

Lawrence Berkeley National Laboratory

Recent Work

Title

Modeling of Coupled Geochemical and Transport Processes: An Overview

Permalink

<https://escholarship.org/uc/item/38r1p965>

Author

Carnahan, C.L.

Publication Date

1989-10-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

EARTH SCIENCES DIVISION

Presented at the International Symposium on the Safety Assessment of Radioactive Waste Repositories, Paris, France, October 9-13, 1989, and to be published in the Proceedings

Modeling of Coupled Geochemical and Transport Processes: An Overview

C.L. Carnahan

October 1989



1 LOAN COPY 1
1 CIRCULATES 1
1 FOR 2 WEEKS 1

Bldg. 50 Library.

LBL-28048

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.

**Modeling of Coupled Geochemical
and Transport Processes: An Overview**

C. L. Carnahan

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

October 1989

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 GEOCHEMICAL AND TRANSPORT PROCESSES:
AN OVERVIEW

C. L. Carnahan
Lawrence Berkeley Laboratory, University of California
Berkeley, California (U.S.A.)

ABSTRACT

Although the physical and mathematical concepts associated with fluid flow and solute transport are well understood, many early coupled models have been limited by assumed conditions of constant temperature, fully saturated fluid flow, and constant pore fluid velocity. More recent developments have included coupling of chemical reactions to variable fields of temperature and fluid flow. These and other imminent developments have generated new requirements for experimental data. As the capabilities of coupled models expand, needs are created for experimental data to be used for both input and validation. It is increasingly important that close cooperation be established between researchers developing the coupled models and numerical simulators on the one hand, and those performing critical experiments on the other hand.

INTRODUCTION

Safety assessments of radioactive waste repositories require the ability to account for the effects of interactions among transport processes and chemical reactions on the migration of radionuclides. Interactions among fields of hydrological potentials, electrochemical potentials, and temperature are expected within radioactive waste repositories, particularly within near-field regions. Here, processes of fluid flow, mass diffusion, and heat flow can influence the homogeneous and heterogeneous chemical reactions that accompany migration of reactive solutes. Coupling, in the sense of the thermodynamics of irreversible processes, can occur among transport processes in low-permeability, permselective media such as bentonite. Such coupling can produce new transport processes that are driven by seemingly unrelated potential gradients (*e.g.*, chemical osmosis, thermal osmosis, ultrafiltration). Finally, variable fields of temperature and composition, the last arising from mass transport and chemical reactions, can cause changes in material properties (*e.g.*, porosity, diffusivity, permeability) that in turn can influence the transport processes.

Modeling of coupled chemical and transport processes can provide predictions of the effects of chemical reactions on the migration rates of radionuclides as well as on major chemical components of ground water. The predictions allow estimations to be made of the travel times and concentrations of radionuclides along critical pathways in the near field and the geosphere to the accessible environment. These estimations are important ingredients in the assessment of biological risk associated with possible disposal options. Necessary prerequisites to the predictions and estimations are site and laboratory investigations of material properties, transport coefficients, chemical properties, and reaction mechanisms. These investigations are best accomplished with guidance from and interaction with the modeling process.

Conceptual and mathematical models that account for various extents of coupling among transport processes and chemical reactions have been formulated and implemented in numerical simulators. These models describe chemical reactions quantitatively by use of thermodynamic data or kinetic data or both. The models are based on fundamental chemical and thermodynamic principles and in this sense are distinguishable from solute transport models that rely on empirical formulations (*e.g.*, K_d 's) for simulation of effects of chemical reactions (*e.g.*, sorption). The present paper will provide an overview of the chemically and thermodynamically rigorous models. For more detailed accounts of the conceptual and numerical bases of these models, the interested reader is referred to several excellent reviews that are available in the recent literature (*e.g.*, [1-3]). Couplings between transport processes, the subject matter of the thermodynamics of irreversible processes, are not discussed here; reviews of this subject are also available (*e.g.*, [4,5]).

FUNDAMENTAL CONCEPTS

This section sets forth, in a general way, the conceptual and mathematical bases of coupled reactive transport modeling. In general, three fundamental problems must be solved: motion of the bulk fluid phase, motion of dissolved components of the fluid phase, and chemical reactions among the components of the flow system, including homogeneous reactions within the fluid phase and heterogeneous reactions involving the solid matrix bounding the fluid phase. If a variable field of temperature is present, an additional problem, the motion of heat, must be solved, and variations of temperature must be accounted for explicitly in descriptions of chemical reactions.

