

**SOFTWARE VALIDATION PLAN AND REPORT FOR
GEOCHEMIST'S WORKBENCH® VERSION 6.0**


Prepared by

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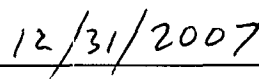
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1 SCOPE OF THE VALIDATION

This document establishes the Software Validation Test Plan and reports the results for validating the installation and functionality of software tools in the Geochemist's Workbench® code (Bethke, 2005a,b). Geochemist's Workbench 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.

A previous Software Release Notice was issued for Geochemist's Workbench Version 6.0 (Software Release Notice for Geochemist Workbench, 2007), this validation was based on Regression testing from the previous Version 5.0 validation; however, it lacked the practical uses of two of the main tools. This validation will supplement the tests performed for the software release notice. This Software Validation Test Plan applies to Geochemist's Workbench Version 6.0 and is intended to validate the set of software tools used to evaluate chemical reactions, calculate phase stability and aqueous speciation, and evaluate sorption and temperature effects. The following software tools are used to perform these geochemical evaluations:

- SpecE8
- React

Each of these software programs includes a large number of user options, including options to format and constrain data, depict modeling results, or control numerical processing methods. These options increase the diversity of site-specific geochemical applications that can be evaluated by the code, but do not alter the general functionality of the individual software tools. This Software Validation Report has been designed to show correct and successful implementation of the underlying theory and algorithms as outlined in the Geochemist's Workbench Version 6.0 User's Manual and required by the Technical Operating Procedure (TOP)-018 (CNWRA, 2007).

Geochemist's Workbench Version 6.0 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
- Microbial metabolism and growth
- Virial methods of calculating species activities

The professional release of Geochemist's Workbench Version 6.0 also includes X1t and X2t modules for reactive transport modeling in one and two dimensions (Bethke, 2005c); these modules 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. This validation report uses much of the same text as the Geochemist's Workbench Version 5.0 validation report (Pabalan, 2005).

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3 ENVIRONMENT

3.1 Software-Introduction

Geochemist's Workbench Version 6.0 (Bethke, 2005a,b) is a package of interactive software programs that run on IBM-compatible personal computers. The main programs in Geochemist's Workbench are named Rxn, Act2, React, Tact, and SpecE8. These programs manipulate chemical reactions (e.g., Rxn), evaluate phase stability (e.g., Act2), calculate aqueous speciation, equilibrium conditions, and reaction pathways (e.g., React), and evaluate temperature-activity relationships (e.g., Tact). An additional software tool, called Gtplot, is also included in the Geochemist's Workbench Version 6.0 package to facilitate processing and visualization of the modeling results. This Geochemist's Workbench suite of programs was developed to support educational, scientific, and practical applications of geochemical modeling. Development of Geochemist's Workbench began in the mid-1980s, and was based on a simpler batch mode code named GT, which had been developed earlier by Bethke. The program Rxn balances chemical reactions between dissolved species, minerals, and gases. The program Act2 calculates and plots information on mineral stabilities and predominant aqueous species for a given combination of dissolved components and environmental conditions. Tact is a program that determines species activities and gas fugacities at different temperatures to show the effect of temperature on mineral stability and the predominance of aqueous species in specific chemical systems. The program React is the geochemical modeling program in the Geochemist's Workbench software package. React performs aqueous speciation calculations and calculates gas fugacities and fluid saturation states with respect to various minerals. This program allows the User to determine the equilibrium state of a chemical system or the influence of kinetic dissolution/precipitation reactions on species concentrations at various times along a reaction pathway.

3.2 Code Description

The following description of Geochemist's Workbench is based mainly on the User's manual (Bethke, 2005b) provided with the Geochemist's Workbench Version 6.0 file. Additional information about the code was obtained from the associated textbook on geochemical reaction modeling (Bethke, 1996).

3.2.1 Input

Each of the geochemical software programs in Geochemist's Workbench (i.e., Rxn, Act2, Tact, SpecE8, and React) 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. The most current chemical system defined by the User can be saved into a dataset described by commands in the format of the specific program or through the interactive input screen. These datasets can be recalled and used as input scripts later.

All the programs use an independent set of aqueous species, known as the basis, to write reactions. Table 3-1 shows the default list of independent basis species used in Geochemist's Workbench. Reactions described by basis species may include dissolved species only, or may also involve various combinations of interacting solid phases and gases. Basis species comprise a portion of all thermodynamic databases included with the Geochemist's Workbench installation package, and can be modified interactively by the User. The same basic process is used to configure calculations in the Rxn, Act2, Tact, SpecE8 and React programs. Basis species can be "swapped" with other aqueous species, minerals, or gases that are anticipated to play an important role in the modeled system. Swapped species may, for example, constrain fugacity conditions or describe minerals co-existing with the system. The next step in the process is to set the system conditions. The User must set a temperature and assign values of concentration, activity, or fugacity to each default and/or swapped basis species in the model system. A variety of options are available to constrain the system. In React, for example, the User can apply a single temperature to the system or define a polythermal reaction pathway. Another option allows the User to linearly adjust gas fugacities or aqueous species activities within a User-defined range. There is a wide variety of different species concentration options, such as molality, molarity, or ppm.

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 user-provided input. 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 6.0 package includes the following thermodynamic databases:

- thermo.dat (employs Debye-Hückel 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)

H ₂ O	Eu ⁺³	Pb ⁺²
Ag ⁺	F ⁻	PUO ₂ ⁺²
Al ⁺³	H ⁺	Ra ⁺²
Am ⁺³	HPO ₄ ⁻²	Rb ⁺
As(OH) ₄ ⁻	Hg ⁺²	Ru ⁺³
Au ⁺	I ⁻	SeO ₃ ⁻²
B(OH) ₃	Fe ⁺²	SiO ₂ (aq)
Ba ⁺²	K ⁺	Sr ⁺²
Br ⁻	Li ⁺	SO ₄ ⁻²
Ca ⁺²	Mg ⁺²	TcO ₄ ⁻
HCO ₃ ⁻	Mn ⁺²	Th ⁺⁴
Cs ⁺	NO ₃ ⁻	Sn ⁺⁴
Cl ⁻	Na ⁺	U ⁺⁴
Co ⁺²	Ni ⁺²	V ⁺³
Cr ⁺³	Np ⁺³	Zn ⁺²
Cu ⁺	O ₂ (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.

- 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 [32–572 °F] at one atm pressure below 100 °C [212 °F] 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 (Bethke, 2005a).

The most commonly used database in the Geochemist's Workbench Version 6.0 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 6.0 software package to maintain compatibility with earlier releases of the software but are neither supported nor recommended for use with Geochemist's Workbench Version 6.0 (Bethke, 2005a). The following validation exercises were taken from the sample problems that accompany the PHREEQC manual (Parkhurst and Appelo, 1999). Validation exercises described in this report use the most appropriate database for each problem. The validation exercise tests the code theories and mathematical functionality; therefore, thermo.dat was not used for every validation problem. However, the quality of the input and thermodynamic data used is just as important. Each validation problem was run with both thermo.dat and thermo.com.v8.r6+.com to view consistency. While each database used supplied various outputs, none was deemed unreasonable or significantly different from expected.

3.2.2 Output

The results from the software packages React, Act2, Tact, and SpecE8 are written to output files React_Output, Act2_Output, Tact_Output, and SpecE8_Output respectively. In addition, the programs Act2 and Tact display a diagram on the User's workstation screen, which can be modified interactively with standard pull-down menus. The program Rxn is usually run interactively, with the output written on the workstation screen. It is possible, however, to divert Rxn's output to a file, by using the "output" command in place of "go" or select run from the drop down menu then view Rxn_Output. The Software Release Notice For Geochemist's Workbench Version 6.0 (2007) has already sufficiently validated packages Rxn, Act2, and Tact. However, for this supplemental validation, only SpecE8 and React will be evaluated.

3.3 Hardware Requirements and Installation

The Geochemist's Workbench Version 6.0 is designed for IBM-compatible personal computers. Successful installation of the code on an IBM-compatible personal computer requires the following system attributes:

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

A computer information systems administrator installed the Geochemist's Workbench software package in accordance with TOP-018 (CNWRA, 2007). An interactive installation program that

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.

4 PREREQUISITES

Prerequisites for successful installation and application of the Geochemist's Workbench software include an appropriate level of hardware capabilities and compliance with Geochemist's Workbench installation process, as described in Section 3.3. Input files will be prepared for all validation tests, as necessary.

