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A COMPARATIVE EVALUATION OF IONSIV® IE-911 AND CHABAZITE ZEOLITE FOR THE REMOVAL OF RADIOSTRONTIUM AND CESIUM FROM WASTEWATER

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ABSTRACT

Natural chabazite zeolite was selected as the baseline treatment technology for the removal of fission products, namely ^{90}Sr and ^{137}Cs, from near-neutral-pH process wastewater and groundwater. The sorbent IONSIV® IE-911, a crystalline silicotitanate manufactured by UOP, was recently tested in this capacity and found to compare extremely well against the baseline material. This paper presents and compares the results of similar batch and column tests performed using both materials, and summarizes the physical and chemical characteristics of the sorbents.

INTRODUCTION

Many DOE facilities generate process wastewater that is contaminated with ^{90}Sr and ^{137}Cs, and/or are responsible for processing groundwater in order to lower levels of these radioactive constituents to acceptable limits. In most cases, the treatment option of choice is ion-exchange, and this material has generally been a type of natural zeolite. Through a grant from the DOE Efficient Separations and Processing (ESP) Crosscut EM-50 Program, several new, promising materials have been evaluated for their capacity to remove these fission products from simulated and actual wastewaters. The materials are evaluated for their capacity in removing ^{90}Sr and ^{137}Cs in the presence of competing alkaline and alkaline-earth cations, which are sometimes present in the waste at levels exceeding 1 million times the concentration of the target radioactive species. Therefore, the most important measure of the success of a material is its selectivity for the fission products. Reduced secondary waste is an indirect, yet equally important result of a more selective ion-exchanger.

As mentioned, the most common material used in treating wastewater for the removal of fission products is natural zeolite; the baseline material in this study is chabazite zeolite obtained from GSA Resources. Crystalline silicotitanate (CST), developed at Texas A&M and Sandia National Laboratories (SNL) for the treatment of high-salt, high pH tank waste, has shown a remarkable ability to remove strontium and cesium from near-neutral-pH wastewater in the presence of other competing cations. It is now commercially available through UOP in a granular (IONSIV® IE-910) or pelletized form (IONSIV® IE-911). Test results using the zeolite and IONSIV® IE-911 in batch and column configurations are presented and compared here.

EXPERIMENTAL

Batch Testing

Process wastewater simulant was prepared by adding dry chemicals to 100 L volumes of nanopure water and adjusting the pH of the column feed by sparging CO_2 gas into the solution for about an hour. The pH of the solution dropped to 5, which enhanced the solubility of the added chemicals. However, the pH stabilized at a value of 7 after equilibrating for a few days to match that of the simulant used in batch testing. The solution was filtered with a 0.45-µm Supor™ filter membrane recommended by the vendor for the clarification of groundwater samples. Stable strontium and cesium were added to the simulant at this point. A sample of the final simulant solution was then analyzed for total metals by ICP. The ^{85}Sr and ^{137}Cs tracers were added to 20-L aliquots of the feed solution; 2-mL samples from each aliquot were retained to determine the initial activity of the feed solution.

Sorption measurements were made in long-term batch equilibrium tests. The solutions and exchanger are 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 point. Solution volumes were determined from the weight and density of the samples. The sorbent was weighed directly and added to the tubes. At the conclusion of the equilibration period, the tubes were centrifuged for 30 min at 5000 relative centrifugal force (rcf). The solutions were clarified further by filtering the centrifuged supernate using a plastic syringe fitted with a 0.2-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. The 2-mL 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. Competing cation concentrations in nonradioactive solutions were determined using a Thermo Jarrel Ash IRIS/CID ICP spectrophotometer on companion untraced experiments. A Perkin-Elmer 5000 atomic absorption (AA) spectrophotometer was used to characterize the cation content of radioactive solutions.

Column Testing

Column testing will define the sorption characteristics of a material under dynamic flow conditions. The dimensions of a sorbent column were selected primarily on the basis of the diameter of the average sorbent particle.[1] Although the optimum column diameter should be at least 40 times greater than the average particle diameter (typically 0.059 cm or 30 mesh), a factor of 20 was deemed adequate for testing. A 1-cm column diameter meets these requirements and was used for comparative testing of the sorbents. The optimum length of the column should be greater than or equal to 4 times the column diameter; the typical column aspect ratio for testing is between 4 and 5. Approximately 2 g of preconditioned sorbent were packed in the 1-cm-ID columns, resulting in a bed volume of 3.85 mL for each test.

The CST column was prepared by slowly adding prepared sorbent from a weighed container to a 1-cm column containing a known volume of water. The sorbent was added to the column to a bed depth of 4.5 cm. The dry sorbent container was reweighed to determine the weight of sorbent added to the column. Excess water above the column bed was collected and weighed. The difference between the initial water volume in the column and the volume of water displaced by sorbent represents the pore volume of the sorbent column. The pore fraction is equivalent to the measured pore volume of the 1-cm column divided by the column volume, calculated on the basis of a 4.5-cm bed height.

A peristaltic pump was used to transfer the traced simulant through a second 0.45-μm Supor™ filter membrane into the base of the sorbent column (Fig. 1). The flow rate of simulant feed was set at 1.2 mL/min (about 19 BV/h) to maintain a linear flow velocity similar to that of successful earlier column tests. The feed was introduced at the bottom of the column to maximize contact of the solution and sorbent within the column. An automatic fraction collector was used to collect the column effluent over 6-h periods (or 460 mL per fraction), and later in the test, at 8-h intervals. Aliquots of each fraction were acidified and submitted for ICP analysis of competing cations through breakthrough of these species. The nuclide content of each fraction was determined using gamma spectrometry.

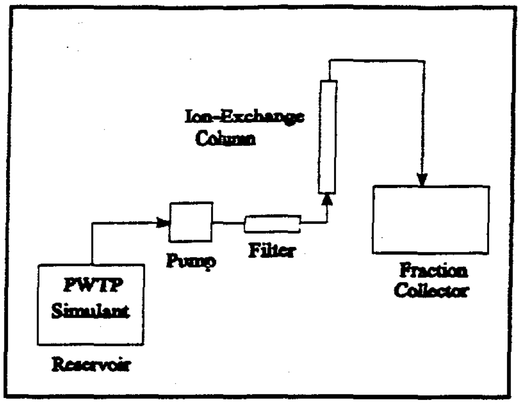

Figure 1. Flow diagram for column test.

The test results were used in the following equations:

$$\text{Decontamination factor, } DF = \frac{G_i}{G_f}\,, \tag{1}$$

$$\text{Sorption ratio, } R_s\ (L/kg) = \frac{(G_i - G_f)\ V}{G_f\ W}\,, \tag{2}$$

$$\text{Final solution concentration, } C_f\ (meq/L) = \frac{C_i G_f}{G_i}\,, \tag{3}$$

and

$$\text{Final concentration on exchanger, } C_x\ (meq/kg) = C_f R_s\,. \tag{4}$$

where:

G_i = gamma count rate of the initial solution;
G_f = gamma count rate of the final solution;
V = volume of the solution treated, mL;
W = exchanger weight, g;
C_i = concentration in initial solution, meq/L;
C_f = concentration in final solution, meq/kg.

The sorption ratio (R_s) is equivalent to the distribution coefficient (K_d) if equilibrium conditions are assumed. The exchanger weight is reported on a dry-weight basis by correcting for moisture content of the sorbent in order to make direct comparison of sorption efficiency among sorbent materials.

