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**OAK RIDGE  
NATIONAL  
LABORATORY**



## **Removal of Cesium, Technetium, and Strontium from Tank Waste Supernatant**

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Chemical Technology Division

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FROM TANK WASTE SUPERNATANT**

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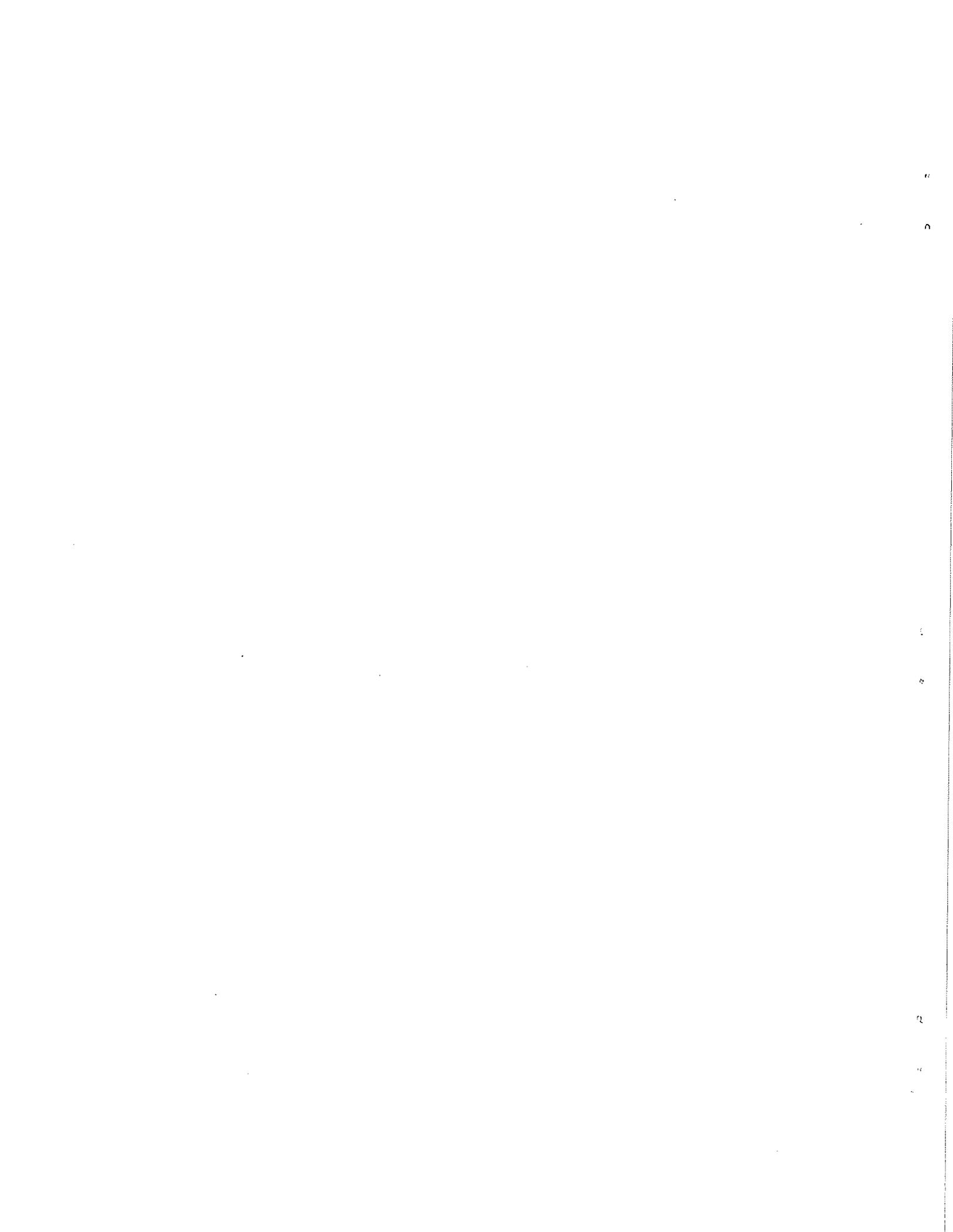
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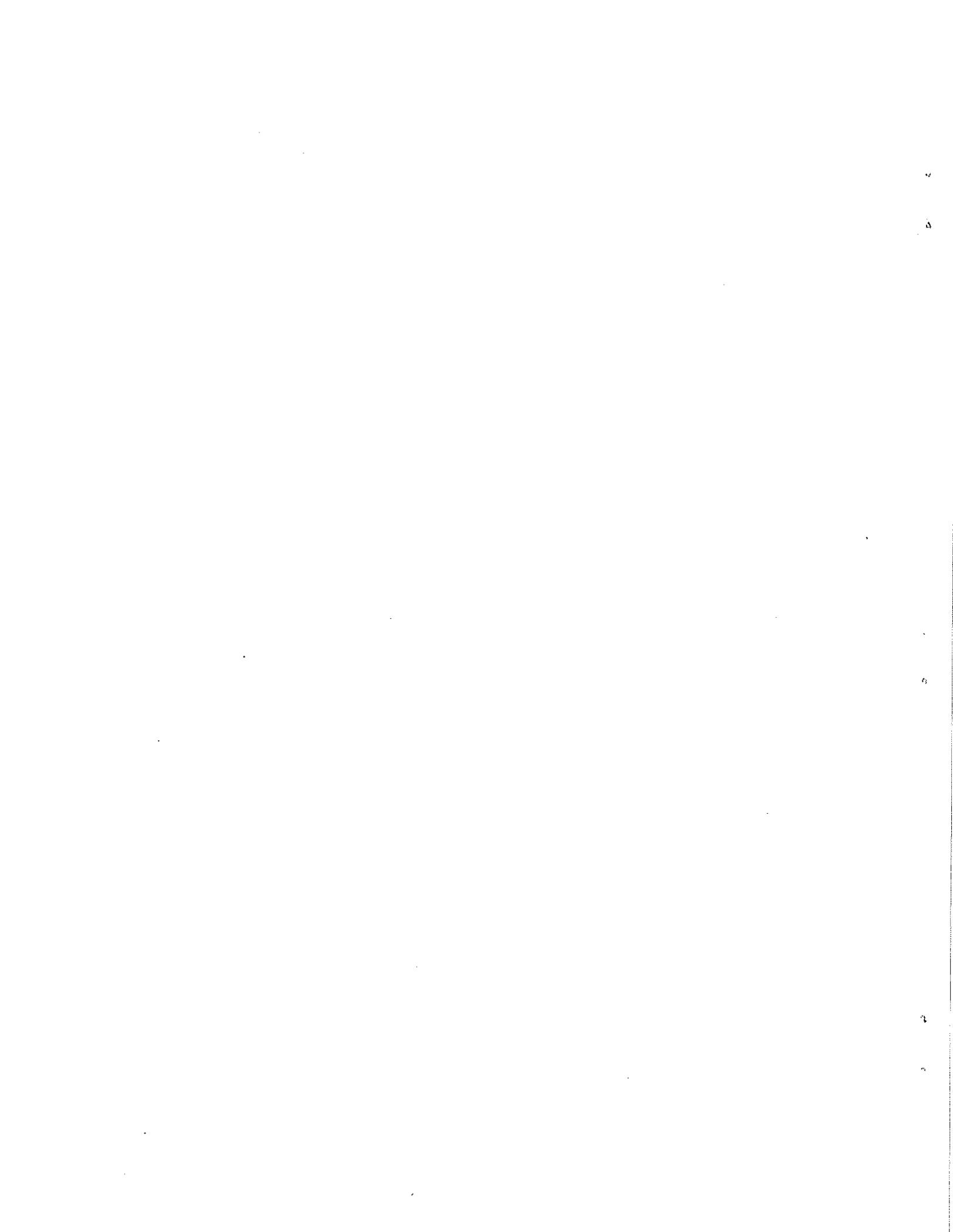
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## SUMMARY

Millions of gallons of radioactive waste stored in underground tanks contain liquid supernatants. The radioactivity is only a small part of the supernatant volume; most of the radioactivity is from cesium, technetium, and strontium. Separation of the radioactive components from the bulk material would reduce the storage requirements for high-level waste and allow the nonradioactive components to be handled and stored as low-level waste.

