SOFTWARE VALIDATION REPORT FOR GEOCHEMIST'S WORKBENCH, VERSION 5.0

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March 30, 2005
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1 SCOPE OF THE VALIDATION

The purpose of this document is to report the results of validation testing for the geochemical code Geochemist's Workbench, Version 5.0 (Bethke, 2004a,b,c) performed under the Geochemist's Workbench Software Validation Test Plan (Browning, 2003a). The Geochemist's Workbench code was developed by Craig Bethke at the University of Illinois at Urbana-Champaign and acquired by the Center for Nuclear Waste Regulatory Analyses (CNWRA) to provide technical assistance to the U.S. Nuclear Regulatory Commission (NRC) in its high-level waste program. The following software programs are used to perform geochemical evaluations in the Geochemist's Workbench, Version 5.0 software package:

- Rxn
- Act2
- Tact
- React
- SpecE8

These programs offer several user options, including options to format and constrain data, depict modeling results, and control numerical processing methods. These options increase the range of site-specific geochemical applications that can be evaluated by the code but do not modify the general functionality of the individual software tools. These software validation tests are designed to provide evidence of correct and successful implementation of the underlying theory and algorithms as outlined in the Geochemist's Workbench Version 5.0 Reference Manual and is required by the Technical Operating Procedure (TOP)–018 (CNWRA, 2004). Geochemist's Workbench, Version 5.0 has several capabilities that are not planned for the CNWRA applications related to the NRC high-level waste program, these capabilities were not tested at this time. Capabilities not tested include:

- Ion exchange
- Sorption onto mineral surfaces
- Microbial metabolism and growth
- Virial methods of calculating species activities

Specifically, SpecE8, a flexible program that models the equilibrium states of geochemical systems that contain an aqueous phase, is a new module in the Geochemist's Workbench, Version 5.0 package that was not available in previous versions of the software. Also, the Professional release of Geochemist's Workbench, Version 5.0 also includes X1t and X2t modules for reactive transport modeling in one– and two–dimensions. SpecE8, X1t, and X2t were not included in the validation testing. If a decision is made to use these code capabilities, the Geochemist's Workbench software validation test plan and report will be modified as necessary.

The software validation report for Geochemist's Workbench, Version 4.0.2 was published in 2003 (Browning, 2003b). Because Geochemist's Workbench, Version 5.0 is very similar to Version 4.0.2, the validation of Version 5.0 presented in this report used the same test cases as those used for validating Version 4.0.2. This validation report uses much of the same text as the previous validation report (Browning, 2003b).

2 THERMODYNAMIC DATA USED IN TESTING

The results from geochemical codes are dependent on the type and quality of the data used in the simulation. These results are typically contained in databases that are searched and read by the code, based on the input provided by the user. Databases are considered separately from the input file that defines the geochemical problem and are not modified within the context of a running simulation.

The Geochemist's Workbench, Version 5.0 package includes the following thermodynamic databases:

- thermo.dat (employs Debye-Huckel equation for calculating activity coefficients)
- thermo.com.V8.R6+.dat (Lawrence Livermore National Laboratory "combined" database, Version 8, Release 6, in which the redox coupling among organic species has been modified somewhat relative to thermo.dat)
- thermo_pitzer.data (contains coefficients needed for Pitzer activity model)
- thermo_hmw.dat (contains coefficients needed for Harvie-Moller-Weare activity model)
- thermo_hdata.dat (contains coefficients needed to calculate activities for saline solutions)
- thermo.phrqpitz (contains coefficients needed for modified Harvie-Moller-Weare activity model)

These thermodynamic databases contain properties of aqueous species, minerals, and gases; and can be accessed by any of the Geochemist's Workbench software programs. The databases also include equilibrium constants for the reactions to form these species and information required to calculate activity coefficients. When available, data are provided for the temperature range 0–300 °C at one atm pressure below 100 °C and along the vapor pressure curve for water at higher temperatures. If information on equilibrium constants is not available at specific temperatures, the omissions are generally denoted by a 500 in the databases. All thermodynamic databases in the Geochemist's Workbench software package can be modified by the user, and new thermodynamic databases can be created.

The most commonly used database in the Geochemist's Workbench, Version 5.0 software package is the thermo.dat database, which calculates activity coefficients using the B dot equation. The thermo.dat database was compiled at Lawrence Livermore National Laboratory for use with the geochemical code EQ3/6 (Wolery, 1992) and is based mainly on the SUPCRT data compilation (Johnson, et al., 1991). The thermo.dat database is the default database for all Geochemist's Workbench software programs. Other databases in the Geochemist's Workbench installation package were designed to support calculations involving high ionic strength solutions, which are applicable to a small subset of geologic problems that can be addressed by thermodynamic and kinetic models. The thermo_hdata.dat and thermo_pitzer.dat databases are included in the Geochemist's Workbench, Version 5.0 software package to maintain compatibility with earlier releases of the software but are neither supported nor recommended for use with Geochemist's Workbench, Version 5.0 (Bethke, 2004a).

Validation exercises described in this report are, therefore, performed using the thermo.dat database. If a decision is made to use thermo.com.V8.R6+.dat, thermo_pitzer.dat, thermo_hdata.dat, thermo_hmw.dat, or thermo.phrqpitz databases in support of the NRC high-level waste program, the validation test plan (Browning, 2003a) will be modified and additional validation exercises will be performed.

3 TEST CASES

The test cases to be used in validation testing have been identified previously (Browning, 2003*a*). The following sections are intended to report the results of the testing.

Validation tests are performed for four of the geochemical software programs in Geochemist's Workbench, Version 5.0 (i.e., Rxn, Act2, Tact, and React). These programs are designed for interactive, rather than batch mode, use. This approach allows the user to configure each Geochemist's Workbench program interactively with a series of commands that modify, run, or save input files. Although input scripts for each of the programs can be written and saved, scripts do not include the history of interactive commands used to generate files. The sequence of interactive commands for each validation test is documented below. Output files can be written for all programs and are automatically generated with the use of the Act2, Tact, and React programs.

Individual input files used in the Geochemist's Workbench, Version 5.0 software validation tests are included in Appendix A and as WordPerfect files in a CD attachment. It is not feasible to include the associated output files in an Appendix to this report, however, because the size of individual output files is typically large. The electronic files for some of the output files are provided in a CD attachment.