RESULTS AND DISCUSSION

Physical Characterization of Sorbents

A number of physical parameters are important in assessing the performance of a given sorbent. Some of these characteristics include the sorbent density, surface moisture content, surface area, pore size, pore volume, particle size, degree of particle swelling, and mechanical stability. Table 1 summarizes the available physical data for each of the sorbents. Much of this information is available for the baseline zeolite sorbent, primarily through the manufacturer's product literature.

Table 1. Physical and chemical parameters for zeolite and CST.

Parameter	Chabazite zeolite[a]	Crystalline silicotitanate (IONSIV® IE-911)
Source	GSA Resources, Inc.	UOP
Particle density (g/cm^3)	1.73	2.0
Surface moisture, wt%	7.1	6.0
Pore size, Å	4.1 - 3.7	4.0[b]
Total pore volume, cm^3/g	0.468	0.24[c]
Dry particle size, μm (as-received)	484 ± 223	409 ± 111
Wet particle size, μm (pretreated)	575 ± 156	418 ± 113
Sodium content, w/w%	6.2	2.13
Ion-exchange capacity, meq/g	2.2	2.5
Pretreatment needs for use in treating near-neutral-pH wastewater	sieve, wash with 2 *M* NaCl, wash with H_2O, air dry	sieve, wash with H_2O, wash with 0.1 *M* HCl

[a] Cabsorb-ZS500A product literature, GSA Resources, Inc., Cortaro, Arizona.

[b] Z. Zeng, et. al., "Ion-exchange of Group I Metals by Hydrous Crystalline Silicotitanates," *Ind. Eng. Chem. Res.*, 35, 4246-4256 (1996).

[c] Miller, J. E. and N. E. Brown, "Development and Properties of Crystalline Silicotitanate (CST) Ion Exchangers for Radioactive Waste Applications," SANDIA REPORT, SAND97-0771, April 1997. This is the pore volume of IONSIV® IE-910.

Sieve analysis[2] was used to determine the particle size of engineered CST (IONSIV® IE-911, Lot No. 9990968/002). Two forms of CST were sized: (1) the as-received material and (2) CST that has been preconditioned by equilibrating it with 2 *M* NaCl, water rinsed, and air dried. Sieving results indicated that 90% of the as-received dry sorbent was in the −30/+60 mesh size range; the average particle size, based on pellet volume, was 409 ± 111 μm (Table 1). When the as-received material was wetted, approximately 10% of the sorbent was removed as fines in the rinse water. Evidently, fines adhere to the larger particles and are not detected separately during dry sieve analysis. The dry particle size of saline-washed CST was 374 ± 107 μm; 90% of the particles were also in the −30/+60 mesh size range. The wet particle sizes of both the as-received and pretreated CST were found to be 415 μm. The sieve results suggest that once fines are removed, the dry particle size is actually 375 μm for both forms of CST. When either form of the sorbent is fully wetted, the volume is approximately 20% greater.

Additional physical parameters pertinent to IONSIV® IE-911 include an approximate pore opening of 4Å, a particle density of 2.0 g/cm^3, and a bulk density of 62.4 lb/ft^3 (960 kg/m^3).[3]

Results of the sieve analysis for chabazite zeolite indicated that the dry, as-received resin was finer than the stated -35/+50 mesh range. The average dry particle sizes of the combined -20/+50 fractions of the as-received zeolite were 536 ± 149 μm, with an average water content of 7.1 wt%. Approximately 2% fines were produced when the sorbent was pretreated. The average wet-particle size of the pretreated zeolite was 575 ± 156 μm. The difference between the average particle size of the wet and dry forms of the zeolite indicated that the volume of the sorbent swelled by a factor of 1.23, where the wet particle size more accurately reflects the particle size of the sorbent during testing.

Chemical Characterization and Pretreatment of Chabazite Zeolite

Natural chabazite zeolite was purchased from GSA Resources, Inc. at a cost of $50/ft^3. A stock supply was pretreated to remove the natural strontium present on the as-received zeolite. This pretreatment was accomplished by washing the zeolite with 2 *M* NaCl, followed by several rinses with deionized water to remove excess sodium ion; thus the natural strontium was displaced, and the zeolite was fully loaded with sodium. The −20/+50 mesh fraction (300–840 μm) of the pretreated zeolite represents the reference sorbent for the remaining studies presented here. Sodium content of the as-received zeolite was confirmed to be 6.2 wt%. The exchange capacity of the zeolite was determined to be 2.2 meq/g zeolite.

Chemical Characterization and Pretreatment of CST

CST sorbent can exist in multiple ionic forms. The form of CST undergoing exchange with strontium and cesium is a function of both the sodium ion concentration and the pH in the waste. In a recent publication, Zheng et al.[4] defined CST functionality in sodium solutions according to the following equilibrium reactions:

$$H^+ + Na_3\text{-CST} = HNa_2\text{-CST} + Na^+ \qquad k_1 = 7.7 \times 10^8 , \tag{5}$$

$$H^+ + HNa_2\text{-CST} = H_2Na\text{-CST} + Na^+ \qquad k_2 = 6.1 \times 10^7 , \tag{6}$$

and

$$H^+ + H_2Na\text{-CST} = H_3\text{-CST} + Na^+ \qquad k_3 = 7.4. \tag{7}$$

The concentration of each CST form can be rewritten in terms of the preceding equilibrium constants,

$$[HNa_2\text{-CST}] = k_1 \frac{[Na_3\text{-CST}]\ [H^+]}{[Na^+]} , \tag{8}$$

$$[H_2Na\text{-CST}] = k_2 \frac{[HNa_2\text{-CST}]\ [H^+]}{[Na^+]} = k_1 k_2 \frac{[Na_3\text{-CST}]\ [H^+]^2}{[Na^+]^2} , \tag{9}$$

and

$$[H_3\text{-CST}] = k_3 \frac{[H_2Na\text{-CST}]\ [H^+]}{[Na^+]} = k_1 k_2 k_3 \frac{[Na_3\text{-CST}]\ [H^+]^3}{[Na^+]^3} ; \tag{10}$$

and summed in a mass balance equation,

$$[CST] = [Na_3\text{-CST}] + [HNa_2\text{-CST}] + [H_2Na\text{-CST}] + [H_3\text{-CST}] . \tag{11}$$

The distribution of CST functionality in a given waste matrix can be determined by combining Eqs. (8–11). For example, the fractional contribution of the trisodium form of CST to the overall IONSIV® IE-911 functionality can be determined as

$$\frac{[\mathrm{Na_3\text{-}CST}]}{[\mathrm{CST}]} = \frac{1}{k_1\frac{[\mathrm{H^+}]}{[\mathrm{Na^+}]} + k_1k_2\frac{[\mathrm{H^+}]^2}{[\mathrm{Na^+}]^2} + k_1k_2k_3\frac{[\mathrm{H^+}]^3}{[\mathrm{Na^+}]^3}} . \tag{12}$$

Each of the other CST forms can be similarly represented. For typical nuclear tank waste containing 5 *M* sodium ion and a pH greater than 11, equilibrium calculations indicate that the trisodium CST will be the primary form of CST undergoing exchange (Fig. 2). However, the monosodium form of CST is the primary form of the exchanger in near-neutral wastewater streams (Fig. 3). Even if the total sodium content is as great as 5 *M*, over 98% of CST will hydrolyze to the monosodium form in a near-neutral, equilibrated solution.

