Multiphase fluid flow and subsequent geochemical transport in variably saturated fractured rocks: 1. Approaches

Tianfu Xu and Karsten Pruess

Earth Sciences Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720

ABSTRACT. Reactive fluid flow and geochemical transport in unsaturated fractured rocks has received increasing attention for studies of contaminant transport, groundwater quality, waste disposal, acid mine drainage remediation, mineral deposits, sedimentary diagenesis, and fluid-rock interactions in hydrothermal systems. This paper presents methods for modeling geochemical systems that emphasize: (1) involvement of the gas phase in addition to liquid and solid phases in fluid flow, mass transport and chemical reactions, (2) treatment of physically and chemically heterogeneous and fractured rocks, (3) the effect of heat on fluid flow and reaction properties and processes, and (4) the kinetics of fluid-rock interaction. The physical and chemical process model is embodied in a system of partial differential equations for flow and transport, coupled to algebraic equations and ordinary differential equations for chemical interactions. For numerical solution, the continuum equations are discretized in space and time. Space discretization is based on a flexible integral finite difference approach that can use irregular gridding to model geologic structure; time is discretized fully implicitly as a first-order finite difference. Heterogeneous and fractured media are treated with a general multiple interacting continua method that includes double-porosity, dual-permeability, and multi-region models as special cases. A sequential iteration approach is used to treat the coupling between fluid flow and mass transport on the one hand, chemical reactions on

the other. Applications of the methods developed here to variably saturated geochemical systems are presented in a companion paper (part 2, this issue).

INTRODUCTION

Reactive fluid flow and geochemical transport in unsaturated fractured rocks has received increasing attention for studies of contaminant transport, groundwater quality, waste disposal, acid mine drainage remediation, mineral deposits, sedimentary diagenesis, and fluid-rock interactions in hydrothermal systems. Examples include supergene copper enrichment in the Atacama Desert, Northern Chile (Alpers and Brimhall, 1988), hydrothermal alteration at a potential high-level nuclear waste repository in volcanic tuff rock formations at Yucca Mountain, Nevada (Sonnenthal and others, 1998), and contamination by volatile organic compounds in unsaturated fractured basalts at the Idaho National Engineering and Environmental Laboratory (Sorenson, Wylie, and Wood, 1996).

Numerical simulation is a powerful tool for understanding and predicting the complex interplay of physical and chemical processes in geologic media. Coupled models for mass transport and chemical reactions in subsurface systems have been presented by a number of investigators (Ortoleva, Merino, and Chadam, 1987; Lichtner, 1988; Ague and Brimhall, 1989; Liu and Narasimhan 1989; Engesgaard and Kipp, 1992; Nienhuis, Appelo, and Willemsen, 1991; Yeh and Tripathi, 1991; Simunek and Suares, 1994; Steefel and Lasaga, 1994; Walter and others 1994; White, 1995; Lichtner, 1996; Steefel and MacQuarrie, 1996; Viswanathan, 1996; Sun and others, 1998; Bolton, Lasaga, and Rye, 1999; and Xu and others, 1999). A detailed summary of subsurface hydrogeochemical processes and numerical models was given by Raffensperger (1996).

Two major approaches have been used to couple multi-species transport and chemistry: (1) direct substitution approach (DSA), which substitutes the chemical reaction equations directly into the transport equations; and (2) sequential iteration approach (SIA), which solves the transport and the reaction equations separately in a sequential manner with an iterative procedure. Detailed discussions of numerical approaches for modeling reactive chemical transport can be found in Yeh and Tripathi (1989), Lichtner (1996), and Steefel and MacQuarrie (1996).

Some of the most difficult aspects of subsurface reactive transport in unsaturated fractured rocks include: (1) involvement of a gas phase in addition to liquid and solid phases in the fluid flow, chemical transport and reaction, (2) treatment of such phenomena in fractured rocks, (3) the effect of heat on fluid flow and reaction properties and processes, and (4) the kinetics of fluid-rock chemical interaction. These difficult aspects have been partly solved by a number of investigators. Steefel and Lasaga (1994) presented a model coupling water flow, solute and heat transport and chemical reactions, in which mineral dissolution and precipitation progress by way of kinetic reactions. The model has been applied to study water-rock interaction in weathering processes and hydrothermal convection systems. Simunek and Suares (1994) have developed a two-dimensional finite element model, UNSATCHEM-2D, for simulating the major ion equilibrium and kinetic nonequilibrium chemistry in variably saturated soils. The code solves the coupled solute and heat transport together with CO_2 gas diffusive transport. White (1995) presented a multiphase non-isothermal reactive transport model with chemical equilibrium assumption and applications to mineral alteration in hydrothermal systems. White's model employs a fully coupled approach where all flow, transport, and reaction equations are solved

simultaneously. Lichtner (1996) also presented a multiphase non-isothermal reactive transport model with chemical equilibrium and kinetics. This model has been applied to various problems such as pyrite oxidation and hydrothermal systems. Recently, Bolton, Lasaga, and Rye (1999) presented a model for long-term flow/chemistry feedback in a porous medium with heterogenous permeability. They examined the dynamics of fluid flow evolution for several geologically relevant permeability distributions under kinetic control of quartz dissolution and precipitation.

Here we present a comprehensive modeling approach and numerical methods for non-isothermal multiphase fluid flow and geochemical transport. These have been implemented in a numerical simulator TOUGHREACT, with novel capabilities for modeling complex geochemical system. In our model, the gas phase is active for fluid flow, chemical transport and reaction. Special techniques are presented for reactive flow and transport in fractured rocks. The integral finite difference (IFD) method (Narasimhan and Witherspoon, 1976) is employed for space discretization. The IFD permits irregular grids for representing geologic features such as fractures, faults, and lithologic discontinuities, and no reference to a global system of coordinates is needed. The use of IFD allows us to deal with classical dual-continua (Warren and Root, 1963) and multiple interacting continua (MINC; Pruess and Narasimhan, 1985) approaches for fractured rocks. The effects of heat are considered, which include water-vapor phase change and temperature-dependence of thermophysical properties such as fluid density and viscosity, and geochemical properties such as thermodynamic and kinetic data. The transient temperature distribution is solved from an energy conservation equation which is fully coupled with the water and air mass conservation equations. Chemical reactions are

treated through a sequential solution approach in an iterative or non-iterative manner. Mineral dissolution/precipitation can proceed either subject to local equilibrium or kinetic constraints.

We first give a brief description of our physical and chemical process model, assumptions, and numerical method. Then we present the treatment of gases and fractured rocks. In the second of this two-part paper (this issue), our model is applied to investigate two important types of geochemical systems.

MODEL DESCRIPTION

Main features. -Our model for fluid flow and geochemical transport has three important features: (1) the gas phase is active for multiphase fluid flow, mass transport and chemical reactions, (2) we consider not only porous media, but also reactive fluid flow and transport in fractured rocks, (3) the effects of heat are considered, including heat-driven fluid flow, and temperature-dependent thermophysical and geochemical properties (such as fluid density and viscosity, and thermodynamic and kinetic data). In unsaturated fractured media, fractures may be dominantly occupied by the gas phase, while the matrix pores may have a large water saturation. In hydrothermal convection systems and nuclear waste disposal sites, heat-driven vaporizing fluid flow is strongly coupled with gas geochemistry (such as CO_2), and is complicated by fracture-matrix interaction. An example is presented in the second of this two-part paper (Xu and others, this issue), which examines coupled thermal, hydrological, and chemical processes induced by emplacement of a strong heat source (for example, high-level nuclear waste) in unsaturated fractured rocks.

Our methods are applicable to one-, two-, or three-dimensional geologic domains with physical and chemical heterogeneity. Transport of aqueous and gaseous species by advection and molecular diffusion is considered in both liquid and gas phases. Any number of chemical species in liquid, gas and solid phases can be accommodated. Aqueous complexation, acid-base, redox, gas dissolution/exsolution, cation exchange, and surface complexation are considered under the local equilibrium assumption. Mineral dissolution and precipitation can proceed either subject to local equilibrium or kinetic conditions. Additional details on the model are given in Xu and Pruess (1998).

