SOFTWARE VALIDATION TEST PLAN FOR

MINTEQA2 FOR WINDOWS VERSION 1.5

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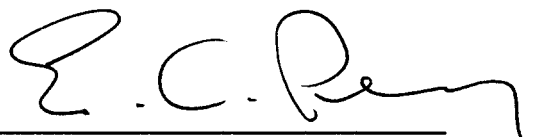

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1 SCOPE OF THE VALIDATION

This document establishes the software validation test plan for validating the installation and functionality of the geochemical equilibrium speciation code MINTEQA2 for Windows, Version 1.5 (Allison Geoscience Consultants, Inc. and Hydrogeologic, Inc., released August 2003). MINTEQA2 for Windows Version 1.5 is an acquired code that uses the same computational algorithms and thermodynamic databases as the DOS version originally developed by the U.S. Environmental Protection Agency (EPA), National Exposure Research Laboratory, Ecosystems Research Division (EPA, 1999a,b). The software is used by staff at 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.

This Software Validation Test Plan applies to MINTEQA2 for Windows Version 1.5 and is intended to validate the software for use in modeling geochemical equilibrium reactions as identified in the test cases described in Section 5. An earlier version, MINTEQA2 Version 4.02, is currently under configuration control in accordance with Technical Operating Procedure (TOP)–018, Development and Control of Scientific and Engineering Software. This validation plan identifies differences from the earlier MINTEQA2 Version 4.02 as necessary. MINTEQA2 for Windows Version 1.5 will be placed under TOP–018 configuration control prior to performing the validation activities outlined in Sections 6 (Test Inputs) and 7 (Test Procedures) of this document.

MINTEQA2 for Windows Version 1.5 includes a number of capabilities that are not planned for use in CNWRA applications. The capabilities that will not be tested at this time are

- Ion Exchange
- Freundlich Isotherm
- Langmuir Isotherm
- Triple-Layer Model
- Constant Capacitance Model
- Composite Organic Liquid Model

If a decision is made to use these code capabilities, this software validation test plan will be modified as necessary.

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3 ENVIRONMENT

3.1 Software—Introduction

MINTEQA2 for Windows Version 1.5 (Allison Geoscience Consultants, Inc. and Hydrogeologic, Inc., released August 2003) is a geochemical equilibrium speciation code for Windows 95/98/2000/XP. It uses the same computational algorithms and thermodynamic database as the DOS version developed in FORTRAN 90 by EPA to model dilute aqueous systems. The original MINTEQ code (Felmy, et al., 1984) was developed at Pacific Northwest National Laboratory to combine the mathematical approach of the earlier MINEQL code (Westall, et al., 1976) with the extensive thermodynamic database of the U.S. Geological Survey code WATEQ3 (Ball, et al., 1981). The code was updated to MINTEQA2 Version 3.11/3.12 (Allison, et al., 1991), and a preprocessing routine called PRODEFA2 was added to help construct the formatted input files used by the code. The most recent DOS version is MINTEQA2 Version 4.02 (released December 1999). Since the original development, MINTEQA2 has become one of the more commonly used codes to simulate geochemical equilibria (e.g., Langmuir, 1997).

3.2 Code Description

The following description of MINTEQA2 is based on the source code and on the user's manuals for MINTEQA2 Version 3.0 (Allison, et al., 1991) and MINTEQA2 for Windows Version 1.5 (Allison Geoscience Consultants, Inc., 2003). The user's manual for MINTEQA2 for Windows Version 1.5 is provided with the software, and the manual for MINTEQA2 Version 4.02 can be downloaded from the EPA website (http://www.epa.gov/ceampubl/mmedia/minteq.htm).

