Multicomponent Solute Transport with Moving Precipitation/Dissolution Boundaries

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Introduction

Multicomponent solute transport problems involving precipitation and dissolution chemical reactions are unique among the wide array of problems encountered in which homogeneous and heterogeneous reactions affect the movement of contaminants in groundwater. The imposition of solubility constraints for various reactive mineral solids may result in the formation or disappearance of moving boundaries which mark the transient location of discontinuities in solid phase concentration, aqueous component flux, and other variables of interest such as porosity. This distinct characteristic of precipitation/dissolution reaction problems poses particular mathematical difficulties to their accurate solution and requires special treatment.

The numerical approaches chosen to solve these types of problems are often suggested directly from the chemical quantities employed as the primary dependent variables (PDVs). While the selection of all species concentrations (Miller and Benson[1]) or the total dissolved concentration of each component (Kirkner et al.[2]) as the PDVs are possible choices, their use results in front-tracking type (FT) schemes in which the moving boundary locations appear explicitly as unknowns in the governing equations. However, choosing the total concentration of each component as the PDV (Walsh et al.[3], Cederburg et al.[4]) removes the explicit presence of the moving boundaries, resulting in formulations that resemble enthalpy-type (ET) methods used for heat flow problems with phase change (Crank[5]). This is an attractive feature which greatly simplifies the numerical approach. However, general finite element ET methods exhibit oscillatory behavior as a result of their inability to accurately simulate the discontinuities across the moving interfaces.

This work will develop and compare fixed-mesh finite element ET and FT formulations for solving precipitation/dissolution chemical transport problems. As will be shown, these schemes result from particular forms of the weak variational statement of the governing differential equations. Throughout the work, it is assumed that all chemical interactions are sufficiently fast that the local equilibrium assumption (LEA) is applicable.

Governing Equations

The following development describes the mass transport of N solute species A_i involved in a precipitation/dissolution reaction with the reactive solid phase C(s) described by

$$C(s) \longleftrightarrow \sum_{i=1}^{N} \upsilon_i A_i \tag{1}$$

, where υ_i represents the stoichiometric coefficient indicating the number of moles of the i th species in one mole of the reactive solid. In this presentation, other chemical reactions such as aqueous complexation and sorption are ignored to simplify the treatment, although they may easily be included.

Mass transport equations for the solute species derived from conservation of mass are given by

$$\frac{\partial}{\partial t}(\phi\, C_i) + \nabla \cdot J_i = \upsilon_i I\,, \quad (i=1,\dots,N) \tag{2a}$$

and for the reactive solid mineral by

$$\frac{\partial}{\partial t}(V_s^{-1}\phi_s) = -I \tag{2b}$$

where C_i denotes the concentration of the i th species, J_i is the mass flux of the i th species, ϕ is the porosity of the porous medium, ϕ_s is the volume fraction occupied by C(s), V_s is the reactive solid molar volume, and I represents the reaction rate expressed in units of moles per unit time per unit bulk volume of porous material. The reaction rate may be eliminated by substituting for I in equation (2a) from equation (2b) resulting in

$$\frac{\partial}{\partial t}\{\phi\, C_i + \upsilon_i V_s^{-1}\phi_s\} + \nabla \cdot J_i = 0\,, \quad (i=1,\dots,N) \tag{3}$$

These mass transport equations must also satisfy the chemical solubility inequality constraint posed by equation (1) expressed as

$$K \geq \prod_{i=1}^{N} \{C_i(x,t)\}^{\upsilon_i} \tag{4}$$

where K denotes the equilibrium constant for the reaction and x the spacial coordinate vector. It is assumed in this development that unit activity coefficients for the solute species hold, and that the activity of the solid phase is unity. To measure the degree of saturation with respect to the reactive solid, the saturation index function (Lichtner et al.[6]) may be introduced as

$$\xi(x,t) = \prod_{i=1}^{N} \{C_i(x,t)\}^{\upsilon_i} - K \tag{5}$$

where ξ is zero or negative if the aqueous solution is in equilibrium or undersaturated, respectively, with respect to the reactive solid C(s).

If the reactive solid is present throughout the domain, equation (3) represents N partial differential equations and equation (4) one algebraic equation for the N+1 unknowns in the system. However, since all regions of the system may not be saturated with respect to the solid phase during a transport episode, a reaction zone will develop that does not contain the reactive solid. This undersaturated zone will be separated from the saturated region by a sharp reaction front across which the solid phase will appear (precipitate) or disappear (dissolve) depending on the saturation index function in each zone.