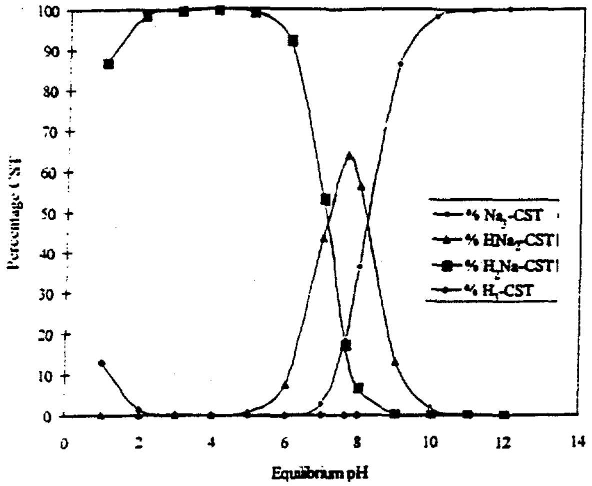

Figure 2. CST functionality in 5 *M* sodium.

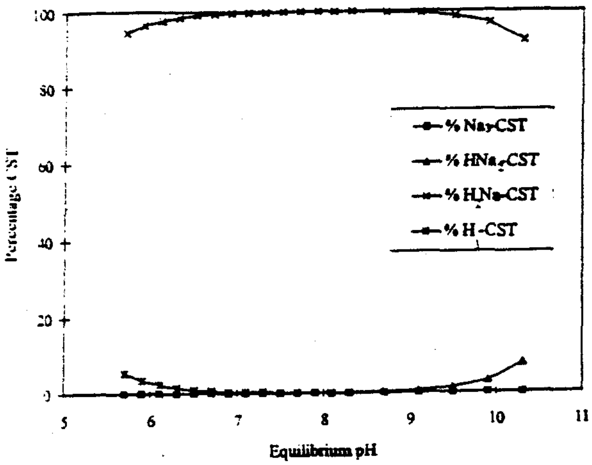

Figure 3. CST functionality in 15 ppm sodium.

The implication of the preceding calculations is that efforts to convert CST to either the trisodium or the trihydrogen form are not particularly effective for wastewater applications. According to directions supplied by UOP, IONSIV® IE-911 should be converted to the trisodium form by pretreating the CST with NaOH. Complete conversion to the trisodium CST ensures that the exchanger will have the greatest exchange capacity in highly alkaline tank matrices and that the pH of the waste is not altered by any exchange of hydrogen on the CST with sodium ion present in the waste solution. However, in near-neutral-pH waste matrices, the formation of the monosodium CST is highly favored, such that trisodium CST immediately hydrolyzes and elevates the pH of the process wastewater. The secondary consequence of CST hydrolysis is the possibility that near-saturation levels of calcium present in groundwater might precipitate as the pH of the waste increases. Conversely, if the CST is pretreated with HCl to form trihydrogen CST, monosodium CST is rapidly formed by the uptake of sodium from process wastewater and the release of hydrogen ion into the waste stream.

The presence of multiple cationic forms of CST must be considered in interpreting laboratory data intended to chemically characterize the inorganic sorbent. According to UOP product literature, the as-received sorbent contains Na_2O, SiO_2, TiO_2 and proprietary oxides.[1] The cationic content was determined by ICP indicating the as-received IONSIV® IE-911 contained 2.13 ± 0.2 wt% Na (0.93 meq/g); only traces of Mg and Ca were observed. Potassium was not detected. For comparison purposes, IONSIV® IE-910, the powder form of CST, contains 10.5–11.5 wt % (4.8 meq/g) ion-exchangeable sodium.[3]

Two procedures were used to remove fines and convert the as-received IONSIV® IE-911 to a single cationic form. The UOP procedure was modified by pretreating the sorbent with 2 *M* NaCl rather than NaOH. It was felt that alkaline preconditioning might result in a basic sorbent that would precipitate alkaline earth metals when the sorbent was used in process wastewater. Following a saline pretreatment procedure that was used previously for zeolite, preconditioned IONSIV® IE-911 was then rinsed several times with nanopure water to remove excess saline. The sodium content of the saline-washed CST, which will be referred to as Sodium-CST, was 3.4 wt % or 1.36 meq Na/g CST. Batch testing results summarized in this report were performed using the Sodium-CST sorbent. In light of the recently published equilibrium reactions [Eqs. (5- 7)], it is evident that this preconditioning method produces primarily H_2Na-CST, rather than Na_3-CST. This conclusion is supported by the fact that the sodium content is approximately one-third that of the trisodium form of CST prepared by Zheng et al.[4] Additionally, when the preconditioned sorbent was introduced into near-neutral-pH simulant, it consistently yielded a basic solution, as the sodium on the CST was displaced with hydrogen in solution. Because there is little difference between the sodium content of the as-received and preconditioned CST, it can be assumed that IONSIV® IE-911 is received primarily in the H_2Na-CST form.

The sorbent used in the column test was prepared by contacting as-received IONSIV® IE-911 with 1*M* HCl. The converted CST was then rinsed with nanopure water until the pH of the resulting rinsate was near neutral. The hydrogen-form CST was air dried; the final sodium content was less than 0.02 wt%. According to the stated equilibria, the acid-washed sorbent, henceforth referred to a Hydrogen-CST, should be in the trihydrogen form.

The exchangeable hydrogen content for both the Sodium-CST and Hydrogen-CST preparations was determined by contacting 0.1 g of the preconditioned CST with 5 *M* NaCl. After five saline contacts, a total of 1 meq H/g was generated from Sodium-CST; linear extrapolation of the data to negligible H_3-CST content suggests that the original Sodium-CST preparation contains 1.18 meq/g exchangeable hydrogen, in addition to the 1.36 meq/g exchangeable sodium. The combined exchangeable cation content indicates that the Sodium-CST in near-neutral-pH applications has a total ion-exchange capacity of 2.5 meq/g sorbent.

Similar data calculations indicate that the Hydrogen-CST generates 10.75 meq H/g after five contacts with 5 *M* NaCl. A logarithmic extrapolation of the data to negligible H_3-CST suggests that the original Hydrogen-CST preparation contains 10.8 meq/g exchangeable hydrogen. This value is four times greater than the combined total of exchangeable sodium and hydrogen in the Sodium-CST. The elevated value might indicate that additional sodium exchange sites were created by treating the CST and binder with strong hydrochloric acid. Anthony et al.[5] found that powdered CST resisted acid dissolution if the pH was greater than 2. Pretreatment of the IONSIV® IE-911 with a less concentrated acid (0.1 *M* HCl) may be advisable to produce the trihydrogen form of CST.

