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Evaluation of Improved Techniques for the Removal of Fission Products from Process Wastewater and Groundwater: FY 1997 Status

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Chemical Technology Division

EVALUATION OF IMPROVED TECHNIQUES FOR THE REMOVAL OF FISSION PRODUCTS FROM PROCESS WASTEWATER AND GROUNDWATER: FY 1997 STATUS

D. T. Bostick, S. M. DePaoli, and B. Guo*

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ABSTRACT

The primary goals of this effort in FY 1997 were to survey local end users of wastewater treatment technology and then to evaluate recently available treatment processes in light of user needs. Survey results indicate that local sites are confronted with a limited, and shrinking, budget for treating aqueous waste streams. Therefore, a process will be selected primarily on the basis of sorbent costs, use of existing equipment, and disposal costs for spent processing materials. Most of the local users will require column technology to conform to current plant operating equipment. Loose sorbents might be used more appropriately in batch operations at the Y-12 West End Treatment Facility and the K-25 Central Neutralization Facility. All facilities would benefit from the use of inorganic, rather than organic, sorbents, for which there are more waste disposal options. Due to limited funding for waste treatment, new EM-50 sorbents must exceed existing processes in regard to nuclide loading capacity, selectivity, and operating costs.

Current laboratory testing and economic studies have been directed toward addressing the technical issues specific to the removal of ^{90}Sr and ^{137}Cs from groundwater and process wastewater. This year's efforts have concentrated on evaluating the engineered form of crystalline silicotitanates (CSTs) for near-neutral-pH applications. Both powder and pellet forms of CST can be obtained through UOP; this task evaluated only the engineered form of the sorbent (Ionsiv® IE-911) for wastewater remediation.

Preliminary experimental efforts included measuring the average particle size, surface water content, total sodium content, ion-exchange capacity, and equilibration mixing time. The as-received material contains approximately 10% fines, which adhere to the CST pellet. Once the sorbent is rinsed free of fines, the average particle size is 409 ± 109 µm; the moisture content of the dried CST is 14%. The sodium content of as-received Ionsiv® IE-911 is 2.1% or 1 meq/g sorbent. The sorbent contains a similar amount of exchangeable hydrogen. The cesium and strontium ion-exchange capacities, based on multiple contacts with 50 ppm of the metal, are 0.8 meq/g and 1.1 meq/g, respectively. Batch tests indicated that an equilibration mixing time of 100 h was required for cesium sorption. Group II cations (Sr, Ca, and Mg) required greater than 500 h. Particle diffusion coefficients were estimated for each of these cations from the batch studies.

Once the initial physical and chemical characteristics of the sorbent were defined, the intention was to spend the remainder of the fiscal year collecting binary sorption data. The data from this series of testing would be used to establish cation selectivity and be incorporated into an equilibrium sorption model. As the binary sorption data were accumulated, it became apparent that, in addition to radionuclide sorption, the CST also hydrolyzed . The primary ionic form of CST in near-neutral-pH applications is H_2Na-CST. However, trisodium and trihydrogen forms are also possible, depending upon solution pH and sodium concentration. The impact of multiple forms of CST on binary testing is discussed more fully in this document. The consensus at the 1997 ESP Mid-year Review was that it would be more expeditious to complete a small-column test to evaluate CST for process wastewater treatment. If the CST exchanger performed well relative to the baseline zeolite exchanger, then it may be worthwhile to complete the extensive batch testing required to model CST sorption for near-neutral applications. To this end, a small column test using the trihydrogen form of Ionsiv® IE-911 was initiated within the first week of May.

Approximately 55,000 bed volumes (BVs) of wastewater simulant have been processed thus far. Column breakthrough indicates that cation selectivity on CST follows the order of Mg < Ca < Na < K < Sr < Cs. Strontium breakthrough at 1% of influent concentration occurred at 14,000 BVs; thus far, cesium has not broken through. In comparison, 1% breakthrough of strontium and cesium on a similarly sized zeolite column occurred at 3000 and 6000 BVs, respectively.

This document summarizes the physical features of engineered CST, presents batch testing and column data acquired to date for Ionsiv® IE-911, and discusses the relative economics of the CST versus the baseline zeolite sorbent.

1. INTRODUCTION

1.1 SCOPE OF TASK

The goal of this task is to adequately understand the needs of those responsible for wastewater treatment, to evaluate emerging treatment materials and then to provide the end users with pertinent information required to select and scale up these new technologies for a given waste stream. A survey of customers within the Oak Ridge Reservation was performed in FY 1997 to define the critical parameters required by the user to implement a technology to remove ^{90}Sr and ^{137}Cs from wastewater. This survey was also supported with end-user input from other Department of Energy (DOE) sites. Survey parameters included the types, quantities, and locations of wastewater within the locality. The survey also attempted to ascertain the level of treatment efforts currently under way, as well as to define the drawbacks that the user experienced in the operation of these processes. Possible drivers that might influence the decision of the user to select a given wastewater treatment or to alter a current process were determined. These drivers included environmental regulatory requirements, limitations in secondary waste generation, operational costs, mandated time frames for waste decontamination, and compatibility with current treatment flow sheets. A letter report summarizing the survey findings is included in the appendix of this document.

Current laboratory testing and economic studies have been directed toward addressing the technical issues specific to the removal of ^{90}Sr and ^{137}Cs from groundwater and process wastewater. Materials/processes that have been investigated in the course of this task include ion exchange on resorcinol-formaldehyde

(R-F) resin, an organic exchanger developed at Savannah River Laboratory and manufactured by Boulder Scientific Company.[1,2] Strontium sorption on sodium nonatitanate, an inorganic exchanger developed by Texas A&M University and AlliedSignal Corporation, has been evaluated and documented in an FY 1996 status report.[2] This year's efforts have concentrated on evaluating the engineered form of crystalline silicotitanates (CSTs) for the removal of both strontium and cesium from wastewaters. CST technology was developed at Sandia National Laboratory and Texas A&M for the remediation of highly alkaline tank waste. Both powder and pellet forms of CST can be obtained through UOP; this task evaluated only the engineered form of the sorbent for wastewater remediation. The purpose of this report is to present the data acquired in FY 1997 and to discuss the utility of the CST sorbent in light of DOE Environmental Management (EM)–30 and EM–40 end-user needs.

1.2 PREVIOUS TASK RESULTS

Laboratory studies have endeavored to obtain a quantitative understanding of the behavior of the new materials and to evaluate their sorption efficiency in reference to a standard benchmark treatment technique. Scoping tests were conducted in which new treatment materials are compared with the baseline sorbent, chabazite zeolite, in batch shaker tests.[3] Equilibrium tests have been conducted under various treatment conditions (pH, temperature, waste composition). Once batch testing of a treatment method is completed, dynamic column tests are performed to obtain the defining column operating parameters for scaling up the technology.

1.2.1 Chabazite Zeolite

The primary effort in FY 1994 and a portion of FY 1995 was the characterization of the baseline treatment technology—that is, radionuclide sorption on natural chabazite zeolite. Cesium and strontium sorption on zeolite was determined for batchwise treatment of both a wastewater simulant and the corresponding actual wastewater. From batch testing, radionuclide sorption on the zeolite was fit to an empirical sorption model so that ^{90}Sr and ^{137}Cs sorption on zeolite columns could be predicted. Zeolite sorption efficiency was determined in the presence of the major cations present in wastewater (e.g. Na, Ca, K, and Mg) to estimate the impact that variations in water compositions might have. A test with a small zeolite column was completed in FY 1995 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.[3] An abbreviated summary of zeolite sorption is presented in Sect. 4.1 of this report. 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.

Laboratory results identified several sorbent characteristics that might impact the selection of chabazite zeolite by EM-30 and EM-40 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.[4] 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 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.

1.2.2 R-F Resin

In lieu of an available new inorganic exchanger, R-F resin was selected in FY 1995 as the first in a series of new sorbents that were tested under this task. A portion of FY 1996 was used to complete this effort. Studies performed in FY 1995 used radioanalytical data to determine the fate of cesium and strontium in solutions treated with the resin. Supporting inductively coupled plasma (ICP) spectrometric data were acquired during FY 1996 to help interpret the nonlinear isotherms observed in FY 1995 strontium sorption tests. Strontium and cesium sorption characteristics on the resin were also observed in a small-column test run in FY 1996.

Comparison of natural chabazite zeolite sorption data with those of R-F resin demonstrated that, in a near-neutral wastewater matrix, the sodium form of the zeolite had a greater sorption capacity for both strontium and cesium. Additionally, the preconditioned zeolite demonstrated a greater selectivity for both of these radionuclides over competing cations common in process wastewater. This was particularly evident in the case of strontium, for which the water-washed R-F resin demonstrated no distinct selectivity over the other alkaline earth metals tested. Consequently, strontium sorption behavior on R-F resin is driven by the overall alkaline earth concentration in the waste. Because there is little selectivity for strontium over other alkaline earth metals, the resin loading capacity will be much lower than that of zeolite. Additionally, the saturation capacity of the resin will also be very dependent on fluctuations in wastewater composition. A water-softening procedure upstream from the R-F resin column might extend the lifetime of the sorbent. However, a preconditioning operation will add to the process complexity and resulting inventory of secondary waste generated by the treatment flow sheet.

Another attribute that might be of concern to EM-30 and EM-40 users is that 60% of the purchased resin had a dry particle size greater than 80 mesh, although the specified manufacturing range is +35 to −50. The wet particle size of the resin conformed more closely to the stated mesh size. Considering the relative cost of the resin over the zeolite, this is a sizable fraction to fall outside manufacturer specifications. The as-received product contains a significant excess (0.6 meq/g) of potassium. Because the molal equilibrium constant suggests that potassium is selected over cesium, the excess potassium will adversely impact cesium sorption from process water and may even impact potassium discharge limits if a large resin column is used. In addition to potassium, a large amount of organic leachables elutes from the resin bed initially. The pH of the treated water will be basic at column startup as the resorcinol resin partially hydrolyzes.

The density of the organic resin is 10% less than that of process waters; slight changes in operating pressure easily disturbed the resin bed in the small-column experiment. The particle size of the resin varies with pH; accommodations must be made in column equipment if the resin is to be stripped with acid for subsequent reuse. With extended contact times, both strontium and cesium desorbed from the resin in batch tests. Both cations also produced elution peaks much greater than the feed concentration in the column test, probably an indication of continuous breakdown of resin structure.

1.2.3 Sodium Nonatitanate

The first new inorganic sorbent selective for strontium became available for evaluation in late FY 1996. Two samples of sodium nonatitanate ($Na_4Ti_9O_{20}{\cdot}xH_2O$) were received from AlliedSignal Research and Technology in the form of a fine powder and as cylindrical pellets. Pretreatment options for the nonatitanate powder were explored; the cation content and ion-exchange capacity of this material were also determined. Equilibrium studies were completed to determine the optimum contact time for nonatitanate powder in 10 mL of either simulant or actual wastewater. Final testing in FY 1996 focused on the competition of other cations for strontium sorption sites on the nonatitanate.

The applicability of nonatitanate to wastewater treatment still needs to be more fully defined. Nonatitanate sorbs Mg and Ca, in addition to Sr. Strontium loading is, therefore, dependent upon alkaline earth metal content in wastewater. The rate of strontium loading is also dependent upon wastewater composition, but this factor becomes less significant as the total metal content of the wastewater increases. Therefore, scaling up the process by incorporating both chemical kinetic parameters, which fluctuate with feed stream composition, and column kinetic parameters will be a sizable task. Employing a water-softening process prior to nonatitanate treatment may simplify column operation by creating a more consistent feed stream composition.

Nonatitanate also partially hydrolyzes in solution; the loading characteristics of the hydrolyzed form differ from those of the sodium form. This effect may also have to be incorporated into scaleup calculations. Finally, the integrity of the pellet form of the sorbent needs to be reviewed. Approximately 40% of the pellets disintegrated to a fine powder in batch studies where long-term mixing (1 week) was used. On a positive note, the generation of an inorganic secondary waste will reduce the effort required to make a stabilized waste form from the spent nonatitanate sorbent.

1.2.4 FEZHEL

Also in FY 1996, a sample of a commercial treatment reagent for cesium removal was received. This material, referred to as FEZHEL (or ANFEZH), is available through JSC "Compomet Cantec" of Yekaterinburg, Russia. It consists of wood cellulose fibers coated with potassium iron hexacyanoferrate. At the request of the DOE Efficient Separations and Processing Crosscutting Program (ESP), a limited evaluation of this sorbent was performed to determine whether the material might have applications for wastewater treatment in the United States. In a short scoping study, the as-received material was sized, the equilibration mixing time was determined, and a single batch isotherm profile was developed.

1.3 OVERVIEW OF FY 1997 TASK EFFORTS

Engineered CST (Ionsiv® IE-911) was received from UOP in early FY 1997. Preliminary experimental efforts included measuring the average particle size, surface water content, total sodium content, ion-exchange capacity, and equilibration mixing time. Once the initial physical and chemical characteristics of the sorbent were defined, the intention was to spend the remainder of the fiscal year collecting binary sorption data. The data from this series of testing would be used to establish cation selectivity and be incorporated into an equilibrium sorption model. As the binary sorption data were accumulated, it became apparent that, in addition to radionuclide sorption, the CST also hydrolyzed. Thus, the binary sorption data actually represented (at least) a ternary sorption system in which hydrogen ion also played a role and in which the CST could be present in multiple ionic forms. After discussing the complexity of the chemical reactions of CST, the consensus of the 1997 ESP Mid-year Review was that it would be more expeditious to complete a small-column test to evaluate CST for process wastewater treatment. If the CST exchanger performed well relative to the baseline zeolite exchanger, then it might be worthwhile to complete the extensive batch testing required to model CST sorption for near-neutral applications. To this end, a small-column test using the hydrogen form of Ionsiv® IE-911 was initiated within the first week of May. This document summarizes the physical features of engineered CST, presents batch testing data acquired to date, and describes Ionsiv® IE-911 performance under dynamic flow conditions for wastewater treatment.

2. TEST PROCEDURES

2.1 FORMULATION OF PROCESS/GROUNDWATER SIMULANT

Accurate comparative testing of new sorbent materials requires that experimentation be performed under defined, consistent conditions. To accomplish this need, each of the sorbent materials was tested by treating a synthetic wastewater of standard composition using a specific experimental protocol detailed in the following discussion. The formulation of the simulant, as presented in Table 1, is based on reviews [5,6] of the compositions of local groundwater and DOE wastewater. The chemical makeup of the ORNL Process Waste Treatment Plant (PWTP) feed was found to be representative of waste streams of these local sites and also falls within the ranges of concentration for the general description for groundwater composition.[7] The chemical composition of the simulant, therefore, is derived from the composition of this particular feed stream. Grab samples of this wastewater provide the source for sorbent testing with actual process water.

In FY 1995 the scope of the evaluation program was broadened to encompass the treatment of contaminated groundwater that is specific to the Oak Ridge National Laboratory (ORNL) site. To this end, a second simulant representing local groundwater was prepared by augmenting the calcium concentration in the wastewater simulant to 100 ppm with the addition of calcium chloride. This upper concentration of calcium represents a typical value observed from a groundwater quality monitoring well located at the down-gradient perimeter to the Waste Area Grouping (WAG) 5 on the Oak Ridge Reservation. Grab samples taken from this location are used to test sorbent in actual groundwater treatment applications.

Strontium was included in the simulants at a level of 0.1 mg/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 total ^{137}Cs added to the simulant was present at a tracer level of 1.12 × 10^6 Bq/L and reflects the upper limit for cesium activity typical of process wastewater.

2.2 BATCH TESTING

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 PWTP simulant or the actual wastewater samples. The sorbent was weighed directly and added to the tubes. The tubes were weighed at the beginning and at the end of the equilibration periods to determine any solution loss. At the conclusion of the equilibration period, the tubes were centrifuged for 30 min at 5000 relative centrifugal force (rcf). The solutions studied were clarified further by filtering the centrifuged supernate using a plastic syringe fitted with a 0.45-µm-pore nylon membrane filter. Due to the finer particle size of the sorbent, the solutions generated in the nonatitanate studies were filtered with a 0.1-µm-pore polyethersulfone membrane filter.

The ^{85}Sr and ^{137}Cs count rates were determined with a Canberra Series 90 gamma spectrometer. Two-milliliter samples were counted for 1000 s in a germanium well detector. Data for ^{85}Sr are 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 are used in the following calculations:

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

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

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

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

where

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

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.

The fate of competing cations in nonradioactive solutions was 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.

2.3 SMALL-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,[8] although results of previous small-column experiments were used to modify initial estimates to allow for practical limitations in preparing large volumes of simulant and in limiting the duration of the column test. 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 was packed in the 1-cm-ID columns, resulting in a bed volume of 4–5 mL.

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.

One hundred liters of simulant was prepared at a time by adding dry chemicals to 100 L 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.

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 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). Actual fraction volumes were determined by multiplying the value for the density of the simulant (0.9965 g/mL) by the tared weight of the solution in the fraction. Aliquots of each fraction were acidified and submitted for ICP analysis. The nuclide content of each fraction was also determined.

3. PHYSICAL AND CHEMICAL CHARACTERIZATION OF CRYSTALLINE SILICOTITANATE

3.1 PHYSICAL CHARACTERIZATION OF CST

Sieve analysis[9] 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 2). 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.