Governing equations. -The primary governing equations for multiphase fluid and heat flow and chemical transport have the same structure, which are derived from the principle of mass (or energy) conservation. These equations are presented in app. A. Major processes considered for non-isothermal fluid and heat flow are: (1) fluid flow in both liquid and gas phases occurs under pressure, viscous and gravity forces; (2) interactions between flowing phases are represented by characteristic curves (relative permeability and capillary pressure), (3) heat flow occurs by conduction, convection, and diffusion. More detail on multiphase fluid and heat flow has been given by Pruess (1987, 1991). Aqueous (dissolved) species are subject to transport in the liquid phase as well as to local chemical interactions with the solid and gas phases. Transport equations are written in terms of total dissolved concentrations of chemical components which are concentrations of their basis species plus their associated aqueous secondary species (Yeh and Tripathi, 1991; Steefel and Lasaga, 1994; Walter and others, 1994; Lichtner, 1996). If kinetically-controlled reactions occur between aqueous species, then additional ordinary differential equations need to be solved to link the total concentrations of the

6

primary species with the evolving concentrations of the secondary species (Steefel and MacQuarrie, 1996). Kinetically-controlled reactions between aqueous species are not considered in our current model. Slow aqueous phase reactions are common in the case of redox reactions and will be addressed in future work. Advection and diffusion processes are considered for both the liquid and gas phases, and their coefficients are assumed to be the same for all species. The local chemical interactions in the transport equations are represented by reaction source/sink terms.

The primary governing equations must be complemented with constitutive local relationships that express all parameters as functions of fundamental thermophysical and chemical variables. Expressions for non-isothermal multiphase flow are given by Pruess (1987). The equations for chemical equilibrium are similar to those by Parkhurst, Thorstenson, and Plummer (1980), Reed (1982), Yeh and Tripathi (1991), Wolery (1992), and Steefel and Lasaga (1994), and are presented in app. B. The activity of aqueous species is equal to the product of the activity coefficient and molar concentration. Aqueous species activity coefficients are calculated from the extended Debye-Hückel equation (Helgeson and Kirkham, 1974). Activities of pure mineral phases and H_2O are assumed to be one. Gases are assumed ideal, therefore, fugacity coefficients are assumed equal to one, and fugacity is equal to partial pressure. Mass conservation in the closed chemical system is written in terms of basis species. The species distribution must be governed by the total concentrations of the components. The oxygen approach is used for formulating redox reactions which is based on attributing the oxidizing potential to the dissolved oxygen (Nordstrom and Muñoz, 1986; Wolery, 1992). In contrast to the free electron in the hypothetical electron approach (Yeh and Tripathi, 1991), oxygen can

be present and be transported in natural subsurface flow systems. Sorption processes, including cation exchange and surface complexation (by double layer model) are included in our reactive transport model. The formulation for cation exchange is similar to Appelo and Postma (1993), and for surface complexation are taken from Dzombak and Morel (1990). Further details are given in Xu and others (1997).

For kinetically-controlled mineral dissolution and precipitation, a general form of rate law (Lasaga, 1984; and Steefel and Lasaga, 1994) is used

$$r_m = sgn[\log(Q_m / K_m)]A_m\, k_m\, f(a_i)\left|1 - \left(\frac{Q_m}{K_m}\right)^\mu\right|^n \qquad (1)$$

where m is mineral index, $sgn[\log(Q_m/K_m)]$ gives the sign of the expression, positive values of r_m indicate dissolution, and negative values precipitation, A_m is the specific reactive surface area per kg H_2O, $f(a_i)$ is some function of the activities of the individual ions in solution such as H^+ and OH^-, k_m is the rate constant (moles per unit mineral surface area and unit time) which is temperature-dependent, K_m is the equilibrium constant for the mineral-water reaction written as the destruction of one mole of mineral m, and Q_m is ion activity product. The parameters μ and n are two positive numbers to be determined experimentally (usually, but not always, they are taken equal to one). The temperature-dependence of the reaction rate constant can be expressed reasonably well via an Arrhenius equation (Lasaga, 1984; and Steefel and Lasaga, 1994). Since many rate constants are reported at 25^oC, it is convenient to write the rate constant at some temperature T as

$$k = k_{25} \exp\left[\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] \qquad (2)$$

where E_a is the activation energy, k_{25} is the rate constant at 25 $^{\circ}$C, and R is gas constant.

For field-scale variably saturated geologic media, the rate law given in eq (1) must be modified to allow for saturation dependence. Following Welch, Dann, and Mehta (1990), we introduce a factor f ($0 \leq f \leq 1$) to represent effective reactive surface area at different water saturations, which can account for the effective sizes of the mineral surfaces that are actively available to react with aqueous species. Welch, Dann, and Mehta (1990) conducted laboratory pyrite oxidation experiments in porous media with different water saturation, and determined a dependence of the factor f on water saturation as given in fig. 1. Their results indicate that at a water saturation of about 0.3 almost all mineral surface is effectively contacted by water. It should be pointed out that $f(S_l)$ is a property of the medium that may vary in space and time.
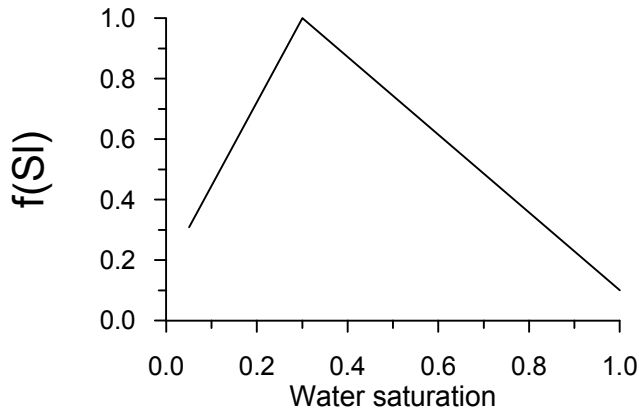
Fig. 1. Water saturation dependent factor f used for kinetic rate expression eq (1).

Active gas phase. -In the present model, gases are considered for fluid flow, chemical transport, and reaction. The gas phase is composed of non-condensible gases such as O_2, CO_2, N_2, etc. as well as water vapor. Currently we treat all chemically reactive gases in a "trace gas" approximation, and we assume that chemical reactions and accompanying changes in partial pressures do not affect overall gas and liquid flow. This is a good approximation for many geochemical systems, but under some conditions the exchange of gaseous reactants may significantly affect gas pressures and flow, requiring a fully coupled treatment (White, 1995).

The gaseous species are subject to transport in the bulk gas phase and react with aqueous species. No gas-gas and gas-solid reactions are considered. In addition to transport of aqueous species in the liquid, advective-diffusive transport of gaseous species in the gas phase is considered. Diffusion coefficients of gaseous species in geologic media are calculated from

$$D_{jg} = \tau_g \phi S_g D_{jg}^0 \qquad (3)$$

where D_{jg}^0 is the j-th gaseous species diffusion coefficient in pure gas phase (for example, according to Vargaftik (1975), $D_{O_2(g)}^0 = 2.20 \times 10^{-5}$ m^{2}s^{-1} at atmospheric pressure and 25 ^{o}C), ϕ is porosity, S_g is gas phase saturation, and τ_g is tortuosity factor of the medium that is computed from the Millington and Quirk (1961) model,

$$\tau_g = \phi^{1/3} S_g^{7/3} \tag{4}$$

Diffusion coefficients of gaseous species in the gas phase are on the order of 10^{-5} to 10^{-6} m^{2}s^{-1} and are three to four orders of magnitude larger than diffusivities of aqueous species in the liquid phase (on the order of 10^{-9} - 10^{-10} m^{2}s^{-1}). Therefore, gaseous diffusion is an important transport process in some variably saturated geologic media.

