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NUMERICAL MODELING OF COUPLED VARIABLY-SATURATED FLUID FLOW
AND
REACTIVE TRANSPORT WITH FAST AND SLOW CHEMICAL REACTIONS

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Abstract

The couplings among chemical reaction rates, advective and diffusive transport in fractured media or soils, and changes in hydraulic properties due to precipitation and dissolution within fractures and in rock matrix are important for both nuclear waste disposal and remediation of contaminated sites. This paper describes the development and application of LEHGC2.0, a mechanistically-based numerical model for simulation of coupled fluid flow and reactive chemical transport, including both fast and slow reactions in variably saturated media. Theoretical bases and numerical implementations are summarized, and two example problems are demonstrated. The first example deals with the effect of precipitation-dissolution on fluid flow and matrix diffusion in a two-dimensional fractured media. Because of the precipitation and decreased diffusion of solute from the fracture into the matrix, retardation in the fractured medium is not as large as the case wherein interactions between chemical reactions and transport are not considered. The second example focuses on a complicated but realistic advective-dispersive-reactive transport problem. This example exemplifies the need for innovative numerical algorithms to solve problems involving stiff geochemical reactions.

Keywords: reactive transport, numerical models, geochemistry, groundwater, remediation.

1. Introduction and Background

More than 10,500 individual contaminated sites have been identified at the Department of Energy (DOE) facilities with pollutants including mixtures of hazardous organics, metals, and radionuclides. Terminal disposal of these wastes requires development of techniques for waste characterization, performance assessment, and long-term monitoring technologies that are cost-effective and result in acceptable risks to human health and the environment. Accurate tools for reliable prediction of contaminant migration and transformation are necessary to support these tasks. Consideration of equilibrium chemistry, kinetic chemistry, and hydrologic transport and the interaction between fluid flow and reactive transport is necessary to be able to reflect the complexity of many real systems. For example, solid phase reactions including precipitation and dissolution can potentially plug pores or open fractures reducing matrix diffusion and promoting rapid flow through fractures.

The development of mechanistically-based reactive chemical transport models has exploded in the last decade

(Yeh and Tripathi, 1989, Steefel and Van Cappellan, 1998). Some models couple transport with equilibrium chemistry, others couple transport with kinetic geochemistry for specific geochemical processes like precipitation-dissolution or adsorption. This paper describes the development and application of a LEHGC 2.0, a mechanistically-based numerical model for simulation of coupled fluid flow and reactive chemical transport in variably saturated media. LEHGC 2.0 can simulate a full suite of kinetic and equilibrium geochemical processes simultaneously. The coupling of this capability with simultaneous modeling of fluid flows and their interactions with reactive transport gives LEHGC 2.0 a robust ability to simulate the geochemistry of the subsurface environment..

2. Governing Equations

The governing equations of LEHGC2.0 includes three modules: a flow equation, a set of hydrologic transport equations, and a set of geochemical equations. A modified Richard equation describes density-dependent fluid flow in variably-saturated media. It can be derived based on continuity of fluid, continuity of solid, motion of fluid (Darcy's law), consolidation of the media, and compressibility of water (Yeh, et al., 1994). The governing equations for a reactive system are mass balance equations for aqueous components, adsorbent components, equivalent-balance equations for ion exchange sites, mass action equations for equilibrium species, and reaction rate expressions for kinetic species. For simplification, we will only present the governing equations for the aqueous components, complexed species, and precipitated species. Neither source/sink nor decay are considered in the following presentation; detailed descriptions of these equations can be found in Yeh et al., 1999.

Hydrologic transport equations for aqueous components -

$$\theta \frac{\partial T_j}{\partial t} + \frac{\partial \theta}{\partial t} P_j = L(C_j) - \frac{\partial \theta}{\partial t} C_j, \quad j \in N_a, \quad (1)$$

where θ is the moisture content, T_j is the total analytical concentration of the j -th aqueous component, P_j is the total precipitated concentration of the j -th aqueous component, C_j is the total dissolved concentration of the j -th aqueous component, N_a is the number of aqueous components, and L is an advection-diffusion/dispersion operator.

