

Screening (BSC 2005 [DIRS 175058]) in FY07 (as described in TWP-MGR-PA-000038). BSC. If the qualification of the ORNL data occurs, a qualification plan will be completed as per LP-SIII.2Q-BSC.

1.2 PRIMARY TASKS

This TWP describes five tasks:

(1) Support revision of the Pitzer database specifically for the IDPS model, in FY06. Revision of the IDPS model report is planned in a separate work plan (TWP-MGR-PA-000038).

(2) Revise the dilute-systems ("B-dot") database *data0.ymp* and the supporting data qualification report (BSC 2004 [DIRS 171916]) in FY06.

(3) Develop other changes to the Pitzer database (i.e., changes not needed for the IDPS model) in FY06, and submit as preliminary data to the Technical Data Management System (TDMS).

(4) Analyze isopiestic data acquired by ORNL and develop revised values of Pitzer parameters for the $Ca(NO_3)_2$-KNO_3-$NaNO_3$-H_2O system consistent with those data, in FY07.

(5) Revise the Pitzer *data0.ypf* database and the supporting data qualification report (BSC 2005 [DIRS 174223]) in FY07, to include database changes arising from tasks (1), (3), and (4).

The following sections detail changes to the databases and the associated documentation. The list below includes CRs and other opportunities for improvement. The discussion assigns each issue to one or more of the five tasks listed above, summarized by Table 1 in Section 1.2.4.

1.2.1 Condition Reports

The CR descriptions presented here have been altered slightly to better present the context of the condition. Each is followed by a discussion of which primary tasks and associated products (i.e., databases and documents) will address the CR.

- **CR 6489: Sensitivity Studies on Form of Sepiolite Used in ANL-EBS-MD-000074, Rev. 00**.

  Description: The IDPS model (EQ3/6 simulations) is used in the *Analysis of Dust Deliquescence for FEP Screening*, ANL-EBS-MD-000074 Rev 00. (Note: The version of the *Analysis of Dust Deliquescence for FEP Screening* cited in CR 6489 is incorrect, the current version is Rev 01 not Rev 00). The IDPS model uses the precipitation of the mineral sepiolite as the primary mechanism controlling magnesium concentrations in brines. The thermodynamic database, *data0.ypf.R0* contains the *log K* value for crystalline sepiolite. Validation of the IDPS model (ANL-EBS-MD-000045 Rev. 02, Section 7.1.1) required changing the *log K* value for sepiolite by 6 log units to match experimental data. The modified *log K* represents an amorphous form of sepiolite rather than the crystalline form. The authors currently did not know how the results of the IDPS model applied to dust deliquescence analysis would change if the *log K* for amorphous sepiolite were used in *data0.ypf.R0.* Modifying the IDPS model with the revised log K for amorphous sepiolite and running the simulations of the brine formed by evaporation would improve the confidence in the results of the model as it applied to dust deliquescence. The issue of the appropriateness of using the log K of amorphous versus crystalline sepiolite will be addressed in the reports (IDPS model ANL-EBS-MD-000045 and *Analysis of Dust Deliquescence for FEP Screening*, ANL-EBS-MD-000074), which are not part of this TWP.

Planned Actions: One or more additional species will be added to the Pitzer and the dilute-system databases, in tasks (1), (2), (3), and (5) listed above; the specific changes are described in Section 2.1.2. These changes will be documented in revisions to *In-Drift Precipitates Salts Model* (BSC 2004 [DIRS 169863]), *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]), and *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]).

- **CR 6731: Discrepancy in thermodynamic data for phosphate species.**

  Description: The CR identifies discrepancies in key thermodynamic data used to develop the *data0.ymp.R0* and successor thermochemical databases (see ANL-WIS-GS-000003 Rev. 00). The *data0.ymp.R0* database is used as a starting point for a Pitzer database in *In-Drift Precipitates/Salts* (ANL-EBS-MD-000045 Rev. 02). Phosphate species are not included in these models, and are likely to be very scarce in the EBS chemical environment. In other models such as *In-Package Chemistry Abstraction* (BSC 2005 [DIRS 174583]) and *Dissolved Concentration Limits of Radioactive Elements* (BSC 2005 [DIRS 174566], however, phosphate may be a significant reactant. Because phosphate forms insoluble precipitates with certain actinides (e.g., U) and other important elements (e.g., Gd), discrepant thermodynamic data for phosphate species may be significant to TSPA abstractions or FEP exclusion. In addition, it has been reported that the stoichiometry of $GdPO_4{:}10H_2O$ cannot be verified from the source cited in the *data0.ymp.R2* database (ANL-WIS-GS-000003 Rev. 00). This is a different but related issue to the one identified in the attachment, and the two issues should be evaluated together.

  Planned Actions: The stoichiometry and equilibrium constants for phosphate species will be updated based on current literature sources. The update of thermodynamic parameters affects a large number of phosphate species. The evaluation of these changes may require analyzing various sources of data and rewriting chemical reactions different from those given in previous versions of the database. This could result in the addition of new phosphate species used in the current data reevaluation. Database changes will be implemented for tasks (2), (3), and (5) listed above; the specific changes are described in Section 2.1.2. The changes will be documented in revisions to database qualification reports *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]) and *Qualification of*

Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems (BSC 2005 [DIRS 171916]).

- **CR 6752: Error in the dissociation constants for two Np(V) aqueous species $NpO_2(OH)_2^-$ and $NpO_2OH(aq)$ in the Pitzer database.**

  Description: The log K values for the dissociation reactions of the aqueous species $NpO_2(OH)^{2-}$ and $NpO_2OH(aq)$ are in error due the incorrect representation of these in output DTNs: SN0504T0502404.010 and SN0504T0502404.011 as association reactions. Further, the *log K* values given in the source need to be corrected for consistency with the thermodynamic properties of the basis species NpO_2^+ adopted in the *data0.ypf.R1* and *data0.ypf.R2* databases. This condition may impact users of the *data0.ypf* and *data0.ymp* databases, including but not limited to *Dissolved Concentration Limits of Radioactive Elements* (BSC 2005 [DIRS 174566]).

  Planned Actions: Tasks (1), (3) and (5) will produce database files and associated documentation that corrects these errors in the Np reactions. The changes will be documented in revisions to *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]) and *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]). In addition, because these are simple corrections, they will also be implemented in revision of *In-Drift Precipitates/Salts Model* (BSC 2004 [DIRS 169863]), although the IDPS model does not include Np. The corrected database submittals will be available for use in planned revisions of *Dissolved Concentration Limits of Radioactive Elements* (BSC 2005 [DIRS 174566]) and *In-Package Chemistry Abstraction* (BSC 2005 [DIRS 174583]), which are planned in a separate work plan (TWP-WIS-MD-000018).

