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Abstract

Transport of oxygen gas from the land surface through an unsaturated zone has a strong influence on oxidative weathering processes. Oxidation of sulfide minerals such as pyrite (FeS_2), one of the most common naturally occurring minerals, is the primary source of acid drainage from mines and waste rock piles. Here we present a detailed numerical model of supergene copper enrichment that involves the oxidative weathering of pyrite (FeS_2) and chalcopyrite (CuFeS_2), and acidification that causes mobilization of metals in the unsaturated zone, with subsequent formation of enriched ore deposits of chalcocite (Cu_2S) and covellite (CuS) in the reducing conditions below the water table. We examine and identify some significant conceptual and computational issues regarding the oxidative weathering processes through the modeling tool. The dissolution of gaseous oxygen induced by the oxidation reduces oxygen partial pressure, as well as the total pressure of the gas phase. As a result, the gas flow is modified, then the liquid phase flow. Results

indicate that this reaction effect on the fluid flow may not be important under ambient conditions, and gas diffusion can be a more important mechanism for oxygen supply than gas or liquid advection. Acidification, mobilization of metals, and alteration of primary minerals mostly take place in unsaturated zone (oxidizing), while precipitation of secondary minerals mainly occurs in saturated zone (reducing). The water table may be considered as an interface between oxidizing and reducing zones. Moving water table due to change of infiltration results in moving oxidizing zone and redistributing aqueous chemical constituents and secondary mineral deposits. The oxidative weathering processes are difficult to model numerically, because concentrations of redox sensitive chemical species such as $O_2(aq)$, SO_4^{2-} and HS^- may change over tens of orders of magnitude between oxidizing and reducing conditions. In order to simulate substantial reaction progress over geologic time, one can benefit from the quasi-stationary state (QSS) approximation. A significant saving of computing time using QSS is demonstrated through the example. In addition, changes in porosity and permeability due to mineral dissolution and precipitation are also addressed in some degree. Even though oxidative weathering is sensitive to many factors, this work demonstrates that our model provides a comprehensive suite of process modeling capabilities, which could serve as a prototype for oxidative weathering processes with broad significance for geoscientific, engineering, and environmental applications.

1. Introduction

Oxidative weathering of sulfide minerals such as pyrite (FeS_2) is fundamental to alteration of primary rock minerals, formation of acid-sulfate soils, and the development of acidity and metal mobilization in natural waters. The acid waters produced by oxidation of sulfide minerals from waste rock, tailings, and open pits typically have a pH values in the range of 2-4 and high concentrations of metals known to be toxic to living organisms (Nordstrom and Alpers, 1997). The process has been studied by many investigators (Singer and Stumm, 1970; Kleinmann et al., 1981; Lowson, 1982; Nordstrom, 1982; McKibben and Barnes, 1986; Ague and Brimhall, 1989; Brown and Jurinak, 1989; Welch et al., 1990; Olson, 1991; Engesgaard and Kipp, 1992; Walter et al., 1994; Wunderly et al., 1996; Nordstrom and Alpers, 1997; and Lefebvre et al. 1998)

Transport of oxygen gas from the land surface through an unsaturated zone has a strong influence on the oxidative weathering geochemistry. The oxygen consumed during oxidation of sulfide minerals is supplied from gaseous oxygen dissolved in the aqueous phase. Dissolved oxygen is replenished by percolating oxygenated rainwater, and by dissolution of oxygen that is present in the gas-filled portion of the pore space. The dissolution of gaseous oxygen reduces oxygen partial pressure, as well as the total pressure of the gas phase. Gaseous oxygen is replenished by diffusion and advection in the gas phase from the land surface boundary. In natural subsurface environments, sulfide mineral oxidation is influenced by many other factors such as climate, bacterial catalysis, physical structure, and vegetation (Nordstrom and Alpers, 1997), which are beyond the scope of this paper.

In the unsaturated zone, the oxidative weathering occurs through a complex interplay of multi-phase flow, transport, and chemical reaction processes. These complex hydrogeochemical processes can be modeled. There will always be inadequate data for the modeling effort. The advantage of modeling is that it can take into account some of the complex interactions between hydrology, geochemistry and size characteristics, to give a general analysis. In this paper, we use modeling tool to examine and identify some important conceptual and computational issues regarding the oxidative weathering process. We begin with a description of mathematical formulation for the reactive chemical system under study. The multi-phase reactive transport computer model TOUGHREACT (Xu and Pruess, 1998) is used, which employs a sequential iteration approach similar to Yeh and Tripathi (1991), Engesgaard and Kipp (1992), and Walter et al (1994). The dissolution of gaseous oxygen induced by sulfide mineral oxidation reduces oxygen partial pressure, as well as the total pressure of the gas phase. As a result, the gas flow is modified, then the liquid phase flow. This reaction effect on the fluid flow is not considered in TOUGHREACT, although advection and diffusion are considered for oxygen transport processes.

Prior to supergene copper enrichment problem, we first chose a problem with only one mineral pyrite (or pyrite oxidation) to examine importance of the reaction effect on fluid flow. Another reactive transport code TOUGH2-CHEM (White, 1995) that employs a fully coupled approach, is also used for pyrite oxidation problem for comparison. The latter code solves equations of flow, multi-component chemical transport and reaction simultaneously, and the reaction effect on the fluid flow is taken into account. We simulated the pyrite oxidation problem in a 1-D variably saturated flow system using the

two codes. We will see that in the unsaturated zone gas diffusion can be a more important mechanism for oxygen supply than gas or liquid advection, and the reaction effect on fluid is not significant. We must mention that this coupling of flow to chemical reaction is not significant under ambient conditions presented in this paper, however when fluid flow and chemical reactions are strongly coupled, such as when boiling takes place in geothermal reservoirs, this could be essential.

