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Sandia National Laboratories

Je-Hun Jang
4100 National Parks Highway
Carlsbad, NM 88220
Phone: (505) 284-2770
Fax: (575) 234-0061
E-mail: jjang@sandia.gov

Date: August 27, 2012

To: Records Center

From: Je-Hun Jang

Subject: Derivation of the solubility product for ferrous iron oxalate dihydrate in NaCl solutions and related Pitzer ion interaction parameter

This memo is written to describe the derivation of (i) the solubility product for ferrous iron oxalate dihydrate ($\text{FeOxalate} \cdot 2\text{H}_2\text{O}(s)$, where $\text{Oxalate}^{2-} = \text{C}_2\text{O}_4^{2-}$ and $2\text{H}_2\text{O}$ is water of hydration) in sodium chloride (NaCl) solutions, and (ii) related Pitzer ion interaction parameter. This derivation is associated with Test Plan TP 08-02, "Iron, Lead, Sulfide, and EDTA Solubilities" (Ismail et al., 2008) and Analysis Plan AP-154, "Analysis Plan for Derivation of Thermodynamic Properties Including Pitzer Parameters for Solubility Studies of Iron, Lead and EDTA", Task 7 in Table 1 therein (Xiong, 2011a). Briefly, an aqueous model for dissolution of $\text{FeOxalate} \cdot 2\text{H}_2\text{O}(s)$ in NaCl solution was fitted to the experimentally measured solubility data. The aqueous model consists of several chemical reactions and related Pitzer interaction parameters (See section 4 below for details). The model is implemented within the aqueous speciation code EQ3/6 v.8.0a (Wolery and Jarek, 2003). Specifically, the 10-based logarithm of the equilibrium constant ($\log K$) for reaction (10) ($\log K_{10}$ hereafter; Table 4) and a Pitzer interaction parameter for the $\text{FeOxalate}(aq)$ and Na^+ pair ($\lambda_{\text{FeOxalate}(aq)/\text{Na}^+}$; Table 5) were fitted to the experimental data (Table 3).

EQ3NR packaged in EQ3/6 v.8.0a was used to calculate the aqueous speciation and saturation index for a given number of EQ3NR input files (*.3i files). A *.3i file represents one set of measurements from an individual experiment. To calculate the aqueous speciation and saturation index, EQ3NR refers to one of the databases (e.g., data0.fm1) for values of $\log K$ s (10-based logarithm of equilibrium constants for reactions) and Pitzer parameters. The saturation index indicates how far the system is from the equilibrium with respect to the solid of interest, and can be calculated from the aqueous speciation. The value could be (i) zero if the system is saturated (equilibrated) with the solid of interest, (ii) positive if the system is supersaturated with the solid of interest, or (iii) negative if the system is undersaturated with the solid of interest. Thus, the smaller the sum of squared saturation indices that the aqueous model calculates for the given number of *.3i files, the more closely the model attributes equilibrium to the individual experiment with respect to the solid of interest.

Hence, we seek $\log K_{10}$ (Table 4) and $\lambda_{\text{FeOxalate}(aq)/\text{Na}^+}$ (Table 5) that make the sum of squared saturation indices as small as possible. To do so, the calculation of aqueous speciation and saturation index was repeated by adjusting the $\log K_{10}$ and $\lambda_{\text{FeOxalate}(aq)/\text{Na}^+}$ in the database (e.g., data0.fm1) until the values of $\log K_{10}$ and $\lambda_{\text{FeOxalate}(aq)/\text{Na}^+}$ were found that make the sum of squared saturation indices the least for the given number of *.3i files. The repetition was driven by a script written in the Python computer language, *EQ3CodeModule.py* (Kirchner, 2012).

1. Experimental data for the fitting

Experimental data used in this analysis is summarized in Table 1 below. The values are from Tables 3-13 and 3-14 in Jang et al. (2012). Note that the concentration units for NaCl solutions are either M or m.

Table 1. Experimental data for derivation of logK and $\lambda_{\text{FeOxalate(aq)}/\text{Na}^+}$.

