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Publication Date
1983-02-01

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February 1983

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TOWARD A COMPREHENSIVE MODEL OF CHEMICAL TRANSPORT IN POROUS MEDIA

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ABSTRACT

A chemical transport model, CHEMTRN, that includes advection, dispersion/diffusion, complexation, sorption, precipitation or dissolution of solids, and the dissociation of water has been written. The transport, mass action and site constraint equations are written in a differential/algebraic form and solved simultaneously. The sorption process is modelled by either ion-exchange or surface complexation. The model has been used to investigate the applicability of a k_D model for simulating the transport of chemical species in groundwater systems, to simulate precipitation/dissolution of minerals, and to consider the effect of surface complexation on sorption.

INTRODUCTION

To be able to assess the long term storage of radionuclides in underground repositories, it is important to be able to predict the migration of chemical species in groundwater systems. To help in this understanding, a numerical model, CHEMTRN, has been developed. Although there are numerous chemical transport models available, most models are either limited to one or two types of chemical mechanisms [1,2,3] or they integrate existing chemical equilibrium distribution codes with a transport model in a two step procedure [4,5,6], i.e. first the fluid is allowed to flow with little or no chemical reactions, then the chemical species are allowed to react until equilibrium is obtained again. Anderson [7] has reviewed the models which were available before 1978. In constrast to these models, CHEMTRN solves the mass action and transport equations simultaneously. It includes sorption via ion-exchange or surface complexation, precipitation or dissolution of solids, formation of complexes in the aqueous phase, dispersion/diffusion, advection, and the dissociation of water. In addition, the structure of the program and the solution procedure are flexible so additional chemical mechanisms can be added with minimal change.

BASIC EQUATIONS

Given a basis set of species $(A_j^{n_j})$, which are the minimum number (N_b) of species needed to define all the chemical species present, one can write a reaction for a complex $B_i^{n_{c_i}}$,

$$\sum_{j=1}^{N_b} a_{ij} A_j^{n_j} \rightleftharpoons B_i^{n_{c_i}}, \tag{R1}$$

or a solid precipitate G_k,

$$\sum_{j=1}^{N_b} s_{kj} A_j^{n_j} \rightleftharpoons G_k, \tag{R2}$$

where a_{ij} and s_{kj} are the stoichiometric reaction coefficients, n_j is the charge of the basis species, and n_{c_i} is the charge of the complex. Assuming chemical equilibrium, mass action expressions can be written for each of these cases. For the formation of complexes,

$$K_i = \frac{\left[B_i^{n_{c_i}}\right]}{\prod_{j=1}^{N_b} [A_j^{n_j}]^{a_{ij}}}, \tag{1}$$
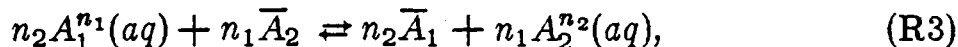
where the square brackets denote the thermodynamic activity of the dissolved species and K_i is the equilibrium constant. For the formation of the precipitates,

$$K_k = \prod_{j=1}^{N_b} [A_j^{n_j}]^{s_{kj}} \tag{2}$$

where the square brackets again denote activities and K_k is the solubility product. The activities of the dissolved species are approximated using an activity coefficient model, and the activity coefficients are approximated using the Davies equation [8].

The mass transfer of ions and complexes from the aqueous phase to the solid phase is simulated by either ion-exchange or a surface complexation. For an ion-exchange process, the charge on the solid remains fixed with the chemical species being sorbed on a fixed number of sorption sites. The species in the aqueous phase are sorbed on the solid phase by displacing ions already on it. Because

the charge on the solid matrix does not change, a species which is sorbed must replace an equivalent amount of charge. For species $A_1^{n_1}$ exchanging with species $A_2^{n_2}$,

$$n_2 A_1^{n_1}(aq) + n_1 \overline{A}_2 \rightleftharpoons n_2 \overline{A}_1 + n_1 A_2^{n_2}(aq), \tag{R3}$$

