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**Evaluation of Improved Techniques for  
the Removal of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  from  
Process Wastewater and Groundwater:  
FY 1995 Status**

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Chemical Technology Division

**EVALUATION OF IMPROVED TECHNIQUES FOR  
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FY 1995 STATUS**

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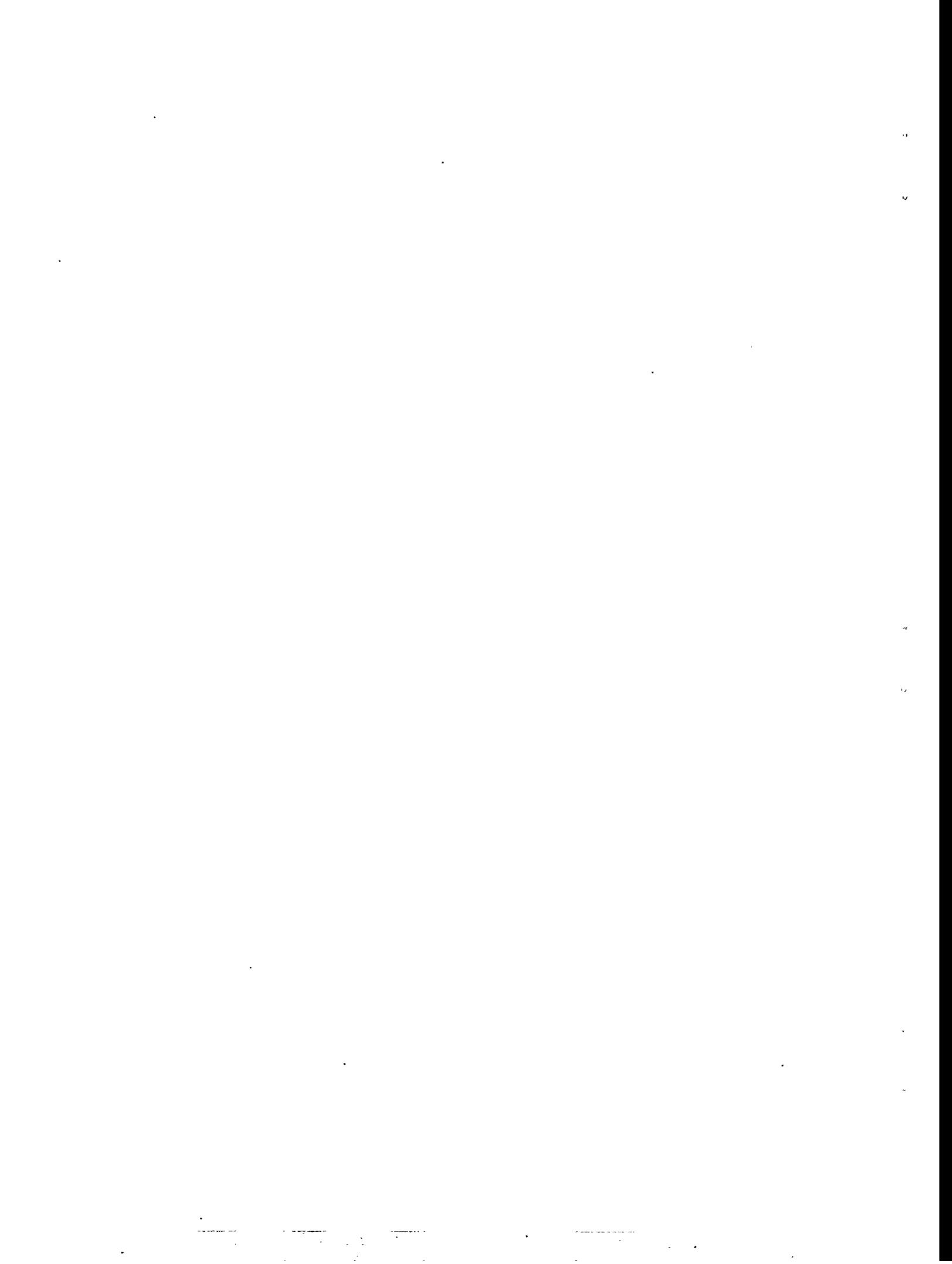
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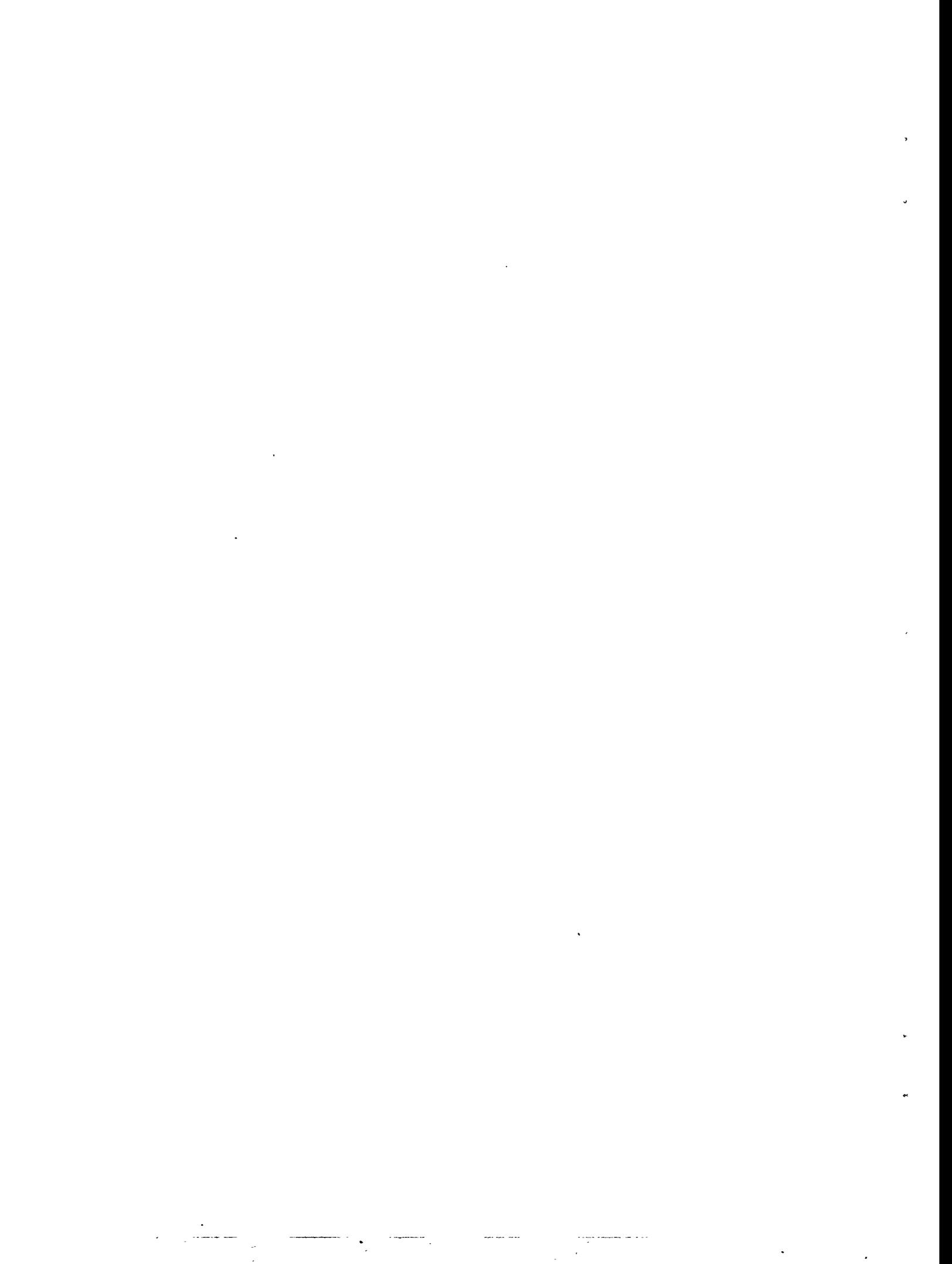
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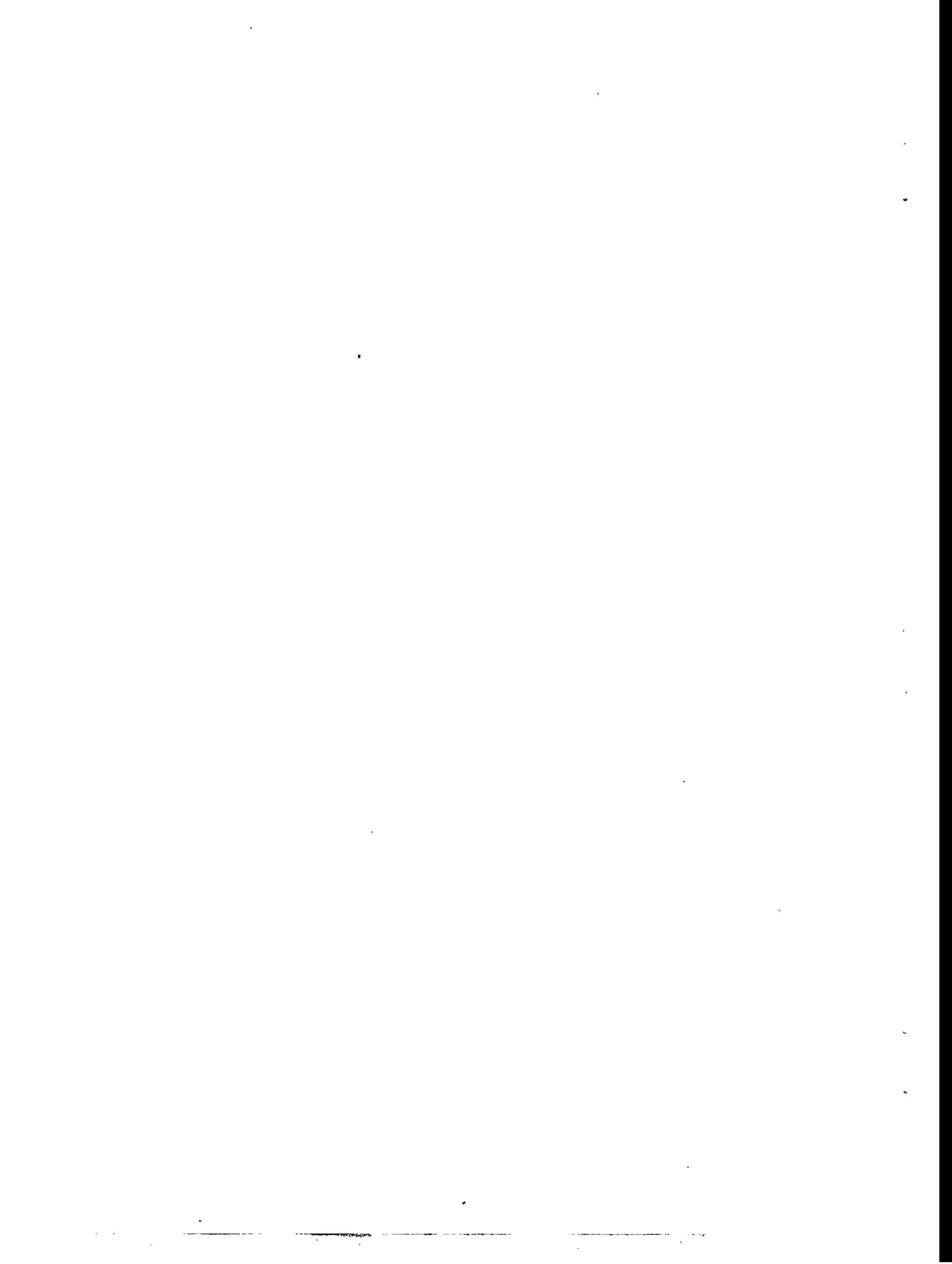
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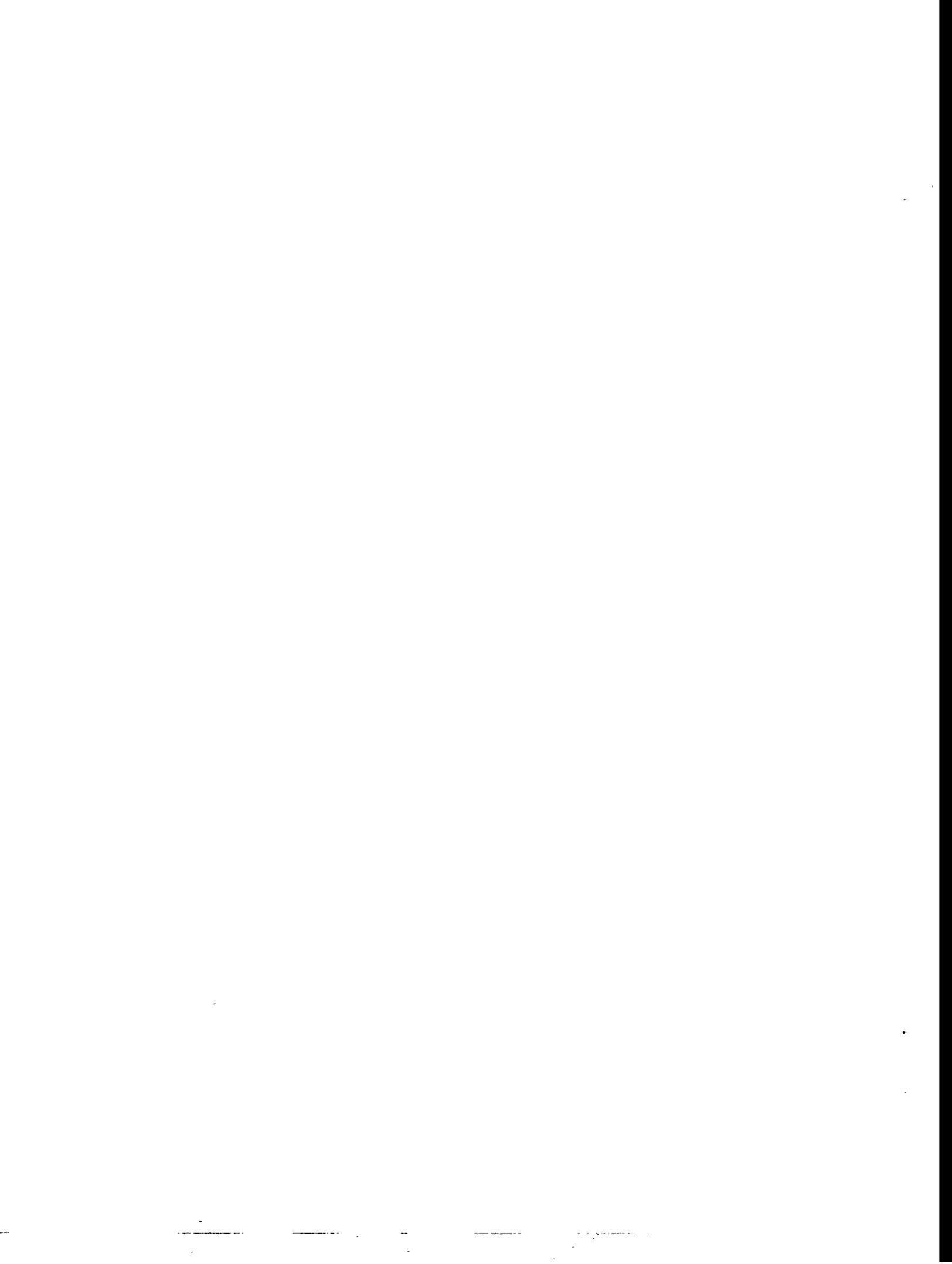
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## ACRONYMS AND ABBREVIATIONS

B.E.T.	Brunauer, Emmett, Teller
BSC	Boulder Scientific Company
BV	bed volume
$C_s$	saturation concentration in solution
DOE	Department of Energy
ESP	efficient separations/processes
FY	fiscal year
ICP	inductively coupled plasma
$K_d$	distribution coefficient
LLW	low-level waste
ORNL	Oak Ridge National Laboratory
PGDP	Paducah Gaseous Diffusion Plant
PWTP	Process Waste Treatment Plant
$Q_s$	amount of nuclide sorbed per unit mass of sorbent
rcf	relative centrifugal force
$R_s$	sorption ratio
R-F	resorcinol-formaldehyde
SRL	Savannah River Laboratory
SRS	Savannah River Site
TRU	transuranic
WAG	Waste Area Grouping



## ABSTRACT

A number of new sorbents are currently being developed for the removal of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  from contaminated, caustic low-level liquid waste (LLLW). These sorbents are potentially promising for use in the cleanup of contaminated groundwater and process wastewater containing the two radionuclides. The goal of this subtask is to evaluate the new sorbents to determine whether their associated treatment technology is more selective for the decontamination of wastewater streams than that of currently available processes.

Activities during fiscal year 1995 have included completing the characterization of the standard treatment technology, ion exchange on chabazite zeolite. Strontium and cesium sorption on sodium-modified zeolite was observed in the presence of elevated concentrations of wastewater components: sodium, potassium, magnesium, and calcium. The most significant loss of nuclide sorption was noted in the first 0- to 4-meq/L addition of the cations to a wastewater simulant. Radionuclide sorption on the pretreated zeolite was also determined under dynamic flow conditions. Cation selectivity on the zeolite was determined to be  $\text{Cs} > \text{Sr} > \text{Ca} > \text{Mg} > \text{Na}$ , as denoted by cation breakthrough from a zeolite column with a 4-mL bed volume (BV). Strontium was first observed in the column effluent at 3000 BVs; incipient cesium breakthrough occurred at 15,000 BVs. The sorption ratio ( $R_s$ ) values for strontium and cesium on the column were calculated to be 16,800 and 53,000 L/kg, respectively.

