IMPORTANT NOTICE: The current official version of this document is available via the Sandia National Laboratories WIPP Online Documents web site. A printed copy of this document may not be the version currently in effect.

SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

AP-176
Revision 0

Analysis Plan for the Development of a Self-Consistent Extension of the WIPP Geochemical Thermodynamic Database that Includes Aqueous Ferrous Iron Chemistry

Task 4.4.2.2.1

Effective Date: June 27, 2016

Authored by:	Je-Hun Jang	*Original signed by Jang, Je-Hun*	*6/27/2016*
	Print Name	Signature	Date
Authored by:	Paul Domski	*Original signed by Shelly R. Nielsen for*	*6-27-16*
	Print Name	Signature	Date
Reviewed by:	Sungtae Kim	*Original signed by Shelly R. Nielsen for*	*6-27-16*
	Print Name Technical Reviewer	Signature	Date
Reviewed by:	Shelly R. Nielsen	*Original signed by Shelly R. Nielsen*	*6-27-16*
	Print Name Quality Assurance Reviewer	Signature	Date
Approved by:	Christi D. Leigh	*Original signed by Christi Leigh*	*6-27-16*
	Print Name Department Manager	Signature	Date

© 2016 Sandia Corporation

Table of Contents

1. Introduction and Objectives **.... 3**

1.1 Introduction 3
1.2 Objectives 3

2 Approach **.... 3**

2.1 An Example of Interim Database.... 6
2.2 Extending the Interim Database in Self-Consistent Way.... 7
2.3 Example of Cross-Fitting over Multiple Experimental Sets: A Scenario 9
2.4 Evaluation of derived parameters for incomplete systems 11
2.5 Parameters to be derived.... 12
2.6 Software List 13
2.7 Acceptance Criteria.... 13

3 Tasks **.... 13**

4 Special Considerations **.... 14**

5 Applicable Procedures **.... 14**

6 References **.... 14**

1. Introduction and Objectives

1.1 Introduction

This analysis plan provides the methods used to fit the experimental data to attain reproducible thermodynamic and Pitzer parameters, and creation of a self-consistent new QA EQ3/6 thermodynamic database. The motivation behind creation of this database is to include the iron(II) system, which includes the major anionic species (hydroxide, chloride, sulfate, sulfide, carbonate, and borate), and organic species (oxalate, citrate, EDTA, and acetate), as well as solid phases.

This analysis plan, as per NP 9-1, is considered a compliance decision analysis.

1.2 Objectives

The objectives of this analysis plan are: 1) To provide a concise standard methodology to implement the fitting procedure used in determining thermodynamic and Pitzer parameters for inclusion in the database; 2) To facilitate a seamless workflow among analysts, including QA staffs; and ultimately 3) To create a single verified self-consistent QA EQ3/6 thermodynamic database which will include the ferrous iron system, Fe(II), - thermodynamic and Pitzer parameters derived under AP-154 and AP-155.

These objectives will be met by following the procedure outlined in the Approach section. The currently verified QA EQ3/6 thermodynamic database, DATA0.FM2, (Xiong and Domski, 2016) will be used as the starting database and by progressively adding and verifying the newly derived parameters interim databases will be created until all of the chemical systems listed in Table 6 are included. The new QA database resulting from this analysis plan will be called DATA0.FM4.

2 Approach

This AP outlines procedures for choosing and fitting thermodynamic and Pitzer parameters, and the creation of a single self-consistent extension of QA EQ3/6 thermodynamic database, which will be built on a previous QA database, DATA0.FM2. The general procedure is outlined below:

1. Define an experimental system with least number of components possible that adequately describes the system.
2. Construction of the interim database. Each task[1] starts with the construction of an interim database. Compile the data to be included in an interim database. This data consists of: (i) Reactions, both equilibrium mineral dissolution/precipitation and aqueous phase speciation reactions together with the base-10 logarithms of their equilibrium constants, and (ii) the Pitzer parameters of the related pairs/triplets of aqueous species. The logK values of

[1] "Task" refers to the tasks defined under AP-154 and AP-155, in some cases two tasks will be combined and fit simultaneously. Task numbers in the APs do not necessarily mean the order of data analysis.

reactions and Pitzer parameters to be included in the interim databases will be critically reviewed and selected from the literature and data0.fm2. Most favorable logK values would be those determined for zero ionic strength under the Pitzer formulation. If such values are not available, use of logK values determined for zero ionic strength under other activity coefficient equations is warrantied to begin with, and the logK values will be examined at Step 3. These data will be formatted in a manner consistent with the appropriate EQ3/6 database data blocks. The data blocks will then be implemented into a working database file that EQ3/6 can recognize and process. The interim database will be named in accordance with the EQ3/6 database naming standard, for example "data0.i01". The file extension "i01" means the interim database numbered 01. Analysts may use their own scheme in using the file extension.

