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Authors

Miller, C.W.
Benson, L.V.

Publication Date

1981-12-01

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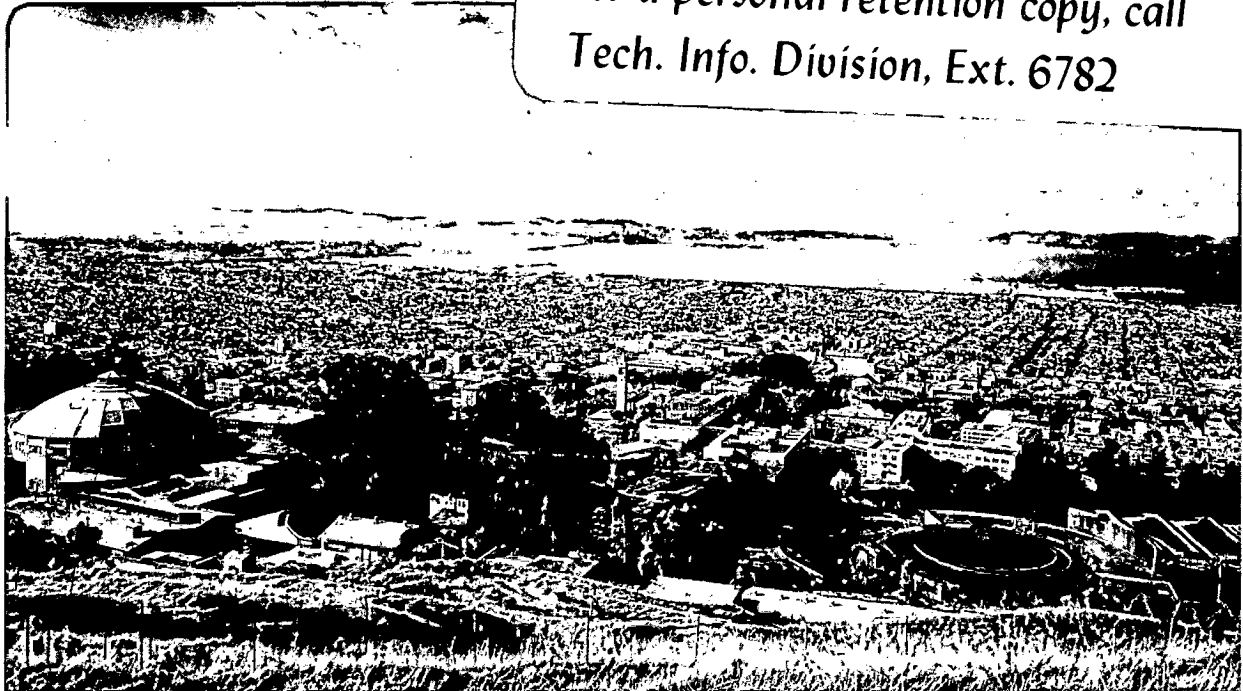
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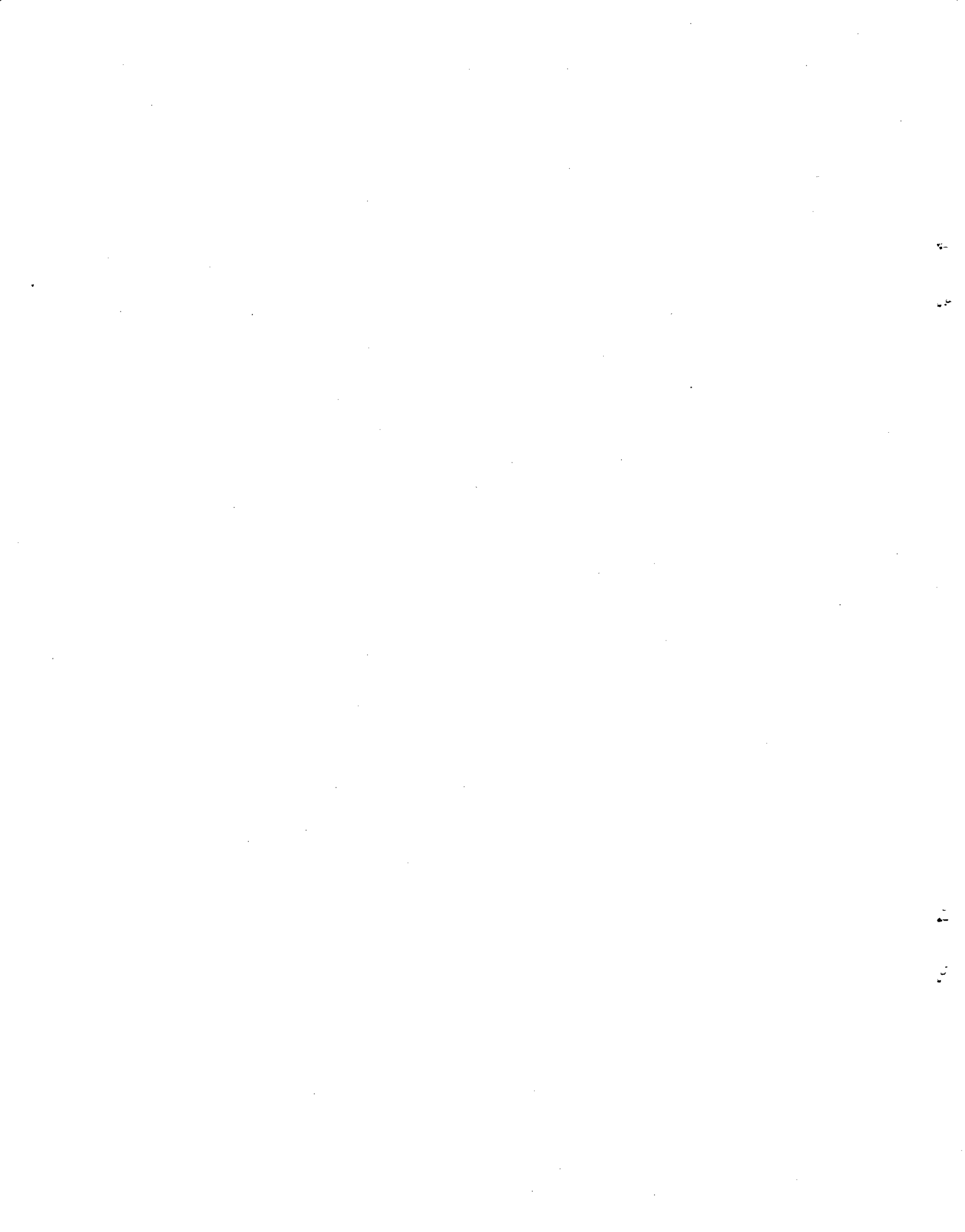Berkeley, California 94720

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C. W. Miller and L. V. Benson

Earth Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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ABSTRACT

The one-dimensional transport of solutes in a saturated porous medium has been solved using a numerical model CHEMTRN. This model includes dispersion/diffusion, convection, sorption, formation of complexes in the aqueous phase, and the dissociation of water. In the mass action equations describing complexation and/or sorption processes, the activities of the species in the aqueous phase are approximated using an activity coefficient model of the aqueous solution. The activity of the sorbed phase was approximated with an ideal mixing model. A solubility constraint was used at the inner boundary. The model was applied to a study of the migration of contaminant chemical species in groundwater. In particular the propagation of strontium and its complexes was studied. The effects of sorption, complexation, and water dissociation were considered. Results show that surface site competition results in cases where low levels of contaminant can be transported at distances much greater than that predicted using a constant k_D model. In addition, the pH level was buffered to a level of 10 near the waste form due to the incorporation of the solubility constraint. For the particular case studied, the incorporation of aqueous complexation did not significantly enhance strontium mobility.

INTRODUCTION

Prediction of the rates of migration of contaminant chemical species in groundwater moving through toxic waste repositories is essential to the assessment of the ability of a repository to meet standards for release rates. A large number of chemical transport models, of varying degrees of complexity, have been devised for the purpose of providing this predictive capability (see, for instance Holly and Fenske, 1968; Routson and Serne, 1972; Rubin and James, 1972; Ahlstrom et al., 1977; Grove and Wood, 1979; Strickert et al., 1979; Charbeneau, 1981; and Valocchi et al., 1981).

Two different methods have been applied to chemical transport models. One method is based on the plate theory of chromatography and integrates existing codes for equilibrium distributions of species with transport algorithms in a two-step procedure. This method was used, for example, by Routson and Serne (1972), Ahlstrom et al. (1977), Grove and Wood (1979), and Strickert et al. (1979). Applications of this method can be differentiated by the manner in which transport by dispersion-diffusion is accounted for. 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 based on a one-step procedure which 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 possessing a constant valued distribution coefficient (k_D). 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 et al. (1981), the method is more soundly based on chemical and thermodynamic principles and leads to a system of simultaneous, non-linear, 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.

The transport of dissolved chemical species through a water-saturated porous medium is influenced by a wide variety of chemical and physical processes including convection, dispersion-diffusion, formation of complexes in the aqueous phase, sorption and chemical precipitation. In general current models do not incorporate complete descriptions of the entire set of phenomena known to affect rates of chemical migration. More particularly, existing models which incorporate certain individual chemical processes suffer from omission of other possibly significant processes. Thus the reliability of predictions made through the application of these models is, at best, difficult to assess.