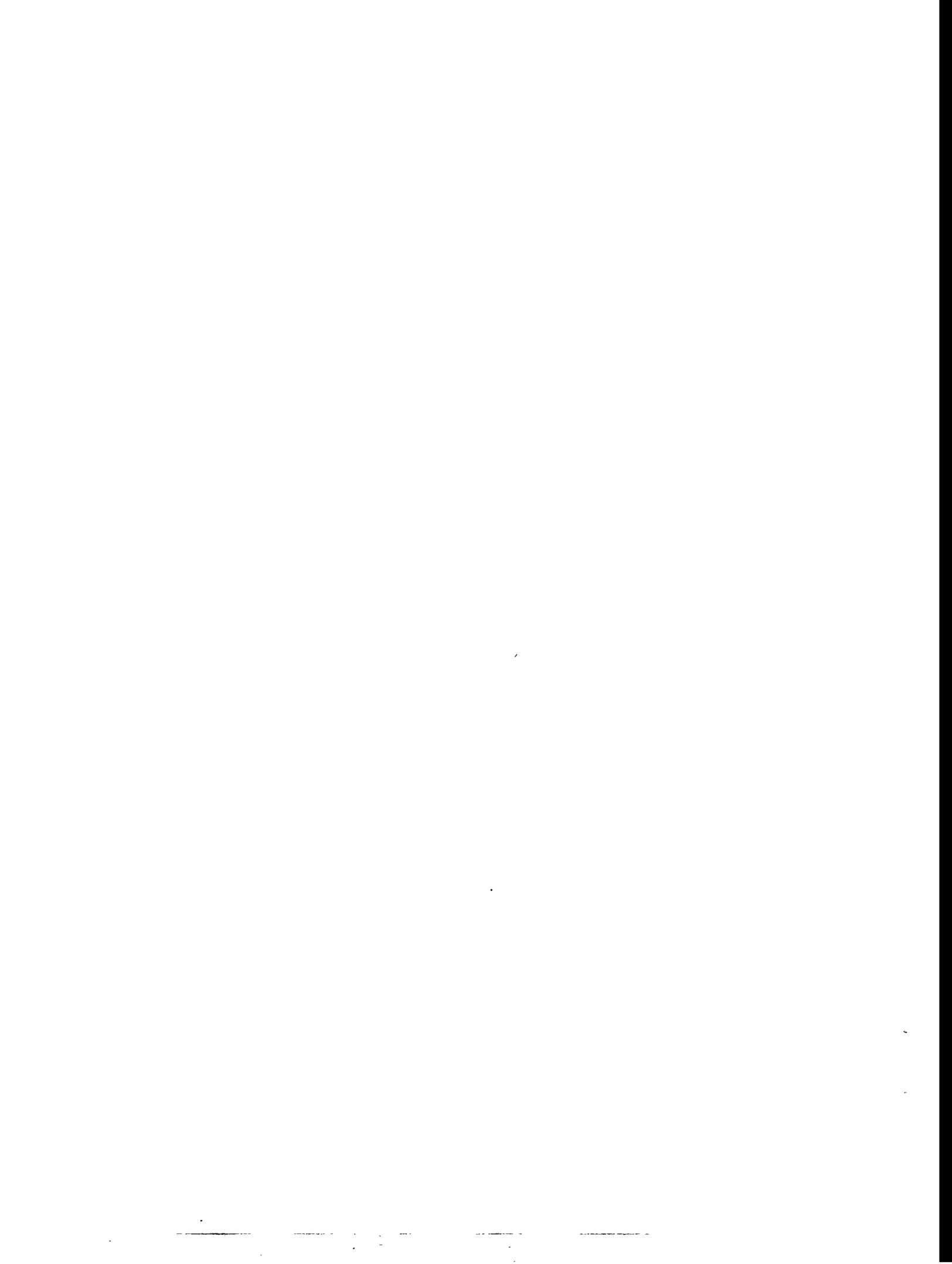
Resorcinol-formaldehyde (R-F) resin, which was developed at the Savannah River Site, was selected as the first new sorbent to be evaluated for wastewater treatment. Nuclide sorption on this resin was greater when the resin had been washed with ultrapure water and air dried

prior to use. Cesium sorption on the pretreated resin was linear with the cesium concentration in the test solution. The cesium  $R_s$  from wastewater simulant containing an initial cesium concentration of  $2.5 \times 10^{-6}$  meq/L was 11,000 L/kg; the sorption capacity of the resin was 0.02 meq/kg. These values are compared with 80,000 L/kg and 0.17 meq/kg, respectively, for pretreated zeolite under identical experimental conditions.

The strontium sorption data can be described using the Brunauer, Emmett, Teller (B.E.T.) model for multilayer adsorption. The strontium  $R_s$  is, therefore, dependent on the sample volume-to-resin mass ratio. When this treatment ratio was greater than a value of 1 mL per milligram of resin, strontium sorption on zeolite exceeded that on the resin; however, the reverse was true when the ratio was less than 1 mL per milligram of resin. This sorption behavior was maintained for process wastewater simulant, actual process wastewater, and actual groundwater samples.

Sorption of strontium and cesium on the R-F resin was suppressed by elevated concentrations of the significant monovalent and divalent cations present in the wastewater. Cesium sorption on pretreated resin was greater than that on the untreated resin, regardless of the quantity of cation in solution. Strontium sorption on the R-F resin appeared to be more strongly affected by the presence of calcium than was observed for zeolite. Although strontium sorption was more efficient on the R-F resin at low concentrations (40 ppm) of calcium, zeolite treatment remained the choice for strontium removal at higher competing cation concentrations.

The characterization of radionuclide sorption of water-washed R-F resin will be completed as part of our FY 1996 activities. Additionally, monosodium titanate will be investigated as a sorbent for wastewater treatment applications.



## 1. INTRODUCTION

The Efficient Separations and Processing (ESP) Crosscutting Program supports activities designed to remove radionuclides and hazardous materials from radioactive defense waste streams throughout the DOE complex. One of the goals of this program is to identify new sorbents, ion-exchange materials, or processes that might be more selective than current treatment methods for the decontamination of wastewater streams. Because the principal radioactive contaminants in DOE wastewater are  $^{90}\text{Sr}$  and  $^{134,137}\text{Cs}$ , the initial focus of the subtask was to evaluate separation techniques that are potentially promising for the removal of these two radionuclides from contaminated groundwater and process wastewater.

Materials and processes to be investigated during the course of this task include the molecular recognition materials that were developed by IBC Advanced Technologies, Inc., (Provo, UT) and immobilized using 3M Corporation technology. The resorcinol-formaldehyde (R-F) resin developed at the Savannah River Site (SRS) and the monosodium titanate and crystalline silicotitanates developed at Sandia National Laboratory and Texas A&M University will also be evaluated. The objectives of the laboratory studies are to obtain a quantitative understanding of the behavior of these new materials and to evaluate their sorption efficiency in reference to a standard benchmark treatment technique.

As the first step in the evaluation procedure, each new material was subjected to a series of scoping tests where it was compared with standard, commercially available materials in batch shaker experiments. Equilibrium tests were then conducted under various treatment conditions (pH, temperature, waste composition) for the most promising materials.

Additional experiments with actual groundwater and process wastewater were conducted

with the most effective treatment methods. Once batch-testing of a treatment method was completed, dynamic studies were performed to define column operating parameters.

Activities during FY 1994 were directed toward laying the groundwork for comparative testing of the new technologies vs a standard treatment technique. Laboratory efforts focused on selecting for treatment studies a process waste stream that typified wastewater encountered at DOE sites. A review of DOE site wastewater streams and groundwater indicated that the influent to the Oak Ridge National Laboratory (ORNL) Process Waste Treatment Plant (PWTP) reflects the general composition of DOE wastewater. A simulant of the waste stream was then formulated so that a standard waste solution could be used for comparative testing of the selected treatment methods. The decontamination efficiency of the standard treatment sorbent, chabazite zeolite, was summarized. Strontium and cesium sorption capacities on the zeolite were determined from batchwise treatment of the simulant. The suppression of nuclide sorption capacity by the sodium and calcium present in contaminated waters was also quantified. An actual sample of the selected waste stream was subsequently treated with the standard technique. The strontium and cesium sorption isotherms for the actual wastewater matched those observed for the simulant. Finally, a test with a small zeolite column was initiated to observe  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  breakthrough characteristics under dynamic flow conditions. The development of a defined waste simulant and the discussion of the decontamination efficiency of the standard treatment technique formed the bases with which to compare the effectiveness of all new treatment technologies to be studied as a part of this subtask.

Activities in FY 1995 included completing the zeolite column test, summarizing the sorption efficiency of chabazite zeolite in a topical report,<sup>1</sup> and evaluating the first new treatment method. Following completion of the zeolite studies, the evaluation of molecular recognition materials was initially scheduled as the first new sorbent to be reviewed. However, although IBC Advanced Technologies, Inc., has developed solid-phase extraction materials for the removal of radionuclides from highly caustic wastes, none of these are suitable for wastewater treatment applications. Therefore, studies using the R-F resin were substituted for those with the molecular materials. This report summarizes the final results of the study with the chabazite zeolite column and compares the sorption efficiency of the R-F resin with that observed for the zeolite.

## **2. FORMULATION OF WASTE STREAM SIMULANT**

### **2.1 SELECTION OF WASTE STREAM**

In a continuation of FY 1994 efforts, studies in FY 1995 included determination of the sorption capacities of sorbents in a process waste stream that typified those encountered generally at DOE sites. An FY 1994 review of the compositions of DOE wastewater and groundwater concluded that the process wastewater treated at the Process Waste Treatment Plant (PWTP) at Oak Ridge National Laboratory (ORNL) would be a representative waste stream that could be used in the testing of actual wastewater samples.

As can be seen in Table 1, the principal chemical constituents previously reported for the PWTP feed were calcium, magnesium, and sodium bicarbonates, which are introduced by the presence of contaminated groundwater in the feed stream. The final column in the table summarizes the spread in concentration of typical groundwater components.<sup>2</sup> The

composition of the PWTP feed wastewater falls within the ranges of concentration of the general description for groundwater composition. It is also similar in content to several groundwaters at other local DOE facilities<sup>3</sup> (Paducah and Portsmouth Gaseous Diffusion plants). 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.

The selection of a waste stream was broadened in FY 1995 to encompass the treatment of contaminated groundwater that is specific to the ORNL site. Table 1 summarizes the composition of seep-water samples collected at three Waste Area Groupings (WAGs) located on the ORNL site. Authentic groundwater samples used in FY 1995 treatment studies were collected from a groundwater quality monitoring well located at the down-gradient perimeter to WAG 5. The well site is located directly south of the main ORNL plant in Melton Valley and includes areas that are devoted to the disposal of solid LLW (Solid Waste Storage Area 5) and the Transuranic (TRU) Waste Storage Area.

## 2.2 FORMULATION OF PWTP SIMULANT

The formulation of the PWTP process wastewater simulant is identical to that used in FY 1994 and is included in Table 2 for reference purposes. A decision was made in FY 1994 to include cations in the simulant that were present in concentrations equal to or greater than 1 ppm in PWTP feed samples. Strontium and cesium are the exceptions to this delineation. Strontium was included at a level of 0.1 mg/L 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 <sup>134</sup>Cs and <sup>137</sup>Cs are normally absent in groundwater but are present at an average level of 300 Bq/L in PWTP influent. The total <sup>137</sup>Cs added to the simulant is present at a tracer level of  $1.12 \times 10^6$  Bq/L

**Table 1. Compositions of DOE site groundwater and process wastewater**

Component	Concentration (mg/L)				
	WAG 5 <sup>a</sup>	WAG 6 <sup>b, c</sup>	WAG 7 <sup>a</sup>	PWTP feed <sup>d</sup>	General <sup>e</sup>
Element					
Al	~0.22	NR <sup>f</sup>	~1.3	0.48	0.003 to 0.083
B	<0.080	<0.88	~0.15	<0.08	0 to 0.50
Ca	95	106	79	75	3.2 to 121
Co	NR	<0.044	~0.0083	<0.004	NR
Cr	NR	0.086	~0.0047	0.008	ND <sup>g</sup> to 0.001
Cu	~0.010	<0.08	~0.0078	0.037	0 to 0.015
Fe	~0.55	<0.55	~1.6	2.2	0.001 to 6.6
K	~2.6	NR	~3.4	2	0.4 to 30
Mg	18	14.0	19	12	0.3 to 120
Mn	0.26	0.031	~0.24	0.16	ND to 0.34
Na	24	8.06	120	64	6.1 to 129
Ni	~0.013	0.161	~0.041	0.024	ND to <0.015
Pb	NR	<0.55	~0.020	<0.2	ND to 0.038
Si	8.4	7.23	8.7	2.6	2.0 to 33.6
Sr	NR	0.219	NR	0.19	0.019 to 6.3
Zn	~0.0078	<0.55	~0.0075	0.27	ND to <0.47

Table 1 (continued)

Component	Concentration (mg/L)				
	WAG-5 <sup>a</sup>	WAG-6 <sup>b,c</sup>	WAG-7 <sup>a</sup>	PWTP feed <sup>d</sup>	General <sup>e</sup>
Anion					
HCO <sub>3</sub> <sup>-</sup>	NR	NR	NR	93	55 to 364
CO <sub>3</sub> <sup>2-</sup>	NR	NR	NR	7	0 to 5
SO <sub>4</sub> <sup>2-</sup>	50	NR	160	28	0.8 to 572
NO <sub>3</sub> <sup>-</sup>	~0.29	NR	~140	11	0.0 to 17
Cl <sup>-</sup>	11	NR	14	11	2.0 to 92
F <sup>-</sup>	~0.14	NR	~0.93	1	0.0 to 7.0
Alkalinity	310	200	300	125	NR
pH	8.5 to 5.9	4.8 to 7.9	8.6 to 6.6	NR	6.7 to 8.7
Conductivity, mS/cm	0.76	0.31	1.1	NR	NR

<sup>a</sup> Oak Ridge Reservation Environmental Report for 1994, Volume 2: Data Presentation, ES/ESH-18/V2.

<sup>b</sup> Oak Ridge Reservation Environmental Report for 1991, Volume 2: Data Presentation, ES/ESH-18/V2.

<sup>c</sup> ORNL Analytical Chemistry Division's analysis of sample submitted on July 30, 1993.

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

<sup>f</sup> NR = not reported.

<sup>g</sup> ND = not detected.

**Table 2. Chemical formulation of 4 L of PWTP feed simulant<sup>a</sup>**

Chemical	Weight (g)	Chemical	Weight (g)
CaCO <sub>3</sub>	0.36604	NaF	0.00707
Ca(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O	0.04037	Na <sub>3</sub> PO <sub>4</sub> · 12H <sub>2</sub> O	0.03362
CaCl <sub>2</sub>	0.00710	Na <sub>2</sub> SiO <sub>3</sub> · 9H <sub>2</sub> O	0.12548
MgSO <sub>4</sub>	0.10174	NaHCO <sub>3</sub>	0.10863
MgCl <sub>2</sub> · 6H <sub>2</sub> O	0.09582	K <sub>2</sub> CO <sub>3</sub>	0.00707
Ferri-Floc <sup>b</sup>	0.160 mL		

<sup>a</sup> Inactive strontium, <sup>85</sup>Sr, and <sup>137</sup>Cs are added to the simulant just prior to experimentation, to reduce the possibility of losing these cations by sorption onto labware.

<sup>b</sup> Solution containing 10,000 ppm iron and 25,800 ppm sulfate.

(equivalent to 0.00034 mg of cesium per liter). The levels of both <sup>85</sup>Sr and <sup>137</sup>Cs in the simulant were selected on the basis of the efficiency of gamma spectrometer counting equipment to be used throughout the sorption studies. The composition of the average PWTP simulant, as well as the compositions of a specific PWTP feed and the WAG 5 groundwater used in the FY 1995 sorbent testing of actual wastewater samples, are summarized in Tables 3 through 5.

**Table 3. Results of chemical analyses<sup>a</sup> of PWTP feed, WAG 5 samples, and PWTP simulant**

Element	Concentration (ppm)		
	Actual PWTP feed	Actual WAG 5 sample	PWTP simulant
Ag	<0.005	<0.005	<0.005
Al	<0.050	<0.050	<0.050
As	<0.050	<0.050	<0.050
B	<0.080	0.160	<0.080
Ba	0.025	0.300	0.0036
Be	<0.001	<0.001	<0.001
Ca	36	100	37.0
Cd	<0.005	<0.005	<0.005
Co	<0.004	0.007	<0.004
Cr	<0.004	<0.004	<0.004
Cs	Na <sup>b</sup>	NA	NA
Cu	<0.007	<0.007	<0.007
Fe	<0.050	1.50	<0.05
K	2.5	2.70	2.0
Li	<0.005	<0.005	<0.005
Mg	7.4	14.0	6.5
Mn	0.0015	8.20	0.0013
Mo	<0.040	<0.040	<0.040
Na	27	12.0	14.0
Ni	<0.010	<0.010	<0.01
P	<0.3	<0.30	0.42
Pb	<0.050	<0.050	<0.05
Sb	<0.050	<0.050	<0.05
Se	<0.050	<0.050	<0.05
Si	1.8	6.30	3.1
Sn	<0.050	<0.050	<0.05
Sr	0.095	0.22	0.023
Ti	<0.020	<0.020	<0.02
V	0.0021	<0.002	<0.002
Zn	0.022	0.74	0.019
Zr	<0.02	<0.02	<0.02

<sup>a</sup> Metal analyses were done by inductively coupled plasma spectroscopy.

<sup>b</sup> NA = not analyzed.

**Table 4. Results of chemical analyses<sup>a</sup> of PWTP feed, WAG 5 samples, and PWTP simulant**

	Concentration (mg/L)		
	Actual PWTP feed	Actual WAG- 5 groundwater	PWTP simulant
Alkalinity <sup>b</sup>	138	398	158 <sup>c</sup>
Anions			
Cl <sup>-</sup>	9.1	12	8.7
F <sup>-</sup>	1.0	<0.1	0.8
Br <sup>-</sup>	0.16	0.20	NA <sup>d</sup>
NO <sub>3</sub> <sup>-</sup>	37	<0.1	5.3
PO <sub>4</sub> <sup>3-</sup>	0.78	<0.5	2.1
SO <sub>4</sub> <sup>2-</sup>	25	10	21.3
pH	9.07	7.06	7.83

<sup>a</sup> Anion analysis was done by ion chromatography.

<sup>b</sup> As CaCO<sub>3</sub>.

<sup>c</sup> Calculated from the following equation:

$$\text{Alkalinity} = 1.219 \times [\text{HCO}_3^-].$$

<sup>d</sup> NA = not analyzed.

**Table 5. Radiochemical analyses of PWTP feed and WAG 5 samples**

Nuclide	Concentration (Bq/L)		
	PWTP feed	WAG 5	Simulant
<sup>134</sup> Cs	0.16	0.5	
<sup>137</sup> Cs	23	0.1	1.1 x 10 <sup>6</sup>
<sup>90</sup> Sr	270	1.3 x 10 <sup>4</sup>	8.8 x 10 <sup>5</sup> <sup>a</sup>

<sup>a</sup> As <sup>85</sup>Sr.

