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Performance assessment of a zeolite treatment wall for removing Sr-90 from groundwater

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Abstract

Laboratory and modeling studies were conducted to assess the potential performance of a permeable reactive barrier constructed of a natural zeolite material at the West Valley Demonstration Project in western New York State. The results of laboratory column tests indicated that the barrier material would be effective at removing strontium from groundwater under natural gradient conditions. Two one-dimensional contaminant transport models were developed to interpret the data. A single-solute retardation factor model provided good agreement with the column test data, but time-consuming extraction and analysis of the zeolite material was required to parameterize the model. A preliminary six-solute model was also developed based on the assumption of competitive cation exchange as the primary removal mechanism. Both models yielded similar predictions of the long-term performance of the barrier, but the cation exchange model predicted higher effluent concentrations during the first 1000 pore volumes of operation. The cation exchange framework has several advantages, including the ability to calibrate the model using only data from column effluent samples, and the ability to account for site-specific

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differences in the groundwater cation composition. However, additional laboratory work is needed to develop a suitably robust model.

Keywords: Groundwater remediation; Strontium; Zeolite; Cation exchange; Permeable reactive barrier

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1. Introduction

1.1. Background

The West Valley Demonstration Project (WVDP) is one of two North American nuclear facilities to recently deploy a sorbing permeable reactive barrier (PRB) for the removal of strontium-90 (Sr^{90}) from groundwater. The barrier consisted of a shallow trench placed in the path of migrating groundwater, filled with a natural clinoptilolite-rich rock. A general overview of the project is provided by Moore et al. (2000). This paper reports the results of laboratory and numerical analysis conducted to characterize the potential performance of the WVDP treatment wall.

Zeolite materials have been used extensively as ion exchange media in wastewater treatment systems. In particular, certain natural zeolites have exhibited a strong selectivity for the radionuclides cesium (Cs) and Sr^{90} (e.g., Robinson et al., 1991) and are in active use in wastewater treatment systems at several nuclear facilities (e.g., Barton et al., 1997). Recently, the application of natural zeolites has been extended to include subsurface permeable reactive barriers (PRBs) for remediating groundwater contamination. At the time of this writing, two North American nuclear facilities have deployed barriers constructed of a natural clinoptilolite-rich rock for removal of Sr^{90} from groundwater: (1) the Chalk River (Canada) facility (Lee et al., 1998), and (2) the West Valley Demonstration Project in western New York State (Moore et al., 2000). A similar PRB had also been considered for the US Department of Energy facility in Hanford, Washington, although the project was discontinued, in part due to stakeholder concerns (USDOE, 1997). The use of surfactant-modified-zeolite to remediate mixtures of organic and inorganic contaminants also has been extensively evaluated through laboratory and pilot testing (Bowman et al., 1999, 2001).

Construction and economic factors have constrained the installed thicknesses of PRBs, including the zeolite-based systems, to less than approximately 2 m in the direction of groundwater flow (e.g., USEPA, 2002; Gavaskar et al., 1998). Since the corresponding solute residence time is expected to be much shorter than the time scale for Sr^{90} decay, replacement of the zeolite media will be required when the sorption capacity is exhausted. Performance assessment has therefore relied on a combination of short-term laboratory experiments and mathematical modeling to predict the PRB time-to-replacement, which significantly influences the economics of the system.

The barrier material installed at WVDP and Chalk River (and considered for use at Hanford) was a clinoptilolite-rich rock supplied by Teague Mineral Products (TMP) of Adrian, Oregon. Removal of aqueous Sr^{90} by clinoptilolite is generally understood to occur via a competitive ion exchange process. In groundwater systems, calcium represents the chief competitor for exchange sites because of its abundance and preference. However, the previous models developed for PRB systems have typically reflected the simplistic assumptions of linear local equilibrium using a single sorption distribution coefficient (K_d) (e.g., Cantrell, 1996; Lee et al., 1998; Moore et al., 2000). Characterization of Sr sorption in terms of a K_d is typically supported by tests conducted under the assumptions of "worst-case" competition and local linear equilibrium partitioning. While some justification for these simplifications has been offered on the basis of limited laboratory experiments (e.g., Cantrell, 1996), the use of the K_d approach is primarily a reflection of resource limitations, the multiple sources of uncertainty associated with assessing long-term PRB performance, and the lack of an established alternative modeling framework.

Estimated K_d values for Sr^{90} and the TMP mineral have exhibited significant variability. For the Chalk River site, Lee et al. (1998) reported K_d values of 1700 and 745 mL/g, based on unpublished column tests. In preliminary testing conducted for the Hanford project, Cantrell (1996) performed batch kinetic and equilibrium sorption tests using synthetic groundwater and Sr^{85}as a surrogate for Sr^{90}. For Sr^{85} concentrations below 10^{-6} M, the estimated K_d was 2600 mL/g. Initial performance assessment for the WVDP project was reported by Fuhrmann et al. (1995), who estimated the Sr^{85} K_d at 650 mL/g, based on data from column tests conducted using site groundwater. As discussed below, the range in the estimated K_d could be influenced by differences in site-specific groundwater chemistry, as well as the testing methods employed.

1.2. Objectives

This paper reports the results and interpretation of column and batch tests performed at the University at Buffalo prior to the WVDP treatment wall installation. Following the deployment of the pilot barrier in 1999, which was assessed using a simplified K_d approach, a more detailed mathematical model was developed to provide additional insight into the competitive ion exchange behavior of the TMP materials. In addition to improving the confidence associated with performance assessment, the development of a mechanistic sorption model was motivated by the desire to extrapolate performance data to sites characterized by different groundwater conditions, particularly with respect to calcium. The application of an accurate mechanistic model could also provide cost savings in the design of laboratory and field studies, since it is often easier to collect data for nonradioactive cations.

The specific objectives of the research included:

- Implementation of laboratory batch and column experiments to characterize the sorption of Sr to the natural zeolite-rich material used in the WVDP treatment wall.
- Development of a simple K_d-based simulation model for preliminary performance assessment.
- Development of a preliminary multi-solute model based on the assumption of competitive cation exchange as the dominant sorption mechanism.
- Comparison the two models in terms of data needs, computational burden, and the predicted treatment wall performance.

- Application of the multi-solute model to assess the sensitivity of the predicted treatment wall performance to potential changes in the aqueous geochemistry.

2. Model development

2.1. Conceptual model

The work reported here represents an initial effort in the development of a general model for zeolite treatment walls that remove contaminants by cation exchange. As a first step, the assumption of physical and chemical equilibrium was considered reasonable because of: (1) the relatively low velocities associated with natural groundwater flow in treatment walls, (2) the relatively small particle size of the TMP material under consideration, and (3) the lack of information regarding the pore geometry and diffusion properties of the specific candidate material, which included approximately 30% non-zeolitic materials. The assumption of rapid sorption was further supported by the batch experiments performed by Cantrell (1996) that indicated near-equilibrium for Sr^{85} sorption after a period of approximately 24 hours. As discussed below, the equilibrium model yielded good model fits across multiple data sets in experiments performed for the WVDP project. However, the influence of nonequilibrium sorption in zeolite-based PRBs is an open research question, and a more comprehensive model that includes intraparticle diffusion is under development.

Several unusual aspects of Sr transport in PRBs are noteworthy. First, while Sr^{90} represents a significant health concern due to its high specific activity, it is typically present in groundwater at very low mass concentrations (e.g., in the ng/L to μg/L range). Second, the level of nonradioactive Sr^{2+} in natural groundwater is much higher (e.g., ~200 μg/L at the WVDP site). However, natural Sr^{2+} is much less prevalent than the other competing cations, which are dominated at the WVDP by Ca^{2+} in the 50 to 250 mg/L range. Third, the natural zeolite-rich materials considered for PRB applications contain significant amounts of all the competing cations, including Sr^{2+}.

