

An Integrated Media, Integrated Processes Watershed Model – WASH123D: Part 8 – Reactive Chemical Transport in Subsurface Media

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ABSTRACT

A watershed system includes river/stream networks, overland regions, and subsurface media. This paper presents a reaction-based numerical model of reactive chemical transport in subsurface media of watershed systems. Transport of M chemical species with a variety of chemical and physical processes is mathematically described by M partial differential equations (PDEs). Decomposition via Gauss-Jordan column reduction of the reaction network transforms M species reactive transport equations into M reaction extent-transport equations (a reaction extent is a linear combination of species concentrations), each involves one and only one linear independent reaction or no reactions. Thus, the reactive transport problem is viewed from two different points of view. Described with a species-transport equation, the transport of a species is balanced by a linear combination of rates of all reactions. Described by a reaction extent-transport equation, the rate of a linear independent reaction is balanced by the transport of the linear combination of species. The later description facilitates the decoupling of fast reactions from slow reactions and circumvents the stiffness of reactive transport problems. This is so because the M reaction extent-transport equations can be approximated with three subsets of equations: N_E algebraic equations describing N_E fast reactions (where N_E is the set of linear independent fast/equilibrium reactions), N_{KI} reactive transport equations of kinetic-variables involving only slow reactions (where N_{KI} is the number of linear independent slow/kinetic reactions), and N_C transport equations of components involving no reactions at all (where $N_C = M - N_E - N_{KI}$ is the number of components). The elimination of fast reactions from reactive transport equations allows robust and efficient numerical integration. The model solves the PDEs of kinetic-variables and components rather than individual chemical species, which reduces the number of reactive transport equations and simplifies the reaction terms in the equations. Two validation examples involving simulations of uranium transport in soil columns are presented to evaluate the ability of the model to simulate reactive transport with reaction networks involving both kinetic and equilibrium reactions. A hypothetical three-dimensional example is presented to demonstrate the model application to a field-scale problem involving reactive transport with a complex reaction network.

1. INTRODUCTION

Due to the rapid development of computer technology in the past two decades, subsurface contaminant transport models have become increasingly powerful popular assessment tools to evaluate the efficacy of alternative remediation techniques prior to incurring expenses in the field. This paper considers the reactive chemical transport modeling in subsurface media that is an integral component of a watershed system (Yeh et al., 1998). The transport and transformation of water quality in river/streams and overland water will be addressed in separate communications.

Reactive chemical transport in the subsurface occurs over a broad range of biogeochemical environments at various space and time scales. Chemical and physical processes can be divided into two classes (Rubin, 1983): (1) fast/equilibrium reactions and (2) slow/kinetic reactions. The former are sufficiently fast compared to the transport time-scale and are reversible, so that local equilibrium may be assumed. The latter are not sufficiently fast compared to the transport time-scale, and local equilibrium conditions cannot be assumed.

Due to computational limitations, existing coupled models for subsurface reactive transport have various capabilities. Some models couple transport with equilibrium chemistry (Yeh and Tripathi, 1991; and Parkhurst and Appelo, 1999), while some couple transport with kinetic chemistry (Adeel et al., 1995; Yeh et al., 1998; and Saiers et al., 2000). Models coupling transport with both equilibrium and kinetic reactions have appeared since the mid-1990s (Steeffel and Lasaga, 1994; Tebes-Stevens et al., 1998; Brun and Engesgaard, 2002; Yeh et al., 2004). Most of these models either implicitly assumes that equilibrium reactions occur only among aqueous species or consider only limited reaction networks. There appears to be few general-purpose transport models that can simulate generic reaction networks including mixed equilibrium/kinetic reactions (Yeh et al., 2004).

This paper presents a general mathematical framework and a three-dimensional numerical implementation to simulate reactive chemical transport in subsurface water subject to both equilibrium and kinetic reactions. The decomposition of the system of species transport equations reduces problem stiffness by eliminating fast reactions from the partial differential equations governing reactive transport and enables robust numerical integration.

