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SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

AP-182
Revision 0

Analysis Plan for Derivation and Addition of Equilibrium Constants and Pitzer Interaction Parameters to the WIPP Geochemical Thermodynamic Database

Task 4.4.2.2.1

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1 Introduction and Objectives

This analysis plan (AP) provides procedures to derive or import thermodynamic quantities that are new to our existing geochemical thermodynamic database, named "data0.fm1". The thermodynamic quantities of interest are: (i) equilibrium constants for reactions, and (ii) Pitzer interaction parameters relevant to aqueous species in the reactions.

The existing thermodynamic database, named "data0.fm1", has been systematically built over decades and used with software qualified for geochemical modeling work relevant to the Waste Isolation Pilot Plant (WIPP), e.g., EQ3/6, version 8.0a (Wolery and Jarek, 2003). The brine model by Harvie et al. (1984) was the template, to which models for complexation of actinides and major brine cations with organic ligands were amended by Choppin et al. (2001) in a consistent manner with Harvie et al. (1984). Because the brine model by Harvie et al. (1984) did not contain borate, therefore a borate speciation model by Felmy and Weare (1986) was adopted into data0.fm1.

New thermodynamic quantities, derived or imported, will be inserted into the data0.fm1 to create data0.fm4 to be used in the Compliance Recertification Application (CRA) for 2019. Therefore this is considered a compliance decision analysis. Decision to keep or reject newly derived thermodynamic quantities will be based on the consistency of the the new data values with respect to data0.fm1.

2 Approach

The derivation procedure to be described in this AP will be based on experimental data available in our own records or in peer-reviewed research literature. The derivation procedure will use the thermodynamic data values existing in data0.fm1 to keep the newly derived thermodynamic quantities consistent with existing ones in data0.fm1. The standard form of the Pitzer activity coefficient equation (PACE) (Pitzer, 1973; Pitzer and Mayorga, 1973; Pitzer and Kim, 1974; Pitzer, 1975; Pitzer, 1991) will be used as implemented in the aqueous speciation code, EQ3/6 version 8.0a (Wolery and Jarek, 2003), with A_φ set to 0.392 at 25 °C. A_φ is one third the Debye-Huckel limiting slope with units of $(kg/mol)^{1/2}$.

Any deviation, that is, replacing the thermodynamic quantities currently in the data0.fm1 database with new ones, shall be noted and explained using the appropriate documentation. Use of equilibrium constants determined using activity coefficient equations other than PACE, such as, specific ion interaction theory (SIT) used in Hummel et al. (2005), Lemire et al. (2013), and Powell et al. (2009), shall be noted and explained using the appropriate documentations. The SIT activity coefficient model is not well-suited to deal with highly concentrated salt solutions (Fanghanel et al., 1994).

The SNL WIPP Geochemistry Program is concerned with the effects of brine concentration on aqueous species of lower concentration, including organic complexes, of iron, lead, etc. Borate aqueous species are also considered capable of forming complexes with iron (Byrne and Thompson, 1997). Concentrations of those species in neutral to alkaline pH range under WIPP conditions are generally less than ~0.001 m (molal or molality, moles of aqueous species per kg of water); much lower than the major background ions in brine, such as sodium, magnesium, and chloride. The speciation of such species is affected by the presence of major background ions. Therefore, the interaction of aqueous species at lower concentrations should be considered, if any, in conjunction with the background ions of higher concentration.

The following is an outline of our approach whose application is elaborated in the next sections.

1. Select set of experimental data for a simplest system, e.g., solubility, isopiestic, emf, etc.

2. Refer to data0.fm1 to retrieve relevant thermodynamic quantities for the system, i.e., equilibrium constants for reactions and Pitzer interaction parameters related to species in the reactions.

3. Model the selected system using the thermodynamic quantities retrieved from data0.fm1 to calculate the total dissolved concentration of component of interest.

