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ABSTRACT

Because of its ability to retard the movement of radionuclides, sodium bentonite is being considered as a packing and backfilling material in a number of nuclear waste isolation programs. Few studies, however, have considered how the chemical properties of the bentonite backfill will vary with distance from the canister and change in time as groundwater constituents diffuse through the bentonite. Of particular importance is the conversion of sodium bentonite to calcium bentonite by ion exchange, which will in turn affect the migration of cationic radionuclides, such as Cs^+ and Sr^{2+} , leaking from a waste canister.

Experiments measuring the movement of trace amounts of radionuclides through compacted bentonite have typically used unaltered bentonite. Models based on experiments such as these may not lead to accurate predictions of the migration through altered or partially altered bentonite of radionuclides that undergo ion exchange. To address this problem, we have modified an existing transport code to include ion exchange and aqueous complexation reactions. The code is thus able to simulate the diffusion of major ionic groundwater components through bentonite and reactions between the bentonite and groundwater. Numerical simulations have been made to investigate the conversion of sodium bentonite to calcium bentonite for a reference groundwater characteristic of deep granitic formations.

INTRODUCTION

Because of its ability to retard the movement of radionuclides, sodium bentonite is being considered as a packing and backfilling material by the nuclear waste isolation programs of several countries. A great deal of effort has been devoted to characterizing the material, structural and chemical properties of bentonite. Of particular importance are the chemical properties of bentonite since they will affect the composition of the groundwater in contact with the waste canister and determine the bentonite's ability to retard the migration of radionuclides. Experimental studies of the chemical properties of bentonite generally fall into two categories: studies of the influence of sodium bentonite on groundwater composition (*e.g.*, [1,2]) and diffusion of radionuclides through compacted bentonite (*e.g.*, [3,4,5]). Experiments in the first category are generally batch experiments in which the bentonite is mixed with a reference groundwater in a clay/water ratio smaller than that of compacted bentonite. Reactions between the bentonite and water proceed, therefore, at a faster rate than they would in compacted bentonite. The effect of the clay/water ratio on the increase of sodium in the solution is noted in [2]. Experimental studies of diffusion of radionuclides through compacted bentonite vary considerably in design and in how the bentonite is prepared before being placed in the experiment cell. Values of diffusivity measured in these experiments are based on the assumptions that sorption occurs instantaneously and that the sorption isotherm is linear. Few, if any, of these studies consider how the chemical prop-

erties of the bentonite will change in time as major ionic components of groundwater diffuse through the bentonite packing and backfill.

Assuming that the length of time before a nuclear waste canister fails is on the order of a thousand years, the chemical properties of the bentonite surrounding the waste canister at time of failure may be quite different from the properties at the time of emplacement. The sodium bentonite may be all or partially converted to calcium bentonite by ion exchange, which in turn may affect the migration of radionuclides released from a failed canister. Results of experiments on diffusion through unaltered bentonite may only be applicable to a repository scenario in which a waste canister fails soon after resaturation. The experimental work mentioned above is, however, very important for understanding what mechanisms are responsible for changes in the chemical properties of bentonite and for providing parameters needed for numerically simulating bentonite-groundwater interactions.

H. Wanner [6,7] developed a "mixing-tank" model to investigate how the chemical properties of compacted bentonite change as the porewater in the bentonite is gradually replaced by groundwater. He calculated ion exchange constants from batch experiments and used a modified version of the speciation code MINEQL/EIR to simulate a titration experiment in which bentonite is added to a groundwater representative of deep granite formations. In this way he was able to determine the porewater composition of a compacted bentonite. The calculated porewater composition was then used as the initial condition for the "mixing tank" model. In the "mixing-tank" model, the compositions of the bentonite and the groundwater are not explicitly calculated as functions of time, but rather as functions of water exchange cycles, where within a water exchange cycle all of the groundwater in contact with the bentonite is replaced by fresh groundwater. Our work extends Wanner's by explicitly accounting for diffusion of ionic components and the resulting changes in the compositions of the bentonite and the groundwater as functions of time and space.

