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Author

Carnahan, C.L.

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Simulation of Chemically Reactive Solute Transport Under Conditions of Changing Temperature

C.L. Carnahan

Earth Sciences Division
Lawrence Berkeley Laboratory
Berkeley, California 94720, USA

ABSTRACT

A numerical code, THCC, has been developed for simulation of multicomponent solute transport in saturated porous media with aqueous complexation and precipitation/dissolution of stable solid phases in the presence of variable temperature. THCC evolved from the isothermal code CHEMTRN and is capable of simulating the diffusion of solutes along a steady gradient of temperature and the mixing of fluids having different initial compositions and temperatures. Example calculations demonstrate the close coupling that can exist between temperature variations and the transport of chemically reactive solutes. This coupling can be an important consideration in the assessment of performance of nuclear waste repositories.

INTRODUCTION

The coupling of heat flow with chemical reactions can affect the transport of chemically reactive solutes in saturated porous media by the influence of changing temperature on chemical reaction rates and equilibria. In the vicinity of nuclear waste canisters, strong gradients of temperature will be established quickly within packing and surrounding geologic materials, and mixing of waste-bearing fluids of differing temperatures and compositions will occur. Prediction of migration of wastes and

assessment of compliance of a waste repository with regulatory standards require the ability to account for effects of interactive coupling between chemistry, temperature, and fluid flow.

In recent years, considerable progress has been made in the development of thermodynamically based computer codes that incorporate chemical reactions, under the assumption of chemical equilibrium, into the solution of multicomponent solute transport equations. This has been accomplished either by iteration between solutions of the transport equations and solutions of usually nonlinear, algebraic equations of chemical equilibrium (the "two-step" method, e.g. Grove and Wood, 1979; Theis et al., 1983; Cederberg et al., 1985), or by simultaneous solution of both transport and chemical equations (the "direct" method, e.g. Rubin and James, 1973; Valocchi et al., 1981; Miller, 1983; Miller and Benson, 1983; Kirkner et al., 1985). These codes provide strong coupling of chemical reactions to the solute transport equations, but the coupling to fluid flow is weak due to the general assumption of a flow field invariant in space and time. The current codes provide only weak coupling to temperature in the sense that temperature can be varied from simulation to simulation, but not within a single simulation.

A computer code (named THCC) incorporating a variable temperature field in the framework of multicomponent, thermodynamically based, reactive chemical transport model has been developed. The starting point for this development was the CHEMTRN code (Miller and Benson, 1983). Here, I describe the THCC code briefly and provide results of simulations of two simple chemical transport problems under conditions of variable temperature.

DESCRIPTION OF THE CODE THCC

In the code THCC it is assumed that heats of chemical reactions do not affect the temperature field, the temperature field does not affect the (constant) fluid flow field, and effects (thermal diffusion, thermal osmosis, chemical osmosis, and ultrafiltration) arising from thermodynamic coupling between flows of heat and matter (Carnahan, 1984, 1985) are absent. These assumptions allow the calculation of heat transport to be done independently of the calculations of solute transport and chemical equilibria.

All partial differential equations of transport, written in one dimension or in radial coordinates, are converted to finite difference form. At each new time, the heat transport equation with initial and boundary conditions is solved and temperatures are assigned to each spatial node. Values of equilibrium coefficients for all chemical reactions at all nodes are calculated using these temperatures. The temperatures and coefficients are

invariant during the subsequent solution of the solute transport equations and the chemical equilibrium equations.

The solute transport equations and the chemical equilibrium equations are solved by the "direct" method in a manner generally similar to that of the CHEMTRN code (Miller and Benson, 1983), but with several differences in detail. In the THCC code, the primary unknowns, found by Newton-Raphson iteration, are concentrations of basis species and solids; concentrations of aqueous complexes are secondary unknowns and are replaced in the numerical solution by mass-action relations. Also in THCC, Jacobian matrix elements are calculated explicitly rather than by divided differences, and the parts of the elements that depend only on invariant quantities are calculated only once during each simulation; the Crank-Nicolson method is used in the finite-difference approximations of the transport equations; and a different algorithm for precipitation/dissolution of solids is used.

The present version of THCC treats formation of complexes in the aqueous phase and reversible precipitation/dissolution of solid phases, and it updates activity coefficients during the Newton-Raphson solution procedure.

Three types of transport problems involving variable temperature can be simulated by the present version of THCC. In the first type, a fluid of constant composition and temperature flows into a one-dimensional porous medium saturated by a fluid of initially different composition and temperature. In the second type, heat and solutes diffuse from a boundary held at constant temperature and composition into a porous medium saturated by an initially different fluid. In the third type, a constant gradient of temperature is imposed on the medium with a given initial composition, and solutes diffuse between boundaries having constant compositions and temperatures. The code also can be run isothermally with either constant-concentration or constant-flux boundary conditions.

EXAMPLE PROBLEMS

Two examples of simple chemical transport problems involving variable temperatures are given. Although the THCC code is capable of treating more complicated chemical systems, the examples shown here have been kept simple chemically in order to emphasize the effects of variable temperatures.