Conservation of mass across this front relates the magnitude of the jump discontinuities in the solute species flux and reactive solid volume fraction to the normal velocity v_n of the front according to the generalized Rankine-Hugoniot equations given by (Lichtner et al.[7])

$$v_n = \frac{-\partial s/\partial t}{n \cdot \nabla s} = \frac{[J_i] \cdot n}{\upsilon_i [\phi_s] V_s^{-1}}\,, \quad (i=1,\dots,N) \tag{6}$$

where v_n denotes the magnitude of the front velocity normal to the surface of discontinuity s with unit outer normal n, and the brackets [ ] represent the jump discontinuity in a quantity

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across the surface s, eg.

$$[J_i] = J_i(s^+,t) - J_i(s^-,t) \tag{7}$$

The moving interface location now represents an additional unknown in the system that may be solved for using equation (6). The choice of the primary dependent variables and the manner in which the requirements of the Rankine-Hugoniot equation are incorporated into the formulation defines the numerical approach to these problem types.

Finite Element Formulation

The transport problem in a single semi-infinite spacial domain will be considered. It is assumed that the solution is initially saturated with respect to the reactive solid phase, and that the reactive solid occupies an initial volume fraction, ϕ_{so}. At time $t = 0$, the concentrations of all species A_i in solution are lowered on the left boundary and subsequently held fixed at $C_i(o,t) = C_i^o$. This results in a dissolution front moving away from the boundary with its location at time t designated as s(t). From equation (3), it is apparent that the following mass transport equations must be satisfied

$$\frac{\partial}{\partial t}(\phi\,C_i) + \frac{\partial J_i}{\partial x} = 0\ , \quad (i = 1,...,N), \quad 0 < x < s(t) \tag{8a}$$

$$\frac{\partial}{\partial t}(\phi\,C_i) + v_i V_s^{-1}\frac{\partial \phi_s}{\partial t} + \frac{\partial J_i}{\partial x} = 0\ , \quad (i = 1,...,N), \ s(t) < x < \infty \tag{8b}$$

The development of a finite element solution requires a weak variational statement of this problem obtained by multiplying equations (8a) and (8b) and the interface boundary condition implied by equation (6) by an arbitrary test function v resulting in

$$\int_0^{s^-}\left[\frac{\partial}{\partial t}(\phi\,C_i) + \frac{\partial J_i}{\partial x}\right]v\ dx + \int_{s^+}^{\infty}\left[\frac{\partial}{\partial t}(\phi\,C_i) + v_i V_s^{-1}\frac{\partial \phi_s}{\partial t} + \frac{\partial J_i}{\partial x}\right]v\ dx$$

$$+ \left([J_i] - v_i V_s^{-1}[\phi_s]\frac{ds}{dt}\right)v(s) = 0\ , \quad \forall\,v, \ (i = 1,...,N) \tag{9}$$

Integrating the flux term by parts, equation (9) becomes

$$\int_0^{\infty}\left(\frac{\partial}{\partial t}(\phi\,C_i)\,v - J_i v'\right)dx + \int_{s^+}^{\infty} v_i V_s^{-1}\frac{\partial \phi_s}{\partial t}v\ dx$$

$$- v_i V_s^{-1}[\phi_s]\,\frac{ds}{dt}\,v(s) = 0\ , \quad (i = 1,...,N) \tag{10}$$

Using generalized function notation, equation (10) may equivalently be written as (Mundell and Kirkner[8])

$$\int_0^{\infty}\left\{\frac{\partial}{\partial t}\left[\phi C_i + v_i V_s^{-1}\phi_s\theta(x-s(t))\right]v - J_i\,v'\right\}dx = 0\ , \quad (i = 1,...,N) \tag{11}$$

where $\theta(x)$ denotes the Heaviside step function. The ET formulation arises from the selection of the total component concentration as the PDV. In equation (11), the expression in the square brackets is recognized as the total concentration of the i th species, C_{Ti}, or

$$C_{Ti} = C_i + v_i\kappa_s\theta(x-s(t))\ , \quad (i = 1,...,N) \tag{12}$$

where $\kappa_s = (\phi_s\,V_s^{-1})/\phi$ denotes the solid phase concentration of C(s) per unit volume of aqueous