The study described here has as its principal objective the determination of the necessity for inclusion of specific chemical processes in models used to predict contaminant transport as well as the level of complexity needed to describe the chemical processes. The starting point for these investigations was a one-dimensional model (MCCTM) of dispersive-convective transport developed by Lichtner and Benson (1980). The model MCCTM provides for complexation in the aqueous phase and treats sorption of cations on the surface phase by equilibrium ion exchange. The ion-exchange algorithm in model MCCTM specifies a constant finite surficial density of ion-exchange sites and accounts for competition among

different cationic species for occupancy of sites. We have extracted the physical and chemical processes treated in model MCCTM and incorporated them in a more sophisticated transport model, CHEMTRN. Model CHEMTRN also includes algorithms describing the dissociation of water and the nonideality of both solvent and solute species. The treatment of pH-dependent reactions can be handled as well as computation of pH itself. An ideal mixing model has been applied to sorbed cationic species, i.e., the activity of a sorbed species has been set equal to its mole fraction.

Basic Equations and Method of Solution

The formation of complexes in the aqueous phase

$$a_{i1}A_1^{n_1} + a_{i2}A_2^{n_2} + \ldots + a_{iN}A_N^{n_N} \rightleftarrows B_i^{n_{c_i}}$$
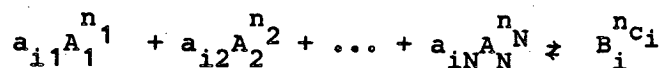
is described by the mass action expression

$$K_i = \frac{\left[B_i^{n_{c_i}}\right]}{\prod_j \left[A_j^{n_j}\right]^{a_{ij}}} \tag{1}$$

where the square brackets denote the thermodynamic activity of the dissolved species, K_i is the equilibrium constant, a_{ij} is the stoichiometric reaction coefficient, n_j is the charge of the bare ion, and n_{c_i} is the charge of the complex. The activities are approximated using the relation,

$$\left[A_j^{n_j}\right] = \gamma_j m_j \tag{2}$$

where γ_j is an activity coefficient and m_j is the concentration (molar) of solute species.

Equation 1 reduces to

$$K_i = \frac{\gamma_{c_i} m_{c_i}}{\prod_j \left(\gamma_j m_j\right)^{a_{ij}}} \tag{3}$$

where m_{c_i} is the molar concentration of the complex B_i.

The activity coefficients of the aqueous species (bare ions and complexes) are functions of temperature, pressure, and chemical composition. For this work, they are approximated using the Davies Equation,

$$\log_{10} \gamma_j = -\frac{1}{2} n_j^2 \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I\right] = \frac{1}{2} n_j^2 G' \tag{4}$$

where I is the ionic strength defined as

$$I = \frac{1}{2} \left[\sum_j n_j^2 m_j + \sum_i n_{c_i}^2 m_{c_i}\right] \tag{5}$$

where summations are taken over all bare ions and all complexes in the aqueous phase and G' is the quantity in the brackets in (4). The activity of water is taken to be unity.

The sorption of ions and complexes on the solid phase is modeled by an ion exchange process. For species $A_1^{n_1}$ exchanging with species $A_2^{n_2}$,

$$n_2 A_1^{n_1}(aq) + n_1 \bar{A}_2 \rightleftharpoons n_2 \bar{A}_1 + n_1 A_2^{n_2}(aq)$$
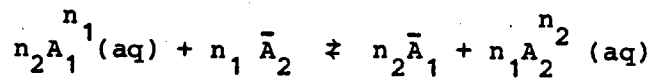
where $\bar{A}_j$ denotes the sorbed component. This reaction can also be described by a thermodynamic equilibrium constant

$$K_{eq} = \frac{\left[\bar{A}_1\right]^{n_2} \left[A_2^{n_2}\right]^{n_1}}{\left[A_1^{n_1}\right]^{n_2} \left[\bar{A}_2\right]^{n_1}} \tag{6}$$

where the square brackets again denote activities. The activities in the aqueous phase are expressed as $\gamma_j m_j$. For the surface phase, an ideal solution is assumed where

$$\left[\bar{A}_j\right] = \bar{m}_j / \bar{m}_T$$

and $\bar{m}_j$ is the concentration of species j on the surface phase and $\bar{m}_T$ is the total concentration sorbed on the surface phase given by

$$\bar{m}_T = \sum_j \bar{m}_j \qquad (7)$$

where the summation is over all sorbed species. The units of $\bar{m}_j$ and $\bar{m}_T$ are expressed as moles/liter solution. These units can be related to the more conventional ones (moles/gm solid) used for the sorbed phase by dividing $\bar{m}_j$ by $\rho_s (1-\varphi) 10^3/\varphi$ where ρ_s is the the density of the solid phase, and φ is the porosity of the porous medium. An effective equilibrium constant, K_2^1, is used to model the ion exchange process and (6) is replaced by

$$K_2^1 = \left[\frac{(\bar{m}_1/\bar{m}_T)^{n_2}}{(\gamma_1 m_1)^{n_2}}\right] \left[\frac{(\gamma_2 m_2)^{n_1}}{(\bar{m}_2/\bar{m}_T)^{n_1}}\right] \quad . \qquad (8)$$

For N_a sorbed species, (8) provides N_a-1 relationships. To complete the set of equations for $\bar{m}_j$, it is assumed that the total number of surface sites per liter solution, N_s, available for ion exchange is constant,

$$N_s = \sum_{j=1}^{N_a} n_j \bar{m}_j \qquad . \qquad (9)$$

This concentration of sites for a solid whose surface density is constant over the pH range of interest can be determined from the cation exchange capacity (meq/gm solid), CEC, or

$$N_S = (CEC) \, \rho_S \, \frac{1 - \phi}{\phi} \quad .$$

Both complexed and bare forms of an ionic component are subject to transport by dispersion/diffusion and convective processes. These forms are also subject to sorption processes and are therefore associated with the surface phase at least a portion of the time. The total concentration of species A_j present in the aqueous phase is

$$W_j = m_j + \sum_{i=1}^{N_c} a_{ij} \, m_{c_i} \qquad (10)$$

where N_c is the total number of complexes in the aqueous phase. Considering the mass balance of species A_j on a volume element of the fluid (in contrast to the porous medium), the one-dimensional transport of A_j is written as

$$L\left(W_j\right) = - \frac{\partial}{\partial t} \bar{m}_j \qquad (11)$$

where the operator L is defined as

$$L = \left(\frac{\partial}{\partial t} - D \frac{\partial^2}{\partial x^2} + v \frac{\partial}{\partial x} \right) \quad . \qquad (12)$$

D is the dispersion/diffusion coefficient and v is the actual fluid velocity, i.e. the Darcy velocity divided by the porosity. For this work both D and v are assumed to be constant. If species j does not sorb, $\bar{m}_j = 0$.

The number of unknowns are $N_b + N_a + N_c$ where N_b is the number of bare ions, N_a is the number of sorbed ions and sorbed complexes, and N_c is the number of complexes present in the aqueous phase. Therefore, $N_a + N_b + N_c$ equations are needed for solution of this system. For (11), $j = 1$ to N_b giving N_b equations. The mass action relation, (3), provides N_c equations for the complexes. There are $N_a - 1$ relationships of the form of (8); and (9) provides the final relationship needed. The activity coefficients are given by (4) with $\bar{m}_T$ defined by (7). Therefore a sufficient number of equations exist and can be used to determine $\bar{m}_j$, m_j and m_{c_i}.

The equations have been solved using the method of lines, i.e. the partial differential equations (11) are discretized in space leading to a set of ordinary differential equations (ODE's). If (11) is discretized in space, the result is

$$\frac{d}{dt} W_{j,n} + \frac{d}{dt} \bar{m}_{j,n} = \frac{D}{(\Delta x)^2} \left(W_{j,n+1} - 2W_{j,n} + W_{j,n-1} \right)$$

$$- \frac{v}{\Delta x} \left(W_{j,n} - W_{j,n-1} \right) \qquad (12)$$

where j denotes the species and n the spatial position. The unknowns are m_j, $\bar{m}_j$ and m_{c_i}. However $\bar{m}_j$ and m_{c_i} can be expressed as a function of all the bare ion concentrations. Using (3), m_{c_i} can be determined i.e.

$$m_{c_i} = \frac{K_i \prod_j (\gamma_j m_j)^{a_{ij}}}{\gamma_{c_i}} \qquad . \quad (13)$$

From (9), an expression for $\bar{m}_j$ can be determined, i.e.,

$$N_s = \sum_{\ell=1}^{N_a} n_\ell \, \bar{m}_\ell = n_j \bar{m}_j + \sum_{j \neq \ell} n_\ell \, \bar{m}_\ell \qquad . \qquad (14)$$

However, using (8)

$$\bar{m}_\ell = \frac{(K_j^\ell)^{(1/n_j)} \, \bar{m}_j^{(n_\ell/n_j)} \, \gamma_\ell m_\ell \, \bar{m}_T^{(1-n_\ell/n_j)}}{(\gamma_j m_j)^{(n_\ell/n_j)}} \qquad ; \qquad (15)$$

$$N_s = n_j \, \bar{m}_j + \sum_{\ell \neq j} \frac{n_\ell (K_\ell)^{(1/n_j)} \, \bar{m}_j^{(n_\ell/n_j)} \, \gamma_\ell m_\ell \, \bar{m}_T^{(1-n_\ell/n_j)}}{(\gamma_j m_j)^{n_\ell/n_j}} \qquad . \qquad (16)$$

The term $\bar{m}_T$ does contain the unknowns $\bar{m}_\ell$ so an iterative procedure is

needed to solve (15) and (16) for $\bar{m}_j$.

