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COUPLING OF PRECIPITATION/DISSOLUTION REACTIONS TO MASS DIFFUSION

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Publication Date

1988-10-01

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Presented at the 196th Annual Meeting of the
American Chemical Society, Division of Geochemistry,
Los Angeles, CA, September 25-30, 1988

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LBL-26183
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**Coupling of Precipitation/Dissolution Reactions
to Mass Diffusion**

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This work was supported by the Director, Office of Civilian Radioactive Waste Management, Office of Facilities Siting and Development, Siting and Facilities Technology Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Coupling of Precipitation/Dissolution Reactions to Mass Diffusion

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Coupling of precipitation/dissolution reactions to diffusive mass transport via porosity changes has been implemented in the computer program THCC, a simulator of reactive chemical transport. The coupling is accomplished without increasing the set of primary unknowns. Porosity is included explicitly in the transport equations and is tracked by accounting for changes of volumes of precipitates. The coupling prevents the volume of a precipitated solid from exceeding available pore volume. Results of calculations are presented for two examples, each done with and without variable porosity.

Computer programs (1-5) that couple chemical reactions 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 can alter the effective mass diffusivities and permeabilities of porous or fractured materials (6,7), and these alterations can affect the subsequent movement of dissolved chemicals. Neglect of these effects not only might produce inaccurate computational results (8), 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 reported (9). However, 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.

The reactive chemical transport simulator THCC (10,11) is being used to study effects on mass transport of precipitation/dissolution reactions. This paper sets forth the mathematical and numerical bases for the coupling from these reactions to mass *diffusion* and presents results of calculations to demonstrate consequences of the coupling.

The Computer Program THCC

The THCC computer program (10,11) 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 by hydrodynamic dispersion or mass diffusion in one-dimensional or cylindrically symmetric geometry. Chemical reactions are assumed to be in a state of local equilibrium. The reactions simulated are complexation, oxidation-reduction, and ionization of water in the aqueous phase, reversible precipitation of solid phases, and ion exchange. Chemical reactions are described by mass action relations among thermodynamic activities of participating species. The THCC program has the capability to simulate systems with temporally and spatially variable fields of temperature and to simulate radioactive decay of selected reactants.

Variable Porosity in THCC

The variable porosity must be included explicitly in the transport equations for mobile species. Values of porosity are related to volumes of reactive solids.

Transport Equations. In a system with fluid-filled porosity ϵ_f , N_p reactive solid phases, and aqueous-phase species consisting of N_b basis species and N_c complexes, the conservation equation for the mass of a basis species i is:

$$\frac{\partial}{\partial t} \left(\epsilon_f W_i + \sum_{k=1}^{N_p} \nu_{ik} P_k \right) = \nabla \cdot \left(\frac{\epsilon_f D}{\tau} \nabla W_i \right), \quad i = 1, \dots, N_b, \quad (1)$$

with

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

and

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

where D is the diffusion coefficient in the fluid phase, τ is the tortuosity, B_i and C_j are concentrations of basis species and complexes (moles per unit volume of fluid), P_k is the concentration of a precipitate (moles per unit volume of matrix), K_j is the temperature-dependent thermodynamic equilibrium constant for formation of complex j , the γ 's are activity coefficients, and the ν 's are stoichiometric coefficients. In the numerical formulation of THCC, Equations (2) and (3) are substituted into Equation (1). Then 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. The

finite-difference analog of Equation (1) provides N_b relations at each node; the remaining N_p relations are provided by residue equations for the reactive solids, as described elsewhere (10). Currently, τ is treated as a constant, although it is expected to exhibit second-order variation with porosity.

The fluid-filled porosity ϵ_f is not a primary unknown because it is determined by the P_k , $k = 1, \dots, N_p$, as shown below. In the iterative Newton-Raphson solution scheme, values of ϵ_f are updated based on new values of the P_k 's at the end of each iteration.

Volumetric Relations. A conservation equation can be written for a unit volume of matrix:

$$\epsilon_m + \epsilon_p + \epsilon_f + \epsilon_g = 1, \quad (4)$$

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

$$\epsilon_p = \sum_{k=1}^{N_p} P_k \bar{V}_k, \quad (5)$$

where \bar{V}_k is the molar volume of reactive solid k and is assumed constant. It follows from Equation (4) that

$$\Delta(\epsilon_f + \epsilon_g) = -\Delta\epsilon_p. \quad (6)$$

In the current numerical formulation if $\epsilon_g > 0$, then $\Delta\epsilon_f = 0$ and $\Delta\epsilon_g = -\Delta\epsilon_p$ until $\epsilon_g = 0$; thereafter, $\Delta\epsilon_f = -\Delta\epsilon_p$.

