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subject: Incorporation of Amorphous Calcium Carbonate into the EQ3/6 HMY Database and Its Modified Version HML

The objective of this memorandum is to document the release of a modified EQ3/6 database to support the analysis of the effects of the consumption of carbon dioxide (CO_2) by calcite ($CaCO_3$) precipitation on the excess factor calculated for the magnesium oxide (MgO) engineered barrier that the U.S Department of Energy is emplacing in the Waste Isolation Pilot Plant.

In particular, this database will be used to simulate the effects of precipitation of amorphous calcium carbonate ($CaCO_3$(am)) on the MgO excess factor. If the precipitation of calcite were inhibited, metastable $CaCO_3$ polymorphs or hydrates such as aragonite ($CaCO_3$), vaterite ($CaCO_3$), $CaCO_3$ monohydrate ($CaCO_3 \cdot H_2O$), ikaite ($CaCO_3 \cdot 6H_2O$), and $CaCO_3$(am) would precipitate instead of calcite; and the brines from which these phases precipitates would retain a higher dissolved Ca concentration than if thermodynamically stable calcite precipitates (e.g., Buchardt et al., 2001). For instance, the formation of $CaCO_3$(am) in nature has been observed (e.g., Aizenberg et al., 2002). $CaCO_3$(am) has the highest solubility product of any of the metastable $CaCO_3$ polymorphs or hydrates that we have identified so far. Therefore, use of the solubility product for $CaCO_3$(am) in simulations of CO_2 consumption by $CaCO_3$ precipitation will provide a conservative test of the effects of precipitation of these metastable phases.

In the previous, modified version of the EQ3/6 database (HMY) that supports the Pitzer activity-coefficient option, earlandite ($Ca_3(C_6H_5O_7)_2 \cdot 4H_2O$), whewellite ($CaC_2O_4 \cdot H_2O$), and aqueous citrate and oxalate species were incorporated (Xiong, 2006). That database, HMY, was modified from the previous EQ3/6 database (HMP) (Xiong, 2004). In turn, the HMY database will be modified to incorporate $CaCO_3$(am).

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1 INCORPORATION OF $CaCO_3$(am) INTO EQ3/6 HMY

There are two recent, independent studies on the solubility product constants of the $CaCO_3$(am) (Brečević and Nielsen, 1989; Clarkson et al., 1992). The solubility reaction for $CaCO_3$(am) can be cast as follows:

$$CaCO_3(am) = Ca^{2+} + CO_3^{2-} \quad (1)$$

In the study of Brečević and Nielsen (1989), a measured volume of $CaCl_2$ solution was placed in a 200 mL reaction vessel. Then, a measured volume of a concentrated Na_2CO_3 solution was added to the vessel, resulting in a total volume of 50 mL. Therefore, their experiments were carried out from the direction of supersaturation. By using the Davies equation, they obtained the following equation for the temperature dependence of the solubility product at infinite dilution in the temperature range from 10 to 55 °C for Reaction 1:

$$-\log K_{sp} = 6.1987 + 5.336 \times 10^{-3} t + 1.096 \times 10^{-4} t^2, \quad (2)$$

in which t is temperature in Celsius. According to Eq. 2, log K_{sp} at 25 °C is calculated to be –6.401.

In the study of Clarkson et al. (1992), precipitation was induced by adding a certain volume of Na_2CO_3 to a solution of $CaCl_2$ in a sealed Pyrex cell. In their undersaturation experiments, $CaCO_3$(am) was prepared by mixing a cold, concentrated Na_2CO_3 solution and a $CaCl_2$ solution, which produced a gel. Then, the solid was dispersed in a solution containing various concentrations of Na_2CO_3 and NaCl. In their calculations of activity coefficients, the Davies equation was also used. Their equation for the temperature dependence of log K_{sp} from 16 to 60 °C is:

$$\log K_{sp} = 1247.0/T - 10.224, \quad (3)$$

in which T is the temperature in Kelvins. According to Eq. 3, the log K_{sp} at 25 °C (298.15 K) is calculated to be –6.042.

In the critical review of Gal et al. (1996), the solubility product of Brečević and Nielsen (1989) was adopted. Hence, the log K_{sp} of Brečević and Nielsen (1989) was selected for use in the modified EQ3/6 database HML.

