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AREST-CT V1.0 SOFTWARE VERIFICATION

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SUMMARY

The Analyzer for Radionuclide Source-Term with Chemical Transport (AREST-CT) is a scientific computer code designed for performance assessments of engineered barrier system (EBS) concepts for the underground storage of nuclear waste, including high-level, intermediate, and low-level wastes. The AREST-CT code has features for analyzing the degradation of and release of radionuclides from the waste form, chemical reactions that depend on time and space, and transport of the waste and other products through the EBS. This document provides a description of the verification testing that has been performed on the initial version of AREST-CT (V1.0). Software verification is the process of confirming that the models and algorithms have been correctly implemented into a computer code. Software verification for V1.0 consisted of testing the individual modules (unit tests) and a test of the fully-coupled model (integration testing). The integration test was done by comparing the results from AREST-CT with the results from the reactive transport code CIRF.A. The test problem consisted of a 1-D analysis of the release, transport, and precipitation of ^{99}Tc in an idealized LLW disposal system. All verification tests showed that AREST-CT works properly and in accordance with design specifications.

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1.0 INTRODUCTION

The Tri-Party agreement (TPA) between the State of Washington Department of Ecology, the U.S. Department of Energy (DOE), and the U.S. Environmental Protection Agency (EPA), specifies vitrification as the encapsulation technology for Hanford low-level wastes (LLW). By DOE Order 5820.2A, before any LLW can be disposed of, a performance assessment covering the disposal facility must be approved by DOE headquarters. The performance assessment is to provide "reasonable assurance" that the disposal activities will not adversely impact long-term human health and safety.

The Hanford Low-Level Waste Performance Assessment Group currently plans to publish an interim performance assessment for the disposal facility in December 1996, followed by a preliminary performance assessment due in June 1998, and a final performance assessment in July 1999. The interim performance assessment will be based on as much site-specific and materials-specific data as possible, to demonstrate a high likelihood that the final performance assessment will be approved, and therefore, support a decision to begin construction of vitrification facilities.

Performance assessments for the disposal of Hanford LLW will require calculating radiation dose to a future population as a result of any release and transport of radionuclides to the unconfined aquifer located approximately 70 m below the disposal facility. The processes controlling release and transport of radionuclides to the unconfined aquifer will be simulated by computer models. A review of currently available computer codes was recently completed (McGrail and Mahoney 1995), where the codes were ranked in terms of the feature sets that match a set of physical, chemical, numerical, and functional capabilities needed to assess radionuclide release rates from a LLW engineered-system. The needed capabilities were identified from an analysis of the important physical and chemical processes expected to affect LLW glass corrosion and the mobility of radionuclides. The highest ranked computer code was found to be the Analyzer of Radionuclide Source-Term with Chemical Transport (AREST-CT) code, developed at PNL for the U.S. Department of Energy for evaluation of arid land disposal sites.

Computer codes selected for performance assessment calculations must undergo software verification and validation testing. Software validation, or more appropriately confirmation (Oresek, Frechette, and Belitz 1994), is the process of demonstrating that the mathematical models or constitutive equations embodied in a computer code are consistent with observational data. Thus, validation is the process of demonstrating that a computer code reasonably represents the actual processes in a system. The validation/confirmation tests planned for the AREST-CT code primarily involve long-duration, unsaturated, flow-through tests in columns packed with low-level waste (LLW) glass, engineered barrier materials, and/or Hanford soils. Results from the confirmation testing of the AREST-CT code will be described in a future document. The subject of this document is software verification, which is the process of testing the mathematical components of a computer code to "verify" that they have been correctly implemented. This document was developed to satisfy quality assurance program requirements of the Pacific Northwest Laboratory (PNL).^(a)

^(a)Pacific Northwest Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-RLO 1830.

2.0 MODEL DESCRIPTION

The AREST-CT code is a scientific computer software system developed at PNL to analyze the engineered barrier system (EBS) of a subsurface disposal site for the storage of nuclear waste. A brief overview of the model is given here. The interested reader should contact the authors to obtain more detailed documentation of the design^(a) or models^(b) used in the AREST-CT code.

Figure 1 is a schematic illustration of a multi-barrier, engineered-system concept for Hanford LLW. The engineered-system is assumed to begin with the water chemistry conditioner and end at the chemical retardation barrier. No specific materials have been selected for any of the engineered components depicted in Figure 1, and some of these components may not be included

Figure 1. Engineered-System Concept for Hanford LLW

^(a) Engel, D.W., B.P. McGrail, J.A. Fort, K.S. Lessor, R.E. Williford, and M.K. Altenhofen. 1995. *Software Design Description for the AREST-CT Code Development*. In Press, Pacific Northwest Laboratory, Richland, Washington.

^(b) Engel, D.W., B.P. McGrail, D.M. Elwood, W.J. Gray, R.E. Einziger, R.E. Williford, W.E. Nichols, and M.K. Altenhofen. 1995. *Mathematical Document for the AREST-CT Code Development*. In Press, Pacific Northwest Laboratory, Richland, Washington.

in the final design of the disposal facility. However, the function of AREST-CT is to calculate the total mass flux of radionuclides exiting the vault (or retardation barrier if it exists in the final design) as a function of time. To accomplish this, a coupled set of equations is solved that describes radionuclide release from the waste form and mass transport constrained by chemical reactions. The fundamental equation system to be solved is given by

$$\frac{\partial \phi \rho_l \theta_l c_\alpha}{\partial t} = -\nabla \cdot \mathbf{q}_\alpha + \sum_{k=1}^{N_r} v_{\alpha k} W_k, \quad \alpha = 1, 2, \dots, N_{aq} \quad (1)$$

where ϕ = porosity
 θ_l = volumetric water content,
 ρ_l = fluid density, kg/m³
 c_α = concentration of species α , mole/kg
 $\mathbf{q}_\alpha$ = total flux of component α , mole/m²·s
 t = time, s
 $v_{\alpha k}$ = stoichiometric coefficient of species α in reaction k
 W_k = reaction rate of k th reaction (mole/m³·sec)
 N_r = number of reactions, including aqueous equilibrium reactions, solid dissolution/precipitation reactions, kinetic controlled aqueous reactions and decay reactions
 N_{aq} = number of aqueous species.

If it is assumed that the phenomenon of hydrodynamic dispersion can be represented by a Fickian type law, then the total flux due to advection, dispersion, and diffusion is given by

$$\mathbf{q}_\alpha = \phi \rho_l \theta_l (c_\alpha \mathbf{V} - \mathbf{D}_\alpha(\theta_l) \cdot \nabla c_\alpha). \quad (2)$$

where $\mathbf{D}_l$ = hydrodynamic dispersion tensor, m²/s
 $\mathbf{V}$ = fluid velocity vector, m/s.

Substituting Equation (2) into Equation (1), one arrives at

$$\frac{\partial \phi \rho_l \theta_l c_\alpha}{\partial t} = -\nabla \cdot (\phi \rho_l \theta_l (c_\alpha \mathbf{V} - \mathbf{D}_\alpha(\theta_l) \cdot \nabla c_\alpha)) + \sum_{k=1}^{N_r} v_{\alpha k} W_k, \quad \alpha = 1, 2, \dots, N_{aq} \quad (3)$$

which is commonly known as the reaction-transport equation. The solution to the system of equations (3) is the core function of the AREST-CT code. A brief overview of the solution method implemented in this version of AREST-CT is given in the next section.

2.1 SOLUTION METHOD

The reactive transport equation system (3) is solved in the AREST-CT code using the method of finite-differences on an arbitrary 1-D or orthogonal 2-D grid. The solution method proceeds by solving the discretized reaction-transport equations at each grid point and each time-step. A solute concentration vector, $\vec{c}$ (mol/kg), is returned that contains the concentration of each aqueous species at that point and time step. This solution method will be referred to as a Type II point-solver.

Using a technique similar to that described by Friedly and Rubin (1992), a series of transformations are applied to Equation (3) to eliminate terms associated with equilibrium chemical reactions. The details of the transformation will not be discussed here but the result is that three equation sets are obtained that correspond to equilibrium reactions, non-reactive transformed species, and reactive transformed species, respectively. The transformed species, both reactive and non-reactive, are linear combinations of chemical species.

The discretized reaction-transport equations are a set of non-linear equations of the form:

$$\vec{F}(\vec{c}) = 0 \quad (4)$$

where

$$\vec{F} = \{F_1, F_2, \dots, F_{N_{aq}}\}^T \quad (5)$$

and

$$\vec{c} = \{c_1, c_2, \dots, c_{N_{aq}}\}^T. \quad (6)$$

To handle the large range of $\vec{c}$ in geochemical problems, the above set of equations is usually written as functions of $\vec{x}$, instead of $\vec{c}$, where

$$\vec{x} = \{x_1, x_2, \dots, x_{N_{aq}}\}^T = \{\ln c_1, \ln c_2, \dots, \ln c_{N_{aq}}\}^T. \quad (7)$$

Thus, Equation (4) reads as:

$$\vec{F} = \vec{F}(\vec{x}) = 0. \quad (8)$$

As mentioned above, Equation (8), which is the discretized form of Equation (3), also consists of three sets of equations. For the N_f equilibrium reactions, applying the law of mass action yields

$$F_k = \sum_{i=1}^{N_{aq}} v_{ij} (\ln \gamma_i + \ln c_i) - \ln K_j^{eq} = 0, \quad k = j, j = 1, 2, \dots, N_f \quad (9)$$

where v_{ij} = stoichiometric coefficient of species i in equilibrium reaction j
 γ_i = activity coefficient of species i
 K_j^{eq} = equilibrium constant of reaction j .

For N_b non-reactive species, we have a set of linear equations

$$F_k = \sum_{i=1}^{N_{aq}} b_{ij} c_i - B_j = 0, \quad k = N_f + j, j = 1, 2, \dots, N_b \quad (10)$$

where b_{ij} is the transformation coefficient of species i in the non-reactive linear transformation, and B_j is the transformed concentration of non-reactive species j . For N_a reactive species, we have the following set of non-linear equations

$$F_k = \sum_{i=1}^{N_{aq}} a_{ij} [p_{1i} c_i + p_{2i} - \Delta t \sum_{l=1}^{N_{fk}} v_{il1}^{fk} W_{l1}^{fk} - \Delta t \sum_{l=2}^{N_{fd}} v_{il2}^{fd} W_{l2}^{fd} - \Delta t \sum_{l=3}^{N_{sr}} v_{il3}^{sr} W_{l3}^{sr} - \Delta t \sum_{l=4}^{N_{sd}} v_{il4}^{sd} W_{l4}^{sd}] = 0, \quad (11)$$

$$k = N_f + N_b + j, j = 1, 2, \dots, N_a$$

where a_{ij} = transformation coefficient of species i for the reactive species j
 p_{1i} = coefficient describing transport properties at the previous time step for species i
 p_{2i} = coefficient describing concentration properties at the previous time step
 v_{il1}^{fk} = stoichiometric coefficient of species i in the kinetically-controlled reaction $l1$
 v_{il2}^{fd} = stoichiometric coefficient of species i in aqueous species decay reaction $l2$
 v_{il3}^{sr} = stoichiometric coefficient of species i in dissolution/precipitation reaction $l3$
 v_{il4}^{sd} = stoichiometric coefficient of species i in solid species decay reaction $l4$.