2. MATHEMATICAL BASIS

The temporal-spatial distribution of M chemical species in reactive transport systems with a variety of chemical and physical processes is mathematically described by the following partial differential equation (PDE).

$$\frac{\partial(\theta\rho_i C_i)}{\partial t} + \alpha_i L(\rho_i C_i) = \theta r_i \Big|_N, \quad i \in M \quad (1)$$

where θ is the moisture content; ρ_i is the phase density associated with species i , C_i is the concentration of species i , t is the time; α_i is 0 for immobile species and 1 for mobile species, $r_i \Big|_N$ is the production rate of species i due to all N reactions, and operator L is defined as

$$L(\rho_i C_i) = \nabla \cdot (\mathbf{V}\rho_i C_i) - \nabla \cdot [\theta \mathbf{D} \cdot \nabla(\rho_i C_i)] - M_i^s. \quad (2)$$

where \mathbf{V} is Darcy velocity; \mathbf{D} is the dispersion coefficient; and M_i^s is the source term other than that due to reactions.

In a reaction-based formulation, $r_i \Big|_N$ is given by the rate summation of all reactions that the i -th species participates in, which results in the transport equations of M chemical species described by

$$\frac{\partial(\theta\rho_i C_i)}{\partial t} + \alpha_i L(\rho_i C_i) = \theta \sum_{k=1}^N (v_{ik} - \mu_{ik}) r_k, \quad i \in M \quad (3)$$

where v_{ik} is the reaction stoichiometry of species i in the k -th reaction associated with the products, μ_{ik} is the reaction stoichiometry of species i in the k -th reaction associated with the reactants, r_k is the rate of the k -th reaction.

In a primitive approach, equation (3) is integrated to yield the distributions and evolutions of chemical species in a region of interest. However, when some fast reactions take place in the system, this approach is not adequate (Fang et al., 2003). Here, we take a diagonalization approach through decomposition. To avoid singularity of the reaction matrix, redundant reactions (i.e., fast reactions that can be derived from other fast reactions) are omitted from the system prior to decomposition. Define N_E as the number of linear independent fast reactions, N_{KI} as the number of linear independent slow reactions, N_{KD} as the number of dependent slow reactions, and $N_C = M - N_E - N_{KI}$ as the number of components. A complete Gauss-Jordan column reduction of the reaction network will result in N_E algebraic equations describing N_E fast reactions, N_{KI} reactive transport equations of kinetic-variables involving only slow reactions, and N_C transport equations of components involving no reaction at all .

Algebraic Equations for Equilibrium Reactions

$$\begin{aligned} \frac{\partial(\theta E_i)}{\partial t} + L(E_i^m) &= \theta \gamma_{kk} r_k + \theta \sum_{j \in N_{KD}} \gamma_{ij} r_j, \quad k \in N_E, i \in M : \\ \frac{\partial(\theta E_i)}{\partial t} + L(E_i^m) &\approx \theta \gamma_{kk} r_k = \infty \quad \exists \quad \begin{array}{l} \text{a thermodynamically} \\ \text{consistent equation} \end{array} \end{aligned} \quad (4)$$

Reactive Transport Equations for Kinetic-Variables

$$\frac{\partial(\theta E_i)}{\partial t} + L(E_i^m) = \theta \gamma_{kk} r_k + \theta \sum_{j \in N_{KD}} \gamma_{ij} r_j, \quad k \in N_{KI}, i \in M \quad (5)$$

Transport Equations for components

$$\frac{\partial(\theta E_i)}{\partial t} + L(E_i^m) = 0; \quad \text{donating } T_k = E_i, \quad k \in N_C, i \in M. \quad (6)$$

where E_i is the total concentration of a reaction extent, which is a linear combination of species concentrations, E_i^m is the mobile part concentration of a reaction extent, and γ is the decomposed reaction matrix.

The M species reactive transport equations are transformed into M reaction extent transport equations each involves one and the only one linear independent reaction or no reaction. Thus, the reactive transport problem is viewed from two different points of view. Described with a species-transport equation, the transport of a species is balanced by a linear combination of rates of all reactions. Described by a reaction extent-transport equation, the rate of a linear independent reaction is balanced by the transport of the linear combination of species. The later description facilitates the decoupling of fast reactions from slow reactions. The elimination of fast reactions from reactive transport equations allows robust and efficient numerical integration. The model solves the PDEs of kinetic-variables and components rather than individual chemical species, which reduces the number of reactive transport equations and simplifies the reaction terms in the equations.