Experiment ID	NaCl	pH	Fe(II) (M)
0.1-FeOx-3	0.1 M	5.188	3.11E-04
1M-FeOx-3	1.0 M	5.321	6.26E-04
2M-FeOx-3	2.0 M	5.171	7.49E-04
3M-FeOx-3	3.0 M	5.036	7.56E-04
4M-FeOx-3	4.0 M	4.977	7.54E-04
5M-FeOx-3	5.0 m	5.587	7.35E-04
0.1-FeOx-4	0.1 M	5.199	3.25E-04
1M-FeOx-4	1.0 M	5.327	5.98E-04
2M-FeOx-4	2.0 M	5.177	7.33E-04
3M-FeOx-4	3.0 M	5.112	7.63E-04
4M-FeOx-4	4.0 M	4.878	7.46E-04
5M-FeOx-4	5.0 m	5.259	7.05E-04

2. Data conversion

Input files for EQ3/6 runs require data to be in molal (m) units. Thus, data given in molar (M) units was converted to molal (m) units by applying the ratio of M to m (M_m in Table 2, the values are in the unit of kg.H₂O/L.solution).

The pH values in Table 1 are those measured by pH electrodes and meters, which are typically calibrated with respect to pH buffers of low ionic strength. Therefore, to account for the bias introduced by higher ionic strength used in the experiments, the value should be converted to pC_{H^+} (negative 10-based logarithm of molar concentration of H^+) using the correction factor defined for NaCl-dominated brines (A_{NaCl}) in Roselle (2011). :

$$A_{\text{NaCl}} (\pm 0.47) = 0.186 \cdot I_M - 0.105 \quad (\text{ii})$$

$$pC_{H^+} = \text{pH} + A_{\text{NaCl}} \quad (\text{iii})$$

where I_M is the molar ionic strength of the solution.

Negative 10-based logarithm of molal concentration of H^+ (pmH in Table 3 below) can be calculated from pC_{H^+} by the equation below:

$$\text{pmH} = -\log[10^{-pC_{H^+}} / (M_m)] \quad (\text{iv})$$

Values for A_{NaCl} and M_m as a function of ionic strength are summarized in Table 2.

Table 2. Solution density and M_m.

NaCl (M)	NaCl (m)	A _{NaCl}	Solution density (g/mL) [#]	M _m (kg.H ₂ O/L.solution) [#]
0.1	0.1	-0.086	1.0047	0.9989
1.0	1.0	0.081	1.0383	0.9799
2.0	2.1	0.267	1.0757	0.9588
3.0	3.2	0.453	1.1131	0.9378
4.0	4.4	0.639	1.1505	0.9167
4.5	5.0	0.738	1.1637	0.9006

[#] The solution density and M_m were calculated by EQ3NR for NaCl solutions of 0.1, 1.0, 2.0, 3.0, and 4.0 M. For 5.0 m NaCl solution, the solution density is from WIPP-Solubility-31, p.11; M_m value for a 5.0 m NaCl solution was calculated from $M_m = (\text{solution density})/[1 + (\text{NaCl molality}) \times (\text{molecular weight of NaCl})]$, where the solution density is in g/mL (or, kg/L) and the molecular weight of NaCl in kg/mole.

3. Data used in the fitting

Using conversion factors in Table 2, the experimental data in Table 1 were converted to numbers in molal unit, which are to be used in the model fitting.

Table 3. Experimental data[#] to be used in the model fitting (in molal unit) and corresponding EQ3NR input files (*.3i).

Experiment ID	Na(I) (m)	Cl(-I) (m)	Fe(II) (m)	pmH	filename
0.1-FeOx-3	0.1	0.1	3.11E-04	5.101	feoxna01.3i
1M-FeOx-3	1.0	1.0	6.39E-04	5.393	feoxna02.3i
2M-FeOx-3	2.1	2.1	7.81E-04	5.420	feoxna03.3i
3M-FeOx-3	3.2	3.2	8.06E-04	5.461	feoxna04.3i
4M-FeOx-3	4.4	4.4	8.22E-04	5.578	feoxna05.3i
5M-FeOx-3	5.0	5.0	8.16E-04	6.279	feoxna06.3i
0.1-FeOx-4	0.1	0.1	3.25E-04	5.112	feoxna07.3i
1M-FeOx-4	1.0	1.0	6.10E-04	5.399	feoxna08.3i
2M-FeOx-4	2.1	2.1	7.64E-04	5.426	feoxna09.3i
3M-FeOx-4	3.2	3.2	8.14E-04	5.537	feoxna10.3i
4M-FeOx-4	4.4	4.4	8.14E-04	5.479	feoxna11.3i
5M-FeOx-4	5.0	5.0	7.83E-04	5.951	feoxna12.3i

[#] Total oxalate concentration was adjusted by EQ3NR to account for the charge imbalance caused by large uncertainty associated with oxalate analysis.

