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## Evaluation of Improved Techniques for the Removal of <sup>90</sup>Sr and <sup>137</sup>Cs from Process Wastewater and Groundwater: Chabazite Zeolite Baseline Study

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**EVALUATION OF IMPROVED TECHNIQUES FOR  
THE REMOVAL OF <sup>90</sup>Sr AND <sup>137</sup>Cs FROM PROCESS  
WASTEWATER AND GROUNDWATER:  
CHABAZITE ZEOLITE BASELINE STUDY**

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## CONTENTS

	<b>Page</b>
LIST OF TABLES .....	v
LIST OF FIGURES .....	vii
ACRONYMS AND ABBREVIATIONS .....	ix
ABSTRACT .....	xi
1. INTRODUCTION .....	1
2. WASTE STREAM SELECTION AND SIMULANT FORMULATION .....	2
2.1 WASTE STREAM SELECTION .....	2
2.2 PWTP SIMULANT FORMULATION .....	5
3. DECONTAMINATION EFFICIENCY OF A STANDARD TREATMENT METHOD .....	9
3.1 SELECTION OF CHABAZITE AS THE BASELINE TREATMENT METHOD .....	9
3.2 PREPARATION OF THE CHABAZITE ZEOLITE .....	11
3.3 KINETIC AND EQUILIBRIUM STUDIES WITH TSM-300 CHABAZITE ZEOLITE .....	11
3.3.1 Test Procedures .....	11
3.3.2 Determination of TSM-300 Equilibration Time .....	13
3.3.3 Sr and Cs Sorption Isotherms of TSM-300 .....	13
3.3.4 Comparison of Washed Versus Unwashed Chabazite Zeolite .....	17
3.3.5 Effect of Calcium, Sodium, Potassium, and Magnesium on Sr and Cs Sorption .....	18
4. TREATMENT OF ACTUAL PWTP FEED PROCESS WATER WITH TSM-300 .....	19
5. SMALL-COLUMN TESTING OF WASHED TSM-300 .....	25
6. SUMMARY .....	30
7. REFERENCES .....	32



## LIST OF TABLES

	<b>Page</b>
1 DOE site groundwater and process wastewater compositions .....	3
2 Chemical analysis of PWTP feed samples and composition of simulant—metal analysis by ICP .....	6
3 Chemical analysis of PWTP feed samples and composition of simulant—anion analysis by ion chromatography .....	7
4. Radiochemical analysis of PWTP feed .....	7
5 Chemical formulation of 4 L of PWTP feed simulant .....	8
6 Sorption ratios for Sr and Cs ( $R_s$ ) on washed and unwashed TSM-300 .....	18
7 Composition of actual PWTP feed wastewater sample .....	22



## LIST OF FIGURES

	<b>Page</b>
1 Sr and Cs equilibration time on washed TSM-300 chabazite zeolite .....	14
2 Sr sorption from PWTP simulant on TSM-300 .....	15
3 Cs sorption from PWTP simulant on TSM-300 .....	16
4 Sr sorption as a function of total cation concentration in PWTP simulant .....	20
5 Cs sorption as a function of total cation concentration in PWTP simulant .....	21
6 Sr sorption from actual PWTP feed and PWTP feed simulant .....	23
7 Cs sorption from actual PWTP feed and PWTP feed simulant .....	24
8 Breakthrough curves for the major cation concentrations with washed TSM-300 .....	28
9 Sr and Cs breakthrough curves for washed TSM-300 zeolite .....	29



## ACRONYMS AND ABBREVIATIONS

ESPIP	Efficient Separations/Processes—Integrated Program
FY	fiscal year
ICP	inductively coupled plasma
$K_d$	distribution coefficient
ORNL	Oak Ridge National Laboratory
PGDP	Paducah Gaseous Diffusion Plant
PWTP	Process Waste Treatment Plant
rcf	relative centrifugal force
$R_s$	sorption ratio
WAG	Waste Area Grouping



## ABSTRACT

Standard waste treatment procedures for the removal of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  from contaminated groundwater and process wastewaters generate large volumes of secondary contaminated wastes. Several new sorbent materials, ion exchangers, and other processes hold the promise of treating large volumes of contaminated water while minimizing the generation of secondary low-level radioactive wastes. As part of the Efficient Separations/Processes—Integrated Program (ESPIP), these new treatment techniques will be compared with standard processes to define their effectiveness for the removal of radioactive strontium (Sr) and cesium (Cs), as well as to gauge the quantity of secondary radioactive waste generated by the new processes.

This report summarizes the efforts made to design standardized testing procedures to evaluate the sorption characteristics of a baseline wastewater treatment technique. Definition of the experimental procedures, as well as a summary of the benchmark sorption technique, will provide the framework with which to compare newly evolving treatment technologies. Accomplishments include selecting the feed stream to the Process Waste Treatment Plant (PWTP) at Oak Ridge National Laboratory as representative of the prototypical contaminated wastewater of many DOE sites. Samples from the PWTP feed stream were collected and analyzed for metals, anions, total Sr and Cs, radioactive Sr and Cs, alkalinity, pH, and density. The cumulative sample data were used to formulate a simulant that will be used as a standard waste surrogate for comparative testing of selected treatment methods.

Based on a literature review of current wastewater treatment technology, Sr and Cs sorption on natural chabazite zeolite was selected as the baseline treatment method for the ESPIP study. A stock supply of TSM-300 zeolite, acquired from Steelhead Specialty Minerals (Spokane, Washington), was prepared by pretreating the sorbent with 2 M NaCl, removing the excess sodium with water, air drying the washed zeolite, and finally selecting the -20 to +50 mesh fraction for testing.

Testing of the standard zeolite treatment included determining the Sr and Cs sorption rates from the wastewater simulant. The Sr and Cs sorption ratios were defined for the prepared

zeolite and compared with those obtained on unwashed TSM-300. The Sr sorption isotherm using batch testing on TSM-300 exhibited a curvilinear response. Strontium loading deviated positively from linearity above a Sr loading of 2 meq/kg. The sorption ratio ( $R_s$ ) at low Sr loading on the washed zeolite is approximately 17,000 L/kg; the comparable  $R_s$  on unwashed zeolite was 30% lower. The Cs sorption isotherm was found to be linear with Cs solution concentration. The  $R_s$  for Cs on prepared zeolite is 80,000 L/kg as compared with 50,000 L/kg on the unwashed TSM-300. The effect of calcium, sodium, potassium, and magnesium on Sr and Cs sorption was also determined over the concentration range at which each cation is typically found in groundwater. Radionuclide sorption decreased as the concentration of any of these cations increased. Potassium exhibited the most significant effect; the  $R_s$  values for both Sr and Cs decrease by 50% over a potassium concentration range of 0.13 to 1.0 meq/L. Magnesium, sodium, and calcium significantly depress zeolite sorption capacity if they are present in the 0- to 4-meq/L concentration range. Further loss of sorption capacity is minimal above this concentration range. A 20% reduction in  $R_s$  of either nuclide is observed when sodium concentration in the simulant is increased from 0.65 to 1.35 meq/L. The  $R_s$  for Cs is reduced by 35% when the calcium concentration in the simulant is doubled from 1.95 to 3.89 meq/L. The  $R_s$  for Sr decreases by 80% over this same calcium concentration range.

The Sr and Cs sorption from actual PWTP feed wastewater on washed TSM-300 was tested, both to serve as the baseline treatment methodology for actual process wastewater and as a means to validate the composition of the PWTP feed simulant that will be used to test the new treatment technologies. The sorption profiles of the actual PWTP feed sample were nearly identical to those obtained with the simulant, although the  $R_s$  values for Sr and Cs were approximately 80% and 90%, respectively, of the corresponding values determined using the simulant solution. Maximum Sr loading in the authentic wastewater was calculated to be 24 meq/kg, and maximum Cs loading was determined to be 0.17 meq/kg.

A small-column test with prepared TSM-300 using wastewater simulant is under way. Elution results indicate that the chabazite zeolite has the following selectivity: Cs > Sr > Ca > Mg > Na. Strontium breakthrough was first noted at approximately 3000 bed volumes; 50% breakthrough was observed at 13,000 bed volumes. Incipient Cs breakthrough occurred at 12,500 bed volumes. On completion of this test, the efficiency of the benchmark waste

treatment method should be defined and work will begin on comparison testing of the new treatment technologies.



## 1. INTRODUCTION

Most U.S. Department of Energy (DOE) sites manage very large volumes of dilute liquid wastes which must be treated before they can be discharged to the environment. The waste is composed principally of contaminated groundwater and cooling water. Process wastewaters generated as a result of research programs and radiochemical production contribute to a lesser extent to the overall DOE inventory. The principal radionuclide contaminants of the radiological wastewaters are  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ , which may also be contaminated with trace quantities of heavy metals and organics.

Current treatment processes for the decontamination of the wastewaters typically involve the removal of the radionuclides by ion exchange on organic resins and/or inorganic zeolites. One of the drawbacks in using these technologies is the generation of large amounts of solid secondary wastes, which must be disposed of as radioactive waste. Because the handling and disposal of large quantities of contaminated solid waste are prohibitively expensive, new processes are needed which will minimize the volume of the secondary waste produced during wastewater treatment.

The goal of Subtask B under TTP OR1-3-20-12 is to test new sorbent materials, ion-exchanger materials, or other processes which might be more selective for the removal of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  than the standard treatment methods. New technologies to be included in the study are those based on the use of engineered crystalline silicotitanates, pillard clays, solid-phase extraction using selective molecular recognition compounds, and advanced ion-exchange and solvent-extraction systems. Initial task activities have been directed toward laying the groundwork for the comparative testing of the new technologies with a standard treatment technique. Samples of the new innovative adsorbents will become available during the next fiscal year. Laboratory efforts have focused on (1) selecting a process waste stream for treatment studies that typified wastewater and groundwater encountered at DOE sites, (2) formulating a simulant of the waste stream so that a standard waste solution can be used for comparative testing of the selected treatment methods, (3) documenting the decontamination efficiency for a benchmark treatment technique, and, finally, (4) treating an actual sample of the selected waste stream with the standard technique. The development of a

defined waste simulant and the determination of the decontamination efficiency of the baseline treatment technique will form the basis with which to compare the effectiveness of all new treatment technologies that will be studied under this subtask.

