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January 1984

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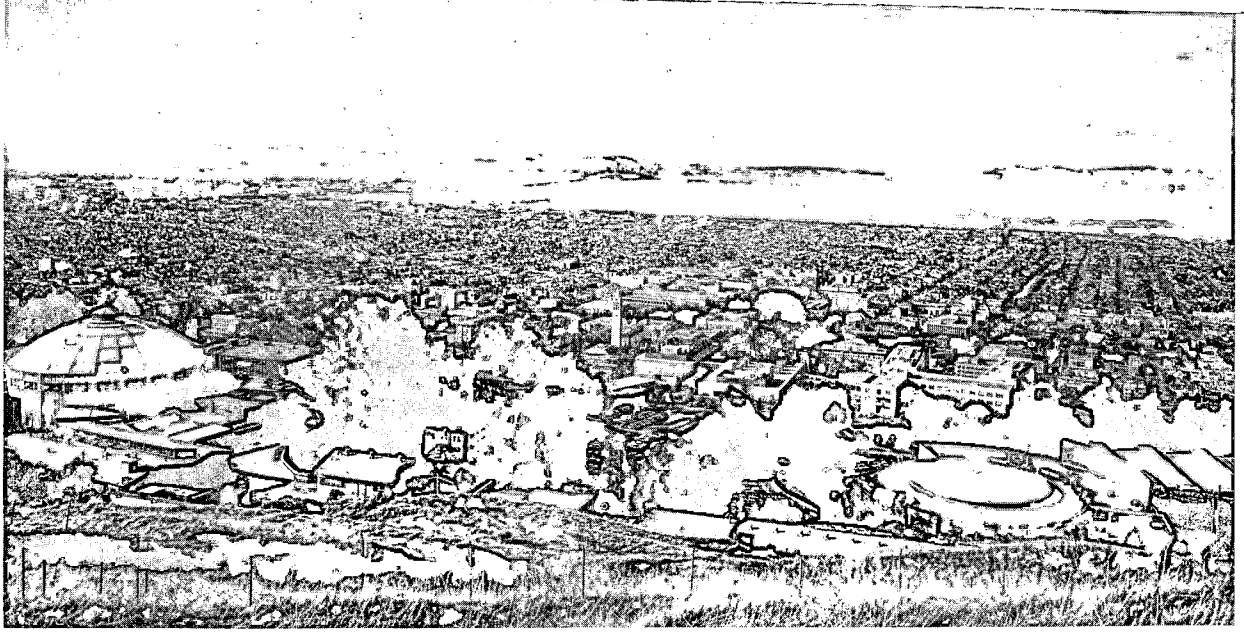

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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VERIFICATION AND IMPROVEMENT OF PREDICTIVE ALGORITHMS FOR RADIONUCLIDE MIGRATION

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ABSTRACT

This research addresses issues relevant to numerical simulation and prediction of migration of radionuclides in the environment of nuclear waste repositories. Specific issues investigated are the adequacy of current numerical codes in simulating geochemical interactions affecting radionuclide migration, the level of complexity required in chemical algorithms of transport models, and the validity of the "constant-k_D concept" in chemical transport modeling. An initial survey of the literature led to the conclusion that existing numerical codes did not encompass the full range of chemical and physical phenomena influential in radionuclide migration. Studies of chemical algorithms have been conducted within the framework of a one-dimensional numerical code that simulates the transport of chemically reacting solutes in a saturated porous medium. The code treats transport by dispersion/diffusion and advection, and equilibrium-controlled processes of interphase mass transfer, complexation in the aqueous phase, pH variation, and precipitation/dissolution of secondary solids. Irreversible, time-dependent dissolution of solid phases during transport can be treated. Mass action, transport, and sorptive site constraint equations are expressed in differential/algebraic form and are solved simultaneously. Simulations using the code show that use of the constant-k_D concept can produce unreliable results in geochemical transport modeling. Applications to a field test and laboratory analogs of a nuclear waste repository indicate that a thermodynamically based simulator of chemical transport can successfully mimic real processes provided that operative chemical mechanisms and associated data have been correctly identified and measured, and have been incorporated in the simulator. Success in the development of an ability to reliably predict the performance of a nuclear watse repositories will depend on close interaction and coordination of effort between experimenters and developers of predictive codes.

INTRODUCTION

Prediction of the rates of migration of radionuclides in ground water moving through engineered barriers and host rocks surrounding underground repositories for nuclear waste is essential to the assessment of the ability of a repository to meet standards for performance. The hydrogeological and geochemical processes that could influence the rates of migration may operate over times spanning many thousands of years and are difficult, if not impossible, to study in real-time laboratory and field experiments. Therefore, recourse is made to numerical simulations of these processes and their spans of time in order to predict, as accurately as possible, the total amounts and the concentrations of radionuclides that might be transported from waste repositories to the accessible environment. Only in this way can the potential hazard to public health and safety arising from nuclear waste repositories be quantified and evaluated.

Issues Addressed by This Research

The principal issues concerning our abilities to numerically simulate, and thus to predict, the migration of radionuclides in a repository environment are:

> What geochemical interactions between radionuclides, water, backfill, and host rock must be considered in order to achieve reliable simulations and predictions?

What experimental and other observational data are required to implement identified geochemical processes as algorithms in simulators of radionuclide transport?

How can the results of numerical simulations of radionuclide transport be verified?

This task addresses these principal issues and, in particular, certain specific issues necessary for their resolution. The specific issues are:

Are currently applied numerical codes adequate to simulate geochemical interactions affecting radionuclide migration?

What level of complexity is required in chemical algorithms of transport models to adequately predict radionuclide migration?

Under what conditions, if ever, is the use of the constant distribution coefficient (k_D) valid in describing sorption and retardation of radionuclides?

Background and Objectives

In general, two methods have been used to simulate transport of chemically reactive solutes.

One method is based on the plate theory of chromatography and uses codes that calculate equilibrium, closed-system distributions of chemical species sequentially with transport algorithms in a two-step procedure. This method was used, for example, by *Routson and Serne* (1972), *Ahlstrom, Foote, Arnett, Cole, and Serne* (1977), *Grove and Wood* (1979), and *Strickert, Friedman, and Fried* (1979). Applications of this method can be differentiated by the manner in which they attempt to account for transport by dispersion/diffusion. Thus, *Ahlstrom et al.* (1977) used a random walk procedure, while *Grove and Wood* (1979) solved the nonreacting convective-dispersive transport equation.

The second method is a one-step procedure that consists of solving a system of equations simultaneously describing chemical reactions and convective-dispersive transport with interphase mass transfer. In its simplest form, exemplified by the work of *Holly and Fenske* (1968), the method assumes uncoupled equilibrium exchange of noncompeting solutes, each with a constant k_D value; in this case, the system of simultaneous equations reduces to a set of independent, linear, partial differential transport equations, one for each exchanging solute. In its more advanced form, exemplified by the work of *Rubin and James* (1973) and *Valocchi, Street, and Roberts* (1981), the method is more soundly based on chemical and thermodynamic principles and leads to a system of simultaneous, nonlinear, partial differential equations coupled to a set of mass action equations. This approach appears to have produced the greatest degree of success in matching experimental laboratory and field data.

Various models have focused on particular physical or chemical phenomena identified to be influential in chemical transport. In general, however, models existing at the beginning of this work did not incorporate complete descriptions of the entire set of chemical phenomena known to affect rates of chemical migration. More particularly, existing models that incorporated individual chemical processes suffered from omission of other possibly significant processes, and the reliability of predictions made by these models was, at best, difficult to assess. Thus, there was an apparent need for a transport model capable of incorporating the essential set of chemical processes necessary for adequate understanding and prediction of migration of radionuclides.