A comparison of the particle size distribution among the −30/+60 mesh sorbents suggests that the R-F resin has the lowest standard deviation in wet particle size, followed by Ionsiv® IE-911, and then zeolite. However, the organic resin swells significantly when wetted; R-F particle diameter is also a function of stream composition. Since variability in particle size plays a significant role in the dispersion observed in column breakthrough curves, the fluctuation in resin diameter due to feed stream composition may be equivalent to the standard deviation in sieve analysis of the inorganic sorbents.

Additional physical parameters pertinent to Ionsiv® IE-911 include an approximate pore opening of 4Å, a particle density of 2.44 g/mL, and a bulk density of 62.4 lb/ft^3 (960 kg/m^3).[10]

3.2 CHEMICAL CHARACTERIZATION 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.[11] defined CST functionality in sodium solutions according to the following equilibrium reactions:

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

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

and

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

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

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

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

and

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

and summed in a mass balance equation,

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

The distribution of CST functionality in a given waste matrix can be determined by combining Eqs. (8–10). For example, the fractional contribution of the trisodium form of CST to the overall Ionsiv® IE-911 functionality can be determined as

$$\frac{[\mathrm{Na_3\text{-}CST}]}{[\mathrm{CST}]} = \frac{1}{k_1 \frac{[\mathrm{H^+}]}{[\mathrm{Na^+}]} + k_1 k_2 \frac{[\mathrm{H^+}]^2}{[\mathrm{Na^+}]^2} + k_1 k_2 k_3 \frac{[\mathrm{H^+}]^3}{[\mathrm{Na^+}]^3}}\ . \tag{12}$$

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.

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 waste matrices, the formation of the monohydrogen 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.

3.2.1 Cationic Composition of Ionsiv® IE-911

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.[8] Permission was received from UOP to determine the quantity of Group I and II metals in Ionsiv® IE-911 to aid in the development of an equilibrium exchange model. The cationic content of engineered CST was determined in-house by dissolving Ionsiv® IE-911 in ultrapure hydrofluoric/hydrochloric acids. Results obtained by ICP indicated that 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.[12]

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 to process wastewater. Following a saline pretreatment procedure that was used previously for zeolite and R-F resin, 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 is referred to as Sodium-CST in the remainder of this document, 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.[12] Additionally, when the preconditioned sorbent was introduced into near-neutral 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. The solution was mixed for 24 h; the pH of the solution was then measured before the sorbent was quantitatively separated from the solution. The sorbent was resuspended in fresh 5*M* NaCl, and the procedure was continued. Table 3 presents the laboratory data for five such saline contacts. The functionality of each CST preparation was calculated by inputting the equilibrium pH and sodium concentration of each saline contact into the equilibrium exchange equations. The pH and solution volume were then used to estimate the milliequivalents of hydrogen generated per gram (meq H/g) of the prepared CSTs. As the data in Table 3 indicate, the fraction of H_2Na-CST for both pretreatment procedures is greater than 95% after the first saline contact and approaches 100% with each successive saline wash. As would be expected, the Sodium-CST contains significantly less H_3-CST content than the Hydrogen-CST. 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 Ionsiv® IE-911 in near-neutral 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.[13] found that powdered CST (TAM-5) resisted acid dissolution if the pH was greater than 2. Pretreatment of the Ionsiv® IE-911 with a less concentrated acid (0.01*M* HCl) may be advisable to produce the trihydrogen form of CST.

3.2.2 Ion-Exchange Capacity and Ion-Exchange Ratio of CST with Radionuclides

Multiple functionality of CST was found to complicate 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 mg/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.[11] 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

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

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 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.[14] A plot representing Eq. (15) was used to confirm a 1:1 exchange between Cs and Na on chabazite zeolite and between Cs and K on R-F resin. Ideally, the slope of the plot should be a value of − 1, validating a charge ratio of one in the case of sodium-cesium exchange on H_2Na-CST. The multiple breaks in cesium data (Fig. 4) suggest 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 wastes streams. 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.

4. COMPARISON OF CST REMOVAL EFFICIENCY WITH BASELINE ZEOLITE

4.1 REVIEW OF RESULTS OF CHABAZITE ZEOLITE SORPTION STUDIES

4.1.1 Zeolite Batch Studies

Natural chabazite zeolite was selected as the benchmark sorbent for removing strontium and cesium from contaminated wastewater. The zeolite was purchased from Steelhead Specialty Minerals (Spōkane, WA) at a cost of $\$50/\mathrm{ft}^3$. A stock supply was pretreated to remove the natural strontium present on the zeolite as received. Pretreatment consisted of washing the zeolite with 2 *M* NaCl, followed by several rinses with deionized water to remove excess sodium ion. The average water content of the −20/+50 mesh fraction of the air-dried chabazite is 7.1 wt %, and the manufacturer's stated density for the material is 1.73 g/cm^3. The −20/+50 mesh fraction (300–840 μm) of the pretreated zeolite represents the reference sorbent for the remaining studies in this subtask.

Testing of the standard zeolite treatment method 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 wastewater simulant samples in which the strontium concentration in the initial solution was 2.28×10^{-3} meq Sr/L. The strontium sorption isotherm exhibited a curvilinear profile; positive deviations from linearity were observed for strontium loadings greater than 2 meq/kg. The 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 fit to the Freundlich sorption model.[2] The distribution coefficient, K_d (L/kg), can be written in terms of the Freundlich constant obtained from this fit. Thus, for strontium, the relationship between C (concentration of strontium in the liquid at equilibrium (in milliequivalents per liter) and K_d is

$$K_d = \frac{2.5 \times 10^3}{C^{0.26}} . \tag{16}$$

Cesium sorption was observed in simulant samples containing an initial cesium concentration of 3.23×10^{-6} meq/L. 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 the Freundlich sorption model,[2] and the comparable equation defining cesium sorption on pretreated zeolite was found to be

$$K_d = \frac{5.6 \times 10^4}{C^{0.02}} , \tag{17}$$

implying that the distribution coefficient is essentially constant over the cesium concentration range studied in these tests. A thermodynamic-based multicomponent ion-exchange model has been developed by Perona et al. to predict the distribution coefficients for both strontium and cesium on chabazite zeolite as a function of competing cation concentrations.[15] This model enables the prediction of Sr and Cs sorption equilibrium outside the concentration ranges of this particular simulant.

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 steam. Maximum strontium and cesium loadings from the actual wastewater sample onto treated TSM-300 were calculated to be 24 and 0.17 meq/kg, respectively.

4.1.2 Zeolite Column Study

A small-column test was initiated in FY 1994 and completed in FY 1995 to determine the breakthrough characteristics of strontium and cesium on zeolite under dynamic flow conditions. 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 1.3 mL/min, 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 1. The column test, which lasted for 120 d, was stopped after 59,000 bed volumes (BVs) 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 BVs) were analyzed by ICP to determine the breakthrough behavior of Na, K, 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 in displacement of Mg beginning at 250 BVs and displacement of Ca beginning at 500 BVs. 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 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. 7. Strontium was 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 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 30 and 0.18 meq/kg measured previously for strontium and cesium, respectively, in batch sorption isotherms.[1] 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.[16] The sorption ratios, although slightly lower, were in good agreement with sorption ratios measured[1] at low loading in batch sorption isotherms:

	Sorption ratio (L/kg)	
Test	Strontium	Cesium
Column	15,800	53,000
Isotherm	17,000	80,000

4.2 RESULTS OF CST SORPTION STUDIES

4.2.1 CST Batch Studies

4.2.1.1 Determination of CST Equilibrium Sorption Times

Equilibration times, corresponding decontamination factors, and sorption ratios were determined for Sodium-CST by mixing a series of samples containing 20 mg of the ion-exchange material in 10 or 15 mL of the traced process water simulant. The sorption parameters and particle diffusion cōefficients were determined for the competing cations, as well as for cesium and strontium.

Sodium-CST sorption ratios for cesium are higher than those of the other cations in the process waste simulant, with maximums of up to 1.6×10^7 L/kg at 200 h (Fig. 8). At equilibrium, an average sorption ratio of about 8×10^6 L/kg is seen for cesium on the CST. Strontium sorption ratios continued to increase up to a maximum of 6×10^5 L/kg at just over 500 h. In comparison, maximum R_s values for strontium and cesium on the baseline zeolite in similar batch experiments were 1.7×10^4 and 8×10^4 L/kg, respectively. 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. Maximum sorption ratios of 100 L/kg and 1400 L/kg were obtained for magnesium and calcium, respectively. These maximum sorption ratios give a selectivity preference of the CST in the following order: Mg < Ca < Sr < Cs. The material's selectivity for Na^+ and K^+ ions was determined in the column tests and is discussed further in Sect. 4.2.2.2.

A plot of the fractional approach to equilibrium of strontium and cesium sorption on Sodium-CST highlighted the fact that greater than 99% of the radioisotopes were removed from solution in under 10 h (Fig. 9). Nevertheless, decontamination factors (DFs) and sorption ratios continued to increase slightly with time. The ^{137}Cs DF continued to increase with time, through approximately 50 h. From 50 to

300 h, the DF for ^{137}Cs removal was fairly constant at approximately 17,000. The strontium DF continued to increase from a value of 352 at 50 h to a maximum of 1200 at 525 h.

4.2.1.2 Calculation of Particle Diffusion Coefficients for CST

Sodium-CST particle diffusion coefficients were determined from the batch equilibrium experiments for Ca, Cs, Mg, and Sr in process waste simulant. Calculations assumed that the particle diffusion coefficient was independent of solution concentration. The mass balance on a single species diffusing into a spherical particle was written based on Fick's second law of diffusion,[16]

$$\frac{\partial C_x}{\partial t} = D_p \left(\frac{\partial^2 C_x}{\partial r^2} + \frac{2}{r} \frac{\partial C_x}{\partial r} \right) \tag{18}$$

where the subscript x denotes the interior of the particle, r is the radial position, t is time, D_p is the interparticle diffusion coefficient, and C_x is the concentration of species in the particle. The experimental conditions allow the simplifying assumption that cation sorption is taking place in an "infinite solution volume," where

$$C_x V_x \ll C V , \tag{19}$$

with C = total concentration of counterions, V_x = total volume of ion-exchange material, and V = solution volume. Based on this assumption, a constant boundary condition is met at the surface of the particle; therefore, an approximate solution to Eq. (18) is valid and can be written in terms of the fractional approach of the exchanging species to equilibrium [i.e., $U(t)$] and particle radius (r_0).[16] This solution is

$$U(t) \cong \left[1 - \exp\left(- \frac{D_p t \pi^2}{r_0^2} \right) \right]^{0.5} . \qquad \textbf{(20)}$$

The preceding equation was fitted to batch experimental data for the species Ca and Mg as well as for Cs and Sr. Figures 10 and 11 show the fractional approach to equilibrium for these cations exchanging on Sodium-CST. Fitting Eq. (20) to the experimental data allowed calculation of the particle diffusion coefficients, which are summarized in Table 4. These values are within the ranges reported in literature. Comparable diffusion coefficients for cesium and strontium on zeolite are 5.5×10^{-9} and 7.4×10^{-9} cm^2/s, respectively. The magnitude of the particle diffusion coefficients indicates that both strontium and cesium diffuse significantly faster within the CST particle, compared with competing cations in the simulant.

4.2.1.3 Binary Sorption Isotherm Data on CST

Cesium-Sodium Sorption Isotherm on CST. At the request of ESP management during the 1996 project review, strontium and cesium removal with CST was described in terms of specific chemical equilibria occurring during the sorption process. It was felt that, since calcium and magnesium play significant roles in wastewater remediation, sorption behavior described by chemical equilibria would be more accurate than the empirical models that had been used in the past. To accomplish this goal, batch testing was performed to observe sorption in binary and ternary combinations of radionuclides with the major wastewater cations. The sorption data would then be fit to a multicomponent equilibrium model that was successfully developed for a five-cation system exchanging on chabazite zeolite.[14] The development of an accurate model of nuclide sorption on the CST would then be used to estimate sorbent efficiency under variable waste stream compositions.

To this end, cesium-sodium binary sorption isotherms were observed by two methods: (1) increasing the sorbent loading from 5 to 100 mg in the presence of 60-ppm cesium solution and (2) increasing the cesium concentration in the presence of 20 mg of Sodium-CST. Cesium sorption was monitored using gamma spectrometry; sodium solution content in equilibrated samples was determined by AA spectrometry. The sorption profile, developed by varying either cesium concentration or sorbent loading, indicates that cesium uptake becomes nonlinear at approximately 1×10^{-3} meq/L Cs in solution (Fig. 12). However, the sodium isotherms differ, depending on whether the sorbent loading or the cesium content was held constant (Fig. 13). 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.

Strontium-Sodium Sorption Isotherm on CST. Batch testing was also performed for the Sr-Na binary exchange reaction. In this case, the isotherm was developed by contacting a 1000-ppm strontium solution (as $SrCl_2$) with 5–100 mg of Sodium-CST (Fig. 14). 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.

The successful development of a thermodynamic equilibrium model requires that batch equilibrium data be representative of process wastewater conditions. At a minimum, it is important to maintain the pH of the batch samples close to that of wastewater and groundwater (pH 8.3). Considering the fact that the preceding sample solutions are the result of sorbent hydrolysis, ion exchange with Na and H, and possibly surface sorption (in the case of Sr), these batch studies are actually multicomponent rather than binary studies. The multiplicity of chemical reactions suggests that the development of the equilibrium model will be complicated, and perhaps compromised by the interplay of the complex reaction system. An extended amount of time will be required to define radionuclide sorption on both the hydrogen and sodium forms of the CST for wastewater applications. In an effort to bring about a more rapid evaluation of CST performance, the ESP 1997 project review staff requested that CST efficiency be estimated in a small-column test using process wastewater simulant. To comply with this request, batch testing was terminated and a small-column test was initiated in early May.

4.2.2 CST Column Study

4.2.2.1 Column Setup

A small-column test, similar to that described for the baseline zeolite in Sect. 4.1.2, using the hydrogen form of Ionsiv® IE-911 was run in order to demonstrate the effectiveness of the CST in removing strontium and cesium from a process wastewater simulant. The competing cation concentrations were those listed in Table 1. 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 BVs/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.

As with the zeolite small-column test, simulant (see Table 1) was prepared in 100-L batches by dissolving high-purity chemicals in distilled deionized water. The adjusted solution was filtered through a 0.45-µm Suporcap 100™ (hydrophilic polyethersulfone) membrane in approximately 20-L batches before the addition of ^{85}Sr and ^{137}Cs tracers. To date, twelve 20-L batches of traced feed, prepared from three 100-L batches of untraced feed, have been used in the test. The column test will be run until 50%

breakthrough of ^{85}Sr and ^{137}Cs is achieved or until the radioactivity of the column requires shutdown of the test.

4.2.2.2 Column Experimental Results

The column has been running for a total of 20 weeks, at an average flow rate of 1.20 mL/min. A total of 240 L of simulant has run through the column to date. Only limited maintenance of the column system has been required. This has included the replacement of worn peristaltic tubing, flow lines, and the prefilter that had evidence of algae growth.

Figure 15 shows the breakthrough curves of the cations Mg, Ca, and Na. All reached 50% breakthrough at under 1300 BVs: 160, 800, and 1225 BVs for Mg, Ca, and Na, respectively. Figure 16 also shows the potassium breakthrough curve, where 50% breakthrough occurred at 15,000 BVs. 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.[17]

The breakthrough curves in Figs. 15 and 16 support the initial batch findings for selectivity of CST (Sect. 4.2.1.1) in the following order, with the addition of potassium and sodium: Mg < Ca < Na < K < Sr < Cs .

The selectivity of cesium over strontium is demonstrated in Fig. 17, which shows the beginning of strontium breakthrough on CST. To date, about 50,000 BVs have been run through the column, and no cesium has broken through. At 47,000 BVs, strontium breakthrough is 14%.

Figure 18 shows the effluent pH for the first 5000 BVs of column operation. 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 BVs. 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 pH will be continuously monitored throughout the column test so that the functionality of CST can be determined at the point of cesium breakthrough.

4.2.2.3 Column Data Analysis

Ion-exchange phenomena can be mathematically and physically described on many different levels of complexity. The level of complexity utilized is tempered by available resources as well as by desired accuracy. However, the goals of all models are identical: to predict parameters that can be used to model the behavior of a sorbent under various conditions and to scale up experimental, bench-scale results to predict full-scale system behaviors. Estimation of mass transfer parameters—such as diffusion coefficients in the liquid, particle distribution coefficients, and mass transfer zones— allows the prediction of performance of an ion exchanger under variable system conditions such as liquid velocity, column size, and influent sorbate/contaminant concentrations.

Breakthrough curves generated by column operation of an ion-exchange system have characteristic features that, when properly evaluated, predict mass transfer and column operational parameters. M. S. Doulah[18] presented a method to analyze breakthrough curves to obtain liquid phase mass transfer coefficients and distribution coefficients, as well as column parameters by fitting the curve to a probability function. This method is used here to evaluate the liquid phase mass transfer coefficients, the corresponding liquid diffusivities, and the distribution coefficients for exchanging cations on CST. Calculations for transfer zone height, zone velocity, number of transfer units, and height of a transfer unit can all be completed using this technique. Assumptions inherent in the model are (1) uniform solute concentration across the cross-sectional area of the bed (no radial dispersion), (2) transfer zones of equal length, (3) fluid velocity greater than the solid phase concentration velocity, and (4) plug flow.