## 2. WASTE STREAM SELECTION AND SIMULANT FORMULATION

### 2.1 WASTE STREAM SELECTION

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

A review of reported data suggested that the feed stream to the Process Waste Treatment Plant (PWTP) at Oak Ridge National Laboratory (ORNL) appeared to have a composition similar to that of typical DOE wastewater and/or groundwater. The wastewater is derived from contaminated groundwater, once-through cooling water, evaporator condensates, and laboratory wastewater generated on-site. The typical radionuclide composition of the feed is 750 Bq/L  $^{90}\text{Sr}$  and 350 Bq/L  $^{137}\text{Cs}$ , although activities as high as 8000 Bq/L  $^{90}\text{Sr}$  and 1000 Bq/L  $^{137}\text{Cs}$  have been observed.<sup>1</sup> As can be seen in Table 1, the principal chemical constituents previously reported for the PWTP feed are calcium, magnesium, and sodium bicarbonates, which are introduced by contaminated groundwater. Table 1 also summarizes the composition of seep water samples collected at three Waste Area Groupings (WAGs) located on the ORNL reservation, as well as the composition of groundwater found at the Paducah Gaseous Diffusion Plant (PGDP). Data describing a Hanford well sample are also included in the table to demonstrate some extremes in sodium, silica, fluoride, and pH values which may be encountered in the processing of low-level contaminated groundwater at DOE sites. The final column in the

Table 1. DOE site groundwater and process wastewater compositions

Element	Concentration (mg/L)						
	WAG-5 <sup>a</sup>	WAG-6 <sup>a,f</sup>	WAG-7 <sup>a</sup>	PWTP feed <sup>c</sup>	PGDP <sup>d</sup>	Hanford <sup>e</sup>	General <sup>f</sup>
Al	0.21	NR	0.22	0.48	NR	NR	0.003 to 0.083
B	0.33	<0.88	NR	<0.08	NR	1.4	0 to 0.50
Ca	130	106	91	75	33.5	1.3	3.2 to 121
Co	0.008	<0.044	0.035	<0.004	NR	NR	NR
Cr	NR	0.086	0.02	0.008	0.071	NR	ND to 0.001
Cu	NR	<0.08	0.016	0.037	0.013	NR	0 to 0.015
Fe	0.65	<0.55	1.1	2.2	0.19	NR	0.001 to 6.6
K	NR	NR	4.1	2	NR	1.9	0.4 to 30
Mg	19	14.0	22	12	8.85	0.02	0.3 to 120
Mn	0.2	0.031	0.24	0.16	NR	NR	ND to 0.34
Na	25	8.06	130	64	19.3	299.2	6.1 to 129
Ni	0.016	0.161	0.11	0.024	0.061	NR	ND to <0.015
Pb	NR	<0.55	0.02	<0.2	NR	NR	ND to 0.038
Si	8.6	7.23	NR	2.6	NR	54.9	2.0 to 33.6
Sr	0.7	0.219	NR	0.19	NR	NR	0.019 to 6.3
Zn	NR	<0.55	NR	0.27	0.015	NR	ND to <0.47

**Table 1 (continued)**

Component	Concentration (mg/L)						
	WAG-5 <sup>a</sup>	WAG-6 <sup>a,f</sup>	WAG-7 <sup>a</sup>	PWTP feed <sup>c</sup>	PGDP <sup>d</sup>	Hanford <sup>e</sup>	General <sup>f</sup>
HCO <sub>3</sub>	NR	NR	NR	93	NR	42.9	55 to 364
CO <sub>3</sub>	NR	NR	NR	7	61.8 <sup>g</sup>	34	0 to 5
SO <sub>4</sub>	58	NR	160	28	11.7	113.4	0.8 to 572
NO <sub>3</sub>	NR	NR	970	11	39	NR	0.0 to 17
Cl	12	NR	13	11	28	214.8	2.0 to 92
F	1	NR	2.2	1	0.12	37.1	0.0 to 7.0
Alkalinity	300	200	280	125	103	NR	NR
pH	6.0 to 8.7	4.8 to 7.9	6.6 to 8.6	NR	6.1 to 7.2	9.9	6.7 to 8.7
Conductivity (ms/cm)	0.4	0.31	0.73	NR	0.4	NR	NR

NR = not reported; ND = not detected.

<sup>a</sup>Oak Ridge Reservation Environmental Report for 1990, Volume 2: Data Presentation, ES/ESH-18/V2.

<sup>b</sup>ORNL Analytical Chemistry Division analysis of sample submitted 07/30/93.

<sup>c</sup>T. E. Kent, S. A. Richardson, A. C. Coroneos, A. J. Lucero, and J. J. Perona, *Zeolite Ion-Exchange System Development for Treatment of ORNL Process Wastewater*, Letter Report, August 1993.

<sup>d</sup>G. D. Del Cul, W. D. Bostick, et al., "Technetium-99 Removal from Process Solutions and Contaminated Groundwater," *Sep. Sci. Technol.*, 28 (1-3), 551 (1993).

<sup>e</sup>G. F. Vandergrift, et al., "Interaction of Groundwater and Basalt Fissure Surfaces and Its Effect on the Migration of Actinides" (1984).

<sup>f</sup>Conrad P. Staub, ed., *Practical Handbook of Environmental Control*, CRC Press, Boca Raton, Fla., 1989.

<sup>g</sup>Total carbonate from alkalinity.

table summarizes the spread in concentrations of typical groundwater components.<sup>2</sup> The composition of the PWTP feed wastewater certainly falls within the ranges of concentration of the general description for groundwater composition. It is also similar in content to groundwater samples of local DOE facilities (e.g., PGDP). The radiological content of the PWTP feed stream is typical of process wastewaters. The radioactivity of process wastewater is generally within 10<sup>3</sup> to 10<sup>6</sup> Bq/L,<sup>3</sup> the primary nuclides being <sup>90</sup>Sr and <sup>137</sup>Cs. As such, the feed to the PWTP appears to be a good selection for the representative waste stream for baseline testing of wastewater treatment techniques for this particular task.

## 2.2 PWTP SIMULANT FORMULATION

The second initiative of the program was to formulate a simulant that would reflect the current composition of the PWTP feed. The simulant would ensure a constant composition of wastewater for the comparative testing of the benchmark technology against new processes. PWTP feed samples were collected on a weekly basis and submitted for inductively coupled plasma (ICP) metal analysis, anion chromatographic analysis, total Sr and Cs content,  $^{90}\text{Sr}$  and  $^{134,137}\text{Cs}$  activity, sample pH, and alkalinity. The analysis of pH and carbonate and bicarbonate content was also determined on the day each sample was collected.<sup>4</sup> The compositions of the individual feed samples and their average compositions are summarized in Tables 2 through 4.

Table 2 identifies the average cation concentrations of the PWTP feed samples. The final column in the table states the concentration of each cation to be included in the simulant. A decision was made to include cations in the simulant that were present in concentrations equal to or greater than 1 ppm in any of the analyzed PWTP feed samples. Strontium and Cs are the exceptions to this delineation. Strontium was included at a level of 0.1 ppm to reflect the average concentration of total Sr in the PWTP feed. This Sr concentration is also typical of process water in the local DOE area and represents a midrange value present in groundwater. Cesium was not detected above the 0.00005-ppm detection limit of the ICP-mass spectrometer. However, an average of 274 Bq/L  $^{134,137}\text{Cs}$  was detected radiochemically, as presented in Table 4. The total Cs added to the simulant is present at a tracer level of  $1.12 \times 10^6$  Bq/L  $^{137}\text{Cs}$  (equivalent to 0.00034 mg/L Cs). Both the levels of  $^{85}\text{Sr}$  and  $^{137}\text{Cs}$  activity in the simulant were selected on the basis of the counting efficiency of the gamma spectrometer to be used throughout the sorption studies.

The added  $^{137}\text{Cs}$  tracer activity also reflects the upper limit for Cs activity typical of process wastewaters. All anions above the detection limit of the ion chromatograph were included in the simulant. Values for the concentration level of each anion in the actual PWTP samples and the selected concentrations for the simulant are listed in Table 3. Note that the selected cation and anion contents in the simulant fall within the concentration ranges reported for general groundwater composition as presented in Table 1.

