Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Bostick, D. T. , Arnold, W. D. , Guo, B. and Burgess, M. W.(1997) 'The Evaluation of Sodium-Modified Chabazite Zeolite and Resorcinol-Formaldehyde Resin for the Treatment of Contaminated Process Wastewater', Separation Science and Technology, 32: 1, 793 — 811

To link to this Article: DOI: 10.1080/01496399708003230

URL: http://dx.doi.org/10.1080/01496399708003230

SEPARATION SCIENCE AND TECHNOLOGY, 32(1-4), pp. 793-811, 1997

THE EVALUATION OF SODIUM-MODIFIED CHABAZITE ZEOLITE AND RESORCINOL-FORMALDEHYDE RESIN FOR THE TREATMENT OF CONTAMINATED PROCESS WASTEWATER

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ABSTRACT

Natural chabazite zeolite has been selected as the baseline treatment technology to compare the performance of emerging sorbent materials for the removal of ^{90}Sr and ^{137}Cs from contaminated process water. The resorcinol-formaldehyde resin, developed at Savannah River Site, is the first sorbent to be evaluated in this study. This paper summarizes the required contact times for maximum strontium and cesium removal, presents sorption isotherms in wastewater simulant and authentic wastewater, and defines the effects of elevated concentrations of K, Mg, Ca, and Na in wastewater for both sorbents.

INTRODUCTION

Standard waste treatment procedures for the removal of ^{90}Sr and ^{137}Cs from contaminated groundwater and process wastewaters generate large volumes of secondary contaminated wastes. Several new sorbent materials hold the promise for treating large volumes of contaminated water while minimizing the generation of secondary low-level radioactive waste. As part of the DOE Efficient Separations and Processing (ESP) Crosscut EM-50 Program, these new treatment techniques are being evaluated in reference to standard treatment processes. This effort will define the effectiveness of the new sorbents for removing ^{90}Sr and ^{137}Cs in wastewater applications, as well as gauge the quantity of radioactive waste generated with their use.

EXPERIMENTAL

Sorption measurements were made in long-term batch equilibrium tests. The 10-mL solutions and exchanger (5-100 mg) were contacted in screw-cap polycarbonate centrifuge tubes by mixing on a Labquake shaker, which rocks the samples from -45° to +45° from horizontal at 20 cycles per minute. Three samples were included in each data set. The sorbent was weighed directly and added to the tubes. Solution volumes were determined by weights and densities of the wastewater samples. At the end of the equilibration period, the tubes were centrifuged for 30 minutes at 5000 relative centrifugal force (rcf). The solutions were further clarified either by transferring the supernate to a 12-mL tube and recentrifuging for 30 min at 5000 rcf or by filtering the centrifuged supernate using a plastic syringe fitted with a 0.45-μm-pore nylon membrane filter.

The extent of strontium and cesium removal was determined by tracing the samples with ^{85}Sr and ^{137}Cs. Strontium-85 was substituted for ^{90}Sr in sorption testing so that the activities of both radionuclides could be counted with a Canberra Series 90 Gamma Spectrometer. Two-milliliter samples were counted for 1000 s in a germanium well detector. Data for ^{85}Sr were corrected for the interference of ^{137}Cs at the 514-keV peak by using a linear regression line developed with ^{137}Cs standards. Test data were used in the following calculations:

Sorption ratio (R_s, L/kg) = $(C_i - C_f)V/C_fW$,

Final concentrations in solution (M_f, meq/L) = $M_i\ C_f/C_f$,

Final concentrations on the exchangers (M_e, meq/kg) = $M_f\ R_s$,

where:

C_i = count rate of the initial solution,

C_f = count rate of the final solution ,

V = initial volume of the solution (mL) ,

W = exchanger weight (g), and

M_i = concentration in initial solution (meq/L)

The exchanger weight was corrected for moisture content of the sorbent in all data used to make direct comparison of sorption efficiency among sorbent materials. The sorption ratio is equivalent to the distribution coefficient (K_d) if equilibrium conditions are assumed.

RESULTS AND DISCUSSION

Waste Stream Selection and Simulant Formulation

The first task of the program was to select a waste stream that typifies groundwater and/or process wastewaters generally encountered at DOE facilities to ensure that data generated in the study would be applicable to other DOE sites. Once the composition of the stream was determined by chemical analysis, a simulant could be formulated and used for the standard testing of the various treatment technologies. The optimum operating parameters of a baseline treatment process would then be determined with the simulant, followed by its evaluation in an authentic sample of the waste stream.

A review of reported data (1-3) suggested that the feed stream to the Process Waste Treatment Plant (PWTP) at Oak Ridge National Laboratory (ORNL) appeared to have a composition similar to regional DOE wastewater and fell within the range of composition range for typical groundwater (4). The wastewater is derived from contaminated groundwater, once-through cooling water, evaporator condensates, and laboratory wastewater generated on-site. The typical radionuclide composition of the feed is 400 Bq/L ^{90}Sr and 350 Bq/L ^{137}Cs, although activities as high as 8000 Bq/L ^{90}Sr and 1000 Bq/L ^{137}Cs have been observed.(1) As can be seen in Table 1, the principal chemical constituents in PWTP feed are calcium, magnesium, and sodium bicarbonates, which are introduced by groundwater. The radiological content of the PWTP feed stream is typical of process wastewaters. The radioactivity of DOE process wastewater is generally within 10^3 to 10^6 Bq/L(2), the primary nuclides being ^{90}Sr and ^{137}Cs.