Doulah[18] writes a simple rate equation to predict fractional conversion of solute from the liquid to solid phase, α, as

$$\frac{d\alpha}{d\theta} = p(1-\alpha) \tag{21}$$

and using a Weibull-type probability function (p) to describe the breakthrough curve, integrates with respect to time and linearizes the result to obtain

$$\log\left[\ln\left(\frac{1}{1-C/C_0}\right)\right] = \beta\log(\theta-\theta_0) - \beta\log\theta_m\ , \tag{22}$$

where C is the concentration in meq/L of the solute at time, θ; C_0 is the initial concentration of solute; β is the shape factor and corresponds to the slope of the equation; θ_0 is the time of initial solute breakthrough (usually taken where C/C_0 is 0.05); and θ_m is the mean time of the function. (In the analysis of CSTs, the initial breakthrough was found to correspond to a C/C_0 of about 0.02 for magnesium and sodium since the breakthrough was very gradual.) This linearized form is then fitted to the experimental data to obtain the constants β and θ_m, where β is the slope and the intercept is equal to $-\beta \log \theta_m$. The mean time of the function, θ_m, corresponds to the point on the breakthrough curve where

$C/C_0 = 0.632$, with corresponding time, $\theta = \theta_m + \theta_0$. The linearized form, Eq. (22) is thus plotted for the range of $C/C_0 = 0.05$ (or 0.02) to $C/C_0 = 0.95$, and the parameters β and θ_m can be determined.

Breakthrough curves for Ca, K, Mg, and Na were analyzed by this method to obtain the pertinent constants. The predicted breakthrough curves are shown in Fig. 15 for Ca, Mg, and Na and in Fig. 16 for K on CST, in comparison with the experimental breakthrough points. The model fit the data reasonably well, thus supporting the utility of the predive method. Cesium and strontium, to date, have not broken through sufficiently in the CST column experiment to calculate similar transfer parameters.

Parameters determined by the Doulah[18] method for the competing cations in this CST study are given in Table 5. The overall liquid phase mass transfer coefficient, K_f (cm/s), multiplied by a, the mass transfer area (cm^{-1}), is given by this method as

$$K_f a = \frac{\beta}{\theta_m} . \tag{23}$$

The mass transfer area for a sphere is found from

$$a = 1.5 \frac{e^2}{d} , \tag{24}$$

where e is the particle voidage and d the particle diameter.

The liquid mass transfer coefficient is related by correlations to the liquid phase diffusion coefficient[18] by

$$K_f = \frac{D}{\delta} , \tag{25}$$

where D is the liquid phase diffusivity (cm^2/s) and δ is the film thickness (cm). The film thickness is a function of the superficial velocity v (cm/s) through the column and the particle radius r_0 (cm).

Helfferich[16] reports an empirical relationship for the film thickness at low velocities:

$$\delta = \frac{0.2r_0}{1 + 70r_0v} . \tag{26}$$

For the CST column study, δ was calculated to be 0.0078 cm, within range of values given in the literature.[19]

Column operational parameters can also be determined using the method presented by Doulah.[17] Table 6 summarizes operational parameters such as mass transfer zone (MTZ); overall number of transfer zones, (N_z), and saturation capacity of the resin (q_0, meq/kg).

The degree of bed saturation, D_{bs}, is the percent of the bed that is saturated at the beginning point of breakthrough (i.e., when time = θ_0). It is found by

$$D_{bs} = \frac{\theta_0}{\theta_0 + \theta_m} . \tag{27}$$

Strontium and cesium mass transfer and bed parameters will be determined after sufficient data have been obtained to define breakthrough on the CST column.

After sufficient breakthrough data have been acquired for cesium and strontium on CST, a direct comparison of mass transfer data for the two exchangers will be made.

5. CONCLUSIONS

5.1 COMPARISON OF CST AND BASELINE ZEOLITE ION-SORPTION EFFICIENCIES

A comparison of distribution coefficients (or maximum R_s) for CST and baseline zeolite is made in Table 7. Both exchangers sorb calcium to approximately the same degree, with maximum sorption ratios of about 1200 L/kg in both batch and column configurations. 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 17,000 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 to date, where cesium has not yet broken through with 50,000 BVs run through the column to date. This K_d ($^{137}Cs^+$ on CST = 8,000,000 L/kg) is two orders of magnitude greater than the K_d of $^{137}Cs^+$ on zeolite in a batch system. A reduction of about 34% in the K_d was seen for cesium removal in moving from a batch to column configuration for the zeolite. A similar reduction in the K_d for cesium removal by CSTs would result in a value of 5,300,000 L/kg.

Breakthrough of cesium has not yet been seen in the CST column study. To date, 55,000 BVs have been 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 BVs and 50% breakthrough occurred at 50,000 BVs.

Strontium breakthrough of 1% occurred at 14,000 BVs in the CST study. Presently, the C/C_0 for strontium, as seen in Fig. 15, is about 14% at 47,000 BVs. The baseline zeolite performed much less effectively for strontium removal, with 1% breakthrough occuring at 3000 BVs, and 50% breakthrough at 15,000 BVs.

Analyzing strontium breakthrough data to date, the strontium removal from PWTP simulant in the CST column study is projected to achieve a maximum possible K_d of about 138,000 L/kg at 50% breakthrough, which is a reduction of 44% from what was seen in the batch equilibration experiments. Based on this reduction, a K_d for cesium removal by CST in this column configuration might be as high as 4,500,000 L/kg.

Physically, the CST has appeared to outperform the zeolite. No problems with plugging have been noted with the CST, whereas the zeolite produced fines that cemented together and prevented column flow at cesium 50% breakthrough (50,000 BVs). To date, 55,000 BVs have passed through the CST, with no noticeable plugging or breakdown of the pellets.

5.2 ECONOMIC EVALUATION OF CSTs

Previous work[1,2] under this ESP program had identified the baseline treatment material, TSM-300 natural chabazite zeolite, for removal of radioactive strontium and cesium from process wastewater and groundwater as the most cost-effective and most technically effective material. This report presents the technical tests and results of using CST for the removal of radioactive strontium and cesium from process wastewater simulant. Results to date have shown CST to outperform the zeolite in a technical capacity. CST is extremely selective for Sr and Cs over competing cations Ca, K, Mg, and Na, which are present in process wastewater at concentrations orders of magnitude greater than the Sr and Cs. Column tests have not yet been completed, so a final numerical factor describing the superiority of CST over the baseline zeolite in a technical capacity cannot yet be provided; however, based on results to date, minimum and maximum factors will be used to present an economic comparison of the two ion exchangers.

Previous sections of this report have summarized and compared maximum sorption ratios (R_s, L/kg) and column breakthrough parameters for zeolites and CST. Table 8 presents these ratios for cesium and strontium sorption on the two materials. Also shown in the table are maximum loadings for cesium and strontium in both batch and column operation. Based on column parameters and data collected to date, the CST removes approximately 4.6 times as much strontium as does zeolite in a similar column configuration at a minimum (taken at 1% breakthrough) and 10 times as much strontium at a maximum (taken at a projected 50% breakthrough). Based on an average PWTP inlet concentration of 270 Bq/L of radioactive strontium and 0.0023 meq/L of stable strontium, and achieving a decontamination factor of 7.3 to meet a discharge limit of 37 Bq/L (the maximum allowable inlet concentration to the Nonradiological Waste Treatment Plant), the CST outperforms the zeolite by a factor of 6.3; this corresponds to a strontium breakthrough of 14%.

Factors such as the operational costs and final disposal costs must be taken into account when comparing the efficiency and cost of different ion-exchangers. By referring to the operations at the ORNL PWTP (which currently uses TSM-300 baseline chabazite zeolite) as a basis, a comparison of the economics of the two exchangers was made. Table 8 summarizes the advantages and disadvantages (and associated costs) of the two exchangers.

Operationally, a column containing zeolite would be changed out more frequently than one containing CST. During operation, problems that have been encountered with zeolite—such as channeling and plugging due to the generation of fines—have caused the premature removal of the zeolite; therefore the zeolite must be changed out before it is fully loaded. Data from the use of chabazite zeolite in the PWTP columns suggest that the material is only 50% loaded. This information implies that using chabazite would be, operationally, more expensive than using CST; again, using the PWTP as a basis, this cost would be a factor of three higher.

5.3 IMPLICATIONS FOR USER NEEDS

A letter report to identify local, potential users of the process and groundwater treatment technology being developed and communicated in this document was written in early FY1997 and is included in this report as Appendix A. Potential local users requiring the removal of ^{90}Sr, ^{137}Cs, ^{99}Tc, and/or ^{3}H from process wastewater and groundwater streams were identified and surveyed in order to ensure that this ESP task provides the pertinent information required to select and scale up a treatment process specific to the user needs.

The report presented in the Appendix identifies the potential users, describes their waste streams, examines current treatment methods (if any) and associated drawbacks, and identifies possible drivers that might influence the user's decision to select a given wastewater treatment or to alter a current process. These drivers include environmental regulatory requirements, limitations in secondary waste generation, operational costs, mandated time frames for waste decontamination, and the need for compatibility with current treatment flow sheets.

6. REFERENCES

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TABLES

Table 1. Molality and activity of process wastewater simulant components

Ionic species	Molality	Estimated activity [a]	Log estimated activity [a]
H^+	1.479×10^{-8}	1.479×10^{-8}	−7.83
Ca^{2+}	9.24×10^{-4}	9.333×10^{-4}	−3.03
K^+	5.12×10^{-5}	5.129×10^{-5}	−4.29
Mg^{2+}	2.70×10^{-4}	2.692×10^{-4}	−3.57
Na^+	6.09×10^{-4}	6.026×10^{-4}	−3.22
Sr^{2+}	1.479×10^{-8}	1.176×10^{-6}	−5.93
Cl^-	2.45×10^{-4}	2.455×10^{-4}	−3.61
NO_3^-	8.55×10^{-5}	8.511×10^{-5}	−4.07
PO_4^{3-}	2.21×10^{-5}	2.188×10^{-5}	−4.66
SO_4^{2-}	2.22×10^{-4}	2.239×10^{-4}	−3.65
CO_3^{2-} (total alkalinity)	1.08×10^{-3}	1.072×10^{-3}	−2.97
F^-	4.21×10^{-5}	4.169×10^{-5}	−4.38

[a] Calculated by MINTEQA2 v3.10 software, U.S. Environmental Protection Agency.

Table 2. Particle size distribution of sorbents tested to date

U.S. sieve range (mesh)	Particle size (µm)	Dry-weight distribution (%)			Wet-weight distribution (%)		
		Zeolite (as received)	R-F resin[a] (as received)	Ionsiv® IE-911 (as received)	Zeolite (NaCl washed)	R-F resin[a] (water washed)	Ionsiv® IE-911 (NaCl washed)
+20	+840	0.30	0.0026	0.00	0.00	0.00	0.00
-20/+30	-840/+590	29.77	0.0289	4.56	50.97	1.45	4.78
-30/+40	-590/+420	25.24	0.4	32.78	26.09	77.11	38.07
-40/+50	-420/+300	25.63	39.73	43.24	20.70	19.34	39.47
-50/+60	-297/+250			12.56	0.79	0.67	12.43
-60/+100	-250/+149			2.93	1.45	1.43	2.68
-50/+80	-300/+212	19.06	32.82				
-80/+100	-177/+149		24.81				
+100	-149		1.14	0.40			0.27
Average size, µm		484	231	409	575	474	418
Std. dev., µm		223	47	111	156	73	113

[a] R-F resin: Lot BSC-187-0210B.

Table 3. CST functionality determined from contacting Na-CST and H-CST forms with 5 M NaCl

CST form	[NaCl]	pH	[H]	% Na_3-CST	% HNa_2-CST	% H_2Na-CST	% H_3-CST	Volume NaCl (mL)	CST (g)	H generated (meq)	H (meq/g)
Na-CST	5	2.58	2.6×10^{-3}	7.7×10^{-9}	3.1×10^{-3}	99.6	0.39	100	0.4854	0.263	0.542
	5	2.58	2.6×10^{-3}	7.7×10^{-9}	3.1×10^{-3}	99.6	0.39	25		0.066	0.135
	5	2.66	2.2×10^{-3}	1.1×10^{-8}	3.7×10^{-3}	99.7	0.32	25		0.055	0.113
	5	2.73	1.9×10^{-3}	1.5×10^{-8}	4.4×10^{-3}	99.7	0.27	25		0.047	0.096
	5	2.77	1.7×10^{-3}	1.8×10^{-8}	4.8×10^{-3}	99.7	0.25	25		0.042	0.087
									Total	0.472	0.973
Na-CST	5	2.58	2.6×10^{-3}	7.7×10^{-9}	3.1×10^{-3}	99.6	0.39	100	0.4737	0.263	0.555
	5	2.56	2.8×10^{-3}	7.0×10^{-9}	3.0×10^{-3}	99.6	0.41	25		0.069	0.145
	5	2.64	2.3×10^{-3}	1.0×10^{-8}	3.6×10^{-3}	99.7	0.34	25		0.057	0.121
	5	2.71	1.9×10^{-3}	1.4×10^{-8}	4.2×10^{-3}	99.7	0.29	25		0.049	0.103
	5	2.75	1.8×10^{-3}	1.7×10^{-8}	4.6×10^{-3}	99.7	0.26	25		0.044	0.094
									Total	0.482	1.018
H-CST	5	1.86	1.4×10^{-2}	2.7×10^{-10}	5.8×10^{-4}	98.0	2.0	100	0.2109	1.380	6.544
	5	1.84	1.4×10^{-2}	2.5×10^{-10}	5.6×10^{-4}	97.9	2.1	25		0.361	1.713
	5	2.15	7.1×10^{-3}	1.1×10^{-9}	1.1×10^{-3}	99.0	1.0	25		0.177	0.839
	5	2.36	4.4×10^{-3}	2.8×10^{-9}	1.9×10^{-3}	99.4	0.64	25		0.109	0.517
	5	2.48	3.3×10^{-3}	4.8×10^{-9}	2.5×10^{-3}	99.5	0.49	25		0.083	0.392
									Total	2.111	10.006
H-CST	5	1.8	1.6×10^{-2}	2.1×10^{-10}	5.1×10^{-4}	97.7	2.3	100	0.2117	1.585	7.487
	5	1.78	1.7×10^{-2}	1.9×10^{-10}	4.8×10^{-4}	97.6	2.4	25		0.415	1.960
	5	2.07	8.5×10^{-3}	7.3×10^{-10}	9.5×10^{-4}	98.8	1.2	25		0.213	1.005
	5	2.28	5.2×10^{-3}	1.9×10^{-9}	1.5×10^{-3}	99.2	0.77	25		0.131	0.620
	5	2.4	4.0×10^{-3}	3.3×10^{-9}	2.0×10^{-3}	99.4	0.59	25		0.100	0.471
									Total	2.443	11.542

Table 4. Particle diffusion coefficients for Ca, Mg, Sr, and Cs on Sodium-CST

Species	Particle diffusion coefficient	
	(cm^2/h)	(cm^2/s)
Ca^{2+}	5.26×10^{-6}	1.46×10^{-9}
Cs^{+}	6.20×10^{-4}	1.72×10^{-7}
Mg^{2+}	7.45×10^{-6}	2.07×10^{-9}
Sr^{2+}	3.90×10^{-4}	1.08×10^{-7}

Table 5. Functions and mass transfer parameters for cations exchanging on Hydrogen-CST

Cation	β	θ_0 (h)	θ_m (h)	K_d (L/kg)	Liquid mass transfer coefficient $K_f a$ (s^{-1})	Liquid film diffusivity (cm^2/s)
Ca^{2+}	1.121	14.6	46.1	1148	6.76×10^{-6}	8.2×10^{-9}
K^{+}	2.836	395.6	509.2	17,103	1.55×10^{-6}	1.9×10^{-9}
Cs^{+}						
Mg^{2+}	0.425	0.9	15.4	308	7.68×10^{-6}	9.3×10^{-9}
Na^{+}	6.705	18.0	57.6	1429	3.23×10^{-5}	3.9×10^{-8}
Sr^{2+}						

Table 6. Operational parameters for cations exchanging on Hydrogen-CST

Cation	Mass transfer zone, MTZ (cm)	Number of zones	Degree of bed saturation (%)	Saturation capacity (meq/kg)
Ca^{2+}	3.68	1.32	24.1	2320
K^+	2.73	1.78	43.7	517
Cs^+				
Mg^{2+}	4.58	1.06	5.6	85.6
Na^+	3.70	1.31	23.8	1150
Sr^{2+}				

Table 7. Distribution coefficients (K_d) for batch and column configurations for cations exchanging on zeolite and Sodium-CST

Cation	Distribution coefficient, K_d (L/kg)			
	TSM-300 chabazite zeolite		Crystalline silicotitanate	
	Batch	Column	Batch	Column
Ca^{2+}		1200	1430	1148
Cs^+	80,000	53,000	8,000,000	TBD
Mg^{2+}		812	109	308
K^+				17,103
Sr^{2+}	17,000	15,800	600,000	TBD

Table 8 . Economic comparison of baseline zeolite and crystalline silicotitanate

Advantage/Disadvantage	Baseline chabazite zeolite	Crystalline silicotitanate (CST)
Maximum sorption ratio, or K_d (L/kg)		
Batch		
Strontium	17,000	600,000
Cesium	80,000	8,000,000
Column		
Strontium	15,800	TBD
Cesium	53,000	TBD
Maximum Sr loading (meq/kg)		
Batch	24	1050
Column	60	TBD
Maximum Cs loading (meq/kg)		
Batch	0.17	800
Column	0.2	TBD
Resin cost, \$/(ft^3)	50	8410
Resin cost to treat 1 × 10^8 gal PWTP wastewater (\$)	20,000[a]	247,300
Backwashing needed	yes	not as frequently
Column plugging	yes	no

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[a] Based on actual operation at PWTP.