Fluid Flow Field

With a few exceptions noted below, coupled reactive transport models currently do not attempt to solve the problem of bulk fluid flow. Instead, they commonly assume that the fluid flow field for the problem at hand has been adequately defined by site investigations and associated hydrological modeling. In fact, the majority of models assume a steady field of fluid flow. (Hydrological modeling is the subject of considerable separate research, and is not directly addressed here.)

Solute Migration

Motions of dissolved components of the fluid phase are caused by advection, mechanical dispersion, and chemical diffusion. To describe these processes mathematically, we consider a unit volume of porous or fractured, fully saturated medium having fluid-filled porosity ϵ_f , and containing N_p reactive solid phases, fluid-phase species consisting of N_b basis species and N_c complexes, and sorbed species consisting of \bar{N}_b basis species and \bar{N}_c complexes, where \bar{N}_b and \bar{N}_c are subsets of N_b and N_c . The set of basis species is the minimum set of chemical species needed to define all chemical species in the system being simulated, including all other aqueous-phase species, all sorbed-phase species, and all solids in reversible equilibrium with aqueous-phase species. Processes of mass transport in the fluid phase and mass transfer between fluid and solid phases by heterogeneous chemical reactions can be described mathematically by a set of partial differential equations expressing conservation of mass in the unit volume (the "transport equations").

The conservation equation for the mass of a component i in the unit volume can be written operationally:

$$\begin{aligned} \left(\frac{\partial}{\partial t} + \lambda_i \right) \left[\epsilon_f \left(B_i + \sum_{j=1}^{N_c} \nu_{ij} C_j + \bar{B}_i + \sum_{j=1}^{\bar{N}_c} \nu_{ij} \bar{C}_j \right) + \sum_{k=1}^{N_p} \nu_{ik} P_k \right] \\ = \left[\nabla \cdot (\epsilon_f D \nabla) - q \cdot \nabla \right] \left(B_i + \sum_{j=1}^{N_c} \nu_{ij} C_j \right), \quad i = 1, \dots, N_b. \end{aligned} \quad (1)$$

Here t is time, D is the effective dispersion/diffusion coefficient, and λ_i is the radioactive decay constant of component i . q is the local volumetric (Darcy) flux of fluid and is related to the local pore fluid velocity, v , by $q = \epsilon_f v$. B_i , $i = 1, \dots, N_b$, is the concentration of the basis species B_i containing component i , C_j , $j = 1, \dots, N_c$, is the fluid-phase concentration of complex C_j , \bar{B}_i , $j = 1, \dots, \bar{N}_b$, is the sorbed-phase concentration of B_i , \bar{C}_j , $j = 1, \dots, \bar{N}_c$, is the sorbed-phase concentration of C_j , and ν_{ij} is the number of moles of B_i per mole of C_j . Concentrations B_i , C_j , \bar{B}_i , and \bar{C}_j are referred to unit volume of the fluid phase. 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 .

There are N_b transport equations, one for each basis species. The transport equations may contain up to $N_b + N_c + \bar{N}_b + \bar{N}_c + N_p$ unknown concentrations:

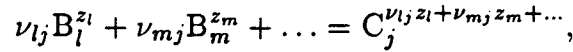
$$\begin{aligned} B_i, i = 1, \dots, N_b; & \quad C_j, j = 1, \dots, N_c; \\ \bar{B}_i, i = 1, \dots, \bar{N}_b; & \quad \bar{C}_j, j = 1, \dots, \bar{N}_c; \\ P_k, k = 1, \dots, N_p. & \end{aligned}$$

To solve the mathematical system, up to $N_c + \bar{N}_b + \bar{N}_c + N_p$ additional relations among the unknowns may be needed.

Chemical Relations

The additional mathematical relations needed are furnished by algebraic mass-action relations for chemical reactions at equilibrium or by ordinary differential equations expressing rates of formation of species involved in nonequilibrium reactions. Chemical reactions usually simulated are speciation and variable pH in the aqueous phase, precipitation-dissolution of solids, and sorption. For the sake of generality, the following development will focus on chemical reactions assumed to be in a state of local equilibrium, an assumption embodied in many coupled reactive chemical transport models. Specific kinetic formulations have been used also by replacing a mass-action relation with an appropriate differential rate equation; however, this can be done only in specific cases for which the reaction mechanisms and rate constants have been well characterized experimentally.