DESCRIPTION OF TIP COMPUTER PROGRAM

The transport code that we have modified is based on the theory of the thermodynamics of irreversible processes [9] and is unique in its coupling of the velocity field with changes in fluid composition. The TIP code is able to simulate heat and mass transport under conditions of changing temperature, pressure and composition. Previous versions of the code were used to study thermodynamically coupled processes in the near-field region of a nuclear waste repository [9,10]. The current version of the program allows for more than one solute and calculates temperature and pressure as well as solute concentrations. In addition, aqueous complexation and ion exchange reactions have been incorporated assuming local chemical equilibrium. In the simulations presented in this work, constant temperature and pressure distributions were assumed, and as a result thermodynamically coupled processes have been ignored, though the

code still retains the flexibility described above.

Transport Equation

Assuming constant temperature and pressure distributions, the set of equations solved by the TIP code [9,10] reduces to a single transport equation

$$\epsilon \frac{\partial}{\partial t} \left(B_j + \overline{B}_j + \sum_{k=1}^{n_c} s_{jk} C_k \right) = -\nabla \left(J_j + \sum_{k=1}^{n_c} s_{jk} J_k \right), \quad (1)$$

where

B_j is the concentration of basis species j in the aqueous phase,

$\overline{B}_j$ is the concentration of basis species j sorbed by ion exchange,

C_k is the concentration of aqueous complex k ,

J_j is the mass flux of basis species j ,

J_k is the mass flux of complex k ,

s_{jk} is the stoichiometric coefficient of basis species j in aqueous complex k ,

t is the time,

ϵ is the porosity,

∇ is the gradient operator in one-dimensional or cylindrical coordinates.

The mass fluxes are defined by

$$J_i = -L_{ii} \frac{RT}{M_i A_i} \nabla A_i, \quad (2)$$

where i refers either to basis species j or to aqueous complex k , and

A_i is the concentration,

L_{ii} is the phenomenological coefficient of mass diffusion,

M_i is the molecular weight,

R is the gas constant,

T is the absolute temperature.

The coefficient of mass diffusion depends on composition, but due to lack of data on how it varies, it is considered to be a constant in TIP. It is related to the usual diffusion coefficient D_i by

$$D_i = L_{ii} \frac{RT}{M_i A_i}, \quad (3)$$

where A_i and i are defined as above.

Chemical Reactions Simulated

The activities of the aqueous species are approximated by the the product of the concentration of the species and its activity coefficient, γ . The activity coefficient is calculated from the Davies equation, where a value of 0.3 has been used for the B coefficient as recommended by Davies [11]. Once the concentrations of the basis species have been determined, the concentration of aqueous complex k may be calculated from the mass action law

$$K_{C_k} = \frac{\gamma_k C_k}{\prod_{j=1}^{n_b} (\gamma_j B_j)^{s_{jk}}}, \quad (4)$$

where K_{C_k} is the formation constant for the complexation reaction,

$$s_{1k} B_1^{\nu_1} + s_{2k} B_2^{\nu_2} + \cdots + s_{n_b k} B_{n_b}^{\nu_{n_b}} = C_k, \quad (5)$$

and ν_j is the valence of basis species j .

The sorbed phase concentrations are not treated as unknowns either, though the procedure for calculating them is considerably more complicated than that for calculating the complex concentrations. In the ion exchange model incorporated into the TIP code, all exchangeable sites are assumed to be filled. Therefore, if n_s ions undergo ion exchange, mass action relations are needed for $n_s - 1$ of the sorbed ions, and the concentration of the remaining ion may be calculated from the site constraint equation,

$$N_s = \sum_{l=1}^{n_s} \nu_l \bar{B}_l, \quad (6)$$

where N_s is the number of exchangeable sites per unit volume of fluid. Using this formalism, one of the exchanging ions is chosen as a flagged species, and the rest of the ion exchange reactions are written in terms of ion exchange with the flagged species. For ion B_l exchanging with the flagged species $\bar{B}_*$, the ion exchange reaction is

$$\nu_* B_l^{\nu_l} + \nu_l \bar{B}_* = \nu_l B_*^{\nu_*} + \nu_* \bar{B}_l. \quad (7)$$

