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INCORPORATION OF AQUEOUS AND SORPTION KINETICS AND BIODEGRADATION INTO TOUGHREACT

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ABSTRACT

The needs for considering aqueous and sorption kinetics and microbiological processes arises in many subsurface problems, such as environmental and acid mine remediation. A general rate expression has been implemented into TOUGHREACT, which considers multiple mechanisms (pathways) and includes multiple product, Monod, and inhibition terms. In this paper, the formulation for incorporating kinetic rates among primary species into the mass balance equations is presented. A batch sulfide oxidation problem is simulated. The resulting concentrations are consistent with simple hand calculations. A 1-D reactive transport problem with kinetic biodegradation and sorption was investigated, which models the processes when a pulse of water containing NTA (nitrylotriacetate) and cobalt is injected into a column. The problem has several interacting chemical processes that are common to many environmental problems: biologically-mediated degradation of an organic substrate, bacterial cell growth and decay, metal sorption and aqueous speciation including metal-ligand complexation. The TOUGHREACT simulation results agree very well with those obtained with other simulators.

INTRODUCTION

The TOUGHREACT (Xu and Pruess, 2001; Xu et al., 2006) is a numerical simulation program for chemically reactive non-isothermal flows of multiphase fluids in porous and fractured media. The program was written in Fortran 77 and developed by introducing reactive geochemistry into the multiphase fluid and heat flow simulator TOUGH2. The program has been distributed to the public through the US Department of Energy's Energy Science and Technology Software Center (email: estsc@adonis.osti.gov; WorldWideWeb: http://www.osti.gov/estsc/). Additional information is available on the TOUGHREACT homepage, at http://www-esd.lbl.gov/TOUGHREACT/

A variety of subsurface thermo-physical-chemical processes are considered under a wide range of conditions of pressure, temperature, water saturation, ionic strength, and pH and Eh. Interactions between mineral assemblages and fluids can occur under local equilibrium or kinetic rates. The gas phase can be chemically active. Precipitation and dissolution reactions can change formation porosity and permeability. The program can be applied to many geologic systems and environmental problems, including geothermal systems, diagenetic and weathering processes, subsurface waste disposal, acid mine drainage remediation, contaminant transport, and groundwater quality.

In natural systems, many redox reactions such as sulfide oxidation that take place homogeneously within the aqueous phase are slow to achieve equilibrium, and therefore violate the local equilibrium assumption inherent in the current formulation of TOUGHREACT. The needs for aqueous and sorption kinetics and microbiological processes arose recently from subsurface problems related to environmental contamination and acid mine drainage.

MATHEMATICAL FORMULATION

The TOUGHREACT formulation for an aqueous equilibrium system was presented in Xu et al. (1999), which is based on mass balances in terms of basis species. In contrast to aqueous equilibrium, species involved in kinetic reactions, such as redox couples, are independent and must be considered as basis (or primary) species (Steefel and MacQuarrie, 1996). For example, for the reaction

$$HS^- + 2O_2(aq) = SO4^{2-} + H^+ \qquad (1)$$

under kinetic conditions, both HS^- and $SO4^{2-}$ must be placed in the basis species list. Thus, all redox reactions making use of these species must be decoupled in the input of thermodynamic database. Based on the previous formulation (Xu et al., 1999), we have added kinetic aqueous reactions with rate expressions discussed in the next section.

Let's first consider the system with only aqueous equilibrium. At time zero (initial), the total concentrations of basis species j are assumed to be known, and are given by

$$T_j^0 = c_j^0 + \sum_{k=1}^{N_x} \nu_{kj} c_k^0 + \sum_{m=1}^{N_p} \nu_{mj} c_m^0 + \sum_{n=1}^{N_q} \nu_{nj} c_n^0 \qquad j = 1 \ldots N_C \tag{2}$$

where superscript 0 represents time zero; c are concentrations (chemical reactions are always solved per kg of water, and concentration units used here are mol/kg which is close to mol/l when water density is close to 1 kg/l); 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; ν_{kj}, ν_{mj}, and ν_{nj} are stoichiometric coefficients of the basis species in the aqueous complexes, equilibrium and kinetic minerals, respectively. After a time step Δt, the total concentration of basis species j is given by

$$T_j = c_j + \sum_{k=1}^{N_x} \nu_{kj} c_k + \sum_{m=1}^{N_p} \nu_{mj} c_m + \sum_{n=1}^{N_q} \nu_{nj} \left(c_n^0 - r_n \Delta t \right) \qquad j = 1 \ldots N_C \tag{3}$$

where r is the kinetic rate of mineral dissolution (negative for precipitation, units used here are moles per kg water per time).