Unless otherwise specified, all geochemical calculations will be conducted using an independent set of aqueous species, known as the basis species. Table 3-1 shows the default list of independent basis species used in Geochemist's Workbench. Reactions described by basis species may involve dissolved species only or interactions with solid phases and gases. Basis species comprise a portion of all thermodynamic databases included in the Geochemist's Workbench installation package and can be modified interactively by the user.

Table 3-1. Basis Species in the Geochemist's Workbench, Version 5.0 Database*†

H_2O	Eu+++	Pb++
Ag+	F-	PUO2++
Al+++	H+	Ra++
Am+++	HPO4--	Rb+
As(OH)4-	Hg++	Ru+++
Au+	I-	SeO3--
B(OH)3	Fe++	SiO2(aq)
Ba++	K+	Sr++
Br-	Li+	SO4--
Ca++	Mg++	TcO4-
HCO3-	Mn++	Th++++
Cs+	NO3-	Sn++++
Cl-	Na+	U++++

Table 3-1. Basis Species in the Geochemist's Workbench, Version 5.0 Database*† (Continued)		
Co++	Ni++	V+++
Cr+++	Np++++	Zn++
Cu+	O2(aq)	

*Johnson, J.W., E.H. Oelkers, and H.C. Helgeson. "SUPCRT92: A Software Package for Calculating the Standard Molal Thermodynamic Properties of Minerals, Gases, Aqueous Species, and Reactions from 1 to 5,000 Bars and 0° to 1,000 °C." Livermore, California: Lawrence Livermore National Laboratory. 1991.
†Wolery, T.J. "EQ3/6, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0)." UCRL–MA–11066 Pt III. Livermore, California: Lawrence Livermore National Laboratory. 1992.

3.1 Installation Check—Results

The Geochemist's Workbench is designed for IBM-compatible personal computers. Successful installation of the code on an IBM-compatible personal computer requires the following system attributes:

- Windows 98/ME/NT/2000/XP
- Pentium-level processor
- 32 MB RAM
- 20 MB free disk space.

Installation of the Geochemist's Workbench software package was performed by a computer information systems administrator in accordance with TOP–018 for CNWRA (2004). An interactive installation program which provides the necessary instructions, guidance, and tests for completing the installation was provided with the software. Installation of the Geochemist's Workbench software package will be considered successful if the individual software packages function as expected.

3.2 Validation Check—Results

TOP–018 for CNWRA (2004) describes acceptable methods for validating commercially available software. These methods were reviewed by staff to determine the most appropriate tests for the Geochemist's Workbench software package.

There are inevitable assumptions and constraints involved in the algorithms, mathematical formulations, data, and conceptual models that are incorporated into simulations generated by most commonly used geochemical codes such as Geochemist's Workbench Version, 5.0 (Bethke, 2004a,b,c), EQ3/6 (Wolery, 1992), and PHREEQC (Parkhurst and Appelo, 1999). It is, therefore, difficult or perhaps even impossible (Oreskes, et al., 1994; Bethke, 1992) to produce a quantitative representation of a complex earth science system that is unique. Validation exercises under TOP–018, thus, emphasize the importance of testing the ability of the code to apply underlying theories accurately by comparing independent applications of those same theories.

Validation of the Geochemist's Workbench software package is based mainly on comparisons of calculation results with published geochemical data from field studies, experiments, and modeling exercises, rather than by direct comparisons with simplistic analytical results (Richardson and McSween, 1989). As described in Browning (2003a), the approach adopted in this report tests the ability of the underlying theory and algorithms in the Geochemist's Workbench software package to accurately represent complex geochemical processes such as those that might result from the emplacement of high-level nuclear waste at Yucca Mountain, Nevada. The, results of Geochemist's Workbench, Version 5.0 calculations, however, are also compared with those from analytical expressions, when appropriate.

3.2.1 Rxn

Fundamental capabilities of the Rxn program are evaluated here by three different tests, as described in Browning (2003a). The software program Rxn balances chemical reactions among minerals, dissolved species, and gases and provides thermodynamic data describing equilibrium conditions for that reaction at different temperatures. Through an iterative process of swapping basis species for other species, minerals, or gases, the user instructs the program to construct balanced reactions and present associated thermodynamic data. To obtain results in the desired forms, species stoichiometries may be manipulated by the program to calculate a transformation matrix that gives the desired balanced reaction and associated equilibrium constant. Alternatively, the Rxn code may obtain this information by addition, subtraction, and multiplication of balanced reactions described in the thermodynamic database until the desired reaction appears on the computer screen. A more detailed description of the underlying equations used to perform reaction balancing in Rxn is described in Chapter 9 of Bethke (1996).

Rxn Test 1: Analcime Dissolution Reaction

This test determines whether the Rxn program can access the thermo.dat database and correctly read its formatted data to construct a reaction that is stoichiometrically and electrically balanced for the mineral analcime.

Geochemist's Workbench Input (also see Rxn_test1.wpd): The input file shows the scripted geochemical constraints used by the Rxn program, and the commands listed below were used to develop that script.

Commands:
> react Analcime
> output
> go

Geochemist's Workbench Output (also see Rxn_test1.wpd):

Analcime + 4 H+ = 3 H2O + Na+ + Al+++ + 2 SiO2(aq)

Geochemist's Workbench thermodynamic database: The following information about analcime is included in the thermo.dat database and will be compared with output from the Rxn program:

```
Analcime                type = zeolite
   formula = NaAlSi2O6:H2O
   mole vol.=  97.100 cc     mole wt. =  220.1539 g
   5 species in reaction
    3.000 H2O            1.000 Na+          1.000 Al+++
    2.000 SiO2(aq)      -4.000 H+
   Log K's (T = 0, 25, 60, 100, 150, 200, 250, and 300 °C, from left to right):
    8.6163   7.2800   5.6735   4.2314
    2.8879   1.8680   0.9663  -0.1538
```

By default, the thermo.dat database represents reactions in terms of mineral dissolution rather than precipitation. A negative sign for species in the reactions indicates it's position on the left side of the reaction.

Rxn validation test 1 results:

A comparison of the basis species listed in Table 3-1 and the Geochemist's Workbench output for Rxn test 1 shows that the Rxn program correctly accessed basis species from the thermo.dat database to write a stoichiometrically and electrically balanced reaction for the analcime. There are 4 positive charges on both the left (e.g., 4 H^+'s) and right sides (e.g., 1 from Na^+ and 3 from Al^{+++}) of the reaction, demonstrating electrical balance. Stoichiometric balance is obtained by comparing the number of elemental components on each side of the reaction. There are 6 H, 1 Na, 1Al, 2 Si, and 4 Si on each side of the reaction demonstrating that the Rxn program has resourced the thermo.dat database correctly to ensure appropriate stoichiometric balance.

