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Coupled to Fluid Flow in Varying Thermal Fields**

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NUMERICAL SIMULATIONS OF HETEROGENEOUS CHEMICAL REACTIONS COUPLED TO FLUID FLOW IN VARYING THERMAL FIELDS

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ABSTRACT

A numerical simulator of reactive chemical transport with coupling from precipitation-dissolution reactions to fluid flow, via changes of porosity and permeability, is applied to precipitation-dissolution of quartz and calcite in spatially and temporally variable fields of temperature. Significant effects on fluid flow are found in the quartz-silicic acid system in the presence of a persistent, strong gradient of temperature. Transient heat flow in the quartz-silicic acid system and in a calcite-calcium ion-carbonato species system produces vanishingly small effects on fluid flow.

INTRODUCTION

Variable thermal fields in the near vicinity of nuclear waste canisters may induce dissolution of minerals, causing transport of dissolved chemical species and reprecipitation of the same mineral or different minerals. Redistribution of materials by heterogeneous chemical reactions and transport processes may produce changes of porosity and permeability. Changes of these properties may affect migration of both radionuclides and major solution components of subsurface fluids.

In the present work, a simulator of reactive chemical transport is used to investigate effects of varying thermal fields on selected heterogeneous chemical reactions in porous media supporting fully saturated fluid flow. A particular focus of the investigations is the possibility of thermally induced precipitation or dissolution of minerals changing porosity (and, thus, permeability) to the extent that significant effects on solute migration (including radionuclides) can be expected. The numerical investigations are restricted to chemical systems that may be relevant in thermally disturbed regions of repositories for high-level nuclear wastes and that involve thermal perturbations of existing mineral-solution equilibria. The investigations consider two types of heterogeneous chemical reactions of different complexities. The simplest type is that in which a single solution species is in equilibrium with a solid, exemplified by the quartz-silicic acid equilibrium:

Here the equilibrium concentration of silicic acid is affected only by temperature. The more complex case involves equilibria among a solid and multiple solution species whose concentrations are influenced by the pH of the groundwater; this case is exemplified by precipitation-dissolution of calcite accompanied by pH-dependent reactions involving carbonato species:

Here the equilibria are affected by temperature, pH, and activities of reacting Ca^{2+}

and carbonate species in solution. This case is a subset of reactions involving variable oxidation potential as well as pH and temperature. For the purpose of this paper, reactions of the latter type are not considered explicitly because their precipitation-dissolution behavior in response to variations of temperature is, in general, similar to that of systems typified by reactions (R-2)–(R-5).

COMPUTER PROGRAM THCVF

The THCVF computer program is a thermodynamically based simulator of multi-component, reactive chemical transport in which the equations of mass transport are fully coupled to the mass-action relations describing chemical equilibria. Effects of pressure variations on the equilibria are ignored. The chemical reactions simulated are complexation, oxidation-reduction, dissociation of water, and reversible precipitation of solid phases. The equation of heat transport is solved concurrently, if necessary. Heat transfer between solid and liquid phases is assumed to be instantaneous. The THCVF program is derived from the older THCC program [1,2] by explicitly accounting for changes of porosity caused by precipitation-dissolution of solid phases [3]. Empirical relations are used to calculate consequent changes of permeability; changes of the fluid flow field are then calculated by Darcy's law. Thus, THCVF retains THCC's couplings among solute transport, chemical reactions, and temperature and introduces a new coupling between chemical reactions and fluid flow.