Strontium and Cesium Ion-Exchange Capacity/Ratio on CST

Multiple functionality of CST complicated the determination of ion-exchange capacity of the sorbent for cesium and strontium. The cesium cation-exchange capacity was estimated by two procedures. The as-received IONSIV® IE-911 was contacted with 0.1 *M* cesium chloride ($CsCl_2$) that had been traced with ^{137}Cs. Final cesium and sodium contents, determined by cesium activity and atomic absorption, respectively, indicate that 1.69 ± 0.09 meq/g cesium was sorbed per 1.48 ± 0.15 meq/g sodium exchanged. Similarly, 1.06 ± 0.01 meq/g cesium was sorbed per 1.03 ± 0.03 meq/g sodium exchanged when the Sodium-CST was contacted with 0.01 *M* $CsCl_2$. The approximate 1:1 exchange of cesium for sodium is in agreement with the description of cesium sorption on CST presented by Zheng et al.[4] Cesium primarily exchanges with only one of the sites on CST, and only if that site is in the sodium form. Zheng represented the chemical equilibrium reaction as

$$\mathrm{Cs}^+ + \mathrm{H_2Na\text{-}CST} \rightleftharpoons \mathrm{H_2Cs\text{-}CST} + \mathrm{Na}^+ \qquad k_4 = 1.5 \times 10^7 \ . \tag{13}$$

The cesium ion-exchange capacity was also determined by mixing duplicate 0.5-g samples on a Labquake shaker overnight with 25 mL of 50 ppm CsCl (pH 5.45) traced with ^{137}Cs. At the end of a 24-h contact, the final pH values of the solutions were determined and the samples were then centrifuged at 5000 relative centrifugal force (rcf) for 45 min. The clarified solutions were removed, counted for cesium activity, and submitted for AA analysis. The separated CST was then contacted with fresh CsCl solution for at least 24 h. Multiple contacts were continued until the cesium concentration of the equilibrated solutions was equivalent to the initial concentration. A total of 11 solution contacts (Fig. 4) were made, in which the sum of 0.8 meq/g cesium sorbed to the CST; 0.96 meq/g sodium and 0.0001 meq/g hydrogen were released into the solution. Cesium data at the two highest sodium concentrations in Fig. 4 represent the solution composition of the first two 50-ppm CsCl contacts. The elevated pH values of these samples indicate that sodium release is the result of both CST hydrolysis and cesium exchange on $\mathrm{H_2Na}$-CST. Beyond the third contact (0.15 *M* sodium), the final pH is more acidic than that of the initial 50-ppm CsCl solution. At this point in the study, cesium appears to be replacing primarily sodium ion—and, only to a very limited extent, hydrogen ion.

For sorption data involving a single ion-exchange reaction of the general form

$$mM^{n+}{}_{(aq)} + nA^{m+}{}_{(s)} \rightleftharpoons mM^{n+}{}_{(s)} + nA^{m+}{}_{(aq)} \ , \tag{14}$$

the equilibrium sorption ratio, or distribution coefficient (K_d), is related to the concentration of exchanging ion by the following equation:

$$\frac{d \log [K_d]_M}{d \log [A^{m+}]_{aq}} = -\frac{n}{m} \ , \tag{15}$$

where $[K_d]_M$ represents the equilibrium sorption ratio of cesium, $[A^{m+}]_{aq}$ represents the aqueous concentration of sodium, and *n*/*m* signifies the charge ratio of cesium to sodium. Equation (15) was plotted and used to confirm a 1:1 exchange between Cs and Na on chabazite; ideally, the slope of the plot should be a value of - 1 for this situation. In the case of sodium-cesium exchange on H_2Na-CST (Fig. 4), multiple breaks in the plot were seen, suggesting the multiplicity of exchange reactions that actually take place in 50 ppm CsCl. No portion of the cesium data can be solely attributed to cesium sorption on monosodium CST, and, therefore, no ion-exchange ratio can be calculated from this form of data treatment.

Strontium chemical equilibria have not been fully defined for highly alkaline wastes, for which the pertinent sorbing species would be the strontium hydroxide cation ($SrOH^+$). Strontium exists as the unassociated divalent cation in near-neutral-pH wastes streams; this was verified through the use of the Environmental Protection Agency's (EPA) public domain program — MINTEQ.[6] Again, no chemical equilibria have yet been established between the Sr(II) cation and H_2Na-CST. Duplicate samples of as-received IONSIV® IE-911 was contacted with 50 ppm $SrCl_2$ (pH 5.44) to determine the strontium ion-exchange capacity. After 12 contacts with the strontium solution, a total of 1.05 meq/g strontium was sorbed, while 1.3 meq/g sodium and 0.0001 meq/g hydrogen were released. Fig. 5 represents the final sodium concentration after *each* contact for the duplicate samples. All final solutions were 0.6–0.8 pH units more acidic than the initial 50-ppm $SrCl_2$ solution, indicating a more complex equilibrium than just sodium displacement. As can be seen in Fig. 5, the majority of strontium was loaded within the first seven contacts. Between contacts 3 and 7, the slope of the data is equivalent to - 0.1, which also suggests that some other mechanism besides simple sodium exchange is involved in strontium sorption.

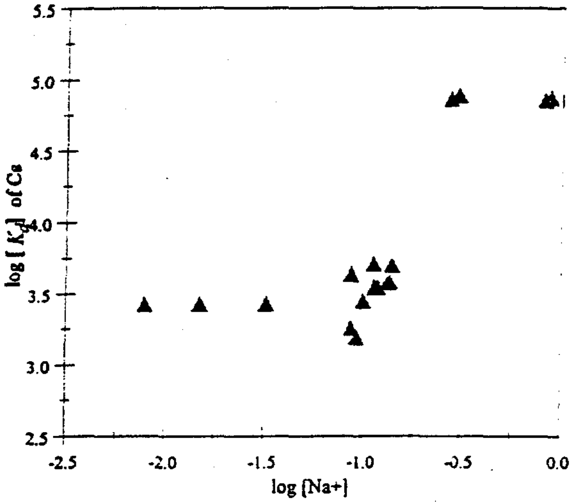

Figure 4. Determination of cesium ion-exchange ratio on as-received IONSIV® IE-911.

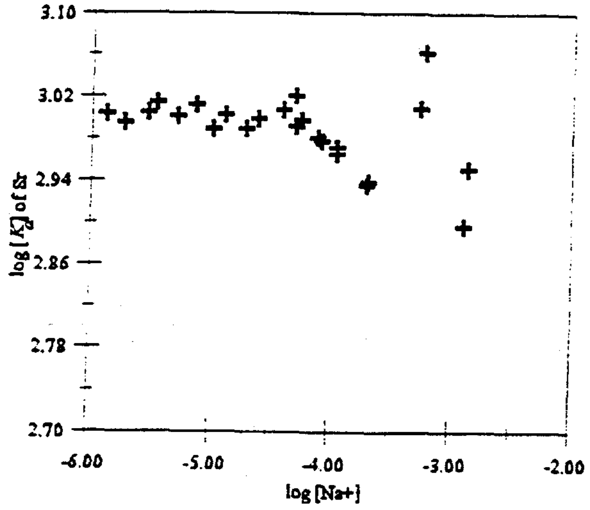

Figure 5. Determination of strontium ion-exchange ratio on as-received IONSIV® IE-911.