Rxn Test 2: Equilibrium Constants for Analcime

This test determines whether the Rxn program can reproduce temperature dependent equilibrium constants (K) for the analcime dissolution reaction from the thermo.dat thermodynamic database (see Rxn test 1).

Geochemist's Workbench Input (also see Rxn_test2.wpd):

Commands:
> react Analcime
> output
> long
>go

Geochemist's Workbench Output (also see Rxn_test2.wpd):

Rxn validation test 2 results:

A comparison of the equilibrium constants (K) displayed in the Rxn test 2 output file and those provided in the thermodynamic database illustrates the successful reproduction of log K values for the analcime dissolution reaction. The expression labeled "polynomial fit" in the Rxn test 2 output file provides an approach for interpolating between log K values for different temperatures.

Rxn Test 3: Basis Species Swap for the Pyrite Dissolution Reaction

This test determines whether the Rxn program can calculate a stoichiometrically and electrically balanced dissolution reaction for a mineral pyrite that is not defined in terms of the default basis species used in Geochemist's Workbench, Version 5.0 (Table 3-1). The test will be performed by swapping HS^- for SO_4^{--} in the pyrite dissolution reaction and, then, checking the output to determine whether the resultant reaction is stoichiometrically and electrically balanced.

Geochemist's Workbench Input (also see Rxn_test3.wpd):

Commands:
> react Pyrite
> swap HS- for SO4--
> go

Geochemist's Workbench Output (also see Rxn_test3.wpd):

Pyrite + H2O = Fe++ + 2 HS- + .5 O2(aq)

Geochemist's Workbench thermodynamic database: The following information about pyrite is included in the thermo.dat database, and will be compared with output from the Rxn program:

```
Pyrite                    type = sulfide
   formula = FeS2
   mole vol. =  23.940 cc     mole wt. =  119.9670 g
   5 species in reaction
    -1.000 H2O          1.000 Fe++          1.750 HS-
     0.250 SO4--        0.250 H+
   Log K's (T = 0, 25, 60, 100, 150, 200, 250, and 300 °C, from left to right):
    -26.5279  -24.7025  -22.8643  -21.4327
    -20.3362  -19.8398  -19.9168  -20.8284
```

As discussed in the description of Rxn test 1, the thermo.dat database describes mineral dissolution reactions in terms of the default basis species (Table 3-1). The thermo.dat representation of the pyrite dissolution reaction is as follows:

Pyrite + H2O + 3.5 O2(aq) = Fe++ + 2 SO4-- + 2 H+

Rxn validation test 3 results:

The Rxn program generated the following reaction for pyrite dissolution:

Pyrite + H2O = Fe++ + 2 HS- + .5 O2(aq)

A comparison of the pyrite dissolution reactions defined by the thermo.dat database and the pyrite dissolution reaction defined by Rxn test 3 demonstrates that HS^- was successfully swapped into the reaction for the default basis species, $SO4^{--}$.

The test 3 reaction has a sum zero charge (e.g., no charged species) on both the left and right sides (e.g., 2 positive charges from Fe^{++} and 2 negative charges from HS^{-}) of the reaction demonstrating electrical balance. Stoichiometric balance is obtained by comparing the number of elemental components on each side of the reaction. There are 2 S, 8 O, 2 H, and 1 Fe on each side of the reaction demonstrating that the Rxn program has resourced the thermo.dat database correctly to ensure appropriate stoichiometric balance.

3.2.2 Act2

In support of the NRC high-level waste program, it is expected that the main function of the Act2 software program will be to develop activity-activity plots. To test the ability of Geochemist's Workbench to accurately calculate activity-activity diagrams, calculations are performed to determine whether the Act2 program is capable of reproducing the series of activity-activity diagrams published on pages 30–31 in Bethke (2004a). The diagrams in Bethke (2004a) are modified in Figure 3-1 to facilitate comparison with the diagrams calculated using Geochemist's Workbench, Version 5.0 (Figure 3-2).

Figure 3-1 shows uranium speciation diagrams for a system at 25 °C and a total uranium species activity of 10^{-10}, (Bethke, 2004a). The individual diagrams show

- uranium speciation as a function of dissolved oxygen and pH (Figure 3-1a)
- uranium speciation as a function of oxygen fugacity and pH (Figure 3-1b)
- Eh versus pH (Figure 3-1c)
- uranium speciation as a function of the activity ratio of Fe^{+++} to Fe^{++} and pH (Figure 3-1d)

Geochemist's Workbench Input (also see Act2a-d_input.wpd): The input files show the scripted geochemical constraints used by the Act2 program, and the commands listed below were used to develop that script.

Commands:
For Figure 3-2a:
> diagram U++++ on O2(aq) vs pH
> log a U++++ = -10
> x from 0 to 14; y from -90 to 0
> go

For Figure 3-2b:
(interactive continuation of previous run)
> swap O2(g) for O2(aq)
> go

For Figure 3-2c:
(interactive continuation of previous run)
> swap e- for O2(aq)
> diagram on Eh
> y from -0.75 to 1.25
> go