**Table 2. Chemical analysis of PWTP feed samples and composition of simulant -- metal analysis by ICP**

Element	Concentration (ppm)				Simulant
	Sample 1	Sample 2	Sample 3	Avg	
Ag	<0.005	<0.005	<0.005	<0.005	—
Al	0.140	<0.050	0.540	0.227	—
As	<0.050	<0.050	<0.050	<0.050	—
B	<0.080	<0.080	<0.080	<0.080	—
Ba	0.031	0.022	0.043	0.032	—
Be	<0.001	<0.001	<0.001	<0.001	—
Ca	35.000	37.000	44.000	38.667	39.0
Cd	<0.005	<0.005	<0.005	<0.005	—
Co	0.052	<0.004	<0.004	0.017	—
Cr	0.049	<0.004	<0.004	0.016	—
Cs	<0.0005	<0.00005	<0.00005	<0.00005	0.00034
Cu	0.020	<0.007	0.034	0.018	—
Fe	0.190	<0.050	1.000	0.397	0.4
K	3.000	<2.000	<2.000	1.000	1.0
Li	0.008	<0.005	<0.005	0.003	—
Mg	7.500	7.900	8.700	8.033	8.0
Mn	0.180	0.003	0.024	0.069	—
Mo	<0.040	<0.040	<0.040	<0.040	—
Na	8.000	12.000	23.000	14.333	15.0
Ni	<0.010	<0.010	<0.010	<0.010	—
P	0.580	1.500	0.460	0.847	2
Pb	<0.050	<0.050	<0.050	<0.050	—
Sb	<0.050	<0.050	<0.050	<0.050	—
Se	<0.050	<0.050	<0.050	<0.050	—
Si	3.400	2.500	3.300	3.067	3
Sn	<0.050	<0.050	<0.050	<0.050	—
Sr	0.089	0.100	0.120	0.103	0.1
Ti	<0.020	<0.020	<0.020	<0.020	—
V	<0.002	<0.002	<0.002	<0.002	—
Zn	0.045	0.024	0.170	0.080	—
Zr	<0.020	<0.020	<0.020	<0.020	—

**Table 3. Chemical analysis of PWTP feed samples and composition of simulant — anion analysis by ion chromatography**

	Concentration (mg/L)				
	Sample 1	Sample 2	Sample 3	Avg	Simulant
Alkalinity <sup>a</sup>	105.0	110.0	120.0	111.7	126
Anions					
Cl <sup>-</sup>	8.3	8.4	9.3	8.7	8.7
F <sup>-</sup>	0.8	0.9	0.8	0.8	0.8
NO <sub>3</sub> <sup>-</sup>	4.3	4.0	7.6	5.3	5.3
NO <sub>2</sub> <sup>-</sup>	<0.1	<0.1	<0.1	<0.1	---
PO <sub>4</sub> <sup>3-</sup>	<0.5	5.5	0.8	2.1	2.1
SO <sub>4</sub> <sup>2-</sup>	21.0	22.0	21.0	21.3	21.3
pH	8.45	8.52	9.30	8.8	8.3

<sup>a</sup>Measured as CaCO<sub>3</sub>.

**Table 4. Radiochemical analysis of PWTP feed**

Nuclide	Concentration (Bq/L)				
	Sample 1	Sample 2	Sample 3	Average	Simulant
<sup>134</sup> Cs	2	0.32	0.12	0.8	---
<sup>137</sup> Cs	450	120	250	273	1.1 × 10 <sup>6</sup>
<sup>89,90</sup> Sr	360	330	370	353	8.8 × 10 <sup>5</sup> (as <sup>85</sup> Sr)

A summation of the average milliequivalents (meq) of cationic and anionic species present in the PWTP samples indicates that ICP and ion chromatographic data are in good agreement. Based on the chemical analysis, approximately 3.3 meq/L cationic species is present in solution as compared with 3.7 meq/L anionic species. Calculation of anionic charge was made by assuming that the silica is present as  $\text{SiO}_3^{2-}$ , that any phosphorus occurs as  $\text{PO}_4^{3-}$ , and that the average alkalinity is the result of 0.3 meq/L  $\text{CO}_3^{2-}$  and 2.26 meq/L  $\text{HCO}_3^-$ . Table 5 describes the formulation of wastewater simulant to prepare a 4-L solution containing the anions and cations at the selected concentrations presented in Tables 2 through 4. Inactive Sr,  $^{85}\text{Sr}$ , and  $^{137}\text{Cs}$  are added to the simulant just prior to experimentation to reduce the possibility of losing these cations by sorption onto labware.

**Table 5. Chemical formulation of 4 L of PWTP feed simulant**

Chemical	Weight (g)	Chemical	Weight (g)
$\text{CaCO}_3$	0.36604	$\text{NaF}$	0.00707
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	0.04037	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	0.03362
$\text{CaCl}_2$	0.00710	$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	0.12548
$\text{MgSO}_4$	0.10174	$\text{NaHCO}_3$	0.10863
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	0.09582	$\text{K}_2\text{CO}_3$	0.00707
Ferri-Floc <sup>a</sup>	0.160 mL		

<sup>a</sup> Solution containing 10,000 ppm iron and 25,800 ppm  $\text{SO}_4$ .

The difficulty encountered in preparing the simulant is that the solubility of  $\text{CaCO}_3$  in water is limited to approximately 14 ppm, whereas the required quantity to prepare the wastewater simulant is 41 ppm. Several batches of the simulant were prepared to test the most effective means to add the reagents to nanopure water in a manner which would reduce the precipitation of the components. The fewest solids were formed when the calcium salts were added to 4 L of stirred nanopure water at room temperature, followed by the addition of the remainder of

the reagents. To improve the solubility of the calcium salts, dry ice was added to the solution to decrease the pH; stirring was continued for an additional hour. The simulant was then allowed to settle for 2 days before the solution was filtered with a 0.45- $\mu\text{m}$  cellulose nitrate membrane filter under house vacuum. Some solids were noted on the filter membrane, suggesting the loss by precipitation of some sparingly soluble salts (e.g., ferric, calcium, and silicate salts.) An acidified aliquot of the filtered solution was submitted for ICP analysis to determine the final concentration of cations in the simulant. According to the analysis, less than 10% of the calcium and magnesium was lost to precipitation. The simulant contained the target concentration of 15 ppm sodium. Ferric ion concentration was not detected above the 0.5-ppm detection limit of the ICP; the silica concentration of the filtrate was 5 ppm (equivalent to 13.6 ppm  $\text{SiO}_3^{2-}$ ). The density of the wastewater simulant was 0.9965 g/L at 27°C. The final simulant solution was stored in a polypropylene container to minimize leaching of minerals or component loss to the storage vessel.

### **3. DECONTAMINATION EFFICIENCY OF A STANDARD TREATMENT METHOD**

#### **3.1 SELECTION OF CHABAZITE ZEOLITE AS THE BASELINE TREATMENT METHOD**

Since the early 1900s, zeolites have been used for water treatment<sup>5</sup> primarily as a means of removing calcium and magnesium in the softening of water. More recently, zeolites have been employed to remove heavy metals from process water and to decontaminate radioactive waste solutions.<sup>6</sup> West Valley Nuclear Services Company,<sup>7,8</sup> the British Nuclear Fuels, and the Savannah River Plant<sup>9</sup> use zeolites to treat process wastewater containing Cs and/or Sr. As a result of a variety of bench-scale and pilot-scale treatability studies performed at ORNL, zeolite treatment has been selected to remove Cs and Sr from PWTP feed wastewater in a scheduled upgrade of the PWTP facility.<sup>10,11,12</sup> Use of zeolites has also been suggested for the decontamination of aqueous solutions generated during in situ soil flushing and leaching at contaminated DOE sites. The process has been demonstrated in bench-scale studies<sup>13</sup> and has been proposed for use in the field. Considering the wealth of information available on zeolite treatment and the prevalent use of zeolites in the decontamination of process wastewater, ion

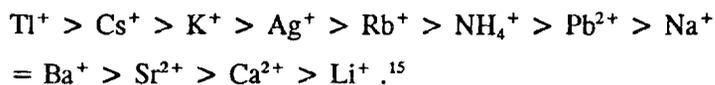
exchange on zeolites was selected as the reference treatment technique from which to compare new treatment technologies studied in this task.

The main body of research concerning the application of zeolites to ORNL wastewater decontamination has been performed using chabazite zeolite. Bench-scale tests indicated that chabazite zeolites have a very high sorption capacity for Cs. The sorption capacity for Sr is much lower than for Cs, although zeolites demonstrate the highest capacity for Sr removal in the presence of nonradioactive ions of any sorbent studied thus far. The natural zeolite was selected over the synthetic zeolite, Ionsiv IE-95, because the former was found to have a higher capacity for <sup>90</sup>Sr sorption.<sup>14</sup>

Stock chabazite zeolite was purchased from Steelhead Specialty Minerals under the product name TSM-300. The natural zeolite is mined from the Bowie deposit in Arizona by GSA Resources, Inc. (Cortaro, Arkansas). The product specification sheet describes the material as Carbasorb-Sodium, a natural herschelite-sodium chabazite (CHA) having a typical anhydrous chemical composition of

SiO<sub>2</sub>: 68.1% Al<sub>2</sub>O<sub>3</sub>: 18.59% Fe<sub>2</sub>O<sub>3</sub>: 2.84% CaO: 0.27% MgO: 0.75% Na<sub>2</sub>O: 8.32%  
K<sub>2</sub>O: 1.12%,

with the dominant cation being sodium. The chabazite has a framework of large ellipsoidal cavities; the entrance to these cavities is through six 8-ring pores having free diameters of 4.1 by 3.7 angstroms. The crystalline lattice structure accounts for the use of the zeolite in gas sorption applications, while limiting ion-exchange sites to the exterior surface of the lattice in liquid applications. The porous zeolite has a surface area of 500 to 600 m<sup>2</sup>/g. The zeolite exchange capacity, determined with ion exchange of ammonium ion, is 2.20 meq/g ammonia. The chabazite is stable to pH 4; below this value the material begins to dealuminate. The approximate exchange selectivities as stated in the product literature are



### **3.2 PREPARATION OF THE CHABAZITE ZEOLITE**

A stock supply of the chabazite zeolite was prepared by first performing a sieve analysis<sup>16</sup> on three 50-g portions of TSM-300 zeolite nominally sized as -20 to +50 mesh. Approximately 20% of the material was discarded as fines, having a mesh size greater than 50. The high fines content in the sample is typical of natural zeolites and is due to the friable nature of the chabazite zeolite, which is easily fractured during storage or handling. The -20/+50 fractions of the three zeolite samples were converted completely to the sodium form to remove any natural Cs or Sr that may be on the surface of the sorbent. The zeolite fractions were initially contacted with 200 mL of 2 N NaCl for 1 h; the samples were stirred constantly on a orbital shaker. After the zeolite samples were centrifuged, fresh NaCl solution was added to the zeolite and the process repeated for three additional saline washes. A fifth NaCl wash was performed by loading the individual fractions of the zeolite in a 1-in.- ID column. The salt solution was pumped upflow through the bed at a flow rate of 5 mL/min. Excess sodium was removed from the zeolite by subsequently passing approximately 1500 mL nanopure water through the column. ICP analysis of the final fraction of wash water indicated that no more than 14 ppm sodium was present in the final water rinsate. This level of free sodium in the water would reflect 7  $\mu\text{g}$  of free sodium per gram of zeolite, an insignificant quantity compared with the sodium content that would be present in 10-mL synthetic PWTP samples used for batch testing with up to 0.1 g of washed zeolite. The converted zeolites were air dried; the final water content of the dried material was determined to be 7.1% (w/w). The dried zeolite fractions represent the stock supply of sorbent for the standard treatment method.