3. EXAMPLES

3.1 Packed column breakthrough curve simulation with uranium (VI) sorption

A glass column 1 cm in diameter by 3 cm long was filled with 2.483 g crushed and sieved soil material with a porosity of 0.66. The soil contained 1.9 percent Fe oxides on a mass basis. A solution with 10 μM U(VI) and 50 mM NaNO_3 was injected at a specific discharge of 1.235 cm/h until breakthrough was observed. The inlet solution was switched to a U(VI) free solution after 614.7 pore volumes (Kim et al., manuscript in preparation, 2006).

In the simulation, the column is discretized with 20 nodes and 4 equal size elements (0.886 cm \times 0.886 cm \times 0.779 cm each). The longitudinal dispersivity of 0.046 cm was determined by fitting the breakthrough curve of the nonreactive tracer Br. The reaction network utilizes 46 species and 39 equilibrium reactions (Lindsay, 1979; Brooks, 2001; Waite et al., 1994; and Langmuir, 1997). The simulation was performed for a total duration of 2500 hours with a constant time-step size of 0.1 hour.

The experimental data and simulation results are shown in Figure 1. The simulation results closely follow the data, reflecting retardation due to reactions on both the leading and tailing portions of the breakthrough curve. The results provide validation of the reaction network employed to simulate uranium (VI) transport and the numerical implementation.

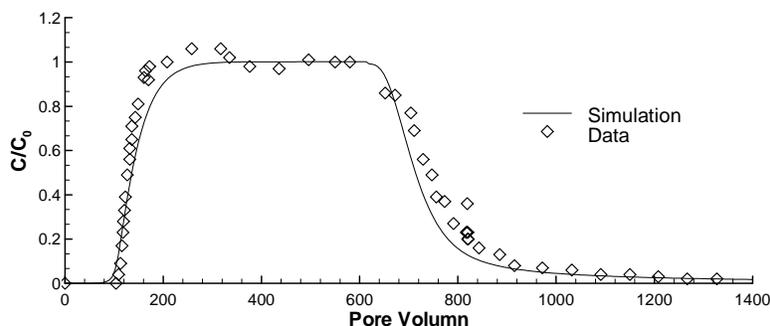


FIGURE 1. U(VI) breakthrough curve for the packed column.

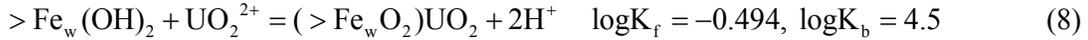
3.2 Undisturbed column breakthrough curve simulation with uranium (VI) sorption

This problem involves similar geochemistry to that of the previous example, but involves an undisturbed soil core. A miscible displacement experiment was conducted at pH 4 under atmospheric $\text{CO}_2(\text{g})$. The core was 15.2 cm in length and 6.19 cm in diameter. Influent solution consisting of 50 mg/L U(VI) in 50 mM CaCl_2 was pumped through the column at a constant flow rate of 7 mL/h, which is equivalent to 26.5 pore volumes per hour at the water content of 0.4. (Pace et al, manuscript in preparation, 2005).

The column was numerically discretized with a simulation grid of 20 nodes and 4 equal sized elements (5.49 cm \times 5.49 cm \times 3.8 cm each). The longitudinal dispersivity of 21.5 cm was determined by fitting the breakthrough curve of the nonreactive tracer Br. The experiment duration of 2448 hours was simulated with a constant time-step size of 12 hours. Simulations were initially performed assuming the same equilibrium reactions as in previous Example. The equilibrium sorption simulation results (upper part of Figure 2) did not accurately predict U(VI) transport through the undisturbed column, indicating that some of the sorption sites may be kinetically hindered resulting in less sorption. Two of the sorption reactions are

considered to be the most kinetically limiting reactions. Therefore, a second simulation was performed with these two reactions as rate-limited.

Forward and backward kinetic rate coefficients for following U(VI) sorption reactions were fitted to the U(VI) breakthrough curve data using a nonlinear parameter estimation procedure yielding



Simulations of U(VI) transport using kinetic parameters (lower part of Figure 2) yielded good agreement with the measured results indicating that U(VI) transport may be kinetically controlled in naturally heterogeneous media.

