Software Release Notice
Acquired Software

1. Software Name: PHREEQCI, Version 2.12.5
Software Version: Version 2.12.5

2. Software Function:
A computer program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations.

3. Summary of Actions:
❑ New Software X Update to Existing Software ❑ Software Retirement

4. Software Installation

4a. Computer Platform(s): PC/100Mhz or faster
4b. Operating System(s): Windows 95,98, NT 4.0, ME, 2000, or XP
4c. Programming Language(s): ANSI C

4d. Installation Testing:
X Passed Performed by: Lynn Sabido Testing Performed On: PC - Windows 2000
Description of Testing Performed:
Performed the 18 installation tests that are described in the Software Validation Report for PHREEQC, version 2.6.

4e. Archive Copy:
X Enclosed ❑ Not Available, Why:

Installation Performed by: Lynn Sabido	Date: 3/6/06

Remarks:

5. Software Assessment

Validation Status:
❑ Full Validation X Limited Validation Date of Validation: 3/6/06
❑ Not Validated, Explain: Regression testing from v. 2.6, Attached scr.

Software User: F. Paul Bertetti, Miriam R. Juckett, Jude McMurry, James Myers, Lynn Sabido, David R. Turner	Date: 3/6/06

Remarks: Software change report done rather than a full validation

6. Approval

Manager: P. C. [signature]	Date: 3/21/2006

Remarks:

7. QA Verification

SRN Number: 382

Verified by: [signature]	Date: 3/29/06

Remarks:

SOFTWARE CHANGE REPORT (SCR)

1. SCR No. (*Software Developer Assigns*):	2. Software Title and Version: PHREEQCI, Version 2.12.5	3. Project No: 20.06002.01.212
4. Affected Software Module(s), Description of Problem(s): New Software version: Update from Phreeqcl, Version 2.8 to Version 2.12.5		
5. Change Requested by: James Myers Date: 3/6/06	6. Change Authorized by (*Software Developer*): James Myers Date: 3/6/06	
7. Description of Change(s) or Problem Resolution (*If changes not implemented, please justify*): Bugs from previous versions fixed, and a few new keywords have been added. See attached list for a full description of changes.		
8. Implemented by: Lynn Sabido	Date: 3/6/06	

9. Description of Acceptance Tests:
Regression testing was completed by running Installation tests and Validation tests from the last Validation (Phreeqc v. 2.6) using Phreeqcl 2.12.5. The Result files were compared for discrepancies. Files with no unexplainable discrepancies are considered successful tests. The comparison files for old and new results are contained in the attached cd.

Acceptable Discrepancies in the files consisted of the following types:

1)Changes in the Ion Activity Product and Log KT values. While these values may have changed the Saturation Index (SI) remains the same (ex1_compare). The difference are due to the *following code changes: Saturation index phases that included water had wrong value if* distribution of species, exchange, or surface not written also. Changed saturation index print out to use reaction and log K defined in PHASES definition. Previously, reaction could be rewritten to predominant redox species.

2)Small, yet insignificant changes in value as a result of rounding differences, e.g. 5.907 changed to 5.898. Some files contained differences of this type, possibly a result of different operating system. A multiple precision version of routine cl1, cl1mp, has been included in version 2.12 for inverse modeling were calculations are carried out to about 30 significant digits, which would produce rounding differences. (Example np-phrq2-new-2.6dat-compare)

3)Changes in format such as spaces, tabs, minor text differences, etc. which do not impact the final data are considered insignificant. (stumm96-new-2.6dat-compare)

4)Changes in values such as iteration numbers, electrical balances, etc. which do not impact the final data are considered insignificant. (Seawater_new_2.6dat_compare)

10. Tested by: Lynn Sabido	Date: 3/6/06

STATUS OF PHREEQC PROGRAMS
November 16, 2005--Phreeqcl, PHAST, PHREEQC

Updates for Batch versions of PHREEQC version 2.9, version 2.10, and version 2.11 are included because they were incorporated into PHREEQC version 2.12, which was then incorporated into PHREEQCI version 2.12.