- **CR 7542: Thermodynamic database (*data0.ymp.R4*) update [$NiCO_3$ solid].**

  Description: The solid mineral $NiCO_3$ (nickel carbonate) has been identified as needing an update in the *data0.ymp.R4* thermodynamic database (DTN: SN0410T0510404.002). The *data0.ymp.R4* data leads to a very high nickel solubility that is realized in the in-package chemistry calculations (ANL-EBS-MD-000037 REV 04). A recent NAGRA/PSI 2002 report (Hummel et al [DIRS 161904]) states how previous databases commonly contained this incorrect solubility product. The updated value from NAGRA/PSI is already contained within *data0.ypf.R2* (DTN: SN0504T0502205.008).

  Planned Actions: This change will be addressed in tasks (2), (3), and (5) listed above. The new data for $NiCO_3(s)$ will be evaluated for inclusion in both the "B-dot" and Pitzer databases. These changes will be documented in revisions to *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]) and *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]). Updated database submittals will be available for use in planned revisions of *Dissolved Concentration Limits of Radioactive Elements* (BSC 2005 [DIRS 174566]) and

In-Package Chemistry Abstraction (BSC 2005 [DIRS 174583]), which are planned in a separate work plan (TWP-WIS-MD-000018).

- **CR 7721**: **Revision of Pitzer interaction parameters for carbonate species.**

  Description: Discrepancies in the prediction of calcite and CO_2(aq) solubilities were found in EQ3/6 equilibrium calculations between the Pitzer and other thermodynamic databases in cases involving high temperature, ionic strength, and CO_2 partial pressure. Moreover, discrepancies with predictions of activity coefficients for CO_2(aq) suggest revisiting the Pitzer parameter data for this species.

  Planned Actions: This condition will be addressed in tasks (1), (3), and (5) listed above, by evaluating the use of updated parameters for description of CO_2 species. The database changes will be documented in revisions of *In-Drift Precipitates/Salts Model* (BSC 2004 [DIRS 169863]) in FY06, and *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]) in FY07. For the IDPS model, the impact on CO_2(aq) solubilities is expected to be small because of the small CO_2 fugacities in the repository, and the limited temperature range for application of the IDPS model.

- **CR 7756**: **Add mineral phases observed in UO_2 drip tests and natural analogue to EQ3/6 databases.**

  Description: A number of secondary minerals observed in UO_2 dissolution experiments and/or at the Peña Blanca uraninite deposit are not included in YMP thermodynamic databases such as *data0.ymp.R4* used in TSPA. They include: haiweeite, dehydrated schoepite (UO_3:0.8-1.0H_2O), becquerelite, compreignacite, sklodowskite, boltwoodite ($KH(UO_2)SiO_4$:1.5H_2O), beta-uranophane (same formula as uranophane), palygorskite, ianthinite, and weeksite ($K_2(UO_2)2Si_6O_{15}$:4H_2O). Because these minerals are observed to form under conditions similar to conditions that could develop at the repository, they should be added to the databases, if data are available. Without these phases in the databases, one can predict neither their potential formation and accumulation nor their potential effects on water composition.

  Planned Actions: The database changes will be implemented in tasks (3) and (5) listed above. The secondary minerals to be included in the databases will be determined based on the consistency and quality of the available data, and may differ for the "B-dot" and Pitzer databases depending on the data characteristics as discussed previously. The database changes will be documented in revisions to *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]) in FY06, and *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]) in FY07.

1.2.2 Additional Updates and Revisions

Other issues to be addressed in this thermodynamic database qualification effort include:

- **Consistent Application of *log K* Values in the Pitzer and "B-dot" Databases**. There is a need to address consistent application of "infinite dilution" *log K* values for dissociation reactions for actinides and transition metal solids and aqueous species common to *data0.ymp.R4* and *data0.ypf.R1*. Consistency does not necessarily mean that identical values for parameters will be used in different databases, as discussed in Section 1.1. The changes will be documented in revisions to database qualification reports *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]) and *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]). This issue will be addressed in tasks (3) and (5) listed above.

- **New Data for Se(VI) and Sn(IV) Species**. The current "B-dot" database (*data0.ymp.R4*) has thermodynamic data for aqueous and solid species involving these two components, but additional data are needed to expand the stability range and number of possible phases that could occur in this system. The application will be in radionuclide transport for certain scenarios of system performance. The new data will be addressed in a revision of the database qualification report *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]), and may also be addressed in a revision of *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]), if appropriate. These changes will be made in task (2), and possibly tasks (3) and (5) as listed above. The changes (*data0.ymp.R5*) will be available for use in revision of *Dissolved Concentration Limits of Radioactive Elements* (BSC 2005 [DIRS 174566]), where a solubility model description for these two chemical species will be documented. These solubility limits are implemented in TSPA, where they are most important for peak dose assessment.

- **Update *log K* Values for Silica Species**. Only the equilibrium constant for the silicic acid aqueous species (delineated by $HSiO_3^-$ in the thermodynamic database) will be revised. This revision will be on the basis of published experimental data including sensitivity of this reaction to ionic strength and temperature. Several solubility experiments at various temperatures have been conducted in the past to determine the log K value of this reaction. It was noted that the current log K value at 25°C was consistently lower (by ~0.2 log units) than those reported in studies for which more confidence is weighed in terms experimental methodologies and data evaluation. This reassessment will be documented in the report describing all the changes to *data0.ymp.R4*. Since this aqueous species is not a 'strictly basis' species in chemical reactions involving aqueous silica in the using the EQ3/6 thermodynamic database, there is no effect on reactions involving silicate phases. Other aqueous species that may be affected are $NaHSiO_3(aq)$, $CaHSiO_3^+$, and $MgHSiO_3^+$ in terms of the Gibbs energy of formation value. It appears that this thermodynamic parameter for these aqueous species was determined based on the Gibbs energy of formation of $HSiO_3^-$ as described in the original source (Sverjensky et al. 1997 [DIRS 150775]) through the reaction

$P^vHSiO_3(aq) = P^v + HSiO_3^-$ where P^v is the complexed species corresponding to Na^+, Ca^{++}, and Mg^{++}. The log K values for these species in accord with the above reaction were based on solubility data for $NaHSiO_3(aq)$ (Seward 1974 [DIRS 177381]) and from the complexation estimates made by Turner (1981 [DIRS 177378]) for $MgHSiO_3^+$ and $CaHSiO_3^+$. Since the log K values of the dissociation reactions in the EQ3/6 database are expressed in terms of $SiO_2(aq)$, these values need to be updated to be consistent with the revised values for $HSiO_3^-$. This will be evaluated as part of the current revision of the thermodynamic databases. These changes will be documented in revisions to *In-Drift Precipitates Salts Model* (BSC 2004 [DIRS 169863]), *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]), and *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]). The changes will be implemented in tasks (1), (2), (3), and (5) listed above. Pot

- **Addition of the Phase $NiMoO_4(s)$.** Thermodynamic data for this Ni-bearing phase have recently been determined by Morishita and Navrotsky (2003 [DIRS 176846]). The changes will be documented in revisions to database qualification reports *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]) and *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]). The changes will be implemented in tasks (2), (3), and (5) listed above.