### **3.3 KINETIC AND EQUILIBRIUM STUDIES WITH TSM-300 CHABAZITE ZEOLITE**

#### **3.3.1 Test Procedures**

Sorption measurements were made in batch equilibrium tests. The 10-mL solutions and exchanger (5-100 mg) were contacted in screw-cap polycarbonate centrifuge tubes by mixing on a Labquake shaker, which rocks the samples from -45° to +45° from horizontal at 20 cycles per minute. Three samples were included in each data set. Solution volumes were

determined by weights and density of the wastewater simulant. The chabazite zeolite was weighed directly and added to the tubes. The tubes were weighed at the beginning and the end of the equilibration periods to determine any solution loss. At the end of the equilibration period, the tubes were centrifuged for 30 min at 5000 relative centrifugal force (rcf). The solutions were clarified again either by transferring the supernate to a 12-mL tube and recentrifuging for 30 min at 5000 rcf or by filtering the centrifuged supernate using a plastic syringe fitted with a 0.45- $\mu$ m-pore nylon membrane filter.

The  $^{85}\text{Sr}$  and  $^{137}\text{Cs}$  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  $^{85}\text{Sr}$  were corrected for the interference of  $^{137}\text{Cs}$  at the 514-keV peak by using a linear regression line developed using  $^{137}\text{Cs}$  standards.

Test data were used in the following calculations:

$$\text{Decontamination factor (DF)} = C_i/C_f,$$

$$\text{Sorption ratio (R}_s, \text{ L/kg)} = (C_i - C_f)V/C_fW,$$

$$\text{Final concentrations in solution (M}_f, \text{ meq/L)} = M_i \times C_i/C_f,$$

$$\text{Final concentrations on the exchangers (M}_e, \text{ meq/kg)} = M_f \times R_s,$$

where:

$C_i$  = count rate of the initial solution,

$C_f$  = count rate of the final solution,

$V$  = initial volume of the solution (mL),

$W$  = exchanger weight (g).

The sorption ratio ( $R_s$ ) is equivalent to the distribution coefficient ( $K_d$ ), if equilibrium conditions are assumed.

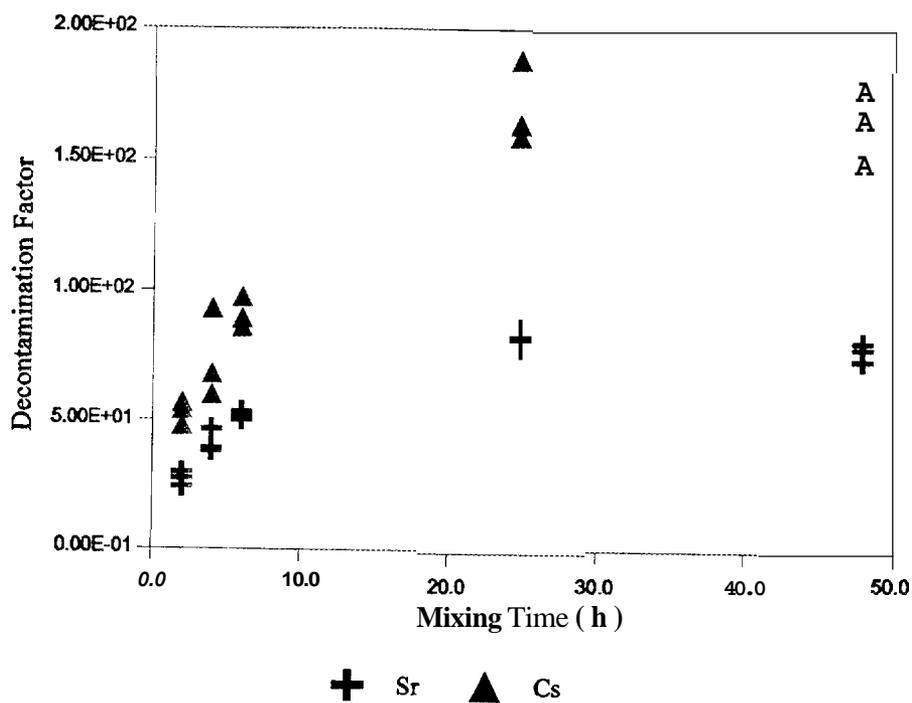
### 3.3.2 Determination of TSM-300 Equilibration Time

The Sr and Cs sorption rates from the simulated wastewater were determined by mixing a series of samples containing 20 mg of the stock TSM-300 in 10 mL of the traced simulant. Blank simulant samples without zeolite were also mixed for the full 48-h duration of the study. Sorption of both Sr and Cs reached steady state in 24 h, as shown in Fig. 1. On the basis of these results, a 24-h mixing time was used in subsequent sorption studies. The sorption ratios ( $R_s$ ) were about 38,000 L/kg for Sr and about 85,000 L/kg for Cs. Analysis of the blank samples indicated that neither Sr nor Cs is lost to the walls of the sample containers over this time period, even at tracer levels 30 times less than those that normally will be present in the wastewater simulant testing.

### 3.3.3 Sr and Cs Sorption Isotherms on TSM-300

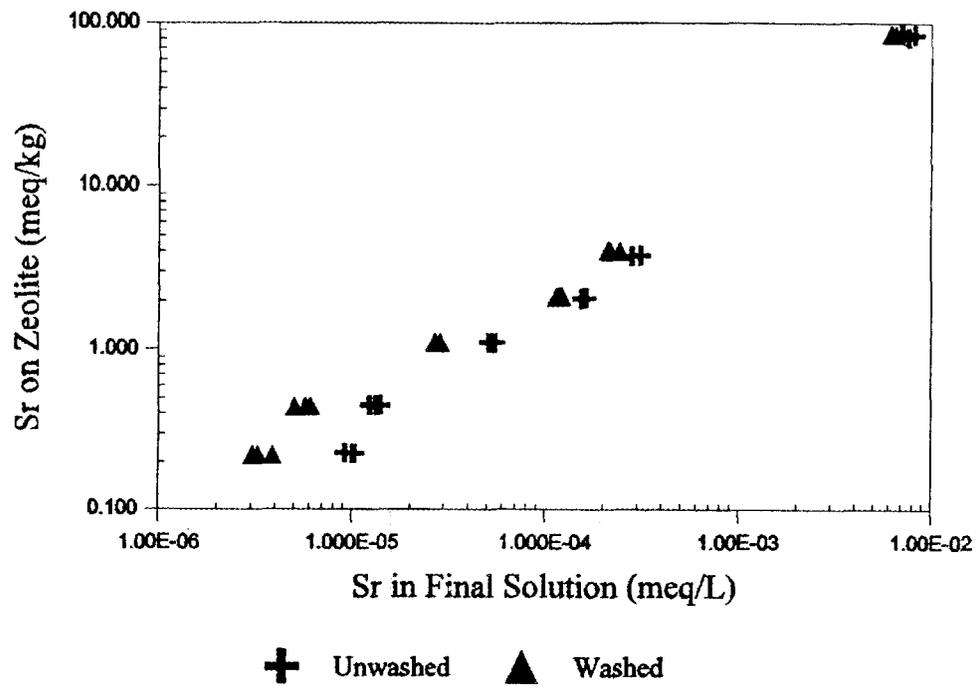
Figures 2 and 3 present the Sr and Cs isotherms on the prepared TSM-300 zeolite. The samples were prepared by adding 10 mL of traced simulant to sample tubes containing 5-100 mg chabazite zeolite. The samples were mixed for 24 h before being centrifuged and the supernates filtered. The isotherms are essentially linear at the low Sr and Cs loadings. The lowest data point on both graphs represents samples containing 100 mg of zeolite; the negative deviation of these points from the majority of the data probably reflects an insufficient mixing time for this quantity of zeolite. Least squares regression analysis of data, excluding the 100-mg zeolite samples, indicates that the  $R_s$  values for Sr and Cs are 16,000 L/kg and 77,000 L/kg, respectively.