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

Flux Condition at Inner Boundary

Both examples given in this paper were calculated with the following condition at the boundary $x = 0$:

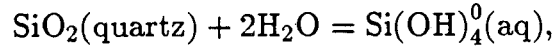
$$- [D \nabla W_i]_{x=0} = J_i \epsilon_f|_{x=0}, \quad i = 1, \dots, N_b, \quad (7)$$

where J_i is the input value of the flux of basis species i referred to unit area of the fluid phase. This formulation allows the incoming flux to decrease in response to decreasing porosity at the boundary.

Examples

The examples involve (1) precipitation along a gradient of temperature and (2) isothermal precipitation of a solid by reaction between two diffusing ions.

Transport of Silica along a Temperature Gradient. This example simulates diffusion of silicic acid into a domain where temperature decreases with increasing distance from the inlet at $x = 0$. The temperature field is steady in time. Quartz precipitates according to the reaction



for which the equilibrium constant, K , is given as a function of absolute temperature, T , by (12)

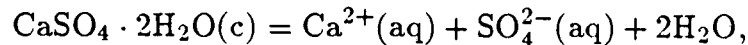
$$\log K = 1.881 - \frac{1560}{T} - 2.028 \times 10^{-3}T. \quad (8)$$

The molar volume of quartz is $0.0227 \text{ dm}^3/\text{mole}$ (13). The quantity D/τ is assumed constant and equal to $10^{-9} \text{ m}^2/\text{s}$. The temperature gradient is $-20 \text{ }^\circ\text{C}/\text{m}$, and the temperature at the boundary $x = 0$ is $150 \text{ }^\circ\text{C}$. The outer boundary is located at $x = 5 \text{ m}$. Initial conditions in the domain $x \geq 0$ were $\epsilon_f = 0.05$, $\epsilon_g = 0$, $\epsilon_m = 0.95$, and zero concentrations of $\text{Si}(\text{OH})_4^0(\text{aq})$ and $\text{SiO}_2(\text{quartz})$. The boundary condition at $x = 0$ is $J(\text{Si}(\text{OH})_4^0(\text{aq})) = 10^{-4} \text{ mole}/\text{m}^2\text{s}$.

Because quartz exhibits prograde solubility, it precipitates along the decreasing temperature profile within the domain $x \geq 0$. However, significant changes of porosity occur only at the boundary $x = 0$. Figure 1 shows the accumulation of quartz at this boundary at times up to 10^9 s for simulations with variable porosity and constant porosity. In the case of constant porosity the non-physical result that the volume of precipitated quartz exceeds available pore space is obtained at about $0.45 \times 10^9 \text{ s}$, when the solid concentration exceeds $2.2 \text{ moles}/\text{dm}^3$ of matrix. On the other hand, in the case of variable porosity the concentration of solid increases gradually with time and does not exceed the critical concentration. This is a result of a decreasing influx of $\text{Si}(\text{OH})_4^0(\text{aq})$ at the boundary caused by the decreasing porosity there, as indicated by Equation (7). Also, the concentration of precipitated solid at the adjacent node is smaller in the variable porosity case than in the constant porosity case for all times, a consequence of reduced effective diffusivity at the boundary as reflected in the term $\epsilon_f D/\tau$ in Equation (1).

Figure 2 shows the porosity at the boundary $x = 0$ as a function of time for the variable porosity case. The decline of porosity appears to be exponential in time, approaching the asymptotic value of zero.

Precipitation of Gypsum at Constant Temperature. This example simulates diffusion of $\text{Ca}^{2+}(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$ into a domain where the two ions react and gypsum precipitates according to the reaction



for which $\log K = -4.50$ at $25 \text{ }^\circ\text{C}$ (14). The molar volume of gypsum is $0.0747 \text{ dm}^3/\text{mole}$ (13). The quantity D/τ is assumed constant and equal to $10^{-9} \text{ m}^2/\text{s}$.

Initial conditions in the domain $x \geq 0$ were $\epsilon_f = 0.05$, $\epsilon_g = 0.$, $\epsilon_m = 0.95$, and zero concentrations of $\text{Ca}^{2+}(\text{aq})$, $\text{SO}_4^{2-}(\text{aq})$, and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{c})$. The boundary condition at $x = 0$ is $J(\text{Ca}^{2+}(\text{aq})) = J(\text{SO}_4^{2-}(\text{aq})) = 10^{-3}$ mole/m²s.