The mass action relation for reaction (7) is

$$K_{\bar{B}_l} = \left(\frac{\bar{B}_l}{\bar{B}_{tot}} \right)^{\nu_*} \left(\frac{\bar{B}_{tot}}{\bar{B}_*} \right)^{\nu_l} \frac{(\gamma_* B_*)^{\nu_l}}{(\gamma_l B_l)^{\nu_*}}, \quad (8)$$

where the activities of the solid phases have been approximated by mole fractions,

$$[\bar{B}_l] = \frac{\bar{B}_l}{\bar{B}_{tot}}, \quad (9)$$

and $\bar{B}_{tot}$ is the total solid phase concentration,

$$\bar{B}_{tot} = \sum_{l=1}^{n_s} \bar{B}_l. \quad (10)$$

Method of Solution

Due to the presence of the terms incorporating complexation and ion exchange reactions, the transport equation (1) is nonlinear. An iterative method, the n-dimensional Newton's method (NDNM) [12], is used to advance the solution in time. The NDNM, also known as the Newton-Raphson method, was chosen because it is widely used [13,14,15] and conceptually easy to implement. In order to apply the NDNM, the system of transport equations is rewritten as a set of nonlinear algebraic equations, called residue equations, by approximating the space derivatives in (1) by finite difference approximations. The elements of the Jacobian matrix, required by the NDNM and corresponding to the set of residue equations, are formed analytically. This ensures that the rate of convergence of the NDNM is second-order and reduces the number of operations required to form the Jacobian matrix. More operations would be involved in calculating the elements of the Jacobian matrix if the partial derivatives were formed from divided differences.

The NDNM requires solving a linear system of equations at each iterative step. The coefficient matrix of the linear system is block tridiagonal, and the system of equations can be easily solved using the method of LU factorization [16]. A set of subroutines written by A. Hindmarsh [17] has been included within the TIP code to perform this part of the solution.

The NDNM is also used to calculate the sorbed phase concentrations from the system of mass action relations (8). The presence of the flagged basis species $\bar{B}_*$ is eliminated from (8) and from (10), the expression for $\bar{B}_{tot}$, using the site constraint equation (6). The result is a set of $n_s - 1$ nonlinear equations for the sorbed phase concentrations. In this case the NDNM leads to a full matrix, and an IMSL routine (f04atf) is used to solve the linear system.

The reason for not treating the sorbed-phase concentrations as unknowns in the transport equation, but rather as functions of the basis species, is to reduce the size of the linear system associated with the NDNM. Doing so decreases the amount of computer memory and computation time required to solve the linear systems during each iteration. The only disadvantage of this scheme is that the form of the Jacobian elements becomes more complicated. The trade-off is well worth it, however. A timing analysis of the TIP code has shown that between 50 and 70 percent of the computation time is spent solving the linear systems resulting from the NDNM formulation.

Verification of the TIP Program

The transport, temperature and pressure calculations in the previous version of the TIP program were verified by comparison with analytical solutions for linearized versions of the governing equations [10]. In the present case, assuming constant temperature and pressure distributions, the only nonlinearities result from the addition of the chemical reaction terms. It is not possible to linearize these equations or to derive analytical solutions, but the calculated concentrations have been checked to see that, in the case of the aqueous complexation, the mass action relations (4) are satisfied, and that, in the case of ion exchange, the mass actions relations (8) and the site constraint equation (6) are satisfied.

INPUT DATA

Most of the input data for the simulations was taken or derived from Wanner's work [7]. Wanner used data from experiments in which samples of sodium bentonite were allowed to interact with synthetic groundwater. Using these data, he calculated ion exchange constants for Na^+ , K^+ , Mg^{2+} and Ca^{2+} . In his calculations, Wanner assumed that the activity coefficient of a sorbed components is unity and thus, that its activity is equal to its concentration. In the TIP program, the solid phase activity of a species is approximated by its mole fraction (9). In addition, Wanner used a value of 0.2 as the B coefficient in the Davies equation, and a value of 0.3, recommended by Davies [11], has been used in TIP. The results of recalculating the ion exchange constants from the data that Wanner used and accounting for the adjustments noted above are given in Table I, where the ion exchange reactions have been written in terms of ion exchange with sorbed sodium.