The study described here addressed two objectives.

The first objective was to evaluate existing transport models with regard to their treatment of chemical processes affecting rates of movement of radionuclides in flowing ground water. The results of work toward this objective, briefly summarized in the preceding paragraphs, have been presented in detail by *Miller, Benson, and Carnahan* (1982).

The second objective was to determine the necessity to include specific chemical processes in models used to predict radionuclide transport, and the level of complexity needed to describe the chemical

processes. This objective has been approached by adding chemical algorithms to an existing computer code and observing the effects of including, omitting, and combining algorithms that describe individual chemical processes on computed histories of radionuclide migration.

Scope of Research

Because the primary emphasis in this research was the study of chemical algorithms, the numerical simulator used as a research tool was based on a very simple fluid flow model. The flow model is one-dimensional and assumes constant fluid velocity, diffusion, and dispersion. However, considerable effort has been spent on coupling the chemical algorithms to the fluid transport algorithm in as chemically and thermodynamically rigorous a manner as possible.

The more advanced form of the one-step approach was used in the simulator of chemical transport, *CHEMTRN*, used in this work. This allows simulation of the transport and chemical reactions of both major and minor chemical species and evaluation of the effects of major species on the transport of minor species, including radioactive species. The chemical equilibrium algorithms included in *CHEMTRN* are complexation in the aqueous phase, sorption of simple ions and complexes by either ion exchange or surface complexation, dissociation of water, and reversible precipitation/dissolution of solid phases. A nonequilibrium algorithm for the simulation of irreversible dissolution of solid phases during transport is included also.

CHEMICAL AND MATHEMATICAL BASES OF THE SIMULATOR, *CHEMTRN*

Chemical Equations

To simplify solution of the transport equations for a given chemical system, a set of *basis species* $A_j^{n_j}$ is defined, where n_j is the ionic charge of the species. This set consists of the minimum number N_b of species necessary to define all species present, either through equilibrium mass action relations or through nonequilibrium rate expressions.

Thermodynamic activities of basis species, $[A_j^{n_j}]$, and of complexes in the aqueous phase, $[C_i^{n_i}]$, (where n_i is the ionic charge of the complex) are approximated by the relations

$$[A_j^{n_j}] = \gamma_j m_{bj} \tag{1}$$

and

$$[C_i^{n_i}] = \gamma_i m_{ci}, \tag{2}$$

where γ_j and γ_i are activity coefficients and m_{bj} and m_{ci} are mass concentrations of basis species and complexes, respectively, in moles per dm^3 of aqueous phase. Activity coefficients are approximated using a modification of the Davies equation given by *Stumm and Morgan* (1970, p. 83, footnote),

$$\log_{10} \gamma_h = -\frac{1}{2} n_h^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right), \tag{3}$$

where subscript h represents either i or j. I is the ionic strength defined by

$$I = \frac{1}{2} \left(\sum_{j=1}^{N_b} n_j^2 m_{bj} + \sum_{i=1}^{N_c} n_i^2 m_{ci} \right), \tag{4}$$

and N_c is the number of complexes in the aqueous phase. The activities of water and of uncharged complexes are assumed to be unity.

Chemical reactions for the formation of complexes $C_i^{n_i}$ and precipitates G_k from basis species $A_j^{n_j}$ are written

$$\sum_{j=1}^{N_b} a_{ij} A_j^{n_j} \rightleftarrows C_i^{n_i} \qquad \text{R1}$$

and

$$\sum_{j=1}^{N_b} s_{kj} A_j^{n_j} \rightleftarrows G_k, \qquad \text{R2}$$

where a_{ij} and s_{kj} are stoichiometric reaction coefficients, which are zero for basis species that do not participate in a given reaction. Under the assumption of chemical equilibrium the mass action relation for the formation of a complex is then

$$K_i = \frac{[C_i^{n_i}]}{\prod_{j=1}^{N_b} [A_j^{n_j}]^{a_{ij}}}, \tag{5}$$

where K_i is the thermodynamic equilibrium constant. Similarly, the mass action relation for the *dissolution* of a precipitate is

$$K_k = \prod_{j=1}^{N_b} [A_j^{n_j}]^{s_{kj}}, \tag{6}$$

where K_k is the thermodynamic solubility product of the solid phase G_k. Activities of solid phases are assumed to be unity.

Interphase mass transfer of basis species and charged complexes by cation exchange takes place by reactions of the type

$$n_2 B_1^{n_1}(aq) + n_1 \overline{B}_2 \rightleftarrows n_2 \overline{B}_1 + n_1 B_2^{n_2}(aq), \qquad \text{R3}$$

where $B_i^{n_i}(aq)$ denotes a positively charged species (basis or complex) in the aqueous phase and $\overline{B}_i$ denotes the sorbed component. Assuming chemical equilibrium, the mass action relation for this reaction is

$$K_{eq} = \frac{[\overline{B}_1]^{n_2}[B_2^{n_2}]^{n_1}}{[\overline{B}_2]^{n_1}[B_1^{n_1}]^{n_2}}. \tag{7}$$

Activities of sorbed components are approximated by assuming that they can be described by an ideal-solution model in which

$$[\overline{B}_j] = \frac{\overline{m}_j}{\overline{m}_T}, \tag{8}$$

where $\overline{m}_j$ is the concentration of species j in the sorbed phase and $\overline{m}_T$ is the total concentration in the sorbed phase. $\overline{m}_T$ is given by

$$\overline{m}_T = \sum_{j=1}^{\overline{N}_b} \overline{m}_{bj} + \sum_{i=1}^{\overline{N}_c} \overline{m}_{ci}, \tag{9}$$

where $\overline{N}_b$ is the number of sorbed basis species and $\overline{N}_c$ is the number of sorbed complexes. The concentrations of sorbed components are expressed as moles per dm^3 of the aqueous phase. The number

of surface sites available for cation exchange is a constant characteristic of the sorbent, and is measured by the cation exchange capacity (CEC). In the *CHEMTRN* code, the number of equivalents of available sites per dm^3 of aqueous phase, N_e, is assumed constant and is given by

$$N_e = \sum_{j=1}^{\overline{N}_b} n_j \overline{m}_{bj} + \sum_{i=1}^{\overline{N}_c} n_i \overline{m}_{ci}. \tag{10}$$

The treatment of interphase mass transfer by surface complexation used in *CHEMTRN* is based on the electrical double layer site-binding model developed by *Davis, James, and Leckie* (1978). In this case, the surface electrical charge is not necessarily conserved and both cations and anions can be sorbed. Thus a neutral surface site denoted by SOH can dissociate to give a negatively charged site SO^-:

$$SOH \rightleftarrows SO^- + H_s^+, \qquad \text{R4}$$

where the subscript s denotes that the hydrogen ion is located at the so-called "surface plane". SOH can react with H^+ at the surface plane to give a positively charged surface complex SOH_2^+:

$$SOH + H_s^+ \rightleftarrows SOH_2^+. \qquad \text{R5}$$

This surface complex can react with an anion such as Cl^- to form a formally neutral surface complex:

$$SOH_2^+ + Cl_\beta^- \rightleftarrows SOH_2^+ Cl^-. \qquad \text{R6}$$

The subscript β denotes the plane where the chloride ion is located when it forms a complex with the surface site. Finally, a SOH site can react with a bivalent cation such as Sr^{2+} to form a charged surface complex:

$$SOH + Sr_\beta^{2+} \rightleftarrows SO^- Sr^{2+} + H^+. \qquad \text{R7}$$

The *CHEMTRN* code treats only those surface complexation reactions involving a single site; reactions involving two or more sites must be simulated by the ion exchange algorithm.

