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SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

AP-170
Revision 0

Analysis Plan for Migration of PHREEQCI Version 2.12.5-669 to PHREEQC Version 3.0 and Comparison of the NEA SIT Model with Pitzer Model for Actinide Chemistry

Task 4.4.1.1.1

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1 Introduction and Objectives

1.1 Introduction

The Waste Isolation Pilot Plant (WIPP) used the Fracture-Matrix Transport (FMT) code (Novak, 1996, ERMS# 210790; see also Babb and Novak, 1995; Babb and Novak, 1997 and addenda; Wang, 1998) for modeling geochemical interactions in the WIPP repository. The WIPP employed the FMT code for calculations for the Compliance Certification Application in 1996 (CCA-1996) (US DOE, 1996), the Compliance Re-certification Application Performance Assessment in 2004 (CRA-2004 PA) (US DOE, 2004), and the Compliance Re-certification Application Performance Assessment in 2009 (CRA-2009 PA) (US DOE, 2009), and the associated calculations for CCA Performance Assessment Verification Test (CCA-PAVT), CRA-2004 Performance Assessment Baseline Calculations (CRA-2004 PABC), and CRA-2009 Performance Assessment Baseline Calculations (CRA-2009 PABC).

The FMT code was migrated to the EQ3/6 platform under EQ3/6 Version 8.0a, and qualified under the WIPP QA program (Wolery et al., 2010; Xiong, 2011a). On September 27, 2011, US EPA approved the migration of the FMT code to EQ3/6 Version 8.0a for WIPP compliance recertification calculations (US EPA, 2011).

The geochemistry part of the FMT and one subroutine of its successor, EQ3/6 Version 8.0a, uses Pitzer's (1973, 1975, 1991) equations to represent the thermodynamic activity coefficients of aqueous species including both solutes and the solvent, water. The standard form of the Pitzer equations is based on molalities and requires data for interaction parameters for pairs and triplets of the solute species included in the model.

The Nuclear Energy Agency (NEA) uses the Specific Ion Interaction Theory (SIT) model for calculation of activity coefficients of aqueous species to systematically evaluate thermodynamic data on the chemical elements relevant to nuclear waste management (i.e., Gamsjäger et al., 2005; 2012). For the background of the SIT model, please refer to Xiong (2006).

The software, PHREEQC Version 3.0 (Parkhurst and Appelo, 2013), is compatible with the SIT model. Under the WIPP QA, a previous version of PHREEQC, PHREEQCI Version 2.12.5-669 (Charlton and Parkhurst, 2002), was qualified for the WIPP use.

The purpose of this Analysis Plan (AP) is two-fold. The first part is to qualify the migration from PHREEQCI Version 2.12.5-669 to PHREEQC Version 3.0. After the separate qualification of the SIT model of PHREEQC Version 3.0 under NP 19-1, the second part is to compare the SIT model with the Pitzer model, side by side, for the same experimental solubility data. This is a programmatic decision.

1.2 Objectives

The objective is to use the qualified PHREEQC Version 3.0 to compare the SIT model with the Pitzer model for the well-defined experimental data, primarily on actinides. A specific objective is to test, head-to-head in WIPP-relevant application, the WIPP thermodynamic model with

EQ3/6 using the Pitzer model against the NEA database with PHREEQC Version 3.0 using the SIT model. This will serve to alleviate any potential concerns about the adequacy of the WIPP thermodynamic model. An additional objective is to include this documentation in revisions of the relevant qualification documents for the previous version. The understanding here is that the software, PHREEQC, which is already qualified, is not being re-qualified. Rather, the documented basis of the qualification is for migration to a higher version, and is being extended for confidence-building.

2 Approach

To achieve the objective of this AP well-defined experimental data will be used to compare with the values predicted by the SIT model with PHREEQC Version 3.0 and by the Pitzer model with EQ3/6 Version 8.0a.

2.1 Test Cases for Migration from PHREEQCI Version 2.12.5-669 to PHREEQC Version 3.0

The test suite from the PHREEQCI Version 2.12.5-669 is utilized to validate the migration from PHREEQCI Version 2.12.5-669 to PHREEQC Version 3.0. The test suite is summarized in Table 1.

Table 1. Summary of Test Cases for Version Migration

#	Name	File Name	Description
1	T1	ex1_dat	Speciation of uranium in seawater
2	T2	ex5_dat	Oxidation of pyrite
3	E1	bo3bufs	Simple speciation of borate pH buffers
4	E2	oxcalhem	Speciation with redox of calcite and hematite in oxygenated waters
5	E3	microhcl	Speciation with emphasis on SI, Microcline in dilute HCl
6	E4	j13wa	Speciation of J13 well water
7	E5	j13wsf	Speciation of J13 well water with actinides in irreversible reaction (degradation of waste package)
8	E6	pquartz	Kinetics of quartz precipitation
9	E7	sr2	Precipitation of solid solutions
10	A1	fractadv	Simple advection of a conservative tracer
11	A2	fractadvdisp_1	Simple advection-diffusion of a conservative tracer
12	A3	ard	Advection-diffusion of reactive tracer (ion exchange)
13	A4	surf3	Advection-diffusion of reactive tracer (surface sorption)
14	H1	invmod	Inverse modeling to determine solid phase balance including isotopic data
15	M1	mixtest_s	Replacement of resident water with an influent water and mixing with a third water
16		iso13c	Vapor-liquid equilibrium with stable and radioactive isotopes – carbon species in soil pore water
17		c22bv	Flow-through reaction path with equilibration with waste package materials and CSNF

All of the above test cases in Table 1 will be regression tested by running PHREEQC Version 3.0 and comparing its outputs with the corresponding outputs from the validation of PHREEQCI Version 2.12.5-669.