To have (12) written in terms of m_ℓ's only, it is necessary to provide

provide $\partial m_{c_i}/\partial m_\ell$ and $\partial \bar{m}_j/\partial m_\ell$. The former expression can be obtained

from (13):

$$\frac{\partial m_{c_i}}{\partial m_\ell} = m_{c_i} \left[\frac{a_{i\ell}}{m_\ell} + \sum_j \frac{a_{ij}}{\gamma_j} \frac{\partial \gamma_j}{\partial m_\ell} - \frac{1}{\gamma_{c_i}} \frac{\partial \gamma_{c_i}}{\partial m_\ell} \right] \qquad | \quad (17)$$

where $\partial \gamma_j / \partial m_\ell$ is obtained from (4). The required expression is

$$\frac{\partial \gamma_j}{\partial m_\ell} = - \gamma_j n_j^2 \frac{\partial G'}{\partial I} \frac{\partial I}{\partial m_\ell} \quad \log_e 10 = - \gamma_j \, n_j^2 \frac{\partial G}{\partial I} \frac{\partial I}{\partial m_\ell} \qquad (18)$$

where

$$\frac{\partial G}{\partial I} = \left(\frac{0.25}{\sqrt{I} \, (1 + \sqrt{I}} - 0.15 \right) 2.3 \qquad (19)$$

and

$$\frac{\partial I}{\partial m_\ell} = \frac{\frac{1}{2} n_\ell^2 + \frac{1}{2} \sum_{i=1}^{N_c} n_{c_i}^2 a_{i\ell} m_{c_i}/m_\ell}{1 + \frac{1}{2} \frac{\partial G}{\partial I}\left[\sum_{i=1}^{N_c} n_{c_i}^2 m_{c_i}\left(\sum_j a_{ij} n_j^2 - n_{c_i}^2\right)\right]}$$

(20)

The expression for $\partial \bar{m}_j / \partial m_\ell$ is obtained from (16):

$$\frac{\partial \bar{m}_j}{\partial m_\ell} = \frac{\bar{m}_j}{m_\ell} \delta_{j\ell} - \frac{n_\ell \bar{m}_\ell \bar{m}_j}{N_s m_\ell} + \frac{\bar{m}_j}{N_s} \frac{\partial G}{\partial I} \frac{\partial I}{\partial m_\ell}\left[\sum_{k \neq j} n_k^2 \bar{m}_k (n_k - n_j)\right]$$

(21)

$$- \frac{\bar{m}_j}{N_s}\left[\frac{n_j \bar{m}_\ell}{N_s m_\ell} - \sum_{k \neq j} n_j n_k \bar{m}_k (n_k - n_j) \frac{1}{N_s} \frac{\partial G}{\partial I} \frac{\partial I}{\partial m_\ell}\right]\left[\sum_{k \neq j} n_k \bar{m}_k \left(1 - \frac{n_k}{n_j}\right)\right]$$

Equation 12 then gives a set of equations for m_j

$$\frac{d}{dt} m_{j,n} + \sum_i a_{ij} \sum_\ell \left(\frac{\partial m_{c_i}}{\partial m_\ell} \frac{dm_\ell}{dt}\right) + \sum_\ell \left(\frac{\partial \bar{m}_j}{\partial m_\ell} \frac{\bar{d}m_\ell}{dt}\right)_n =$$

$$\frac{D}{(\Delta x)^2}\left[m_{j,n+1} - 2m_{j,n} + m_{j,n-1} + \sum_i a_{ij}\left(m_{c_i,n-1} - 2m_{c_i,n} + m_{c_i,n-1}\right)\right]$$

$$\frac{-v}{\Delta x}\left[m_{j,n} - m_{j,n-1} + \sum_i a_{ij}\left(m_{c_i,} - m_{c_i,n-1}\right)\right].$$

(22)

Given the initial and the boundary conditions, these equations were solved using the solver LSODI (Hindmarsh 1980).

Initially, uniform conditions are assumed throughout the porous medium. The total aqueous concentration of each species is given and (3) is used to determine an equilibrium distribution of species. The concentration of sorbed ions is determined from (8) and the total concentration of sites available for sorption. Different boundary conditions are possible with CHEMTRN. At the inner boundary, a concentration boundary condition was used where the magnitude of the concentration at that boundary was determined using a solubility constraint,

$$K_{12} = [A_1] [A_2].$$

(23)

A semi-infinite system is modelled. Far from the waste form, a no flux condition was imposed. This boundary condition was imposed far enough away from the inner nodes so it did not affect the solution at these points.

In many chemical systems, the hydrogen ion can be considered a master variable since many chemical reactions can be written in terms of its activity or concentration. In an aqueous solution, the dissociation of water is an important source of hydrogen ions, i.e,

$$H_2O = H^+ + OH^-. \tag{24}$$

Current chemical transport models do not incorporate reaction (24). Since calculations involving solubility, sorption, and complexation often depend on pH, failure to account for the dissociation of water results in incorrect estimates of chemical migration; therefore, we have included this chemical phenomenon in CHEMTRN.

To avoid convergence problems, CHEMTRN solves for a dummy concentration, y, defined by

$$y = m_{H^+} - m_{OH^-} \tag{25}$$

This method is employed since consideration of a mass balance equation for either H^+ or OH^- must include a change in the concentration of water, a change which is extremely small relative to changes in the hydrogen ion concentration.

To solve for y, a slight modification must be made to the mass balance equations for H^+ and OH^-. The mass balance equation for hydrogen is

$$L \left(m_{H^+} + \sum_i a_{i,H^+} m_{c_i} \right) + \frac{\partial}{\partial t} \bar{m}_{H^+} = - \frac{\partial}{\partial t} m_{H_2O}, \tag{26}$$

and for the hydroxyl ion

$$L \left(m_{OH^-} + \sum_i a_{i,OH^-} \, m_{c_i} \right) = - \frac{\partial}{\partial t} \, m_{H_2O} \tag{27}$$

If (26) is subtracted from (25), the result is

$$L \left[y + \sum_i \left(a_{i,H^+} - a_{i,OH^-} \right) m_{c_i} \right] + \frac{\partial}{\partial t} \, \bar{m}_{H^+} = 0 . \tag{28}$$

An additional relationship is obtained from the mass action equation for

the dissociation of water i.e.,

$$[H^+] \, [OH^-] = K_W \tag{29}$$

where K_W s the equilibrium coefficient for (24) and is given as $10^{-13.99}$

at 25 C. Given (25), (28) and (29), the changes in H^+ and OH^- can be

determined without solving explicitly for changes in the concentration

water.

APPLICATION TO CONTAMINANT TRANSPORT

Model CHEMTRN was used to investigate the magnitudes of various chemical

processes on the propagation of radionuclides through a porous medium.

One-dimensional flow was assumed. A radionuclide source function (waste-

form) is located at x = 0 and is open to the groundwater system. Although

there exist many radioactive species that could be studied, the decision was

made to simulate the propagation of strontium and its complexes. This system

was chosen primarily because of consideration of the availability of data.

In order to test the effects of composition on radionuclide propagation,

the initial groundwater (supporting electrolyte) composition was varied.

The supporting electrolyte consisted of NaCl or mixtures of NaCl and CaCl$_2$ dissolved in water. In all cases, a background level of 10^{-12} M SrCO$_3$ was used. In order to illustrate the application of (1) through (29) an example calculation is outlined in the Appendix.

A constant-concentration boundary condition at the canister was assumed. However, the actual concentration level for each situation was determined using the strontianite (SrCO$_3$) solubility constraint at 25 C

$$[Sr^{2+}] \ [CO_3^{2-}] = 10^{-9.25} \ . \tag{30}$$

and calculating the activity coefficients of Sr^{2+} and CO$_3^{2-}$. Because of variation in the initial groundwater compositions, the concentration of strontium at the boundary in equilibrium with strontianite was different for the various cases considered.

Variations of the total concentrations of strontium and carbonate at the inner boundary result from changes of ionic strength. As the ionic strength of groundwater is increased, the activity coefficients of Sr^{2+} and CO$_3^{2-}$ decrease. In order to maintain the relation indicated by (30), the concentrations of both Sr^{2+} and CO$_3^{2-}$ must therefore increase. The second boundary condition used was a zero-flux condition ($\partial m/\partial x = 0$) that was assumed to hold at a distance far from the canister.

Several different cases were run to illustrate the relative importance of the different chemical processes. In all examples, a diffusion/dispersion coefficient of 0.013 m^2/yr, a Darcy velocity of 0.04 m/yr, a porosity of 40 percent, and a solid density of 2.0 g/cm^3 were used. These numbers are reasonable values but rather arbitrary choices. The cation exchange capacity

(CEC) was 0.033 meq/g. This value was chosen so that the difference between the propagation rates of nonsorbed and sorbed species were not so great that their concentration fronts could not be displayed on the same grid. The sorptive properties of the ion exchanger correspond to a material having the ion exchange equilibrium coefficients characteristic of Camp Berteau montmorillonite and the cation exchange capacity of quartz (~1/300 the CEC of montmorillonite).

The first example (Figure 1) illustrates the general importance of the sorption process on radionuclide retardation. The figure shows the concentration of Sr^{2+} in the aqueous phase as a function of distance after a time period of five years. Two cases were considered. In the first case, Sr^{2+} was not allowed to sorb; in the second case, Sr^{2+} was allowed to sorb via an ion exchange model. The initial NaCl background concentration used for this calculation was 0.001 M. In these calculations, aqueous-phase activity coefficients were set equal to unity and complexes were not permitted to form. Therefore, the boundary value concentration of Sr^{2+} was held at 2.37×10^{-5} M via the constraint indicated by (30). The results of these calculations illustrate the fundamental importance of sorption (ion exchange) on Sr^{2+} mobility. Figure 1 shows that the sorption of Sr^{2+} (as measured by the position of the leading edge) decreases the mobility by approximately 90 per cent. Note in this and subsequent figures that the distance traveled by a sorbable cation should be divided by 300 in order to scale properly the transport distance of the cation relative to montmorillonite's actual CEC.