3. Obtain the logK values. This Step 3 is to determine if the logK values of the reactions properly delineate the experimental data. This is accomplished by manual execution of the EQ3/6 input files ("*.3i" files) using "data0.i01". The measured concentration of the key component and the EQ3/6 calculated concentration of the same component versus background electrolyte concentration will be plotted to determine how well the interim database fits the measured data. The fit will be evaluated by visual inspection.

   3.1. If the fit is acceptable per analyst's discretion, then record the residual calculated using Excel spreadsheet and proceed to 3.3. Note that the Pitzer parameters will not be fit in this step. Residual is defined under 3.3.

   3.2. If the fit is poor and analyst believes that poor fit is an indication that the logK values are of low confidence, then those logK values will be adjusted using the Python script (Kirchner, 2012) in step 6.2 until the sum of squared differences reaches a minimum. Note that the Pitzer parameters will not be fit in this step. Once a fit to the logK values are obtained, then record the residual and proceed to 3.3. Residual is defined under 3.3.

   3.3. Once an acceptable fit is achieved, either by inspection (3.1) or use of the Python script (3.2), then the residual and the corresponding logK values will be recorded. The residual is defined as the followings:

$$\text{Residual} = \Sigma(\log [C]_{measured} - \log [C]_{calculated})^2,$$

   where [C] means total dissolved concentration of a component of interest.

4. Update the interim database with the logK values from Step 3. Inspect the model-calculated speciation in the EQ3 output files (*.3o) from Step 3, and make a list of major aqueous species in the descending order of the concentrations. Ions of the background electrolytes should not be included in the list. The purpose of making the list is to identify major aqueous species specific to the selected experimental system. One of the major species will be a member of pairs/triplets whose Pitzer parameters are to be derived.

   4.1. Select one species of highest concentration, and make up one pair and/or triplet one member of which being the selected species. The other member in the pair, or two other members in the triplet should be ion(s) of the background electrolytes. Determine if the new pair or triplet already exists in the interim database. This action is critical in building a self-consistent database.

4.2. If the pair/triplet exists in the interim database, then proceed to the species of next highest concentration and repeat Step 4.1 until new pair and/or triplet of interest is identified. Do not alter the Pitzer parameters of the pairs and/or triplets that are already in the interim database. Doing so will compromise the self-consistency of the final database.

4.3. Avoid creating pairs and/or triplets consisting of minor species solely without one or two background ion(s) because the use of such pairs and/or triplets could result in numerical artifacts deficient of geochemical meaning.

4.4. Avoid making up pairs and/or triplets the members of which are already considered in the set of reactions.

5. Format and insert text blocks that implement the ion interaction of pair and/or triplet of Step 4 into the working database file, "data0.i01".

5.1. Format the text blocks to be inserted in the database by using similar text blocks from the QA database (data0.fm2) and editing them accordingly.

5.2. Insert the text blocks that implement the ion interaction of pairs and/or triplets of Step 5.1 into the working database file, "data0.i01". All relevant value(s) in the text blocks are set to: (i) 0.0, or (ii) the values as prescribed in Table 1 of AP-154, Revision 2 (Xiong, 2013) for the cases of binary cation-anion pairs.

6. Performing the fitting

6.1. If logK values were confirmed in Step 3.1, then execute the Python script (Kirchner, 2012) to fit the Pitzer value(s) from Step 5 to find better delineation of the experimental data. Record the minimized residual and the fitted Pitzer value(s) that gives the minimized residual. Check if the new residual is smaller than the residual obtained at Step 3.1. If so, fitting is numerically successful so far.

6.2. If logK values were fitted at Step 3.2, execute the Python script (Kirchner, 2012) to fit both the logK values and the Pitzer values in the text blocks inserted at Step 5, to obtain a better fit of the experimental data. Record the minimized residual, the new logK values, and the fitted Pitzer values that give the minimized residual. Compare the new residual with the residual obtained at Step 3.2 to determine which is the smallest. If the residual obtained in this step is the smallest, then fitting is numerically successful so far.

6.3. If the logK values and the Pitzer pairs/triplets in Steps 6.1 and 6.2 are of concern to other experimental systems, then cross-fitting with the combined systems may be warranted.