Now let's add aqueous kinetic reactions to the system, according to mass conservation, we have

$$T_j^0 = T_j - \sum_{l}^{N_a} \nu_{lj} r_l \tag{4}$$

where l is aqueous kinetic reaction index, N_a is total number of aqueous kinetic reactions, and r_l is the kinetic rate which is in terms of generation of one mol of product species such as $SO4^{2-}$ per unit time Therefore, for product species the stoichometric coefficient ν_{lj} are positive, for reactant species they are negative. For reaction (1), ν_{lj} for $SO4^{2-}$ and H^+ are 1, for HS^- is –1, and for $2O_2(aq)$ is -2

The set of nonlinear chemical reactions is solved by the Newton-Raphson iterative method. The use of this method requires lumping all the terms in the right-hand side in a single term (or residual function which is zero in the limit of convergence), and we denote this term by F_j^c

$$F_j^c = T_j - T_j^0 - \sum_{l}^{N_a} \nu_{lj} r_l \Delta t = 0 \tag{5}$$

By substituting Eqs. (2) and (3) into Eq. (5), we obtain

$$F_j^c = c_j + \sum_{k=1}^{N_x} \nu_{kj} c_k + \sum_{m=1}^{N_p} \nu_{mj} c_m - \sum_{n=1}^{N_q} \nu_{nj} r_n \Delta t - \sum_{l=1}^{N_a} \nu_{lj} r_l \Delta t - U_j^0 = 0 \qquad j = 1 \ldots N_C \tag{6}$$

where

$$U_j^0 = c_j^0 + \sum_{k=1}^{N_x} \nu_{kj} c_k^0 + \sum_{m=1}^{N_p} \nu_{mj} c_m^0 \tag{6a}$$

According to mass action equations, concentrations of aqueous complexes c_k can be expressed as functions of concentrations of the basis species c_j. Kinetic rates r_n and r_l are functions of c_j. No explicit expressions relate equilibrium mineral concentrations c_m, to c_j. Therefore, N_P additional mass action equations (one per mineral) are needed. Details on solution of the nonlinear-system of equations by Newton-Raphson iterative method are given in (Xu et al., 1999).

RATE EXPRESSIONS

Following the expression of Curtis (2003) and adding multiple mechanisms (or pathways), a general rate law is used,

$$r_i = \sum_{s=1}^{Mech} \left[k_i \times \prod_{j=1}^{N_l} \left(\gamma_j^{\nu_{i,j}} C_j^{\nu_{i,j}} \right) \times \prod_{k=1}^{N_m} \frac{C_{i,k}}{K_{Mi,k} + C_{i,k}} \times \prod_{p=1}^{N_p} \frac{K_{Ii,p} + C_{i,p}}{C_{i,p}} \right] \tag{7}$$

where r_i is the reaction rate of the *i*th reaction, *Mech* is number of mechanisms or pathways and *s* is the mechanism counter, k_i is a rate constant, (often denoted v_{max} in the Monod formulation), γ_j is the activity coefficient of species *j*, C_j is the concentration of species *j*, $v_{i,j}$ is a stoichiometric coefficient, N_l is the number of reacting species in the forward rate term (called product terms), N_m is the number of Monod factors (Monod terms), $C_{i,k}$ is the concentration of the *k*th Monod species, $C_{Ii,p}$ is the concentration of the *p*th inhibiting species, $K_{Mi,k}$ is the *k*th monod half-velocity coefficient of the *i*th species, N_P is the number of inhibition factors (inhibition terms), $K_{Ii,p}$ is the *p*th inhibition constant. Equation (7) accounts for multiple mechanisms, multiple

product, Monod, and inhibition terms, which can cover many rate expressions.