Studies of coupled transport and ion exchange in porous media have been reported for both engineered and natural systems. For engineered systems, emphasis has been placed on characterizing the kinetic behavior in batch reactors (e.g., DePaoli and Perona, 1996; Ma et al., 1996). For transport in natural soil systems, equilibrium approaches have predominated, and a number of conceptual models have been used to represent the sorption of cations in the advective-dispersive-reactive equation. Valocchi et al. (1981) coupled a one-dimensional transport model with single-site cation exchange model based on the Gaines–Thomas (GT) convention (Gaines and Thomas, 1953). Similar approaches were adopted by others (Selim et al., 1987; Mansell et al., 1988) and extended to consider alternative conventions including the Vanselow and statistical thermodynamic approaches (Grant et al., 1995) and mass action equations expressed in terms of the equivalent fraction (Cernik et al., 1994). Subsequent work has suggested that the performance of transport models could be improved by extending the simple cation exchange framework to include multiple exchange sites (Vulava et al., 2000, 2002; Voegelin et al., 2000). In some cases, additional reactions have been coupled with cation exchange, including specific adsorption (Voegelin et al., 2001) and precipitation (Spalding and Spalding, 2001).

For this work, the single-site GT convention was adopted, which has performed well in comparisons of cation exchange models (Grant et al., 1995; Vulava et al., 2000, 2002; Voegelin et al., 2000; Carlyle et al., 2004). Although this convention is implemented in public domain reactive transport codes such as PHREEQC (Parkhurst and Appelo, 1999), a new model was developed to provide needed flexibility in column and field boundary conditions, and to effectively utilize available parallel computing platforms.

2.2. Numerical model

In this work, both single-solute and multi-solute models for Sr transport in zeolite were developed and compared. Both approaches were represented by the one-dimensional advective-dispersive-reactive equation. Following the general approach of Perona (1993), the multi-species model was formulated to consider exchange reactions involving Sr^{2+} (nonradioactive), Sr^{90}, Ca^{2+}, Na^{+}, Mg^{2+}, and K^{+}. The total cation exchange capacity was assumed to be occupied only by these solutes, and the equilibrium relationships were formulated using the GT convention with Na^{+} as the reference solute; the Davies equation (e.g., Stumm and Morgan, 1996) was used to calculate the aqueous activity coefficients. In modeling Sr exchange in zeolites, some researchers have proposed the use of more complex expressions for sorbed phase activity such as the Wilson equation (e.g., Perona, 1993), which requires two additional empirical "interaction parameters" for each ion pair. Given the limitations of available data and the lack of a compelling argument for use of the more complex formulation, the simpler GT convention was considered adequate.

A complication associated with Sr^{90} exchange is the treatment of sorbed phase decay. Although the radioactive decay process is understood to result in the disappearance of both aqueous and sorbed Sr^{90} at the known rate, it is unclear whether the daughter products occupy exchange sites. Because the most prevalent reaction product (zirconium) is not known to participate in the ion exchange process, the model was formulated both with and without the decay of sorbed Sr^{90}.

The cation exchange reactions were coupled to an existing transport model using a "two-step" split-operator algorithm (Miller and Rabideau, 1993; Rabideau and Khandelwal, 1998; Rabideau et al., 1999). For scenarios in which Sr^{90} decay was included, an additional step was added to each reaction solution in which aqueous and sorbed Sr^{90} decay was calculated analytically following equilibration (i.e., a "three-step" approach). The advective-dispersive equations were solved using a quadratic finite element approximation of the spatial derivatives and a Crank–Nicholson finite difference approximation of the time derivative. Each system of nodal cation exchange equations was solved by the Newton–Raphson method. Because the majority of the computational demand was associated with the reaction steps, operator-splitting was implemented using the "alternating" approach (e.g., Miller and Rabideau, 1993). The multispecies cation exchange model was implemented on a variety of single-processor and parallel computers located at the Center for Computational Research at the University at Buffalo (www.ccr.buffalo.edu). Parallel implementation was accomplished using both the Message

Passing Interface (MPI) and the OpenMP approaches. A single-processor version of the model is available for download (Rabideau, 2004).

For both laboratory and field applications, a finite (zero-gradient) boundary condition was applied at the domain exit. In modeling column effluent data, a specified concentration entrance condition was used. For field applications, the entrance boundary concentration was treated as time-dependent to represent the movement of an increasing concentration plume through the treatment wall. For column experiments that measured the sorbed phase at the end the experiment, a mass-conserving 3rd-type inlet boundary condition was necessary (e.g., Rabideau et al., 2001).

Extensive numerical experimentation was performed to establish confidence in model accuracy by: (1) verifying convergence of simulation results with spatial and temporal step refinement, and (2) comparing the results of single-solute analytical solutions with multi-solute predictions in which the cation exchange parameters were specified to mimic noncompetitive linear isotherms. A focused sensitivity analysis was then performed to characterize to identify parameters that strongly influence barrier time-to-replacement, based on a hypothetical field-scale PRB similar to the WVDP system.

3. Experimental methods

3.1. Materials

The material used in the WVDP treatment wall was a natural clinoptilolite-rich rock (henceforth denoted “clino”) supplied by Teague Mineral Products (TMP) of Adrian Oregon. Relevant physical and chemical properties are summarized in Tables 1–3. The two materials are denoted CH20 × 50 and CH14 × 50, where CH denotes the location of the zeolite source and the numbers refer to standard sieve sizes. Both size fractions had a clinoptilolite content of 68–70%. Grain size analyses were conducted according to ASTM Method D422. Hydraulic conductivity was measured using a Boart Longyear constant-head permeameter according to ASTM D2434-68, which reflects the “loose packing” approach. To assess the possible role of field compaction, an ad hoc follow-up test was conducted in which the zeolite was compacted with a hammer in the permeameter cell, in a manner similar to the standard Proctor test. All sorption tests were conducted using the

Table 1
Selected material properties reported by Teague Mineral Products (TMP)

Parameter	Value	Source
Cation exchange capacity (CEC)	1.65 meq/g	Average of 3 tests performed by Hazen Research (Golden CO) on CH 14 × 50
Strontium content	152.5 mg/kg	Average of two X-ray fluoresence tests performed by DCM Science Laboratory (Wheat Ridge, CO) on CH 14 × 50
Particle density	2.2 g/cm^3	20 × 50, TMP Information bulletin
Bulk density (loose)	0.78 g/cm^3	20 × 50, TMP Information bulletin
Bulk density (packed)	0.85 g/cm^3	20 × 50 TMP Information bulletin

Table 2
Mineral phases for study materials

Mineral	Weight percentage		
	UB 20 × 50	UB 14 × 50	TMP 14 × 50
Clinoptilolite	70	68	70
Smectite	8	9	6
Opal CT	17	18	19
Feldspar	3	3	3
Quartz	<1	<1	<1
Unidentified	<3	<3	<3

UB=actual materials used in this work.
TMP=general information provided by Teague Mineral Products.
All tests performed by DCM Science Laboratory (Wheat Ridge, CO).

20 × 50 fraction, although the field design for both Chalk River and WVDP was eventually changed to the 14 × 50 fraction because of the higher hydraulic conductivity and lower cost.

For the preliminary batch isotherm and column tests, site groundwater was collected by West Valley Nuclear Services (WVNS) personnel from a monitoring well located outside of the contaminant (Sr^{90}) plume. The water was shipped in headspace-free 5-l plastic containers and stored in a temperature controlled chamber at 10 °C. Several of the bags contained water that became discolored (light brown) presumably due to oxygenation; these were excluded from use in the experiments. Chemical constituents relevant to this work are summarized in Table 4. For all experiments reported here, nonradioactive Sr^{2+} was used as a surrogate for Sr^{90}.

3.2. Preliminary isotherm

To provide an initial estimate of the sorption capacity, a preliminary batch sorption test was conducted using material that was pre-washed with Nanopure water to remove fines. Preliminary kinetic experiments were not conducted; the 14-day period was considered adequate to establish a an approximate estimate of the overall media sorption capacity. A

Table 3
Grain size analyses

Sieve	Percent passing					
	CH 20 × 50			CH 14 × 50		
	UBu	UBw	TMP	UBu	UBw	TMP
10 (2 mm)	100	100	100	100	100	100
20 (0.85 mm)	75.7	71.5	79.9	75.7	71.5	77.9
30 (0.60 mm)	40.4	33.1	45.2	40.4	33.1	45.2
40 (0.43 mm)	16.9	11.0	19.4	16.9	11.0	19.4
50 (0.30 mm: fines)	2.8	1.2	3.1	2.8	1.2	3.1

UBu=materials used in this research (average of 3 samples, unwashed).
UBw=materials used in this research (average of 2 samples, prewashed).
TMP=general information provided by Teague Mineral products.

