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**Simulation of Reactive Chemical Transport in a
Varying Thermal Field with Reaction-Flow Coupling**

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SIMULATION OF REACTIVE CHEMICAL TRANSPORT IN A VARYING THERMAL FIELD WITH REACTION-FLOW COUPLING

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ABSTRACT

A computer program, THCVP, simulates coupling between advective/diffusive solute transport and chemical reactions, coupling of the reactions to heat transport, and feedback from precipitation/dissolution reactions to fluid flow. A simple simulation of transport of dissolved silicic acid along a gradient of temperature shows how precipitation of quartz at low temperatures can drastically reduce advective transport of all solution components including trace contaminants.

INTRODUCTION

Computer programs that simulate the movement of reactive chemical species in subsurface waters are important tools for the assessment of performance and, ultimately, safety of nuclear waste repositories. An aspect of geochemical behavior that can have important consequences in performance assessment is the effect of a variable thermal field on (1) the movement of major solution components and dissolved waste radionuclides and (2) the stabilities of minerals exposed to the changing thermohydrochemical environment. Variable thermal fields can arise in the near vicinity of nuclear waste canisters and from mixing of fluids having different temperatures. Such fields imposed on previously stable or metastable fracture minerals can induce dissolution of existing minerals, transport of dissolved chemical species, and precipitation of new solid phases. Redistribution of materials within fractures by chemical reactions and transport can produce changes of physical properties such as porosity, mass diffusivity, and permeability. Changes of these parameters can affect transport of both radionuclides and major components of subsurface fluids.

Computer programs¹⁻⁵ that couple chemical reactions, including precipitation/dissolution, to mass transport processes have not, in general, accounted for the effects of precipitation/dissolution reactions on the transport processes. In particular, changes in the sizes of pores or apertures of fractures caused by precipitation/dissolution reactions accompanying mixing of fluids of different compositions can alter the effective mass diffusivities and permeabilities of porous or fractured materials⁶, and these alterations can affect the subsequent

movement of dissolved chemicals. Neglect of these alterations not only might produce inaccurate computational results⁷, but might also lead to physically unrealizable consequences such as the calculated volume of a precipitate exceeding available pore space.

An examination of calculated permeability changes associated with chemical changes accompanying simulated acidization of sandstone with HCl/HF mixtures has been reported⁸. Calculations of the permeability changes were done separately from the reactive chemical transport simulations; thus, there was not complete coupling between precipitation/dissolution reactions and fluid flow in the simulations.

Reaction-transport feedback in advecting systems with chemical disequilibrium has been described and has been simulated by the computer program REACTRANS to demonstrate the origins of patterned states ("geochemical self-organization") in rocks^{9,10}. These calculations did not consider the effects of varying thermal fields.

BASIS FOR THE COMPUTER PROGRAM THCVP

The reactive chemical transport simulator THCVP is an extension of the simulator THCC^{11,12}, and is being used to study effects on mass transport of precipitation/dissolution reactions in the presence of varying thermal fields. The THCVP computer program is a thermodynamically based simulator of multicomponent, reactive chemical transport using the direct method of solution. The program simulates transport of reactive chemical species by advection and hydrodynamic dispersion or mass diffusion in one-dimensional linear or cylindrically symmetric geometry. Chemical reactions are assumed to be in a state of local equilibrium. The reactions simulated are complexation, oxidation-reduction, ionization of water, reversible precipitation of solid phases, and ion exchange. Chemical reactions are described by mass action relations among thermodynamic activities of participating species. The THCVP program has the capability to simulate systems with temporally and spatially variable fields of temperature.

In a system with fluid-filled porosity ϵ_f , N_p reactive solid phases, and nonsorbed aqueous-phase species consisting of N_b basis species (the smallest set of species

needed to define the chemical system in the aqueous phase) and N_c complexes, the conservation equation for the mass of a component i is

$$\frac{\partial}{\partial t} (\epsilon_f W_i + \sum_{k=1}^{N_p} \nu_{ik} P_k) = \nabla \cdot [(\epsilon_f D_d + aq) \nabla W_i - q W_i], \quad i = 1, \dots, N_b, \quad (1)$$

where t is time, D_d is the diffusion coefficient in the fluid phase, a is the dispersivity, q is the volumetric flux of fluid (Darcy flux), P_k is the concentration (referred to unit volume of porous matrix) of a precipitate P_k , and the ν_{ik} 's are the number of moles of basis species B_i per mole of solid P_k . W_i is the total concentration (referred to unit volume of the fluid phase) of component i and is defined by