Three major subroutines have been added for aqueous kinetic reactions. The first reads data related to define aqueous kinetic reactions and rate expressions. The second calculates kinetic rates based on updated concentrations of basis species. The third calculates derivatives of the rate with respect to concentrations of basis species using a numerical method. The advantage of numerical derivatives is that if one changes the rate expressions the derivative subroutine is not required to change. Sorption kinetics and biodegradation reactions are accommodated in the framework of the aqueous kinetics. Adsorbed species and biomass are placed in the list of primary species but are not subject to transport (see test problem 2).

TEST

Sulfide oxidation

Let's recall the sulfide oxidation example of Equation (1). We use a rate expression for generation of $SO4^{2-}$ or H^+ as first order in $[HS^-]$ and $[O_2(aq)]$

$$r = k\,[HS^-]\,[O_2(aq)] \qquad (8)$$

In such case, only the product terms of Equation (7) are used. We considers one grid block, a batch system. Initial concentrations are 1×10^{-4} mol/kg for HS^-, 2.528×10^{-4} for $O_2(aq)$, 1×10^{-8} for $SO4^{2-}$, a pH of 7. A rate constant of $k = 1\times10^{-5}$ mol/kg s is used. The concentration evolution for 100 days is presented in Figure 1. Concentration changes are close to linear. Final concentrations are 9.793×10^{-5} mol/kg for HS^-, 2.487×10^{-4} for $O_2(aq)$, 2.084×10^{-6} for $SO4^{2-}$, a pH of 5.691. For simplicity, we use average concentrations for calculating r, or $[HS-] = (1\times10^{-4} + 9.793\times10^{-5})/2 = 9.897\times10^{-5}$, $[O_2(aq)] = (2.528\times10^{-4} + 2.487\times10^{-4})/2 = 2.508\times10^{-4}$. Therefore, $r = 1\times10^{-5}\times9.897\times10^{-5}\times 2.508\times10^{-4} = 2.482\times10^{-13}$ mol/kg s. Based on this rate, we have $[SO4^{2-}] = 1\times10^{-8} + r\Delta t = 1\times10^{-8} + 2.482\times10^{-13}\times(100\times86400) = 1\times10^{-8} + 2.144\times10^{-6} = 2.154\times10^{-6}$, which is close to the simulation result of 2.121×10^{-6}. Similarly, $[HS-] = 1\times10^{-4} - r\Delta t = 1\times10^{-4} - 2.144\times10^{-6} = 9.786\times10^{-5}$, which is close to 9.789×10^{-5}. $[O_2(aq)] = 2.528\times10^{-4} - 2r\Delta t = 1\times10^{-4} - 4.288\times10^{-6} = 2.485\times10^{-4}$, which is close to 2.486×10^{-4}. The hand calculations agree well with the simulation results.

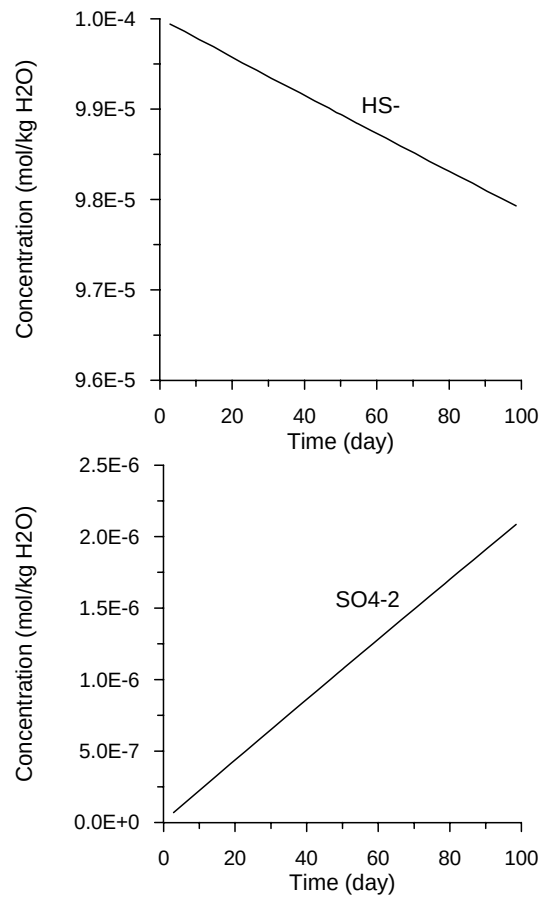

Figure 1. Concentrations vs. time for batch sulfide oxidation problem.