Table 4
WVDP major groundwater constituents ([a]=typical field measurements from source well; others were measured from column reservoir)

Constituent	Value
Ca^{2+}	100 mg/L
Mg^{2+}	15 mg/L
K^{+}	3.5 mg/L
Na^{+}	68 mg/L
Sr^{2+}	0.2[a] mg/L
pH	6.9[a]
Cl^{-}	120[a]mg/L
HCO_3^{-}	270[a]mg/L
SO_4^{2-}	64[a] mg/L

replicated series of tests was performed using 20-mL glass vials, 4 grams of pre-washed CH 20 × 50, and groundwater spiked with Sr^{2+} stock solution at 10 concentration levels. The bottles were allowed to equilibrate for 14 days on a shake table. At the end of the equilibration period, solid/liquid separation was accomplished by centrifugation followed by filtration at 0.45 μm, and the aqueous Sr^{2+} concentrations were measured. Due to the presence of naturally occurring Sr in the zeolite, the sorbed concentrations were computed as follows:

$$q = \frac{V\left(C_0 - C_f\right) + q_0 M}{M} \tag{1}$$

where q is the final sorbed concentration, C_0 is the initial aqueous concentration (estimated from blanks), C_f is the final measured aqueous concentration, V is the liquid volume, q_0 is the initial sorbed concentration, and M is the zeolite mass.

3.3. Column performance studies

Characterization of strongly sorbing materials using column experiments is inherently difficult, and is usually accomplished using one or more of the following strategies (Rabideau et al., 2001): (1) short columns, realistic flow rates, and long experiments (e.g., thousands of pore volumes) to generate complete effluent breakthrough curves, (2) artificially high velocities that accelerate breakthrough at the expense of possible artifacts due to nonequilibrium sorption, and (3) measurement of the spatial, rather than temporal, contaminant distributions, which requires extraction of the solid phase and more complex interpretive models. The third approach was adopted in this work to enable the use of realistic velocities within the constraint imposed by a two-month study schedule. To provide insight into the possible role of kinetic and nonlinear effects, duplicate columns were operated for different durations.

Eight column experiments were initiated as a replicated set of four. The experiments were labeled using a number (10, 20, 40, 60) to designate the nominal duration in days and a letter (a, b) to designate the replicate group. The columns were constructed of borosilicate glass, each 2.5 cm in diameter and 15 cm in length, and housed in a temperature-controlled chamber maintained at 10 degrees Celsius, the approximate average groundwater temperature at the WVDP. The clino material (20 × 50) was introduced into the columns in layers by sequentially adding small amounts of Nanopure water and clino, with considerable care taken to minimize the potential for the formation of voids. A zone of glass beads (approximately 0.5 cm in length) was placed at each end of the column. Once the columns were filled, they were flushed with Nanopure water for 48 h prior to introduction of the groundwater.

Two reservoirs of source groundwater were prepared using 20-l plastic carboys, one for each set of 4 columns. Because of the potential for incomplete penetration of Sr^{2+} during the time-limited column tests, $SrCl_2$ was added to the site groundwater to raise the source concentration from approximately 200 μg/l to 1 mg/L. After the initial 48-h flush was completed, the groundwater was fed to the columns in an upflow mode using two peristaltic pumps, each operated to produce a fluid velocity of approximately 0.4 m/d, which is at the high end of the range of velocities observed at the WVDP and similar to the value previously used for performance assessment by Furhmann et al. (1995). Samples were collected from the influent reservoirs at periodic intervals and analyzed for pH, turbidity, Sr^{2+}, and Ca^{2+}.

Effluent samples were collected daily from each column over a period of approximately 8 h. The average flow rates were determined gravimetrically and the pumps were adjusted when significant deviations (± 10%) from the design flow rate were noted. Each effluent sample (approximately 50 mL) was analyzed for pH and turbidity, then split into two subsamples. One subsample from each set was filtered using a 0.1 mm syringe filter. Both filtered and unfiltered samples were analyzed at periodic intervals for Sr^{2+}. Selected effluent samples from column C60a were also analyzed for Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}.

Flow to the individual columns was terminated after intervals of approximately 10, 20, 40, or 60 days. After flow was stopped, free water was drained from the column. The clino was then removed by carefully lifting the solids from the end of the column in 0.5-cm increments using a stainless steel scoop. The individual segments were dried, weighed, and subjected to microwave-assisted acid digestion, followed by analysis for Sr^{2+}. Six samples of unprocessed clino were also digested and analyzed to determine the level of background Sr^{2+}.

A column tracer test was conducted to determine the dispersion coefficient and effective porosity. Due to a limited supply of site groundwater, synthetic groundwater was used for this test, consisting of Nanopure water with 100 mg/L $CaCO_3$, buffered to pH 7 with the addition of NaOH. Because the experimental columns had been sacrificed to obtain measurements of sorbed Sr, a new column was assembled using the same TMP source material. The column was flushed with dionized water for 24 h, at which point a modified source water was introduced containing Br^{-}at approximately 1000 mg/L (added as NaBr). The bromide solution was fed to the column for approximately 24 h, after which the original solution was reintroduced and flushing continued for an additional 24 h. Effluent samples were collected at 30-min intervals and analyzed for Br^{-}.

3.4. Analytical methods

Analysis of aqueous samples for Sr^{2+} was performed using a Perkin Elmer Aanalyst 300 atomic absorption (AA) spectrophotometer equipped with a graphite furnace

(Standard Methods 3133). Analyses of selected aqueous samples for other cations (Ca^{2+}, K^+, Na^+, Mg^{2+}) were conducted by Advanced Environmental Services (Niagara Falls, NY) by Inductively Coupled Plasma (ICP) according to EPA method 200.7. Aqueous samples from the column tracer tests were analyzed for bromide using a Shimadzu LC10AS ion chromatograph with an anion column (Shimadzu IC-A1) and a conductivity detector operating at 40 °C (SW846-7780 or Standard Methods, 4110).

The clino cation exchange capacity (CEC) was measured by Mineral Associates (Clarkson, NY) using a modified version of the method described by Sumner and Miller (1996). A 1-g<60 mesh sample of clino material was mixed with three separate doses of 0.5 M NH_4Cl, for 5, 5, and 390 min, with centrifugation and supernate decantation in between the doses. Interstitial salts were removed by shaking the clino for the same lengths of time in deionized water. The NH_4 was then extracted by shaking the washed product for the same periods of time with 1 M KCl, combining the supernates. The combined liquid was brought to 100 ml volume and the pH was adjusted to 2. The ammoniacal nitrogen content of the liquid was then analyzed using an ion-selective electrode. The initial concentrations of Na^{2+}, Mg^{2+}, Ca^{2+}, Fe^{2+}, Ba^{2+}, and Sr^{2+} were determined by ICP analysis of the liquid collected during the NH_4 saturation step.

Some clino samples were subjected to a microwave-assisted acid digestion procedure (EPA Method SW846-3051). Ten ml of 0.1 M nitric acid were combined with 0.5 g zeolite and placed in a CEM MDS2000 digestion unit for 20 min. Solid/liquid separation was accomplished by filtration (0.45 μm), and the liquid was analyzed for Sr^{2+} or other cations by ICP.

4. Results

4.1. Hydraulic conductivity

The results of hydraulic conductivity testing, along with published results from other studies, are summarized in Table 5. As discussed below, a concern arose that the standard “loose packing” methodology may not adequately represent the behavior of the TMP material in the field. Supplemental tests performed using an ad hoc compaction procedure suggested that compacting the zeolite could reduce the observed hydraulic conductivity by at least an order of magnitude, with results similar to those observed subsequently in monitoring well slug tests.