where $\overline{A}_j$ denotes the sorbed component. This reaction is described by a thermo-dynamic equilibrium constant,

$$K_{eq} = \frac{\left[\overline{A}_1\right]^{n_2} \left[A_2^{n_2}\right]^{n_1}}{\left[A_1^{n_1}\right]^{n_2} \left[\overline{A}_2\right]^{n_1}}, \tag{3}$$

where the square brackets again denote activites. Because of the lack of real data, the surface phase has been assumed to be an ideal solution where the activity of the sorbed phase for species j is the ratio of the molar concentration of that species in the sorbed phase to the total molar concentration of all sorbed species.
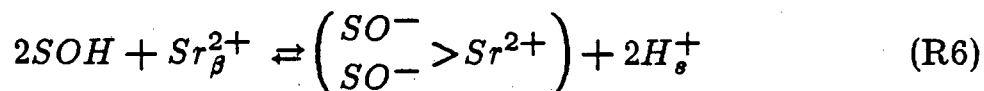
For a surface complexation model, a neutral site denoted as SOH can dissociate to give a negatively charged site, SO^-,

$$SOH \rightleftharpoons SO^- + H_s^+ \tag{R4}$$

where the subscript s denotes the ion at the surface, or SOH can react with a H^+ ion to give a positively charged site SOH_2^+,

$$SOH + H_s^+ \rightleftharpoons SOH_2^+. \tag{R5}$$

In contrast to the ion-exchange model, the charge on the solid surface changes and both cations and anions can be sorbed. In addition, because of the variable surface charge, an ion does not necessarily have to displace an equal amount of charge when it forms a complex with the surface site. For example, in an ion-exchange model, the sorption of Sr^{2+} on the solid phase would require a reaction with two surface sites,

$$2SOH + Sr_\beta^{2+} \rightleftharpoons \begin{pmatrix} SO^- \\ SO^- \end{pmatrix} > Sr^{2+} \end{pmatrix} + 2H_s^+ \tag{R6}$$

while in a surface complexation model a reaction with only one site is possible,

$$SOH + Sr_\beta^{2+} \rightleftharpoons SO^- Sr^{2+} + H_s^+. \tag{R7}$$
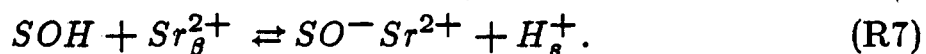
The subscript β denotes the plane where the Sr^{2+} ion is located when it forms a complex with the surface site. In an ion-exchange model, the s and β planes

are the same while in the surface complexation model, the β plane is displaced a distance from the solid surface. Following the discussion by Davis et al. [9], the equilibrium constant for reaction R4 is

$$K = \frac{[SO^-][H_s^+]}{[SOH]}.$$

(4)

The activity of H^+ at the surface is related to the activity in the bulk solution by

$$[H_s^+] = [H^+]\exp\left(-\frac{e\psi_i}{kT}\right),$$

(5)

where ψ_i is the change of potential when a species moves from the bulk phase to the solid phase. A similar expression can be written for reactions R6 and R7. However, the sorbed Sr^{2+} ion resides at the β plane and only moves through a potential difference of ψ_β. Therefore, the activity of Sr^{2+} at the β plane is related to the bulk activity by a term $\exp(-e\psi_\beta/kT)$. The potentials ψ_i and ψ_β are functions of the charge distribution developed between the bulk fluid and the solid surface. A complete discussion of this surface complexation model for sorption is given in reference [9].