- **Review of Complexation Data for the Species $Th(CO_3)_5^{(-6)}$.** Consistency of the current value adopted in the Pitzer database (which is from *data0.ymp.R4*) with the Pitzer parameters obtained for this species needs to be reevaluated. The changes will be documented in revisions to database qualification reports *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]) and *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]). . This evaluation is directed to more defensible solubility calculations, since the activity model for highly charged species can have a strong effect on solubility, particularly where there is a high concentration of dissolved carbonate in solution.. Changes will be made, as appropriate, in tasks (3) and (5) listed above.

- **Add Kogarkoite (Na_3SO_4F) to the Databases.** This phase has been identified as a product of the experimental evaporation of synthetic seepage solutions. Thermodynamic properties for this phase have been determined by Gurevich et al. (1999 [DIRS 176845]). The changes will be documented in revisions to database qualification reports *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]) and *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]). Addition of this solid will be implemented in tasks (1), (2), (3), and (5) listed above.

- **Change Basis Species for Cr Species.** This issue is related to the basis aqueous species used in dissociation reactions for the solid eskolaite (Cr_2O_3) and aqueous species CrO_3Cl^- that are currently written as redox reactions. Changing the basis aqueous species in the reaction within the database file to the one corresponding to the redox state of the solid or aqueous species in question would facilitate suppressions in the problem definition in the computer software package EQ3/6 EQ3/6 input file. The changes will be documented in the revision to database qualification report *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]). The change will be implemented in task (2) as listed above.

- **Incorporate Tabulated Data Corrections**. This issue involves incorporation of the corrections for *log K* values in *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916], Section 7; DTN: SN0410T0510404.002) into the updated version of the *data0.ymp.R4* database file. The change will be documented in the revision to database qualification report *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]). The changes will be implemented in task (2) as listed above.
- **Update Pitzer Parameters for Published Data on Nitrate Salts**. This issue involves updating temperature-dependent Pitzer parameter data for $Mg(NO_3)_2$, $NaNO_3$, and $Ca(NO_3)_2$. Updated data for these three salts have been determined by Rard et al. (2004 [DIRS 173816]) and Wijesinghe and Rard (2005 [DIRS 176847]). The changes will be documented in revisions to database qualification reports *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]) and *In-Drift Precipitates/Salts Model* (BSC 2004 [DIRS 169863]). The changes will be implemented in tasks (1), (3), and (5) listed above.

1.2.3 Analyze Oak Ridge National Laboratory Isopiestic Data

ORNL generated experimental isopiestic data to better constrain the system $Ca(NO_3)_2$-KNO_3-$NaNO_3$-H_2O at elevated temperatures and further enhance the current Pitzer parameters in the database for this system. In FY07 analysis of these experimental data within the formalism of Pitzer equations will be initiated once the data are available and qualified in the Technical Data Management System (TDMS). This activity will also entail a comprehensive examination of literature data available for this system. The resulting enhanced Pitzer database (*data0.ypf.R3*) will support calculations in a revision of *Analysis of Dust Deliquescence for FEP Screening* (BSC 2005 [DIRS 175058]) in FY07 (as described in TWP-MGR-PA-000038 Rev. 00). This activity will be implemented in tasks (4) and (5) listed above.

1.2.4 Summary of Primary Tasks

Implementation of the database changes listed above, in the five tasks identified at the beginning of Section 1.2, is summarized in Table 1.

Table 1. Summary of Chemical Database Change Implementation in Primary Tasks

Database Change	Task 1	Task 2	Task 3	Task 4	Task 5
CR 6489 (Add Mg-silicate Phases)	X	X	X		X
CR 6731 (Inconsistent Treatment of Phosphates)		X*	X		X
CR 6752 (Np Speciation Reactions Reversed)	X		X		X
CR 7542 (Add $NiCO_3$ Species)		X*	X		X
CR 7721 (Revise Pitzer Parameters for Carbonates)	X		X		X
CR 7756 (Add UO_2 Mineral Phases)			X		X
Consistent Application of *log K* Values			X		X
New Data for Se(VI) and Sn(IV) Species		X	X		X
Update *log K* Values for Silica Species	X	X	X		X
Addition of $NiMoO_4(s)$		X*	X		X
Review of Complexation Data for the Species $Th(CO_3)_5^{(-6)}$			X		X
Add Kogarkoite (Na_3SO_4F) to the Databases	X	X*	X		X
Change Basis for Cr Aqueous Species		X*			
Incorporate Tabulated Data Corrections into Database File(s)		X*			
Update Pitzer Parameters for Nitrate Salts	X		X		X
Analyze ORNL Isopiestic Data for Nitrates				X	X
Evaluate and Address Consistency of THC and IDPS Databases	X		X		X

NOTES: Asterisk (*) indicates information requested by authors of the in-package chemistry report (BSC 2005 [DIRS 174583]).

Task 1: Support revision of IDPS Pitzer database (FY06).

Task 2: Issue revised *data0.ymp* database and qualification report (BSC 2004 [DIRS 171916]) for dilute systems (FY06).

Task 3: Issue preliminary revised DTN for Pitzer database (FY06).

Task 4: Analyze experimental data from ORNL (FY07).

Task 5: Revise Pitzer database qualification report (BSC 2005 [DIRS 174223]) (FY07).

1.3 RESPONSIBLE ORGANIZATIONS

The Near-Field Environment team, currently part of the Post Closure Activities department in the Licensing and Nuclear Safety organization, is responsible for the execution of the new work identified in this plan. The technical work will be done mainly by personnel at Sandia National Laboratories (SNL) and Lawrence Livermore National Laboratory. In FY07, ORNL will participate in task (4).

1.4 TESTING AND PRETEST PREDICTIONS

The work scope covered by this TWP includes no scientific testing activities.

2. SCIENTIFIC APPROACH OR TECHNICAL METHODS

This section establishes the implementation plan and work controls to perform the primary tasks.

2.1 WORK ACTIVITIES

2.1.1 Intended Use of Products

The overall intended purpose of this TWP is describe the necessary improvements to the existing Pitzer database (*data0.ypf.R1*) and the existing dilute-system database (*data0.ymp.R4*), generating new versions of these files, as well as the revision of the two data qualification reports supporting these databases (ANL-WIS-GS-000001 and ANL-WIS-GS-000003). Technical exchanges will involve interfacing with other departments that are part of the Licensing and Nuclear Safety organization, such as Criticality in the Licensing and Analysis department, and TSPA in the Performance Assessment department. Analysis and model reports that are directly downstream of these reports and thermodynamic databases are broken down by organization in Section 10.