Governing equations for complexed species -

$$x_i = \alpha_i^x \prod_{k=1}^{N_i} c_k^{a_{ik}^x}, \quad i \in (N_x - K_x), \quad (2)$$

$$\frac{\partial(\theta x_i)}{\partial t} = L(x_i) - k_i^{bx} x_i + \alpha_i^{fx} \prod_{k=1}^{N_i} c_k^{a_{ik}^x}, \quad i \in K_x, \quad (3)$$

Governing equations for precipitated species -

$$1 = \alpha_i^p \prod_{k=1}^{N_i} c_k^{a_{ik}^p}, \quad i \in (N_p - K_p), \quad (4)$$

$$\frac{\partial(\theta p_i)}{\partial t} = A_i \left(-\alpha_i^{bp} + \alpha_i^{fp} \prod_{k=1}^{N_i} c_k^{a_{ik}^p} \right), \quad i \in K_p \quad (5)$$

where c_k , x_i , and p_i are the concentrations of the k -th aqueous component species, the i -th complexed species, and the i -th precipitated species, respectively; N is the number of reactions; K is the number of kinetic reactions; a_{ij} is the stoichiometric coefficient of the j -th component in the i -th reactions; α_i is the apparent stability constant for the i -th equilibrium reaction; k_i is the backward rate constant of the i -th kinetic reaction; α_i^b and α_i^f are the modified backward and forward rate constant of the i -th kinetic reactions, respectively. The “x” and “p” in the superscript or subscript position of the notations in the above equations are used to describe the association of these notations with complexation and precipitation/dissolution reactions, respectively. $A_i = 0$ if the i -th kinetic precipitation/dissolution reaction is not to occur or $A_i = 1$ if the reaction is to occur.

Coupling between fluid flows and reactive transport -

The density-dependence of fluid flows are described via the following constitutive relationships

$$\rho = \rho_o + \sum_{j=1}^{N_s} C_j M_j, \quad \mu = \mu_o + \sum_{j=1}^{N_s} a_j C_j M_j \quad (6)$$

where ρ and μ are fluid density and fluid dynamic viscosity with dissolved chemical concentrations, ρ_o and μ_o are fluid density and fluid dynamic viscosity in pure water, M_j and C_j are the molecular weight and total dissolved concentration of the j -th aqueous component, respectively, and a_j is a weighting parameter for the j -th component.

The interactions between reactive transport and fluid flows are described by the following dependencies of moisture content (θ), saturated hydraulic conductivity tensor (K_{so}), and dispersion coefficient tensor (D) on

concentrations of minerals

$$\theta = \frac{S\theta_{so}}{1 + S\phi_p} \quad \text{and} \quad K_{so} = K_{soo} \left(\frac{1}{1 + S\phi_p} \right)^n \quad (7)$$

$$D = D_0 \left[\phi^{m-1} (1 - \phi_p)^m \right] \quad (8)$$

where θ_{so} is the effective saturated moisture content without the effect of solid species; S is the degree of saturation of water which is a function of the pressure head; $\phi_p = \sum p_i V_i$, where p_i is the precipitated concentration of the i -th mineral [mole/dm³ of water] and V_i is the molar volume of the i -th mineral [dm³ of solid/mole]; K_{soo} is the reference saturated hydraulic conductivity tensor (ignoring the effect of density and solid concentration); n is the fractal for estimating hydraulic conductivity based on particle size and packing structure; D_0 is dispersion coefficient tensor computed without the effect of solid species; and m is the "cementation exponent" (Dullien, 1979).

3. Numerical Solutions

In LEHGC 2.0 the flow equations are discretized with the Galerkin finite element method. The transport equations are discretized with either conventional finite element methods or a hybrid Lagrangian-Eulerian finite element method. Nonlinearities in the fluid flow, reactive transport, and their interaction are solved with using Picard linearization, and any nonlinearity in geochemistry are solved with Newton-Raphson linearization.