4. Model description

An aqueous model consists of aqueous reactions, dissolution reactions, and related Pitzer interaction parameters. The reactions for this model are summarized in Table 4 and Pitzer parameters in Table 5.

Table 4. Reactions and 10-based logarithms of their equilibrium constants (logK's) used in this model fitting. LogK for reaction (10) (logK₁₀) was fitted to the experimental data in this memo.

Reactions	logK	Source
<u>Aqueous reactions</u>		
(1) $H^+ + OH^- = H_2O$	13.9967	data0.fm1 ^a
(2) $H_2Oxalate(aq) = 2H^+ + Oxalate^{2-}$	-5.6532	data0.fm1
(3) $HOxalate^- = H^+ + Oxalate^{2-}$	-4.2596	data0.fm1
(4) $FeOH^+ + H^+ = Fe^{2+} + H_2O$	9.3148	data0.ymp.R2 ^b
(5) $FeOxalate(aq) = Fe^{2+} + Oxalate^{2-}$	-4.05	Harrison and Thyne (1992)
<u>Dissolution</u>		
(6) $H_2Oxalate.2H_2O(s) = 2H^+ + Oxalate^{2-} + 2H_2O$	-5.6615	data0.fm1
(7) $NaHOxalate.H_2O(s) = Na^+ + H^+ + Oxalate^{2-} + H_2O$	-6.0608	data0.fm1
(8) $Na_2Oxalate(s) = 2Na^+ + Oxalate^{2-}$	-2.4051	data0.fm1
(9) $NaCl(s) = Na^+ + Cl^-$	1.5704	data0.fm1
(10) $FeOxalate.2H_2O(s) = Fe^{2+} + Oxalate^{2-} + 2H_2O$	TBD ^c	This memo

^a data0.fm1: See Xiong (2011b)

^b data0.ymp.R2 is one of the EQ3/6 databases that comes within the installation package for EQ3/6 v.8.0a.

^c TBD: To Be Determined

Table 5. Pitzer interaction parameters used in this model fitting. The Pitzer parameter for FeOxalate(aq)/Na⁺ pair ($\lambda_{FeOxalate(aq)/Na^+}$) was fitted to the experimental data in this memo.

<i>i</i>	<i>j</i>	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^ϕ	Source
Na ⁺	Cl ⁻	0.0765	0.2664	-	0.00127	data0.fm1 ^a
Na ⁺	OH ⁻	0.0864	0.253	-	0.0044	data0.fm1
Na ⁺	HOxalate ⁻	-0.2448	0.29	-	0.068	data0.fm1
Na ⁺	Oxalate ²⁻	-0.2176	1.74	-	0.122	data0.fm1
H ⁺	Cl ⁻	0.1775	0.2945	-	0.0008	data0.fm1
Fe ²⁺	Cl ⁻	0.3359	1.5322	-	-0.00861	Pitzer (1991)
<i>i</i>	<i>j</i>	$\theta_{cc'} \text{ or } \theta_{aa'}$			Source	
Na ⁺	H ⁺	0.036			data0.fm1	
Na ⁺	Fe ²⁺	0.08			Nemer et al. (2011)	
Cl ⁻	OH ⁻	-0.05			data0.fm1	
<i>i</i>	<i>j</i>	$\lambda_{nc} \text{ or } \lambda_{na}$			Source	
FeOxalate(aq)	Na ⁺	TBD ^b			This memo	
<i>i</i>	<i>j</i>	<i>k</i>	$\psi_{cc'a} \text{ or } \psi_{aa'c}$			Source
Na ⁺	H ⁺	Cl ⁻	-0.004			data0.fm1
Cl ⁻	OH ⁻	Na ⁺	-0.006			data0.fm1

^a data0.fm1: See Xiong (2011b)

^b TBD: To Be Determined

5. Text blocks required to update an EQ3/6 database (e.g., data0.fm1) for the model fitting

The following eight text blocks should be copied to appropriate places in an EQ3/6 database (e.g., data0.fm1) for the model fitting described in this memo.