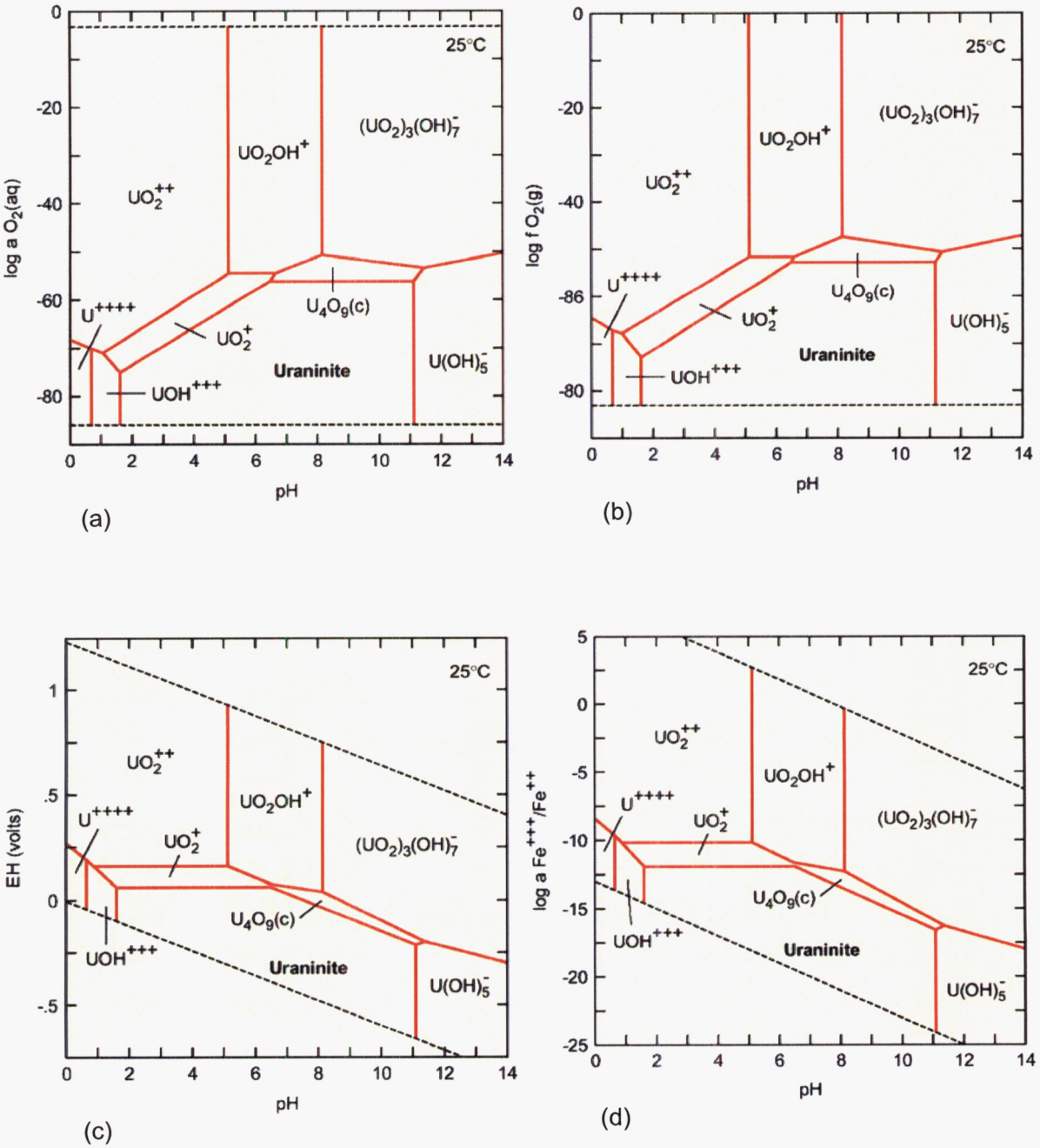

Figure 3-1. Uranium Speciation Diagrams Modified After Bethke (2004a), Assuming a Total Uranium Activity of 10^{-10}

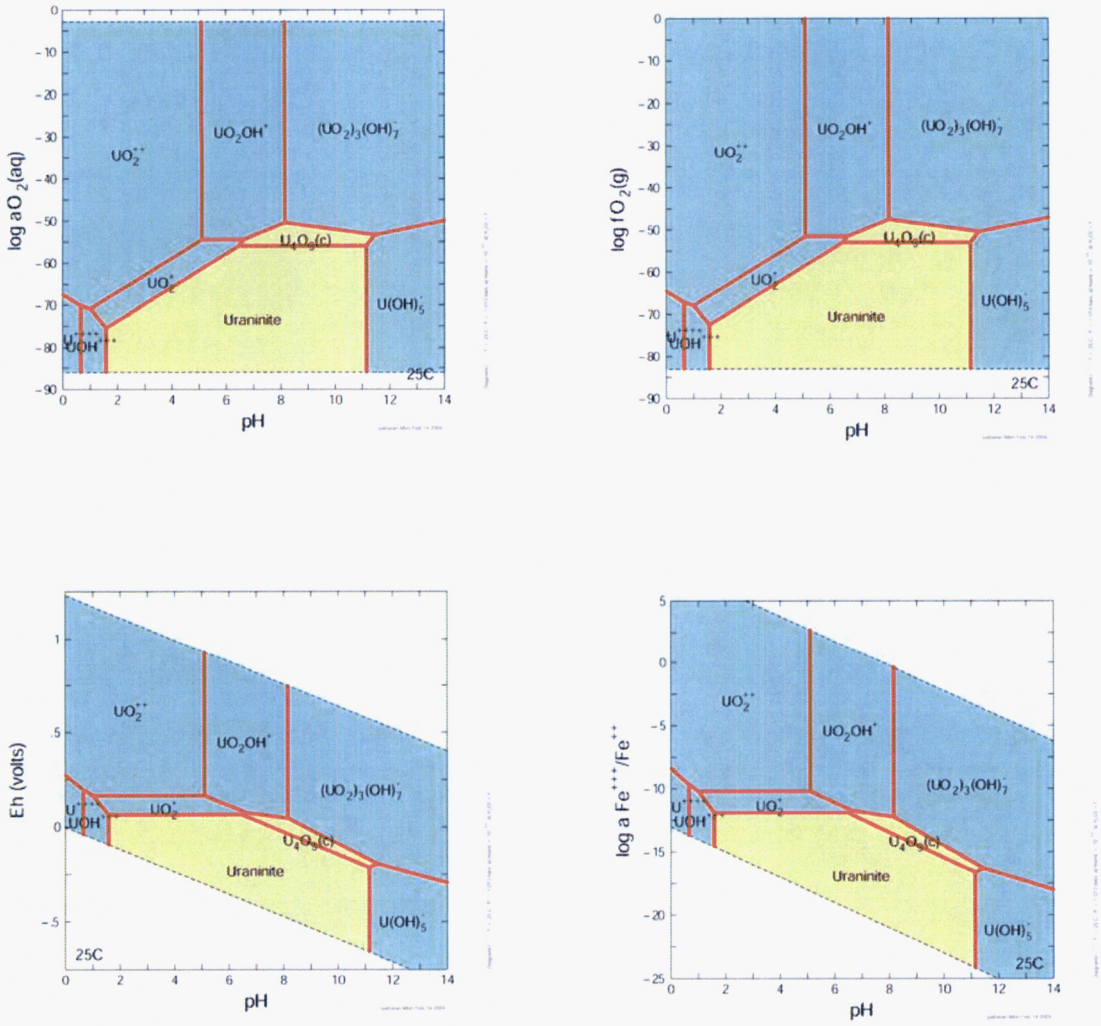

Figure 3-2. Uranium Speciation Diagrams Calculated Using the Act2 Program, Assuming a Total Uranium Activity of 10^{-10}

For Figure 3-2(d):
(interactive continuation of previous run)
> swap Fe+++/Fe++ for O2(aq)
> y from -25 to 5
> go

Act2 validation test results:

Figure 3-2 shows the uranium activity diagrams generated by the Act2 program for comparison with diagrams from Bethke (2004a) that employ the same geochemical constraints (Figure 3-1). Accurate reproduction of the uranium activity diagrams from Bethke (2004a) would constitute adequate validation of the Act2 program, based on the expected usage of this program for the NRC client. The underlying Act2 program capabilities being tested in this report are the ability to perform geochemical speciation calculations and generate accurate activity-activity diagrams using this information. Requisite visual comparisons between Figures 3-1 and 3-2 are accomplished by examining the numerical intersection points of stability lines on X-Y axes and the relative orientation of the various stability fields.