Based on the log K_{sp} of Brečević and Nielsen (1989), the free energy change for Reaction 1 is calculated according to the following equation:

$$\log K_{sp} = -\Delta_r G^\circ/(2.3026 \times R \times T), \quad (4)$$

in which R is the gas constant (1.98719 cal mol^{-1} K^{-1}), and T is absolute temperature (T = 298.15 K at 25 °C). The free energy change for Reaction 1 at 25 °C is listed in Table 1.

The free energy change for a chemical reaction is expressed in the following general equation:

$$\Delta_r G = \sum_j \Delta_f G_{j,product} - \sum_i \Delta_f G_{i,reac.} \quad (5)$$

According to Eq. 5, and based on $\Delta_r G^o$ listed in Table 1 and $\Delta_f G^o$ for Ca^{2+} and CO_3^{2-} listed in Table 2, the free energy of formation for $CaCO_3$(am) is derived from Reaction 1 and listed in Table 2.

In the HMY database, the association reaction for CO_3^{2-} is given as:

$$CO_3^{2-} + H^+ = HCO_3^-, \quad (6)$$

which has a log K of 10.3392 (Table 3). The combination of Reaction 1 with Reaction 6 yields the following dissolution reaction:

$$CaCO_3(am) + H^+ = Ca^{2+} + HCO_3^- \quad (7)$$

The equilibrium constant for Reaction 7 is 3.938 (see Table 3), which is calculated as the difference between the equilibrium constants for Reactions 6 and 1 (10.3392 – 6.401). This value is used in the modified database.

2 HML DATABASE

Using the equilibrium constant listed in Table 3 to modify HMY, the HML database is formally established. This database has been successfully run by EQPT, an executable in the EQ3/6 geochemical software package (Wolery, 1992), and files "output.hml" (an formatted output file) and "data1f.hml" (a formatted data file) have been generated. File comparisons between "output.hml" and "output.hmy", and between "data1f.hml" and "data1f.hmy" indicate that the only differences between HML and HMY are those of entries of the above species. An electronic copy of this database will be placed on a floppy disk containing the "EQ3/6 HML Database" to be submitted along with this memo.

REFERENCES

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Xiong, Y.-L. 2006. "Incorporation of Calcium Citrate Hydrate, Earlandite; Calcium Oxalate Monohydrate, Whewellite; and Aqueous Species of Citrate and Oxalate into the EQ3/6 HMP Database and Its Modified Version HMY." Memorandum to L.H. Brush, October 18, 2006. Carlsbad, NM: Sandia National Laboratories. ERMS 544529.

Table 1. The Free Energy Change at Reference Sate (298.15 K and 1 bar) Calculated in This Memorandum.

Reaction	$\Delta_r G^o$, cal mol^{-1}	Reference
Reaction 1	8733	Calculated from log K_{sp} from Brečević and Nielsen (1989)

Table 2. Standard Free Energies of Formation for Ca^{2+}, CO_3^{2-} and $CaCO_3$(am) at Reference State (298.15 K and 1 bar).

Species	$\Delta_f G^o$, cal mol^{-1}	References
Ca^{2+}	–132,302	HMY database (Xiong, 2006)
CO_3^{2-}	–126,166	HMY database (Xiong, 2006)
$CaCO_3$(am)	–267,201	This memorandum

Table 3. Dissolution Constant of $CaCO_3$(am) at Reference Sate (298.15 K and 1 bar) Used in the Modified EQ3/6 Database.

