570188

Sandia National Laboratories
Operated for the U.S. Department of Energy by
Sandia Corporation

4100 National Parks Highway
Carlsbad, NM 88220

Phone: (575) 234-0056
Fax: (575) 234-0061
Internet: psdomsk@sandia.gov

date: July 30, 2018

to: SNL WIPP Records Center
Defense Waste Management Programs

from: Paul S. Domski

subject: Comparison of Hydromagnesite5424 Log K_{sp} Values

It has been demonstrated (Xiong and Domski, 2016) that the equilibrium that exists between brucite ($Mg(OH)_2$) and hydromagnesite has a strong influence on the pH and carbon dioxide fugacity in the near-field environment of the WIPP. Both the pH and carbon dioxide fugacity have an impact on the actinide solubilities, and likewise impact performance assessment (PA), rendering hydromagnesite solubility an important parameter for PA. The purpose of this memo is to compare the solubility product (K_{sp}) of hydromagnesite5424 of Robie and Hemmingway (1973) that is included in the DATA0.FM1 EQ3/6 database with the data measured in the laboratory as reported in Xiong (2010), and the solubility product calculated from this data by Xiong (2010 and 2015) to determine which value to use for WIPP calculations.

The dissolution of hydromagnesite5424 follows the reaction:

$$Mg_5(CO_3)_4(OH)_2.4H_2O + 6H^+ = 5Mg^{2+} + 4HCO_3^- + 6H_2O$$

The value of log K_{sp} used in DATA0.FM1 (Xiong 2011) for the dissolution of hydromagnesite5424 is 32.2529 (Robie and Hemmingway, 1973). Robie and Hemmingway (1973) calculated the log Ksp of hydromagnesite5424 from the Gibb's free energy of formation, which in turn were calculated from calorimetric measurements, and thus, do not represent actual solubility data. Xiong (2010) calculated the hydromagnesite 5424 log K_{sp} for the SIT model to be 30.2528, and Xiong (2015) converted the SIT value to the Pitzer ion-activity model value for hydromagnesite5424 to be 29.3328, the value which would be included in the DATA0.FM2 database (Domski and Xiong, 2015).

Method

The experiments as described in Xiong (2010) were executed by creating NaCl stock solutions at 0.1, 1.0, 2.1, 3.2, and 4.4 molality, and adding an excess of synthetic hydromagnesite5424 to each vessel. Details of hydromagnesite synthesis can be found in Xiong (2010). The vessels were open to atmospheric carbon dioxide at a partial pressure of $10^{-3.4}$ atm. Each vessel was well mixed to insure equilibrium with both the CO_2(g) and the solid hydromagnesite. Samples were collected on a semi-regular basis for each stock solution for up to 5 years, prior to sample removal the pH of each was measured. The details of the analytical procedures can be found in Xiong (2010).

Information Only

WIPP:4.2.1:PA:QA-L:540715

For comparison purposes an EQ3/6 run was setup to emulate the experimental conditions of Xiong (2010) as outlined above. An EQ3NR input file was created which set the constituent ions in the system (Na^+, $Ca2^+$, Cl^-, $HCO3^-$, and H^+) to a nominal value of 1.0×10^{-18} m, except for pH which was set equal to 7.0. Creation of the EQ3NR input file is required by EQ6 which uses the EQ3NR "pickup" file which sets the initial conditions for the subsequent EQ6 simulation.

The EQ6 code is a reaction-path simulator, in other words it uses the initial fluid composition specified in the EQ3NR pickup file, and then incrementally reacts user specified reactants with the fluid, in accordance to the reactions in the thermodynamic database, while keeping a record of all of the important chemical, and some physical properties, of the specified chemical system. Thus, as mineral phases reach saturation in the solution they will be begin to "precipitate", in complex systems multiple phases can be forming simultaneously, while phases which had formed previously may become unstable and dissolve back into solution. The EQ6 reaction path terminates either when the system comes to equilibrium, or when the reactants are expended. The detail that EQ6 provides is very useful for simulating well constrained laboratory experiments, and complex theoretical problems.

To simulate Xiong's (2010) hydromagnesite experiments the phase Hydromagnesite5424 was included as a reactant using the EQ6 keyword "Pure Mineral" with an excess of 10 moles available for reaction. Also specified was Na^+ and Cl^- which were specified as "Aqueous Species" with their total mole values set to 4.4 moles, the maximum concentration of Xiong's (2010) stock solutions. In addition to these reactants, $CO_2(g)$ was specified as a "Fixed Fugacity Gas", at a fugacity of $10^{-3.4}$ bars. Note that at every step in the reaction path $CO_2(g)$ was maintained at this fugacity.