A comparison of Figures 3-1 and 3-2 demonstrates excellent agreement between the uranium activity diagrams calculated by the Geochemist's Workbench, Version 5.0 Act2 program and those calculated by Bethke (2004a). Uranium speciation calculations performed by Act2 predicted that the dominant dissolved species for all four validation test cases are UO_2^{++}, UO_2^{+}, $U(OH)_5^{-}$, UO_2OH^{+}, $(UO_2)_3(OH)_7^{-}$, U^{++++}, UOH^{+++}, and that the stable solids are $U_4O_9(c)$ and Uraninite. These results (Figure 3-2) are consistent with those determined by Bethke (2004a), as shown in Figure 3-1. A comparison of Figures 3-1 and 3-2 also shows that the relative orientation of all solid and dissolved uranium species calculated by Geochemist's Workbench, Version 5.0 matches with those calculated by Bethke (2004a). Geochemist's Workbench, Version 5.0 calculated pH dependent field boundaries among UO_2^{++} and UO_2OH^{+}, UO_2OH^{+} and $(UO_2)_3(OH)^{-}_7$, and uraninite and $U(OH)_5^{-}$ at values of 5, 8, and 11 consistent with those calculated by Bethke (2004a). Comparisons of other calculated stability fields are also favorable. For example, the Eh condition between the UO_2^{++} and the U^{++++} stability fields in Figures 3-1c and 3-2c both occur at a value of 0.25 volts at pH 0.

3.2.3 Tact

The program Tact calculates and plots mineral stabilities and the predominance of specific species or gases as a function of temperature. In support of the NRC high-level waste program, it is expected that the main function of the Tact2 software program will be to construct diagrams showing the stability fields for minerals and aqueous species at different temperatures. Two validation exercises were developed by Browning (2003a) to test the basic capabilities of the Tact software, and the results are described below.

Tact Validation Test 1: Phosphate Speciation as a Function of pH and Temperature

This test determines whether the Tact program can accurately calculate and plot the stability regions for different phosphate species on a diagram of pH versus temperature. The results of these Geochemist's Workbench Version 5.0 calculations will be compared with the published temperature-pH relations for phosphate species shown on page 42 in Bethke (2004a) and in Figure 3-3a.

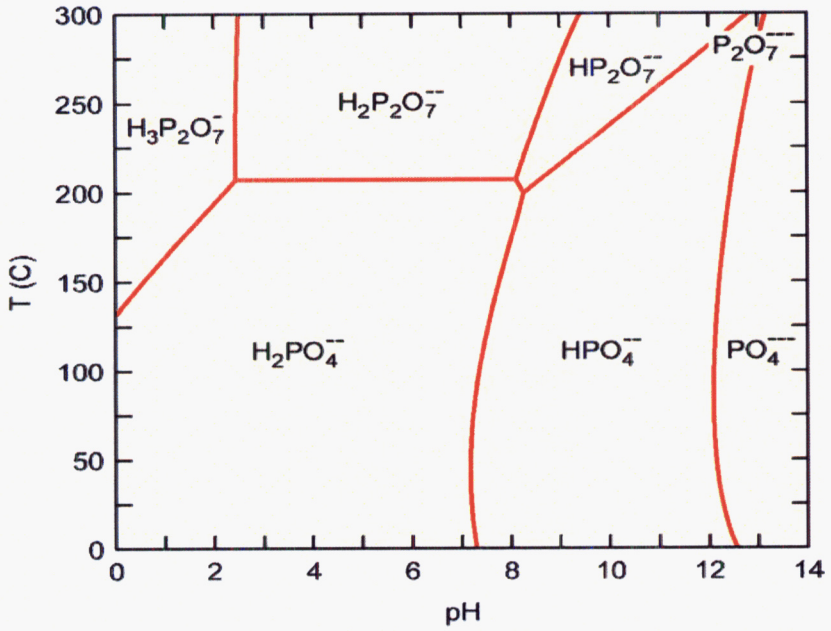

Figure 3-3a. pH Versus Temperature Diagram for Different Phosphate Species Modified After Bethke (2004a)

Geochemist's Workbench Input (also see Tact_input.wpd): The input files show the scripted geochemical constraints used by the Tact program, and the commands listed below were used to develop that script.

Commands:
> diagram HPO4-- vs pH
> a HPO4-- = 10^-3
> x from 0 to 14
> go

Tact validation test 1 results:

Figure 3-3b shows the results of the Tact calculations performed for this validation test. A comparison of Figures 3-3a and 3-3b illustrates excellent agreement between the two sets of temperature-dependent calculations. Both diagrams illustrate that the predominant dissolved phosphate species are $H_3P_2O_2^-$, $HP_2O_7^-$, $H_2P_2O_7^{--}$, $H_2PO_4^{--}$, and PO_4^-. The numerical value of intersection points for stability field lines in both diagrams match well. For example, the $H_2PO_4^-$ and HPO_4^- fields in both diagrams are separated at a pH of approximately 7.2 at a temperature of 0 °C.