5 ASSUMPTIONS AND CONSTRAINTS

It is difficult, or perhaps even impossible (Oreskes, et al., 1994) to produce a quantitative representation of a complex earth science system that is unique. Assumptions, constraints, and limitations are unavoidable in quantitative geochemical models. This is, in part, because there are different, and yet often equally valid, equations to describe geochemical processes, such as reaction rates or nonideal speciation behavior. Two different modelers may conceptualize the same chemical system in different ways, electing to include different minerals and aqueous species in his or her model or to evaluate the same data with somewhat different equations. In addition, thermodynamic data for a given phase often vary from dataset to dataset. Bethke (1992) demonstrates how modelers may obtain different results due to the presence of multiple mathematical roots to a single set of governing equations by employing slightly different sets of initial assumptions and constraints to a model. There are thus assumptions and constraints involved in the algorithms, the mathematical formulations, the data, and the conceptual models generated by Geochemist's Workbench. Other geochemical codes, such as EQ3/6 (Wolery, 1992) or PHREEQC (Parkhurst and Appelo, 1999) have similar limitations. It is thus important to clarify what aspect of Geochemist's Workbench Version 6.0 is being validated here. This software validation test plan is designed to provide evidence only that the Geochemist's Workbench Version 6.0 software package successfully implements the main underlying theory and algorithms described in the Geochemist's Workbench User's manual, as required by TOP-18 (CNWRA, 2007).

6 TEST CASES

The test cases to be used in validation testing have been identified previously (Parkhurst and Appelo, 1999). The following sections report the results of the testing. Validation tests are performed for two of the geochemical software programs in Geochemist's Workbench Version 6.0 (i.e., SpecE8 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. Output files can be written for all programs and are automatically generated using the SpecE8 and React programs (Bethke, 2005a).

Individual input files used in the Geochemist's Workbench Version 6.0 software validation tests are included in the appendix and as text 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 Version 6.0. 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 the user can modify them interactively (Bethke, 2005a).

6.1 Validation Results

TOP-018 (CNWRA, 2007) describes acceptable methods for validating commercially available software. Staff reviewed these methods 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 6.0 (Bethke, 2005a,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 (CNWRA, 2007) thus emphasize the importance of testing the ability of the code to accurately apply underlying theories 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). 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 waste at Yucca Mountain, Nevada. The results of Geochemist's Workbench Version 6.0 calculations, however, are also compared with those from analytical expressions, when appropriate.

6.1.1 SpecE8

SpecE8 is a flexible module that models the equilibrium states of geochemical systems that contain an aqueous fluid. The module calculates the equilibrium distribution of aqueous species in a fluid, the fluid's saturation state with respect to minerals, the sorption of aqueous species onto various types of surfaces, and the fugacities of gases dissolved in the fluid. SpecE8 produces as output a dataset "SpecE8_output.txt" that shows calculation results in tabular form, and a dataset "SpecE8_plot.aqp" that passes more complete information to the graphics module Aqplot (Bethke, 2005a).

SpecE8 Test 1: Seawater Speciation Calculation With Uranium

Parkhurst and Appelo (1999) provide an example to calculate the distribution of aqueous species in seawater, the saturation state of seawater at 25 °C [77 °F], and a fixed O₂ log fugacity of 0.7 relative to a set of minerals. A representative major element composition of seawater can be seen in Table 6-1.

As originally posed in the PHREEQC Version 2.12.5 User's Manual (Parkhurst and Appelo, 1999), the speciation problem specified thermodynamic equilibrium constants for the uranium aqueous speciation in the input file. However, both programs contain the Wateqa2 database, which contains the desired uranium species and was therefore used in the runs. The original formulation of the problem in the PHREEQC Version 2.12.5 User's Manual (Parkhurst and Appelo, 1999) also used the NO₃⁻/NH₄⁺ redox couple to control the oxidation state of uranium, while controlling the distribution of the other redox sensitive elements (iron and manganese) by the overall redox equilibrium with atmospheric oxygen. The Geochemist's Workbench Version 6.0 database does not allow the user to specify individual redox controls, so the entire problem was formulated to control all redox reactions, including uranium speciation, only by atmospheric oxygen. To make PHREEQC's output more compatible to that of Geochemist's Workbench, the electron potential was not specified as it was in the original example problem. Because of the large number of aqueous species in a multicomponent solution like seawater, only a few representative species concentrations are included in Table 6-2. The speciation results for PHREEQC and Geochemist's Workbench models are very similar. A graphical comparison of the calculated concentration of aqueous species (Figure 6-1) shows a reasonable, although not perfect, correlation among the results. Species with a zero concentration were not included in the figure. Most calculated values agree within a factor of two. Calculated mineral saturations (Table 6-3) also show reasonable agreement of the predictions of saturation and undersaturation between the two codes.

Cl ⁻	.5458
Na ⁺	.4680
SO ₄ ⁻⁻	.0282
Mg ⁺⁺	.0531
Ca ⁺⁺	.0103
K ⁺	0.102
HCO ₃ ⁻	.0023
SiO ₂ (aq)	8.3242 × 10 ⁻⁶ – 1.6648 × 10 ⁻⁴
O ₂ (aq)	3.1269 × 10 ⁻⁶ – 1.8762 × 10 ⁻⁴

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

Table 6-2. Comparison of Geochemist's Workbench Version 6.0 and PHREEQC Version 2.12.5 Calculated Concentrations of Selected Component Species, Carbonate Species, and Redox Sensitive Species; T = 25 °C [77 °F]		
Species	Aqueous Concentration (molal) Geochemist's Workbench Version 6.0	Aqueous Concentration (molal) PHREEQC Version 2.12.5
Non-Redox/Non-Carbonate Species		
K ⁺	1.005 × 10 ⁻²	1.005 × 10 ⁻²
Na ⁺	4.624 × 10 ⁻¹	4.624 × 10 ⁻¹
Cl ⁻	5.459 × 10 ⁻¹	5.459 × 10 ⁻¹
Carbonate Species		
CO ₃ ²⁻	4.144 × 10 ⁻⁵	3.698 × 10 ⁻⁵
HCO ₃ ⁻	1.656 × 10 ⁻³	1.478 × 10 ⁻³
NaHCO ₃	1.774 × 10 ⁻⁴	1.583 × 10 ⁻⁴
UO ₂ CO ₃	1.302 × 10 ⁻¹²	1.62 × 10 ⁻¹²
Redox-Sensitive Species		
U(IV) _{total}	1.954 × 10 ⁻⁴¹	7.344 × 10 ⁻²⁶
U(V) _{total}	6.879 × 10 ⁻²⁸	4.98 × 10 ⁻²⁰
U(VI) _{total}	1.386 × 10 ⁻⁸	1.386 × 10 ⁻⁸
U ^{VI} O ₂ (CO ₃) ₂ ²⁻	1.006 × 10 ⁻⁹	1.117 × 10 ⁻⁹
U ^V O ₂ (CO ₃) ₃ ⁵⁻	1.448 × 10 ⁻³²	7.452 × 10 ⁻²⁵
U ^{VI} O ₂ (CO ₃) ₃ ⁴⁻	1.284 × 10 ⁻⁸	1.272 × 10 ⁻⁸
Saturation Indices (SI) with respect to solid phases		
Anhydrite	-0.857	-0.860
Calcite	0.783	0.73
Halite	-2.534	-2.53
Schoepite	-5.380	-5.24
Uranophane	-11.14	-11.5

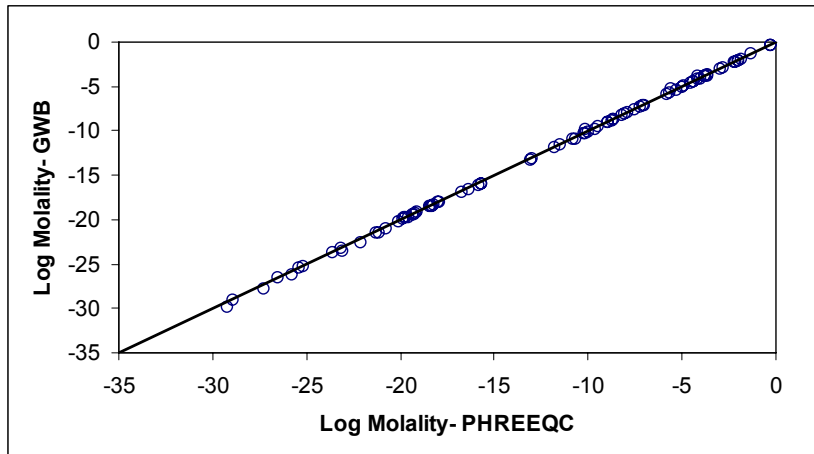


Figure 6-1. Comparison of the Calculated Concentration of Aqueous Species Between PHREEQC Version 2.12.5 and Geochemist's Workbench Version 6.0

6.1.2 React

React is the primary equilibrium and kinetic reaction pathway modeling module in the Geochemist's Workbench Version 6.0 software package. The module 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). Four tests of the React module will be performed to validate the underlying theory and algorithms to calculate the equilibrium chemical system and a kinetic reaction pathway.