The two subsystems of equations describing coupled hydrologic transport and mixed geochemical equilibrium/kinetic reaction problems are solved iteratively. Three different approaches may be used in LEHGC 2.0 to reach a convergent solution. The first approach is complete iteration between two subsystems, the second approach is the use of operator splitting, and the third approach is the employment of the predictor-corrector method. For each time step, a sequential iteration approach is also applied to solve coupled fluid flows and reactive chemical transport equations until the pressure head, total analytical concentrations of aqueous and adsorbent components, and concentrations of kinetically controlled complex species meet prescribed convergent criteria.

4. Examples

Nineteen example problems have been developed to demonstrate the ability of LEHGC-2.0 to solve a variety of mixed subsurface flow, solute transport, and chemical reaction problems (Yeh et al., 1999). However, due to space limitation, only two numerical experiments are described in this paper.

4.1. Example 1: Coupled Fracture Flow, Matrix Diffusive, and Reactive Transport

The first example deals with the effect of precipitation on fluid flow and matrix diffusion in a two-dimensional fractured media. The domain of interest was based on a longitudinal cross-section of a 0.76 meter high column with a 120 μm wide fracture in the center, running the length of the column. Due to symmetry, one-half of the cross-section can be used as shown in Figure 1 with a 6×10^{-4} dm wide fracture on the left hand side. The fractured media is simulated by the three left-hand columns of elements with a moisture content, θ , of 1.0 when precipitated chemical species are not present. The top and bottom surfaces are held at a Dirichlet head of 7.615 dm and 7.6 dm, respectively. The upper boundary of the domain is assumed to maintain a constant concentration, Dirichlet boundary. Neumann boundaries are used for the other three boundaries with $\partial C/\partial x = 0$ for the two vertical boundaries and $\partial C/\partial z = 0$ for the bottom boundary. The reference saturated hydraulic conductivity K_{soo} in the z-direction for the matrix is $K_z = 2.16 \times 10^{-6}$ dm/; in the fracture, $K_z = 237.0$ dm/hr for material 2, $K_z = 222.0$ dm/hr for material 3, and $K_z = 90.0$ dm/hr for material 4. The matrix elements have a moisture content (without the presence of precipitated species), tortuosity and bulk density of 0.35, 0.1, and 1.7 kg/dm³, respectively. The molecular diffusion coefficient is 3.6×10^{-4} dm²/hr. Longitudinal dispersivity (α_L) and lateral dispersivity (α_T) for all elements is set to 7.6 dm and 0.0 dm, respectively. A detailed description of the finite element grid is found in Yeh et al., 1999.

Two cases are simulated in this example; in the first case, the flow and reactive transport are coupled through the effect of precipitation on hydraulic conductivity, porosity, and hydrodynamic dispersion. To reflect the effect of mineral precipitation on flow, the fractal exponent for adjusting the hydraulic conductivity (Eq. 7) is set equal to 2.5. The cementation exponent in Archie's law is set equal to 2.0 to adjust the dispersion coefficient (Eq. 8). Molar volumes (V_i) of 0.03 dm³/mol and 0.037 dm³/mol are assumed for portlandite, $\text{Ca}(\text{OH})_2$ (s), and calcite, CaCO_3 (s), respectively. In the second case, although the effects of precipitation/dissolution on flow, conductivity and dispersion are not considered, solute transport and chemical reaction still need to be coupled because heterogeneous reactions

(precipitation/dissolution reactions) are involved in the system. A time step size of 0.24 hour was used; a total of six days (144 hours) is simulated using 600 time steps.