The composition of the simulant in the final equilibrated simulant solution is essentially the same as the initial sample composition minus nuclide activity. The data obtained from the 100-mg zeolite samples indicate that the majority of Sr and Cs was removed from the 10-mL sample solution. Based on these results,  $2 \times 10^{-5}$  meq of Sr and  $3 \times 10^{-8}$  meq of Cs were exchanged with sodium on the zeolite. The incremental amount of sodium displaced into the 10-mL sample by sorption of Sr and Cs on the zeolite changed the soluble sodium concentration by less than 3%. The slight difference between the initial and final simulant



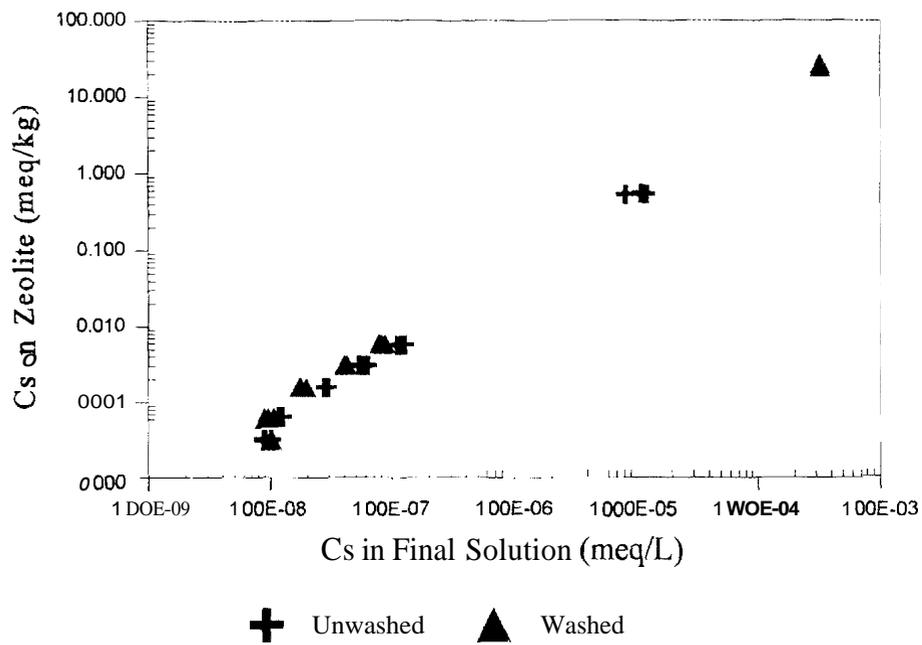
**Fig. 1. Sr and Cs equilibration time on washed TSM-300 chabazite zeolite.**

(Test conditions: 20 mg washed TSM-300 in 10 mL simulant, 0.00228 meq/L Sr and  $3.23 \times 10^{-6}$  meq/L Cs initial concentration; Labquake mixing at 20 cycles/min, samples centrifuged at 5000 rcf for 30 min.)



**Fig. 2. Sr sorption from PWTP simulant on TSM-300.**

(Test Procedure: 0.005-0.100 g TSM-300 in 10 mL solution; 24-h equilibration time; 0.00228 meq/L Sr initial concentration for lower data points; 0.05 meq/L Sr initial concentration for upper data point.)



**Fig. 3. Cs sorption from PWTP simulant on TSM-300.**

(Test Procedure: 0.005-0.100 g TSM-300 in 10mL simulant: 24-h equilibration time:  $3.237 \times 10^{-6}$  meq/L Cs initial concentration for lower data points; 0.00032 meq/L Cs for upper data points.)

composition from batch processing most likely implies that sorption results from batch testing should be directly applicable in determining zeolite column performance with the simulant.

### 3.3.4 Comparison of Washed Versus Unwashed Chabazite Zeolite

Figures 2 and 3 also present the logarithmic graph of Sr and Cs isotherms for unwashed TSM-300; the numerical data for this study are summarized in Table 6. Again, the samples were prepared by adding 10 mL of traced PWTP feed simulant to sample tubes containing 5-100 mg chabazite zeolite. Two sources of zeolite were used: the first was the sodium-washed zeolite that is the standard stock for this task, and the second was zeolite that had been sieved to remove the fines, but had not been previously equilibrated with NaCl. The uppermost point in the Sr and Cs isotherms reflects the addition of higher levels of these cations to the wastewater simulant to determine the loading capacity of the zeolites at 0.05 meq/L Sr and 0.00032 meq/L Cs.

Experimental data indicate that the log-log plot of the Cs sorption isotherm is linear up to the maximum Cs loading of 180 meq/kg. The only deviation from this behavior with either the washed or the unwashed zeolite is seen in the 100-mg zeolite data.

The Sr sorption on washed zeolite exhibits a slightly curvilinear behavior; Sr loading on the zeolite deviates positively from linearity above a value of 2 meq Sr/kg. This behavior is apparent for both the washed and unwashed TSM-300. The approximate  $R_s$  at low Sr loading is 15,400 L/kg.

The sorption profiles of washed versus unwashed zeolite indicate that Sr and Cs sorption are improved in samples containing the sodium-washed zeolite. The least squares regression analysis of the unwashed zeolite data indicates that the  $R_s$  for Cs is 50,000 L/kg as compared with 80,000 L/kg for the washed zeolite. Data pertaining to the washed zeolite samples indicate that the maximum loading capacity in the PWTP feed simulant is approximately 0.23 meq/kg Cs on TSM-300. The maximum Cs loading on the unwashed zeolite at a comparable Cs simulant concentration is slightly lower, 0.17 meq/kg. The sorption of Sr on TSM-300 is more dependent on zeolite washing. This, in fact, should be the case since one of the primary

reasons for washing the natural zeolite is to remove natural Sr present on the TSM-300 as received. The maximum loading capacity of the simulant containing 0.1 ppm Sr is 29% greater when the zeolite is pretreated with NaCl. A loading capacity of about 31 meq/kg can be obtained on the pretreated zeolite as compared with 23 meq/kg on the untreated sorbent. The difference in Sr loading between treated and untreated zeolite at the lower Sr solution

**Table 6. Sorption ratios for Sr and Cs ( $R_s$ ) on washed and unwashed TSM-300**

Initial Sr (meq/L)	Initial Cs (meq/L)	TSM-300 (g)	Avg Sr $R_s$ (L/kg)		Avg Cs $R_s$ (L/kg)	
			Washed	Un- washed	Washed	Un- washed
$2.28 \times 10^{-3}$	$3.23 \times 10^{-6}$	0.0050	18,000	12,400	74,600	49,900
$2.28 \times 10^{-3}$	$3.23 \times 10^{-6}$	0.0100	17,900	12,900	76,600	54,000
$2.28 \times 10^{-3}$	$3.23 \times 10^{-6}$	0.0200	39,300	20,600	85,800	54,600
$2.28 \times 10^{-3}$	$3.23 \times 10^{-6}$	0.0500	79,600	34,000	65,800	53,100
$2.28 \times 10^{-3}$	$3.23 \times 10^{-6}$	0.1000	65,900	22,800	31,300	36,100
$2.28 \times 10^{-3}$	$3.20 \times 10^{-4}$	0.0050	21,400	--	80,500	--
$5.00 \times 10^{-2}$	$3.23 \times 10^{-6}$	0.0050	23,300	--	76,300	--

concentrations is more typically 25%. It is obvious that removal of natural Sr from the chabazite zeolite is beneficial in cases where the  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  must compete for a relatively small number of available binding sites on the zeolite.

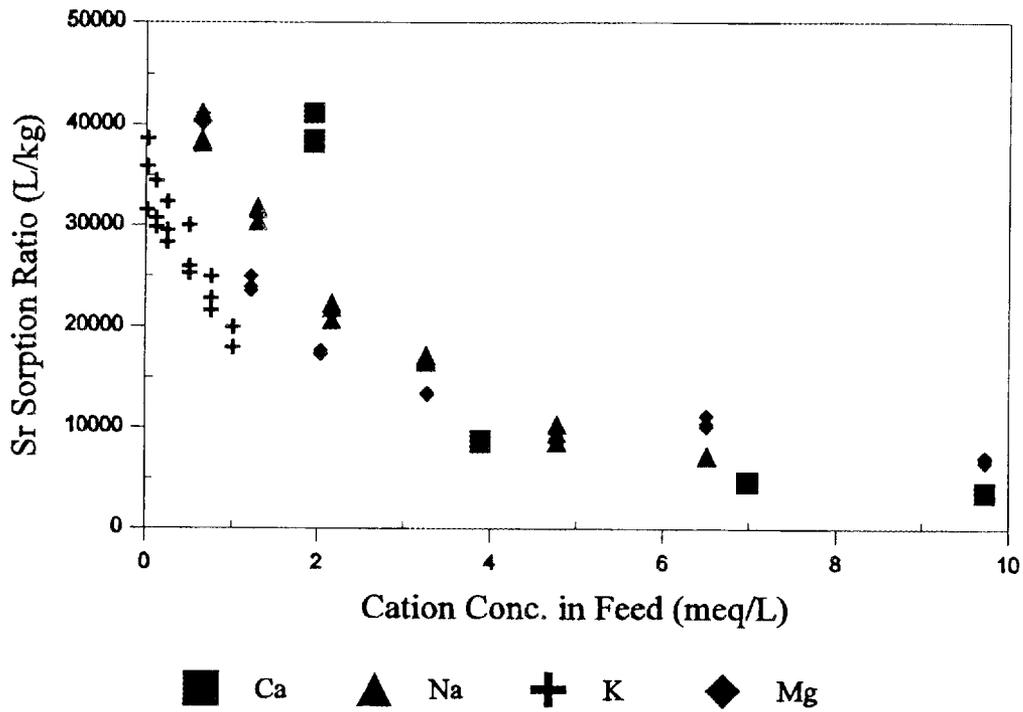
### 3.3.5 Effect of Calcium, Sodium, Potassium, and Magnesium on Sr and Cs Sorption

The effect of elevated calcium, sodium, potassium, and magnesium concentration on Sr and Cs sorption was studied using the washed TSM-300 zeolite stock. Higher concentrations of the individual cations were added as the chloride salts to the wastewater simulant to cover the concentration ranges of the individual cations found in typical groundwater. The total calcium ion in the simulant samples covered a range of 2-20 meq/L (as compared to 0.16-6 meq/L calcium in groundwater). The total sodium concentration in a second study covered a range of

0.5-6.5 meq/L (0.26-5.4 meq/L sodium present in groundwater). Potassium concentration was varied over the 0.025-1.03 meq/L range (0.01-0.8 meq/L potassium found in groundwater) to develop a third set of isotherms. In the final experiment, the magnesium concentration was adjusted to between 0.3 and 5 meq/L (0.025-10 meq/L magnesium in groundwater). The plots of Sr and Cs sorption ratios,  $R_s$ , as a function of cation concentration in the wastewater simulant are given in Figs. 4 and 5. All cations depress the sorption capacity of the zeolite for Sr and Cs, particularly in the 0-4 meq/L concentration range of each cation. In agreement with vendor literature, potassium ion had the most significant effect on Sr and Cs sorption capacity in the low cation concentration range. The  $R_s$  for both Sr and Cs decreased by approximately 50% in simulant containing up to 1 meq/L potassium. The effect of 0-4 meq/L magnesium, calcium, or sodium on radionuclide sorption appears to be roughly equivalent in these batch experiments. The sorption ratio for Sr and Cs decreased by 82% and 64%, respectively, for the range of magnesium typically encountered in groundwater. The effect of calcium was not as significant as that of potassium, although its effect in the 2-5 meq/L calcium range appears to be more significant than that of sodium. Above approximately 8 meq/L of either calcium or sodium, the sorption ratios for Sr and Cs are essentially constant.