The oxidative weathering of sulfide minerals is influenced by the presence of other minerals. A wide variety of homogeneous and heterogeneous reactions could take place simultaneously in the reactive fluid-rock system. For this purpose, the example of supergene copper enrichment in a unsaturated-saturated medium is presented, which involves the oxidative weathering of pyrite (FeS_2) and chalcopyrite (CuFeS_2) and associated acidification that causes mobilization of metals in the unsaturated zone, with subsequent formation of enriched secondary copper bearing sulfide mineral deposits chalcocite (Cu_2S) and covellite (CuS) in the reducing conditions below the water table. Acidification, mobilization of metals and alteration of primary minerals mostly take place in unsaturated zone (oxidizing), precipitation of secondary minerals mainly occur in saturated zone (reducing). The water table can be considered as a interface between oxidizing and reducing zones. Water table drop due to decreasing infiltration results in moving oxidizing zone and redevelopment of secondary mineral deposit. The alteration of primary rock minerals and the development of secondary minerals predicted by our model are consistent with observations in supergene copper deposits in the Atacama Desert, Northern Chile (Ague and Brimhall, 1989).

Oxidative weathering processes are difficult to model numerically, because redox sensitive chemical species such as $O_2(aq)$, SO_4^{2-} and HS^- could change over tens of orders of magnitude between oxidizing and reducing conditions. In order to simulate substantial oxidative weathering progress over a large geologic time (such as 100000 years), one can benefit from the "quasi-stationary state" (QSS; Lichtner, 1988) approximation. After a brief transient evolution, the reactive system settles into a QSS, during which aqueous concentrations of all chemical species remain essentially constant. Dissolution of primary and precipitation of secondary minerals proceed at constant rates. In fact, no complex calculations are necessary and only abundance of mineral phases needs to be updated. This state terminates when one or more minerals dissolve completely at any of the grid blocks. A tremendous saving of computing time (99%) using QSS approximation is demonstrated from the supergene copper enrichment example.

Mineral dissolution and precipitation over geological time may result in considerable changes in porosity. As a result, permeability is changed and then fluid flow. Changes in porosity and permeability were implemented in our compute model. However, these changes require a smaller time step, and quasi-stationary state for reactive chemical transport is never reached. It is difficult to complete a large geological time (100000 years) simulation. In this work, only changes in porosity are allowed. Changes in permeability and the feedback on fluid flow are not considered. This is not true for real world, but does give us rough picture how dissolution and precipitation changes porosity.

Even though oxidative weathering is sensitive to many factors, this work demonstrates that our model provides a comprehensive suite of process modeling

capabilities, which could serve as a prototype for oxidative weathering processes with broad significance for geoscientific, engineering, and environmental applications.

2. Mathematical model and numerical implementation

2.1. Mathematical model

In the present work, major assumptions are made as follows: (1) aqueous chemical concentration changes do not influence fluid thermophysical properties such as density and viscosity; (2) changes in partial pressure of oxygen gas other than H_2O and air (i.e. trace gas) due to chemical reactions do not affect overall gas and liquid flow, the accuracy of this assumption is discussed in section 3; (3) the effect of porosity and permeability change from mineral dissolution/precipitation on fluid flow is neglected, the detailed discussion is given in section 6; and (4) heat generation due to chemical reactions is neglected.

All flow and transport equations have the same structure, and can be derived from the principle of mass (or energy) conservation. Table 1 summarizes these equations and Table 2 gives the meaning of symbols used. The non-isothermal multi-phase flow consists of fluid flow in both liquid and gas phases, and heat transport, which has been discussed in detail by Pruess (1987 and 1991). Aqueous (dissolved) species are subject to transport in the liquid phase as well as to local chemical interactions with the solid and gaseous 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 et al., 1994).

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.

Table 1. Governing equations for fluid and heat flow, and chemical transport. Symbol meanings are given in Table 2.

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

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

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

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

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

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

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

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

Table 2. Symbols used in Table 1.

C	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	Subscripts:	
k _r	relative permeability	a	air
g	gravitational acceleration, m s ⁻²	g	gas phase
M	mass accumulation, kg m ⁻³	h	heat
N	number of chemical components	j	chemical component in liquid phase
p	pressure, Pa	k	chemical component in gas phase
q	source/sink	l	liquid phase
S	saturation	s	solid phase
T	temperature, °C	w	water
U	internal energy, J kg ⁻¹	κ	governing equation index
u	Darcy velocity, m s ⁻¹	β	phase index
X	mass fraction		
φ	porosity		

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

The primary governing equations given in Table 1 must be complemented with constitutive local relationships that express all parameters as functions of thermophysical and chemical variables. These expressions for non-isothermal multiphase flow are given by Pruess (1987). The expressions for reactive chemical transport are given below. The primary governing equations are nonlinear due to these local relationships.