Many workers in the area of radionuclide transport have assumed that radionuclide retardation can be calculated using a constant retardation

factor. For a system containing strontium, this factor is related to the amount of strontium sorbed on the solid and the amount of strontium left in the liquid by the expression

$$\bar{c} = k_D c$$

where $\bar{c}$ is in moles/g solid, c is in moles/cm^3, and k_D is the constant retardation factor (cm^3 solution/g solid), commonly known as the distribution coefficient. Elementary ion exchange theory predicts that the distribution coefficient is approximately constant when the concentration of the ion of interest is extremely low relative to the concentration of the supporting electrolyte. Under these conditions the ionic strength of the solution is determined mainly by the supporting electrolyte and is approximately constant; therefore, activity coefficients of both sorbed and dissolved species remain constant. In addition, since the anionic composition of the solution remains constant, the degree and effects of complexation are invariant.

For example, given a binary ion-exchange of equally-charged ionic species, the distribution coefficients are given by

$$k_{D_1} = \frac{10^3 CEC}{n\left(c_1 + \dfrac{1}{K_{eq}} \dfrac{\gamma_2 c_2}{\gamma_1}\right)}$$

$$k_{D_2} = \frac{10^3 CEC}{n\left(c_2 + K_{eq} \dfrac{\gamma_1 c_1}{\gamma_2}\right)}$$

where n is the ionic charge, K_{eq} is an equilibrium constant for the reaction $A_1^n(aq) + \bar{A}_2 = \bar{A}_1 + A_2^n(aq)$ and the units of c_1 and c_2 are as given above.

If $c_1 \gg c_2$ and remains so, then site competition is not important and the distribution coefficient will not change significantly. However, when the aqueous phase concentrations of sorbable ions are comparable, then site competition, complexation, and ionic strength effects are expected to result in variable distribution coefficients.

To investigate the effects of these chemical phenomena on the variability of the distribution coefficient, several calcualations of strontium transport were made. There are five general categories of calculations which differ in their degree of chemical complexity (Table 1):

1. Binary ion exchange of Sr^{2+} for Na^+ on a Na-loaded substrate.

2. Ternary ion exchange wherein Na^+, Ca^{2+}, and Sr^{2+} ions compete for a finite number of sites initially occupied by Na^+ and Ca^{2+}.

3. Binary ion exchange coupled with complexation in the presence of a single supporting electrolyte.

4. Binary ion exchange coupled with complexation and water dissociation in the presence of a single supporting electrolyte.

5. Ternary exchange coupled with complexation and water dissociation.

In Table 1 are listed the initial concentrations of Na^+ and Ca^{2+}. As noted before, the initial concentration of Sr^{2+} is always assumed to be 10^{-12} M. Also included in the table is the total amount of Sr^{2+} at the boundary determined from the solubility constraint. The reactions (Table 2) included in each case are also indicated in Table 1, as well as distribution coefficients for both Sr^{2+} and Na^+ calculated from initial concentrations, $k_{D,i}$, and from boundary concentrations $k_{D,b}$. Table 2 shows that k_D values can vary significantly across the front where the concentration of Sr^{2+} changes from its boundary to its initial value.

Figures 2a through 2d are graphs of the aqueous concentration of Sr^{2+} as a function of distance. These figures illustrate the effects of different values of concentrations of the NaCl supporting electrolyte on Sr^{2+} transport. Reactions 1 and 2 (Table 2) are considered. It is obvious from the figures that the higher the NaCl concentration, the lower the degree of Sr^{2+} sorption.

Macroscopically the tendency of an ion to be sorbed depends on its concentration in the aqueous phase relative to the concentration of other sorbable ions, the selectivity of the sorptive substrate for an ion relative to other ions, and the number of sites on the sorptive substrate. Given similar concentrations of sorbable ions in the aqueous phase, the selectivity of Sr^{2+} is higher than the selectivity of Na^+. However, as the concentration of Na^+ is increased, the enhanced selectivity for Sr^{2+} is outweighed by the Na^+ concentration effect and the distribution coefficient of Sr^{2+} decreases.

As the concentration of Na^+ is decreased relative to that of Sr^{2+} a very interesting phenomenon occurs. The amount of Na^+ displaced from the clay by Sr^{2+} increases across the sharp front depicted in Figures 2a through 2d. The enhanced Na^+ concentration propagates downstream together with a depleted Sr^{2+} concentration resulting in a "enhanced concentration effect" wherein low levels of Sr^{2+} are mobilized well beyond the region of the sharp front.

Figure 2b shows this effect when the initial background level of Na^+ is 1×10^{-4} M. This effect increases significantly as the Na^+ level is decreased to 7×10^{-5} M (Figure 2c) and to 3×10^{-5} M (Figure 2d). The Sr^{2+} ion transits ahead of the steep front at a slightly higher level than

its initial concentration in the supporting electrolyte and can propagate to significant distances ahead of the front. In Figures 2d and 3 the aqueous concentration of Sr^{2+} is plotted as a function of distance at 10 years and at 20 years respectively. It is evident that concentration levels an order of magnitude higher than the initial concentration occur far downstream from the location of the base of the sharp front.

Groundwaters generally contain several cations other than sodium which compete with strontium and with each other for exchange sites. To examine the effects of this phenomenon a third cation, calcium, was added to the supporting electrolyte mixture in amounts consistent with its occurrence in natural ground waters (Table 1).

Figures 4a and 4b illustrate the effects of adding a third sorbable ion to the aqueous system. The reactions 1, 2, and 3 (Table 2) are pertinent. (Note that each of these reactions involve aqueous and sorbed hydrogen ions; equilibrium constants for exchange reactions between the other cations, Na^+, Sr^{2+}, and Ca^{2+}, are computed by combining appropriate pairs of these reactions; therefore, the concentrations of aqueous and sorbed hydrogen ions cancel out of the computations).

Table 1 also shows that calculated k_D's have been reduced from the case where Ca^{2+} is not included in the ground water. For 10^{-3} M Na^+, the boundary k_D is reduced from about 1900 to approximately 50 when a concentration of 10^{-3} M Ca^{2+} is added to the ground water.

When Ca^{2+} is omitted from the supporting electrolyte, sorption of Sr^{2+} causes the strontium concentration in the aqueous phase to drop to its initial value (10^{-12} M) at a distance of 0.1 m after ten years. However, the addition

of 10^{-3} M Ca^{2+} lowers the degree of strontium sorption such that the aqueous Sr^{2+} concentration remains above its initial value for a full meter after ten years.

It is also interesting to note that, when both Na^+ and Ca^{2+} are present in the groundwater, the clay sites are largely occupied by calcium. For a groundwater containing 10^{-4} M Na^+ and 10^{-5} M Ca^{2+}, Ca^{2+} occupies about 100 sites to every one site occupied by Na^+. Therefore when Sr^{2+} is sorbed, Ca^{2+} is the ion which is principally displaced (see Figure 4b). This increase in the aqueous phase concentration of Ca^{2+} leads again to the enhanced concentration effect observed in the case of binary exchange (Figures 2 and 3). The depleted level of Sr^{2+} must now compete with an increased Ca^{2+} concentration downstream, resulting in Sr^{2+} transiting ahead of the steep front.

The ions in the aqueous phase can also form complexes. It is possible for a radionuclide to propagate downstream from the canister as a complex to much greater distances and at much greater rates than would the bare ion, especially if that complex is uncharged or is negatively charged. To illustrate the effects of complexation, equilibrium complexation constants for $SrCO_3^0$ and $NaCO_3^-$ were added to the data base. Activity coefficients of solute species were calculated using the Davies equation. Figure 5a is a plot of the concentrations of bare ions (Sr^{2+} and Na^+) in the aqueous phase as a function of distance after five years for the binary ion exchange case with the complexes $SrCO_3^0$ and $NaCO_3^-$ forming in the aqueous phase (reactions 1, 2, 4, 6 of Table 2). Concentrations of the complexes ($SrCO_3^0$ and $NaCO_3^-$) are plotted in Figure 5b as a function of distance. The relative concentrations of these particular complexes are not particularly high. However, the effect of complexation on the transport of strontium is evident in Figure 5b where a low,

broad front of the strontium complex exists far in advance of the relatively

sharp front of the bare ion, Sr^{2+} (Figure 5a). The magnitude of the enhanced

concentration effect due to complexation is certainly trivial in this system;

however, certain other radionuclides can exist in highly complexed states,

e.g., the actinides. In such highly complexed systems this effect may signifi-

cantly effect the migration of radionuclides.

Inclusion of the dissociation of water can have significant effects on

the mobility of various solute species. Complexes such as HCO_3^-, $H_2CO_3^o$,

$SrOH^-$, $NaHCO_3^o$ and $NaOH^o$ can be included in the model. The formation of

these complexes affects the hydrogen ion balance (pH) in the aqueous phase

which, in turn, affects the solubilities of radionuclide-bearing solids,

their kinetics of dissolution, and the hydrogen ion concentration on exchange

sites.

Figures 6a and 6b illustrate the effects of both dissociation of water

and complexation on the transport of strontium (reactions 1, 2, 4-7 were

modeled). One effect is that a pH of approximately 10 is maintained near

the boundary despite the fact that the initial pH was varied from 6 to 10.