6.4. If fitting is not satisfactory, increase the number of pairs/triplets or logK value to be fit by one and execute the properly revised Python script. Check if the new residual is smaller than the residual obtained at step 6.1, 6.2, or 6.3. If so, the fitting is numerically successful so far.

6.5. The total number of Pitzer pairs/triplets and logK values to be fitted per experimental system is preferably less than or equal to two. Justification needs to be provided if the total number is equal to or larger than three.

7. Update the "data0.i01" with new values fitted at step 6.
8. Continue to next experimental system.
9. Build an interim database, from "data0.i01", that includes reactions and the Pitzer parameters specific to the experimental system under consideration as per Step 2.
10. This step is essential to develop a self-consistent database: Compare the interim database of step 9 with "data0.i01" updated at step 7 in order to identify any overlapping reactions and pairs/triplets.
    10.1. If any overlapping reactions and pairs/triplets are found at Step 10, they should be kept the same and the values of logKs and Pitzer parameters are not allowed to be fitting variables for the current experimental system. If there are shared chemical entities between systems, then cross-fitting may be required.
    10.2. For newly introduced reactions and pairs/triplets in the interim database of Step 9, insert the corresponding text blocks into "data0.i01", and save it under different name, such as, "data0.i02". Do not discard "data0.i01" for future reference.
11. Repeat steps 3 through 6, and update the "data0.i02" with the fitted values.
12. Repeat steps 8 through 11 to create "data0.i03". Do not discard "data0.i02" for future reference.
13. Repeat steps 3 through 12 until the last set of experimental data is analyzed.

If the number of experimental sets is nn, the file extension of the working database file will be "data0.inn", which is the final database developed in a self-consistent manner. Do not discard "data0.i(nn-1)" for future reference. If cross-fitting is performed using m experimental systems simultaneously, increase the file extension number by m at Step 7, so that the final database file has the extension of inn. "data0.inn" will be renamed "data0.fm4", the final product of this analysis plan.

2.1 An Example of Interim Database

The following is provided as an example of the approach outlined in Section 2 as applied to an actual data set. To simulate the solubility of ferrous iron hydroxide ($Fe(OH)_2(s)$) in sodium chloride (NaCl) solutions using the Pitzer activity coefficient model, the reactions in Table 1 and the Pitzer parameters in Table 2 are required. Note that (i) all the reactions and Pitzer parameters for non-Fe(II) chemistry are from data0.fm2 (Xiong and Domski, 2016), and (ii) the reactions and Pitzer parameters for Fe(II) to be used were imported from literature, or are to be determined through model fitting processes to better match the experimental data.

Table 1. Reactions of an example interim database for $Fe(OH)_2(s)$-NaCl-H_2O System.

Aqueous reactions	logK[C]	Source
$H^+ + OH^- = H_2O$	13.9967	data0.fm2[A]
$FeOH^+ + H^+ = Fe^{2+} + H_2O$	9.3148	data0.ymp.R2[B]
$Fe(OH)_3^- + 3H^+ = Fe^{2+} + 3H_2O$	31.0000	data0.ymp.R2
Dissolution	**logK**	**Source**
$NaCl(s) = Na^+ + Cl^-$	1.5704	data0.fm2
$Fe(OH)_2(s) + 2H^+ = Fe^{2+} + 2H_2O$	12.95	Nemer et al. (2011)

[A] Xiong and Domski (2016).
[B] data0.ymp.R2 is one of the EQ3/6 databases that comes within the installation package for EQ3/6 v.8.0a (Wolery and Jarek (2003). This software is available at "https://missions.llnl.gov/energy/technologies/geochemistry" as of April, 2015.
[C] 10-based logarithm of equilibrium constant of a reaction.

Table 2. Pairs/Triplets of aqueous species and their Pitzer interaction parameters of an example interim database for $Fe(OH)_2(s)$-NaCl-H_2O System.

