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SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

AP-173
Revision 1

Analysis Plan for the Compilation and Testing of Selected Parameters from AP-134, Revision 3, AP-154, Revision 2 and AP-155, Revision 3 for Incorporation in a New QA EQ3/6 Thermodynamic Database

Task 4.4.2.2.1

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1 *Introduction and Objectives*

1.1 Introduction

This analysis plan guides the addition of thermodynamic parameters to a current quality assured EQ3/6 thermodynamic database with the ultimate creation of a new QA EQ3/6 thermodynamic database. The motivation behind creation of this database is to address EPA comments regarding the adequacy of the EQ3/6 database with regard to PABC 2014. Due to the timing of the completion of the tasks under TP 08-02, TP 10-01, AP-154, and AP-155 it will be not possible to include all of the chemical species' thermodynamic parameters outlined in those documents. In addition to the parameters derived under AP-154 and AP-155, the thermodynamic parameters for the dissolution of hydromagnesite (Xiong, 2010b and Xiong, 2015), the speciation of americium - EDTA complexes (Xiong, 2013c), and the speciation of americium – borate complex (Xiong, 2010c) will also be included. Therefore, this analysis plan provides a list of the parameters to be included, and a method to QA them for inclusion in a new QA database. This analysis plan, as per NP 9-1, is considered a compliance decision analysis.

1.2 Objectives

The objective of this analysis plan is to create one verified QA EQ3/6 thermodynamic database which will include parameters derived under AP-154 and AP-155 by using the currently verified QA EQ3/6 thermodynamic database, DATA0.FMT.R2, also known as DATA0.FM1 (Xiong, 2011c) as the starting database. The new QA database resulting from this analysis plan will be called DATA0.FM2.

2 Approach

This AP outlines the procedure for the creation of a single QA EQ3/6 thermodynamic database, which will be built on a previous QA database, DATA0.FM1. The general procedure in the creation of this QA database includes the compilation and testing of an interim database, and final QA approval of the database. Below are described the methods for database creation using the data derived under AP-154 and AP-155.

Testing of the preliminary database will consist of running the Python scripts from specific AP-154 and AP-155 tasks to insure consistency of the derived parameters. If discrepancies are encountered during testing, then the parameters derived under AP-154 or AP-155 may need to be reevaluated and the pertinent documentation revised.

It is the intent of this analysis plan that the parameters that will be included in this new database will include the lead inorganic and organic complexes from AP-154, Revision 2, and the borate complexes from AP-155, Revision 3. However, a subset of the lead and borate parameters may not be included in the QA database because of time constraints. The iron complexes will not be included because the iron related tasks under AP-154, Revision 2 are not complete at this time. A listing of the proposed parameters from AP-154 and AP-155 to be included DATA0.FM2 may be found in Table 1.

Table 1. Parameters to be included in DATA0.FM2.

AP	Task	Description
154	14	Pitzer binary interaction parameter of $PbCl^+$—HCO_3^-
154	15	Pitzer binary interaction parameter of $PbCl^+$—CO_3^{2-}
154	18	Pitzer binary interaction parameter of Na^+— $PbEDTA^{2-}$
154	19	Pitzer binary interaction parameter of Mg^{2+}— $PbEDTA^{2-}$
154	20	Pitzer binary interaction parameter of Na^+— $PbCit^-$
154	21	Pitzer binary interaction parameter of Mg^{2+}— $PbCit^-$
154	23	Pitzer λ parameter of Mg^{2+}— PbOx(aq)
154	24	Pitzer λ parameter of Cl^-— PbOx(aq)
154	28	Pitzer binary interaction parameter of Na^+—$CaCit^-$
154	29	Pitzer binary interaction parameter of Na^+—$HEDTA^{3-}$
154	30	Pitzer binary interaction parameter of Mg^{2+}—$HEDTA^{3-}$
154	31	Determination of solubility constant of di-calcium ethylenediaminetetraacetic acid (Ca_2EDTA), $Ca_2C_{10}H_{12}N_2O_8$(s)
154	32	Pitzer λ parameter of Na^+ — CaOxalate(aq) Pitzer λ parameter of Mg^{2+} — CaOx(aq)
154	35	Pitzer binary interaction parameter Mg^{2+}—$CaCit^-$
155	3	Determination of formation constant PbB_4O_7(aq)
155	4.1	Pitzer binary interaction parameter of $PbB(OH)_4^+$—Cl^-
155	4.2	Pitzer binary interaction parameter of $PbB(OH)_4^+$—SO_4^{2-}
155	4.3	Pitzer binary interaction parameter of Na^+— $Pb[B(OH)_4]_3^-$
155	4.4	Pitzer binary interaction parameter of Mg^{2+}— $Pb[B(OH)_4]_3^-$
155	4.5	Pitzer binary interaction parameter of $MgB(OH)_4^+$—SO_4^{2-}
155	4.7	Pitzer λ parameter of Na^+— $NaB(OH)_4$(aq)
155	4.6	Pitzer binary interaction parameter of $CaB(OH)_4^+$—SO_4^{2-}
155	4.8	Pitzer λ parameter of Mg^{2+}— $NaB(OH)_4$(aq)
155	4.9	Derivation of Pitzer ξ of $NaB(OH)_4$(aq) with NaCl + $MgCl_2$
155	4.10	Derivation of Pitzer λ of Na^+ - PbB_4O_7(aq)
155	4.11	Derivation of Pitzer λ of Mg^{2+} - PbB_4O_7(aq)
155	4.12	Derivation of Pitzer ξ of PbB_4O_7(aq) with NaCl + $MgCl_2$