Both batch and column tests have been conducted at Oak Ridge National Laboratory (ORNL) using supernatants from tanks at the Melton Valley Storage Tank (MVST) facility to evaluate over 25 sorbents for removing cesium, strontium, and technetium. The greatest effort was directed toward cesium removal since  $^{137}\text{Cs}$  is responsible for a large fraction of the radioactivity in tank supernatants at ORNL, Hanford, and other Department of Energy sites.

The "best" sorbent for a particular application depends on several considerations. Different sorbents are more stable and usable in different pH ranges and acid and base concentrations. Some of the sorbents are more easily eluted, allowing recovery and concentration of the radionuclide, while the radionuclides cannot be readily removed from other sorbents. Also, some of the sorbents are more adaptable to storage in final waste forms; therefore, the sorbent of choice depends on the ultimate objective as well as the characteristics of the supernatant.

Crystalline silicotitanate (CST), potassium cobalt hexacyanoferrate (KCoCF), resorcinol-formaldehyde (R-F) resin, and SuperLig<sup>®</sup> 644C effectively removed cesium from supernatants. The commercial form of CST, IONSIV IE-911, gave the most-favorable all-around results in both batch and column tests. It is also a reasonable sorbent for strontium. It is effective over a wide range of pH values and has good physical properties. The cesium is not readily recoverable from CST. However, it might be feasible to incorporate the loaded CST directly in glass for final disposal. Potassium cobalt hexacyanoferrate had the highest cesium distribution coefficient in the batch tests but was unstable in the column tests in which the pH of the supernatants was  $>12.5$ . It is most stable below pH 12. Also, cesium cannot be readily eluted from KCoCF. The R-F resin showed some inconsistency in loading and elution. Potassium has a greater effect on cesium removal with R-F than with CST. In contrast to the CST and KCoCF, the cesium can be eluted and recovered from R-F.

Technetium removal is very dependent on technetium speciation. In our tests, technetium was added to the supernatant solutions as ammonium pertechnetate. A significant fraction of technetium in the Hanford

tanks exists as nonpertechnetate. Consequently, anion exchangers would not be expected to be completely effective in removing all the technetium from all the Hanford tank supernatants. Several anion exchangers, including Reillex HPQ and Eichrom ABEC-5000, were effective in removing pertechnetate from supernatants. Elution of the technetium from Reillex HPQ required reduction of the technetium with stannous chloride and complexation with ethylenediamine. Technetium can be eluted from ABEC-5000 with water, which is a great advantage. Both sorbents exhibited significant volume changes during loading and elution. Also, the densities of these sorbents are similar to those of some of the supernatants; consequently, the sorbents may float and require bed stabilization. Furthermore, in batch or column tests conducted with these sorbents using effluent from column tests in which Superlig<sup>®</sup> 644C resin was used to remove the cesium from MVST W-27 supernatant, very little technetium was removed. These data indicated that the Superlig<sup>®</sup> 644C decomposition product(s) may have reduced the pertechnetate ions to lower valence forms that were not sorbed.

Amberlite IRC-718, Duolite, sodium titanate, CST, sodium titanate in a polyacrylonitrile matrix, titanium monohydrogen phosphate, and C-467 were effective in removing strontium from MVST supernatant solutions. R-F resin also has some capacity for strontium removal. Generally, the inorganic sorbents were more effective than the resins. The presence of carbonate can significantly reduce the strontium solubility, while complexing agents in the supernatant can increase strontium solubility and reduce removal by ion exchange.

## 1. INTRODUCTION

Releases of radioactivity into the environment have always been a concern. The concern over additional releases has increased the need for remediation of the nuclear wastes stored in underground tanks at sites managed by the Department of Energy (DOE). The hundred million gallons of waste stored in hundreds of tanks at various managed sites consist predominantly of sludges and supernatants. Although the quantities of these wastes are quite substantial, the bulk consists of nonradioactive chemicals. Separation of the radioactive components from the bulk material would reduce the storage requirements for high-level waste and allow the nonradioactive components to be handled and stored as low-level waste. This separation and removal could benefit several DOE-managed programs, including the Tank Waste Remediation System, by reducing the radioactive waste volume.

Achieving this goal will be difficult because the supernatants in the tanks were derived from combined wastes from various chemical processes over the last 50 years. Consequently, identifying the best method to treat these materials is a considerable task. The radioactive constituents comprise only a small part of the volume of the supernatants in the tanks; most of this activity is from the cesium, technetium, and strontium present. Precipitation, ion exchange, evaporation, and solvent extraction are some processes used to separate these materials. However, any separation of radionuclides from the supernatants can be affected by the high concentrations of sodium, potassium, and nitrates. Ion-exchange may be the best method for treatment of the supernatants, since ion exchange is effective under a broad range of conditions. Ion-exchange separation has the added advantage of potentially producing small quantities of secondary wastes. The large amount of material being treated and subsequent costs will greatly influence the selection of a process for treating the supernatants.

A survey of the literature resulted in the identification of several sorbents for testing.<sup>1-16</sup> From an initial screening of these sorbents, several were selected for batch tests using tank waste simulants to reduce the number of materials used for additional testing. Since unidentified complexants in actual supernatants can alter the behavior of the multivalent cations, selecting the best materials for column studies from these screening tests requires using actual supernatant samples. Experiments conducted at Oak Ridge National Laboratory (ORNL) have used actual supernatant samples from tanks at the Melton Valley Storage Tank (MVST) facility. These tests were used for evaluating sorbents to remove cesium, strontium, and technetium. Several sorbents were selected for evaluation in column tests. This report includes a summary of the batch studies and the results obtained from column studies conducted during FY 1996 and FY 1997 and compares the results.

## 1.1 RELATED STUDIES

Work has been conducted at several DOE sites using both actual supernatant samples and supernatant simulants for evaluating sorbents to remove cesium, technetium, and strontium.<sup>1-16</sup> A variety of sorbents have been tested in both batch and column tests. Several of these sorbents, some experimental and some commercially available, are listed in Tables 1 (cesium), 2 (technetium), and 3 (strontium). The results from some of these studies are summarized in the following sections.

### 1.1.1 Batch Studies

Simulants were prepared by Brooks et. al.<sup>17</sup> to cover the concentration range found in the underground storage tanks. Several sorbents were evaluated in simulants designated as neutralized current acid waste (NCAW), double-shell slurry feed (DSSF), and West Valley Alkaline Supernatant. The sorbents selected for testing to remove the cesium from these supernatants included Duolite CS-100, IONSIV IE-95, Duolite ARC-359, Amberlite IRC-718, Duolite ARC-9359, Durasil 210, resorcinol-formaldehyde (R-F) resin, Duolite C-3, Lewatit DN-KR, Amberlite IRC-76, Duolite DP-1, RT 3972, TP-207, Durasil 230, and IONSIV IE-96. The cesium distribution ratios for these sorbents indicated that the R-F resin was more effective, with  $K_d$  values of  $10^2$  mL/g in the NCAW and DSSF, while the  $K_d$  values for CS-100, Duolite C-3, and TIE-96 were on the order of 10 mL/g in the various simulants.