Thermodynamic equilibrium constants for reactions R4–R7 are formed in the usual manner. Following the discussion by *Davis, James, and Leckie* (1978), the activity of a species B^n in the s or β plane is related to its activity in the bulk solution by

$$[B_p^n] = [B^n] \exp\left(-\frac{ne\psi_p}{kT}\right), \tag{11}$$

where ψ_p is the change of electrical potential when the species moves from the bulk solution to the plane denoted by p, k is the Boltzmann constant, T is the absolute temperature, and e is the electronic charge.

Irreversible dissolution of a solid phase along the path of transport is treated in the following way. A stoichiometric equation is written for dissolution of one mole of the solid such that the reactants and products consist of the solid and basis species only. Given a rate of dissolution of the solid expressed as moles per dm^3 of aqueous phase per unit time, the stoichiometric equation determines rates of production or consumption of each basis species. These rates are specified as part of the input data for each basis species, and are added or subtracted at each finite difference node during the solution procedure. It is noted that this method does not account for changes of dissolution rates caused by changes of aqueous phase composition.

Transport Equations

Basis species and complexes are transported by advection with velocity v and by hydrodynamic dispersion (mechanical dispersion plus molecular diffusion) with dispersion coefficient D. W_j, the total

concentration of a component A_j in the aqueous phase, is defined by

$$W_j = m_{bj} + \sum_{i=1}^{N_c} a_{ij} m_{ci}, \tag{12}$$

and $\overline{W_j}$, the total concentration of component A_j in sorbed phases, is defined by

$$\overline{W_j} = \overline{m}_{bj} + \sum_{i=1}^{\overline{N}_c} a_{ij} \overline{m}_{ci}. \tag{13}$$

Then, if N_p precipitates are present, the mass balance for component A_j is expressed by

$$\left(\frac{\partial}{\partial t} + v\frac{\partial}{\partial x} - D\frac{\partial^2}{\partial x^2}\right)W_j = -\frac{\partial}{\partial t}\overline{W_j} - \frac{\partial}{\partial t}\sum_{k=1}^{N_p} s_{kj} m_{pk} + d_j, \tag{14}$$

where m_{pk} is the equivalent, aqueous-phase concentration of a compound removed by reversible precipitation (negative values of m_{pk} correspond to addition of the compound by reversible dissolution) and d_j is the incremental concentration of A_j added per unit time by irreversible dissolution of a solid phase. The number of unknowns equals $N_b + \overline{N}_b + N_c + \overline{N}_c + N_p$. There are N_b transport equations having the form of (14). The mass action relations, (5), provide N_c equations. N_p equations are provided by (6). There are $\overline{N}_b + \overline{N}_c - 1$ mass action relations for ion exchange or surface complexation having the form of (7), and one site-constraint equation, (10). The activity coefficients are given by (3) and (4), and $\overline{m}_T$ is given by (9). These equations are sufficient to determine the m_{jb}, $\overline{m}_{bj}$, m_{ci}, $\overline{m}_{ci}$, and m_{pk}.

Boundary Conditions

The *CHEMTRN* simulator accepts either constant-flux or constant-concentration boundary conditions. Semi-infinite systems are simulated by imposing outer boundary conditions at a distance large enough that they do not noticeably perturb solutions computed at inner nodes, in the region of interest.

Method of Solution

The transport equations (14) are discretized in space and time to give a set of finite difference equations which are solved simultaneously with the algebraic equations given in the preceding sections. The Newton-Raphson method is used for the solution, and special techniques are used for precipitation and the treatment of pH changes. A detailed description of the method of solution has been given by *Miller and Benson* (1983).

APPLICATIONS AND RESULTS

In this section we discuss applications of the *CHEMTRN* simulator to an investigation of the validity of the constant-k_D concept, to a field experiment in which the principal chemical process acting during transport was multicomponent ion exchange, and to simulations of laboratory experiments on the sorption of neptunium on basalt surfaces. Simulations of systems involving reversible precipitation and surface complexation have been discussed by *Miller* (1983) and by *Miller and Benson* (1983).

Validity of the Constant-k_D Concept

Transport of contaminants in ground water often has been simulated under the assumption that the solid/fluid distribution coefficient (k_D) for a chemical species is constant throughout its transport path. Increasingly, this assumption is being questioned (e.g., *Reardon*, 1981).

It can be shown that the k_D of an exchanging ion depends on the exchange capacity of the sorbent, the concentration(s) of other exchanging ion(s), and the ionic strength of the aqueous phase (e.g., *Miller and Benson*, 1983). If these quantities change during transport, then it must be expected that the k_D will change also. This situation will occur when the concentrations of exchanging ions in the aqueous phase are comparable. On the other hand, if the concentration of the ion of interest is very small relative both to the concentration of the supporting electrolyte and the cation exchange capacity, then the k_D for this ion will be independent of its concentration.

Figure 1 shows the results of simulations by *CHEMTRN* when competition for sites on the sorbent affects sorption of cations. The aqueous phase initially contained $10^{-4}\,M$ Na^+, $10^{-5}\,M$ Ca^{2+}, $10^{-8}\,M$ Sr^{2+}, $4.5 \times 10^{-5}\,M$ CO_3^{2-}, and $3 \times 10^{-5}\,M$ Cl^-, where M has the units moles per dm^3. At the inner boundary, the concentration of Sr^{2+} was maintained slightly in excess of $10^{-5}\,M$. The k_D calculated for Sr^{2+} was 5000 initially and 2000 at the inner boundary. For comparison with the *CHEMTRN* results, Figure 1 also shows the results obtained when the sorption of Sr^{2+} is assumed to follow a constant-k_D model with k_D equal to 2000. It is seen that the latter model predicts a slower rate of movement of Sr^{2+} than is predicted when competition for sorptive sites is accounted for.

In some situations the constant-k_D model can give acceptable results even though the value of k_D varies during transport. Figure 2 shows concentrations of Sr^{2+} computed by *CHEMTRN* for the system used above, but with a much smaller concentration of Ca^{2+}. In this case the Sr^{2+} exchanges primarily with Na^+, and the amount of the latter that is displaced from the sorbent by ion exchange does not change the composition of the aqueous phase enough to affect the value of k_D significantly. Results computed using a constant value of k_D equal to 2000 agree closely with the results computed by *CHEMTRN*.

In general, the results of simulations of transport with multicomponent ion exchange and surface complexation done with *CHEMTRN* show the following. If the major ion content of ground water remains unaltered during transport and if the sorbed concentration of a trace ion is small relative to the exchange capacity of the sorbent, then a constant-k_D model could be used to simulate the transport of the trace ion. However, the k_D value used would have to be measured or calculated for exactly the conditions postulated to exist in the chemical transport system. On the other hand, if the concentration of the ion of interest is comparable to the concentrations of major, exchanging ions or if the number of sorptive sites is a function of pH, then a constant-k_D model is not adequate to simulate the chemical transport process.

Simulation of a Field Experiment

CHEMTRN was used to simulate a field experiment in which treated municipal waste water was injected into a shallow aquifer in the Palo Alto (California) Baylands region. During the period of injection, water samples were collected at several observation wells and were analyzed for their chemical composition. Also, tests were performed to evaluate physical characteristics of the aquifer. The test has been described and results of measurements have been given by *Valocchi, Street, and Roberts* (1981).