4. Gauge the quality of the fit by calculating the residual defined in the following equation;

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

   where [C] means total dissolved concentration of a component of interest. Decadic (base 10) logarithm scale of the concentrations is used to equally represent each data point.

5. Select major species of the component of interest through aqueous speciation to obtain binary pairs with the highly concentrated background ion. Avoid considering ion association (or ion pairing) reactions with Pitzer ion interaction parameterization simultaneously in the model, i.e., model redundancy or "double counting". Exceptions can be made as a deviation from this AP. For tasks to be processed by this AP, mainly work with binary pairs of ionic species having different charge signs, i.e., cation-anion, neutral-cation, or neutral-anion.

6. Improve the fit to minimize the residual defined above in (4) by adjusting the Pitzer interaction parameter(s) of the species pair(s) selected above. See the following examples for a guidance to select Pitzer interaction parameters to be adjusted. The PACE used for this AP is implemented in the aqueous speciation code, EQ3/6, version 8.0a (Wolery and Jarek, 2003). Pitzer formulations are given elsewhere and interested readers are referred to Harvie et al. (1984) and Pitzer (1991) for details on PACE.

7. Compare the activity coefficients of the species in the chosen pair(s) calculated by the newly adjusted, non-zero interaction parameter(s) with activity coefficients of similarly charged species. This is done to check if the value of the newly calculated activity coefficients (i) exceed the conventional range defined by the Debye-Huckel limiting law, and (ii) deviate noticeably from activity coefficients of similarly charged species. These are often indicated by abrupt changes in the species distribution as a function of ionic strength or pH.

8. If one or more of the non-conventional observations noted above is made, the model fit of the system cannot be improved by solely adjusting the selected Pitzer interaction parameters. Consider adjusting Pitzer interaction parameters for another pair(s). Unreasonable equilibrium constants or low quality experimental data can be the culprit.

The above outline is elaborated in the following two examples. Guidances to select species pairs are also given. A few more details and precautionary steps will be noted in the examples.

3 *Example I. Solubility of Glushinskite*

Glushinskite is the mineralogical name for magnesium oxalate dihydrate ($MgC_2O_4•2H_2O(s)$, $C_2O_4^{-2}$ = Oxalate^{-2}) that could limit the total dissolved concentration of Oxalate^{-2}. Two sets of solubility data for glushinskite are available in our record (e.g., Jang and Kim, 2016); one in $MgCl_2$ solutions (Mg^{+2} - Oxalate^{-2} - Cl^- - H^+ - H_2O system), and the other in NaCl solutions (Mg^{+2} - Oxalate^{-2} - "Na^+" - Cl^- - H^+ - H_2O system). The solubility data in the carbonate-free 0.01 – 2.4 molal $MgCl_2$ solutions will be discussed in this AP prior to the data in NaCl solutions because of its simplicity, i.e., less numbers of components and thermodynamic quantities. This is an example of systems for which only part of the required thermodynamic quantities are retrievable from data0.fm1 (Table 1 for the relevant reactions; Table 2 for Pitzer interaction parameters).

Note that the equilibrium constant for glushinskite dissolution reaction is not available from data0.fm1.

Table 1. Reactions Retrieved from data0.fm1 for the Dissolution of Glushinskite in $MgCl_2$ Solutions

Reactions	LogK	Source
Aqueous reactions		
$H^+ + OH^- = H_2O$	13.99	Harvie et al. (1984)
$MgOH^+ + H^+ = Mg^{+2} + H_2O$	11.80	Harvie et al. (1984)
H_2Oxalate(aq) = $2H^+$ + Oxalate$^{-2,\ A}$	-5.65	Choppin et al. (2001)
HOxalate$^-$ = H^+ + Oxalate^{-2}	-4.25	Choppin et al. (2001)
MgOxalate(aq) = Mg^{+2} + Oxalate^{-2}	-3.79	Giambalvo (2002) using data in Choppin et al. (2001)
Mg(Oxalate)$_2^{-2}$ = Mg^{+2} + 2Oxalate^{-2}	-5.24	Determined by applying the same approach of Giambalvo (2002) onto data in Choppin et al. (2001)