The second initiative of the task was to formulate a simulant that would reflect the current composition of the PWTP feed and ensure a constant composition of wastewater for the comparative testing of the benchmark technology against new processes. A decision was made to include cations in the simulant that were present in concentrations equal to or greater than 1 ppm in PWTP feed samples. Strontium and cesium are the exceptions to this delineation. Strontium was included at a level of 0.1 ppm to reflect the average concentration of total Sr in the PWTP feed. This Sr concentration is also typical of process water in the local DOE area and represents a mid-range value present in groundwater. Sr-85, substituted in place of ^{90}Sr for analytical purposes, was added to the simulant at a level of 8.8×10^5 Bq/L. Cesium is not detected above the 0.00005-ppm detection limit of the

TABLE 1. COMPOSITION OF ACTUAL PWTP FEED AND PWTP SIMULANT

	Concentration (mg/L)			Concentration (mg/L)	
Component	Actual PWTP Feed	Simulant	Component	Actual PWTP Feed	Simulant
Cations by ICP			Anions by anion chromatography		
Na^+	14.3	15.0	Cl^-	8.7	9.6
K^+	1.0	1.0	F^-	0.8	0.8
Mg^{2+}	8.0	8.0	NO_3^-	5.3	5.3
Ca^{2+}	38.7	39	SiO_3^-	8.3	8.4
Sr^{2+}	0.1	0.1[d]	SO_4^{2-}	21.3	21.3
			PO_4^{3-}	2.1	2.1
pH	9.1	7.8	Alkalinity[a]	138[b]	126[c]

[a] As $CaCO_3$

[b] Calculated as Alkalinity = $([CO_3^{2-}] X 1.668) + ([HCO_3^-] X 1.640)$

[c] Calculated as Alkalinity = $[HCO_3^- X 1.219]$

[d] Non-radioactive strontium added to simulant as $SrCl_2$ just prior to use.

ICP-mass spectrometer, although 350 Bq/L $^{134,137}Cs$ is typically present in the PWTP feed. Cesium was added to the simulant at a tracer level of 1.12 × 10^6 Bq/L ^{137}Cs (equivalent to 0.00034 mg/L Cs). The levels of both ^{85}Sr and ^{137}Cs activity in the simulant were selected on the basis of the counting efficiency of the gamma spectrometer to be used throughout the sorption studies. The added ^{137}Cs tracer activity also reflects the upper limit for Cs activity typical of process wastewaters.

The difficulty encountered in preparing the simulant is that the solubility of $CaCO_3$ in water is limited to approximately 5.6 ppm Ca, whereas the required concentration to prepare the wastewater simulant is 37 ppm. To improve the solubility of the calcium salts, dry ice was added to the solution to decrease the pH; stirring was continued for an additional hour.

The simulant was then allowed to settle for 2 days before the solution was filtered with a 0.45-μm cellulose nitrate membrane filter under house vacuum. Some solids were noted on the filter membrane, suggesting the loss by precipitation of some sparingly soluble salts (e.g., ferric, calcium, and silicate salts.) ICP analysis showed that less than 10% of the calcium and magnesium was lost to precipitation. The density of the wastewater simulant was 0.9965 g/L at 27°C. The final simulant solution was stored in a polypropylene container to minimize leaching of minerals or component loss to the storage vessel.

Characterization of the Baseline Treatment Technology--Chabazite Zeolite

Since the early 1900s, zeolites have been used for water treatment (3) primarily as a means for removing calcium and magnesium in the softening of water. More recently, zeolites have been employed to remove heavy metals from process water and to decontaminate radioactive waste solutions.(4), (5),(6), (7) As a result of a variety of bench-scale and pilot-scale treatability studies performed at ORNL, zeolite treatment has been selected to remove cesium and strontium from PWTP feed wastewater in a scheduled upgrade of the PWTP facility (1),(8). The main body of research concerning the application of zeolites to ORNL wastewater decontamination has been performed using chabazite zeolite. The natural zeolite was selected over the synthetic zeolite, Ionsiv IE-95, because it was found to have a higher capacity for ^{90}Sr sorption.(9) Based on these considerations, ion exchange on chabazite zeolite was selected as the reference treatment technique from which to compare new treatment technologies studied in this task.

Chabazite zeolite was purchased from Steelhead Specialty Minerals under the product name TSM-300. The natural zeolite is mined from the Bowie deposit in Arizona by GSA Resources, Inc. (Cortaro, AZ)and can now be obtained directly from this company. A stock supply of the zeolite was prepared by first performing a sieve analysis(10) on 50-g portions of TSM-300 zeolite nominally sized as -20 to +50 mesh. Approximately 20% of the material was discarded as fines, having a mesh size greater than 50. The -20/+50 fraction was converted to the sodium form by contacting the zeolite with 2 *M* NaCl , followed by several water rinses to remove excess sodium. The converted zeolites were air dried; the final water content of the dried material was determined to be 7.1% (w/w). The dried zeolite fractions represent the stock supply of sorbent for the standard treatment method.

The Sr and Cs sorption rates from the simulated wastewater were determined by mixing a series of samples containing 20 mg of the stock TSM-300 in 10 mL of the traced simulant. Blank simulant samples without zeolite were also mixed for the full 48-h duration of the study. Sorption of both Sr and Cs reached steady state in 24 h. Analysis of the blank samples indicated that neither Sr nor Cs is lost to the walls of the sample containers over this time period, even at tracer levels 30 times less than those that normally will be present in the wastewater simulant testing.