5.1. Block for reaction (4) in Table 4.

The block below addresses the reaction (4) in Table 4. This block should be copied under "aqueous species" section of an EQ3/6 database. The information in this block comes from "data0.ymp.R2", and the extra information therein was trimmed out, so that the format of this block is consistent with that of "data0.fm1". "data0.ymp.R2" is one of the EQ3/6 databases that come within the installation package for EQ3/6 v.8.0a.

```
+-----+
FeOH+                FeOH+
charge = 1.0
****
3 element(s):
 1.0000 H                1.0000 Fe                1.0000 O
****
4 species in aqueous dissociation reaction:
-1.0000 FeOH+                -1.0000 H+
 1.0000 Fe++                1.0000 H2O
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
      No_Data    9.3148    No_Data    No_Data
      No_Data    No_Data    No_Data    No_Data
* Source: data0.ymp.R2
+-----+
```

5.2. Block for reaction (5) in Table 4.

The block below addresses the reaction (5) in Table 4. This block should be copied under "aqueous species" section of an EQ3/6 database.

```
+-----+
FeOxalate(aq)        FeC2O4(aq)
charge = 0.0
****
3 element(s):
 2.0000 C                1.0000 Fe                4.0000 O
****
3 species in aqueous dissociation reaction:
-1.0000 FeOxalate(aq)        1.0000 Fe++
 1.0000 Oxalate--
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
      No_Data    -4.05    No_Data    No_Data
      No_Data    No_Data    No_Data    No_Data
* Source: -4.05, Harrison and Thyne (1992)
+-----+
```

5.3. Block for reaction (10) in Table 4.

The block below addresses the reaction (10) in Table 4. This block should be copied under "solids" section of an EQ3/6 database.

```
+-----+
FeOxalate.2H2O(s)    FeC2O4.2H2O
V0PrTr = 0.000 cm**3/mol [source: ]
****
4 element(s):
 2.0000 C                4.0000 H                1.0000 Fe
+-----+
```

```

6.0000 0
****
4 species in aqueous dissociation reaction:
-1.0000 FeOxalate.2H2O(s)          1.0000 Fe++
2.0000 H2O                          1.0000 Oxalate--
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
      No_Data    0.0000   No_Data   No_Data
      No_Data   No_Data   No_Data   No_Data
* Source: -8.2965, per this memo. 0.0000 is place holder.
+-----+

```

5.4. Block for Pitzer parameters for ion pair of Fe++ and Cl- in Table 5.

The block below addresses the Pitzer parameters for ion pair of Fe++ and Cl- in Table 5. This block should be copied under "ca combinations: beta(n)(ca) and Cphi(ca) [optional: alpha(n)(ca)]" section of an EQ3/6 database.

```

+-----+
Fe++          Cl-
alpha(1) = 2.0
alpha(2) = 12.0
beta(0)
  a1 = 0.33590
  a2 = 0.
  a3 = 0.
  a4 = 0.
beta(1)
  a1 = 1.53220
  a2 = 0.
  a3 = 0.
  a4 = 0.
beta(2)
  a1 = 0.0
  a2 = 0.
  a3 = 0.
  a4 = 0.
Cphi:
  a1 = -0.00861
  a2 = 0.
  a3 = 0.
  a4 = 0.
* Source: Pitzer (1991)
+-----+

```

5.5. Block for Pitzer parameters for ion pair of Na+ and Fe++ in Table 5.

The block below addresses the Pitzer parameters for ion pair of Na+ and Fe++ in Table 5. This block should be copied under "cc' and aa' combinations: theta(cc') and theta(aa')" section of an EQ3/6 database.

```

+-----+
Na+          Fe++
theta:
  a1 = 0.08
  a2 = 0.
  a3 = 0.
  a4 = 0.
* Source: Nemer et al. (2011)
+-----+

```

5.6. Block for Pitzer parameters for the pair of FeOxalate(aq) and Na+ in Table 5.

The block below addresses the Pitzer parameters for the pair of FeOxalate(aq) and Na+ in Table 5. This block should be copied under "nc and na combinations: lambda(nc) and lambda(na)" section of an EQ3/6 database.

```
+-----+
FeOxalate(aq)          Na+
lambda:
  a1 = 0.0
  a2 = 0.
  a3 = 0.
  a4 = 0.
* Source: -0.061992, per this memo. 0.0 is place holder.
+-----+
```