[A] Oxalate^{-2}: $C_2O_4^{-2}$

Table 2. Pitzer Interaction Parameters Retrieved from data0.fm1 for the Dissolution of Glushinskite in $MgCl_2$ Solutions

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	Harvie et al. (1984)
Na^+	OH^-	2.0/12.0	0.0864	0.253	0.0	0.0044	Harvie et al. (1984)
Mg^{+2}	Cl^-	2.0/12.0	0.35235	1.6815	0.0	0.00519	Harvie et al. (1984)
$MgOH^+$	Cl^-	2.0/12.0	-0.10	1.658	0.0	0.0	Harvie et al. (1984)
H^+	Cl^-	2.0/12.0	0.1775	0.2945	0.0	0.0008	Harvie et al. (1984)
i	j	θ_{ij}	Source		k	ψ_{ijk}	Source
Mg^{+2}	H^+	0.10	Harvie et al. (1984)		Cl-	-0.011	Harvie et al. (1984)
Mg^{+2}	$MgOH^+$	0.0[C]	See footnote [C]		Cl-	0.028	Harvie et al. (1984)
Cl-	OH^-	-0.05	Harvie et al. (1984)				
i	j	λ_{ij}					
MgOxalate(aq)[B]	Cl^-	0.0189					Giambalvo (2002)

[A] α_1 and α_2 are pre-set constants used in the Pitzer activity coefficient equation. α_1 and α_2 apply for only 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] $Oxalate^{-2}$: $C_2O_4^{-2}$

[C] Set to zero to have ψ for $Mg^{+2}/MgOH^+/Cl^-$ in Harvie et al. (1984).

One required information to properly model the solubility of glushinskite in $MgCl_2$ solution is the equilibrium constant for dissolution of glushinskite;

> $MgOxalate \bullet 2H_2O(s) = Mg^{+2} + Oxalate^{-2} + 2H_2O$; LogK(Glush) = -6.4(±0.2)
> (Hummel et al., 2005).

Since the logK(Glush) is not available in the data0.fm1, a literature value of -6.4 is chosen from Hummel et al. (2005). This is a NOTEWORTHY information because Hummel et al. (2005) used the SIT activity model to determine the logK(Glush) = -6.4 at infinite dilution. Thus, use of logK(Glush) = -6.4 from Hummel et al. (2005) in combination of PACE would be considered inconsistent application of two different activity models.

To properly model the dissolution of glushinskite in NaCl solutions (i.e., Mg^{+2} - $Oxalate^{-2}$ - "Na^+" - Cl^- - H^+ - H_2O system), additional Pitzer interaction parameters retrievable from data0.fm1 should be considered (See Table 3).

Table 3. Pitzer Interaction Parameters Retrieved from data0.fm1 for the Dissolution of Glushinskite in NaCl Solutions