This TWP describes five tasks:

(1) Support revision of the Pitzer database specifically for the IDPS model, in FY06. A revision of *In-Drift Precipitates/Salts Model* (BSC 2004 [DIRS 169863]) is planned in a separate work plan (TWP-MGR-PA-000038).

(2) Revise the dilute-systems ("B-dot") database *data0.ymp* and the supporting data qualification report (BSC 2004 [DIRS 171916]) in FY06. The results of this work will support revisions (described in other TWPs) to the following documents: *Engineered Barrier System: Physical and Chemical Environment* (BSC 2005 [DIRS 175083]); *In-Package Chemistry Abstraction* (BSC 2005 [DIRS 174583]); *Dissolved Concentration Limits of Radioactive Elements* (BSC 2005 [DIRS 174566]); *Geochemistry Model Validation Report: Material Degradation and Release Model* (BSC 2001 [DIRS 156790]); *Geochemistry Model Validation Report: External Accumulation Model* (BSC 2001 [DIRS 156324]); and Sections 2.3.5 and 2.3.7 of the LA Safety Analysis Report.

(3) Develop other changes to the Pitzer database (i.e., changes not needed for the IDPS model) in FY06, and submit as preliminary data to the Technical Data Management System (TDMS). This information will be used in FY07 for the revision of *Analysis of Dust Deliquescence for FEP Screening* (BSC 2005 [DIRS 175058]).

(4) Analyze isopiestic data acquired by ORNL and develop revised values of Pitzer parameters for the $Ca(NO_3)_2$-KNO_3-$NaNO_3$-H_2O system consistent with those data, in FY07. This information will be used in FY07 for the revision of *Analysis of Dust Deliquescence for FEP Screening* (BSC 2005 [DIRS 175058]).

(5) Revise the Pitzer *data0.ypf* database and the supporting data qualification report (BSC 2005 [DIRS 174223]) in FY07. This information will be used in FY07 for the revision of *Analysis of Dust Deliquescence for FEP Screening* (BSC 2005 [DIRS 175058]).

2.1.2 Scientific Approach and Technical Methods

This work will be conducted following standard scientific analysis practices, and using the commercial software identified in Section 9. This work scope does not include any field work. Consideration of alternative conceptual models is not applicable for this activity.

The overall scientific approach adopted in this work is based on the methods delineated in the procedure LP-SIII.9Q-BSC, but invoking LP-SIII.2Q-BSC for data qualification methods. The applicable methods based on this procedure are explained later in this section. Initially, the methods adopted for correction and/or updating of thermodynamic data parameters will mainly involve reviewing and/or corroboration with literature data: for example, in the form of solubility predictions using the qualified computer software package EQ3/6 (V8.1), and comparing the parameter values with alternate data. If alternate data are not available for comparison, the evaluations will be done on the basis of technical assessment. It should be noted that previous qualification activities of thermodynamic databases were done successfully by using only the corroborating data and technical assessment methods. Emphasis is placed on the latter method, which was used extensively in previous scientific analysis reports (BSC 2005 [DIRS 174223]; BSC 2005 [DIRS 171916]). The evaluation of thermodynamic parameters will be conducted using exempted software like MS Excel and the qualified computer software package EQ3/6 (V8.1).

The Office of Civilian Radioactive Waste Management (OCRWM) procedure for qualifying data (LP-SIII.2Q-BSC) lists five methods for qualifying data, of which the following two are selected for use in this scientific analysis activity:

Method 2—*Corroborating Data.* This method involves the application of independently measured data to substantiate or confirm parameter values. It requires that data be available for comparison to the unqualified data sets, and that inferences drawn to corroborate the unqualified data be clearly identified, justified, and documented.

Method 5—*Technical Assessment.* This method is used when it is determined that independent assessment of the data, by a subject matter expert, is needed to raise the confidence of the data to the proper level for intended use. Technical assessments may be required if the confidence in the data is in question because data collection procedures are unavailable for review, the procedures are not adequate, or if documentation or proof of proper data acquisition is unavailable for review. The technical assessment must include one or more of the following requirements:

(1) Determination that the employed *methodology* is acceptable

(2) Determination that *confidence* in the data acquisition or developmental results is warranted

(3) Confirmation that the data have been *used* in similar applications (e.g., by the U.S. Nuclear Regulatory Commission or the Environmental Protection Agency, by nationally or internationally recognized organizations, or by the scientific community including publications, peer reviews, etc.).

Corroborative data in the form of independently derived parameter values or of thermodynamic data for chemical analogues will be used where available. Technical assessments will be carried out by the data qualification team to determine if requirements (1), (2), and (3) are met. Closure of CRs described in Section 1.2.1 will be done according to the corrective action plan summarized in the corresponding CR descriptions.

Planned approaches to assess the issues delineated in Section 1.2.1 involving CRs in accordance with the above-mentioned technical methods are as follows:

- **CR 6489:** The thermodynamic databases will be updated with the modified *log K* of "amorphous sepiolite" considered in the IDPS validation. Furthermore, the databases will also be updated with *log K* values for the dissociation reaction of poorly crystalline antigorite based on the analysis of solubility and thermodynamic data given by Gunnarsson et al. (2005 [DIRS 176844). This phase has been identified as a potential solubility-controlling solid for Mg in geothermal waters.

- **CR 6731:** This work will encompass a detailed evaluation of key thermodynamic and compositional data for the affected phosphate species from various sources including handbook data tabulations and peer-reviewed scientific journals. This evaluation will examine the potential sources for error and assessment of the effects (if any) caused by these discrepancies in computer software package EQ3/6 calculations as used in the affected model reports.

- **CR 6752**: This activity will mainly involve corrections of a calculation in the source spreadsheets and database DTN files and evaluation of the effects of the discrepancy in the thermodynamic data for the basis species NpO_2^+.

- **CR 7542**: This task will comprise the evaluation and subsequent update of thermodynamic data for $NiCO_3$ (nickel carbonate) and recent reviews of thermodynamic data for this phase. A reassessment of the Ni system was conducted in the development of the database *data0.ypf.R1.*

- **CR 7721**: This work may entail revisions of Pitzer and other related thermodynamic parameters for the carbonate system valid at temperatures above 25°C. It will involve literature searches and recent reviews focusing on the evaluation of solubility of carbonate solids at elevated temperatures and ionic strength.

- **CR 7756**: This activity will mainly consist of literature searches for thermodynamic and/or solubility data for the phases delineated in the CR. There are also plans to explore the examination of estimation methods to obtain thermodynamic parameters of these phases.

Planned approaches to assess the issues delineated in Section 1.2.2 in accordance with the above-mentioned technical methods are as follows:

- "Consistency evaluation between infinite dilution *log K* values of dissociation reactions for actinides and transition metal species solids and aqueous species common to *data0.ymp.R4* and *data0.ypf.R1*": This evaluation will be initially accomplished by a systematic comparison of *log K* values between the two databases. Differences in *log K* values will be examined, and to the extent possible these will evaluated based on uncertainties reported by the sources.