The EQ6 input file was copied into two separate folders each to be executed using a different database. In the first case EQ6 was run using DATA0.FM1, and in the second case it was run using DATA0.HYD. The only difference between these databases was the value of Log K_{sp} for Hydromagnesite5424, where DATA0.FM1 contains the Robie and Hemmingway (1973) value of 32.2529, and DATA0.HYD implements the Xiong (2015) value of 29.3328.

Results

The results of the EQ6 simulations are displayed in Figures 1 – 3, and are tabulated in *2010_Hydromag_data.xlsx*[1]. Data were extracted from the EQ6 output files using the Excel macro *GetEQData_v101f.xls* included with the file package. These data show that for the entire reaction path, for both DATA0.FM1 and DATA0.HYD, that Hydromagnesite5424 was saturated, i.e., Log Q/K = 0.0, and likewise the $CO_2(g)$ fugacity was maintained at $10^{-3.4}$.

The Figure 1 plot shows the total magnesium concentration versus the NaCl concentration. The measured data from all sample dates are plotted with the most aged samples plotted in blue. It might concluded that based on the spread of the measured data in relation to where the most aged samples plot that the oldest samples are not any more representative of equilibrium conditions than any of the other sample dates. Figure 1 clearly shows that Xiong's Log K_{sp} provides a better fit to the data than does the Robie and Hemmingway (1973) value.

Figure 2 shows the pmH ($-\log_{10}$ of the H^+ molality) versus NaCl molality. Although the spread in the pmH data is large, the fit using Xiong's (2010) Log K_{sp} for Hydromagnesite5424 is much better than the

[1] files may found at: /nfs/data/CVSLIB/WIPP_EXTERNAL/APPENDIXGEOCHEM/Files

Information Only

fit using the value of Robie and Hemmingway. Note that due to a typographic error the measured pmH values for 4.4 m NaCl from Table 4 of Xiong (2010) were in error by a factor of ten, this error was corrected in a memo by Xiong (2018). The 4.4 m NaCl data as listed in Table 4 (Xiong, 2010) should be divided by ten.

Finally, Figure 3 shows the model output total inorganic carbon, all of which is some form of carbonate, versus NaCl molality, unfortunately no carbonate data were collected for the samples so there is no point of reference. As expected, Xiong's lower value of Log K_{sp} provides less carbonate to the system than Robie and Hemmingway's value.

