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to: SNL WIPP Records Center
Defense Waste Management Programs

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subject: Memo AP-154, Task 10 EQ3/6 Database Update

This memo documents the steps used to update the EQ3/6 thermodynamic database parameters estimated in AP-154 and AP-155. The steps are as follows:

1) The official QA EQ3/6 database, data0.fmt.R2, aka, data0.fm1 is copied to a task specific interim database, which is updated only with the parameters that are being estimated for the task at hand, and any supporting parameters.
2) The Python script specific to the problem, and which calls the parameter optimization script "*EQ3CodeModule.py*" (Kirchner, 2012), is executed and the specified parameters are estimated.
3) The output of the Python script, a text file named "results.txt", which consists of the parameter estimates and the calculated residual, is evaluated in Excel to determine the parameter(s) which corresponds to the smallest value of the residual. The parameter value is plotted versus the residual to evaluate the nature of the minimum and if a global minimum has been found by the optimization routine.
4) If a global minimum has not been found the EQ3 problem will be evaluated and reposed to better constrain the parameters being estimated, and steps 2 and 3 will again be executed.
5) If a global minimum has been found, then the fitted parameters will be documented and added to the official cumulative interim database which will contain all of the new parameters from all of the AP-154 and AP-155 tasks. This cumulative interim database called data0.psd, is a copy of the official QA database data0.fm1, but contains the additional data documented by the tasks of AP-154 and AP-155, and will form the blue print for the future official QA database.

AP-154, Task 10 Parameters

A total of three parameters were estimated for AP-154, Task 10. These parameters were estimated by use of the inverse method(s) implemented in the Python script "*EQ3CodeModule.py*" (Kirchner, 2012).

The parameters were estimated simultaneously using the Python script, and included the three Pitzer binary interaction parameters for the Na^+ and $FeEDTA^{2-}$ pair ($\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ}).

In order to estimate these parameters additional parameters had to be added to the database, these included the element iron, Fe, the basis species ferrous iron, Fe^{2+}, two aqueous species, $FeOH^+$ and $FeEDTA^{2-}$(aq) (Jang 2012), the solid phase $Fe(OH)_2$(s), the Pitzer parameters for the interaction of

Fe^{2+} with Cl^- and Fe^{2+} with Na^+, and finally the parameters that were to be estimated, the Pitzer parameter for Na+ and $FeEDTA^{2-}$(aq).

A total of eight data blocks for the above described parameters were added to a pristine version of data0.fm1 and the resulting database was renamed data0.pd5. The Python script *"FeEDTA_Na.py"* (Jang, 2012) was created to call the parameter estimation script, *"EQ3CodeModule.py"* (Kirchner, 2012), with the specifics of which database to use and which parameters to fit.

The data blocks included in data0.pd5 are listed below:

1) Element Iron

```
Fe          55.84500
```

Note iron was included in the database data0.fm1, but was commented out, it was simply uncommented in data0.pd5.

2) Basis Species Ferrous Iron

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

3) Aqueous Species – $FeOH^+$

```
+--------------------------------------------------------------------
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
+--------------------------------------------------------------------
```

4) Aqueous Species – $FeEDTA^{2-}$

```
+--------------------------------------------------------------------
FeEDTA--                     FeC10H12O8N2--
     charge  =  -2.0
****
     5 element(s):
     10.0000 C             12.0000 H             1.0000 Fe
      2.0000 N              8.0000 O
****
     3 species in aqueous dissociation reaction:
    -1.0000  FeEDTA--                       1.0000  Fe++
     1.0000  EDTA----
*
**** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
```

```
          No_Data    -16.100    No_Data    No_Data
          No_Data    No_Data    No_Data    No_Data
   * Source: -16.1 Morel and Hering (1993), p.339, I=0, 25 degree C
   +-----------------------------------------------------------------
```

5) Pitzer Parameters for Fe^{2+} and Cl^-

```
+-----------------------------------------------------------------
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 and Mayorga (1973), Pitzer (1991)
+-----------------------------------------------------------------
```

6) Pitzer Parameters for Na^+ and Fe^{++}

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

7) Log K for the solid phase $Fe(OH)_2$

```
   +-----------------------------------------------------------------
   Fe(OH)2-Hex                 Fe(OH)2
        V0PrTr  =     24.630 cm**3/mol [source: supcrt92 ]
   ****
        3 element(s):
         2.0000 H              1.0000 Fe             2.0000 O
   ****
        4 species in aqueous dissociation reaction:
       -1.0000  Fe(OH)2-Hex                -2.0000  H+
        1.0000  Fe++                        2.0000  H2O
   *
   **** logK grid [0-25-60-100C @1.0132bar; 150-200-250-300C @Psat-H2O]:
          No_Data    12.9500    No_Data    No_Data
          No_Data    No_Data    No_Data    No_Data
   * Source: 12.95, Nemer et al. (2011)
   +-----------------------------------------------------------------
```

8) Pitzer Parameters for Na^+ and FeOxalate(aq) – fitting parameter

```
+------------------------------------------------------------------
Na+                          FeEDTA--
  alpha(1) = 2.0
  alpha(2) = 12.0
  beta(0)
    a1 = 0.0
    a2 = 0.
    a3 = 0.
    a4 = 0.
  beta(1)
    a1 = 0.0
    a2 = 0.
    a3 = 0.
    a4 = 0.
  beta(2)
    a1 = 0.0
    a2 = 0.
    a3 = 0.
    a4 = 0.
  Cphi:
    a1 = 0.0
    a2 = 0.
    a3 = 0.
    a4 = 0.
* Source: Memo by Jang (2012)
+------------------------------------------------------------------
```

Results

The following table lists the results:

Parameter	Fit Value	Residual	Results file	Python Script
Na^+ - $FeEDTA^{2-}$ $\beta^{(0)}$	-8.43	0.854	*"Results_AP154_task10.xlsx"*	*"FeEDTA_Na.py"*
Na^+ - $FeEDTA^{2-}$ $\beta^{(1)}$	52.49			
Na^+ - $FeEDTA^{2-}$ C^{ϕ}	3.41			

References

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

Jang, J.-H., 2012. "Derivation of Pitzer ion interaction parameters for the pair of Na^+ and $FeEDTA^{2-}$". Memorandum to Records. Carlsbad, NM: Sandia National Laboratories.

Xiong, Y.-L. 2011. "Analysis Plan for Derivation of Thermodynamic Properties Including Pitzer Parameters for Solubility Studies of Iron, Lead, and EDTA" AP-154, Revision 0. Carlsbad, NM: Sandia National Laboratories.