4.2. CEC tests

The CEC values measured by Mineral Associates (1.31, 1.25 meq/g) were significantly lower than the generic values reported by TMP (1.65 meq/L). The reason for this discrepancy was not clear, although it may have been influenced by differences in both the test material and measurement technique. The sum of the five major exchangeable cations (1.14 meq/g for both samples) was slightly less than the total measured CEC, presumable due to experimental error (concentrations of exchangeable iron and barium were also measured, but were negligible.) Potassium dominated the exchanger phase, representing slightly more than half the CEC. The measurements from

Table 5
Summary of hydraulic conductivity tests

Study	Material	K (cm/s)	Method
Rabideau et al. (this study)	20 × 50 unwashed (0.3–0.85 mm)	0.11–0.14	ASTM D2434
	20 × 50 washed	0.13–0.14	ASTM D2434
	14 × 50 unwashed (0.3–1.4 mm)	0.16–0.40	ASTM D2434
	14 × 50 washed	0.33–0.35	ASTM D2434
	14 × 50 unwashed, compacted	0.004	Modified ASTM D2434
West Valley Nuclear Services (2001)	14 × 50 field	0.0016–0.003	7 slug tests
Aloysius (1995)	20 × 50 unwashed	0.027	FH
	20 × 50 washed	0.9	CH
Cantrell (1996)	20 × 50 unwashed	0.065	CH
	5 × 20 unwashed (0.85–4.0 mm)	0.15	CH
	4 × 8 unwashed (2.4–4.8 mm)	0.31	CH
	3/8 × 5 unwashed (4–19 mm)	0.36	CH
Abadzic and Ryan (2001)	20 × 50 unwashed (0.3–0.85 mm)	0.12	column max
	20 × 50 washed	0.12	column max
	20 × 50 calcined	0.13	column max
	5 × 50 unwashed	0.20	column max
	5 × 50 washed	0.20	column max
	5 × 50 calcined	0.21	column max
Bowman et al. (2001)	14 × 40 unwashed (0.4–1.4 mm)	0.1–0.2	CH, FH, SC
	14 × 40 field	0.02	slug test, SC

CH=constant head, FH=falling head, SC=St. Cloud mine (all other results are for TMP).

the sample with the better mass balance were used to establish initial conditions for modeling, as summarized in Table 6.

The measurements of natural Sr^{2+} obtained using the digestion procedure were significantly higher (0.0034 + 0.0004 meq/g for 6 samples) than the CEC-based values (0.002 meq/g). In the original experimental design, it was assumed that all Sr^{2+} removed from the zeolite by digestion represented “exchangeable” cations bound by a reversible process that could be described by either of the conceptual models (K_d or competitive cation exchange). However, the lower values obtained from the CEC-based tests suggested that a portion of Sr^{2+}associated with the solid phase was non-exchangeable. Therefore, the “exchangeable” portion of naturally occurring Sr^{2+} was quantified using the value from the CEC tests, and the inferred “nonexchangeable” portion (0.0014 meq/g) was subtracted from subsequent measurements obtained using the digestion procedure.

4.3. Isotherm

The primary purpose of the initial batch isotherm test was to develop a preliminary model for the columns for use in experimental design. The isotherm data were well-described by the Langmuir expression [$q = bQ_0C/(1+bC)$], with the best-fit parameters determined by nonlinear regression assuming constant relative error in the estimated sorbed concentrations ($b = 1.92$ L/mg and $Q_0 = 1692$ mg/kg). At low concentrations (below 200 μg/L), the isotherm was approximately linear, with an estimated $K_d = 2965$ mL/g. The latter value is similar to the results of the Hanford study of $K_d = 2650$ mL/g (Cantrell,

Table 6

a. Parameters used in column modeling (common)

Parameter	Value	Comment
Diameter (cm)	2.5	
Flow rate (L/d)	0. 1237 (C10a–C60a) 0.1324 (C10b-C60b)	Average over study period
Sr^{2+} influent (mg/L)	0.98 (C10a–C60a) 1.03 (C10b–C60b)	Average of 9 measurements
Dispersivity (cm)	0.51	Tracer test calibration
K_d (mL/g, K_d model only)	2045	Calibrated from C60b spatial data
Initial sorbed Sr^{2+} (meq/g) (both models)	0.002	Measured by mineral associates
Cation exchange model		
CEC (meq/g)	1.14	Sum of exchangeable cations measured by mineral associates
Initial sorbed Ca^{2+} (meq/g)	0.23	Measured by mineral associates
Initial sorbed Mg^{2+} (meq/g)	0.01	Measured by mineral associates
Initial sorbed Na^{+} (meq/g)	0.26	Measured by mineral associates
Initial sorbed K^{+} (meq/g)	0.64	Measured by mineral associates
$K_{\text{Na-Sr}}$	4714	Calibrated from column C60a effluent
$K_{\text{Na-Ca}}$	333	Calibrated from column C60a effluent
$K_{\text{Na-Mg}}$	295	Calibrated from column C60a effluent
$K_{\text{Na-K}}$	26	Calibrated from column C60a effluent

b. Parameters used in column modeling (individual)

Parameter	Column value							
	C10a	C20a	C40a	C60a	C10b	C20b	C40b	C60b
Bulk density (g/cm^3)	0.78	0.77	0.77	0.83	0.84	0.80	0.86	0.80
Porosity	0.63	0.63	0.63	0.61	0.60	0.62	0.59	0.62
Length (cm)	14.0	13.7	13.7	13.5	13.2	13.8	12.7	13.0

1996) and is higher than the batch value of 765 mL/g reported previously by Furhmann et al. (1995) using WVDP groundwater. The estimated maximum sorption capacity ($Q_0 = 1692$ mg/kg $= 0.038$ meq/g) was considerably lower than the typical measured CEC (1.14 meq/g).

The preliminary isotherm was calculated without the correction for “nonexchangeable” Sr^{2+} described above. However, since the purpose of the isotherm test was only to provide preliminary data for the design of the column studies, further interpretation of these results was not pursued. The estimated sorption capacity was used to establish the design flow rate for the columns, with the objective of achieving measurable penetration of Sr^{2+} during the 10–60 day experimental periods.

4.4. Column tests: sorbed Sr^{2+}

For the eight spatial data sets, elevated levels of total Sr^{2+} (aqueous plus sorbed) were observed over the first few centimeters of the 15-cm columns, with the remainder of the column samples exhibiting levels consistent with the initial background Sr^{2+}. In general, excellent agreement was noted between replicate columns. The spatial data from the eight columns are presented in Fig. 1, along with the modeling calibration and predictions discussed below. These results highlight a drawback to the use of nonradioactive Sr^{2+}as a surrogate for Sr^{90}: limited resolution at the leading edge of the Sr^{2+}front due to the presence of background Sr^{2+}.

As a check on the accuracy of the column results, the Sr mass balance was computed for each column as follows:

$$\%\ \text{mass recovered} = 100 \times \frac{\text{effluent mass} + \text{final sorbed mass}}{\text{influent mass} + \text{initial sorbed mass}} \tag{2}$$

with the components estimated as follows:

- The final sorbed mass was computed directly by summing the measured Sr^{2+} mass from each digested zeolite segment.
- The influent mass was computed as the product of the average column flow rate and the average source reservoir Sr^{2+} concentration, multiplied by the duration of the column test.
- The effluent mass was computed as the product of the column flow rate and the area under the effluent Sr^{2+} concentration curve (estimated by numerical integration).
- The initial sorbed mass was computed by multiplying the total zeolite mass by the initial (background) sorbed Sr^{2+} mass fraction, which was estimated as 150 mg/kg based on multiple measurements of unprocessed zeolite.

The eight computed mass balances ranged from 97% to 115%, with an average of 103%. Together with the good agreement between replicate columns, the mass balance results indicated that the spatial data were of high quality and provided a good picture of column behavior.

4.5. Column tests: effluent

The breakthrough curve and model fit for the bromide tracer test are shown in Fig. 2. Column calibrations were performed using a modified version of the CXTFIT program (Parker and van Genuchten, 1984) for fitting the advective-dispersive-reactive equation. The data were used to estimate the dispersivity and confirm that the effective porosity was equivalent to the value calculated from the measured bulk density. A small degree of early breakthrough and tailing was observed, but application of a “two region” model did not significantly improve the overall quality of model fit, presumably because the single mass transfer coefficient was inadequate to capture the nonideal behavior at both the leading and tailing edges of the breakthrough curve.

For the 60-day columns, the effluent pH exhibited a gradual trend from an initial value of approximately 7.5 to a final value of approximately 8.5. This trend directly mirrored a gradual increase in the influent pH, which was attributed to the slow release of dissolved carbon dioxide from the source groundwater. Previous work has suggested that Sr sorption to zeolite is insensitive to pH over the range 3–9 (USDOE, 1997), which is consistent with the hypothesized cation exchange mechanism.