i	*j*	α_1/α_2[A]	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{φ}	Source
Na^+	Cl^-	2.0/12.0	0.0765	0.2664	0.0	0.00127	data0.fm2[D]
Na^+	OH^-	2.0/12.0	0.0864	0.253	0.0	0.0044	data0.fm2
H^+	Cl^-	2.0/12.0	0.1775	0.2945	0.0	0.0008	data0.fm2
Fe^{2+}	Cl^-	2.0/12.0	0.37324	1.13499	0.0	-0.02152	Moog et al. (2004)
$FeOH^+$	Cl^-	2.0/12.0	a_1	a_2	a_3	a_4	TBD[B]
Na^+	$Fe(OH)_3^-$	2.0/12.0	b_1	b_2	b_3	b_4	TBD[B]
i	***j***		$\theta_{cc'}$ or $\theta_{aa'}$				**Source**
Na^+	H^+		0.036				data0.fm2
Cl-	OH^-		-0.050				data0.fm2
Na^+	Fe^{2+}		0.08				Nemer et al. (2011), Ptacek (1992)
H^+	Fe^{2+}		0.0				Set to zero[C]
Na^+	$FeOH^+$		c_1				TBD[B]
$Fe(OH)_3^-$	Cl^-		d_1				TBD[B]
i	***j***	***k***	$\psi_{cc'a}$ or $\psi_{aa'c}$				**Source**
Na^+	H^+	Cl^-	-0.004				data0.fm2
Cl-	OH^-	Na^+	-0.006				data0.fm2
Fe^{+2}	Na^+	Cl^-	-0.014				Ptacek (1992)
Fe^{+2}	H^+	Cl^-	0.0				Set to zero[C]
Fe^{+2}	$FeOH^+$	Cl^-	0.0				Set to zero[C]

[A] α_1 and α_2 are pre-set constants used in the Pitzer activity coefficient equation. α_1 and α_2 appliy for cation-anion binary pairs. α_2 is not applied when $\beta^{(2)}$ is zero or not used. Unit for α_1 and α_2 is $kg^{1/2}\cdot mol^{-1/2}$.
[B] To be determined.
[C] Pitzer parameters for these pairs are considered insignificant.
[D] Xiong and Domski (2016).

2.2 Extending the Interim Database in Self-Consistent Way

When building a self-consistent database, it is essential to maintain the values for (i) logKs of common reactions, and (ii) the Pitzer parameters of common pairs/triplets of aqueous species at each step leading up to the final QA database. The reason being, the values of the Pitzer parameters and logKs to be determined are dependent on the logK values of common reactions and the Pitzer parameters of common pairs/triplets that were used in the previous steps.

Reactions and Pitzer parameters in Table 1 and Table 2 in section 2.1 are common for all systems that contain Fe^{2+}, Na^+, Cl^-, H^+, and H_2O as system components. We want to further characterize the system by determining the Pitzer parameters for the pairs of iron species and dominating background cations/anions, i.e., $FeOH^+/Cl^-$, $Na^+/Fe(OH)_3^-$, $Na^+/FeOH^+$, and/or $Fe(OH)_3^-/Cl^-$ (Table 2). This determination will be based on the values of (i) logKs for $FeOH^+$,

$Fe(OH)_3^-$, and $Fe(OH)_2(s)$ in Table 1, and (ii) the Pitzer parameters for pairs/triplets other than the four pairs of $FeOH^+/Cl^-$, $Na^+/Fe(OH)_3^-$, $Na^+/FeOH^+$, and/or $Fe(OH)_3^-/Cl^-$ (Table 2). Once determined, the new Pitzer parameters of the four pairs (a_1 to a_4, b_1 to b_4, c_1, and d_1; bold font in Table 2) should be part of the common Pitzer parameters used in determining the Pitzer parameter(s) in more complicated systems that have other components in addition to Fe^{2+}, Na^+, Cl^-, H^+, and H_2O.

In the manner described above, an interim database for $FeOxalate.2H_2O(s)$ in NaCl system could be constructed from the data shown in Table 3 and Table 4 below ($Oxalate^{-2} = C_2O_4^{-2}$), including the Pitzer parameters for the four pairs mentioned in the previous paragraph for the $Fe(OH)_2(s)$ - NaCl - H_2O system. Note that the data for the oxalate reactions in Table 3 from reliable sources, which includes $H_2Oxalate(aq)$, $HOxalate^-$, FeOxalate(aq), and $Fe(Oxalate)_2^{-2}$. These four species, i.e., reactions, are new entries in the common reactions that are required, in addition to $FeOH^+$ and $Fe(OH)_3^-$, for any experimental systems containing Fe^{2+}, H^+, H_2O, and $Oxalate^{-2}$. Other reactions are the same as in Table 1. As new oxalate species are included, the number of the required Pitzer parameters increases. Two newly added Pitzer parameters are those for the pairs of $Na^+/HOxalate^-$ and $Na^+/Oxalate^{-2}$, which are from the data0.fm2 (Table 4). Also note that one Pitzer parameter for the pair of $FeOxalate(aq)/Na^+$ is introduced (marked *italic* $\boldsymbol{e_1}$ in Table 4), which could be one of the fitting variables for the $FeOxalate.2H_2O(s)$-NaCl-H_2O system. When determining the lambda of $FeOxalate(aq)/Na^+$, all the Pitzer parameters in Table 2 plus the Pitzer parameters for the four pairs (marked in bold fonts, to be determined) should be transferred as they are into Table 4 in order to develop a self-consistent database.