2.2 Test Cases for the SIT Model in PHREEQC Version 3.0

The SIT model for the PHREEQC Version 3.0 will be tested for the following test cases using the default SIT database, SIT.DAT, distributed along with the PHREEQC Version 3.0. If necessary, the database will be modified with the required parameters from the literature needed for the specific tests. As the SIT model is valid usually to 3.5 mol•kg^{-1}, the tests will not go beyond 4.0 mol•kg^{-1} at most.

The test cases listed in Table 2 are designed to validate the SIT model in PHREEQC Version 3.0. The SIT interaction parameters with high precision evaluated from experimental data by Xiong (2006) will be incorporated into the SIT.DAT database. Then, a series of runs will be performed. The activity coefficients for a specific solution output by PHREEQC Version 3.0 will be compared with the activity coefficients hand-calculated with the same SIT interaction parameters.

Table 2. Summary of Test Cases for the SIT Model in PHREEQC Version 3.0

#	Name	File Name	Description
18	SIT1	SITHCl	Activity coefficients of HCl to I = 4.0 mol•kg^{-1}
19	SIT2	SITNaCl	Activity coefficients of NaCl to I = 4.0 mol•kg^{-1}
20	SIT3	SITMgCl2	Activity coefficients of $MgCl_2$ to I = 4.0 mol•kg^{-1}
21	SIT4	SITCaCl2	Activity coefficients of $CaCl_2$ to I = 4.0 mol•kg^{-1}
22	SIT5	SITEuCl3	Activity coefficients of $EuCl_3$ to I = 4.0 mol•kg^{-1}
23	SIT7	SITSmCl3	Activity coefficients of $SmCl_3$ to I = 4.0 mol•kg^{-1}
24	SIT6	SITKOH	Activity coefficients of KOH to I = 4.0 mol•kg^{-1}
25	SIT8	SITNaAc	Activity coefficients of NaAc to I = 4.0 mol•kg^{-1}

2.3 Comparing Results: Pitzer Model with EQ3/6 8.0a vs. SIT Model with PHREEQC 3.0

This set of test cases for the head-to-head comparisons is not designed for qualification tests. Instead, they serve as benchmark test cases for comparing the two activity coefficient models (i.e., SIT and Pitzer models) in reproducing experimental solubility data. The intent of these test cases is to show which model can more accurately reproduce the experimental data. As the Pitzer model is valid to much higher ionic strengths, the head-to-head tests will be limited the ionic strength range valid to the SIT model. Once the benchmark test cases are established, other tests can be made in any other publications when necessary.

The test cases in this suite are summarized in Table 3. The first test case in this suite is to calculate gypsum ($CaSO_4$•$2H_2O$) solubilities at 25°C as a function of ionic strength in NaCl solutions up to 4.0 mol•kg^{-1}. Then, the solubilities predicted by the SIT model in PHREEQC Version 3.0 and by the Pitzer model in EQ3/6 Version 8.0a will be compared with the experimental data to evaluate their respective accuracies with regard to the experimental data.

The second test case in this suite is to calculate brucite [$Mg(OH)_2$] solubilities at 25°C as a function of pmH/pH_m (negative logarithm of hydrogen ion concentration on a molal scale, i.e., $pmH / pH_m = -\log m_{H^+}$) in a 3.2 mol•kg^{-1} NaCl solution. Then, the solubilities predicted by the SIT model in PHREEQC Version 3.0 and by the Pitzer model in EQ3/6 Version 8.0a will be compared with the experimental data from Xiong (2008) to evaluate their respective accuracies with respect to the experimental data.

The third test case in this suite is to calculate hydromagnesite [$Mg_5(CO_3)_5(OH)_2$•$4H_2O$] solubilities at 25°C as a function of pmH/pH_m at f_{CO_2} = $10^{-3.4}$ atm in a 3.2 mol•kg^{-1} NaCl solution. Then, the solubilities predicted by the SIT model in PHREEQC Version 3.0 and by the Pitzer model in EQ3/6 Version 8.0a will be compared with the experimental data from Xiong (2011b) to evaluate their respective accuracies with respect to the experimental data.

The fourth test case in this suite is to calculate solubilities of $NaAm(CO_3)_2$·$6H_2O$/$NaAm(CO_3)_2$·$5H_2O$ in Na_2CO_3 and $NaHCO_3$ solutions at 25°C. Then, the solubilities predicted by the SIT model in PHREEQC Version 3.0 and by the Pitzer model in EQ3/6 Version 8.0a will be compared with the experimental data to evaluate their respective accuracies with respect to the experimental data.

