LBL-26393 c2

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

EARTH SCIENCES DIVISION

RECEIVED
LAWRENCE
BERKELEY LABORATORY

MAR 1 7 1989

LIBRARY AND
DOCUMENTS SECTION

Presented at the Workshop on Modeling of Dispersion Processes in the Ground, Bro, Sweden, November 29–30, 1988, and to be published in the Proceedings

Modeling of Coupled Chemistry and Chemical Transport in Groundwater Systems

C.L. Carnahan

November 1988

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks.

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

LBL-26393 c2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-26393

Modeling of Coupled Chemistry and Chemical Transport in Groundwater Systems

C. L. Carnahan

Earth Sciences Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, California 94720

November 1988

Workshop on Modeling of Dispersion Processes in the Ground
Lejondals Slott, Bro, Sweden, November 29–30, 1988

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Engineering and Geosciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Modeling of Coupled Chemistry and Chemical Transport in Groundwater Systems

C. L. CARNAHAN

Coupling of chemical reactions with mass transport in groundwater flow systems has been accomplished, in general, by two approaches: the "one-step" and "two-step" methods. This paper focuses on experiences with the "one-step" method as it has been used in computer programs descended from, or similar to, the CHEMTRN program. The "one-step" method incorporates rigorous treatment of chemical reactions, both homogeneous and heterogeneous, directly into the solutions of equations describing mass transport of multiple chemical species. Coupling to heat transport and variation of oxidation potential have been accomplished in the THCC program. Kinetics of calcite precipitation/dissolution and fractionation of carbon isotopes have been modelled by the CHMTRNS program. Coupling among processes transporting heat, fluid, and solutes has been implemented in the TIP program; this approach allows simulation of coupled processes such as chemical osmosis and thermal osmosis. New areas of research include simulation of effects of variable porosity arising from precipitation/dissolution reactions on transport coefficients such as permeability and mass diffusivity.

In recent years, considerable progress has been made in the development of computer programs that simulate migration of multiple chemical species in groundwater together with chemical reactions among the mobile species and reactive solids. These programs, in general, treat specific chemical reactions occurring in a fluid phase whose components are subject to diffusion, advection, and possibly other mass transport processes. Chemical reactions are described quantitatively by use of thermodynamic data or kinetic rate constants or both. These programs are based rigorously on chemical thermodynamic principles and in this sense are distinguishable from solute transport programs that rely on K_d's or other empirical formulations.

In general, two approaches have been used to link chemical reactions to mass transport processes in the reactive chemical transport programs. One approach, the "two-step" method, consists of attaching an existing geochemical speciation program to an existing program that simulates solute transport. At each simulated time level, the programs are run sequentially; thus, the programs separately find "solutions", consisting of sets of solute concentrations distributed over a spatial network, first to a nonreactive solute transport problem and then to a static chemical distribution-of-species problem that may include heterogeneous reactions [e.g., *Narasimhan et al.*, 1986; *Sharland et al.*, 1987]. A variant of this method provides iteration between the two programs at the current time level until a convergence criterion has been satisfied [*Cederberg et al.*, 1985]. The other approach, the "one-step" method, consists of simultaneously solving the equations of mass

transport together with thermodynamic mass action relations and kinetic rate equations. This approach is exemplified by the work of *Walsh et al.* [1982], *Walsh et al.* [1984], and *Bryant et al.* [1986], by the CHEMTRN program [*Miller*, 1983; *Miller and Benson*, 1983], and by the REACTRAN program [*Ortoleva et al.*, 1987]. The remainder of this paper will be concerned mainly with experiences with the "one-step" method as it has been applied in the CHEMTRN program and similar computer programs.

Coupling between Solute Transport and Chemical Reactions: The CHEMTRN Program

The CHEMTRN program assumes all chemical reactions to be at equilibrium at constant temperature and oxidation potential. Chemical reactions simulated are speciation and variable pH in the aqueous phase, precipitation/dissolution of solids, cation exchange, and surface complexation. Mass transport processes simulated are advection with constant fluid velocity, hydrodynamic dispersion, and chemical diffusion in one-dimensional (linear or cylindrical) geometry. The primary unknowns in CHEMTRN are the concentrations of basis species (the minimum set of aqueous species needed to define all other species and solids in the system), complexes, sorbed species and solids.

Figure 1 illustrates the coupling among transport processes and chemical reactions in CHEMTRN. Full coupling exists between solute transport and equilibrium chemical reactions, but there is no coupling to fluid transport (because of the constant fluid velocity) and no coupling to heat transport (because of the constant temperature).

The CHEMTRN program has been applied to a large number of problems involving migration of reactive chemical species in groundwater. However, modeling capabilities beyond those of CHEMTRN are needed to treat systems with variable temperature and oxidation potential as well as systems supporting nonequilibrium chemical reactions and coupled transport processes. These capabilities have been provided by the computer programs THCC, CHMTRNS, and TIP.

Coupling of Heat Transport to Chemical Reactions: The THCC Program

The CHEMTRN program is constrained to operate under conditions of constant temperature and constant (or unspecified) oxidation potential. However, certain important applications (e.g., hydrothermal regions, geologic repositories for nuclear wastes) require consideration of effects of temperature variations on transport of reactive solutes. Also, certain important materials (e.g., the actinide elements) can exist in several oxidation states that exhibit distinctly different chemical behaviors. These considerations led to the development of the THCC program.

Couplings in the THCC program are shown in Figure 2. Relative to CHEMTRN, the only additional coupling is from heat transport to equilibrium chemical reactions. In THCC, equilibrium constants are temperature-dependent and are calculated from thermodynamic expressions. During simulations in which temperature varies with time, the equation of heat transport is solved at each new time level; this is not required in the case of fixed gradients of temperature. Effects of variable temperature on mass transport processes are ignored in THCC.

Oxidation-reduction reactions are treated by either of two methods in THCC. One method assumes that the oxidation potential of the simulated system is determined solely by chemical reactions included in the simulation. The other method assumes that the oxidation potential is controlled externally, either by poising by one or more dominant oxidation-reduction couples not included explicitly in the simulation or by an imposed electrical potential.

The primary unknowns in THCC are the concentrations of basis species and reactive solids. Concentrations of complexes and sorbed species appearing in the transport equations are replaced by mass action relations involving only the basis species. Concentrations of the secondary unknowns are calculated from basis species concentrations found as solutions to the transport equations at each time level.