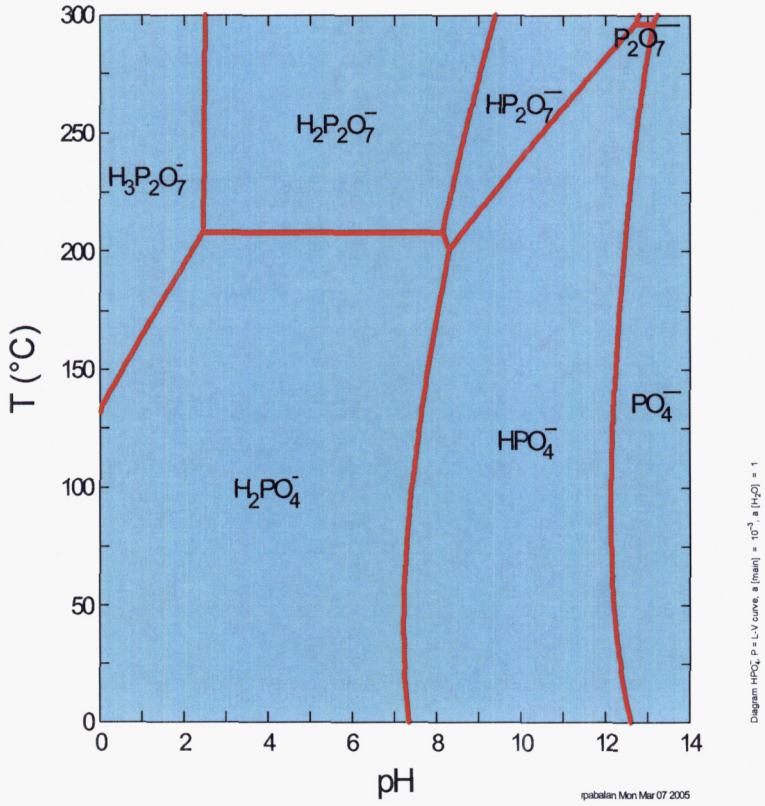

Figure 3-3b. pH Versus Temperature Diagram Generated by the Tact Program Showing Stability Regions for Different Phosphate Species

Tact Validation Test 2: Quartz Solubility as a Function of Temperature

This test determines whether the Tact program can accurately calculate and plot the solubility of quartz as a function of temperature. The results of these Geochemist's Workbench, Version 5.0 calculations will be compared with solubility data for quartz described in the thermo.dat database at discrete temperatures.

Geochemist's Workbench Input (also see Tact_input.wpd): The input files show the scripted geochemical constraints used by the Tact program, and the commands listed below were used to develop that script.

Commands:
> diagram SiO2(aq) vs SiO2(aq)
> x from -5 to -1
> go

Geochemist's Workbench thermodynamic database: The following information about quartz is included in the thermo.dat database and will be compared with output from the Tact program:

Quartz type = silica
formula = SiO2
mole vol. = 22.688 cc mole wt. = 60.0843 g
1 species in reaction
1.000 SiO2(aq)
Log K's (T = 0, 25, 60, 100, 150, 200, 250, and 300 °C, from left to right):
-4.5021 -3.9993 -3.5026 -3.0951
-2.7176 -2.4272 -2.1943 -2.0106

The thermo.dat representation of the quartz dissolution reaction is as follows:

Quartz = SiO2(aq)

Quartz solubility is measured directly by the value of K at a prescribed temperature, because $K = a_{SiO2}/a_{quartz}$, where the activity of quartz, a pure mineralogical phase, is defined as one.

Tact validation test 2 results:

Figure 3-4 shows the results of the Geochemist's Workbench, Version 5.0 calculations of quartz solubility as a function of temperature. The solubility of quartz increases with temperature. Log K values for quartz at discrete temperatures defined in the database agree with the log $SiO_2(aq)$ values for those same temperatures that are plotted in Figure 3-4. The interpolation technique used by the Geochemist's Workbench, Version 5.0 program has defined a smooth and continuous solubility curve between the discrete Log K values identified in the database, as would be required by a user simulating quartz solubilities at alternative temperatures.

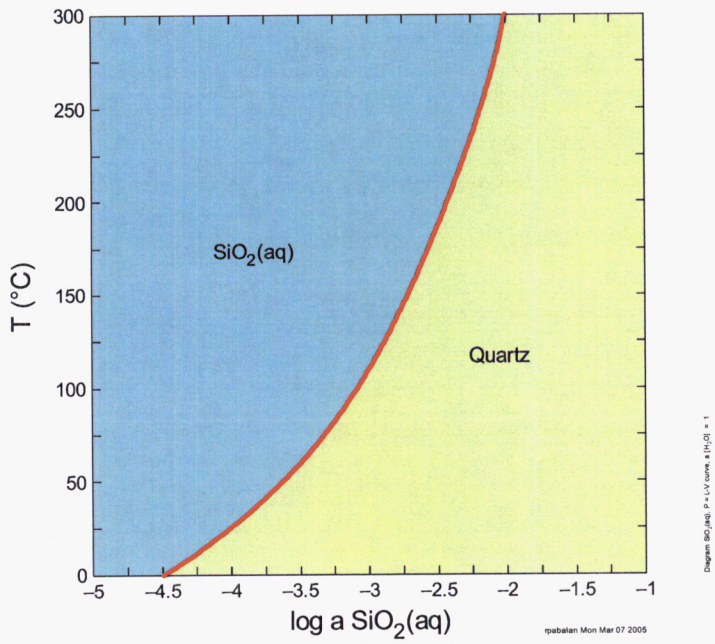

Figure 3-4. Quartz Solubility as a Function of Temperature

3.2.4 React

React is the primary equilibrium and kinetic reaction pathway modeling program in the Geochemist's Workbench, Version 5.0 software package. The program calculates the equilibrium of aqueous speciation relationships, the saturation state of fluid with respect to solid phases, and gas fugacities and can simulate the rate dependence of specified mineral dissolution/precipitation reactions. The underlying theory and algorithms used in React are described in Chapters 5, 7, and 14 of Bethke (1996). Two tests of the React program will be performed to validate the underlying theory and algorithms for calculation of the equilibrium chemical system and a kinetic reaction pathway.

React Test 1: Calculation of Activity Coefficients and Fluid Saturation States

Garrells and Thompson (1962) first calculated the distribution of species in surface seawater, and much work has since been done to refine our understanding of the major element composition of the ocean, species concentrations, and fluid saturation states for co-existing solids (Drever, 1988; Holland, 1978; McDuff and Morel, 1980).

Using the major element composition of seawater in Table 3-2 as input, the React program was used to calculate the activities of the predominant dissolved species and the corresponding fluid saturation states with respect to various solid precipitates. Tables 3-3 and Table 3-4 compare calculated species activities and fluid saturation states, respectively, with those published in Bethke (1996).