Coupling between Chemical Reactions and Fluid Flow

In a system with fluid-filled porosity ϵ_f , N_p reactive solid phases, and nonsorbable 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

$$\frac{\partial}{\partial t} \left\{ \epsilon_f \left[B_i + \sum_{j=1}^{N_c} \nu_{ij} \frac{K_{cj}}{\gamma_j} \prod_{l=1}^{N_b} (\gamma_l B_l)^{\nu_{lj}} \right] + \sum_{k=1}^{N_p} \nu_{ik} P_k \right\} =$$

$$L \left[B_i + \sum_{j=1}^{N_c} \nu_{ij} \frac{K_{cj}}{\gamma_j} \prod_{l=1}^{N_b} (\gamma_l B_l)^{\nu_{lj}} \right], \quad i = 1, \dots, N_b, \quad (1)$$

where the spatial operator L is defined by

$$L\{ \} = \nabla \cdot [(\epsilon_f D_d + a q) \nabla - q] \{ \}. \quad (2)$$

Here t is time, D_d is the diffusion coefficient in the fluid phase, a is the dispersivity, and q is the volumetric (Darcy) flux of fluid. B_i , $i = 1, \dots, N_b$, is the concentration (referred to unit volume of the fluid phase) of the basis species i and ν_{ij} is the number of moles of i per mole of complex j , $j = 1, \dots, N_c$. K_{cj} is the temperature-dependent thermodynamic equilibrium constant for formation of complex j from the set of basis species, and the γ 's are activity coefficients estimated by the modified Davies equation [4]. P_k is the concentration (referred to unit volume of porous matrix) of precipitate k , $k = 1, \dots, N_p$, and the ν_{ik} 's are the number of moles of basis species i per mole of solid k .

Eq. (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 numerical solution scheme, new values of ϵ_f are calculated from current values of the P_k 's.

A conservation equation can be written for a unit volume of porous medium:

$$\epsilon_m + \epsilon_p + \epsilon_f = 1, \quad (3)$$

where ϵ_m is the volume fraction of nonreactive 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

$$\epsilon_p = \sum_{k=1}^{N_p} P_k \bar{V}_k, \quad (4)$$

where $\bar{V}_k$ is the molar volume of reactive solid k and is assumed constant. It follows from Eq. (3) that

$$\Delta\epsilon_f = -\Delta\epsilon_p. \quad (5)$$

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

The Darcy flux, q , obeys Darcy's law:

$$q = -K_f(\epsilon_f)\nabla h, \quad (6)$$

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 ; the present work uses a relation similar to the Kozeny-Carmen equation:

$$K_f = C_f \frac{\epsilon_f^3}{(1 - \epsilon_f)^2}, \quad (7)$$

where C_f is a constant [5]. THCVF accounts for variations of K_f and ∇h over the spatial domain, and computes q under the assumptions that there are no sources or sinks of fluid flow in the domain and that the total drop of hydraulic head across the domain is constant in time. It is noted that, although q is fixed at any given time level, the pore fluid velocity can vary spatially due to spatial variations of ϵ_f . Further details of the computation of q are given by [3].

EQUILIBRIUM CONSTANTS AS FUNCTIONS OF TEMPERATURE

In addition to the isothermal mode, three kinds of thermal variations can be simulated by THCC and THCVF: (1) mixing of advecting fluids having different temperatures, (2) diffusion of heat from a constant-temperature boundary, and (3) a constant gradient of temperature between two boundaries. In the first two cases, spatial and temporal variations of temperature are simulated by numerical solution of a heat-transport equation. To account for its variation with temperature, the equilibrium constant for a chemical reaction is calculated by the thermodynamic relation of Clarke and Glew [6]:

$$\log K(T) = A + \frac{B}{T} + C \log T + D T \quad (8)$$

where $K(T)$ is an equilibrium constant evaluated at absolute temperature T and the coefficients A , B , C , and D are related to the changes of standard Gibbs free energy, enthalpy, and heat capacity for the reaction. The coefficients used in the computations reported here were obtained either directly from the literature [7] or by calculating them from published values of $K(T)$'s [8] or from tabulated thermodynamic functions [9]. Table I lists values of the coefficients for Eq. (8) that were used in this work.