For a velocity v and a dispersion coefficient D, both the basis species and the complexes are subject to transport by advection and dispersion/diffusion. In addition they are subject to sorption and precipitation or dissolution. One can write a mass balance for the concentration of each species. If W_j is the total concentration of species A_j in the aqueous phase, given by

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

(6)

where m denotes the molar concentration of a species and N_c is the total number of complexes, and if $\overline{W}_j$ is the total concentration of the sorbed species A_j, given by

$$\overline{W}_j = \overline{m}_j + \sum_{i=1}^{\overline{N}_c} a_{ij} \overline{m}_{c_i},$$

(7)

where $\overline{m}$ is the molar concentration of the sorbed phase, and $\overline{N}_c$ is the total number of sorbed complexes, and if N_p is the total number of precipitates, then

$$\left(\frac{\partial}{\partial t} + v\frac{\partial}{\partial x} - D\frac{\partial^2}{\partial x^2}\right)W_j = -\frac{\partial}{\partial t}\overline{W}_j - \frac{\partial}{\partial t}\sum_{k=1}^{N_p} s_{kj} G_k.$$

(8)

The dissociation of water is handled by solving for a dummy variable y, which is the difference in concentration between the molar concentration of the H^+ and the OH^- ions. The dummy variable is used because a mass balance for either the H^+ or OH^- ions would require including the changes in water concentration. To avoid numerical difficulties, a mass balance was computed for this dummy variable. Details of this aspect of the model are given by Miller and Benson [10].

The spatial terms in the transport equation (8) are finite differenced and combined with the mass action equations (1,3,4), solubility product (2) and a site constraint equation to give a set of differential/algebraic equations in the form of

$$A(m, t)\frac{dm}{dt} + G(m, t) = 0. \qquad (9)$$

These equations are solved using a Newton-Raphson iteration technique. Given the initial conditions and boundary conditions, a guess is made for the values of the concentrations at all the node points at a new time level. These guesses are then used in equation (9) and the residue, R, of these equations is calculated. In addition, the Jacobian, J, is calculated where $J = \partial R/\partial m$. The Jacobian is used to predict the next approximation to the new concentrations. This method has been used by Kee and Miller [11] to model chemically reacting boundary layer flow. To save time a new Jacobian is not calculated at every interation nor at every time step. One is calculated only if convergence is slow. Once convergence is fairly rapid, the time step is increased. Details of the solution procedure are given by Miller and Benson [10].

After each time step, the solubility constraint for every precipitate that is being considered is tested at all the node points. If any of the solubility constraints is exceeded at a node point, the total amount of each basis species is computed and a new re-distribution of species is done at that node point. All the solubility constraints are considered when the new equilibrium is calculated. From that point on, the solubility constraint is satisfied for any precipitate which has formed at the node point and is included in the system of differential/algebriac equations which are solved simultaneously. The transport equation at that node point will now include an additional term which is the change in the amount of precipitate at that point. For dissolution, the opposite occurs: if $[A][B] < K_k$, a new equilibrium distribution of species is calculated. If the precipitate has redissolved, the solubility constraint equation will no longer be satisfied at that node point.

SIMULATION OF CHEMICAL TRANSPORT

The numerical model CHEMTRN has been used to simulate the transport of chemical species away from a nuclear waste repository. Three different cases are considered here. The first case is a set of three examples. It compares the numerical solution to a known analytical solution, and it looks at the validity of using a k_D type of model to simulate sorption of radionuclides. The second case illustrates the ability of the model to handle precipitation and dissolution of solids as well as complexation and sorption. The last example uses the surface complexation model for the sorption of the chemical species.

To illustrate that CHEMTRN gives reasonable results, it has been used to simulate the transport of a chemical species in a semi-infinite medium where the initial concentration of the species is c_i for $0 < x < \infty$ and where at time $t > 0$, the concentration at $x = 0$ is maintained at c_b. Far from this boundary, the concentration of the species remains at the initial concentration. For this particular case, the sorption of the species was not considered. The analytical solution for the concentration of the species as a function of time and position is known and given by

$$\frac{(c - c_i)}{(c_b - c_i)} = \frac{1}{2}\text{erfc}\left(\frac{x - vt}{2\sqrt{Dt}}\right) + \frac{1}{2}\exp\left(\frac{vx}{D}\right)\text{erfc}\left(\frac{x + vt}{2\sqrt{Dt}}\right) \tag{10}$$

Figure 1 is a comparison between this analytical solution and the numerical solution of the same problem using CHEMTRN. The velocity used was 0.1 m/hr and the dispersion coefficient was 1.0 v. The comparison was made at 10 and 20 hrs. However, in the numerical solution a boundary condition of $\partial c/\partial x = 0$ was imposed 4.75 m downstream. The deviation of the numerical model from the analytical solution occurs only when the influence of this boundary is felt.