Table 3. Reactions of an example interim database for $FeOxalate.2H_2O(s)$-NaCl-H_2O System. This set of reactions was expanded from Table 1 in self-consistent way.

Aqueous reactions	logK[C]	Source
$H^+ + OH^- = H_2O$	13.9967	data0.fm2[A]
$H_2Oxalate(aq) = 2H^+ + Oxalate^{2-}$, [E]	-5.6532	data0.fm2
$HOxalate^- = H^+ + Oxalate^{2-}$	-4.2596	data0.fm2
$FeOH^+ + H^+ = Fe^{2+} + H_2O$	9.3148	data0.ymp.R2[B]
$Fe(OH)_3^- + 3H^+ = Fe^{2+} + 3H_2O$	31.0000	data0.ymp.R2
$FeOxalate(aq) = Fe^{2+} + Oxalate^{2-}$	-4.05	Harrison and Thyne (1992)
	-3.97	Gustaffson (2015)
$Fe(Oxalate)_2^{-2} = Fe^{2+} + 2Oxalate^{2-}$	-5.90	Gustaffson (2015)
Dissolution	**logK**	**Source**
$NaCl(s) = Na^+ + Cl^-$	1.5704	data0.fm2
$Fe(OH)_2(s) + 2H^+ = Fe^{2+} + 2H_2O$	12.95	Nemer et al. (2011)
$FeOxalate.2H_2O(s) = Fe^{2+} + Oxalate^{2-} + 2H_2O$	-6.68	Oxtoby et al. (2012)[D], to begin with

[A] Xiong and Domski (2016). [B] data0.ymp.R2 is one of the EQ3/6 databases that comes within the installation package for EQ3/6 v.8.0a (Wolery and Jarek, 2003). This software is available at "https://missions.llnl.gov/energy/technologies/geochemistry" as of April, 2015. [C] 10-based logarithm of equilibrium constant of a reaction. [D] Not traceable to original research. To be determined. [E] $Oxalate^{-2} = C_2O_4^{-2}$

Table 4. Pairs/Triplets of aqueous species and their Pitzer interaction parameters of an example interim database for FeOxalate.2H_2O(s)-NaCl-H_2O System. Numbers in bold fonts are from previous section and they are to be used in the determination of λ of FeOxalate(aq)/Na^+ pair (marked in *italic* font). This set of Pitzer parameters was expanded from Table 2 in self-consistent way.

i	*j*	α_1/α_2 [A]	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{φ}	Source
Na^+	Cl^-	2.0/12.0	0.0765	0.2664	0.0	0.00127	data0.fm2 [E]
Na^+	OH^-	2.0/12.0	0.0864	0.253	0.0	0.0044	data0.fm2
Na^+	$HOxalate^-$	2.0/12.0	-0.2448	0.29	-	0.068	data0.fm2
Na^+	$Oxalate^{2-}$ [C]	2.0/12.0	-0.2176	1.74	-	0.122	data0.fm2
H^+	Cl^-	2.0/12.0	0.1775	0.2945	0.0	0.0008	data0.fm2
Fe^{2+}	Cl^-	2.0/12.0	0.37324	1.13499	0.0	-0.02152	Moog et al. (2004)
$FeOH^+$	Cl^-	2.0/12.0	$\mathbf{a_1}$	$\mathbf{a_2}$	$\mathbf{a_3}$	$\mathbf{a_4}$	As shown in Table 2
Na^+	$Fe(OH)_3^-$	2.0/12.0	$\mathbf{b_1}$	$\mathbf{b_2}$	$\mathbf{b_3}$	$\mathbf{b_4}$	As shown in Table 2
i	***j***		**$\theta_{cc'}$ or $\theta_{aa'}$**				**Source**
Na^+	H^+		0.036				data0.fm2
Cl^-	OH^-		-0.050				data0.fm2
Na^+	Fe^{2+}		0.08				Nemer et al. (2011), Ptacek (1992)
H^+	Fe^{2+}		0.0				Set to zero [D]
Na^+	$FeOH^+$		$\mathbf{c_1}$				As shown in Table 2
$Fe(OH)_3^-$	Cl^-		$\mathbf{d_1}$				As shown in Table 2
i	***j***		**λ_{nc} or λ_{na}**				
FeOxalate(aq)	Na^+		***e_1***				TBD [B]
i	***j***	***k***	**$\psi_{cc'a}$ or $\psi_{aa'c}$**				**Source**
Na^+	H^+	Cl^-	-0.004				data0.fm2
Cl-	OH^-	Na^+	-0.006				data0.fm2
Fe^{+2}	Na^+	Cl^-	-0.014				Ptacek (1992)
Fe^{+2}	H^+	Cl^-	0.0				Set to zero [D]
Fe^{+2}	$FeOH^+$	Cl^-	0.0				Set to zero [D]