Table I. Coefficients for Temperature Dependence of Equilibrium Constants

Reactions	A	B	C	D
$\text{SiO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) = \text{Si}(\text{OH})_4(\text{aq})$	1.881	-1560.	0.	-2.028×10^{-2}
$\text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) = \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^-$	-29.08	-2383.	13.75	-3.051×10^{-2}
$\text{HCO}_3^- + \text{OH}^- = \text{CO}_3^{2-} + \text{H}_2\text{O}(\text{l})$	154.095	-3086.9	-60.29	3.051×10^{-2}
$\text{HCO}_3^- + \text{H}_2\text{O}(\text{l}) = \text{H}_2\text{CO}_3 + \text{OH}^-$	-40.25	-522.0	13.54	4.150×10^{-3}
$\text{H}_2\text{O}(\text{l}) = \text{H}^+ + \text{OH}^-$	-76.985	-1506.4	31.25	-3.110×10^{-2}

SIMULATIONS OF QUARTZ PRECIPITATION IN VARYING THERMAL FIELDS

The simulations of quartz precipitation consider two types of temperature variations: (1) linear gradient of temperature between two boundaries, constant in time; (2) mixing of advecting fluids with different temperatures to produce a transient temperature field. All simulations assume a is 0.1 m and D_d is 1×10^{-9} m²/s.

Constant Gradient of Temperature

The inner boundary ($x = 0$) of the spatial domain is held at 90° C and the outer boundary ($x = 1$ m) is held at 30° C. Temperature varies linearly in space between these two limits. The initial porosity of the domain is 0.05, and the fluid phase contains silicic acid in equilibrium with quartz at the appropriate temperature. Silicic acid in equilibrium with quartz at 90° C flows into the domain at $x = 0$; the initial Darcy flux is 1×10^{-5} m/s. Quartz is more soluble at 90° C than at lower temperatures, and as the influent solution progresses down the gradient of temperature, quartz precipitates. The simulations consider the case in which deposition of quartz reduces porosity, using $\bar{V}(\text{quartz})$ equal to 0.0227 dm³/mole [10], and the case in which porosity and Darcy flux are held constant ($\bar{V} = 0$).

With passage of time, significant quantities of quartz are deposited, as shown in Fig. 1 for $x = 0.497$ m. In the constant-porosity case, the quantity of precipitated quartz (which has $\bar{V} = 0$) increases without limit and eventually exceeds the theoretical volumetric capacity of the pore space, a physically unacceptable result. In the variable-porosity case, the non-zero $\bar{V}$ causes reduction of inflow of hot silicic acid solution, and the amount of deposited quartz asymptotically approaches the pore capacity. In this case, filling of pore space causes significant reductions of K_f , as shown in Fig. 2, and of Darcy flux, q , as shown in Figs. 3a and 3b.

An analytical solution for the constant-porosity case can be derived by considering that, at equilibrium with quartz, the concentration of silicic acid must be invariant in time. In Eq. (1) with $N_c = 0$, the time derivative of B (silicic acid) is zero on the LHS, while the spatial terms on the RHS can be calculated using the known dependencies of B on temperature from Eq. (8) and Table 1 and of temperature on x . This allows expression of B as an explicit function of x and integration of the time derivative of P (quartz) on the LHS. Then, noting the constancies of ϵ_f and q , it is found that,

$$P(x, t) = P_o(x) + [(\epsilon_f D_d + qa)B''(x) - qB'(x)]t, \quad (9)$$

where $P_o(x)$ is an initial value and $B'(x)$ and $B''(x)$ are respectively the first and second space derivatives of $B(x)$. Values of $P(x, t)$ for $x = 0.497$ m obtained from the analytical solution are shown in Fig. 1.

Figure 1. Deposition of quartz at 0.497 m, constant ∇T .

Figure 2. Hydraulic conductivity vs. distance, constant ∇T .

Figure 3a. Log Darcy flux vs. log time, constant ∇T .

Figure 3b. Darcy flux vs. time, constant ∇T .