React Test 1: Mineral Solubility (Barite)

Richardson and McSween (1989) present two worked problems to investigate the solubility of barite (BaSO_4) at 25 °C [77 °F] in pure water (Worked Problem 3-7) and in a 0.2 m NaCl solution (Worked Problem 3-8). Using an iterative solution of the congruent barite dissolution reaction, Richardson and McSween (1989) demonstrated that barite solubility increases with ionic strength. The results for barite solubility calculated by Geochemist's Workbench Version 6.0 in pure water and in a 0.2 m NaCl solution were calculated using the phreeqc.dat database. The Geochemist's Workbench Version 6.0 solubilities are comparable to the results obtained from PHREEQC Version 2.12.5. The results for barite solubility reported in Richardson and McSween (1989) differ slightly from the results calculated by Geochemist's Workbench Version 6.0 (Table 6-3). The results differ by less than 2 percent and are likely due to slight differences in the activity coefficient formulation and a more complete handling of the geochemical system in Geochemist's Workbench and PHREEQC. For example, the Davies equation is used in Geochemist's Workbench Version 6.0 (Bethke, 2005b), versus the Debye-Hückel formulation used in Richardson and McSween (1989). Geochemist's Workbench Version 6.0 also includes the dissociation products of water (H^+ and OH^-) in the geochemical

Table 6-3. Comparison of Barite Solubility Results for Richardson and McSween (1989), Geochemist's Workbench Version 6.0, and PHREEQC Version 2.12.5				
Result Source	$m_{\text{Ba}^{2+}}$ (molal)	$m_{\text{SO}_4^{2-}}$ (molal)	$\gamma_{\text{Ba}^{2+}}$ (D-H)	$\gamma_{\text{SO}_4^{2-}}$ (D-H)
Problem 3-7 (pure H₂O)				
Geochemist's Workbench Version 6.0	1.067×10^{-5}	1.067×10^{-5}	0.97010	0.97010
PHREEQC Version 2.12.5	1.055×10^{-5}	1.055×10^{-5}	0.97010	0.97010
Richardson and McSween (1989)	1.051×10^{-5}	1.051×10^{-5}	0.9704	0.9704
Blount (1977)	1.060×10^{-5}	1.06×10^{-5}	N/R	N/R
Problem 3-8 (0.2 m NaCl)				
Geochemist's Workbench Version 6.0	3.981×10^{-5}	3.080×10^{-5}	0.29820	0.29280
PHREEQC Version 2.12.5	3.937×10^{-5}	3.047×10^{-5}	0.29820	0.29270
Richardson and McSween (1989)	3.611×10^{-5}	3.611×10^{-5}	0.2987	0.2671
Blount (1977)	3.700×10^{-5}	3.700×10^{-5}	N/R	N/R
N/R not reported				

system, resulting in small changes in calculated ionic strength. Geochemist's Workbench Version 6.0, PHREEQC Version 2.12.5, and Richardson and McSween (1989) solubility calculations are in good agreement with the experimental data of Blount (1977) as reported in Richardson and McSween (1989).

React Test 2: Sorption—Surface Complexation Modeling

Parkhurst and Appelo (1999) provide an example to calculate Zn^{2+} sorption on ferrihydrite (HFO) using the diffuse-layer surface complexation model and parameters described in Dzombak and Morel (1990). While SpecE8 has sorption capabilities, it was not used for this problem, which required the pH to slide from 5 to 8. Sorption at 25 °C [77 °F] is investigated for two Zn^{2+} concentrations (10^{-4} and 10^{-7} molal), and the results are presented in terms of dissolved and sorbed Zn^{2+} molality as a function of pH.

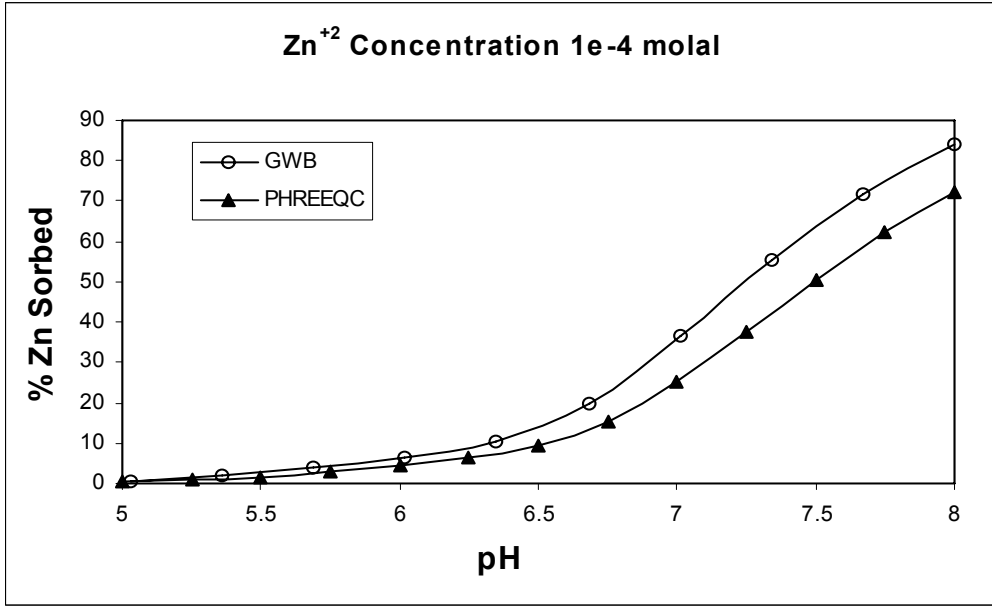
PHREEQC used the DLM Constants from Dzombak and Morel (1990), while Geochemist's Workbench was modeled using the FeOH.dat database that accompanies the program. The log K values vary slightly; however, the results from Geochemist's Workbench Version 6.0 and PHREEQC Version 2.12.5 show good agreement in trend but are off by as much as 38 percent. Geochemist's Workbench was updated using the PHREEQC log K values for the surface complex reactions. Once the files were rerun, the results between Geochemist's Workbench Version 6 and PHREEQC Version 2.12.5 improved, indicating that the surface complexation modeling subroutines are performing as expected. Model results are given in Table 6-4 (percent sorbed), and a comparison of results using different and the same log K values is shown in Figure 6-2(a–d) (surface complex concentration).

Table 6-4. Comparison of Geochemist's Workbench Version 6.0 and PHREEQC Version 2.12.5 Results for Zinc Sorption on Ferrihydrite (Percent Sorbed) With the Same Log K Values				
pH	Zn_T = 1 × 10⁻⁴ molal		Zn_T = 1 × 10⁻⁷ molal	
	Geochemist's Workbench Version 6.0 (% sorbed)	PHREEQC Version 2.12.5 (% sorbed)	Geochemist's Workbench Version 6.0 (% sorbed)	PHREEQC Version 2.12.5 (% sorbed)
5.00	0.35	0.31	0.38	0.33
5.25	0.88	0.77	1.03	0.90
5.50	1.91	1.68	2.75	2.42
5.75	3.42	3.02	7.15	6.32
6.00	5.09	4.51	17.32	15.48
6.25	7.07	6.26	36.38	33.24
6.50	10.44	9.26	61.10	57.61
6.75	17.08	15.17	81.32	78.88
7.00	27.90	24.99	92.43	91.20
7.25	41.49	37.55	97.19	96.66
7.50	55.54	50.58	99.00	98.78
7.75	68.23	62.50	99.65	99.56
8.00	78.66	72.39	99.88	99.84