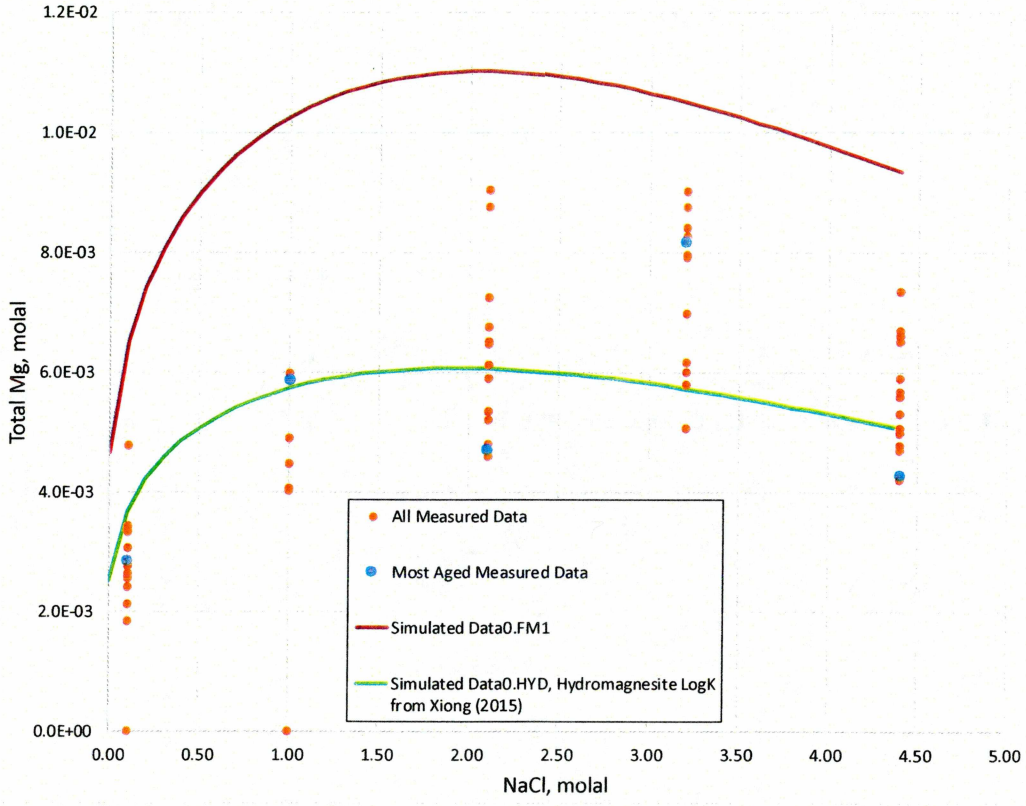


Figure 1. Plot of total magnesium versus sodium chloride concentration.

Information Only

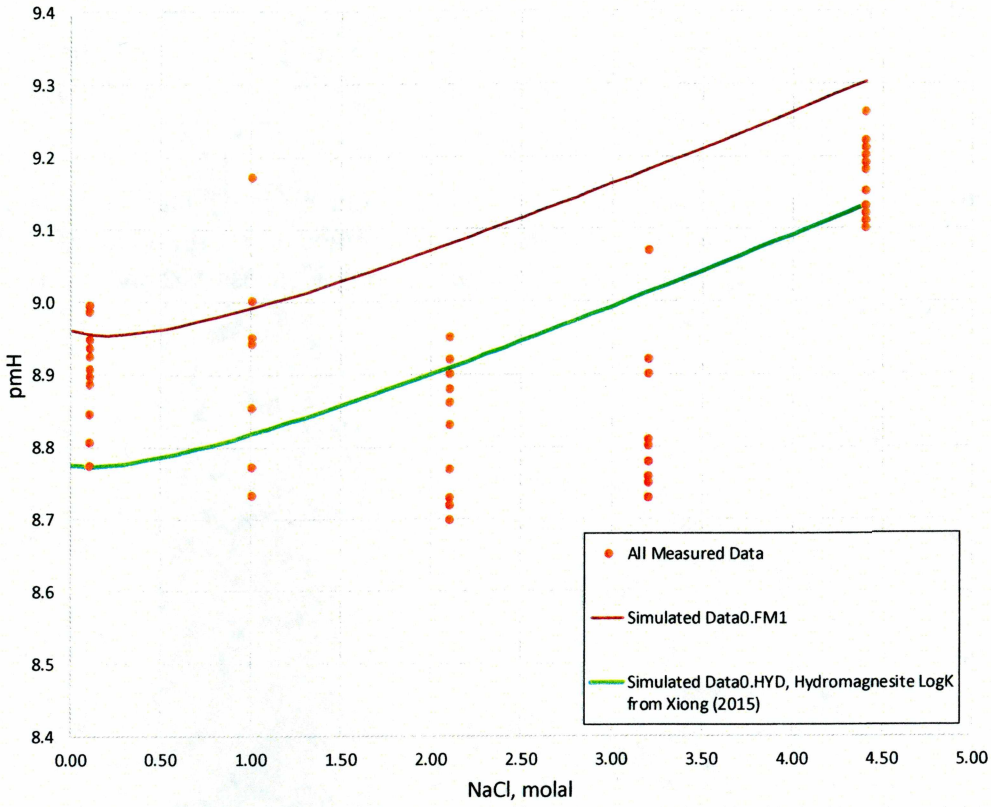


Figure 2. Plot of pmH versus sodium chloride concentration.