Strontium sorption on sodium-modified zeolite was observed in samples containing an initial solution concentration of 2.28×10^{-3} meq Sr/L. Sorption data on the pretreated zeolite were fit to the Freundlich sorption model (Fig. 1). The sorption data were approximately linear when the log value of the equilibrium Sr concentration in solution (meq/L) was plotted versus the log value of Sr sorbed on the zeolite (meq/kg). The slight deviation from linearity reflects the influence of concomitant cations competing for sorption sites at low strontium concentrations. The slope of the Freudlich relationship is 0.74 and the intercept is 3.4; the correlation coefficient for a linear fit is 0.98. The equation defining Sr sorption from PWTP simulant on pretreated zeolite is thus:

$$\text{Log } Q_e = \text{Log } K_F + 1/n \text{ Log } C \tag{1}$$

or

$$\text{Log } Q_e = 3.4 + 0.74 \text{ Log } C, \tag{2}$$

where Q_e is the quantity of Sr on the sorbent (meq/kg)at equilibrium; K_F is the Freundlich constant; C is the equilibrium concentration in solution; and 1/n is the sorption intensity(11). Since the distribution coefficient, K_d, is equivalent to

$$K_d = Q_e / C, \tag{3}$$

it can be calculated in terms of Sr equilibrium concentration using the Freundlich constants:

$$K_d = 2500 \times C^{-0.26}. \tag{4}$$

Cesium sorption was observed in samples containing an initial concentration of 3.23×10^{-6} meq/L Cs. The cesium sorption data were also fit to the Freundlich sorption model (Fig 2). The slope of the curve was 0.98 and the intercept was 4.75. Cesium data fit the Freundlich model better than that of strontium, as demonstrated by a higher linear correlation coefficient of 0.996. The comparable equation defining cesium sorption on pretreated zeolite is, thus,

$$K_d = 56{,}000 \times C^{-0.02}. \tag{5}$$

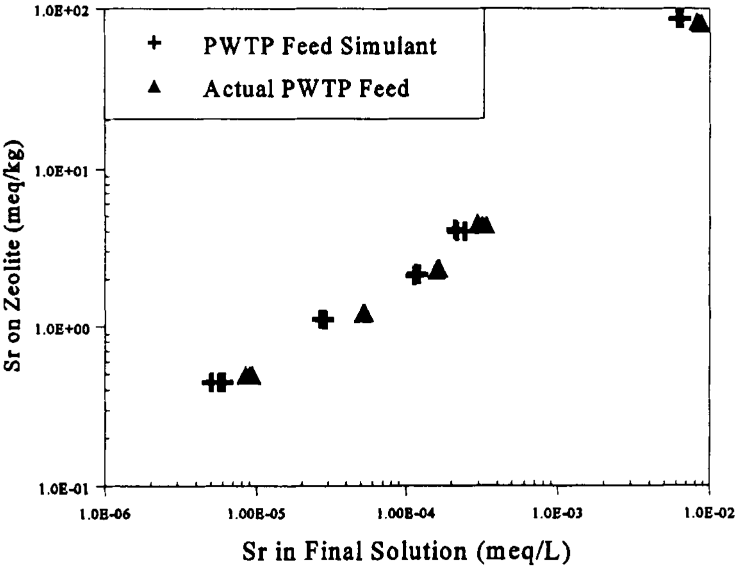

FIGURE 1. Sr sorption from actual PWTP feed and PWTP feed simulant.

Test Procedure: 0.005-0.100 g TSM-300 zeolite in 10 mL solution; 24-h equilibration time; 0.00228 meq/L Sr initial simulant concentration for lower data points; 0.05 meq/L Sr initial simulant concentration for upper data points; 0.00251 meq/L Sr in actual PWTP feed sample.

On completion of testing with the simulant, the Sr and Cs sorption from actual PWTP feed wastewater was observed on the pretreated chabazite. As can be seen in Figures 1 and 2, the sorption profiles in the actual PWTP feed sample were nearly identical to those obtained with the simulant, indicating the close match between the chemical composition of the simulant and actual waste steam. Maximum loading from the actual wastewater sample onto treated zeolite was calculated to be 24 meq/kg Sr and 0.17 meq/kg Cs.

A small column test was run to verify the sorption capacity and K_d of strontium and cesium on zeolite under dynamic flow conditions. A 1-cm-diam column containing about 1.9 g of sodium-modified TSM-300 zeolite was used to treat PWTP simulant. The zeolite bed in the column was 4.9 cm deep, and the bed volume (BV) was 3.85 mL. At a nominal PWTP simulant flow rate of 1.3 mL/min, the superficial velocity through the bed was 1.6 cm/min. The packed density of the column was 0.535 g/mL, and the nominal solution residence time in the column was about 3 min.

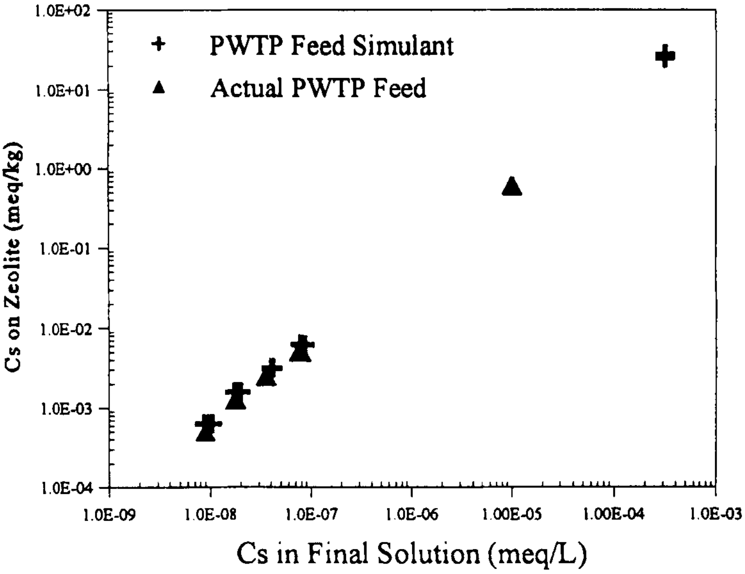

FIGURE 2. Cs sorption from actual PWTP feed and PWTP feed simulant.