Marsh, Svitra, and Bowen<sup>2-6</sup> tested sorbents in several solutions simulating Hanford tank supernatants exhibiting slightly different chemistries. In most of the batch tests, a 250-mg sample of the air-dried sorbent was contacted with 6 or 8 mL of the simulant for 30 min, 2 h, and 6 h. Results from the tests using the different simulants indicated that dissolved organics did not interfere with cesium separation, with similar  $K_d$  values for the initial simulant and the simulant that was hydrothermally treated. Actually, hydrothermal treatment of the simulant appeared to increase the cesium distribution significantly with potassium cobalt hexacyanoferrate (KCoCF) sorbent. Dilution of the supernatant simulant increased the cesium distribution for crystalline silicotitanate (CST) and R-F resin.

Marsh, Svitra, and Bowen<sup>2-6</sup> also tested several sorbents for removing strontium from different supernatant simulants. The strontium concentration in the simulants was 3  $\mu\text{g/L}$ . As with the cesium batch tests, a 250-mg sample of the air-dried sorbent was contacted with 6 or 8 mL of the simulant for 30 min, 2 h, and 6 h. The strontium  $K_d$  values using a Hanford tank 102-SY supernatant simulant were  $>9000$  mL/g for CST, and 2734 mL/g for Duolite C-467. Hydrothermally treated 101-SY simulant gave strontium  $K_d$  values  $>16,000$  mL/g for sodium titanate, 5000 mL/g for KCoCF, 487 mL/g for Duolite C-467, and 1383 mL/g for

Table 1. Sorbents used for cesium batch-contact studies

Organic sorbents	
Amberlyst™ XN-1010	LIX™-54—a beta-diketone extractant bead
Bone char	Savannah River resorcinol-formaldehyde resin (R-F resin)
Clinoptilolite	Superlig™ 644
Diphonix™	Synthetic zeolite in a polyacrylonitrile (PAN) matrix (NaY-PAN)
Duolite™ C-467	Synthetic mordenite in a PAN matrix (M315-PAN)
Duolite™ CS-100 resin	Tannin
Durasil™ 230	TRW CS-WA—treated coal
IONSIV™ IE-96	
IONSIV™ TIE-96	
Inorganic sorbents	
Ammonium molybdophosphate (AMP) in a PAN matrix (AMP-PAN)	Nickel hexacyanoferrate/manganese dioxide (NM) in a PAN matrix (NM-PAN)
Amorphous hydrous titanium oxide (HTO)	Nickel ferrocyanide (NiFC) in a PAN matrix (NiFC-PAN)
Barium/calcium sulfate [Ba(Ca)SO <sub>4</sub> ] in a PAN matrix [Ba(Ca)SO <sub>4</sub> -PAN]	Potassium hexacyanoferrate (KCoFC) in powder and crystalline form
Cobalt hexacyanoferrate (CoFC) in a phenolsulfonic-formaldehyde matrix (CoFC-PSF)	Sodium titanate (NaTiO) in a PAN matrix (NaTiO-PAN)
Crystalline silicotitanate (CST)—several batches	Titanium dioxide (TiO) in a PAN matrix (TiO-PAN)
IONSIV™ IE-910 (CST)	Titanium hexacyanoferrate (TiFC) in a PSF matrix (TiFC-PSF)
Magnesium oxide (MgO) in a PAN matrix (MgO-PAN)	

Table 2. Sorbents used for technetium batch-contact studies

Organic sorbents		
Aliquat™ 336	IONSIV™ TIE-96	PNPK-2
Bone char	Isobutyl-Reillex™ HP	Purolite™ A-520-E
CMPO-diisopropylbenzene beads	LIX™-26 (8-hydroxyquinoline) beads	Reillex™ HPQ
Crypt-DER polymer resin	LIX™-54	R-F resin
Cyanex™ 923	M315-PAN	Sr-Spec™
DHDECMP	N-Butyl-HP	Sybron (Et) <sub>3</sub> N resin
DHDECMP-DIPB	N-Hexyl-HP	Sybron (Pr) <sub>3</sub> N resin
Diphonix™	N-Octyl-HP	Tannin
Dow™ XFS-4195	N-Butyl-Reillex™ HP	TEVA-Spec™
Duolite™ C-467	N-Hexyl-Reillex™ HP	TRU-Spec
Ionac™ SR-3	Nusorb™ LP-70-S	
Ionac™ SR-6	PNPK-1	
Inorganic sorbents		
Ba(Ca)SO <sub>4</sub> -PAN	NiFC-PAN	Titanium dioxide (TiO)
CoFC-PSF	Niobium pentoxide (NbO)	TiO-PAN
HTO	NaTiO-PAN	ZrO
MgO-PAN	TiFC-PSF	

Table 3. Sorbents used for strontium batch-contact studies

Organic sorbents		
Aliquat™ 336	IONSIV™ IE-96	NK 120B
Amberlite™ DP-1	IONSIV™ TIE-96	Nusorb™ Ferrocabon A
Amberlite™ IRC-718	Isobutyl-HP	Nusorb™ Unitane
Bone char	KW-4-40x (pillared, layered material)	PS-3,3-LICAMS (functionalized polymer)
Chelex™ 100	KW-4-41x (pillared, layered material)	PS-CATS (functionalized polymer)
Clinoptilolite	Lewatit™ TP-207 resin	Purolite A-520-E
Cyanex™ 923	LIX™-54	R-F resin
Diphonix™	M315-PAN	Superlig™ 644
Dow™ XFS-4195	MgAlHT (hydrotalcite)	Tannin
Duolite™ C-467	N-Butyl-HP	TRW CS-WA
Duolite™ CS-100	N-Hexyl-HP	TRW CS-SA
Fithian Clay		
Inorganic sorbents		
AMP-PAN	Manganese dioxide in a PAN matrix (MnO-PAN)	TiFC-PSF
Ba(Ca)SO <sub>4</sub> -PAN	Monosodium titanate	TiO-PAN
CoFC-PSF	NiFC-PAN	Titanium phosphate (TiP)
Crystalline polyantimonic acid in a PAN matrix (CSbA-PAN)	Nickel hexacyanoferrate/manganese dioxide (NM) in a PAN matrix (NM-PAN)	Titanium phosphate in a PAN matrix (TiP-PAN)
CST	Sodium nanotitanate (RC-2-62A)	Zirconium dioxide in a PAN matrix (ZrO-PAN)
HTO	NaTiO-PAN	Zirconium Oxide (ZrO)
IONSIV™ IE-910 (crystalline silicotitanate)	Stannic antimonate in a PAN matrix (SnSbA-PAN)	Zirconium oxide (ZrO) in a PAN matrix (ZrO-PAN)
KCoFC powder and crystals	Tantalum tungstate (KW-3-85x)	Zirconium phosphate in a PAN matrix (ZrP-PAN)
KCoFC in a PAN matrix (KCoFC-PAN)	Titanium antimonate (TiSbA) in a PAN matrix (TiSbA-PAN)	Zirconium oxide/zirconium phosphate in a PAN matrix (ZrOP-PAN)
MgO-PAN		

IONSIV IE-910 (a commercial form of CST). The results indicated that the presence of organics in the alkaline solutions reduced the  $K_d$  values for strontium by as much as two orders of magnitude. This was presumably due to the complexation of the strontium by the organics forming neutral or anionic complexes that were not removed by cation exchangers.<sup>18</sup>

Marsh, Svitra, and Bowen<sup>2-6</sup> also measured the technetium distribution using several supernatant simulants containing trace quantities (2 pg/L) of technetium and various sorbents. Their results indicated that organics appeared to have some effect on the removal of technetium from the alkaline solutions, with technetium  $K_d$  values increasing somewhat (generally less than a factor of 2) when the simulant was hydrothermally treated. From the batch tests using a 6-h mixing time, the technetium  $K_d$  values for the 102-SY simulant were 370 mL/g for Reillex HPQ and 620 mL/g for Purolite A-520-E. For the 101-SY simulant, the  $K_d$  values were 669 and 1301 mL/g and increased to 931 and 1887 mL/g for the hydrothermally treated simulant.