After a transient period of several pore volumes, during which fine particles were washed from the columns, the effluent turbidity stabilized at values in the range of 0.3–0.5 NTU, slightly lower than the corresponding influent value, which averaged 0.46 NTU. Comparisons between filtered and unfiltered samples showed no systematic deviation, which, together with the low effluent turbidity, suggests that particle-facilitated transport was not a significant factor. However, the loss of fine particles may have reduced the effective column CEC, as discussed below.

Effluent concentrations for Sr^{2+}, Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} from column C60a are shown in Fig. 3, along with predictions generated by the calibrated multi-solute model (discussed below). The development of an ion exchange front is apparent, in which the

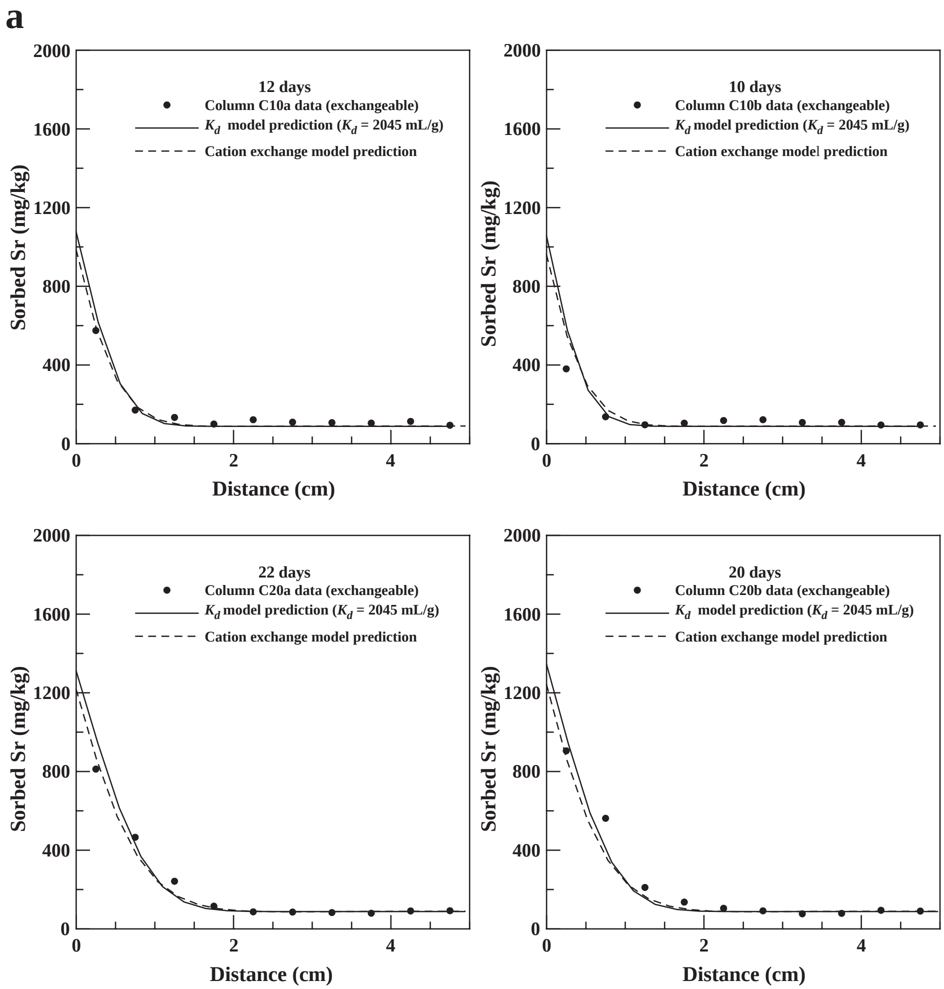

Fig. 1. a. Spatial concentrations and model predictions for 10- and 20-day columns. b. Spatial concentrations and model calibration/predictions for 40-and 60-day columns.

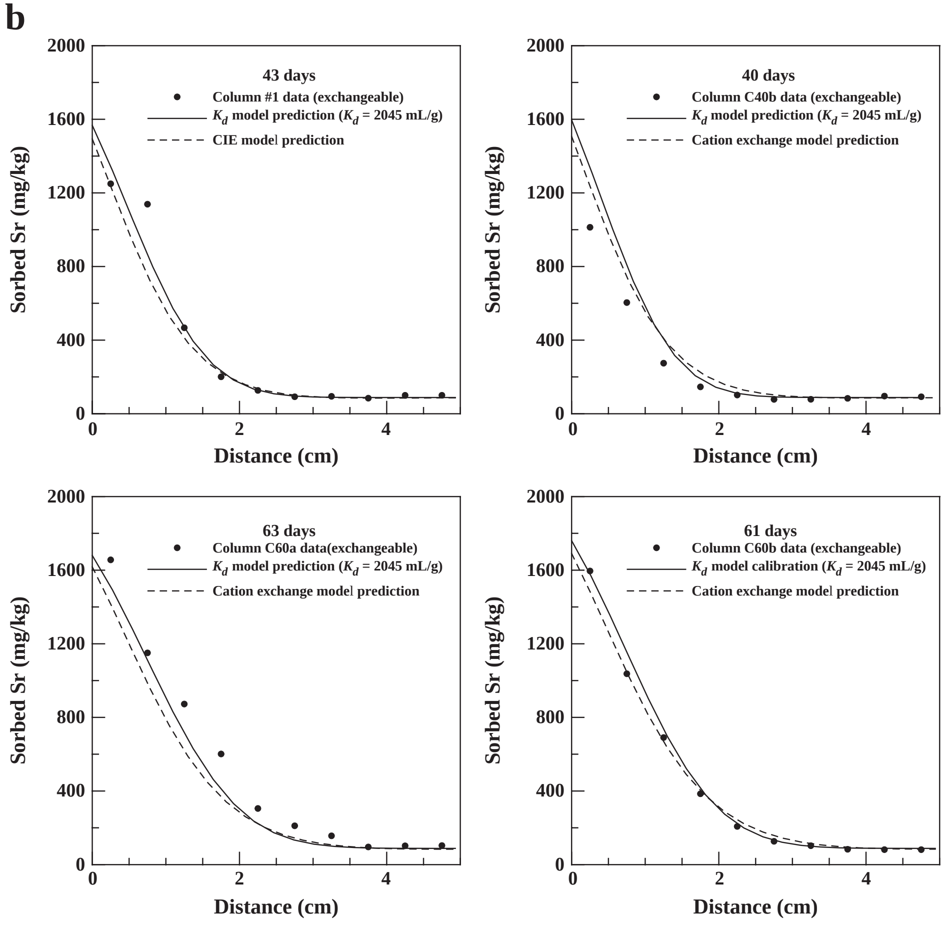

Fig. 1 (*continued*).

dominant divalent cations in the influent groundwater (Ca^{2+}, Mg^{2+}) gradually displace Na^+ and K^+ from the clino. During the approximately 200 pore volumes of column operation, only Mg^{2+} reached an effluent concentration similar to its influent value. The presence of Sr^{2+} in the effluent (approximately 35 μg/L, increasing to approximately 80 μg/L) is attributed to removal of the background Sr^{2+}initially present in the zeolite. Similar Sr^{2+} behavior was observed for the other 7 columns.