3.2.1 Input

A MINTEQA2 for Windows Version 1.5 user typically has a problem relevant to a natural chemical system. This system is described in terms of its physiochemical conditions (e.g., temperature) and the concentrations of chemical components, species, solids, and gases that are present. MINTEQA2 for Windows Version 1.5 uses a main window to specify system variables and parameters, chemical total concentrations, and optional constraints or reactions. A formatted input file is generated to identify the components of interest, read the concentrations, construct the chemical equilibrium model, and solve for aqueous speciation and the distribution of species between the solid, gas, and liquid phases. This main window replaces the preprocessor PRODEFA2 that was developed and refined for DOS versions to help the user describe the geochemical problem and, through a series of menus, create the formatted input file necessary for a MINTEQA2 simulation.

3.2.2 Output

The aqueous and solid phase speciation and the distribution of species between the solid, gas, and liquid phases are performed by selecting the "Equilibrate" button from the main window. This button replaces the MINRUN.BAT command used in DOS versions. The results from the equilibrium geochemical speciation calculation are automatically displayed as a summary output within the main window and written to an output file. The detailed results can be viewed by selecting Full Output. The output can also be viewed at any time by selecting "View Output" from the main window. MINTEQA2 for Windows Version 1.5 will overwrite previously existing files with the same name. In all cases, the full output includes an echo of the input to verify that the input file was read correctly and a time stamp to verify the time of the run. Additional types of output include writing equilibrium mass distribution chemical component species (or aqueous species) to a tab-delimited text file that can be imported into commercial spreadsheets. The equilibrium concentration of the element(s) of interest is reported in molarity (moles contaminant/L H_2O) as distributed between the dissolved, sorbed, and precipitated phases.

3.2.3 Graphic Output

Results for the MINTEQA2 for Windows Version 1.5 runs involving a single equilibration point and multiple equilibration points in a sensitivity analysis can be viewed graphically. For a single equilibration point, the distribution of any component among its aqueous species or among phases can be displayed as a pie chart. For a sensitivity analysis, the following can be displayed as a function of the sensitivity parameter on an X-Y plot.

Dissolved Species Concentration
Components: Percent Dissolved

Components: Percent Sorbed
Components: Percent Precipitated
Species Saturation Indices
Ionic Strength
Charge Imbalance
System pH
System pE

The format of the graphs can be customized by the user and saved as a graphics file in any of a variety of commonly used formats.

3.3 Hardware Requirements and Installation

MINTEQA2 for Windows Version 1.5 is designed for the IBM personal computer (PC) family of microcomputers or compatible systems with a 486 or faster processor and at least 8 MB of memory. MINTEQA2 for Windows Version 1.5 runs on Microsoft Windows 95/98/2000/XP operating systems.

To install MINTEQA2 for Windows Version 1.5, insert the installation CD into the CD drive. The setup program will begin automatically if autorun is enabled on the computer. If setup does not begin automatically, select "Start" from the menu bar at the bottom of the desktop, then select "Run" on the Windows start menu and enter D:\setup (assuming D is the drive designation for the CD drive). After setup begins, follow the on-screen instructions.

4 ASSUMPTIONS AND CONSTRAINTS

The results from geochemical equilibrium speciation codes are dependent on the type and quality of the data used in the simulation. These are typically contained in databases that are searched and read by the code based on the input provided by the user. While these databases can be modified by the user to incorporate additional species or different thermodynamic data, they are considered separately from the input file that defines the geochemical problem and should not be modified in the context of running the simulation. MINTEQA2 for Windows Version 1.5 uses several databases to construct and execute a geochemical equilibrium model. All of these databases must be present in the working directory for the code to run. Thermodynamic data for component species and reaction species can be added or edited using the MINTEQA2 for Windows database editor that is provided with the program. The thermodynamic data are presented in a Microsoft® Excel spreadsheet for easy editing. Once changes are complete, the program automatically converts the modified databases to binary files used by MINTEQA2 for Windows Version 1.5.