Functions of the THCC program and the method of solution used have been described in detail elsewhere [*Carnahan*, 1986a, 1987a,b,c] and examples of applications have been given [*Carnahan*, 1987b, 1988a,b]. One example [*Carnahan*, 1987b] is described briefly here.

The THCC program was used to simulate transport of aqueous uranium species within a porous matrix in the presence of a constant radial temperature distribution varying from 90 °C at the inner boundary to 50 °C at a distance of 10 m. A constant flux of uranium dissolved in a source fluid enters the porous matrix in a field of flow having a pore fluid velocity of 3×10^{-8} m/s (approximately 1 m/y), with a dispersivity of 0.05 m and a diffusion coefficient of 1×10^{-11} m^2/s. The fluid present in the porous matrix has an initial composition approximating a basalt groundwater with pH equal to 10, Eh equal to -0.36 v, total carbonate equal to 9×10^{-4} M, and ionic strength equal to 0.016 M, and is saturated with respect to amorphous silica. The source fluid has a temperature of 90 °C, 9×10^{-4} M total carbonate and ionic strength of 0.016 M but no dissolved silica. The source fluid is assumed to be in equilibrium with solid uraninite [UO_2(c)] at a pH of 6 and an Eh of 0.0 v. It is assumed that oxidation potentials in the initial and influent fluids are poised by chemical reactions external to the simulation.

Figure 3 shows profiles of temperature, oxidation potential, and total dissolved uranium concentrations at a simulated time of 1×10^7 s (approximately 0.3 y). Also shown is the theoretical solubility of coffinite [$USiO_4$(c)] calculated for prevailing values of pH, Eh, and temperature. Filled symbols in the uranium concentration curve designate finite-difference nodes where precipitates of coffinite exist. The uranium species in the source fluid are predominantly $UO_2CO_3^0$ and $UO_2(CO_3)_2^{2-}$ with smaller concentrations of UO_2OH^+, UO_2^+, and $U(OH)_4^0$. At the simulated time of 1×10^7 s, coffinite (more stable here than uraninite) has precipitated at the first four nodes beyond the source, lowering dissolved uranium concentrations by a factor of more than 10^4 relative to the source concentration. Because of the decrease of oxidation potential and increase of pH, the dominant solution species of uranium in the domain of transport is $U(OH)_5^-$. An interesting feature of Figure 3 is the minimum in the concentration profile of dissolved uranium near the source. This has happened because of precipitation of coffinite in the near-source region followed by further lowering of uranium concentrations caused by upstream diffusion of reducing species and silicic acid.

Coupling of Nonequilibrium Chemical Reactions to Solute Transport: The CHMTRNS Program

Laboratory and field investigations have shown that imposing the constraint of equilibrium on chemical reactions can be a serious deficiency when modeling certain chemical systems. For example, comparison of computer simulations that assume chemical equilibrium with observed geothermal fluid compositions and associated mineral assemblages has revealed dissimilarities indicative of kinetic hindrance of certain reactions. Thus, for many problems the slowness of reaction rates necessitates the implementation in computer programs of time-dependent, nonequilibrium chemical calculations.

The CHMTRNS program began as a modification of the CHEMTRN program to simulate kinetic precipitation/dissolution of calcite in flowing groundwater [*Noorishad et al.*, 1985]. In this and later versions of CHMTRNS all existing functions of CHEMTRN were retained. Further additions to CHMTRNS consisted of capabilities to simulate kinetic precipitation/dissolution of various silica phases and irreversible dissolution of glass. Capabilities to treat variable temperature and variable oxidation potential in the manner of the THCC program were added. An especially interesting addition is the capability to simulate fractionation of ^{13}C during transport with both equilibrium and nonequilibrium reactions involving carbonate species and calcite [*Noorishad et al.*, 1986]. Figure 4 shows that the extent of coupling in CHMTRNS is identical to that in THCC, but that chemical reaction kinetics has been added.

Detailed descriptions of the functions of the CHMTRNS program, the method of solution used, and several example simulations have been given by *Noorishad et al.* [1987]. One example is described briefly here.

The CHMTRNS program was used to simulate the fractionation of ^{13}C in recharging water containing dissolved CO_2 gas as the water percolates through, and reacts with, marine carbonate rocks. The $\delta^{13}C$ values are assumed to be $-25\,‰$ in the water initially and $0\,‰$ in the rock. When this rock-water system has come to equilibrium with respect to the chemical reaction

$$CO_2(g) + H_2O + CaCO_3(c) = Ca^{2+} + 2HCO_3^-,$$

the $\delta^{13}C$ value in the aqueous solution is expected to be $-12.5\,‰$. Three scenarios were simulated: (1) batch kinetic dissolution of calcite, (2) equilibrium dissolution with transport, and (3) kinetic dissolution with transport. The batch scenario simply contacts the initial recharging water, having $P(CO_2) = 10^{-1.5}$ atm, pH = 5, and $\delta^{13}C = -25\,‰$, with calcite having $\delta^{13}C = 0\,‰$ and allows the system to proceed to equilibrium without any transport. In the two scenarios with transport the recharging water, having the same chemical characteristics as in the batch scenario, flows into a one-dimensional domain in which water with pH = 5 and zero $\delta^{13}C$ has been allowed to come into chemical equilibrium with calcite; the influent recharging water mixes with and displaces the initial water and reacts with the calcite either instantaneously (equilibrium scenario) or in finite time (kinetic scenario).

Figure 5 shows plots of $\delta^{13}C$ in the fluid phase versus time for the three scenarios; for the two scenarios with transport, results are shown at a point located 0.012 m downstream from the inlet where recharging water enters the system. In the batch kinetic and

equilibrium transport scenarios the $\delta^{13}C$ in the fluid phase has reached the equilibrium value of $-12.5\,‰$ by a time of one year. However, in the kinetic transport scenario the $\delta^{13}C$ at 0.012 m has decreased to $-18\,‰$ at this time; the rate of dissolution of calcite is evidently too slow, relative to the influx of water lighter in ^{13}C, to allow achievement of equilibrium at this place and time.