Reactions involving aqueous and gaseous species are assumed to be at equilibrium, governed by the mass-action law. For low pressures (in the range of atmospheric pressure), the gaseous species are assumed to behave like an ideal mixture, and the fugacity coefficients are assumed equal to one. At higher temperatures and pressures, such as boiling conditions in hydrothermal systems, the assumption of ideal gas and ideal mixture is not valid. In these cases, the fugacity coefficients will depend on the temperature and pressure of the system (Spycher and Reed, 1988).

Simplifying approximations. -Hydrodynamic dispersion is an important solute transport mechanism which arises from an interplay between non-uniform advection and molecular diffusion. In geologic media, velocities of fluid parcels are spatially variable due to heterogeneities on multiple scales, all the way from the pore-scale to basin-scale.

The process is often represented by a Fickian diffusion analog (convection-dispersion equation), which has fundamental flaws and limitations, as has been demonstrated in numerous studies in the hydrogeology literature of the last 20 yrs. Although field tracer tests can generally be matched with the convection-dispersion equation, such matching and associated parameters have little predictive power. There is much evidence that when a Fickian dispersion model is calibrated to field tracer data, such success does not indicate that a realistic description of in-situ solute distribution has been attained. Dispersivities are generally found to increase with space and time scale of observation (Gelhar, Welty, and Remfeldt, 1992). Observed dispersivities are only partly due to mixing and dilution in-situ; they also reflect the mixing that occurs when subsurface flow systems are observed (perturbed) and sampled, as when fluids are extracted from wells (Chesnut, 1994). It has been established that Fickian dispersion implies an unrealistically large level of mixing and dilution (Kapoor, Gelhar, and Miralles-Willem, 1997). Fickian plumes represent a probability distribution, not a distribution of solute; they strongly overestimate dilution in any particular representation of a heterogeneous medium. This can produce erroneous predictions for transport and even more unrealistic consequences for reactions that depend on concentrations in a non-linear manner. Fickian dispersion also gives rise to spurious upstream dispersion opposing the direction of advective flow. For these reasons, we are not using a Fickian model for dispersion. Instead, hydrodynamic dispersion is modeled through appropriate spatial resolution on multiple scales, using multiple continua (or multi-region) models (Pruess and Narasimhan, 1985; Gwo and others, 1996) to describe interactions between fluid regions with different velocities.

The basic idea of using a multi-region approach to model dispersion is to explicitly resolve domains with different advective velocities through appropriate spatial discretization (gridding). This approach is applicable for heterogeneous media in which regions of higher permeability form spatially-extensive correlated structures. Hydrodynamic dispersion then arises from an interplay between different advective velocities, and diffusive exchange between subdomains (Bibby, 1981). An example of a two-region model for fractured media is the double-porosity concept, in which separate overlapping continua are used to represent fractures and unfractured rock, respectively (see below). In such a system, hydrodynamic dispersion arises from advective and diffusive exchange between faster flow in the fracture continuum and slower flow (or possibly even immobile water) in the rock matrix. A more accurate representation of dispersive processes in fractured media can be achieved with the method of "multiple interacting continua" (MINC; see below), in which matrix rock is partitioned into several interacting continua that are defined based on the distance from the nearest fracture. Similar conceptualizations have been used in studies of chemical migration in soils to represent the interplay between fast advective transport in rootholes, wormholes, and cracks, with slow flow and diffusive transport in the soil matrix (Gwo and others, 1996). Lake and Hirasaki (1981) showed that in layered porous media, diffusive exchange between layers with different permeability will give rise to a broadening of the solute mixing zone that is analogous to Taylor's dispersion of flow in capillary tubes (Taylor, 1953). Harvey and Gorelick (2000) presented an analysis of macrodispersion in a heterogeneous sedimentary aquifer which does not use the Fickian model; instead, hydrodynamic dispersion arises from solute transfer between mobile and immobile

domains. Apart from the vast difference in scale, their conceptualization is analogous to the "dead end" pore model of Coats and Smith (1964).

Temporal changes in porosity and permeability due to mineral dissolution and precipitation processes can modify fluid flow. This feedback between transport and chemistry can be important (Raffensperger, 1996), but a rather large computational penalty that has to be paid if this is modeled explicitly (Xu, Pruess, and Brimhall, 1999b). We presently monitor changes in porosity during the simulation from changes in mineral volume fractions, but we neglect their effects on fluid flow. Another difficulty arises from the complex relationship between porosity and permeability. The porosity-permeability correlation in geologic media depends on a complex interplay of many factors, such as pore size distribution, pore shapes, and connectivity (Verma and Pruess, 1988), and a simple functional porosity-permeability relationship is not realistically attainable (Raffensperger, 1996). By neglecting porosity and permeability change we obtain quasi-steady flow conditions. This greatly simplifies the numerical solution and makes it possible to consider geochemistry in great detail. The changes in porosity remain small over limited time spans. For example, for the supergene copper enrichment system presented in the second of this two-part paper (this issue), simulated changes in porosity are less than 0.6 percent over a 1000-yr period (see fig. 2). Furthermore, we use Kozeny-Carman grain model based on spheres to illustrate changes in permeability due to changes in porosity (see Bolton, Lasaga, and Rye, 1999, p. 5). Kozeny-Carman equation relates the permeability k (in m^2) to the porosity (ϕ) by

$$k = \frac{R_0^2}{45}\left(\frac{\phi^3}{(1-\phi)^2}\right) \tag{5}$$

where R_0 is the initial local spherical close pack radius. Based on eq (5), the ratio of the permeability k to initial permeability k_0 can be expressed as

$$\frac{k}{k_0} = \left(\frac{\phi}{\phi_0}\right)^3\left(\frac{1-\phi_0}{1-\phi}\right)^2 \tag{6}$$

where ϕ_0 is the initial porosity. In the example presented in fig. 2 we used a ϕ_0 of 0.1. Based on the example and eq (6), we calculated permeability ratios for a number of changes in porosity $\Delta\phi$ which is listed in table 1. The table indicates that a change of porosity results in a considerable change of permeability. A less than 0.6 percent porosity change causes a less than about 20 percent permeability change. Nevertheless, changes in permeability may remain small over limited time spans such as a 1000-yr period for the example. The effects of changes in porosity and permeability on fluid flow will be fully addressed in the future works.

TABLE 1

List of changes in permeability (k/k_0) due to changes in porosity ($\Delta\phi$) based on the fig. 2 example and eq (6)

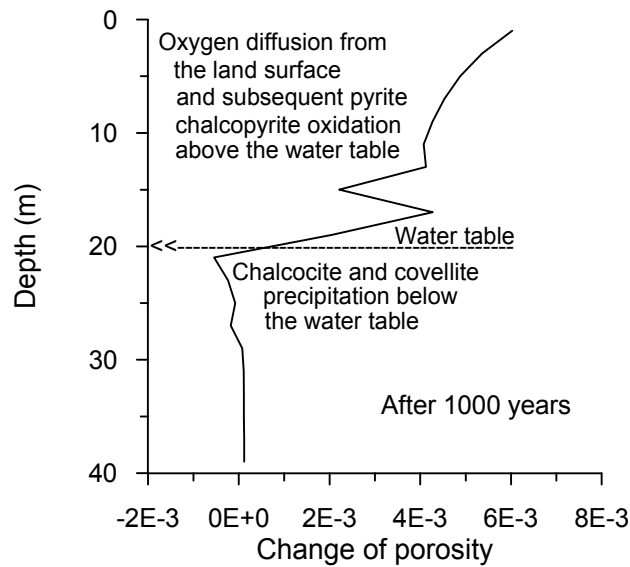| $\Delta\phi$	0.006	0.01	0.02	0.03	0.04	-0.01	-0.02	-0.03	-0.04
k/k_0	1.199	1.346	1.767	2.273	2.872	0.721	0.5	0.332	0.207

Fig. 2. Simulated changes in porosity after 1000 yrs for a one-dimensional supergene copper enrichment system, which involves oxygen diffusion from the land surface, subsequent pyrite and chalcopyrite oxidative dissolution, intense alteration of primary minerals in the unsaturated zone, and precipitation of secondary copper ore compounds. The detailed problem description is given in the second of this two-part paper (this issue).