FIGURES

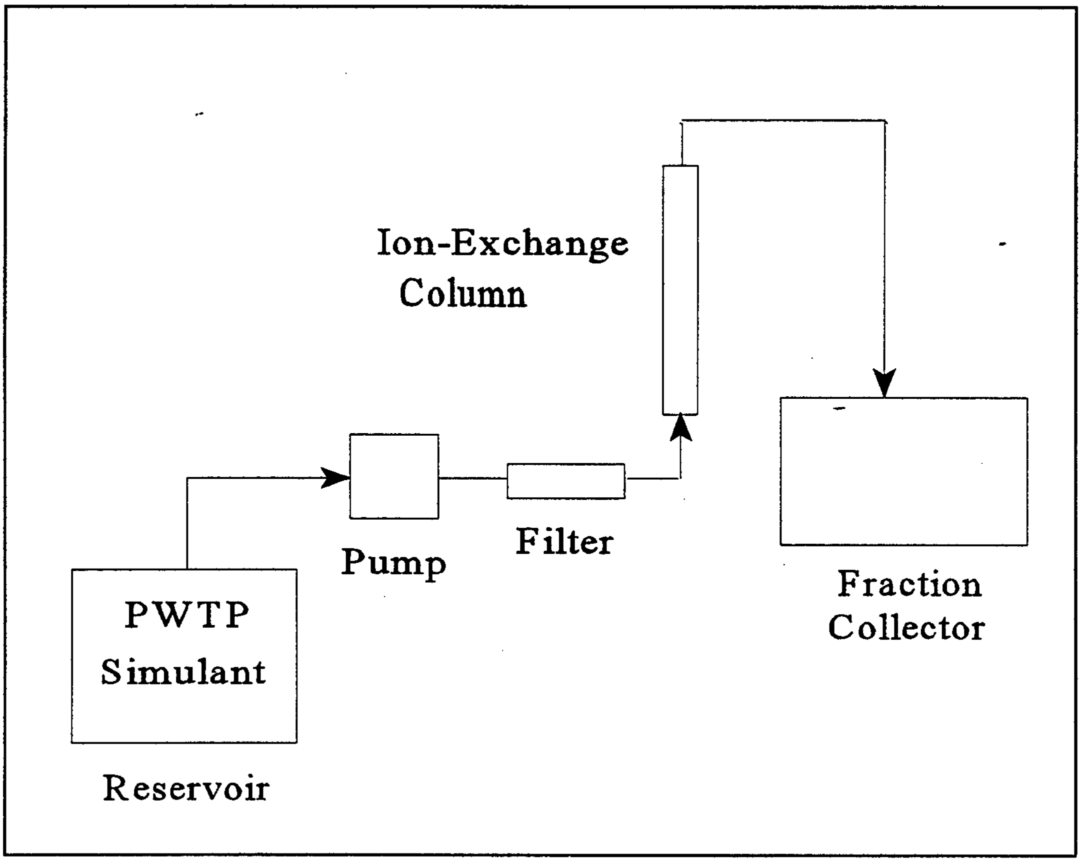


Fig. 1. Flow diagram for column test.

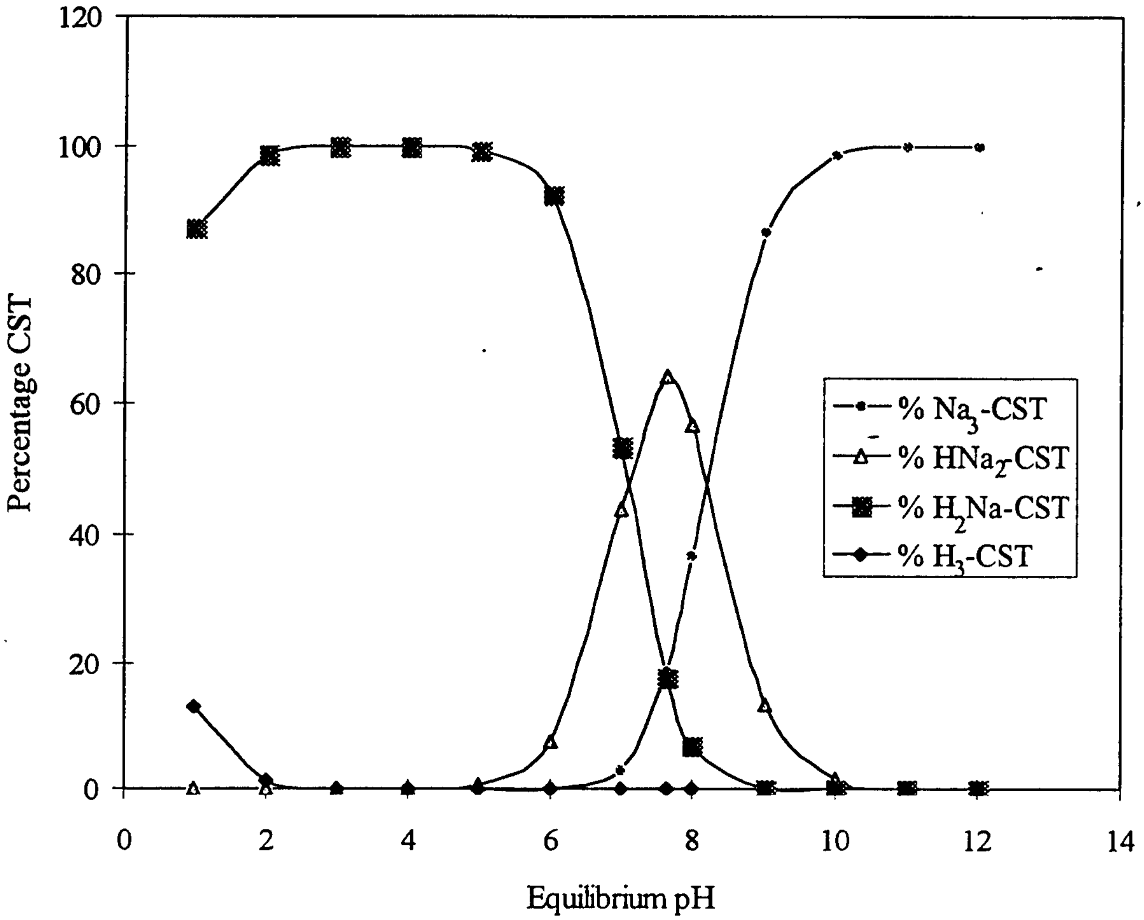


Fig. 2. CST functionality in 5 *M* NaCl.

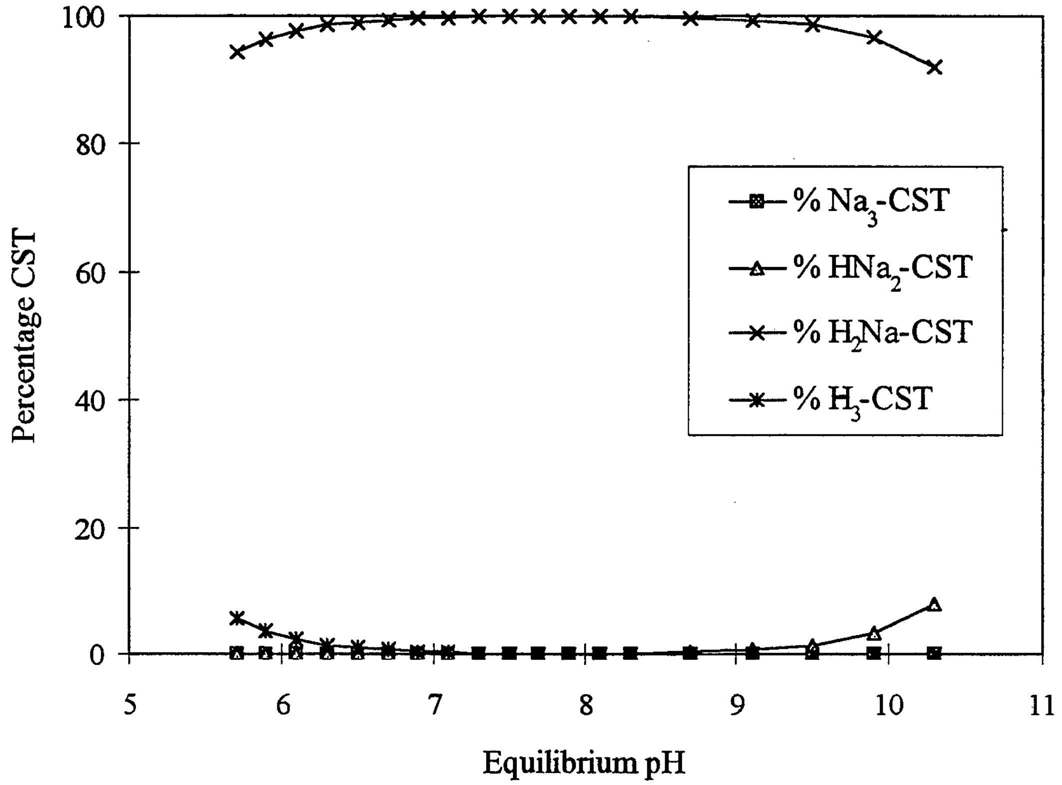


Fig. 3. CST functionality in 15 ppm sodium.

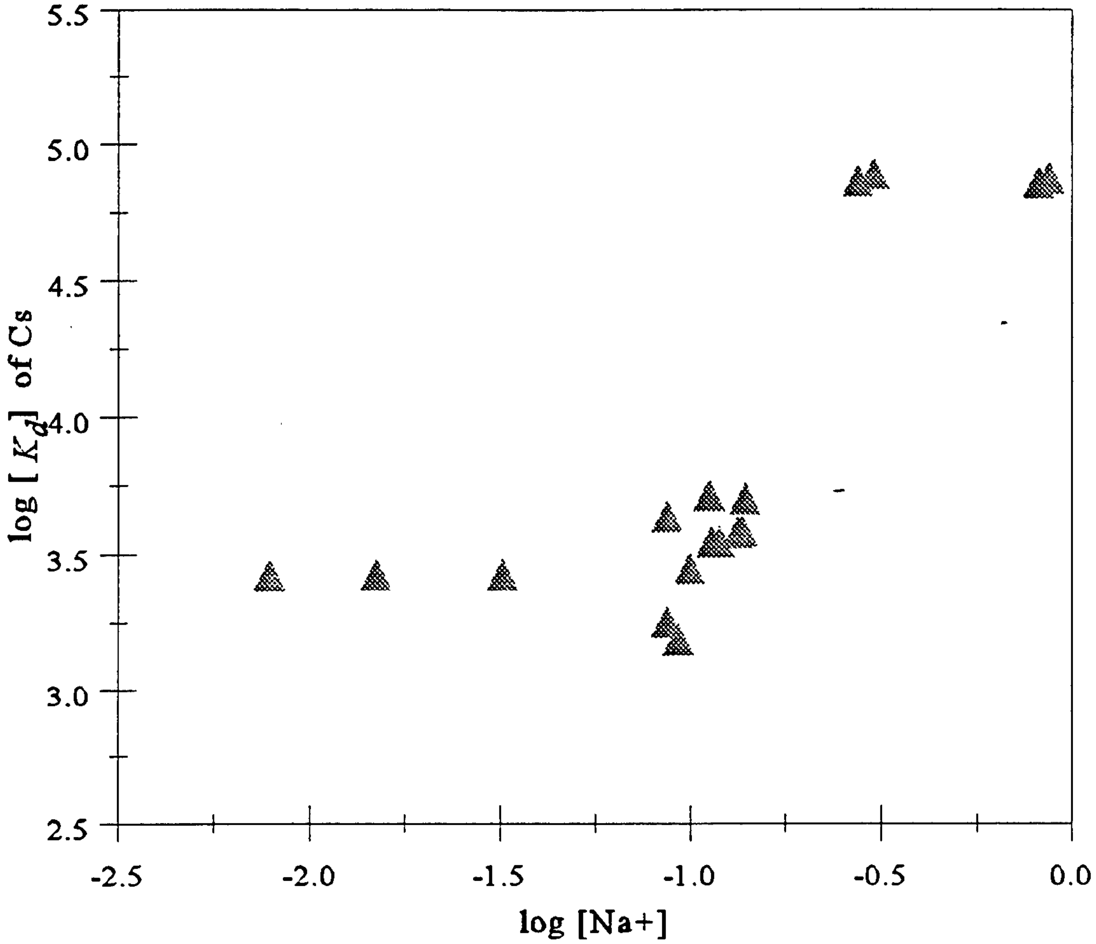


Fig. 4. Determination of cesium ion-exchange ratio on as-received Ionsiv® IE-911 CST. Test conditions: Eleven contacts of 50 mg CST; each contact solution, 25 mL of 50 ppm CsCl.

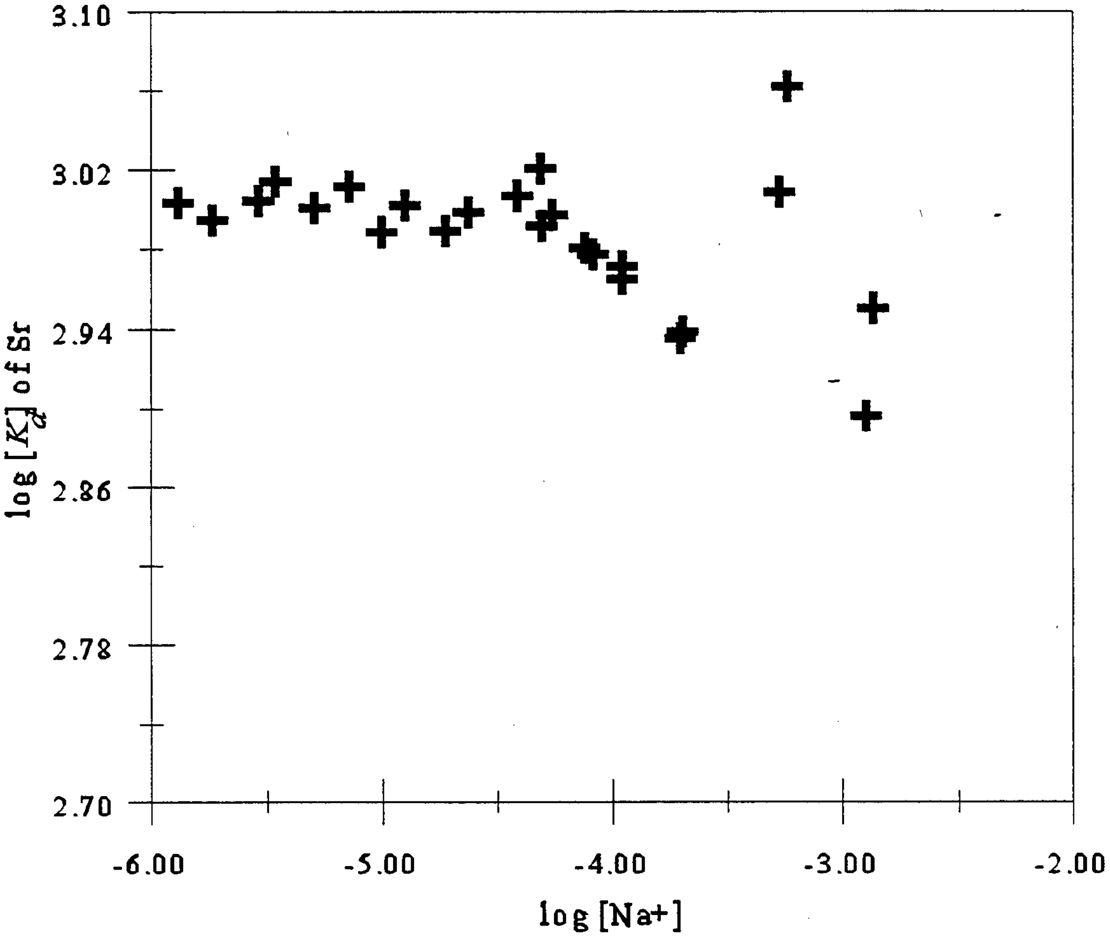


Fig. 5. Determination of strontium ion-exchange ratio on as-received Ionsiv® IE-911 CST. Test conditions: Twelve duplicate contacts of 50 mg CST; each contact solution, 25 mL of 50 ppm $SrCl_2$.