The initial composition of ground water at observation well S23, 16 m from the injection well, was 1990 mg/dm^3 Na^+, 444 mg/dm^3 Ca^{2+}, 436 mg/dm^3 Mg^{2+}, and 5700 mg/dm^3 Cl^-. The waste water was injected at an average rate of 21 m^3/hour and had an average composition of 216 mg/dm^3 Na^+, 85 mg/dm^3 Ca^{2+}, 12 mg/dm^3 Mg^{2+}, and 320 mg/dm^3 Cl^-. The aquifer thickness was 2 m, the density of the solid matrix was 2500 kg/m^3, the cation exchange capacity was 0.1 equivalent/kg, and

the porosity was 0.25. Measured selectivity coefficients (expressed in the mole fraction convention used in *CHEMTRN*) were 1.0 for Ca^{2+} replacing Na^{+} and 0.65 for Mg^{2+} replacing Na^{+}. (*Valocchi et al.*, 1981)

A *CHEMTRN* simulation was done for the composition of the fluid arriving at well S23 as a function of time since the start of injection. The chemical mechanism simulated was ion exchange between Na^{+}, Ca^{2+}, and Mg^{2+}. Radial flow was assumed with the fluid velocity v at a distance r from the injection well proportional to $Q/(2\pi b\phi r)$, where Q is the rate of injection, b is the aquifer thickness, and ϕ is the porosity. The dispersion coefficient used was approximately $1.3v$; about 20 percent of this value is attributable to numerical dispersion.

Figures 3–6 are comparisons between measured and simulated histories of concentrations of Ca^{2+} and Mg^{2+} at well S23. In each figure the solid curves are the "best fit" simulations, and the discrete points are the measured values. The dashed curves are results of simulations using values of fluid velocity, density of exchange sites in units of sites/dm^3 of aqueous phase, and selectivity coefficients at the extrema of their ranges of uncertainty. These ranges were estimated from uncertainties in the reported data. Examination of Figures 3–6 shows that the "best fit" simulations provide very good matches to the measured concentration histories and are within the ranges of uncertainty of the parameters used.

Simulation of a Laboratory Experiment

Experiments with laboratory analogs of the BWIP site are being conducted at Argonne National Laboratory (*Seitz, Gerding, Vandegrift, Bowers, and Fried*, 1982). In an experiment, synthetic ground water is pumped through basalt chips and bentonite, contacts a glass frit containing radionuclide tracers which simulates a glass waste form, flows through more bentonite, and then flows through the fissure in a split basalt core before leaving the apparatus. In several experiments the basalt core was removed after periods of time varying from 90 to 150 days, and the surface of the fissure was scanned radiometrically to detect residual ^{237}Np. The results of three such measurements are shown in Figure 7.

The data in Figure 7 show, generally, a plateau region near the inlet to the rock face. (Fluctuations in this region are attributed to variations of the flow rates.) The plateau merges into a diffuse leading edge as distance from the inlet increases. These sorbed-phase distributions are similar to distributions resulting from ion-exchange equilibria between previously sorbed cations and a different, incoming cation (in this case a positively charged neptunium species) being transported in the fluid phase. Therefore, we attempted to simulate the experimental data using this mechanism of transport with interphase mass transfer. It should be noted, however, that the chemical mechanisms actually operating to produce the distributions observed in these experiments have not been identified.

Details of the analog experiments, including the composition of the simulated ground water, have been given by *Seitz et al.* (1982). The total concentration of neptunium entering the system was approximately $1.5 \times 10^{-8}\ M$. The total carbonate content of the ground water was $1.26 \times 10^{-3}\ M$, the concentration of Na^{+} was $1.36 \times 10^{-2}\ M$, and the pH was 10. Published thermodynamic data (*Benson and Teague*, 1980; *Nitsche and Edelstein*, 1982) indicate that the neptunium species present under these conditions are the oxo cation of neptunium(V), NpO_2^{+}, and its complexes NpO_2OH^0, $NpO_2HCO_3^0$, $NpO_2CO_3^{-}$, and $NpO_2(CO_3)_3^{5-}$, the last being the dominant species. Preliminary calculations of distributions of species by the *CHEMTRN* code showed that ion exchange reactions of Ca^{2+} and Mg^{2+} and complexation with SO_4^{2-} and F^{-} were not significant influences in the simulations. The transport of neptunium with sorption on the rock surface was then simulated by ion exchange between NpO_2^{+} and Na^{+} and complexation of NpO_2^{+} in the aqueous phase to form the tris(carbonato) complex. The formation constant of this complex has been reported to be $2 \times 10^{16}\ M^{-3}$ (*Nitsche and Edelstein*, 1982). The cation exchange capacity of the basalt was assumed to be 0.02 equivalent/kg, as reported by *Barney* (1980) for Umtanum basalt. Equilibria between CO_3^{2-}, HCO_3^{-}, and $H_2CO_3^0$ were included in the simulations.

Unknown quantities were the equilibrium constant for the ion-exchange reaction between NpO_2^+ and Na^+, and the linear velocity of the fluid phase through the fissure in the basalt core. We assumed a velocity of 0.088 m/day (32 m/year), based on data reported by *Seitz et al.* (1982), for the second analog experiment. This experiment was terminated at 150 days, and from the data in Figure 7 we estimated that in this time the midpoint of the leading edge of the sorbed neptunium distribution had migrated 0.072 m from the inlet. Under the assumption of constant retardation (which is approximately valid under the conditions of this part of the analog experiments), we calculated a retardation factor of 180 for neptunium. When the complexation of NpO_2^+ in the aqueous phase is accounted for, this value of retardation requires that the equilibrium constant for $NpO_2^+(aq)$ replacing sorbed Na^+ by ion exchange be equal to 7.2×10^{11}. This value was used in all simulations of the analog experiments.

The results of the simulations are shown in Figures 8–10, where relative concentrations of sorbed neptunium are plotted against distance from the inlet at the times of termination of each experiment. To facilitate comparison with the experimental data, computed concentrations of sorbed NpO_2^+ are expressed as ratios to the concentrations at the inlet, and similar normalizations were done to the experimental data. (Estimated inlet "concentrations" for data points in experiments 1, 2, and 3 were 62, 52, and 32 counts per 1000 seconds, respectively.) The computed distributions correspond to linear flow velocities of 0.066, 0.088, and 0.153 m/day and diffusion coefficients of 1.4×10^{-6}, 1.2×10^{-6}, and 1.9×10^{-6} m^2/day for experiments 1, 2, and 3. Agreement between simulations and experimental data is reasonably good at the leading edges of the distributions.

It must be noted that considerable uncertainty exists about the chemical mechanisms producing the observed distributions. In the numerical simulations, two critical items of information — the velocity of the fluid through the fissure and the equilibrium constant for the assumed ion-exchange reaction — were not known and were adjusted to make the simulations match the data. Independent evaluation of these quantities would permit evaluation of the validity of the mechanisms assumed in these simulations. We cannot eliminate the possibility that other chemical mechanisms such as nonequilibrium reactions, surface complexation of anionic species, precipitation, and heterogeneous electron-transfer reactions may have produced or contributed to the observed distributions. Until the correct mechanisms have been identified unequivocally by appropriate experiments, numerical simulations based on plausible, but hypothetical, mechanisms must be regarded as speculative at best. Furthermore, given a correct mechanism, numerical simulations will remain speculative until reliable values of all chemical and physical parameters associated with the mechanism have been obtained experimentally.