The terms W_{l1}^{fk} , W_{l2}^{fd} , W_{l3}^{sr} , and W_{l4}^{sd} are the rates of the kinetically-controlled reaction $l1$, aqueous species radioactive decay reaction $l2$, solid dissolution/precipitation reaction $l3$, and solid species radioactive decay reaction $l4$, respectively. Equations (9) thru (11) are the fundamental equation sets solved by the AREST-CT code. The Newton-Raphson iteration method is used to solve this highly nonlinear equation system.

In AREST-CT, activity coefficients (γ_i) are computed using the B-dot formulation as is used in the EQ3/6 code (Wolery 1992). The four different types of aqueous species allowed are 1) charged species, 2) water, 3) neutral polar species, and 4) neutral non-polar species. The equations used to calculate the activity coefficients of the four types are:

1) For charged species:

$$\ln \gamma_i = \ln(10.0) \cdot \left\{ B^* I - \frac{Z_i^2 A I^{1/2}}{1 + a_i \dot{B} I^{1/2}} \right\} \quad (12)$$

where the ionic strength, I , is given by

$$I = \frac{1}{2} \sum_{i=1}^{N_{aq}} Z_i^2 c_i = \frac{1}{2} \sum_{i=1}^{N_{aq}} Z_i^2 e^{x_i} \quad (13)$$

where a_i is the closest distance (radius) of species i ; A , B^* , $\dot{B}$ are three parameters as functions of temperature, and Z_i is the charge of species i .

2) For water:

$$\ln \gamma_w = - \frac{\sum_{i \neq w} c_i}{\Omega} + \frac{\ln(10)}{\Omega} \cdot \left[\frac{2}{3} A I^{3/2} \sigma(a_w B I^{1/2}) - B I^2 \right] - \ln \lambda_w \quad (14)$$

where $\Omega = 1000.0/M_{\text{water}}$, (M_{water} is the molecular weight of water), λ_w is the mole fraction of water in the solution, $a_w = 4.0$ (Å), and

$$\sigma(x) = \frac{3}{x^3} \left[1 + x - \frac{1}{1+x} - 2 \ln(1+x) \right]. \quad (15)$$

3) For non-polar neutral species:

$$\ln \gamma_i = (C + FT + \frac{G}{T})I - (E + HT) \left(\frac{I}{I+1} \right) \quad (16)$$

where, T is the temperature (K), and $C = -1.0312$, $F = 0.0012806$, $G = 255.9$, $E = 0.4445$, $H = -0.001606$.

4) For polar neutral species:

$$\ln \gamma_i = 0. \quad (17)$$

This concludes the discussion of the AREST-CT model. The verification tests that were performed on the computerized implementation of this model are discussed in the next section.

3.0 VERIFICATION TESTING

This section discusses the specific confirmation tests performed to verify that the reactive transport modules in AREST-CT were correctly implemented, along with a description of the evaluation method and acceptance criteria. The actual test case results and input data are given in the appendices. This format was intentionally adopted so that revisions to this document can be easily made as new versions of the code are developed. All testing for AREST-CT V1.0 was performed on a Sun[™] SparcStation 10/20, running SunOs 4.1.1.

3.1 UNIT TESTING

Unit testing consists of evaluating individual code modules against hand calculations, analytical solutions, or other numerical codes to verify that the algorithms implemented in the module correctly solve the governing equations. The AREST-CT code consists of the 8 modules shown in Table 1. Each module was unit tested separately before being implemented into AREST-CT. The results are described below.

Table 1. AREST-CT Modules for Unit Testing

<u>Module Name</u>	<u>Function</u>
TRANSP	Transport
READIN	input data structure
QRDCMP	Q-R decomposition
EQCONST	equilibrium constant calculation
RCONST	rate constant calculation
DHACTV	activity coefficient correction
EQPT	point solver I (boundary condition setup)
RTPT	point solver II (coupled reaction with transport)

3.1.1 TRANSP

The transport module uses an upwinding scheme, with the Crank-Nicolson algorithm to achieve second-order truncation error in space and time. Five test cases have been analyzed and compared to analytical solutions. The input data are given in Appendix A, Tables A.1 thru A.8, and the results of the analyses are shown in Figures A.1 thru A.8. The results from each test case are briefly described as follows:

- 1) 1-D pure diffusion. The input data to analyze a one-dimensional diffusive transport case is listed in Table A.1. The resulting concentrations as a function of time and distance were plotted against an analytical solution (Haberman 1987) and are shown in Figure A.1. The numerical solution and analytical results compare to within the acceptable relative error for the plotted time steps.
- 2) 1-D pure convection. The input data to analyze the one-dimensional convective dominated case is shown in Table A.2. The numerical results are compared to results from an analytical solution in Figure A.2. Qualitatively, the results are similar, i.e., peaks are at the same location in space. However, the magnitude and sharpness of the moving front is not captured accurately with the numerical solution. This is a consequence of numerical dispersion inherent with any upwind finite-difference scheme used to solve a hyperbolic partial differential equation. Resolution of the numerical solution can be increased by increasing the number of grid nodes and increasing the number of time steps, although neither of these solutions is practicable for large, 2-D problems. Higher-order transport schemes are available that provide better front-tracking. However, these schemes typically use a flux limiter to ensure that the solution to the PDE is total variation diminishing (TVD) throughout the spatial domain. The method works very well for pure transport problems but we have not implemented these schemes in V1.0 of AREST-CT because chemical reactions tend to dominate the shape and position of any moving front, and so can increase the total variation of the solution, independent of transport. As a result, reactive chemical transport problems can become nonconvergent when using a standard TVD flux-limiter algorithm. A modified TVD scheme is under development for use in reactive transport problems.
- 3) 1-D diffusion + convection. The input data to analyze the one-dimensional diffusive plus convective transport case is shown in Table A.3. The results of this analysis are shown in Figure A.3. The numerical results were compared to results from an analytical solution (Sauty 1980). The numerical and analytical results compare quite well for this problem. As in the previous case, the numerical model could be refined by increasing the number of grid nodes and time steps.
- 4) 2-D diffusion + convection with uniform X-direction flow ($V_x > 0$ and $V_y = 0.0$). The input data to analyze the two-dimensional diffusion plus convection case with uniform flow in the X-direction is shown in Table A.4. For this case, the flow in the X-direction is in the positive direction; the flow is zero in the Y-direction. The results of this analysis, compared to an analytical solution (Fried 1975) are shown in Figure A.4. Essentially, the test case is a point source problem. Because of the singularity at the point source, it is difficult to obtain an

accurate value of the analytical solution and numerical solution near the point source. However, qualitatively, the results are similar as the peaks are located at the same point and the peak height increases with increasing time.

- 5) 2-D diffusion + convection with different uniform flow directions. Four cases were analyzed to look at the transport given a flow in one direction, (a) $V_x > 0$ & $V_y = 0.0$; (b) $V_x < 0$ & $V_y = 0.0$; (c) $V_x = 0.0$ & $V_y > 0$; and (d) $V_x = 0.0$ & $V_y < 0$. The input data for these four test cases are listed in Tables A.5 thru A.8. The results of the analyses are shown in Figures A.5 thru A.8. The results of the test cases show the same behavior for flow in all four directions. Thus, the results verify that the correct solution is obtained for all flow directions.

3.1.2 READIN

The input structure was tested by comparing the input file (listed in Appendix B, Table B.1) against an output file that contains most of the input information (also listed in Appendix B, Table B.2). Several simple operations are carried out by the input module and are listed below (these calculations have been compared against hand calculations):

- 1) eliminate zero stoichiometric coefficients of aqueous species in reactions, including fast reactions, solid reactions, fluid-species radioactive decay, and solid-species radioactive decay
- 2) calculate molecular weights for each aqueous and solid specie according to its formula weight
- 3) calculate porosity of each lithology unit according to volume fractions of each solid species
- 4) calculate number densities of solid species in each lithology unit. A negative radius of the solid species is an indication (flag) that the initial volume fraction of the species is actually zero, and that the input volume fraction and the absolute value of the radius should be used to calculate the number density of the species. The result is actually the number of nucleation sites.

3.1.3 QRDCMP

The Q-R decomposition module, which is used to determine the linear transformation performed on Equation (3), was tested by comparing the results from AREST-CT to results calculated externally. The CIRF.A reaction model (Chen et al. 1995) was used for this test.

The input file for AREST-CT is shown in Appendix C, Table C.1. The same input values were input into CIRF.A for the comparison. The general reaction matrix, qrxntot, is listed in Table C.2 and C.3. Several criteria were used to judge if the Q-R decomposition was correctly implemented into AREST-CT:

- 1) The square of each A-vector should be 1.0
- 2) The dimensions of [A x qrxntot] are naxvct by nrxt
- 3) The first nfrxn (number of equilibrium reactions) columns of [A x qrxntot] should be zero or very close to zero and the matrix should have the property of upper triangular.

The output file containing the general reaction matrix [qrxntot], the A-vector [avector], and [A x qrxntot] are also shown in Appendix C, Table C.2. These results compare favorably with the results from CIRF.A for qavector and [A x qrxntot] shown in Table C.3.

3.1.4 EQCONST, RCONST, DHACTV

This section combines the testing of the respective modules for calculation of 1) equilibrium constant as a function of temperature for each reaction, 2) rate constant of kinetic reactions as a function of temperature, and 3) activity coefficients using the B-DOT equation.

The input file for the analysis is shown in Appendix D, Table D.1. The results of this analysis are shown in Table D.2. In the input file, equilibrium constants are expressed as zeroth to fourth order polynomial functions of temperature. The thermodynamic data are from the EQ3/6 (Wolery 1992) database (Table D.3), which were fit as polynomial functions of temperature using *Mathematica*[™]. Calculated values (Table D.2) were compared against the original data from EQ3/6 and the results compare well to four significant digits.