In addition to being transported downstream, a species can be sorbed onto the solid matrix. A typical method of handling sorption is to assume that the amount of sorbed material is proportional to the concentration of that species in the aqueous phase, $\overline{m} = k_D m$. When this k_D type of model is appropriate, one can consider the same problem as above but with the species sorbing as well as being transported. The analytical solution is obtained by replacing both v and D by an effective velocity and dispersion coefficient, v' and D', where $v' = v/(1 + k_D)$ and $D' = D/(1 + k_D)$. Figure 2 is a comparison between the analytical solution and the numerical simulation when Sr^{2+} is being transported downstream in a groundwater consisting of 10^{-3} M Na^+, 10^{-4} M Ca^{2+}, 10^{-8} M Sr^{2+}, 4.5 x 10^{-5} M CO_3^{2-}, 1.11 x10^{-3} M Cl^-. Equilibrium constants of 0.66 for Sr^{2+} replacing Na^+ and 0.66 for Ca^{2+} replacing Na^+ were used. At $x = 0$, a solubility product for strontium carbonate was used to calculate the amount of Sr^{2+} and CO_3^{2-} entering the groundwater. For both the initial conditions and the boundary conditions, the k_D as defined above is 450. Note
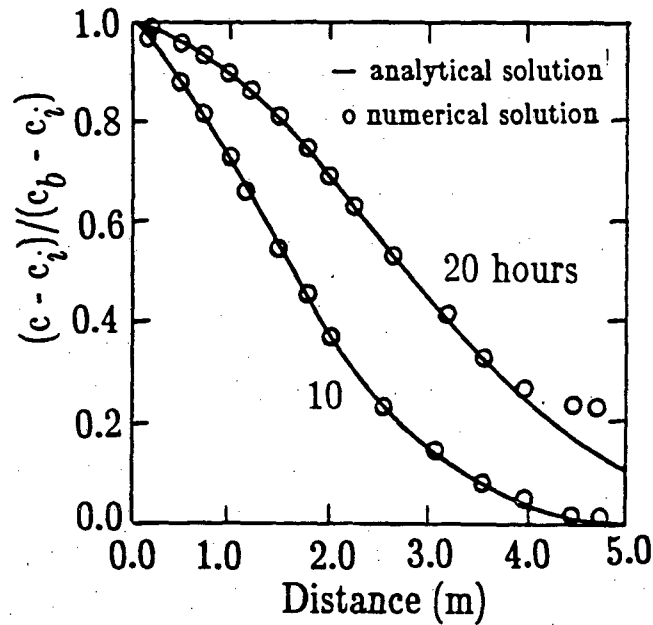
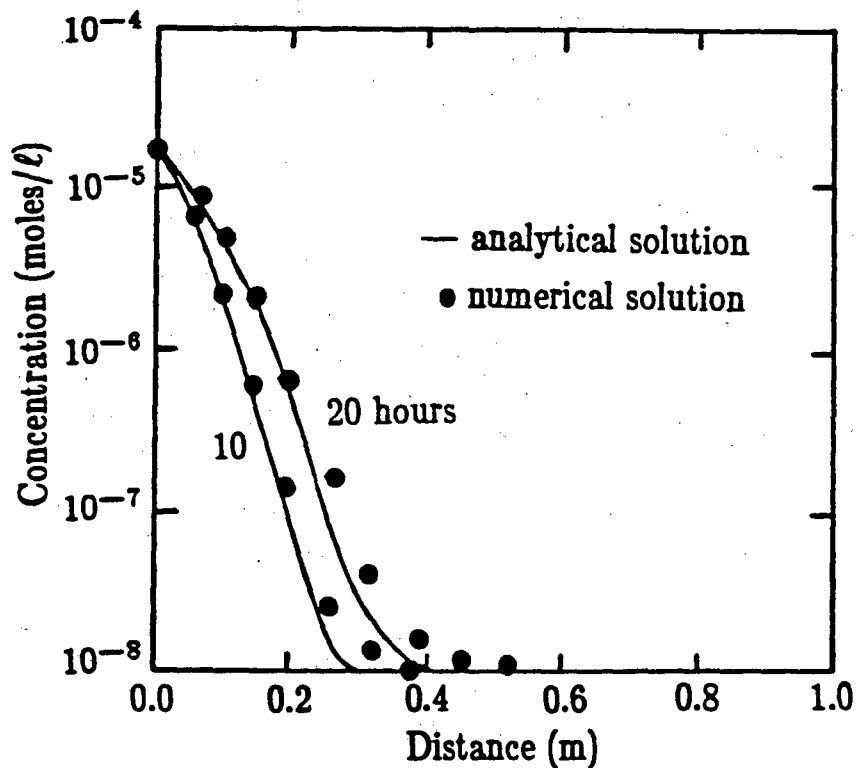Figure 1. Comparison of analytical solution and numerical simulation using CHEMTRN