Technetium distribution studies were conducted by Schroeder et. al.<sup>8</sup> at Los Alamos National Laboratory using a double-shell slurry supernatant simulant and a 1:3 dilution of the simulant with Reillex HPQ anion exchanger. The effects of solution/sorbent ratio, temperature, and mixing time were evaluated. Using liquid-to-solid ratios of 5:1 to 10,000:1, a constant  $K_d$  of approximately 350 mL/g was obtained for ratios <250. Increasing the temperature from 25 to 60°C decreased the technetium distribution coefficients for all mixing times between 5 and 120 min in both the simulant and the diluted simulant. The technetium distribution ratios for the simulant were about 280 mL/g after 5 min in the 25°C solution and decreased to 180 mL/g at 60°C. Diluting the simulant increased the technetium  $K_d$  from 280 to 380 mL/g.

### 1.1.2 Column Studies

Several sorbents that gave good results in batch tests have been evaluated in column tests to verify batch results and establish column parameters for large-scale operation. More column studies have involved cesium removal since cesium is the major radioactive component in most tank supernatants.

Bray, Elovich, and Carson<sup>9</sup> used R-F resin to remove cesium from a simulant of a Savannah River Site alkaline waste. The column volume was about 200 mL. It took an average of 220 column volumes (CV) to reach 50 % cesium breakthrough. Approximately 99% of the cesium was eluted in 10 CV of 1 M formic acid.

Brown et al.<sup>19</sup> conducted column loading and elution studies to evaluate cesium removal from simulants of supernatants and actual supernatants from Hanford tanks 241-SY-101 and 241-SY-103. The supernatants used were obtained by mixing two samples of supernatants from each tank. The results from the column tests

indicated that cesium removal from the simulant and the actual supernatants was very similar. The 50% cesium breakthrough occurred for simulant and actual supernatant after about 41 and 37 CV, respectively. Elution of cesium loaded from the simulant and the supernatant required slightly different amounts of eluant. For the cesium loaded onto the sorbent from the simulant, 3.5 CV of the 0.5 M HNO<sub>3</sub> was required. Eluting cesium from the sorbent loaded from actual supernatant required 4.1 CV, an additional 0.6 CV of 0.5 M HNO<sub>3</sub>.

Column studies were conducted at Hanford by Hendrickson using similar equipment and procedures as used by Lee at ORNL.<sup>20</sup> Cesium removal was evaluated using a supernatant sample from Hanford tank 241-AW-101 with both R-F resin and IONSIV IE-911 (CST). The supernatant was diluted with water to reach a target sodium concentration of about 5 M. Comparison of the column data from ORNL MVST and Hanford DSSF supernatants showed reasonable agreement and predictability, especially for the IONSIV IE-911. It was suggested that differences in the R-F behavior could be related to the chemical stability of the resin and prior degradation during storage.

It is interesting to note that in the period from April 1961 to August 1964, almost 2,000,000 Ci of <sup>137</sup>Cs was recovered from Hanford Purex supernatant 103A, a basic 9 M sodium nitrate solution, and transported to ORNL for cesium source fabrication.<sup>21</sup> Aged Purex waste was centrifuged, and the supernatant was passed through a shielded transfer tank containing 400 gal of Decalso, a synthetic aluminosilicate sorbent, until about 50,000 Ci of <sup>137</sup>Cs was loaded. The casks were shipped from Hanford to ORNL on a modified gondola car. The cesium was eluted (>97%) at ORNL with 1000–1200 gal of 5 M ammonium nitrate at 80°C, and the ion-exchange tanks were returned to Hanford and reloaded with cesium. The cycle was repeated until 1.93 MCi of <sup>137</sup>Cs was recovered and transferred.

Blanchard et al.<sup>22,23</sup> evaluated Reillex HPQ and Eichrom ABEC-5000 in column studies at Pacific Northwest National Laboratory (PNNL) for technetium removal from Hanford supernatants. For these tests, supernatants obtained from tank AW-101, which is a DSSF, were diluted to 5 M Na<sup>+</sup>. Tracer quantities of <sup>99m</sup>Tc were added as ammonium pertechnetate (1.5 μCi/L), which did not add significantly to the 4.2 ppm <sup>99</sup>Tc already in the supernatant. Using flow rates of 10 and 9 bed volumes (BV)/h for loading the Reillex HPQ and Eichrom ABEC-5000, respectively, the 50% technetium breakthrough occurred after approximately 140 BV for Reillex HPQ and 60 BV for Eichrom ABEC-5000.

## 2. MATERIALS

### 2.1 MVST SUPERNATANT

Supernatant was taken from MVST W-25, W-27, and W-29 or by transferring pH-adjusted supernatant in tank W-27 to tank W-29 for use in sorption studies. The compositions of the original "as-received" supernatants are shown in Table 4. Supernatant samples were used in tests "as received," after pH adjustment, or after cesium removal by batch ion exchange or column chromatography. The "treated" supernatants (MVST W-27T and MVST W-29T) were prepared by removing cesium from the supernatants using a R-F resin followed by mixing with granular KCoCF. Table 5 shows the constituents in the treated supernatants.

Treating the W-27 supernatant to remove the cesium (MVST W-27T) also removed significant amounts of aluminum, barium, and calcium. Similar results were obtained by treating the W-29 supernatant (comparing the W-29 data in Table 4 and the MVST W-29T data in Table 5). Also shown in Table 5 is the composition of a W-27 supernatant after addition of sodium hydroxide to adjust the pH to 14 (MVST W-27pH). Many of the Hanford tank supernatants have a pH closer to 14 and a higher cesium concentration than the MVSTs.

Solids in all supernatant samples were removed by filtration of both the "as-received" and "treated" supernatant. For batch tests and column studies conducted in a hood, a filter with a maximum pore size of 0.22  $\mu\text{m}$  was used to filter the supernatant before conducting batch tests. For the column tests conducted in a hot cell, the supernatant was passed through in-line filters with a pore size of 0.45  $\mu\text{m}$ , located upstream and downstream from the column.

For technetium batch and column tests, ammonium pertechnetate, containing  $^{99}\text{Tc}$ , was added to the "treated" supernatant to give a final technetium concentration of about  $3 \times 10^{-5} \text{ M}$ . This technetium concentration more closely represents that in Hanford tank supernatants. Before use, all solutions were mixed for several days to ensure equilibrium, filtered, and analyzed for technetium.

