Application of a Competitive Cation Exchange Model for Simulating Removal of Strontium in a Zeolite Permeable Reactive Barrier

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Introduction

Permeable reactive barriers (PRBs) are engineered treatment walls consisting of a shallow trench placed in the path of a contaminated groundwater and filled with a permeable material that reacts to remove the contaminant. The West Valley Demonstration Project (WVDP) in western NY State is one of two North American nuclear facilities where sorbing permeable reactive barriers have been constructed for the removal of Sr-90 from groundwater. At the WVDP site, the barrier material is a natural zeolite contained in a clinoptilolite-rich rock that removes Sr-90 by ion exchange.

PRBs present unique and challenging problems in terms of design and performance evaluation. There are sharp discontinuities in both physical and chemical parameters between barrier materials and the native aquifer, the chemistry occurring within the barrier may be complex, and the long time horizons of interest in barrier performance make the use of physical scale models difficult. Consequently, mathematical models are essential tools for PRB design. In this paper, we report on the implementation of a competitive cation exchange model for evaluation of Sr-90 removal in a natural zeolite PRB. The motivation for a cation exchange model is that it represents a more realistic representation of reactions occurring in the zeolite PRB than the traditional K_d approach. The cation exchange reaction module has been incorporated in a 1-D transport model that has been adapted so as to take advantage of the efficiencies offered through multi-processor parallel computing.

Methods

Experimental laboratory column studies were conducted. Two types of data were collected. First, laboratory columns were operated for various time periods and then sectioned and Sr content of the zeolite was determined (microwave-assisted digestion and AA analysis) to provide spatial resolution of Sr penetration in the column. Duplicate columns were operated for about 10, 20, 40, and 60 days. Second, at the startup of one of the columns, effluent samples were collected as a function of time (analysis by ICP) that showed the initial cation exchange front as ions on the zeolite were exchanged with native ions and Sr in the WVDP groundwater. For the sectioned columns, spatial Sr data were interpreted using a single-solute linear isotherm approach. A multi-solute competitive cation-exchange model was used to interpret column effluent data. In addition, a column tracer test was also conducted to determine the dispersion coefficient and effective porosity of the zeolite material.

Both single-solute and multi-solute models for Sr transport in zeolite can be represented by the general one-dimensional advective-dispersive-reactive (ADR) equation. For single solute transport under the assumption of local equilibrium sorption, the retardation factor is defined as $R_f = 1 + \rho_b K_d / n$ where K_d is the sorption distribution coefficient [$M^{-1}L^3$].

For the multi-solute cation exchange model, additional equations are needed to describe the cation exchange process. One equation is provided by a constraint on the total cation exchange capacity. Additional equations are developed by writing mass action expressions for each binary ion exchange reaction, with Na^+ chosen as the reference species. The general form of the equilibrium relationship is:

$$K_{Na,i} = \left(\frac{a_{Na}}{y_{Na}} \right)^m \left(\frac{y_i}{a_i} \right)$$

where *a* represents the aqueous phase activity, *y* is the sorbed phase activity, *m* is the charge of solute *i*, and $K_{Na,i}$ is the equilibrium constant. In this work, the sorbed phase activity was equated with the equivalent fraction as proposed by Gaines and Thomas (1953):

The model equations were solved using a split-operator approach. The split-operator algorithm was implemented in a FORTRAN program developed using a modular structure established in other studies of reactive transport. Each system of nodal cation exchange equations was solved by the Newton-Raphson method.

The multispecies cation exchange model was implemented on both single-processor and massively parallel (MP) computers. The primary MP platform was a Silicon Graphics Origin 2100 located at the Center for Computation Research at the University at Buffalo. Parallel implementation was accomplished using both the Message Passing Interface (MPI) and the OpenMP protocols.

Results

Shown in Figure 1 are the single-solute (K_d approach) modeling results applied to spatially-resolved data from the four laboratory columns (C1-C4). The single-solute model was fit to the data from Column C2, which was selected based on the long duration (63-day) and the good calculated Sr mass balance (97 percent). The calibrated K_d of 2030 mL/g was then used to generate model *predictions* for the other columns, with no adjustment of model parameters. Calibration of the multi-solute cation exchange model to column effluent data is shown in Figure 2. Although some deviations between the model and the data are evident, the trends in the ion exchange front are correctly captured by the model. Finally, a comparison of barrier life based on the two modeling approaches is shown in Figure 3. Both models provide similar predictions, with the treatment goal of 1000 pCi/L for Sr-90 being reached in about 15 years. Because the multi-solute data are much simpler to obtain than spatial data, and also because the multi-solute model allows for testing of variations in the relative concentrations of background cation composition, it is the preferred approach for assessing the performance of alternative barrier materials. Also, once calibrated for a given barrier material, the multi-solute model could be applied to groundwater conditions at any site. The K_d values obtained in this study are specific to WVDP groundwater only. Future work will focus on calibrating the CEC model to multiple ion exchange fronts produced by varying the concentrations of cations in the source water for the column.