Coupling among Transport Processes: The TIP Program

Certain argillaceous materials are known to exhibit semipermeability, or permselectivity. These materials include naturally occurring clays and shales as well as clayey materials that might be used in engineering applications such as linings of waste disposal pits and as buffers around nuclear waste canisters. In the presence of gradients of temperature, pressure, and fluid composition, coupled transport processes — thermal osmosis, thermal filtration, chemical osmosis, and ultrafiltration — can occur in semipermeable materials simultaneously with the direct processes — heat conduction, advection, and chemical diffusion — described individually by Fourier's law, Darcy's law, and Fick's law.

The computer program TIP is based on the thermodynamics of irreversible processes and solves the coupled equations of heat, fluid and solute flow under conditions of spatially and temporally varying fields of temperature, pressure, and fluid composition. Accounts of the theoretical background and applications of the TIP program have been given by *Carnahan* [1984, 1985, 1986b], *Carnahan and Jacobsen* [1988], and *Jacobsen and Carnahan* [1986, 1988a]. In its original form, the TIP program did not account for chemical reactions. Capabilities to simulate equilibrium chemical reactions, using the methodology of the THCC program, were added later [*Jacobsen and Carnahan*, 1988b]. Because the chemical version of TIP retains all functions of the original version, it is a very powerful tool and extends the reactive chemical transport capabilities of the THCC program to applications involving variable fields of fluid flow. The resulting scheme of coupling among transport processes and chemical reactions is shown in Figure 6.

The TIP program has been used to simulate coupled transport processes (without chemical reactions) in a buffer of sodium bentonite surrounding a nuclear waste canister [*Jacobsen and Carnahan*, 1988a]. TIP has been used also to investigate the effects of major groundwater cations on the cation-exchanging properties of such a buffer [*Jacobsen and Carnahan*, 1988b]. The two applications are described briefly here.

A heat source emitting 10 W/m^2 occupies a cylindrical region of radius 0.15 m in a semipermeable medium extending to infinity. The initial temperature in the medium is $52\,°C$, the initial pressure is 10^7 Pa, and the medium is saturated with a fluid containing a solute with a concentration of 0.4 kg/m^3. The solute enters the medium at the inner boundary at the rate of 10^{-11} $kg/(m^2 \cdot s)$, but no fluid enters. Phenomenological coefficients for the coupled and direct transport processes in bentonite were either obtained directly or estimated from data reported in the literature [*Jacobsen and Carnahan*, 1988a]. Simulations of the evolution of this system were done for cases with no coupling, with chemical osmosis the only coupled process, with thermal osmosis the only coupled process, and with both chemical and thermal osmosis; the direct processes (heat conduction, Darcian fluid flow, and Fickian diffusion) were simulated in all cases. Some results of the simulations are shown in Figure 7, which displays radial profiles of solute concentrations and total fluxes at a simulated time of 1000 years. The profiles of solute concentrations for the cases of no

coupling, chemical osmosis only, and combined chemical and thermal osmosis are distinct near the inner boundary, but converge as radial distance increases. The cases of no coupling and thermal osmosis only coincide throughout. The profiles of total solute fluxes at and near the inner boundary coincide in all cases because of the constant-flux boundary condition imposed there. As radial distance increases, the total solute fluxes for different cases diverge with the exception of the cases of no coupling and thermal osmosis only, which coincide. In the fully coupled case, solute migrates away from the inner boundary at higher rates than in any other case even though this case shows the lowest concentrations and gradients of concentration of solute. The coincidence of profiles for the cases of no coupling and thermal osmosis only is consistent with the results of an approximate, steady state analysis by *Oliver* [1986] which showed that thermal osmotic flows arising near a spherical heat source would be canceled exactly by an opposing Darcian flow.

An annulus of sodium bentonite with inner radius of 0.315 m and outer radius of 1.85 m is equilibrated with a groundwater containing the following initial concentrations of cations (M): Na^+, 0.176; K^+, 1.15×10^{-3}; Ca^{2+}, 0.0216; Mg^{2+}, 1.07×10^{-4}. The equilibration displaces Na^+ from exchange sites on the bentonite and replaces it with varying quantities of the other cations. Cations from the original groundwater then diffuse radially into the bentonite from the outer boundary, where cationic concentrations are held constant. At the inner boundary, cationic concentrations and composition of the sorbed phase are held at the values resulting from the initial equilibration. Figure 8 shows the concentrations of cations in the fluid and sorbed phases as functions of radius at 1000 years after diffusion has started. It is seen that strong sorption of of Ca^{2+}, accompanied by significant displacement of Na^+, has occurred in the outermost 0.1 m of the annulus. Further inward, decreased concentrations of diffusing Ca^{2+} have allowed increased sorption of K^+ and Mg^{2+}.

Coupling from Chemical Reactions to Mass Transport: Effects of Variable Porosity on Permeability and Mass Diffusivity

Until recently, computer programs that couple chemical reactions to mass transport processes have not 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 permeabilities and mass diffusivities of porous or fractured materials, and these alterations can affect the subsequent movements of dissolved chemicals. Neglect of these effects not only might produce inaccurate computational results, but also might lead to physically unrealizable consequences such as the calculated volume of a precipitate exceeding available void space.

Coupling from heterogeneous chemical reactions to fluid flow has been demonstrated recently by *Ortoleva et al.* [1987] in the REACTRN program and by *Steefel and Lasaga* [1988]. The coupling scheme is shown in Figure 9. The coupling from reactions to fluid flow is accomplished by monitoring the changes of volume accompanying precipitation/dissolution of reactive solids, and changing the permeability of the medium accordingly. Thus, *Haskin et al.* [1988] used the REACTRN program to simulate permeability changes due to kinetic precipitation/dissolution of anhydrite accompanying acid stimulation of oil wells. In another application, *Steefel and Lasaga* [1988] simulated two-dimensional "fingering" caused by locally enhanced permeability during kinetic dissolution of silica cement embedded in an unreactive porous matrix.

Coupling from precipitation/dissolution reactions to diffusion in the absence of fluid flow has been accomplished by a modification of the THCC program to account for changes of effective mass diffusivity accompanying changes of porosity [*Carnahan*, 1988c]. An example calculation is described briefly here.