An aqueous-phase complex, C_j , is formed by reactions among basis species, thus:



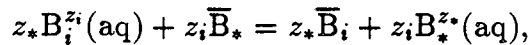
where the z_i are signed ionic charges of the basis species. The concentration of complex C_j is given by the mass action relation,

$$C_j = \frac{K_{cj}}{\gamma_j} \prod_{l=1}^{N_b} (\gamma_l B_l)^{\nu_{lj}}, \quad j = 1, \dots, N_c, \quad (2)$$

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

Sorption of aqueous-phase species at solid surfaces has been described by several mechanisms of which those used most prominently in coupled models are ion exchange and surface complexation [e.g., 6,7]. Here, we consider the mass-action and other relations appropriate to ion-exchange processes. Corresponding relations for surface-complexation processes have been developed along similar lines [8].

There are $\bar{N}_b + \bar{N}_c - 1$ mass action relations for sorption by cation exchange of basis species and complexes. One basis species is flagged and all ion exchange reactions are referred to the flagged species, B_* . Then, for exchange of basis species according to the chemical reactions

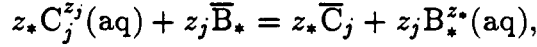


the mass action relations are

$$K_*^i = \frac{(\bar{B}_i / \bar{m}_T)^{z_*} (\gamma_* B_*)^{z_i}}{(\bar{B}_* / \bar{m}_T)^{z_i} (\gamma_i B_i)^{z_*}}, \quad i = 1, \dots, \bar{N}_b - 1, \quad (3)$$

where K_*^i is the temperature-dependent equilibrium constant for the reaction in which basis

species B_i in the aqueous phase replaces basis species B_* in the sorbed phase. Similarly, for exchange involving positively charged complexes according to the chemical reactions



the mass action relations are

$$K_*^j = \frac{(\bar{C}_j / \bar{m}_T)^{z_*} (\gamma_* B_*)^{z_j}}{(\bar{B}_* / \bar{m}_T)^{z_j} (\gamma_j C_j)^{z_*}}, \quad j = 1, \dots, \bar{N}_c, \quad (4)$$

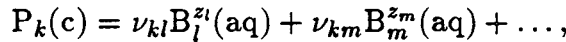
where K_*^j is the temperature-dependent equilibrium constant for the reaction in which complex C_j in the aqueous phase replaces basis species B_* in the sorbed phase. Activities of sorbed species are approximated here by their mole fractions in the sorbed phase (the ideal solution approximation). The quantity \bar{m}_T in (3) and (4) is the total sorbed-phase concentration defined by

$$\bar{m}_T = \sum_{i=1}^{\bar{N}_b} \bar{B}_i + \sum_{j=1}^{\bar{N}_c} \bar{C}_j. \quad (5)$$

The required relations for ion exchange are completed by an equation expressing constancy of the concentration of singly valent sorptive sites:

$$S = \sum_{i=1}^{\bar{N}_b} z_i \bar{B}_i + \sum_{j=1}^{\bar{N}_c} z_j \bar{C}_j. \quad (6)$$

Finally, there are N_p mass action relations for reversible precipitation of solid phases. If a solid phase is in equilibrium with basis species in the aqueous phase according to the chemical reaction,



then the corresponding mass action relation is the solubility product,

$$K_{pk} = \prod_{l=1}^{\bar{N}_b} (\gamma_l B_l)^{\nu_{kl}}, \quad (7)$$

where K_{pk} is the temperature-dependent equilibrium constant for reversible precipitation-dissolution of mineral P_k .

APPROACHES TO COUPLING SOLUTE MIGRATION WITH CHEMICAL REACTIONS

The two principal approaches to coupling chemical reactions to mass transport processes are discussed here.

Linked-Module Method

This approach, also called the "two-step" method, consists of linking a geochemical speciation program module to a separate program module that simulates conservative solute transport. At each simulated time level, the modules are run sequentially; thus, the modules separately find solutions, consisting of sets of solute concentrations distributed over a spatial network, first to a conservative solute transport problem [similar to that posed by equation (1) without the terms involving P_k] and then to a static chemical distribution-of-species problem that may include heterogeneous reactions [as posed by equations (2)–(7)]. The process is repeated at each succeeding time level. An example of use of this method is the CHEQMATE code [9], which includes an electromigration term in the transport equation. Another example is the DYNAMIX code [10], in which the mass-transport module simulates fluid flow as well as solute migration. A variant of this method is the TRANQL code [11], which provides iteration between the two modules at the current time level until a convergence criterion has been satisfied by the solute concentrations calculated in each module.