Batch Test Results

Direct comparison of the two sorbents is valid only if the test conditions are identical and the treated waste streams are identical. In all of the results presented here, the wastewater simulant used had the composition shown in Table 2. This is a simulant based on the process wastewater treated at Oak Ridge National Laboratory's (ORNL) Process Waste Treatment Plant (PWTP), the composition which is also shown in Table 2. This waste stream was choosen to be used as a simulant since it typifies regional DOE wastewater and falls within the regional composition of typical groundwater. [7, 8, 9,10]

Strontium was included in the simulant at a level of 0.1 mg/L or 0.00228 meq/L (which included 1 × 10^6 Bq/L ^{85}Sr tracer) to reflect the average concentration of total strontium in the PWTP feed. This strontium concentration is also typical of process water in the local DOE area and represents a midrange value for groundwater. Both ^{134}Cs and ^{137}Cs are normally absent in local on-site groundwater but are present at an average level of 300 Bq/L in PWTP influent. The ^{137}Cs added to the simulant was present at a tracer level of 1.12 × 10^6 Bq/L (3.4 × 10^{-4} ppm, 2.5 × 10^{-6} meq/L) and reflects the upper limit for cesium activity typical of process wastewater.

Table 2. PWTP actual wastewater and simulant compositions.

Component	Concentration (mg/L)	
	PWTP, actual	PWTP, simulant
Ca^{2+}	35 - 40	45
Cs^{+}	9.4 × 10^{-8} (3.0 × 10^2 Bq/L)	3.4 × 10^{-4} (1.12 × 10^6 Bq/L)
K^{+}	1 - 3	1.2
Mg^{2+}	7 - 8	8.8
Na^{+}	14 - 30	18.3
Sr^{2+} (total)	0.1	0.1
Sr^{2+} (radioactive)	5.3 × 10^{-8} as ^{90}Sr (2.70 × 10^2 Bq/L)	1.14 × 10^{-6} as ^{85}Sr (1.0 × 10^6 Bq/L)
pH	6.7 - 9	7 - 8

Batch Tests: Chabazite Zeolite

Natural chabazite zeolite was selected as the benchmark sorbent for removing strontium and cesium from contaminated wastewater. Standard testing of the zeolite included determination of the strontium and cesium sorption rates using batch test procedures. Twenty-four hours was required to achieve sorption equilibrium in 10-mL batch samples containing 0.005 to 0.05 g of zeolite.

Strontium sorption on pretreated zeolite was observed in PWTP simulant samples in which the total strontium concentration in the initial solution was 0.1 ppm Sr. The strontium sorption isotherm exhibited a curvilinear profile; positive deviations from linearity were observed for strontium loadings greater than 2 meq/kg. The sorption ratio, R_s, at low strontium loading on washed zeolite was approximately 17,000 L/kg, while the comparable R_s on unwashed zeolite was 30% lower. The difference in the behavior of the two preparations of zeolite indicates the availability of additional sorption sites that were created when the natural strontium was removed during saline washing of chabazite.

Data for strontium sorption on the pretreated zeolite were successfully fit to the Freundlich sorption model.[6] Cesium sorption was observed in simulant samples containing an initial cesium concentration of 3.4×10^{-4} ppm. The sorption isotherm was found to be directly proportional to the concentration of cesium in solution. The R_s for cesium on the prepared zeolite was 80,000 L/kg as compared with 50,000 L/kg on the unwashed zeolite. Cesium sorption data were also fit to a Freundlich sorption model, the results of which implied that the distribution coefficient is essentially constant over the cesium concentration range studied in these tests.[7]

On completion of testing with the simulant, the sorption of strontium and cesium from actual PWTP feed wastewater was observed on washed zeolite. The sorption profiles of the actual PWTP feed sample were nearly identical to those obtained with the simulant, indicating a close match between the chemical compositions of the simulant and the actual waste stream. Maximum strontium and cesium loadings from the actual wastewater sample (or simulant) onto treated chabazite were calculated to be 24 and 0.17 meq/kg, respectively. Sorption results from these batch studies are summarized for zeolite, and compared to results for crystalline silicotitanate under identical experimental conditions, in Table 3.

Batch Tests: IONSIV® IE-911

Equilibration times, corresponding decontamination factors, and sorption ratios were determined for Sodium-CST by mixing a series of samples containing up to 20 mg of the ion-exchange material in 10 or 15 mL of the traced process water simulant (Table 2).

Table 3. Batch experimental results for sorption of cesium and strontium from PWTP simulant using zeolite and IONSIV® IE-911.

Batch sorbent parameter	Cesium		Strontium	
	Chabazite zeolite	IONSIV® IE-911	Chabazite zeolite	IONSIV® IE-911
Sorption ratio, Rs (L/kg)	17,000	95,000	80,000	1,300,000
max. loading, (meq/kg)	0.17	5	24	200
maximum DF	170	17,000	80	1200

Cesium and strontium sorption equilibrium times were initially determined on the Sodium-CST. Cesium sorption on the Sodium-CST reached equilibrium at approximately 200 h. Strontium sorption ratios continued to increase, reaching a maximum at just over 500 h. The kinetic characteristics for both Mg and Ca are similar to that of Sr. In the process wastewater simulant, it appears that these divalent cations require at least 500 h to achieve equilibrium concentrations on the solid. Based on the maximum sorption ratios obtained in the equilibrium time experiments, the selectivity preference of the CST in the PWTP simulant is: Mg < Ca << Sr<< Cs. The material's selectivity for Na^+ and K^+ ions was determined in the column tests.

Greater than 99% of the strontium and cesium were removed from solution by Sodium-CST in under 10 h. Nevertheless, decontamination factors (DFs) and sorption ratios continued to increase slightly with time. The ^{137}Cs DF increased steadily through approximately 50 h, up to 17,000. The strontium DF continued to increase from a value of 352 at 50 h to a maximum of 1200 at 525 h.

Batch testing for the removal of cesium and strontium from the PWTP simulant was performed as described previously. Maximum sorption ratios are given in Table 3. The cesium R_s was 1,300,000 L/kg in the CST, whereas the comparable value for sorption of cesium on zeolite was 80,000 L/kg. Likewise, for the strontium the sorption ratio was much higher on the CST as compared to the zeolite: 95,000 L/kg on CST and 17,000 L/kg on zeolite.

Maximum loadings for cesium and strontium from PWTP simulant on CST far exceeded those on zeolite (Table 3). Cesium loading on CST was 5 meq/kg compared to 0.17 meq/kg for the zeolite, and a strontium loading of 200 meq/kg was obtained for CST compared to 24 meq/kg of Sr on zeolite.

Cesium-sodium and strontium-sodium binary sorption isotherms were observed for the CST. The

Cs-Na exchange ratio varied between 0.6 and 1; the pH of the equilibrated solutions became more acidic with increasing initial cesium concentration. Again, binary sorption tests reflect the fact that several competing reactions are taking place on the preconditioned CST pellets. Sodium is removed from the CST either by ion-exchange with cesium or by hydrolysis of the sorbent as the sodium is replaced by hydrogen ion in solution. Additionally, cesium appears to exchange with both the sodium sites and, to a lesser extent, with the hydrogen sites (which are formed as a result of CST hydrolysis). The CST hydrolysis reaction will yield a basic sample solution, whereas cesium exchange with available hydrogen sites will yield an acidic solution.