Kinetic biodegradation and sorption

Problem setup

A problem for reactive biogeochemical transport originally developed by Tebes-Steven and Valocchi (1998) was used for the test. This problem was also used by others for verification of PHREEQC (Parkhurst and Appelo, 1999) and Bio-CORE2D (Zhang, 2001). The problem has several interacting chemical processes that are common to many environmental problems: biologically-mediated degradation of an organic substrate, bacterial cell growth and decay, metal sorption, and aqueous speciation including metal-ligand complexation. The problem models the transport processes when a pulse of water containing NTA (nitrylotriacetate) and cobalt is injected into a column, including advection and dispersion in the column, aqueous equilibrium reactions, and kinetic reactions for NTA degradation, growth of biomass, and cobalt sorption. The dimension and hydrological properties of the column are given in Table 1.

Table 1. List of hydrological properties of the column.

Property	Value
Length of column	10 m
Porosity	0.4
Bulk density	1.5×10^3 kg/m^3
Grams of sediment per liter water (from porosity and bulk density	3.75×10^3 g/l
Pore water velocity	1 m/hr
Longitudinal dispersivity	0.05 m

Aqueous Chemistry

The aqueous chemical model defined by Tebes-Steven and Valocchi (1998) was used. Activity coefficients of aqueous species were assumed to be 1.0. Aqueous complexes considered and their stoichiometric coefficients and equilibrium constants are summarized in Table 2.

Table 2. List of stoichiometric coefficients and equilibrium constants for aqueous complexes.

Complex	Stoichiometric coefficients					$Log_{10}K$
	H^+	H_2CO_3	NH_4^+	NTA^{3-}	Co^{2+}	
H_3NTA	3			1		-14.9
H_2NTA^-	2			1		-13.3
$HNTA^{2-}$	1			1		-10.3
$CoNTA^-$				1	1	-11.7
$CoNTA_2^{4-}$				2	1	-14.5
$CoNTA^{2-}$	-1			1	1	-0.5
$CoOH^+$	-1				1	9.7
$Co(OH)_2$	-2				1	22.9
$Co(OH)_3^-$	-3				1	31.5
HCO_3^-	-1	1				6.35
CO_3^{2-}	-2	1				16.68
$NH_3(aq)$	-1		1			9.3
OH^-	-1					14.0

Table 3. List of concentrations for injection and background waters.

Component	Mobile	Injection concentration (mol/l)	Initial concentration (mol/l)
H^+	Yes	10×10^{-6}	10×10^{-6}
Total carbon	Yes	4.9×10^{-7}	4.9×10^{-7}
NH_4^+	Yes	0.0	0.0
$O_2(aq)$	Yes	3.125×10^{-5}	3.125×10^{-5}
NTA^{3-}	Yes	5.23×10^{-6}	
Co^{2+}	Yes	5.23×10^{-6}	
Na	Yes	1.0×10^{-3}	1.0×10^{-3}
Cl^-	Yes	1.0×10^{-3}	1.0×10^{-3}
Biomass	No	---	1.36×10^{-4}
CoNTA(ads)	No	---	0.0
Co(ads)	No	---	0.0

Biodegradation

The initial concentrations in the column are listed in Table 3. The column contains no NTA and cobalt initially, but has a biomass of 1.36×10^{-4} g/l. An injection water with NTA and cobalt is applied at the inlet of the column for a time period of 20 hours. The injection concentrations are also given in Table 3. After 20 hours, the background (initial) water is introduced at the inlet until the experiment ends after 75 hours.