We currently neglect deformation of the porous skeleton. Heat effects from chemical reactions are neglected in our current model, as are changes in thermophysical properties of fluid phases (such as viscosity, surface tension, and density) due to changes in chemical composition.

SOLUTION METHOD

The process model discussed above was implemented in a computer program TOUGHREACT, which is based on the framework of the non-isothermal multi-phase fluid and heat flow simulator TOUGH2 (Pruess 1991). The numerical solution of multi-phase flows in TOUGH2 employs space discretization 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 discretization approach used in the IFD method and the definition of the geometric parameters are illustrated in fig. 3. The basic mass- (for water, air, and chemical component) and energy (for heat) balance equations are written in integral form for an arbitrary domain V_n

$$V_n \frac{\Delta M_n}{\Delta t} = \sum_m A_{nm} F_{nm} + V_n q_n \tag{7}$$

where subscript n labels a grid block, subscript m labels grid blocks connected to grid block n, Δt is time step size, and M_n is the average mass or energy density in grid block n. Surface integrals are approximated as a discrete sum of averages over surface segments A_{nm}, F_{nm} is the average flux (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 grid block n per unit volume. Time is discretized fully implicitly as a first-order finite difference to achieve unconditional stability. More detail on the numerical discretization is given in Pruess and

Narasimhan (1985). The IFD method gives a flexible discretization for geologic media that allows us to use irregular grids, which is well suited for simulation of flow, transport, and fluid-rock interaction in multi-region heterogeneous and fractured rock systems (see the following section).
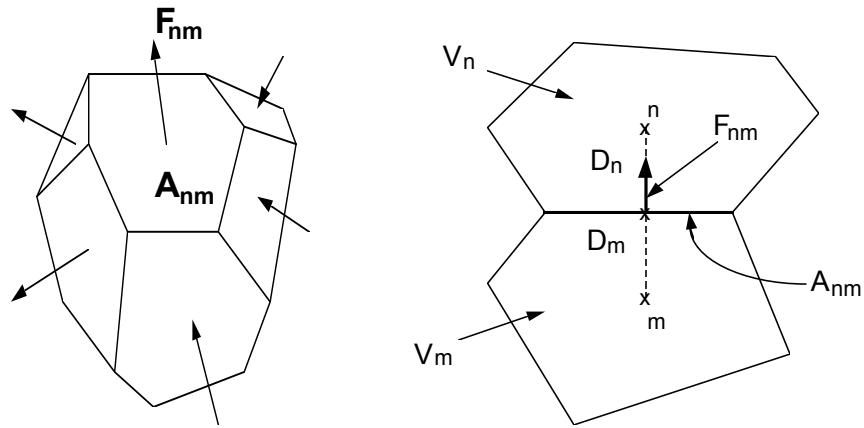

Fig. 3. Space discretization and geometry data in the integral finite difference method.

Time discretization of fluid and heat flow equations results in a set of coupled non-linear algebraic equations for the thermodynamic state variables in all grid blocks as unknowns. These are solved by Newton-Raphson iteration method as implemented in the original TOUGH2 simulator (Pruess, 1991). The set of coupled linear equations arising at each iteration step is solved either by sparse direct matrix methods or iteratively by means of preconditioned conjugate gradient methods (Moridis and Pruess, 1998).

TOUGHREACT uses a sequential iteration approach similar to Yeh and Tripathi (1991), Engesgaard and Kipp (1992), Simunek and Suares (1994), and Walter and others (1994). 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

basis. The resulting concentrations obtained from the transport are substituted into the chemical reaction model. The system of chemical reaction equations is solved on a grid-block basis by Newton-Raphson iteration, similar to Parkhurst (1980), Reed (1982), and Wolery (1992). The chemical transport and reactions are iteratively solved until convergence. The reaction time step Δt_r is very important for convergence of the system of reaction equations. During a transport time step Δt_t, depending on the convergence of the reaction equations, multiple steps with $\sum \Delta t_r = \Delta t_t$, can be used. The Δt_r pattern may be different from grid block to grid block depending on the convergence behavior of the local chemical reaction system. For example, at the redox front a small Δt_r may be required. 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 toward the end of a QSS.

As an alternative to the fully iterative sequential approach (SIA), a sequential non-iterative approach (SNIA) may be used, in which the sequence of transport and reaction equation is solved only once (Walter and other, 1994; Steefel and MacQuarrie, 1996; and Xu and other, 1999). Xu and others (1999) analyzed the accuracy of SIA and SNIA using several test cases. They concluded that the accuracy of SNIA depends mainly on the Courant number, which is defined as $C = v\Delta t/\Delta x$, where v is fluid velocity and Δx is grid spacing. For small Courant numbers, satisfying the stability condition $C \leq 1$, the differences between SNIA and SIA are generally small. The accuracy of SNIA also depends on the type of chemical process. Therefore, the applicability of the decoupling of chemical reactions from transport will depend on time and space discretization parameters, the nature of the chemical reactions, and the desired accuracy (Xu and others,

1999). When SNIA is used, the Courant number condition $C \leq 1$ is automatically enforced during the simulation.

When analyzing water flow through partially saturated porous media, gas phase advection can often be disregarded by assuming the gas phase to be immobile (Richards, 1931; de Marsily, 1986). This means that for the purpose of solving for water flow, the entire gas phase is at the same pressure (usually the atmospheric pressure). TOUGHREACT allows a choice of considering saturated-unsaturated liquid phase flow in which case only molecular diffusion can be considered for gaseous species transport. Alternatively, the full non-isothermal multi-phase flow equations (liquid, gas, and heat) may be solved. To test the immobile air approach under ambient conditions, Xu and others (2000a) performed numerical simulation experiments on pyrite oxidation in a variably saturated porous medium. They found that under ambient conditions the effects of partial pressure reduction due to oxygen consumption on the fluid flow is not significant, and oxygen diffusion is the dominant gas phase transport process. However, when fluid flow and chemical reactions are strongly coupled, for example, in boiling hydrothermal reservoirs, gas phase advection could be essential (White, 1995).

The numerical model was first developed on a PC and then tested on VAX and UNIX computer systems. Later the simulator was ported to the high-performance Cray T3E, and a parallelized version was developed, resulting in significant improvements of computing efficiency.

TREATMENT OF FRACTURED ROCK

For chemical transport in variably saturated fractured rocks, global fluid flow and transport of aqueous and gaseous species occurs primarily through a network of interconnected fractures, while chemical species may penetrate into tight matrix blocks primarily through relatively slow diffusive transport in gas and liquid phases. Methods developed for fluid flow in fractured rock can be applied to geochemical transport (Warren and Root, 1963; Pruess, 1983; Pruess and Narasimhan, 1985; Tsang and Neretnieks, 1998; Liu, Doughty, and Bodvarsson, 1998).

Effective continuum model. -The simplest approach for flow in fractured porous media is the effective continuum model (ECM). The role of individual fractures is considered to be similar to that of individual pores in porous media. In each computational grid block, ECM assumes that fractures and matrix have the same state valuables such as pressure, temperature, and chemical concentrations. The validity of this approximation depends on the relative time scales for global flow in the reservoir, and local exchange and equilibriation between fractures and matrix rock (Pruess, Wang, and Tsang, 1990).