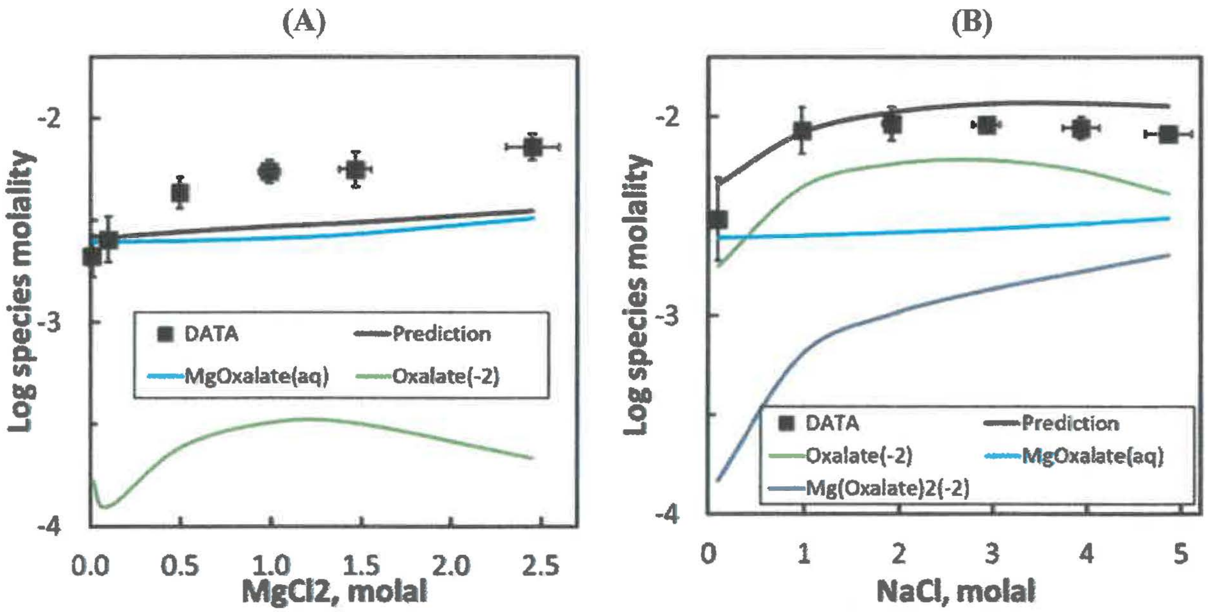
i	j	α_1/α_2[A]	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{φ}	Source
Na^+	$HOxalate^-$	2.0/12.0	-0.2448	0.29	0.0	0.068	Choppin et al. (2001)
Na^+	$Oxalate^{-2}$[B]	2.0/12.0	-0.2176	1.74	0.0	0.122	Choppin et al. (2001)
i	j	θ_{ij}	Source		k	ψ_{ijk}	Source
Na^+	Mg^{+2}	0.07	Harvie et al. (1984)		Cl^-	-0.012	Harvie et al. (1984)
Na^+	H^+	0.036	Harvie et al. (1984)		Cl^-	-0.004	Harvie et al. (1984)
Cl-	OH^-	-0.05	Harvie et al. (1984)		Na^+	-0.006	Harvie et al. (1984)

[A] α_1 and α_2 are pre-set constants used in the Pitzer activity coefficient equation. α_1 and α_2 apply for only 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] $Oxalate^{-2}$: $C_2O_4^{-2}$

Using the thermodynamic quantities in the three Tables above and the logK(Glush) anchored at -6.4, the fitting qualities are fair-to-poor for both experiments in $MgCl_2$ and NaCl solutions, the residuals being 1.053 for $MgCl_2$ experiment, 0.068 in NaCl experiment (Figure 1).

Figure 1. Model calculations using the thermodynamic quantities retrieved from the existing data0.fm1 and the logK(Glush) anchored at -6.4 (±0.2) as in Hummel et al. (2005). (A) Experiments in $MgCl_2$ solutions, (B) Experiments in NaCl solutions. Data are modified from Jang and Kim (2016). Note that the logK(Glush) = -6.4 was determined using SIT approach, not PACE.



Species distribution indicates that the major oxalate species is MgOxalate(aq), a neutral species, in the $MgCl_2$ experiment (Figure 1(A)). In the NaCl experiment, the second major species is MgOxalate(aq) (Figure 1(B)). Note that Pitzer interaction parameters for Na^+/$Oxalate^{-2}$ are already considered and will not be adjusted any further to keep the internal model consistency intact with the thermodynamic quantities retrieved from the data0.fm1 database (Table 1 to Table 3).