CONCLUSIONS

The results of simulations with several chemical algorithms in the simulator *CHEMTRN*, presented here and also previously by *Miller* (1983) and *Miller and Benson* (1983), identify a minimum set of requirements that should be imposed on geochemical transport codes considered for use as part of an assessment of the performance of a nuclear waste repository. Specifically, the assumption of a constant distribution coefficient (k_D) for interphase mass transfer cannot be relied upon to adequately account for changes of chemical composition of major, minor, or trace chemical components of ground water in the vicinity of a repository. A higher level of chemical complexity is required. This includes using thermodynamic equilibrium constants for all chemical reactions, using nonideality corrections via activity coefficients, accounting for changes in ionic strength, accounting for finite exchange or sorptive capacity of the solid phase and competition for sorptive sites among aqueous species, accounting for complexation of aqueous species, the ability to compute variations of pH, the ability to account for precipitation/dissolution equilibria of secondary solid phases, and the ability to simulate both equilibrium and nonequilibrium processes.

In addition, systems with variable oxidation potential require algorithms for electron-transfer reactions, and significant precipitation or dissolution will require the ability to simulate changes of flow velocity caused by decreases or increases of permeability. These effects have not been included in the

present version of the *CHEMTRN* simulator, but are regarded as necessary components of an adequate chemical transport code.

These requirements for adequacy in numerical simulations of geochemical transport imply corresponding needs for chemical, thermodynamic, kinetic, and mineralogical data to be used as input to chemical algorithms. These data include identities of reaction mechanisms and the species participating in them, solubilities of solid phases and identities of the species in equilibrium with them, and thermodynamic equilibrium constants for both homogeneous and heterogeneous chemical reactions involving species that are influential on migration of nuclear waste. Unfortunately, practically all of the measurements of k_D values made over the past fifteen to twenty years are useless as input to thermodynamically based chemical algorithms.

RECOMMENDATIONS

The following recommendations are based on the findings and conclusions of this research effort, and are directed to the objective of improving the ability to assess long-term performance of nuclear waste repositories.

> Use of the k_D concept in models of waste transport should be abandoned. This concept has little, if any, chemical and thermodynamic contents and can produce misleading results if applied uncritically. It should be replaced by thermodynamically based chemical algorithms that describe experimentally identified chemical mechanisms.
>
> Experimental programs for measurement of k_D values should be redirected toward identification of chemical mechanisms influential in waste transport, identification of aqueous and sorbed species involved in the mechanisms, and measurement of thermodynamic and chemical-kinetic data associated with species and mechanisms. These efforts should include characterization of solid phases active in chemical reactions during waste transport. Many of these important data are currently lacking, but are required for development and application of a capability to predict repository performance.
>
> Conceptual and numerical models of reactive chemical transport should be extended to include collateral processes (hydrothermal, thermochemical, thermomechanical) that are coupled both mathematically and thermodynamically to chemical reactions, fluid flow, and solute transport. Only in this way can a comprehensive description of the entire repository system and its evolution in time and space be developed.
>
> Our research during the past several years has made us keenly aware of the necessity for close interaction between those investigators making measurements in the field or laboratory, and those attempting to develop the ability to predict the behavior of the complex chemical systems anticipated to exist at a nuclear waste repository. Each group can, and should, provide guidance and input to the other. Communication between the two groups and coordination of their activities is vital to the successful development of an ability to reliably assess the performance of a repository.

PLANNED RESEARCH

Future research in this program will include extension of chemical algorithms to include nonequilibrium reversible and irreversible reactions and electron-transfer reactions. Chemical algorithms will be combined with broadly based thermohydromechanical simulators and the range of phenomena covered

will be extended to include thermodynamic coupling among transport processes. These efforts will have the objective of providing more comprehensive predictors of repository evolution and performance.

ACKNOWLEDGEMENT

We are grateful to Drs. Martin Seitz and George Vandegrift of Argonne National Laboratory for providing us with data and guidance relevant to the laboratory analog experiments.

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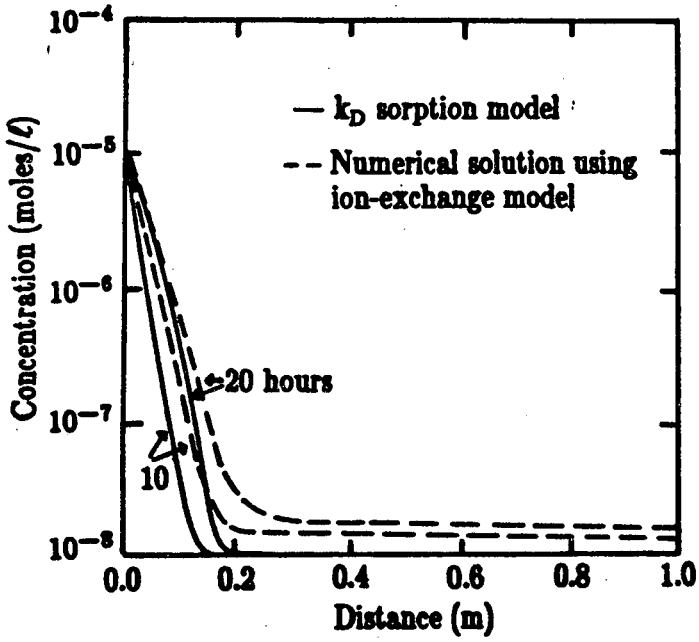

Fig. 1: Comparison of ion-exchange model with a constant-k_D sorption model when changes in background electrolyte concentrations are important.

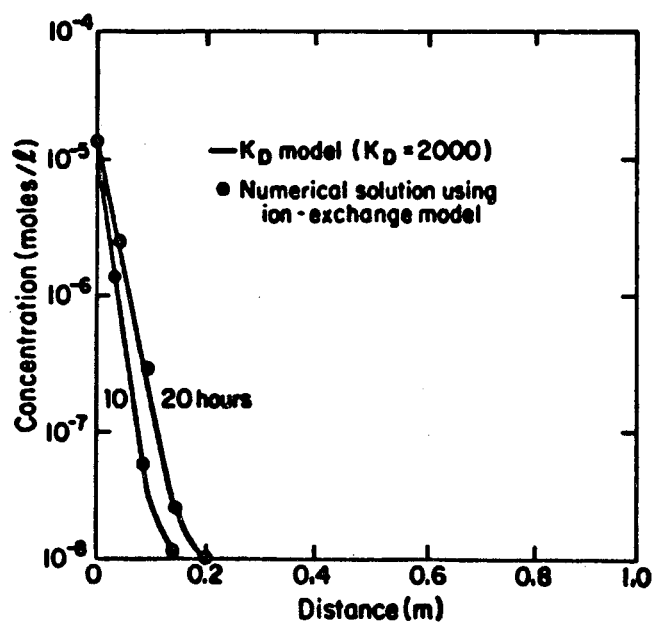

Fig. 2: Comparison of ion-exchange model with a constant-k_D sorption model when changes in background electrolyte concentrations are not important.