A chemical species is defined as any chemical entity distinguishable from the rest due to (1) its elemental composition, and (2) by the phase in which it is present. For instance, gaseous O₂ is a different species from aqueous O₂. Not all species are needed to fully describe the chemical system. The subset of species which is strictly necessary is made up of what are known as basis or master or primary species, or components (Parkhurst et al., 1980; Reed, 1982; Yeh and Tripathi, 1991; Wolery, 1992; Steefel and Lasaga, 1994). The remaining species are called secondary species consisting of aqueous, precipitated

(mineral), and gaseous species. The secondary species can be represented as a linear combination of the set of the basis species (Table 3). Aqueous complexation and gas dissolution/exsolution are assumed to proceed according to the local equilibrium. Mineral dissolution/precipitation can proceed either subject to local equilibrium or kinetic constraints. Three types of equations are required for solving the chemical reaction system: mass action equations for equilibrium, rate expressions for kinetics, and mass balances for the basis chemical species (Table 3). To help understand the formulation for chemical reactions, we selected a simple illustrative example in Table 3; in fact, our model is valid for any geochemical system. All reactions in Table 3 are written in dissociation forms, which are useful for facilitating mathematical modeling. For the mass action equations of aqueous dissociation, the activity 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 a pure mineral phase 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 (in bar). Only mineral dissolution and precipitation are allowed to proceed subject to kinetics. The rate expression used is taken from Lasaga et al. (1994). Mass conservation in the closed chemical system is written in terms of basis species. The species distribution must be governed by the total concentration of the component.

Table 3. List of chemical reaction equations: mass action, rate expression and mass balance (illustrated by specific examples; in fact the model is valid for general geochemistry). Symbol meanings are given in Table 4.

General dissociation reactions	$S_i^s = \sum_{j=1}^{N_c} v_{ij} S_j^p$
(1) General mass action equations:	$K_i a_{S_i^s} = \sum_j^{N_c} (a_{S_j^p})^{v_{ij}}$
Aqueous dissociation: $\text{HSO}_4^- = \text{SO}_4^{2-} + \text{H}^+$	$K_{\text{HSO}_4^-} \gamma_{\text{HSO}_4^-} c_{\text{HSO}_4^-} = \gamma_{\text{SO}_4^{2-}} c_{\text{SO}_4^{2-}} \gamma_{\text{H}^+} c_{\text{H}^+}$
Mineral dissolution: $\text{pyrite}(\text{FeS}_2) = 2\text{SO}_4^{2-} + \text{Fe}^{2+} + 2\text{H}^+ - 3.5\text{O}_2(\text{aq}) - \text{H}_2\text{O}$	$K_{\text{pyrite}} = (\gamma_{\text{SO}_4^{2-}} c_{\text{SO}_4^{2-}})^2 (\gamma_{\text{Fe}^{2+}} c_{\text{Fe}^{2+}}) (\gamma_{\text{H}^+} c_{\text{H}^+}) (\gamma_{\text{O}_2(\text{aq})} c_{\text{O}_2(\text{aq})})^{-3.5}$
Gas dissolution: $\text{O}_2(\text{g}) = \text{O}_2(\text{aq})$	$K_{\text{O}_2(\text{g})} f_{\text{O}_2(\text{g})} = \gamma_{\text{O}_2(\text{aq})} c_{\text{O}_2(\text{aq})}$
(2) Rate expressions:	$r_m = k_m A_m [1 - (Q_m / K_m)^\theta]^\eta \quad \text{negative for precipitation}$
Pyrite dissolution rate (first order):	$r_{\text{pyrite}} = k_{\text{pyrite}} A \left(1 - \frac{Q_{\text{pyrite}}}{K_{\text{pyrite}}} \right)$
	$Q_{\text{pyrite}} = (\gamma_{\text{SO}_4^{2-}} c_{\text{SO}_4^{2-}})^2 (\gamma_{\text{Fe}^{2+}} c_{\text{Fe}^{2+}}) (\gamma_{\text{H}^+} c_{\text{H}^+}) (\gamma_{\text{O}_2(\text{aq})} c_{\text{O}_2(\text{aq})})^{-3.5} = K_{\text{pyrite}} \quad \text{at equilibrium}$
(3) Mass conservation for the basis species	

Table 4. Symbols used in Table 3. Note that some symbols that have been used in Table 1 have different meanings here.

A	specific reactive surface area, $\text{m}^2 \text{kg}^{-1}$	T	total concentration of component, mol l^{-1}
a	thermodynamic activity	S^p	basis species
C	total dissolved concentration of component, mol l^{-1}	S^s	secondary species
c	species concentration, mol l^{-1}	γ	thermodynamic activity coefficient
f	partial pressure of gas species, bar	v	Stoichiometric coefficient
Q	ion activity product		
K	Equilibrium constant		
k	kinetic rate constant, $\text{mol m}^{-2} \text{s}^{-1}$	Subscript:	
N_c	number of component (basis species)	i	secondary species index
r	net dissolution rate, $\text{mol l}^{-1} \text{s}^{-1}$	j	basis species index
S	species chemical formula	m	mineral index
		n, θ , η	experimental parameters

Two major approaches have been used for formulating redox reactions: (1) the oxygen approach which is based on attributing the oxidizing potential to the dissolved oxygen (Nordstrom and Muñoz, 1986; Wolery, 1992), such as, $\text{HS}^- = \text{SO}_4^{2-} - 2\text{O}_2(\text{aq}) + \text{H}^+$; and (2) the hypothetical electron approach in which each half redox reaction is completed by adding electrons as transferable species, for example, $\text{HS}^- = \text{SO}_4^{2-} - 4\text{H}_2\text{O} + 8\text{e}^- + 9\text{H}^+$. Using these two approaches, mathematical equations for redox reactions have the same form as aqueous complexation reactions. In this paper we use the oxygen approach, because in contrast to the free electron, oxygen can be present and be transported in natural subsurface flow systems. Using this approach $\text{O}_2(\text{aq})$ is selected as the basis species for redox instead of e^- .