* Notice that the parameters listed were those proposed when the test plans (TP) were written, and some of them may not necessarily be the parameters that would best describe the respective systems in modeling. Under such circumstances, the parameters that best describe the respective systems will be presented.

Table 2 provides the parameters that are not covered under AP-154 or AP-155 that will be included in the DATA0.FM2 database.

Table 2. Additional parameters to be included in DATA0.FM2.

Description	Reference
Hydromagnesite (5424) Log K_{sp}	Xiong 2010b and 2015
Pitzer binary interaction parameter Na^+ - $Am(EDTA)^-$	Xiong 2013c
Pitzer binary interaction parameter $AmHB_4O_7^{2+}$ - Cl^- $4B(OH)_4^- + 3H^+ + Am^{3+} = AmHB_4O_7^{2+} + 9H_2O(l)$	This AP

It should be noted that when Borkowski et al. (2010) (also see Xiong, 2010c) presented the stability constant (log β_1) for the following reaction,

$$Am^{3+} + HB_4O_7^- = AmHB_4O_7^{2+} \quad (1)$$

it was based on the following speciation scheme for boron species: $H_2B_4O_7(aq)$, $HB_4O_7^-$ and $B_4O_7^{2-}$. That speciation scheme is different from that in the WIPP thermodynamic database, which is $B(OH)_3(aq)$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, and $B_4O_5(OH)_4^{2-}$. Therefore, the stability constant proposed by Borkowski et al. (2010) cannot be directly employed in the WIPP thermodynamic database. Consequently, the raw data presented in Borkowski et al. (2010) are modelled according to the following reaction,

$$4B(OH)_4^- + 3H^+ + Am^{3+} = AmHB_4O_7^{2+} + 9H_2O(l) \quad (2)$$

in order that it be consistent with the WIPP thermodynamic database. The derivation of thermodynamic parameters for $AmHB_4O_7^{2+}$ will follow the methods outlined in AP-154 and AP-155 via the use of the Python script EQ3CodeModule.py.

2.1 Software List

The software to be used is EQ3/6 Version 8.0a (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011b), and DATA0.FM1 (Xiong, 2011a). In addition, off the shelf software such as Microsoft Excel, and the Excel macro *GetEQData_v101f.xls* will be used to extract data from the EQ3/6 output files, and the open source text editor Notepad++ may be used to edit the preliminary and final databases.

2.2 Acceptance Criteria

During the testing phases of the preliminary and interim databases comparisons between fitted parameters and EQ3/6 output will be made in Microsoft Excel. Parameters and simulation output will be considered acceptable if they are they agree in the first three significant figures, i.e., variation in the third and greater significant figures will be considered acceptable.

3 Tasks

There is one task under this AP, which will result in the creation of a QA thermodynamic database. The subtasks for this task includes the creation of a preliminary database, testing of the preliminary database, evaluation of the test results, evaluation of errors and re-testing as necessary, and issuance of the final QA database(s). The final QA databases will be documented in an analysis report which will accompany the issuance of the QA database, DATA0.FM2.

Table 3 lists the task, database name, and completion date for AP-173.

Table 3. Task list and completion date.

Task	Database	Completion Date
1	DATA0.FM2	09/01/2015

Paul Domski will be the primary analyst performing the tasks under this AP, estimated dates for completion are contingent upon the completion of the tasks under AP-154 and AP-155. Therefore, it is expected that the final QA databases will be complete, a memo of notification will be issued to users, and the final database will be submitted to WIPP records to be stored in the CVS under the Sun platform/Solaris OS with all accompanying documentation. Yongliang Xiong will be responsible for modeling the raw data of Borkowski et al. (2010) for the equilibrium constant and associated Pitzer parameters for Reaction (2). Yongliang Xiong will generate the EQ3/6 input files and Python script for modeling, and Paul Domski will perform the official confirmation run.

4 Special Considerations

Depending on the results of database testing, it may be necessary to revise documents submitted under AP-154 and AP-155.

5 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*.

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