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Publication Date

1998-04-01

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April 1998

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This work was supported by the Laboratory Directed Research and Development Program of the Ernest Orlando Lawrence Berkeley National Laboratory under the U.S. Department of Energy, Contract No. DE-AC03-76SF00098.

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Abstract. Reactive chemical transport occurs in a variety of geochemical environments, and over a broad range of space and time scales. Efficiency of the chemical speciation and water-rock-gas interaction calculations is important for modeling field-scale multi-dimensional reactive transport problems. An improved efficient model, REACT, for simulating water-rock-gas interaction under equilibrium and kinetic conditions, has been developed. In this model, equilibrium and kinetic reactions are solved simultaneously by Newton-Raphson iteration. The iteration scheme uses the relative concentration increments as unknowns rather than their absolute values. The REACT speciation model was coupled with the multi-dimensional non-isothermal multiphase flow and mass transport code TOUGH2, resulting in the general purpose reactive chemical transport simulator TOUGHREACT. An application to supergene copper enrichment of a typical copper protore that includes the sulfide minerals pyrite (FeS_2) and chalcopyrite (CuFeS_2) is presented. The efficiency and convergence of the present model is demonstrated from this numerically difficult application that involves huge variations in the concentrations of oxygen, and sulfide and sulfate species. TOUGHREACT provides a detailed description of water-rock-gas interactions during fully transient, multi-phase, non-isothermal flow and transport in hydrologically and

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geochemically heterogeneous media. The code is helpful for assessment of acid mine drainage remediation, geothermal convection, waste disposal, contaminant transport, and water quality.

Key Words: Speciation algorithm, Equilibrium-kinetics, Redox reactions, Variably saturated subsurface flow, Reactive transport.

Introduction

Reactive chemical transport occurs in a variety of geochemical environments, and over a broad range of space and time scales. Different numerical approaches are available to model the coupled processes of chemical mass transport and water-rock-gas interaction in subsurface systems (Yeh and Tripathi, 1991; Potdevin et al., 1992; Steefel and Lasaga, 1994; White, 1995; Lichtner, 1996). Among them, the sequential iteration approach (SIA), which solves the transport and the reaction equations separately in a sequential manner with an iterative procedure, is widely used (Cederberg et al., 1985; Liu and Narasimhan, 1989; Ague and Brimhall, 1989; Nienhuis et al., 1991; Yeh and Tripathi, 1991; Engesgaard and Kipp, 1992; Appelo, 1994; Simunek and Soares, 1994; Walter et al., 1994; Zysset et al., 1994; Lichtner, 1996; Xu, 1996; and Neretnieks et al., 1997). The transport equations are solved on a chemical component basis, while the reaction equations are solved on a grid-block (or node) basis. Most of the CPU time of reactive transport simulations is consumed by performing the chemical speciation and water-rock interaction calculations (Yeh and Tripathi, 1991; and Xu, 1996). Efficiency of geochemical calculations is important for modeling field-scale multi-dimensional reactive transport problems. Several geochemical reaction path and reaction-transport models, such as EQ3/6 (Wolery, 1992) and KGEOFLOW (Sevougian et al., 1995), decouple kinetics from equilibrium calculations. Newton-

Raphson iteration is used for thermodynamic equilibrium calculations, whereas kinetic dissolution/precipitation is treated separately using Taylor series expansions. Using this approach, one cannot integrate the kinetic reactions over a significant time step without applying the equilibrium constraints. General geochemical codes such as EQ3/6 and PHREEQE [Parkhurst et al., 1980] are designed for batch reaction systems and keep track of the full chemical database during the entire simulation. This may be not efficient and practical for simulating field-scale multi-dimensional reactive transport problems.

An improved efficient geochemical speciation model, REACT, for simulating water-rock-gas interaction under simultaneous equilibrium and kinetic conditions, has been developed. This reaction model is well suited for coupling with flow and mass transport simulators. In this model, equilibrium and kinetics are solved simultaneously by Newton-Raphson iteration, which allows a larger time step to be applied. Mineral dissolution and precipitation can be treated by the local equilibrium approximation, by kinetic rates, or a mixed formulation. In addition, the Newton-Raphson iteration scheme in the REACT has been modified such that the unknowns are the relative concentration increments as opposed to their absolute values. By doing this, the modified Jacobian matrix is symmetric and better conditioned, improving convergence. The REACT model has been coupled with the multi-dimensional (one, two, or three) non-isothermal multiphase flow and mass transport code TOUGH2 (Pruess, 1991), resulting in the general purpose reactive chemical transport code TOUGHREACT. This code provides a detailed description of rock-fluid interactions during fully transient, multi-phase, non-isothermal flow and transport in hydrologically and geochemically heterogeneous media. To demonstrate the capability of the model, we present a simulation of supergene copper enrichment of a typical copper protore that includes the sulfide minerals pyrite (FeS_2) and chalcopyrite (CuFeS_2). The oxidative weathering and acidification