$$W_i = B_i + \sum_{j=1}^{N_c} \nu_{ij} C_j, \quad i = 1, \dots, N_b, \quad (2)$$

where B_i , $i = 1, \dots, N_b$, is the concentration of the basis species B_i containing component i and ν_{ij} is the number of moles of B_i per mole of complex C_j , $j = 1, \dots, N_c$, having concentration C_j . C_j is formed by reactions among basis species, thus:

$$\nu_{i1} B_1^{z_1} + \nu_{mj} B_m^{z_m} + \dots = C_j^{\nu_{ij} z_i + \nu_{mj} z_m + \dots},$$

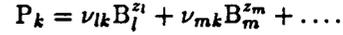
where the z_i are signed ionic charges of the basis species. The concentration of complex C_j is given by the mass action relation,

$$C_j = \frac{K_{cj}}{\gamma_j} \prod_{l=1}^{N_b} (\gamma_l B_l)^{\nu_{lj}}, \quad j = 1, \dots, N_c, \quad (3)$$

where K_{cj} is the temperature-dependent thermodynamic equilibrium constant for formation of complex C_j and the γ 's are activity coefficients.

In the numerical formulation of THCVP, equations (2) and (3) are substituted into equation (1). The resulting set of N_b partial differential equations is transcribed into N_b finite-difference equations, using central differencing in space and the Crank-Nicolson method to obtain second-order accuracy in time. The set of unknowns consists of B_i , $i = 1, \dots, N_b$, and P_k , $k = 1, \dots, N_p$, at each finite-difference node. Residue equations for the basis species are formed by algebraically summing all terms in the finite-difference forms of the transport equations. The finite-difference analogs of equation (1) provide N_b residue equations at each node; the remaining N_p residue equations are provided by the solubility products for the reactive solids.

A reactive solid P_k dissolves to form its constituent basis species, thus:



The activity product, Q_{sk} , for this reaction is given by

$$Q_{sk} = \prod_{l=1}^{N_b} (\gamma_l B_l)^{\nu_{lk}}. \quad (4)$$

If the the basis species formed by dissolution of solid P_k are in chemical equilibrium with the solid, then the activity product, Q_{sk} , is equal to the thermodynamic solubility product, K_{sk} . Values of K_{sk} at different temperatures are calculated using tabulated thermodynamic functions¹³. Residue equations for the solids are formed by an algorithm that provides a residue equation for each solid at each node and eliminates the need to alter the number of unknowns at nodes where solids have precipitated or dissolved.

The residues ($N_b + N_p$ at each node) are reduced to "zero" (a small positive number fixed by specifying an error tolerance at input) iteratively by computing corrections to current values of the unknowns using the Newton-Raphson method¹⁴. Elements of the Jacobian matrix required by this method are computed from analytical expressions. The system of equations to be solved for the corrections has block tridiagonal form and is solved by use of a published software routine¹⁵.

Temperature variations during transport and reaction of chemical components are simulated by numerical solution of a heat-transport equation within THCVP. Three kinds of thermal variations can be simulated: (1) mixing of advecting fluids having different temperatures, (2) diffusion of heat from a constant-temperature boundary, and (3) a constant linear gradient of temperature between two boundaries.

COUPLING BETWEEN CHEMICAL REACTIONS AND POROSITY

Equation (1) accounts for changes of porosity, ϵ_f , and fluid flow velocity, q , as well as changes of chemical concentrations. The fluid-filled porosity ϵ_f is not a primary unknown because it is determined by the P_k , $k = 1, \dots, N_p$. In the iterative Newton-Raphson solution scheme, new values of ϵ_f are calculated from values of the P_k 's at the end of each iteration. A conservation equation can be written for a unit volume of porous medium:

$$\epsilon_m + \epsilon_p + \epsilon_f = 1, \quad (5)$$

where ϵ_m is the volume fraction of unreactive solid (constant), ϵ_p is the volume fraction of reactive solids, and ϵ_f is the volume fraction of fluid phase. ϵ_p is calculated from the current concentrations of reactive solids by

$$\epsilon_p = \sum_{k=1}^{N_p} P_k \bar{V}_k, \quad (6)$$

where \bar{V}_k is the molar volume of reactive solid k and is assumed constant. It follows from equation (5) that

$$\Delta\epsilon_f = -\Delta\epsilon_p. \quad (7)$$

To simulate constant porosity in a system with precipitation/dissolution reactions, all \bar{V}_k 's are given input values of zero.