2.2. Numerical implementation

The above mentioned mathematical equations of flow, transport and reaction, has been implemented in the computer model TOUGHREACT (Xu and Pruess, 1998). This is based on the framework of the non-isothermal multi-phase flow simulator TOUGH2 (Pruess 1991). The numerical solution of the multi-phase flow and reactive chemical transport equations employs space discretization by means of integral finite differences (Narasimhan and Witherspoon, 1976) and fully implicit first-order finite differences in time. TOUGHREACT uses a sequential iteration approach similar to Yeh and Tripathi (1991), Engesgaard and Kipp (1992), and Walter et al (1994). The multi-phase flow and transport and reaction equations are solved sequentially. 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 by means of chemical reaction source/sink terms from the previous reaction iteration. The resulting concentrations obtained from the transport are substituted into the chemical speciation model. The system of chemical reaction equations is solved on a grid-block basis by Newton-Raphson iterative method similar to Parkhurst (1980), Reed (1982), and Wolery (1992). The chemical transport and reactions are iteratively solved until convergence.

TOUGHREACT can work with two different fluid flow modules, known as EOS9 and EOS3. Using EOS9, only saturated-unsaturated liquid phase flow is considered (Richards' equation). In this case only the oxygen diffusion process can be considered for gaseous species transport. Using EOS3, the full non-isothermal multi-phase flow equations (for liquid, gas and heat) are solved. The dissolution of gaseous oxygen induced by pyrite oxidation reduces oxygen partial pressure, as well as the total pressure of the gas phase. As a result, the gas flow is modified, then the liquid phase flow. This reaction effect on the fluid flow is not considered, although advection and diffusion are considered for oxygen transport processes. To examine importance of this effect, another TOUGH2 family reactive transport code TOUGH2-CHEM (White, 1995) that employs a fully coupled approach, is also used for comparison (see the next section). The latter code solves the multi-component chemical transport simultaneously with the heat and mass flow problem so that equations of flow and multi-component transport are fully coupled and the reaction effect on the fluid flow is taken into account.

3. Pyrite oxidation

A one-dimensional flow system is modeled. Only reactions directly associating pyrite (FeS_2) oxidation were considered. This problem is based on Xu et al. (1999). Here it is employed again to illustrate importance of reaction effect on fluid flow and oxygen gas diffusion to the oxidative weathering processes. Two computer simulators TOUGHREACT (using EOS9 flow module, only saturated-unsaturated liquid phase flow is considered) and TOUGH2-CHEM based on different numerical approaches are used.

The flow model is a vertical column extending from the atmosphere through an unsaturated and a saturated zone and extending below the water table (see Figure 1). Oxygen is supplied to the top of the column as a dissolved species in infiltrating rainwater and is also transported by the gas phase from the land surface. Because TOUGH2-CHEM includes a coupling between the gas (and liquid) phase flows and chemical reaction it is not possible to solve identical problems with the two codes when the gas phase is included. For the variably saturated medium, TOUGH2-CHEM must include an extra component, nitrogen, to correctly model the gas phase. The initial flow conditions are set by specifying the rate of water infiltration into the top of the model (0.07 m yr^{-1}) and a constant pressure of 3.5 bar at the bottom. The steady state water saturation obtained by ignoring chemical reactions are used as initial conditions for the calculation of reactive chemical transport. Physical parameters for this unsaturated-saturated medium are listed in Table 5.

Figure 1. Schematic representation of the unsaturated-saturated flow system used for pyrite oxidation.

Table 5. Physical parameters used for the unsaturated-saturated flow system.

Parameter	Value
Infiltration (m yr^{-1})	0.07
Depth (m)	50
Grid size (m)	1
O_2 partial pressure at the land surface (bar)	0.2
Permeability (m^2)	7×10^{-12}
gas O_2 diffusivity ($\text{m}^2 \text{s}^{-1}$)	4.4×10^{-5}
Tortuosity	0.1
Porosity	0.1
Relative permeability and capillary Pressure (van Genuchten curves, 1980):	
λ	0.457
S_{lr}	0.05
S_{ls}	1.0
$P_0(\text{Pa})$	1.96×10^3

The initial water composition corresponds to a dilute reducing water with aqueous oxygen concentration, $C_{\text{O}_2(\text{aq})}$, of $1.0 \times 10^{-70} \text{ mol l}^{-1}$. The infiltration water compositions

correspond to a dilute oxidizing water with $C_{O_2(aq)} = 2.53 \times 10^{-4}$ which is at equilibrium with an atmospheric O_2 partial pressure of 0.2 bar. Initial pyrite abundance is 9% by volume. Aqueous dissociation and gas dissolution are assumed to proceed according to local equilibrium. Pyrite oxidation is subject to kinetic rates. The rate constant used is $2 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$, and specific surface area is $58.7 \text{ m}^2 \text{ m}^{-3}$ medium. In addition to pyrite oxidative dissolution and oxygen gas dissolution, The following aqueous species are considered: (1) component species, H^+ , H_2O , SO_4^{2-} , Fe^{2+} , and $O_2(aq)$; (2) secondary species, HS^- , $H_2S(aq)$, Fe^{3+} , OH^- , HSO_4^- , and $FeSO_4(aq)$. Thermodynamic equilibrium constants used are from the EQ3/6 database (Wolery, 1992).