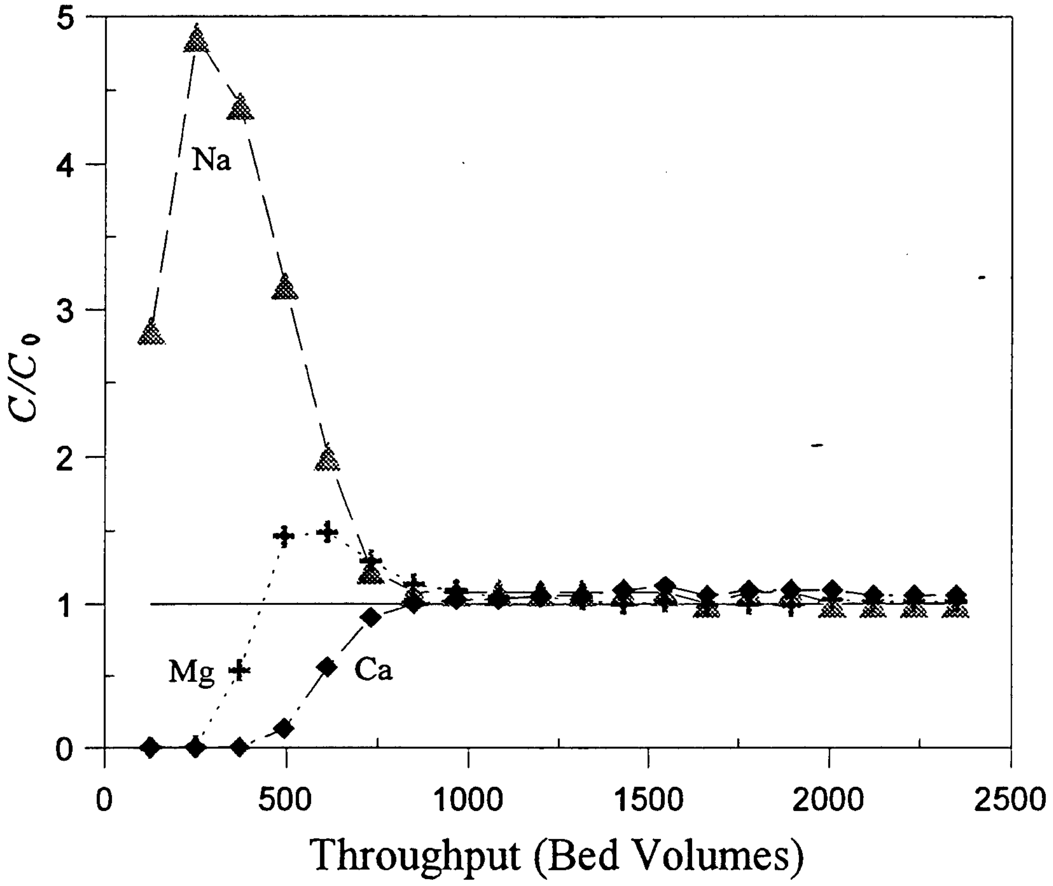
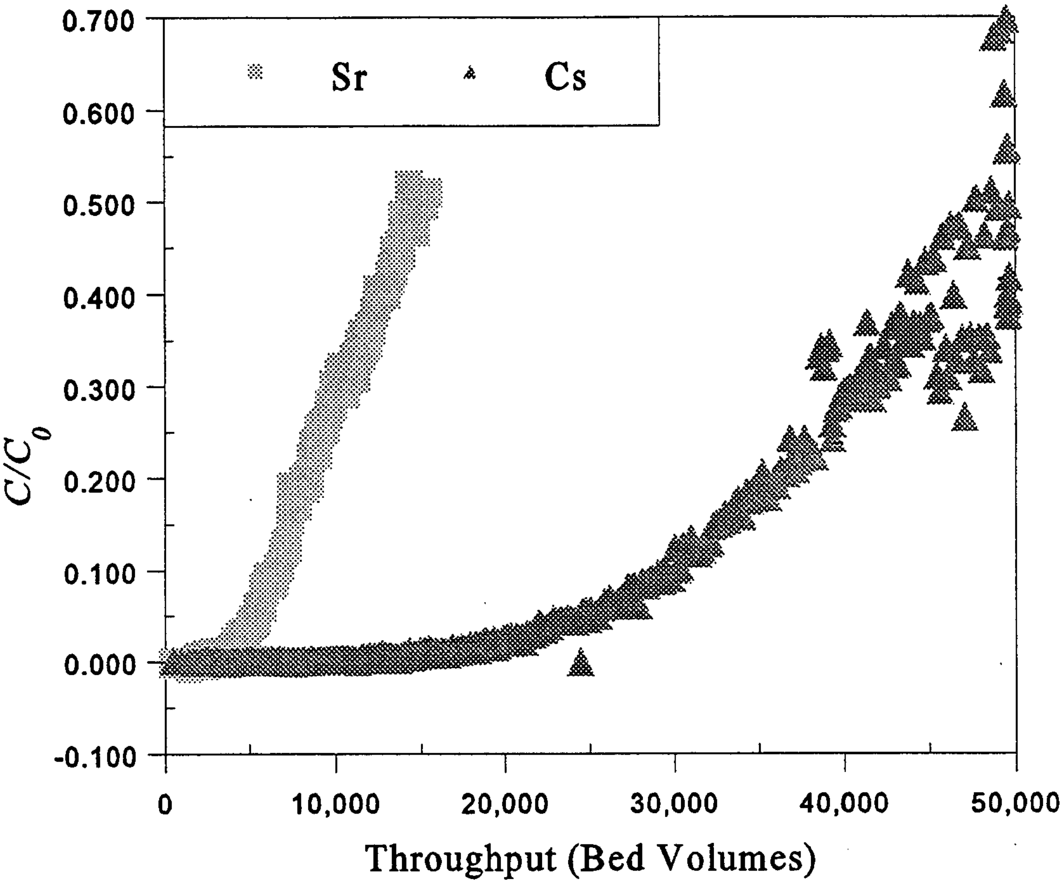


Fig. 6. Curves showing breakthrough of Na, Mg, and Ca from sodium-modified zeolite. Column parameters: 2.2 g of sodium chloride–washed zeolite contained in a 1-cm-diam column having a bed volume of 3.85 mL. The wastewater simulant flow rate was 1.3 mL/min.



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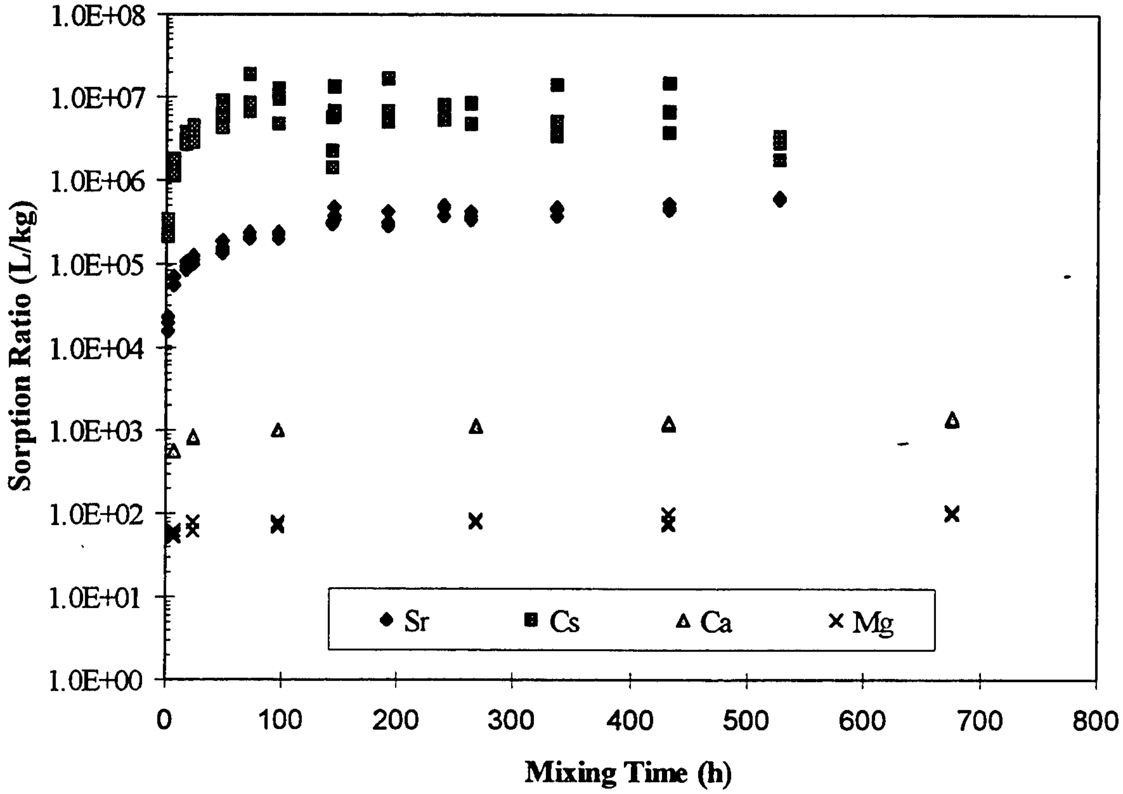


Fig. 8. Sorption ratios for Ca, Cs, Mg, and Sr on Sodium-CST as a function of mixing time. Test conditions: 20 mg of Sodium-CST equilibrated in 10 mL of PWTP simulant.

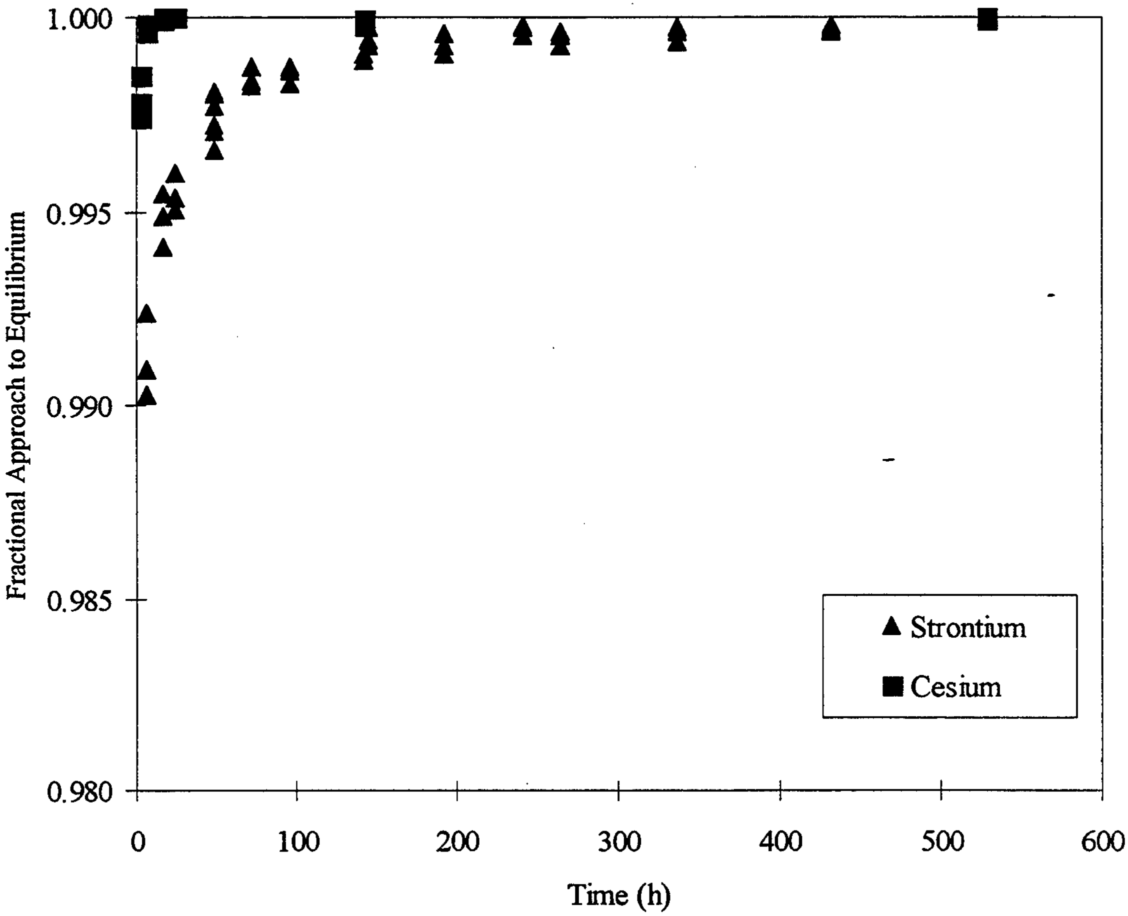


Fig. 9. Fractional approach to equilibrium for cesium and strontium on Sodium-CST in PWTP simulant. Test conditions: 20 mg of Sodium-CST equilibrated in 10 mL of PWTP simulant.

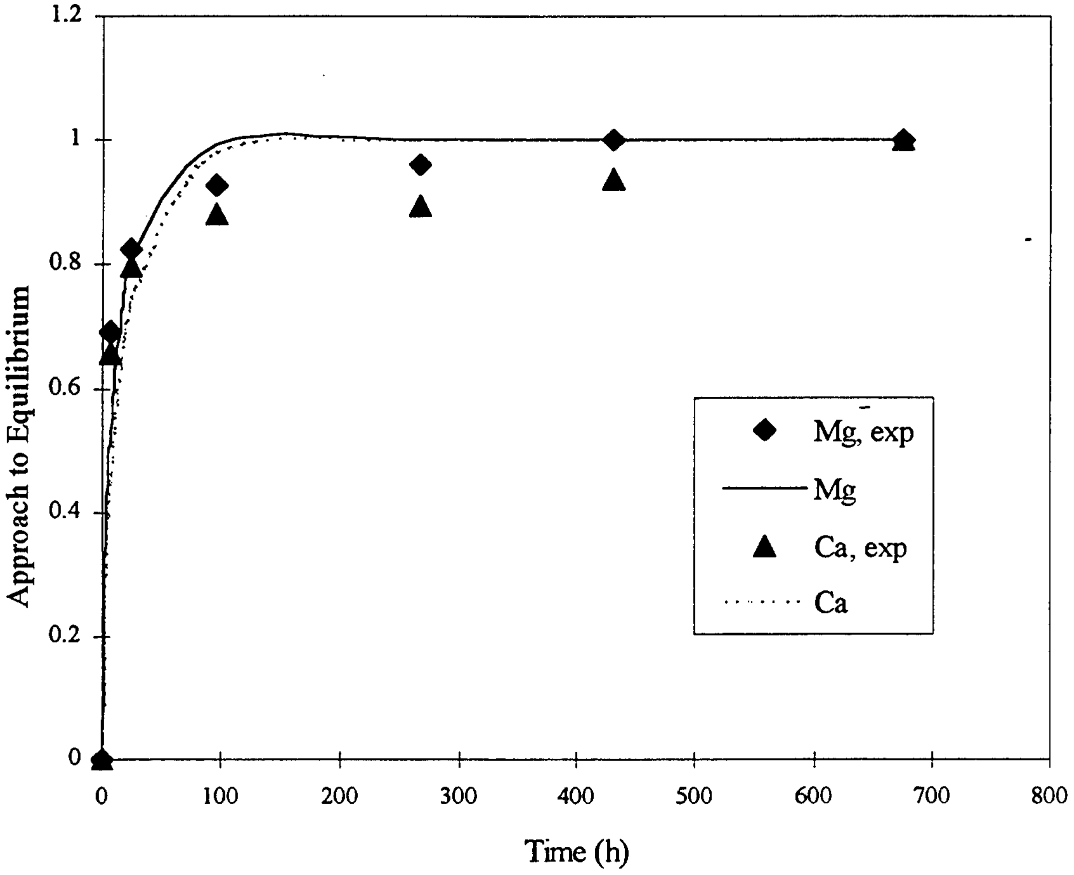


Fig. 10. Fractional approach to equilibrium of magnesium and calcium on Sodium-CST, experimental and predicted. Test conditions: 20 mg of Sodium-CST equilibrated in 10 mL of PWTP simulant.