Rate constants (k) are calculated internally in AREST-CT using $k = k_o e^{E_a/RT}$, where k_o is the rate coefficient (assumed = 1.0E-2) and E_a is the activation energy (assumed = 10.0 kJ/mol). The calculated rate constants were compared against results calculated with *Mathematica* at different temperatures. These results also agree to within four significant digits.

Four types of aqueous species are considered in calculating activity coefficients. They are: charged species, water, polar neutral species, and non-polar neutral species. In the input file, all four types of aqueous species are included. The output contains their calculated activity coefficients at different temperatures. The activity coefficients were also calculated with *Mathematica*. The results were the same to within machine precision.

[™] Mathematica is a registered trademark of Wolfram Research, Inc.

3.1.5 EQPT

The EQPT module is a so-called point solver of type I that calculates concentrations at each grid point according to the specified total concentration and equilibrium reactions without transport. In AREST-CT, this module is used to set up the initial and boundary conditions for a problem. Five types of reactions are considered including: 1) fast aqueous, 2) kinetically controlled aqueous, 3) fluid species radioactive decay, 4) solid species dissolution/precipitation, and 5) solid species radioactive decay. Aqueous reactions are usually assumed to be fast reactions and so may be treated as in local chemical equilibrium. However, AREST-CT allows the user to specify whether aqueous reactions are kinetically-controlled or assumed to be in local equilibrium.

The initial concentration of each species must also be specified for the point solver Type I. When total concentration is specified, one can either state the concentration of one species or the total concentration of one component and let the program do speciation calculations. One has to remember that the number of reactions in local equilibrium plus the number of specified total concentrations must exactly equal the number of aqueous species. Problem input data that under-specifies or over-specifies these conditions cannot be solved, and the code will issue an error message and stop execution.

The input test file for verifying the point solver I is shown in Appendix E (Table E.1). The output from this test case is shown in Table E.2. In the output, the equilibrium constants of each equilibrium reaction, k , are listed along with the ion activity products (Q) and saturation index (Q/K). If the calculation is accurate, all Q/K values should be equal to 1.0. Also listed are the specified total concentrations and the calculated total concentrations. Mass conservation requires that they be equal.

3.1.6 RTPT

The RTPT module is the so-called point solver of type II discussed in section 2.1, and is the main driver routine for calculating coupled chemical reactions with transport. Several existing routines are called by RTPT, including: 1) `y_getabb`; 2) `y_getacoef`; 3) `y_getacoedx`; 4) `b_ludcmp` and 5) `b_lubksb`. The first three routines have been tested in the activity coefficient

module (shown in Appendix D), and the last two routines were taken from a standard text -- "Numerical Recipes" (Press et al. 1986). Thus, no unit testing was considered necessary for these five routines.

Because no analytical solutions are available to test against the output from this module, no unit testing was possible. Consequently, several extra steps were taken to ensure accurate implementation and coding. The equation derivation given in section 2.1 has been carefully examined by the authors. Also a code "walk-through" was done, where each FORTRAN statement in the subroutines was checked. Several coding errors were discovered during this process and were corrected. Additional testing of this module will be done as part of the integration testing phase.

3.2 INTEGRATION TESTING

Integration testing is the process of testing a computer code as a whole object. One purpose of integration testing is to examine the logical relationships between submodules, which can be achieved by examining the qualitative behavior of simulation results, with judgment based on geochemical common sense. Another purpose is to ensure that the results are quantitatively correct. However, because there are no analytical solutions for the reaction-transport problems AREST-CT is designed to solve, at least to the authors' knowledge, such comparisons were not possible. The next best alternative is to benchmark the code against simulation results from a similar reaction-transport code. For this purpose, we have used the CIRF.A code which has some of the same functions as AREST-CT, and which has been applied to different types of problems in the past few years.

The test case we have selected is a 1-D idealization of a LLW engineering system that is illustrated schematically in Figure 2. The system consists of 7 solids and 12 aqueous species (Appendix F, Tables F.1 and F.2). Two types of reactions are considered: (1) equilibrium aqueous reactions (Table F.3) and solid dissolution/precipitation reactions (Table F.4). Water enters the system at the left side, infiltrates through the system and exits at the right side boundary. The infiltration velocity is assumed to be a constant 5.2 cm/year and the temperature is assumed uniform and constant at 25°C. Initial conditions are uniform concentrations

Figure 2. Schematic of One-dimensional Integration Test Problem. Mineral percentages are given in volume percent.

throughout the whole domain. At the left side boundary, concentrations are specified (Dirichlet type boundary conditions). At the right side boundary, zero diffusive flux conditions were used.

Simulations with AREST-CT and CIRF.A were carried out with exactly the same system configurations as described above, except for infiltration velocity. CIRF.A adopts a fully coupled model. In this model, the infiltration velocity changes with porosity as a result of solid dissolution/precipitation reactions. The initial design of AREST-CT required that the water velocity be computed externally and used as an input to the code. Consequently, Version 1.0 of AREST-CT cannot simulate changes in the fluid velocity field as a result of chemical reactions.^(a) Thus, AREST-CT simulations were carried out under uniform and constant infiltration velocity, but the CIRF.A simulation was carried out under non-uniform, time-varying infiltration velocity. Other input parameters, such as equilibrium constants and rate constants were exactly the same.

Simulation results at 5166 years are presented in Appendix F (Figure F.1 - F.9). Solid lines are from AREST-CT calculation, while dashed lines are from CIRF.A calculation. Figure F.1 shows that the pH increases in the iron/soil barrier. This occurs because the dissolution reaction of natural iron consumes H^+ (reaction 1 in Table F.4). In this same region, the HCO_3^- should

^(a) An unsaturated flow solver is being implemented and will be included in the next version of AREST-CT.

increase and $\text{CO}_2(\text{aq})$ should decrease, corresponding to the increase in pH. This occurs because the total carbonate ($\text{CO}_2(\text{aq}) + \text{HCO}_3^-$) is fixed as specified in the initial and inlet boundary conditions. So, to maintain equilibrium in reaction 2 in Table F.3, the increase in pH results in higher concentrations of HCO_3^- and lower concentrations of $\text{CO}_2(\text{aq})$. These expected changes are reflected in Figures F.2 and F.3.

Figure F.4 shows that the concentration of TcO_4^- increases with the penetration depth into the vault until it reaches a maximum and then drops to near zero. The increase in concentration with penetration depth is caused by the release of Tc from the waste glass (reaction 7 in Table F.4). The decrease is due to the reduction of TcO_4^- to Tc^{3+} (reaction 1 of Table F.4) that occurs in the iron/soil barrier, as shown in Figure F.5. Reaction 4 in Table F.4 then controls the precipitation of the highly insoluble $\text{Tc}_3\text{O}_4(\text{s})$, as shown in Figure F.6, so that the total flux of Tc exiting the iron/soil barrier is essentially zero. Qualitatively, the simulation results are consistent with expectations from theoretical analysis.

Quantitatively, the AREST-CT simulations compare very well with the CIRF.A results, especially for the solid species (Figures F.7-F.9). There are some exceptions, e.g., in Figure F.1, the CIRF.A calculation has an extra spike that is believed to be numerical noise. There are other small differences in the profiles of aqueous species concentrations (Figures F.1-F.3 and F.5). We suspect that the time-varying velocity field in CIRF.A is the cause of these differences. This hypothesis will be tested in the near future after an unsaturated flow solver is coupled with the AREST-CT code.

4.0 CONCLUSION

Verification testing of AREST-CT (version 1.0) has been completed. Testing will continue on this version, to get a good understanding of the capabilities of the code and to find possible bugs. Specifically, the resolution will be increased (more grid nodes and smaller time steps) for the one-dimensional transport test cases (diffusion, convection, and diffusion + convection), to match the analytical solutions more closely. Integration testing showed that AREST-CT works properly and no significant errors were found. However, the testing so far is for relatively simple cases. Several other functions of AREST-CT have yet to be tested, including mechanisms of radioactive decay and decay chain ingrowth, and the 2-D simulation capability. Additional integration testing is planned to test these functions.

5.0 REFERENCES

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APPENDIX A

Verification of Transport Module (Upwinding)

APPENDIX A

Verification of Transport Module (Upwinding)

This appendix contains the input data and results of the test case runs to verify the implementation of the upwinding numerical transport model.

Table A.1. Input Data File for 1-D Pure Diffusion Case

```
C
C Test input file for AREST reaction-transport module
C
C format: 20 lines of comments
C line1: nxp,nyp,naqs,ntstep
C line2: vx,vy [m/sec]
C line3: porosity
C line4: water saturation (Sw)
C line5: dispersion coefficient [m**2/year]
C line6: density of aqueous solution [kg/m**3]
C line7: xlength, ylength [m]
C line8: time step length [seconds]
C line9: initial condition
C line10: boundary conditions
C
C Creating Date: 12/14/94 by: Yueting Chen
C Purpose: testing AREST-CT module
C ----- Data start -----
101  2    1    500
0.0  0.0
0.25
1.00
3.0
1.0E+3
10.0 10.0
1000.0
1.00
1.00 0.001 0.1 0.001
C ----- control flags -----
1      ! LF1, 1D or 2D (=2) simulation
1      ! LF2, boundary condition types; 1: type 1; 2: type 2
1      ! LF3, Aitken extrapolation scheme; 1: on; 0: off
1      ! LF4, diff/conv switch for anal. solutions; 1: d, 2: c; 3:d+c
0      ! not used
0      ! not used
0      ! not used
0      ! not used
0      ! not used
0      ! not used
C ----- parameters -----
1.0    ! PA1, Max CFL
0.50   ! PA2, Crank-Nicklson parameter
1.0E-7 ! PA3, acceptable relative err for concentration
0.0    ! PA4, the position of initial wave front
0.0    ! not used
0.0    ! not used
0.0    ! not used
0.0    ! not used
```

```

0.0 ! not used
0.0 ! not used