4.6. Column tests: modeling

Using a modified version of the CXTFIT model, the single solute equilibrium model was fit to the data from column C60b, which was selected because the experimental Sr^{2+} mass balance (97%) was slightly better than the replicate column (C60a). As discussed above, the sorbed Sr concentrations (measured using the digestion procedure) were first

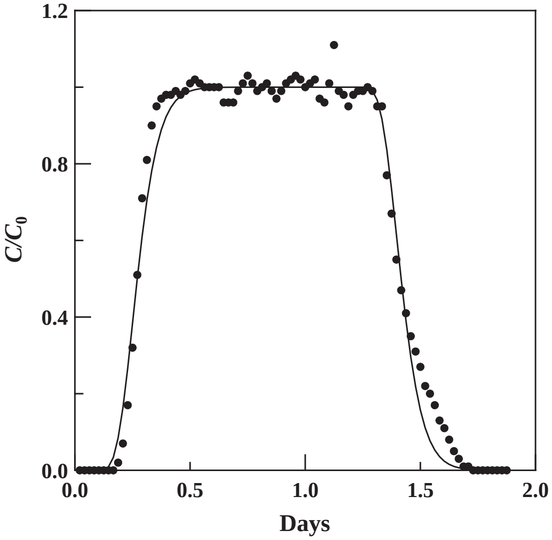

Fig. 2. Bromide tracer test data and model fit.

adjusted by subtracting the "nonexchangeable" portion. All parameters were estimated independently except for the sorption coefficient (K_d), which was calibrated using the data from the first 5 cm of the column. The calibrated K_d of 2045 mL/g was then used to generate model predictions for the other 7 columns, with no adjustment of model

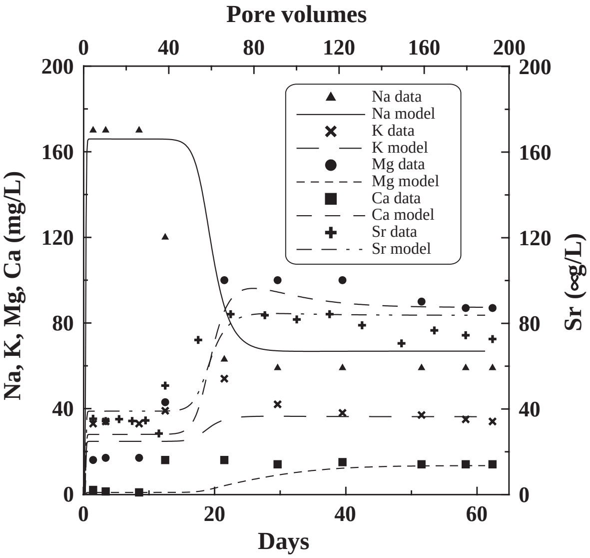

Fig. 3. Cation effluent data from column C60a and model fit (Sr^{2+} in μg/L, all others in mg/L).

parameters, as shown in Fig. 1. Other key model parameters are summarized in Table 6. The agreement between the data and single-solute model predictions was considered excellent; where systematic differences were observed, they were attributed to the small experimental mass balance errors.

The multi-solute ion exchange model was calibrated by nonlinear regression to the effluent data from Column C60a using the public domain parameter estimation model OSTRICH (Matott, 2003). The initial conditions and calibrated selectivity coefficients are summarized in Table 6. It is likely that the removal of fines during the early portion of the column flushing may have altered the effective CEC; however, lacking appropriate data, the initial conditions of the column were assigned to the initial measured values. Because the mass concentrations of the effluent Sr^{2+} were much lower than the other solutes, various schemes were used to increase the corresponding weight in the least squares objective function. In general, the estimated selectivity coefficients were not sensitive to the weighting scheme, although the size of the calculated linearized confidence intervals changed a function of the relative weights. In all cases, the selectivity coefficients for Sr^{2+} and Ca^{2+} were strongly correlated. The calculated statistic proposed by Linssen (1975) indicated that the objective function was weakly nonlinear with respect to the parameters. For this reason the calculated confidence intervals, which are based on the assumption of linearity, are not reported.

Reasonable agreement was noted between the effluent cation data and model calibration, particularly for $Ca^{2+}$and Sr^{2+}. The calibrated cation exchange model was then used to predict the Sr spatial data for all 8 columns, as shown in Fig. 1, with results similar to those obtained using the calibrated K_d model. Although the ability of both models to reproduce the spatial concentration data is encouraging, assessment of the models was hampered by the relatively limited penetration of Sr^{2+} into the columns.

5. Performance assessment

5.1. Simulation of WVDP treatment wall

Based on the results of the column tests, modeling predictions were generated for performance of an installed barrier, according to the assumptions listed in Table 7. The barrier thickness (1.5 m) and "increasing source" scenario were based on conservative estimates provided by WVDP personnel, while the velocity was selected from the high end of field observations. For Sr^{90}, the initial concentration was set to zero, decay in both phases was included, and the inlet boundary condition was modified to reflect the time-dependent source scenario.

A plot of the predicted effluent concentrations is shown in Fig. 4. The predictions generated by the two models differed significantly at early times, with the cation exchange model predicting higher effluent concentrations. At later times, the two models converged to similar values. The different predictions at early times reflect, in part, the fact that the K_d was estimated from spatial data recorded after the initial ion exchange front has passed through the column. For a target breakthrough activity of 1000 pCi/L, both models give similar results, with a predicted a barrier life exceeding 30 years. However, a lower target

Table 7
Barrier simulation parameters (sorption parameters given in Table 6a)

Model parameter	Value	Comment
Wall thickness	1.5 meters	WVDP
Wall porosity	0.6	Typical lab value
Media bulk density	0.80 g/mL	Typical lab value
Groundwater velocity	0.39 m/d	F
Dispersivity	0.15 m	Typical field value
Initial inlet activity	10,000 pCi/L	WVDP
Rate of inlet activity increase	50% per year for 2 years, 5% per year afterwards	WVDP
Sr^{90} decay rate	6.59×10^{-5} day^{-1}	literature

WDVP=suggested by WVDP personnel, UB=current study, F=Fuhrmann et al., (1995).

activity would correspond to a much shorter time-to-breakthrough, with significant differences between the two models.

5.2. Sensitivity analysis

The sensitivity of predicted treatment wall performance to modeling parameters was further explored using the multi-solute model. The physical/chemical parameters considered in the sensitivity analysis are summarized in Table 8. The "base case" was based loosely on the measurements from the WVDP project and preliminary model fits, with most of the "low" and "high" values representing perturbations of the individual parameters by a factor of 2. The resulting groundwater conditions were intended to represent typical values that could occur across sites characterized by different aquifer materials, while the zeolite parameters reflect uncertainty in characterization of the cation

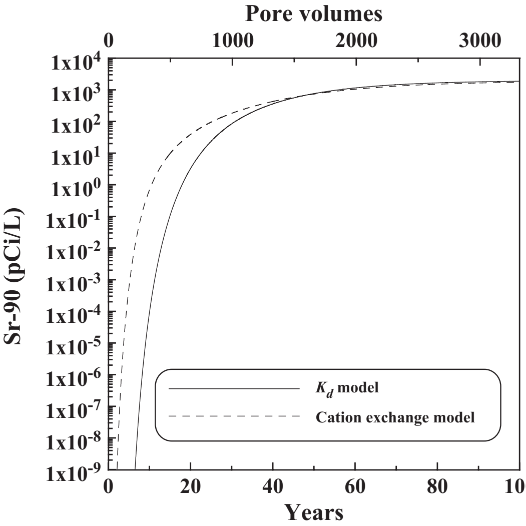

Fig. 4. Predicted Sr^{90} effluent from hypothetical treatment wall.

Table 8
Sensitivity analysis parameters

Parameter	Low	Base	High
Groundwater			
Ca^{2+}(mg/L)	50	100	200
Mg^{2+}(mg/L)	7.5	15	30
K^{+}(mg/L)	1.75	3.5	7.5
Na^{+}(mg/L)	34	68	136
Sr^{+}(mg/L)	0.1	0.2	0.4
Zeolite			
CEC (meq/g)	0.71	1.42	2.84
$K_{Na\text{-}Sr}$	2400	4800	9600
$K_{Na\text{-}Ca}$	175	350	700
$K_{Na\text{-}Mg}$	150	300	600
$K_{Na\text{-}K}$	14	28	56
Bulk density (g/mL)	0.6	0.8	1.2
Sr^{90} sorbed phase decay rate (day^{-1})	0.0	6.6e-05	–

exchange properties. Preliminary simulations indicated that the results were not sensitive to the initial cation distribution in the sorbed phase. Therefore, for simulations involving modification to the overall CEC, the initial cation concentrations were simply adjusted proportionately. The consideration of bulk density was intended to address the unknown in situ packing condition, while consideration of sorbed phase decay reflects the unknown influence of the Sr decay products with respect to cation exchange.

The field PRB configuration was similar to the WVDP system, with a zeolite barrier thickness of 1.5 m, a constant Sr^{90} influent of 5.37e-06 mg/L (10,000 pCi/L), and a specific discharge (Darcy velocity) of 0.2 m/d. The performance of the zeolite for this system was characterized in terms of the predicted time-to-breakthrough, as defined by the effluent Sr-90 reaching 10% of the constant influent value (5.37e-05 mg/L). The results of the sensitivity analysis are summarized in Fig. 5. The results follow the expected trends, with the predicted breakthrough time exhibiting particular sensitivity to the level of background Ca^{2+} in the groundwater. The results are also very sensitive to uncertainty in the selectivity coefficients. The sensitivity of the treatment wall performance to groundwater velocity was assessed only indirectly, as the fluid velocity for a specified discharge is influenced by changes to the bulk density and corresponding porosity. However, the time to breakthrough is expected to decrease in a manner approximately proportionate to an increase in the specific discharge.