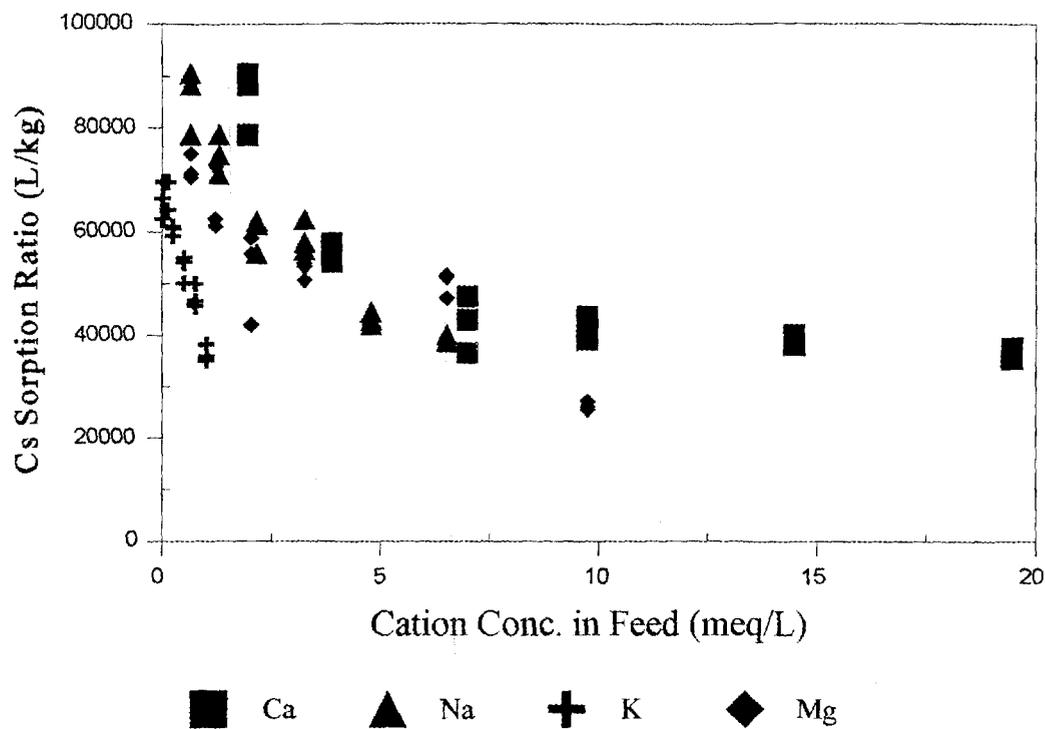
#### **4. TREATMENT OF ACTUAL PWTP FEED PROCESS WATER WITH TSM-300**

The Sr and Cs sorption from actual PWTP feed wastewater on washed TSM-300 was tested, both to serve as the baseline treatment process for actual process wastewater and as a means to validate the composition of the PWTP feed simulant that will be used in the testing of new technologies. Approximately 2 L of actual PWTP feed wastewater was collected and filtered through a 0.45- $\mu$ m cellulose nitrate filter membrane. A portion of the filtrate was acidified for ICP analysis of metal content; aliquots were also submitted for anion chromatography and radiological analysis of Sr and Cs radionuclides. The filtered wastewater was analyzed in the laboratory for carbonate and bicarbonate content on the day the sample was collected. The major components of the actual wastewater sample are summarized in Table 7. Comparison



**Fig. 4. Sr sorption as a function of total cation concentration in PWTP simulant.**

(Test procedure: 0.020 g TSM-300 in 10 mL simulant; 24-h equilibration time;  $2.26 \times 10^{-3}$  meq/L Sr initial concentration, cations added as chloride salts.)



**Fig. 5. Cs sorption as a function of total cation concentration in PWTP simulant.**

(Test procedure: 0.020 g washed TSM-300 in 10 mL simulant; 24-h equilibration time;  $2.56 \times 10^{-6}$  meq/L Cs initial concentration; cations added as the chloride salts.)

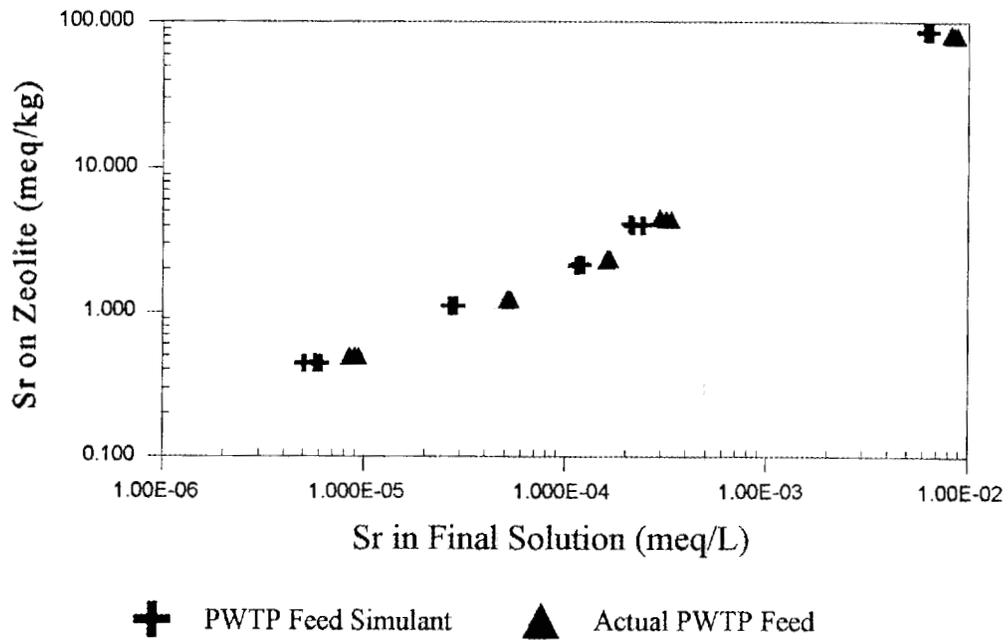
**Table 7. Composition of actual PWTP feed wastewater sample<sup>a</sup>**

Component	Concentration
ICP metals, ppm	
Calcium	38
Magnesium	6.8
Sodium	18.5
Silicon	2.8
Strontium (total)	0.11
Anions, ppm	
Chloride	3.8
Nitrate	34.5
Sulfate	22
Bicarbonate	152.5
Carbonate	3.4
Radionuclides, Bq/L	
<sup>134</sup> Cs	0.29
<sup>137</sup> Cs	2.50
<sup>89,90</sup> Sr	400

<sup>a</sup>Sample density is 0.9935g/L at 24.2°C.

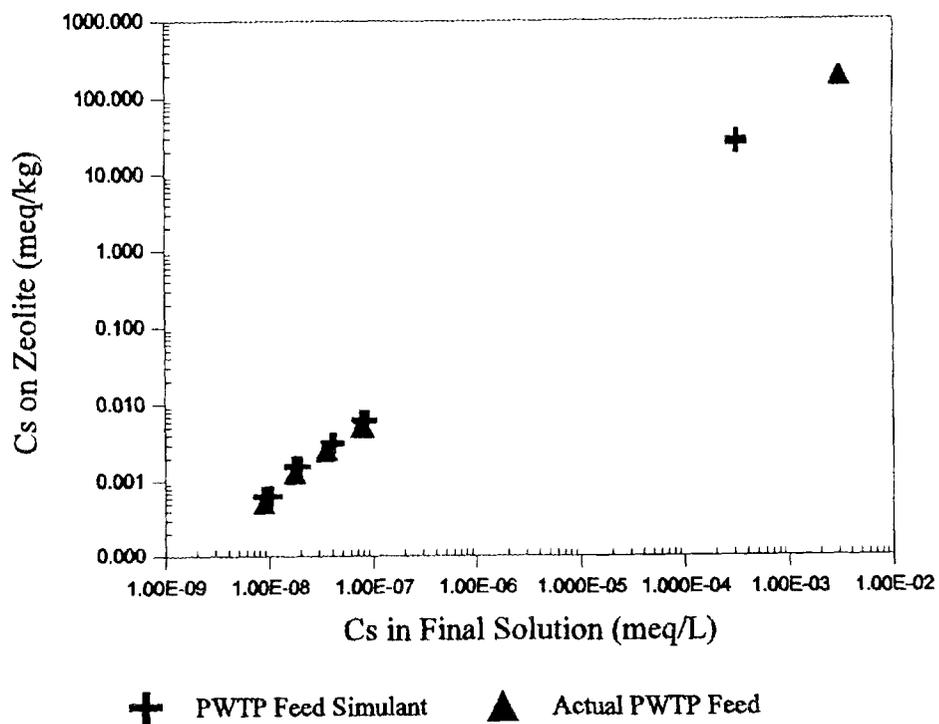
of the composition of this particular PWTP feed sample with that of the feed samples drawn earlier to establish the characteristics of the PWTP simulant indicates that only the nitrate concentration is slightly higher than the value selected for the simulant.

Batch testing of the actual PWTP feed sample was performed in a manner identical to that of the simulant samples. The filtered wastewater sample was traced at a level analogous to the simulant samples to meet the analytical detection limits of the gamma counting equipment in the laboratory. Additional inactive Sr and Cs were added to one PWTP feed sample set to provide sorption data at a high loading in this sample matrix. The 10-mL samples were mixed with 0.005-0.05 g of the washed TSM-300 zeolite for 24 h. Sorption results for the actual PWTP samples versus the PWTP simulant are presented in Figs. 6 and 7.