Table I. Ion Exchange Coefficients

<u>ion exchange reaction</u>	<u>log K</u>
$\overline{\text{Na}} + \text{K}^+ = \overline{\text{K}} + \text{Na}^+$	0.39
$2\overline{\text{Na}} + \text{Mg}^{2+} = \overline{\text{Mg}} + 2\text{Na}^+$	-0.20
$2\overline{\text{Na}} + \text{Ca}^{2+} = \overline{\text{Ca}} + 2\text{Na}^+$	0.54

Formation of the following aqueous complexes was considered: NaOH , KOH , CaOH^+ , MgOH^+ , NaCO_3^- , CaCO_3 , MgCO_3 , HCO_3^- , NaHCO_3 , CaHCO_3^+ , MgHCO_3^+ , and H_2CO_3 . The formation constants for these complexes were taken from a data base compiled by Benson and Teague [18]. All of the complexes listed above were considered in preliminary equilibrium calculations, but complexes with concentrations more than four orders of magnitude smaller than the concentrations of the bare ions forming them were not included in the simulations. The only complexes excluded from the simulations were NaOH , KOH , and CaOH^+ .

The initial and boundary conditions for the system were taken from Wanner's report as well. The initial concentrations listed in Table II describe the speciation of porewater in equilibrium with a compacted sodium bentonite. As discussed earlier, Wanner calculated the values in column 1 using a speciation code, but did not consider sorption of Sr^{2+} . The concentrations of the groundwater constituents diffusing into the bentonite are given in column 2.

Table II. Composition of Equilibrated Porewater and Incoming Groundwater
(concentrations in mol/dm^3)

	<u>porewater</u>	<u>incoming GW</u>
Na^+	2.33×10^{-1}	1.76×10^{-1}
K^+	3.63×10^{-4}	1.15×10^{-3}
Ca^{2+}	1.32×10^{-5}	2.16×10^{-2}
Mg^{2+}	2.03×10^{-5}	1.07×10^{-4}
Sr^{2+}		2.40×10^{-4}
CO_3^{2-}	2.64×10^{-3}	9.72×10^{-7}
pH	9.67	6.78

Wanner's report also provided values of porosity (ϵ), bulk density (ρ_s) and cation exchange capacity (CEC) for sodium bentonite MX-80, the same material used in the experiments to determine the ion exchange coefficients. The values used in the simulations are $\epsilon = 0.38$; $\rho_s = 1.7 \times 10^3 \text{ kg/m}^3$; $\text{CEC} = 76.4 \text{ meq/100g}$. The CEC is converted to N_s , the concentration of exchangeable sites, using $N_s = \text{CEC} \rho_s \times 10^{-3} / \epsilon$. The coefficients of mass diffusion were calculated from (3) using the initial porewater concentrations listed in Table II and a value of D equal to $5 \times 10^{-10} \text{ m}^2/\text{s}$ [19].

NUMERICAL SIMULATIONS

The TIP code was used to simulate the radial diffusion of groundwater constituents into a compacted, saturated annulus of sodium bentonite. The inner radius of the bentonite is 0.315 m, and the outer radius is 1.85 m. These values were chosen so that the geometry used in the simulations would approximate that of a Swiss HLW repository. The Swiss HLW program [20] proposes emplacement of a series of canisters 2 m in length, 0.5 m in radius, separated, in the longitudinal direction, by a distance of 3 m and surrounded by a packing of bentonite with a thickness of 1.85 m, measured from the centerline of the canisters. Thus the volume of a long cylinder of radius 0.315 m is approximately equal to that of a series of canisters with the dimensions and spacing of the Swiss HLW program.