Reaction	log K	References
Reaction 6	10.3392	HMY database (Xiong, 2006)
Reaction 7	3.938	This memorandum, based on log K_{sp} for Reaction 1 from Brečević and Nielsen (1989), and log K for Reaction 6 from HMY (Xiong, 2006)

```
Comparing files data1f.hmy and DATA1F.HML
***** data1f.hmy
   11   12
data0.hmy.v8.R6
CII: GEMBOCHS.V2-EQ8-data0.hmp.v8.R6
THERMODYNAMIC DATABASE
***** DATA1F.HML
   11   12
data0.hml.v8.R6
CII: GEMBOCHS.V2-EQ8-data0.hml.v8.R6
THERMODYNAMIC DATABASE
*****

***** data1f.hmy
Output package:  eq3
Data set:        hmy
+------------------------------------------------------------------------
***** DATA1F.HML
Output package:  eq3
Data set:        hml
+------------------------------------------------------------------------
*****

***** data1f.hmy
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
Calcite                         3    4
       100.087   0.    36.934
***** DATA1F.HML
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
CaCO3(am)                       3    4
       100.087   0.    36.934
*****

***** data1f.hmy
     3.0000  O
    -1.0000  Calcite                    -1.0000  H+
***** DATA1F.HML
     3.0000  O
    -1.0000  CaCO3(am)                  -1.0000  H+
     1.0000  Ca++                       1.0000  HCO3-
 3.938000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
Calcite                         3    4
       100.087   0.    36.934
     1.0000  C          1.0000  Ca
     3.0000  O
    -1.0000  Calcite                    -1.0000  H+
*****
```

```
Comparing files output.hmy and OUTPUT.HML
***** output.hmy

 Run  09:53:06  18Oct2006

***** OUTPUT.HML

 Run  16:51:44  26Oct2006

*****

***** output.hmy

 data0.hmy.V8.R6
 CII: GEMBOCHS.V2-EQ8-data0.hmp.V8.R6
 THERMODYNAMIC DATABASE
***** OUTPUT.HML

 data0.hml.V8.R6
 CII: GEMBOCHS.V2-EQ8-data0.hml.V8.R6
 THERMODYNAMIC DATABASE
*****

***** output.hmy
 Output package:  eq3
 Data set:        hmy
 +------------------------------------------------------------------------
***** OUTPUT.HML
 Output package:  eq3
 Data set:        hml
 +------------------------------------------------------------------------
*****

***** output.hmy
    13 CaCl2:4H2O
    14 Calcite
    15 Carnallite
    16 Chloromagnesite
    17 Dolomite
    18 Earlandite
    19 Epsomite
    20 Gaylussite
    21 Glauberite
    22 Gypsum
    23 Halite
    24 Hexahydrite
    25 Hydromagne5424
    26 Hydromagne4323
    27 K2CO3:1.5H2O
    28 K3H(SO4)2
    29 K8H4(CO3)6:3H2O
    30 KNaCO3:6H2O
    31 Kainite
    32 Kalicinite
    33 Kieserite
    34 Leonite
    35 Lime
    36 Magnesite
    37 Mercallite
    38 Mirabilite
    39 Misenite
    40 Na2CO3:7H2O
    41 Na3H(SO4)2
    42 Na4Ca(SO4)3:2H2O
    43 Nahcolite
    44 Natron
    45 Nesquehonite
    46 Oxychloride-Mg
    47 Periclase
    48 Picromerite
    49 Pirssonite
    50 Polyhalite
    51 Portlandite
    52 Sylvite
    53 Syngenite
    54 Tachyhydrite
    55 Thenardite
    56 Thermonatrite
    57 Trona
```

```
    58 Trona-K
    59 Whewellite

***** OUTPUT.HML
    13 CaCl2:4H2O
    14 CaCO3(am)
    15 Calcite
    16 Carnallite
    17 Chloromagnesite
    18 Dolomite
    19 Earlandite
    20 Epsomite
    21 Gaylussite
    22 Glauberite
    23 Gypsum
    24 Halite
    25 Hexahydrite
    26 Hydromagne5424
    27 Hydromagne4323
    28 K2CO3:1.5H2O
    29 K3H(SO4)2
    30 K8H4(CO3)6:3H2O
    31 KNaCO3:6H2O
    32 Kainite
    33 Kalicinite
    34 Kieserite
    35 Leonite
    36 Lime
    37 Magnesite
    38 Mercallite
    39 Mirabilite
    40 Misenite
    41 Na2CO3:7H2O
    42 Na3H(SO4)2
    43 Na4Ca(SO4)3:2H2O
    44 Nahcolite
    45 Natron
    46 Nesquehonite
    47 Oxychloride-Mg
    48 Periclase
    49 Picromerite
    50 Pirssonite
    51 Polyhalite
    52 Portlandite
    53 Sylvite
    54 Syngenite
    55 Tachyhydrite
    56 Thenardite
    57 Thermonatrite
    58 Trona
    59 Trona-K
    60 Whewellite

*****

***** output.hmy

 Completed processing the pitzer data file data0.hmy.V8.R6.

***** OUTPUT.HML

 Completed processing the pitzer data file data0.hml.V8.R6.

*****

***** output.hmy

          Start time = 09:53:06  18Oct2006
            End time = 09:53:06  18Oct2006

           run time =  0.400     seconds

***** OUTPUT.HML

          Start time = 16:51:44  26Oct2006
            End time = 16:51:45  26Oct2006

           run time =  0.440     seconds
```

*****