The two lambda (λ) parameters for the species pairs MgOxalate(aq)/Mg^{+2} ($MgCl_2$ experiment) and MgOxalate(aq)/Na^+ (NaCl experiment) were adjusted to seek better fits. Since logK(Glush) = -6.4 (Hummel et al, 2005) was determined under SIT activity model, the value for logK(Glush) was also adjusted simultaneously with the two λ's to see how the logK(Glush) = -6.4 by Hummel et al. (2005) would be affected by the application of PACE.

Residuals became smaller: 0.049 and 0.028 for $MgCl_2$ and NaCl experiments, respectively, with the adjusted values for logK(Glush) = -6.41, λ(MgOxalate(aq)/Mg^{+2}) = -0.20, and λ(MgOxalate(aq)/Na^+) = 0.19.

However, a non-conventional value for activity coefficient of the neutral species MgOxalate(aq) was observed, resulting in abrupt change in the speciation of $Oxalate^{-2}$ in NaCl experiment. The value for activity coefficient for MgOxalate(aq), γ(MgOxalate(aq)) hereafter, in NaCl experiments increased from unity to ~10 as NaCl molality increases 0.1 to 5, making the calculated concentration of MgOxalate(aq) in NaCl experiment plummets below the concentration of $Mg(Oxalate)_2^{-2}$ at a NaCl molality > 2. Considering the pH ranges from 7 to 9 and total dissolved concentration of oxalate not exceeding 0.01 molal over the entire range of NaCl molality, the change in expected oxalate aqueous speciation is to be considered a result of overparameterization.

Therefore, for NaCl experiment, it is necessary to decrease the concentrations of both MgOxalate(aq) and $Mg(Oxalate)_2^{-2}$ together by adjusting $\beta^{(0)}$ parameter for species pair $Na^+/Mg(Oxalate)_2^{-2}$ with α_1 set to 2.0. The changes in the residuals are not significant: 0.049 and 0.027 for $MgCl_2$ and NaCl experiments, respectively, with the adjusted values for logK(Glush) = -6.41, $\lambda(MgOxalate(aq)/Mg^{+2}) = -0.20$, and $\lambda(MgOxalate(aq)/Na^+) = 0.08$, and $\beta^{(0)}(Na^+/Mg(Oxalate)_2^{-2}) = 0.07$. No abrupt changes in Oxalate speciation was observed, and conventional value of unit activity coefficient of neutral species MgOxalate(aq) was observed.

A better-looking fit with a smaller residual for $MgCl_2$ experiment could be achieved by adjusting $\beta^{(1)}(Mg^{+2}/Oxalate^{-2})$ to be -4.41 with $\alpha_1 = 1.4$ (Domski, 2018). However, this adjustment triggers the model redundancy issue, i.e., considering ion interaction and ion association together; two association reactions for Mg^{+2} and $Oxalate^{-2}$ are already considered by use of two aqueous species, i.e., MgOxalate(aq) and $Mg(Oxalate)_2^{-2}$. Furthermore, this scheme causes an abrupt change in $Oxalate^{-2}$ speciation without significant changes in pH, simply because the overfitted $\beta^{(1)}(Mg^{+2}/Oxalate^{-2})$, -4.41, makes the values of $\gamma(Oxalate^{-2})$ exceed Debye-Huckel limiting law would calculate in $MgCl_2$ experiments.

Therefore, derivation of thermodynamic quantities for solubility of glushinskite in $MgCl_2$ and NaCl solutions using the Pitzer approach can be evaluated using the following parameters: logK(Glush) = -6.41, $\lambda(MgOxalate(aq)/Mg^{+2}) = -0.20$, and $\lambda(MgOxalate(aq)/Na^+) = 0.08$, and $\beta^{(0)}(Na^+/Mg(Oxalate)_2^{-2}) = 0.07$.