### 3. TEST PROCEDURES

Sorption measurements were made in long-term batch equilibrium tests. The solutions and exchanger were contacted in screw-cap polycarbonate centrifuge tubes by mixing on a Labquake™ shaker, which rocked 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 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 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 were clarified again by filtering the centrifuged supernate using a plastic syringe fitted with a 0.45- $\mu\text{m}$ -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 with  $^{137}\text{Cs}$  standards. Test data were used in the following calculations:

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

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

$$\text{Concentrations in solution (M}_p, \text{ meq/L)} = M_i \times C_f/C_b$$

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

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;

$M_i$  = concentration in initial solution, meq/L; and

$M_f$  = 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 was corrected for moisture content of the sorbent in all the data used to make direct comparison of sorption efficiency among sorbent materials.

#### 4. DECONTAMINATION EFFICIENCY OF THE BASELINE TREATMENT METHOD

##### 4.1 REVIEW OF RESULTS OF CHABAZITE ZEOLITE BATCH STUDY IN FY 1994

Natural chabazite zeolite was selected as the benchmark sorbent for removing strontium and cesium from contaminated wastewater. The zeolite (TSM-300) was purchased from Steelhead Specialty Minerals (Spokane, WA) at a cost of \$50/ft<sup>3</sup>. A stock supply of TSM-300 was pretreated to remove the natural strontium present on the zeolite as received. Pretreatment consisted of washing the TSM-300 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 TSM-300 is 7.1 wt %, and the manufacturer's stated density for the material is 1.73 g/cm<sup>3</sup>. The -20/+50 mesh fraction (300-840  $\mu\text{m}$ ) of the pretreated TSM-300 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. A longer mixing time was required for samples containing greater amounts of pretreated TSM-300.

Strontium sorption on pretreated TSM-300 was observed in PWTP simulant samples where the strontium concentration in the initial solution was  $2.28 \times 10^{-3}$  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 TSM-300.

Data for strontium sorption on the pretreated zeolite were fit to the Freundlich sorption model. The sorption data were approximately linear when the log value of the equilibrium concentration of strontium (meq/L) was plotted vs the log value of strontium sorbed per unit weight (meq/kg) on the zeolite. The slope of the relationship was 0.74, and the intercept was 3.4; the correlation coefficient for a linear fit was 0.98. The Freundlich equation defining strontium sorption from PWTP simulant on pretreated zeolite is, therefore,

$$\log Q_e = \log K_F + 1/n \log C \quad (1)$$

or

$$\log Q_e = 3.4 + 0.74 \log C, \quad (2)$$

where  $Q_e$  is the quantity of strontium on the sorbent (meq/kg) at equilibrium;  $K_F$  is the Freundlich constant;  $C$  is the equilibrium concentration in solution, and  $1/n$  is the sorption intensity.<sup>4</sup> Since the distribution coefficient,  $K_d$ , can be rewritten as

$$K_d = Q_e / C, \quad (3)$$

it can be expressed in terms of the strontium equilibrium concentration using the Freundlich constant

$$K_d = 2.5 \times 10^{+3} / C^{0.26}. \quad (4)$$

Cesium sorption was observed in simulant samples containing an initial cesium concentration of  $3.23 \times 10^{-6}$  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 TSM-300. When the cesium sorption data were fit to the Freundlich sorption model, the slope of the curve was 0.98 and the intercept was 4.75. The data for cesium fit the Freundlich model better than did the strontium data, as demonstrated by a higher linear correlation coefficient of 0.996. The comparable equation defining cesium sorption on pretreated zeolite is, therefore,

$$K_d = 5.6 \times 10^{+4} / C^{0.02}, \quad (5)$$

implying that the distribution coefficient is essentially constant over the cesium concentration range studied in these tests.

On completion of testing with the simulant, the sorption of strontium and cesium 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 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.

## **4.2 RESULTS OF CHABAZITE ZEOLITE STUDY IN FY 1995**

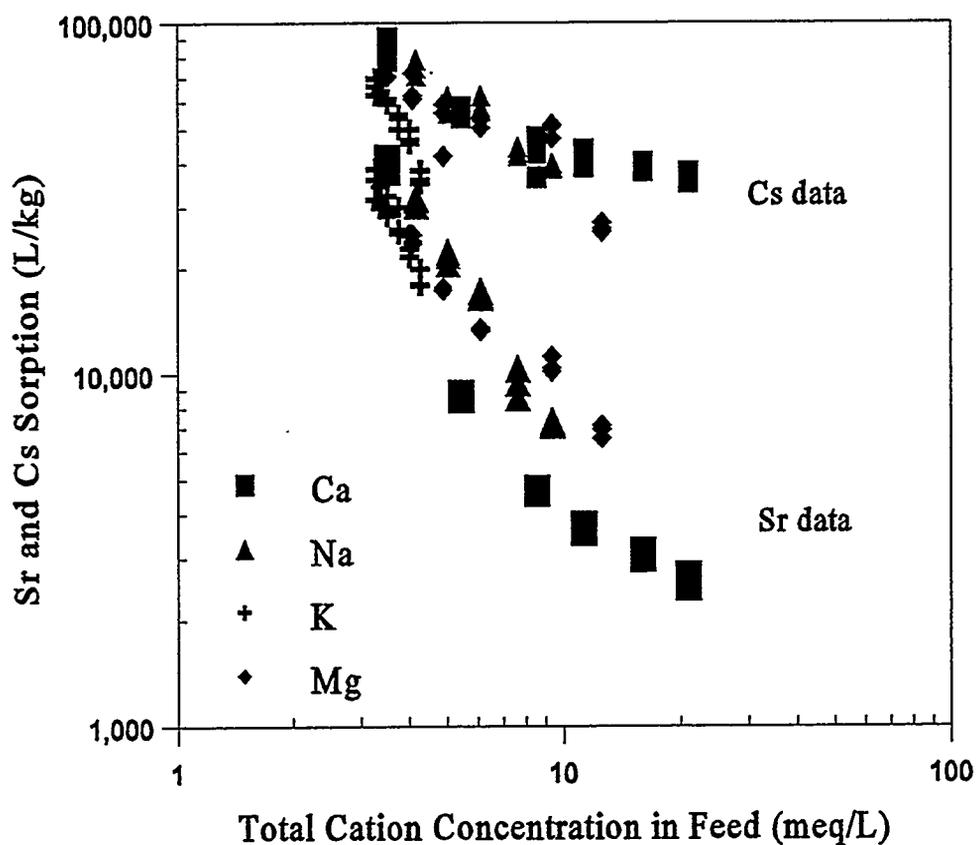
### **4.2.1 Batch Studies in FY 1995**

A series of four batch experiments was begun in FY 1994 and completed in FY 1995 to determine the effects of K, Mg, Na, and Ca cations on radionuclide sorption. In separate tests, higher concentrations of the individual cations, as the chloride salts, were added to the wastewater simulant to cover the concentration ranges of the individual cations found in typical groundwater. The total calcium concentration in the simulant samples covered a range of 2 to 20 meq/L (as compared with 0.16 to 6 meq/L in groundwater). In a second study, the total sodium

concentration covered a range of 0.5 to 6.5 meq/L (0.26 to 5.4 meq/L present in groundwater). The potassium concentration was varied from 0.025 to 1.03 meq/L (0.01 to 0.8 meq/L found in groundwater). In the final experiment, the magnesium concentration was adjusted to a value between 0.6 and 10 meq/L (between 0.025 and 10 meq/L in groundwater). The plots of strontium and cesium sorption ratios,  $R_s$ , as a function of total cation concentration in the wastewater simulant are given in Fig. 1. All cations tested depress the sorption capacity of the zeolite for strontium and cesium, particularly in the 0- to 4-meq/L concentration range of each cation. The  $R_s$  values for both strontium and cesium decreased by approximately 50% in simulants with potassium concentrations up to 1 meq/L. The sorption ratio for strontium and cesium decreased by 82 and 64%, respectively, for the range of magnesium concentration typically encountered in groundwater. The effect of calcium on strontium sorption was more significant than that observed for cesium sorption. Above approximately 8 meq/L of either Ca or Na, the sorption ratios for strontium and cesium were essentially constant.

#### 4.2.2 Study Using Small Zeolite Column

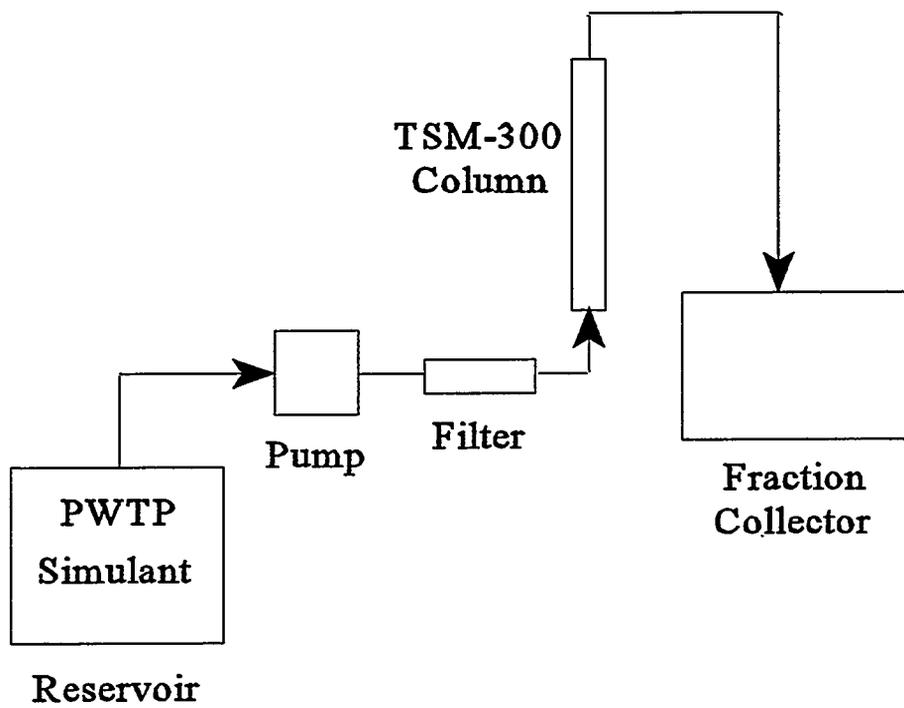
A small column test was initiated in FY 1994 and completed in FY 1995 to determine the breakthrough characteristics of strontium and cesium under dynamic flow conditions. A 1-cm-diam column containing about 2 g of sodium-modified TSM-300 zeolite was used to treat PWTP simulant. Cation breakthrough was 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 PWTP 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.



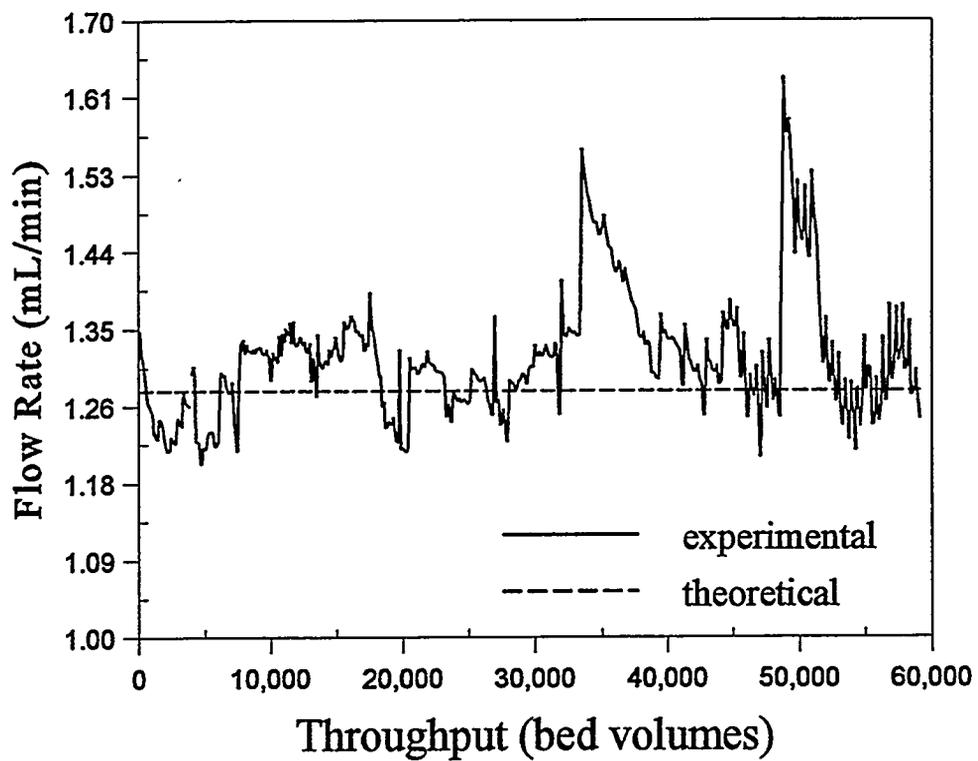
**Fig. 1. Strontium and cesium sorption as a function of total cation concentration in PWTP simulant. Test procedure: 0.020 g of washed TSM-300 zeolite in 10 mL of simulant; 24-h equilibration time; initial cesium and strontium concentrations,  $2.56 \times 10^{-6}$  and 0.00228 meq/L, respectively; cations added as the chloride salts.**

PWTP simulant (see Table 3) for the test was prepared in 100-L batches by dissolving high-purity chemicals in distilled deionized water. Calcium carbonate was dissolved by sparging the simulant solution with CO<sub>2</sub> gas. The solution pH decreased from 9.8 after all the chemicals had been added to 5.2 after the CO<sub>2</sub> addition; however, it gradually increased to about 7 as the solution was stirred and equilibrated with the atmosphere for several days. No postprecipitation of simulant components was observed over this time period. The adjusted solution was filtered through a 0.45- $\mu$ m Suporcap 100™ (hydrophilic polyethersulfone) membrane in approximately 20-L batches before the addition of <sup>85</sup>Sr and <sup>137</sup>Cs tracers. Twelve 20-L batches of traced feed, prepared from three 100-L batches of untraced feed, were used in the test.

A flow diagram for the column test is shown in Fig. 2. Filtered PWTP simulant was pumped from a reservoir through an in-line 0.45- $\mu$ m polyethersulfone membrane in an upflow mode through the zeolite bed. Column effluent samples were collected with a fraction collector in 6- or 8-h (approximately 500- or 700-mL) increments, which were weighed to determine the solution flow rate. A flow rate profile for the test is shown in Fig. 3. The test, which lasted for 120 d, was stopped after 59,000 BVs because the zeolite particles were beginning to cement together. The polyvinyl chloride tube used in the peristaltic pump tends to flatten on extended use, resulting in decreased flow; consequently, the tube was replaced several times during the test. Patches of green algae were observed in the in-line filter and in the 1/16-in. Teflon tube connecting the pump and the filter. The line connecting the pump and the filter was replaced after 31,000 BVs, and the filter was replaced after 48,000 BVs. The filter did not remove any measurable amount of <sup>85</sup>Sr or <sup>137</sup>Cs activity from the solution that passed through it.



**Fig. 2. Flow diagram for column test.**

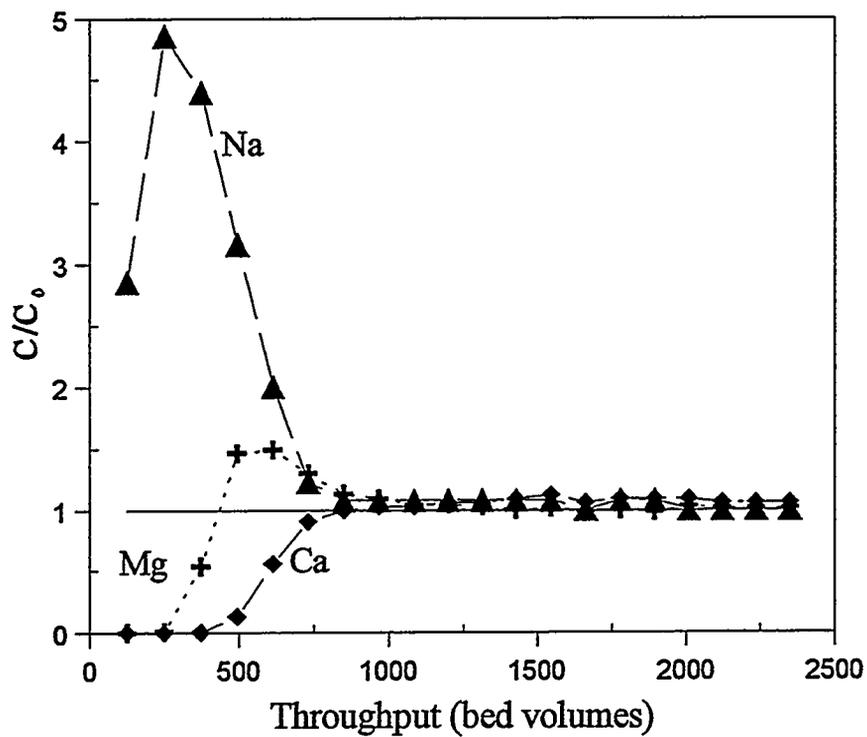


**Fig. 3. Flow rate profile for column test with washed TSM-300 zeolite.** Column parameters: 2.2 g of sodium chloride-washed zeolite contained in a 1-cm-diam column having a bed volume of 3.85 mL. The PWTP simulant flow rate was 1.3 mL/min.