Double porosity and dual permeability. -Another commonly used method for fractured media is the double porosity approach, in which fractures and matrix are treated as two separate interacting continua. Fig. 4 illustrates the classical dual-continua concept for modeling flow in fractured-porous media as first developed by Barenblatt, Zheltov, and Kochina (1960), and Warren and Root (1963). Matrix blocks of low permeability are embedded in a network of inter-connected fractures. Global flow occurs only through the

fracture system, which is described as an effective porous continuum. Rock matrix and fractures may exchange fluid locally by means of "interporosity flow," which is driven by the difference in pressures between matrix and fractures. Warren and Root approximated the interporosity fluid flow as being "quasi-steady," with rate of matrix-fracture interflow proportional to the difference in local average pressures (or temperatures, species concentrations). As an extension to the double-porosity approach, global flow may be considered in both fracture and matrix continua, which is known as dual-permeability approach.
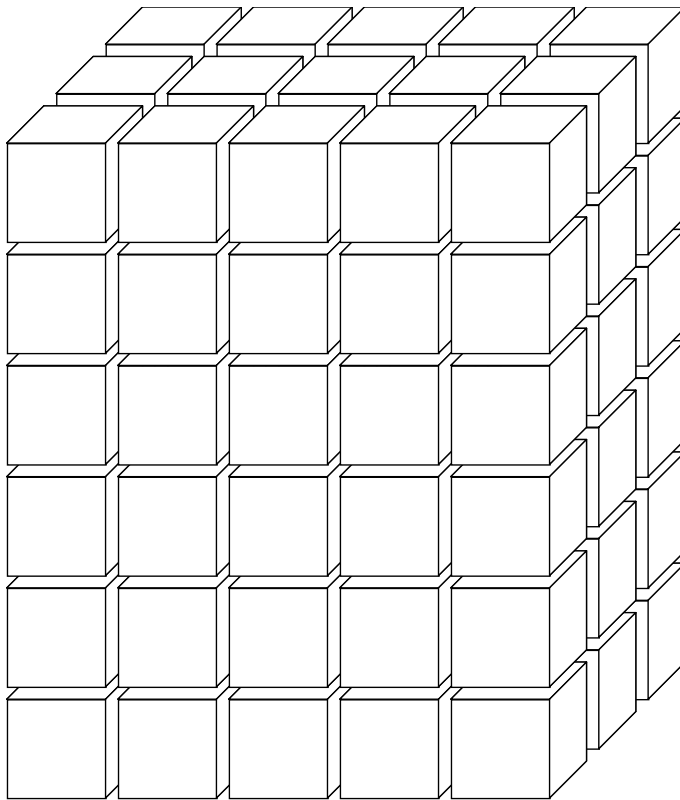
Fig. 4. Idealized "double porosity" model of a fractured porous medium.

The quasi-steady approximation is applicable to isothermal single phase flow of fluids with small compressibility, where pressure diffusivities are large, so that pressure changes in the fractures penetrate quickly all the way into the matrix blocks. However, for multiphase fluid flow and chemical transport, the transient periods for interporosity fluid flow and chemical transport can be very long (tens of years or more), so that the quasi-steady approximation for interporosity flow may become poor.

Multiple interacting continua. -In order to describe accurately transient interporosity flow and transport, it is necessary to resolve the driving pressure, temperature and chemical concentration gradients at the fracture-matrix interface. This is accomplished with the method of "multiple interacting continua" (MINC), as presented by Pruess (1983) and Pruess and Narasimhan (1985) for multiphase fluid and heat flow in fractured media. In this model, the resolution of gradients near the fracture-matrix interface is achieved by appropriate subgridding of the matrix blocks, as shown in fig. 5. The MINC concept is based on the notion that changes in fluid pressures, temperatures, phase compositions, and chemical concentrations will propagate rapidly through the fracture system, while invading the tight matrix blocks only slowly. Therefore, changes in matrix conditions will (locally) be controlled by the distance from the fractures. Fluid and heat flow and chemical transport between fractures and the matrix blocks can then be modeled by means of one-dimensional strings of nested grid blocks, as shown in fig. 5.
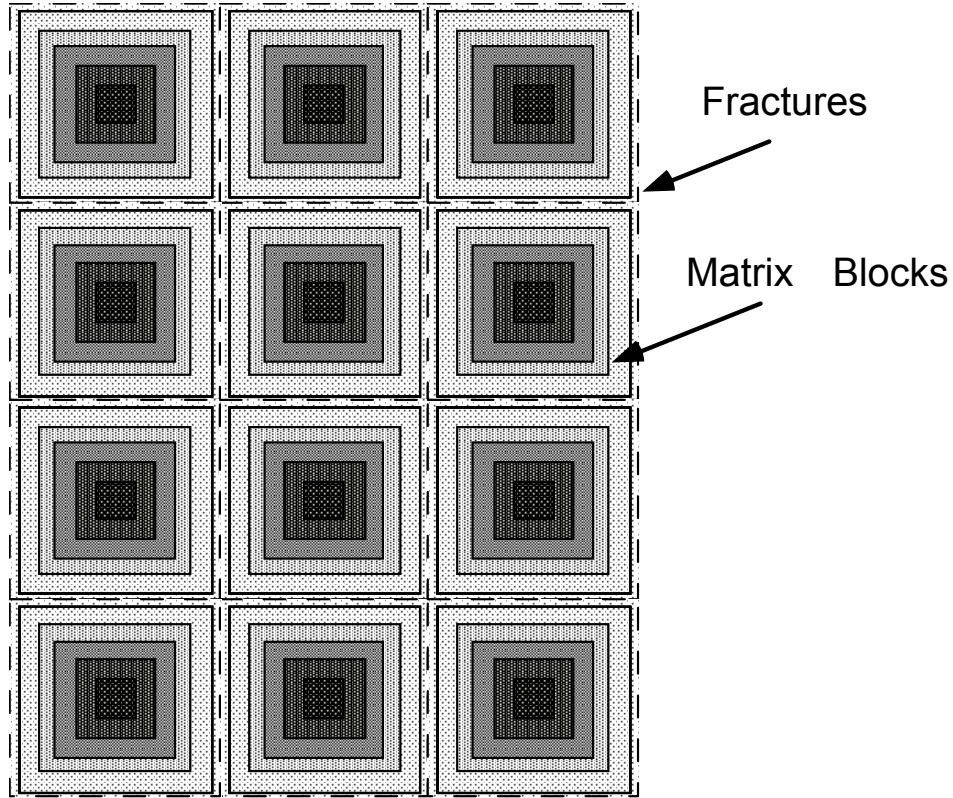
Fig. 5. Subgridding in the method of "multiple interacting continua" (MINC).

In general it is not necessary to consider explicitly subgrids in all the matrix blocks separately. Within a certain subdomain (corresponding to a finite difference grid block), all fractures will be lumped into continuum # 1, all matrix material within a certain distance from the fractures will be lumped into continuum # 2, matrix material at larger distance becomes continuum # 3, and so on. Quantitatively, the subgridding is specified by means of a set of volume fractions VOL(j), j = 1, ..., J, into which the "primary" porous medium grid blocks are partitioned. The information on fracturing (spacing, number of sets, shape of matrix blocks) required for this is provided by a "proximity function" PROX(x) which expresses, for a given domain V_0 , the total fraction

of matrix material within a distance x from the fractures (Pruess and Karasaki, 1982). If only two continua are specified (one for fractures, one for matrix), the MINC approach reduces to the conventional double-porosity or dual permeability methods.

The MINC method is similar to the "shrinking core" model as used for sulfide mineral oxidation by Wunderly and others (1996). In this model, it is assumed that the reactive minerals form spherical particles, which are analogous to rock matrix in fractured media. As the reaction between oxygen and sulfide minerals within the particles progresses the radius of the unreacted core will gradully decrease, while the thickness of the oxidized shell increases. Thus the oxygen flux from the outside of the particle surface to the unreacted core decreases with time.

The MINC-method as implemented in TOUGHREACT can also describe global matrix-matrix fluid flow and chemical transport. Fig. 6 shows the most general approach, often referred to as "dual permeability," in which global flow occurs in both fracture and matrix continua.
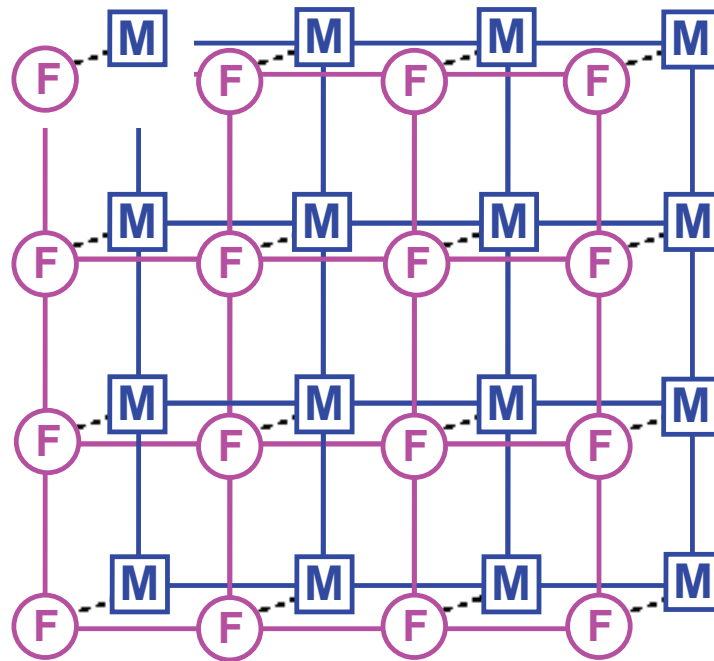
Fig. 6. Flow connections in the "dual permeability" model. Global flow occurs between both fracture (F) and matrix (M) grid blocks. In addition there is F-M interporosity flow.

