FEB 0 8 1989

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

EARTH SCIENCES DIVISION

Presented at the Twelfth International Symposium
on the Scientific Basis for Nuclear Waste Management,
Berlin, FRG, October 10-13, 1988, and
to be published in the Proceedings

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LBL--26395

DE89 006653

**Numerical Simulation of Cesium and Strontium Migration
through Sodium Bentonite Altered by Cation Exchange
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This work was supported by the Director, Office of Civilian Radioactive Waste Management, Office of External Relations and Policy, Policy and Program Relations Division, of the U.S. Department of Energy, as part of the DOE/NAGRA Joint Research Project on Flow and Transport in Fractured Media, under Contract No. DE-AC03-76SF00098.

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ABSTRACT

Numerical simulations have been used to investigate how spatial and temporal changes in the ion exchange properties of bentonite affect the migration of cationic fission products from high-level waste. Simulations in which fission products compete for exchange sites with ions present in groundwater diffusing into the bentonite are compared to simulations in which the exchange properties of bentonite are constant.

INTRODUCTION

The mechanism by which the fission products, $^{135}\text{Cs}^+$, $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$, are sorbed by sodium bentonite is reversible cation exchange. In this work we consider the migration of these fission products through both a pure sodium bentonite and a bentonite that has been altered by ion exchange with groundwater constituents. The fission product $^{135}\text{Cs}^+$ is of interest because of its extremely long half-life (2.3 million years). Though $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$ have shorter half-lives, 30 years and 29 years, respectively, they are of interest because of their initially high levels of activity in spent reactor fuel [1].

The present study extends our previous work in which a numerical simulator was used to investigate changes in ion exchange properties of bentonite resulting from the inward diffusion of groundwater constituents [2]. A groundwater, high in calcium and characteristic of a deep granitic formation [3], was used. At a simulation time of 1000 years, the concentration of sorbed sodium, near the interface between the host rock and the bentonite packing material, decreased by a factor of two as it was replaced primarily by calcium. Dissolution of calcite present in the bentonite, which was neglected in previous simulations, has been included in the present work.

DESCRIPTION OF THE ION EXCHANGE MODEL USED

Most investigators seeking to describe the sorptive character of clay materials have focused on measuring a distribution coefficient, or K_d , for each species of interest. Values of the distribution coefficient are known to depend on the concentration of the species and on the pH and ionic strength of the solution containing it [4]. Such dependencies limit the usefulness of the " K_d approach" to modeling radionuclide migration through bentonite because the composition of the pore fluid in the bentonite will vary spatially and temporally as groundwater from the host rock diffuses through the bentonite. The use of distribution coefficients to describe sorption of species that are sorbed by ion exchange has two additional shortcomings. The K_d approach does not account for the presence of other ions in the solution competing for exchange sites or for the fact that the cation exchange capacity of the bentonite is fixed [6].

In this work we use an ion exchange model based on the thermodynamic equilibrium constant, which in contrast to the distribution coefficient, "is an integral quantity characteristic of the whole isotherm surface and is a true constant depending on temperature only" [5]. For a reaction in which cation B_1 replaces the sorbed cation $\bar{B}_2$,

the equilibrium constant is defined by

$$K_{B_1} = \frac{[B_1]^{\nu_1} [B_2]^{\nu_2}}{[B_2]^{\nu_1} [B_1]^{\nu_2}}, \quad (2)$$

where the square brackets denote the activity of a species and ν_1 and ν_2 are the valences of species 1 and 2. In the numerical simulator described in the following section, the Davies equation is used to approximate the activity coefficients of aqueous species, and the solid phase activities are approximated by mole fractions.

DESCRIPTION OF THE THCC COMPUTER PROGRAM

The computer program used to perform the simulations is the THCC program developed by C. Carnahan [7,8]. THCC simulates the transport of reactive chemical species in a one-dimensional nonisothermal system and has been used to simulate transport of uranium species under conditions of changing temperature and oxidation potential [7] and to study the effect of data base variations on numerical simulations of uranium migration [8].

The chemical reactions included in THCC are aqueous complexation, ionization of water, oxidation-reduction and precipitation-dissolution. Prior to performing the simulations reported in this work, ion exchange reactions and radioactive decay were added. Chemical reactions have been incorporated into THCC using the "one-step" method. In the one-step method, the mass action laws describing chemical reactions are inserted directly into the transport equations in contrast to the two-step method in which the equilibrium (speciation) calculation is performed in a step separate from the solution of the transport equations. The advantages and disadvantages of using the one-step and two-step approaches to simulate reactive chemical transport have been discussed by Jennings et al. [9].