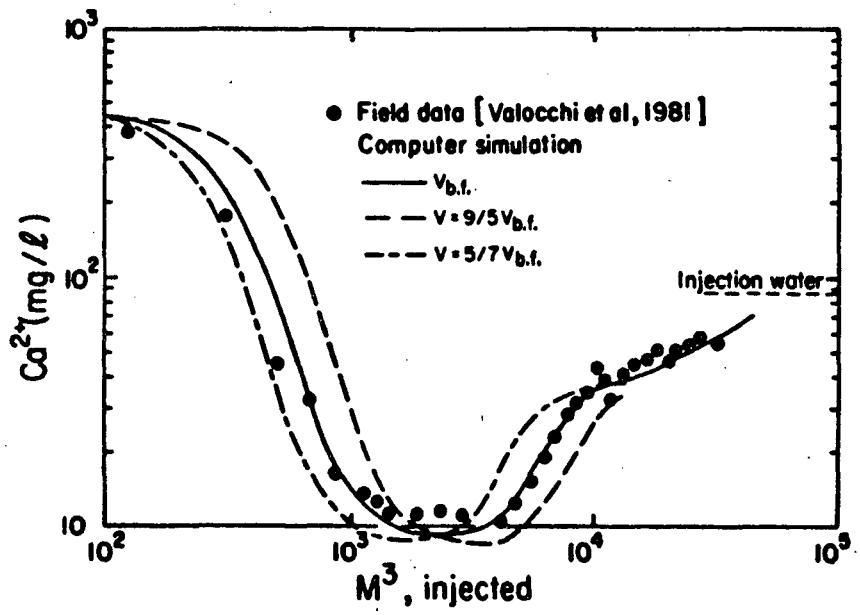

Fig. 3: Effects on numerical simulations of varying fluid velocity about the best-fit value ($v_{b.f.}$).

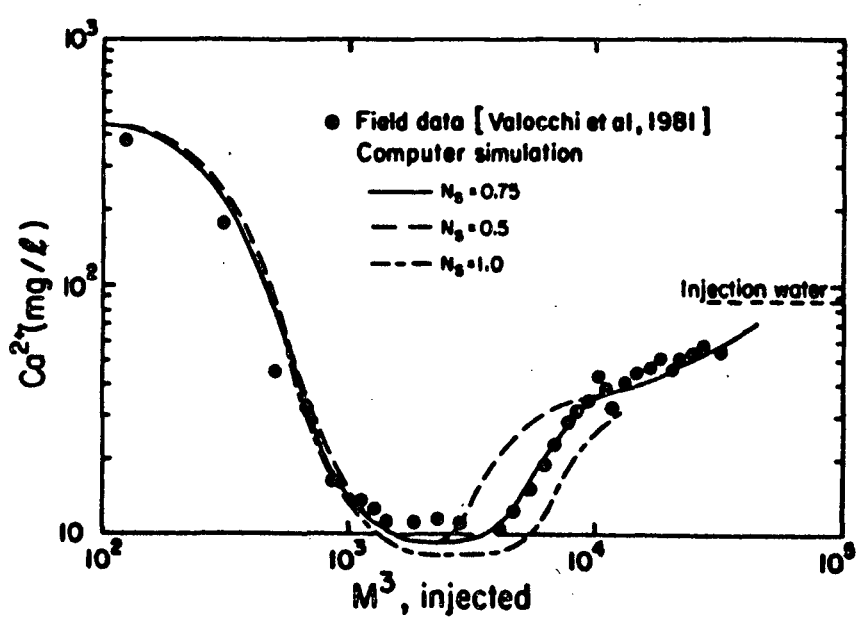

Fig. 4: Effects on numerical simulations of varying cation exchange capacity about the best-fit value (N_s=0.75).

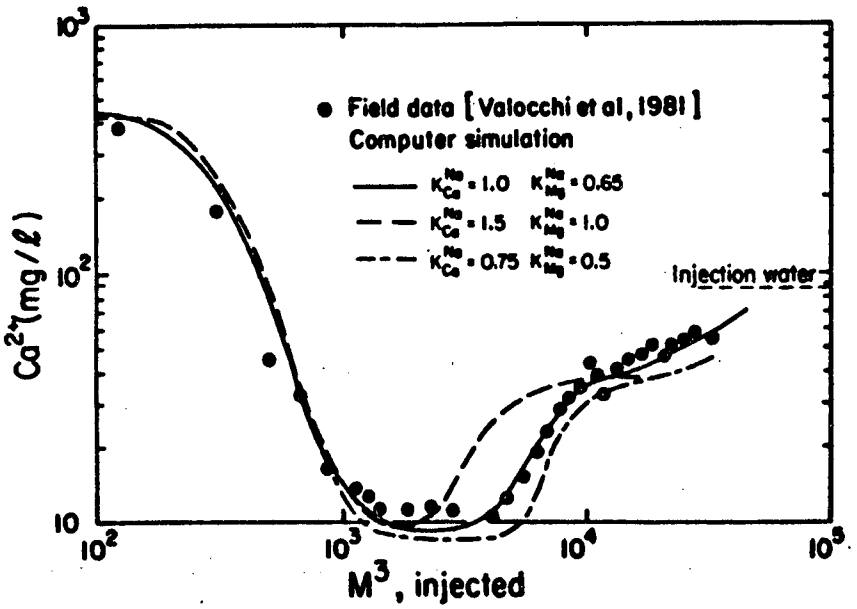

Fig. 5: Effects on numerical simulations of varying equilibrium exchange constants about the best-fit values (K_{Ca}^{Na}=1.0, K_{Mg}^{Na}=0.65).

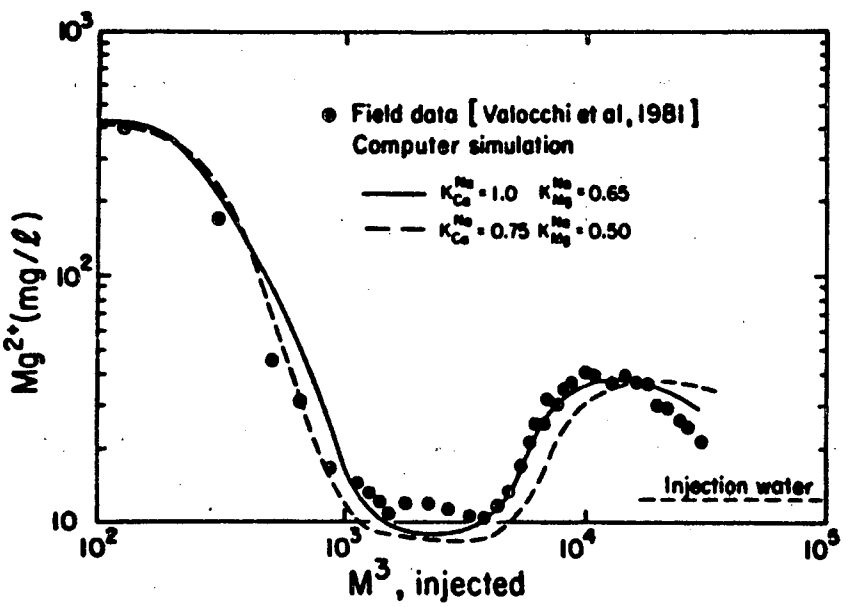

Fig. 6: Effect on numerical simulations of varying equilibrium exchange constants from the best-fit values (K_{Ca}^{Na}=1.0, K_{Mg}^{Na}=0.65).