```

Table A.2. Input Data File for 1-D Pure Convection Case

```

C
C Test input file for AREST reaction-transport module
C
C format: 20 lines of comments
C line1: nxp,nyp,naqs,ntstep
C line2: vx,vy [m/sec]
C line3: porosity
C line4: water saturation (Sw)
C line5: dispersion coefficient [m**2/sec]
C line6: density of aqueous solution [kg/m**3]
C line7: xlength, ylength [m]
C line8: time step length [seconds]
C line9: initial condition
C line10: boundary conditions
C
C Creating Date: 12/14/94 by: Yueting Chen
C Purpose: testing AREST-CT module
C ----- Data start -----
101 2 1 100
0.02 0.0
0.25
1.00
0.0
1.0E+3
20.0 10.0
1000.0
1.00
0.100 0.001 1.0 0.001
C ----- control flags -----
1 ! LF1, 1D or 2D (=2) simulation
1 ! LF2, boundary condition types; 1: type 1; 2: type 2
1 ! LF3, Aitken extrapolation scheme; 1: on; 0: off
2 ! LF4, diff/conv switch for anal. solutions; 1: d, 2: c; 3:d+c
1 ! LF5, Upwinding/TVD flag, 1: upwinding; 2: TVD
0 ! not used
0 ! not used
0 ! not used
0 ! not used
0 ! not used
C ----- parameters -----
0.50 ! PA1, Max CFL
0.50 ! PA2, Crank-Nicklson parameter
1.0E-7 ! PA3, acceptable relative err for concentration
0.1 ! PA4, the position of initial wave front
0.0 ! not used
0.0 ! not used
0.0 ! not used
0.0 ! not used
0.0 ! not used
0.0 ! not used

```


Table A.3. Input Data File for 1-D Diffusion + Advection Case

```
C
C Test input file for AREST reaction-transport module
C
C format: 20 lines of comments
C line1: nxp,nyp,naqs,ntstep
C line2: vx,vy [m/sec]
C line3: porosity
C line4: water saturation (Sw)
C line5: dispersion coefficient [m**2/sec]
C line6: density of aqueous solution [kg/m**3]
C line7: xlength, ylength [m]
C line8: time step length [seconds]
C line9: initial condition
C line10: boundary conditions
C
C Creating Date: 12/14/94 by: Yueting Chen
C Purpose: testing AREST-CT module
C ----- Data start -----
101  2      1      200
5.0  0.0
0.25
1.00
0.40
1.0E+3
20.0 10.0
1000.0
1.00
1.00 0.001 0.0 0.001
C ----- control flags -----
1      ! LF1, 1D or 2D (=2) simulation
1      ! LF2, boundary condition types; 1: type 1; 2: type 2
1      ! LF3, Aitken extrapolation scheme; 1: on; 0: off
3      ! LF4, diff/conv switch for anal. solutions; 1: d, 2: c; 3:d+c
1      ! LF5, Upwinding/TVD flag, 1: upwinding; 2: TVD
0      ! not used
0      ! not used
0      ! not used
0      ! not used
0      ! not used
C ----- parameters -----
0.25  ! PA1, Max CFL
0.50  ! PA2, Crank-Nicklson parameter
1.0E-7 ! PA3, acceptable relative err for concentration
0.1   ! PA4, the position of initial wave front
0.0   ! not used
0.0   ! not used
0.0   ! not used
0.0   ! not used
0.0   ! not used
0.0   ! not used
```

Table A.4. Input Data File for 2-D Diffusion + Convection Case with Uniform X-Direction Flow

```
C
C Test input file for AREST reaction-transport module
C
C format: 20 lines of comments
C line1: nxp,nyp,naqs,ntstep
```

```

C line2: vx,vy [m/sec]
C line3: porosity
C line4: water saturation (Sw)
C line5: dispersion coefficient [m**2/sec]
C line6: density of aqueous solution [kg/m**3]
C line7: xlength, ylength [m]
C line8: time step length [seconds]
C line9: initial condition
C line10: boundary conditions
C
C Creating Date: 12/14/94 by: Yueting Chen
C Purpose: testing AREST-CT module
C ----- Data start -----
51 51 1 100
0.0 -8.0
0.25
1.00
3.0
1.0E+3
20.0 20.0
1000.0
1.00
1.00 0.001 0.0 0.001
C ----- control flags -----
2 ! LF1, 1D or 2D (=2) simulation
1 ! LF2, boundary condition types; 1: type 1; 2: type 2
1 ! LF3, Aitken extrapolation scheme; 1: on; 0: off
4 ! LF4, diff/conv switch for anal. sol.; 1: d, 2: c; 3:d+c;4: 2D
1 ! LF5, not used
0 ! not used
0 ! not used
0 ! not used
0 ! not used
0 ! not used
C ----- parameters -----
0.25 ! PA1, Max CFL
0.50 ! PA2, Crank-Nicklson parameter
1.0E-7 ! PA3, acceptable relative err for concentration
0.1 ! PA4, the position of initial wave front
0.5 ! PA5, the injection rate at point (26,26),for 2-D testing only
0.0 ! not used
0.0 ! not used
0.0 ! not used
0.0 ! not used
0.0 ! not used

```

Table A.5. Input Data File for 2-D Diffusion + Convection Case with Different Uniform Flow Directions ($V_x > 0$ & $V_y = 0$)

```

C
C Test input file for AREST reaction-transport module
C
C format: 20 lines of comments
C line1: nxp,nyp,naqs,ntstep
C line2: vx,vy [m/sec]
C line3: porosity
C line4: water saturation (Sw)
C line5: dispersion coefficient [m**2/sec]
C line6: density of aqueous solution [kg/m**3]
C line7: xlength, ylength [m]

```

```

C line8: time step length [seconds]
C line9: initial condition
C line10: boundary conditions
C
C Creating Date: 12/14/94 by: Yueting Chen
C Purpose: testing AREST-CT module
C ----- Data start -----
51      51      1      100
8.0      0.0
0.25
1.00
3.0
1.0E+3
20.0 20.0
1000.0
1.00
1.00 0.001 0.0 0.001
C ----- control flags -----
2      ! LF1, 1D or 2D (=2) simulation
1      ! LF2, boundary condition types; 1: type 1; 2: type 2
1      ! LF3, Aitken extrapolation scheme; 1: on; 0: off
4      ! LF4, diff/conv switch for anal. sol.; 1: d, 2: c; 3:d+c;4: 2D
1      ! LF5, not used
0      ! not used
0      ! not used
0      ! not used
0      ! not used
0      ! not used
C ----- parameters -----
0.25 ! PA1, Max CFL
0.50 ! PA2, Crank-Nicklson parameter
1.0E-7 ! PA3, acceptable relative err for concentration
0.1 ! PA4, the position of initial wave front
0.5 ! PA5, the injection rate at point (26,26), for 2-D testing only
0.0 ! not used
0.0 ! not used
0.0 ! not used
0.0 ! not used
0.0 ! not used

```

Table A.6. Input Data File for 2-D Diffusion + Convection Case with Different Uniform Flow Directions ($V_x < 0$ & $V_y = 0$)

```

C
C Test input file for AREST reaction-transport module
C
C format: 20 lines of comments
C line1: nxp,nyp,naqs,ntstep
C line2: vx,vy [m/sec]
C line3: porosity
C line4: water saturation (Sw)
C line5: dispersion coefficient [m**2/sec]
C line6: density of aqueous solution [kg/m**3]
C line7: xlength, ylength [m]
C line8: time step length [seconds]
C line9: initial condition
C line10: boundary conditions
C
C Creating Date: 12/14/94 by: Yueting Chen
C Purpose: testing AREST-CT module

```

```

C ----- Data start -----
51      51      1      100
-8.0    0.0
0.25
1.00
3.0
1.0E+3
20.0    20.0
1000.0
1.00
1.00    0.001 0.0    0.001
C ----- control flags -----
2      ! LF1, 1D or 2D (=2) simulation
1      ! LF2, boundary condition types; 1: type 1; 2: type 2
1      ! LF3, Aitken extrapolation scheme; 1: on; 0: off
4      ! LF4, diff/conv switch for anal. sol.; 1: d, 2: c; 3:d+c;4: 2D
1      ! LF5, not used
0      ! not used
0      ! not used
0      ! not used
0      ! not used
0      ! not used
C ----- parameters -----
0.25    ! PA1, Max CFL
0.50    ! PA2, Crank-Nicklson parameter
1.0E-7   ! PA3, acceptable relative err for concentration
0.1     ! PA4, the position of initial wave front
0.5     ! PA5, the injection rate at point (26,26), for 2-D testing only
0.0     ! not used
0.0     ! not used
0.0     ! not used
0.0     ! not used
0.0     ! not used

```

Table A.7. Input Data File for 2-D Diffusion + Convection Case with Different Uniform Flow Directions ($V_x = 0$ & $V_y > 0$)

```

C
C Test input file for AREST reaction-transport module
C
C format: 20 lines of comments
C line1: nxp,nyp,naqs,ntstep
C line2: vx,vy [m/sec]
C line3: porosity
C line4: water saturation (Sw)
C line5: dispersion coefficient [m**2/sec]
C line6: density of aqueous solution [kg/m**3]
C line7: xlength, ylength [m]
C line8: time step length [seconds]
C line9: initial condition
C line10: boundary conditions
C
C Creating Date: 12/14/94 by: Yueting Chen
C Purpose: testing AREST-CT module
C ----- Data start -----
51      51      1      100
0.0     8.0
0.25
1.00
3.0

```

```

1.0E+3
20.0 20.0
1000.0
1.00
1.00 0.001 0.0 0.001
C ----- control flags -----
2      ! LF1, 1D or 2D (=2) simulation
1      ! LF2, boundary condition types; 1: type 1; 2: type 2
1      ! LF3, Aitken extrapolation scheme; 1: on; 0: off
4      ! LF4, diff/conv switch for anal. sol.; 1: d, 2: c; 3:d+c;4: 2D
1      ! LF5, not used
0      ! not used
0      ! not used
0      ! not used
0      ! not used
0      ! not used
C ----- parameters -----
0.25   ! PA1, Max CFL
0.50   ! PA2, Crank-Nicklson parameter
1.0E-7 ! PA3, acceptable relative err for concentration
0.1    ! PA4, the position of initial wave front
0.5    ! PA5, the injection rate at point (26,26),for 2-D testing only
0.0    ! not used
0.0    ! not used
0.0    ! not used
0.0    ! not used
0.0    ! not used