November 16, 2005: Phreeqcl, PHAST, PHREEQC re-released

All PHREEQC and PHAST programs were rebuilt for distribution. Several bugs and installation errors have been fixed over the last month. All programs are now at subversion level 669.

October 11, 2005: Phreeqcl Version 2.12-590, Bug Fix

Phreeqcl version 2.12-590 fixes an incorrect message about which solver is used for INVERSE_MODELING.

October 10, 2005: Phreeqcl Version 2.12-587, Bug Fix

Phreeqcl Version 2.12-577 and 581 contained did not include the multiprecision option for inverse modeling. Phreeqcl version 2.12-587 includes the inverse modeling multiprecision capability and the INVERSE_MODELING screen (first tab) allows invoking the option and setting the parameters.

October 5, 2005: Phreeqcl Version 2.12-581, Bug Fix

Phreeqcl Version 2.12-577 contained an error in the Pitzer calculations. The first time a file was run after opening Phreeqcl, results were correct. Calculations in subsequent file runs were incorrect, because of incorrect re-initialization of Chebyschev parameters related to temperature. The batch versions of PHREEQC are unaffected by the problem. The bug is fixed in Phreeqcl version 2.12-581.

September 28, 2005: Phreeqcl Version 2.12 Released

Phreeqcl Version 2.12 contains the batch version of **PHREEQC, version 2.12**. This version of Phreeqcl fixes a bug related to long lines in SOLUTION_SPREAD.

September 28, 2005: PHREEQC Version 2.12 Released

PHREEQC version 2.12 has been released, including batch versions for Windows and Linux. SunOS versions are no longer distributed, but there should be no problem compiling a batch version of PHREEQC on any Unix operating system.

Version 2.12 includes an implementation of the Pitzer specific-interaction activity coefficient formulation. To use the Pitzer activity coefficients, use the "pitzer.dat" database. All PHREEQC capabilities are available with the Pitzer activity coefficients except the explicit diffuse layer calculation (rarely used). A new keyword PITZER has been added, which is used to define the Pitzer interaction parameters (B0, B1, B2, C0, theta, lambda, zeta, and psi). The only other option in the PITZER data block is -MacInnes T/F, which uses the MacInnis assumption [gamma(Cl-) = gamma(K+)] to scale the individual ion activity coefficients or leaves the individual ion activity coefficients unscaled. The PHREEQC implementation of the Pitzer

approach is based largely on the program PHRQPITZ (Plummer, L.N., Parkhurst, D.L., Fleming, G.W., and Dunkle, S.A., 1988, A Computer Program Incorporating Pitzer's Equations for Calculation of Geochemical Reactions in Brines: U.S. Geological Survey Water-Resources Investigations Report 88-4153).

A multiple precision version of routine cl1, cl1mp, has been included in version 2.12 for inverse modeling. Cl1mp uses the Gnu Multiple Precision package (gmp). #Define statements are used to include or exclude this routine when compiling. PHREEQC. By using cl1mp, calculations are carried out to about 30 significant digits. Cl1mp may help in some inverse modeling calculations where roundoff errors are a problem, but it is still possible that roundoff errors will cause cl1mp to fail to find a solution to an optimization problem.

Other modifications and bug fixes for version 2.12 are detailed in the file RELEASE.TXT, which is included in all distributions.

February 7, 2005: Phreeqcl Version 2.11 Released

PhreeqcI Version 2.11-148 contains the batch version of PHREEQC, version 2.11-136. This version of PhreeqcI has the bug fixes related to **PHREEQC version 2.11**.

February 7, 2005: PHREEQC Version 2.11 Released

PHREEQC version 2.11 has been released, including batch versions for Windows, Linux, and SunOS.

A new database, minteq.v4.dat has been translated from version 4.02 of MINTEQA2. An older version of the MINTEQA2 database is retained in file minteq.dat.