causes mobilization of metals in the unsaturated zone, with subsequent formation of enriched ore deposits in the reducing conditions below the water table. Redox reactions pose difficult challenges for numerical modeling because they result in huge variations in the concentrations of aqueous species involved. For example, in systems where pyrite (FeS_2) is oxidized in the vadose zone through contact with atmospheric oxygen, aqueous oxygen concentrations may vary over 70 orders of magnitude. Similarly, between oxidizing and reducing conditions the concentrations of sulfide and sulfate species may range over more than 90 orders of magnitude. For comparison purposes, by coupling TOUGH2 with the speciation and reaction path code EQ3/6, the code TOUGH2-EQ3/6 has been developed. For the application case presented in this paper, the TOUGHREACT code achieves a speedup by a factor of about 94 in comparison to TOUGH2-EQ3/6.

Solution method for mixed equilibrium-kinetics system

We assumed that aqueous complexation and gas dissolution/exsolution proceed according to local equilibrium, while mineral dissolution/precipitation are subject to equilibrium and/or kinetic conditions. Only pure mineral phases are considered in this paper. Gas dissolution/exsolution is included in the model and treated in a similar way as equilibrium mineral dissolution/precipitation. The formulation is based on mass balances in terms of basis species as used by Parkhurst et al. (1980) and Reed (1982) for the equilibrium chemical system. The kinetic rate expressions for mineral dissolution/precipitation is directly added to the mass balances of basis species. At time zero (initial), the total analytical concentrations of basis species j in the system are assumed to be known, and are given by

$$T_j^0 = c_j^0 + \sum_{k=1}^{N_x} v_{kj}^x x_k^0 + \sum_{m=1}^{N_p} v_{mj}^p p_m^0 + \sum_{n=1}^{N_q} v_{nj}^q q_n^0 \quad j=1, \dots, N_C \quad (1)$$

where superscript 0 represents time zero; subscripts j, k, m, and n are the indices of basis 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 the corresponding species and minerals; c, x, p and q are their concentrations; v_{kj}^x , v_{mj}^p , and v_{nj}^q are stoichiometric coefficients of the basis species in the aqueous complexes, equilibrium and kinetic minerals, respectively. After a time step Δt_r , the total analytical concentration of basis species j is given by

$$T_j = c_j + \sum_{k=1}^{N_x} v_{kj}^x x_k + \sum_{m=1}^{N_p} v_{mj}^p p_m + \sum_{n=1}^{N_q} v_{nj}^q (q_n^0 - r_n \Delta t_r) \quad j=1, \dots, N_C \quad (2)$$

where r is the kinetic dissolution rate (negative for precipitation). For a closed system, according to mass conservation, we have $T_j = T_j^0$. By subtracting (1) from (2), we obtain

$$F_j^c = c_j + \sum_{k=1}^{N_x} v_{kj}^x x_k + \sum_{m=1}^{N_p} v_{mj}^p p_m - \sum_{n=1}^{N_q} v_{nj}^q r_n \Delta t_r - U_j^0 = 0 \quad j=1, \dots, N_C \quad (3)$$

where

$$U_j^0 = c_j^0 + \sum_{k=1}^{N_x} v_{kj}^x x_k^0 + \sum_{m=1}^{N_p} v_{mj}^p p_m^0 \quad (3a)$$

According to mass action equations, concentrations of aqueous complexes x_k can be expressed as functions of concentrations of the basis species c_j (Equation A1.2 in Appendix 1). Kinetic rates r_n are functions of c_j (Equation A1.5 in Appendix 1). No explicit expressions relate equilibrium mineral concentrations p_m , to c_j . Therefore, N_p additional mass action equations must be added to the system of N_c equations (3). At equilibrium we have

$$F_m^p = \log_{10} SI_m = 0 \quad m = 1, \dots, N_p \quad (4)$$

where SI_m is the m -th equilibrium mineral saturation index which is a function of c_j (see Equations A1.3 and A1.4 in Appendix 1). N_c equations in (3) and N_p in (4) constitute a complete set of equations needed for $N_c + N_p$ primary variables, $(c_1, c_2, \dots, c_{N_c}, p_1, p_2, \dots, p_{N_p})$. This system of nonlinear equations is solved by Newton-Raphson iteration. Denoting the set of primary variables collectively as X_i ($i=1, 2, \dots, N_c + N_p$), we have