Silicic acid diffuses into a domain where temperature decreases with increasing distance from the inlet at $x = 0$. Initially the domain of transport has a porosity of 0.05. Quartz 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 10 shows the accumulation of quartz at this boundary at times up to 10^9 s for simulations with constant and variable porosity. In the case of constant porosity the non-physical result that the volume of precipitated quartz exceeds available void volume is obtained. On the other hand, in the case of variable porosity the accumulation of quartz increases gradually with time and the its volume never exceeds the available porosity. This is a result of decreasing flux of silicic acid caused by the reduction of the effective mass diffusivity of this reactant. Figure 11 shows the porosity at the boundary $x = 0$ as a function of time for the case of variable porosity. The porosity appears to decline exponentially in time, asymptotically approaching zero.

Concluding Remarks

The "one-step" method of coupling chemical reactions to mass transport has proven very flexible, and this has allowed considerable progress to be made toward fully coupled systems. The coupling from heterogeneous chemical reactions (precipitation/dissolution) to the fluid flow process is a topic of considerable interest currently. Its applicability to a large variety of chemically reactive fluid flow systems is limited by a general lack of data relating changes of porosity to changes of permeability. Modeling of chemical processes accompanying transport in the unsaturated zone will require coupling to equations of unsaturated fluid flow.

Acknowledgment

This work was supported by the Director of Energy Research, Office of Basic Energy Sciences, Engineering and Geosciences Division, of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

Literature Cited

Bryant, S. L., Schechter, R. S., and Lake, L. W., 1986. Interactions of precipitation/dissolution waves and ion exchange in flow through permeable media. *Am. Inst. Chem. Eng. J., 32*, 751–764.

Carnahan, C. L., 1984. Thermodynamic coupling of heat and matter flows in near-field regions of nuclear waste repositories. In McVay, G. L., ed., *Scientific Basis for Nuclear Waste Management VII, Mater. Res. Soc. Symp. Proc., vol. 26*, North-Holland, New York, pp. 1023–1030.

Carnahan, C. L., 1985. Thermodynamically coupled mass transport processes in a saturated clay. In Jantzen, C. M., Stone, J. A., and Ewing, R. C., eds., *Scientific Basis for Nuclear Waste Management VIII, Mater. Res. Soc. Symp. Proc., vol. 44*, Materials Research Society, Pittsburgh, Pa., pp. 491–498.

Carnahan, C. L., 1986a. A simulator of solute transport in saturated porous media incorporating variable temperature and oxidation potential (abstract). *Eos Trans. Am. Geophys. Union, 67*, 965.

Carnahan, C. L., 1986b. Thermal osmosis near a buried heat source. *Internat. Comm. Heat Mass Transfer, 13*, 659–664.

Carnahan, C. L., 1987a. Simulation of chemically reactive solute transport under conditions of changing temperature. In Tsang, C.-F., ed., *Coupled Processes Associated with Nuclear Waste Repositories*, Academic Press, Orlando, Fla., pp. 249–257.

Carnahan, C. L., 1987b. Simulation of uranium transport with variable temperature and oxidation potential: the computer program THCC. In Bates, J. K., and Seefeldt, W. B., eds., *Scientific Basis for Nuclear Waste Management X, Mater. Res. Soc. Symp. Proc., vol. 84*, Materials Research Society, Pittsburgh, Pa., pp. 713–721.

Carnahan, C. L., 1987c. Simulation of oxidation-reduction reactions in multicomponent solute transport (abstract). *Eos Trans. Am. Geophys. Union, 68*, 1274, 1987c.

Carnahan, C. L., 1988a. Some effects of data base variations on numerical simulations of uranium migration. *Radiochimica Acta*, in press.

Carnahan, C. L., 1988b. Simulation of effects of redox and precipitation on diffusion of uranium solution species in backfill. In Apted, M. J., and Westerman, R. E., eds., *Scientific Basis for Nuclear Waste Management XI, Mater. Res. Soc. Symp. Proc., vol. 112*, Materials Research Society, Pittsburgh, Pa., pp. 293–302.

Carnahan, C. L., 1988c. Coupling of precipitation/dissolution reactions to mass diffusion. Paper presented at Symposium on Chemical Modeling in Aqueous Systems II, 196th Annual Meeting of American Chemical Society, Division of Geochemistry, Los Angeles, Calif., 25–30 Sept. 1988; Lawrence Berkeley Laboratory Report LBL-26183.

Carnahan, C. L., and Jacobsen, J. S., 1988. Coupled Transport Processes in Semipermeable Media, Part I: Theoretical Basis. Lawrence Berkeley Laboratory Report LBL-25618.

Cederberg, G. A., Street, R. L., and Leckie, J. O., 1985. A groundwater mass transport and equilibrium chemistry model for multicomponent systems. *Water Resour. Res., 21*, 1095–1104.

Haskin, H. K., Moore, C. H., and Ortoleva, P. J., 1988. Modeling acid stimulation of the Halfway Formation, Canada, using a geochemical computer model. Paper presented at 63rd Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, Houston, Tex., 2–5 Oct. 1988.

Jacobsen, J. S., and Carnahan, C. L., 1986. Chemical osmosis and thermal osmosis near a heat source buried in a saturated, semi-permeable medium (abstract). *Eos Trans. Am. Geophys. Union, 67*, 965.

Jacobsen, J. S., and Carnahan, C. L., 1988a. Coupled Transport Processes in Semipermeable Media, Part II: Numerical Method and Results. Lawrence Berkeley Laboratory Report LBL-25619.

Jacobsen, J. S., and Carnahan, C. L., 1988b. Numerical simulation of alteration of sodium bentonite by diffusion of groundwater components. In Apted, M. J., and Westerman,

R. E., eds., *Scientific Basis for Nuclear Waste Management XI, Mater. Res. Soc. Symp. Proc., vol. 112*, Materials Research Society, Pittsburgh, Pa.

Miller, C. W., 1983. Toward a comprehensive model of chemical transport in porous media. In Brookins, D. G., ed., *Scientific Basis for Nuclear Waste Management VI, Mater. Res. Soc. Symp. Proc., vol. 15*, North-Holland, New York, pp. 481–488.

Miller, C. W., and Benson, L. V., 1983. Simulation of solute transport in a chemically reactive hetereogeneous system. *Water Resour. Res., 19*, 381–391.

Narasimhan, T. N., White, A. F., and Tokunaga, T., 1986. Groundwater contamination from an inactive uranium mill tailings pile, 2. application of a dynamic mixing model. *Water Resour. Res., 22*, 1820–1834.