- "Additions of thermodynamic data for Se(VI) and Sn(IV) solids and aqueous species": These two chemical species can exist as long-lived fission products, and concentrations of these can be attenuated by solubility-controlling solids. The amorphous phase SnO_2(am) has been observed to form at 25°C, and recent solubility of this solid along with aqueous speciation data extends to fairly alkaline pH values (Amaya et al. 1997 [DIRS 176843]). The plan is to add infinite dilute *log K* values for SnO_2(am) along with additional aqueous species to the already existing data in the current version of the thermodynamic database *data0.ymp.R4*. Plans are considered to add a solubility-controlling solid for the soluble selenate (SeO_4^{--}) aqueous species to the revised version of the database *data0.ymp.R4*.

- "Revision of the *log K* value for the reaction involving silicic acid $HSiO_3^- + H^+ = SiO_2(aq) + H_2O$ as compared to published experimental data": The assessment of this reaction plus evaluation of the aqueous species $NaHSiO_3$(aq), $CaHSiO_3^+$, and $MgHSiO_3^+$, in case these need any revision, will be assessed mainly through comparisons with experimentally determined solubility data. The effect of ionic strength along with temperature on silicic acid stability will also be explored depending on data availability.

- "Addition of the phase $NiMoO_4$(s)": Standard thermodynamic data obtained from the calorimetric study by Morishita and Navrotsky (2003 [DIRS 176846]) for this nickel molybdate phase, along with existing thermodynamic data of the aqueous species in *data0.ymp.R4*, will be used to evaluate its solubility.

- "Review of complexation data or *log K* values for the species $Th(CO_3)_5^{(-6)}$": This task will involve a data consistency evaluation between the *log K* value adopted in *data0.ymp.R4* and that in *data0.ypf.R1*. Recent studies have assessed the solubility of ThO_2(s) in solutions containing carbonate. These studies have elucidated differences in retrieved thermodynamic parameters to explain ThO_2(s) solubility and advance revised *log K* values for several Th aqueous complexes along with new solubility data. Examination of these data will determine if there is any need for an update in equilibrium constants relative to what is already in the thermodynamic databases. Aqueous Th-carbonate species are important in effecting ThO_2(s) solubility from near-neutral to alkaline pH values, particularly in solutions containing fair amounts of dissolved carbon.

- "Add the phase kogarkoite (Na_3SO_4F) to the database": As mentioned in Section 1.2.2, this phase was identified in the evaporation of synthetic seepage solutions. Standard thermodynamic data have been determined experimentally from calorimetric measurements by Gurevich et al. (1999 [DIRS 176845]). Evaluation for this phase solubility will be conducted using Gibbs energies of formation retrieved from thermodynamic data given by Gurevich et al. (1999 [DIRS 176845]) and data for aqueous species in *data0.ymp.R4*.

- "Change the basis aqueous species used in dissociation reactions for the solid eskolaite (Cr_2O_3) and aqueous species CrO_3Cl^- that are currently written as redox reactions": The solubility reactions for these two species will be rewritten according to their corresponding Cr aqueous basis species. The *log K* value of the resulting reactions will be obtained by linearly combining the *log K* values of the redox reactions involving Cr(III) and Cr(VI) aqueous species with those described above.

- "Incorporate all tabulated corrections of *log K* values in *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]) into the updated version of the *data0.ymp.R4* database file": The corrected values are tabulated in the database qualification report *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]). The update will involve transcribing the corrected values in the report in the data blocks within the thermodynamic data file used by EQ3/6. These corrected *log K* values are also available in DTN: SN0410T0510404.001.

- "Update temperature-dependent Pitzer parameter data for $Mg(NO_3)_2$, $NaNO_3$, and $Ca(NO_3)_2$": The Pitzer parameters for $Mg(NO_3)_2$, $NaNO_3$, and $Ca(NO_3)_2$ will be updated using the recent parameter data published in data analyses by Rard et al. (2004 [DIRS 173816]) and Wijesinghe and Rard (2005 [DIRS 176847]). This will involve transcribing the temperature-dependent Pitzer parameter coefficient data if it coincides with the function used by the computer software package EQ3/6. If this is not the case, the parameters will be refitted to the temperature-dependent function in EQ3/6. This could be done using off-the-shelf commercial software such as Excel or Mathematica.

Planned approaches to assess the issues delineated in Section 1.2.3 in accordance with the above-mentioned technical methods are as follows:

- Qualification of Oak Ridge National Laboratory Isopiestic Data: As described in Section 1.2.3, ORNL conducted experiments to obtain high-temperature isopiestic data for the system $Ca(NO_3)_2$-KNO_3- $NaNO_3$-H_2O. The quality assurance (QA) program followed to conduct this activity was that of ORNL, and all records and data produced as a result of this activity needs to comply with OCRWM QA procedures. Therefore, prior to beginning any data evaluation activity, all records and data must be compliant under OCRWM QA procedures. Pertinent activities to determine the evaluation approaches of the experimental isopiestic data to obtain the necessary Pitzer parameters for the chemical system of interest will begin once QA compliance is established and all relevant data can be retrieved through the TDMS. Data evaluation activities will include assessments of the experimental data collection, including calibrations and standards according to the experimental method, analysis of the experimental data treatments (if any) such as corrections and statistical examinations, and comparisons of these data sets with others if similar data is available in the scientific literature. This last activity would allow for the identification of data gaps, for example, with respect to temperature and salt concentration. Applicability of these approaches will depend on the nature of data available with respect to the compositional and physical variables considered for the retrieval of Pitzer parameter data. Isopiestic data will then be appropriately evaluated with Pitzer equations to extract parameter data as a function of temperature and ionic strength. This evaluation will be done using off-the-shelf commercial software such as Excel or Mathematica.

2.1.3 Data Collection, Reduction, and Recording Methodology

Collection of scientific data is restricted to acquisition of parameter values from the scientific literature. In particular, thermodynamic data to be collected from literature values is limited to those relevant for intended use and support of chemical models (see Section 2.1.1). There are no plans for obtaining data by carrying out experiments in this activity. However, experimental data generated as part of previous activities could be used once OCRWM QA compliance is established and the data is available through the TDMS. Therefore, data as a result of a testing task will not be collected in association with these activities.

2.1.4 Unexpected Test Results, Test Conditions, or Off-Normal Event Occurrence

The work scope described by this TWP includes no scientific testing activities.

2.1.5 Features, Events, and Processes

No screening argument for features, events, and processes (FEPs) is directly associated with this work

2.2 ADDITIONAL MODELING AND SCIENTIFIC ANALYSIS ACTIVITIES

Model validation activities are N/A because the work described in this TWP constitutes a scientific analysis activity. The work does not involve model development.