$$\sum_{i=1}^{N_c + N_p} \frac{\partial F_j}{\partial X_i} \Delta X_i = -F_j \quad j = 1, \dots, N_c + N_p \quad (5)$$

where j is a row index and i is a column index (this is opposite to conventional mathematical notation, since j in this paper denotes basis species index and mass balance equations are written in terms of them). In matrix form Eqs. (5) reduces to

$$\mathbf{J}\Delta\mathbf{X} = \mathbf{B} \quad (6)$$

where $\mathbf{J}$ is the so-called Jacobian matrix and $\mathbf{B}$ the vector of residuals. The Jacobian matrix elements are evaluated in Appendix 2. The values of $\Delta\mathbf{X}$ are used to update the primary variables:

$$X_i^{l+1} = X_i^l + \Delta X_i \quad (7)$$

where l labels iteration number. $|\Delta X_i|$ are expected to decrease in successive iterations. The system of equations is considered satisfactorily solved when

$$\max_j \left(\frac{|F_j^c|}{T_j^0} \right) \leq \tau \quad j = 1, \dots, N_C \quad (8)$$

where τ are specified tolerance limit. In order to avoid negative values for concentrations, the relative change is restricted to one (called under-relaxation), or $|\Delta X_i|/X_i < 1$ ($i = 1 \dots N_C$). As a consequence, although the iteration method becomes more robust, the rate of convergence may slow down in some cases. When a negative value of X_i ($i = N_C + 1, \dots, N_C + N_p$) is obtained, the corresponding mineral is considered exhausted and must be removed from the chemical system, and its corresponding equation disappears (Reed, 1982).

In the Newton-Raphson iteration scheme, the absolute concentration increments would normally be taken as the unknowns. However, as will be seen below, it is advantageous for

numerical solution to rewrite Eqs. (5) so that for the basis species the relative concentration increments will be used as unknowns.

$$\sum_{i=1}^{N_C} \left[X_i \frac{\partial F_j}{\partial X_i} \right] \Delta X_i^* = -F_j \quad j=1, \dots, N_C \quad (9)$$

where

$$\Delta X_i^* = \frac{\Delta X_i}{X_i} \quad (10)$$

Note that for the equilibrium minerals ($i = N_C + 1, \dots, N_C + N_p$) the absolute increments as in Eqs. (5) are used as unknowns. The primary variables are now updated by

$$\begin{aligned} X_i^{l+1} &= X_i^l (1 + \Delta X_i^*) & i &= 1, \dots, N_C \\ X_i^{l+1} &= X_i^l + \Delta X_i & i &= N_C + 1, \dots, N_C + N_p \end{aligned} \quad (11)$$

The resulting matrix in the modified Newton-Raphson iteration scheme is symmetric (if neglecting derivatives of activity coefficients). It is also by diagonal dominant if the most abundant species are selected as the basis species. The detailed derivation is given in Appendix 2. This matrix is better conditioned and has a smaller condition number. The condition number is a measure of how round-off errors are propagated through the numerical solution algorithm. The solution of a system of equations having a large condition number will contain large round-off errors. If too large, these errors may completely mask the correct solution. This is especially important in dealing with variables which may take on extremely low values, such as the concentration of

species SO_4^{2-} in reducing conditions. In the application to supergene copper enrichment presented later, the condition number of the matrix corresponding to absolute concentration increments is 3.15×10^{12} . This number is reduced by seven orders of magnitude to 4.2×10^5 when working with relative concentration increments, providing much better convergence. Basis species switching, as suggested by Wolery (1992) and Steefel and Lasaga (1994), may also improve convergence. However, much more programming work is required. There is no comparison of efficiency of both methods since the latter is not implemented in our model.

The solution of the reaction system requires knowing initial total concentrations of basis species j in the equilibrium system (aqueous and mineral) or U_j^0 in Eqs. (3a), and the time step Δt_r . Adding kinetic mineral dissolution/precipitation processes does not require additional primary equations, because the reaction rate is a function of the concentrations of the basis species. Once the concentrations of the basis species are obtained, all other secondary variables can be computed in a straightforward manner.