The TOUGHREACT includes oxygen diffusion in the gas phase in addition to aqueous transport processes. Using an active gas phase in TOUGH2-CHEM not only invokes oxygen diffusion in the gas phase, but also includes an overall advective gas flow, in response to reduction of gas phase pressures from oxygen consumption. Because of these different process descriptions, some differences are expected (see Figure 2). Even though TOUGH2-CHEM provides a more complete process description, both results agree reasonably well. This indicates that gas diffusion provides a much stronger mechanism for oxygen supply than aqueous advection. When analyzing water flow through partly saturated porous media, usually the role of the gas phase can be disregarded by assuming the gas phase to be immobile. This is consistent with the statement of de Marsily (1986), using the mobile air phase approach does not give results significantly different from the immobile approach, except for very special cases. This means that for the purpose of solving the water flow, the whole gas phase is at the same

pressure (usually the atmospheric pressure). In addition, the sequential code TOUGHREACT is much more efficient than the fully coupled TOUGH2-CHEM. The former requires 3 minutes (on a Pentium 200 PC) for a simulation of 150 years, while the latter requires 90 minutes on the same computer for the same simulation time.

Figure 2. pH (a) and total dissolved S (b) obtained from TOUGHREACT and TOUGH2-CHEM. TOUGHREACT results consider oxygen gas diffusion in addition to chemical transport in the liquid phase, while TOUGH2-CHEM results consider reaction effect on the fluid flow, gas advection and diffusion.

To further illustrate the importance of gas transport processes on oxidative weathering geochemistry, we also present results that did not include gas transport processes (Figure 3). When oxygen gas transport processes are considered in addition to chemical transport in the liquid phase, much lower pH (compare Figure 2a to 3a) and a higher dissolved concentrations (compare Figure 2b to 3b) are obtained. This indicates again that gas diffusion provides a much stronger mechanism for oxygen supply. In

addition, results obtained from both codes agree very well when only chemical transport in the liquid phase is considered.

Figure 3. pH (a) and total dissolved S (b) obtained by considering only chemical transport in the liquid phase.

From the simulations of this unsaturated-saturated pyrite oxidation problem, we may draw the following conclusions: (1) the effects of partial pressure reduction due to reactions on the fluid flow may be not significant under ambient conditions, (2) gas diffusion can be a more important mechanism for oxygen supply than gas or liquid advection. We must mention that this coupling of flow to chemical reaction is not significant in the examples presented in this paper, however when fluid flow and chemical reactions are strongly coupled, such as when boiling takes place in geothermal reservoirs, this could be essential.

4. Supergene copper enrichment

Supergene enrichment involves hydrochemical differentiation by near-surface weathering processes in which water transports metals from a source region or leached zone to a locus of an enrichment blanket zone where these ions are reprecipitated as secondary ore compounds (Figure 4). The geochemistry for this work was based on field and laboratory studies of supergene copper systems as carried out by Brimhall and Alpers (1985), and Ague and Brimhall (1989). The model system as shown in Figure 4 captures, in simplified manner, conditions of desertification in Northern Chile that led to oxidation and chemical enrichment of copper deposits at certain times in the past when downward movements in the ground water table exposed sulfides to unsaturated conditions.

Figure 4. A schematic representation of a supergene copper enrichment system according to Ague and Brimhall (1989).

Supergene copper enrichment involves oxidative weathering of pyrite (FeS_2) and chalcopyrite (CuFeS_2) and acidification that causes mobilization of metals in the oxidizing

zone and alteration of primary minerals, with subsequent formation of enriched secondary copper bearing sulfide mineral deposits (enrichment blanket) in the reducing conditions just below water table. Such oxidative weathering driven processes have produced some of the world's largest copper deposits (Ague and Brimhall, 1989). The sequential iteration approach code TOUGHREACT was employed. Only gas diffusion is considered for gas transport processes, which is believed to be a more important oxygen supply mechanism under ambient conditions.

4.1. Model system

The model system is shown in Figure 5. Oxygen is supplied to a protore containing pyrite and chalcopyrite (Table 6) as a dissolved species in infiltrating rainwater, as well as by gaseous diffusion from the land surface boundary. A vertical column of 40 m thickness is used, which is discretized into 20 grid blocks with a constant spacing of 2 m. A gaseous diffusion coefficient of $4.38 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ and a tortuosity of 0.1 are used. In the first period of 20000 years, a infiltration of 0.07 m yr^{-1} is assumed, and water table is located at a depth of 16 m. After 20000 years, the infiltration is assumed to reduce to 0.015 m yr^{-1} , the water table moves down to a depth of 24 m. In real world, infiltration decrease and water table drop is achieved gradually. However, compared to the total simulation time of 102500 years, they can be assumed immediately. Two steady-state water flow regimes are assumed (see Figure 6).

Figure 5. Model setup of a one-dimensional supergene copper enrichment system

Figure 6. Steady-state water saturation distribution along the unsaturated-saturated medium.

The column is initially filled entirely with a protore mineral assemblage as listed in Table 6. The dissolution of the primary minerals is kinetically controlled. The kinetic rate constants and specific surface areas used are also given in Table 6. These two parameters may vary over a wide range in the field, and are not well-known. Surface areas are also changed dynamically due to dissolution and precipitation processes. These uncertainties are not taken into account in the present work. Chemical formulae and dissociation stoichiometries of the primary minerals are given in Table 7. Oxygen is treated as an ideal gas, and its interaction with the aqueous solution is assumed at equilibrium. The precipitation of secondary minerals (Table 8) during the simulation progress is also assumed to proceed at equilibrium.

