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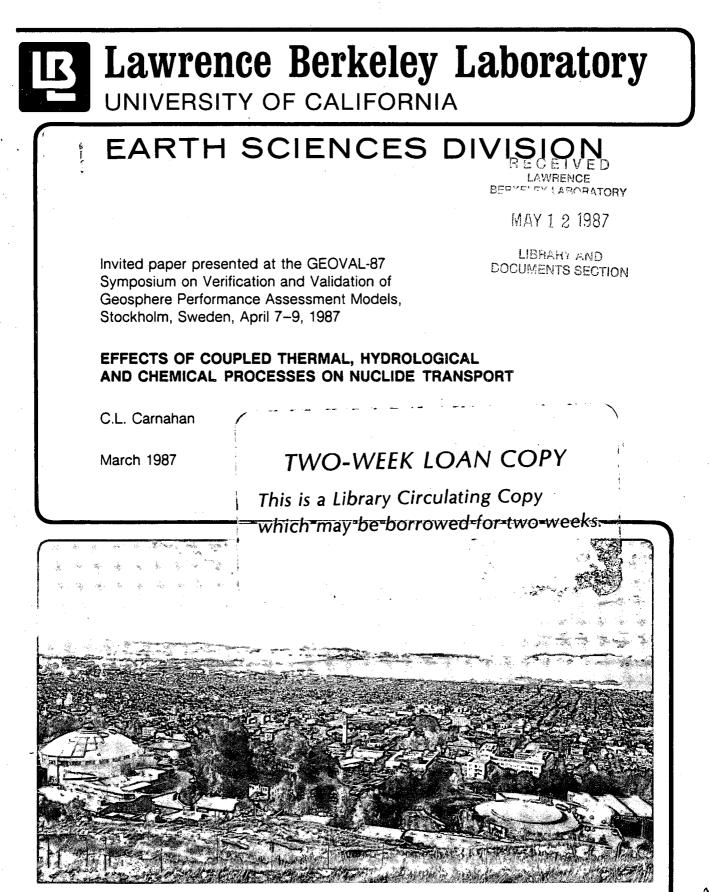
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EFFECTS OF COUPLED THERMAL, HYDROLOGICAL AND CHEMICAL PROCESSES ON NUCLIDE TRANSPORT

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ABSTRACT

Coupled thermal, hydrological and chemical processes can be classified in two categories. One category consists of the "Onsager" type of processes driven by gradients of thermodynamic state variables. These processes occur simultaneously with the direct transport processes. In particular, thermal osmosis, chemical osmosis and ultrafiltration may be prominent in semipermeable materials such as clays. The other category consists of processes affected indirectly by magnitudes of thermodynamic state variables. An important example of this category is the effect of temperature on rates of chemical reactions and chemical equilibria. Coupled processes in both categories may affect transport of radionuclides. Although computational models of limited extent have been constructed, there exists no model that accounts for the full set of THC-coupled processes. In the category of Onsager coupled processes, further model development and testing is severely constrained by a deficient data base of phenomenological coefficients. In the second category, the lack of a general description of effects of heterogeneous chemical reactions on permeability of porous media inhibits progress in quantitative modeling of hydrochemically coupled transport processes. Until fundamental data necessary for further model development have been acquired, validation efforts will be limited necessarily to testing of incomplete models of nuclide transport under closely controlled experimental conditions.

1. INTRODUCTION

Interactions between fields of temperature, hydraulic potential, and electrochemical potentials are expected to occur in the vicinity of canisters of high-level nuclear wastes located in deep geological repositories. Prediction of the extent that a repository is able to comply with regulatory standards governing the escape of radionuclides requires the ability to account for the effects of these interactions on the movement of the radionuclides. To this end, conceptual and mathematical models of both direct and coupled transport processes have been devised and have been rendered into computer programs intended for numerical simulation of the processes under consideration. Here, I shall review the transport processes and associated material properties that require simulation. I then shall review the

merits and deficiencies of current simulators, with regard to meeting these requirements. Finally, I shall suggest a strategy for future model development and laboratory experimentation that could provide at least partial validation of our concepts of the factors controlling migration of radionuclides.