This numerical model for solving the mixed equilibrium-kinetics reaction system was implemented in the code REACT, which was then coupled with the multi-dimensional (one, two, or three) non-isothermal multiphase flow and mass transport code TOUGH2 (Pruess, 1991), resulting in the general purpose reactive chemical transport code TOUGHREACT. Our model of flow and reactive chemical transport in geologic media is based on space discretization by means of integral finite differences (Narasimhan and Witherspoon, 1976). Time is discretized as a first-order finite difference, and all flow, transport and reaction terms are evaluated fully implicitly, using a sequential iteration approach (SIA). More details on the mathematical and numerical formulation for multiphase flow and transport are given in Xu et al. (1997). The reaction time step Δt_r is very important for convergence of a mixed equilibrium-kinetics system. During a transport time

step Δt_r , depending on the convergence of the reaction, multiple steps with $\sum \Delta t_r = \Delta t_i$, can be used. An automatic time stepping scheme is implemented in the TOUGHREACT. If the number of iterations for the reaction calculation is greater than a specified value such as 30, Δt_r is reduced by a factor of 2, while if the number of iterations is less than a smaller number such as 3, Δt_r is increased by a factor of 1.5.

Verification and Validation

The TOUGHREACT code was extensively verified against analytical solutions and other numerical simulators such as TRANQL (Cederberg, 1985) and DYNAMIX (Liu and Narasimhan, 1989) and PHREEQM (Nienhuis, 1991) for a wide range of physical and chemical processes (Xu et al, 1998). Here we only present the verification of reactive transport with mineral dissolution under kinetic conditions against an analytical solution. This solution corresponds to one-dimensional transport of two hypothetical species A and B which originate from the dissolution of a mineral phase AB_s , $AB_s \rightleftharpoons A + B$. A semi-infinite water saturated medium under a steady-state uniform velocity flow regime is considered. For this case, an analytical solution is given in Xu (1996). Parameters used in the TOUGHREACT simulation are listed in Table 1. The numerical results agree well with those of the analytical solution (see Figure 1).

Table 1. Parameters used for the TOUGHREACT verification of the kinetic mineral dissolution.

Parameter	value
Length (m)	1.0
Grid size (m)	0.4
Velocity (m day ⁻¹)	0.1
Porosity	0.4
Equilibrium constant	10 ⁻⁸
Kinetic rate constant (mol m ⁻² s ⁻¹)	2×10 ⁻¹⁰
Specific surface area (m ² kg ⁻¹)	1.0
Initial concentrations (mol kg ⁻¹)	
Species A	10 ⁻⁴
Species B	10 ⁻⁴
Boundary concentrations (mol kg ⁻¹)	
Species A	10 ⁻⁵
Species B	10 ⁻⁴

Figure 1. Spatial distribution of analytical and numerical concentration data at steady-state (after 20 days) for TOUGHREACT verification of the kinetic mineral dissolution.

The code TOUGHREACT has been validated (Sonnenthal et al., 1998) by comparison with a plug-flow reactor experiment for quartz dissolution conducted at Lawrence Livermore National Laboratory by Johnson et al. (1997). On the inlet pure water was injected, and aqueous silica concentrations were measured at the outlet. Experimental and model parameters are listed in Table 2. Dissolution causes some increase in the porosity, which is not modeled in the current simulation. An average porosity of 0.435 was used. The kinetic rate constant for quartz dissolution used in the simulation is based on the empirical equation given by Tester et al. (1994):

$$k_{\text{quartz}} = (276 \pm 193) \exp \left[- \frac{90.1 \pm 2.5}{RT} \times 10^3 \right] \quad (12)$$

where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is absolute temperature. Average values in (12) are used for this quartz dissolution simulation. Three runs were performed using three different trial values of specific reactive surface area, σ_{quartz} . The TOUGHREACT results and the measured values of outlet aqueous silica concentrations are presented in Figure 2a. It can be seen that rapid attainment (approximately 1/2 hour) of a steady-state outlet concentration in the simulation generally matches experimental observations although no measurements are available for comparison with early-time predictions. Simulated values with $\sigma_{\text{quartz}} = 25.18 \text{ m}^2/\text{kg H}_2\text{O}$ provide an optimal match to the measured data. From the simulations it can be seen that results are sensitive to specific reactive surface areas. The early time transient from the TOUGHREACT simulation is presented in Figure 2b.

Table 2. Parameters describing the plug-flow experiment of quartz dissolution. Data are from Johnson et al. (1997) and Sonnenthal et al. (1998)

Parameter	value
Temperature ($^{\circ}\text{C}$)	239
Plug length (cm)	3.1
Plug diameter (cm)	0.66
Initial bulk porosity (vol.%)	42.50
Flow rate (ml day^{-1})	24.8
Duration (days)	12.7
Darcy flux ($\text{m}^3 \text{m}^{-2} \text{yr}^{-1}$)	264.4
Fluid velocity (m yr^{-1})	622.1
Average grain diameter (μm)	100
Permeability (m^2)	6.51×10^{-12}
Fluid residence time (hours)	0.44
Final bulk porosity (vol.%)	44.55

Figure 2a. Outlet aqueous silica concentrations predicted from TOUGHREACT simulation, using different specific reactive surface areas, compared with measured data from a plug-flow reactor experiment (Johnson et al., 1997).