The bentonite is assumed to have been equilibrated with a Swiss Reference Groundwater. The chemical species included in the simulation were discussed in the

previous section, and the initial concentrations and the composition of the incoming groundwater are given in Table II. One shortcoming of the current version of TIP is that the concentration of all species were held equal to their initial values at the inner boundary throughout the simulation. In future calculations this constant-concentration boundary condition will be replaced by a zero-flux boundary condition.

A constant temperature of 55°C was used in (2). The $\log K$ values that Wanner calculated, and from which the $\log K$ values in Table I were determined, are based on experiments performed at 25°C. Because of a lack of data [6], it was not possible to correct the $\log K$ values in Table I for temperature.

Calculations of the changes in the fluid phase and sorbed phase concentrations were made for simulated times up to 1000 years. The results of the simulations at selected times are shown in Figures 1 and 2. The concentrations of both the bare ions (Fig. 1) and the sorbed ions (Fig. 2) have been plotted. With the exception of Na^+ , the concentrations of the exchanging ions in the incoming groundwater are larger than their concentrations in the initial porewater. Therefore, the fluid phase concentrations of all ions except Na^+ increase with time at the outer boundary.

In contrast, the solid phase concentrations of K^+ and Mg^{2+} initially increase (Fig. 2a), and thereafter decrease (Figs. 2b and 2c). The solid phase concentration of Na^+ monotonically decreases with time. The decrease in the sorbed phase concentrations of ions other than Ca^{2+} is a result of competition with Ca^{2+} . The concentration of Ca^{2+} in the incoming groundwater is two orders of magnitude larger than its concentration in the initial porewater. As the concentration of Ca^{2+} in the porewater near the outer boundary increases due to the inward diffusion of calcium, so does the competition for ion exchange sites between Ca^{2+} and the other exchanging ions.

Table II shows that the concentration of Sr^{2+} in the incoming groundwater is greater than that of Mg^{2+} . Simulations were made in which Sr^{2+} was included in both the initial porewater and incoming groundwater. Including Sr^{2+} had a greater effect on Mg^{2+} than on any other ion, but at early times, the sorption of all ions was affected. At a simulation time of 1000 years, the differences between the simulations with and without Sr^{2+} were much less evident: only the concentration of sorbed Mg^{2+} differed noticeably.

SUMMARY AND CONCLUSIONS

Chemical reactions of aqueous complexation and ion exchange have been incorporated into an existing transport code, unique in its coupling of fluid flow and changes in chemical composition. The new version of the program preserves the capability of the previous version for simulating the effects of thermodynamically coupled processes on heat and mass transport, though these effects were not included in the current simulations. The chemical reactions were included in such a way as to not increase the

number of unknowns.

The code was used to simulate the effect on the chemical properties of saturated sodium bentonite of inwardly diffusing groundwater. Our results show that changes in the bentonite occur quite slowly. At a simulation time of 1000 years, the concentration of sorbed sodium has decreased by a factor of two, but only in an annulus 0.5 m thick. The decrease of sorbed sodium is due to an increase of calcium in the porewater caused by the high concentration of calcium in the incoming groundwater. Though 1000 years was our longest simulation time, it is clear the direction of change that the bentonite is undergoing, for the chemical system considered. Including Sr^{2+} in the initial porewater and incoming groundwater did affect the sorption of the other ions considered. The sorbed concentrations of Mg^{2+} and Ca^{2+} are somewhat smaller than in the simulations in which Sr^{2+} was omitted, but at long simulation times, the differences are quite small.

One important reaction not yet included in the TIP code is that of dissolution of calcite, which may significantly affect the concentration of Ca^{2+} in the porewater. The next version of TIP will, therefore, include precipitation/dissolution reactions. Once this modification has been completed, we will be able to begin investigations of how the migration of cationic radionuclides, specifically Cs^+ and Sr^{2+} , through bentonite will be affected by changes in the ion exchange properties of bentonite.

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Figure 1. Concentrations of bare ions at simulation times of (a) 10 years, (b) 100 years, and (c) 1000 years.

Figure 2. Concentrations of sorbed ions at simulation times of (a) 10 years, (b) 100 years, and (c) 1000 years.