Transient Temperature Field

A solution of silicic acid in equilibrium with quartz at 90°C flows into a domain of length 10 m. The spatial domain has initial porosity of 0.05, filled with silicic acid solution in equilibrium with quartz at the initially uniform temperature of 30°C . The initial Darcy flux is 1×10^{-5} m/s. The rate of progress of the 60°C isotherm is $1/6$ of the pore fluid velocity (2×10^{-4} m/s) due to transfer of heat from the fluid to the solid matrix. Examination of results shown in Fig. 4 reveals that deposition of quartz occurs only during passage of the thermal "front" and diminishes with increasing distance from the inlet. The quantities of quartz deposited are too small to affect hydraulic conductivity and fluid flow. At steady state, the largest deposition is at $x = 0$ and corresponds to a volume fraction of $\sim 3 \times 10^{-5}$; at other distances the volume fractions of precipitate are an order of magnitude smaller.

Figure 4. Quartz deposition and temperature, transient case

SIMULATIONS OF THERMAL EFFECTS ON CALCITE

The precipitation-dissolution behavior of calcite is complicated by the pH dependence of its solubility and of the distribution of solution species in equilibrium with the solid. For this reason, simulations of precipitation-dissolution of calcite under transient thermal conditions were compared to isothermal simulations. In both cases, a solution of nominally 1×10^{-3} molar CaCl_2 in equilibrium with calcite at pOH equal to 5 flows into a spatial domain of porosity ~ 0.05 occupied by an aqueous phase in equilibrium with calcite at 30°C with pOH equal to 7 (pH ~ 6.8). In the isothermal case, the influent solution has a concentration of Ca^{2+} equal to 1.07×10^{-3} molar and pH of 8.8. In the case of transient temperature, the influent solution at 90°C has a Ca^{2+} concentration of 1.19×10^{-3} molar and pH of 7.4. $\bar{V}(\text{calcite})$ is $0.0369 \text{ dm}^3/\text{mole}$ [10]. In both cases, the initial Ca^{2+} concentration in the spatial domain is 5.7×10^{-3} molar, a is 0.1 m , and D_d is $1 \times 10^{-9} \text{ m}^2/\text{s}$. Under these conditions, the influent solution is expected to dissolve calcite in the spatial domain. (In the isothermal case, dissolution of calcite arises solely from the dispersive property of the porous matrix.)

Figs. 5–8 show that the effects of variable temperature and pH are interactive. Larger quantities of calcite are dissolved in the transient case than in the isothermal case. This behavior is attributed largely to the depression of the pH caused by the temperature dependence of reaction (R-5), dissociation of water. The equilibrium constant for (R-5)

Figure 5. Calcite dissolution and temperature at 0.04 m.

Figure 6. pH and temperature at 0.04 m.

Figure 7. Calcite dissolution and temperature at 0.49 m.

Figure 8. pH and temperature at 0.49 m.

increases by a factor of ~ 25 from 30°C to 90°C , while the equilibrium constant for reaction (R-2), hydrolytic dissolution of calcite, increases by a factor of only ~ 3.5 over the same range. The effect of temperature to decrease pH is clearly visible in Fig. 8, while Figs. 5 and 6 show that lower pH levels dissolve more calcite. In both cases, the amounts of calcite dissolved are too small to affect fluid flow; they represent increases of porosity of no more than $\sim 2 \times 10^{-6}$.

CONCLUSIONS

In the simulations presented here, it is evident that changes of porosity, hydraulic conductivity, and fluid flow occurred only in the presence of a gradient of temperature. In the cases involving transient changes of temperature during advection and mixing of fluids with different initial temperatures, the gradients were not present for times sufficient to produce significant changes of porosity. Only in the case of quartz deposition in the presence of a constant, strong gradient of temperature (60°C/m) did this occur. Temperature gradients may persist for considerable times within the thermally disturbed region of a repository for high-level nuclear waste. The methods used in the THCVS simulator provide a tool for assessment of possible changes of fluid flow in this region due to thermally induced, heterogeneous chemical reactions.

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