Figure 2b. The TOUGHREACT predicted outlet aqueous silica concentrations during the early-time transient period.

Application: Supergene copper enrichment

The geochemistry for this application was based on field and laboratory studies of supergene copper systems and their dynamics under conditions of climatic change as carried out by Brimhall and Alpers (1985), and Ague and Brimhall (1989). A schematic representation of the model system is shown in Figure 3. Oxygen is supplied to a protore containing pyrite and chalcopyrite (Table 3) as a dissolved species in infiltrating rainwaters, as well as by gaseous diffusion from the land surface boundary. A vertical column of 20 m thickness is used, which is discretized into 10 grid blocks with a constant spacing of 2 m. The top 5 blocks represent the unsaturated zone (water saturation: 0.43, 0.43, 0.44, 0.48, 0.72 from the top to the bottom), while the bottom 5 blocks represent the water saturated zone. A steady-state water flow regime is assumed throughout the simulation. Mineral dissolution/precipitation effects on porosity are not considered

in the current simulation. A diffusion coefficient of $4.38 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ and a tortuosity of 0.1 are used for gaseous oxygen.

Figure 3. Schematic representation of a supergene enrichment system

The column is initially filled entirely with a protore mineral assemblage as listed in Table 3. The dissolution of the protore minerals is kinetically controlled. We use the rate expression given in Equation A1.5 (in Appendix 1). The term for the catalytic effect of H^+ is not taken into account. The exponential terms are set equal to one (first order kinetics). The kinetic rate constants and specific surface areas used are listed in Table 3. The chemical formulae of the primary minerals are given in Table 4. The interaction of O_2 gas with the aqueous solution is assumed at local equilibrium. The precipitation of secondary minerals (Table 5) during the simulation progress is model as instantaneous.

Table 3. Chemical properties of protore mineral reactants. Volume fraction, rate constant and specific surface area are based on Ague and Brimhall (1989) and Gerard et al. (1997). Abundance is calculated from volume fractions (in this table) and mole volumes presented in the EQ3/6 database (Wolery, 1992).

Mineral	Volume fraction (%)	Abundance (mol/dm ³ medium)	Rate constant (mol/cm ² /s)	Surface area (cm ² /dm ³ medium)
Pyrite	9.0	3.76	4.0×10^{-15}	5866.7
Chalcopyrite	4.5	1.05	4.0×10^{-15}	5866.7
Magnetite	4.5	1.01	2.0×10^{-15}	5866.7
K-feldspar	18.0	1.65	3.1×10^{-16}	58666.7
Albite	9.0	0.9	3.1×10^{-16}	69813.4
Anorthite	9.0	0.89	1.5×10^{-16}	29920.0
Annite	4.5	0.29	2.4×10^{-18}	29333.3
Muscovite	9.0	0.64	2.4×10^{-18}	17600.0
Quartz	18.0	7.93	4.3×10^{-18}	61600.1
Anhydrite	4.5	0.98	1.5×10^{-16}	5866.7
Total=90				
Void=10				

Table 4. Chemical reaction equations for oxygen gas and the primary mineral reactants. The thermodynamic equilibrium constants are from the EQ3/6 database (Wolery, 1992)

Mineral (or gas)	Reactions equation	log K (25°C)
Oxygen gas	$O_2(g) = O_2(aq)$	-2.898
Pyrite	$FeS_2 + H_2O + 3.5O_2(aq) = 2SO_4^{--} + Fe^{++} + 2H^+$	217.4
Chalcopyrite	$CuFeS_2 + 4O_2(aq) = 2SO_4^{--} + Fe^{++} + Cu^{++}$	244.07
Magnetite	$Fe_3O_4 + 8H^+ = Fe^{++} + 2Fe^{+++} + 4H_2O$	10.4724
K-feldspar	$KAlSi_3O_8 + 4H^+ = K^+ + Al^{+++} + 3SiO_2(aq) + 2H_2O$	-0.2753
Albite	$NaAlSi_3O_8 + 4H^+ = Na^+ + Al^{+++} + 3SiO_2(aq) + 2H_2O$	2.7645
Anorthite	$CaAl_2Si_2O_8 + 8H^+ = Ca^{++} + 2Al^{+++} + 2SiO_2(aq) + 4H_2O$	26.5780
Annite	$KFe_3AlSi_3O_{10}(OH)_2 + 10H^+ = K^+ + 3Fe^{++} + Al^{+++} + 3SiO_2(aq) + 6H_2O$	29.4693
Muscovite	$KAl_3Si_3O_{10}(OH)_2 + 10H^+ = K^+ + 3Al^{+++} + 3SiO_2(aq) + 6H_2O$	13.5858
Quartz	$SiO_2 = SiO_2(aq)$	-3.9993
Anhydrite	$CaSO_4 = Ca^{++} + SO_4^{--}$	-4.3064