[A] α_1 and α_2 are pre-set constants used in the Pitzer activity coefficient equation. α_1 and α_2 appliy for cation-anion binary pair. α_2 is not applied when $\beta^{(2)}$ is zero or not used. Unit for α_1 and α_2 is $kg^{1/2}\cdot mol^{-1/2}$.
[B] To be determined.
[C] $Oxalate^{-2} = C_2O_4^{-2}$.
[D] Pitzer parameters for these pairs are considered insignificant.
[E] Xiong and Domski (2016).

2.3 Example of Cross-Fitting over Multiple Experimental Sets: A Scenario

We have two sets of experimental data for the solubility of MgOxalate.2H_2O(s); one measured in $MgCl_2$ solutions, the other in NaCl solutions.

These two data sets are closely related. As analyzed in Table 5 below, the modeling of experimental data in NaCl solutions will need just one additional component compared to the $MgCl_2$ solution due to the presence of Na^+. From these data sets, we wish to determine the logK of MgOxalate.$2H_2O$(s) and the Pitzer parameters (λ) for the interaction of two species pairs; MgOxalate(aq)/Na^+ and MgOxalate(aq)/Mg^{+2}.

In theory, the value of logK for MgOxalate.$2H_2O$(s) should be constant regardless of the ionic media used. However, the experimentally measured solubility data are prone to errors. If the derivation of logK of MgOxalate.$2H_2O$(s) and lambda of MgOxalate(aq)/Mg^{+2} is performed by individual fitting using the experimental data of $MgCl_2$ solutions only, the derived values of logK and lambda will be biased in favor of the errors associated with $MgCl_2$ experiments. Considering the necessity of using common reactions and the Pitzer parameters for self-consistency, the only difference in the solubility model for NaCl experiment, compared to the $MgCl_2$ experiment is the use of lambda for MgOxalate(aq)/Na^+. If the values for logK of MgOxalate.$2H_2O$(s) and lambda of MgOxalate(aq)/Mg^{+2} are biased in favor of the errors associated with $MgCl_2$ experimental data, the individually fitted lambda for the pair of MgOxalate(aq)/Na^+ using the experimental data in NaCl solution will deviate from the expected range, depending on the bias impregnated into the values of logK and lambda MgOxalate(aq)/Mg^{+2} derived from the individual fitting using $MgCl_2$ data only.

Care should be taken in examining the progression of individual fittings to decide whether the cross-fitting should be performed over multiple sets of experimental data. Analysts would not know whether the cross-fitting would be required or not, unless the analysts had gone through all the individual fittings.

Table 5. Number of components to model the solubility of MgOxalate.$2H_2O$(s) in pure water, $MgCl_2$, and NaCl solutions. Arrows mean "Refer to the entity to the left".

Solid	MgOxalate.$2H_2O$(s)	←	←
Media	Pure Water	$MgCl_2$	NaCl
Number of Components	4; Mg^{+2}, $Oxalate^{-2}$, H^+, H_2O	5; plus Cl^-	6; plus Na^+ and Cl^-
Reactions			
OH^-	←	←	←
MgOxalate.$2H_2O$(s)	←	←	←
$MgOH^+$	←	←	←
MgOxalate(aq)	←	←	←
H_2Oxalate(aq)	←	←	←
$HOxalate^-$	←	←	←
Species interactions			
λ: MgOxalate(aq)/Mg^{+2}	Insignificant	TBD[B]	←
λ: MgOxalate(aq)/Na^+	NA[A]	NA[A]	TBD[B]
λ: MgOxalate(aq)/Cl^-	NA[A]	data0.fm2[C]	←

[A] Not Applicable
[B] To Be Determined
[C] Xiong and Domski (2016).

2.4 Evaluation of derived parameters for incomplete systems

There may be cases where all of the supporting parameters (logK values and/or Pitzer parameters) for a chemical system may not be available at the time when a parameter set is being analyzed. For example, the values of a_1 to a_4, b_1 to b_4, c_1, and d_1, as noted in bold letters in Table 4 may not be available when an analyst completes the derivation of e_1. This means that the value e_1 has been derived in the absence of the values a_1 to a_4, b_1 to b_4, c_1, and d_1 in the interim database. In such case, the sensitivity of e_1 with respect to the values a_1 to a_4, b_1 to b_4, c_1, and d_1 will be analyzed by examining the change in the residuals. Refer to the following definitions and see discussion below.