Table 3-2. Major Element Composition of Seawater*

Chemical component	Concentration (mg/kg)
Cl^-	19,350
Na^+	10,760
SO_4^{--}	2,710
Mg^{++}	1,290
Ca^{++}	411
K^+	399
HCO_3^-	142
$SiO_2(aq)$	0.5–10
$O_2(aq)$	0.1–6

*Drever, J. I. *The Geochemistry of Natural Waters*, 2nd ed. Prentice-Hall, Englewood Cliffs, New Jersey. 1988.

Table 3-3. Log Activity Coefficients (*a*) of the Most Abundant Species in Seawater*		
Species	**Log *a****	**Log *a*, Calculated For This Report**
Cl^-	-0.462	-0.4619
Na^+	-0.50	-0.4958
Mg^{++}	-1.90	-1.9009
SO_4^{--}	-2.57	-2.5657
K^+	-2.19	-2.1881
$MgCl^+$	-2.21	-2.2125
$NaSO_4^-$	-2.3	-2.3676
Ca^{++}	-2.83	-2.8334
$MgSO_4$	-2.24	-2.2391
$CaCl^+$	-2.60	-2.5953

*Bethke, C.M. *Geochemical Reaction Modeling: Concepts and Applications*. New York City, New York: Oxford University Press. 1996.

Table 3-4. Saturation Indices for Various Minerals in Seawater		
Mineral	**SI (log Q/K)***	**SI (log Q/K); this report**
Antigorite	44.16	44.16
Tremolite	7.73	7.73
Talc	6.68	6.68
Chrysotile	4.72	4.72
Sepiolite	3.93	3.93
Anthophyllite	3.48	3.48
Dolomite	3.46	3.46
Dolomite-ord	3.46	3.46
Magnesite	1.02	1.02
Calcite	0.81	0.81

*Bethke, C.M. *Geochemical Reaction Modeling: Concepts and Applications*. New York City, New York: Oxford University Press. 1996.

Geochemist's Workbench Input (also see React1_input.wpd): The input files show the scripted geochemical constraints used by the React program, and the commands listed below were used to develop that script.

Commands:
> swap CO2(g) for H+
> swap O2(g) for O2(aq)
> log f CO2(g) = -3.5
> f O2(g) = 0.2
> TDS = 35080
> Cl- = 19350 mg/kg
> Ca++ = 411 mg/kg
> Mg++ = 1290 mg/kg
> Na+ = 10760 mg/kg
> K+ = 399 mg/kg
> SO4-- = 2710 mg/kg
> HCO3- = 142 mg/kg
> SiO2(aq) = 6 mg/kg
> print species = long
> go

Geochemist's Workbench Output (also see Numerical values only: React1_output.wpd): Some values extracted from the React1_output.wpd file are also shown in Tables 3-3 and 3-4.

React validation test 1 results:

The React program within the Geochemist's Workbench, Version 5.0 software package succeeded in reproducing the geochemical characteristics of seawater published in Bethke (1996). Tables 3-3 and 3-4 list activity coefficients and fluid saturated states for predominant phases in sea water, respectively. A comparison of the data in the second and third columns of Tables 3-3 and 3-4 shows that values calculated using the React program in Geochemist's Workbench, Version 5.0 are equivalent to those reproduced from Bethke (1996). In Table 3-3, the favorable comparison demonstrates that the React program calculated reasonable activity coefficients for different dissolved species in seawater and then correctly predicted which of the dissolved species would be most abundant. These calculations validate the ability of the React program to correctly apply the B dot form of the Debye-Huckel equation to complex solution compositions. Similarly, the excellent match between data in the second and third columns of Table 3-4 indicates that the React program is correctly reading log K values from the thermo.dat database, utilizing calculated activity coefficients, and calculating ion activity products for the various minerals based on these data.

React Test 2: Calculation of Reaction Rates in An Unequilibrated Solution

Many mineral phases and geochemical conditions associated with the emplacement of nuclear waste in a potential repository at Yucca Mountain, Nevada, will likely be controlled by kinetic processes. Validation of the React program's ability to correctly apply kinetic rate laws is, therefore, important. In this test, the React program is used to calculate the reaction rate of quartz sand at 100 °C according to the rate law described in Rimstidt and Barnes (1980). A specific surface area of 1,000 cm^2/g is assumed. Analytical calculations are then performed to

determine the amount of quartz expected to dissolve under these conditions, and the results are compared with the calculated volume losses for quartz.

Geochemist's Workbench Input (also see React2_input.wpd): The input files show the scripted geochemical constraints used by the Tact program, and the commands listed below were used to develop that script.

Commands:
> time begin = 0 days, end = 5 days
> T = 100
> SiO2(aq) = 1 umolal
> react 5000 g Quartz
> kinetic Quartz rate_con = 2.e-15 surface = 1000
> go

Geochemist's Workbench Output (alse see Numerical values only: React2_output.wpd):

React validation test 2 results: (analytical calculations: React2_calcs.xls); estimated number of moles of quartz dissolved in five days.

The React program within the Geochemist's Workbench, Version 5.0 software package was used to calculate the number of moles of quartz that would dissolve in five days under a specific set of geochemical conditions. The simulations depict the kinetically-controlled dissolution of 5,000 grams of quartz in deionized water spiked with negligible silica at 100 °C and assume a fixed specific surface area of 1,000 cm^2/g and an intrinsic rate constant for quartz of 2×10^{-15} mol/cm^2 s. To validate these simulations, the total number of moles of dissolved quartz calculated by React is compared to the results of analytical calculations. The total number of moles of dissolved quartz is estimated analytically by employing the ion activity product values calculated by React and the following rate law for quartz dissolution given by Rimstidt and Barnes (1980):

$$r_{qtz} = A_S K_+ \left(\frac{Q}{K} - 1 \right) \tag{3-1}$$

where r_{qtz} is the rate of quartz dissolution in mol/s, A_s is the surface area (cm^2), K_+ is the intrinsic rate constant for quartz, and Q/K is the saturation state for quartz. This is a simplified form of the rate law used in the React program of the Geochemist's Workbench, Version 5.0 software package.

Results of the React simulations indicate that the dissolution rate of quartz slows over time as the reaction approaches equilibrium. The solution becomes saturated with quartz after about 3.5 days, at which time the dissolution rate for quartz becomes negligibly slow. At all times, the saturation state for quartz at 100 °C is defined by the ion activity product for quartz (Q) divided by the equilibrium constant for quartz dissolution at 100 °C (e.g., log K = -3.0951, or $K = 8.03 \times 10^{-4}$) that is recorded in the thermo.dat database (also see above section on Tact Validation Test 2). React calculations indicate that a total of 0.0007985 moles of quartz have been dissolved after five days.