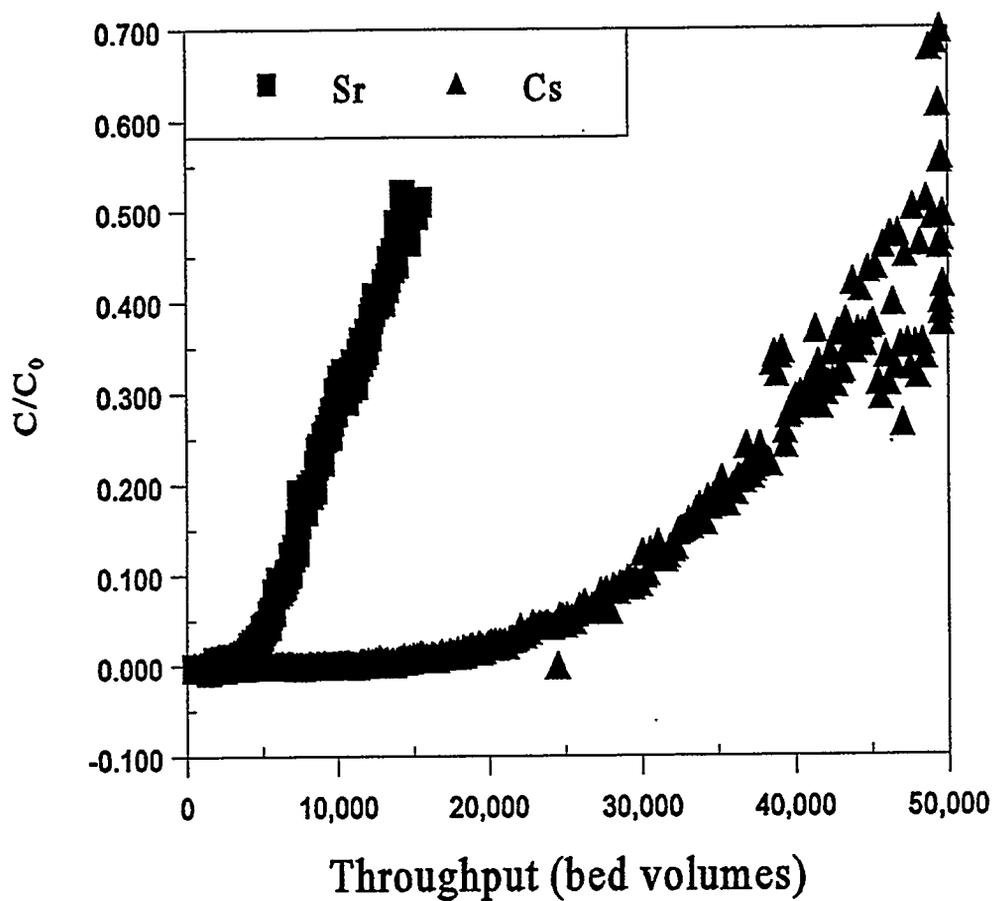
The breakthrough curves for the major cations are presented in Fig. 4, where the fractional breakthrough ( $C/C_0$ ), defined as the ratio of the cation concentration in the column effluent to the concentration in the feed, is plotted as a function of the volume of solution passed through the column. The initial effluent fractions (about 2500 BVs) were analyzed by ICP in the ORNL Analytical Services Organization 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 detection limit of 0.1 mg/L. Figure 4 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 strontium and cesium onto the zeolite resulted 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:  $Ca > Mg > Na$ . The fractional breakthrough of the above cations stabilized to a value of 1.0 at approximately 800 to 1400 BVs.

The  $^{85}\text{Sr}$  and  $^{137}\text{Cs}$  count rates of the effluent fractions were compared with those of the feed solutions to determine breakthrough points, which are shown in Fig. 5. 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 Sr loading for the zeolite was about 60 meq/kg at 50% strontium breakthrough; the Cs loading was 0.2 meq/kg at 50% cesium breakthrough. These loadings,



**Fig. 4. Curves showing breakthrough of sodium, magnesium, and calcium from washed TSM-300 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 PWTP simulant flow rate was 1.3 mL/min.**



**Fig. 5. Curves showing breakthrough of strontium and cesium from sodium chloride-washed zeolite. Column parameters: 2.2 g of washed zeolite contained in a 1-cm-diam column having a bed volume of 3.85 mL. The PWTP simulant feed flow rate was 1.3 mL/min.**

particularly the Sr 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.<sup>1</sup> The breakthrough data were used to construct logarithmic-probability plots of strontium and cesium breakthrough vs column throughput (Fig. 6). These plots were used to estimate sorption ratios, which are approximately equal to the number of bed volumes at 50% breakthrough.<sup>5</sup> The sorption ratios, although slightly lower, were in good agreement with sorption ratios measured<sup>1</sup> at low loading in batch sorption isotherms:

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

The heights of the mass transfer zones (MTZs) for strontium and cesium were calculated<sup>6</sup> by analysis of the breakthrough curves generated in the column test. The MTZ is the depth of the zeolite bed from the point of complete zeolite exhaustion (i.e., the zeolite is in equilibrium with solution containing approximately the feed concentration of the ion being sorbed) to the point that the sorbing ion in solution is barely detectable. The calculation required extrapolation of the breakthrough curves to 100% fractional breakthrough, assuming that the breakthrough curve is symmetrical. The MTZs, calculated between 99 and 1% fractional breakthrough, were 7.2 cm for strontium and 7.0 cm for cesium. The depth of the zeolite in the column was less than the MTZs for both strontium and cesium; thus, better breakthrough characteristics could probably be obtained by using either a longer column or a slower flow velocity. The results of this study can be used in conjunction with those from planned column tests at different flow rates to determine the height of the MTZ as a function of superficial flow velocity and to estimate the mass transfer coefficients and related quantities.

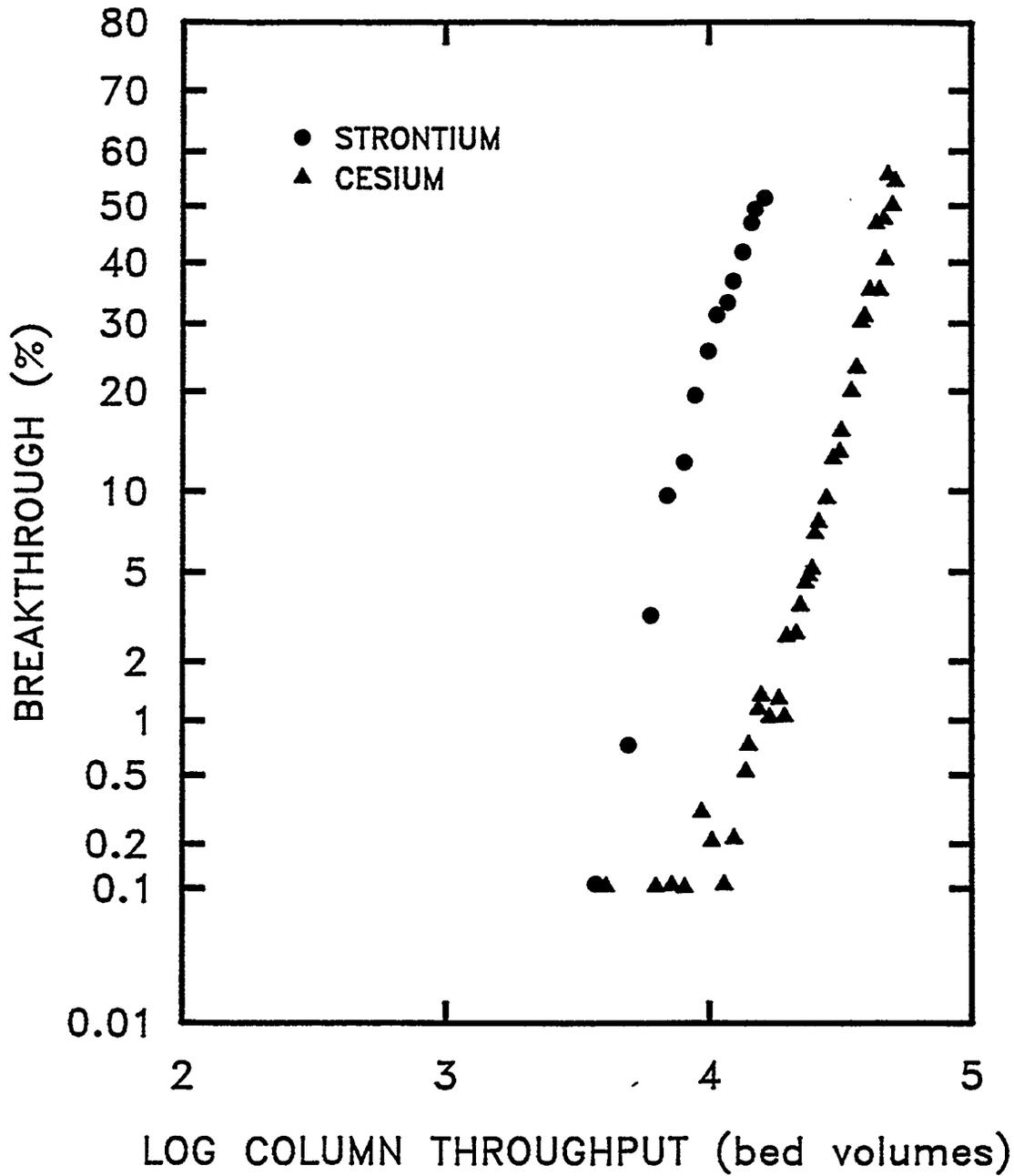


Fig. 6. Logarithmic-probability plots of strontium and cesium breakthrough vs column throughput. Column parameters: 2.2 g of sodium-modified TSM-300 zeolite contained in a 1-cm-diam column having a bed volume of 3.85 mL. The PWTP simulant flow rate was 1.3 mL/min.

## 5. SORPTION CHARACTERISTICS OF SRS RESORCINOL-FORMALDEHYDE ION-EXCHANGE RESIN

### 5.1 RESORCINOL-FORMALDEHYDE ION-EXCHANGE RESIN

Ion exchange on organic resins is a common technique for the processing of liquid nuclear waste. The organic resins are typically composed of rigid, three-dimensional polymers in which the polymeric chains are held together by chemical cross-linking groups. As with the inorganic zeolites, this type of resin contains positively or negatively charged functional groups that can exchange a counterion for either a negatively or positively charged species, respectively, that is present in solution. The R-F resin was developed at the SRS as an ion exchanger for removing cesium from caustic solutions containing high concentrations of sodium.<sup>7</sup> The two hydroxyl groups of resorcinol function as the active exchange groups of this particular resin. The resin is prepared by condensing the potassium salt of resorcinol with formaldehyde in an aqueous solution; cross-linkage is accomplished by drying the resulting gel at about 100 °C. Gram quantities of the resin were prepared at the SRS using this procedure. The Boulder Scientific Company (BSC) has employed a similar technique to prepare kilogram quantities for commercial use.

A mixed sodium-potassium (Na/K) form of the BSC resin can be prepared by passing a 2 M NaOH solution through a resorcinol-formaldehyde resin column. This form of the resin is typically used to remove cesium ion from caustic liquid waste having high sodium concentrations. Samples of the resin can be converted to the hydrogen form by passing a dilute solution of nitric acid (HNO<sub>3</sub>) or hydrochloric acid (HCl) through a column containing the potassium form of the resin. This treatment is used to regenerate a resorcinol-formaldehyde resin column by displacing any cesium that had previously sorbed onto the resin with hydrogen

ion. The compositions of the various forms of the resin are shown in Table 6. The ion-exchange capacity and the bulk density of the Na/K-form are also included.<sup>8</sup>

**Table 6. Elemental analyses for Na/K-, H-, and K-forms of the resorcinol-formaldehyde resin<sup>a</sup>**

Element	Na/K-form	H-form	K-form
C, %	45.90	59.46	42.20
H, %	5.35	5.67	5.37
Na, %	2.01	<0.5	0.015
K, %	7.68	<0.5	8.94
O, %	38.13	33.82	41.33
Total	99.07	98.95	97.86

<sup>a</sup>From J. P. Bibler, R. M. Wallace, and L. A. Bray, paper presented at the Waste Management '90 Symposium, Tucson, Ariz., Feb. 25-Mar. 1, 1990.

## 5.2 PRETREATMENT OF THE RESORCINOL-FORMALDEHYDE RESIN

Approximately 100 g of R-F resin (BSC, Lot BSC187-0210 ) was received from Lane Bray of Battelle, Pacific Northwest Division, Hanford, Washington. A 100-g portion of the resin can be purchased directly from the BSC (Mead, CO) for \$50.00. A sieve analysis<sup>9</sup> was performed in-house on a 50-g portion of as-received resin nominally sized as -20/+60 mesh. The size distribution of the resin particles is presented in Table 7. Approximately 58% of the material was considered as fines (i.e., having a mesh size greater than 80). Only 0.0026% of the sorbent had a mesh size less than 20. The -20/+50 mesh fractions were used for all batch equilibration studies so as to match the size range used in the zeolite sorption studies. The water content of the resin, as received, was determined to be 19.1 wt %, determined by weight loss after heating

1 g of resin to 104 °C for 24 h. This water content is greater than twice that observed with the sodium-modified chabazite zeolite (7.1 wt %).

**Table 7. Sieve analyses of resorcinol-formaldehyde resin (Lot BSC187-0210)**

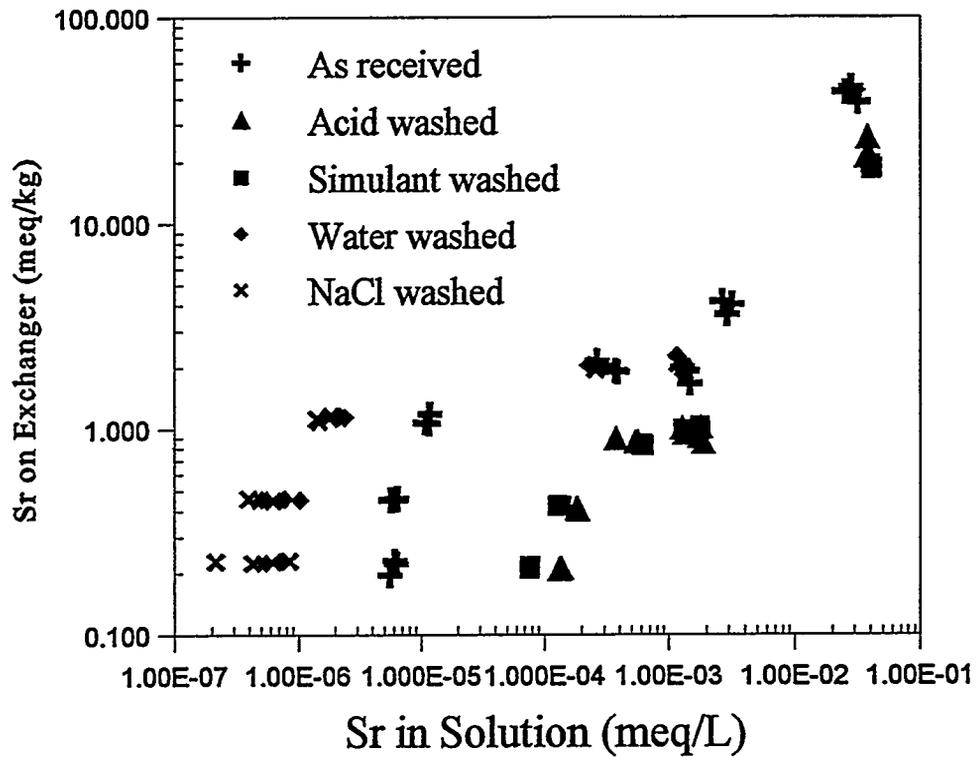
U.S. sieve No.	Particle size (µm)	Percent total weight
+20	>840	0.0026
-20/+30	590-840	0.029
-30/+40	420-590	0.40
-40/+50	297-420	38.7
-50/+80	177-297	32.5
-80/+100	149 -177	24.8
-100	<149	1.14
<b>sum</b>		<b>97.6</b>

Sorption results from several resin pretreatment methods were compared with sorption isotherms developed by using as-received resin. The pretreatment methods included: (1) rinsing the resin with deionized, distilled (ultrapure) water prior to air drying; and (2) prewashing the resin with 2 M sodium chloride (NaCl) followed by several rinses with ultrapure water to remove excess sodium ion. This treatment is similar to that used for pretreating the zeolite sorbent used in the baseline sorbent studies. (3) A third resin-conditioning step included prewashing the resin with PWTP simulant six times, followed by water rinses and air drying. A final resin treatment, which was recommended by J. P. Bibler of SRL,<sup>10</sup> was to prewash the resin with 1 M HCl followed by several rinses with ultrapure water to remove excess hydrogen ion.

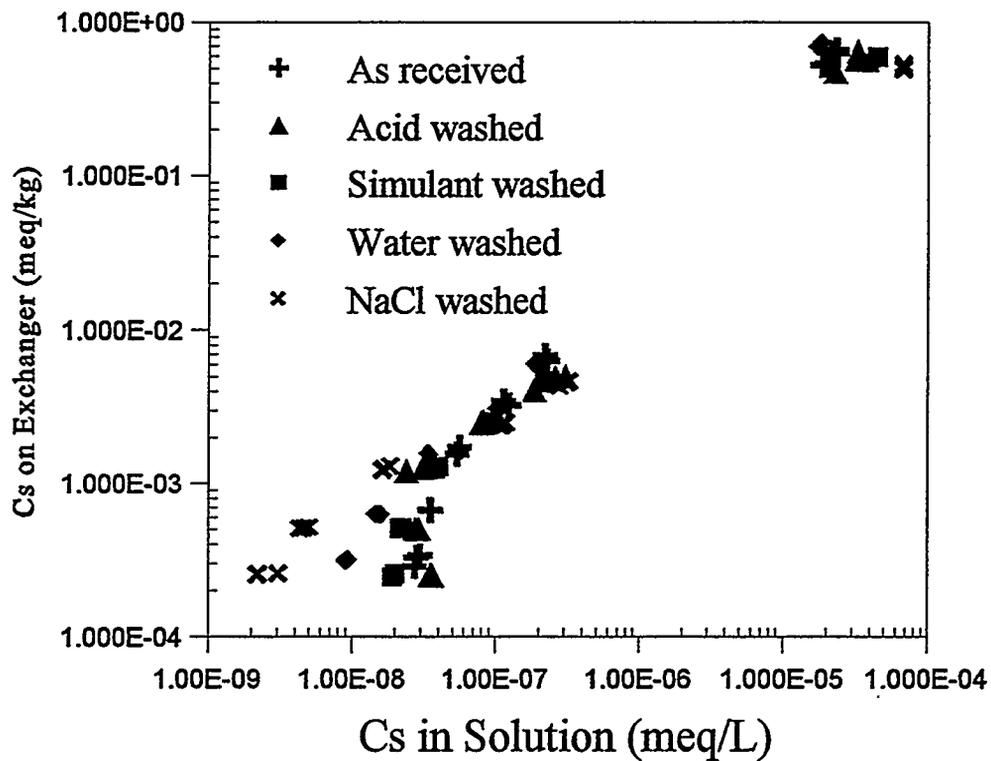
In all methods of resin pretreatment, approximately 5 g of resin was combined with ten volumes of conditioning solution and mixed on a Labquake mixer for 1 h. The washes were repeated until the wash solution was no longer colored; four to six wash cycles were required to obtain a colorless solution. The resin was then mixed with 100 mL of ultrapure water for 1 h on the Labquake unit. The pretreated resin was subsequently air-dried and stored in a sealed polypropylene vial for later use.