The fifth test case in this suite is to calculate solubilities of ThO_2(am) as a function of pmH/pH_m in a 3.2 mol•kg^{-1} NaCl solution at 25°C. Then, the solubilities predicted by the SIT model in PHREEQC Version 3.0 and by the Pitzer model in EQ3/6 Version 8.0a will be compared with the experimental data to evaluate their respective accuracies with respect to the experimental data.

The sixth test case in this suite is to calculate solubilities of hydrated NpO_2OH(am) as a function of pmH up to 10 in a 3.2 mol•kg^{-1} $NaClO_4$ solution at 25°C. Then, the solubilities predicted by the SIT model in PHREEQC Version 3.0 and by the Pitzer model in EQ3/6 Version 8.0a will be compared with the experimental data to evaluate their respective accuracies with respect to the experimental data.

Table 3. Summary of Test Cases for the Head-to-Head Comparisons for SIT Model in PHREEQC Version 3.0 the Pitzer Model in EQ3/6 Version 8.0a in Reproducing Experimental Solubility Data

#	Name	File Name	Description
26	SIT_Pit1	GYPSUM.*	Solubility of gypsum in NaCl to I = 4.0 mol•kg^{-1}
27	SIT_Pit2	BRUCITE.*	Solubility of brucite as a function of pmH in NaCl at I = 3.2 mol•kg^{-1}
28	SIT_Pit3	HYDROMAG.*	Solubility of hydromagnesite(5424) as a function of pmH in NaCl at I = 3.2 mol•kg^{-1}
29	SIT_Pit4	NaAmCO3	Solubility of $NaAm(CO_3)_2$·$6H_2O$/$NaAm(CO_3)_2$·$5H_2O$ in Na_2CO_3 and $NaHCO_3$ solutions
30	SIT_Pit5	ThO2_am	Solubility of ThO_2(am) as a function of pmH in NaCl at I = 3.2 mol•kg^{-1}
31	SIT_Pit6	NpO2OH	Solubility of NpO_2OH(am) as a function of pmH in $NaClO_4$ at I = 3.2 mol•kg^{-1}

3 Software List

The WIPP codes to be used for this analysis are listed in Table 4. These codes will be used for comparative calculations for the qualification of the migration from PHREEQCI Version 2.12.5-669 to PHREEQC Version 3.0, and for the qualification of the SIT model in PHREEQC Version 3.0, as described above in Section 2. These codes will be executed on the machines listed in Table 5. Commercial off-the-shelf (COTS) software such as MATHEMATICA®, MATLAB®, MathCAD®, Excel®, Visio®, CorelDRAW®, Corel Paint Shop Pro X®, or Origin®, running on MS Windows 7- and 10-based PC workstations may also be utilized. The use of any COTS application for routine calculations will be justified per NP 9-1, Appendix C and NP 19-1 as appropriate.

Table 4. Codes to be used for this Analysis Plan (AP)

Code	Version	Use
EQ3/6*	8.0a	Software comparison
PHREEQC*	3.0	Version migration and Software comparison

* - Qualified

Table 5. Platforms to be used for this Analysis Plan (AP)

Platform Description	ID Number	Operating System	Location	User(s)
Dell Precision Workstation T3600	S952878	MS Window 7®	SNL, Carlsbad	Xiong
Dell Precision Workstation T3500	S923775	MS Window 7®	SNL, Tijeras	Domski

In addition, the Python minimization script tested under the execution platform of EPD Python 2.7.2, where EPD stands for Enthought Python Distribution, is also available for use.

4 Tasks

The tasks of this AP are listed below, and milestones for each task are tabulated in Table 6:

Table 6. Milestones for each individual task

Task	Description	Responsible Individuals	Estimated Completion Date
1	*Qualification of PHREEQC Version 3.0 under NP 19-1:* Regression tests for migration from PHREEQCI Version 2.12.5-669 to PHREEQC Version 3.0 under Subsection 2.1	Domski, Xiong	12/31/2016
2	Head-to-head comparison tests for the SIT model in PHREEQC Version 3.0 and the Pitzer model in EQ3/6 Version 8.0a under Subsection 2.3	Xiong, Domski	05/31/2017
3	Complete Summary Report Deliverable (regarding NP 19-1)	Xiong, Domski	06/30/2017

Paul Domski will do the official runs for the head-to-head comparison tests.

5 Special Considerations

No special considerations have been identified.

6 Applicable Procedures

All applicable WIPP QA procedures will be followed when conducting this AP.

- Training of personnel will be conducted in accordance with the requirements of NP 2-1, *Qualification and Training*.
- Analyses will be conducted and documented in accordance with the requirements of NP 9-1, *Analyses*.
- All software used will meet the requirements laid out in NP 19-1, *Software Requirements* and NP 9-1, as applicable.
- The analyses will be reviewed following NP 6-1, *Document Review Process*.
- All required records will be submitted to the WIPP Records Center in accordance with NP 17-1, *Records*.
- NP19-1, *Software Requirements.*

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