2.2.1 Schedule of Review Sessions

The Responsible Manager will schedule separate meetings to review quality issues pertaining to the scientific analysis reports with (a) the report Originator prior to starting the work, (b) the Checker prior to the document going into checking, and (c) the Independent Technical Reviewer before or concurrent with checking. Section 8.3 has more detail on the content and purpose of these meetings.

3. INDUSTRY STANDARDS, FEDERAL REGULATIONS, DOE ORDERS, REQUIREMENTS, AND ACCEPTANCE/COMPLETION CRITERIA

This section discusses applicable standards, criteria from *Yucca Mountain Review Plan, Final Report* (YMRP) (NRC 2003 [DIRS 163274]), level of accuracy of activity results, acceptance criteria, and other requirements as they apply to the scientific analysis reports described in this TWP.

3.1 STANDARDS

There are no industry or technical standards applicable to this work.

3.2 REGULATORY REQUIREMENTS

The applicable federal regulations and technical requirements related to the work activities associated with this TWP are generally implemented through the appropriate implementing procedures identified in Section 4. In particular, the requirements identified in 10 CFR 63.114 (a), (b), (c), and (g) are implemented through procedures LP-SIII.9Q-BSC and LP-SIII.10Q-BSC. There are no U.S. Department of Energy (DOE) orders applicable to the scope of work identified in this TWP.

The YMRP acceptance criteria that will be addressed by the reports documenting the updates to the two thermodynamic databases are provided below.

Quantity and Chemistry of Water Contacting Waste Packages and Waste Forms (NRC 2003 [DIRS 163274], Section 2.2.1.3.3.3)—from 10 CFR 63.114(a)–(c) and (e)–(g):

- **Acceptance Criterion 1**—System Description and Model Integration Are Adequate:

  (5) Sufficient technical bases and justification are provided for total system performance assessment assumptions and approximations for modeling coupled thermal-hydrologic-mechanical-chemical effects on seepage and flow, the waste package chemical environment, and the chemical environment for radionuclide release. The effects of distribution of flow on the amount of water contacting the engineered barriers and waste forms are consistently addressed, in all relevant abstractions.

  (6) The expected ranges of environmental conditions within the waste package emplacement drifts, inside the breached waste packages, and contacting the waste forms and their evolution with time are identified.

  (12) Guidance in NUREG–1297 and NUREG-1298 (Altman et al. 1988 [DIRS 103597]; Altman et al. 1988 [DIRS 103750]), or other acceptable approaches, is followed.

- **Acceptance Criterion 2**—Data Are Sufficient for Model Justification:

  (1) Geological, hydrological, and geochemical values used in the license application are adequately justified. Adequate description of how the data were used, interpreted, and appropriately synthesized into the parameters is provided.

- **Acceptance Criterion 3**—Data Uncertainty Is Characterized and Propagated Through the Model Abstraction:

  (1) Models use parameter values, assumed ranges, probability distributions, and bounding assumptions that are technically defensible, reasonably account for

uncertainties and variabilities, and do not result in an under-representation of the risk estimate.

(2) Parameter values, assumed ranges, probability distributions, and bounding assumptions used in the total system performance assessment calculations of quantity and chemistry of water contacting engineered barriers and waste forms are technically defensible and reasonable, based on data from the Yucca Mountain region (e.g., results from large block and drift-scale heater and niche tests), and a combination of techniques that may include laboratory experiments, field measurements, natural analog research, and process-level modeling studies.

(3) Input values used in the total system performance assessment calculations of quantity and chemistry of water contacting engineered barriers (e.g., drip shield and waste package) are consistent with the initial and boundary conditions and the assumptions of the conceptual models and design concepts for the Yucca Mountain site. Correlations between input values are appropriately established in the U.S. Department of Energy total system performance assessment. Parameters used to define initial conditions, boundary conditions, and computational domain in sensitivity analyses involving coupled thermal-hydrologic-mechanical-chemical effects on seepage and flow, the waste package chemical environment, and the chemical environment for radionuclide release, are consistent with available data. Reasonable or conservative ranges of parameters or functional relations are established.

(4) Adequate representation of uncertainties in the characteristics of the natural system and engineered materials is provided in parameter development for conceptual models, process-level models, and alternative conceptual models. The U.S. Department of Energy may constrain these uncertainties using sensitivity analyses or conservative limits. For example, the U.S. Department of Energy demonstrates how parameters used to describe flow through the engineered barrier system bound the effects of backfill and excavation-induced changes.

Radionuclide Release Rates and Solubility Limits (NRC 2003 [DIRS 163274], Section 2.2.1.3.4.3)—from 10 CFR 63.114(a)–(c) and (e)–(g):

- **Acceptance Criterion 1**—System Description and Model Integration Are Adequate.

  (4) 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 thermal-hydrologic-mechanical-chemical processes;

  (8) Guidance in NUREG–1297 and NUREG–1298 (Altman et al. 1988 [DIRS 103597]; Altman et al. 1988 [DIRS 103750]), or other acceptable approaches for peer reviews and data qualification, is followed.

- **Acceptance Criterion 2**—Data Are Sufficient for Model Justification.

  (1) Geological, hydrological, and geochemical values used in the license application are adequately justified. Adequate description of how the data were used, interpreted, and appropriately synthesized into the parameters is provided.

- **Acceptance Criterion 3**—Data Uncertainty Is Characterized and Propagated Through the Model Abstraction.

  (1) Models use parameter values, assumed ranges, probability distributions, and bounding assumptions that are technically defensible, reasonably account for uncertainties and variabilities, and do not result in an under-representation of the risk estimate.

  (2) 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.

  (3) 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.

  (4) 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.

  (8) 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.

3.3 LEVEL OF ACCURACY, PRECISION, AND REPRESENTATIVENESS OF RESULTS

The reports generated from this work will state the level of accuracy, precision, and representativeness for the results of the analyses, and how these were determined. Each product developed for the activities in this work plan will be technically checked in accordance with the appropriate procedure. The procedures provide general guidelines for required accuracy and precision. The documentation of the inputs, assumptions, implementation and uncertainties will demonstrate confidence in the databases. The documentation of the uncertainties will be presented in Section 7 as required by LP-SIII.9Q-BSC, in ANL-WIS-GS-000003 and ANL-WIS-GS-000001.