Strontium nitrate, traced with  $^{85}\text{Sr}$ , was added to the "treated" supernatant to provide a strontium concentration of 2.0 mg/L for batch and column work. After mixing for several days, the solution was sequentially filtered through 0.45- and 0.2- $\mu\text{m}$  nylon filters to remove any strontium particulates and then analyzed by gamma counting. The final strontium concentration in the supernatant was 1.5 mg/L

Table 4. Analytical data for original MVST supernatants

	Tank			
	W-25	W-27	W-29	W-27/W-29
	(pH = 12.6)	(pH = 12.9)	(pH = 13.2)	(pH = 13.3)
<b>Radionuclides, Bq/L</b>				
<sup>137</sup> Cs	2.5E+08	3.2E+08	2.2E+08	3.2E+08
<sup>134</sup> Cs	7.4E+06	1.4E+06	3.4E+06	1.4E+06
<sup>60</sup> Co	6.3E+06	6.8E+05	4.0E+05	6.8E+05
<sup>154</sup> Eu	1.1E+05	NM <sup>a</sup>	BDL <sup>b</sup>	NM <sup>a</sup>
<sup>90</sup> Sr	1.0E+06	6.5E+07	2.4E+06	6.5E+07
<sup>99</sup> Tc	2.1E+04	NM <sup>a</sup>	2.0E+04	NM <sup>a</sup>
<b>Other metals, mg/L</b>				
Al	453	0.85	0.43	0.847
Ba	1.2	8.04	0.36	8.04
Ca	9.5	89.1	3.5	89.1
Cs	0.19	0.94	0.57	0.935
Cr	51	2.96	2.2	2.96
Cu	0.7	<0.03	0.2	<0.0319
K	14,000	10,800	11,400	10,300
Na	89,000	113,000	102,000	113,000
Pb	12.8	0.01	7.1	0.0092
Sr	0.4	NM <sup>a</sup>	1.0	NM <sup>a</sup>
Tc	0.032	NM <sup>a</sup>	0.031	NM <sup>a</sup>
Th	0.3	<0.44	<0.1	NM <sup>a</sup>
U	4.3	<1.00	1.3	<1.0
Zn	9.5	<0.47	61	0.473
<b>Anions, mg/L</b>				
Br <sup>-</sup>	345	288	<50	288
Cl <sup>-</sup>	3,740	3,180	3,000	3,180
F <sup>-</sup>	371	<7.5	<5	
NO <sub>3</sub> <sup>-</sup>	236,000	322,000	280,000	322,000
PO <sub>4</sub> <sup>3-</sup>	BDL <sup>b</sup>	<30	<50	
SO <sub>4</sub> <sup>2-</sup>	2,370	1,540	670	1,540

<sup>a</sup>NM = not measured.<sup>b</sup>BDL = below detection limit.

Table 5. Analytical data for treated supernatants

	MVST W-27T <sup>a</sup> (pH = 13.2)	MVST W-27pH <sup>b</sup> (pH = 14)	MVST W-29T <sup>a</sup> (pH = 12.68)
<b>Radionuclides, Bq/L</b>			
<sup>137</sup> Cs		3.4E+08	2.7E+05
<sup>60</sup> Co		3.3E+05	BDL <sup>c</sup>
<sup>154</sup> Eu		NM <sup>d</sup>	BDL <sup>c</sup>
<sup>90</sup> Sr		3.1E+07	1.1E+05
<sup>99</sup> Tc		NM <sup>d</sup>	NM <sup>d</sup>
<b>Other metals, mg/L</b>			
Al	<0.321	<0.14	0.23
Ba	<0.0154	5.61	0.08
Ca	<0.0858	3.1	1.0
Cs	NM <sup>d</sup>	9.95	0.0007
Cr	2.53	3.49	1.0
Cu	<0.0462	0.15	0.1
K	11,600	12,000	13,100
Na	125,000	127,000	88,600
Pb	NM <sup>d</sup>	<10	7.1
Sr	<0.055	26.3	1.5
Tc	NM <sup>d</sup>	NM <sup>d</sup>	0.031
Th	<0.534	<0.243	0.05
U	<1.00	0.485	1.1
Zn	<0.325	<0.148	23
<b>Anions, mg/L</b>			
Br <sup>-</sup>	335	<50	<50
Cl <sup>-</sup>	3,135	2,960	3,000
F <sup>-</sup>	50	<5	<5
NO <sub>3</sub> <sup>-</sup>	316,250	298,000	296,000
PO <sub>4</sub> <sup>3-</sup>	20	<10	<20
SO <sub>4</sub> <sup>2-</sup>	1,485	1,380	758

<sup>a</sup>Treated with R-F resin and potassium cobalt hexacyanoferrate to remove cesium.

<sup>b</sup>Adjusted to pH 14 with NaOH.

<sup>c</sup>BDL = below detection limit.

<sup>d</sup>NM = not measured.

( $1.7 \times 10^{-5} M$ ). Subsequent tests showed no further changes in the strontium concentration during the time that the batch tests were conducted.

## 2.2 SORBENTS

The best sorbent candidates for use in initial batch experiments were identified by a survey of the literature. Both organic and inorganic materials were identified for radionuclide removal. Organic materials selected for tests to remove cesium included Duolite CS-100, R-F resin, and SuperLig<sup>®</sup> 644C (IBC Advanced Technologies). CST, IONSIV IE-911 (an engineered granular form of CST), KCoCF, hydrous titanium oxide microspheres embedded with KCoCF powder (HTiO-KCoCF  $\phi$ ), and titanium monohydrogen phosphate microspheres embedded with sodium cobalt hexacyanoferrate powder (TiHP-NaCoCF  $\phi$ ) were the inorganic sorbents evaluated to test their effectiveness in removing cesium.

For technetium, the sorbents selected for testing included Amberlite IRA-400, Amberlite IRA-904, Eichrom ABEC-5000, Purolite A520E, Reillex 402, Reillex HP, and Reillex HPQ. No inorganic sorbents were identified that are specific for technetium removal from solutions at high pH and high salinity.

The most promising organic sorbents identified for strontium separation included Amberlite IRC-718, Chelex 100, Duolite C-467, MERSORB-S, and R-F resin. Sodium titanate (NaTiO), CST, IONSIV IE-911, sodium titanate in a polyacrylonitrile matrix (NaTiO-PAN), titanium monohydrogen phosphate (TiHP) microspheres, and titanium monohydrogen phosphate in a polyacrylonitrile matrix (TiHP-PAN) were the inorganic materials selected.

## 3. BATCH EXPERIMENTS

Sorbent effectiveness for cesium, technetium, and strontium removal was evaluated using batch equilibration tests. Supernatant was added to 15-mL, screw-cap, polypropylene centrifuge tubes containing the individual sorbents. The tubes were placed on a Labquake<sup>™</sup> shaker. Mixing the contents consisted of a back-and-forth rocking motion at ~20 cycles per minute. Volumes of supernatant used were calculated using the supernatant density. Any material loss was determined by weighing the tubes at the end of the equilibration period. The tubes were centrifuged for 30 min at 3000 rpm with an International Equipment Company Centra 7 tabletop centrifuge. Approximately 2 mL of the clarified supernatants was pipetted into clean centrifuge tubes and centrifuged for 30 min. Any remaining fine particulates were removed from these clarified supernatants by filtering successively through 0.45- and 0.22- $\mu$ m nylon filters, using a syringe filtering system.

Cesium and strontium analysis was by gamma spectroscopy using an LKB Wallac 1282 CompuGamma universal counter. Sample size was 0.5 mL. Liquid scintillation and inductively coupled plasma-mass spectroscopy (ICP-MS) were used to measure technetium in the samples. For liquid scintillation, a 0.5-mL sample was used for analysis.

Mixing times from 0 to 144 h and solution-to-sorbent ratios from 10:1 to 1000:1 were used to measure radionuclide removal. Varying the masses of sorbents while maintaining a constant supernatant volume of 10 mL was used to obtain loading and isotherm data. The most promising sorbents were selected for column studies.

#### 4. COLUMN EXPERIMENTS

Additional evaluation of sorbents was completed using chromatographic columns. Column studies can provide additional information on sorbent loading, identify potential kinetic and equilibrium problems, and quantity changes in sorbent-bed characteristics in a flowing system. The columns had an inside diameter of 1.5 cm and a total height of 15 cm with polypropylene end fixtures. Each sorbent was prepared as recommended by the provider or manufacturer. Air bubbles were removed by flowing liquid up through the bed, which allowed them to rise and escape; stirring the material in the column; or both. The amount of sorbent contained in the column (the column volume) was calculated from the bed height of the wetted material.