It is the relative extent of CST hydrolysis as compared with the Cs-H exchange that defines the equilibrium pH and the observed Cs-Na exchange ratio in a batch sample. At constant initial cesium concentration, the solution pH becomes more basic as the sorbent loading increases. Additionally, the Cs-Na exchange ratio of the solution drops as the sodium concentration increases when more sorbent is available for hydrolysis. At constant sorbent loading, the amount of sodium produced by sorbent hydrolysis remains constant. However, the overall sodium increases concentration linearly with cesium concentration through an ion-exchange process. The equilibrium pH approaches a value of 3 when the initial quantity (milliequivalents) of cesium in solution exceeds the amount of exchangeable sodium on the sorbent. At these high cesium concentrations, the cesium also exchanges with hydrogen ion sites and the observed Cs-Na exchange ratio increases. The pH data suggest that at cesium solution concentrations above 1 meq/L, at least 10% of the cesium exchange on the prepared CST is with hydrogen.

Batch testing was also performed for the Sr-Na binary exchange reaction. After a 600-h mixing time, the pH of the equilibrated solutions ranged from 4.4 at 5-mg loading to 3.9 at 100 mg of sorbent. Strontium sorption onto CST becomes more favorable at elevated strontium solution concentrations. The Sr-Na exchange ratio varies from 8.5 for 5 mg loading to 1.5 for 100 mg sorbent. The Sr-H ratio is approximately 6×10^4. Ion-exchange with either sodium or hydrogen does not appear to be the only mechanism for strontium removal by CST.

Column Test Results

Column Test: Baseline Sorbent, Chabazite Zeolite

Laboratory results identified several sorbent characteristics that might impact the selection of chabazite zeolite by end users. Natural zeolite has a significant heat of hydration. Consequently, steam is initially generated when water is added to a column of fresh, dry zeolite and may produce voids in the column packing. Natural zeolite is friable; fines are created in the transportation to and charging of a column. With continued column use, zeolite fines and algae cement the column packing so that spent zeolite cannot be easily sluiced from the column.[9] If it is deemed cost-effective, the natural zeolite should be charged with concentrated saline to displace the natural strontium already present on the sorbent. Care must be taken to remove any excess sodium entrained in the column packing by this pretreatment process, so that it will not affect column performance. If this process is done properly, the lifetime of the zeolite column will be enhanced by about 30%. Some of the positive operational features of this particular sorbent are that the inorganic material does not swell significantly when wetted and the fact that the particle size does not change with compositional fluctuations in the waste matrix. The material is relatively dense; consequently, the column packing is not easily disturbed with changes in column operating pressures. Finally, waste immobilization procedures using grout/cement have already been defined for the final disposal of spent zeolite; and the zeolite cost is extremely low compared to the cost other, new sorbents.

A test with a small zeolite column was completed in order to observe ^{90}Sr and ^{137}Cs breakthrough characteristics under dynamic flow conditions. The performance of the chabazite zeolite for the treatment of process/groundwater samples has been summarized in ORNL topical reports.[9] The combination of sorption data and column performance served to define zeolite characteristics, as well as to establish standardized testing procedures for the direct comparison of the baseline treatment with emerging sorbent technology in the future. A 1-cm-diam column containing about 2 g of sodium-modified zeolite was used to treat wastewater simulant. Cation breakthrough was followed by ICP analysis of the effluent, and the radiostrontium and cesium breakthrough was monitored using gamma spectrometry. The zeolite bed in the column was 4.9 cm deep, and the bed volume was 3.85 mL. At a nominal simulant flow rate of 1.25 mL/min (19 bed volumes (BV)/h), the superficial velocity through the bed was 1.6 cm/min. The void volume was 2.52 mL, and the nominal solution residence time in the column was about 3 min. Details of the test can be found in Reference 7. The column test, which lasted for 120 d, was stopped after 59,000 BV because the cementation of fractured zeolite particles plugged the column.

The breakthrough curves for the major cations are presented in Fig. 6, where the fractional breakthrough (C/C_0), defined as the ratio of the cation concentration in the column effluent to the concentration in the feed, is plotted as a function of the volume of solution passed through the column. The initial effluent fractions (about 2500 BV) were analyzed by ICP to determine the breakthrough behavior of Na, Mg, and Ca. The sorption behavior of potassium could not be determined because the potassium concentration in all of the feed and effluent samples was at or below the ICP detection limit of 0.1 mg/L. Figure 6 also illustrates the initial displacement of sodium ion from the prepared zeolite as the cations in the feed were sorbed onto the column. Continued sorption of Sr and Cs onto the zeolite resulted in displacement of Mg beginning at 250 BV and displacement of Ca beginning at 500 BV. These curves imply that the selectivity of the treated zeolite is as follows: Ca > Mg > Na. The fractional breakthrough of these cations stabilized to a value of 1.0 at approximately 800 to 1400 BV.

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. 7. Strontium was first observed in the column effluent at approximately 3000 BV. Fractional breakthrough of 10 and 50% occurred at 6600 and 15,000 BV, respectively. Under these conditions, cesium breakthrough was 1% after about 15,000 BV, 10% after about 30,000 BV, and 50% after about 50,000 BV. The strontium loading for the zeolite was about 60 meq/kg at 50% strontium breakthrough; the cesium loading was 0.2 meq/kg at 50% cesium breakthrough. These loadings, particularly the strontium 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.[9] The breakthrough data were used to construct logarithmic probability plots of strontium and cesium breakthrough vs column throughput. These plots were used to estimate sorption ratios, which are approximately equal to the number of bed volumes at 50% breakthrough.[10] The sorption ratios, although slightly lower, were in good agreement with sorption ratios measured[7] at low loading in batch sorption isotherms:

	Sorption ratio (L/kg) on chabazite zeolite	
Test	Strontium	Cesium
Column	15,800	53,000
Batch	17,000	80,000

Column Test: IONSIV® IE-911

Engineered CST (IONSIV® IE-911) was received from UOP. A small-column test using the hydrogen form of IONSIV® IE-911 was carried out over a period of 10 months, in order to compare its performance to that of the baseline zeolite in removing strontium and cesium from a process wastewater simulant. A description of the IONSIV® IE-911 performance under dynamic flow conditions for wastewater treatment follows.

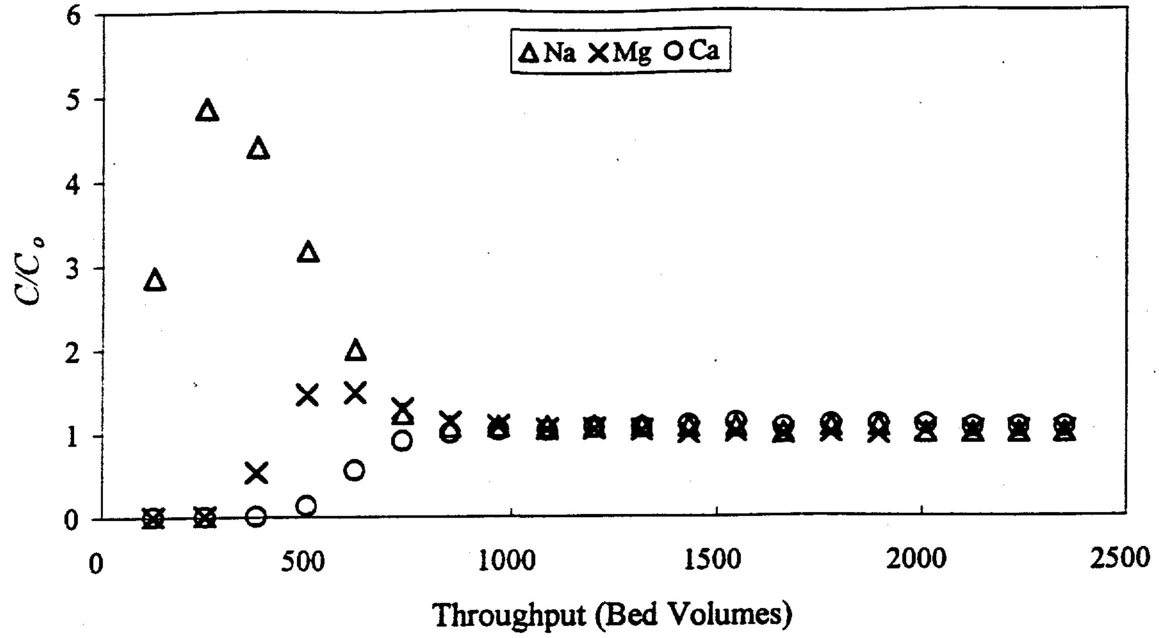

Figure 6. Cation breakthrough curves on chabazite zeolite.