Under the isothermal condition imposed in this example, gypsum precipitates only at the boundary $x = 0$ in both constant porosity and variable porosity cases. Significant changes of porosity occur at this location in the variable porosity case. Figure 3 shows the accumulation of gypsum at this location at times up to 10^7 s for the two cases. The results are qualitatively similar to the results of the previous example. In the case of constant porosity the volume of precipitated gypsum exceeds available pore space at times greater than about 0.14×10^7 s. In this example, the critical concentration of solid is 0.67 mole/dm³ of matrix. In the variable porosity case the solid concentration rises asymptotically toward the critical value, again as a result of decreasing influxes of reactants at the boundary caused by decreasing porosity there.

Figure 4 shows the porosity at the boundary $x = 0$ as a function of time for the variable porosity case. As in the previous example, the porosity declines steadily and approaches zero asymptotically.

Discussion

The method described here to account for variations of porosity and mass diffusivity associated with precipitation/dissolution of reactive solids provides a previously absent coupling in the direction from chemical reactions to mass transport. The method does not allow the non-physical exceedance of available pore volume by precipitated solids.

It is important to note that in systems of the type considered here variations of porosity and mass diffusivity *do not affect fluid-phase concentrations of reactants in equilibrium with a reactive solid*; only the rate of accumulation of the solid is affected. In the present examples the profiles of fluid-phase concentrations of reactants were identical in the cases with and without porosity variations *whenever the reactive solid was present*. This is a necessary consequence of the assumption of chemical equilibrium in the precipitation/dissolution process. However, in simulations involving dissolution of a previously precipitated solid and transport of the dissolution products, the limitation imposed by available porosity on quantities of precipitate may have to be considered.

Acknowledgment

This work was supported by the Director, Office of Civilian Radioactive Waste Management, Office of Facilities Siting and Development, Siting and Facilities Technology Division, of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Figure Captions

Figure 1. Quartz precipitated at boundary $x = 0$.

Figure 2. Porosity at boundary $x = 0$ for quartz precipitation.

Figure 3. Gypsum precipitated at boundary $x = 0$.

Figure 4. Porosity at boundary $x = 0$ for gypsum precipitation.