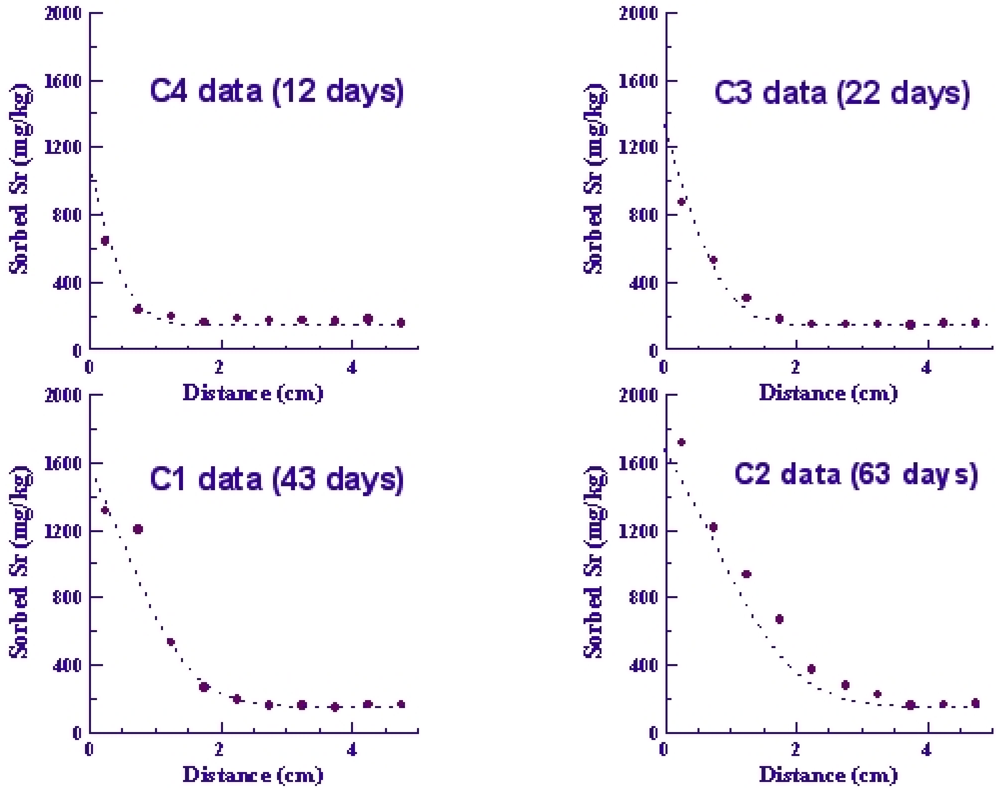

Fig 1. Laboratory column spatial data (symbols) and single-solute modeling results (lines). K_d = 2030 mL/g

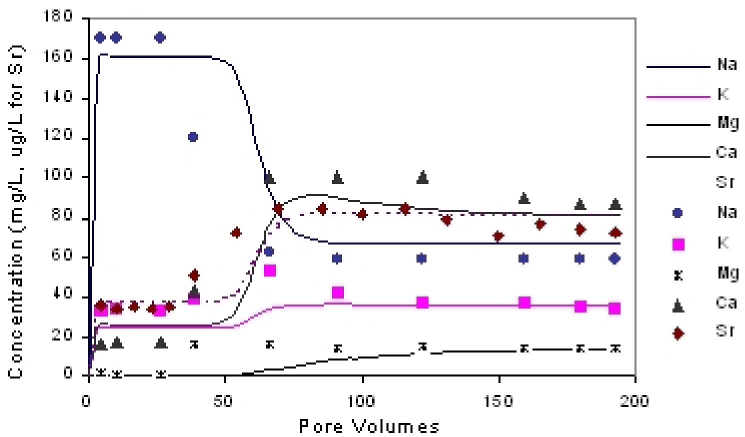

Fig 2. Multi-solute CEC model results

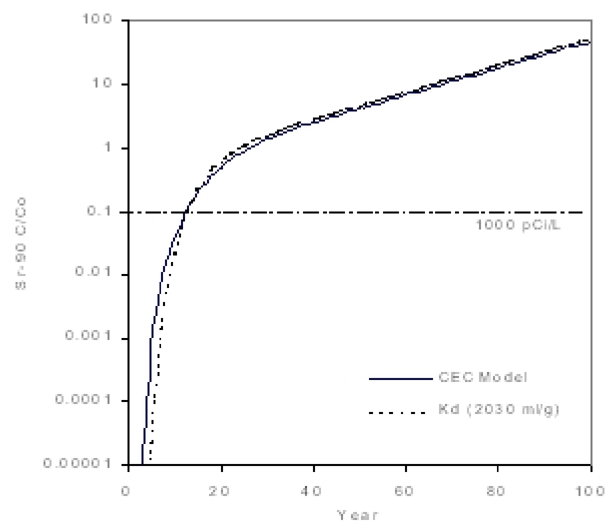

Fig 3. Comparison of modeling approaches for barrier life