Direct Solution Method

This approach, also called 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 Bryant, Lake, Schechter, and Walsh [12–14] (henceforth referred to as BLSW), by the CHEMTRN program [6,7], and by the THCC [15,16] and CHMTRNS [17] programs, both descended from the CHEMTRN program.

Both the BLSW work and the CHEMTRN program assume all chemical reactions to be at equilibrium at constant temperature. The primary unknowns are the concentrations of basis species, complexes, sorbed species and solids. Thus, these programs solve a system of partial differential and nonlinear algebraic equations. In the case of the CHEMTRN program and assuming ion exchange is the sorption process, the total number of primary unknowns is $N_b + N_c + \bar{N}_b + \bar{N}_c + N_p$. The system is solved by the Newton-Raphson method.

In the THCC program the number of primary unknowns is $N_b + N_p$; the unknowns are the concentrations of basis species and solid phases at each node:

$$B_i, i = 1, \dots, N_b; P_k, k = 1, \dots, N_p.$$

The equation set to be solved consists of N_b transport equations and, within the Newton-Raphson scheme, an additional N_p residue equations. After the Newton-Raphson procedure has converged on a solution for the primary unknowns, values of the secondary unknowns $C_j, j = 1, \dots, N_c$, and $\bar{B}_i, i = 1, \dots, \bar{N}_b$, are calculated. (The THCC program does not include ion exchange by complexes.) Reducing the number of primary unknowns and thus the size of the linear system associated with the Newton-Raphson solution in the THCC program decreases the amount of computer memory required to solve the linear system during each iteration, relative to the memory required by the CHEMTRN program for the identical problem.

Verification and Benchmarking

Because the chemical mass-action relations are nonlinear, it is not possible to derive analytical solutions to the transport equations [*e.g.*, equation (1)] when they are coupled to chemical reactions. Thus, verification of computer programs simulating coupled reactive chemical migration is possible only by inter-program comparisons.

Results of calculations by the chemical speciation and solute migration parts of the CHEMTRN program were compared separately to results obtained from two uncoupled programs (PHREEQE for speciation, GEO1 for conservative migration) [18]. The comparisons showed excellent agreement.

The degradation of cement in a one-dimensional section in contact with water at one boundary was simulated by the CHEQMATE program and the results were compared to those obtained by a version of the THCC program using the same chemical reaction scheme [19]. The two sets of results showed very good agreement and provided a useful comparison between coupled programs using the direct coupling (THCC) and the linked modular (CHEQMATE) methods.

Further coupled-program comparison studies currently are being undertaken by the international CHEMVAL project [20].

INCORPORATION OF OTHER COUPLING

Specific problems may require consideration of the coupling of additional processes with chemical reactions. These processes include heat transport, isotopic exchange accompanying nonequilibrium reactions, and fluid flow.

Coupling of Heat Transport with Chemical Reactions

Modeling of chemical processes affecting solute migration in near-field regions of repositories for nuclear wastes requires consideration of effects of temperature variations on migration of reactive solutes. For the purpose of simulating migration of reactive solutes, the principal effect of a variable temperature field will be the attendant changes in rates and equilibrium states of chemical reactions. These considerations led to the development of the THCC program [16,17], which accounts for the effects of temperature variations on chemical equilibria coupled to solute migration. In the THCC program, 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. The program also can simulate a system with a steady-state gradient of temperature. Effects of variable temperature on fluid flow are ignored.

Nonequilibrium, Heterogeneous Reactions with Isotopic Exchange

Laboratory and field investigations have shown that imposing the constraint of equilibrium on chemical reactions can be a serious deficiency when modeling certain geochemical 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. Often, additional useful data on geochemical systems is available from comparative isotopic analyses

of fluids and rocks along paths of fluid flow, and the ability to include isotopic exchange reactions in simulations of such systems is desirable. This ability could be useful in the interpretation of geochemical observations during characterization of a potential site for disposal of nuclear wastes.

The CHMTRNS program began as a modification of the CHEMTRN program to simulate kinetic precipitation-dissolution of calcite in flowing groundwater. Later additions to CHMTRNS consisted of capabilities to simulate kinetic precipitation-dissolution of various silica phases, irreversible kinetic dissolution of glass, and the capability to treat variable temperature in the manner of the THCC program. An especially interesting feature is the capability to simulate fractionation of ^{13}C during transport with both equilibrium and nonequilibrium reactions involving carbonate species and calcite [18]. A mathematical quantity related to the isotopic shift, $\delta^{13}\text{C}$, in solution is defined and is treated numerically as though it were another basis species. The possibility exists of extending this capability to include other naturally occurring isotopes used as ground-water "tracers".