Figure 2. Comparison of analytical solution and numerical simulation using CHEMTRN for transport of a sorbing species. Analytical solution assumes a k_D type of model for sorption.

that k_D is unitless as defined here because both m and $\overline{m}$ have been expressed in the same units of moles/ℓ solution. The comparison is done on semi-log paper where differences between the exact solution and the numerical calculations are more evident. Again, the numerical model agrees well with the exact solution. The slight deviation of the numerical calculation from the analytical solution is because of the size of the finite grid spacing used.

Figure 3 shows calculations done using CHEMTRN when the competition for sites on the solid matrix affect the sorption of the radionuclides. In this case the groundwater consisted of 10^{-4} M Na$^+$, 10^{-5} M Ca^{2+}, 10^{-8} M Sr^{2+}, 4.5 x 10^{-5} M CO$_3^{2-}$, and 3 x 10^{-5} M Cl$^-$. In this example, the calculated value of k_D varies from 5000 at the initial conditions to 2000 at the boundary. Plotted in the figure is the solution assuming that the sorption of Sr^{2+} follows a k_D type of model with $k_D = 2000$. The numerical solution shows that site competition makes the k_D model inaccurate. As Sr^{2+} is sorbed, Ca^{2+} and Na$^+$ are displaced from the solid matrix. The Sr^{2+} must now compete with a higher level of background electrolyte downstream. The bulk of the Sr^{2+} is transported at a slightly faster rate than predicted by a k_D model with a k_D of 2000. The sorption of Sr^{2+} depends on the changes of Na$^+$ and Ca^{2+} as well as Sr^{2+} concentrations in the aqueous phase. When the changes in concentration of these background ions becomes important, the k_D model overpredicts the sorption of Sr^{2+}. It is also noted that low levels of Sr^{2+} are transported for much longer distances at a level just slightly greater than the background level. However, the Sr^{2+} concentration plotted consists of both the strontium from the waste form and that which was initially sorbed on the rock matrix.