COUPLING BETWEEN POROSITY AND FLUID FLOW

The fluid flux, q , is calculated from Darcy's law:

$$q = -K_f(\epsilon_f)\nabla h, \quad (8)$$

where $K_f(\epsilon_f)$ is the local hydraulic conductivity, a function of porosity, and ∇h is the local hydraulic gradient. A number of empirical relations are available to relate local values of K_f to ϵ_f ; currently, THCVF uses a relation similar to the Kozeny-Carmen equation:

$$K_f = C_f \frac{\epsilon_f^3}{(1 - \epsilon_f)^2}, \quad (9)$$

where C_f is a constant.

The computer program THCVF assumes a constant hydraulic head drop, h_t , across a finite one-dimensional domain divided into $n - 1$ segments by n nodes numbered $1, \dots, k, \dots, n$. Associated with each node and adjacent segment is the current value of porosity, $\epsilon_{f,k}$, and the current value of hydraulic conductivity, $K_{f,k}$, from equation (9). Because there are no sources or sinks of fluid flow in the domain, the Darcy flux, q , at any time must be constant throughout the spatial domain. Then it can be shown that at any simulated time level, the Darcy flux in linear geometry is given by

$$q = h_t \left(\sum_{k=1}^{n-1} \frac{x_{k+1} - x_k}{K_{f,k}} \right)^{-1}, \quad (10)$$

where $x_{k+1} - x_k$ is the spatial separation between nodes k and $k + 1$. Here it is assumed that the hydraulic head drops from h_t at node 1 to zero at node n . Values of hydraulic head, h_k , at intermediate nodes are given by

$$h_k = h_t - q \sum_{i=1}^{k-1} \frac{x_{i+1} - x_i}{K_{f,i}}. \quad (11)$$

In radial coordinates, the geometric variations of q and h_k must be accounted for, and equations (10) and (11) become

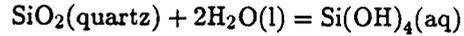
$$q = h_t \left(x_1 \sum_{k=1}^{n-1} \frac{x_{k+1} - x_k}{K_{f,k} x_{k+1}} \right)^{-1}, \quad (12)$$

and

$$h_k = h_t - x_1 q \sum_{i=1}^{k-1} \frac{x_{i+1} - x_i}{K_{f,i} x_{k+1}}. \quad (13)$$

EXAMPLE SIMULATION

A simple chemical reaction, the precipitation of quartz from saturated solution of silicic acid, illustrates the effect of varying temperature on porosity, hydraulic conductivity, and fluid flow. A constant temperature gradient is imposed on a finite spatial domain, the temperature varying from 90 °C at $x = 0$ to 50 °C at $x = 1$ m. The domain has initial porosity, ϵ_f , of 0.05 and is saturated with silicic acid at the local temperature. The variation with temperature of the equilibrium constant, K_{SP} , for the reaction,



is given by¹³

$$\log K_{SP} = 1.881 - \frac{1560}{T} - 2.028 \times 10^{-3}T, \quad (14)$$

where T is the absolute temperature in kelvins. The molar volume of quartz is 0.0227 dm³/mole¹⁶. The constant C_f in equation (9) is taken to be 0.045 m/s, corresponding to a fracture hydraulic conductivity of 10⁻⁴ m/s¹⁷ at a porosity of 0.12¹⁸. At the simulated initial porosity of 0.05, the initial hydraulic conductivity is then 6.2 × 10⁻⁶ m/s. (The fracture porosity was reduced from 0.12 to 0.05 in these simulations to reduce computing time.) A constant hydraulic head gradient of unity is imposed on the system, the head dropping from 1 m at $x = 0$ to zero at $x = 1$ m. Under the influence of the head gradient, fluid saturated with silicic acid at 90 °C enters the domain at $x = 0$ and is advected in the direction of increasing x . Due to decreasing temperature and the decreasing solubility of silicic acid, quartz is deposited in the region near $x = 0$; the "concentrations" (moles of quartz per dm³ of matrix) of deposited solid are shown in Fig. 1 as functions of time for nodes located at $x = 0$ and $x = 0.05$ m. Fig. 2 shows values of porosity at the same two nodes. The deposited solid concentration rises to a steady-state value of about 2.2 mole/dm³ at time 2.7 × 10⁷ s, while the porosity drops to about 0.0004 at this time. Fig. 3 shows the Darcy flux with time, and is plotted semilogarithmically to emphasize the sudden decrease of fluid flow near 2.5 × 10⁷ s and the non-zero steady-state value of about 6.7 × 10⁻¹¹ m/s, a decrease of about five orders of magnitude from the initial value. Finally, Fig. 4 shows spatial profiles of hydraulic head at various times, indicating the effect of accumulation of solid quartz near the fluid inlet.