Test Procedure: 0.005-0.100 g TSM-300 zeolite in 10 mL solution; 24-h equilibration time; 2.46 x 10^{-6} meq/L Cs initial simulant concentration for lower data points; 3.2 x 10^{-4} meq/L Cs initial simulant concentration for upper data points; 2.57 x 10^{-6} meq/L Cs in actual PWTP feed sample.

The initial effluent fractions (about 2500 BVs) were analyzed by ICP to determine the breakthrough behavior of Na, Mg, and Ca. (The sorption behavior of potassium could not be determined because its concentration in all of the effluent samples was below the ICP detection limit of 0.1 mg/L.) Initial displacement of Na from the zeolite was observed immediately. Continued sorption of strontium and cesium onto the zeolite resulted in displacement of Mg beginning at 250 BVs and displacement of Ca beginning at 500 BVs. Cation breakthrough from the column implies that the selectivity of the treated zeolite is: Cs > Sr > Ca > Mg > Na. The fractional breakthrough (C/C_0) of the competing cations, defined as the ratio of the cation concentration in the column effluent to the concentration in the feed, stabilized to a value of 1.0 at approximately 800 to 1400 BVs.

The ^{85}Sr and ^{137}Cs count rates of the effluent fractions were compared with those of the feed solutions to determine breakthrough points, which are shown in Fig. 3. Strontium was

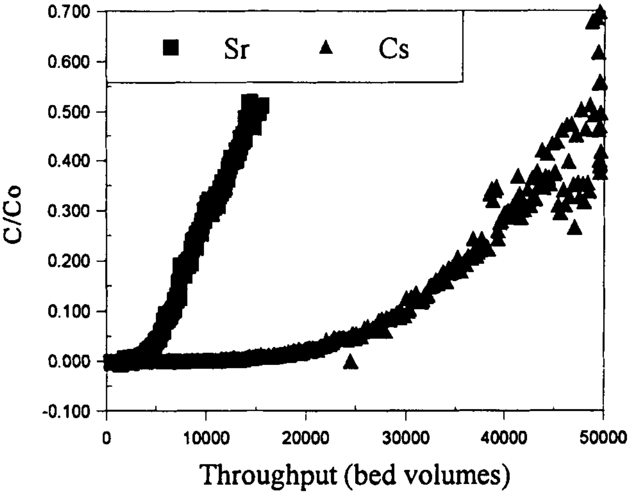

FIGURE 3. Sr and Cs breakthrough curves on sodium-modified zeolite

Column parameters: 1.9 g sodium-modified zeolite contained in a 1-cm-ID column having a bed volume of 3.85 cm^3. The simulant flow rate is 1.28 mL/min.

first observed in the column effluent at approximately 3000 BVs. Fractional breakthrough of 10 and 50 % occurred at 6600 and 15, 000 BVs, respectively. Under these conditions, cesium breakthrough was 1% after about 15,000 BVs, 10% after about 30,000 BVs, and 50% after about 50,000 BVs. The Sr loading for the zeolite was about 60 meq/kg at 50% strontium breakthrough; the Cs loading was 0.2 meq/kg at 50% cesium breakthrough. These loadings, particularly the Sr loading, are higher than the saturation loadings of about 24 and 0.17 meq/kg measured previously for strontium and cesium, respectively, in batch sorption isotherms. The breakthrough data were used to construct logarithmic-probability plots of strontium and cesium breakthrough vs column throughput. These plots were used to estimate column K_d s, which are approximately equal to the number of bed volumes at 50% breakthrough. (12) The K_d values for the radionuclides, although slightly lower, were in good agreement with those predicted in batch sorption isotherms:

	K_d (L/kg)	
Zeolite Test	Strontium	Cesium
Column	15,800	53,000
Batch Isotherm	17,000	80,000

The above batch and column tests were performed at a single simulant composition. Additional batch tests were performed to determine the effect of variations of K, Mg, Na and Ca concentrations at other than simulant concentrations. Higher concentrations of the individual cations, up to those values found in typical groundwater, were added as the chloride salts to the wastewater simulant. The plots of Sr and Cs sorption ratios as a function of cation concentration in the wastewater simulant are given in Fig. 4. All cations depress the sorption capacity of the zeolite for Sr and Cs, particularly in the 0-4 meq/L concentration range of each cation. As indicated by the column breakthrough profiles, the selectivity of the zeolite for strontium over competing cations is less than that for cesium. The impact of cation selectivity on nuclide sorption is emphasized in results presented in Fig. 4, in which the sorption ratio for strontium is significantly more affected than cesium for the same addition of competing cation.

A multicomponent ion-exchange equilibrium model has been developed by J. J. Perona. to predict the distribution coefficients for both strontium and cesium on chabazite zeolite as a function of the aforementioned competing cations.(13) This model has recently been extended to include a pore diffusion model that more accurately predicts the transient uptake rates of cations in multicomponent ion exchange on the zeolite(14).