Precipitation/dissolution of solids is also included in the model. To illustrate the capability of CHEMTRN in this respect, it was used to simulate precipitation when a Na$^+$-rich solution flows into a one-dimensional column of porous medium which has Ca^{2+} sorbed on the solid. Initially, the fluid in the column consists of 1.5 x 10^{-3} M Ca^{2+}, 10^{-5} M Na$^+$, 6.6 x 10^{-4} M CO$_3^{2-}$, a pH of 8 and enough Cl$^-$ to balance the solution electrically. Then a solution that has a higher level of Na$^+$ (1.1 x 10^{-2} M) is fed into the column. The Ca^{2+} ion is displaced from the solid matrix. The conditions of the fluid were set so that the solubility product of CaCO$_{3(s)}$ would be exceeded downstream from the boundary. The boundary condition maintained at $x = 0$ is a constant concentration condition although a flux boundary condition could also be imposed. The dissociation of water and the formation of the complexes NaCO$_3^-$, NaHCO$_3^0$, NaOH^0, HCO$_3^-$, H$_2$CO$_3^0$, CACO$_3^0$, CaHCO$_3^+$, and CaOH$^+$ were included in the calculation. Plotted in Figure 4 is the amount of precipitate CaCO$_{3(s)}$ that forms as the Na$^+$ flows into the column. As the time increases from 0.1 hr to 10 hrs, more precipitate forms downstream. After 5 hrs, the level of Ca^{2+} near the boundary starts to decrease and some of the precipitate begins to redissolve. We see that after 10 hrs, all the
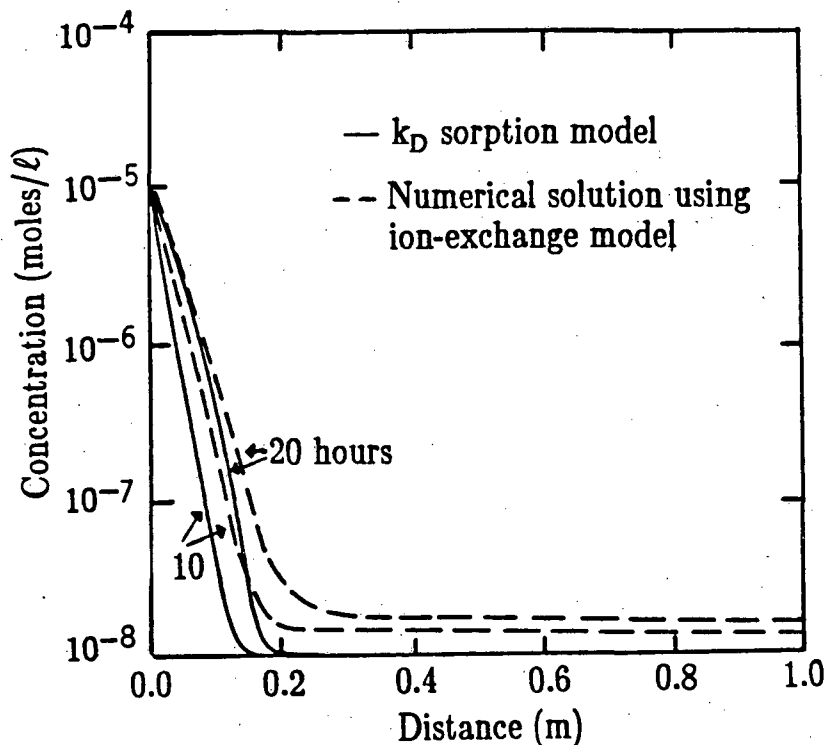
Figure 3. Comparison of ion-exchange model with a k_D type of sorption model when changes in the background electrolyte concentrations are important
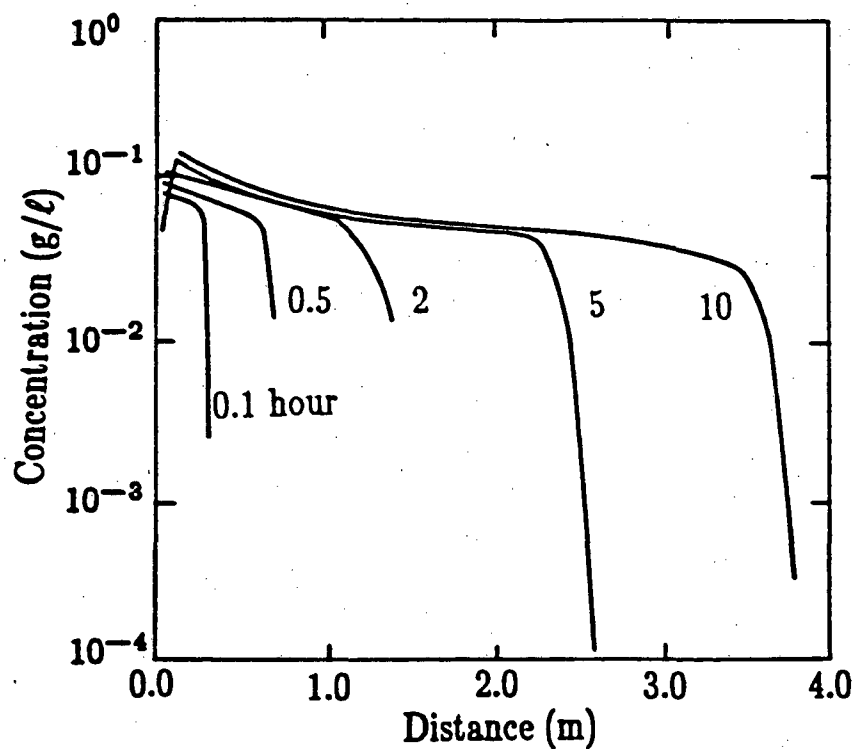
Figure 4. Precipitation of $CaCO_{3(s)}$ as a function of time and position.