This buffering effect is principally due to the strontianite activity pro-

duct constraint coupled with the dissociation of water. It is an effect of

fundamental importance, since it suggests that the toxic waste form

can control certain facets of its surrounding chemical environment.

Accounting for the dissociation of water also allows the solution pH

to vary as a function of transport distance. Therefore, the amounts of OH^-

and CO_3^{2-} available for complexation also vary in a realistic manner, affect-

ing the amount of these species available for complexation with strontium

(Figure 6b). The effect of varying pH on the mobility of strontium is

negligible in this system since strontium is never strongly complexed
but the effect of pH variation on the mobility of the actinides could well
be significant.

Figures 7a and 7b show concentrations of bare ions and complexes respec-
tively as a function of distance after five years for a more complex case:
a ternary ion exchange process with an increased number of complexes. All
reactions in Table 2 were used for this case. Again, the pH near the waste
canister is buffered and remains approximately 10. The strontium is trans-
ported farther downstream in this case because of the presence of the calcium
ion.

SUMMARY AND CONCLUSIONS

CHEMTRN, a transport model which accounts for most chemical processes common to hydrochemical systems, has been developed and applied to a hypothetical study of contaminant transport. CHEMTRN provides for complexation in the aqueous phase and treats sorption as an equilibrium ion exchange process. The ion exchange algorithm specifies a constant finite surficial density of exchange sites and accounts for. competition among different cationic species for occupancy of those sites. CHEMTRN also includes algorithms describing the dissociation of water and the nonideality of both solvent and solute species.

Several calculations were made with CHEMTRN in order to determine the necessity for inclusion of specific chemical processes in this and other models used to predict contaminant transport. The hypothetical waste disposal system consisted of a strontianite waste source surrounded by a water-saturated porous backfill composed of montmorillonite.

From the results of these calculations, several conclusions can be drawn:

1. When the concentration of a positively charged radionuclide such as Sr^{2+} is extremely small, relative to the concentration of the supporting electrolyte (e.g., NaCl), the transport of the trace cation can be simulated adequately with a transport model based on a constant distribution coefficient (k_D). However, the distribution coefficient should be measured or calculated in a manner designed to duplicate exactly the situation expected to exist in the near-canister region at the time of loss of canister integrity. In addition, it should be noted that the definition of "trace" for each cation of interest should be determined experimentally.

2. When the concentration of the radionuclide is comparable to the concentration of the supporting electrolyte, a constant distribution coefficient model is inadequate to simulate the mass transport process. This fact is evidenced by the orders of magnitude difference in the value of the distribution coefficient calculated to exist across the propagating front.

3. Migration of a non-trace radionuclide far forward of its sharp front was found to occur when surface site constraints were accounted for in the model. This phenomenon is not adequately accounted for in models which employ constant distribution coefficients.

4. When the scope of the model was broadened to account for competition for a fixed number of surface sites by more than two species, a significantly greater degree of mobility of strontium was noted.

5. Incorporation of aqueous complexation in the model does not significantly enhance the mobility of strontium, but the calculation does serve to illustrate qualitatively the importance of such phenomena. Other radionuclides such as the actinides will be strongly complexed in groundwater to the point that only a minimal fraction of the element may exist as positively charged species (Langmuir, 1978). Therefore, the incorporation of complexation phenomena in models of radionuclide transport appears a necessity for these radionuclides.

6. Allowing water to dissociate resulted in profound effects on the chemistry of the system. The dissociation of water coupled with boundary solubility constraint buffered the pH of the groundwater near the waste form at a value of 10, regardless of the value of the pH of groundwater. In addition, the inclusion of the dissociation

of water allows pH to vary along the transport path. This, in turn, causes changes in both the saturation state of the system and in the amount and type of radionuclide complexes.

In the future CHEMTRN will be modified in order to account for chemical precipitation phenomena. In addition a model of sorption which includes surface ionization and complexation will also be provided as an alternative to the existing ion exchange model. This option will provide a more realistic treatment of earth materials whose surficial site density is not constant, but is a function of pH.

ACKNOWLEDGEMENTS

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Appendix 1

An example is given below to illustrate the use of (1) - (29).
The particular system chosen has Na^+, Sr^{2+}, H^+, CO_3^{2-}, Cl^-, OH^- as
basis species. These species can react to give $SrCO_3^o$, $SrOH^+$, $NaOH^o$,
$NaCO_3^-$, $NaHCO_3^o$, HCO_3^-, and $H_2CO_3^o$ as the principal complexes. Given
the equilibrium coefficients for each of these reactions, seven
equations of the form (3) can be written. For example, the reaction

$$2H^+ + CO_3^{2-} \rightleftharpoons H_2CO_3^o$$
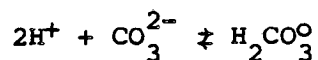
gives the equation

$$K_{H_2CO_3} = \frac{m_{H_2CO_3}}{\left(\gamma_{H^+} \, m_{H^+}\right)^2 \left(\gamma_{CO_3^{2-}} \, m_{CO_3^{2-}}\right)} \tag{A1}$$

The activity coefficient, $\gamma_{H_2CO_3}$, is equal to one since the valence is
zero. The activity coefficients of H^+ and CO_3^{2-} are determined from (4)
given the ionic strength of the aqueous phase. The ionic strength of
this system is calculated from

$$I = \frac{1}{2} \left(m_{Na^+} + 4m_{Sr^{2+}} + m_{H^+} + 4m_{CO_3^{2-}} + m_{Cl^-} \right.$$

$$\left. + m_{OH^-} + m_{NaCO_3^-} + m_{SrOH^+} + m_{HCO_3^-} \right) \tag{A2}$$

The porous material is assumed to have a negative charge so that
the only species which can sorb by an ion exchange process are Na^+,
Sr^{2+}, H^+ and $SrOH^+$. Ion exchange equilibrium constants for the reaction
of Na^+ and Sr^{2+} exchanging with H^+ are available (Benson, 1980); however,
data for $SrOH^+$ is not available. Therefore only Na^+, Sr^{2+} and H^+ are
assumed to sorb.

For the reaction

$$Na^+{}_{(aq)} + \bar{H} \rightleftharpoons \bar{Na} + H^+{}_{(aq)}$$
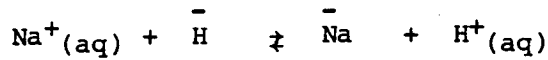
we can write

$$K^{\bar{Na}}_{\bar{H}} = \frac{\left(\bar{m}_{Na^+}/\bar{m}_T\right)\left(\gamma_{H^+}\,m_{H^+}\right)}{\left(\gamma_{Na^+}\,m_{Na^+}\right)\left(\bar{m}_{H^+}/\bar{m}_T\right)} \tag{A3}$$

where $\bar{m}_T = m_{Na^+} + m_{H^+} + m_{Sr^{2+}}$. When the exchanging ions have the same valence, the term $\bar{m}_T$ cancels out. For the three exchanging species, only two equations of the form A3 are available. However, the total number of sites is assumed to be constant so

$$N_s = \bar{m}_{Na^+} + 2\bar{m}_{Sr^{2+}} + \bar{m}_{H^+} . \tag{A4}$$

Transport equations for the change in the total concentration of each of the basis species at a point can be written:

$$L\left(W_{Sr}\right) + \frac{\partial}{\partial t}\,\bar{m}_{Sr} = 0 \tag{A5}$$

where m_{Sr} is the total concentration of strontium in the aqueous phase and is given by $m_{Sr^{2+}} + m_{SrOH^+} + m_{SrCO_3^o}$. The concentrations of the complexes are written as functions of the bare ion concentrations. For example from (A1), the concentration of H_2CO_3 is calculated to be

$$m_{H_2CO_3} = K_{H_2CO_3}\left(\gamma_{H^+}\,m_{H^+}\right)^2\left(\gamma_{CO_3^{2-}}\,m_{CO_3^{2-}}\right) . \tag{A6}$$

and is a function of $m_{Sr^{2+}}$, m_{OH^-}, etc. as well as a function of m_{H^+} and $m_{CO_3^{2-}}$. The activity coefficients are a function of the ionic strength which in turn is a function of all charged species (A2). Each of the complex concentrations can be written in a similar manner to (A6).