To analytically calculate the total number of moles of quartz dissolved over five days using Eq. 3-1, continuous changes in the average saturation states for quartz calculated by the React program are approximated as five constant saturation states corresponding to each of the simulated days of dissolution. As shown in the React2_calcs.xls file, ion activity values calculated by the React program for 0.5, 1.5, 2.5, 3.5, and 4.5 days were adopted as representative values for days 1 through 5. These saturation states, plus the geochemical input constraints used to define the React input files, are applied to the Rimstidt and Barnes (1980) rate law (Eq. 3-1). Specific surface area and initial mass of quartz in the system used by the React calculations are converted to surface area (cm^2) in the following manner:

As = specific surface area of quartz * total number of grams quartz =
= 1000 $cm^2/g \times 5000$ g = 5e6 cm^2

Analytical calculations are provided electronically in the file React2_calcs.xls. React calculated a total loss of 7.985×10^{-4} moles of quartz in 5 days, whereas a loss of 7.66×10^{-4} moles was estimated analytically. This represents a less than 5 percent difference between the total numbers of moles of dissolved quartz calculated analytically and by the React program. Because the time dependent saturation states for quartz calculated by React were simplified as 5 constant values to support the analytical estimates, this difference was expected and is insignificant. This validation test demonstrates that the React program is able to correctly apply kinetic rate laws.

4 SUMMARY AND CONCLUSIONS

Comparisons for a variety of geochemical problems show that Geochemist's Workbench, Version 5.0 produces results that are consistent with those produced by other methods such as hand calculations and other computer codes. Validation tests performed for this report demonstrate that the Geochemist's Workbench, Version 5.0 software package will correctly execute a variety of fundamental geochemical calculations, including the correct calculation of activity coefficients, mineral solubilities, activity-activity diagrams, temperature dependent aqueous speciation, and time-dependent mineral dissolution. A less than 5 percent difference between the results of analytical calculations and those performed by the Geochemist's Workbench, Version 5.0 was judged to be satisfactory, because the differences resulted from known simplifications in the analytical treatment of the problem.

Overall, the agreement of trends and results between Geochemist's Workbench, Version 5.0 and the various calculational methods used in the model validation exercise indicate that the code is correctly and consistently applying the underlying geochemical theorems and algorithms needed to evaluate the equilibrium and kinetic behavior of geochemical systems.

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APPENDIX A

Rxn Test 1:

```
# Rxn script, saved Mon Feb 14 2005 by rpabalan
data = "c:\program files\gwb\gtdata\thermo.dat" verify
react Analcime
activity H2O = ?
activity Na+ = ?
activity Al+++ = ?
activity SiO2(aq) = ?
activity H+ = ?
```

Rxn Test 2:

```
# Rxn script, saved Mon Feb 14 2005 by rpabalan
data = "c:\program files\gwb\gtdata\thermo.dat" verify
react Analcime
activity H2O = ?
activity Na+ = ?
activity Al+++ = ?
activity SiO2(aq) = ?
activity H+ = ?
long
```

Rxn Test 3:

```
# Rxn script, saved Mon Feb 14 2005 by rpabalan
data = "c:\program files\gwb\gtdata\thermo.dat" verify
react Pyrite
swap HS- for SO4--
activity H2O = ?
activity Fe++ = ?
activity HS- = ?
activity H+ = ?
activity O2(aq) = ?
```

Act2 Figure 3-1a:

```
# Act2 script, saved Mon Feb 14 2005 by rpabalan
data = "c:\program files\gwb\gtdata\thermo.dat" verify
diagram U++++ on O2(aq) vs pH
log activity main = -10
x-axis from 0 to 14 increment 1
y-axis from -90 to 0 increment 5
```

Act2 Figure 3-1b:

```
# Act2 script, saved Mon Feb 14 2005 by rpabalan
data = "c:\program files\gwb\gtdata\thermo.dat" verify
swap O2(g) for O2(aq)
diagram U++++ on O2(g) vs pH
log activity main = -10
x-axis from 0 to 14 increment 1
y-axis from -90 to 0 increment 5
```

Act2 Figure 3-1c:
# Act2 script, saved Mon Feb 14 2005 by rpabalan
data = "c:\program files\gwb\gtdata\thermo.dat" verify
swap e- for O2(aq)
diagram U++++ on Eh vs pH
log activity main = -10
x-axis from 0 to 14 increment 1
y-axis from -.75 to 1.25 increment .25

Act2 Figure 3-1d:
# Act2 script, saved Mon Feb 14 2005 by rpabalan
data = "c:\program files\gwb\gtdata\thermo.dat" verify
swap Fe+++/Fe++ for O2(aq)
diagram U++++ on Fe+++/Fe++ vs pH
log activity main = -10
x-axis from 0 to 14 increment 1
y-axis from -25 to 5 increment 2.5

Tact test 1:
# Tact script, saved Mon Feb 14 2005 by rpabalan
data = "c:\program files\gwb\gtdata\thermo.dat" verify
diagram HPO4--vs pH
log activity main = -3
x-axis from 0 to 14 increment 1
y-axis from 0 to 300 increment 25

Tact test 2:
# Tact script, saved Mon Feb 14 2005 by rpabalan
data = "c:\program files\gwb\gtdata\thermo.dat" verify
diagram SiO2(aq) vs SiO2(aq)
x-axis from -5 to -1 increment .25
y-axis from 0 to 300 increment 25

React test 1:
# React script, saved Mon Feb 14 2005 by rpabalan
data = "c:\program files\gwb\gtdata\thermo.dat" verify
temperature = 25
swap CO2(g) for H+
swap O2(g) for O2(aq)
1 kg H2O
-3.5 log fugacity CO2(g)
.2 fugacity O2(g)
balance on Cl-
19350 mg/kg Cl-
411 mg/kg Ca++
1290 mg/kg Mg++
10760 mg/kg Na+
399 mg/kg K+
2710 mg/kg SO4--

142 mg/kg HCO3-
6 mg/kg SiO2(aq)
TDS = 35080

printout species = long

React test 2:
# React script, saved Mon Feb 14 2005 by rpabalan
data = "c:\program files\gwb\gtdata\thermo.dat" verify
time start = 0 days, end = 5 days
temperature = 100 °C
1 kg H2O
1 umolal SiO2(aq)
kinetic Quartz 5000 gram
kinetic Quartz rate_con = 2e-15 surface = 1000