Table 5. The chemical reaction equations for secondary minerals. The thermodynamic equilibrium constants are from the EQ3/6 database (Wolery, 1992)

Mineral	Reaction equation	log K (25°C)
Covellite	$\text{CuS} + \text{H}^+ = \text{Cu}^{++} + \text{HS}^-$	22.8310
Chalcocite	$\text{Cu}_2\text{S} + \text{H}^+ = 2\text{Cu}^+ + \text{HS}^-$	-34.7342
Bornite	$\text{Cu}_5\text{FeS}_4 + 4\text{H}^+ = \text{Cu}^{++} + 4\text{Cu}^+ + \text{Fe}^{++} + 4\text{HS}^-$	-102.44
Goethite	$\text{FeOOH} + 3\text{H}^+ = \text{Fe}^{+++} + 2\text{H}_2\text{O}$	-0.283
Hematite	$\text{Fe}_2\text{O}_3 + 6\text{H}^+ = 2\text{Fe}^{+++} + 3\text{H}_2\text{O}$	0.1086
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 2\text{Al}^{+++} + 2\text{SiO}_2(\text{aq}) + 5\text{H}_2\text{O}$	6.8101
Alunite	$\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2 + 6\text{H}^+ = \text{K}^+ + 3\text{Al}^{+++} + 2\text{SO}_4^{--} + 6\text{H}_2\text{O}$	-0.3479
Amorphous silica	$\text{SiO}_2 = \text{SiO}_2(\text{aq})$	-2.7136

A dilute oxidizing water with an oxygen fugacity (partial pressure) of 0.2 bar is initially placed in the five uppermost (unsaturated) grid blocks, while a reducing water with a fugacity of 1.0×10^{-70} bar is assumed for the remaining (saturated) grid blocks. The infiltration water composition is the same as the initial unsaturated water. A total of 52 aqueous species are considered. The aqueous complexation is assumed at local equilibrium. Detailed results for the chemical evolution, simulated with TOUGHREACT, are given in Figures 4 and 5.

Figure 4. Change of mineral abundances (in moles per cubic meter medium) after 90 years. Negative values indicate dissolution, positive indicate precipitation.

(a)

(d)

(b)

(e)

(c)

Figure 5. Total dissolved concentration distribution along the vertical column.

In the unsaturated zone, pyrite and chalcopyrite are oxidized and dissolved (Figure 4a). As aqueous phase oxygen is depleted through reaction with pyrite and chalcopyrite, it is replenished by dissolution from the gas phase, and by diffusive transport from the atmospheric boundary at the land surface. The pH decreases downward (Figure 5a), and the total dissolved Cu and S concentrations increase (Figures 5c and 5d) due to pyrite and chalcopyrite oxidation. When the aqueous solution reaches the reducing saturated zone, the secondary copper bearing minerals chalcocite and covellite are precipitated (Figure 4b), forming the enrichment blanket immediately below the water table (Ague and Brimhall, 1989). In addition, goethite precipitates in the unsaturated zone.

At the same time magnetite, K-feldspar, albite, anorthite, annite and muscovite dissolve throughout the column due to decrease of pH (Figures 4a, 4c and d). Magnetite dissolution (Figure 4a) creates additional Fe^{2+} and Fe^{3+} . Fe^{3+} also acts as an oxidant, which contributes to pyrite and chalcopyrite oxidation. Dissolution of K-feldspar, albite, anorthite, annite and muscovite produces Na, K, Ca, Al and $\text{SiO}_2(\text{aq})$. As a result, amorphous silica precipitates throughout the column (Figure 4e). Kaolinite occurs only in the bottom 3 grid blocks of the saturated zone (Figure 4b), while alunite appears only in the top 7 grid blocks of the column (Figure 4e). There is no quartz dissolution as this mineral is stable in our simulation, as it is in nature.

The chemical changes and secondary mineral assemblages predicted by our model are consistent with observations in supergene copper deposits (Ague and Brimhall, 1989).