In the foregoing discussion, an idealized fractured medium with three perpendicular sets of infinite, plane, parallel fractures of equal aperture and spacing was assumed for illustrative purposes. However, any fracture geometry can be considered by the MINC method. For any given fractured medium, selection of the most appropriate gridding scheme must be based on a careful consideration of the physical, chemical, and geometric conditions of flow, transport, and fluid-rock interaction. The MINC approach is not applicable to systems in which fracturing is so sparse that the fractures cannot be approximated as a continuum. The MINC method allows very general connectivity between grid blocks, corresponding to different continua. Multi-region models, considering regions of immobile water, and regions with different pore sizes and water velocities, are contained in the MINC method as special cases (Gwo and others, 1996).

Compared to classical dual-continua approaches, the MINC approach can more accurately describe reactive flow and transport in fractured rocks. Nevertheless, this approach has larger computational requirements due to the further detailed discretization of a rock matrix. As computers become increasingly powerful (such as high-performance massively parallel machines), simulation of large-scale problems (such as 10^5 grid blocks) over reasonable time spans using the MINC method is possible.

VERIFICATION

The accuracy of numerical approximations for multiphase fluid and heat flow has been discussed by Pruess (1987, 1991) and Pruess and others (1996). A broad range of reactive geochemical transport processes was verified against available analytical solutions, other numerical simulators, and field data by Xu and Pruess (1998), and Xu, Pruess, and Brimhall (1999a). As an example, we note a simulation of water quality in the Aquia aquifer (Maryland), where original saline water is flushed by fresh water recharge (Chapelle and Knobel, 1983). The water quality in this aquifer shows zonal bands with changes in concentrations of major cations that have been attributed to cation exchange and calcite dissolution/precipitation. Simulation results obtained by Xu and Pruess (1998) agree quite well with the field concentration observations. Full details on verification and validation for reactive transport are given in Xu and Pruess (1998) and in Xu, Pruess, and Brimhall (1999a).

CONCLUSIONS

We have presented a comprehensive methodology for non-isothermal multiphase fluid flow and subsequent geochemical transport. Embodied, in the computer program TOUGHREACT, this methodology employs a sequential solution approach. The simulation techniques presented here are applicable to reactive geochemical transport in variably saturated fracture rocks. The gas phase is considered active for multiphase fluid flow, species transport, and chemical reactions. Our model is applicable to porous media as well as to fractured rocks. An integral finite difference (IFD) technique is employed for space discretization. The IFD can deal with irregular grids, does not require reference to a global system of coordinates, and includes classical dual-continua, multiple interacting continua, and multi-region models for heterogeneous and fractured rocks as special cases. Non-isothermal effects are considered, including water-vapor phase change and air partitioning between the liquid and gas phases, temperature-dependence of thermophysical properties such as phase density and viscosity, and chemical properties such as thermodynamic and kinetic parameters.

Chemical reactions considered under the local equilibrium assumption include aqueous complexation, acid-base, redox, gas dissolution/exsolution, cation exchange, and surface complexation. Mineral dissolution/precipitation can proceed either subject to local equilibrium or kinetic conditions. In the second of this two-part paper (this issue), our model is applied to explore two important types of geochemical systems, (1) supergene copper enrichment in unsaturated-saturated media where oxygen gas diffusion from the land surface through fractured rock plays an important role in primary mineral

28

alteration and secondary mineral deposition, and (2) coupled thermal, hydrological, and chemical processes induced by emplacement of a strong heat source in unsaturated fractured volcanic tuffs to represent a high-level nuclear waste repository. The latter system features strong fracture-matrix interactions, CO_2 degassing, and heat-driven vaporizing fluid flow, and their effects on mineral alteration.

APPENDIX A

The governing equations for multiphase fluid and heat flow, and chemical transport

The governing equations for multiphase fluid and heat flow and chemical transport are derived from the principle of mass (or energy) conservation and have the same structure, regardless of the nature and number of fluid phases and chemical species present. Table A1 summarizes these equations, and table A2 gives the meaning of symbols used.

Primary governing equations for fluid and heat flow, and chemical transport. Symbol

meanings are given in table A2

General governing equations: $\dfrac{\partial M_\kappa}{\partial t} = -\nabla F_\kappa + q_\kappa$

Water: $M_w = \phi(S_l\rho_l X_{wl} + S_g\rho_g X_{wg})$ $F_w = X_{wl}\rho_l\mathbf{u}_l + X_{wg}\rho_g\mathbf{u}_g$

$q_w = q_{wl} + q_{wg}$

Air: $M_a = \phi(S_l\rho_l X_{al} + S_g\rho_g X_{ag})$ $F_a = X_{al}\rho_l\mathbf{u}_l + X_{ag}\rho_g\mathbf{u}_g$

$q_a = q_{al} + q_{ag}$

Heat: $M_h = \phi(S_l\rho_l U_l + S_g\rho_g U_g) + (1-\phi)\rho_s U_s$ $F_h = \sum\limits_{\beta=l,g} h_\beta\rho_\beta\mathbf{u}_\beta - \lambda\nabla T$ q_h

where $\mathbf{u}_\beta = -k\dfrac{k_{r\beta}}{\mu_\beta}\left(\nabla P_\beta - \rho_\beta\mathbf{g}\right)$ $\beta = l,g$ (Darcy's Law)

Chemical components in the liquid phase ($j = 1,2,...,N_l$):

$M_j = \phi S_l C_{jl}$ $F_j = \mathbf{u}_l C_{jl} - D_l\nabla C_{jl}$ $q_j = q_{jl} + q_{js} + q_{jg}$

Chemical components in the gas phase ($k = 1,2,...,N_g$):

$M_k = \phi S_l C_{kl}$ $F_k = \mathbf{u}_{gl} C_{kg} - D_g\nabla C_{kg}$ $q_k = -q_{jg}$

where $C_{kg} = f_{kg} / RT$ (gas law)

Symbols used in table A1

C	total component concentration, mol l^{-1}	ρ	density , kg m^{-3}
D	diffusion coefficient, m^{2}s^{-1}	μ	viscosity, kg m^{-1}s^{-1}
F	mass flux, kg m^{-2}s^{-1} (*)	λ	heat conductivity, W m^{-1}K^{-1}
f	gaseous species partial pressure, bar		
k	permeability, m^2		
k$_r$	relative permeability	Subscripts:	
g	gravitational acceleration, m s^{-2}	a	air
M	mass or energy accumulation, kg m^{-3} or Jm^{-3}	g	gas phase
N	number of chemical components	h	heat
p	pressure, Pa	j	chemical component in liquid phase
q	source/sink	k	chemical component in gas phase
S	saturation	l	liquid phase
T	temperature, ^{o}C	s	solid phase
U	internal energy, J kg^{-1}	w	water
u	Darcy velocity, m s^{-1}	κ	governing equation index
X	mass fraction	β	phase index
ϕ	porosity		

(*) For chemical transport and reaction calculations, molar units are used.