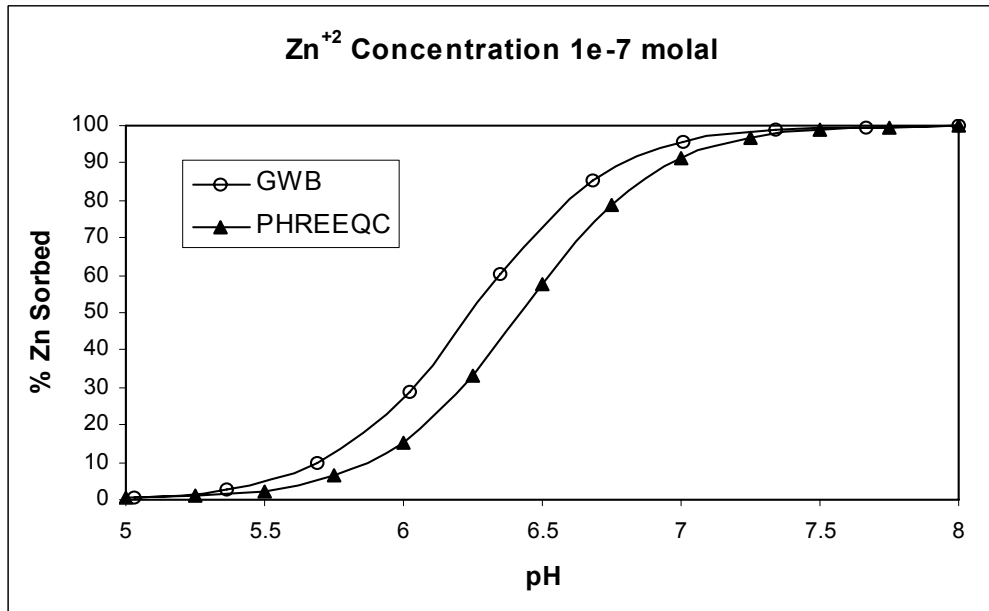
React Test 3: Temperature Effects

Parkhurst and Appelo (1999) provide an example of the use of PHREEQC to calculate the solubility of gypsum and anhydrite in pure water over a range in temperature from 25 to 75 °C [77 to 167 °F]. Only the pH and temperature are used to define a pure water solution. Gypsum and anhydrite are allowed to react to equilibrium, and the initial phase assemblage has 1 mol of each mineral. Each mineral will react either to equilibrium or until it is exhausted in the assemblage. For both Geochemist's Workbench Version 6.0 and PHREEQC Version 2.12.5, the degree of saturation with respect to a given mineral is indicated by the saturation index (SI), such that

$$SI = \log \frac{IAP}{K} \quad (3-1)$$

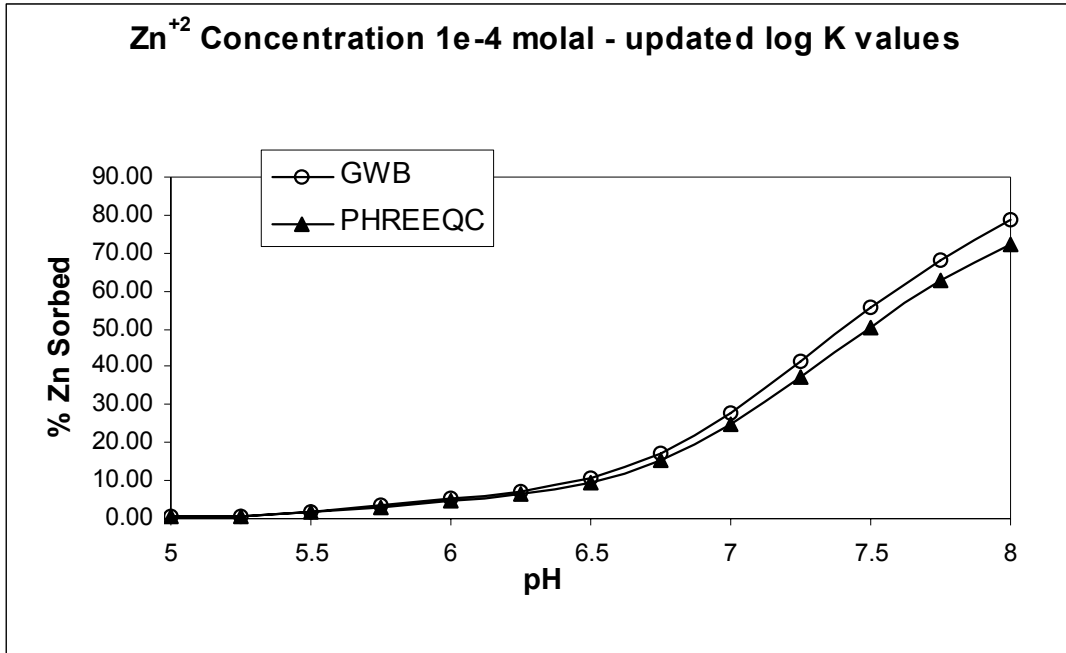


(a)

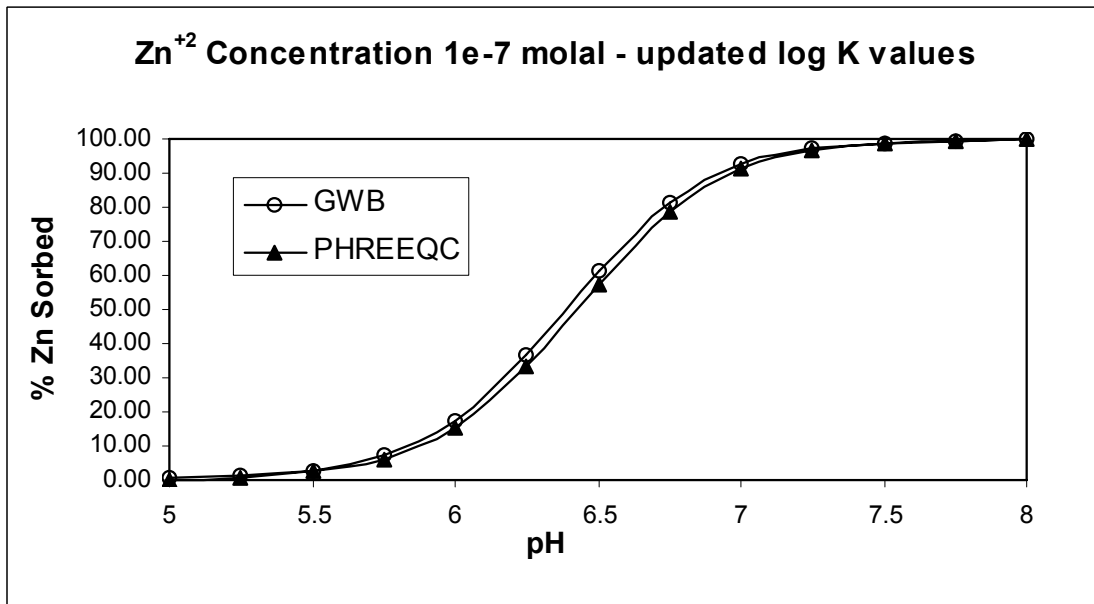


(b)

Figure 6-2. Sorbed Zn⁺² Molaity as a Function of pH. (a) Zn⁺² 10⁻⁴ Molal; (b) Zn⁺² 10⁻⁷ Molal; (c) Zn⁺² 10⁻⁴ Molal Same log K Values; (d) Zn⁺² 10⁻⁷ Molal Same log K Values.



(c)



(d)

Figure 6-2. Sorbed Zn⁺² Molaity as a Function of pH. (a) Zn⁺² 10⁻⁴ Molal; (b) Zn⁺² 10⁻⁷ Molal; (c) Zn⁺² 10⁻⁴ Molal Same log K Values; (d) Zn⁺² 10⁻⁷ Molal Same log K Values (continued).

where IAP is the ion activity product, and K is the equilibrium constant. When a solution is undersaturated with respect to a given mineral, $SI < 0$. Under supersaturated conditions, $SI > 0$, and $SI = 0$ at equilibrium.

As a default, both Geochemist's Workbench Version 6.0 and PHREEQC Version 2.12.5 use the Van't Hoff relationship and enthalpies of reaction (ΔH_r°) to correct equilibrium constants for the effects of temperature. PHREEQC Version 2.12.5 provides a polynomial expression in the phreeqc.dat database for both anhydrite and gypsum to calculate K at temperatures above 25 °C [77 °F] [Eq. (3-1)].

$$\log_{10}K = A1 + A2T + A3/T + A4\log_{10}T + A5/T^2 \quad (3-2)$$

where T is Kelvin.

The thermo_phreeqc.dat database was used with Geochemist's Workbench Version 6.0 for this problem. Log K values were calculated as a function of temperature using the analytic method from PHREEQC.

If the same thermodynamic data and polynomial expressions are used, both codes should produce similar results. Comparing the results in Table 6-5 and Figure 6-3 shows very similar SI values calculated by Geochemist's Workbench Version 6.0 and PHREEQC Version 2.12.5. Differences (in the third significant digit) may be due to an accumulation of rounding errors.

React Test 4: Evaporation of Central Oklahoma Rainwater

Parkhurst and Appelo (1999) provide an example of the use of PHREEQC to simulate concentration of rainwater from central Oklahoma at 25 °C [77 °F]. The concentration was approximately twentyfold, achieved by removing 95 percent of the water, which is referred to as solution 2. They then multiply the moles of solution 2 by 20 for all elements in the solution. This effectively increases the composition of solution 2 20 times to create solution 3. The evaporated solution 2 and the resultant mixing of the evaporated solution 3 should have the same concentrations, but the mass of water will increase from 0.05 kg to approximately 1 kg [1.76 to 35.27 oz].