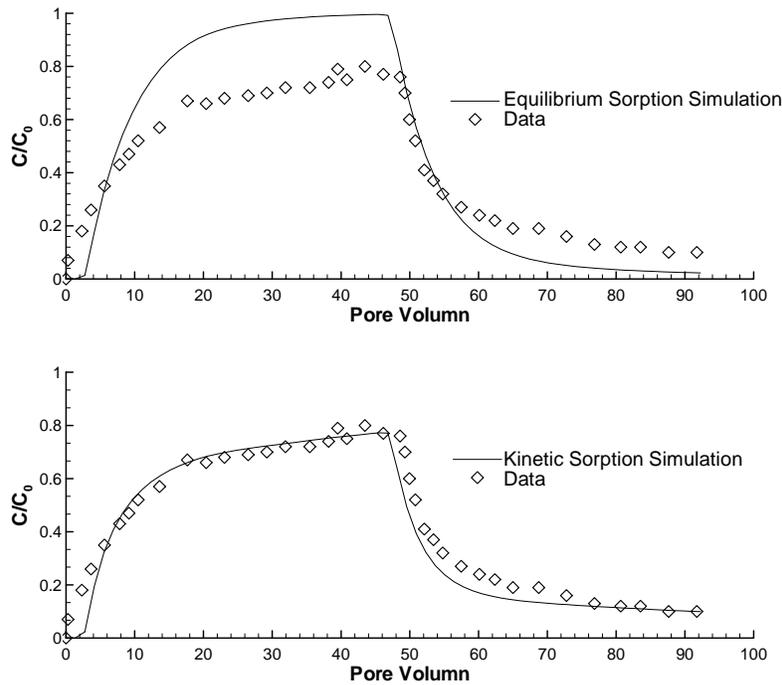


FIGURE 2. U(VI) breakthrough curve for the undisturbed column.

3.3 Three-dimensional reactive uranium (VI) transport simulation

This example was undertaken to assess the model capability to handle complex geochemistry within a three-dimensional subsurface domain. A 600 m long, 400 m wide, and 200 m deep region is considered and discretized with uniform hexahedral elements with size of 60 m \times 50 m \times 40 m (Figure 3).

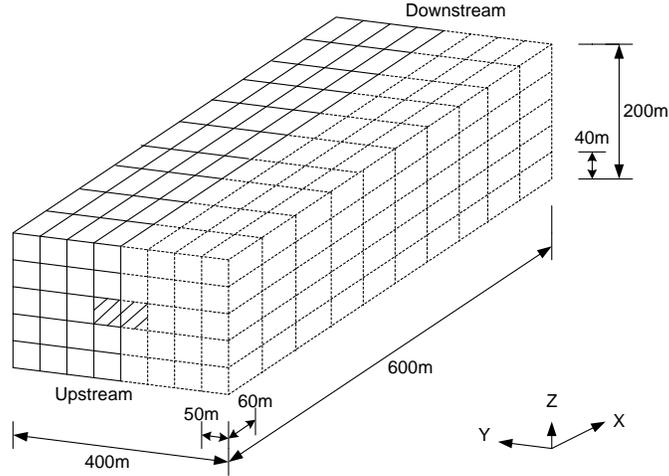


FIGURE 3. Simulation domain and discretization for example 3.3.

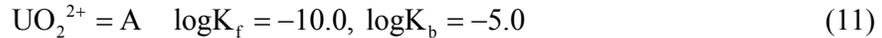
A steady state flow field was simulated using FEMWATER. Dirichlet boundary conditions were applied to the upstream boundary ($x = 0$ m) with total head of 190 m and to the downstream boundary ($x = 600$ m) with total head of 180 m. A flux boundary condition was applied to the top boundary ($z = 200$ m) with an infiltration rate of 0.0015 m/d. We assumed a constant effective porosity of 0.3 and saturated hydraulic conductivity of $K_{xx} = K_{yy} = 1.0$ and $K_{zz} = 0.1$ m/d throughout the domain. The following two equations were employed to describe the unsaturated hydraulic properties.

$$\theta = 0.1 + (0.3 - 0.1) / (1 + 4h^2) \quad (9)$$

$$Kr = \left[0.1 + (0.3 - 0.1) / (1 + 4h^2) \right] / 0.3 \quad (10)$$

where θ is the moisture content and Kr is the relative conductivity. The calculated moisture content varied from 0.1 to 0.3 and Darcy velocity from 0.0014 to 0.021 m/day.