We started using Subversion for our version control system. The number included in distribution files (for example, "136" in phreeqc-2.11-136.Linux.tar.gz) is the Subversion revision number corresponding to the set of files used to build the current version. Subversion revision numbers change whenever any repository file is changed, so the number uniquely defines all files used in the current version.

Modifications include:

(1)Fixed error in selected output file with mixing reaction. MIX number was written to two columns, should be one.

(2) Fixed memory leak with PAD function.

(3) Modified and rewrote make files for compilation and distribution.

(4) Fixed bug with PRINT; -warnings n. Use of this option generally eliminated all warning messages instead of all messages after the nth. Default number of warning messages printed in now 100 per simulation.

(5) Fixed memory leaks in cvode. These leaks caused phreeqci to crash. New distribution of PhreeqcI is imminent. Now uses PHRQ_malloc in cvode in case of other memory leaks. Also fixed potential memory error with PAD malloc.

(6) Saturation index phases that included water had wrong value if distribution of species, exchange, or surface not written also.

(7) Fixed error message in cvode, if max iterations exceeded the error caused a segmentation fault.

(8) Made printing of parameter combination message a warning message so that it could be turned off.

November 2, 2004: PHREEQC version 2.10 Released

PHREEQC version 2.10 has been released, including batch versions for Windows, Linux, and SunOS, and the graphical user interface PhreeqcI. All features of PHREEQC version 2.10,

except those related to isotopes (keywords ***ISOTOPES*** , ***NAMED_EXPRESSIONS*** , ***ISOTOPE_ALPHAS*** , ***ISOTOPE_RATIOS*** , ***ISOTOPE_ALPHAS*** , and ***CALCULATE_VALUES***). PHREEQC version 2.10 contains only minor bug fixes relative to version 2.9.

Changes in version 2.10 include (1) Rearranged i/o for PHREEQC and reorganized driver subroutine. The object of these changes is to make the program more functional as a module for other programs (PHAST) and eventually to produce a callable C and Fortran module. (2) Fixed a problem with surface related to a phase, when phase was not part of system (for example, Fe(OH)3a when there is no iron in system. (3) Added convergence parameter set that requires mineral transfers to produce positive concentrations in the event that negative concentrations have been produced in the prior Newton-Raphson iteration. (4) Fixed bug with kinetics formulas; did not account for stoichiometric coefficient correctly when using phase names. Generalized to allow multiple phase names in the -formula definition.

September 20, 2004: Batch versions of PHREEQC version 2.9 Released

PHREEQC version 2.9 released, including batch versions for Windows, Linux, SunOS, and Mac. PhreeqcI and Phreeqc For Windows have not yet been updated to version 2.9.

New features include:

New keyword ***COPY*** that can be used with any reactant that is identified with an index number (***SOLUTION*** , ***EQUILIBRIUM_PHASES*** , ***EXCHANGE*** , ***GAS_PHASE*** , ***KINETICS*** , ***MIX*** , ***REACTION*** , ***REACTION_TEMPERATURE*** , ***SOLID_SOLUTION*** , ***SURFACE)*** .

Added new Basic functions

b$ = PAD(a$, 20) pads a$ to a total of 20 characters;

i = INSTR(a$, b$) sets i to the character position of string b$ in a$;

b$ = LTRIM(a$) trims white space from beginning of string a$ and stores result in b$;

b$ = RTRIM(a$) trims white space from end of string a$ and stores result in b$;

b$ = TRIM(a$) trims white space from beginning and end of string a$ and stores result in b$.;

Added new Basic function SYS that calculates the to total amount of an element in all phases (solution, equilibrium_phases, surfaces, exchangers, solid solutions, and gas phase). KINETIC reactions are not included. The function has two forms: (1) one element name as an argument (variable names are user specified)

10 tot = SYS("As") the function will return the total arsenic in the system.