The input file for PHREEQC Version 2.12.5 was altered slightly; the N(5) and N(-3) input concentrations were based on the formula weight of NO_3^- and NH_4^+ to accommodate the input limitations of Geochemist's Workbench Version 6.0. The Geochemist's Workbench Version 6.0 file was run using thermo.dat, and the input file is seen in the appendix. The altered PHREEQC input file will accompany this report on CD. After evaporation, solution 2 is still undersaturated with respect to calcite, dolomite, and gypsum and has a mass of water approximately equal to 0.05 kg [1.76 oz]. The number of moles of chloride (mol) was unaffected by the removal of water; however, the concentration of chloride (mol/kgw) increased because the amount of water decreased. There is good agreement between PHREEQC Version 2.12.5 and Geochemist's Workbench Version 6.0 (Table 6-6). The rainwater analysis contained data for both ammonium and nitrate, but none for dissolved nitrogen. Although nitrate and ammonium should not coexist at thermodynamic equilibrium, the speciation calculation of PHREEQC Version 2.12.5 allows

Table 6-5. Comparison of Saturation Indexes (SI) Calculated by Geochemist's Workbench Version 6.0 and PHREEQC Version 2.12.5 for Anhydrite and Gypsum as a Function of Temperature				
T(°C)	Geochemist's Workbench Version 6.0 Limited 1mol (Figure A)		PHREEQC Version 2.12.5	
	SI(Anhy)	SI(Gyp)	SI(Anhy)	SI(Gyp)
25	-0.2178	0	-0.2197	0
30	-0.1978	0	-0.1977	0
35	-0.1713	0	-0.1713	0
40	-0.1407	0	-0.1406	0
45	-0.106	0	-0.106	0
50	-0.0678	0	-0.0678	0
55	-0.0261	0	-0.0261	0
60	0	-0.0188	0	-0.0187
65	0	-0.0666	0	-0.0665
70	0	-0.1172	0	-0.1171
75	0	-0.1704	0	-0.1704

redox disequilibria and accepts the concentrations of the two redox states of nitrogen that are defined by the input data, regardless of thermodynamic equilibrium. Geochemist's Workbench Version 6.0 accepts the input and then converts the nitrate to dissolved nitrogen before it brings the system to equilibrium. During the (evaporation) step, redox equilibrium is attained for the aqueous phase, which causes ammonium to be oxidized and nitrate to be reduced, generating dissolved nitrogen [N₂(aq)]. The simulation (solution 2) contains the equilibrium distribution of nitrogen, which consists of ammonium and dissolved nitrogen, but no nitrate (Table 6-6).

The second simulation increased the mass of water and the moles of each element by a factor of 20. There is good agreement between Geochemist's Workbench Version 6.0 and PHREEQC Version 2.12.5. The moles of chloride increased, but the chloride concentration remained the same in solution 2 and 3 for both models because the mass of water increased proportionately, just as predicted (Table 6-6). Geochemist's Workbench Version 6.0 is not set up to take the results of one simulation to use for another, which made it necessary to create a separate file for the second simulation. In this input file, the pH and pE needed to be fixed to preserve the equilibrium distribution of nitrogen.

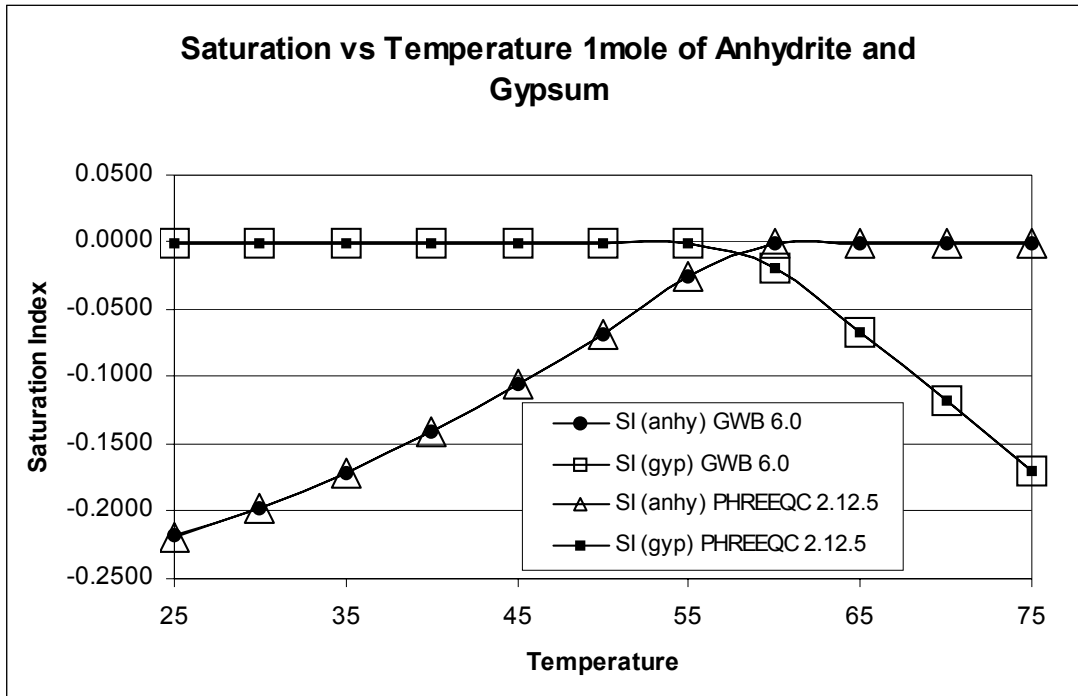


Figure 6-3. Comparison of Saturation Indexes Calculated by Geochemist's Workbench Version 6.0 and PHREEQC Version 2.12.5 for Anhydrite and Gypsum as a Function of Temperature

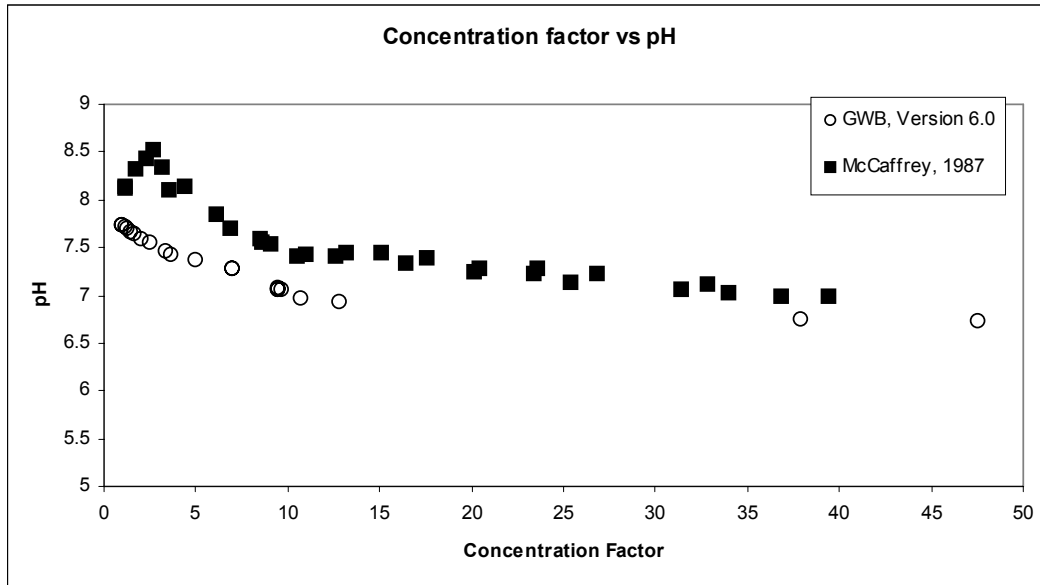
Constituent	Geochemist's Workbench Solution 1	PHREEQC Solution 1	Geochemist's Workbench Solution 2	PHREEQC Solution 2	Geochemist's Workbench Solution 3	PHREEQC Solution 3
Mass water, kg*	1	1	0.05	0.05	1	1
C, μm	11.3	10.9	11.3	10.9	226	218
Ca, μm	9.58	9.58	9.58	9.58	192	192
Cl, μm	6.66	6.66	6.66	6.66	133	133
K, μm	0.92	0.92	0.92	0.92	18.4	18.4
Mg, μm	1.77	1.77	1.77	1.77	35.4	35.4
N, μm	15.4	15.4	15.4	15.4	300	307
Na, μm	6.13	6.13	6.13	6.13	123	123
S, μm	13.5	13.5	13.5	13.5	271	271
Cl, $\mu\text{m mol/kg}$	6.66	6.66	133	133	133	133
HCO ₃ ⁻ , $\mu\text{m mol/kg}$	0.15	0.14	0.17	0.16	0.07	0.16