One difficulty in pretreating the resin is defining the ionic form of the resin at the completion of resin conditioning. Assuming that the as-received resin is completely in the potassium form, a portion of the potassium will exchange with the sodium when the resin is pretreated with NaCl. In the pretreatment tests, the pH of each of the multiple water rinsates used to remove excess sodium ion after pretreatment was above 10.5. This indicates that hydrogen ion from the water displaced a portion of either the potassium or the sodium, or both, from the resin. In the case of the acid-washed resin, the water washes were consistently acidic (pH ~4.5); it appears that the acid slowly leaches from the resin over an extended period. Both the simulant-washed and the ultrapure water-washed resin batches yielded slightly basic solutions on completion of the batch sorption experiments. Thus, the actual cation content of the treated resin in low-ionic-strength solutions is in question and may have to be resolved through elemental analysis of the treated resin batches.

Exploratory studies of the pretreated resin batches included developing strontium and cesium isotherms for each resin in the PWTP wastewater simulant. The sorption characteristics for all batches of resin are presented in Figures 7 and 8. Cesium sorption was equivalent for all forms



**Fig. 7. Strontium sorption on pretreated resorcinol-formaldehyde resin.** Test conditions: 0.005 to 0.100 g of resin in 10 mL of PWTP of simulant; 24-h equilibration time; initial concentration of strontium in simulant for lower data points, 0.00228 meq/L; initial concentrations of strontium and cesium in simulant for upper data points, 0.05 and 0.04 meq/L, respectively.



**Fig. 8. Cesium sorption on pretreated resorcinol-formaldehyde resin.** Test conditions: 0.005-0.100 g of resin in 10 mL of PWTP simulant; 24-h equilibration time; initial concentration of strontium in simulant for lower data points, 0.00228 meq/L; initial concentrations of strontium and cesium in simulant for upper data points, 0.05 and 0.04 meq/L, respectively.

of the resin when the cesium concentration in the solution was greater than 0.1 neq/L. There was a slight enhancement of cesium sorption below this concentration for pretreated resin. Strontium sorption on resin is very dependent on the method of resin pretreatment. The strontium isotherm has two inflection points, possibly indicating a multilayer sorption process. The upper inflection point occurs at a strontium concentration of  $1 \times 10^{-3}$  meq/L and is independent of the method of resin pretreatment. The strontium sorption ratio increases sharply above this inflection point. The location of the lower inflection point of the strontium isotherm varies between  $10^{-6}$  and  $10^{-3}$  meq of strontium per liter, depending on the method of resin pretreatment. In the acidic pretreatment procedure, the distance between the two inflection points could be reduced by additional water rinses of the acid-washed resin. The greatest strontium sorption in simulant containing very low strontium concentration was obtained when the resin had been initially washed with ultrapure water; the second best performance was observed with the saline-washed resin batches.

Pretreating the resin with ultrapure water only was selected as the approach to use in developing cesium and strontium isotherms in all remaining batch studies. Of the various treatment options, it is the most convenient procedure and does not risk inadvertent introduction of elevated levels of sodium into the test simulant. The formalized procedure for pretreating the resin for the remainder of the studies included washing a -20/+50 mesh fraction (~3.5 g) of the resin with 100 mL of ultrapure water to remove the residual colored components from the resin. The resin fraction was initially contacted with the water overnight on a Labquake™ shaker. After the wash water was decanted, a similar volume of fresh water was added to the resin and the process was repeated for five additional washes (until the wash water was colorless). The prepared resin sample was air dried and then stored in a sealed

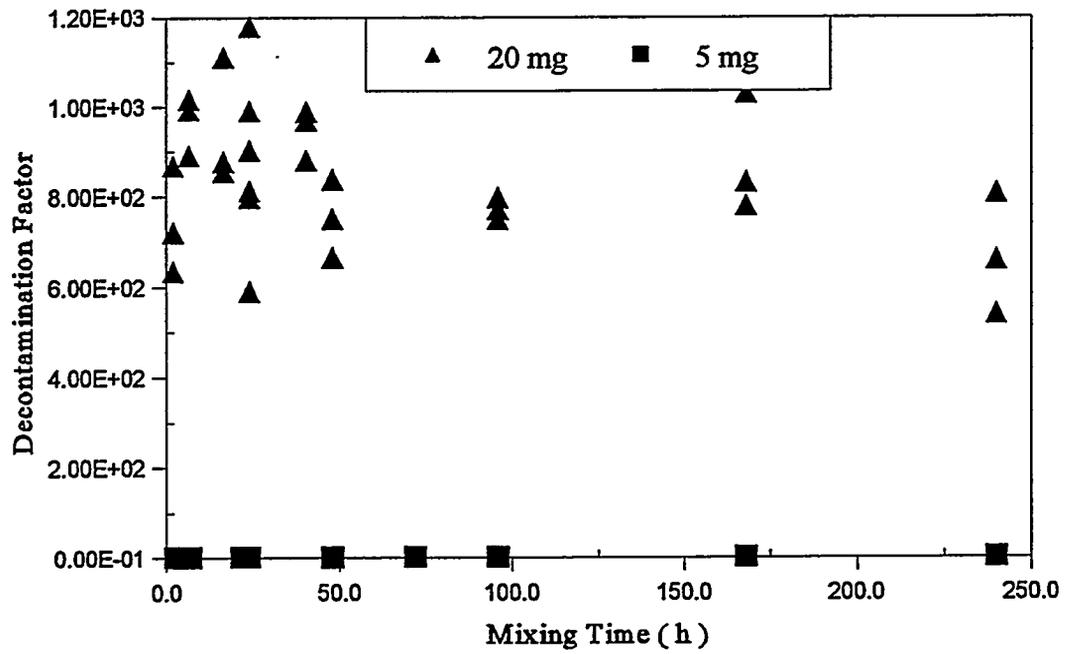
polypropylene bottle to avoid potential air-oxidation of the resin and reduce the uptake of moisture.

### **5.3 KINETIC AND EQUILIBRIUM STUDIES WITH RESORCINOL-FORMALDEHYDE RESIN**

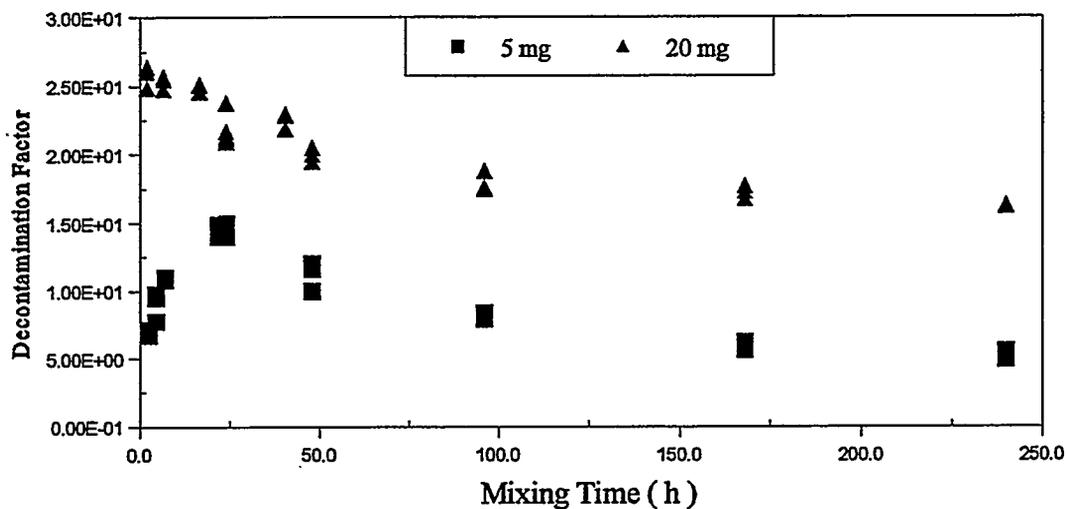
#### **5.3.1 Determination of Equilibration Time for Resorcinol-Formaldehyde Resin**

The strontium and cesium sorption rates were determined by mixing a series of samples containing either 20 or 5 mg of water-washed R-F resin in 10 mL of the traced PWTP simulant. Maximum cesium sorption in the 5-mg resin samples was observed after 24 h; the sorption ratio decreased with longer contact times. It steadily declined in 20-mg resin samples, with only 80% of the cesium initially sorbed being found on the resin after 100 h of contact. The sorption of strontium onto 5 mg of resin reached steady state in 24 h. The sorption of strontium onto 20-mg resin samples peaked at 24 h and stabilized at 80% of the maximum value within 50 h of contact. Figures 9 and 10 present the results of the equilibrium studies. On the basis of these results, a 24-h mixing time was used in subsequent sorption studies.

Analysis of the simulant samples that did not contain any sorbent<sup>1</sup> indicated that neither strontium nor cesium is lost to the walls of the sample containers over this period, even at tracer levels 30 times less than those that normally would be present in the PWTP simulant. The sorption ratio ( $R_s$ ) values for a 24-h equilibration were about 1440 and about 7600 L/kg for strontium and cesium, respectively, on 5 mg of resin; they were 410,000 L/kg for strontium and about 11,000 L/kg for cesium in the presence of 20 mg of water-washed resin.



**Fig. 9. Strontium equilibration time on water-washed resorcinol-formaldehyde resin.** Test conditions: 5 or 20 mg of washed R-F resin in 10 mL of simulant; initial strontium and cesium concentrations, 0.00228 and  $3.23 \times 10^{-6}$  meq/L, respectively; Labquake mixing at 20 cycles/min; samples centrifuged at 5000 rcf for 30 min.



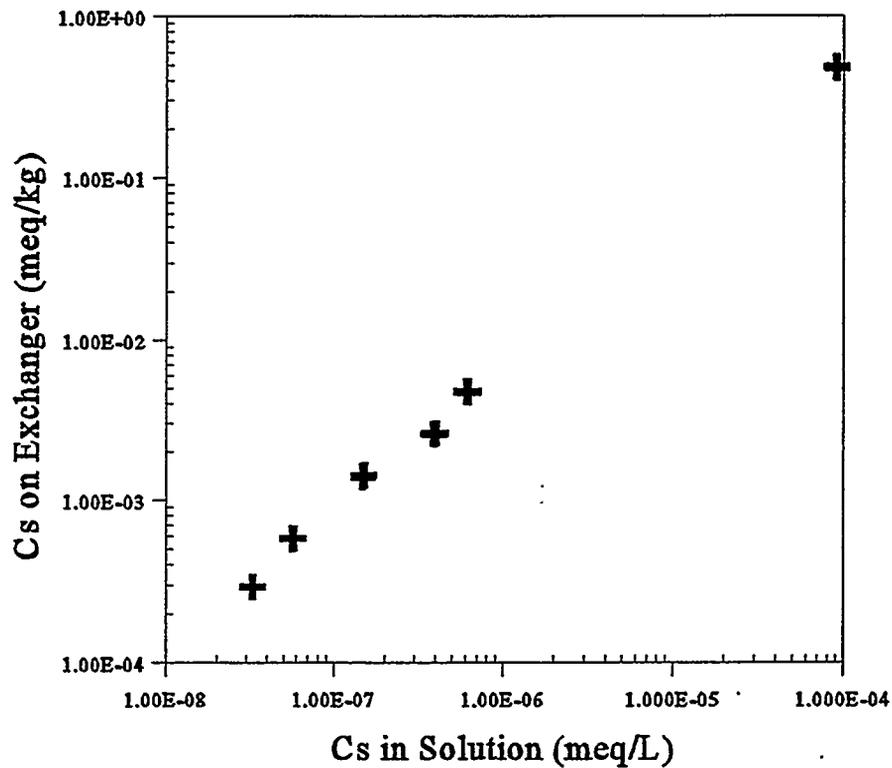
**Fig. 10. Cesium equilibration time on water-washed resorcinol-formaldehyde resin.** Test conditions: 5 or 20 mg of washed R-F resin in 10 mL of simulant; initial concentrations of strontium and cesium,  $0.00228$  and  $3.23 \times 10^{-6}$  meq/L, respectively; Labquake mixing at 20 cycles/min; samples centrifuged at 5000 rcf for 30 min.

### 5.3.2 Strontium and Cesium Sorption Isotherms on Resorcinol-Formaldehyde Resin

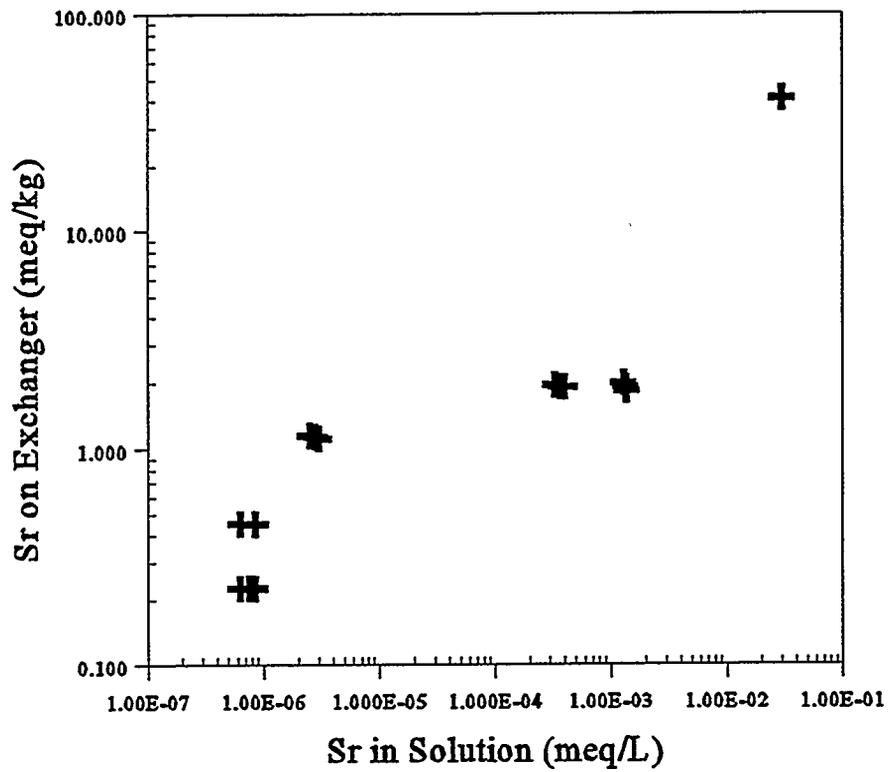
Strontium and cesium isotherms were developed by adding 10 mL of traced PWTP feed simulant to sample tubes containing from 5 to 100 mg of water-washed R-F resin. The samples were mixed for 24 h before being centrifuged and the supernates filtered. The isotherm profiles are presented in Figs. 11 and 12. As observed with the chabazite zeolite, the cesium isotherm is essentially linear in the wastewater simulant. The lowest data point on the cesium isotherm graph represents samples containing 100 mg of resin. The least-squares regression analysis of cesium data indicates that the  $R_s$ , equivalent to the slope of the regression line, is 6,300 L/kg. The cesium sorption capacity on the resin is 0.02 meq/kg. Comparable values for the  $R_s$  and sorption capacity on the sodium-modified zeolite are 80,000 L/kg and 0.17 meq/kg, respectively.

The strontium isotherm shows two inflection points, possibly indicating a multilayer sorption mechanism. If strontium sorption characteristics are the result of the formation of multilayer sorption sites (rather than due to an experimental artifact), the strontium sorption ratio,  $R_s$ , should be a function of the ratio of sample volume to the resin mass used in batch tests.

Table 8 shows the variation in strontium and cesium sorption ratios with the change in the ratio of the sample volume to the resin mass. The data are plotted in Fig 13. The strontium  $R_s$  increases with the ratio of sample volume to resin mass for values greater than 0.1 and less than 1. However, the cesium  $R_s$  remains constant as the ratio of sample volume to resin mass is varied, as does the strontium  $R_s$  for ratios greater than 1. The fact that the cesium  $R_s$  is constant is a good indication that the variations in the strontium  $R_s$  are due to differences in sorption mechanism, rather than to an experimental artifact such as a difference in mixing efficiency for different resin masses.



**Fig. 11. Cesium sorption on water-washed resorcinol-formaldehyde resin.** Test conditions: 0.005 to 0.100 g of resin in 10 mL of solution; 24-h equilibration time; cesium initial concentration for lower data points,  $2.3 \times 10^{-6}$  meq/L; cesium initial concentration for upper data points,  $3.2 \times 10^{-4}$  meq/L.



**Fig. 12. Strontium sorption on water-washed resorcinol-formaldehyde resin.** Test conditions: 0.005 to 0.100 g of resin in 10 mL of solution; 24-h equilibration time; strontium initial concentration for lower data points, 0.00228 meq/L; strontium initial concentration for upper data points, 0.05 meq/L.

**Table 8. Strontium and cesium  $R_s$  values in wastewater simulant, using water-washed resorcinol-formaldehyde resin<sup>a</sup>**

Sample volume (mL)	Resin weight (mg)	Sample volume-to-resin mass ratio (mL/mg)	Strontium $R_s$ (L/kg)	Cs $R_s$ (L/kg)
3	5	0.6	$2.47 \times 10^5$	$2.47 \times 10^4$
3.75	5	0.75	$3.38 \times 10^4$	$8.89 \times 10^3$
5	5	1	$6.90 \times 10^3$	$7.33 \times 10^3$
10	5	2	$1.44 \times 10^3$	$7.60 \times 10^3$
10 <sup>b</sup>	5	2	$1.35 \times 10^3$	$5.23 \times 10^3$
10 <sup>c</sup>	5	2	$1.22 \times 10^3$	$7.55 \times 10^3$
10	10	1	$5.26 \times 10^3$	$6.52 \times 10^3$
10	20	0.5	$4.1 \times 10^5$	$9.31 \times 10^3$
10	50	0.2	$5.89 \times 10^5$	$9.87 \times 10^3$
10	100	0.1	$3.07 \times 10^5$	$8.84 \times 10^3$
15	5	3	$1.13 \times 10^3$	$8.47 \times 10^3$
20	5	4	$9.97 \times 10^2$	$9.28 \times 10^3$

<sup>a</sup> Initial strontium concentration was 0.00228 meq/L; initial cesium concentration was  $2.6 \times 10^{-6}$  meq/L.