(2) 5 arguments

10 tot = SYS("As", count_species, names$, types$, moles) will return the total arsenic in the system to tot; count_species--the number of species that contain arsenic, including solution, equilibrium_phases, surfaces, exchangers, solid solutions, and gas phase species; names$--a character array that has the name of each species; type$--a character array that specifies the type of phase for the species, aq, equi, surf, ex, s_s, gas, diff. Diff refers to the amount of the element in the diffuse layer of a surface when the explicit diffuse layer calculation is used; moles--an array containing the number of moles of the element in the species. The sum of moles(i) is equal to tot. SYS has several special arguments for the form SYS("arg", count, names$, types$, values). Arg is one of the options listed below; count is a single numeric value and is the number of elements in the following arrays; name$ is an array of string values; type$ is an array of string values; values is an array of numeric values. Values of arg: elt_name returns total number of moles of element in system, count is the number of species for the element in the system, including aqueous, exchange, surface, equilibrium_phase, solid solution component, and gas phase "species", arrays are filled for each "species"; values are moles; "elements" returns total number of moles of dissolved elements other than H and O; count is number of elements, valence states, exchangers, and surfaces, arrays are filled for each element and valence state, type is "dis"; exchanger, type is "ex", and surface, type is "surf". Values are moles; "phases" returns saturation

indices of all phases; count is number of phases in system, arrays are filled for each phase, values are saturation indices; "aq" returns sum of moles of all aqueous species, count is number of aqueous species in system, arrays are filled with each aqueous species, values are moles; "ex" returns sum of moles of all exchange species, count is number of exchange species in system, arrays are filled with each exchange species, values are moles; "surf" returns sum of moles of all surface species, count is number of surface species in system, arrays are filled with each surface species, values are moles; "s_s" returns sum of moles of all solid solution components, count is number of solid solution components in system, arrays are filled with each solid solution component, values are moles; "gas" returns sum of moles of all gas components, count is number of gas components in system, arrays are filled with each gas component, values are moles.

Added new Basic function, DESCRIPTION, that has the value defined for the description field of the ***SOLUTION*** keyword line.

Added alternative ordinary differential equation solver called CVODE, a set of C routines from the Lawrence Livermore National Labs. CVODE is part of the SUNDIALS package. CVODE is used in place of the Runge Kutta method when " ***-cvode true*** " is used within a ***KINETICS*** data block.

Bug fixes include:

In inverse modeling, program terminates if sum of initial solutions and phases is > 32.

Fixed bug with isotopes. Log activity estimate after initial solution calculation was inf under some conditions. An initial surface calculation failed when using D.

Changed saturation index print out to use reaction and log K defined in ***PHASES*** definition. Previously, reaction could be rewritten to predominant redox species.

Fixed incorrect print of elapsed time for kinetics in advection.

Added phrqproto.h prototype file and phrqtype.h for switching compilation to long double.

Fixed incorrect printout of kinetics delta moles with advection.

Added convergence parameter set that skips mineral equations for first 5 iterations.

Added entity_exists for module.

Fixed bug with mix index incorrect (-2) for mixing with kinetics.

Fixed error in ***SOLUTION_SPREAD*** , defining -redox did not set the default redox for the solutions that were defined; pe was always used as default.

Modified code to allocate space differently for PHAST: pp_assemblage, exchange, surface, gas_phase, kinetics, and s_s_assemblage. Enough space is allocated,at beginning of distribute_initial_conditions. Speeds up phast initialization and makes better use of available memory.

Changed gfw of water to 18 if isotopes of water are included. Solvent is [1H]2[16O].

Fixed a bug in surface integration where order of ions in the list of g's was incorrect.

Pyrite rate was not 0 if supersaturated in *phreeqc.dat* and *wateq4f.dat* .

Segmentation error if a surface species was not defined with an equation that contained another surface species. In this case, the surface master species had been redefined to be an aqueous species (***SOLUTION_SPECIES***).

April 15, 2003: PHREEQC 2.8 and Phreeqcl 2.8 Released