In reducing thermodynamic data, especially from a tabulated database, it is important that the starting data often are not original measurements, rather are values calculated from measurements. The ability to create a compact database from data in standardized form and then use this for a wide range of applications is one of the great powers of thermodynamics. Typically, there is some variation in the types of tabulated data, but standard Gibbs free energies of formation, standard enthalpies of formation, entropies, and heat capacities are most common. There are also data tabulations specific to log K values for reactions and to solubilities in simple chemical systems. Although tabulated solubilities are generally actual measurements, standard Gibbs free energies of formation, for example, are calculated. Unfortunately, the uncertainties that go with the data cannot generally be treated like the data. The uncertainty assigned to a tabulated value that is not a measurement reflects both the uncertainty in the original measured parameter and the uncertainties in any other parameters used to obtain the tabulated value. It may also reflect additional uncertainties in the use of thermodynamic models for solution behavior (e.g., ionic strength corrections). Not only do such models introduce additional parameters with their own uncertainties, but also the approximate nature of such models may add additional uncertainty. Also, failing to recognize how uncertainties are correlated, a much larger uncertainty than the one actually associated with the measurement could be calculated. Much tabulation of thermodynamic data, particularly Gibbs free energies, does not include associated uncertainties. Furthermore, estimates of uncertainties in thermodynamic data often do not take a standard form such as the standard deviation. Even when replicates are used, it can be difficult to calculate a standard deviation with any statistical rigor. Apparent bounds or an informally defined scale of measurement are the approaches most likely to be encountered.

A common approach to characterizing uncertainty in thermodynamic data is to estimate uncertainty for classes of thermodynamic data that share commonality in type and method of best-tabulated log K values for complexation reactions, for example, tend to have an uncertainty of about 0.02 log unit or less, and many such values have an uncertainty within 0.1 log unit. As

Detailed in the sources of the log K's, the majority of log *K* values for actinide solids have nominal uncertainties in the neighborhood of plus or minus one log unit. For a detailed discussion of the treatment of uncertainties in thermodynamic data, we refer to the NEA guidelines on the subject (Wanner and Osthols 1999 [DIRS 159222]). The NEA-sponsored volumes on the thermodynamics of radionuclide elements (e.g., Grenthe et al. 1992 [DIRS 101671], on uranium; Silva et al. 1995 [DIRS 102087], on americium; OECD 2001

[DIRS 159027], on neptunium and plutonium) are excellent examples of expert treatment of thermodynamic data and uncertainties.

3.4 COMPLETION CRITERIA

Requirements allocated to the science activity from the Requirements Management System as per LP-2.15Q-BSC, were reviewed and all of the applicable requirements to this TWP are captured in the procedures located in Section 4. Other than the requirement to address acceptance criteria from *Yucca Mountain Review Plan, Final Report* (NRC 2003 [DIRS 163274]) that address 10 CFR Part 63 (see Section 3.2), the requirement to state any sections of the Code of Federal Regulations, key technical issues, and additional information is not applicable because none is identified. There are no U.S. Department of Energy orders directly addressed by the activities in this TWP that are not identified by contract or procedural interfaces.

This work will satisfy the requirements of AP-16.1Q, *Condition Reporting and Resolution*, to enable closure of the CRs identified in Section 1.2, and any other relevant CRs, which may be generated by the Corrective Action Program.

3.5 OTHER REQUIREMENTS

There are no requirements in engineering, performance assessments, or other source documents (e.g. engineering interface documents) that apply to this work.

4. IMPLEMENTING DOCUMENTS

The following procedures, as appropriate to individual tasks within the work packages, will be used to perform the work. The most recent applicable procedures will be used. Non-Q work will not be performed.

- AP-7.5Q, *Establishing Deliverable Acceptance Criteria and Submitting and Reviewing Deliverables*
- AP-16.1Q, *Condition Reporting and Resolution*
- AP-17.1Q, *Records Management*
- AP-SIII.3Q, *Submittal and Incorporation of Data to the Technical Data Management System*
- IT-PRO-0009, *Control of the Electronic Management of Information*
- IT-PRO-0011, *Software Management*
- LP-2.9Q-BSC, *Establishment and Verification of Required Education and Experience of Personnel*
- LP-2.29Q-BSC, *Planning For Science Activities*

- LP-3.15Q-BSC, *Managing Technical Product Inputs*
- LP-6.3Q-BSC, *Document Control*
- LP-SIII.2Q-BSC, *Qualification of Unqualified Data*
- LP-SIII.9Q-BSC, *Scientific Analyses*
- PA-PRO-0601, *Document Review*
- TQ-PRO-1001, *Personnel Training and Qualification.*

5. EQUIPMENT

The technical product of this activity will be prepared using project standard desktop computers. No field or laboratory work will be conducted as part of this plan. No calibration or other test equipment will be used.

6. RECORDS

Records generated as a result of implementing procedures listed in Section 4 will be collected and submitted to the Records Processing Center in accordance with AP-17.1Q.

7. QUALITY VERIFICATIONS

Any quality assurance verification, other than regularly scheduled audits and surveillances, is not required during the execution of the work package.

8. PREREQUISITES, SPECIAL CONTROLS, ENVIRONMENTAL CONDITIONS, PROCESSES, OR SKILLS

8.1 QARD REQUIREMENTS

The work scope described in this TWP was determined to be subject to the requirements in *Quality Assurance Requirements and Description* (QARD) (DOE 2006 [DIRS 176927]), since it involves the analysis of data to support performance assessment and is relevant to investigations of items or barriers in *Q-List* (BSC 2005 [DIRS 175539]).

8.2 NON-Q WORK

This TWP does not describe the conduct of non-Q activities.

8.3 PREREQUISITES

Administrative considerations, as appropriate, to complement the procedural requirements for doing this work include "time-out-for-quality" briefings. These include Near-Field Environment team management-facilitated discussion of upcoming activities and associated requirements at the following junctures:

1. Before starting work

- What procedures will be used, including revision and interim change notice? Are these expected to change during production?
- Who will be working on the change/revision? Do they have position descriptions, Verification of Education and Experience, and updated training?
- Is there an approved TWP and does it fit the task? Does it include data qualification or model validation?
- What software will be used? If baselined software will be used, an appropriate Software User Request must be presented to the Near-Field Environment team management prior to use.
- Is the Statement of Work clearly defined? Where?
- What CRs and items listed as To Be Verified will be addressed?
- Are there any outstanding CRs open?
- Which input data will be used? State differences from previous version.
- Does project scheduling accurately capture the work, with contingency for delays and time off, and with activities defined so they can be effectively statused? Author/checker should own the schedule from Day 1.
- Who will status the work?
- Have laboratory/subcontractor Subcontract Change Requests and Statements of Work been updated and approved?
- Have the Quality Engineer and publications support staff been notified of the schedule?

2. Before checking starts

- Check the Document Input Reference System for completion and unverified references.
- Provide copies of any sources not in the Technical Information Center.
- Is data qualification completed and documented?
- Are output document tracking numbers submitted to the TDMS?

3. Before review

    - Review list of action items to complete for final approval.
    - Identify the reviewers. To whom will comments be escalated?
    - Have appropriate review criteria been developed? Will output data be included in the review?
    - Who is the Review Coordinator, and what is the schedule for completion of the review?

4. Before a concurrence draft is circulated

    - Have all comments been responded to with responses from the reviewers?
    - Are there any unresolved issues, and have they been escalated?
    - Are there changes in output since checking?
    - Prepare itemized responses for changes.
    - Have any references been superseded since checking?