```

Table A.8. Input Data File for 2-D Diffusion + Convection Case with Different Uniform Flow Directions ($V_x = 0$ & $V_y < 0$)

```

C
C Test input file for AREST reaction-transport module
C
C format: 20 lines of comments
C line1: nxp,nyp,naqs,ntstep
C line2: vx,vy [m/sec]
C line3: porosity
C line4: water saturation (Sw)
C line5: dispersion coefficient [m**2/sec]
C line6: density of aqueous solution [kg/m**3]
C line7: xlength, ylength [m]
C line8: time step length [seconds]
C line9: initial condition
C line10: boundary conditions
C
C Creating Date: 12/14/94 by: Yueting Chen
C Purpose: testing AREST-CT module
C ----- Data start -----
51      51      1      100
0.0     -8.0
0.25
1.00
3.0
1.0E+3
20.0 20.0
1000.0
1.00
1.00 0.001 0.0 0.001

```

```

C ----- control flags -----
2      ! LF1, 1D or 2D (=2) simulation
1      ! LF2, boundary condition types; 1: type 1; 2: type 2
1      ! LF3, Aitken extrapolation scheme; 1: on; 0: off
4      ! LF4, diff/conv switch for anal. sol.; 1: d, 2: c; 3:d+c;4: 2D
1      ! LF5, not used
0      ! not used
0      ! not used
0      ! not used
0      ! not used
0      ! not used
C ----- parameters -----
0.25   ! PA1, Max CFL
0.50   ! PA2, Crank-Nicklson parameter
1.0E-7 ! PA3, acceptable relative err for concentration
0.1    ! PA4, the position of initial wave front
0.5    ! PA5, the injection rate at point (26,26),for 2-D testing only
0.0    ! not used
0.0    ! not used
0.0    ! not used
0.0    ! not used
0.0    ! not used

```

No. of grids: 101, time step: 0.01 years

Figure A.1. Results from the 1-D Pure Diffusion Case

Figure A.2. Results from the 1-D Pure Convection Case

Figure A.3. Results from the 1-D Diffusion + Convection Case

Figure A.4. Results from the 2-D Diffusion + Convection Case, Uniform Flow in the X-Direction

Figure A.5. Results from the 2-D Diffusion + Convection Case with Different Uniform Flow Directions ($V_x > 0$, $V_y = 0$)

Figure A.6. Results from the 2-D Diffusion + Convection Case with Different Uniform Flow Directions ($V_x < 0$, $V_y = 0$)

Figure A.7. Results from the 2-D Diffusion + Convection Case with Different Uniform Flow Directions ($V_x = 0$, $V_y > 0$)

Figure A.8. Results from the 2-D Diffusion + Convection Case with Different Uniform Flow Directions ($V_x = 0$, $V_y < 0$)

APPENDIX B

Verification of READIN Module

APPENDIX B

Verification of READIN Module

This appendix contains the input data and results of the test case runs to verify the implementation of the READIN input module.

Table B.1. Input Data File for Testing Input Module

```
C
C   Test input file for AREST reaction-transport module
C
C   format: 20 lines of comments
C   line1: nxp,nyp,ntstep
C   line2: vx,vy [m/sec]
C   line3: water saturation (Sw)
C   line4: dispersion coefficient [m**2/sec]
C   line5: density of aqueous solution [kg/m**3]
C   line6: xlength, ylength [m]
C   line7: temperature [C]
C
C   Creating Date: 12/14/94 by: Yueting Chen
C   Purpose: testing AREST-CT module
C   ----- Data start -----
51      2      100
0.02   0.0
1.00
3.0
1.0E+3
20.0   1.0
25.0
C   ----- control flags -----
2      ! LF1, 1D or 2D (=2) simulation
1      ! LF2, boundary condition types; 1: type 1; 2: type 2
1      ! LF3, Aitken extrapolation scheme; 1: on; 0: off
0      ! LF4, column scan switch, 0: off, 1: on while LF1=2
0      ! LF5, 0: uniform lithology even more than 1 units in file.
0      ! not used
0      ! not used
0      ! not used
0      ! not used
0      ! not used
C   ----- parameters -----
0.25   ! PA1, Max CFL
0.50   ! PA2, Crank-Nicklson parameter
1.0E-7 ! PA3, acceptable relative err for concentration
0.0    ! PA4, not used
0.0    ! PA5, not used
0.0    ! not used
0.0    ! not used
0.0    ! not used
0.0    ! not used
0.0    ! not used
C   =====
C   aqueous species and solid species
C   =====
```

```

4          number of aqueous species
C -----
1          2
SiO2(aq)
1.0       14
2.0       8
0.0       4.0
C -----
2          2
H2O
2.0       1
1.0       8
0.0       4.0
C -----
3          1
H+
1.0       1
1.0       4.0
C -----
4          2
OH-
1.0       1
1.0       8
-1.0      4.0
C ===== end of aqueous species
2          number of solid species
C -----
1          2
Quartz
1.0       14
2.0       8
2.6
C -----
2          1
Gold
1.0       79
2.6
C ===== end of solid species
1          number of fast reactions
C =====
1          3          1001 H2O
C -----
-1.0      2          H2O
1.0       3          H+
1.0       4          OH-
C ----- equil. constant
1          1.0
-14.0
C ===== end of fast reactions
1          number of slow reactions
C =====
1          1          2001 Quartz
C ----- reacting solid
-1.0      1          Quartz
C -----
1.0       1          SiO2(aq)
C ----- equil. constant
1          1.0
-6.0
C ----- rate constant and Ea
-36.0      0.0

```

```

C ===== end of slow reactions
      1      number of fluid decay
C =====
      1      2      1001      H2O
C -----
      -1.0      2      H2O
      1.0      3      H+
C ----- decay constant
      1.0E-7
C ===== end of fluid decay
      1      number of solid decay
C =====
      1      0      2001      Quartz      0 aqueous or gas product
C -----
      -1.0      1      quartz      decay reactant
C -----
      1.0      2      gold      decay product
C ----- decay constant
      1.0E-5
C ===== end of solid decay
      1      number of lithology units
C =====
      1
sandstone
C -----
      1      0.700      0.001      Quartz
      2      0.001      -0.001      Gold
C ===== end of lithology
      2      Number of Boundary Segments
C =====
      1      1      segment 1(left) type 1
C -----
      0      in equilibrium with number of solids
C -----
C -----
      3      number of specified concentrations
C -----
      1      1      condition 1, 1 species
      1.0      1      SiO2(aq) stoichio. coeff. and species
number
      1.0E-6      total concentration
C -----
      2      1      condition 2, 1 species
      1.0      2      H2O
      1.0      total concentration
C -----
      3      1      condition 3, 1 species
      1.0      3      H+
      1.0E-7      total concentration
C ===== end of segment 1
      2      1      segment 2(right) type 1
C -----
      0      in equilibrium with number of solids
C -----
C -----
      3      number of specified concentrations
C -----
      1      1      condition 1, 1 species
      1.0      1      SiO2(aq)
      1.0E-4      total concentration
C -----

```



```

          2      1      condition 2, 1 species
          1.0    2      H2O
          1.0      total concentraion
C  -----
          3      1      condition 3, 1 species
          1.0    3      H+
          1.0E-8      total concentration
C  ===== end of segment 2
          0      initial conditions 0: the same as the inlet
C  ===== The end

```

Table B.2. Output Data File for Testing Input Module

```

=====

AREST-CT REACTION-TRANSPORT SIMULATOR

Pacific Northwest Laboratory

Version 1.0, 1995

=====
Limitations of This Executable File
=====

*   Grids at X-axis           :   201   *
*   Grids at Y-axis           :    2    *
*   Aqueous species           :    5    *
*   Solid species             :    2    *
*   Fast reactions            :    2    *
*   Slow reactions            :    2    *
*   Fluid decay               :    2    *
*   Solid decay               :    2    *
*   Lithology units           :    3    *

===== AREST-CT SIMULATION OUTPUT =====

THE INPUT FILE IS : test001.actin

THIS SIMULATION STARTS AT :Mon Feb  6 09:58:59 1995

@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@

THE INPUT DATA FOR THIS SIMULATION

@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@

The numbers of grids used for this simulation are:
npx =   51      nyp =    2

The domain size is :   20.0 X      1.0  Meters

The fluid velocity are:
Vx =   0.20000E-01 m/year;   Vy =      0.      m/year

```

The density of the fluid is: 1000.00 [kg/m³]
 The dispersion coefficient is: 3.00000[m²/sec]
 The initial water saturation is: 1.000
 The temperature is : 25.0 [C]

Total number of aqueous species: 4

 SiO2(aq) consists of 2 elements
 1.00 Si
 2.00 O
 The molecular weight of the species is: 60.084
 Its charge is: 0. Its closet distance is: 4.00

H2O consists of 2 elements
 2.00 H
 1.00 O
 The molecular weight of the species is: 18.015
 Its charge is: 0. Its closet distance is: 4.00

H+ consists of 1 elements
 1.00 H
 The molecular weight of the species is: 1.008
 Its charge is: 1. Its closet distance is: 4.00

OH- consists of 2 elements
 1.00 H
 1.00 O
 The molecular weight of the species is: 17.007
 Its charge is: -1. Its closet distance is: 4.00

Total number of solid species: 2

 Quartz consists of 2 elements
 1.00 Si
 2.00 O
 The molecular weight of the species is: 60.084
 Its mass density is: 2600.0000[kg/m³]
 Its molar density is: 43272.5354 [moles/m³]

Gold consists of 1 elements
 1.00 Au
 The molecular weight of the species is: 196.966
 Its mass density is: 2600.0000[kg/m³]
 Its molar density is: 13200.2142 [moles/m³]

=====

Number of fast reactions: 1

 Fast reaction 1 involves 3 species

-1.00 H2O
 1.00 H+
 1.00 OH-

1 terms in the equil. const. polynomial

 -14.000 T** 0

```

Exponential factor for this reaction is:      1.
=====
Number of fluid decays:      1
-----
Fluid decay      1      involves      2species
-----
      -1.00      H2O
      1.00      H+
-----
Its decay constant is:      0.1000E-06
=====
Number of slow reactions:      1
-----
Slow reaction      1      involves 1 solid      Quartz
and      1      aqueous species
-----
      1.00      SiO2(aq)
-----
      1 terms in the equil. const. polynomial
-----
      -6.0000      T** 0
-----
Exponential factor for this reaction is:      1.
-----
Rate coeff. is:      -36.00
The activation energy is :      0.
=====
Number of solid decays:      1
-----
The reactant of this solid decay is:      Quartz
The product of this solid decay is:      Gold
0 aqueous species involve in this solid decay
-----
Its decay constant is:      0.1000E-04
=====
      1 lithology units
-----
Unit      1      sandstone
-----
Quartz      0.7000      0.0010      0.1671E+09
Gold      0.0000      0.0000      0.2387E+06
Porosity is:      0.3000
=====
      2 segments of boundary
-----
Boundary segment      1 with type      1 conditions
-----
Fluid is in equilibrium with      0 solids
-----
      3 specified concnetrations
-----
condition      1      1 Species
SiO2(aq)      1.00000
Total concentration is :      0.10000E-05
-----
condition      2      1 Species
H2O      1.00000
Total concentration is :      1.0000
-----
condition      3      1 Species

```

H+ 1.00000
Total concentration is : 0.10000E-06

Boundary segment 2 with type 1 conditions

Fluid is in equilibrium with 0 solids

3 specified concentrations

condition 1 1 Species
SiO2(aq) 1.00000
Total concentration is : 0.10000E-03

condition 2 1 Species
H2O 1.00000
Total concentration is : 1.0000

condition 3 1 Species
H+ 1.00000
Total concentration is : 0.10000E-07

Initial condition type: 0
=====

Control Flags

LF1 = 2
LF2 = 1
LF3 = 1
LF4 = 0
LF5 = 0
LF6 = 0
LF7 = 0
LF8 = 0
LF9 = 0
LF10 = 0

Control Parameters

PA1 = 0.2500
PA2 = 0.5000
PA3 = 0.1000E-06
PA4 = 0.
PA5 = 0.
PA6 = 0.
PA7 = 0.
PA8 = 0.
PA9 = 0.
PA10 = 0.
=====

APPENDIX C

Verification of QRDCMP Module

APPENDIX C

Verification of QRDCMP Module

This appendix contains the input data and results of the test case runs to verify the implementation of the Q-R decomposition module.

