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TOUGHREACT Version 2.0: A simulator for subsurface reactive transport under non-isothermal multiphase flow conditions

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ABSTRACT

TOUGHREACT is a numerical simulation program for chemically reactive non-isothermal flows of multiphase fluids in porous and fractured media, and was developed by introducing reactive chemistry into the multiphase fluid and heat flow simulator TOUGH2 V2. The first version of TOUGHREACT was released to the public through the U.S. Department of Energy's Energy Science and Technology Software Center (ESTSC) in August 2004. It is among the most frequently requested of ESTSC's codes. The code has been widely used for studies in CO_2 geological sequestration, nuclear waste isolation, geothermal energy development, environmental remediation, and increasingly for petroleum applications. Over the past several years, many new capabilities have been developed, which were incorporated into Version 2 of TOUGHREACT. Major additions and improvements in Version 2 are discussed here, and two application examples are presented: (1) long-term fate of injected CO_2 in a storage reservoir and (2) biogeochemical cycling of metals in mining-impacted lake sediments.

1. Introduction

TOUGHREACT is a numerical simulation program for chemically reactive nonisothermal flows of multiphase fluids in porous and fractured media (Xu and Pruess, 2001; Spycher et al., 2003; Sonnenthal et al., 2005; Xu et al., 2006; Xu, 2008; Zhang et al., 2008; Zheng et al., 2009). The program was written in Fortran 77 and developed by introducing reactive chemistry into the multiphase fluid and heat flow simulator TOUGH2 (Pruess, 2004). The program can be applied to one-, two- or three-dimensional porous and fractured media with physical and chemical heterogeneity. The code can accommodate any number of chemical species present in liquid, gas, and solid phases. A variety of subsurface thermal, physical, chemical, and biological processes are considered under a wide range of conditions of pressure, temperature, water saturation, ionic strength, and pH and Eh.

Processes for fluid flow and heat transport are the same as in the original TOUGH2. Transport of aqueous and gaseous species by advection and molecular diffusion is considered in both liquid (aqueous) and gas phases. Depending on computer memory and CPU performance, any number of chemical species in the liquid, gas, and solid phases can be accommodated. In the 2004 version (Version 1.0) of TOUGHREACT, aqueous complexation, acid-base, redox, gas dissolution/exsolution, and single-site cation exchange were considered under the local equilibrium assumption. Mineral dissolution and precipitation could proceed either subject to local equilibrium or kinetic conditions.

Over the past several years, many new capabilities have been developed within different research projects at Lawrence Berkeley National Laboratory. We have incorporated these new capabilities into Version 2.0 of TOUGHREACT. Major additions and improvements in Version 2.0 include:

- intra-aqueous reaction kinetics and biodegradation;
- surface complexation models including double layer;
- multi-site cation exchange;
- improvements on reactive surface area algorithm for mineral–water reactions, and fugacity coefficient corrections for gas–water reactions;
- improvements on mineral solid solution model that is an ideal model and only available for minerals reacting under kinetic constraints;
- improvements in coupling and mass balances between the chemistry and physics parts, including changes in rock and fluid properties due to reactions, and accounting for CO_2 fixed as carbonates in the flow simulation (for using ECO2N module; Pruess and Spycher, 2007);
- improvement on functionalities such as printouts of mineral reaction rates, and aqueous component and species concentrations in different user-selectable units; and
- improvements in computational efficiency.

TOUGHREACT V2.0 is written in FORTRAN 77 with some Fortran-90 extensions. It has been tested on various computer

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platforms, including Microsoft Windows- and Linux-based PCs, Apple Macintosh G4 and G5, and Intel-based computers. An effort was made for the TOUGHREACT source code to comply with the ANSIX3.9-1978 (FORTRAN 77) standard, and on most machines the code should compile using Fortran 95, Fortran-90, and some Fortran 77 compilers, and run without modification. TOUGHREACT (like TOUGH2 V2) requires 64-bit arithmetic (eight byte word length for floating point numbers) for successful execution; the code is intrinsically double-precision, to achieve 64-bit arithmetic on the commonly used 32-bit processors. The computer memory required by TOUGHREACT depends on the problem size such as numbers of grid blocks, aqueous and gaseous species, and minerals. Array dimensions are set in parameter statements in the INCLUDE files.

The correct implementation, setup, problem formulation, and interpretation of the results of TOUGHREACT requires knowledge of the basic equations of multiphase non-isothermal fluid flow and transport in geologic media, and a basic understanding of the numerical solution of the equations that are used to describe these processes. In addition, the formulation of the geochemical problem requires familiarity with geochemical modeling and an in-depth understanding of the system that is being modeled and of the data used for input to the model. The model boundary conditions, time step length, convergence criteria, and grid properties are crucial elements for a realistic and accurate solution to a problem.

We first present the general formulation for solving flow, transport, and reaction equations. To illustrate new features and applicability of TOUGHREACT Version 2, we then present two applications examples.