5. At approval

    - Check that procedures are the same versions in effect at start.
    - Check for To Be Verified items in the Document Input Reference System (there should be none).

8.4 IT-PRO-0009 (QARD SUPPLEMENT V) REQUIREMENTS

A process control evaluation for work activities under this TWP was conducted and documented in accordance with IT-PRO-0009 through the use of the IT-PRO-0009 Attachment 3 checklist. As a result, the following methods will be used for the control of electronic management of information:

1. Upon completion of work activities, QA and non-QA records will be submitted to the Records Processing Center (RPC) in accordance with applicable implementing procedures. These records will be retained, protected, and dispositioned in accordance with the requirements of LP-6.3Q-BSC.

2. During the conduct of work activities, electronic information will be backed up and readily available on network drives. Reports will be available in InfoWorks with restricted write privileges. Data are maintained and available in the TDMS and/or Record Information System. Electronic information on personal computers and on network drives can be retrieved instantly.

3. The model reports, data, and software are retained on network drives. Electronic information that may be stored on password-protected personal computers during the conduct of work activities will be retained until the QA and non-QA information associated with the work activity becomes part of the records system. Information on personal computers will be backed up on network drives.

4. Electronic information that may be stored on hard drives on password-protected personal computers will be transferred to the RPC on compact disks. Disks and all other removable backup media will be labeled with the following: generating program, originator, date, document number, and content description. This information will be retained on the password-protected personal computers until confirmation by the RPC that the information has become part of the record system.

5. Completeness and accuracy of the input information is assured through compliance with the checking, quality engineering review, and technical review requirements of the procedure controlling the work activity (e.g., LP-SIII.9Q-BSC). Changes to this information will be made in accordance with the revision requirements in that procedure.

6. Security and integrity of the electronic information developed during the work activity are maintained by storing the information on network drives and on hard drives of password-protected personal computers, and by limiting write-access. After transfer to the RPC and TDMS, integrity is maintained by RPC access controls.

7. Minimization of errors resulting from the transfer of electronic information from one media to another will be accomplished through originator review of the transferred information prior to transmittal. Developed data submitted to the TDMS will be checked for consistency in accordance with TDMS procedures.

8.5 ENVIRONMENTAL CONTROLS

The analytical work will be performed mainly at SNL and the Bechtel SAIC Company, LLC, Summerlin office complex. Thus, Special environmental conditions are not required.

8.6 TRAINING/QUALIFICATION

Training requirements will be established in the Licensing and Nuclear Safety Group training matrix and administered for compliance by the same. If the staff member is affiliated with one of the national laboratories providing support for this work scope (SNL), his or her training requirements are established by that national laboratory in accordance with the laboratory's contract to Bechtel SAIC Company, LLC. Compliance with the training requirements will be met through the contractual mechanisms associated with the contract. Additionally, personnel performing the work activity are subject to verification of education and experience in accordance with LP-2.9Q-BSC.

9. SOFTWARE

Off-the-shelf commercial software to be used in this work scope includes Microsoft Word, Microsoft Excel, and Mathematica (Wolfram Research), and will be used with Microsoft Windows 2000 Professional Edition. Microsoft Word will be used to edit and modify the documents, while Excel and Mathematica will be used for data evaluation, calculations, graphing, and summarizing model output data in spreadsheets. Use of the off-the-shelf commercial software will be conducted on project-standard desktop and laptop computers. The main desktop platform to be used is a Dell Optiplex GX260 (R437068), and a Dell Latitude laptop (R404820) will be used.

The qualified software to be used in these activities is listed below (Table 2). The reaction-path chemical speciation computer software package EQ3/6 V8.1 will be used for evaluation of thermodynamic parameters by computing solubilities as a function of temperature and ionic strength where applicable. Data will be extracted from the EQ3/6 output files using the post-processor GetEQData V1.0.1. SUPCRT92 V1.0 could be considered for use in this effort for calculation of thermodynamic parameters regarding data evaluation. However, the planned use of this software is not definite and will be determined by the needs of this activity.

The use of continuous-use software is not planned in this report.

Table 2. Use of Qualified Software

Software Name and Version	Software Tracking Number
EQ3/6 V.8.1	10813-8.1-00
GetEQData V1.0.1	10809-1.0.1-00
SUPCRT92 V1.0	10058-1.0-00

10. ORGANIZATIONAL INTERFACES

The work scope identified in this TWP is being performed by the Near-Field Environment team. The Near-Field Environment team is in the Post Closure Activities department, part of the Licensing and Nuclear Safety organization. The Near-Field Environment team has the responsibility to conduct analyses and simulations, evaluate the results, and revise the report accordingly. The two data qualification reports *Pitzer Database Expansion to Include Actinides and Transition Metal Species (data0.ypf.R1)* (BSC 2005 [DIRS 174223]) and *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]) generate the thermodynamic databases (to be named *data0.ypf.R1 and* data0.ymp.R5*)* for use with the computer software package EQ3/6. Technical exchanges will involve interfacing with other departments that are part of the Licensing and Nuclear Safety organization, such as Criticality in the Licensing and Analysis department, and TSPA in the Performance Assessment department. Analysis and model reports that are directly downstream of these reports and thermodynamic databases are as follows (broken down by organization):

Near-Field Environment:

ANL-EBS-MD-000045 Rev 02: *In-Drift Precipitates/Salts Model* (BSC 2004 [DIRS 169863])

ANL-EBS-MD-000074 Rev 01: *Analysis of Dust Deliquescence for FEP Screening* (BSC 2005 [DIRS 175058])

ANL-EBS-GS-000002 Rev 00: *Geochemistry Model Validation Report: External Accumulation Model* (BSC 2001 [DIRS 156324])

ANL-EBS-MD-000033 Rev 05: *Engineered Barrier System: Physical and Chemical Environment* (BSC 2005 [DIRS 175083]),

Engineered Systems:

In-Package Chemistry Abstraction (BSC 2005 [DIRS 174583])

Dissolved Concentration Limits of Radioactive Elements (BSC 2005 [DIRS 174566]),

Criticality:

Geochemistry Model Validation Report: Material Degradation and Release Model (BSC 2001 [DIRS 156790])

Licensing and Nuclear Safety:

Sections 2.3.5 and 2.3.7 of the LA Safety Analysis Report

The data qualification report *Qualification of Thermodynamic Data for Geochemical Modeling of Mineral-Water Interactions in Dilute Systems* (BSC 2005 [DIRS 171916]) uses data obtained from the following upstream report:

Near-Field Environment:

ANL-NBS-HS-000043 Rev 00: *Data Qualification for Thermodynamic Data Used to Support THC Calculations* (BSC 2004 [DIRS 170268])

11. PROCUREMENT

Procurement activities are not associated with the work scope of this TWP.

12. REFERENCES

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