2. COUPLED PROCESSES AND ASSOCIATED MATERIAL PROPERTIES

The thermodynamic variables affecting the transport of chemicals in aqueous solution are temperature, pressure, gravitational potential, and electrochemical potential, the last consisting of the composition-dependent part of the chemical potential and the (usually inseparable) electrical potential. Gradients of these variables are the driving forces for the "Onsager" coupled transport processes as well as the direct processes described by the phenomenological laws of Fourier, Darcy, Fick, and Ohm. Magnitudes of the thermodynamic variables influence material properties of fluid and solid phases, influence rates of chemical reactions, and affect transport processes indirectly.

2.1 Coupled transport processes

The Onsager coupled transport processes are flows of heat, mass, and electrical current that are driven by seemingly unrelated forces. The thermodynamics of irreversible processes can be used to describe both coupled and direct processes quantitatively [8,10]. In this formalism, the volumetric rate of production of entropy, σ, in a system undergoing irreversible processes plays a central role analogous to the role played in equilibrium thermodynamics by the Gibbs free energy. With the assumption that the state functions used in equilibrium thermodynamics can be carried over to systems supporting irreversible processes, it can be shown that σ is given, in general, by

$$\sigma = \sum_{i=1}^{n} J_i X_i, \tag{1}$$

where J_i is a flow and X_i is the driving force conjugate to that flow ($e.g.$, the force conjugate to heat flow is the gradient of temperature). Next, it is assumed that each flow is related linearly to every force acting within the system, thus:

$$J_i = \sum_{j=1}^{n} L_{ij} X_j, \quad i = 1, \ldots, n, \tag{2}$$

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where the L_{ij} are the phenomenological coefficients. The theory predicts the "reciprocal relations",

$$L_{ij} = L_{ji}, \tag{3}$$

which require that the coupled processes occur in pairs. The reciprocal relations have been validated in many systems supporting irreversible, vector processes [20].

Table 1 is a diagram of the processes contributing to flows of heat, volume (specific discharge), mass (diffusional flows of solutes relative to motion of water), and electrical current. The flows are driven by gradients of temperature, pressure (or hydraulic potential), compositional chemical potential, and electrical potential. The direct processes (flow driven by its conjugate force) lie on the main diagonal of the array of processes, and the coupled processes are the off-diagonal elements of the array. Reciprocal processes are located in symmetrical positions with respect to the main diagonal. In geological materials, the most prominent of the coupled processes are the osmotic processes and ultrafiltration, which occur in materials such as clays and shales that exhibit varying degrees of semipermeability. Previous studies of occurrences of these processes in geological settings have been catalogued as part of a recent review [23] of groundwater flow in low-permeability environments. In the context of nuclear waste repositories, approximate calculations of flows of volume and solute mass under conditions of free flow at boundaries of clay packing materials have been reported [2,3]. Thermal osmosis in packing material around a heat-emitting waste canister has been discussed theoretically [6,25].

Table 1. Direct and coupled flows driven by gradients of temperature (T), pressure (P), chemical potential (μ), and electrical potential (ψ)

Flow	∇T	∇P	$\nabla \mu$	$\nabla \psi$
heat	Fourier's law	thermal filtration	Dufour effect	Peltier effect
volume	thermal osmosis	Darcy's law	chemical osmosis	electro-osmosis
mass diffusion	Sorêt effect	ultra-filtration	Fick's law	electro-phoresis
electrical current	Seebeck effect	streaming current	sedimentation current	Ohm's law

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2.2 Material properties and coupling

In systems with spatially and temporally varying fields of the thermodynamic potentials, complex interactions can take place between these fields and certain physical and chemical properties of the system's components. These interactions constitute a form of coupling dependent on magnitudes, rather than gradients, of the potentials. The interactions can change the magnitudes of the material properties (including transport coefficients) and thus influence the migration of dissolved chemicals.