Table 6-6. Concentration, Water Mass, and Moles of Chloride for Solutions 1 Through 3 (continued)						
Constituent	Geochemist's Workbench Solution 1	PHREEQC Solution 1	Geochemist's Workbench Solution 2	PHREEQC Solution 2	Geochemist's Workbench Solution 3	PHREEQC Solution 3
Nitrate(5) $\mu\text{m mol/kg}$	0	0	0	0	0	0
Nitrogen (0-aq) $\mu\text{m mol/kg}$	204	204	204	204	204	204
Ammonium (-3) $\mu\text{m mol/kg}$	11.53	5.16	103	103	103	103
Calcite Saturation Index	-9.07	-9.21	-9.09	-9.29	-9.08	-9.29
Dolomite Saturation Index	-19.51	-19.02	-19.54	-19.19	-19.54	-19.19
Gypsum Saturation Index	-5.48	-5.35	-3.04	-2.9	-3.04	-2.9

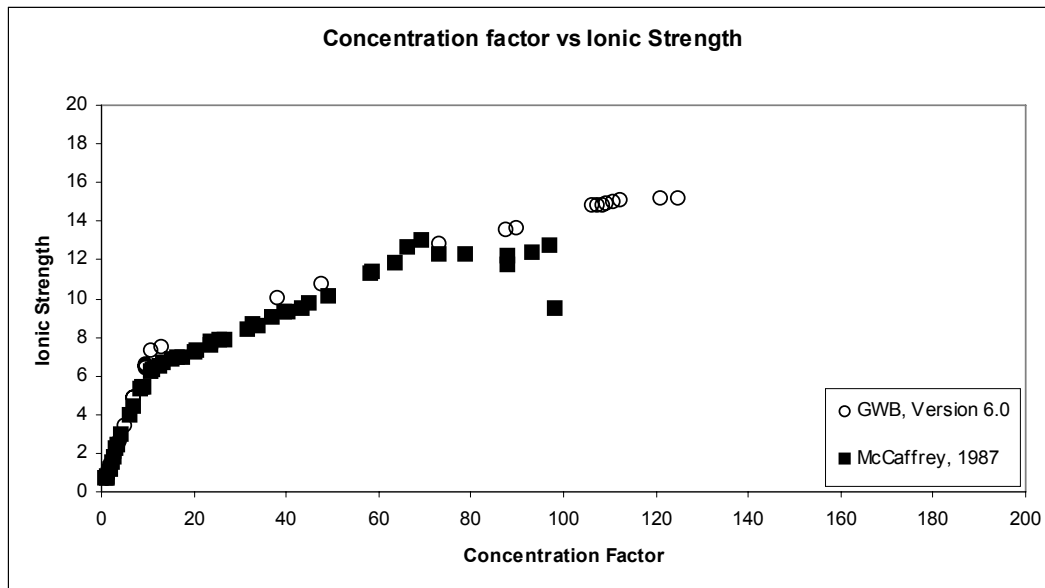
*Kg = kilograms, μm micro moles (10^{-6} moles)

React Test 5: Seawater Evaporation With Harvie-Moller-Weare Database

Thermodynamic simulations of seawater evaporation were conducted using the React module of the Geochemist's Workbench Version 6.0 database. The simulations were done for a temperature of 25 °C [77 °F] at various concentration factors using the Harvie-Moller-Weare database of Pitzer model parameters. The log fugacity of CO₂ was fixed at -3.50. The seawater composition used in the calculation and the evaporation path of seawater and the co-precipitation of Br⁻ and K⁺ with halite was taken from McCaffrey, et al. (1987). For calculation purposes, a value of HCO₃⁻ concentration (not reported by McCaffrey, et al., 1987) was assumed equal to 142 mg/L, based on the Stoughton and Lietzke (1965) value. Bromide ion, which is also listed by McCaffrey, et al. (1987), was not included in the Geochemist's Workbench Version 6.0 database calculations, because there are no Pitzer model parameters for bromide in the Harvie-Moller-Weare database. Charge balance was done using Cl⁻ as the balancing species. Figure 6-4(a,b) compares pH and ionic strength versus concentration factor for the Geochemist's Workbench and McCaffrey, et al. (1987) data (if available). A comparison of the major element concentrations of seawater for both Geochemist's Workbench Version 6.0 database and McCaffrey, et al. (1987) is shown in Figure 6-5(a-f). These figures show good agreement between the results computed by Geochemist's Workbench Version 6.0 database and the data from McCaffrey, et al. (1987). However, in Geochemist's Workbench Version 6.0, K⁺ concentrations begin to decrease after concentrations reach 40 times that of seawater. McCaffrey, et al. (1987) does not demonstrate this same trend, because they did not account for potassium-bearing phases that precipitate at that degree of evaporation and higher. Geochemist's Workbench indicates that polyhalite begins to control potassium concentrations around concentrations 45 times that of seawater.

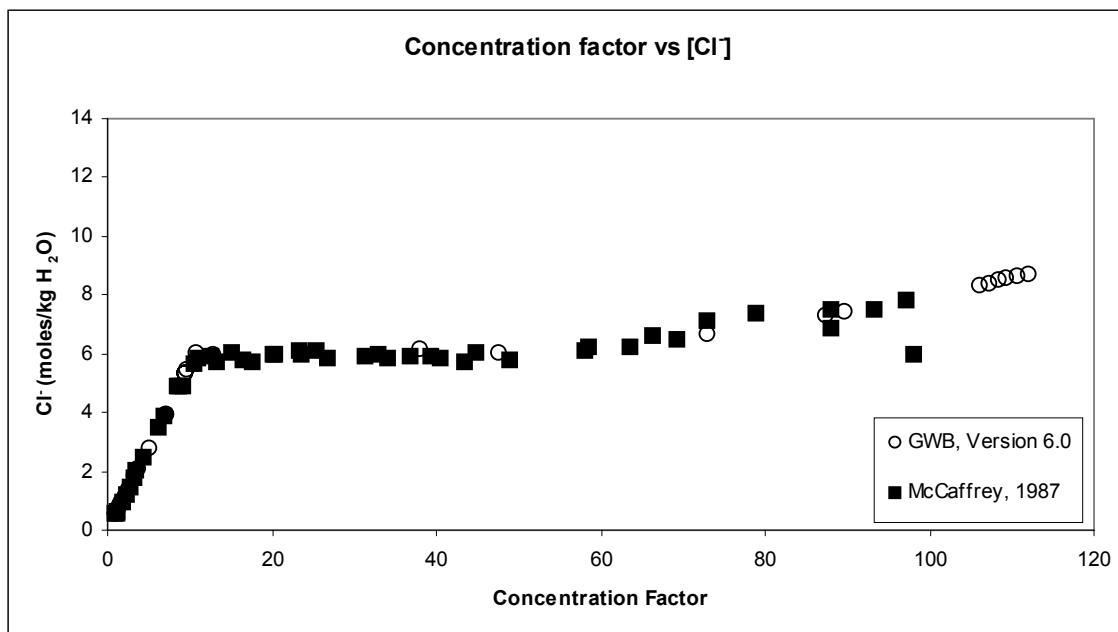


(a)

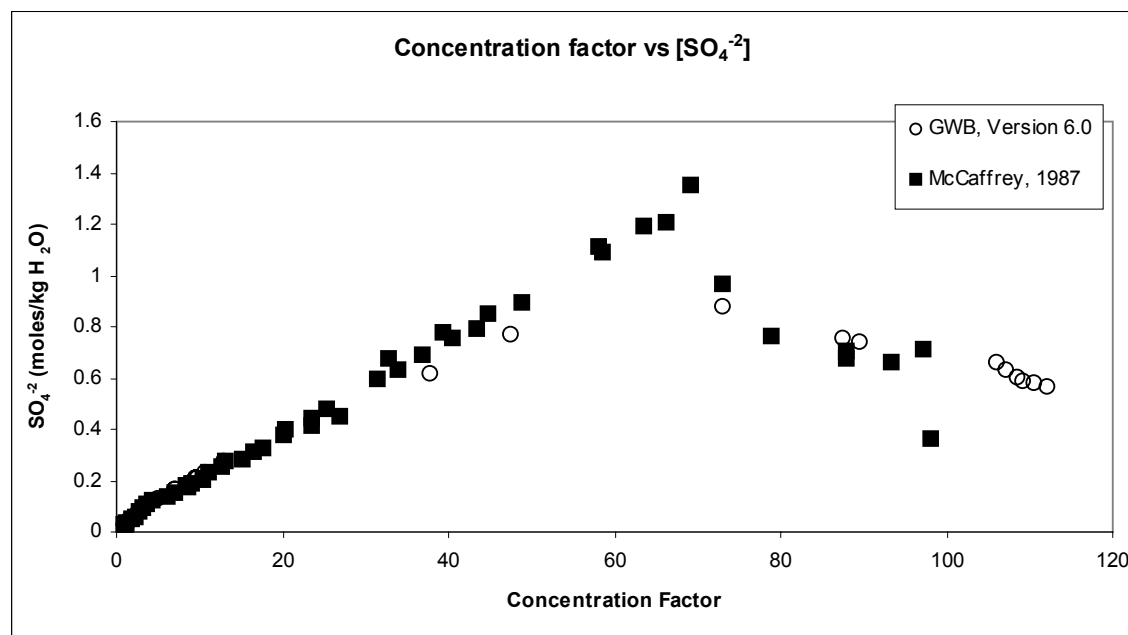


(b)

Figure 6-4. Seawater Evaporation With Harvie-Moller-Weare Database Results for Geochemist's Workbench Version 6.0 and PHREEQC Version 2.12.5. (a) pH Versus Concentration Factor; (b) pH Versus Concentration Factor.