In addition, the sorbed ion concentrations, $\bar{m}_j$, can be written as functions of bare ion concentrations. First it is possible to write $\bar{m}_{Sr^{2+}}$ and $\bar{m}_{Na^+}$ in terms of $\bar{m}_{H^+}$ and the m_j's. For $\bar{m}_{Na^+}$, we have

$$\bar{m}_{Na^+} = \frac{K^{\bar{H}}_{\bar{Na}} \ \bar{m}_{H^+} \ \gamma_{Na^+} \ m_{Na^+}}{\gamma_{H^+} \ m_{H^+}} \tag{A7}$$

using (A3). After solving for $\bar{m}_{Sr^{2+}}$, and substituting into (A4), an equation for $\bar{m}_{H^+}$ results in

$$N_s = \bar{m}_{H^+} + 2 \ \frac{K^{\bar{H}}_{\bar{Sr}} \ \bar{m}_{H^+} \ \gamma_{Sr^{2+}} \ m_{Sr^{2+}}}{\gamma_{H^+} \ m_{H^+}} + \frac{K^{\bar{H}}_{\bar{Na}} \ \bar{m}_{H^+} \ \gamma_{Na^+} \ m_{Na^+}}{\gamma_{H^+} \ m_{H^+}} . \tag{A8}$$

If the derivatives of m_{c_i} and $\bar{m}_j$ are replaced by $\sum_{\ell} (\partial \bar{m}_{c_i}/\partial m_{\ell}) dm_{\ell}$ and $\sum_{\ell} (\partial \bar{m}_j/\partial m_{\ell}) \, dm_{\ell}$, as in (22) then the transport equations can be expressed in terms of m_j's only. For example

$$\frac{\partial m_{H_2CO_3}}{\partial m_{H^+}} = m_{H_2CO_3} \left(\frac{2}{m_{H^+}} + \frac{2}{\gamma_{H^+}} \ \frac{\partial \gamma_{H^+}}{\partial m_{H^+}} + \frac{1}{\gamma_{CO_3^{2-}}} \ \frac{\partial \gamma_{CO_3^{2-}}}{\partial m_{H^+}} \right) \tag{A9}$$

$$\frac{\partial m_{H_2CO_3}}{\partial m_{Sr^{2+}}} = m_{H_2CO_3} \left(\frac{1}{\gamma_{H^+}} \ \frac{\partial \gamma_{H^+}}{\partial m_{Sr^{2+}}} + \frac{1}{\gamma_{CO_3^{2-}}} \ \frac{\partial \gamma_{CO_3^{2-}}}{\partial m_{Sr^{2+}}} \right) \tag{A10}$$

and

$$\frac{\partial m_{HCO_3^-}}{\partial m_{H^+}} = m_{HCO_3^-} \left(\frac{1}{m_{H^+}} + \frac{1}{\gamma_{H^+}} \ \frac{\partial \gamma_{H^+}}{\partial m_{H^+}} + \frac{1}{\gamma_{CO_3^{2-}}} \ \frac{\partial \gamma_{CO_3^{2-}}}{\partial m_{H^+}} - \frac{1}{\gamma_{HCO_3^-}} \ \frac{\partial \gamma_{HCO_3^-}}{\partial m_{H^+}} \right) \tag{A11}$$

The derivative $\partial \gamma_{H_2CO_3}/\partial m_j$ is not included because $\gamma_{H_2CO_3} = 1$.

The term $\partial \gamma_{H^+}/\partial m_{H^+} = -\gamma_{H^+} (\partial G/\partial I)(\partial I/\partial m_{H^+})$ where

$$\frac{\partial I}{\partial m_{H^+}} = \frac{\frac{1}{2}\left(1 + m_{HCO_3^-}\big/m_{H^+}\right)}{1 + \frac{1}{2}\frac{\partial G}{\partial I}\left[4\,m_{NaCO_3^-} + 4\,m_{HCO_3^-} - m_{SrOH^+}\right]} \qquad (A12)$$

An example of the expressions for $\partial \bar{m}_\ell/\partial m_j$ is

$$\frac{\partial \bar{m}_{Na^+}}{\partial m_{H^+}} = -\frac{\bar{m}_{Na^+}\,\bar{m}_{H^+}}{N_s\,m_{Na^+}} + \frac{\bar{m}_{Na^+}}{N_s}\frac{\partial G}{\partial I}\frac{\partial I}{\partial m_{H^+}}\,4\,\bar{m}_{Sr^{2+}} \qquad (A13)$$

$$- \frac{\bar{m}_{Na^+}}{N_s}\left(\frac{\bar{m}_{H^+}}{N_s\,m_{H^+}} - 2\frac{\bar{m}_{Sr^{2+}}}{N_s}\frac{\partial G}{\partial I}\frac{\partial I}{\partial m_{H^+}}\right)\left(-2\bar{m}_{Sr^{2+}}\right)$$

and

$$\frac{\partial \bar{m}_{H^+}}{\partial m_{H^+}} = \frac{\bar{m}_{H^+}}{m_{H^+}} - \frac{\bar{m}_{H^+}^{-2}}{N_s\,m_{H^+}} + \frac{\bar{m}_{H^+}}{N_s}\frac{\partial G}{\partial I}\frac{\partial I}{\partial m_{H^+}}\,4\bar{m}_{Sr^{2+}} \qquad (A14)$$

$$- \frac{\bar{m}_{H^+}}{N_s}\left[\frac{\bar{m}_{H^+}}{N_s\,m_{H^+}} - \frac{2\,\bar{m}_{Sr^{2+}}}{N}\frac{\partial G}{\partial I}\frac{\partial I}{\partial m_{H^+}}\right]\left[-2\,\bar{m}_{Sr^{2+}}\right]$$

and

$$\frac{\partial \bar{m}_{Sr^{2+}}}{\partial m_{H^+}} = \frac{-\bar{m}_{H^+}\,\bar{m}_{Sr^{2+}}}{N_s\,m_{Sr^{2+}}} + \frac{\bar{m}_{H^+}}{N_s}\frac{\partial G}{\partial I}\frac{\partial I}{\partial m_{H^+}}\left[-\bar{m}_{H^+} - \bar{m}_{Na^+}\right]$$

$$\frac{-\bar{m}_{Sr^{2+}}}{N_s}\left[\frac{2\,\bar{m}_{H^+}}{N_s\,m_{H^+}} + \left(\frac{2\,\bar{m}_{H^+} + 2\,\bar{m}_{Na^+}}{N_s}\right)\frac{\partial G}{\partial I}\frac{\partial I}{\partial m_{H^+}}\right]\left(\frac{\bar{m}_{H^+} + \bar{m}_{Na^+}}{2}\right)$$

The terms $\bar{m}_j$ have already been expressed in terms of the m_j's.

These derivatives can then be substituted into equations of the form A5. The space derivatives are then finite differenced resulting in a set of ODE's.

Table 1 Input data and desired data for runs of model CHEMTRN.

Important chemical effects	Na	Ca	Sr (boundary)	pH	γ_{Na}	γ_{Sr}	$K_{D_1}(Sr)$	$K_{D_b}(Sr)$	$K_{D_1}(Na)$	$K_{D_b}(Na)$	Reaction equations (see Table 4-1)
1. Binary ion exchange	1×10^{-2}	-	2.37×10^{-5}	-	1.0	1.0	10^3	598	10	7.0	1, 2, 15
	1×10^{-3}	-	2.37×10^{-5}	-	1.0	1.0	10^5	1894	10^2	10	
	1×10^{-4}	-	2.37×10^{-5}	-	1.0	1.0	10^7	2088	10^3	10	
	7×10^{-5}	-	2.37×10^{-5}	-	1.0	1.0	2×10^8	2095	1429	10	
	3×10^{-5}	-	2.37×10^{-5}	-	1.0	1.0	10^9	2103	3326	10	
2. Ternary ion exchange	1×10^{-3}	1×10^{-3}	2.37×10^{-5}	-	1.0	1.0	49	48	1.5	1.5	1, 2, 3, 15
	1×10^{-3}	1×10^{-5}	2.37×10^{-5}	-	1.0	1.0	4215	1356	16	8.6	
	1×10^{-4}	1×10^{-4}	2.37×10^{-5}	-	1.0	1.0	497	402	5.0	4.5	
	1×10^{-4}	1×10^{-5}	2.37×10^{-5}	-	1.0	1.0	4920	1471	16	8.6	
3. Ion exchange with complexation	1×10^{-1}	-	6.15×10^{-5}	-	0.82	0.46	6.8	6.6	1	1	1, 2,
	1×10^{-2}	-	3.30×10^{-5}	-	0.93	0.74	862	481	10	6.8	4, 6, 15
	1×10^{-3}	-	2.67×10^{-5}	-	0.98	0.90	9.5E4	1686	100	9.9	
	1×10^{-1}	1×10^{-3}	6.81×10^{-4}	-	0.82	0.46	5.7	5.5	0.8	0.8	1, 2, 3,
	1×10^{-2}	1×10^{-3}	4.5×10^{-5}	-	0.92'	0.71	42	40	1.7	1.7	4, 6, 11,
	1×10^{-3}	1×10^{-3}	4.1×10^{-5}	-	0.95	0.81	49	48	1.7	1.7	15
4. Ion exchange, complexation and water dissociation	1×10^{-3}	-	5.83×10^{-5}	8	0.98	0.91	9.5E4	808	100	6.7	1, 2, 4, 5,
	1×10^{-3}	-	4.17×10^{-5}	10	0.97	0.90	9.5E4	1102	100	8	6, 7, 8, 9,
	1×10^{-2}	-	6.53×10^{-5}	8	0.93	0.74	861	339	10	5	10, 14, 15
5. Ternary ion exchange, complexation and water dissociation	1×10^{-3}	1×10^{-3}	6.95×10^{-5}	8	0.95	0.81	47	46	1.7	1.6	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15