<sup>b</sup> Concentrations of strontium and cesium in initial sample were 0.05 and  $3.23 \times 10^{-4}$  meq/L, respectively.

<sup>c</sup> Concentrations of strontium and cesium in initial sample were 0.15 and  $2.6 \times 10^{-6}$  meq/L, respectively.

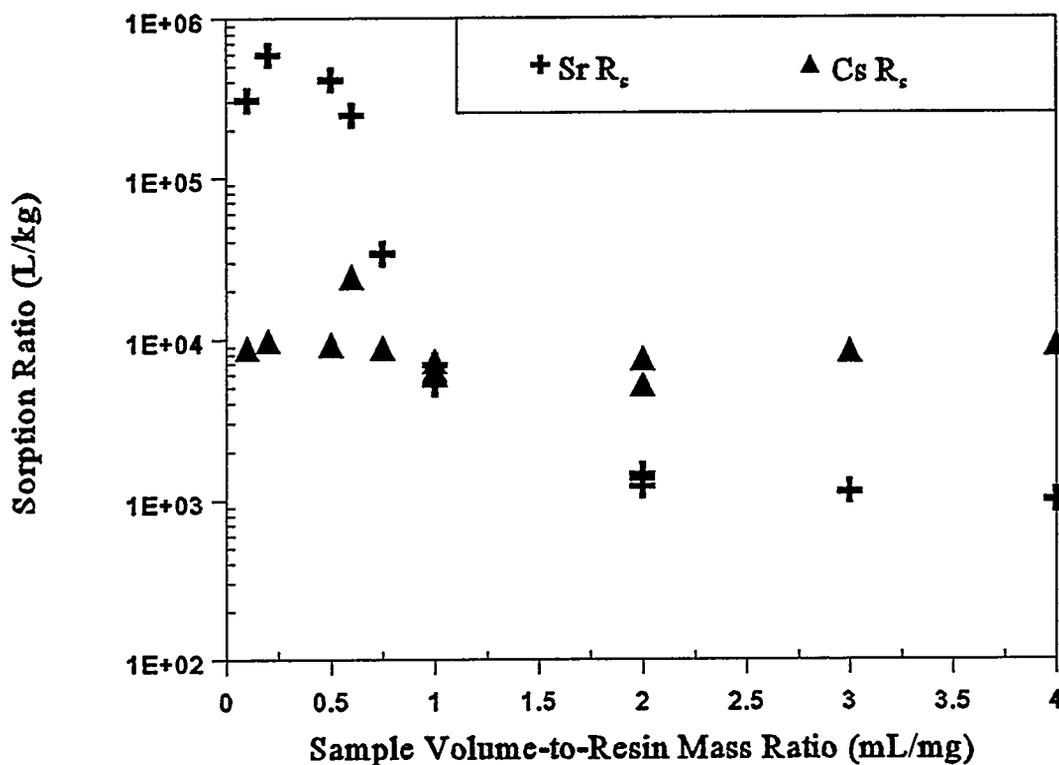


Fig. 13. Sorption ratio,  $R_s$ , vs sample volume-to-resin mass ratio. Test conditions: 0.005 to 0.100 g of resin in 3 to 20 mL of PWTP simulant; 24-h equilibration time; initial strontium and cesium concentrations in simulant of 0.00228 to 0.15 meq/L and  $2.6 \times 10^{-6}$  to  $3.23 \times 10^{-4}$  meq/L, respectively.

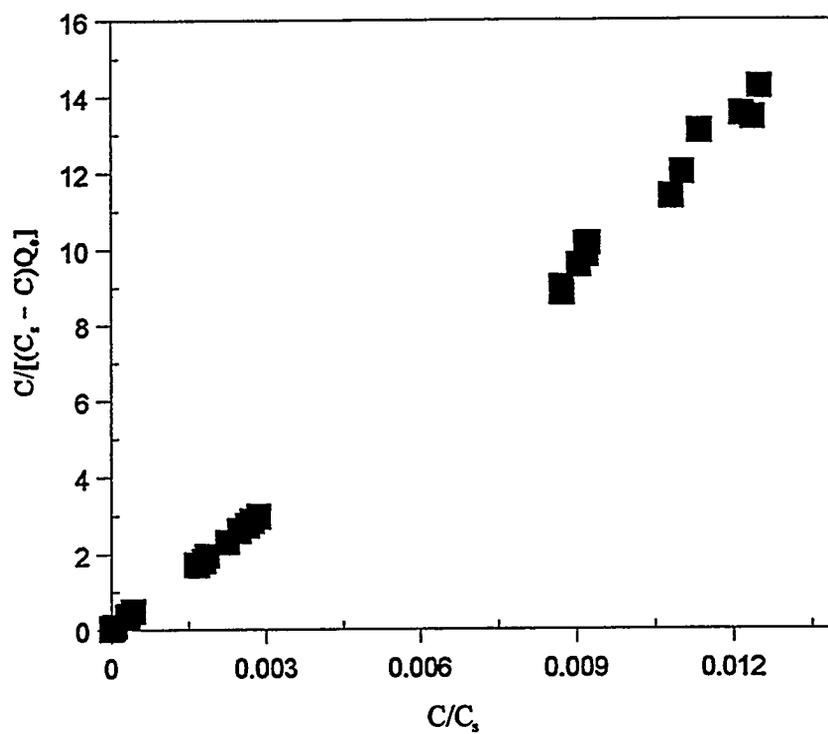
### 5.3.3 Mechanism for Sorption of Strontium and Cesium on Resorcinol-Formaldehyde Resin

Additional samples, spanning wider concentration ranges of strontium and cesium, were treated with the water-washed resin to more fully define the Cs and Sr sorption mechanisms. As can be seen in Fig. 14, strontium sorption appears to fit the Brunauer, Emmett, Teller (B.E.T.) model<sup>4</sup> for multilayer adsorption. A linear relationship is observed when the sorption data are applied to the following equation:

$$\frac{C}{(C_s - C)Q_e} = \frac{1}{BQ^0} + \frac{B-1}{BQ^0} \times \left(\frac{C}{C_s}\right), \quad (6)$$

where  $C$  represents the equilibrium concentration of strontium in solution in units of mol/L,  $C_s$  represents the saturation concentration of strontium in solution,  $B$  is a fitted parameter reflecting energy interaction, and  $Q_e$  is equivalent to the moles of strontium sorbed per kilogram of resin. The strontium saturation concentration was chosen as  $7.5 \times 10^{-5}$  mol/L, representing the uppermost strontium concentration of 6.5 ppm that is found in typical groundwater. The linear correlation coefficient of the regression line was 0.997, indicating that the sorption data fit the B.E.T. model quite well.

The slope and intercept of the relationship were equivalent to  $1102 \pm 9$  kg/mol and  $0.08 \pm 0.4$  kg/mol, respectively. These values were used to calculate the  $Q^0$ , the mol of strontium sorbed per unit weight of resin required to complete a monolayer on the surface of the sorbent. The calculated  $Q^0$  is 0.9 mmol of strontium per kilogram of resin. The calculated value of the  $B$  term is -14,000, a constant related to the energy of interaction with the resin surface. Considerable



**Fig. 14. Strontium sorption data fit to B.E.T. sorption model.** Test conditions: 0.005 to 0.100 g of resin in 3 to 10 mL of solution; 24-h equilibration time; initial strontium concentration for lower data points, 0.00228 meq/L; initial strontium concentration for upper data points, 0.05 and 0.15 meq/L.  $C$  = concentration of strontium remaining in solution at equilibrium (mol/L);  $C_s$  = saturation concentration of strontium in the solution at room temperature ( $7.5 \times 10^{-5}$  mol/L);  $Q_e$  = amount of strontium sorbed per unit mass of resin (mol/kg).

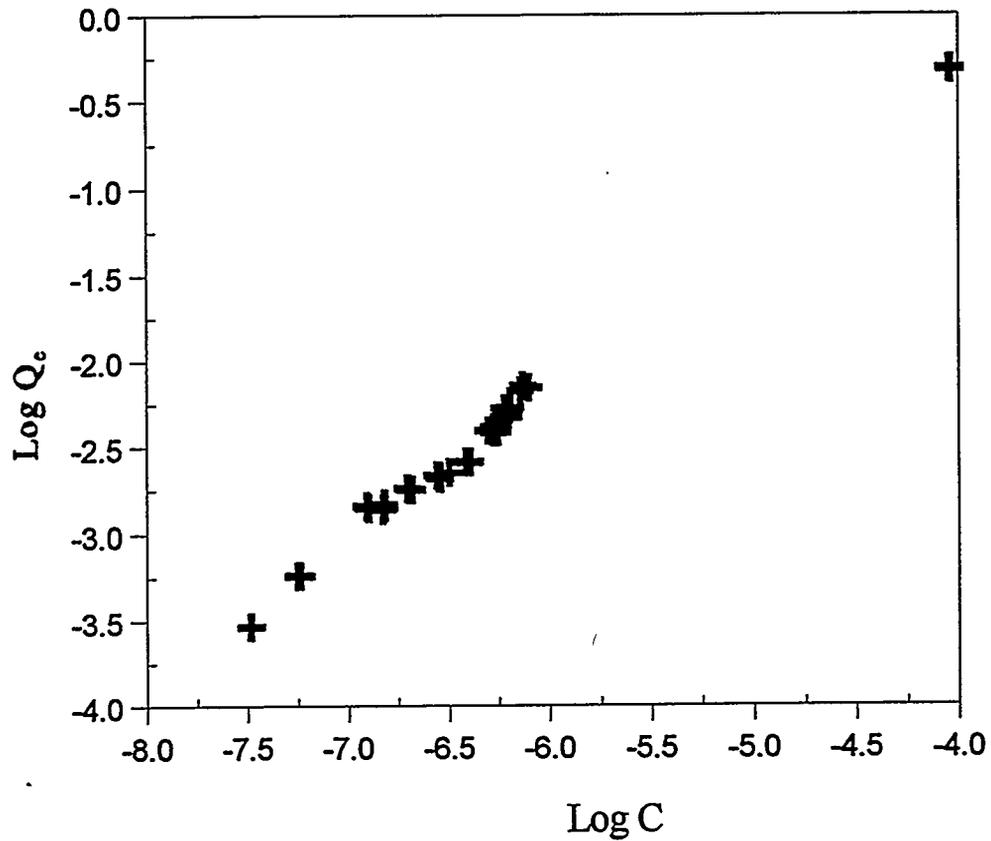
error will be associated with the estimates of  $Q^0$  and  $B$  because of the uncertainty in the determination of the intercept of the B.E.T. graph.

The cesium data, including the data representing various sample volume-to-resin mass ratios, fit the Freundlich model [Eq. (1)] best. A linear relationship was obtained between the log value of the final concentration of cesium in solution (meq/L) and the log value of cesium sorbed per unit weight (meq/kg) on the resin (Fig. 15). However, a slight curvature in the midconcentration range indicates that variation in the sample volume-to-resin mass ratio slightly affects the cesium sorption ratio. This dependence may be the result of the difference in equilibration time required for varying amounts of resin, as observed in Fig. 11. The slope of the line and the intercept are equivalent to 0.92 and 3.4, respectively, with a correlation coefficient for the linear fit of 0.995. Therefore, the equation governing cesium sorption on water-washed resin is

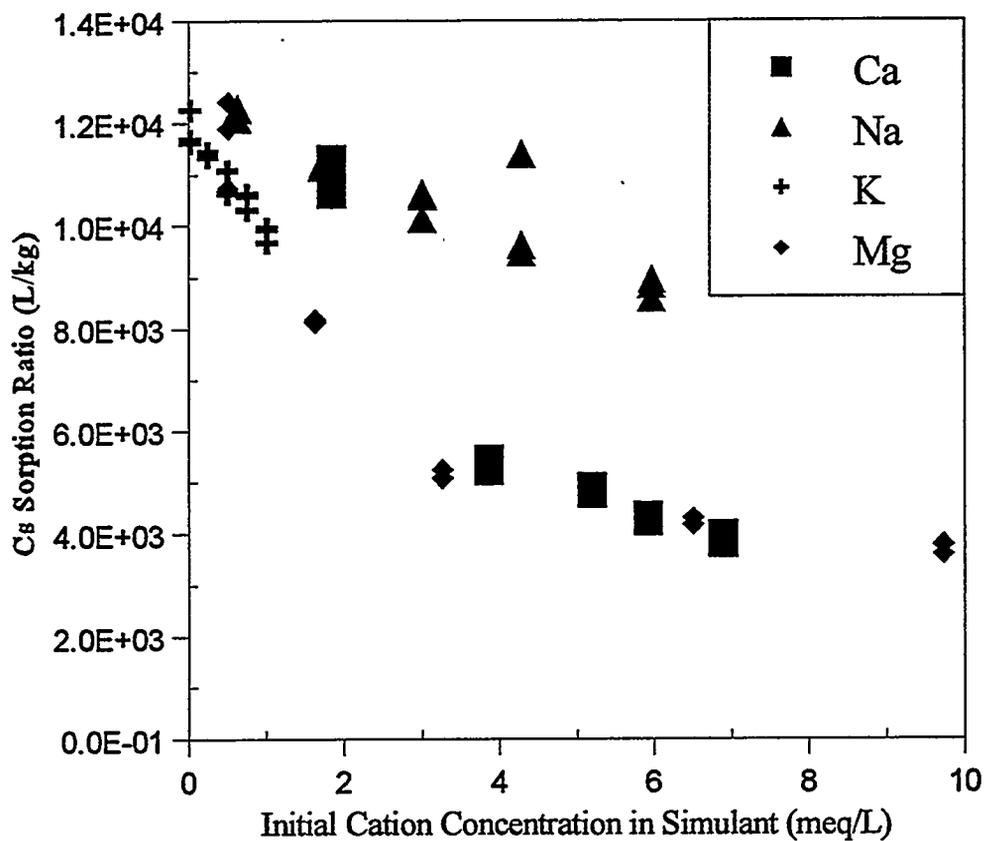
$$K_d = \frac{(2.5 \times 10^3)(C^{0.92})}{C} = \frac{(2.5 \times 10^3)}{C^{0.08}} \quad (7)$$

#### 5.3.4 Effects of Calcium, Sodium, Potassium, and Magnesium on Strontium and Cesium Sorption

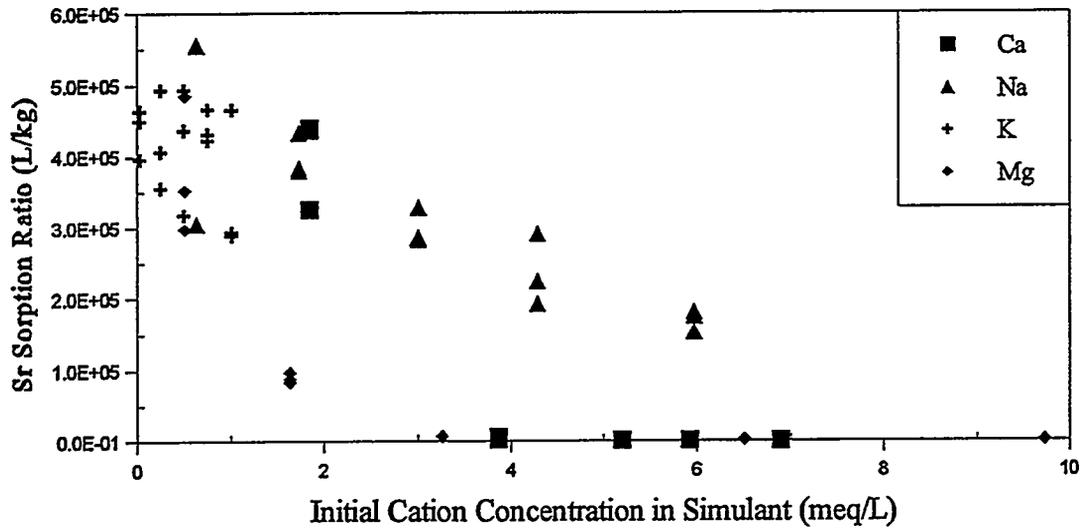
The effects of elevated Ca, Na, K, and Mg concentrations on Sr and Cs sorption were studied using the water-washed R-F resin. Higher concentrations of the individual cations were added, as the chloride salts, to the process wastewater simulant to cover the concentration ranges of the individual cations found in typical groundwater. Twenty milligrams of resin was used to treat 10-mL volumes of the simulant samples; the results of this study are presented in Figs. 16 and 17. Sorption of both strontium and cesium is suppressed as the concentration of each cation is increased above the concentration initially in the wastewater simulant. Within the cation



**Fig. 15. Cesium sorption fit to Freundlich sorption model.** Test conditions: 0.005 to 0.100 g of R-F resin in 3 to 10 mL of solution; 24-h equilibration time; initial cesium concentration for lower data points,  $2.6 \times 10^{-6}$  meq/L; initial cesium concentration for upper data points,  $3.23 \times 10^{-4}$  meq/L. C = cesium remaining in solution at equilibrium (mol/L);  $Q_e$  = amount of cesium adsorbed per unit mass of resin (mol/kg).



**Fig. 16. Effects of cations on cesium sorption on water-washed resorcinol-formaldehyde resin.** Test procedure: 0.020 g of water-washed resin in 10 mL of simulant; 24-h equilibration time; initial strontium and cesium concentrations of 0.00228 and  $2.6 \times 10^{-6}$  meq/L, respectively; cations added as chloride salts.



**Fig. 17. Effects of cations on strontium sorption with water-washed resorcinol-formaldehyde resin. Test procedure: 0.020 g of water-washed resin in 10 mL of simulant; 24-h equilibration time; initial strontium and cesium concentrations of 0.00228 and  $2.6 \times 10^{-6}$  meq/L, respectively; cations added as chloride salts.**

concentration range of 0 to 4 meq/L, the order of increasing effect on strontium sorption is  $\text{Na} \leq \text{K} < \text{Mg} \leq \text{Ca}$ , as compared with the order  $\text{Na} \leq \text{Mg} < \text{K} < \text{Ca}$  on the chabazite zeolite. The effect of potassium on cesium sorption is similar to that observed with doubly charged cations. The greatest difference in composition between PWTP feed and WAG 5 groundwater is the calcium concentration. Prepared zeolite is significantly better for cesium removal and marginally better for strontium removal in simulant samples containing high calcium concentrations.