CONCLUSION

The computer program THCVP provides a capability to simulate coupling and feedback among processes of saturated fluid flow, transport of reactive solutes, and chemical reactions under conditions of varying temperature. A simple simulation shows the significant effect on advective fluid flow of mobilization and subsequent precipitation of quartz from silicic acid solution. Reduction of flow by mineralization involving major solution components can result in decreased migration rates of trace contaminants as well as major components.

ACKNOWLEDGMENT

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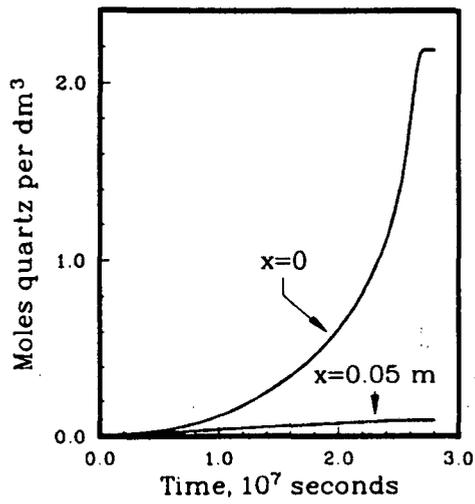


Figure 1. Moles of quartz precipitated per dm^3 of matrix vs. time at $x = 0$ and $x = 0.05$ meter.

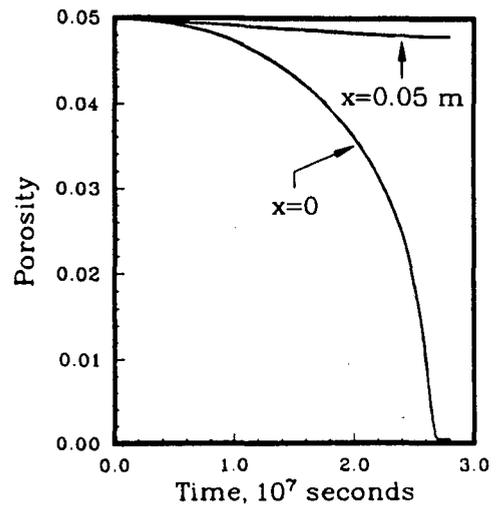


Figure 2. Porosity vs. time at $x = 0$ and $x = 0.05$ meter.

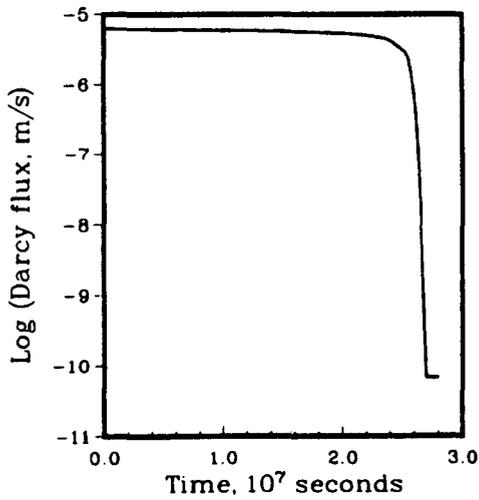


Figure 3. Areal flow rate (Darcy flux) of water vs. time.

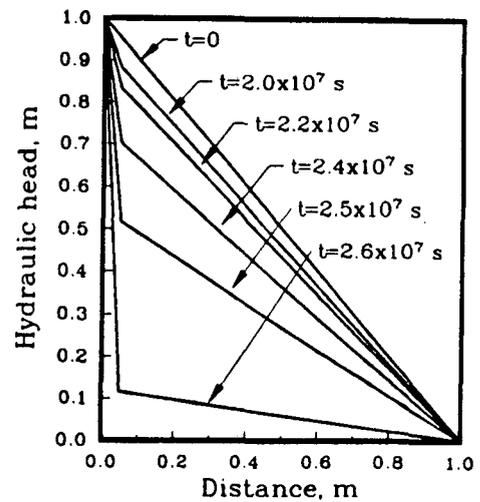


Figure 4. Hydraulic head vs. distance for various simulated times.

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