Figure 1

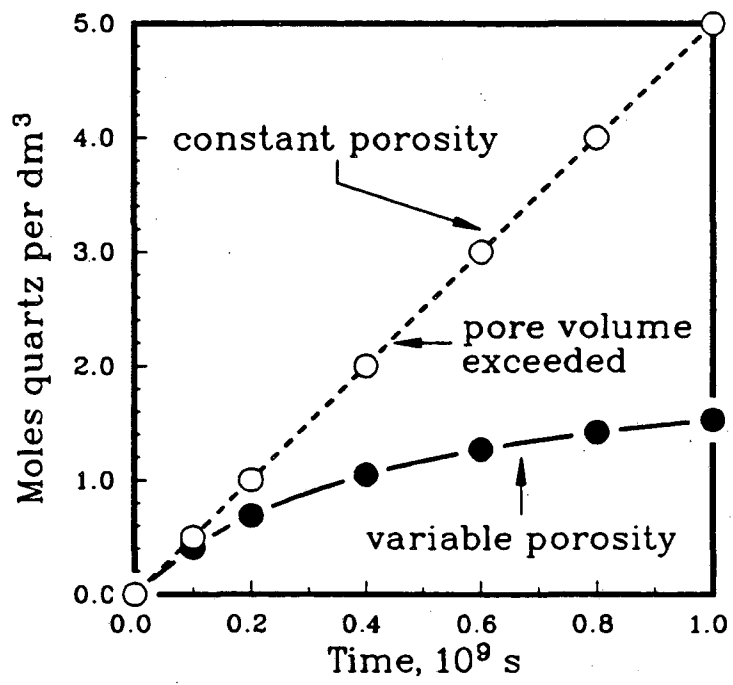


Figure 2

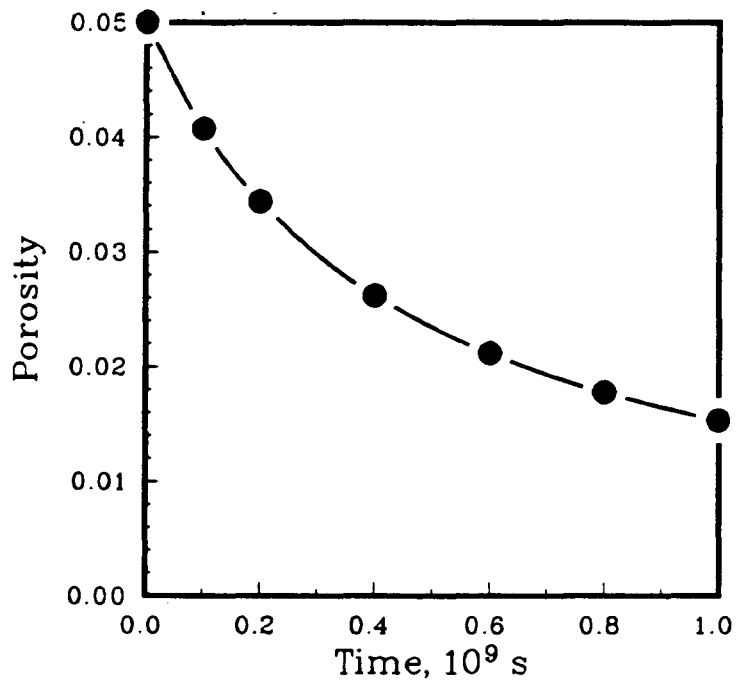


Figure 3

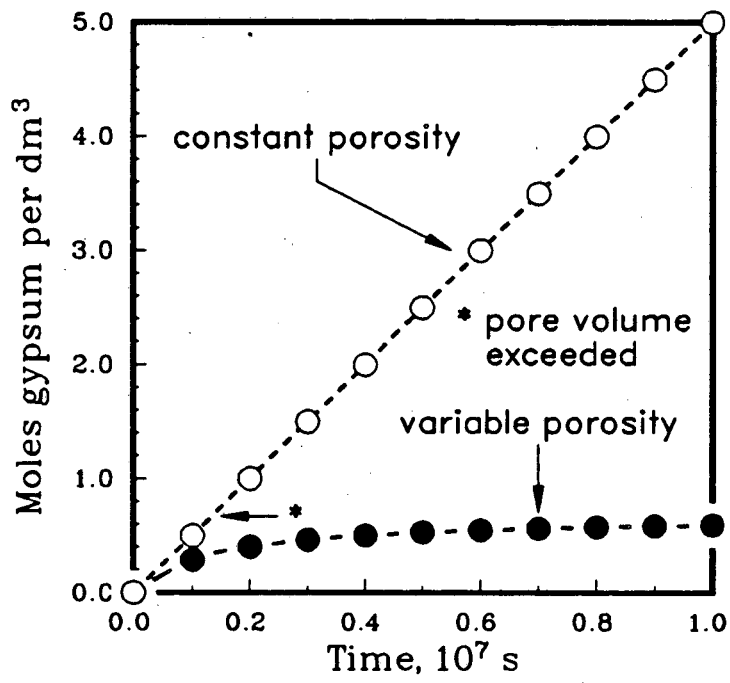
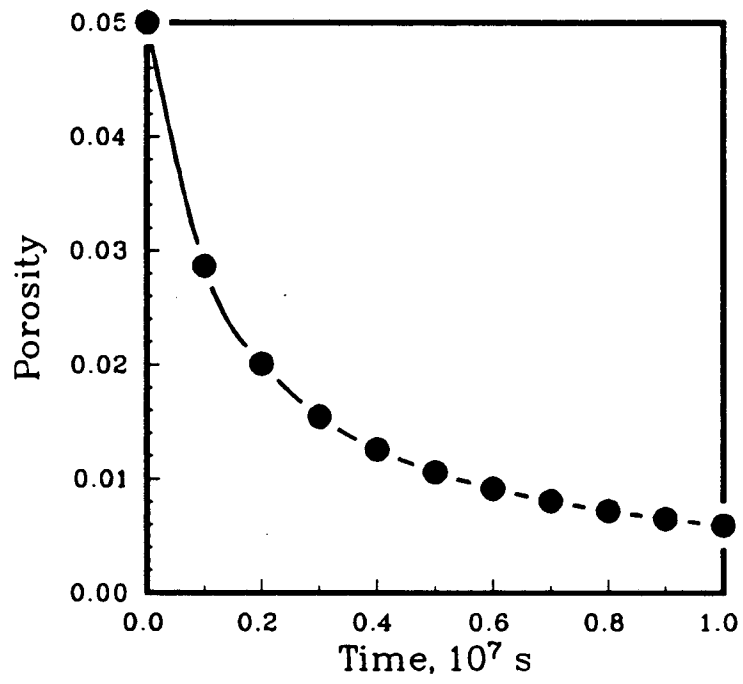


Figure 4



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