4 Example II. Solubility of Ferrous Iron Hydroxide

Ferrous iron hydroxide (FIH, $Fe(OH)_2(s)$) is considered a product of anoxic corrosion of steel. However, thermodynamic quantities related to solubility of FIH in NaCl solutions, i.e., Fe^{+2} - Na^+ - Cl^- - H^+ - H_2O system, is not available in data0.fm1. Thermodynamic quantities retrievable from data0.fm1 for the system concern only the pure NaCl solution. Thus, we need to experimentally verify the quality of thermodynamic quantities available elsewhere. This is an example for how to analyze a set of solubility data using imported thermodynamic quantities, i.e., reactions and the related Pitzer interaction parameters, that are totally new to the data0.fm1.

Table 4 and Table 5 list the thermodynamic quantities that are retrieved from data0.fm1 to model NaCl solution. No reactions of Fe^{+2} and the related Pitzer interaction parameters exist in data0.fm1.

Table 4. No Reactions Available in data0.fm1 for Solubility of $Fe(OH)_2(s)$.

Reactions	logK	References
Aqueous reactions		
$H^+ + OH^- = H_2O$	13.99	Harvie et al. (1984)

Table 5. Pitzer Interaction Parameters Retrieved from data0.fm1 to Model the Solubility of $Fe(OH)_2(s)$ in NaCl Solutions. Note that no Pitzer Interaction Parameters for Fe^{+2} are in data0.fm1.

i	j	α_1/α_2 [A]	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{φ}	Reference
Na^+	Cl^-	2.0/12.0	0.0765	0.2664	0.0	0.00127	Harvie et al. (1984)
Na^+	OH^-	2.0/12.0	0.0864	0.253	0.0	0.0044	Harvie et al. (1984)
H^+	Cl^-	2.0/12.0	0.1775	0.2945	0.0	0.0008	Harvie et al. (1984)
i	**j**	**θ_{ij}**	**Reference**	**k**	**ψ_{ijk}**	**Reference**	
Na^+	H^+	0.036	Harvie et al. (1984)	Cl^-	-0.004	Harvie et al. (1984)	
Cl-	OH^-	-0.05	Harvie et al. (1984)	Na^+	-0.006	Harvie et al. (1984)	

[A] α_1 and α_2 are pre-set constants used in the Pitzer activity coefficient equation. α_1 and α_2 apply for only 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 $kg^{1/2}\cdot mol^{-1/2}$.

From literature, the following thermodynamic quantities are available (See Table 6).

Table 6. Reactions Necessary to Model the Solubility of $Fe(OH)_2(s)$.

Reactions	logK	References
Aqueous reactions		
$FeOH^+ + H^+ = Fe^{2+} + H_2O$	9.31	Shock et al. (1997), YMP
$Fe(OH)_2(aq) + 2H^+ = Fe^{2+} + 2H_2O$	20.82	Stumm and Morgan (1996)
Dissolution		
$Fe(OH)_2(s) + 2H^+ = Fe^{2+} + 2H_2O$	12.95 [A]	Nemer et al. (2011)

[A] At ambient room temperature and pressure.

Higher order hydrolysis products of Fe^{+2}, i.e., $Fe(OH)_3^-$, $Fe(OH)_4^{-2}$ will not be considered because they are not major species in our experimental conditions, i.e., pH ~9 in the WIPP.

The logK(FIH) = 12.95(±0.13) was once co-derived together with the θ parameter for Na^+/Fe^{+2} of 0.08 in Nemer et al. (2011). The binary cation-anion interaction parameters for species pair Fe^{+2}/Cl^-, i.e., $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{φ}, were adopted from Pitzer (1991) in Nemer et al. (2011), which covers ionic strength up to 2 molal. At the time of the analysis in Nemer et al. (2011), authors were not aware of more plausible sets of Pitzer parameters were available from isopiestic experiments by Moog et al. (2004).

Below are the Pitzer interaction parameters to be used in conjunction with the thermodynamic quantities in Table 4 to Table 6.