Noorishad, J., Carnahan, C. L., and Benson, L. V., 1985. Development of a kinetic-equilibrium chemical transport code (abstract). *Eos Trans. Am. Geophys. Union, 66*, 274.

Noorishad, J., Carnahan, C. L., and Benson, L. V., 1986. Simulation of fractionation of ^{13}C during nonequilibrium reactive solute transport in geologic systems (abstract). *Eos Trans. Am. Geophys. Union, 67*, 939.

Noorishad, J., Carnahan, C. L., and Benson, L. V., 1987. Development of the Non-equilibrium Reactive Chemical Transport Code CHMTRNS. Lawrence Berkeley Laboratory Report LBL-22361.

Oliver, D. L. R., 1986. Effects of thermal osmosis near a buried isolated heat source. *Internat. Comm. Heat Mass Transfer, 13*, 295–304.

Ortoleva, P., Merino, E., Moore, C., and Chadam, J., 1987. Geochemical self-organization I: reaction-transport feedbacks and modeling approach. *Am. J. Sci., 287*, 979–1007.

Sharland, S. M., Tasker, P. W., and Tweed, C. J., 1987. The coupling of chemical and transport processes in near-field modelling. In Bates, J. K., and Seefeldt, W. B., eds., *Scientific Basis for Nuclear Waste Management X, Mater. Res. Soc. Symp. Proc., vol. 84*, Materials Research Society, Pittsburgh, Pa., pp. 683–694.

Steefel, C. I., and Lasaga, A. C., 1988. The space-time evolution of dissolution patterns: permeability change due to coupled flow and reaction. Paper presented at Symposium on Chemical Modeling in Aqueous Systems II, 196th Annual Meeting of American Chemical Society, Division of Geochemistry, Los Angeles, Calif., 25–30 Sept. 1988.

Walsh, M. P., Bryant, S. L., Schechter, R. S., and Lake, L. W., 1984. Precipitation and dissolution of solids attending flow through porous media. *Am. Inst. Chem. Eng. J., 30*, 317–328.

Walsh, M. P., Lake, L. W., and Schechter, R. S., 1982. A description of chemical precipitation mechanisms and their role in formation damage during stimulation by hydrofluoric acid. *J. Petrol. Tech., Sept. 1982*, 2097–2112.

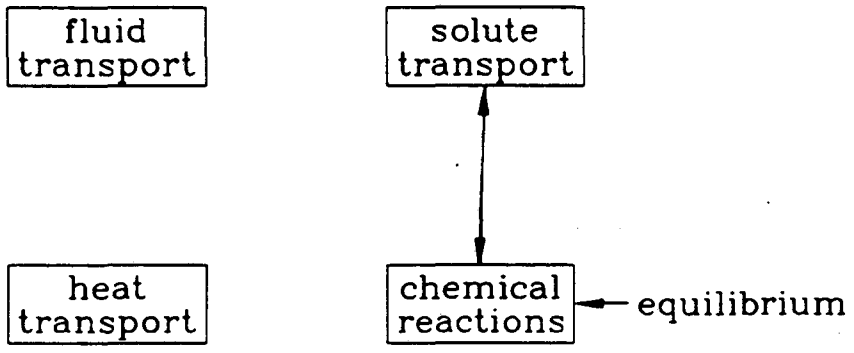

Figure 1. Coupling of processes in the CHEMTRN program.

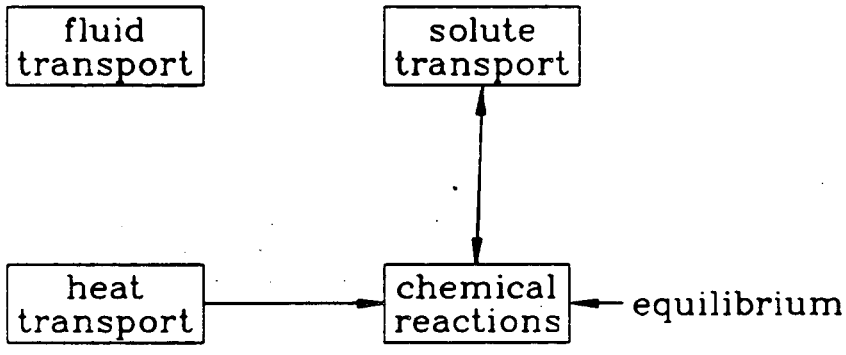

Figure 2. Coupling of processes in the THCC program.