Sorption Characteristics of Resorcinol-Formaldehyde (RF) Ion-Exchange Resin

Comparative tests were initiated to evaluate resorcinol-formaldehyde (RF) resin, the first alternate sorbent to be reviewed in this program. The RF resin was developed at the Savannah River Site as an ion exchanger for Cs removal in caustic solutions containing high concentrations of sodium.(15) The two hydroxyl groups of resorcinol function as the active exchange sites of this particular resin.

A sieve analysis was performed on a 50-g portion of resin (Boulder Scientific, Lot #BSC187-0210), nominally sized as -20 to +60 mesh. Approximately 58% of the material was considered as fines, having a mesh size greater than 80. Only 0.0026% of the sorbent had a mesh size less than 20. The -20/+50 mesh fractions were used for all batch equilibration studies, to match the size range used in the zeolite sorption studies. The water content of the resin, as received, was determined to be 19.1% (w/w). This water content is greater than double that observed with the sodium-modified chabazite zeolite (7.1% w/w).

Sorption results from several resin pretreatment methods were compared to sorption isotherms developed using the resin as received. The pretreatment methods included: 1)

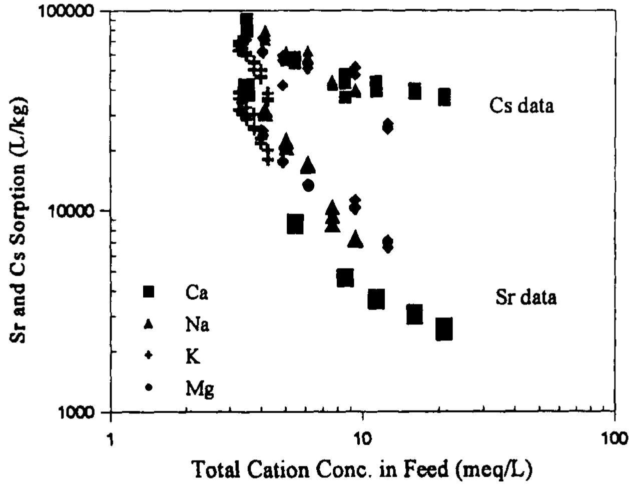

FIGURE 4. The effect of cations on Sr and Cs sorption with sodium-modified zeolite

Test Procedure: 0.020 g sodium-modified zeolite in 10 mL simulant; 24-h equilibration time; 0.00228 meq/L Sr initial concentration and 2.6 × 10^{-6} meq/L Cs initial concentration; cations added as chloride salts.

rinsing the resin with deionized, distilled (ultrapure) water prior to air drying; 2) prewashing the resin with 2 *M* sodium chloride (NaCl) followed by several rinses with the ultrapure water to remove excess sodium ion, a treatment similar to that used for pretreating the zeolite sorbent used in the baseline sorbent studies; 3) prewashing the resin with PWTP simulant six times, followed by water rinses and air drying; and 4) washing the resin with 1 *M* HCl followed by several rinses with ultrapure water to remove excess hydrogen ion.

Sorption isotherms for each resin in the PWTP wastewater simulant are presented in Figures 5 and 6. Because of the selectivity of the resin for cesium, sorption is equivalent for all forms of the resin if the cesium solution concentration is greater than 0.01 µeq/L. There is a slight enhancement of cesium sorption below this solution concentration if the resin is pretreated to remove excess potassium ion present in the as-received resin.

Strontium sorption on resin is very dependent upon the method of resin pretreatment. The strontium isotherm has two inflection points; the breadth of the isotherm is very dependent upon the method of resin pretreatment. In the acidic pretreatment procedure, the distance between the two inflection points increases with additional water rinses which hydrolyze the acid-washed resin. The greatest Sr sorption in simulant containing very low Sr

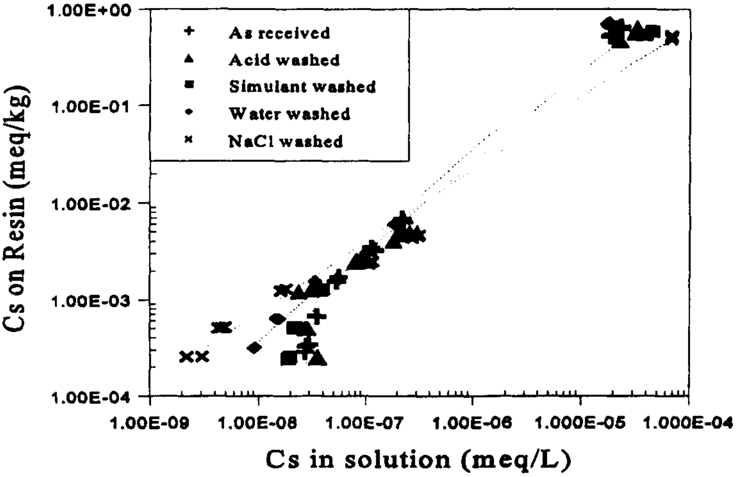

FIGURE 5. Cs sorption on pretreated RF resin

Test conditions: 0.005-0.100 g RF resin in 10 mL PWTP simulant; 24-h equilibration time; 0.00228 meq/L Sr initial simulant concentration for lower data points; 0.05 meq/L Sr and 0.04 meq/L Cs initial simulant concentrations for upper data points.