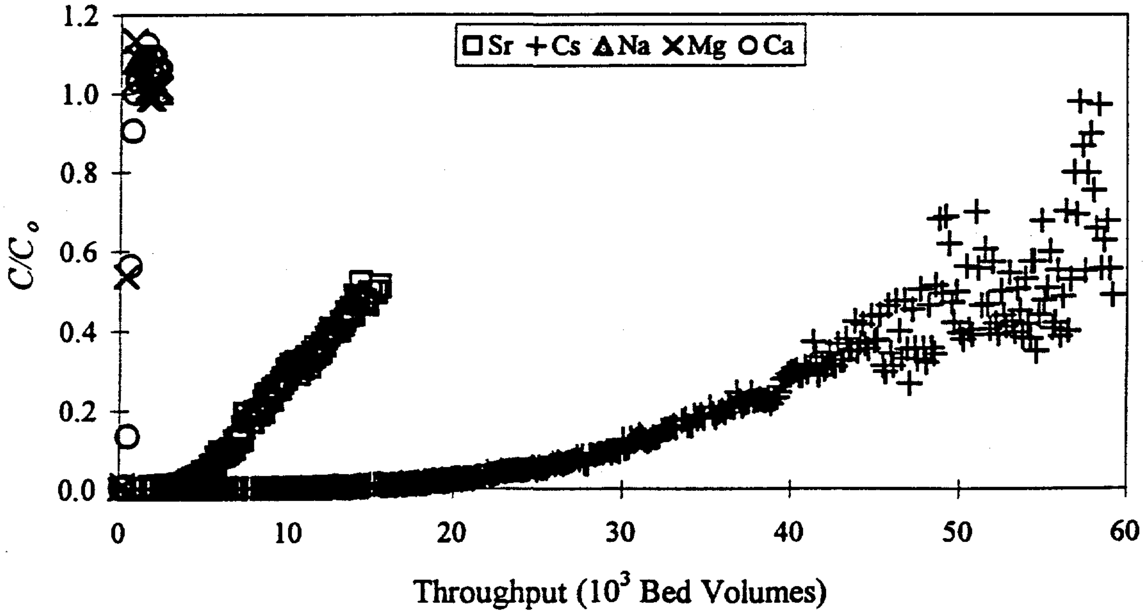

Figure 7. Strontium and cesium breakthrough curves on chabazite zeolite.

The column experiment was run with the PWTP simulant feed stream, whose concentrations were given in Table 2. The column properties, flow rates, and cation concentrations were identical to those used in the zeolite column test, in order to make possible direct comparisons of the two ion-exchange materials.

A 1-cm-diam column containing about 2 g of Hydrogen-CST was used to treat wastewater simulant. Cation breakthrough was followed by ICP analysis of the effluent, and the radiostrontium and cesium breakthrough was monitored using gamma spectrometry. The height of the CST bed in the column was 4.85 cm, and the bed volume was 3.81 mL. At a nominal simulant flow rate of 1.2 mL/min (19 BV/h), the superficial velocity through the bed was 1.53 cm/min. The nominal solution residence time in the column was about 3.2 min. A column void volume of 0.6 was assumed.

The column was run for a total of 10 months; a total of 120,000 BV were processed by the 3.8 mL column during this time. Only limited maintenance of the column system was required. This included the replacement of worn peristaltic tubing, flow lines, and the prefilter that had evidence of algae growth.

Figure 8 shows the breakthrough curves of the cations Mg, Ca, and Na. All reached 50% breakthrough at under 1300 BV: 160, 800, and 1225 BV for Mg, Ca, and Na, respectively. Figure 8 also shows the potassium breakthrough curve, where 50% breakthrough occurred at 16,000 BV. All cation breakthrough curves have a sharp front (i.e., initial part of the breakthrough curve) and a diffuse, or drawn-out, tail. The shape of the curves is indicative of a slow approach to equilibrium concentration, which may signify the rate-controlling step is diffusion of the species in the solid, particle phase as opposed to a rate-controlling step in the liquid phase.[11]

The CST selectivity of cesium over strontium is demonstrated in Fig. 9, which shows the beginning of strontium breakthrough. Cesium breakthrough was not seen, even up to 120,000 BV (10 months operation). Strontium breakthrough was approximately 15% at 120,000 BV. The pH was tracked over the length of the column test. Based on the effluent pH and sodium concentration, the functionality of the Hydrogen-CST in the column was calculated as function of column throughput. Equilibrium calculations indicate that the Hydrogen-CST is initially in the form of H_3-CST. In continuous contact with a sodium-bearing feed stream, the CST is completely converted to H_2Na-CST by 1100 BV. Therefore, sorption of Ca, Mg, and Na is accomplished when the column is primarily in the trihydrogen form. Sorption of K, Sr, and Cs takes place when the CST is present as the monosodium form.

The breakthrough curves in Figs. 8 and 9 support the initial batch findings for selectivity of CST in process wastewater simulant in the following order, with the addition of potassium and sodium:
$Mg < Ca < Na < K < Sr << Cs$.