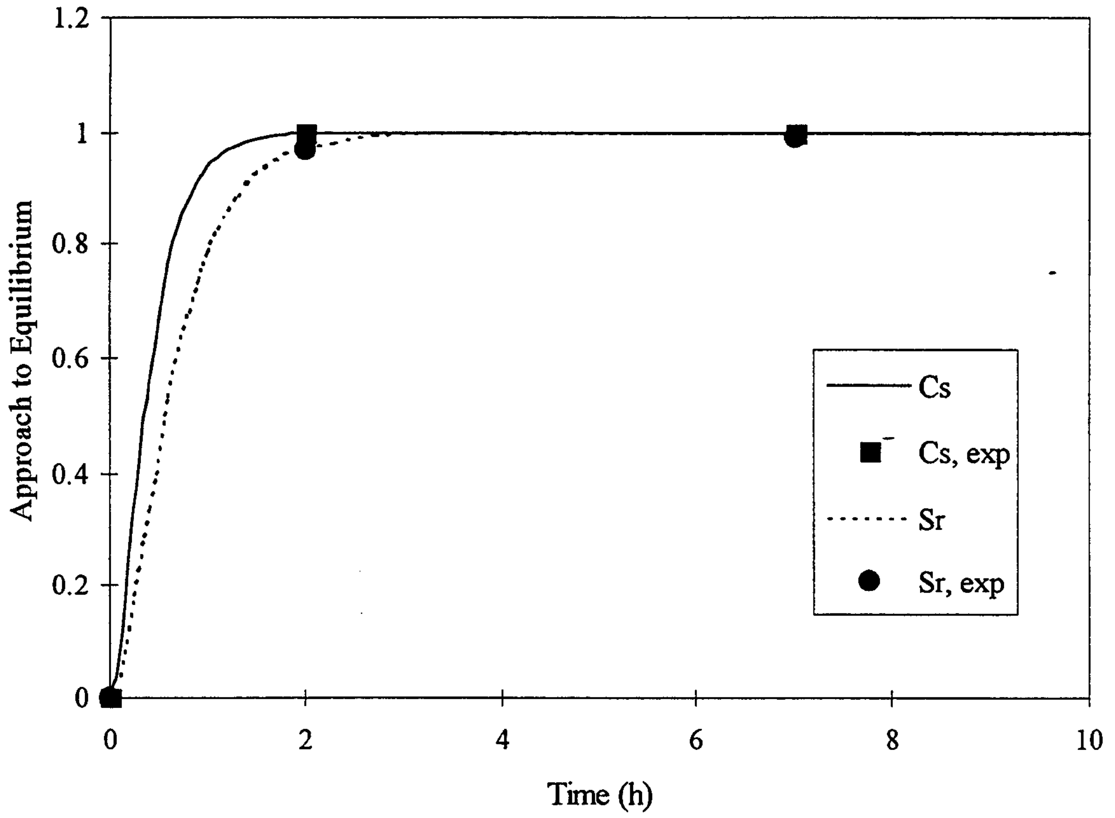
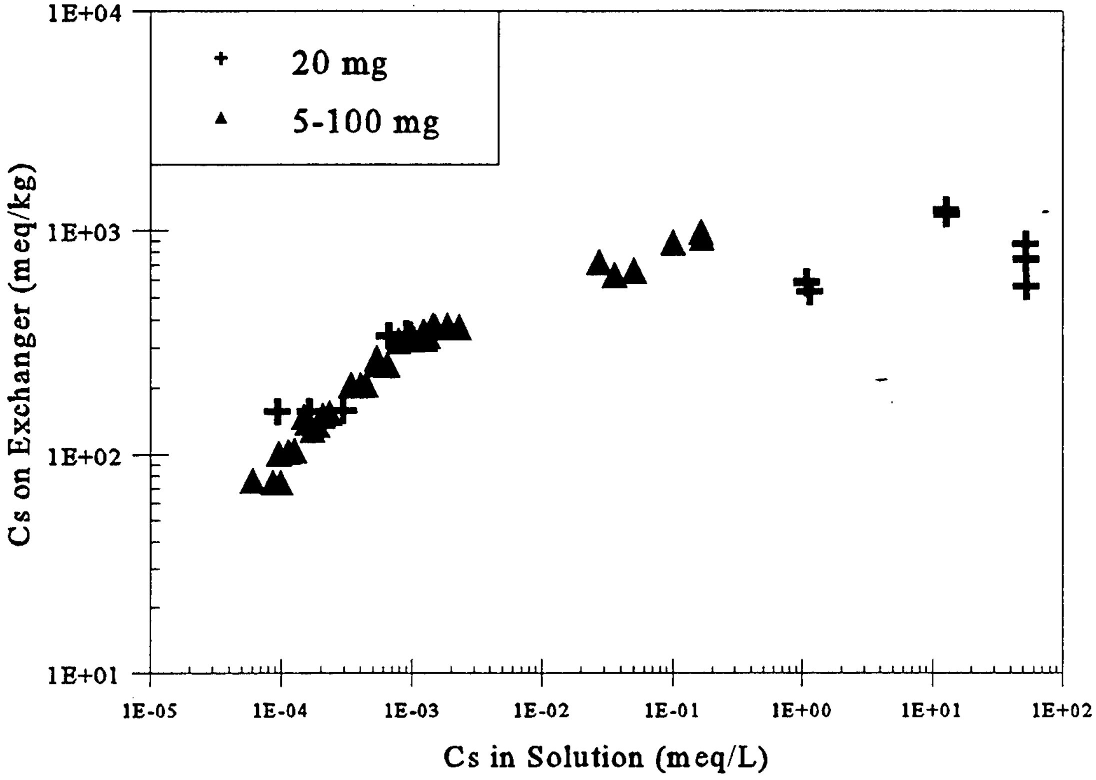


Fig. 11. Fractional approach to equilibrium of cesium and strontium on Sodium-CST, experimental and predicted. Test conditions: 20 mg of Sodium-CST equilibrated in 10 mL of PWTP simulant.



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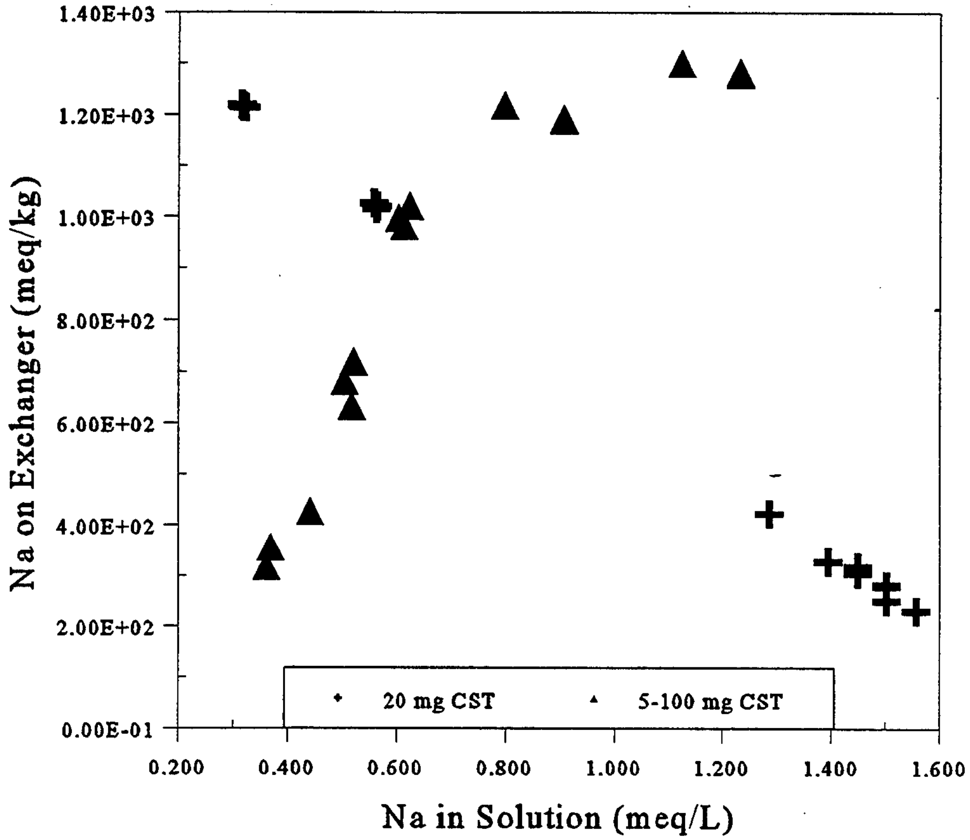
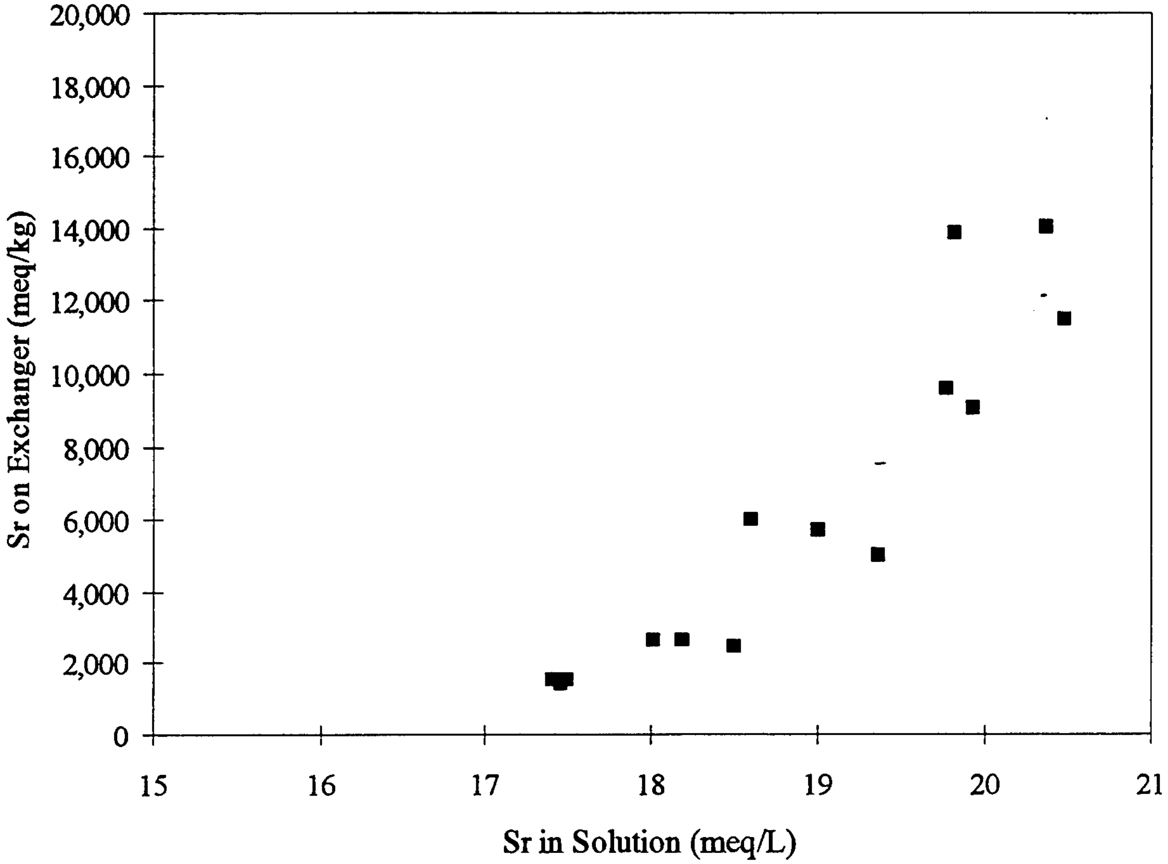


Fig. 13. Sodium sorption isotherm on Sodium-CST in Cs-Na binary system.



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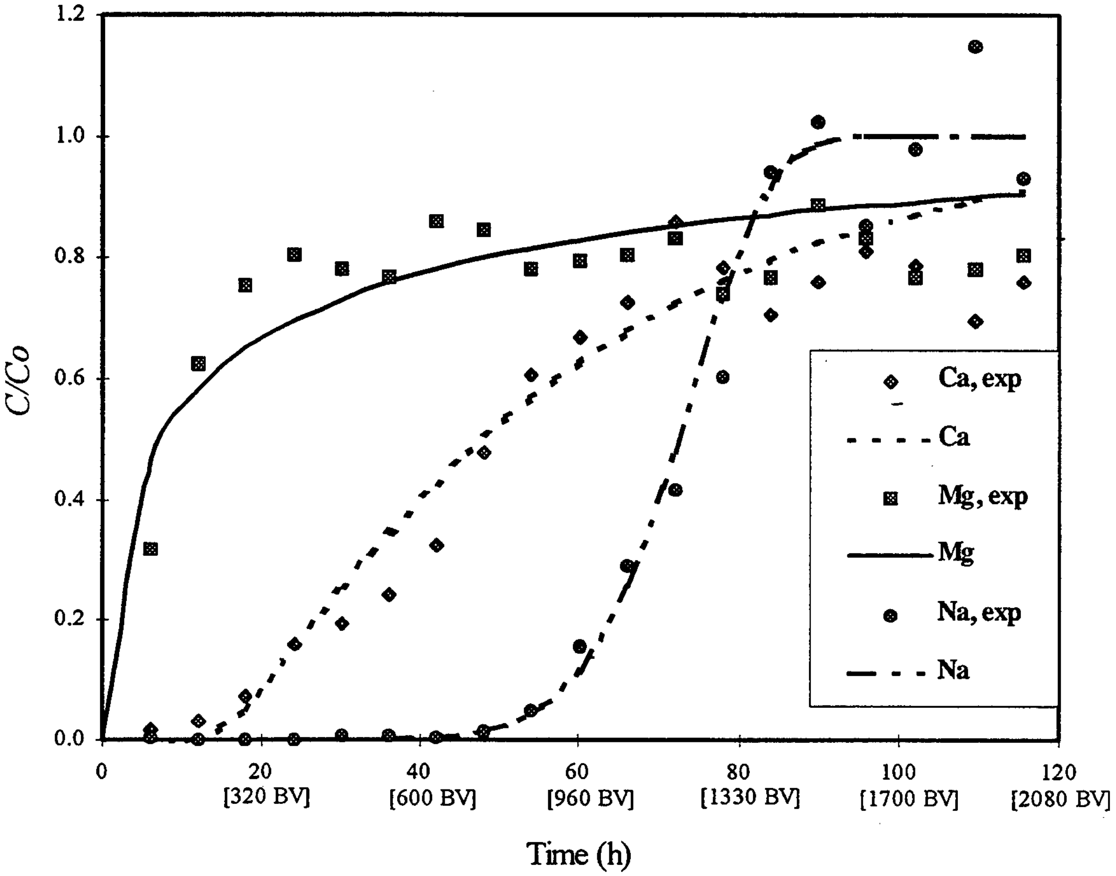

Fig. 15. Calcium, magnesium, and sodium breakthrough on Hydrogen-CST, experimental and predicted. Test conditions: 2 g Hydrogen-CST in a 1-cm-ID column; bed volume, 3.85 cm^3; process wastewater simulant flow rate, 1.21 mL/m.

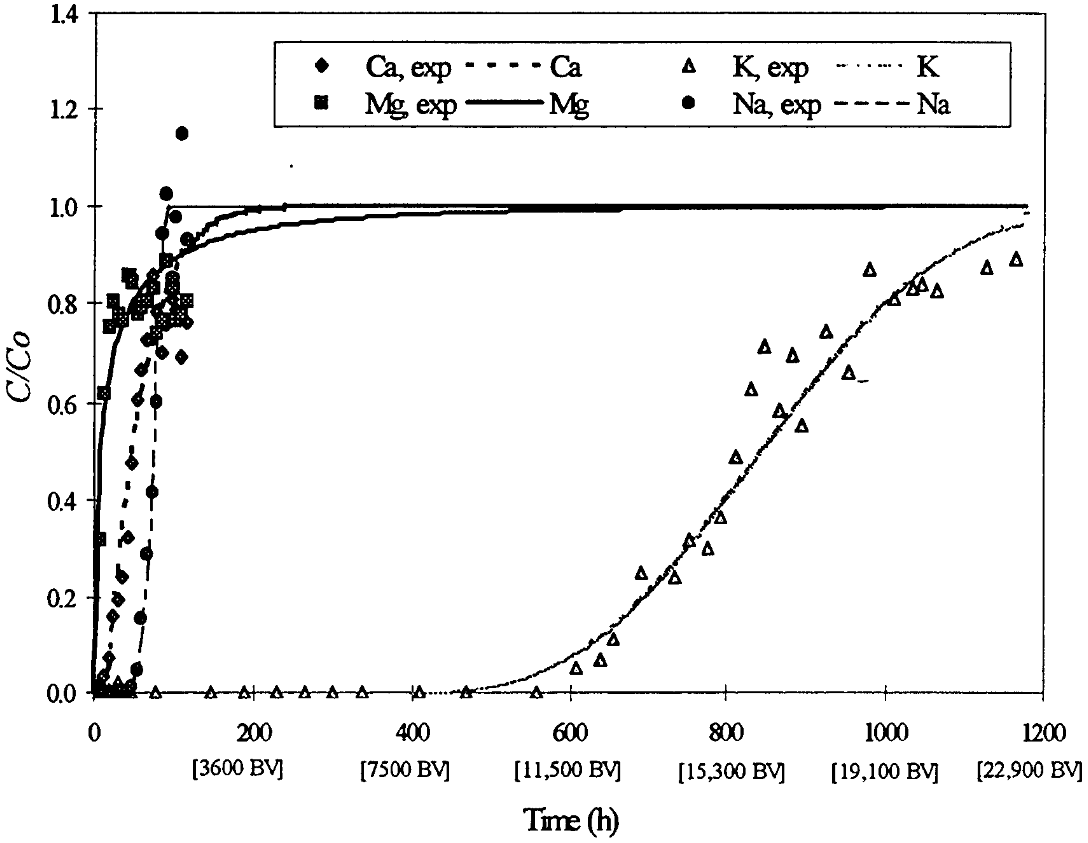

Fig. 16. Calcium, magnesium, potassium, and sodium breakthrough on Hydrogen-CST, experimental and predicted. Test conditions: 2 g Hydrogen-CST in a 1-cm-ID column; bed volume, 3.85 cm^3; process wastewater simulant flow rate, 1.21 mL/m.

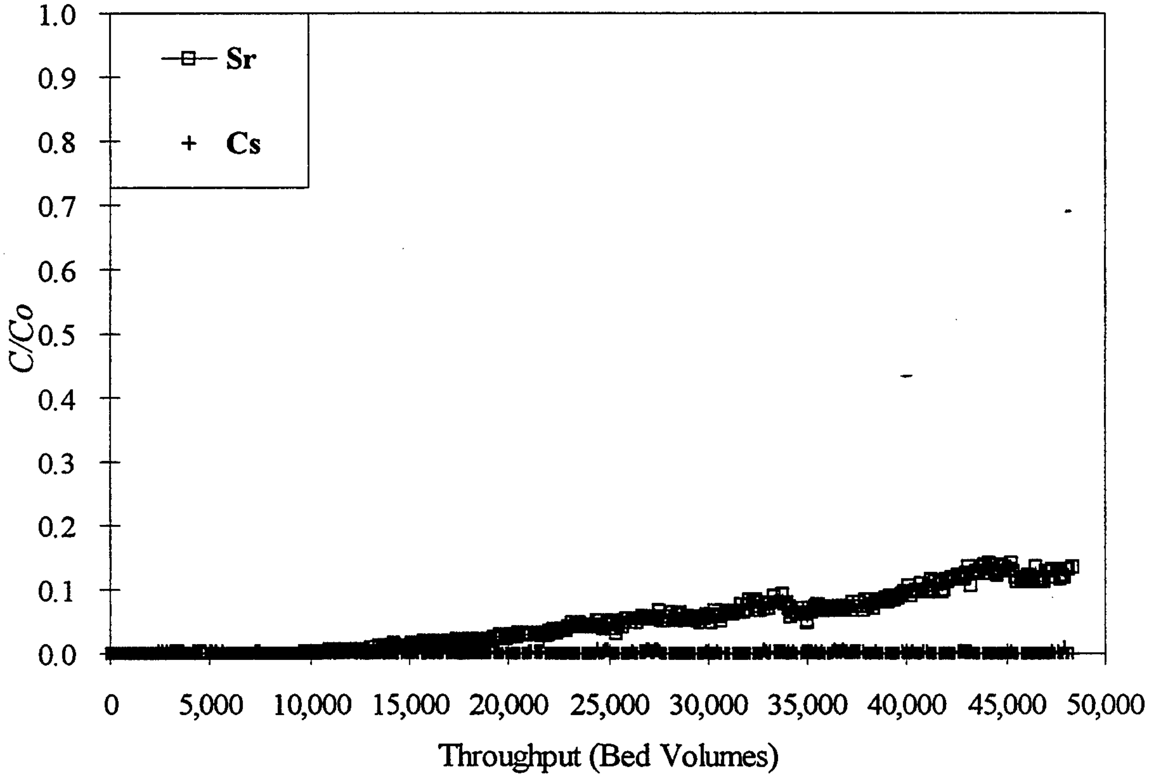

Fig. 17. Strontium and cesium breakthrough curves on Hydrogen-CST. Test conditions: 2 g Hydrogen-CST in a 1-cm-ID column; bed volume, 3.85 cm^3; process wastewater simulant flow rate, 1.21 mL/m.