A column run consisted of pumping the supernatant from the feed tank to the column until a liquid level of about 3 to 5 cm above the resin was reached and maintained throughout the run. Effluent fractions were collected and analyzed for radionuclide content. Column flow rates (i.e., the volume of liquid passing through the column for a designated period of time) were determined using two methods: (1) measuring the time for the liquid level in the column to drop a specified distance or (2) collecting samples over a given time interval and weighing each collected fraction. The specific gravity of the supernatant was used to determine the volume collected. For hot cell experiments, cesium in the effluent was determined using an in-line counter. Several fractions were taken and analyzed using other gamma spectroscopic equipment. In column tests conducted for removal of strontium and technetium, samples of effluent were collected as a function of time. ICP-MS of selected fractions was used to measure the technetium in the effluent. Strontium-85 in the effluent was determined using gamma spectroscopy by counting 0.5-mL samples.

## 5. CALCULATIONS

Batch test results are reported as percent removal (%R) and distribution ratio (D) at time  $t$ . These values are calculated in the following manner:

$$\%R = 100 \left( \frac{C_o - C_t}{C_o} \right),$$

$$D = \left( \frac{C_o - C_t}{C_t} \right) \times \left( \frac{V}{m} \right) \text{ (units are mL/g) ,}$$

where

- $C_o$  = initial counts per minute of sample (counts per minute before contact),
- $C_t$  = final counts per minute of sample at time  $t$  (counts per minute of sample after contact time  $t$ ),
- $V$  = volume of supernatant added,
- $m$  = mass of sorbent added (based on dry weight).

The sorbent necessary to treat a given volume of solution can be estimated by calculating D at equilibrium. The equilibrium value of D is designated as  $K_d$ .

## 6. BATCH RESULTS

Sorbents identified through a literature search were tested for separation of cesium, technetium, and strontium from MVST supernatants. Those identified as the best sorbents under the defined experimental conditions were selected for use in ORNL's Hot Cell Tests and subsequent Cesium Removal Demonstration Project (CsRD) for the Tank Focus Area. A summary of the batch experiments conducted at ORNL follows.

### 6.1 CESIUM

Batch tests were conducted using available MVST W-25 and W-29 supernatant. Samples of CST, Duolite CS-100, HTiO/KCoCF microspheres ( $\phi$ ), KCoCF (granular and powder forms), SuperLig® 644C, R-F

resin, and TiHP/NaCoCF  $\phi$  were used. In these experiments a solution-to-sorbent ratio of 200:1 was used for a mixing time of 24 h. Table 6 shows the results of these tests. The KCoCF powders and granular materials gave the highest cesium distribution ratio. The cesium distribution ratios for the granular KCoCF were 36,900 and 32,700 mL/g in the MVST W-25 and W-29 supernatants, respectively. Mixing the KCoCF powder with the MVST W-25 supernatant gave a higher D value for cesium, 66,800 mL/g. Of the commercial materials, the CST was the most effective for removing cesium. For batch studies conducted using CST, the cesium distribution ratio was 672 mL/g for MVST W-25 and 1190 mL/g for MVST W-29. In the batch tests using W-29 supernatant, the D values obtained for R-F resin and SuperLig 644 were 528 and 430 mL/g, respectively.

Table 6. Typical results from batch tests for removing cesium from MVST supernatants  
(Solution/sorbent = 200:1, mixing time = 24 h)

Sorbent	D (mL/g)	
	MVST W-25	MVST W-29
Duolite CS-100	34	NM <sup>a</sup>
R-F resin	736	528
CST (fp) <sup>b</sup>	672	1,190
KCoCF (gr) <sup>c</sup>	36,900	32,700
TiHP/NaCoCF $\phi$ <sup>d</sup>	3,150	NM
HTiO/KCoCF $\phi$ <sup>d</sup>	5,550	2,560
SuperLig <sup>®</sup> 644C	NM	430
KCoCF (powder)	66,800	NM

<sup>a</sup>NM = not measured.

<sup>b</sup>fp = fine powder.

<sup>c</sup>gr = granular.

<sup>d</sup> $\phi$  = microspheres.

Additional batch tests were conducted using MVST W-25 supernatant and samples of CST, Duolite CS-100, HTiO/KCoCF  $\phi$ , KCoCF (granular and powder forms), R-F resin, and TiHP/NaCoCF  $\phi$  for mixing times from 0.25 to 144 h (Table 7 and Fig. 1). The highest cesium removal was obtained with KCoCF. The

**Table 7. Batch adsorption data showing the effect of the mixing time on the removal of cesium from MVST W-25 supernatant<sup>a</sup>**

Sorbent <sup>b</sup>	Mixing time (h)														
	0.25			2			24			72			144		
	D	% R	pH	D	% R	pH	D	% R	pH	D	% R	pH	D	% R	pH
CS-100	34	15.3	12.2	35	20.0	12.2	34	15.0	12.2	42	20.0	12.6	44	22.0	12.6
R-F resin	138	41.0	12.6	763	79.3	12.6	736	79.5	12.6	764	79.2	12.6	641	78.7	12.6
CST	451	71.5	12.6	662	77.4	12.6	672	77.5	12.6	672	77.7	12.6	958	83.8	12.6
KCoCF (gr)	36,900	99.5	12.3	46,200	99.6	12.3	36,900	99.5	12.3	36,300	99.5	12.2	26,000	99.3	12.2
KCoCF (fp)				49,900	99.6	12.3	66,800	99.7	12.3	18,600	99.0	12.2			
TiHP/NaCoCF $\phi$				1,140	96.9	9.4	3,105	98.8	9.4	3,960	99.1	9.4			
HTiO/KCoCF $\phi$				110	72.3	12.3	5,550	99.3	12.3	5,500	99.3	12.3	5,530	99.3	12.3

<sup>a</sup>With the exception of the composite microspheres, each batch test was conducted by mixing 50 mg of adsorber with 10 mL of tank W-25 supernatant for the times indicated. For the composite microspheres, the masses of microspheres that contained 50 mg of the NaCoCF or KCoCF were used. The initial concentration of cesium in the supernatant was 0.19  $\mu\text{g/mL}$ .

<sup>b</sup>R-F = resorcinol-formaldehyde resin (425 to 595  $\mu\text{m}$ ); CST = crystalline silicotitanate (fine powder); KCoCF (gr) = granular potassium cobalt hexacyanoferrate (250 to 595  $\mu\text{m}$ ); KCoCF (fp) = potassium cobalt hexacyanoferrate sorbent (fine powder); TiHP/NaCoCF  $\phi$  = titanium monohydrogen phosphate microspheres containing ~20 wt % sodium cobalt hexacyanoferrate; and HTiO/KCoCF  $\phi$  = hydrous titanium oxide microspheres containing ~20 wt % potassium cobalt hexacyanoferrate.