solid precipitate has redissolved at the first node point.

The last example is a case where surface complexation has been used to model the sorption of lead in the form of Pb^{2+} and $PbOH^+$ on γ-Al_2O_3. The data for the reactions and the needed constants are taken from Davis and Leckie [12]. For the dissocation of a site (reaction R4) a pK of 11.5 was used and for the formation of a site with a positive charge (reaction R5) a pK of 5.7 was used. The background electrolyte was $NaCLO_4$ and the pK's for the sorption of the background cation and anion were 9.2 and 7.9 respectively. Following the discussion of Davis and Leckie [12], Pb^{2+} primarily forms a complex with only one surface site instead of two. For this example, the total concentration of Pb in the aqueous phase was assumed to be 2.9×10^{-4} moles/ℓ solution and the pH of the solution was 7 initially. Then a feed solution with a velocity of 0.1 m/hr equivalent to the inital solution but with a pH of 4.5 was introduced at $x = 0$. Plotted in Figure 5 are the concentrations of Pb^{2+}, $PbOH^+$, H^+ and the sorbed Pb in the form of (SO^-Pb^{2+}) and (SO^-PbOH^+) and the sorbed H^+ in the form of SOH after 5 hrs. As seen in the figure, the concentration of the Pb^{2+} ion in the aqueous phase is approximately constant. The ratio of the total amount of sorbed Pb to the total aqueous phase concentration varies from 18 initially to almost 0 at the boundary. This surface complexation model clearly gives a vastly different extent of sorption than the simple k_D model.

The surface complexation model has not been directly compared to the ion exchange model because of the fundamently different types of reactions which are considered in the two cases, i.e. Pb^{2+} is forming a bond with only one surface site in the surface complexation case while it must form a bond with two sites in the ion exchange case. However, the equations describing ion exchange would produce a change in sorption proportional to $[PbOH^+][SOH]/[H^+]$ which is not the case here. This quantity changes from a value of 2 initially to a value of 4.8×10^{-5} at the boundary. The variation results from the change in the number of available sites for sorption because of the change in the surface charge for different pH values.