APPENDIX B

The governing equations for chemical equilibrium

The governing equations for chemical equilibrium are shown in table B1. To help understand the formulation on chemical reactions, we selected a simple illustrative example in table B1; in fact, our model is applicable to any geochemical system. All reactions in table B1 are written in dissociation forms, which are convenient for mathematical modeling.

TABLE B1

List of equations governing chemical equilibrium (illustrated by specific examples; in fact the model is valid for general geochemistry). Symbol meanings are given in table B2

General dissociation reactions	$S_i^s = \sum\limits_{j=1}^{N_C} v_{ij} S_j^p$
General mass action equations:	$K_i a_{S_i^s} = \sum\limits_{j}^{N_C} (a_{S_j^p})^{v_{ij}}$
Aqueous dissociation: $HCO_3^- = CO_3^{2-} + H^+$	$K_{HCO_3^-} \gamma_{HCO_3^-} c_{HCO_3^-} = \gamma_{CO_3^{2-}} c_{CO_3^{2-}} \gamma_{H^+} c_{H^+}$
Mineral dissolution: $CaCO_3(s) = CO_3^{2-} + Ca^{2+}$	$K_{CaCO_3(s)} = \gamma_{Ca^{2+}} c_{Ca^{2+}} \gamma_{CO_3^{2-}} c_{CO_3^{2-}}$
Gas dissolution: $CO_2(g) = CO_2(aq)$	$K_{CO_2(g)} f_{CO_2(g)} = \gamma_{CO_2(aq)} c_{CO_2(aq)}$

TABLE B2

Symbols used in table B1

a	thermodynamic activity		γ	thermodynamic activity coefficient
f	gaseous species partial pressure, bar		v	Stoichiometric coefficient
K	Equilibrium constant			
N_C	number of component (basis species)		Subscript:	
S^p	basis (primary) species		i	secondary species index
S^s	secondary species		j	basis (primary) species index

REFERENCES

Alpers, C. A., and Brimhall, G. H, 1988, Middle Miocene climatic change in the Atacama Desert, northern Chile, Evidence from supergene mineralization at La Escondida: American Geological Society, v. 100, p.1640-1655.

Appelo, C. A. J., and Postma, D., 1993, Geochemistry, groundwater and pollution: Rotterdam, The Netherlands, Balkema, 536 p.

Barenblatt, G. E., Zheltov, I. P., and Kochina, I. N., 1960, Basic concepts in the theory of seepage of homogeneous liquids in fissured rocks: Journal of Applied Mathematics, v. 24, p. 1286-1303.

Bibby, R., 1981, Mass transport of solutes in dual-porosity Media: Water Resources Research, v. 17, (4), p. 1075-1081, 1981.

Bolton, E. W., Lasaga, A. C., and Rye, D. M., 1999, Long-term flow/chemistry feedback in a porous medium with heterogenous permeability: Kinetic control of dissolution and precipitation: American Journal of Science, v. 299, p. 1-68.

Chapelle, F. H., and Knobel, L. L., 1983, Aqueous geochemistry and exchangeable cation composition of glauconite in the Aquia aquifer, Maryland: Ground Water, v. 21, p. 343-352.

Chesnut, D. A., 1994, Dispersivity in heterogeneous permeable media, proceedings, Fifth annual international high-level radioactive waste management conference, Las Vegas, NV, v. 4, p. 1822 - 1841, American Nuclear Society, La Grange Park, IL, May 1994.

Coats, K. H., and Smith, B. D., 1964, Dead-end pore volume and dispersion in porous media: Society of Petroleum Engineer's Journal, March (1964), p. 73-84.

de Marsily, G., 1986, Quantitative hydrogeology: San Diego, California, Academic Press Inc., 440.

Dzombak, D. A., and Morel, F. M. M., 1990, Surface complexation modeling: New York, Wiley Interscience, 431 p.

Engesgaard, P., and Kipp, K. L., 1992, A geochemical transport model for redox-controlled movement of mineral fronts in groundwater flow systems: A case of nitrate removal by oxidation of pyrite, Water Resource Research, v. 28, p. 2829-2843.

Gelhar, L. W., Welty, C., and Remfeldt, K. R., 1992, A critical review of data on field-scale dispersion in aquifers, Water Resource Research, v. 28, p. 1955-1974.

Gwo, J. P., Jardine, P. M., Wilson, G. V., and Yeh, G. T., 1996, Using a multiregion model to study the effects of advective and diffusive mass transfer on local physical nonequilibrium and solute mobility in a structured soil: Water Resource Research, v. 32, p. 561-570.

Harvey, C., and Gorelick, S. M., 2000, Rate-limited mass transfer or macrodispersion: Which dominates plume evolution at the Macrodispersion Experiment (MADE) site?, Water Resources Research, v. 36, (3), p. 637-650.

Helgeson, H. C., and Kirkham, D. H., 1974, Theoretical prediction of the thermodynamic behaviour of aqueous electrolytes at high pressures and temperatures: II. Debye-Hückel parameters for activity coefficients and relative partial molal properties: American Journal of Science, v. 274, p. 1199-1261.

Hewett, T. A., and Behrens, R. A., 1990, Considerations affecting the scaling of displacements in heterogeneous permeability distributions: Paper SPE-20739, presented at the 65th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, New Orleans, LA, September 1990.

Kapoor, V., Gelhar, L. W., and Miralles-Willem, F., 1997, Bimolecular second-order reactions in spatially varying flows: Segregation induced scale-dependent transformation rates, Water Resource Research, v. 33, p. 527-536.

Lake, L.W., and Hirasaki, G. J., 1981, Taylor's dispersion in stratified porous media: Society of Petroleum Engineer's Journal, August (1981), p. 459-468.

Lasaga, A. C., 1984, Chemical kinetics of water-rock interactions: Journal of Geophysical Research, v. 89, p. 4009-4025.

Lichtner, P. C., 1988, The quasi-stationary state approximation to coupled mass transport and fluid-rock interaction in a porous medium: Geochimica et Cosmochimica Acta, v. 52, p. 143-165.

Lichtner, P. C., 1996, Continuum formulation of multicomponent-multiphase reactive transport, in Lichtner, P. C., Steefel, C. I., and Oelkers, E. H. (eds.), Reactive transport in porous media: Reviews in Mineralogy, Mineral Society of America, v. 34, p. 1-79.

Liu, H. H., Doughty, C., and Bodvarsson, G. S., 1998, An active fracture model for unsaturated flow and transport in fractured rocks: Water Resource Research, v. 34, p. 2633–2646.

Liu, C. W., and Narasimhan, T. N., 1989, Redox-controlled multiple species reactive chemical transport, 1. Model development: Water Resource Research, v. 25, p. 869-882.

Millington, R. J., and Quirk, J. P., 1961, Permeability of porous solids: Trans. Faraday Soc., v. 57, p. 1200-1207.

Moridis, G., and Pruess, K., 1998, T2SOLV: An enhanced package of solvers for the TOUGH2 family of reservoir simulation codes: Geothermics, v. 27, p. 415-444.

Narasimhan, T. N., and Witherspoon, P. A., 1976, An integrated finite difference method for analyzing fluid flow in porous media: Water Resource Research, v. 12, p. 57–64.

Nienhuis, P., Appelo, C. A. T., and Willemsen, A., 1991, Program PHREEQM, Modified from PHREEQE for use in mixing cell flow tube: Amsterdam Free University, The Netherlands.

Nordstrom, D. K., and Muñoz, J. L., 1986, Geochemical Thermodynamics: The Benjamin/Cummings Pub. Co., Menlo Park, California, 477 p.

Ortoleva, P., Merino, E., and Chadam, J., 1987, Geochemical self-organization, 2. Reaction-transport feebacks and modeling approach: American Journal of Science, v. 287, p. 979-1007.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980, PHREEQE: A computer program for geochemical calculations: US Geological Survey, Water Resource Investigation 80-96, 174 p.

Pruess, K., and Karasaki, K., 1982, Proximity functions for modeling fluid and heat flow in reservoirs with stochastic fracture distributions, in Proceedings: Eighth workshop on geothermal reservoir engineering: p. 219-224, Stanford University, Stanford, California.