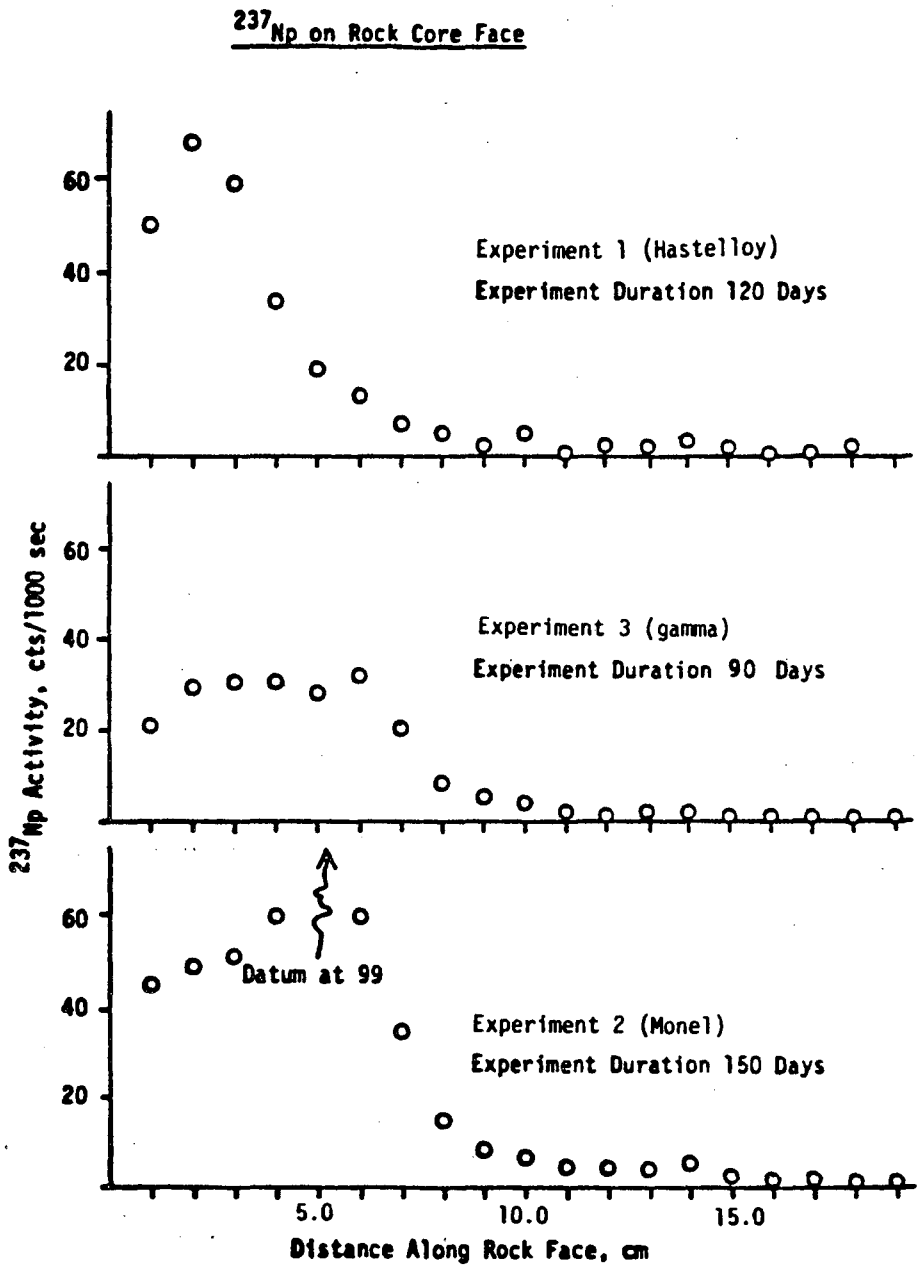

Fig. 7: Neptunium Distribution on the Surface of Split Basalt Cores from Three Analog Experiments. (Reproduced from Seitz et al., 1982)

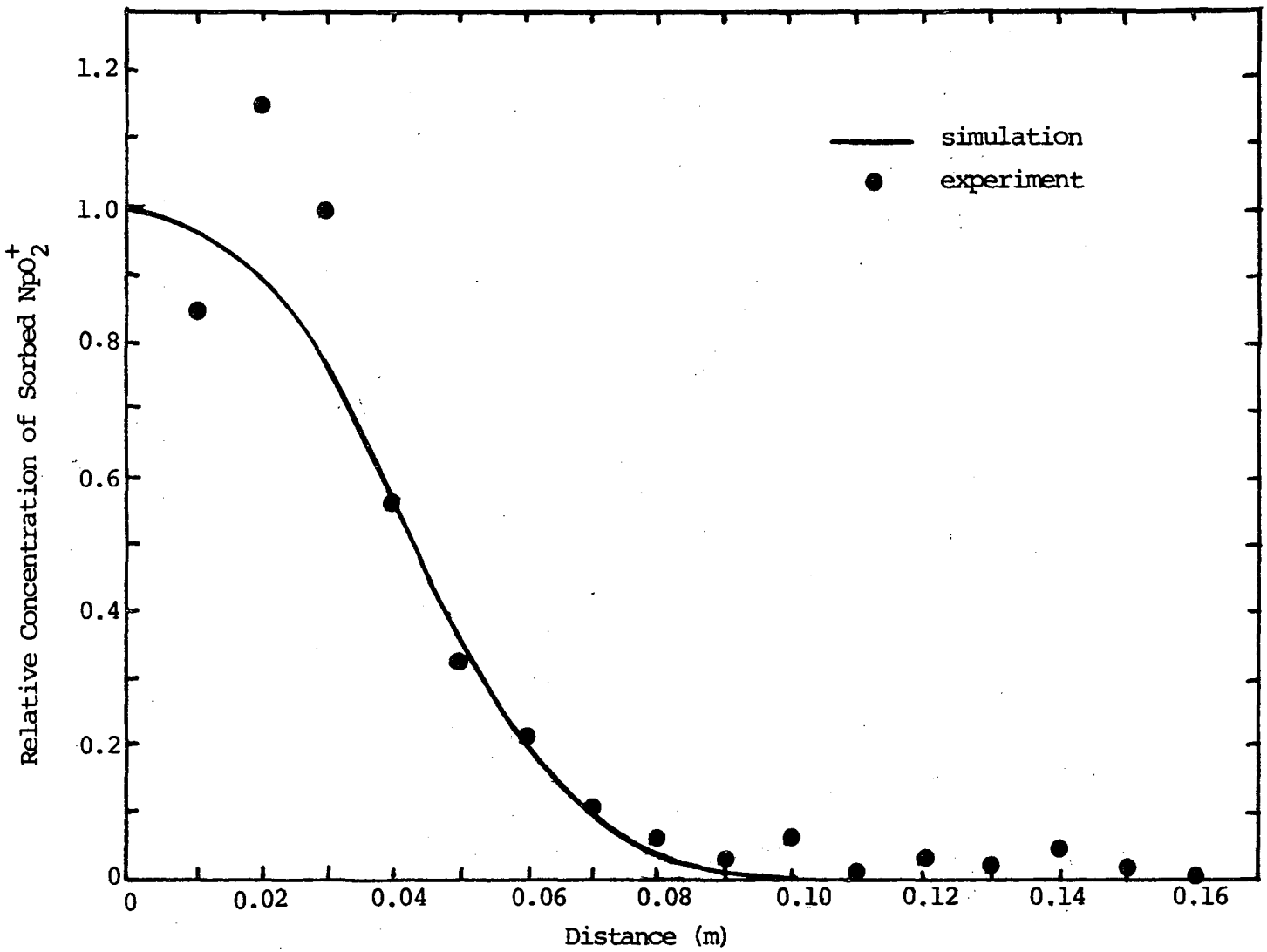

Fig. 8: Concentration of sorbed NpO_2^+ relative to sorbed concentration at inlet for Analog Experiment 1 at 120 days and fluid velocity of 0.066 m/day.