2. Mathematical formulation

TOUGHREACT uses a sequential iteration approach similar to Yeh and Tripathi (1991).

After solution of the flow equations, the fluid velocities and phase saturations are used for chemical transport simulation. The chemical transport is solved on a component-by-component basis. The resulting concentrations obtained from solving transport equations are substituted into the chemical reaction model. The system of mixed equilibrium-kinetic chemical reaction equations is solved on a grid block by grid block basis by Newton–Raphson iteration. Optionally, the chemical transport and reactions are solved iteratively until convergence. An automatic time stepping scheme is implemented in TOUGHREACT, which includes an option to recognize “quasi-stationary states” (QSS; Lichtner, 1988) and perform a “large” time step towards the end of a QSS.

2.1. Solution of flow and transport equations

The numerical solution of multi-phase fluid and heat flow proceeds as in TOUGH2. Space discretization is made by means of integral finite differences (IFD; Narasimhan and Witherspoon, 1976). Because chemical transport equations (derived from mass conservation) have the same structure as fluid and heat flow equations, the transport equations can be solved by the same numerical method. The basic mass—(for water, air, and chemical components) and energy—(for heat) balance equations are written in an integral form for an arbitrary domain with a volume of V_n

$$V_n \frac{\Delta M_n}{\Delta t} = \sum_m A_{nm} F_{nm} + V_n q_n \tag{1}$$

where subscript n labels a grid block, subscript m labels grid blocks connected to the grid block n, Δt is the time step size, and M_n is the average mass or energy density in the grid block n. Surface integrals are approximated as a discrete sum of averages over surface segments A_{nm}, F_{nm} is the average flux (of mass or energy) over the surface segment A_{nm} between volume elements n and m, and q_n is the average source/sink rate in the grid block n per unit volume. Time is discretized fully implicitly as a first-order finite difference to achieve an unconditional stability. More detail on the discretization approach and the definition of the geometric parameters are given in Xu and Pruess (2001) and Pruess (2004). The IFD method gives a flexible discretization for geologic media that allows the use of irregular unstructured grids, which is well suited for simulation of flow, transport, and fluid–rock interaction in multi-region heterogeneous and fractured rock systems. For systems with regular grids, an IFD is equivalent to conventional finite differences.

The time discretization of fluid and heat flow equations results in a set of coupled non-linear algebraic equations for the unknown thermodynamic state variables in all grid blocks. These equations are solved by Newton–Raphson iteration as implemented in the original TOUGH2 simulator (Pruess, 2004). The set of coupled linear equations arising at each iteration step is solved iteratively by means of preconditioned conjugate gradient methods.

2.2. Solution of chemical system

The equations for the chemical system are based on mass-balance in terms of primary (basis) species. In contrast to an aqueous equilibrium, species involved in kinetic reactions, such as redox couples, are independent and must be considered as primary species (Steefel and MacQuarrie, 1996). For example, for the reaction

$$\mathrm{HS^- + 2O_2(aq) = SO_4^{2-} + H^+} \tag{2}$$

under kinetic conditions, both $\mathrm{HS^-}$ and $\mathrm{SO_4^{2-}}$ must be placed in the primary species list. Thus, all redox reactions making use of these species must be decoupled in the input of the thermodynamic database.

Details on the formulation for solving the mixed equilibrium-kinetics system of equations are given in Xu (2008). Here, we present the final Jacobian equations only. By denoting residuals of mass-balance of each component j as F_j^c (which are zero in the limit of convergence), we have

$$\begin{aligned} F_j^c = {} & (c_j - c_j^0) \quad \text{primary species} \\ & + \sum_{k=1}^{N_x} v_{kj}(c_k - c_k^0) \quad \text{equilibrium aqueous complexes} \\ & + \sum_{m=1}^{N_p} v_{mj}(c_m - c_m^0) \quad \text{equilibrium minerals} \\ & - \sum_{n=1}^{N_q} v_{nj} r_n \Delta t \quad \text{kinetic minerals} \\ & - \sum_{l=1}^{N_a} v_{lj} r_l \Delta t \quad \text{kinetics among primary species} \\ = {} & 0 \quad j = 1 \ldots N_c \end{aligned} \tag{3}$$

where superscript 0 represents time zero; Δt is the time step; c are concentrations; subscripts j, k, m, and n are the indices of primary species, aqueous complexes, minerals at equilibrium, and minerals under kinetic constraints, respectively; N_c, N_x, N_p, and N_q are the number of corresponding species and minerals; v_{kj}, v_{mj}, and v_{nj} are stoichiometric coefficients of the primary species in the aqueous complexes, equilibrium, and kinetic minerals, respectively; r_n is the kinetic rate of mineral dissolution and precipitation (positive for dissolution and negative for precipitation-units used here are moles of mineral per kilogram of water per time), for which a general multi-mechanism rate law was used (see next section and Appendix A); l is the aqueous kinetic reaction (including biodegradation) index, N_a is