5.7. Elemental iron.

The line below should be inserted under "elements" section of an EQ3/6 database (Domski, 2012).

```
Fe          55.84500
```

5.8. Block to add ferrous iron cation (Fe++) as a basis species.

The block below defines the ferrous iron cation (Fe++) as a basis species for aqueous speciation calculation. This block should be copied under "basis species" section of an EQ3/6 database (Domski, 2012).

```
+-----+
Fe++
  charge = 2.0
***
  1 element(s):
    1.0000 Fe
+-----+
```

6. Results and discussion

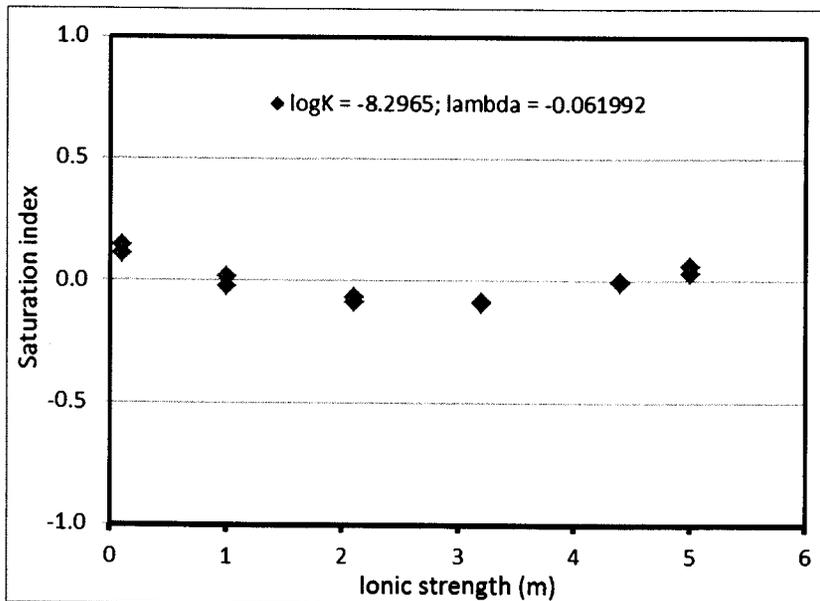
Fitting started with initial guesses of $\log K_{10} = -8.0$ and $\lambda_{\text{FeOxalate(aq)/Na+}} = 0.0$.

Fitting concluded with $\log K_{10} = -8.29$ and $\lambda_{\text{FeOxalate(aq)/Na+}} = -0.0619$. The minimized sum of squared saturation indices is 0.0658. Numbers were truncated to report three digits only. For those who may want to reproduce the results of this memo using the Python script and EQ3NR input files (*.3i files), $\log K_{10} = -8.29653070551$ and $\lambda_{\text{FeOxalate(aq)/Na+}} = -0.0619921553824$. The minimized sum of squared saturation indices is 0.0658006054.

The values of saturation indices from 12 experiments are confined within the narrow range of -0.093 to 0.142 over the entire ionic strength investigated (Figure 1). This indicates that the aqueous model (Table 4 and 5), including newly updated $\log K_{10}$ and $\lambda_{\text{FeOxalate(aq)/Na+}}$, predicts the equilibria with respect to FeOxalate.2H2O(s) for all the 12 experiments very closely.

Fitting procedure in this memo was reproduced independently by Paul Domski. See APPENDIX for his email regarding the reproduction of this fitting.

Figure 1. Plot of saturation index over ionic strength.



7. Files to be submitted

7.1. EQ3NR input files (*.3i, 12 files in total) and output files (*.3o, 12 files in total)

Input files: feoxna01.3i, feoxna02.3i, feoxna03.3i, feoxna04.3i, feoxna05.3i, feoxna06.3i, feoxna07.3i, feoxna08.3i, feoxna09.3i, feoxna10.3i, feoxna11.3i, feoxna12.3i.

Output files: feoxna01.3o, feoxna02.3o, feoxna03.3o, feoxna04.3o, feoxna05.3o, feoxna06.3o, feoxna07.3o, feoxna08.3o, feoxna09.3o, feoxna10.3o, feoxna11.3o, feoxna12.3o.