> R_1: residual when e_1 was derived <u>without</u> a_1 to a_4, b_1 to b_4, c_1, and d_1 in the interim database.
>
> R_2: residual calculated <u>with</u> a_1 to a_4, b_1 to b_4, c_1, d_1, and e_1 in the interim database.
>
> Percent difference between R_2 and R_1: $|R_2 - R_1|/R_1 \times 100$ in %, where $| z |$ means absolute value of the number z.

If the percent difference is less than or equal to 10 %, the value e_1 is acceptable.

If the percent difference exceeds 10 %, a new value for lambda of FeOxalate(aq)/Na^+, $\underline{e}_1$, will be sought <u>with</u> a_1 to a_4, b_1 to b_4, c_1, and d_1 in the interim database. The value $\underline{e}_1$ replaces e_1 if the new value $\underline{e}_1$ give new residual, R_3, that must be smaller than the smallest of R_1 and R_2.

If the R_3 is larger than the largest of R_1 and R_2, the value e_1 is acceptable and the value $\underline{e}_1$ does <u>not</u> replace e_1.

The 10 % criteria described above will be applied to the cases where more than one fitting parameter or more than one set of fitting parameters are available in the literature for certain reaction, pair, or triplet of dissolved species.

> R_1: residual when e_1 was derived <u>with</u> the first selected (set of) parameter(s) a_1 to a_4, b_1 to b_4, c_1, and/or d_1 in the interim database.
>
> R_2: residual calculated <u>with</u> the second selected (set of) parameter(s) a_1 to a_4, b_1 to b_4, c_1, d_1, and e_1 in the interim database. The value e_1 is the parameter that gives the residual R_1 above.
>
> Percent difference between R_2 and R_1: $|R_2 - R_1|/R_1 \times 100$ in %, where $|z|$ means absolute value of the number z.

If the percent difference is less than or equal to 10 %, the value e_1 is acceptable and the first and second (set of) fitting parameters are compatible.

If the percent difference exceeds 10 % and the use of the second (set of) fitting parameter(s) is justified for some reasons, a new value for lambda of FeOxalate(aq)/Na^+, $\underline{e}_1$, will be sought <u>with</u> the second (set of) parameter(s) a_1 to a_4, b_1 to b_4, c_1, and/or d_1 in the interim database. The value $\underline{e}_1$ replaces e_1 if the value $\underline{e}_1$ give new residual, R_3, that must be smaller than the smallest of R_1 and R_2.

If the R_3 is larger than the largest of R_1 and R_2, the value e_1 is acceptable along with the first (set of) parameter(s) and the value $\underline{e}_1$ does <u>not</u> replace e_1.

2.5 Parameters to be derived

It is the intent of this analysis plan that the parameters that will be included in this new database will include the iron inorganic and organic complexes from AP-154, Revision 2. A listing of the proposed parameters from AP-154 to be included DATA0.FM4 may be found in Table 6.

Table 6. Parameters to be included in DATA0.FM4.

AP	Task	Description
154	1	Determination of solubility constant of $Fe_2(OH)_3Cl(cr)$
		Derivation of $\theta_{Na^+, Fe^{2+}}$
		Derivation of Pitzer binary interaction parameter of $FeOH^+$—SO_4^{2-}
154	2	Derivation of Pitzer binary interaction parameter of $FeOH^+$—CO_3^{2-}
154	3	Derivation of Pitzer binary interaction parameter of $FeOH^+$—HS^-
154	4	Derivation of Pitzer binary interaction parameter of Fe^{2+}—HS^-
154	5	Derivation of Pitzer binary interaction parameter of Na^+—$Fe(OH)_3^-$
154	6	Derivation of Pitzer binary interaction parameter of Ca^{2+}—$Fe(OH)_3^-$
154	7	Derivation of Pitzer λ parameter of Na^+—FeOx(aq)
154	8	Derivation of Pitzer λ parameter of Mg^{2+}—FeOx(aq)
154	9	Derivation of Pitzer λ parameter of Cl^-—FeOx(aq)
154	10	Derivation of Pitzer binary interaction parameter of Na^+—$FeEDTA^{2-}$
154	11	Derivation of Pitzer binary interaction parameter of Mg^{2+}—$FeEDTA^{2-}$
154	12	Derivation of Pitzer binary interaction parameter of Na^+—$FeCit^-$
154	13	Derivation of Pitzer binary interaction parameter of Mg^{2+}—$FeCit^-$
154	25	Derivation of Pitzer binary interaction parameter of Na^+—HS^-