solution. Thus, equation (11) is the weak variational statement corresponding to the local form of the conservation of mass for the total concentration of solute species A_i. Note that the introduction of C_{Ti} into equation (11) as the PDV removes the explicit presence of s(t) in the variational statement. Employing linear basis functions for C_{Ti}, C_i, and v leads to the semi-discrete approximation

$$M\dot{c}_{Ti} + Kc_i = f_{oi}, \quad (i = 1,...,N) \tag{13}$$

where M and K denote standard mass and coefficient matrices, respectively, for the mass flux conditions specified, and c_{Ti} and c_i are the vector of nodal values of $C_{Ti}(x,t)$ and $C_i(x,t)$, and f_{oi} is the vector containing the boundary condition contribution for the i th solute species. Equation (11) may be fully discretized using the generalized trapezoidal scheme and solved using Newton methods, function iteration, or modifications to these (Mundell and Kirkner[8]).

If equation (10) is rewritten as

$$\int_0^\infty \left\{ \left[\frac{\partial}{\partial t}(\phi C_i) + \upsilon_i V_s^{-1} \frac{\partial \phi_s}{\partial t} \theta(x-s(t)) \right] v - J_i v' \right\} dx$$
$$- \upsilon_i V_s^{-1} [\phi_s] \frac{ds}{dt} v(s) = 0, \quad (i = 1,...,N) \tag{14}$$

it is apparent that the unknown value of the interface is explicitly contained in the weak variational statement. Use of all species concentrations as the PDVs suggested by equation (14) leads directly to finite element front-tracking schemes in which s(t) becomes part of the solution. This is also true for the case of the use of the total aqueous concentration when soluble complexation reactions are involved in mass transport.

For the case of dissolution without precipitation, the finite element discretization of equation (14) has been shown[8] to yield the following set of nonlinear ordinary differential equations

$$M\dot{c}_i + Kc_i = f_{oi} + \upsilon_i V_s^{-1} \phi_{so} \frac{ds}{dt} \psi(s), \quad (i = 1,...,N) \tag{15}$$

where $\psi(s)$ is the vector of global linear shape functions evaluated at s. Time discretization using the generalized trapezoidal rule results in the same set of fully discretized equations as for transport without chemical reaction except for the addition of a vector that must be updated by a search algorithm for s[8].

Sample Problem

The one-component diffusion dissolution problem demonstrates the behavior of the ET formulation in comparison to an FT scheme. The problem, originally posed by Lichtner et al.[6], involves a system containing a single aqueous component A in local equilibrium with a reactive solid mineral phase C(s). This requires that the initial concentration of species A everywhere in the domain be constant and equal to the equilibrium constant, K. The reactive solid phase occupies some initial volume fraction ϕ_{so} which is very small in comparison to the system porosity, ϕ. At time t = 0, the concentration of A on the left boundary is reduced and subsequently held fixed at $C_a(0,t) = C_a^o$ such that the aqueous solution is undersaturated with respect to C(s) and a moving dissolution boundary begins to propagate through the domain.

The problem is completely analogous to the one-phase heat conduction problem with phase change[5] and reduces to solving for the concentration profile in the domain to the left of the moving front. Nondimensionalization of the mass transport equation to the left of the

interface results in the parabolic diffusion equation with the leading constant of unity

$$\frac{\partial \hat{c}}{\partial \hat{t}} = \frac{\partial^2 \hat{c}}{\partial \hat{x}^2} \ , \quad 0 < \hat{x} < \hat{s}(\hat{t}) \tag{16}$$

where $\hat{c} = (C_a - C_a^o)/(K - C_a^o)$, $\hat{x} = x/L$, $\hat{s} = s/L$, $\hat{t} = Dt/L^2$, and D denotes the diffusion coefficient. The interface condition becomes

$$\frac{\partial \hat{c}(\hat{s}^-, \hat{t})}{\partial \hat{x}} = \lambda \frac{d\hat{s}}{d\hat{t}} \tag{17}$$

where the parameter $\lambda = \kappa_s/(K - C_a^o)$ is the dimensionless solid phase concentration and $1/\lambda$ is the so-called Stefan number. It is obvious that λ uniquely controls the velocity of the moving dissolution boundary, and therefore defines the general behavior of the problem.