Diffusion of Silica along a Gradient of Temperature

A linear temperature gradient equal to $200^{\circ}\text{C}/\text{m}$ is imposed on a 1-m domain with temperatures of 230°C and 30°C at the inner and outer boundaries, respectively. Initially, the domain contains a total concentration of

silica equal to 0.02 mole per dm³ of fluid phase, distributed between fluid and solid phases according to the value of the solubility of amorphous silica along the temperature gradient. The solubility governed by the reaction

is calculated from (Rimstidt and Barnes, 1980):

$$\log K = 0.338 - \frac{840.1}{T} - 7.889 \times 10^{-4} T, \quad (2)$$

where T is the temperature in K. After the initial equilibration, diffusion is allowed to occur with concentrations of silicic acid at the boundaries fixed at their initial values. A constant diffusion coefficient equal to 10^{-9} m²/s is used. Figure 1 shows the initial concentration profile of amorphous silica, the concentration profile at an elapsed time of 10^9 s, and the concentration of silicic acid. Because the latter concentration must be invariant in time, diffusion of silicic acid along its own concentration gradient (created by the temperature gradient) results in an accumulation of

Figure 1. Diffusion of silica along a gradient of temperature ($\nabla T = 200$ K/m): concentration of $\text{Si}(\text{OH})_{4(aq)}^0$ and moles $\text{SiO}_{2(am)}$ per dm³ of fluid phase at times zero and 10^9 s.

amorphous silica that increases toward the cold end of the domain, where the solubility decreases. Thus, the gradient of temperature has caused a transport of amorphous silica from the hot to the cold end of the domain with no change in the concentration of silicic acid in the fluid phase. This process could lead to filling of pores and decreased permeability in the cold region. THCC has no ability to simulate such effects.

Mixing of Two Fluids Equilibrated with Uraninite

A one-dimensional porous medium with a porosity of 0.1 is saturated initially with a neutral (pOH 6.627) solution equilibrated with uraninite at 50°C. Another solution, at 150°C, also neutral (pOH 5.788) and equilibrated with uraninite, flows into the first solution at the boundary $x = 0$ with a pore fluid velocity of 10^{-3} m/s. In each fluid, the total concentration of aqueous U(IV) species plus uraninite is initially 4×10^{-11} mole per dm^3 of fluid phase. The porous medium is assumed to have a dispersivity of 0.1 m. The heat capacity of the fluid phase is 4.2×10^5 and of the solid phase is 1.1×10^6 joule/($\text{m}^3 \cdot \text{K}$), and the thermal conductivity of the saturated porous medium is 6.4×10^{-3} joule/($\text{m} \cdot \text{s} \cdot \text{K}$), all referred to unit volume or area of porous medium. In this situation it is evident that spreading of the thermal front is dominated by thermal dispersion, the contribution of thermal conductivity being relatively negligible.

Dissolution of uraninite is assumed to be controlled by the reaction

with

$$\log K = -7.25 - \frac{1590.6}{T} - 2.028 \times 10^{-3} T \quad (4)$$

(D. Langmuir, personal communication, 1985). The aqueous complex $\text{U}(\text{OH})_{5(aq)}^-$ forms by the reaction

with formation coefficient given by

$$\log K = 1.66 + \frac{2296.5}{T}, \quad (6)$$

derived from enthalpies and free energies of formation given by Langmuir (1978). Under the conditions of this simulation, concentrations of the aqueous complex $\text{U}(\text{OH})_{3(aq)}^+$ are negligible, and this complex was omitted

from consideration. The ion product of water as a function of temperature was calculated by polynomial expressions derived from data given by Marshall and Franck (1981).

Results of the simulation at elapsed times of 2000 s and 4000 s are presented in Figures 2-4. It is noted that if a nonreactive tracer, such as $\text{Na}_{(aq)}^+$, had been added to the system with the inflowing fluid, the midpoints of its breakthrough curves at these elapsed times would be located at approximately 2 m and 4 m, respectively. However, in Figure 2 it is seen that the midpoints of the pOH curves have reached only about one-fourth of these distances in the given times. This is because the concentration of $\text{OH}_{(aq)}^-$ is controlled by the ion product of water, which is a function of temperature. Movement of the thermal front through this system is retarded, relative to the pore fluid velocity, by a factor of approximately four because heat carried by the fluid phase must be expended in heating the solid phase. By comparing the temperature profiles shown in Figure 2 to the chemical profiles in Figures 2-4, it is seen that the transport of reactive chemical species in this example is closely coupled to the flow of heat.

Figure 3 shows the concentrations of $\text{U}(\text{OH})_{4(aq)}^0$, which decrease with decreasing temperature, and the formation constant of $\text{U}(\text{OH})_{5(aq)}^-$, which

Figure 2. Mixing of two fluids equilibrated with $\text{UO}_{2(c)}$: temperature and pOH at times 2000 and 4000 s.

Figure 3. Mixing of two fluids equilibrated with $\text{UO}_{2(c)}$: concentration of $\text{U(OH)}_4^0(aq)$ ($\times 10^{13}$) and formation coefficient of $\text{U(OH)}_5^-(aq)$ ($\times 10^{-7}$) at times 2000 and 4000 s.

increases rapidly with decreasing temperature. These opposing effects, combined with decreasing concentrations of $\text{OH}^-(aq)$ toward the cold boundary, result in almost constant concentrations of the dominant aqueous U(IV) species, $\text{U(OH)}_5^-(aq)$, near the hot end of the system, as shown in Figure 4. Also shown in Figure 4 are concentrations of uraninite, which is being dissolved at the hot end in order to support the $\text{U(OH)}_5^-(aq)$ concentration and is being transported downstream at a rate about equal to the rate of motion of the thermal front.

CONCLUSION

The examples given here, while simple in the chemical sense, demonstrate the possibility of strong coupling between transport of reactive chemical species and the thermal environment in which the transport takes place. Both steady-state gradients of temperature and transient flows of heat can control migration of solutes in the aqueous phase and can mobilize stable solid phases which might otherwise be considered immo-

Figure 4. Mixing of two fluids equilibrated with $\text{UO}_{2(c)}$: concentration of $\text{U}(\text{OH})_5(\text{aq})$ and moles $\text{UO}_{2(c)}$ per dm^3 of fluid phase at times 2000 and 4000 s.

bile. It seems highly desirable to account for such thermochemical coupling in the prediction and assessment of performance of repositories for nuclear waste materials.

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