There are a number of material properties that are important in the present context. These include, in the fluid phase, viscosity, density, and mass diffusivity; in the solid phase, porosity, permeability, and dispersivity; and in both phases, thermal conductivity, heat capacity, and phenomenological coefficients (L_{ij}) for the coupled transport processes. All of these properties can be affected, to some degree, by variations of temperature, pressure, composition, and electrical potential.

The effects of temperature on material properties may be the most important of these interactions. In particular, temperature can have significant effects on the rates of reaction and equilibrium configurations of reactive chemical systems. Chemical reactions that must be simulated for purposes of performance assessment are complexation and oxidation-reduction in the fluid phase, sorption, solubility of primary and secondary solid phases, and dehydration, devitrification, and hydrothermal alteration of packing and backfill materials. Precipitation and dissolution of solid phases can alter the permeability of porous or fractured media, and thus alter the field of fluid flow. Further alteration can arise from the dependence of fluid viscosity on temperature. Alteration of the flow field can, in turn, affect the advection of dissolved chemicals. Other transport processes also can be affected by temperature dependence of the associated transport coefficients. Thus, temperature is clearly coupled, albeit indirectly, to fluid flow, solute transport, and chemical reactions. Similarly, pressure, composition, and electrical potential can be expected to interact with heat and mass flow processes through the associated transport coefficients, chemical reaction rate constants, and chemical equilibrium constants.

It is clear that in order to simulate radionuclide transport by direct and coupled processes, the modeler needs to have available a comprehensive data base of material property coefficients as well as the data and methods necessary to evaluate effects of variable

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thermodynamic potential fields on the coefficients.

3. PRESENT STATUS OF CHEMICAL TRANSPORT MODELS

For the purpose of this discussion, I consider three categories of models intended to simulate movement of water and solutes through porous or fractured geological media: reactive chemical transport models, geothermal system models, and coupled transport models. I exclude from consideration nonreactive chemical transport models, chemical transport models that attempt to describe sorption by use of distribution coefficients, and geochemical equilibrium models that do not include transport.

3.1 Reactive chemical transport models

Table 2 lists characteristics of seventeen computer programs intended to simulate chemical transport with chemical reactions coupled to mass transport processes. The list of programs is arranged in chronological order and is intended to be illustrative — it is not comprehensive. Coupling between chemical reactions and solute transport equations has been accomplished by two numerical approaches. The "two-step" method solves the transport equations and the usually nonlinear equations of chemical equilibrium or reaction rates separately at each time level. (An improved version of this method [7] iterates between the two equation sets at each time level until the two solution sets agree.) The "direct" method solves the two equation sets simultaneously, either explicitly [*e.g.*, 19,24] or implicitly [*e.g.*, 4,5]. All of the programs listed except three [16,24,26] assume that all chemical reactions achieve equilibrium instantaneously, all except one [4,5] are isothermal, and all except one [22] assume that the velocity of the fluid phase is invariant in time.

The merits of these programs are that they provide strong coupling between solute transport equations (conservation of mass of solutes) and chemical reactions, and they provide coupling between temperature and chemical reactions through equilibrium constants or reaction rate constants. Their inadequacies are that they provide no coupling between solute transport, temperature, and chemical reactions on the one hand, and fluid flow on the other hand; they do not consider the effects of Onsager coupled processes; and they consider only one (liquid) mobile phase.