7.2. Python scripts

feoxna_12_nos.py (to be copied into the same folder as EQ3NR input files above; this file drives the fitting procedure)

EQ3CodeModule.py (to be copied into either the same folder as EQ3NR input files above or C:\Python27\Lib for versatile access; this file contains Python modules necessary for the fitting)

7.3. Excel files

GetEQData_v101e.xls (contains excel macro that extracts numbers from EQ3NR output files, *.3o)

Feox_NaCl.xls (contains ionic strength, saturation indices, and their plot, generated using excel macro in the file above)

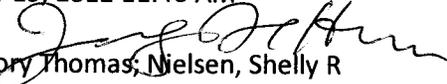
7.4. Email from Paul Domski on 7/19/2012

AP-154 Task 7 Fe - Oxalate Parameter Estimation.msg (See APPENDIX for its content)

8. References

- Domski, P.S. (2012) Memo to Records Center, Memo AP-154, Task 7 EQ3/6 Database Update. (This reference is cited in APPENDIX below)
- Harrison, W. J. and G.D. Thyne (1992) Predictions of diagenetic reactions in the presence of organic-acids, *Geochimica et Cosmochimica Acta* 56, 565-586.
- Ismail, A.E., M.B. Nemer, G.T. Roselle, and Y.-L. Xiong (2008) Iron, Lead, Sulfide, and EDTA Solubilities Test Plan, Sandia National Laboratories, TP 08-02. ERMS 548467.
- Jang, J.-H., Y.L. Xiong, S. Kim, and M.B. Nemer (2012) Second Milestone Report on Test Plan TP 08-02, "Iron, Lead, Sulfide, and EDTA Solubilities", Sandia National Laboratories, ERMS 557198.
- Kirchner, T.B. (2012) User's manual for the EQ3CodeModule, ERMS 557360.
- Nemer, M.B., Y.L. Xiong, A.E. Ismail, and J.-H. Jang (2011) Solubility of $\text{Fe}_2(\text{OH})_3\text{Cl}$ (pure-iron end-member of hibbingite) in NaCl and Na_2SO_4 brines. *Chemical Geology*, v. 280, pp. 26-32. (SAND2010-6500J)
- Pitzer, K.S. (1991) Ion interaction approach: theory and data correlation, in Pitzer, K.S., ed. *Activity Coefficients in Electrolyte Solutions*, 2nd edition, Chapter 3, p. 75-153, CRC Press, Boca Raton, Florida. TIC: 251799.
- Roselle, G.T. (2011) Determination of pC_{H^+} correction factors in brines, Sandia National Laboratories, ERMS 556699.
- Wolery, T. J. and R. L. Jarek (2003) Software User's Manual, EQ3/6, Version 8.0. 10813-UM-8.0-00. Albuquerque, NM: Sandia National Laboratories, ERMS 548926.
- Xiong, Y.-L. (2011a) Analysis Plan for Derivation of Thermodynamic Properties Including Pitzer Parameters for Solubility Studies of Iron, Lead and EDTA, AP-154, Sandia National Laboratories, ERMS 555374.
- Xiong, Y.-L. (2011b) Email from Yongliang Xiong to Jennifer Long on 3/9/2011, Release of EQ3/6 Database data0.fm1, ERMS 555152.

APPENDIX: Email from Paul Domski to Je-Hun Jang on 7/19/2012

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From: Domski, Paul S
Sent: Thursday, July 19, 2012 11:40 AM
To: Jang, Je-Hun 
Cc: Roselle, Gregory; Thomas, Nielsen, Shelly R
Subject: AP-154 Task 7 Fe - Oxalate Parameter Estimation

Dear Je-Hun,

I have independently reproduced the values that you estimated in your memo using the inputs that you provided to me in your draft memo entitled "Memo_Pitzer_FeOx_NaCl.docx". The parameters and values that I estimated using the Python script include the log K for FeOxalate(s) and the Pitzer Parameter, Lambda, for the ion pair of Na⁺ and FeOxlate(aq). I will document the method and results in a memo to the records center. The results that I got were: log K FeOxalate(s) = -8.2965, and lambda Na⁺ - FeOxlate(aq) = -0.061992.

Paul Domski
S.M. Stoller Corp
(505) 604-6736

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Note: Memo related to this email is Domski (2012).