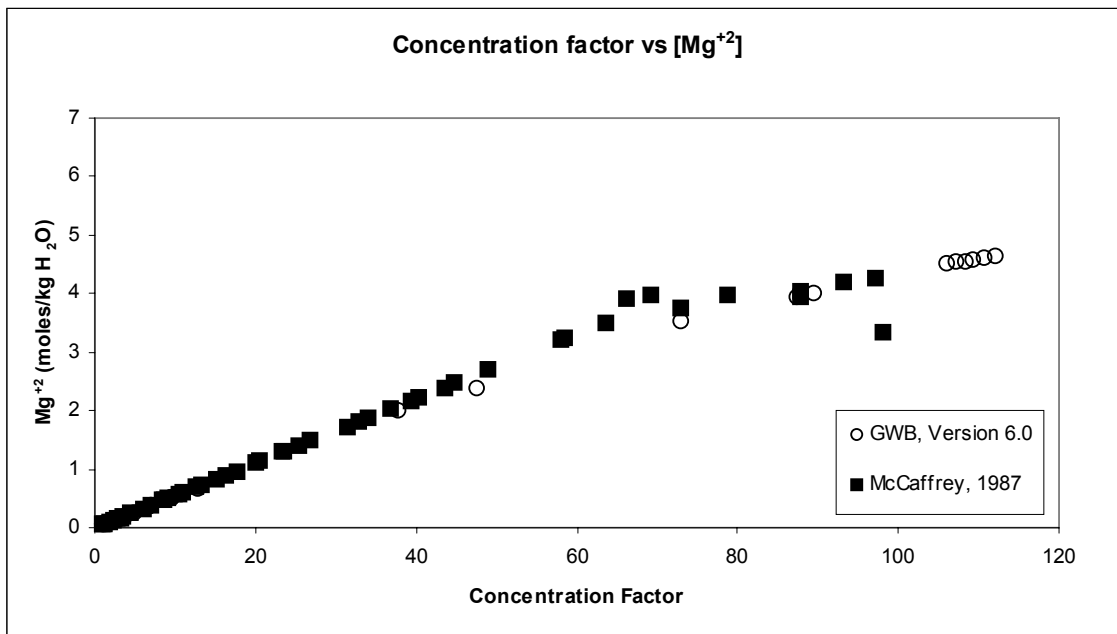


(a)

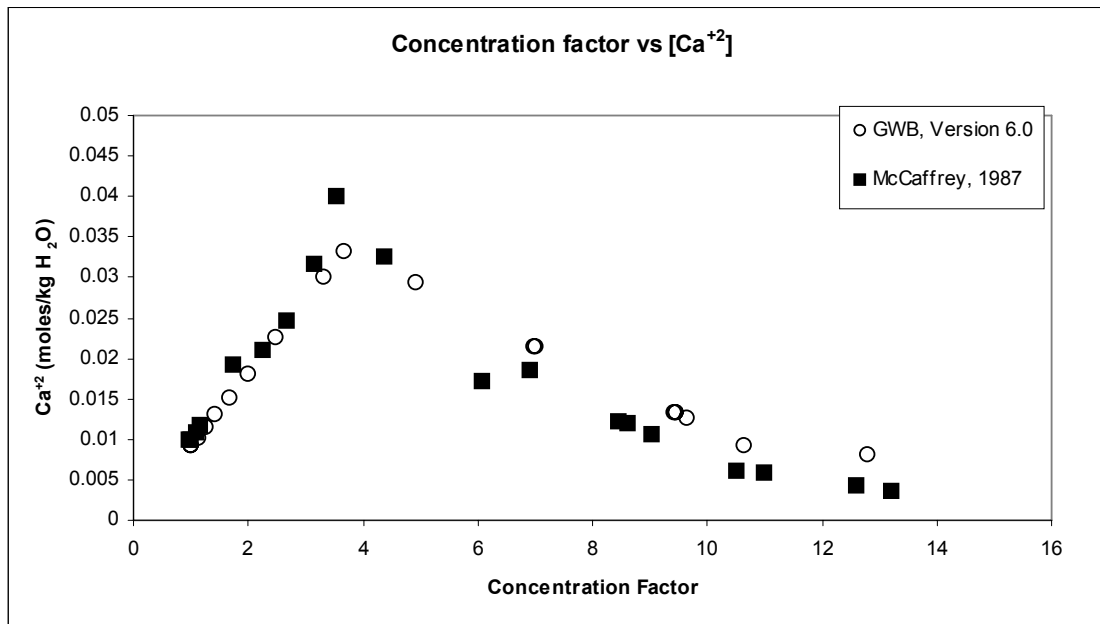


(b)

Figure 6-5. Seawater Evaporation With Harvie-Moller-Weare Database Results for Geochemist's Workbench Version 6.0 and PHREEQC Version 2.12.5. (a) Cl⁻, (b) SO₄⁻², (c) Mg⁺², (d) Ca⁺², (e) K⁺, (f) Na⁺.

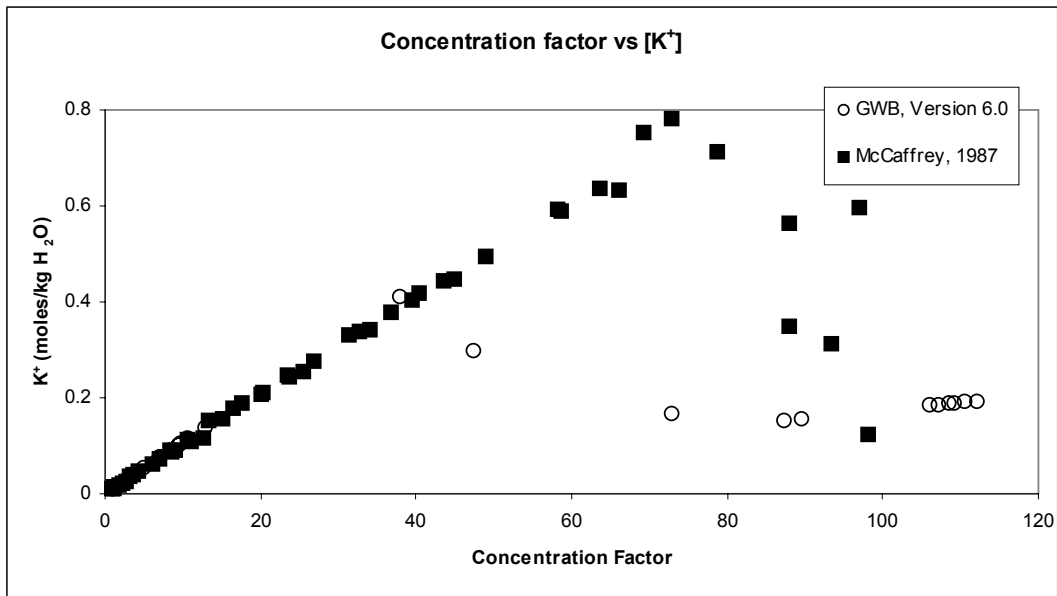


(c)