The chemistry of the system is relatively simple: the chemical components of the systems are Ca^{2+} , CO_3^{2-} , H^+ , and a conservative tracer. Calcite is present in the matrix ($8.642 \times 10^{-5} \text{ M}$) in equilibrium with the pore water and fracture water which contain 10^{-3} M Ca^{2+} and CO_3^{2-} (total concentrations). During the simulation, a solution 10x-richer in both total calcium and total carbonate is injected in the fracture. The complexed species include OH^- , CaCO_3 , CaHCO_3^+ , CaOH^+ , HCO_3^- , and H_2CO_3 . Calcite ($\text{CaCO}_3(\text{s})$) is included as solid species subject to kinetic precipitation and dissolution. The reaction stoichiometries, equilibrium constants and rate constants can be found in Yeh et al., 1999.

The results of the simulation are summarized by the profiles of tracer concentration shown in Figure 2a (precipitation-flow coupling) and 2b (no coupling). In the first case, diffusion into the matrix is diminished due to calcite precipitation in the matrix. The concentrations of tracer in the matrix zone in this case are lower than those without the precipitation effect. In addition, since less tracer can diffuse into the matrix, a larger amount of tracer remains in the fracture zone. As seen in the figures, the concentrations of the conservative tracer in the fracture zone are much higher when the precipitation effect is included. Examination of the simulated flow field (not shown) shows that the change of flow velocity is very small because the calcite precipitation in the fracture zone fills only a small portion of the fracture zone.

4.2. *Example 2: Advective-Dispersive Reactive Transport to Demonstrate Species Switching.*

The second example involves the transient simulation of advection-dispersion and equilibrium complexation/precipitation reactions to demonstrate the successful application of species switching in LEHGC-2.0. This technique is required when the calculated concentration of an aqueous component species becomes very low and causes a mass balance error. In this example, the system domain is a $10 \text{ dm} \times 5000 \text{ dm}$ porous medium, with 200 equal size elements, a moisture content of 0.3, a constant flow field of 155.5 dm/day , and a longitudinal dispersivity of 150 dm (Fig. 3). The chemical system includes 7 aqueous components, 20 equilibrium complexed species, and 4 equilibrium precipitated species; thermodynamic data for the chemical reactions are given in Table 1. Figure 3 shows the distributions of the initial total concentrations of each component in the domain. Three compositional zones are indicated by differences in solution composition and precipitated solids content: Zone 1 contains goethite; Zone 2

contains goethite, gypsum and gibbsite, and Zone 3 contains calcite with minor amounts of gypsum and gibbsite. Variable boundary conditions with the incoming total dissolved concentrations as listed in Table 2 are assigned on the top (nodes 401 and 402) and bottom (nodes 1 and 2) sides. On the right and left sides, a zero flux condition is imposed.

A constant time step size of 0.025 day was used for 400 time steps resulting in a total simulation time of 10 days. Without species switching, the simulation stops during the first precipitation cycle of the first time step at node 299 while checking the mass balance of the Al^{3+} component at the first nonlinear iteration (between solving solute transport and chemical reaction). When the species switching option was used to resolve the error in the mass balance, the aqueous complexed species $\text{Al}(\text{OH})_4^-$ was selected by LEHGC-2.0 to replace Al^{3+} as the new component at several nodes. Subsequently, successful simulations for all 400 time steps were carried out.

Calculated concentration profiles for each of the components are given in Yeh et al., 1999. Due to space limitation, only the results for pH and aluminum are given in Figure 4, where the transport of contaminants is shown with respect to the z-coordinate (any two nodes having the same z-coordinate are identical) with flow going from right to left. Figure 4a shows the pH values computed in this system at different times. When $t \leq 2.5$ days, the region between $z = 4000$ dm and $z = 4550$ dm becomes more acidic with time. This is accompanied by increases in total dissolved aluminum (Fig. 4b), sulfate, and iron and dissolution of gibbsite (Fig 4c). When $t > 2.5$ days, the system becomes more alkaline with time because of the significant increase of the incoming total carbonate and the major decrease of incoming total sulfate. This also causes the reprecipitation of gibbsite $\text{Al}(\text{OH})_3$ (s) (Fig. 4c) in the region between $z = 4000$ dm and $z = 5000$ dm.