Historically, the original MINTEQA2 databases have been modified to include extensive thermodynamic data for toxic elements such as Cd, Zn, Pb, As, Hg, and Cu, as well as organic ligands such as ethylenediaminetetraacetate (EDTA), citrate, and acetate. Additional modifications at CNWRA have included the addition of thermodynamic data (ΔH_r° and log K) for almost 600 aqueous species and solids involving 14 potentially important radioelements: U, Pu, Th, Np, Am, Sr, Cs, Ra, Sn, Zr, Tc, Ru, Eu, and Co (Turner, 1993; Turner, et al., 1993). Thermodynamic data for U, Pu, Np, Am, and Tc are from the Nuclear Energy Agency Thermodynamic Database Project (Grenthe, et al., 1992; Silva, et al., 1995; Rard, et al., 1999;

Lemire, et al., 2001). The source for other data is the EQ3/6 database (Release Gembochs.v2-eq8-data0.alt.r2, 02Aug95).

5 TEST CASES

Although geochemical equilibrium modeling can be performed using hand calculations (Richardson and McSween, 1989), the large number of chemical component species present in natural systems can make for extremely complex calculations. Validation of MINTEQA2 for the Windows Version 1.5 model results against hand calculations for simple systems can be accomplished to test basic code functions, but more rigorous testing of the code and its databases is needed.

One way to address the issue of complexity in code validation and build confidence in model results is to test MINTEQA2 for Windows Version 1.5 against results from the validated previous version of the MINTEQA2 Version 4.02 code (Turner, 2002). The results for MINTEQA2 for Windows Version 1.5 and MINTEQA2 Version 4.02 are expected to agree within a few percent. Any differences are likely due to minor changes in the thermodynamic databases.

The MINTEQA2 Version 4.02 code was validated against another geochemical speciation code, PHREEQC Version 2.4.2 (Parkhurst and Appelo, 1999). The approach followed is outlined in the test cases below. Simple worked problems from standard geochemistry textbooks (e.g., Richardson and McSween, 1989; Stumm and Morgan, 1996; Langmuir, 1997) and test problems in the user's manual for PHREEQC Version 2.4.2 were selected to test different geochemical processes (e.g., speciation and solubility calculations) and adapted to MINTEQA2 Version 4.02 input requirements. To test MINTEQA2 Version 4.02, the same intensive properties (temperature, pressure) were used, and all chemical reactions were written in terms of the appropriate component species for MINTEQA2 Version 4.02. Some differences in how PHREEQC Version 2.4.2 and MINTEQA2 Version 4.02 compute ionic strength corrections (extended Debye-Hückel versus Davies equation) led to differences in speciation that were examined and resolved as necessary (Turner, 2002). For simple systems of a few components, the same thermodynamic data {e.g., log K at 25 °C [77 °F]} were used to ensure consistency between calculational results. For more complicated systems involving seawater, the problems were run using the overall databases. Resulting differences were evaluated and resolved as necessary. It was demonstrated that MINTEQA2 Version 4.02 test results generally agreed with hand calculations and PHREEQC Version 2.4.2 calculations within a few percent. Differences between MINTEQA2 Version 4.02 and PHREEQC Version 2.4.2 calculations were attributed to differences in computational approach and minor differences in thermodynamic databases. These types of variations are commonly observed between geochemical speciation codes (Morrey, et al., 1986; Emren, et al., 1999). The differences did not appear to represent errors in the formulation of MINTEQA2 Version 4.02 (Turner, 2002).

5.1 Installation Check

The first validation test will be to ensure that the MINTEQA2 for Windows Version 1.5 software is installed correctly on the PC platform. Following instructions outlined in Section 3.2 of this test plan, MINTEQA2 for Windows Version 1.5 will be installed. Twelve example problems are included as part of MINTEQA2 Version 4.02. These problems were developed to demonstrate the different capabilities of MINTEQA2 Version 4.02. The geochemical parameters for these example problems will be submitted to MINTEQA2 for Windows Version 1.5 and the output will

be compared to the files provided in the MINTEQA2 Version 4.02 installation package. With the exception of the time and date stamp, these files should produce results identical to those provided by the MINTEQA2 Version 4.02 developers.