Coupling of Chemical Reactions with Fluid Flow

Until recently, computer programs that couple chemical reactions to solute migration 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 in the REACTRN program [21,22]. 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 porous medium according to empirical prescriptions such as the Kozeny-Carmen equation. The REACTRN program has been used to simulate permeability changes due to kinetic precipitation-dissolution of anhydrite accompanying acid stimulation of oil wells [23]. Another program has been developed to simulate two-dimensional "fingering" caused by locally enhanced permeability during kinetic dissolution of silica cement embedded in an unreactive porous matrix [24]. Finally, coupling from precipitation-dissolution reactions to diffusion in the absence of advective fluid flow has been accomplished by a modification of the THCC program to account for changes of effective mass diffusivity accompanying changes of porosity [25].

UNCERTAINTIES: IMPLICATIONS FOR FUTURE RESEARCH

Upon reviewing the present status and capabilities of existing numerical simulators of coupled reactive solute migration, it is clear that opportunities for further development exist in several areas. Perhaps the most prominent of these areas include the provision of coupling to variable fields of fluid flow, consideration of migration processes in the unsaturated zone, and the ability to account for subsurface heterogeneities. In principle, these and other developmental needs can be satisfied, to a large extent, by straightforward extensions of existing methods. For example, an existing simulator of unsaturated fluid flow might be linked to a program such as CHEQMATE or THCC. However, application of

both existing and extended coupled programs to large-scale simulations involving heterogeneous media, as well as the authentication of their computations, will depend strongly on the existence of adequate experimental data from the field and laboratory.

Although the physical and mathematical concepts associated with fluid flow and solute migration in homogeneous media are well understood, our ability to describe and simulate large-scale heterogeneities in the subsurface are very limited. Thus, given a reasonably complete chemical reaction scheme, we can apply coupled reactive chemical migration models to relatively small homogeneous regions of a repository with a high level of confidence. (The simulations of cement degradation mentioned earlier are examples of this level of application.) However, we approach the problem of simulation of larger regions containing significant heterogeneities in material properties and chemical compositions with considerably less confidence. In such cases, uncertainties arise equally from the abilities of coupled models to simulate strongly heterogeneous regions and from the present means to obtain field data sufficient for the characterization of such regions.

The extension of computer programs to incorporate increasingly complex processes and couplings creates needs for two types of field and experimental data. First, fundamental data on the hydrological, geological, and geochemical properties of the region to be simulated, on thermodynamic properties of chemical components of fluids and minerals, on mechanisms and rates of chemical reactions, and on properties of materials (*e.g.*, transport coefficients, porosity-permeability relations, relative permeabilities as functions of phase compositions) are needed in order to perform realistic calculations. Second, the calculations having been done, independent data describing the behavior of real systems are needed to validate the calculations. At present, it seems fair to say that the area of greatest uncertainty in coupled transport modeling is the lack of data adequate to perform realistic calculations that can be validated by comparison with field and laboratory experiments. In this regard, coupled models can play an important role in designing field and laboratory experiments by identifying critical material properties and chemical reactions that should be investigated. High priority should be given to future research involving close cooperation and interaction between modelers and experimenters.

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.

REFERENCES

1. Rubin, J. : "Transport of Reacting Solutes in Porous Media: Relation Between Mathematical Nature of Problem Formulation and Chemical Nature of Reactions", *Water Resour. Res.*, 19 (1983), 1231-1252.
2. Willis, C., and Rubin, J. : "Transport of Reacting Solutes Subject to a Moving Dissolution Boundary: Numerical Methods and Solutions", *Water Resour. Res.*, 23 (1987), 1561-1574.
3. Yeh, G. T., and Tripathi, V. S. : "A Critical Evaluation of Recent Developments in Hydrogeochemical Transport Models of Reactive Multichemical Components", *Water Resour. Res.*, 25 (1989), 93-108.