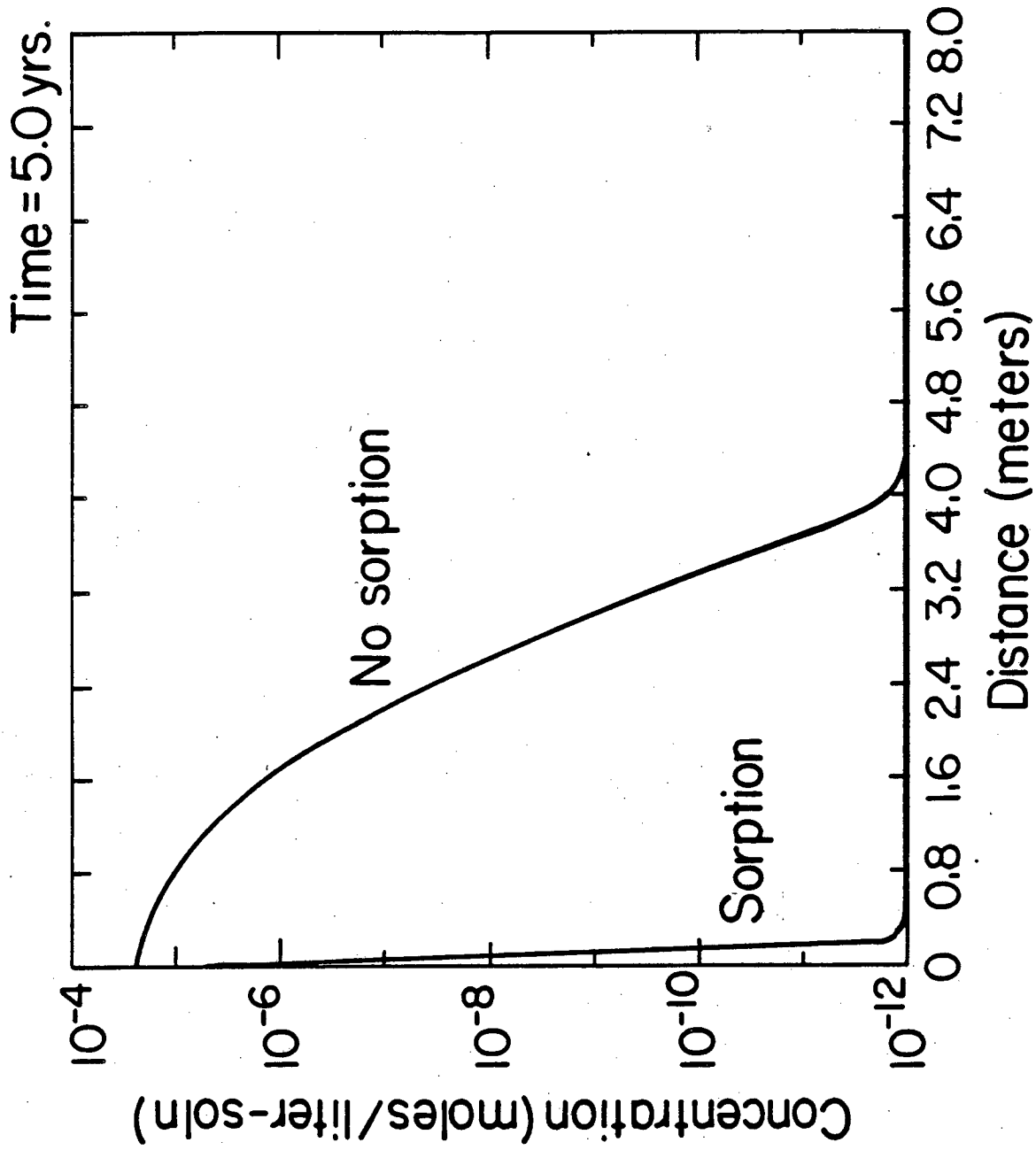Table 2. Chemical reactions and log K values at 25 C.

Reaction			Log K
		Ion exchange *	
1.	$Na^+ + \bar{H}$	$= H^+ + \bar{Na}$	-0.176
2.	$\frac{1}{2}Sr^{2+} + \bar{H}$	$= H^+ + \bar{Sr}_{\frac{1}{2}}$	-0.176
3.	$\frac{1}{2}Ca^{2+} + \bar{H}$	$= H^+ + \bar{Ca}_{\frac{1}{2}}$	-0.181
		Complexation **	
4.	$Sr^{2+} + CO_3^{2-}$	$= SrCO_3^o$	3.0
5.	$Sr^{2+} + OH^-$	$= SrOH^+$	0.799
6.	$Na^+ + CO_3^{2-}$	$= NaCO_3^-$	0.960
7.	$Na^+ + H^+ + CO_3^{2-}$	$= NaHCO_3^o$	10.08
8.	$Na^+ + OH^-$	$= NaOH^o$	-0.213
9.	$H^+ + CO_3^{2-}$	$= HCO_3^-$	10.3
10.	$2H^+ + CO_3^{2-}$	$= H_2CO_3^o$	16.7
11.	$Ca^{2+} + CO_3^{2-}$	$= CaCO_3^o$	3.15
12.	$Ca^{2+} + H^+ + CO_3^{2-}$	$= CaHCO_3^+$	11.33
13.	$Ca^{2+} + OH^-$	$= CaOH^+$	1.32
		Dissociation of water	
14.	H_2O	$= H^+ + OH^-$	-13.99
		Dissolution of strontianite	
15.	$SrCO_3 (s)$	$= Sr^{2+} + CO_3^{2-}$	-9.25

*(Benson, 1980)

** (Benson and Teague, 1980)

FIGURE CAPTIONS

1. Transport of Sr^{2+} through a porous clay illustrating the effect of sorption on radionuclide mobility.

2a. Transport of Sr^{2+} in background solution of 10^{-3} M NaCl including sorption on clay; concentration of Na^+ is also plotted.

2b. Transport of Sr^{2+} in background solution of 10^{-4} M NaCl including sorption on clay; concentration of Na^+ is also plotted.

2c. Transport of Sr^{2+} in background solution of 7×10^{-5} M NaCl including sorption on clay; concentration of Na^+ is also plotted.

2d. Transport of Sr^{2+} in background solution of 3×10^{-5} M NaCl after 10 years including sorption on clay; concentration of Na^+ is also plotted.

3. Transport of Sr^{2+} in background solution of 3×10^{-5} M NaCl including sorption on clay after 20 years; concentration of Na^+ is also plotted.

4a. Transport of Sr^{2+} in background solution of 10^{-3} M NaCl and 10^{-3} M $CaCl_2$ including sorption on clay; concentrations of Na^+ and Ca^{2+} are also plotted.

4b. Transport of Sr^{2+} in background solution of 10^{-4} M NaCl and 10^{-5} M $CaCl_2$ including sorption on clay; concentrations of Na^+ and Ca^{2+} are also plotted.

5a. Transport of Sr^{2+} in background solution of 10^{-3} M NaCl including complexation and sorption; concentrations of Na^+ and CO_3^{2-} are also plotted

5b. Transport of complexes corresponding to Figure 5a.

6a. Transport of Sr^{2+} in background solution of 10^{-3} M NaCl including complexation, water dissociation, and sorption; concentrations of Na^+, H^+, CO_3^{2-}, and OH^- are also plotted.

6b. Transport of complexes corresponding to Figure 6a.