Pruess, K., 1983, GMINC: A mesh generator for flow simulations in fractured reservoirs: Lawrence Berkeley Laboratory Report LBL-15227, Berkeley, California.

Pruess, K., and Narasimhan, T. N., 1985, A practical method for modeling fluid and heat flow in fractured porous media: Society of Petroleum Engineers Journal, v. 25, p. 14-26.

Pruess, K., 1987, TOUGH user's guide: Nuclear Regulatory Commission, report NUREG/CR-4645 (also Lawrence Berkeley Laboratory Report LBL-20700, Berkeley, California).

Pruess, K., Wang, J. S. Y., and Tsang, Y. W., 1990, On thermohydrological conditions near high-level nuclear wastes emplaced in partially saturated fractured tuff, Part 2, Effective continuum approximation: Water Resource Research, v. 26, p. 1249-1261.

Pruess, K., 1991, TOUGH2: A general numerical simulator for multiphase fluid and heat flow: Lawrence Berkeley Laboratory Report LBL-29400, Berkeley, California.

Pruess, K., Simmons, A., Wu, Y. S., and Moridis, G., 1996, TOUGH2 software qualification: Lawrence Berkeley National Laboratory Report LBNL-38383, Berkeley, California.

Raffensperger, J. P., 1996, Numerical simulation of sedimentary basin-scale hydrochemical processes, In Corapcioglu, Y. C., (ed.), Advances in Porous Media: Amsterdam, The Netherlands, Elsevier Science, 440 p.

Reed, M. H., 1982, Calculation of multicomponent chemical equilibria and reaction processes in systems involving minerals, gases and aqueous phase: Geochimica et Cosmochimica Acta, v. 46, p. 513-528.

Richards, L. A., 1931, Capillary conduction of liquids through porous mediums: Physics, v. 1, p. 318-333.

Simunek, J., and Suares, D. L., 1994, Two-dimensional transport model for variably saturated porous media with major ion chemistry: Water Resource Research, v. 30, p. 1115-1133.

Sonnenthal, E., Spycher, N., Apps, J. A., and Simmons, A., 1998, Thermo-hydro-chemical predictive analysis for the drift-scale heater test: Yucca Mountain Project Level 4 Milestone SPY289M4, Lawrence Berkeley National Laboratory Report, Berkeley, California.

Sorenson, K. S., Wylie, A. H., Wood, T. R., 1996, Test area north hydrogeologic studies test plan operable unit 1-07B: Rep. INEL-96/0105, Idaho National Engineering and Environmental Laboratory, Idaho falls, Idaho.

Spycher, N. F., and Reed M. H., 1988, Fugacity coefficients of H_2, CO_2, CH_4, H_2O and of H_2O-CO_2-CH_4 mixtures: A virial equation treatment for moderate pressures and temperatures applicable to calculations of hydrothermal boiling: Geochimica et Cosmochimica Acta, v. 52, p. 739-749.

Steefel, C. I., and Lasaga, A. C., 1994, A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with applications to reactive flow in single phase hydrothermal system: American Journal of Science, v. 294, p. 529-592.

Steefel, C. I., and K. T. B. MacQuarrie, 1996, Approaches to modeling of reactive transport in porous media, In Lichtner, P. C., Steefel, C. I., and Oelkers, E. H. (eds.), Reactive transport in porous media: Reviews in Mineralogy, Mineral Society of America, v. 34, p. 83-129.

Sun, Y., Petersen, J. N., Clement, T. P., and Hooker, B. S., 1998, Effect of reaction kinetics on predicted concentration profiles during subsurface bioremediation: Journal of Contaminant Hydrology, v. 31, p. 395-372.

Taylor, G., 1953, Dispersion of soluble matter in solvent flowing slowly through a tube: Proc. Roy. Soc., Ser. A, v. 219, p. 186-203, London.

Tsang, C. F., and Neretnieks, I., 1998, Flow channeling in heterogeneous fractured rocks: Reviews of Geophysics, v. 36, p. 275-298.

Vargaftik, N. B., 1975, Tables on the thermophysical properties of liquids and gases: Second edition, John Wiley and Sons, New York.

Verma, A., and Pruess, K., 1988, Thermohydrological conditions and silica redistribution near high-level nuclear wastes emplaced in saturated geological formations: Journal and Geophysical Research, v. 93, p. 1159-1173.

Viswanathan, H. S., 1996, Modification of the finite element heat and mass transfer code (FEHM) to model multicomponent reactive transport: Los Alamos National Laboratory Report LA-13167-T, Los Alamos, New Mexico, 105 p.

Walter, A. L., Frind, E. O., Blowes, D. W., Ptacek, C. J., and Molson, J. W., 1994, Modeling of multicomponent reactive transport in groundwater, 1, Model development and evaluation: Water Resource Research, v. 30, p. 3137-3148.

Warren, J. E., and Root, P. J., 1963, The behavior of naturally fractured reservoirs: Society of Petroleum Engineers Journal, Trans., AIME, v. 228, p. 245-255.

Welch, V. S. II, Dann, M. W., and Mehta, B., 1990, Predicting oxygen depletion in reservoir environments: Society of Petroleum Engineers paper SPE 20721.

White, S. P., 1995, Multiphase non-isothermal transport of systems of reacting chemicals: Water Resource Research, v. 31, p. 1761-1772.

Wolery, T. J., 1992, EQ3/6: A software package for geochemical modeling of aqueous systems: Package overview and installation guide (version 7.0): Lawrence Livermore National Laboratory Report UCRL-MA-110662 PT I, Livermore, California.

Wunderly, M. D., Blowes, D. W., Frind, E. O., and Ptacek C. J., 1996, Sulfide mineral oxidation and subsequent reactive transport of oxidation products in mine tailings impoundments: A numerical model: Water Resource Research, v. 32, p. 3173-3187.

Xu, T., Gérard, F., Pruess K., and Brimhall, G., 1997, Modeling non-isothermal multiphase multi-species reactive chemical transport in geologic media: Lawrence Berkeley National Laboratory Report LBNL-40504, Berkeley, California, 78 p.

Xu, T., and Pruess, K., 1998, Coupled modeling of non-isothermal multiphase flow, solute transport and reactive chemistry in porous and fractured media: 1. Model development and validation: Lawrence Berkeley National Laboratory Report LBNL-42050, Berkeley, California, 38 p.

Xu, T., E.L. Sonnenthal, N. Spycher, K. Pruess, and G. Brimhall, 1998, Coupled modeling of non-isothermal multiphase flow, solute transport and reactive chemistry in porous and fractured media: 2. Model applications: Lawrence Berkeley National Laboratory Report LBNL-42051, Berkeley, California, 54 p.

Xu, T., J. Samper, C. Ayora, M. Manzano, and E. Custodio, 1999, Modeling of non-isothermal multi-component reactive transport in field-scale porous media flow system: Journal of Hydrology, v. 214, p. 144-164.

Xu, T., Pruess, K., and Brimhall, G., 1999a, An improved equilibrium-kinetics speciation algorithm for redox reactions in variably saturated flow systems: Computers & Geosciences, v. 25(6), p. 655-666.

Xu, T., Pruess, K., and Brimhall, G., 1999b, Oxidative weathering chemical migration under variably saturated conditions and supergene copper enrichment: Lawrence Berkeley National Laboratory Report LBNL-43129, Berkeley, California, 41 p.

Xu, T., White, S. P., Pruess, K., and Brimhall G., 2000a, Modeling of pyrite oxidation in saturated and unsaturated   subsurface flow systems: Transport in porous media, v. 39, p. 25-56.

Xu, T., Sonnenthal, E., Spycher, N., Pruess, K., Brimhall, G., and Apps, J., 2000b, Modeling multiphase non-isothermal fluid flow and reactive geochemical transport in variably saturated fractured rocks: 2. Applications to supergene copper enrichment and hydrothermal flows: the second one of this two-part paper, this issue.

Yeh, G. T., and Tripathi, V. S., 1991, A model for simulating transport of reactive multispecies components: model development and demonstration: Water Resource Research, v. 27, p. 3075-3094.