6. Discussion

6.1. Hydraulic performance

The laboratory measurements of the hydraulic conductivity of the TMP material ranged from 0.1 to 0.4 cm/s, which is similar to other reported results (Table 4). However, field

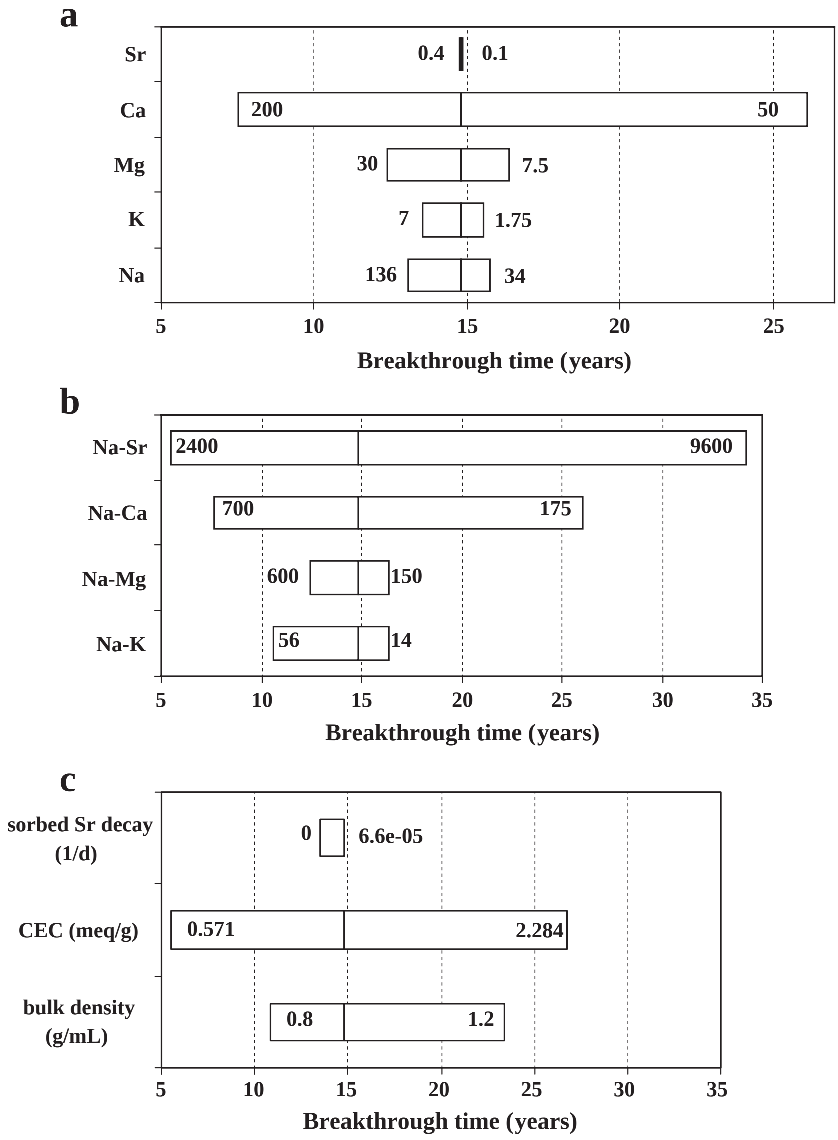

Fig. 5. a. Sensitivity of hypothetical treatment wall performance to groundwater cations. b. Sensitivity of hypothetical treatment wall performance to cation exchange selectivity coefficients. c. Sensitivity of hypothetical treatment wall performance to media properties.

measurements from slug tests of the TMP and other natural materials suggest the in-place conductivity might be significant lower, as much as 1-2 orders of magnitude. The hydraulic conductivity is a critical parameter in the design of PRB systems to achieve full capture of the contaminant plume. Until a more complete understanding of the field behavior of natural zeolite materials is obtained, laboratory measurements should be interpreted with extreme caution and/or the hydraulic component of PRB design should incorporate suitable safety factors.

6.2. Chemical performance

Several factors may contribute to the differences in K_d values observed across the various previous studies, including the source water used, differences in experimental design, and the modeling approach used for data interpretation. These differences highlight the importance of allocating significant resources to the collection and interpretation of laboratory data, particularly if the project economics are highly sensitive to the estimated PRB lifetime. The multi-solute cation exchange modeling framework may be particularly useful in this regard because it allows a more general interpretation of laboratory observations. For example, measurement of effluent breakthrough concentrations is much simpler and cheaper than extracting sorbed Sr from the solid media, and may be sufficient to parameterize a multi-solute model. However, a more complete experimental study is needed to support robust model parameterization.

The performance of a zeolite barrier for removing Sr^{90} will be strongly influenced by the geochemical characteristics of the site groundwater, particularly the level of Ca^{2+} and, to a lesser extent, Mg^{2+}. The results of the sensitivity analysis performed using the calibrated cation exchange model indicate that the time-to-replacement of a zeolite PRB will be roughly proportional to the amount of hardness in the site groundwater. Unless sufficient data are available to support the development of a robust geochemical model for a specified zeolite material, site-specific bench-scale testing is highly recommended. Extrapolation of estimated K_d values to other sites should be avoided unless the geochemical characteristics are similar.

Although it is difficult to draw firm conclusions from the limited data, the close agreement between the long-term predictions of the cation exchange and K_d-based models is encouraging, and suggests that the retardation factor approach may be useful for performance assessment if based on appropriate site-specific experiments. In particular, laboratory tests should be conducted under conditions that are conservative with respect to Ca^{2+} competition. The approach of “pre-washing” the zeolite is insufficient in this regard because it does not mimic the effect of continuous permeation with high-calcium groundwater. This observation is supported by the model sensitivity analysis, which showed that PRB performance is insensitive to the initial distribution of sorbed cations.

6.3. Limitations of cation exchange model

The performance assessment study was not designed to provide an extensive data set for development of a mechanistic cation exchange model, and as such the model is regarded as an initial step in the development of a more complete and robust model. The primary motivation for developing such a model lies in ability to extrapolate the behavior of a well-characterized PRB material to different geochemical conditions, which is not possible with a site-specific K_d-based approach. The limited scope of the WVDP experiments suggest that the calibrated model parameters, particularly selectivity coefficients, are unlikely to be unique, and considerable caution should be used in extrapolating the results.

In developing a more robust model, the following improvements should be considered:

- More rigorous characterization of CEC. More focused attention should be directed to the CEC measurement technique, which may be subject to artifacts related to the diffusional behavior of zeolitic materials. Also, the removal of fine particles during the early stages of column flushing may alter the effective CEC, suggesting that the media CEC should be measured at both the beginning and end of experiments.
- Inclusion of other sorption/leaching processes. Since the natural materials used for PRBs may contain a significant fraction of non-zeolite minerals, it is likely that other reaction processes may influence system behavior, such as specific adsorption and precipitation/dissolution.
- Inclusion of sorption kinetics. While the assumption of rapid sorption may be adequate under low flow conditions, it may not be valid for high groundwater flow rates and/or large grain sizes. A more general model that includes intraparticle diffusion is under development.
- Improved understanding of Sr^{90} behavior. The assumption of equivalence between Sr^{2+} and Sr^{90} sorption, while reasonable, has not been verified experimentally. For example, possible differences in kinetic behavior and isotopic dilution should be investigated. Also, as demonstrated in the sensitivity analysis, decay of sorbed Sr^{90} could contribute significantly to the predicted performance of the PRB. However, studies on the ion exchange behavior of the Sr^{90} decay products were not located.
- Field porosity data. The in-place porosity and bulk density of the zeolite are important model parameters, and the absence of a consolidating pressure under laboratory conditions suggest that field conditions may be different. However, these parameters influence multiple aspects of barrier performance (hydraulic conductivity, seepage velocity, sorption capacity) in a manner that is too complex to support generalizations.

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References

Aloysis, D.L., 1995. "Sorbent material testing and evaluation for passive filter wall design," report submitted to West Valley Nuclear Services, Dames and Moore, Orchard Park, NY.