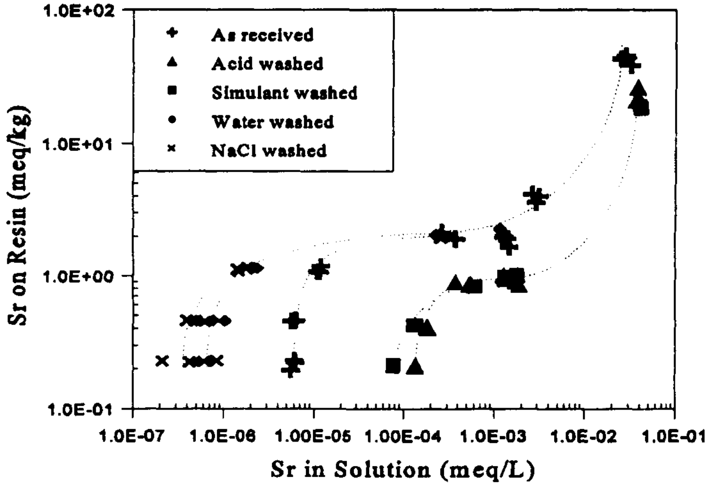

FIGURE 6. Sr sorption on pretreated RF resin

Test conditions: 0.005-0.100 g RF resin in 10 mL PWTP simulant; 24-h equilibration time; 0.00228 meq/L Sr initial simulant concentration for lower data points; 0.05 meq/L Sr and 0.04 meq/L Cs initial simulant concentrations for upper data points.

concentration is obtained if the resin is initially washed with ultrapure water; the second best performance is observed using the saline-washed resin. Pretreating the resin with only ultrapure water was selected for all remaining batch studies. Of the various treatment options, it is the most convenient procedure and does not risk inadvertently introducing elevated levels of sodium into the test simulant.

The time required to obtain maximum Sr and Cs sorption was determined by mixing a series of samples containing either 5 mg or 20 mg of water-washed RF resin in 10 mL of the traced PWTP simulant. Maximum cesium sorption in the 5-mg resin samples was observed after 24 hours. The cesium sorption ratio in 20-mg resin samples decreased with longer contact times; only 80% of the cesium initially sorbed remained on the resin after the first 100 h of contact. The sorption of Sr onto 5 mg of resin reached steady state in 24 hours. Sorption of Sr in 20-mg resin samples peaked at 24 h and stabilized to 80% of the maximum value after 50 h of contact. On the basis of these results, a 24-hour mixing time was used in subsequent batch studies.

Strontium and cesium isotherms were developed by adding 10 mL of traced PWTP feed simulant to sample tubes containing from 5 to 100 mg water-washed RF resin. The samples were mixed for 24 hours before being centrifuged; the supernates were then filtered. As observed with the chabazite zeolite, the Cs isotherm is essentially linear in the wastewater simulant (Fig. 5). The Cs sorption capacity on the resin is 0.02 meq/kg as compared to 0.17 meq/kg on the sodium-modified zeolite. The cesium data fit the Freundlich model (eq. 1) best. A linear relationship was obtained between the log value of the final concentration of cesium in solution (meq/L) and the log value of cesium sorbed per unit weight (meq/kg) on the resin. The slope of the line is equivalent to 0.93 and the intercept is equivalent to 3.77, with a correlation coefficient for the linear fit of 0.998. Therefore, the equation governing cesium sorption on water-washed resin is

$$K_d = 5900 \times C^{-0.07}. \qquad (6)$$

The Sr isotherm has two inflection points (Fig. 6), that at first glance might indicate a multilayer sorption mechanism. However, if the cation content of the final treated simulant is determined by ICP, one finds that Mg and Ca are also significantly sorbed by the resin. Strontium sorption was observed in a series samples in which the total metal(II) concentration was varied, as well as the ratio of Mg–to–Ca initial concentrations in the simulant. A Freundlich plot of sorption results, presented in Fig. 7, indicates that the

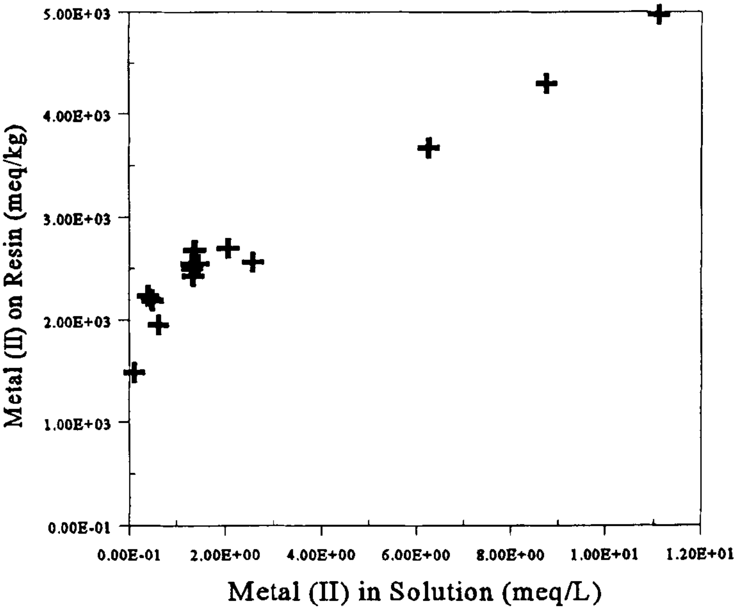

FIGURE 7. Metal(II) sorption data on water-washed RF resin

Test conditions: 0.010-0.200 g RF resin in 20 mL PWTP simulant; 24-h equilibration time; 0.00228 meq/L Sr initial simulant concentration; 0.5-11.1 meq/L total metal(II) concentration.

sorption of total metal(II), i.e. Ca + Mg + Sr, in solution is linear with total metal sorbed onto the resin. The quantity of the individual divalent ions sorbed onto the resin is calculated as the equivalent ionic fraction of that ion relative to the total equivalents of alkaline earth metals present in the solution at equilibrium:

$$\text{Sr on exchanger (meq/kg)} = \text{Sr equiv. fraction} \times 2410\ \text{meq/kg} \times [\text{Total Metal(II)}_{\text{liq}}]^{(0.22)} \quad (7)$$

The strontium K_d then can be determined by dividing the calculated quantity sorbed on the exchanger by the concentration of strontium, in units of meq/L, at equilibrium. The resulting calculation reduces to:

$$K_d = 2410\ \text{meq/kg} \times [\text{Total Metal(II)}_{\text{liq}}]^{(-0.78)} \quad (8)$$

where the concentration of total metal(II) is given in units of meq/L.