Table 6. Chemical properties of initial protore mineral reactants. Volume fraction, rate constant and specific surface area are based on Ague and Brimhall (1989) and Gerard *et al.* (1997).

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}	586.7
Chalcopyrite	4.5	1.05	4.0×10^{-15}	586.7
Magnetite	4.5	1.01	2.0×10^{-15}	586.7
K-feldspar	18.0	1.65	3.1×10^{-16}	2710.0
Albite	9.0	0.9	3.1×10^{-16}	1360.0
Anorthite	9.0	0.89	1.5×10^{-16}	1420.0
Annite	4.5	0.29	2.4×10^{-18}	586.7
Muscovite	9.0	0.64	2.4×10^{-18}	1230.0
Quartz	18.0	7.93	4.3×10^{-18}	850.0
Anhydrite	4.5	0.98	1.5×10^{-16}	510.0
	Total=90			
	Void=10			

Table 7. Chemical reactions 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	$FeS_2 + H_2O + 3.5O_2(aq) = 2SO_4^{2-} + Fe^{2+} + 2H^+$	217.4
Chalcopyrite	$CuFeS_2 + 4O_2(aq) = 2SO_4^{2-} + Fe^{2+} + Cu^{2+}$	244.07
Magnetite	$Fe_3O_4 + 8H^+ = Fe^{2+} + 2Fe^{3+} + 4H_2O$	10.4724
K-feldspar	$KAlSi_3O_8 + 4H^+ = K^+ + Al^{3+} + 3SiO_2(aq) + 2H_2O$	-0.2753
Albite	$NaAlSi_3O_8 + 4H^+ = Na^+ + Al^{3+} + 3SiO_2(aq) + 2H_2O$	2.7645
Anorthite	$CaAl_2Si_2O_8 + 8H^+ = Ca^{2+} + 2Al^{3+} + 2SiO_2(aq) + 4H_2O$	26.5780
Annite	$KFe_3AlSi_3O_{10}(OH)_2 + 10H^+ = K^+ + 3Fe^{2+} + Al^{3+} + 3SiO_2(aq) + 6H_2O$	29.4693
Muscovite	$KAl_3Si_3O_{10}(OH)_2 + 10H^+ = K^+ + 3Al^{3+} + 3SiO_2(aq) + 6H_2O$	13.5858
Quartz	$SiO_2 = SiO_2(aq)$	-3.9993
Anhydrite	$CaSO_4 = Ca^{2+} + SO_4^{2-}$	-4.3064

Table 8. The chemical reactions for secondary minerals. The thermodynamic equilibrium constants are from the EQ3/6 database (Wolery, 1992).

Mineral	Reaction equation	log K (25°C)
Covellite	$CuS + H^+ = Cu^{2+} + HS^-$	22.8310
Chalcocite	$Cu_2S + H^+ = 2Cu^+ + HS^-$	-34.7342
Bornite	$Cu_5FeS_4 + 4H^+ = Cu^{2+} + 4Cu^+ + Fe^{2+} + 4HS^-$	-102.44
Goethite	$FeOOH + 3H^+ = Fe^{3+} + 2H_2O$	-0.283
Hematite	$Fe_2O_3 + 6H^+ = 2Fe^{3+} + 3H_2O$	0.1086
Kaolinite	$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2SiO_2(aq) + 5H_2O$	6.8101
Alunite	$KAl_3(OH)_6(SO_4)_2 + 6H^+ = K^+ + 3Al^{3+} + 2SO_4^{2-} + 6H_2O$	-0.3479
Amorphous silica	$SiO_2 = SiO_2(aq)$	-2.7136

A dilute oxidizing water with an oxygen partial pressure of 0.2 bar is initially placed in the unsaturated zone, while a reducing water with a oxygen partial pressure of 1×10^{-70} bar is assumed for the saturated zone. The infiltration water composition is the same as the

initial unsaturated water. A total of 52 aqueous species are considered (Table 9). The aqueous complexation is assumed at equilibrium.

Table 9. Aqueous species considered in the TOUGHREACT simulations of supergene copper enrichment. Secondary species can be expressed in terms of the primary (basis) species.

Primary species:	Secondary species:		
H ⁺	OH ⁻	Al ₂ (OH) ₂ ⁴⁺	CaOH ⁺
H ₂ O	HSO ₄ ⁻	Al ₃ (OH) ₄ ⁵⁺	Cu ⁺
O ₂ (aq)	H ₂ SO ₄ (aq)	HAIO ₂ (aq)	CuOH ⁺
SO ₄ ²⁻	NaSO ₄ ⁻	AlO ₂ ⁻	CuCl ₂ (aq)
Fe ²⁺	KSO ₄ ⁻	FeCl ²⁺	CuCl ₂ ⁻
Cu ²⁺	CaSO ₄ (aq)	FeCl ₂ ⁺	CuCl ₄ ²⁻
Na ⁺	FeSO ₄ (aq)	FeOH ⁺	CaCl ⁺
K ⁺	Fe(SO ₄) ₂ ⁻	FeOH ²⁺	KCl(aq)
Ca ²⁺	FeSO ₄ ⁺	Fe(OH) ₂ ⁺	Fe ³⁺
Al ³⁺	FeCl ⁺	Fe ₂ (OH) ₂ ⁴⁺	HS ⁻
SiO ₂ (aq)	AlSO ₄ ⁺	Fe(OH) ₂ (aq)	H ₂ S(aq)
Cl ⁻	Al(SO ₄) ₂ ⁻	Fe(OH) ₃ (aq)	HSiO ₃ ⁻
	AlOH ²⁺	Fe ₃ (OH) ₄ ⁵⁺	NaHSiO ₃ (aq)
	Al(OH) ₂ ⁺		