NTA is assumed to degrade in the presence of biomass and oxygen by the reaction:

$$HNta^{2-} + 1.62O_2(aq) + 1.272H_2O + 2.424H^+ = 0.576C_5H_7O_2N + 3.12H_2CO_3 + 0.424NH_4^+$$

The NTA reaction converts 1 mol $HNTA^{2-}$ ($C_6H_7O_6N$) to 0.576 mol $C_5H_7O_2N$, where the latter is chemically inert so that its concentration can be discarded. The following multiplicative Monod rate expression is used to describe the rate of NTA degradation:

$$r_{HNTA^{2-}} = k_{biom} X_{biom} \left(\frac{C_{HNTA^{2-}}}{K_s + C_{HNTA^{2-}}} \right) \left(\frac{C_{O_2}}{K_a + C_{O_2}} \right) \tag{9}$$

where $r_{HNTA^{2-}}$ is the rate of $HNTA^{2-}$ degradation (mol/l/hr), k_{biom} is the maximum specific rate of substrate utilization (mol/g cells/hr), X_{biom} is the biomass (g cells/l), K_s is the half-saturation constant for the substrate NTA (mol/l), K_a is the half-saturation constant for the electron acceptor O_2 (mol/l), and C donates concentration of species (mol/l). Rate expression (9), compared to the general form (7), has only one mechanism, one product term X_{biom}, and two Monod terms.

The rate of biomass production is dependent on the rate of substrate utilization and a first-order decay rate for the biomass:

$$r_{biom} = -y r_{HNTA^{2-}} - b X_{biom} \tag{10}$$

where r_m is the rate of cell growth (g cells/l/hr), y is the microbial yield coefficient (g cells/mol NTA), and b is the first-order biomass decay coefficient (hr^{-1}). The parameter values for Equations (9) and (10) are listed in Table 4. Rate expression (10) consists of two mechanisms using Equation (7).

Table 4. List of kinetic rate parameters used in Equations (9) and (10).

Parameter	*Description*	*Value*
K_s	half-saturation constant for donor	7.64×10^{-7} mol/l
K_a	half-saturation constant for acceptor	6.25×10^{-6} mol/l
k_{biom}	maximum specific rate of substrate utilization	1.418×10^{-3} mol/g cells/hr
y	microbial yield coefficient	65.14 g cells/mol NTA
b	first-order biomass decay coefficient	0.00208 hr^{-1}

Kinetic sorption

The rate expressions for kinetic sorption reactions for Co^{2+} and $CoNTA^-$ are given by

$$r_i = -k_m\left(C_i - \frac{S_i}{K_d}\right) = -k_m C_i - \frac{k_m}{K_d} S_i \qquad (11)$$

where i is either Co^{2+} or $CoNTA^-$ (mol/L), S_i is the sorbed concentration (mol/g sediment), k_m is the mass transfer coefficient (hr^{-1}), and K_d is the distribution coefficient (L/g). The values of the coefficients are given in Table 5. The values of K_d were defined to give retardation coefficients of 20 and 3 for Co^{2+} and $CoNTA^-$ respectively. Two mechanisms involved in the sorption kinetics are each represented by a product term, using Equation (7).

Table 5. Sorption coefficients for Co^{2+} and $CoNTA^-$.

Species	k_m	K_d
Co^{2+}	1 hr^{-1}	5.07×10^{-3} l/g
$CoNTA^-$	1 hr^{-1}	5.33×10^{-4} l/g

Comparison of results

The evolution of aqueous and immobile constituents at the outlet of the column is shown in Figure 2. In the experiment, two pore volumes of water with NTA and cobalt were introduced to the column over the first 20 hours and then followed by 5.5 pore volumes of background water over the next 55 hours. At 10 hours, $HNta^{2-}$ begins to appear at the column outlet along with a rise in the pH. If NTA and cobalt were conservative and dispersion was negligible, the graph would show square pulses that increase at 10 hours and decrease at 30 hours. However, the movement of the NTA and cobalt is retarded relative to conservative movement by the sorption reactions. The peak in NTA and cobalt concentrations occurs in the CoNta complex between 30 and 40 hours. The peak in Co^{2+} concentration is even more retarded by its sorption reaction and does not show up until near the end of the experiment. The sorbed $CoNta^-$ concentration peaks between 30 and 40 hours and slightly lags behind the peak in the dissolved concentration of the $CoNta^-$ complex. Initially, no NTA is present in the column and the biomass decreases slightly over the first 10 hours because of the first-order decay rate for the biomass. As the NTA moves through the column, the biomass increases as the NTA substrate becomes available. After the peak of NTA has moved through the column, biomass concentrations level off and then begin to decrease because of decay. The *Kd* for cobalt sorption relates to a greater retardation coefficient than the *Kd* for $CoNta^-$ sorption, and the sorbed concentration of Co^{2+} appears to be still increasing at the end of the experiment. The TOUGHREACT simulation results agree well with those of Bio-CORE2D and PHREEQC, and also with the original results given by Tebes-Steven and Valocchi (1997, 1998).