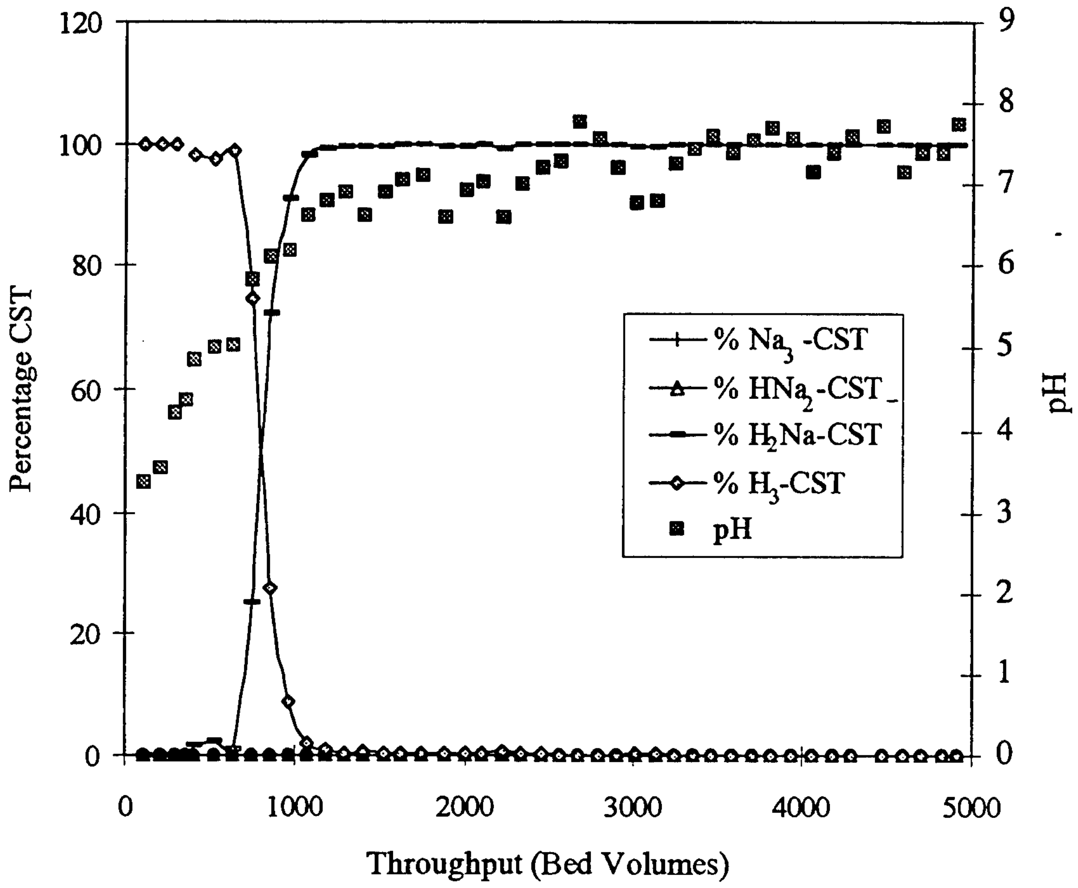

Fig. 18. CST functionality during column operation. Test conditions: column loaded with 2 g Hydrogen-CST; 1-cm-ID column; bed volume, 3.85 cm^3; process wastewater simulant flow rate, 1.21 mL/m.

APPENDIX

ORNL CF-97/20

Local User Survey for the Evaluation of Emerging Sorbents in the Removal of Fission Products -

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April 29, 1997

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1. INTRODUCTION

The purpose of this report is to summarize results of a survey initiated to better understand the treatment needs of local end-users in terms of new EM-50 wastewater treatment technology. The survey specifically addresses the need for the removal of Sr-90, Cs-137, Tc-99 and H-3 from local process wastewater and groundwater streams. Once user needs have been identified, laboratory testing and technical and economic studies, undertaken as part of task TTP OR16C312 of the Efficient Separations/Processing (ESP) Crosscutting Program, will be directed toward addressing these technical issues. Survey results will ultimately ensure that this ESP task provides local end-users with the pertinent information required to select and scale-up a treatment process specific to their needs.

To implement this survey, facility managers and engineers from the following sites within the local Oak Ridge area were canvassed: Oak Ridge National Laboratory (Oak Ridge, TN), Y-12 Site (Oak Ridge, TN), K-25 Site (Oak Ridge, TN), Paducah Gaseous Diffusion Plant (Paducah, KY), and Portsmouth Gaseous Diffusion Plant (Portsmouth, OH). Interview topics included the types, quantities, and locations of the wastewater streams within the site. The extent of current treatment efforts was also ascertained, as well as the drawbacks the user encountered in the operation of these processes. Possible drivers that might influence the decision of a user to select a given wastewater treatment or to alter a current process were addressed. These drivers included environmental regulatory requirements, limitations in secondary waste generation, operational costs, mandated time frames for waste decontamination, and need for compatibility with current treatment flowsheets.

User appraisal forms were devised to document survey comments; completed forms are included in the appendix. The body of this report serves to summarize the survey results and identify primary needs as defined by the survey participants.

2. PROCESS DESCRIPTIONS

A general description of the wastewater treatment activities and sources of nuclide contamination are given in this section. A more complete description of wastewater composition at each site is given in Table 1. Facility operating details are referenced in Table 2.

Table 1. General groundwater and process water composition of local Oak Ridge sites.

	Concentration (ppm)			
Element	**ORNL PWTP feed**	**ORNL WAG 5**	**Y-12 NT-1 water[a]**	**Y-12 GW-087 (BYBY) water**
Al	<0.050	<0.050	8.5, 0.96	0.07, 0.08
Ba	0.025	0.300	19, 15	0.13, 0.11
Ca	36	100	2,270; 1,800	46, 57
Cd	<0.005	<0.005	0.6, 0.06	0.004, 0.004
Fe	<0.050	1.50		
K	2.5	2.70	43	8, 4
Mg	7.4	14.0	314, 400	6.6, 5.1
Mn	0.0015	8.20	130, 140	0.94, 0.69
Na	27	12.0	354, 640	13, <5
Ni	<0.010	<0.010	2.7, 4.6	0.025, <0.0025
Sr	0.095	0.22		
U			0.008	0.24
Zn	0.022	0.74	0.10, 0.09	0.03, 0.08
Alkalinity	125	300	150	142, 174
Chloride ion	11	11	223, 258	9, 16
Fluoride ion	1	~0.2	48	<1
Nitrate	11	0.2-140	7,940; 12,400	<1
Sulfate ion	28	50-160	13, 50	26, 24
pH	6.7 - 8.7	6-8.5	6.04, 5.80	6. 96, 6.72
	Radioactivity (Bq/L)			
H-3	10,000	50,000		
Cs-137	23	0.1		
Sr-90	270	20,000	<DL	
Tc-99			<DL	
Total activity			700	55, 0.4

Table 1 (continued)

Element	Concentration (ppm)			
	Paducah Well 66[a]	Portsmouth X-705 raffinate[a]	K-25 TSCA Blowdown	General groundwater[d]
Al		8.5	<56[b]	0.003- 0.083
Ba		0.47	41[b]	
Ca	33.5		3-400[c]	3.2 to 121
Cr	0.07	<0.1		ND to 0.001
Fe	0.2	<0.04		0.001 to 6.6
K				0.4 to 30
Mg	9		1-150[c]	0.3 to 120
Mn		<0.5	1.1	ND to 0.34
Na	19	20	8-7000[c]	6.1 to 129
Ni	0.06	<0.1	24[b]	ND to <0.015
Sr			0.3[c]	0.019 to 6.3
U	≤0.001	<0.3		
Zn	0.015	<0.01	56[b]	ND to <0.47
Alkalinity	103			
Chloride ion	28		present[c]	2.0 to 92
Fluoride ion	0.12		present[c]	0.0 to 7.0
Nitrite ion				
Nitrate	39	94,500		0.0 to 17
Sulfate ion	28	330	present[c]	0.8 to 572
pH	61 – 7.2	8.5	8-9	6.7 to 8.7
Tc-99 (Bq/L)	77	8.3×10^6		
Gross alpha (Bq/L)		<1665		

DL=Detection limit. ND = Not detected.

[a] G. D. Del Cul, W. D. Bostick, et al., "Technetium-99 Removal from Process Solutions and Contaminated Groundwater," *Sepn. Sci. Technol.* **28** (1-3), 551 (1993).

[b] L. V. Gibson, et al., *Partitioning of Strontium and Cesium in the TSCA Incinerator*, K/ASD-033 Rev. (Oct. 1994).

[c] A. C. Coroneous et al., *Bench-Scale Treatability Studies for Simulated Incinerator Scrubber Blowdown Containing Radioactive Cesium and Strontium*, ORNL/TM-12823 (Dec. 1994).

[d] Conrad P Staub, ed., Practical Handbook of Environmental Control, CRC Press, Boca Raton, FL, 1989.

Table 2. Current end-user wastewater processing.

DOE user/site	Volume treated	Nuclide contaminants	Treatment process/contaminant removed; treatment rate
		Process wastewater	
ORNL /PWTP	70,000,000 gal/y[a]	Sr-90; Cs-13, H-3	Dowex HCR-S and Zeolite/Sr-90, Cs-137; 130-160 gal/min
Y-12/CPCF			Phase separator, neutralization, filtration
Y-12/WETF	2,500,000 gal/y[b]	U, Tc-99	Neutralization, bioreactor, carbonate precipitation, iron coprecipitation, activated carbon filter/U, Tc-99, PCB
K-25/CNF	2,000,000 gal/y	U (other nuclides depending on TSCA waste source)	Iron coprecipitation, neutralization, sludge removal; 17,000-gal batches
Portsmouth/X-705		U, Tc-99	Neutralization, filtration, Dowex -1/U, Tc-99
		Groundwater	
ORNL/Seep C		Sr-90, Cs-137, H-3	Passive french drain, ion exchange on zeolite/Sr-90, Cs-137
Y-12/Bear Creek Valley water shed (NT) Seep Collection	2-30 gal/min		Passive french drains, filtration, oil skimmer/U, PCB; 2-30 gal/min
Y-12/BYBY		U, Tc-99	
Paducah/NW Plume	2,000,000 gal/y	Tc-99	Ion Exchange (Purolite A-520-E)/Tc-99; 200 gal/min
Portsmouth	2,000,000 gal/y	Tc-99	Filtration/TCE, Tc-99

[a] S. M. Robinson, S. M. DePaoli, T. E.. Kent, 14th Annual U.S. DOE Low-Level Radioactive Waste Management Conf., Phoenix, AZ., Nov. 18-20, 1992.

[b] *Process Summary Data Sheets for ORR Low-Level and Mixed Waste Treatment Facilities*, prepared by Engineering Division, X-OE-387, September, 1987.

2.1 Site-Specific Treatment of Process Wastewater

2.1.1 Oak Ridge National Laboratory–Process Waste Treatment Plant (PWTP)

The Office of Waste Management and Remedial Actions, ORNL, operates the PWTP. The facility is designed to remove small quantities of Sr-90 and Cs-137 from liquid process wastewater generated as the result of various research programs, reactor operations, and isotope production and purifications procedures. The process wastewater, together with contaminated groundwater collected within the laboratory confines, is accumulated in feed tanks and fed continuously to the PWTP at an average rate of 130-160 gal/min and average Cs and Sr levels of 23 and 270 Bq/L, respectively. A fuller description of the composition of the PWTP feed stream is presented in Table 1. The influent is first chemically softened by the addition of sodium hydroxide and Ferri-Floc ($Fe_2(SO_4)_3$), which removes the majority of calcium and magnesium and some of the radioactive cations. Clarification and filtration steps then remove the precipitated cations in order to extend the lifetime of the ion exchange columns. The sludge from the clarifier is passed through a filter press to reduce the liquid content and is then packed in drums for on-site storage as solid low-level waste. The softened wastewater is passed through a series of Dowex-HCR-S (hydrogen-form) strong cation exchange resin columns to remove the remaining radioactive cations. When the influent flow or Cs-137 concentration exceeds the capacity of the Dowex column, a 15 cu ft. (112 gal) chabazite zeolite column can be placed in parallel or in series to add additional treatment capability to the system. The organic ion exchange columns are regenerated with a nitric acid solution. The regenerant solution is sent to an evaporator, where part of the nitric acid is recovered and recycled; the concentrate is stored as liquid low-level waste in an underground storage tank. The discharge from the PWTP is sent to the Nonradiological Waste Treatment Plant (NRWTP) where it is further treated to remove Resource Conservation and Recovery Act (RCRA) metals and organics prior to discharge through a National Pollutant Discharge Elimination System (NPDES) monitoring station to White Oak Creek.

2.1.2 Y-12 Site–West End Treatment Facility (WETF) and Effluent Polishing Unit (EPU)

The WETF denitrifies process wastewater by biodenitrification. Approximately 2.5 million gal/yr of acidic wastewater is neutralized with lime, biological nutrients are added, and the solution transferred to a bioreactor for anaerobic denitrification. Bio-oxidation is used to remove soluble organics; the sludge is removed by gravitational sedimentation. The clarified wastewater is transferred to the EPU facility, where the pH is reduced to disassociate uranyl carbonate complexes. The solution is sparged to remove the carbon dioxide, and ferric sulfate is added to coprecipitate uranium and heavy metals. Lime is added to readjust the pH to a slightly alkaline value, and a flocculating polymer is added to enhance the settling of the particulates. The metal-free supernate is passed through a granulated activated carbon filter, followed by cartridge filters, and then released at an NPDES station into East Fork Poplar Creek.[1]

2.1.3 K-25 Site–Central Neutralization Facility (CNF)

The CNF provides treatment for radiologically contaminated effluent derived from the Toxic Substance Control Act (TSCA) mixed-waste incinerator, potentially contaminated runoff rainwater, and aqueous wastes from decontamination activities. The bulk of the dissolved solids in the aqueous stream consists of the chloride and sulfate salts of calcium and sodium (see Table 1).[2] Currently, the primary radiological contaminant is uranium. However, if ORNL wastes are incinerated at TSCA both Sr-90 and Cs-137 are expected in the TSCA blowdown liquors.[3] Alternatively, if TSCA wastes originate from the Hanford site, H-3 may also be present in TSCA effluent wastewater. The contaminated effluent is treated in 17,000-gallon batches in the F-24B reaction tank. The waste is initially treated with 30% hydrochloric acid to reduce the pH below 5. Under acidic conditions, dissolved carbonate is removed through the generation of carbon dioxide. The primary treatment of the wastewaters is by iron coprecipitation. Ferri-Floc is added to a final concentration of 14 ppm iron to coprecipitate colloidal ash and some soluble heavy metal constituents. The treated waste is stirred with a mechanical agitator, and air is sparged through the solution to remove the remaining carbon dioxide. Sodium hydroxide is added to readjust the pH to a value between 7.5 and 8.5. After neutralization, Betz 1138 polymer is added to a final dosage of 10 ppm to aid in flocculation as the waste is transferred to a sludge thickener. The clarified wastewater from the sludge thickener is transferred to one of two settling basins. Four batches of wastewater are transferred to a settling basin before being discharged to an NPDES monitoring station. Finally, the wastewater is transferred to a mixing basin, where the wastewater is augmented with 3500 gal/min Clinch River water before being discharged to Poplar Creek. [1]

2.1.4 Portsmouth Gaseous Diffusion Plant–Building X-705 Decontamination Facility

Decontamination of process equipment takes place in the X-705 facility, where surface contamination from uranium and Tc-99 is removed with nitric acid. Subsequently, the uranium is recovered by solvent extraction, with the majority of the Tc-99 (typical initial concentration as shown in Table 1) remaining in the aqueous raffinate. The raffinate stream contains RCRA metals, high levels of nitric acid, and relatively low radioactivity (see Table 1).[4] Treatment of this stream consists of i) dilution with an equal volume of water; ii) pH adjustment with NaOH to a value of pH 8.5 to precipitate the hydrolyzable heavy metals, iii) filtration of the slurry to yield a heavy metal sludge (HMS) filtrate, iv) removal of Tc-99 by ion exchange with a strong base anion exchange resin (Dowex SRB), and v) biodenitrification of the column effluent.