4.2. Results

4.2.1. Before water table drop

In the unsaturated zone, pyrite and chalcopryrite are oxidized and dissolved (Figure 7a). As aqueous phase oxygen is depleted through reaction with pyrite and chalcopryrite, it is replenished by dissolution from the gas phase, and by diffusive transport from the atmospheric boundary at the land surface (see Figure 8a). The pH decreases downward (Figure 8b). The total dissolved S concentration (Figure 8c) increase downward. Total dissolved Cu and Al (Figure 8d) also increase. When the aqueous solution reaches the

reducing saturated zone, the secondary copper bearing minerals chalcocite and covellite are precipitated (Figure 7c), forming the enrichment blanket immediately below the water table (Ague and Brimhall, 1989). In addition, goethite (Figure 6d) precipitates in the unsaturated zone.

At the same time magnetite (Figure 4a), K-feldspar, albite, anorthite (Figure 4b), annite and muscovite dissolve throughout the column due to decrease of pH. Magnetite dissolution (Figure 6a) 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 7d). Kaolinite (Figure 7c) and alunite (Figure 7d) precipitation occurs only in the bottom of the saturated zone. There is no quartz dissolution as this mineral is stable in our simulation, as it is in nature.

(a)

(b)

(c)

(d)

Figure 7. Change of mineral abundance (in volume fraction) after 20000 years. Negative values indicate dissolution, and positive indicate precipitation.

(a)

(b)

(c)

(d)

Figure 8. Dissolved oxygen concentration (a), pH (b), dissolved S and Si concentrations (c) and dissolved Cu and Al concentrations (d) at 20000 years.

4.2.2. After water table drop

After water table drops down from 16 to 24 m depth, the transition zone or the first enrichment blanket becomes water unsaturated and oxidizing. As a result, the secondary sulfide mineral chalcocite and covellite (Figure 9c), which is stable before water table drop, are oxidized and dissolved in addition to the primary protore mineral pyrite and chalcopyrite oxidative dissolution (Figure 9a). The first enrichment blanket gradually disappears. The new enrichment zone is formed just below the second water table (Figure 9c). Consequentially, the other mineral dissolution and precipitation (Figures 9b and 9d), and aqueous concentration (Figures 10a-d) are redistributed. The water table drop results in not only aqueous chemical movement, but also secondary sulfide mineral migration. The latter is much slower. In this example it takes approximately 80000 years. The time required to migrate the minerals depends on many factors such as kinetic dissolution rates, reactive surface, atmospheric oxygen partial pressure, medium tortuosity, infiltration, water table depth, which are out of the scope of this paper.

The alteration of the primary minerals and development of secondary mineral assemblages predicted by our model are consistent with observations in supergene copper deposits (Ague and Brimhall, 1989).

We initially supposed the different secondary mineral assemblages in the second enrichment blanket. Some numerical experiments were performed with the codes TOUGH2-EQ6 and TOUGHREACT. The simulation results indicate that The secondary mineral assemblages in the second blanket are approximately the same as those in the first enrichment blanket.

(a)

(b)

(c)

(d)

Figure 9. Change of mineral abundance (in volume fraction) after 102500 years. Negative values indicate dissolution, and positive indicate precipitation.

(a)

(b)

(c)

(d)

Figure 10. Dissolved oxygen concentration (a), pH (b), dissolved S and Si concentrations (c) and dissolved Cu and Al concentrations (d) at 102500 years.

5. Quasi-stationary states and time stepping

Reactive transport of sulfide mineral weathering chemicals occurs on a broad range of geological time scales. After a brief transient evolution, the reactive system settles into a "quasi-stationary state" (QSS; Lichtner, 1988), during which aqueous concentrations of all chemical species remain essentially constant. Dissolution of primary and precipitation of secondary minerals proceed at constant rates. In fact, no complex calculations are necessary and only abundance of mineral phases needs to be updated. This state terminates when one or more minerals dissolve completely at any of the grid blocks. A relative concentration change, δ_c , and a relative dissolution (or precipitation) rate change, δ_r , are used to monitor attainment of the QSS conditions,

$$\delta_c = \max_{\substack{\text{all components} \\ \text{all grid blocks}}} \left| \frac{C^{k+1} - C^k}{C^k} \right| < \epsilon_c \quad (1a)$$

$$\delta_r = \max_{\substack{\text{all minerals} \\ \text{all grid blocks}}} \left| \frac{r^{k+1} - r^k}{r^k} \right| < \epsilon_r \quad (1b)$$

where k is the transport time step index, C are dissolved component concentrations, r are dissolution or precipitation rates, and ϵ_c and ϵ_r are the QSS tolerances (see Figure 11). After some 50 years relative concentration changes (Figure 11a) are reduced to 10^{-5} , while dissolution rate changes (Figure 11b) are not very stable. Concentration changes are

controlled by both chemical reaction and transport, while dissolution rate changes only depend on reaction and strongly affected by local chemical system. Some mineral in the saturated zone precipitates at a extremely low rate in the order below $10^{-20} \text{ mol s}^{-1} \text{ m}^{-3}$, which has a significant influence on ϵ_r . The maximum relative dissolution rate changes by excluding these extremely low values are shown in Figure 12. After 15 years, the rates essentially remain constant. The observed numerical sensitivities suggest that criteria for the quasi-stationary state need to be carefully specified. In the simulation given in section 4, tolerances ϵ_c and ϵ_r are set equal to 10^{-5} and 10^{-4} , respectively. After 50 years, a QSS is reached. This QSS is maintained until 14200 years when chalcopyrite is dissolved completely at the first top grid block and the QSS is terminated. Then the simulation is extrapolated from 50 years to 14200 years. A total of 99.6 % of computing time is saved. After some time, a new QSS is reached. A number of QSS states are encountered in the supergene copper enrichment example. Use of the QSS is of considerable practical importance, because substantially larger time steps should be possible during periods where a QSS is present (Neretnieks et al., 1997).