Equation 8 demonstrates the dependency of strontium sorption on the concentration of total alkaline earth metals in wastewater. The relative concentrations of Sr, Mg, and Ca in the waste simulant are 3.11×10^{-3}, 0.54, and 1.87 meq/L, resp. Therefore, Mg and Ca concentrations are the primary parameters defining the magnitude of the strontium K_d in wastewater. Using eq. 8, the calculated K_d for strontium in the simulant is 1200 L/kg. The strontium sorption capacity is, therefore, 3.6 meq/kg on the resin.

In light of eq. 8, the curved profiles for strontium sorption presented in Fig. 6 are the result of removing strontium from solutions containing varying concentrations of total metal(II) cations. Washing the resin with either water or saline partially hydrolyzes the resin or converts the resin to the sodium form. Both of these resin forms enhance the non-selective removal of metal(II) cations. Preloading the resin with Mg and Ca during simulant washing or converting the resin to the hydrogen form linearizes the isotherm by minimizing further Mg and Ca (and, thus, strontium) sorption from the simulant.

The lack of selectivity between +2 cations is further demonstrated in results from the breakthrough profile obtained from a small column test run under conditions similar those for zeolite characterization (Fig. 8). The packed density of the resin column was 0.43 g per mL, as compared to 0.55 g per mL for the earlier zeolite column. The feed solution in the column test contained 0.0023 meq/L total strontium and $2.4 \times^{-6}$ meq/L total cesium. The average flow rate of the feed through the resin column was 1.23 mL/min. Sodium and potassium cations eluted from the resin column immediately. Alkaline earth cations, including strontium, eluted simultaneously and were present in column effluent after 400 BVs of simulant had been treated. Fifty percent breakthrough for strontium and cesium occurred at 525 and 6,400 BV, resp. Comparable 50% breakthrough values observed for the zeolite column were 15,000 and 50,000 BV, resp. The column breakthrough curves were used to estimate the column K_ds, tabulated below, for strontium and cesium. The close comparison of batch test predictions and column performance indicates that a Freundlich sorption model can adequately estimate strontium and cesium column breakthrough on washed RF resin with this particular wastewater composition.

	K_d (L/kg)	
RF Test	Strontium	Cesium
Column	1260	15,400
Batch Isotherm	1200	14,500

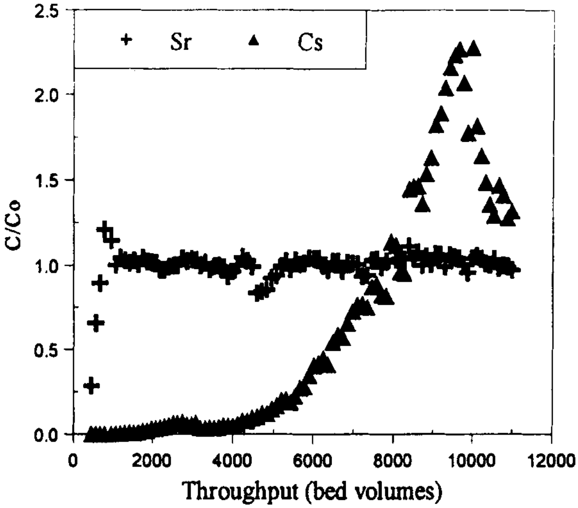

FIGURE 8. Sr and Cs breakthrough curves on water-washed RF resin

Column parameters: 1.6 g water-washed RF resin contained in a 1-cm-ID column having a bed volume of 3.85 cm^3. The simulant flow rate is 1.23 mL/min.

The effects of elevated calcium, sodium, potassium, and magnesium concentrations on Sr and Cs sorption were studied by adding higher concentrations of the individual cations to the simulant. As shown in Figures 9 and 10, sorption of both Sr and Cs is suppressed as the concentration of each cation is increased above the concentration initially present in the simulant. The effect of potassium on cesium sorption is similar to that observed for doubly charged cations on strontium sorption. The enhanced impact of elevated Mg and Ca on Sr sorption on the resin, as compared to the zeolite, can be understood in light of the nonselectivity of the resin for Sr over Mg and Ca.