Abadzic, S.A., Ryan, J.N., 2001. Particle release and permeability reduction in a natural zeolite (clinoptilolite) porous medium. Environ. Sci. Technol. 35, 4502–4508.

Barton, W.D., Craig, P.M., Stone, W.C., 1997. Proceedings of the 1997 International Containment Conference and Exhibition, St. Petersburg, FL, 9–12 February, 1997, pp. 827–834.

Bowman, R.S., Li, Z., Roy, S., Burt, T., Johnson, T., Johnson, R.L., 1999. "Surface altered zeolites as permeable barriers for in situ treatment of contaminated groundwater," Phase II Topical Report, submitted to the U.S. Department of Energy under Contract #DE-AR21-95MC32108.

Bowman, R.S., Li, Z., Roy, S., Burt, T., Johnson, T., Johnson, R.L., 2001. Pilot test of a surfactant-modified zeolite permeable barriers for groundwater remediation. In: Smith, J., Burns, S. (Eds.), Physical/Chemical Subsurface Remediation. Kluwer Publishers.

Cantrell, K., 1996. A permeable reactive wall composed of clinoptilolite for containment of Sr-90 in Hanford groundwater. Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management, 1358–1365. American Nuclear Society, Inc., La Grange Park, Il.

Carlyle, H.F., Tellam, J.H., Parker, K.E., 2004. The use of laboratory determined ion exchange parameters in the predictive modeling of field-scale major cation migration in groundwater over a 40-year period. J. Contam. Hydrol. 68, 55–81.

Cernik, M., Barmettler, K., Grolimund, D., Rohr, W., Borkovec, M., Sticher, H., 1994. Cation transport in natural porous media on laboratory scale: multicomponent effects. J. Contam. Hydrol. 16, 319–337.

DePaoli, S.M., Perona, J.J., 1996. Model for Sr-Cs-Ca-Mg-Na ion exchange kinetics on chabazite. AIChE J. 42 (12), 3434–3441.

Furhmann, M., Aloysius, D., Zhou, H., 1995. Permeable, subsurface sorbent barrier for ^{90}Sr: laboratory studies of natural and synthetic materials. Waste Manage. 15 (7), 485–493.

Gaines, G.L., Thomas, H.C., 1953. Adsorption studies of clay minerals. II. A formulation of the thermodynamics of exchange adsorption. J. Chem. Phys. 21, 714–718.

Gavaskar, A.R., Gupta, N., Sass, B., Janosy, R.J., Sullivan, D., 1998. Permeable Barriers for Groundwater Remediation. Battelle Press.

Grant, S.A., Mansell, R.S., Bloom, S.A., Rhue, R.D., 1995. Simulated transport of three cations through porous media: effect of different approaches to modeling cation exchange reactions. Water Resour. Res. 31 (1), 185–198.

Lee, D.R., Smith, D.J., Shikaze, S.G., Jowett, R., Hartwig, D.S., Milloy, C., 1998. Wall-and-curtain for passive collection/treatment of contaminant plumes. Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Battelle Press, Columbus, OH.

Linssen, H.N., 1975. Nonlinearity measures: a case study. Stat. Neerl. 29, 93–99.

Ma, Z., Whitley, R.D., Wang, N., 1996. Pore and surface diffusion in multicomponent adsorption and liquid chromatography systems. AIChE J. 42 (5), 1244–1262.

Mansell, R.S., Bond, W.J., Bloom, S.A., 1988. Simulated cation transport during water flow in soil: two approaches. Soil Sci. Soc. Am. J. 52, 1533–1540.

Matott, L.S., 2003. OSTRICH: An Optimization Software Tool. Department of Civil Structural, and Environmental Engineering, University at Buffalo, Buffalo, NY (available from http://www.groundwater.buffalo.edu).

Miller, C.T., Rabideau, A.J., 1993. Development of split-operator Petrov–Galerkin methods for simulating transport and diffusion problems. Water Resour. Res. 29 (7), 2227–2240.

Moore, H.R., Steiner, R.E., Fallon, E., Repp, C.L., Hemann, M.R., Rabideau, A.J., 2000. Permeable treatment wall pilot project at the West Valley demonstration project. Proceedings of Waste Management 2000, 27 February– 2 March, 2000, Tucson, AZ.

Parker, J.C., van Genuchten, M.Th., 1984. Determining transport parameters from laboratory and field tracer experiments, Virginia Agricultural Experiment Station, Bulletin, vol. 84-3. Virginia Polytechnic Institute and State University, Blacksburg, VA.

Parkhurst, D.K., Appelo, C.A.J., 1999. User's Guide to PHREEQC (Version 2) — a computer program for speciation, batch reaction-path, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water Resources Investigations Report, pp. 99–4259.

Perona, J.J., 1993. Model for Sr-Cs-Ca-Mg-Na ion exchange equilibria on chabazite. AIChE J. 39 (10), 1716–1720.

Rabideau, A.J., 2004. MOUSER: A Moderately User-Friendly Reactive Transport Model, Version 1. Department of Civil Structural, and Environmental Engineering, University at Buffalo, Buffalo, NY (available from http://www.groundwater.buffalo.edu).

Rabideau, A.J., Khandelwal, A., 1998. Analysis of nonequilibrium sorption in soil/bentonite slurry walls. ASCE J. Environ. Eng. 124 (4), 329–335.

Rabideau, A.J., Blayden, J.M., Ganguly, C., 1999. Field performance of air sparging for removing TCE from groundwater. Environ. Sci. Technol. 33 (1), 157–162.

Rabideau, A.J., Van Benschoten, J.E., Khandelwal, A., Patel, A., Repp, C.L., 2001. Sorbing vertical barriers. In: Smith, J., Burns, S. (Eds.), Physical/Chemical Subsurface Remediation. Kluwer Publishers.

Robinson, S.M., Arnold, W.D., Byers, C.H., 1991. Multicomponent ion exchange equilibria in zeolite. In: Tedder, D.W., Pohland, F.G. (Eds.), ACS Symposium Series, 486, Emerging Technologies in Hazardous Waste Treatment.

Selim, H.M., Schulin, R., Fluher, H., 1987. Transport and ion exchange of calcium and magnesium in an aggregated soil. Soil Sci. Soc. Am. J. (5), 876–884.

Spalding, B.P., Spalding, I.R., 2001. Chemical equilibria model of strontium-90 adsorption and transport in soil in response to dynamic alkaline conditions. Environ. Sci. Technol. 35, 365–373.

Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry. Wiley, New York, NY.

Sumner, M.E., Miller, W.P., 1996. Cation exchange capacity and exchange coefficients. In: Sparks, D.L., et al., (Eds.), Methods of Soil Analysis, Part 3 Chemical Methods. Soil Science Society of America, Madison WS.

U.S. Department of Energy, 1997. In situ treatability test plan, DOE/RL-95-109 Rev. 1, Richland WA.

U. S. Environmental Protection Agency, 2002. Field Applications of in situ Remediation Technologies: Permeable Reactive Barriers. Office of Solid Waste and Emergency Response, Washington DC.

Valocchi, A.J., Street, R.L., Roberts, P.V., 1981. Transport of ion-exchanging solutes in groundwater: chromatographic theory and field simulation. Water Resour. Res. 17 (5), 1517–1527.

Voegelin, A., Vulava, V.M., Kuhnen, F., Kretzschmar, R., 2000. Multicomponent transport of major cations predicted from binary adsorption experiments. J. Contam. Hydrol. 46, 319–338.

Voegelin, A., Vulava, V.M., Kretzschmar, R., 2001. Reaction-based model describing competitive sorption and transport of Cd, Zn, and Ni in an acidic soil. Environ. Sci. Technol. 35, 1651–1657.

Vulava, V.M., Kretzschmar, R., Grolimund, D., Westall, J.C., Borkovec, M., 2000. Cation competition in a natural subsurface material: modeling of sorption equilibria. Environ. Sci. Technol. 34, 2149–2155.

Vulava, V.M., Kretzschmar, R., Grolimund, D., Westall, J.C., Borkovec, M., 2002. Cation competition in a natural subsurface material: prediction of transport behavior. Water Resour. Res. 38 (5).

West Valley Nuclear Services, 2001. Technology Evaluation of the Pilot Permeable Treatment Wall and Recommended Path Forward. West Valley, NY.