## **6. TREATMENT OF ACTUAL PWTP FEED PROCESS WATER AND WAG 5 GROUNDWATER WITH WATER-WASHED RESORCINOL-FORMALDEHYDE RESIN**

### **6.1 PREPARATION AND CHEMICAL ANALYSES OF ACTUAL WATER SAMPLES**

The sorption of strontium and cesium was next observed in actual PWTP feed wastewater and WAG 5 groundwater. Approximately 2 L of actual PWTP feed wastewater and 500 mL of WAG 5 groundwater were collected and filtered through 0.45- $\mu\text{m}$  cellulose nitrate filter membranes. Portions of each filtrate were acidified and submitted for ICP analysis of metal content; aliquots were also submitted for anion chromatography and radiological analysis for strontium and cesium radionuclides. Both the filtered wastewater and the groundwater were analyzed titrimetrically for carbonate and bicarbonate contents. The analytical results for the major components of the actual wastewater and the groundwater are summarized in Tables 3-5.

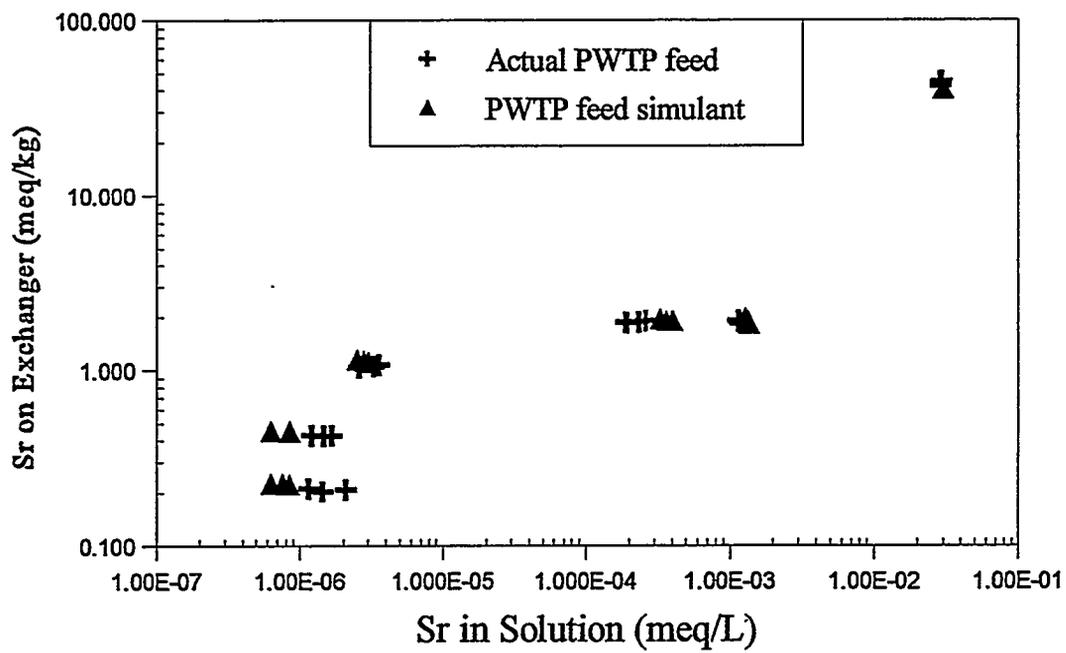
Batch sorption tests were performed with actual PWTP feed wastewater and WAG 5 groundwater in a manner identical to that used for the simulant samples. The actual PWTP feed and groundwater samples were traced with  $^{85}\text{Sr}$  and  $^{137}\text{Cs}$  at levels analogous to those in the simulant samples in order to comply with the analytical detection limits of the gamma counting

equipment in the laboratory. Additional inactive strontium and cesium were added to one set of the PWTP wastewater and WAG 5 groundwater samples to provide sorption data in a high loading situation. The 10-mL samples were mixed with 5 to 100 mg of the water-washed resin for 24 h.

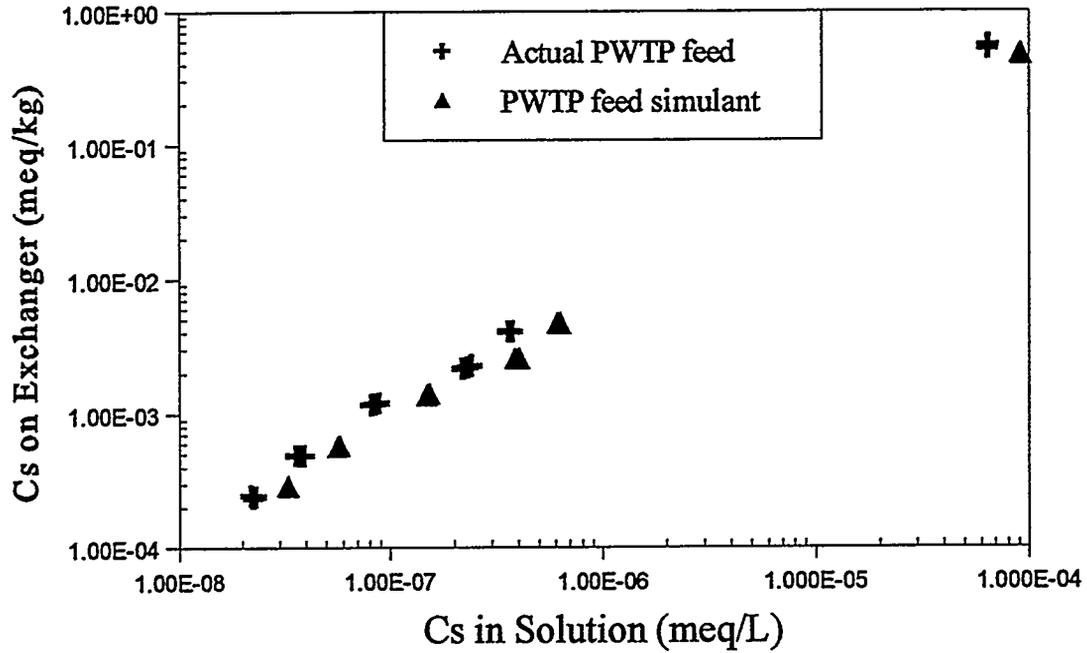
## 6.2 SORPTION FROM ACTUAL PWTP PROCESS WASTEWATER

Sorption results for the actual PWTP feed samples and the PWTP simulant are presented in Figs. 18 and 19. The actual PWTP wastewater sample contained 1 ppm less Ca, 12 ppm greater Na, and 1 ppm greater Mg than are present in the wastewater simulant. Even with the slight difference in chemical composition, the strontium isotherm in the actual wastewater was essentially the same as that observed in the simulant. The slope of the B.E.T. plot was  $1070 \pm 6$  kg/mol, and the intercept was  $0.04 \pm 0.07$  kg/mol; the least-squares linear correlation coefficient was 0.9996. The values for  $Q^\circ$  (0.9 mmol strontium per kilogram of resin) and  $B$  ( $3 \times 10^4$ ) were calculated from these data using Eq. (7). The cesium sorption ratio in the actual PWTP sample is approximately 60 % higher than that of the simulant. The cesium sorption capacity in the actual wastewater was 0.024 meq/kg, as compared with 0.017 meq/kg in the simulant when the initial cesium concentration in either sample was  $2.5 \times 10^{-6}$  meq/L.

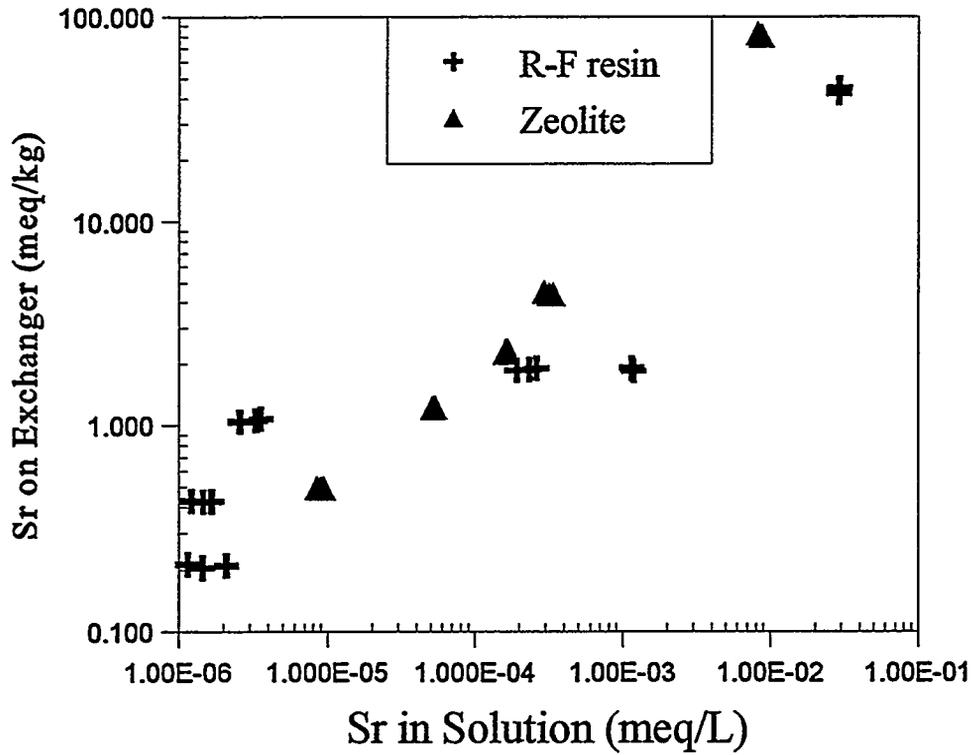
Figures 20 and 21 present a comparison of strontium and cesium sorption on chabazite zeolite and the R-F resin. As can be seen from the two plots, strontium sorption on the zeolite exceeds that of the R-F resin when the ratio of the PWTP sample volume to the resin mass is greater than 1. However, strontium sorption is greater on the R-F resin if this ratio is less than 1. The zeolite is uniformly more effective than the R-F resin for cesium sorption in the actual PWTP process wastewater.



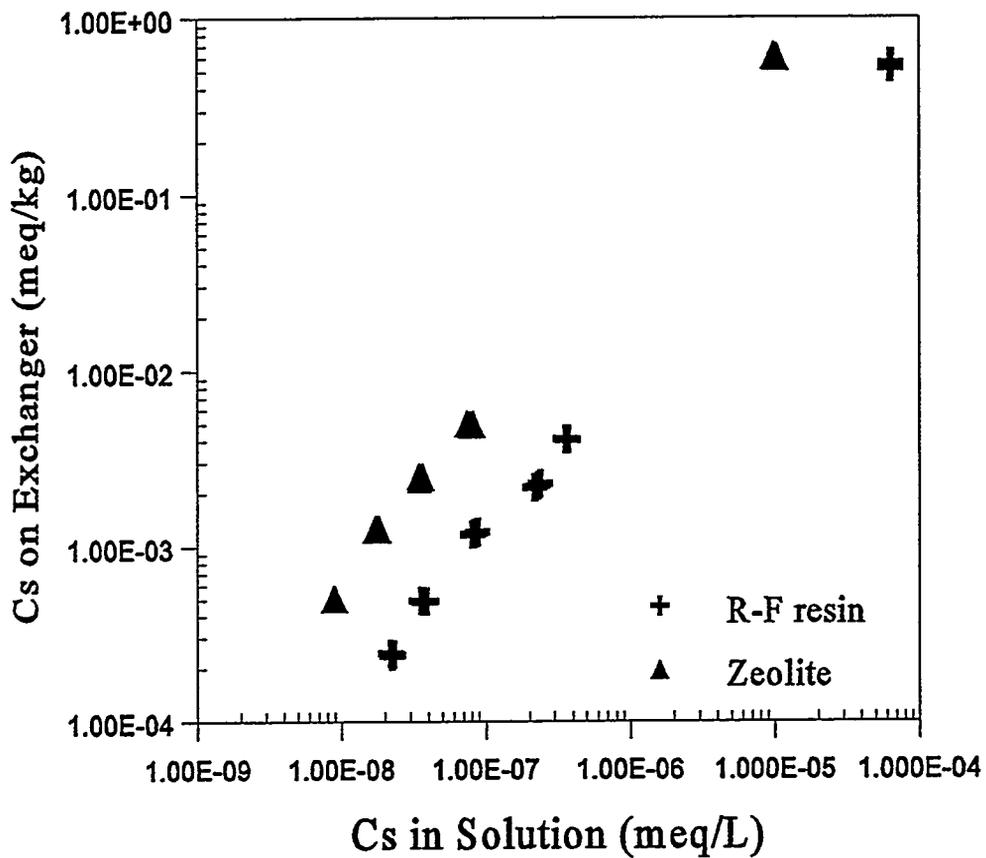
**Fig. 18. Strontium sorption from actual PWTP feed and PWTP simulant.** Test procedure: 0.005 to 0.100 g of water-washed R-F resin in 10 mL of solution; 24-h equilibration time; initial strontium concentration in simulant for lower data points, 0.00228 meq/L; initial strontium concentration for upper points, 0.05 meq/L; initial strontium concentration in actual PWTP sample, 0.00217 meq/L.



**Fig. 19. Cesium sorption from actual PWTP feed and PWTP feed simulant.** Test procedure: 0.005 to 0.100 g of water-washed R-F resin in 10 mL of solution; 24-h equilibration time; initial cesium concentration in simulant for lower data points,  $2.5 \times 10^{-6}$  meq/L; initial cesium concentration in simulant for upper points,  $3.2 \times 10^{-4}$  meq/L; initial cesium concentration in actual PWTP sample,  $2.5 \times 10^{-6}$  meq/L.



**Fig. 20. Strontium sorption from actual PWTP feed on resorcinol-formaldehyde resin and chabazite zeolite. Test procedure: 0.005 to 0.100 g of water-washed R-F resin and NaCl-washed chabazite zeolite in 10 mL of actual PWTP solution; 24-h equilibration time; initial strontium concentration in simulant for lower data points, 0.00228 meq/L; initial strontium concentration for upper points, 0.05 meq/L; initial strontium concentration in actual PWTP sample, 0.00217 meq/L.**

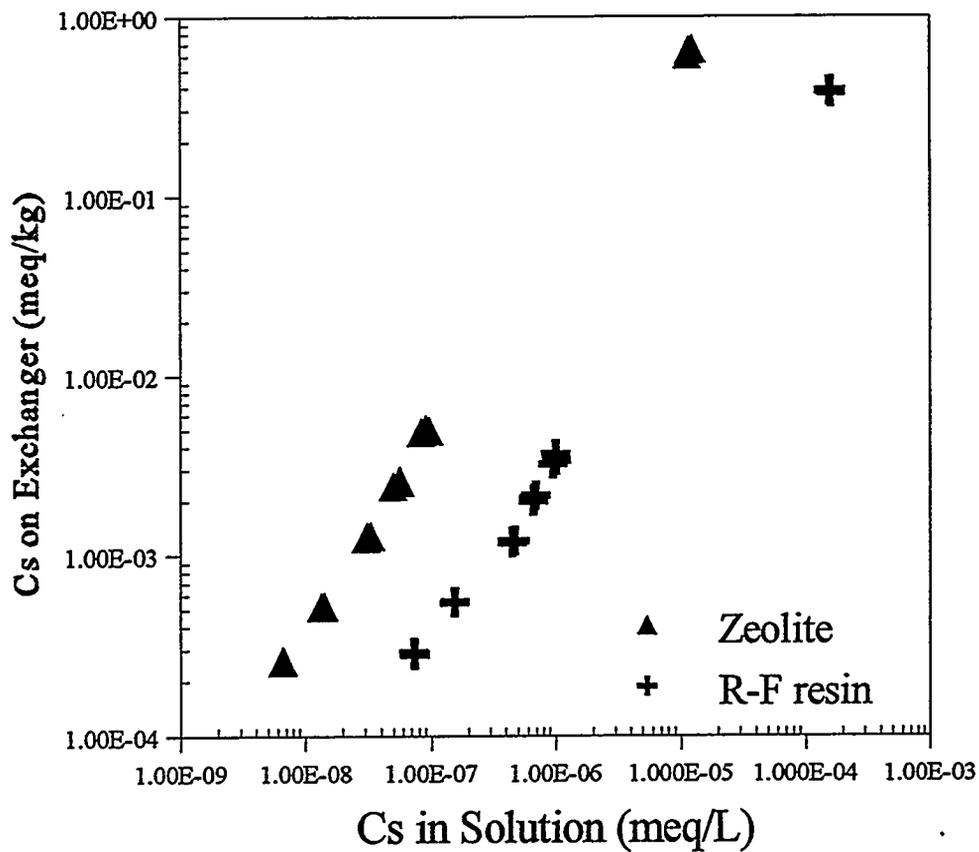


**Fig. 21. Cesium sorption from actual PWTP feed on resorcinol-formaldehyde resin and chabazite zeolite.** Test procedure: 0.005 to 0.100 g of water-washed R-F resin or NaCl-washed chabazite zeolite in 10 mL of actual PWTP solution; 24-h equilibration time; initial cesium concentration in simulant for lower data points,  $2.5 \times 10^{-6}$  meq/L; initial cesium concentration for upper points,  $3.2 \times 10^{-4}$  meq/L; cesium concentration in actual PWTP sample,  $2.5 \times 10^{-6}$  meq/L.

### 6.3 SORPTION FROM ACTUAL GROUNDWATER

Figures 22 and 23 compare the sorption characteristics of cesium and strontium in actual WAG 5 groundwater. Before the addition of  $^{85}\text{Sr}$  and  $^{137}\text{Cs}$  tracers, the  $^{90}\text{Sr}$  content in the groundwater sample was  $1.3 \times 10^4$  Bq/L;  $^{137}\text{Cs}$  was not found in the sample. The total strontium concentration was 0.2 ppm. Bicarbonate, which was present at a concentration of 484 ppm, was the major anion.