Conclusions

Redox reactions under multiphase (unsaturated) flow conditions involve a mix of equilibrium and kinetic reactions, and an enormous range of aqueous concentrations. This poses severe challenges for numerical simulation. We have presented an improved approach in which heterogeneous kinetic reactions are directly embedded into the system of equilibrium-controlled speciation reactions. The speciation problem is then solved in a fully coupled manner by Newton-Raphson iteration. By switching to relative concentration increments as unknowns, substantial improvement was achieved for matrix conditioning and convergence rates.

The improved treatment of simultaneous equilibrium and kinetically controlled speciation reactions was implemented in a computer program "REACT" and was coupled with the general-purpose multiphase flow simulator TOUGH2. The coupled code, "TOUGHREACT," achieved stable convergence behavior and geochemically reasonable results for a problem of supergene copper enrichment, in which concentrations of key species vary by 70 orders of magnitude. The improved speciation treatment resulted in approximately two orders of magnitude decrease in computing time. TOUGHREACT provides a detailed description of water-rock-gas interactions during fully transient, multi-phase, non-isothermal flow and transport in hydrologically and geochemically heterogeneous media. The code is helpful for assessment of acid mine drainage remediation, geothermal convection, waste disposal, contaminant transport, and water quality.

Appendix 1. Mathematical formulation of chemical reactions

For representing a geochemical system, it is convenient to select a subset of N_C aqueous species as basis species (or component or primary species). All other species are called secondary species that include aqueous complexes, precipitated (mineral) and gaseous species (Reed, 1982; Yeh and Tripathi, 1991; Steefel and Lasaga, 1994; Lichtner, 1996). The number of secondary species must be equal to the number of reactions. Any of the secondary species can be represented as a linear combination of the set of basis species such as

$$S_i^s = \sum_{j=1}^{N_C} v_{ij} S_j^p \quad i = 1, \dots, N_R \quad (A1.1)$$

where S_j^p is the chemical formula of the j-th basis species, S_i^s is the chemical formula of the i-th secondary species, N_R is the number of reactions (or secondary species), and v_{ij} is the stoichiometric coefficient of j-th basis species in the i-th reaction.

Aqueous complexation. These reactions are assumed to be at local equilibrium. By making use of the mass action equation to the dissociation of the i-th aqueous complex (Eq. A1.1), concentrations of aqueous complexes can be expressed as functions of the concentrations of basis species:

$$x_i = K_i^{-1} \gamma_i^{-1} \prod_{j=1}^{N_c} c_j^{v_{ij}^x} \gamma_j^{v_{ij}^x} \quad (\text{A1.2})$$

where x_i is molal concentration of the i -th aqueous complex, and c_j is molal concentration of the j -th basis species, γ_i and γ_j are thermodynamic activity coefficients which can be calculated from the extended Debye-Hückel equation or other equations (i.e. Parkhurst, 1990), and K_i is the equilibrium constant.

Equilibrium mineral dissolution/precipitation. The mineral saturation ratio can be expressed as

$$\Omega_m = X_m^{-1} \lambda_m^{-1} K_m^{-1} \prod_{i=1}^{N_c} c_i^{v_{mi}^p} \gamma_i^{v_{mi}^p} \quad m = 1 \dots N_p \quad (\text{A1.3})$$

where m is the equilibrium mineral index, X_m is the mole fraction of the m -th mineral phase, λ_m is its thermodynamic activity coefficient (for pure mineral phases X_m and λ_m are taken equal to one), and K_m is the corresponding equilibrium constant. At equilibrium, we have

$$\text{SI}_m = \log_{10} \Omega_m = 0 \quad (\text{A1.4})$$

where SI_m is called the mineral saturation index.

Kinetic mineral dissolution/precipitation. Kinetic rates can be expressed as functions of the concentrations of the basis species. In this model, we use a rate expression given by Lasaga et al. (1994):

$$r_n = f(c_1, c_2, \dots, c_{N_C}) = k_n \sigma_n a_{H^+}^\beta (1 - \Omega_n^\theta)^\eta \quad n = 1 \dots N_q \quad (A1.5)$$

where positive values of r_n indicate dissolution, and negative values precipitation, k_n is the rate constant (moles per unit mineral surface area and unit time) which is temperature dependent and may have different values for dissolution and precipitation, σ_n is the specific reactive surface area per kg H_2O , Ω_n is the kinetic mineral saturation ratio defined in a similar way as in (A1.3) but with index n instead of m . The parameters θ and η must be determined from experiments; usually, but not always, they are taken equal to one. The term $a_{H^+}^\beta$ accounts for the catalytic effect of H^+ where the value of β is determined experimentally.