Table 7. Pitzer interaction parameters adopted from Moog et al. (2004) to model the solubility of $Fe(OH)_2(s)$ in NaCl solutions.

i	J	α_1/α_2^A	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{φ}	Reference
Fe^{+2}	Cl^-	2.0/12.0	0.37324	1.13499	0.0	-0.02152	Moog et al. (2004)
i	J	θ_{ij}	Reference	k	ψ_{ijk}	Reference	
Na^+	Fe^{+2}	0.10945	Moog et al. (2004)	Cl^-	-0.01605	Moog et al. (2004)	

^A α_1 and α_2 are pre-set constants used in the Pitzer activity coefficient equation. α_1 and α_2 apply for only 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 $kg^{1/2}\cdot mol^{-1/2}$.

Using logK(FIH) = 12.95(±0.13), the species distribution indicates that the major species is free, non-bound Fe^{+2}, consistent with the observed pH < 9. The Pitzer interaction parameters for Fe^{+2} are adopted from Moog et al. (2004) as shown in Table 7 above. Thus, the logK(FIH) was slightly modified to accommodate the use of binary interaction parameters in Moog et al. (2004). The new logK value is 12.89. The change in logK(FIH) is minimal, but this value ensures the internal consistency of our database with smaller residual. No more rationale for further adjustment of thermodynamic quantities can be sought.

5 Other Cautions and Guideline

1. Avoid creating and fitting ternary pairs and their interaction parameters that do not exist in the data0.fm1: Pitzer interaction parameters should be better determined, if available, by isopiestic data where the water activity is sensitive to the concentrations of species of interests. Most of our solubility data are not adequate for fitting ternary interaction parameters. Simply use those existing in the data0.fm1. In case of creating and fitting ternary interaction parameters, this should be noted and explained using proper documentation.

2. If necessary, consider the recommended values for $\beta^{(1)}$ cation-anion binary parameters as in Choppin et al. (2001) and Borkowski et al. (2001) when these help significantly in improving the fitting quality. Set those values to zero if these do not reduce the residual, or if any abnormal speciation issues are observed; abrupt changes in species concentration, unreasonable values of activity coefficients, etc. The recommended values by Choppin et al. (2001) and Borkowski et al. (2001) were given in Xiong (2013) (Table 8). Other references, e.g., Kim and Frederick (1988a; 1988b), might have information necessary to perform the parameter analysis.

Table 8. Values for $\beta^{(1)}$ that Could be Used with Cautions to be Noted in Documentation.

Ion combination	$\beta^{(1)}$
M^+, X^-	0.29
M^+, X^{-2} and M^{+2}, X^- (1:2 or 2:1 interaction)	1.74
M^+, X^{-3} and M^{+3}, X^- (1:3 or 3:1 interaction)	5.22
M^+, X^{-4} and M^{+4}, X^- (1:4 or 4:1 interaction)	11.6
M^{+2}, X^{-2} (2:2 interaction)	3.27[A]

[A] Average of $\beta^{(1)}$ values for Mg^{+2}/SO_4^{-2} and Ca^{+2}/SO_4^{-2}.

3. Set $\beta^{(2)} = 0$ if the chosen cation-anion binary pair contains univalent ion. For 2:2 ion pairs, a $\beta^{(2)}$ value of -45.74 (Average of $\beta^{(2)}$ values for Mg^{+2}/SO_4^{-2} and Ca^{+2}/SO_4^{-2} pairs; Xiong, 2013) could be used upon analysts' decision if the value helps significantly reduce the fitting residual. Otherwise, set the value to zero.

6 Software List

EQ3/6, version 8.0a (Wolery and Jarek, 2003) is the main speciation code for this AP. When iteration of the code is required to adjust the necessary thermodynamic quantities, a Python program, EQ3CodeModule, version 1.00 (Kirchner, 2012), will be used to control the iteration of the EQ3/6. Microsoft Excel can be used to calculate the residuals.

7 Tasks

A list of tasks will be provided in AP-183 (Sisk-Scott, 2019). Paul Domski will be the primary analyst of this AP performing the tasks.

8 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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