**Fig. 6. Sr sorption from actual PWTP feed and PWTP feed simulant.**

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



**Fig. 7. Cs sorption from actual PWTP feed and PWTP feed simulant.**

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

The sorption profiles of the actual PWTP wastewater samples are nearly identical to those of the simulant, although the  $R_s$  values for Sr and Cs in the actual waste are 80% and 90%, respectively, of the corresponding values determined using the simulant solution. The maximum Sr loading in the actual wastewater sample was calculated to be 24 meq/kg as compared to 31 meq/kg in the simulant. The maximum loading capacity of Cs in the actual PWTP feed sample was determined to be 0.17 meq/kg as compared to 0.23 meq/kg in the simulant. The close agreement between the actual wastewater results and the simulant suggests that the simulant composition is a close match with that of the PWTP feed waste stream and, as such, validates its use as a test matrix for studying other treatment technologies for wastewater decontamination. The sorption data also imply that the decontamination factors for Sr and Cs in this particular sample will be approximately 7-30 and 30-300, respectively.

#### 5. SMALL-COLUMN TESTING OF WASHED TSM-300

Small-column testing with washed TSM-300 will more accurately define the sorption characteristics of the benchmark material for treatment of actual PWTP feed wastewater. The dimensions of such a column were selected primarily on the basis of the diameter of the average zeolite particle,<sup>17</sup> although results of previous small zeolite experiments were used to modify initial estimates to allow for practical limitations in preparing large volumes of simulant and in the duration of the column test. According to the literature report, the optimum column diameter should be at least 40 times greater than the average zeolite particle diameter of 0.059 cm (30 mesh). Therefore, the column diameter should be 2.36 cm or greater. The optimum length of the column should be greater than or equal to four times the column diameter, indicating that the zeolite column should be at least 9.44 cm in length. The volume of the zeolite bed would thus be 41.3 cm<sup>3</sup>. TSM-300 zeolite has a wet-packed density of 0.43 g/cm<sup>3</sup>, indicating that the amount of zeolite required to fill the optimum-sized column is 17.7 g. The Sr loading capacity for the zeolite from the simulant containing 0.1 ppm Sr (0.00228 meq/L) was determined in sorption isotherms to be about 30 meq/kg. Previous column testing has shown that a fairly complete breakthrough curve can be obtained by providing about half the amount of sorbent needed for saturation of the exchanger. For Sr sorption on TSM-300 from the PWTP feed simulant, this is 11.6 mg Sr for the 0.0177-kg zeolite column. This amount of Sr is contained in 116 L solution or 2820 bed volumes (BV).

An 8-mL/min flow rate of simulant through the column was selected on the basis of successful small-column zeolite tests run previously in the lab. The 8-mL/min flow rate for the 17.7 g TSM-300 column would require 10 days if optimum column parameters were used. The Cs capacity of the zeolite from the wastewater simulant containing  $3.5 \times 10^{-4}$  ppm was about 0.2 meq/kg as measured in the sorption isotherms. About 0.24 mg Cs will be needed (or 692 L simulant) to reach 50% of the Cs column capacity. At a flow rate of 8 mL/min of simulant, approximately 60 days will be required to observe Cs breakthrough.

The difficulty in preparing such large quantities of simulant and maintaining column equipment for 60 continuous days of operation suggested that the zeolite column should be downsized to improve the chance of completing the column test successfully. Therefore, the small-column zeolite test was performed in a 1.0-cm column rather than in the optimum diameter of 2.4 cm. The 1.0-cm column diameter is about 17 times the average particle size of the -20/+50 mesh zeolite. Results from previously reported column tests performed with 30 to 35 mesh Ionsiv IE-96<sup>18</sup> were made in 1.0-, 1.5-, and 2.54-cm columns. Breakthrough results for magnesium, calcium, Sr, and Cs were about the same in the three columns when the bed depth-to-diameter ratio and the throughput rates were the same for the three column sizes. By inference, reducing the zeolite column diameter to 1 cm while maintaining the optimum values of the remaining parameters should not significantly alter the elution pattern of simulant components from the column. The smaller column would require the preparation of only 100 L of simulant and decrease the overall column test to 30 days.

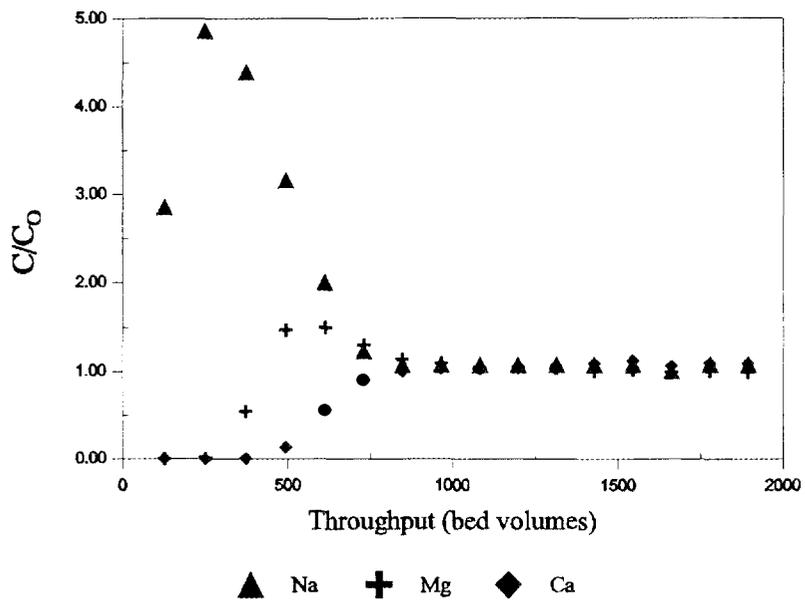
A 1-cm column was prepared by slowly adding prepared TSM-300 stock zeolite from a weighed container to a 1-cm column containing a known volume of water. The zeolite was added to the column to a bed depth of 4.5 cm. The dry zeolite container was reweighed to determine the weight of zeolite added to the 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 zeolite represents the pore volume of the zeolite column. The pore fraction is equivalent to the pore volume of the 1-cm column (2.5 mL) divided by the column volume calculated on the basis of a 4.5-cm bed height. The pore fraction of the 3.8-cm<sup>3</sup> column was 0.655 cm<sup>3</sup>.

The 100-L simulant was prepared by adding dry chemicals to 100 L of nanopure water and adjusting the pH of the column feed by sparging CO<sub>2</sub> gas into the solution for about an hour. The pH of the solution would drop to 5; however, the pH stabilized to a value of 7 after equilibrating for a few days. The solution was filtered with a 0.45- $\mu$ m Supor<sup>TM\*</sup> filter membrane recommended by the vendor for the clarification of groundwater samples. Stable Sr and Cs were added to the simulant at this point. A sample of the final simulant solution was analyzed for ICP metals and nuclide content. The <sup>85</sup>Sr and <sup>137</sup>Cs tracers were added to the first 15 L of the feed solution. Only <sup>137</sup>Cs tracer was added to the remainder of the simulant solution to reduce the radiological dose rate accumulated in the column. A Rainin Rabbit peristaltic pump was used to transfer the simulant through a second 0.45- $\mu$ m Supor filter membrane into the zeolite column. The flow rate of simulant feed was set at 1.28 mL/min to maintain a linear flow velocity similar to that in the earlier zeolite column tests. An automatic fraction collector was used to collect the column effluent over a 6-h period (or 460 mL). The actual fraction volume was 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.

The breakthrough curves for the major cations, Sr and Cs, are presented in Figs. 8 and 9. The fractional breakthrough ( $C/C_0$ ), defined as the ratio of the concentration of the cation in the column effluent as compared to the cation concentration in the feed, has been plotted against the number of BV of feed treated in the column. Figure 8 illustrates the initial displacement of sodium ion from the prepared zeolite as the cations in the feed are sorbed onto the column. Continued sorption of Sr and Cs on the zeolite results in the displacement of magnesium, beginning at 250 BV. Calcium is then displaced beginning at 500 BV. These curves imply that the selectivity of the treated zeolite is Ca > Mg > Na. The fraction breakthrough of the above cations stabilizes to a value of one at approximately 800 BV.

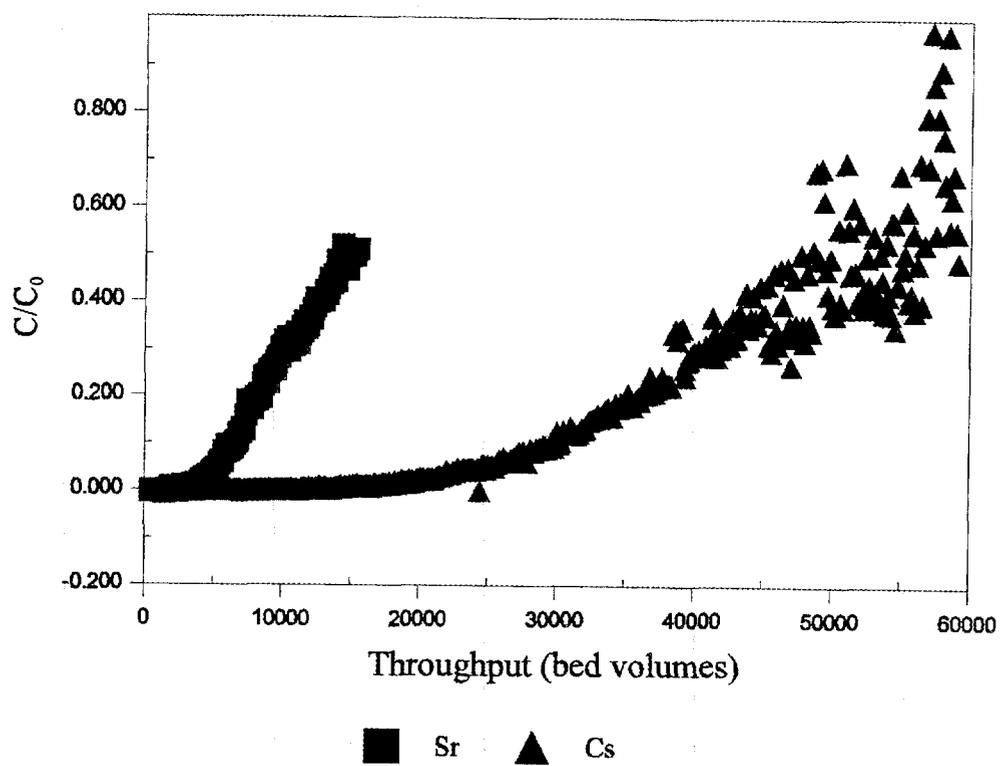
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**Fig. 8. Breakthrough curves for the major cation concentrations with washed TSM-300.**

(Column parameters: 2.2 g washed TSM-300 zeolite contained in a 1-cm -ID column having a bed volume of 3.84 cm<sup>3</sup>. The PWTP simulant feed flow rate is 1.25 mL/min.)