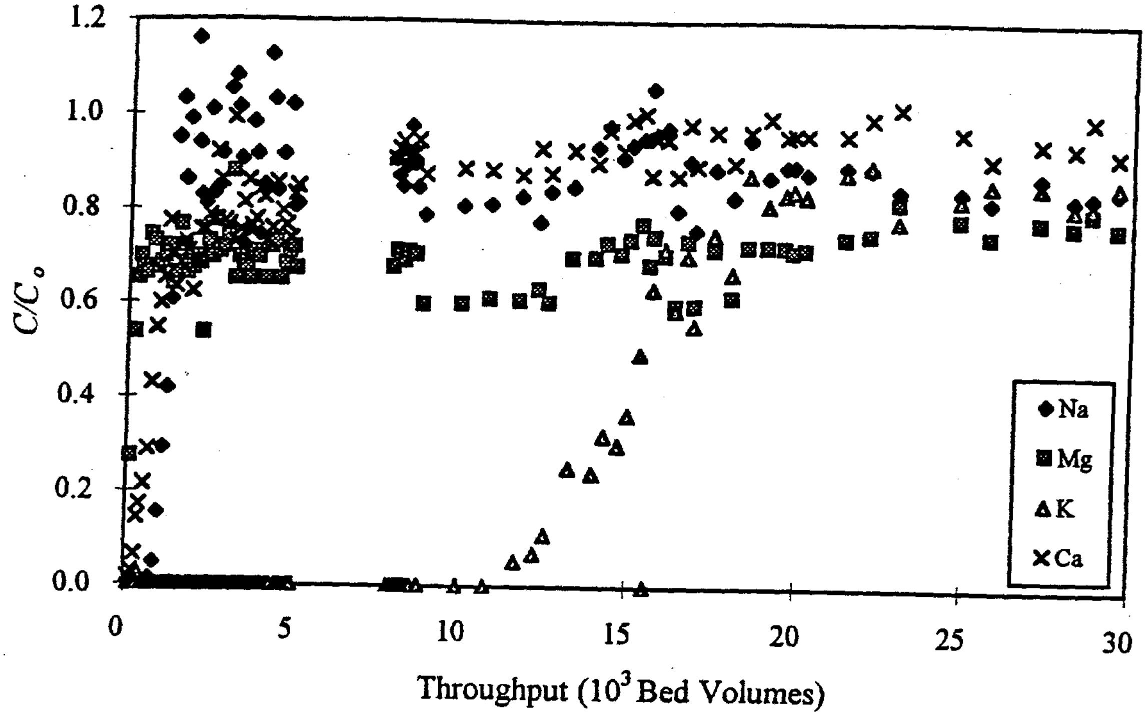

Figure 8. Cation breakthrough curves on CST, IONSIV® IE-911.

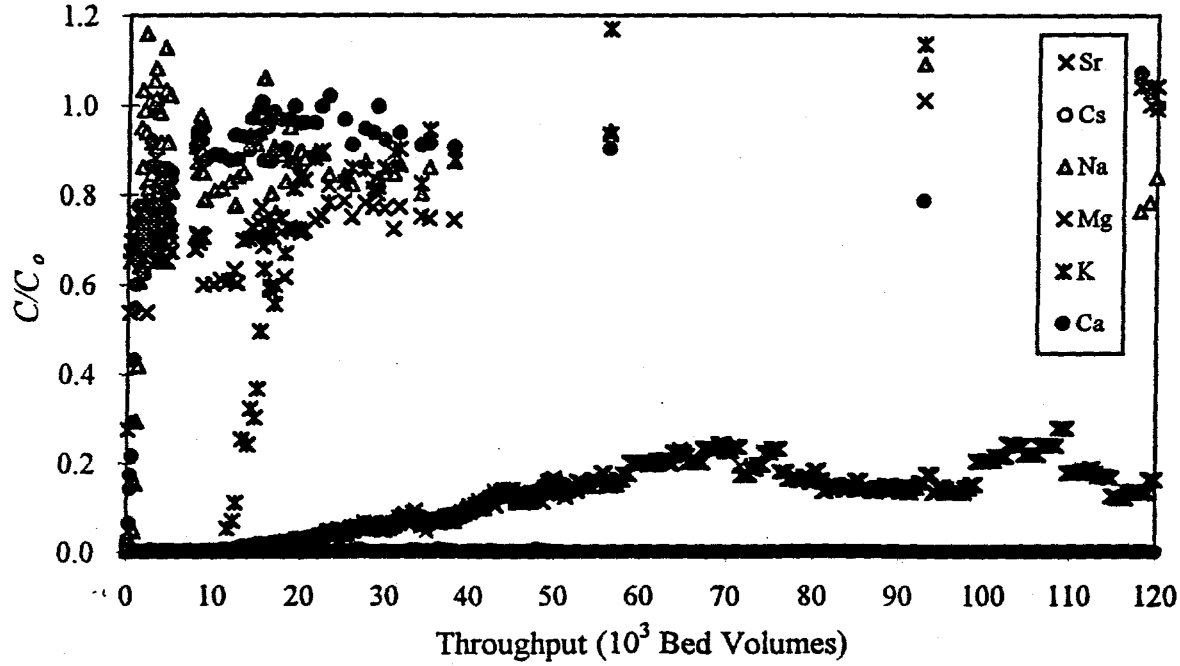

Figure 9. Strontium and cesium breakthrough curves on CST, IONSIV® IE-911.

CONCLUSIONS

A comparison of Cs and Sr distribution coefficients (or maximum R_d) for CST and baseline zeolite in batch studies was made in Table 3. Table 4 gives the distribution coefficients (maximum sorption ratios) as determined in the column studies. The values for both Cs and Sr on CST were estimated.

Table 4. Distribution coefficients for cations on chabazite zeolite and IONSIV® IE-911.

Cation	Column distribution coefficients (L/kg)	
	Chabazite zeolite	Crystalline silicotitanate (IONSIV® IE-911)
Calcium	600	800
Cesium	53,000	2,300,000[a]
Potassium	ND	16,000
Magnesium	400	160
Sodium	< 100	1200
Strontium	15,800	169,000[a]
Selectivity in PWTP simulant	Na<Mg<Ca<Sr<Cs	Mg<Ca<Na<K<Sr<<Cs

[a]Estimated based on column and batch studies.
ND=Not determined.

Both exchangers sorb calcium to approximately the same degree. Magnesium is more strongly exchanged on zeolite compared with CST by almost a factor of three. Potassium appears to be strongly exchanged on the CST, with a column distribution coefficient of about 16,000 L/kg. Data for potassium exchanging on the zeolite are not available because the potassium concentration in the simulant was below the ICP detection limit at that time.

The K_d's measured during batch tests with CST show an enormous distribution of ^{137}Cs on the solid in equilibrium with the liquid. This affinity for ^{137}Cs is supported by the column work. Breakthrough of cesium was not obtained in the CST column study. A total of 120,000 BV were passed through the CST bed, without even 1% breakthrough noted. Comparably, in the zeolite small- column test, with all test conditions similar (PWTP simulant feed, flow rate of 1.2 mL/min, same column size, same volume of exchanger, etc.), 1% cesium breakthrough occurred at 15,000 BV and 50% breakthrough occurred at 50,000 BV.

Strontium breakthrough of 1% occurred at 14,000 BV in the CST study. At the end of the test, C/C_0 for strontium (Fig. 9) was about 15% at 120,000 BV. The baseline zeolite performed much less effectively for strontium removal, with 1% breakthrough occuring at 3000 BV, and 50% breakthrough at 15,000 BV.

Analysis of this incomplete strontium breakthrough data suggests a maximum possible sorption ratio of about 169,000 L/kg at 50% breakthrough. This is about 1.8 times higher than the R_s obtained from batch data. Applying that factor to the maximum cesium R_s obtained in batch experiments suggests that 50% breakthrough would not occur until over 2×10^6 BV had been processed, almost 17 years of operation!

Physically, the stability of the CST material has far exceeded that of the zeolite. No problems with plugging or channeling were noted with the CST after ten months of operation, whereas the zeolite produced fines that cemented together and prevented column flow by 50,000 BV, or six months operation.

Many factors must be included in a cost comparison of the two sorbents. While a direct comparison of the initial cost of the sorbents undoubtedly points to the much less expensive sorbent, zeolite, as the most cost effective choice, the cost of operating columns (i.e. column sluicing and changeout of sorbent) and the disposal of the loaded sorbent all must be taken into consideration. These costs normally far outweigh the cost of the ion-exchange material. Also, since each waste stream has different cation compositions, and therefore different loading capacities for cesium and strontium, the economics must be calculated and compared on the basis of the waste stream being treated.

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