5.2 Aqueous Speciation

Parkhurst and Appelo (1999) provide an example to calculate the distribution of aqueous species in seawater and the saturation state of seawater relative to a set of minerals. To demonstrate how to expand the model to new elements, uranium is added to the aqueous model defined by the PHREEQC Version 2.4.2 database.

Output to be compared includes, but is not limited to

- Percent of different aqueous species such as CO_3^{-2} and $Ca(OH)_2$ (aq)
- Solubility indices [log (Ion Activity Product)—log K_{eq}] for minerals such as halite, calcite, and SiO_2

5.3 Mineral Solubility

Richardson and McSween (1989) present two worked problems to investigate the solubility of barite at 25 °C [77 °F] in pure water (Worked Problem 3-6) and in a 0.2 molal NaCl solution (Worked Problem 3-8). The results of the problems are expressed in terms of $m_{Ba^{++}}$.

Output to be compared includes, but is not limited to

- Molality of Ba^{++}
- Solubility indices [log (Ion Activity Product)—log K_{eq}] with respect to Ba^{++}

5.4 Gas Chemistry

Stumm and Morgan (1996) present several aqueous carbonate speciation problems. Included is Example 7.8, where calcite ($CaCO_3$) is equilibrated in sea water at 25 °C [77 °F], and open to atmosphere (fixed $P_{CO}^2 = 3.55 \times 10^{-4}$ atm). This problem can be used to test the gas chemistry subroutines of MINTEQA2 for Windows Version 1.5.

Output to be compared includes, but is not limited to

- Total carbonate species (e.g., HCO_3^-, CO_3^{-2})
- pH
- Alkalinity

5.5 Sorption—Surface Complexation Modeling

Parkhurst and Appelo (1999) provide an example to use PHREEQC Version 2.4.2 to calculate Zn^{++} sorption on ferrihydrite (HFO) using the diffuse-layer surface complexation model and parameters described in Dzombak and Morel (1990). Sorption at 25 °C [77 °F] is investigated for two Zn^{++} concentrations (10^{-4} and 10^{-7} molal), and the results are presented in terms of dissolved and sorbed Zn^{++} molality as a function of pH.

Output to be compared includes, but is not limited to

- Total dissolved Zn^{++} as a function of pH
- Total sorbed Zn^{++} as a function of pH

5.6 Redox Conditions

Stumm and Morgan (1996) present a number of relatively simple calculations to determine redox equilibrium. These include calculating electron activity (pe) for Fe and Mn systems open to atmosphere (Example 8.2) and equilibrium distribution in the SO_4^{2-}–HS^- system (Example 8.4). These calculations will provide a good check of redox equilibrium in MINTEQA2 for Windows Version 1.5, which uses pE as a master variable to control redox potential.

Output to be compared includes, but is not limited to

- Calculated equilibrium pE for the three solutions presented in Example 8.2 (Stumm and Morgan, 1996)
- Equilibrium distributions of sulfur compounds as a function of pE for the conditions presented in Example 8.4 (Stumm and Morgan, 1996)

5.7 Temperature Effects

Parkhurst and Appelo (1999) provide an example to use PHREEQC Version 2.4.2 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]. This example provides an opportunity to independently check the ability of MINTEQA2 for Windows Version 1.5 to both calculate solubility (see Section 6.3 of this test plan) and the correction of equilibrium for the effects of temperature. Only the pH and temperature are used to define a pure water solution. Gypsum and anhydrite are allowed to react to equilibrium (saturation index equal to 0.0), 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. Temperature is measured at 1° intervals from 25–75 °C [77–167 °F].

Both MINTEQA2 for Windows Version 1.5 and PHREEQC Version 2.4.2 use the Van't Hoff relationship and enthalpies of reaction ($\Delta H_r°$) to correct equilibrium constants for the effects of temperature. If the same thermodynamic data are used, both codes should produce the same results.