**Fig. 9. Sr and Cs breakthrough curves for washed TSM-300 zeolite.**

(Column parameters: 2.2 g washed TSM-300 zeolite contained in a 1-cm-ID column having a bed volume of 3.85 cm<sup>3</sup>. The PWTP simulant feed flow rate is 1.28 mL/min.)

Potassium concentration in the column effluent was not observed above the 1.5-mg/L detection limit of the ICP spectrophotometer. Strontium is first observed in the column effluent at approximately 3000 BV. Fractional breakthrough of 10% and 50% Sr occurs at 6500 and 13,000 BV, respectively. Under these experimental conditions, incipient breakthrough of Cs is noted at 12,500 BV. This experiment will be continued until full breakthrough of Sr and Cs is documented.

## 6. SUMMARY

The basic framework for comparing a baseline wastewater treatment technique with newly emerging treatment processes has been developed. A prototypical waste stream has been selected for the study so that a standard simulant can be formulated based on its composition. The feed stream to the PWTP facility at ORNL was selected as the water source because it is composed of radiologically contaminated groundwater and wastewater and matches the composition of wastewaters prevalent at other DOE installations. Several samples of the PWTP feed stream were collected and sampled for ICP metals, anions, and radionuclide composition. A simulant of the feed stream was formulated that contained calcium, sodium, and magnesium as the primary dissolved metal components. Bicarbonate, sulfate, chloride, and nitrate represent the bulk of the anionic species. Inactive Sr was added at a level of 0.1 ppm to the simulant; approximately  $1 \times 10^6$  Bq/L of  $^{85}\text{Sr}$  and  $^{137}\text{Cs}$  was added to the simulant so that the decontamination efficiency of the treatment methods could be followed adequately with available gamma counting equipment.

Natural chabazite zeolite was selected as the benchmark sorbent for the removal of Sr and Cs from contaminated wastewater. The zeolite (TSM-300) was purchased from Steelhead Specialty Minerals, located in Spokane, Washington. A stock supply of TSM-300 was pretreated to remove the natural Sr present on the zeolite as received. Pretreatment consisted of washing the TSM-300 with 2 M NaCl, followed by a water rinse to remove excess sodium ion. The -20 to +50 mesh fraction of the air-dried TSM-300 represents the reference sorbent for the remaining studies in this task.

Testing of the standard zeolite treatment included determining the Sr and Cs sorption rates using batch testing procedures. Twenty-four hours is required to reach sorption equilibrium in 10-mL batch samples containing 0.005 to 0.05 g zeolite. A longer mixing time is required for samples containing greater amounts of TSM-300.

Strontium sorption on pretreated TSM-300 was observed in samples containing an initial solution concentration of  $2.28 \times 10^{-3}$  meq Sr/L. The Sr sorption isotherm exhibited a curvilinear profile; Sr loading deviated positively from linearity above a Sr loading of 2 meq/kg. The  $R_s$  at low Sr loading on washed zeolite is approximately 17,000 L/kg; the comparable  $R_s$  on unwashed zeolite is 30% lower. The difference in the behavior of the two sources of zeolite indicates the availability of additional sorption sites created when the natural Sr is removed during saline washing of TSM-300.

Cesium sorption was observed in samples containing an initial concentration of  $3.23 \times 10^{-6}$  meq/L Cs. The Cs sorption isotherm was found to be linear with Cs solution concentration. The  $R_s$  for Cs on the prepared zeolite is 80,000 L/kg as compared with 50,000 L/kg on the unwashed TSM-300. The effect of potassium, magnesium, sodium and calcium on Sr and Cs sorption was determined on washed zeolite and found to depress radionuclide sorption, particularly over the 0-8 meq/L range.

On completion of testing with the simulant, the Sr and Cs sorption from actual PWTP feed wastewater was observed on washed TSM-300. The sorption profiles of the actual PWTP feed sample were nearly identical to those obtained with the simulant, indicating the close match between the chemical composition of the simulant and actual waste steam. Maximum loading from the actual wastewater sample onto treated TSM-300 was calculated to be 24 meq/kg Sr and 0.17 meq/kg Cs.

A small-column test has been initiated using a 1-cm-diameter column and 2.2 g of washed TSM-300 zeolite. The elution pattern of the major cations in the simulant suggests that the treated chabazite zeolite has a selectivity order of  $Cs > Sr > Ca > Mg > Na$ . Although the potassium elution front could not be observed during column testing, results from batch tests imply that potassium selectivity falls above that of calcium. Strontium breakthrough was first noted at approximately 3000 BV; 50% breakthrough was observed at 13,000 BV.

Incipient Cs breakthrough occurred at 12,500 BV. The column will be run to exhaustion in order to observe complete Sr and Cs breakthrough.

This report concludes the development of the testing procedures required to define the sorption behavior of the zeolite baseline wastewater treatment techniques. New sorbents will be similarly tested so that a direct comparison of sorption capacity can be made with the benchmark method. The relative merits of SuperLiq<sup>®</sup> molecular recognition sorbents and the Savannah River Laboratory resorcinol formaldehyde resin will be evaluated in the near future.

## 7. REFERENCES

1. S. M. Robinson and J. R. Parrott, Jr., *Pilot-Scale Demonstration of Process Wastewater Decontamination Using Chabazite Zeolites*, ORNL/TM-10836, December 1989.
2. C. P. Staub (ed.), *Practical Handbook of Environmental Control*, CRC Press, Boca Raton, Florida, 1989.
3. L. E. McNeese, J. B. Berry, G. E. Butterworth III, E. D. Collins, T. H. Monk, B. D. Patton, and J. W. Snider, *Overall Strategy and Program Plan for Management of Radioactively Contaminated Liquid Wastes and Transuranic Sludges at the Oak Ridge National Laboratory*, ORNL/TM-10757, December 1988.
4. M. A. Franson (ed.), *Standard Methods for the Examination of Water and Wastewater*, 18th ed., American Public Health Association, Washington, D.C., 1992, pp. 2-23 to 2-28.
5. G. V. James, *Water Treatment: A Guide to the Treatment of Water and Effluents Purification*, 3rd ed, The Darien Press Ltd., Edinburgh, United Kingdom, 1965, pp. 107-127.
6. A. Dyer and D. Keir, *Zeolites*, **4**, 215-217 (1984).
7. P. Burns, et al., *AIChE Symp. Ser.*, **83** (259), 66-73 (1987).
8. D. C. Grant, et al., *Effects of Process Variables on the Removal of Contaminants from Radioactive Waste Streams Using Zeolites*, presented at the Waste Management '87 Symposium, Tucson, Arizona, March 1987.
9. R. H. Hawkins and J. H. Horton, *Zeolite Prefilter to Reduce Pluggage in Zeolite Cesium Removal Column*, DP-1245, Savannah River Laboratory, Aiken, South Carolina, January 1971.
10. S. M. Robinson and J. R. Parrot, Jr., *Pilot-Scale Demonstration of Process Wastewater Decontamination Using Chabazite Zeolites*, ORNL/TM-10836, December 1989.

11. S. M. Robinson and J. M. Begovich, *Treatment Studies at the Process Waste Treatment Plant at Oak Ridge National Laboratory*, ORNL/TM-10352, March 1991.
12. T. E. Kent, S. A. Richardson, A. C. Coroneous, A. J. Lucero, and J. J. Perona, *Zeolite Ion-Exchange System Development for Treatment of ORNL Process Wastewater*, Draft Letter Report, Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, August 31, 1991.
13. R. L. Siegrist et al., *DOE In Situ Remediation Integrated Program: In Situ Physical/Chemical Treatment Technologies — Subarea Program Plan*, Environmental Sciences Division Publication 4238, Oak Ridge National Laboratory, June 1994.
14. S. M. Robinson, T. E. Kent, W. D. Arnold, and J. R. Parrott, Jr., *The Development of a Zeolite System for Upgrade of the Process Waste Treatment Plant*, ORNL/TM-12063, October 1993.
15. T. E. Eyde, "Using Zeolites in the Recovery of Heavy Metals from Mining Effluents," in *Proceedings of the Extraction and Processing Division*, TMS Annual Meeting, ed. J. P. Hager, Denver, Colorado (Feb. 21-25, 1993).
16. *Testing Sieves and Their Uses, Handbook 53*, 1962 ed., The W. S. Tyler Company.
17. J. F. Relyea, "Theoretical and Experimental Considerations for Use of the Column Method for Determining Retardation Factors," *Radioact. Waste Manage. Nuc. Fuel Cycle*, 3, 151-156 (1982).
18. S. M. Robinson, W. D. Arnold, Jr., and C. W. Byers, *Multicomponent Liquid Ion Exchange with Chabazite Zeolites*, ORNL/TM-12403, October 1993.



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