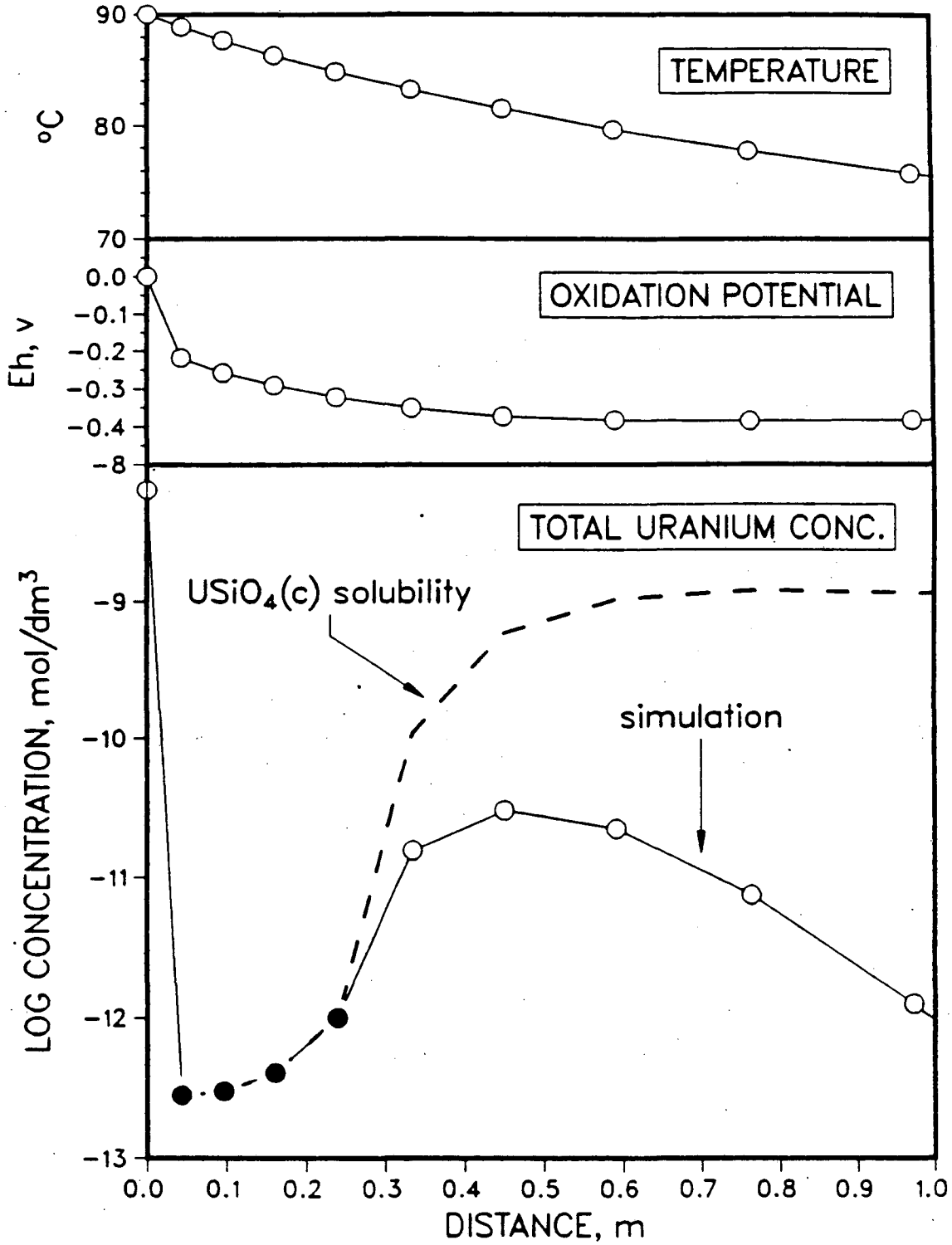

Figure 3. Temperature, oxidation potential, and logarithm of total uranium concentration vs. distance at a simulated time of 1×10^7 s computed by THCC. Filled circles denote presence of coffinite. Theoretical solubility of coffinite shown as dashed line.

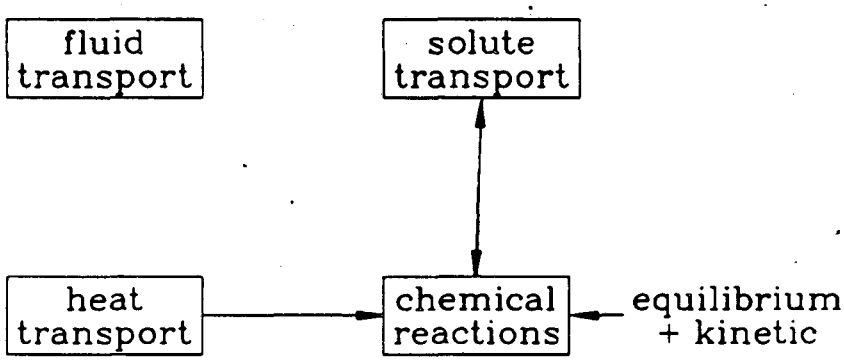

Figure 4. Coupling of processes in the CHMTRNS program.

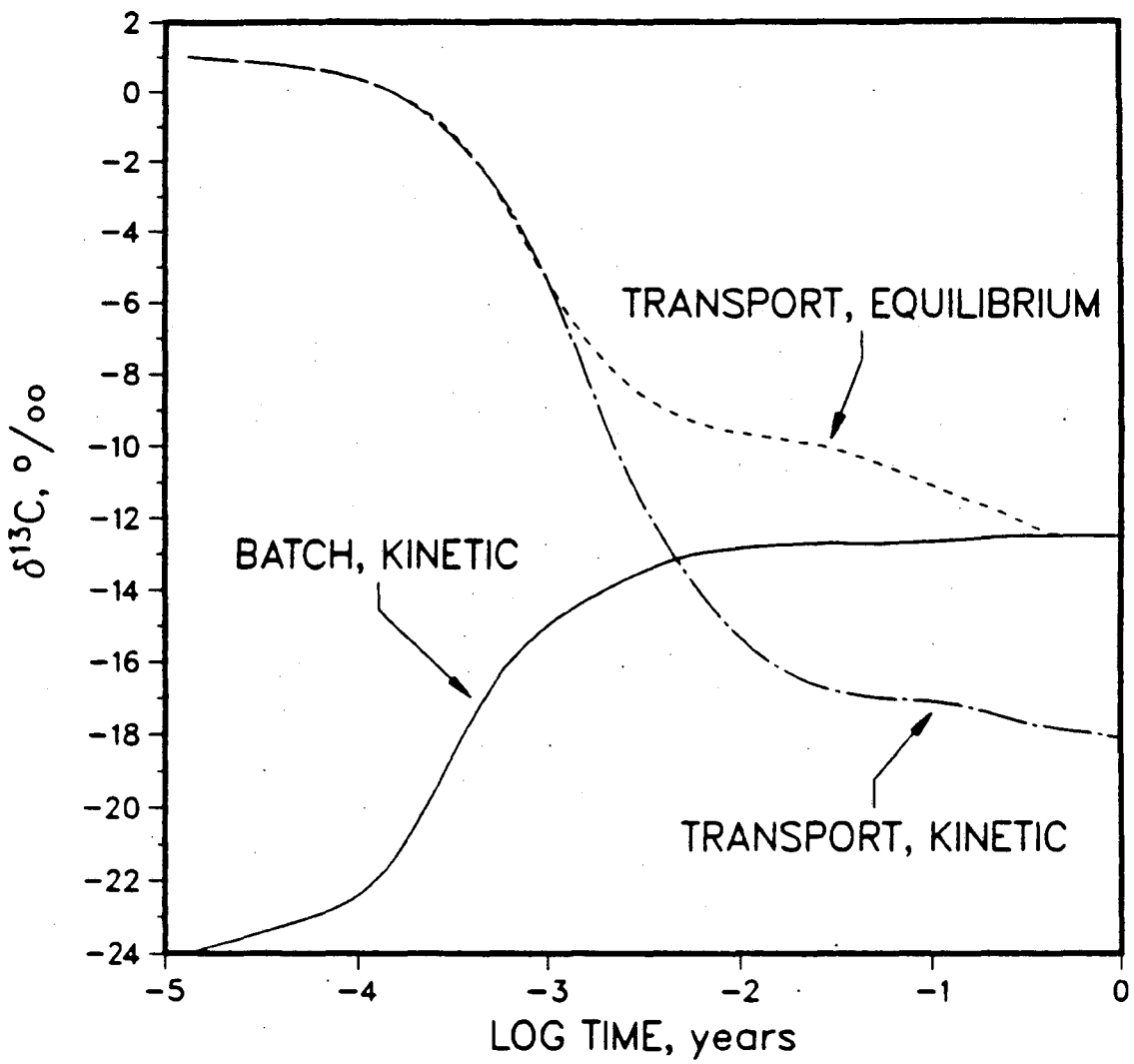

Figure 5. $\delta^{13}C$ vs. logarithm of simulated time at distance 0.012 m from inlet for three scenarios computed by CHMTRNS.