SUMMARY

A flexible chemical transport model has been written. It includes many of the chemical mechanisms which are important in modelling the transport of chemical species away from nuclear waste repositories. It has been used to model precipitation, sorption via an ion-exchange or surface complexation model, aqueous phase complexation and water dissociation. The small number of calculations done here illustrate the ability of the model. It has also been used to show the inadequacy of the simpler k_D type of sorption modelling.
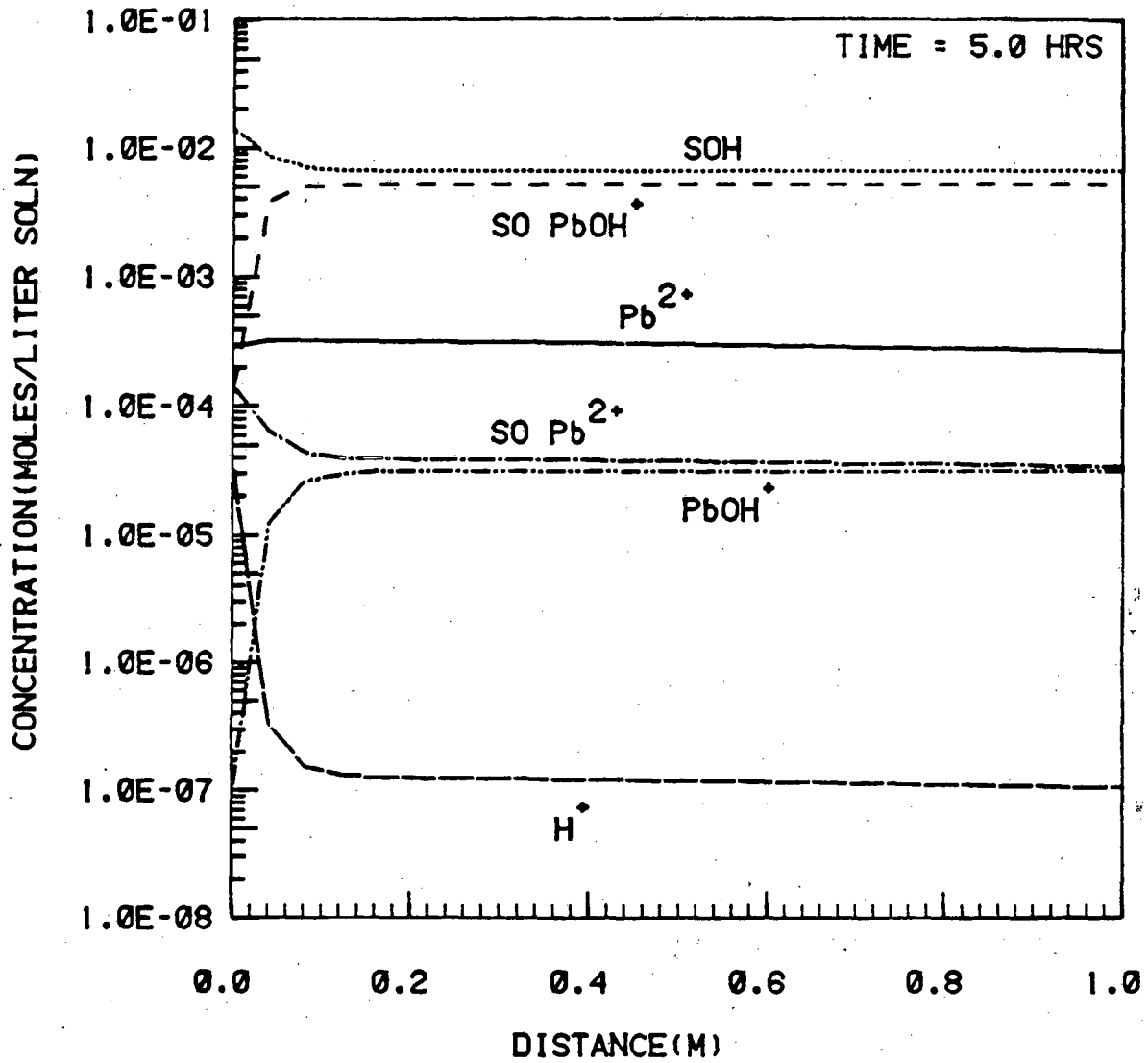
Figure 5. Sorption of lead using a surface complexation model

ACKNOWLEDGEMENTS

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