4. Carnahan, C. L., and Jacobsen, J. S. : "Coupled Transport Processes in Semipermeable Media, Part I: Theoretical Basis", Lawrence Berkeley Laboratory Report LBL-25618 (1988).
5. Miller, D. G. : "The Onsager Relations; Experimental Evidence", in Delgado Domingos, J. J., Nina, M. N. R., and Whitelaw, J. H., eds. : Foundations of Continuum Mechanics, MacMillan Press, London (1974), 185-214.
6. Miller, C. W. : "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., 15, North-Holland, New York (1983), 481-488.
7. Miller, C. W., and Benson, L. V. : "Simulation of Solute Transport in a Chemically Reactive Heterogeneous System", Water Resour. Res., 19 (1983), 381-391.
8. Kent, D. B., Tripathi, V. S., Ball, N. B., Leckie, J. O., and Siegel, M. D. : "Surface-Complexation Modeling of Radionuclide Adsorption in Subsurface Environments", U. S. Nuclear Regulatory Commission Report NUREG/CR-4807 (1988).
9. Sharland, S. M., Tasker, P. W., and Tweed, C. J. : "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., 84, Materials Research Society, Pittsburgh, Pa. (1987), 683-694.
10. Liu, C. W., and Narasimhan, T. N. : "Redox-Controlled Multiple-Species Reactive Chemical Transport 1. Model Development", Water Resour. Res., 25 (1989), 869-882.
11. Cederberg, G. A., Street, R. L., and Leckie, J. O. : "A Groundwater Mass Transport and Equilibrium Chemistry Model for Multicomponent Systems", Water Resour. Res., 21 (1985), 1095-1104.
12. Walsh, M. P., Lake, L. W., and Schechter, R. S. : "A Description of Chemical Precipitation Mechanisms and Their Role in Formation Damage during Stimulation by Hydrofluoric Acid", J. Petrol. Tech., Sept. 1982, 2097-2112.
13. Walsh, M. P., Bryant, S. L., Schechter, R. S., and Lake, L. W. : "Precipitation and Dissolution of Solids Attending Flow through Porous Media", Am. Inst. Chem. Eng. J., 30 (1984), 317-328.
14. Bryant, S. L., Schechter, R. S., and Lake, L. W. : "Interactions of Precipitation/Dissolution Waves and Ion Exchange in Flow through Permeable Media", Am. Inst. Chem. Eng. J., 32 (1986), 751-764.
15. Carnahan, C. L. : "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., 84, Materials Research Society, Pittsburgh, Pa. (1987), 713-721.
16. Carnahan, C. L. : "Some Effects of Data Base Variations on Numerical Simulations of Uranium Migration", Radiochim. Acta, 44/45 (1988), 349-354.
17. Noorishad, J., Carnahan, C. L., and Benson, L. V. : "Simulation of Fractionation of ¹³C During Nonequilibrium Reactive Solute Transport in Geologic Systems: Formulation and Example Calculation", Water Resour. Res., 25 (1989), 754-756.

18. Read, D., Williams, D. R., and Liew, S. K. : "A Coupled Approach to Radioelement Migration Modelling in the United Kingdom", in Tsang, C.-F., ed. : Coupled Processes Associated with Nuclear Waste Repositories, Academic Press, Orlando, Fla. (1987), 309-324.
19. Haworth, A., Sharland, S. M., and Tweed, C. J. : "Modelling of the Degradation of Cement in a Nuclear Waste Repository", in Lutze, W., and Ewing, R. C., eds. : Scientific Basis for Nuclear Waste Management XII, Mater. Res. Soc. Symp. Proc., 127, Materials Research Society, Pittsburgh, Pa. (1989), 447-454.
20. Read, D., and Broyd, T. W. : "Verification and Validation of Predictive Computer Programs Describing the Near and Far-Field Chemistry of Radioactive Waste Disposal Systems", Radiochim. Acta, 44/45 (1988), 407-415.
21. Ortoleva, P., Merino, E., Moore, C., and Chadam, J. : "Geochemical Self-Organization I: Reaction-Transport Feedbacks and Modeling Approach", Am. J. Sci., 287 (1987), 979-1007.
22. Ortoleva, P., Chadam, J., Merino, E., and Sen, A. : "Geochemical Self-Organization II: The Reactive-Infiltration Instability", Am. J. Sci., 287 (1987), 1008-1040.
23. Haskin, H. K., Moore, C. H., and Ortoleva, P. J. : "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.
24. Steefel, C. I., and Lasaga, A. C. : "The Space-Time Evolution of Dissolution Patterns: Permeability Change Due to Coupled Flow and Reaction", in press, ACS Symposium Series, 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.
25. Carnahan, C. L. : "Coupling of Precipitation-Dissolution Reactions to Mass Diffusion", in press, ACS Symposium Series, 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 (1988).

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720