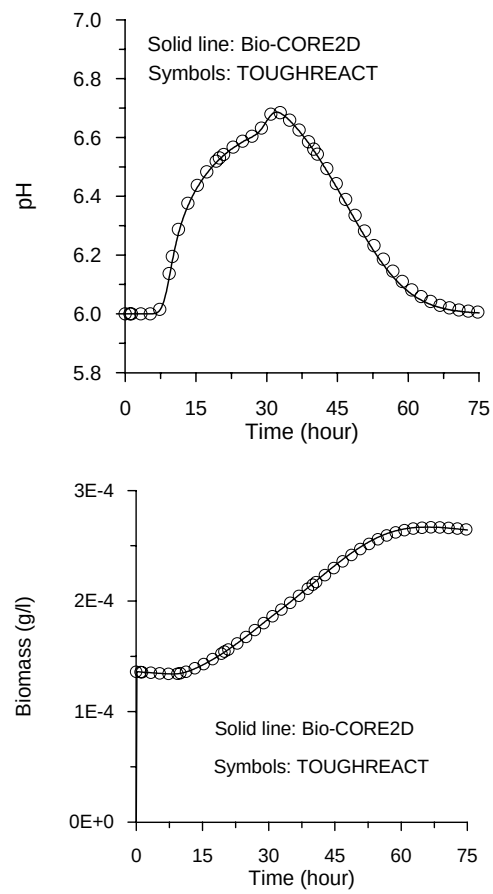

Figure 2. Concentrations vs. time for batch sulfide oxidation problem.

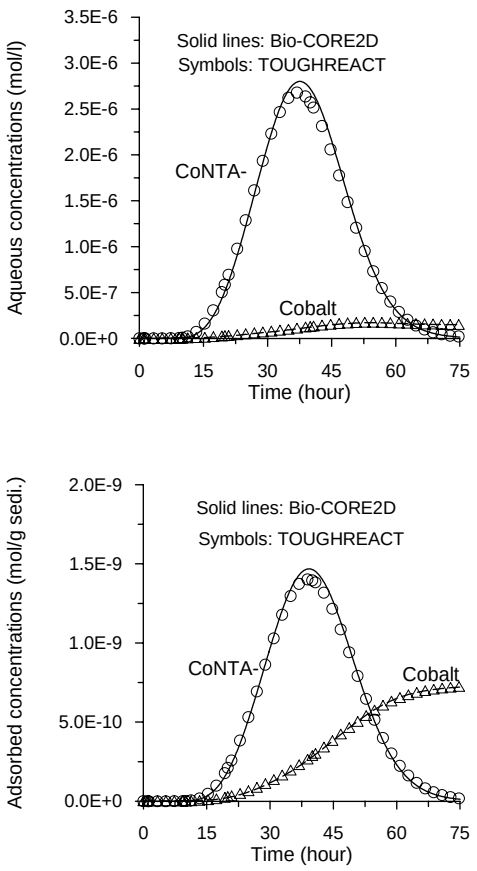

Figure 2 (continued). Concentrations vs. time for batch sulfide oxidation problem.

CONCLUSIONS

Aqueous and sorption kinetics and microbiological processes have been incorporated into TOUGHREACT. A 1-D reactive transport problem with kinetic biodegradation and sorption was investigated. The simulation results agree very well with those obtained with other simulators. The resulting biogeochemical transport simulation capabilities will be useful for many subsurface problems such as (1) acidic mine drainage remediation, (2) organic matter decomposition, oil and gas maturation, and sulfite reduction in oil field, and (3) effective environmental remediation of groundwater contamination.

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