(a)

(b)

Figure 11. Maximum relative concentration and dissolution (precipitation) rate changes for the TOUGHREACT simulation of supergene copper enrichment (given in the previous section).

Figure 12. Maximum relative dissolution (precipitation) rate change by excluding extremely low rate values.

A huge variation of concentration of species involves in redox reactions. For example sulfite and sulfide (SO_4^{2-} and HS^-) species concentrations vary over tens of orders of magnitude between oxidizing and reducing conditions. A very small time step is required in order to give a close initial estimate for convergence. Time steps can be increased gradually up to a maximum value when approaching a QSS. An automatic time stepping scheme is implemented in TOUGHREACT. Two time step levels are used. The global time step, Δt_1 , is controlled by the solution of the transport equations. During a time interval of Δt_1 , depending on convergence, multiple steps Δt_2 , with $\sum \Delta t_2 = \Delta t_1$ can be used for reaction calculations. The Δt_2 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_2 may be required.

5. Porosity change

The changes in porosity caused by mineral dissolution and precipitation can be easily related to mineral volume changes

$$\Delta\phi = -\sum_i^{N_m} \Delta f_i \quad (2)$$

where ϕ is porosity, i is mineral index, N_m is the number of minerals including primary and secondary, and f is the mineral volume fraction. The permeability change associated with

this change in porosity is a complex problem because the porosity-permeability correlation depends on many factors such as pore size distribution, pore shapes, and connectivity (Verma and Pruess, 1988). Effect of changes in porosity and permeability on fluid flow is considered in TOUGHREACT model. However, a trial run indicated that considering this effect results in a very slow convergence and requires a smaller time step, and quasi-stationary state for fluid flow and reactive chemical transport is never reached. It is difficult to complete a large geological time simulation with the current computer power (even a high performance supercomputer). In the example of supergene copper enrichment, only changes in porosity due to mineral dissolution and precipitation are calculated (see Figure 13). The feedback of these changes on fluid flow is not considered. This is not true for real world, but does give us rough picture how dissolution and precipitation changes porosity. Figure 13a shows that: (1) in unsaturated zone porosity has a positive change, indicating that dissolution is dominant, and it has a maximum value at the land surface and gradually decreases downward; (2) from the water table to a depth of 30 m porosity also has a positive change, this is because in this zone silica-alumina minerals still dissolve, secondary copper bearing sulfide minerals (chalcocite and covellite) precipitate, and have high densities; (3) at the bottom of saturated zone (below a depth of 30 m) porosity has a negative change, indicating precipitation is dominant. After water table drops from 16 to 24 m depth, the transition zone becomes oxidizing. Not only primary minerals dissolve, but also secondary sulfide minerals dissolve again, resulting in porosity increase significantly (Figure 13b).

Figure 13. Cumulative changes in porosity at 20000 (a) and 102500 (b) years for the simulation of supergene copper enrichment example. Feedback of porosity changes on fluid flow is not considered.

7. Conclusions

The effects of oxygen partial pressure reduction due to oxidative weathering on the fluid flow may be not significant, and oxygen gas diffusion can be a more important mechanism for oxygen supply than gas or liquid advection. We must mention that this coupling of flow to chemical reaction is not significant under ambient conditions in the examples presented in this paper, however when fluid flow and chemical reactions are strongly coupled, such as when boiling takes place in geothermal reservoirs, this could be essential.

The simulation of supergene copper enrichment indicates acidification, mobilization of metals and alteration of primary minerals mostly take place in unsaturated zone

(oxidizing), precipitation of secondary minerals mainly occur in saturated zone (reducing). The water table can be considered as a interface between oxidizing and reducing zones. Water table drop due to infiltration decrease results in oxidizing zone drop and secondary sulfide mineral migration. The alteration of primary rock minerals and the development of secondary minerals predicted by our model are consistent with observations in supergene copper deposits in the Atacama Desert, Northern Chile.

Oxidative weathering of sulfide minerals is difficult to model numerically, because redox sensitive chemical species concentrations vary over tens of orders of magnitude between oxidizing and reducing zones. In order to simulate substantial reaction process and precipitation of secondary minerals over large geologic time, one can benefit from the quasi-stationary state (QSS) approximation. Substantial saving of computing time has been seen from the example. Oxidative weathering over geological time may result in large changes in porosity. As a result, permeability is changed and then fluid flow. However, if the latter effects are taken into account, simulation progresses very slow and the QSS for fluid flow and reactive chemical transport is never reached. Consequently, it is difficult to simulate over a large geological time.

Even though oxidative weathering processes are sensitive to many factors, this work has demonstrated that our model provides a comprehensive suite of process modeling capabilities, which could serve as a prototype for oxidative weathering processes with broad significance for geoscientific, engineering, and environmental applications. For better understanding the problem, we have only presented the case in one-dimensional flow domain. In fact, the model can be applied to two or three-dimensional problems with physical and chemical heterogeneity.

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