AP	Task	Description
154	27	Derivation of Pitzer mixing interaction parameter of Cl^{-}—HS^{-}
154	32	Determination of stability constant of CaOxalate(aq)
154	33	Derivation of Pitzer mixing parameter of Cl^{-} - $FeEDTA^{-2}$
154	34	Derivation of Pitzer mixing parameter of Na^{+} - $FeOH^{+}$

* 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.

2.6 Software List

The software to be used is EQ3/6 Version 8.0a (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011), and DATA0.FM2 (Xiong and Domski, 2016). 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.

2.7 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 simulations using the final interim database will be considered acceptable if they agree to within 10%. Details are addressed in section 2.4.

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 database will be documented in an analysis report which will accompany the issuance of the QA database, DATA0.FM4.

Table 7 lists the task, database name, and completion date for AP-176.

Table 7. Task list and completion date.

Task	Database	Completion Date
1	DATA0.FM4	09/30/2016

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 database 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 CMS and/or the CVS with all accompanying documentation.

4 Special Considerations

The thermodynamic properties including Pitzer interaction parameters derived in this AP will be summarized in memos/analysis report that will be submitted to the WIPP Records Center. 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*.

6 References

Kirchner, T.B., 2012. User's Manual for The EQ3CodeModule Version 1.00. Carlsbad, NM: Sandia National Laboratories. ERMS 557360.

Moog, H. C., Hagemann, S., and Rumyantsev, A. V., 2004. Isopiestic investigation of the systems $FeCl_2$-(Na, K, Mg, Ca)Cl_n-H_2O at 298.15 K. *ZEITSCHRIFT FUR PHYSIKALISCHE CHEMIE-INTERNATIONAL JOURNAL OF RESEARCH IN PHYSICAL CHEMISTRY & CHEMICAL PHYSICS* **218**, 1063-1087.

Nemer, M.B., Y.L. Xiong, A.E. Ismail, and J.-H. Jang (2011) Solubility of $Fe_2(OH)_3Cl$ (pure-iron end-member of hibbingite) in NaCl and Na_2SO_4 brines. Chemical Geology, v. 280, pp. 26-32. (SAND2010-6500J)

Ptacek, C. J., 1992. Experimental Determination of Siderite Solubility in High Ionic-Strength Aqueous Solutions, University of Waterloo, Ph.D. Thesis.

Wolery, T. 2008. "Analysis Plan for EQ3/6 Analytical Studies." AP-140, Rev. 0, May 15, 2008, Carlsbad, NM: Sandia National Laboratories. ERMS 548930.

Wolery, T.W., and R.L. Jarek. 2003. "Software User's Manual: EQ3/6, Version 8.0." Software Document No. 10813-UM-8.0-00. Albuquerque, NM: Sandia National Laboratories.

Wolery, T.W., Y.-L. Xiong, and J.J. Long. 2010. "Verification and Validation Plan/Validation Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10." Carlsbad, NM: Sandia National laboratories. ERMS 550239.

Xiong, Y.-L., 2011. "WIPP Verification and Validation Plan/Validation Document for EQ3/6 Version 8.0a for Actinide Chemistry, Revision 1. Supersedes ERMS 550239." May 12, 2011, Carlsbad, NM. Sandia National Laboratories. ERMS 555358.

Xiong, Y.-L., 2013. "Analysis Plan for Derivation of Thermodynamic Properties Including Pitzer Parameters for Solubility Studies of Iron, Lead and EDTA", AP-154, Revision 2. Carlsbad, NM: Sandia National Laboratories. ERMS 561114.

Xiong, Y.-L. and P.S. Domski, 2016. "*Updating the WIPP Thermodynamic Database*". Analysis Report, Sandia National Laboratories.

This work of authorship was prepared as an account of work sponsored by an agency of the United States Government. Accordingly, the United States Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so for United States Government purposes. Neither Sandia Corporation, the United States Government, nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately-owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by Sandia Corporation, the United States Government, or any agency thereof. The views and opinions expressed herein do not necessarily state or reflect those of Sandia Corporation, the United States Government or any agency thereof.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Parties are allowed to download copies at no cost for internal use within your organization only provided that any copies made are true and accurate. Copies must include a statement acknowledging Sandia Corporation's authorship of the subject matter.