7a. Transport of Sr^{2+} in background solution of 10^{-3} M NaCl and 10^{-3} M $CaCl_2$ including complexation, water dissociation and sorption.
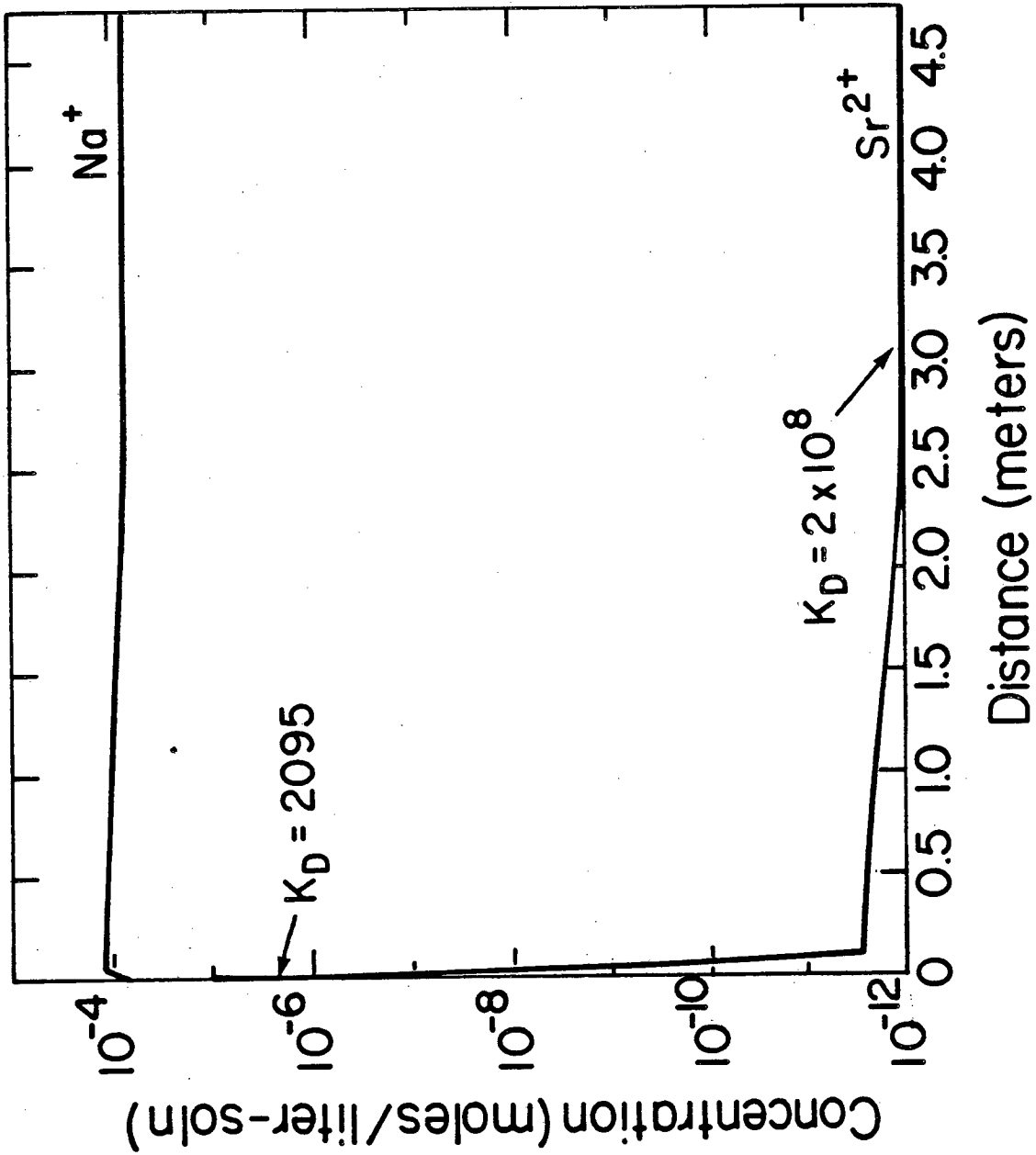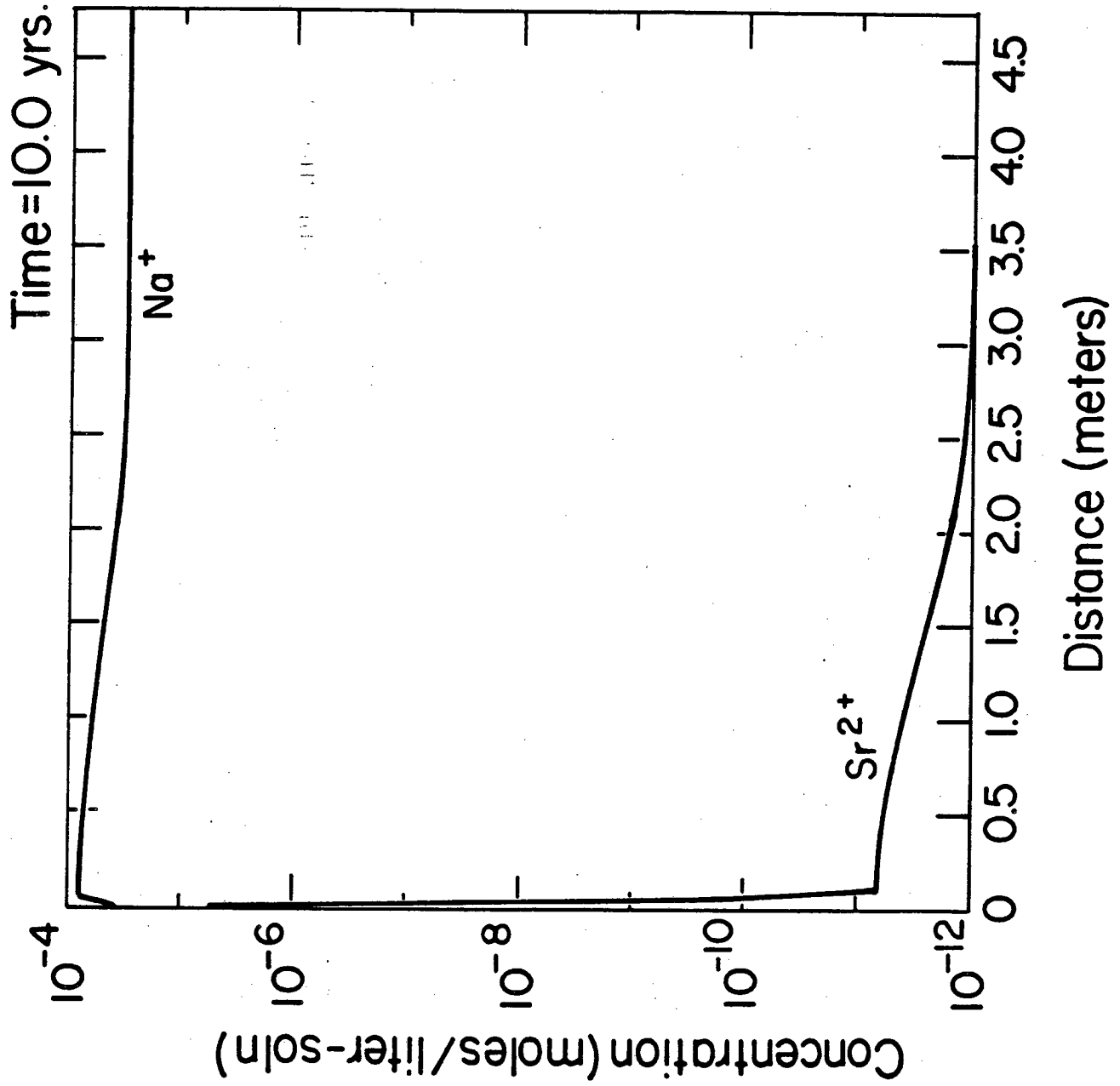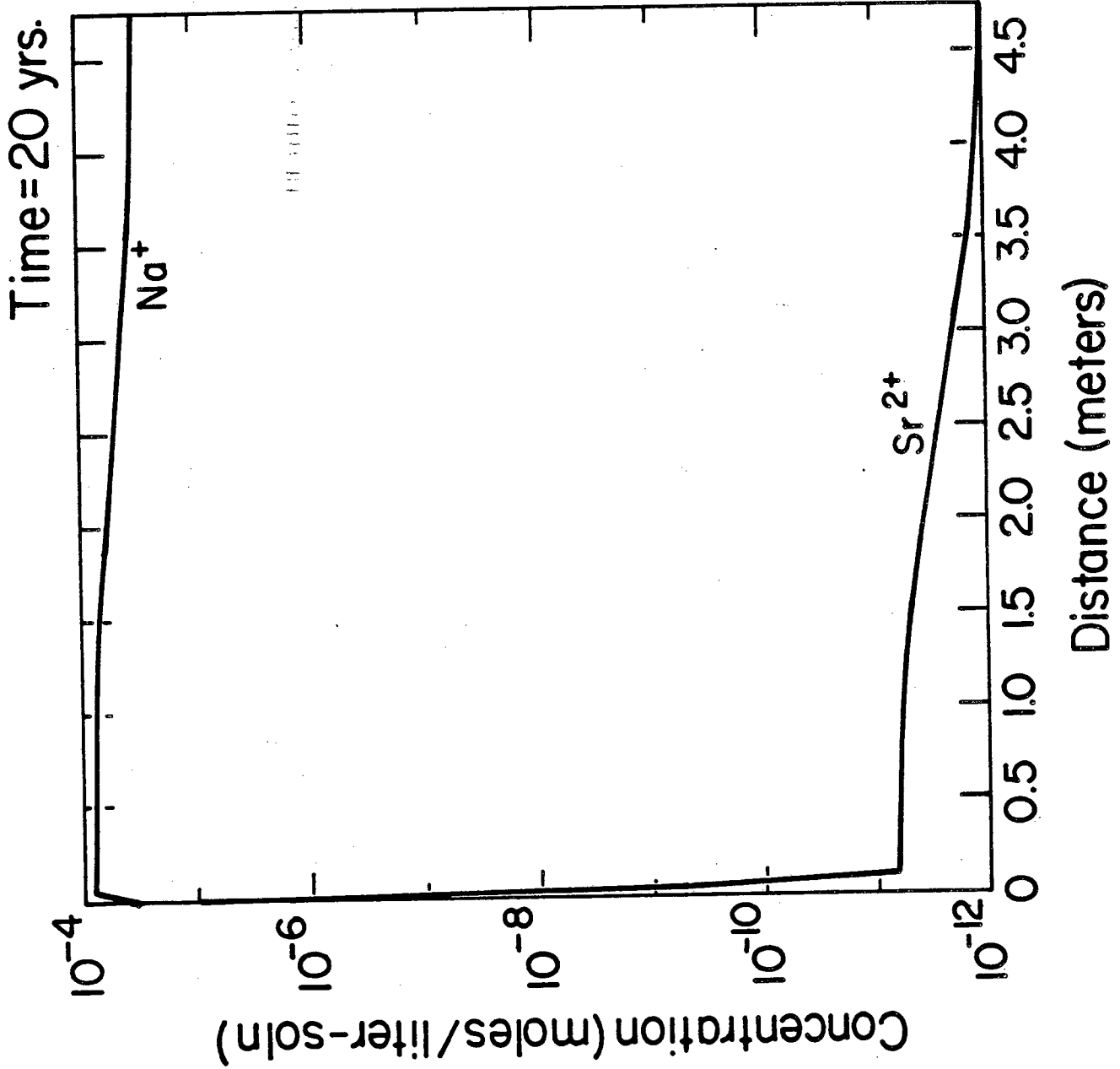
7b. Transport of complexes corresponding to Figure 7a.

Figure 1

3.5

Time = 5.0 yrs.

No sorption

Sorption

Concentration (moles/liter-soln)

Distance (meters)

XBL 8110-1497

Time = 10.0 yrs.

Na⁺

Sr²⁺

Distance (meters)

Concentration (moles/liter-soln)

XBL 8110-1494

Figure 2b

Figure 2c

XBL 8110-7393

Figure 2d

XBL 8110 − 7392

Figure 3

Figure 3

XBL8110-7390

Figure 4a

XBL8110-12145

XBL 8110−7391

Figure 5a

XBL8110-12144

Figure 5b. Time=5.0 yrs.

XBL8110-12143

Figure 6a

Time = 5.0yrs.

Na$^+$

OH$^-$

H$^+$

Sr^{2+}

CO$_3^{2-}$

Distance (meters)

Concentration (moles/liter-soln)

XBL8110−7396

Time = 5.0 yrs.

XBL8110-12141

Figure 7a

XBL 8110-12142

Figure 7b

XBL 8110−7389