THCC uses the finite difference method to approximate the spatial derivatives in the transport equations and the Newton-Raphson method to solve the nonlinear finite difference equations. Ion exchange reactions were incorporated into THCC in such a way as to not increase the number of unknowns that must be solved for at each point in the finite difference grid [2]. The sorbed phase concentrations are not treated as unknowns, but as functions of the concentrations of the species in the fluid phase. An iterative method is used to calculate the sorbed phase concentrations at each finite difference grid point from the fluid phase concentrations at that point. This method of incorporating ion exchange is consistent with the one-step formulation used by THCC because the presence of the sorbed phase concentration of a species is explicitly accounted for in determining the residue equations and Jacobian elements, both of which are required by the Newton-Raphson solution of the transport equations. By taking this approach we have increased the complexity of the chemical system that may be simulated using THCC without increasing the amount of computer memory required at each time step.

INITIAL AND OUTER BOUNDARY CONDITIONS AND CHEMICAL DATA

The initial conditions for the simulations consisted of specifying the composition of the porewater in the bentonite and the concentrations of species sorbed by ion exchange. The initial conditions were determined using the equilibrium routine in THCC. A solution containing major components of a Swiss reference groundwater [3, p. 36] was numerically equilibrated with a compacted bentonite having a cation exchange capacity of 76.4 meq/100 g [3, p. 18]. Several equilibrium calculations that differed by the number of aqueous complexes considered were performed. Initially twelve complexes were considered, but based on the equilibrium calculations, only five, HCO_3^- , $H_2CO_3^*$,

NaCO_3^- , NaHCO_3^0 and MgCO_3^0 , were considered to be present at significant concentration levels and were retained in the transport simulations. Ionization of water was also included. Table I gives the initial composition of the porewater in the bentonite.

The second column in Table I gives the concentrations of the groundwater constituents at the outer boundary of the problem domain, i.e., at the interface between the bentonite and host rock. The concentrations are the same as those in Swiss reference groundwater. Zero initial concentrations and zero concentrations at the outer boundary were used for $^{135}\text{Cs}^+$, $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$.

Table I. Composition of Equilibrated Porewater and Incoming Groundwater
(concentrations in mol/dm³)

	porewater	incoming GW
Na^+	2.64×10^{-1}	1.76×10^{-1}
K^+	3.55×10^{-3}	1.15×10^{-3}
Ca^{2+}	2.43×10^{-4}	2.16×10^{-2}
Mg^{2+}	6.05×10^{-6}	1.07×10^{-4}
Sr^{2+}	5.86×10^{-6}	2.40×10^{-4}
CO_3^{2-}	2.62×10^{-4}	9.73×10^{-7}
pH	8.88	6.78

The formation constants for the complexes and the solubility product constant for calcite were taken from data tabulated by Benson and Teague [10]. The exchange constants for ion exchange reactions involving K^+ , Ca^{2+} and Mg^{2+} were derived from exchange constants determined by Wanner [3] as explained in [2]. Exchange constants for Cs^+ and Sr^{2+} were taken from data compiled by Bruggenwert and Kamphorst [11]. All of the exchange constants used were measured in experiments with Wyoming bentonite at 25°C. Table II gives the ion exchange reactions and equilibrium constant used in the simulations.

Table II. Ion Exchange Reactions and Exchange Constants
ion exchange reaction log K

$\text{Na}^- + \text{K}^+ = \text{K}^- + \text{Na}^+$	0.39
$2\text{Na}^- + \text{Mg}^{2+} = \text{Mg}^{2-} + 2\text{Na}^+$	-0.20
$2\text{Na}^- + \text{Ca}^{2+} = \text{Ca}^{2-} + 2\text{Na}^+$	0.54
$\text{Na}^- + \text{Cs}^+ = \text{Cs}^- + \text{Na}^+$	0.89
$2\text{Na}^- + \text{Sr}^{2+} = \text{Sr}^{2-} + 2\text{Na}^+$	0.18

PROBLEM GEOMETRY AND INNER BOUNDARY CONDITIONS

To simplify the problem geometry, an infinite cylinder was used to approximate a series of waste canisters emplaced horizontally in a circular drift. The cylinder is surrounded by an annulus of compacted, saturated bentonite with an inner radius of 0.315 m and an outer radius of 1.85 m. These dimensions give the same volume of bentonite packing as there would be around a series of waste canisters 2 m in length and 0.5 m in radius, which are separated from end to end by 3 m [1].

At the inner boundary, flux boundary conditions were imposed for all species: zero fluxes for the groundwater species and time-dependent fluxes for the fission products. For each fission product, the time-dependent flux incorporates the initial mass and decay constant of the fission product and the rate of dissolution of the waste form. A constant value of 1.157×10^{-11} kg/m²s was used for the rate of dissolution [12]. The initial masses in the waste form used in the simulations are 4.304×10^{-1} kg of $^{135}\text{Cs}^+$, 6.330×10^{-1} kg of $^{137}\text{Cs}^+$ and 2.805×10^{-1} kg of $^{90}\text{Sr}^{2+}$. These values correspond to forty years after unloading of the fuel elements [1].