CONCLUSIONS

The comparison of natural chabazite zeolite with RF resin demonstrated that, in this particular waste matrix, the sodium form of the zeolite has a greater sorption capacity for both strontium and cesium. Radionuclide sorption on the sodium-modified zeolite and the water-washed resin from this wastewater can be estimated using a Freundlich sorption

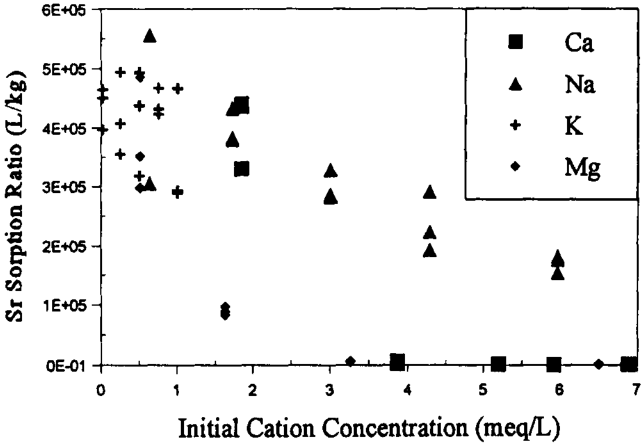

FIGURE 9. The effect of cations on Sr sorption with water-washed R-F resin

Test Procedure: 0.020 g water-washed R-F resin in 10 mL simulant; 24-h equilibration time; 0.00228 meq/L Sr initial concentration and 2.6 × 10^{-6} meq/L Cs initial concentration; cations added as chloride salts.

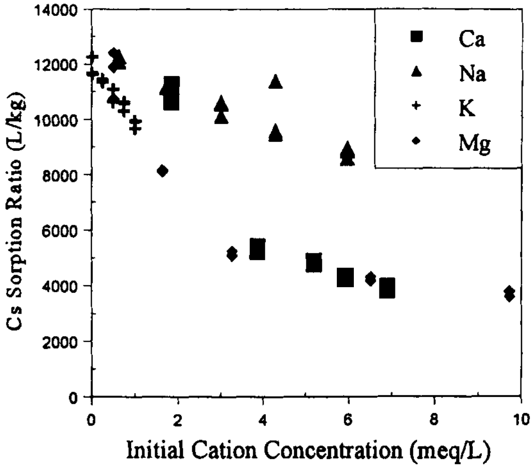

FIGURE 10. The effect of cations on Cs sorption on water-washed R-F resin

Test Procedure: 0.020 g water-washed R-F resin in 10 mL simulant; 24-h equilibration time; 0.00228 meq/L Sr initial concentration and 2.6 × 10^{-6} meq/L Cs initial concentration; cations adds as chloride salts.

model. The prepared zeolite demonstrated a greater selectivity for both these radionuclides over competing cations common in process waste water. This is particularly evident in the case of strontium, for which the water-washed RF resin demonstrated no distinct selectivity over the alkaline earth metals tested. The Sr sorption behavior on RF resin is driven by overall metal(II) concentration.

REFERENCES

1. S. M. Robinson and J. R. Parrott, Jr., Pilot-Scale Demonstration of Process Wastewater Decontamination using Chabazite Zeolites, Report ORNL/TM-10836, U. S. Department of Energy, Oak Ridge, Tennessee, 1989.

2. L. E. McNeese, J. B. Berry, G. E. Butterworth II, E. D. Collins, T. H. Monk, B. D. Patton, and J. W. Snider, Overall Strategy and Program Plan for Management of Radioactively Contaminated Liquid Wastes and Transuranic Sludges at the Oak Ridge National Laboratory, Report ORNL/TM-10757, U. S. Department of Energy, Oak Ridge, Tennessee, 1988.

3. G. V. James, Water Treatment: A Guide to the Treatment of Water and Effluents Purification, 3rd ed., The Darien Press, Ltd., Edinburgh, United Kingdom, 1965, pp. 107-127.

4. A. Dyer and D. Keir, Zeolites, 4, 215-217 (1984).

5. P. Burns, et al., AIChE Symp. Series 83 (259), 66-73 (1987).

6. D. C. Grant, et al., "Effects of Process Variables on the Removal of Contaminants from Radioactive Waste Stream Using Zeolites," presented at the Waste Management '87 Symposium, Tucson, Arizona, March, 1987.

7. R. H. Hawkings and J. H. Horton, Zeolite Prefilter to Reduce Pluggage in Zeolite Cesium Removal Column, Report DP-1245, Savannah River Laboratory, Aiken, South Carolina, 1971.

8. S. M. Robinson and J. M. Begovich, Treatment Studies at the Process Waste Treatment Plant at Oak Ridge National Laboratory, Report ORNL/TM-10352, U. S. Department of Energy, Oak Ridge, Tennessee, 1991.

9. S. M. Robinson, T. E. Kent, W. D. Arnold, and J. R. Parrott, Jr., The Development of a Zeolite System for Upgrade of the Process Waste Treatment Plant, Report ORNL/TM-12063, U. S. Department of Energy, Oak Ridge, Tennessee, 1993.

10. Testing Sieves and Their Uses Handbook 53, 1962 ed., The W. S. Tyler Company.

11. W. J. Weber, Jr, Physiochemical Processes for Water Quality Control; John Wiley & Sons: New York, 1972; Chapter 5.

12. E. D. Collins, D. O. Campbell, L. J. King, J. B. Knauer, and R. M. Wallace, *Evaluation of Zeolite Mixtures for Decontaminating High-Activity-Level Water at the Three Mile Island Unit 2 Nuclear Power Station*, IAEA-EC-518/4, June 1984.

13. J. J. Perona, A Multicomponent Ion-Exchange Equilibrium Model for Chabazite Columns Treating ORNL Wastewaters, Report ORNL/TM-12272, Oak Ridge National Laboratory, Oak Ridge, TN (June 1993).

14. S. M. DePaoli and J. J. Perona, "A Model for Sr-Cs-Ca-Mg-Na Ion Exchange Uptake Kinetics on Chabazite", AIChE (in press).

15. J. P. Bibler, "Ion exchange pretreatment of alkaline radwaste for cesium removal", CONF-940853-7: Summer Meeting of the American Institute of Chemical Engineers, Denver, CO, 14-17 Aug 1994, p 17.