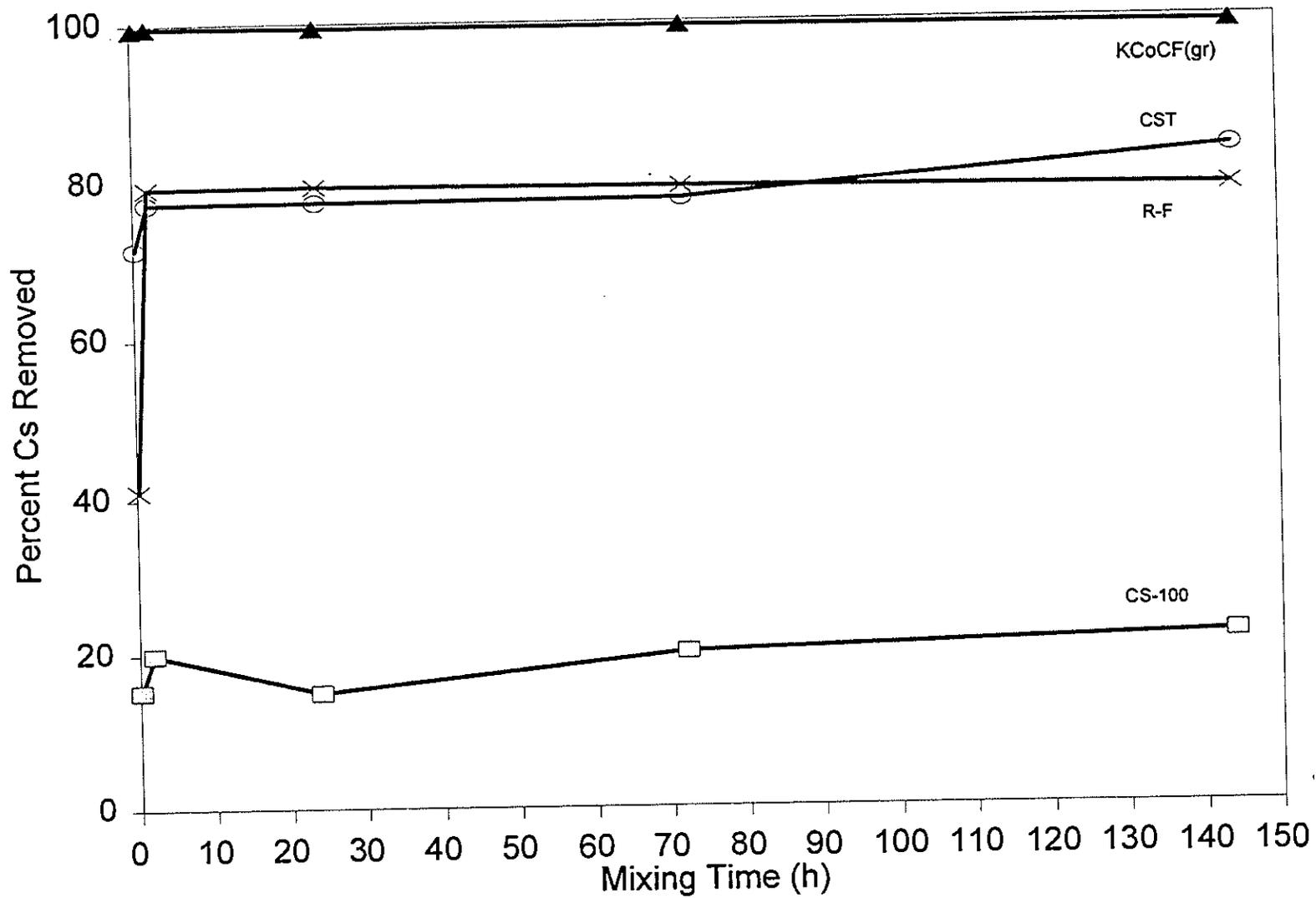


Fig. 1. Percent cesium removed from MVST W-25 as a function of mixing time.

D values ranged from 18,600 to 66,800 mL/g; the %R range was 99.0 to 99.7. CS-100 was the least effective in removing cesium; the highest D and %R values were 44 mL/g and 22%, respectively. R-F and CST performed similarly in sorbing cesium from the supernatant, with the D values ranging from 138 to 764 mL/g for the R-F and 451 to 958 mL/g for the CST. After mixing for 144 h, the R-F and CST removed 78.7 and 83.8% of the cesium, respectively. In the shorter, 0.25-h tests, the CST removed 71.5% and the R-F removed 41% of the cesium. For the tests with microspheres, a mass of microspheres was used that contained 0.050 g of embedded KCoCF or NaCoCF. Separate tests with titanium phosphate and hydrous titanium oxide microspheres (250 to 600  $\mu\text{m}$ ) were also conducted. These materials without the embedded hexacyanoferrates removed <5% of the cesium from the MVST W-25 supernatant after mixing times of 2 and 72 h. The microspheres that contained KCoCF or NaCoCF removed >70% of the cesium. For the longer mixing times, the percentages of cesium removed were similar to the values obtained using granular KCoCF. The D values obtained for the microspheres containing hexacyanoferrate were lower than for the granular material because the total mass of the microspheres was used in the calculations. If the 0.050 g of the embedded KCoCF or NaCoCF, rather than the total mass of microspheres, were used in the calculation, the D values would be similar to those obtained for the granular KCoCF. In the 2-h tests, only ~72% of the cesium was removed by the HTiO/KCoCF microspheres, compared with ~97% for the TiHP/NaCoCF microspheres. However, for the longer mixing times, the percentage removed by the HTiO/KCoCF microspheres increased. Diffusion of cesium ions into the matrix of the microspheres seems to be enhanced by increased hydration. The HTiO microspheres swell more in aqueous solution than do the TiHP microspheres, but the swelling of the HTiO occurs more slowly.

Parallel cesium adsorption tests were conducted with R-F, CST, and granular KCoCF sorbents where the supernatant/exchanger (S/E) ratio was varied from 2000:1 to 100:1 (milliliters per gram). This was accomplished by using a constant volume of supernatant (10 mL) and varying the mass of sorbent from 0.005 to 0.1 g. The S/E ratio used for the R-F and CST tests covered the range of 1000:1 to 100:1; an S/E range of 2000:1 to 200:1 was examined for KCoCF because it showed higher cesium sorption. Measurements were made for 0.25, 2, 24, 72, and 144 h, with results summarized in Table 8.

For equilibration tests conducted for 144 h, the D values for cesium from MVST W-25 supernatant ranged from 562 to 1400 mL/g for R-F, 615 to 958 mL/g for CST, and 26,200 to 75,600 mL/g for KCoCF (gr). The cesium % R ranged from 63.2 to 87.3 for R-F, 45.7 to 90.9 for CST, and 96.9 to 99.4 for KCoCF (gr).

**Table 8. Batch adsorption data showing the effect of the mixing time and the supernatant-to-exchanger ratio on the removal of cesium from MVST W-25 supernatant<sup>a</sup>**

Sorbent <sup>b</sup>	S/E <sup>c</sup> (mL/g)	Mixing time (h)									
		0.25		2		24		72		144	
		D (mL/g)	%R	D (mL/g)	%R	D (mL/g)	%R	D (mL/g)	%R	D (mL/g)	%R
R-F	1,000	293	24.1	370	28.9	1,500	63.4	1,500	63.4	1,400	63.2
R-F	400	227	33.0	315	45.0	1,070	75.4	1,170	76.5	1,080	76.1
R-F	200	138	41.0	763	79.3	736	79.5	764	79.2	641	78.7
R-F	100	84	45.7	459	82.6	597	85.8	619	87.0	562	87.3
CST	1,000	505	32.6	652	39.5	1,120	55.3	1,020	54.9	615	45.7
CST	400	337	47.8	477	55.4	744	68.6	643	66.6	616	67.1
CST	200	451	71.5	662	77.4	672	77.5	672	77.7	958	83.8
CST	100	297	73.8	321	77.2	686	88.5	976	91.2	843	90.9
KCoCF	2,000	1,240	37.8	29,800	93.9	68,400	97.5	68,400	97.6	48,400	96.9
KCoCF	1,000	630	65.0	17,200	95.0	31,300	97.2	59,700	98.5	75,600	98.7
KCoCF	400	330	83.3	44,000	99.2	58,400	99.3	19,300	98.2	54,500	99.4
KCoCF	200	36,900	99.5	46,200	99.6	36,900	99.5	36,200	99.5	26,200	99.3

<sup>a</sup>Each batch test was conducted by mixing 5, 10, 25, 50, or 100 mg of adsorber with 10 mL of MVST W-25 supernatant for the time indicated. The initial concentration of cesium in the supernatant was 0.19  $\mu\text{g/mL}$ .