2.2 Hydrology and Treatment of Contaminated Groundwater

2.2.1 Oak Ridge National Laboratory

ORNL is divided into three hydrological areas: i) Bethel Valley (Waste Area Group-WAG 1) containing the main laboratory facility; ii) White Oak Creek Watershed containing a variety of waste disposal pits, storage areas, trenches and auger holes (WAGS 2,7, 9), and iii) the Hydrofracture Facility (WAG 10) which is also located in the White Oak Creek Watershed. Gunite tanks, located in Bethel Valley, pose a potential risk of Sr-90, Pb-210, and Ra-228 release to the groundwater. Plans are to empty these tanks in the near future. WAG 1 also contains the source of a Sr-90 release that discharges to the upper tributaries of the White Oak Creek Watershed. Trichloroethane (TCE) is also present in the plume. The surface water from this area accounts for 22% of the Sr-90 loading at White Oak Dam.

Most of the waste associated with the operations at ORNL are stored within the White Oak Creek Watershed. This area is currently undergoing a Remediation Investigation (RI)/Feasibility Study (FS) to arrive at a Record of Decision with the Environmental Protection Agency (EPA) for treatment of the site. The solid waste disposal areas cover 20-60 acres and contain more than 3,000,000 cu ft of solid waste stored in long, shallow trenches and pits. Some of the trenches are partially flooded at times, resulting in Sr-90 migration from the burial sites. WAG 5 contains 210,000 Ci of radioactivity, present as Sr-90, H-3, Cs-137, Co-60, curium, plutonium, americium, uranium and radium. This particular storage area is the primary source of Sr-90 and H-3 in surface waters in White Oak Creek. Interceptor trenches have been installed at WAG 5 to collect and remove Sr-90 from seep water using chabazite zeolite. The full-scale system consists of eight drums of zeolite arranged in a lead-lag configuration. An elevation drop of 5 feet from the french drain to the zeolite provides gravity feed to the drums; the effluent then flows through an air lock and into Melton Branch. The flow rate averages 1.4 L/min and the treatment system removes 99% of incoming Sr-90.[5]

Liquid wastes at the Hydrofracture Facility were mixed with grout and injected into shale bedrock at depths of 600-1000 feet until the mid-1980s. Mobile contaminants have migrated laterally from the injection zone. If radioactivity is to be removed from the plume, the treatment method must be amenable to use in corrosive, saline groundwater. [6]

2.2.2 Y-12 Site–West End Groundwater Treatment Facility (WEGTF)

Y-12 operates a facility to treat groundwater from closed and capped waste burial grounds. The associated contaminant plume extends 2.5 miles long and 2000 ft deep from this site through the Bear Creek Valley Watershed. The plume contains depleted U, Sr-90, H-3, Tc-99, high nitrate concentration, and PCBs. Seep waters from the burial ground (i.e. groundwater NT-1 as shown in Table 1) are collected by french drains and pumped to five reservoirs. The water is then trucked to the WEGTF for treatment. The water is filtered through three successive stages of filters with 100, 10, and 1 micron pore apertures, respectively. The majority of radioactive components are removed as solids. An oil skimmer is used to remove oil and entrained PCBs; the wastewater is then pumped through an air stripper and granulated activated carbon columns to remove trace organics. Effluents are monitored for compliance with NPDES effluent limitations before release into East Fork Poplar Creek.[1]

2.2.3 K-25 Site–Groundwater Plumes

There are 214 groundwater wells throughout the K-25 site that are infrequently monitored. The area contains a large number of underground cavities, making it difficult to track the flow of groundwater. The flowrate of the groundwater is estimated to be 200 gal per day. Uranium is present at 1500 pCi/L; Tc-99 is localized in "hot" spots at levels of up to 1500 pCi/L. The site review is in a pre-remedial investigation mode.

2.2.4 Paducah Gaseous Diffusion Plant–Northwest Plume Containment System

Technetium-99 concentration in site groundwater has been observed at levels as high as 40,000 pCi/L. The groundwater plume extends over 1,300 acres. Solid Waste Management Units 7 and 30 (or C400 Building) spills are believed to be the source of the Tc-99 in the groundwater plume. Within the past year a pump-and-treat facility has been installed and is currently under evaluation. The containment system is equipped with four ion exchange columns originally loaded with four different resins: Ionac SR 3, Reillex HPQ Polymer, Dowex SBR-Cl, and Purolite A 520-E. The Dowex SPR-Cl resin reduces the Tc-99 influent levels of approximately 2,000 pCi/L to effluent levels of less than 50 pCi/L; the effluent activity is considerably below the operational goal of 900 pCi/L. Based on the operational experience over the first year of operation of the facility, Dowex SBR-Cl and Purolite A 520-E were selected for continued evaluation. The remaining three columns in the treatment system currently contain the Purolite A-520E resin.[7]

2.2.5 Portsmouth Gaseous Diffusion Plant–Groundwater Treatment

Four pump-and-treat systems are operated near capped burial grounds containing RCRA-hazardous waste. French drains are used to collect the water from the plume areas; the major contaminants are volatile organic carbons (VOC), primarily TCE, and a low level of Tc-99. The pumped systems use air stripping and carbon cartridges in a continuous operating mode. Technetium-99 is incidentally removed in the carbon cartridges through the filtration of suspended solids.

3. USER NEEDS AND PREFERENCES

Insight into the current and future needs of local wastewater treatment technology was ascertained in a series of personal interviews with the managers and engineers of each of the treatment facilities. The information derived from these interviews is summarized below and in Table 3; comments from specific facility staff are documented in the interview forms located in the appendix of this report.

3.1 Oak Ridge National Laboratory–Process Wastewater and Groundwater Treatment

Treatment needs for both process wastewater and groundwater at ORNL were discussed with Chris Scott, manager of the ORNL Liquid and Gaseous Waste Operation Department, ORNL. Chris Scott directs the operations for the PWTP and remediation efforts for groundwater from Seep C and D sites (WAG 5), located next to ORNL waste burial grounds. Chabazite zeolite is used to remove Sr-90 and Cs-137 from both sources of wastewater. Problems associated with the use of zeolite at the PWTP include: sorbent fines produced during shipping and handling of the material; steam generation during wetting of the dry, as-received zeolite; removal of spent zeolite that requires a hands-on operation; and column plugging which limits loading the sorbent to full capacity. The major difficulty in implementing zeolite technology at the Seep C site is that the treatment system is passive, so that a prefiltering operation cannot be easily incorporated into the system to remove suspended iron oxide particles present in the seep water. The formation of iron oxide ultimately plugs the zeolite drums. Active pumping is used at the Seep D site, and is recommended because it allows greater flexibility for treatment options at the site. Advantages of the zeolite process are that is it economical, and spent sorbent can be air-dried and stored in B-25 boxes on-site until final disposition of the waste is determined.

If an alternative EM-50 process is to be competitive with zeolite processing, it will need to be implemented using existing equipment at PWTP. This implies that the sorbent will be used primarily in column applications. Because available storage space is limited, the EM-50 process must have a higher sorption capacity and greater

Table 3. Needs and preferences of local end-users.

DOE user/site	Current needs	Preferences
	Process wastewater	
ORNL /PWTP	Reduce zeolite plugging	Column process, inorganic sorbent, limited calcium uptake, mechanically rugged sorbent, limited secondary waste generation
Y-12/CPCF		
Y-12/WETF	Removal of chelated nickel, reduce infiltration of storm runoff	
K-25/CNF	Better solids removal, automate system, need for approval for final waste disposition, Sr-90, Cs-137, H3 removal from off-site waste streams in future	Limited floor space requires use of batch process
Portsmouth/X-705	More selective resin for Tc-99 removal	
	Groundwater	
ORNL/Seep C	Iron oxide plugs zeolite system, steam generation on initial wetting of zeolite	Pumped system
Y-12/Bear Creek Valley water shed Seep Collection		
Y-12/Bear Creek Valley Watershed, Groundwater	Reduce storm runoff	Use passive, rather than pump and treat system, lower operating costs
Paducah/NW Plume		Sorbents should not require system changes, no leachable, non-hazardous wastes, adequate aquifer pumping, Tc-99 recovery
Portsmouth	Disposal of Tc-99 loaded organic resin, reduced funding level foreseen, pump level must be controlled to reduce DNAPL contamination	Column-based system
Overall Groundwater	Active barriers, source control	

selectivity for the nuclides, thus reducing the amount of secondary waste generated by the process. In addition, the cost of the new process must be competitive on a treatment basis. If impending CERCLA regulations require that additional site streams be treated, economics and secondary waste generation will be of even greater concern. An inorganic sorbent is preferred for groundwater applications because of disposal issues with organic resins. A sorbent having a lesser tendency to plug, particularly in the presence of rust particles, would be particularly useful. With increasing regulatory pressure to remove heavy metals (and in particular, mercury) from ORNL aqueous waste streams, a technology that could also remove RCRA metals might be advantageous.

3.2 Y-12 Bear Creek Valley Watershed

Chris Smith, project engineer supporting the Y-12 Bear Creek Valley restoration effort, was interviewed to determine wastewater treatment needs at the Y-12 site. Chris Smith is also familiar with the operation of the Y-12 WEGTF. Groundwater is treated according to Best Management Practice standards. Radioactive species in the treated water are below DOE 5400.5 limits (see Table 4) when discharged, therefore technologies specific for the removal of radionuclides are not currently required. Primary customer concerns include the fact that in the future the Y-12 site will be governed by CERCLA regulations, which will require more stringent discharge limits and the treatment of additional streams. At that time, treatment processes specific for U, Tc-99, and possibly Sr-90, may be required. Facility managers would prefer a pump-and-treat system at the seep site to alleviate the current need for trucking wastewater to a treatment facility. Additionally, construction of wastewater collection equipment must be such that it reduces the introduction of non-contaminated, storm run-off water into the system.

3.3 K-25 Site–Central Neutralization Facility

Representatives from the Central Waste Management, K-25 Site were surveyed to determine operation needs at CNF. Comments from K-25 Site staff include those of Tommy Bowers, senior manager of K-25 Central Waste Management, and Daren Hendren, of CNF Engineering Support. The driver for additional treatment needs appears to be defined by the source of waste burned at the TSCA Incinerator. If the waste is derived from ORNL, TSCA blowdown is predicted to contain sufficient Sr-90 and Cs-137 to require an additional decontamination operation at CNF specific for these nuclides. Because of the high salt content of CNF wastewater, neither chabazite nor clinoptilolite zeolite are suitable for the removal of Sr-90 or Cs-137 from the stream.[2] Due to the limited funding level and available floor space, preferred treatment options will be

Table 4. Regulatory limits–DOE 5400.5.

Isotope	Derived concentration guides (DCG values)* μCi/mL	Bq/L
H3	2.0 e-03	74,000
Sr-90	1.0 e-06	37
Tc-99	1.0 e-04	3700
Cs-137	3.0 e-06	111

*For mixtures of radionuclides, the sum of the fractions must be less than 1.0.

those that take advantage of existing tank-mixing equipment. Therefore, the addition of loose, powdered sorbent to the waste tank for batch operation will be preferred over column technology. The use of powdered crystalline silicotitanate (CST) may meet this particular customer's need. The powdered CST is available in a variety of mesh sizes and it is selective for both Sr-90 and Cs-137. Bench-scale testing is still required to demonstrate its utility in the high-salt waste matrix. If column parameters match those of the existing activated carbon column located downstream from the mixing tank, perhaps use of the engineered form of CST may be possible. The TSCA incinerator may also process waste from the Hanford site. In this case, the TSCA blowdown most probably will contain tritium. A treatment process for tritium removal at CNF has not been defined.

3.4 Paducah Gaseous Diffusion Plant–Northwest Plume

Debora Jolley, program manager in Environmental Restoration Division, was interviewed to determine the needs for the Paducal Northwest Plume remediation activity. The customer's primary concern was the final disposal of Tc-99 contaminated, organic resin. The use of an inorganic sorbent with a higher loading capacity would diminish and simplify secondary waste disposal. Alternatively, an economical system to regenerate spent Purolite resin might be advantageous. At present, no changes in the operation of the pump-and-treat system or alterations in the discharge limits are anticipated. For an alternative technology to be considered, a sorbent would have to result in significant operational cost savings and/or yield an inorganic secondary waste that would minimize final waste disposal efforts. Additionally, replacement technology will most likely have to be column-based to make use of existing facility components.

3.5 Portsmouth Gaseous Diffusion Plant

3.5.1 Ion Exchange Recovery, Building 705 Decontamination Facility

L. E. Deacon-process chemist, John Urik-former facility engineer, and Burch Upham-former plant design engineer were interviewed to assess the current needs and future requirements of the Ion Exchange Recovery process at the Decontamination Facility. No organic leachable or column plugging problems have been experienced with the strong anion exchanger, Dowex-1, currently used to remove Tc-99 from the near-neutral, high-nitrate waste stream. The resin column is typically replaced once or twice per month. The spent resin is classified as hazardous, due to the presence of mercury introduced from the decontamination of process equipment. The 55-gal drums of spent resin are stored in a holding area until they are transfer off-site to an independent contractor for regeneration at a cost of $150/cu ft. The customer is interested in a resin that is more selective for pertechnetate anion relative to nitrate. To be considered, any new sorbent/process would need to have a 2-year payback range and generate a secondary waste that can be easily stabilized. Because funding is extremely limited, a column operation that can be easily implemented with existing facility equipment is preferable. Finally, the Nuclear Regulatory Commission (NRC) will assume control of this facility in the near future. It is anticipated that more stringent procedures will be required for operating the Ion Exchange Recovery process.

3.5.2 Groundwater Treatment

Contacts for groundwater treatment at Portsmouth Gaseous Diffusion Plant include Tom Houk, Department Head, Technology Applications, and Frank Bullock, Groundwater Program Manager. The Portsmouth site treats 2 million gal of groundwater per year to remove TCE; a portion of the Tc-99 is incidentally removed by filtration of the suspended solids in the present pump-and-treat system. There are no current plans to incorporate a process specific for the removal of Tc-99 from Portsmouth groundwater at this time.

3.6 Overall Groundwater Needs

Overall groundwater treatment needs were assessed by interviewing Drew Diefendorf, Oak Ridge Operation, STCG Hydrology Subgroup Leader and Technology Applications Manager for Lockheed Martin Energy Systems ER/WM Program. Mr. Diefendorf makes recommendations for the ER/WM program for groundwater remediation at all five ORO sites, and as a representative for the Groundwater Program, Environmental Science Division, ORNL, he provides technical support to Paducah Gaseous Diffusion Plant. Mr. Diefendorf feels that pump-and-treat systems are quite expensive to operate and would rather see reactive barriers, source control, and bio-treatment options used in groundwater remediation efforts. However, costs associated with decontamination of installation equipment, disposal of contaminated soil, and disposal of spent sorbents or filtering materials must be considered in determining the most economical route for groundwater treatment. Because such large volumes of groundwater at ORNL contain Sr-90 and H-3 at very low concentrations, efforts to cut-off or contain the contamination at the source might be more economical. If these nuclides can be stabilized in place, or their release minimized, then remediation could rely on the relatively short half-lives of Sr-90 (30 y) and H-3 (12 y) to reduce the radioactivity and risks at these sites.

4. SUMMARY

It appears that economics, regulatory permitting, and secondary waste disposal will determine the type of processing selected by each site. All sites are confronted with a limited, and shrinking, budget for treating aqueous waste streams. Therefore, a process will be selected on the basis of sorbent costs, use of existing equipment, and disposal costs of spent processing materials. Most of the local users will require column technology to conform to current plant operating equipment. Loose sorbents might more appropriately be used at the Y-12 WETF and K-25 CNF facilities in their batch operations. All facilities would benefit from the use of inorganic, rather than organic, sorbents for which there are more waste disposal options. As the state and national environmental agencies become more restrictive in defining discharge limits, it is anticipated that the number and volumes of aqueous waste streams that must be treated for radionuclides at each site will increase. These regulatory drivers which govern the users needs are summarized in Table 5 along with the expected impacts to each site interviewed for this report. Considering the limited funds for this effort, new EM-50 sorbents, such as the CSTs, must exceed existing processes in regard to nuclide loading capacity, selectivity, and, ultimately, operating costs.

Table 5. Regulatory drivers for local end-users.

DOE user/site	Regulatory driver	Impending changes	Impact
	Process wastewater		
ORNL /PWTP	CERCLA, Record of Decision (90% activity removed), NPDES	FFA	Require treatment of greater waste volume, Hg treatment
Y-12/CPCF			
Y-12/WETF	DOE Order 5400A, NPDES	CERCLA	Require treatment of greater waste volumes
K-25/CNF	DOE Order 5400.5, NPDES	Origin of wastes alters radioactive contaminants	
Portsmouth/X-705	RCRA 1976, Consent Order	NRC to assume facility control	More stringent operating procedures will be required
	Groundwater		
ORNL/Seep C	FFA, DOE 5400.1(?)		
Y-12/Bear Creek Valley water shed , Seep Collection	DOE order 5400.5	CERCLA	Require treatment of greater waste volume
Y-12 /Bear Creek Valley Watershed, Groundwater	NPDES		
Paducah/NW Plume	Kentucky KPDES outfall limit 81 ppb TCE, DOE order 5400.5 (Tc-99 treatment goal: 900 pCi/L), CERCLA	Kentucky KPDES outfall limit 5 ppb TCE	
Portsmouth/Groundwater	RCRA 1976, Consent Orders; State discharge limit 10 ppb TCE		

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