5. Summary and Conclusion

This paper communicates the development of a mechanistically-based coupled fluid flow and reactive chemical transport model including both fast and slow reactions in variably saturated media. The theoretical bases and numerical techniques of the code were summarized and two example problems were presented. The first problem examined the effects of precipitation on fluid flow and matrix diffusion in fractured porous media. Although the flow field was not significantly affected by the precipitation, the diffusion of a conservative tracer was significantly reduced and transport of the tracer through the fracture was enhanced by this effect. The example demonstrated the ability of LEHGC 2.0 to

show that chemical reactions between major solutes and rocks along transport pathways will affect contaminant retardation by matrix diffusion. The second example demonstrated the use of species switching by LEHGC 2.0 to solve an advective-dispersive-reactive transport problem in which large changes in the concentration of an aqueous component species caused numerical instability. This example exemplified the need for innovative numerical algorithms to solve problems involving stiff geochemical reactions. Robust mechanistically-based numerical models like LEHGC 2.0 provide tools to more reliably predict the migration and transformation of chemicals in the subsurface environment. Such capabilities could enhance the ability of environmental scientists, engineers and decision makers to analyze the impact of subsurface contamination and to evaluate the efficacy of alternative remediation techniques prior to incurring expense in the field.

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Fig. 1. Problem definition for Example 1

(a)

(b)

Fig. 3. Concentration profiles of conservative tracer: (a) with the precipitation effect and (b) without the precipitation effect for Example 1 at $t = 144$ hours.

Fig. 3. Problem domain, discretization, and initial total concentrations for Example 2.

(a)

(b)

(c)

Fig. 4. Concentration profiles of (a) pH, (b) total dissolved aluminum, and (c) precipitation of gibbsite at different times for Example 2.

Table 1. List of Thermodynamic Data for Example 2.

Components Stoichiometric Coefficient								
Species	Ca ²⁺	CO ₃ ²⁻	Al ³⁺	SO ₄ ²⁻	H ⁺	Fe ³⁺	Na ⁺	logK _e
OH ⁻	0	0	0	0	-1	0	0	-14.00
FeOH ²⁺	0	0	0	0	-1	1	0	-2.19
Fe(OH) ₂ ⁺	0	0	0	0	-2	1	0	-5.67
Fe(OH) ₃	0	0	0	0	-3	1	0	-12.56
Fe(OH) ₄ ⁺	0	0	0	0	-4	1	0	-21.60
AlOH ²⁺	0	0	1	0	-1	0	0	-5.00
Al(OH) ₂ ⁺	0	0	1	0	-2	0	0	-10.20
Al(OH) ₄ ⁻	0	0	1	0	-4	0	0	-23.00
Al(OH) ₃	0	0	1	0	-3	0	0	-17.20
HCO ₃ ⁻	0	1	0	0	1	0	0	10.33
H ₂ CO ₃	0	1	0	0	2	0	0	16.68
CaCO ₃	1	1	0	0	0	0	0	3.22
CaHCO ₃ ⁺	1	1	0	0	1	0	0	11.44
HSO ₄ ⁻	0	0	0	1	1	0	0	1.99
CaSO ₄	1	0	0	1	0	0	0	2.30
AlSO ₄ ⁺	0	0	1	1	0	0	0	3.50
Al(SO ₄) ₂ ⁻	0	0	1	2	0	0	0	5.00
FeSO ₄ ⁺	0	0	0	1	0	1	0	4.04
Fe(SO ₄) ₂ ⁻	0	0	0	2	0	1	0	5.42
NaSO ₄ ⁻	0	0	0	1	0	0	1	0.07
CaCO ₃ (s)	1	1	0	0	0	0	0	8.48
Al(OH) ₃ (s)	0	0	1	0	-3	0	0	-9.11
Fe(OH) ₃ (s)	0	0	0	0	-3	1	0	-4.89
CaSO ₄ (s)	1	0	0	1	0	0	0	4.58

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