Table C.1. Input Data File for Testing the Q-R Decomposition Module

```
C
C      Test input file for AREST reaction-transport module
C
C      format: 20 lines of comments
C      line1: nxp,nyp,ntstep
C      line2: vx,vy [m/sec]
C      line3: water saturation (Sw)
C      line4: dispersion coefficient [m**2/sec]
C      line5: density of aqueous solution [kg/m**3]
C      line6: xlength, ylength [m]
C      line7: temperature [C]
C
C      Creating Date: 12/14/94 by: Yueting Chen
C      Purpose: testing AREST-CT module
C      ----- Data start -----
51      2      100
0.02    0.0
1.00
3.0
1.0E+3
20.0    1.0
25.0
C      ----- control flags -----
2      ! LF1, 1D or 2D (=2) simulation
1      ! LF2, boundary condition types; 1: type 1; 2: type 2
1      ! LF3, Aitken extrapolation scheme; 1: on; 0: off
0      ! LF4, column scan switch, 0: off, 1: on while LF1=2
0      ! LF5, 0: uniform lithology even more than 1 units in file.
0      ! not used
0      ! not used
0      ! not used
0      ! not used
0      ! not used
C      ----- parameters -----
0.25    ! PA1, Max CFL
0.50    ! PA2, Crank-Nicklson parameter
1.0E-7   ! PA3, acceptable relative err for concentration
0.0     ! PA4, not used
0.0     ! PA5, not used
0.0     ! not used
0.0     ! not used
0.0     ! not used
0.0     ! not used
0.0     ! not used
C      =====
C      aqueous species and solid species
C      =====
```

```

4          number of aqueous species
C -----
1          2
SiO2(aq)
1.0      14
2.0       8
0.0      4.0
C -----
2          2
H2O
2.0       1
1.0       8
0.0      4.0
C -----
3          1
H+
1.0       1
1.0      4.0
C -----
4          2
OH-
1.0       1
1.0       8
-1.0     4.0
C ===== end of aqueous species
2          number of solid species
C -----
1          2
Quartz
1.0      14
2.0       8
2.6
C -----
2          1
Gold
1.0      79
2.6
C ===== end of solid species
1          number of fast reactions
C =====
1          3          1001 H2O
C -----
-1.0  2          H2O
1.0   3          H+
1.0   4          OH-
C ----- equil. constant
1          1.0
-14.0
C ===== end of fast reactions
1          number of slow reactions
C =====
1          1          2001 Quartz
C ----- reacting solid
-1.0  1          Quartz
C -----
1.0   1          SiO2(aq)
C ----- equil. constant
1          1.0
-6.0
C ----- rate constant and Ea
-36.0          0.0

```

```

C      ===== end of slow reactions
C      1      number of fluid decay
C      =====
C      1      2      1001      H2O
C      -----
C      -1.0    2      H2O
C      1.0     3      H+
C      ----- decay constant
C      1.0E-7
C      ===== end of fluid decay
C      1      number of solid decay
C      =====
C      1      0      2001      Quartz      0 aqueous or gas product
C      -----
C      -1.0    1      quartz      decay reactant
C      -----
C      1.0     2      gold      decay product
C      ----- decay constant
C      1.0E-5
C      ===== end of solid decay
C      1      number of lithology units
C      =====
C      1
C      sandstone
C      -----
C      1      0.700      0.001      Quartz
C      2      0.001      -0.001      Gold
C      ===== end of lithology
C      2      Number of Boundary Segments
C      =====
C      1      1      segment 1(left) type 1
C      -----
C      0      in equilibrium with number of solids
C      -----
C      3      number of specified concentrations
C      -----
C      1      1      condition 1, 1 species
C      1.0     1      SiO2(aq) stoich. coeff. and species
number      1.0E-6      total concentration
C      -----
C      2      1      condition 2, 1 species
C      1.0     2      H2O
C      1.0     total concentration
C      -----
C      3      1      condition 3, 1 species
C      1.0     3      H+
C      1.0E-7      total concentration
C      ===== end of segment 1
C      2      1      segment 2(right) type 1
C      -----
C      0      in equilibrium with number of solids
C      -----
C      3      number of specified concentrations
C      -----
C      1      1      condition 1, 1 species
C      1.0     1      SiO2(aq)
C      1.0E-4      total concentration
C      -----

```



```

      2      1      condition 2, 1 species
      1.0    2      H2O
      1.0      total concentraion
C -----
      3      1      condition 3, 1 species
      1.0    3      H+
      1.0E-8      total concentration
C ===== end of segment 2
      0      initial conditions 0: the same as the inlet
C ===== The end

```

Table C.2. AREST-CT Output Data File for Testing the Q-R Decomposition Module

grxmtot

```

      0.00000E+00      0.00000E+00      0.00000E+00      0.10000E+01      0.50000E+00
    -0.10000E+01     -0.10000E+01     -0.10000E+01      0.00000E+00      0.00000E+00
      0.10000E+01      0.10000E+01      0.10000E+01      0.00000E+00      0.10000E+01
      0.10000E+01      0.00000E+00      0.00000E+00      0.00000E+00      0.00000E+00
      0.00000E+00     -0.10000E+01      0.00000E+00      0.00000E+00      0.00000E+00
      0.00000E+00      0.10000E+01      0.00000E+00      0.00000E+00      0.00000E+00

```

avector

```

    -0.10000E+01      0.00000E+00      0.00000E+00      0.00000E+00      0.00000E+00      0.00000E+00
      0.00000E+00     -0.47434E+00     -0.79057E+00      0.31623E+00     -0.15811E+00      0.15811E+00
      0.00000E+00      0.63246E+00      0.00000E+00      0.63246E+00     -0.31623E+00      0.31623E+00
      0.00000E+00      0.00000E+00      0.00000E+00      0.00000E+00      0.70711E+00      0.70711E+00

```

avector *grxmtot

```

      0.00000E+00      0.00000E+00      0.00000E+00     -0.10000E+01     -0.50000E+00
      0.00000E+00     -0.11102E-15     -0.31623E+00      0.00000E+00     -0.79057E+00
    -0.11102E-15     -0.22204E-15     -0.63246E+00      0.00000E+00      0.00000E+00
      0.00000E+00      0.11102E-15      0.00000E+00      0.00000E+00      0.00000E+00

```

Table C.3. CIRF.A Output Data File for Testing the Q-R Decomposition Module

grxmtot

```

      0.00000E+00      0.00000E+00      0.00000E+00      0.10000E+01      0.50000E+00
      0.10000E+01      0.10000E+01      0.10000E+01      0.00000E+00      0.00000E+00
      0.10000E+01      0.10000E+01      0.10000E+01      0.00000E+00      0.10000E+01
      0.10000E+01      0.00000E+00      0.00000E+00      0.00000E+00      0.00000E+00

```

0.00000E+00	0.10000E+01	0.00000E+00	0.00000E+00	0.00000E+00
-------------	-------------	-------------	-------------	-------------

0.00000E+00	0.10000E+01	0.00000E+00	0.00000E+00	0.00000E+00
-------------	-------------	-------------	-------------	-------------

avector

-0.10000E+01	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
--------------	-------------	-------------	-------------	-------------	-------------

0.00000E+00	-0.47434E+00	-0.79057E+00	0.31623E+00	0.15811E+00	-0.15811E+00
-------------	--------------	--------------	-------------	-------------	--------------

0.00000E+00	0.63246E+00	0.00000E+00	0.63246E+00	-0.31623E+00	0.31623E+00
-------------	-------------	-------------	-------------	--------------	-------------

0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00	0.70711E+00	0.70711E+00
-------------	-------------	-------------	-------------	-------------	-------------

avector *grxmtot

0.00000E+00	0.00000E+00	0.00000E+00	-0.10000E+01	-0.50000E+00
-------------	-------------	-------------	--------------	--------------

0.00000E+00	-0.11102E-15	-0.31623E+00	0.00000E+00	-0.79057E+00
-------------	--------------	--------------	-------------	--------------

-0.11102E-15	-0.22204E-15	-0.63246E+00	0.00000E+00	0.00000E+00
--------------	--------------	--------------	-------------	-------------

0.00000E+00	0.11102E-15	0.00000E+00	0.00000E+00	0.00000E+00
-------------	-------------	-------------	-------------	-------------

APPENDIX D

Verification of EQCONST, RCONST, and DHACTV Modules

APPENDIX D

Verification of EQCONST, RCONST, and DHACTV Modules

This appendix contains the input data and results of the test case runs to verify the implementation of the equilibrium constants, rate constants, and activity coefficient modules.