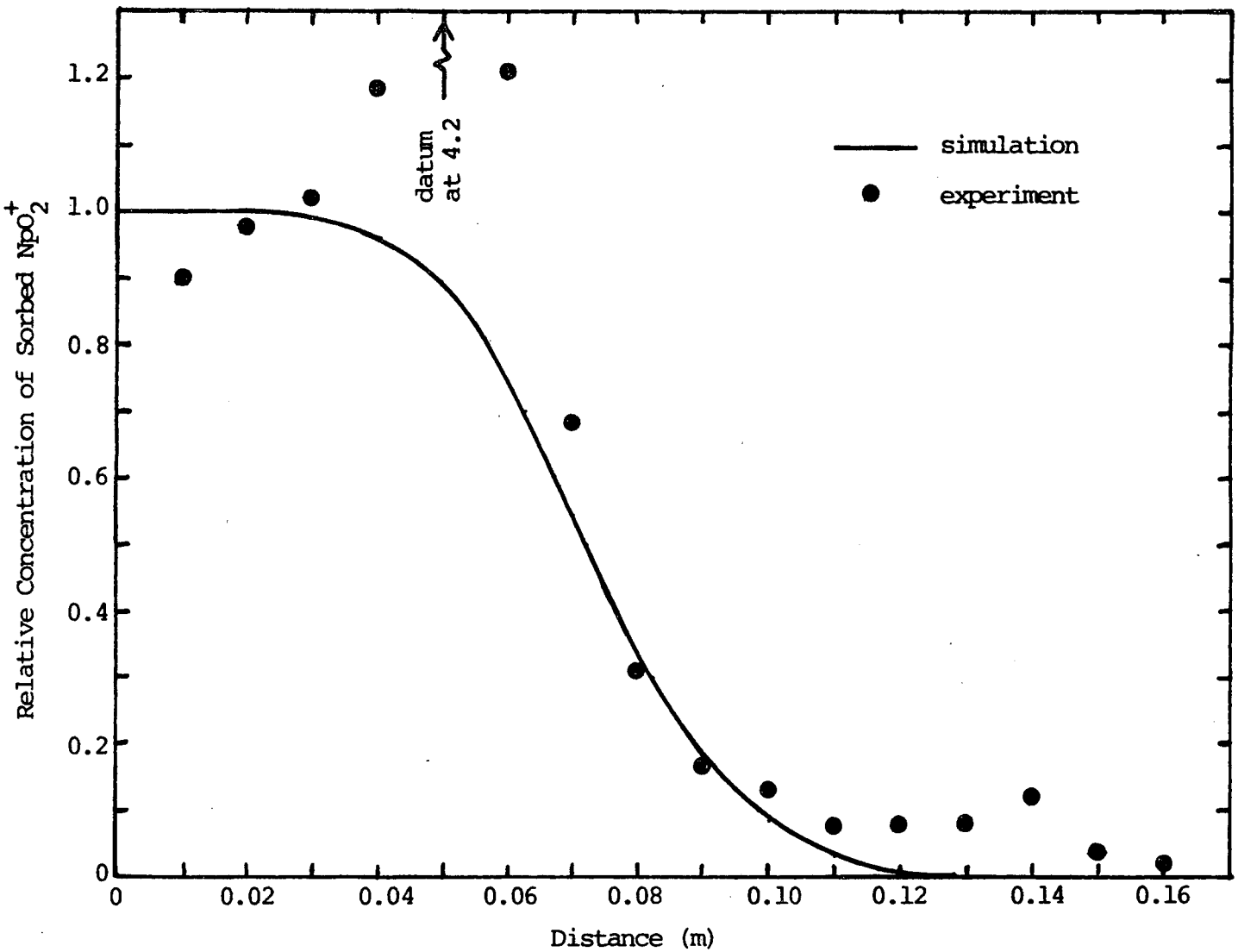

Fig. 9: Concentration of sorbed NpO_2^+ relative to sorbed concentration at inlet for Analog Experiment 2 at 150 days and fluid velocity of 0.088 m/day.

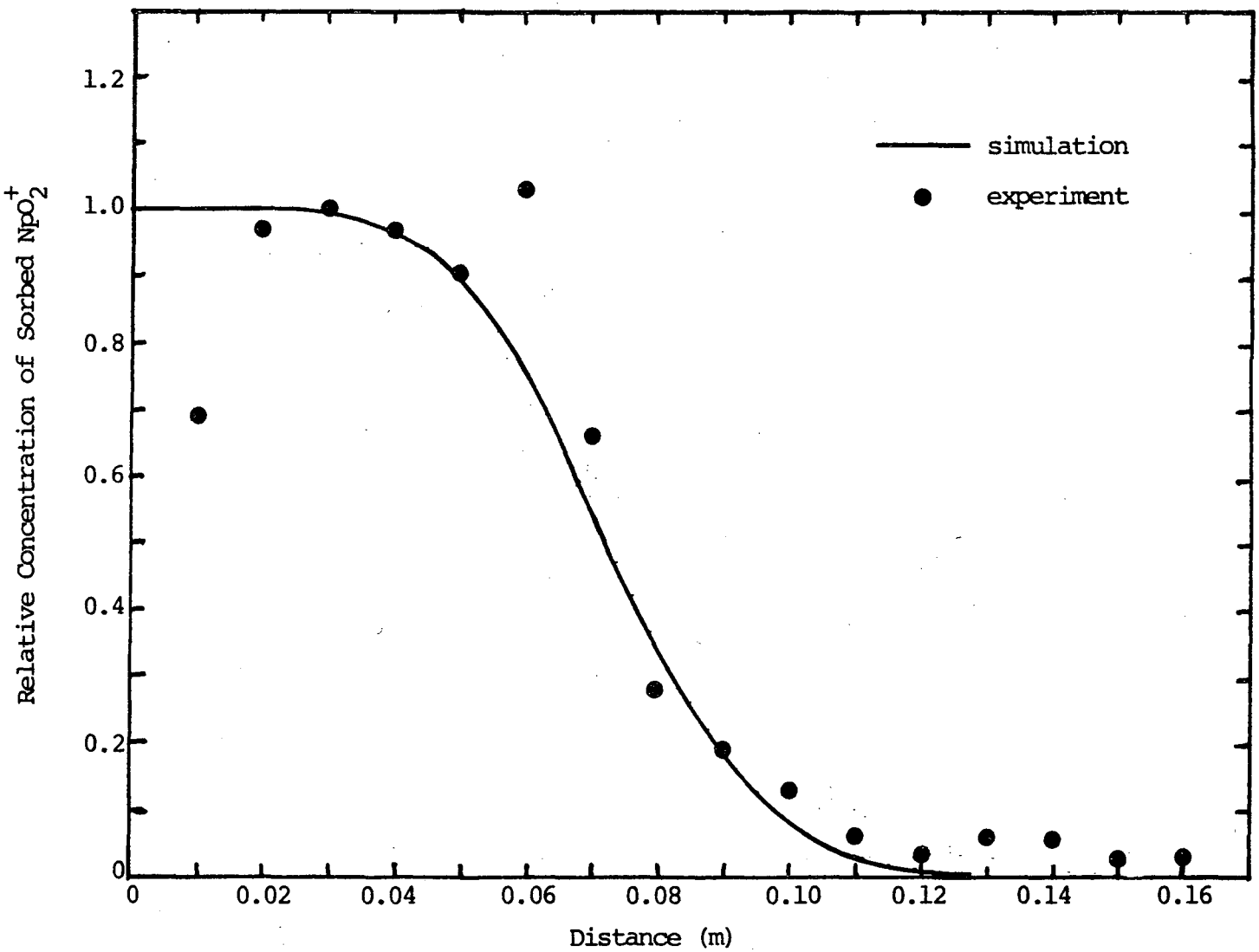

Fig. 10: Concentration of sorbed NpO_2^+ relative to sorbed concentration at inlet for Analog Experiment 3 at 90 days and fluid velocity of 0.153 m/day.

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