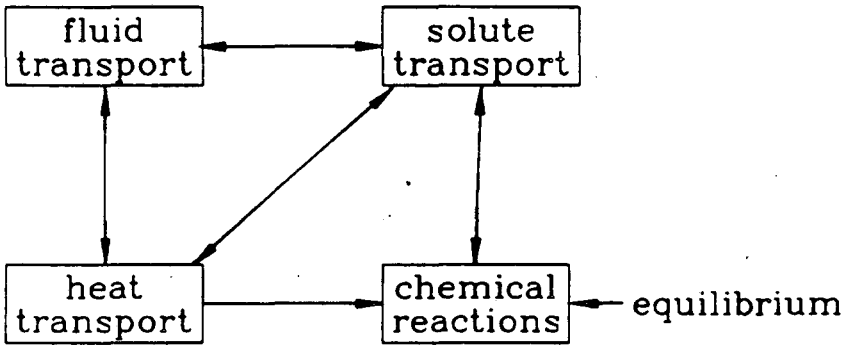

Figure 6. Coupling of processes in the TIP program.

Solute concentration and total solute flux at 1000 years: initial solute concentration = 0.4 kg/m^3, incoming solute flux = 10^{-11} kg/m^{2}s.

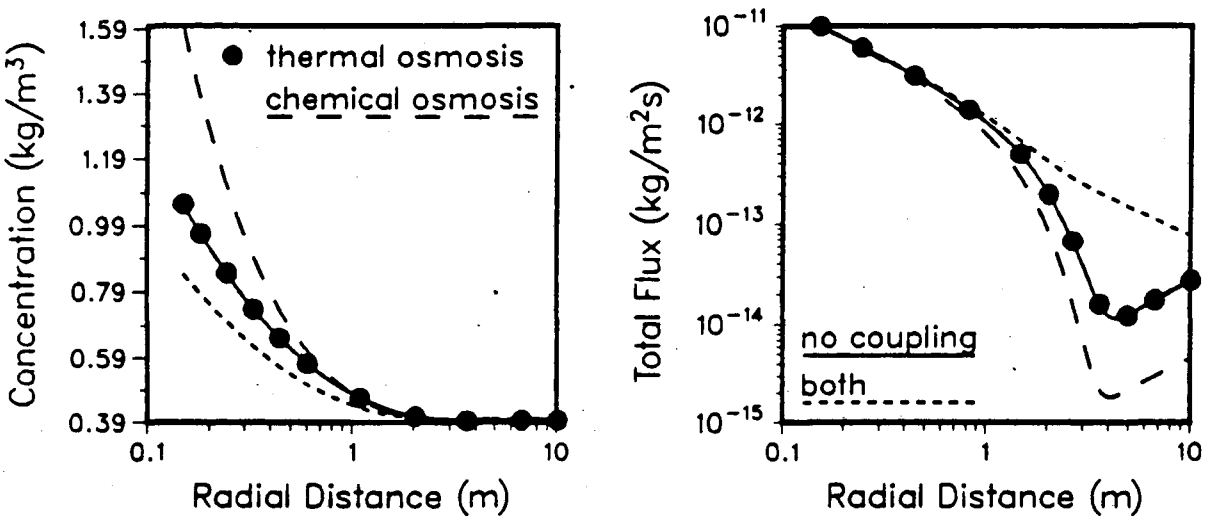

Figure 7. Solute concentration (left) and logarithm of solute flux (right) vs. logarithm of radial distance at simulated time of 1000 y computed by TIP. Legends apply to both plots.