Figure 1 illustrates the behavior of the concentration solutions for fully implicit ET and FT schemes with $\Delta \hat{x} = 0.025$, $\Delta \hat{t} = 0.0167$, and $\lambda = 100$ at the fixed spacial coordinate $\hat{x} = 0.075$. The greater oscillatory behavior of the ET solution is apparent in comparison to the FT solution, and results from the inability of the ET scheme to accurately describe the discontinuous nature of the total component concentration across the dissolution interface. The L_2 error norm (which measures the root-mean-square of the error over the domain) for the ET method solution of Figure 1 is plotted versus the nondimensional interface location in Figure 2. The magnitude of the L_2 error norm varies considerably as the dissolution front travels through the domain, reaching maximum values when the front moves through the center of an element, and minimum values as it passes through a nodal location.
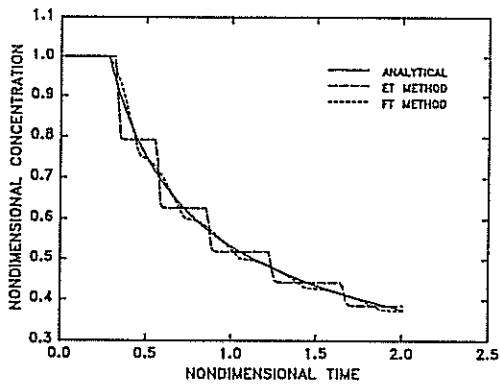

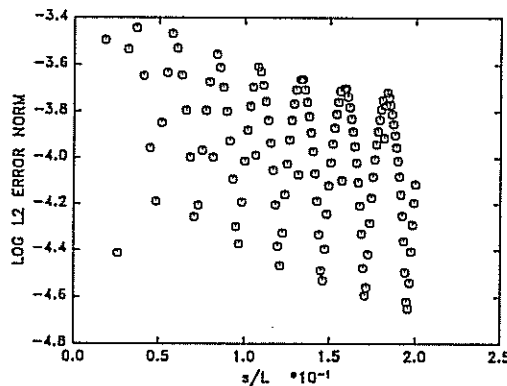Figure 1. One-component diffusion dissolution ($\lambda = 100$).

Figure 2. L_2 error norm for the ET scheme in Figure 1.

To determine the effect that the size of the solid discontinuity at the interface has on the magnitude of the error in the concentration solution, the value of λ was varied over a wide range and simulations were performed. The results for fully implicit ET and FT schemes using a fixed domain discretization of $\Delta \hat{x} = 0.025$ are summarized in Figure 3. The mean L_2 error norms between $\hat{s} = 0.0$ and 0.2 were calculated from graphs similar to Figure 2. The results show the superior performance of the FT scheme for values of λ greater than about 10. However, for problems with lower solid concentrations in comparison to solute

concentrations, the ET formulation yielded more accurate concentration distributions using less computational effort than the FT method.
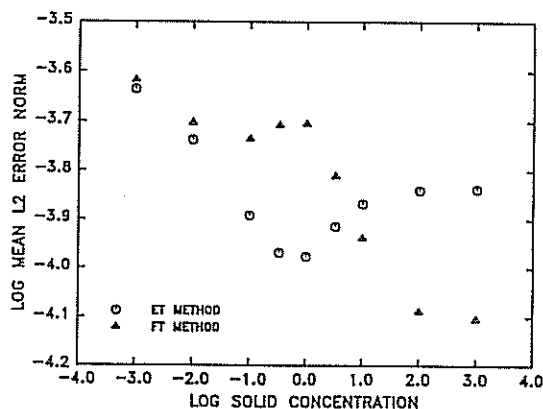

Figure 3. Effect of λ on mean L_2 error norm between s/L = 0.0 and 0.2.

Conclusions

Two fixed-mesh finite element approaches have been presented for solving solute transport problems involving precipitation/dissolution reactions. The results of simulations for one-component diffusion dissolution indicate that despite oscillations inherent in the aqueous concentration profile produced by enthalpy-type (ET) formulations, greater accuracy may be achieved with less computational effort and numerical complexicity than with front-tracking type (FT) schemes for large classes of transport episodes in which the reactive solid concentration does not significantly exceed the aqueous concentration of the solute species. The retention of the simplicity of ET methods is a desirable element in the development of a general multicomponent code for modeling more complex problems involving multiple precipitation/dissolution fronts with aqueous complexation and sorption.

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