In addition to the chemical species and reactions considered in Example 3.2, one more dissolved species A is assumed to undergo a hypothetical kinetic reduction/oxidation reaction



Initial aqueous and adsorbed concentrations are assumed to be zero. The initial concentration of the precipitate $Fe(OH)_3$ is assumed to be 0.0523 mol/kg and the pH is 4.6 throughout the region. The boundary conditions for the transient transport simulation are: no flux for the bottom ($z = 0$ m), the front ($y = 0$ m) and the back ($y = 400$ m) boundaries, outflow variable boundary condition for the downstream boundary ($x = 600$ m); inflow variable boundary condition for the top ($z = 200$ m) and the upstream boundary ($x = 0$ m) with zero incoming concentration for each mobile species except at the two shaded boundary faces shown in Figure 3, where the inflow contains UO_2^{2+} of 1.15×10^{-5} mol/L, NO_3^- of 0.05 mol/L, and a nonreactive tracer of 1.15×10^{-5} mol/L. The longitudinal dispersivity is 60 m, the transverse

dispersivity is 6 m, and the molecular diffusion coefficient is assumed to be zero. A 100 years simulation was performed.

Simulation results within the bisected simulation domain are illustrated in Figure 4 for nonreactive tracer and aqueous uranium (VI). The two variable boundary faces (shaded in Figure 3) on the upstream boundary represent the source of tracer and aqueous U(VI). The nonreactive tracer is transported into the domain along with subsurface flow. However, due to the sorption reactions, most of the mobile aqueous U(VI) is transformed into immobile sorbed U(VI) in the region close to the source. Therefore, U(VI) plume migration is much slower than that of the nonreactive tracer. The calculated percentage of sorbed uranium ranges from 0.56 to 0.96, which illustrates that a single value of the distribution coefficient is not able to simulate the spatially variable retardation under the conditions for this example.

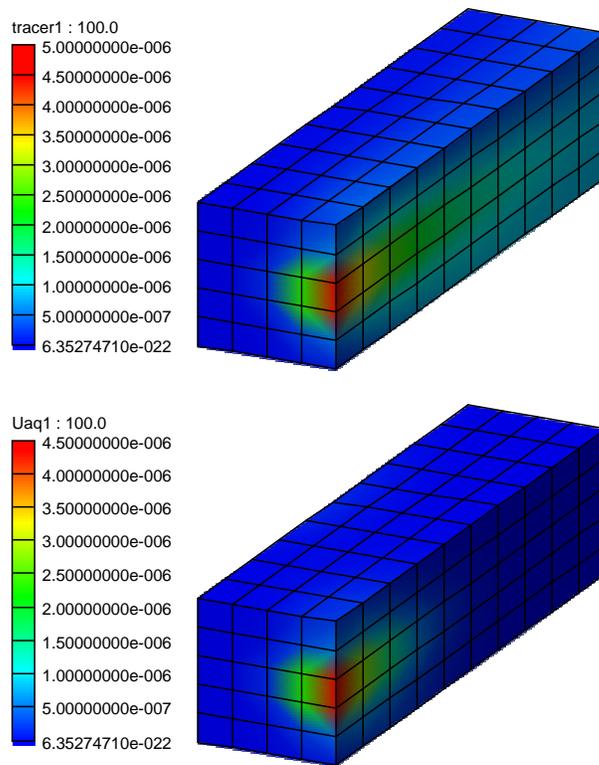


FIGURE 4. Simulated concentration fringes at time = 100 years for example 3.3.
upper: nonreactive tracer; and lower: aqueous U(VI)

4. SUMMARY

This paper presents a numerical model for transient simulation of biogeochemical transformation of chemical species as they are transported in subsurface. Chemical and physical processes are completely defined by the reaction network. Transport equations based on the principle of mass balance are used to describe temporal-spatial distributions of water qualities. Through the decomposition of the system of species transport equations, reaction

extent variables (including kinetic-variables and components) rather than individual species are considered as primary dependent variables.

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