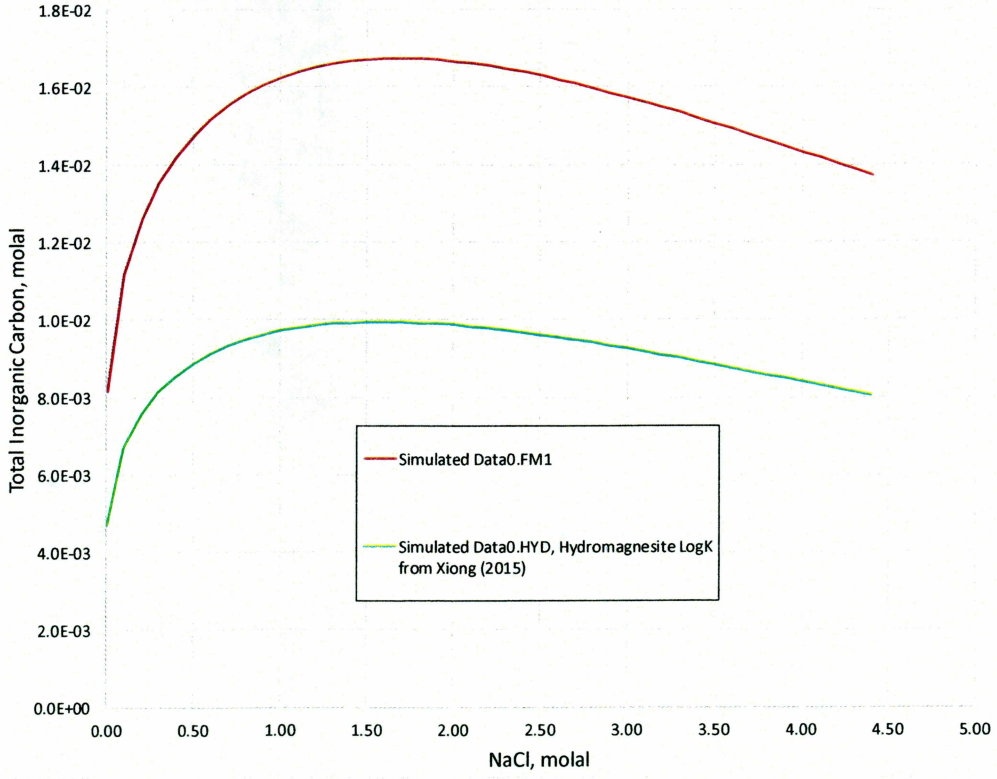


Figure 3. Plot of total inorganic carbon versus sodium chloride concentration.

Information Only

Discussion

Xiong (2010) also performed experiments, as described above, using natural hydromagnesite from two localities, one from Staten Island, NY and the other Gabbs, NV. Both of these yielded SIT Log K_{sp} values lower than the synthetic hydromagnesite value. Xiong attributes the lower log K_{sp} to higher crystallinity and possible impurities of these natural materials, and thus they were not included for use on the WIPP project. However, the lower solubility of the natural hydromagnesite samples lends some credence to the experimental procedures given that it would be expected for higher crystallinity material to have lower solubility.

Conclusions

Based on this modeling exercise it may be concluded that the value of Log K_{sp} derived by Xiong (2010 and 2015) better represents the measured hydromagnesite5424 data, both the solubility data and the pH data, than the value implemented in DATA0.FM1 of Robie and Hemmingway (1973). For this reason it recommended that Xiong's (2010 and 2015) Log K_{sp} be used for future WIPP recertification work.

References

Domski, P.S. and Y.L. Xiong, 2015. "Analysis Plan for the Compilation and Testing of Selected Parameters from AP-134, Revision 3, AP-154, Revision 2 and AP-155, Revision 3 for Incorporation in a New QA EQ3/6 Thermodynamic Database". Carlsbad, NM: Sandia National Laboratories. ERMS: 564585.

Robie, R.A., and Hemingway, B.S., 1973. The enthalpies of nesquehonite, $MgCO_3 \cdot 3H_2O$, and hydromagnesite, $5MgO \cdot 4CO_2 \cdot 5H_2O$. US Geological Survey Journal of Research 1, No.5, 543–547.Xiong, Y.-L., 2010. "Experimental Determination of Solubility Constant of Hydromagnesite (5424) in NaCl Solutions up to 4.4 m at Room Temperature", SAND2010-7132J. Carlsbad, NM: Sandia National Laboratories.

Xiong, Y.-L., 2011. "Release of EQ3/6 Database Data0.FM1." E-mail to Jennifer Long, March 9, 2011, Carlsbad, NM. Sandia National Laboratories. ERMS 555152.

Xiong, Y.-L., 2015. "Recalculation of Solubility Constants of Synthetic Hydromagnesite(5424) Using the Pitzer Model". Memo to WIPP Records Center. Carlsbad, NM: Sandia National Laboratories. ERMS564356.

Xiong, Y.-L., 2018. "Addendum to "Experimental Determination of Solubility Constant of Hydromagnesite (5424) in NaCl Solutions up to 4.4 m at Room Temperature." (Xiong, 2010)". Memo to WIPP Records Center. Carlsbad, NM: Sandia National Laboratories.

Xiong Y.L. and P.S. Domski. 2016. "Prediction of Baseline Actinide Solubilities with an Updated EQ3/6 Thermodynamic Database (DATA0.FM2) in Response to EPA Completeness Comment 3-C-2 for CRA 2014. Carlsbad, NM: Sandia National Laboratories. ERMS 565032.

Information Only