Gas dissolution/exsolution. Reactions involving aqueous and gaseous phases are usually assumed to be at equilibrium. According to the Mass-Action Law, one has:

$$P_i^g \Gamma_i^g K_i^g = \prod_{j=1}^{N_C} c_j^{v_{ij}^g} \gamma_j^{v_{ij}^g} \quad (A1.6)$$

where P_i^g is the partial pressure (pressure fraction) of the i -th gaseous species, Γ_i^g is the gas fugacity coefficient, v_{ij}^g is the stoichiometric coefficient of the j -th basis species in the i -th gaseous

species, and K_1^g is the equilibrium constant of the reaction. For low pressures (in the range of atmospheric pressure), the gaseous phase is assumed to behave like an ideal mixture, and the fugacity coefficient Γ_i^g are assumed equal to one.

Appendix 2: Evaluation of the Jacobian matrix

The structure of the Jacobian matrix in (6) is:

$$\begin{array}{cc} & \begin{array}{c} N_C \quad N_P \end{array} \\ \begin{array}{c} N_C \\ N_P \end{array} & \begin{array}{cc} \frac{\partial F_j^c}{\partial c_i} & \frac{\partial F_j^c}{\partial p_i} \\ \frac{\partial F_j^p}{\partial c_i} & \frac{\partial F_j^p}{\partial p_i} \end{array} \end{array}$$

Based on (A1.3) and (A1.5), and by neglecting the derivatives of activity coefficients with respect to the concentration of basis species, the entries of the Jacobian matrix are

$$J^{cc} = \frac{\partial F_j^c}{\partial c_i} = \delta_{ji} + \sum_{k=1}^{N_x} v_{kj}^x v_{ik}^x \frac{x_k}{c_i} + \sum_{n=1}^{N_q} v_{nj}^q v_{ni}^q \frac{k_n \sigma_n \Omega_n}{c_i} \quad (A2.1)$$

$$J^{cp} = \frac{\partial F_j^c}{\partial p_i} = v_{mj}^p \quad (A2.2)$$

$$J^{pc} = \frac{\partial F_j^p}{\partial c_i} = \frac{v_{mj}^p}{c_i} \quad (A2.3)$$

$$J^{pp} = \frac{\partial F_j^p}{\partial p_i} = 0 \quad (A2.4)$$

Let J^{cc} , J^{cp} , J^{pc} and J^{pp} be the submatrices expressed in (A2.1) through (A2.4), then the Jacobian system of equations can be written as

$$\begin{bmatrix} J^{cc} & J^{cp} \\ J^{pc} & J^{pp} \end{bmatrix} \begin{bmatrix} \Delta c \\ \Delta p \end{bmatrix} = \begin{bmatrix} -F^c \\ -F^p \end{bmatrix} \quad (A2.5)$$

where $-F^c$ and $-F^p$ are the residual terms that can be calculated from (3) and (4), respectively.

In terms of relative concentration increments, (A2.5) become

$$\begin{bmatrix} (J^{cc})^* & J^{cp} \\ (J^{pc})^* & J^{pp} \end{bmatrix} \begin{bmatrix} \Delta c / c \\ \Delta p \end{bmatrix} = \begin{bmatrix} -F^c \\ -F^p \end{bmatrix} \quad (A2.6)$$

where

$$(J^{cc})^* = \delta_{ji} c_i + \sum_{k=1}^{N_x} v_{kj}^x v_{ik}^x x_k + \sum_{n=1}^{N_q} v_{nj}^q v_{ni}^q k_n \sigma_n \Omega_n \quad (A2.7)$$

$$(J^{pc})^* = v_{mj}^p \quad (A2.8)$$

Notice that submatrices $(J^{cc})^*$ and J^{pp} are symmetric (J^{cc} in Equation A2.5 is not). In addition, $(J^{pc})^*$ coincides with the transpose of J^{cp} (J^{cp} and J^{pc} in Equation A2.5 do not), therefore the entire Jacobian matrix in Eq. (A2.6) is symmetric. Notice also that if the most abundant species are selected as the primary species, the Jacobian matrix is diagonal by dominant (see Equation A2.7).

Acknowledgement

The authors appreciate stimulating discussions with Tom Wolery, John Apps, Frederic Gérard, Eric Sonnenthal, and Nicolas Spycher. We thank our latter two colleagues for suggesting using mass-action equations in logarithmic form and including kinetic formulation in the Jacobian matrix, and for their careful review of this manuscript. This work was supported by the Laboratory Directed Research and Development Program of the Ernest Orlando Lawrence Berkeley National Laboratory, under Contract No. DE-AC03-76SF00098 with the U.S. Department of Energy.

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