Output to be compared includes, but is not limited to

- Gypsum and anhydrite solubility as a function of temperature from 25–75 °C [77–67 °F]

5.8 Modified Database

The purpose for checking the main code function in this section of the test plan is to ensure that the MINTEQA2 for Windows Version 1.5 database that was modified to include Nuclear Energy Agency radionuclide thermodynamic data is correct and produces reasonable results. If thermodynamic data are the same, different geochemical equilibrium speciation codes should produce similar results. The most straightforward way to test this is to compare aqueous speciation results from several different codes. This approach has been used before (Turner, 1993; Turner, et al., 1993) to examine the modified MINTEQA2 Version 3.11/3.12 database.

Speciation checks for uranium and neptunium will be performed using results from MINTEQA2 for Windows Version 1.5 and PHREEQC Version 2.4.2. Identical thermodynamic data for neptunium and uranium will be used to examine speciation as a function of pH, both under CO_2-free and atmospheric CO_2 conditions. Temperature will be fixed at 25 °C [77 °F]. Low concentrations will be used to avoid the complications of precipitation of pure phases. The focus of the check is the CNWRA-modifications to the MINTEQA2 for Windows Version 1.5 database, and very simple solutions will be used to minimize the effects of major ions, (e.g., Ca^{2+} and Mg^{++}). Although both MINTEQA2 for Windows Version 1.5 and PHREEQC Version 2.4.2 are reported to use the WATEQ data compilations, small differences are likely to persist in thermodynamic data for many of the chemical component systems that are beyond the intended scope of this validation test plan.

Output to be compared includes, but is not limited to

- Percent of different uranium and neptunium aqueous species as a function of pH

6 TEST INPUTS

In all test cases, the test input files will be prepared using the MINTEQA2 for Windows Version 1.5 main project window. Chemical conditions in the input file, such as temperature, component concentration, and gas pressure, will be set at values consistent with the problems described in Section 5 of this software validation test plan. For simple test problem systems, identical thermodynamic data will be used to facilitate the comparison of results. For complex test problem systems such as those involving seawater, the problem will be run using the MINTEQA2 for Windows Version 1.5 and PHREEQC Version 2.4.2 thermodynamic databases. Differences will be evaluated and resolved as necessary.

7 TEST PROCEDURES

In all test cases, the formatted input file described in Section 6 will be equilibrated in MINTEQA2 for Windows Version 1.5. Results from MINTEQA2 for Windows Version 1.5 (i.e., the output file created by each run) will be evaluated as summarized in the following sections.

7.1 Installation Check

The input files test problems provided with the MINTEQA2 Version 4.02 installation package will be run using MINTEQA2 for Windows Version 1.5. The results of these batch runs will be compared to the output files provided with the MINTEQA2 Version 4.02 installation package.

7.2 Comparison With Hand Calculations

The test problems described in Sections 5.3 (Mineral Solubility) and 5.4 (Gas Chemistry) involve comparing MINTEQA2 for Windows Version 1.5 results against the results of hand calculations. The results, including component concentration and mineral saturation, will be compared in tabular form.

7.3 Comparison With PHREEQC Version 2.4.2 Simulations

For test problems involving comparison to PHREEQC Version 2.4.2 simulations, output from the two computer programs will be compared in several ways.

- Comparison of component concentrations—This will be done in tabular form for a limited suite of dominant aqueous species.

- Comparison of mineral saturation indices—This will be done in tabular form for a limited set of dominant minerals.

- Graphic comparison of aqueous speciation—This is an effective means of comparing model results for speciation and sorption as a function of independent variables, such as pH, pe, and P_{CO}^2.

It is anticipated that results from the two codes will agree within a few percent, although there may be differences due to disparities between the thermodynamic databases used in the code. Any differences resulting from these comparisons will be documented, evaluated, and resolved as necessary. It is important to remember that it is beyond the scope of this validation test plan to resolve all differences between the MINTEQA2 for Windows Version 1.5 and PHREEQC Version 2.4.2 thermodynamic databases.