Table 2. Summary of computer programs coupling chemical reactions and transport

Authors	Coupling Method	Dimen-sions	Aqu. Spec.	Sorp-tion	Precip-itation	Activity Coeff.	Chem.	Temp.
Rubin & James [30]	direct	1	no	IE	no	no	equil.	const.
Grove & Wood [11]	2-step	1	yes	IE	yes	D-H	equil.	const.
Valocchi et al. [33]	direct	2	no	IE	no	no	equil.	const.
Jennings et al. [15]	direct	1	yes	SC	no	no	equil.	const.
Walsh et al. [34]	2-step	1	yes	L	yes	Davies	equil.	const.
Miller [18]; Miller & Benson [19]	direct	1	yes	IE, SC	yes	Davies	equil.	const.
Schulz & Reardon [31]	2-step	2	no	IE	yes	no	equil.	const.
Felmy et al. [9]	2-step	1	yes	L	yes	Davies, D-H	equil.	const.
Theis et al. [32]	2-step	1	yes	L	no	Davies	equil.	const.
Kirkner et al. [17]	2-step	1	yes	IE	no	no	equil.	const.
Morrey & Hostetler [21]	2-step	1	yes	IE, SC	yes	Davies, D-H	equil.	const.
Ortoleva [26]	direct	1	no	no	yes	no	equil., kinetic	const.
Noorishad & Carnahan [24]	direct	1	yes	IE	yes	Davies	kinetic, equil.	const.
Kirkner et al. [16]	direct	1	yes	L	no	no	kinetic	const.
Cederberg et al. [7]	2-step	1	yes	SC	no	no	equil.	const.
Narasimhan et al. [22]	2-step	2	yes	no	yes	Davies	equil.	const.
Carnahan [4,5]	direct	1	yes	no	yes	Davies	equil.	varies

Note: D-H = extended Debye-Hückel, IE = ion exchange, SC = surface complexation, L = Langmuir sorption.

3.2 Geothermal system models

Considerations of chemical transport appear not to have played an important role in the evolution of geothermal system models. However, these models, exemplified by [1,12,29], possess capabilities that would be very useful additions to models of reactive chemical transport. In particular, the geothermal system models are capable of treating variable flow of two-phase fluids and of accounting for variations of fluid properties accompanying variations of temperature and salinity — the kind of interaction defined in Section 2.2 of this paper.

On the other hand, the geothermal system models generally provide only minimal, if any, treatment of chemical reactions, and they do not consider coupled processes of the Onsager type.

3.3 Coupled transport models

Very little work has been done on the simulation of evolution of systems supporting the Onsager type of THC-coupled processes. Although the phenomenological equations have been studied extensively experimentally, principally with a view toward validation of the reciprocal relations [20], it appears that only one computer program has been constructed to combine the phenomenological equations with appropriate conservation equations and to solve the complete, nonlinear equation set. The program that does this has been conditionally verified and has been applied to analysis of coupled transport processes expected to occur in saturated clay surrounding a nuclear waste canister [13]. At present, the program treats heat conduction, advection, chemical diffusion, thermal and chemical osmosis, ultrafiltration, and thermal diffusion. It does not treat chemical reactions and electrokinetic coupled processes.

3.4 Competence of existing models of THC-coupled processes

The present situation with respect to the competence of THC-coupled transport models is as follows.

Individual models can describe a limited number of coupled or interactive processes at reasonable levels of confidence, and a few (e.g., [11,19,33]) have been validated against field data. However, no single model presently describes the full range of coupled and

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interactive processes anticipated to occur in packing, backfill, and host rock during either thermally active or inactive periods. As examples, we have seen that not one of the many reactive chemical transport models listed in Table 2 includes Onsager coupled transport processes, while the only model accounting for some of these processes does not include chemical reactions. Thus, in the strict sense, the current models cannot be considered adequate to provide *unique* solutions for systems supporting processes that have not been treated explicitly within the models. (Under favorable conditions, non-unique solutions can be [and sometimes have been] obtained by a process called "tweaking the model"; this practice can be misleading in predictive applications.)