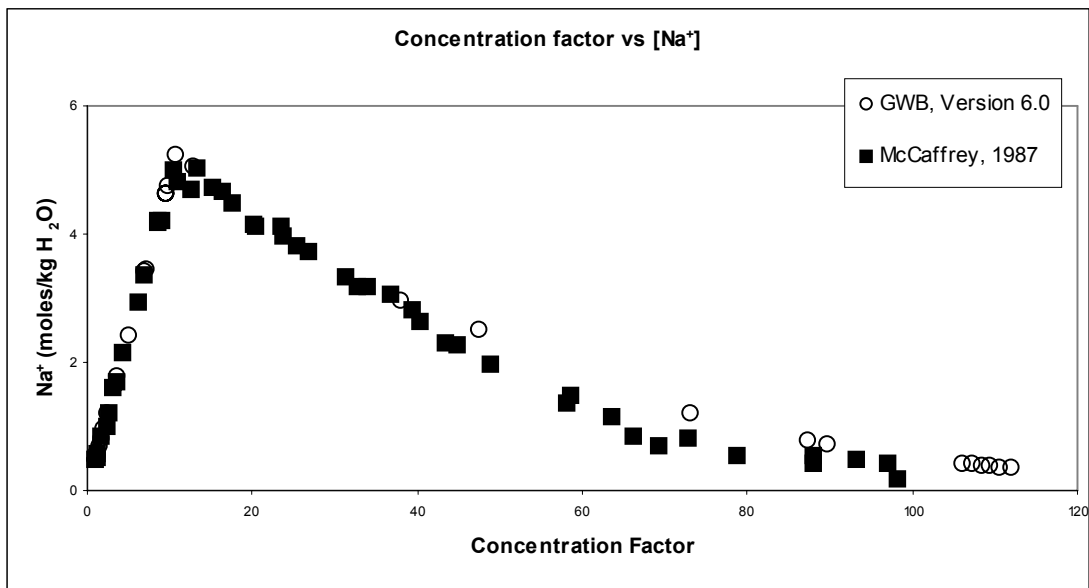


(d)

Figure 6-5. Seawater Evaporation With Harvie-Moller-Weare Database Results for Geochemist's Workbench Version 6.0 and PHREEQC Version 2.12.5. (a) Cl⁻, (b) SO₄⁻², (c) Mg²⁺, (d) Ca²⁺, (e) K⁺, (f) Na⁺ (continued).



(e)



(f)

Figure 6-5. Seawater Evaporation With Harvie-Moller-Weare Database Results for Geochemist's Workbench Version 6.0 and PHREEQC Version 2.12.5. (a) Cl^- , (b) SO_4^{2-} , (c) Mg^{+2} , (d) Ca^{+2} , (e) K^+ , (f) Na^+ (continued).

7 SUMMARY AND CONCLUSIONS

Comparisons for a variety of geochemical problems show that Geochemist's Workbench Version 6.0 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 6.0 software package will correctly execute a variety of fundamental geochemical calculations, including the correct calculation of activity coefficients, mineral solubilities, temperature-dependent aqueous speciation, and sorption calculations. A less than 5 percent difference between the results of analytical calculations and those performed by the Geochemist's Workbench Version 6.0 database 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 6.0 database and the various calculational methods used in the model validation exercise indicates 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.

APPENDIX

SpecE8 Test 1 - Speciation with Uranium:

```
# SpecE8 script, saved Tue Dec 05 2006 by Isabido
data = "C:\Program Files\Gwb\Gtdata\thermo_wateq4f.dat" verify
temperature = 25
decouple NH4+
swap O2(g) for O2(aq)
swap U++++ for UO2++
1 kg H2O
8.22 pH
412.3 mg/l Ca++
1291.8 mg/l Mg++
10768 mg/l Na+
399.1 mg/l K+
.002 mg/l Fe++
2e-4 mg/l Mn++
19353 mg/l Cl-
2712 mg/l SO4--
.29 mg/l NO3-
.03 mg/l NH4+
-.7 log fugacity O2(g)
141.682 mg/l CO3--
14.417 mg/l H4SiO4
.0033 mg/l U++++
balance off
```

React Test 1a - Barite Solubility:

```
# React script, saved Wed Dec 06 2006 by Isabido
data = "C:\Program Files\Gwb\Gtdata\thermo_phreeqc.dat" verify
temperature = 25
1 kg H2O
1e-10 mg/l Ba++
1e-10 mg/l SO4--
balance off
react 10 mol of Barite

suppress HSO4- BaOH+
printout minerals = long
```

React Test 1b - Barite Solubility 0.2 m NaCl solution :

```
# React script, saved Wed Dec 06 2006 by Isabido
data = "C:\Program Files\Gwb\Gtdata\thermo_phreeqc.dat" verify
temperature = 25
1 kg H2O
1e-10 mg/kg Ba++
1e-10 mg/kg SO4--
.2 molarity Na+
.2 molarity Cl-
```

balance off
react 10 mol of Barite

suppress HSO4- BaOH+
printout minerals = long

React Test 2 - Sorption: 1e-4 mmol Zn⁺⁺

```
# React script, saved Thu Jul 13 2006 by Isabido
data = "c:\program files\gwb\gtdata\thermo.dat" verify
surface_data = "C:\Program Files\Gwb\Gtdata\FeOH.dat"
temperature = 25
swap Hematite for Fe++
1 kg H2O
.09 gram Hematite
1e-4 mmol Zn++
balance on Na+
100 mmol Na+
100 mmol NO3-
4.7 pH
100 mmol O2(aq)
slide log activity of H+ to -8
```

React Test 2 - Sorption b: 0.1 mmol Zn⁺⁺

```
# React script, saved Fri Mar 30 2007 by Isabido
data = "c:\program files\gwb\gtdata\thermo.dat" verify
surface_data = "C:\Program Files\Gwb\Gtdata\FeOH.dat"
temperature = 25
swap Hematite for Fe++
1 kg H2O
.09 gram Hematite
.1 mmol Zn++
balance on Na+
100 mmol Na+
100 mmol NO3-
4.7 pH
100 mmol O2(aq)
slide log activity of H+ to -8
```

React Test 3 - Temperature Effects a:

```
# React script, saved Thu Mar 29 2007 by Isabido
data = "C:\Program Files\Gwb\Gtdata\thermo_phreeqc.dat" verify
temperature initial = 25, final = 75
1 kg H2O
1e-10 mg/kg Ca++
1e-10 mg/kg SO4--
```

7 pH
1e-10 mg/kg Cl-
balance off
react 1 mol of Gypsum
react 1 mol of Anhydrite

React Test 3 - Temperature Effects b:

```
# React script, saved Mon Jul 03 2006 by Isabido
data = "C:\Program Files\Gwb\Gtdata\thermo_phreeqc.dat" verify
temperature initial = 25, final = 75
swap Calcite for Ca++
swap Anhydrite for SO4--
1 kg H2O
1 mol Calcite
1 mol Anhydrite
7 pH
1e-8 mg/kg CO3--
balance off
```

React Test 4a - Evaporation of Central Oklahoma Rainwater:

```
# React script, saved Mon Apr 02 2007 by Isabido
data = "c:\program files\gwb\gtdata\thermo.dat" verify
temperature = 25
swap CO2(g) for HCO3-
swap NH4+ for O2(aq)
1 kg H2O
-3.5 log fugacity CO2(g)
.384 mg/l Ca++
.043 mg/l Mg++
.141 mg/l Na+
.036 mg/l K+
.236 mg/l Cl-
4.5 pH
1.3 mg/l SO4--
.237 mg/l NO3-
.208 mg/l NH4+
balance off
react -52.73 mol of H2O
printout species = long minerals = long
```

React Test 4b - Evaporation of Central Oklahoma Rainwater:

```
# React script, saved Mon Apr 09 2007 by Isabido
data = "C:\Program Files\Gwb\Gtdata\thermo.dat" verify
temperature = 25
swap NH4+ for NO3-
```



```

swap e- for O2(aq)
swap CO2(aq) for HCO3-
.05 kg H2O
.000307 molality NH4+
1.5192 pe
.000226 molality CO2(aq)
.000191 molality Ca++
3.53e-5 molality Mg++
.000123 molality Na+
1.84e-5 molality K+
.000133 molality Cl-
3.223 pH
.00027 molality SO4--
balance off
react .95 kg of H2O
react .000182 mol of Ca++
react 3.36e-5 mol of Mg++
react .000117 mol of Na+
react 1.75e-5 mol of K+
react .000126 mol of Cl-
react .000257 mol of SO4--
react .000146 mol of N2(aq)
react .000215 mol of CO2(aq)
fix pH
fix pe
printout species = long minerals = long

```

React Test 5 - Seawater Evaporation With Harvie-Moller-Weare Database

```

# React script, saved Wed Apr 04 2007 by Isabido
data = "C:\Program Files\Gwb\Gtdata\thermo_hmw.dat" verify
temperature = 25
decouple ALL
swap CO2(g) for H+
1 kg H2O
.000316227766 fugacity CO2(g)
11300 mg/l Na+
427 mg/l K+
390 mg/l Ca++
1300 mg/l Mg++
2880 mg/l SO4--
balance on Cl-
20500 mg/l Cl-
142 mg/l HCO3-
fix fugacity of CO2(g)
react -996 gram of H2O
dump
delxi = 1e-4 linear
dxplot = 0

```