Sorption isotherms were developed using both sodium-modified chabazite zeolite and water-washed R-F resin in the actual groundwater sample. The cesium sorption data for both the treated zeolite and the resin fit the Freundlich sorption model, as presented in Fig. 22. Using the sodium-modified zeolite, the slope ( $1/n$ ) of the line is 1.046; the intercept of the Freundlich plot is 4.98, and the linear correlation coefficient is 0.998. These results suggest that the sorption coefficient ( $K_d$ ) in units of L/kg is governed by the relationship  $95,000 \times [\text{Cs}]^{0.045}$ , where the units for cesium concentration at equilibrium are meq/L. Cesium sorption on the resin also fit the Freundlich model, although the relationship indicated a very slight curvature in the midconcentration range of the profile. The slope of the line is 0.945, the intercept is 3.158, and the linear correlation coefficient is 0.997. The comparative equation for the calculation of  $K_d$  using the resin is  $1884/[\text{Cs}]^{0.055}$ . Again, the units for the  $K_d$  are L/kg, and the cesium solution concentration at equilibrium is in units of meq/L. The sorption capacities for cesium from this particular groundwater sample were 0.12 and 0.07 meq per kilogram of dry sorbent for the sodium-modified zeolite and water-washed resin, respectively.



**Fig. 22. Cesium sorption from WAG 5 groundwater on both sodium-form zeolite and water-washed resorcinol-formaldehyde resin. Test procedure: 0.005 to 0.100 g of R-F resin and sodium-form chabazite zeolite in 10 mL of solution; 24-h equilibration time; initial cesium concentration for lower data points,  $2.43 \times 10^{-6}$  meq/L; initial cesium concentration for upper points,  $3.2 \times 10^{-4}$  meq/L.**

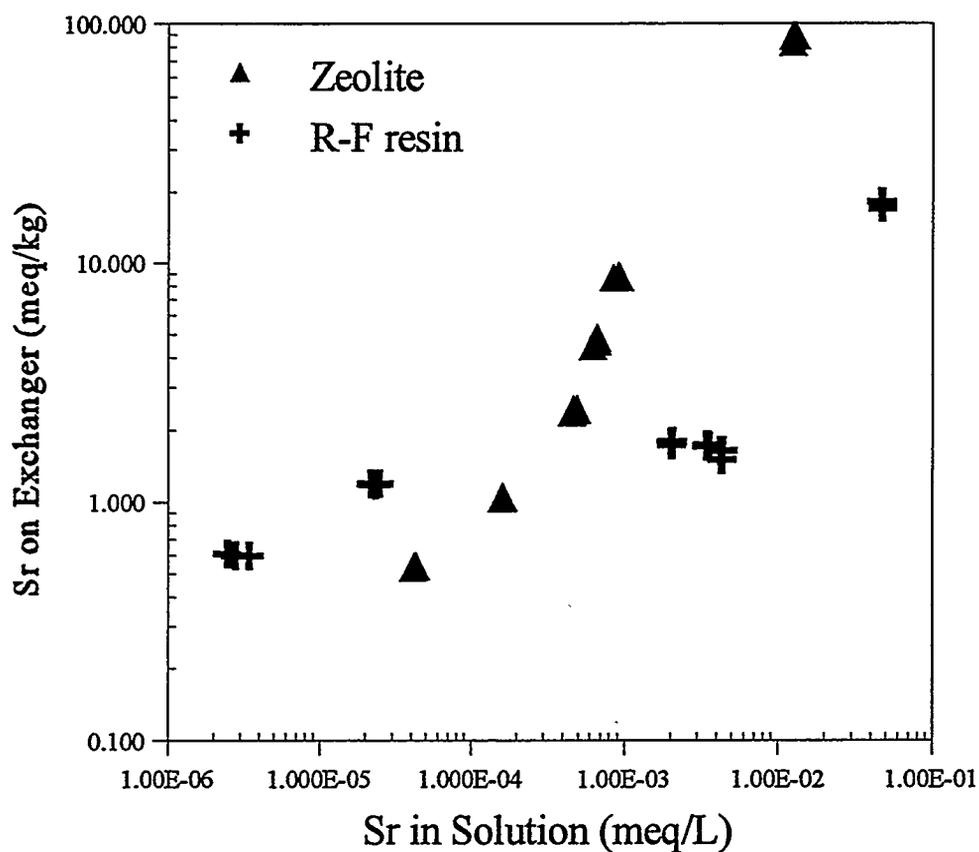
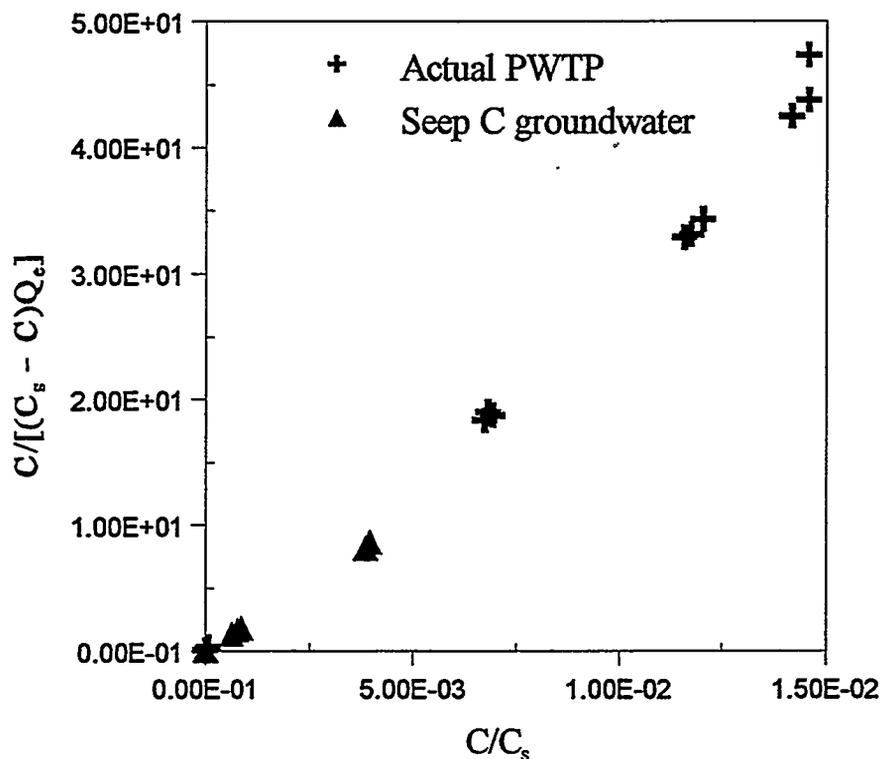


Fig. 23. Strontium sorption from WAG 5 groundwater on both sodium-form zeolite and water-washed resorcinol-formaldehyde resin. Test procedure: 0.005 to 0.100 g of water-washed R-F resin and sodium-form chabazite zeolite in 10 mL of solution; 24-h equilibration time; initial strontium concentration for lower data points, 0.005 meq/L; initial strontium concentration for upper points, 0.05 meq/L.

Strontium sorption on water-washed resorcinol-formaldehyde resin fits the B.E.T. model for groundwater samples. A linear relationship is obtained if the data are plotted as  $C/C_s$  vs  $C/[(C_s - C)Q_s]$ , as presented in Fig. 24. The saturation concentration was set at 0.074 mmol/L (6.5 ppm), the upper concentration of strontium found in typical groundwater. The linear correlation coefficient for the fit of 15 data points to the B.E.T. model was 0.993. The slope ( $1490 \pm 34$  kg/mol) and intercept ( $-0.4 \pm 1.5$  kg/mol) of the relationship were then used to calculate the  $Q^\circ$ . The calculated  $Q^\circ$  is 0.7 mmol of strontium per kilogram of resin from the actual groundwater sample, as compared with the value of 0.9 mmol per kilogram of resin observed in either the PWTP simulant or the actual feed sample. The calculated value of  $B$ , a constant indicating the energy of interaction with the resin surface, is -3500.

Strontium sorption on sodium-modified zeolite fit the Freundlich sorption model best (Fig. 23), although the correlation coefficient for the linear regression analysis is only 0.97. When the log value of the final strontium concentration in solution ( $C$  in meq/L) is plotted against the log value of strontium sorbed per unit weight (meq/kg) on the resin, the resulting slope is equivalent to 0.93 and the intercept is 3.6. These results imply that the equation governing the sorption coefficient,  $K_d$ , can be defined as  $(4.5 \times 10^3)/[Sr]^{0.07}$ . The comparable strontium sorption capacity in WAG 5 groundwater is 20 meq/kg for the zeolite. Because strontium sorption on the resin is dependent on the ratio of the sample volume to the sorbent mass, the sorption capacity for the groundwater sample must be defined in terms of this ratio. A maximum of approximately 2 meq of strontium per kilogram is sorbed from the groundwater if the treatment ratio is higher than 2 mL of sample per milligram of resin. The sorption capacity of the resin will be at least as high as that observed with the zeolite if the treatment ratio is equal to or less than 0.5 mL sample per milligram of resin.



**Fig. 24. Strontium sorption data fit to B.E.T. sorption model.**  
 Test conditions: 0.005 to 0.100 g of R-F resin in 10 mL of solution; 24-h equilibration time; initial strontium concentration, 0.00228 meq/L.  
 $C$  = concentration of strontium remaining in solution at equilibrium (mol/L);  
 $C_s$  = saturation concentration of strontium in solution at room temperature (mol/L); and  $Q_e$  = the amount of strontium adsorbed per unit weight of resin (mol/kg).

## 7. CONCLUSIONS

Progress to date has included the characterization of the baseline treatment technology—nuclide sorption on natural chabazite zeolite. Cesium and strontium sorption capacities on sodium-modified zeolite have been determined for batchwise treatment of both a wastewater simulant and the corresponding actual wastewater. The suppression of nuclide sorption capacity by the major cations present in groundwater (Ca, Na, Mg, and K) was also quantified. A test with a small zeolite column was completed to observe  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  breakthrough characteristics under dynamic flow conditions. Elution results indicate that the chabazite zeolite has the following selectivity:  $\text{Cs} > \text{Sr} > \text{Ca} > \text{Mg} > \text{Na}$ . The strontium concentration in the effluent at 3500 BVs was 1% of the initial feed concentration of 0.1 ppm strontium. One percent cesium breakthrough was observed at approximately 15,000 BVs; column operation was terminated when 55% cesium breakthrough was observed at about 60,000 BVs. The summation of sorption data and column performance served to characterize the baseline zeolite characteristics, as well as to establish standardized testing procedures for the direct comparison of the baseline treatment with emerging sorbent technology. A description of the performance of the chabazite zeolite for the treatment of process/groundwater samples has been summarized in an ORNL topical report.<sup>1</sup>

The R-F resin was selected as the first in a series of new sorbents that will be tested as part of this task. Although the resin was initially developed for the removal of cesium in highly alkaline waste streams, it has demonstrated promise in removing both cesium and strontium from the wastewater simulant. Batchwise testing of the material was conducted to determine the optimum

conditions for nuclide removal in the simulant. Sorption results from several resin pretreatment methods were compared with sorption isotherms developed by using the as-received resin.

Pretreatment methods included (1) washing the resin with 1 *M* HNO<sub>3</sub>, followed by rinsing the resin with ultrapure (nanopure) water until a neutral rinsate was obtained; (2) rinsing the resin with nanopure water only; (3) washing the resin with groundwater simulant that contained neither strontium nor cesium; and (4) prewashing the resin with 2 *M* NaCl, followed by rinsing with nanopure water to remove excess sodium ion. This latter treatment is similar to that used for pretreating the zeolite sorbent used in the baseline sorbent studies. The best pretreatment methods included rinsing the resin with nanopure water prior to air drying and prewashing the resin with 2 *M* NaCl, followed by a rinse with nanopure water. The water-wash pretreatment procedure was adopted for the remainder of the resin studies because (1) the required preparation time is shorter, and (2) there is less likelihood of introducing excess sodium ion inadvertently into test samples.

Cesium sorption on either the treated or the untreated resin was equivalent for cesium solution concentrations above 0.1 neq/L. A slight enhancement of cesium sorption occurred below this solution concentration when the resin was pretreated. The cesium isotherms were linear for simulant with cesium concentrations greater than 0.01 neq/L; the cesium sorption ratio in the linear range was 6,300 L/kg. The cesium sorption capacity in the wastewater simulant was approximately 0.02 meq/kg, which is a factor of 10 lower than that found using the chabazite zeolite treatment. Strontium sorption on the resin was very dependent on the method of resin pretreatment. Again, the greatest sorption in PWTP simulant containing very low strontium concentrations was obtained when the resin was initially washed with either water or saline solution. The strontium isotherm has two inflection points, possibly indicating a multilayer

sorption mechanism. The sorption capacity, therefore, is dependent on the ratio of the sample volume to resin mass used in the batch test. For a ratio less than 0.5 mL per milligram of resin, the strontium sorption capacity on the resin was 600 meq/kg. When the ratio of sample volume to resin mass was greater than 2 mL/mg, the strontium sorption capacity in the simulant was only 4 meq/kg. The strontium sorption capacity from the same simulant using pretreated zeolite was 30 meq/kg.

The effects of elevated Na, K, Mg, and Ca concentrations on Sr and Cs sorption were studied. Higher concentrations of the individual cations were added to the wastewater simulant to cover the concentration ranges of the individual cations found in typical groundwater. As the concentration of each cation increased above that originally found in the simulant, both strontium and cesium sorption on the resin was significantly suppressed. Within the 0- to 4-meq/L cation concentration range, the order of increasing effect on strontium sorption was:  $\text{Na} \leq \text{K} < \text{Mg} \leq \text{Ca}$ . The effect of potassium on cesium sorption was more equivalent to that observed with doubly charged cations than that observed for simply charged cations. Strontium sorption on the R-F resin was more strongly affected by the presence of interfering cations, as compared with that observed for the zeolite. After the addition of 4 meq of interfering cation per liter of wastewater simulant, the strontium sorption ratio was reduced to 0.3% of its original value. The cesium sorption was reduced by 50% for the same addition of cation.

Both water-washed R-F resin and pretreated zeolite were used to develop cesium and strontium isotherms for samples of actual wastewater and actual groundwater. In each case, the sorption isotherm for the sorbents in the authentic PWTP wastewater was similar to that observed for the simulant. The cesium data for the sorbents in both water matrices fit the Freundlich sorption

model, in which the sorption data exhibit a linear relationship between the log value of the final concentration of cesium in solution vs the log value of cesium sorbed, per unit weight, on the sorbent. The slope ( $1/n$ ) of the line was 1.046, the intercept of the Freundlich plot was 4.98, and the linear correlation coefficient was 0.998, using the sodium-modified zeolite in actual groundwater. These results suggest that the sorption coefficient ( $K_d$ ), in units of L/kg, is governed by the relationship  $95,000 \times [Cs]^{0.045}$ , where the units for cesium concentration at equilibrium are meq/L. The resin data for cesium sorption in the groundwater fit the Freundlich model, although the relationship indicated a very slight curvature in the midconcentration range of the profile. The slope of the line was 0.945, the intercept was 3.158, and the linear correlation coefficient was 0.997. The comparative equation for the calculation of  $K_d$  using the resin was  $1884/[Cs]^{0.055}$  for groundwater samples. Again, the units for the  $K_d$  are L/kg, and the concentration of cesium in solution at equilibrium is in units of meq/L.

Strontium sorption on the R-F resin fits the B.E.T. model in both water matrices. When the strontium saturation concentration was set at 0.074 mmol/L (6.5 ppm), 0.7 mmol of strontium per kilogram of resin was required to form a monolayer on the sorbent contained in an actual groundwater sample. This value compares with 0.9 mmol of strontium per kilogram of resin in actual PWTP wastewater.

The actual groundwater sample contains 100 ppm of calcium, as compared with 37 ppm in the process wastewater. Because Ca suppresses nuclide sorption on either zeolite or resin, both Sr and Cs sorption capacities from actual groundwater are lower than those observed in the actual PWTP wastewater sample. Treated zeolite appears to have the greatest sorption capacity for strontium and cesium in the groundwater samples. The removal of strontium from process

wastewater may be greater using the water-washed zeolite, provided that the ratio of sample volume to resin mass, in units of L/kg, is less than 1.

Planned activities in FY 1996 will focus on completing the efforts begun in FY 1995. They will include reviewing data obtained from a test with a small zeolite column in which strontium and cesium breakthrough were observed in the treatment of a wastewater simulant. Breakthrough data will be used to define the basic operating parameters of the zeolite column, such as the height of a transfer unit and the number of transfer units required for simulant treatment. Collaboration, available either at ORNL or through university contacts, will be pursued to obtain the modeling software required to evaluate column breakthrough data and to help define the transfer mechanisms operating in the column.

Additionally, studies will be completed to compare the treatment efficiency of the R-F resin with that of the baseline sorbent, chabazite zeolite. Final experimentation may include either a small-column test using the resin to treat a wastewater simulant or a small, stirred batch reactor to determine cation selectivity in the simulant.

A sample of monosodium titanate powder has been received recently from Allied Signal Research and Technology (Des Plaines, IL). A 15% slurry of the sorbent in sodium hydroxide has been ordered from the BSC (Mead, CO). Both of these sources of sodium titanate will be evaluated for effectiveness in removing strontium from the wastewater simulant. The critical kinetic and equilibrium data will be determined for the removal of strontium from small batch samples. Then the loose sorbent powder will then be tested using actual process wastewater and groundwater samples. The granular form of the sodium titanate is scheduled for production at

Allied Signal Research and Technology early in FY 1996. When it is available, the sorption characteristics of the granular material will be compared with that of the powder. If the performance of the granular sodium titanate warrants the investment of time and materials, a small-column test will be planned. Results of this activity will be submitted for journal publication or as a milestone draft report, as required.

If the granular sodium titanate material cannot be obtained in a timely manner or the performance of the sorbent does not suggest the need for dynamic column testing, the remaining time in FY 1996 will be devoted to assessing another new technology for wastewater treatment. If the materials are available commercially, it would be advantageous to evaluate molecular recognition products for the removal of strontium or cesium in groundwater. Evaluation of such materials was originally scheduled for FY 1995; however, materials suitable for groundwater applications have not yet been released from IBC Advanced Technologies (Provo, UT). If these molecular recognition materials become available, their performance will be compared with the more standard chabazite zeolite treatment. The remainder of FY 1996 can be used to review the performance of pillared clays or engineered crystalline silicotitanate if the molecular materials have not yet become available.

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