The obvious remedy for this situation is to extend existing models to include a larger variety of coupled and interactive processes. Activities of this kind are going on at several research centers. However, there are significant obstacles to be overcome in two areas. In the area of the Onsager coupled processes, further development is severely constrained by the lack of a data base of phenomenological coefficients (and their variations with temperature and composition), and by the current lack of experimental data needed for even partial validation of coupled models. In the area of interaction between chemical reactions and fluid flow, it has been pointed out [27,28] that there is no generally accepted relation between porosity and permeability in porous media that can be used to simulate the effects of precipitation and dissolution of solids on the local field of flow. The situation appears better in the case of such heterogeneous reactions in fractures, where an accepted relation between permeability and fracture aperture does exist [27,28].

The limitations of existing models of coupled and interactive transport processes, and the present lack of fundamental theoretical concepts and experimental data in areas critical to further development of the models, will exert significant influence on efforts to validate the models.

4. A STRATEGY FOR VALIDATION OF THC-COUPLED MODELS

Given the present status of computer programs intended to simulate THC-coupled processes, a discussion of approaches to validation of the programs might best begin with an examination of the philosophy underlying their development and uses.

The desirability of continually expanding computer programs to include ever larger vari-

eties of physical and chemical phenomena is often taken as an article of faith. It is assumed that the more complex a program is, the more faithfully will it reproduce Nature as manifested at a repository for nuclear waste. Often it is not acknowledged (or recognized) that the more complex a program is, the more intractably will it resist efforts to verify, validate, and interpret its results.

In June 1984, I attended a workshop, sponsored by the OECD Nuclear Energy Agency, concerned with the coupling of geochemical and fluid flow models. Among the conclusions of the workshop (which have not been published) were the following statements.

1. Some level of coupling between geochemical and hydrological models is needed in performance assessment.

2. The development of "megacodes" (large, directly coupled hydrogeochemical computer programs) is undesirable.

3. Basic understanding of physical and chemical processes occurring in waste repositories is indispensable.

4. Application of relatively simple coupled models to specific problems and experimental observation of specific systems are important aids to understanding.

These conclusions seem as valid today as they did in 1984.

These considerations lead one to the conclusion that a balance should be achieved between the complexity of a coupled-process model and the extent of validation required for the model. Although the models described above can easily tolerate further development, such development should not be so complex as to obscure understanding of the evolution of the system being simulated. Models constructed in this manner could be validated under closely controlled experimental conditions, and could themselves be used to validate components of more complex models, should the latter be deemed necessary in the future.

It seems clear that full-scale field experiments cannot be relied on for validation of the present, incomplete models. Phenomena may occur in the field that are beyond the scope of present models, or even of contemplated, modest extensions of them.

Validation of existing models will require validation of their individual components as well as the acquisition of much experimental data constituting the models' data bases.

Coupled models incorporating chemical reactions require validation of data bases of ther-

modynamic data (for equilibrium models) or of reaction mechanisms and kinetic rate constants (for kinetic models). The procedures for chemical data-base validation are currently being implemented for geochemical programs that do not include transport [14]. Validation of the chemical components of THC-coupled programs can be accomplished by benchmarking them against validated geochemical programs. The transport components of the models can be validated first in chemically nonreactive systems; validation of transport in reactive systems will require controlled experiments of progressively increasing complexity.

Validation of models of Onsager coupled processes will require the acquisition of a data base of phenomenological coefficients as well as independent investigations of the evolution of systems supporting these processes. The phenomenological coefficients are measured most efficiently in systems that have evolved to a steady state; the systems can be designed so that only one or two coupled processes are allowed to occur. Acquisition of a comprehensive data base will allow not only simulation of the coupled processes, but also evaluation of their significance, relative to the direct transport processes, in given systems with given boundary conditions. Validation of the simulated results can be accomplished by comparison to experimental results obtained in transient states.

A vital ingredient of a successful validation is close cooperation between modelers and experimenters. The modeler must inform the experimenter of his data needs and assist in guiding the experiments; the experimenter must design his experiments to exclude unwanted processes and must assist the modeler toward a correct description of the processes being observed. The model *cum* computer program is not an end in itself; it is a tool to be used in company with experimental science to increase knowledge and understanding of Nature.

5. ACKNOWLEDGEMENT

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