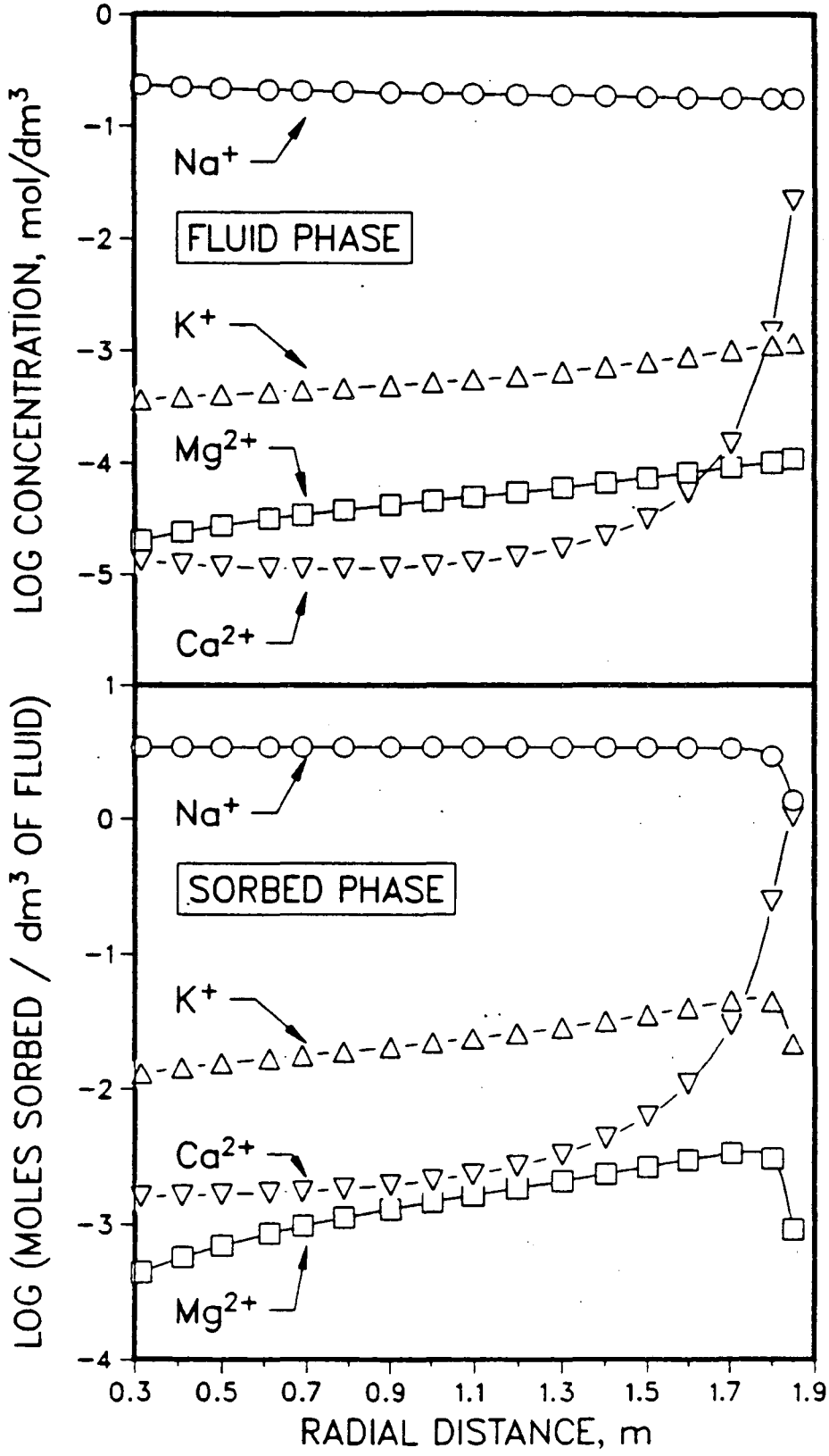

Figure 8. Logarithms of concentrations of cations in fluid phase (above) and in sorbed phase (below) vs. radial distance at simulated time of 1000 y computed by TIP.

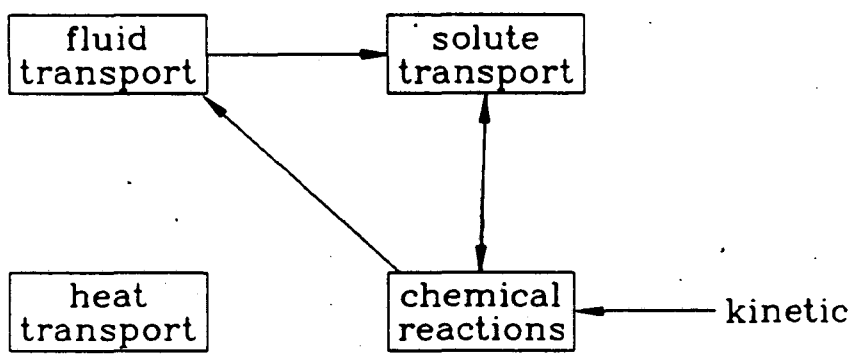

Figure 9. Coupling of processes in the models of *Ortoleva et al.* [1987] and *Steefel and Lasaga* [1988].

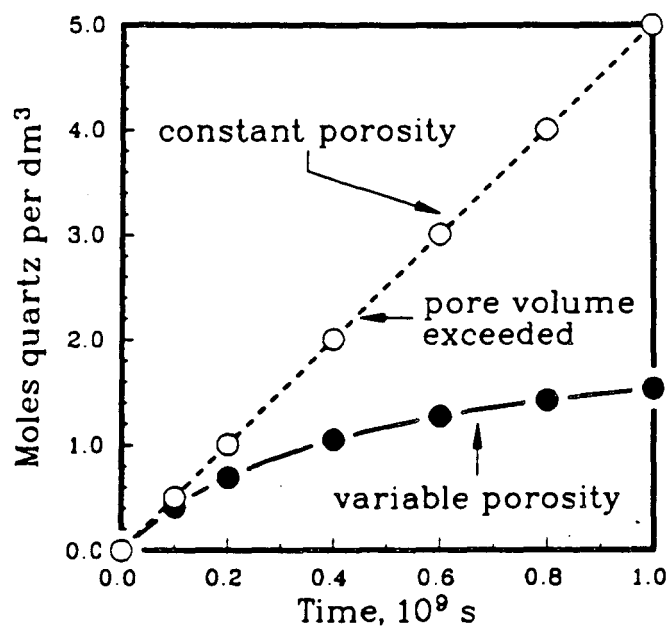

Figure 10. Precipitation of quartz at $x = 0$ vs. time for cases of constant and variable porosity computed by THCC. Transport is by diffusion only.

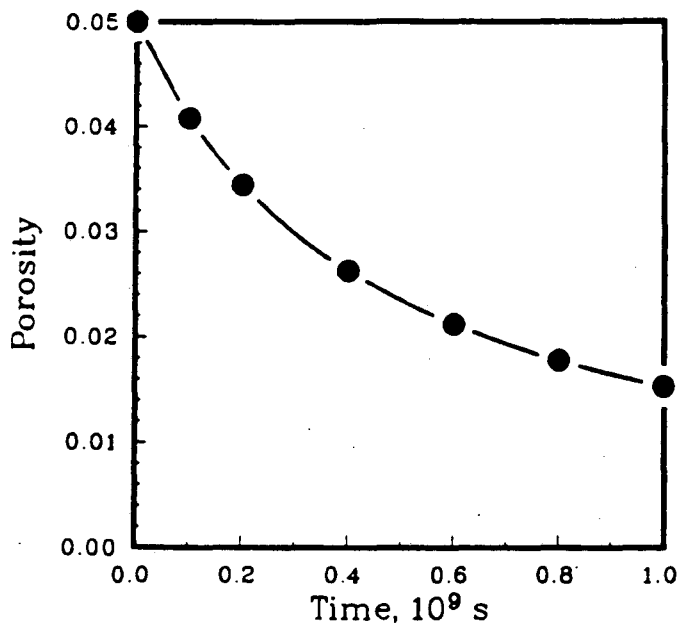

Figure 11. Porosity at $x = 0$ vs. time for case of variable porosity computed by THCC.

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720