Table D.1. Input Data File for Testing the Equilibrium Constants, Rate Constants, and Activity Coefficient Modules

```
C
C   Test input file for AREST reaction-transport module
C
C   format: 20 lines of comments
C   line1: nxp,nyp,ntstep
C   line2: vx,vy [m/sec]
C   line3: water saturation (Sw)
C   line4: dispersion coefficient [m**2/sec]
C   line5: density of aqueous solution [kg/m**3]
C   line6: xlength, ylength [m]
C   line7: temperature [C]
C
C   Creating Date: 12/14/94 by: Yueting Chen
C   Purpose: testing AREST-CT module
C   ----- Data start -----
51      2      100
0.02  0.0
1.00
3.0
1.0E+3
20.0  1.0
25.0
C   ----- control flags -----
2      ! LF1, 1D or 2D (=2) simulation
1      ! LF2, boundary condition types; 1: type 1; 2: type 2
1      ! LF3, Aitken extrapolation scheme; 1: on; 0: off
0      ! LF4, column scan switch, 0: off, 1: on while LF1=2
0      ! LF5, 0: uniform lithology even more than 1 units in file.
0      ! not used
0      ! not used
0      ! not used
0      ! not used
0      ! not used
C   ----- parameters -----
0.25  ! PA1, Max CFL
0.50  ! PA2, Crank-Nicklson parameter
1.0E-7 ! PA3, acceptable relative err for concentration
0.0   ! PA4, not used
0.0   ! PA5, not used
0.0   ! not used
0.0   ! not used
0.0   ! not used
0.0   ! not used
0.0   ! not used
C   =====
```

```

C          aqueous species and solid species
C          =====
C          6          number of aqueous species
C          -----
C          1          2
C          SiO2(aq)
C          1.0        14
C          2.0         8
C          0.0         4.0
C          -----
C          2          2
C          H2O
C          2.0         1
C          1.0         8
C          0.0        -4.0
C          -----
C          3          1
C          H+
C          1.0         1
C          1.0         9.0
C          -----
C          4          2
C          OH-
C          1.0         1
C          1.0         8
C          -1.0        3.0
C          -----
C          5          2
C          CO2(aq)
C          1.0         6
C          2.0         8
C          0.0         0.0
C          -----
C          6          3
C          HCO3-
C          1.0         1
C          1.0         6
C          3.0         8
C          -1.0        4.0
C          ===== end of aqueous species
C          2          number of solid species
C          -----
C          1          2
C          Quartz
C          1.0        14
C          2.0         8
C          2.6
C          -----
C          2          1
C          Gold
C          1.0        79
C          2.6
C          ===== end of solid species
C          2          number of fast reactions
C          =====
C          1          3          1001  H2O
C          -----
C          -1.0        2          H2O
C          1.0         3          H+
C          1.0         4          OH-
C          ----- equil. constant

```

	5	1.0		
	12.3441			
	-6.08839E-3			
	3.58697E-5			
	-8.58931E-8			
	1.06773E-10			
C	-----			
	2	4	1002	CO2 (aq)
C	-----			
	-1.0	5		CO2 (aq)
	-1.0	2		H2O
	1.0	3		H+
	1.0	6		HCO3-
C	-----			
				equil. constant
	5	1.0		
	21.2959			
	-0.107557			
	2.18665E-4			
	-3.33969E-7			
	1.01998E-10			
C	=====			
				end of fast reactions
	1			number of slow reactions
C	=====			
	1	1	2001	Quartz
C	-----			
				reacting solid
	-1.0	1		Quartz
C	-----			
	1.0	1		SiO2 (aq)
C	-----			
				equil. constant
	5	1.0		
	12.3441			
	-6.0884E-3			
	3.5870E-5			
	-8.5893E-8			
	1.0677E-10			
C	-----			
				rate constant and Ea
	-2.0		10.0	
C	=====			
				end of slow reactions
	1			number of fluid decay
C	=====			
	1	2	1001	H2O
C	-----			
	-1.0	2		H2O
	1.0	3		H+
C	-----			
				decay constant
	1.0E-7			
C	=====			
				end of fluid decay
	1			number of solid decay
C	=====			
	1	2	2001	Quartz
C	-----			
				1 aqueous or gas product
	-1.0	1		quartz
C	-----			
				decay reactant
	1.0	2		gold
C	-----			
				decay product
C	-----			
				aqueous species
	1.0	3		OH-
	0.5	1		H+
C	-----			
				decay constant
	1.0E-5			
C	=====			
				end of solid decay
	1			number of lithology units

```

C =====
  1
sandstone
C -----
  1      0.700      0.001      Quartz
  2      0.001      -0.001      Gold
C ===== end of lithology
  2      Number of Boundary Segments
C -----
  1      1      segment 1(left) type 1
C -----
  0      in equilibrium with number of solids
C -----
C -----
  4      number of specified concentrations
C -----
  1      1      condition 1, 1 species
      1.0      1      SiO2(aq) stoichio. coeff. and species
number      1.0E-6      total concentration
C -----
  2      1      condition 2, 1 species
  1.0      2      H2O
  1.0      total concentration
C -----
  3      1      condition 3, 1 species
  1.0      3      H+
  1.0E-7      total concentration
C -----
  4      1      condition 4, 1 species
  1.0      5      CO2(aq)
  1.0E-4      total concentration
C ===== end of segment 1
  2      1      segment 2(right) type 1
C -----
  0      in equilibrium with number of solids
C -----
C -----
  4      number of specified concentrations
C -----
  1      1      condition 1, 1 species
  1.0      1      SiO2(aq)
  1.0E-4      total concentration
C -----
  2      1      condition 2, 1 species
  1.0      2      H2O
  1.0      total concentraion
C -----
  3      1      condition 3, 1 species
  1.0      3      H+
  1.0E-8      total concentration
C -----
  4      1      condition 4, 1 species
  1.0      5      CO2(aq)
  1.0E-4      total concentration
C ===== end of segment 2
  0      initial conditions 0: the same as the inlet
C ===== The end

```

Table D.2. Output Data File for Testing the Equilibrium Constants, Rate Constants, and Activity Coefficient Modules

<u>Temperature</u>	<u>Equilibrium and Rate Constants</u>				
	log k ₁ (calc)	log k ₁ (EQ3)	log k ₂ (calc)	log k ₂ (EQ3)	rate const
0.01	12.3440	12.3460	21.2948	21.2950	1.22376E-04
25.00	12.2130	12.2091	18.7385	18.7390	1.77002E-04
60.00	12.0908	12.0918	15.5589	15.5565	2.70422E-04
100.00	12.0187	12.0214	12.4031	12.4046	3.98217E-04
150.00	12.0021	12.0011	9.00680	9.00960	5.82816E-04
200.00	12.0449	12.0426	6.02254	6.01750	7.87016E-04
250.00	12.1389	12.1412	3.25338	3.25660	1.00346E-03
300.00	12.2916	12.2910	0.51767	0.51700	1.22633E-03

Input Values From EQ3/6

Temperature	A	B	B*
0.01000	0.49390	0.32530	0.03740
25.00000	0.51140	0.32880	0.04100
60.00000	0.54650	0.33460	0.04400
100.00000	0.59950	0.34210	0.04600
150.00000	0.68550	0.35250	0.04700
200.00000	0.79940	0.36390	0.04700
250.00000	0.95930	0.37660	0.03400
300.00000	1.21800	0.39250	0.00000

Calculated Value from Polynomial Fit.

0.01000	0.49463	0.32533	0.03739
25.00000	0.51015	0.32876	0.04108
60.00000	0.54621	0.33458	0.04388
100.00000	0.60092	0.34216	0.04584
150.00000	0.68571	0.35252	0.04764
200.00000	0.79739	0.36381	0.04625
250.00000	0.96088	0.37667	0.03440
300.00000	1.21760	0.39248	-0.00008

Log10(Activity Coefficients)

0.10000E-01	0.	-0.93978E-04	-0.10459E-01	-0.10910E-01	0.55288E-04	-0.10832E-01
25.000	0.	-0.93976E-04	-0.10778E-01	-0.11249E-01	0.53870E-04	-0.11167E-01

60.000	0.	-0.93972E-04	-0.11527E-01	-0.12039E-01	0.56269E-04	-0.11951E-01
100.00	0.	-0.93965E-04	-0.12665E-01	-0.13240E-01	0.63598E-04	-0.13140E-01
150.00	0.	-0.93953E-04	-0.14426E-01	-0.15100E-01	0.77609E-04	-0.14983E-01
200.00	0.	-0.93939E-04	-0.16744E-01	-0.17551E-01	0.95413E-04	-0.17411E-01
250.00	0.	-0.93917E-04	-0.20139E-01	-0.21142E-01	0.11592E-03	-0.20968E-01
300.00	0.	-0.93884E-04	-0.25466E-01	-0.26785E-01	0.13843E-03	-0.26556E-01

Table D.3. Original Data From EQ3/6

```

C  Fit
C  Parameters (A, B and B*) in Extended Debye-Huckel equation and
C  equilibrium constants at different temperatures.
c  From EQ3/6 Database: data.com.R16
c
c  temperatures
c      0.0100    25.0000    60.0000    100.0000
c      150.0000  200.0000  250.0000  300.0000
c  debye huckel a (adh)
c      0.4939    0.5114    0.5465    0.5995
c      0.6855    0.7994    0.9593    1.2180
c  debye huckel b (bdh)
c      0.3253    0.3288    0.3346    0.3421
c      0.3525    0.3639    0.3766    0.3925
c  bdot
c      0.0374    0.0410    0.0440    0.0460
c      0.0470    0.0470    0.0340    0.0000

*  log k grid (0-25-60-100/150-200-250-300 c) =
      12.3460    12.2091    12.0918    12.0214
      12.0011    12.0426    12.1412    12.2910

*  log k grid (0-25-60-100/150-200-250-300 c) =
      21.2950    18.7390    15.5565    12.4046
      9.0096     6.0175     3.2566     0.5170

```

APPENDIX E

Verification of EQPT Module

APPENDIX E

Verification of EQPT Module

This appendix contains the input data and results of the test case run to verify the implementation of the EQPT, point solver type I module.