RESULTS OF NUMERICAL SIMULATIONS

Migration of $^{135}\text{Cs}^+$, $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$ through compacted sodium bentonite was simulated under three sets of conditions, denoted below and in the figures by (a), (b) and (c). The three cases are: (a) no chemical reactions included; (b) ion exchange reactions between the fission products and a pure sodium bentonite were included; (c) the ion exchange reactions in (b) were included as were ion exchange reactions between the bentonite and constituents in the inwardly diffusing groundwater, aqueous complexation reactions among the groundwater constituents and dissolution of calcite present in the bentonite. In all cases, the transport mechanism was diffusion. An additional assumption made was that the waste canister fails immediately upon emplacement.

The results of the simulations are shown in Figures 1, 2 and 3. Due to space limitations the figures serve to illustrate our results rather than document them in detail.

Figure 1 shows the concentration of $^{137}\text{Cs}^+$ in the bentonite at a simulation time of 100 years. The concentration profile for case (a) exceeds that for the other two cases because the migration of $^{137}\text{Cs}^+$ has not been retarded by sorption by ion exchange. Whereas the concentrations for case (a) decrease by less than an order of magnitude in 0.7 m, the concentrations for cases (b) and (c) decrease by nearly five orders of magnitude.

The concentration profiles for $^{90}\text{Sr}^{2+}$ at a simulation time of 100 years are shown in Figure 2. Because the exchange coefficient of Sr^{2+} is smaller than that of Cs^+ , the difference between cases (a) and (c) is not as large for $^{90}\text{Sr}^{2+}$ as that for $^{137}\text{Cs}^+$. Though not shown, the concentration profiles for $^{135}\text{Cs}^+$ for the three cases at a simulation time of 100 years exhibit the same qualitative behavior as that of $^{137}\text{Cs}^+$.

Figure 1. Concentration of $^{137}\text{Cs}^+$ at a simulation time of 100 years. Curve (a) ignores all ion exchange reactions. Curve (b) accounts only for ion exchange between $^{137}\text{Cs}^+$ and Na^+ . Curve (c) includes the ion exchange reaction in (b) and also accounts for ion exchange between groundwater constituents and bentonite and for dissolution of calcite.

Figure 3 shows the concentration profiles for $^{135}\text{Cs}^+$ at a simulation time of 1000 years. Concentration profiles for $^{90}\text{Sr}^{2+}$ and $^{137}\text{Cs}^+$ (not shown) for the three cases resemble those for $^{135}\text{Cs}^+$, but due to radioactive decay, the concentrations of the two short-lived fission products have significantly decreased compared to those shown in Figures 1 and 2. The trends in Figure 3 are similar to those shown in Figures 1 and 2, but the differences between curves (a) and (c), though significant, are not as large.

Figure 2. Concentration of $^{90}\text{Sr}^{2+}$ at a simulation time of 100 years. Curve (a) ignores all ion exchange reactions. Curve (b) accounts only for ion exchange between $^{137}\text{Cs}^+$ and Na^+ . Curve (c) includes the ion exchange reaction in (b) and also accounts for ion exchange between groundwater constituents and bentonite and for dissolution of calcite.

Figure 3. Concentration of $^{135}\text{Cs}^+$ at a simulation time of 1000 years. Curve (a) ignores all ion exchange reactions. Curve (b) accounts only for ion exchange between $^{135}\text{Cs}^+$ and Na^+ . Curve (c) includes the ion exchange reaction in (b) and also accounts for ion exchange between groundwater constituents and bentonite and for dissolution of calcite.

At a simulation time of 100 years, the ratio of sorbed phase to fluid phase concentration for all three fission products is constant for the range of data plotted in Figure 1. At a simulation time of 1000 years, however, the ratio of sorbed phase to fluid phase concentration for case (c) decreases with distance from the inner boundary due to the inward diffusion of the groundwater ions and the resulting increase in competition for ion exchange sites.

SUMMARY AND CONCLUDING REMARKS

As groundwater diffuses through sodium bentonite, the ion exchange properties of the bentonite will change as ion exchange takes place between Na^+ and cations present in the groundwater. The numerical simulations described previously show that neglecting spatial and temporal variations in the ion exchange properties of bentonite results in overpredicting the amounts of $^{133}\text{Cs}^+$, $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$ sorbed by bentonite. When competition for exchange sites between the groundwater cations and fission products is accounted for, the ratio of the sorbed phase to fluid phase concentration of the fission products is not constant, but varies spatially and temporally.

In the future, the THCC numerical simulator will be further modified to treat a bi-layered medium with each layer having different chemical and physical properties. When this modification is completed, we will be able to investigate the effect of the properties of the host rock on the migration of radionuclides through the near-field.

ACKNOWLEDGEMENTS

The authors would like to thank Piet Zuidema for discussions concerning this work. This work was supported by the Office of Civilian Radioactive Waste Management, U. S. Department of Energy, as part of the DOE/NAGRA Joint Research Project on Flow and Transport in Fractured Media, under Contract No. DE-AC03-76SF00098.

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