Table E.1. Input Data File for Testing the Point Solver I Module

```
C
C      Test input file for AREST reaction-transport module
C
C      format: 20 lines of comments
C      line1: nxp,nyp,ntstep
C      line2: vx,vy [m/sec]
C      line3: water saturation (Sw)
C      line4: dispersion coefficient [m**2/sec]
C      line5: density of aqueous solution [kg/m**3]
C      line6: xlength, ylength [m]
C      line7: temperature [C]
C
C      Creating Date: 12/14/94 by: Yueting Chen
C      Purpose: testing AREST-CT module
C      ----- Data start -----
51      2      100
0.02    0.0
1.00
3.0
1.0E+3
20.0    1.0
25.0
C      ----- control flags -----
2      ! LF1, 1D or 2D (=2) simulation
1      ! LF2, boundary condition types; 1: type 1; 2: type 2
1      ! LF3, Aitken extrapolation scheme; 1: on; 0: off
0      ! LF4, column scan switch, 0: off, 1: on while LF1=2
0      ! LF5, 0: uniform lithology even more than 1 units in file.
2      ! LF6, skip factor for eq. point solver in N-R iteration
2      ! LF7, skip factor for transp. point solver in N-R iteration
0      ! not used
0      ! not used
0      ! not used
C      ----- parameters -----
0.25    ! PA1, Max CFL
0.50    ! PA2, Crank-Nicklson parameter
1.0E-7   ! PA3, acceptable relative err for concentration
1.0E-7   ! PA4, error tolerance in eq. point solver
1.0E-3   ! PA5, error tolerance in transp. point solver
0.0      ! not used
0.0      ! not used
0.0      ! not used
0.0      ! not used
0.0      ! not used
C      =====
C      aqueous species and solid species
C      =====
```

	9	number of aqueous species
C	-----	
	1	2
	SiO2(aq)	
	1.0	14
	2.0	8
	0.0	4.0
C	-----	
	2	2
	H2O	
	2.0	1
	1.0	8
	0.0	-4.0
C	-----	
	3	1
	H+	
	1.0	1
	1.0	9.0
C	-----	
	4	2
	OH-	
	1.0	1
	1.0	8
	-1.0	3.0
C	-----	
	5	2
	CO2(aq)	
	1.0	6
	2.0	8
	0.0	0.0
C	-----	
	6	3
	HCO3-	
	1.0	1
	1.0	6
	3.0	8
	-1.0	4.0
C	-----	
	7	1
	Fe+++	
	1.0	26
	3.0	9.0
C	-----	
	8	1
	Fe++	
	1.0	26
	2.0	6.0
C	-----	
	9	1
	O2(g)	
	2.0	8
	0.0	3.0
C	=====	
		end of aqueous species
C	2	number of solid species
C	-----	
	1	2
	Quartz	
	1.0	14
	2.0	8
	2.6	
C	-----	

```

2      1
Gold
1.0    79
2.6

C      =====
          2      number of fast reactions
C      =====
          1      3      1001  H2O
C      -----
          -1.0  2      H2O
          1.0  3      H+
          1.0  4      OH-
C      -----
          1      1.0
          -14.0
C      -----
          2      4      1002  CO2(aq)
C      -----
          -1.0  5      CO2(aq)
          -1.0  2      H2O
          1.0  3      H+
          1.0  6      HCO3-
C      -----
          1      1.0
          -6.5
C      =====
          1      number of kinetic aqueous reactions
C      =====
          1      5      2001  fe+++
C      -----
          -1.0  7      Fe+++
          -0.5  2      H2O
          1.0  8      Fe++
          1.0  3      H+
          0.25  9      O2(g)
C      -----
          1      1.0
          -4.0
C      -----
          -2.0      0.0
C      =====
          rxn      =====
          1      number of slow reactions
C      =====
          1      1      3001  Quartz
C      -----
          -1.0  1      Quartz
C      -----
          1.0  1      SiO2(aq)
C      -----
          1      1.0
          -4.6
C      -----
          -2.0      10.0
C      =====
          1      number of fluid decay
C      =====
          1      2      1001  H2O
C      -----
          -1.0  2      H2O
          1.0  3      H+

```

end of solid species

equil. constant

equil. constant

end of fast reactions

end of kinetic aqu.

reacting solid

equil. constant

rate constant and Ea

end of slow reactions

```

C ----- decay constant
      1.0E-7
C ===== end of fluid decay
      1      number of solid decay
C =====
      1      2      2001      Quartz      1 aqueous or gas product
C -----
      -1.0  1      quartz      decay reactant
C -----
      1.0  2      gold      decay product
C ----- aqueous species
      1.0  3      OH-
      0.5  1      H+
C ----- decay constant
      1.0E-5
C ===== end of solid decay
      1      number of lithology units
C =====
      1
sandstone
C -----
      1      0.700      0.001      Quartz
      2      0.001      -0.001      Gold
C ===== end of lithology
      2      Number of Boundary Segments
C =====
      1      1      segment 1(left) type 1
C -----
      1      in equilibrium with number of solids
C -----
      1      Quartz
C -----
      1      kinetic aqu. rxn. in equil.
C -----
      1      Fe+++
C -----
      5      number of specified concentrations
C -----
      1      1      condition 1, 1 species
      1.0      2      H2O
      1.0      total concentration
C -----
      2      1      condition 2, 1 species
      1.0      3      H+
      1.0E-3      total concentration
C -----
      3      1      condition 43, 1 species
      1.0      5      CO2(aq)
      1.0E-4      total concentration
C -----
      4      1      condition 54, 1 species
      1.0      7      Fe+++
      1.0E-9      total concentration
C -----
      5      1      condition 65, 1 species
      1.0      8      Fe++
      1.0E-7      total concnetration
C ===== end of segment 1
      2      1      segment 2(right) type 1
C -----
      0      in equilibrium with number of solids

```

```

C -----
C -----
C      0      kinetic aqu. rxn. in equil.
C -----
C -----
C      7      number of specified concentrations
C -----
C      1      1      condition 1, 1 species
C      1.0    1      SiO2(aq)
C      1.0E-4      total concentration
C -----
C      2      1      condition 2, 1 species
C      1.0    2      H2O
C      1.0      total concentraion
C -----
C      3      1      condition 3, 1 species
C      1.0    3      H+
C      1.0E-8      total concentration
C -----
C      4      1      condition 4, 1 species
C      1.0    5      CO2(aq)
C      1.0E-4      total concentration
C -----
C      5      1      condition 5, 1 species
C      1.0    7      Fe+++
C      1.0E-9      total concentration
C -----
C      6      1      condition 6, 1 species
C      1.0    8      Fe++
C      1.0E-7      total concentration
C -----
C      7      1      condition 7, 1 species
C      1.0    9      O2(g)
C      1.0E-10
C ===== end of segment 2
C      0      initial conditions 0: the same as the inlet
C ===== The end

```

Table E.2. Output Data File for Testing the EQPT Module

```

EQPT.TEST

32 Newton-Raphson iterations

point solver y_pteqsol converges

The relative error =      0.70421E-07

      species      cvar      log(cvar)      log(gamma)
SiO2(aq)    0.2512E-04    -4.600      0.
H2O          1.000      0.      -0.8738E-05
H+          0.1000E-02    -3.000      -0.1068E-01
OH-         0.1052E-10    -10.98      -0.1114E-01
CO2(aq)     0.1000E-03    -4.000      0.5282E-04
HCO3-       0.3325E-07    -7.478      -0.1106E-01
Fe+++       0.1000E-08    -9.000      -0.9628E-01
Fe++        0.9080E-30    -30.04      -0.4368E-01
O2(g)       0.1000E-19    -20.00      0.

      ln(K)      ln(Q)      Q/K
-32.2362    -32.2362      1.00000
-14.9668    -14.9668      1.00000
-66.7750    -66.7750      1.00000
-10.5919    -10.5919      1.00000

Specified Total C.    Calculated Total C.
1.0000      1.0000
0.10000E-02    0.10000E-02
0.10000E-03    0.10000E-03
0.10000E-08    0.10000E-08
0.10000E-19    0.10000E-19

```


APPENDIX F
Integration Test Results

APPENDIX F

Integration Test Results

This appendix contains the input data and results of the integration test case for the AREST-CT code. All results are shown at 5166 years into the simulation.

Table F.1. Aqueous Species List

1	TcO_4^-
2	H^+
3	Fe^{2+}
4	H_2O
5	Tc^{3+}
6	Fe^{3+}
7	OH^-
8	$\text{Fe}(\text{OH})_{2(\text{aq})}$
9	$\text{Fe}(\text{OH})_{3(\text{aq})}$
10	CO_2
11	HCO_3^-
12	$\text{SiO}_{2(\text{aq})}$

Table F.2. Solid Species List

1	Natural Iron $\text{Fe}_{(\text{s})}$
2	$\text{Fe}(\text{OH})_{2(\text{s})}$
3	$\text{Fe}(\text{OH})_{3(\text{s})}$
4	$\text{Tc}_3\text{O}_{4(\text{s})}$
5	Glass (SiO_2)
6	Quartz (SiO_2)
7	Tc waste (TcO_4^-)

Table F.3. Equilibrium Aqueous Reactions

1	$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$
2	$\text{CO}_2 + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-$
3	$\text{Fe}^{2+} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_{2(\text{aq})} + 2\text{H}^+$
4	$\text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_{3(\text{aq})} + 3\text{H}^+$

Table F.4. Dissolution/Precipitation Reactions

1	$2\text{Fe}_{(s)} + 8\text{H}^+ + \text{TcO}_4^- = \text{Tc}^{3+} + 2\text{Fe}^{2+} + 4\text{H}_2\text{O}$
2	$\text{Fe}(\text{OH})_{2(s)} + 2\text{H}^+ = \text{Fe}^{2+} + 2\text{H}_2\text{O}$
3	$\text{Fe}(\text{OH})_{3(s)} + 3\text{H}^+ = \text{Fe}^{3+} + 3\text{H}_2\text{O}$
4	$\text{Tc}_3\text{O}_{4(s)} + 8\text{H}^+ + \text{Fe}^{3+} = 3\text{Tc}^{3+} + \text{Fe}^{2+} + 4\text{H}_2\text{O}$
5	$\text{Glass (SiO}_{2(s)}) = \text{SiO}_{2(aq)}$
6	$\text{Quartz} = \text{SiO}_{2(aq)}$
7	$\text{Tc Waste} = \text{TcO}_4^-$

Figure F.2 Simulated Profiles of $\text{CO}_2(\text{aq})$ by AREST-CT and CIRF.A

Figure F.3 Simulated HCO_3^- Concentrations From AREST-CT and CIRF.A

Figure F.4. TcO_4^- Profiles From AREST-CT and CIRF.A

Figure F.5. Tc^{3+} Profiles From AREST-CT and CIRF.A

Figure F.6. Comparison of the Amount of $Tc_3O_4(s)$ Precipitated in Volume Fraction from the AREST-CT and CIRF.A Codes

Figure F.7. Calculated Profiles of $Fe(s)$ from AREST-CT and CIRF.A

Figure F.8. Profiles of Tc Concentration in the Waste Glass

Figure F.9. Profiles of Glass Remaining After 5166 Years

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