<sup>b</sup>R-F = resorcinol-formaldehyde resin (425 to 595  $\mu\text{m}$ ); CST = crystalline silicotitanate (fine powder); and KCoCF = granular potassium cobalt hexacyanoferrate (210 to 595  $\mu\text{m}$ ).

<sup>c</sup>S/E = volume of supernatant to mass of exchanger.

For tests conducted for the shortest mixing time period (0.25 h), the *D* values for cesium removal from the supernatant ranged from 84 to 293 mL/g for R-F, 297 to 505 mL/g for CST; and 330 to 36,900 mL/g for KCoCF (gr). The cesium %R ranged from 24.1 to 45.7 for R-F, 32.6 to 73.8 for CST, and 37.8 to 99.5 for KCoCF (gr).

The maximum cesium loading was ~2.8 meq/kg for KCoCF, 0.9 meq/kg for R-F, and 0.8 meq/kg for CST. The maximum cesium sorption on KCoCF was achieved after 24 h, and the sorption then decreased; the maximum cesium sorption on R-F and CST occurred after 72 h and then decreased.

Batch tests were conducted to examine the effect of varying the cesium concentration in MVST W-25 supernatant on the sorption of cesium by the sorbents R-F, CST, and KCoCF. The Hanford supernatants have wide ranges of Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup> concentrations; the Cs<sup>+</sup> concentration ranges from 0.024 to 0.86 mg/L. A  $7.52 \times 10^{-2} M$  CsCl stock solution (<sup>133</sup>Cs only) was added to W-25 supernatant to obtain cesium concentrations of 0.19 to 726 mg/L. The Na<sup>+</sup> and K<sup>+</sup> concentrations were 3.87 *M* and 0.36 *M*, respectively. In each test, ~50 mg of sorbent was mixed with ~5 mL of supernatant for ~24 h at room temperature. The maximum cesium sorbed by the different sorbents was 11 g/kg for R-F resin, 50 g/kg for CST, and 71 g/kg for KCoCF (gr) (Fig. 2). The ranges of distribution coefficients (milliliters per gram) for the sorbents were 45 to 560 for R-F, 226 to 970 for CST, and 5000 to 37,400 for KCoCF (Fig. 3). The percentages of cesium removed from the supernatant samples (%R) ranged from 31 to 87 for R-F, 70 to 91 for CST, and 98 to 99.7 for KCoCF. The *D* and %R values were fairly constant for supernatant samples with cesium concentrations up to 351 mg/L for CST and up to 183 mg/L for KCoCF; this was also the case for R-F for the batch tests conducted with supernatants with cesium concentrations in the range of 30.4 mg/L to 181.6 mg/L. The *D* and %R values for R-F were much higher at the lower Cs<sup>+</sup> concentrations.

A sample of SuperLig<sup>®</sup> 644C (lot 3695-GM1121), which is a polymer resin of the covalently bound SuperLig<sup>®</sup> 644C macrocycle family of sequestering ligands from IBC Advanced Technologies (American Fork, Utah), was supplied by Lane Bray of PNNL. This sorbent was received too late to be included in the batch test studies with the MVST W-25 supernatant. However, batch equilibration tests were conducted with samples of this resin to determine its effectiveness in removing cesium from filtered samples of MVST W-29 and MVST W-27 supernatants.

Duplicate tests (in some cases, triplicate tests) were run with the MVST W-29 supernatant (Table 9) using samples of Superlig<sup>®</sup> 644C resin that were pretreated with 0.1 *M* NaOH for 4 h and with samples that received no pretreatment. The *D* and %R values that were obtained for the mixing times were as follows: 160 mL/g and 44% for 0.25 h, 270 mL/g and 57% for 2 h, and 390 mL/g and 64% for 24 h. For the samples

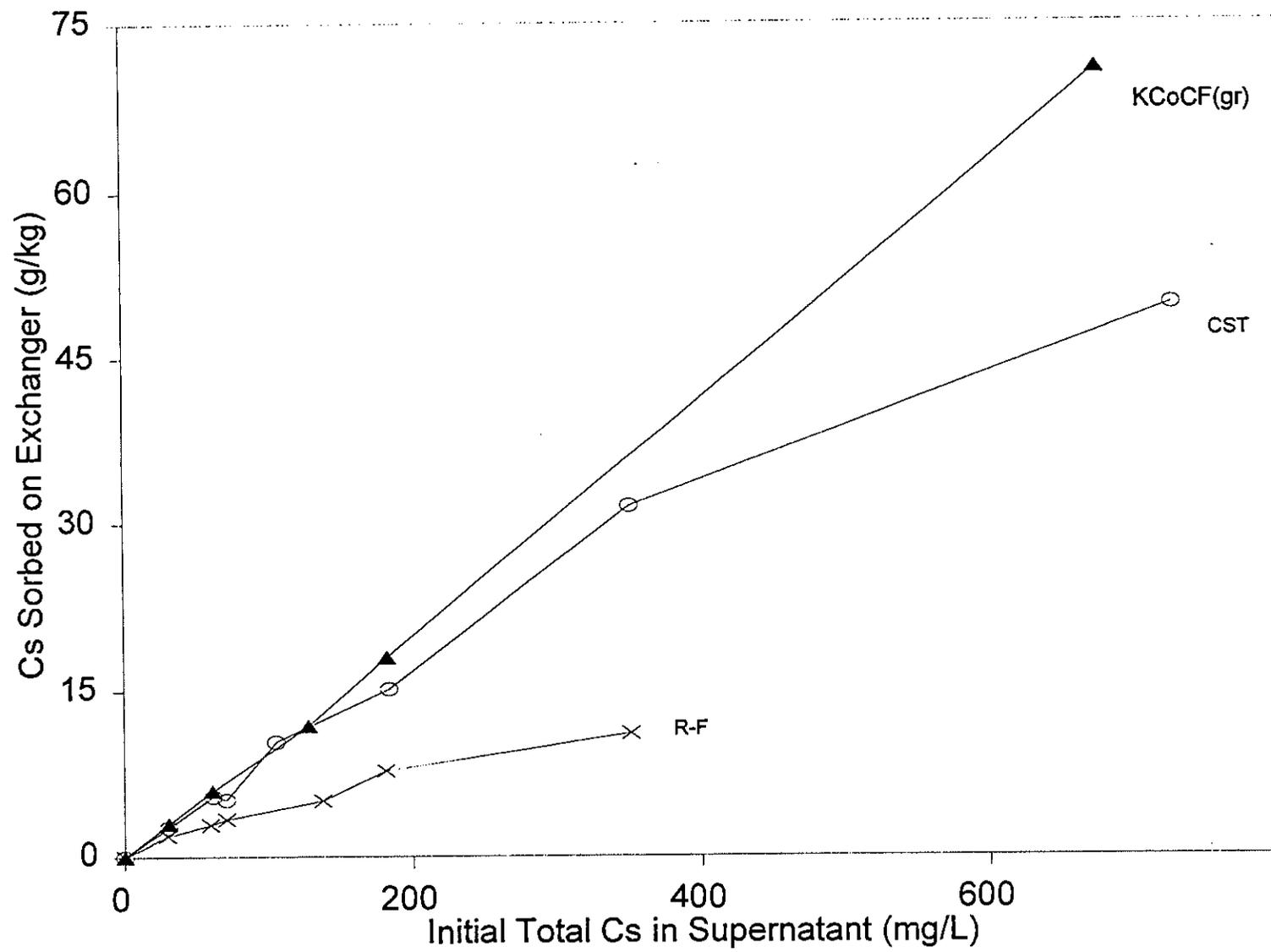


Fig. 2. Cesium sorbed on exchangers vs initial cesium concentration in supernatant.

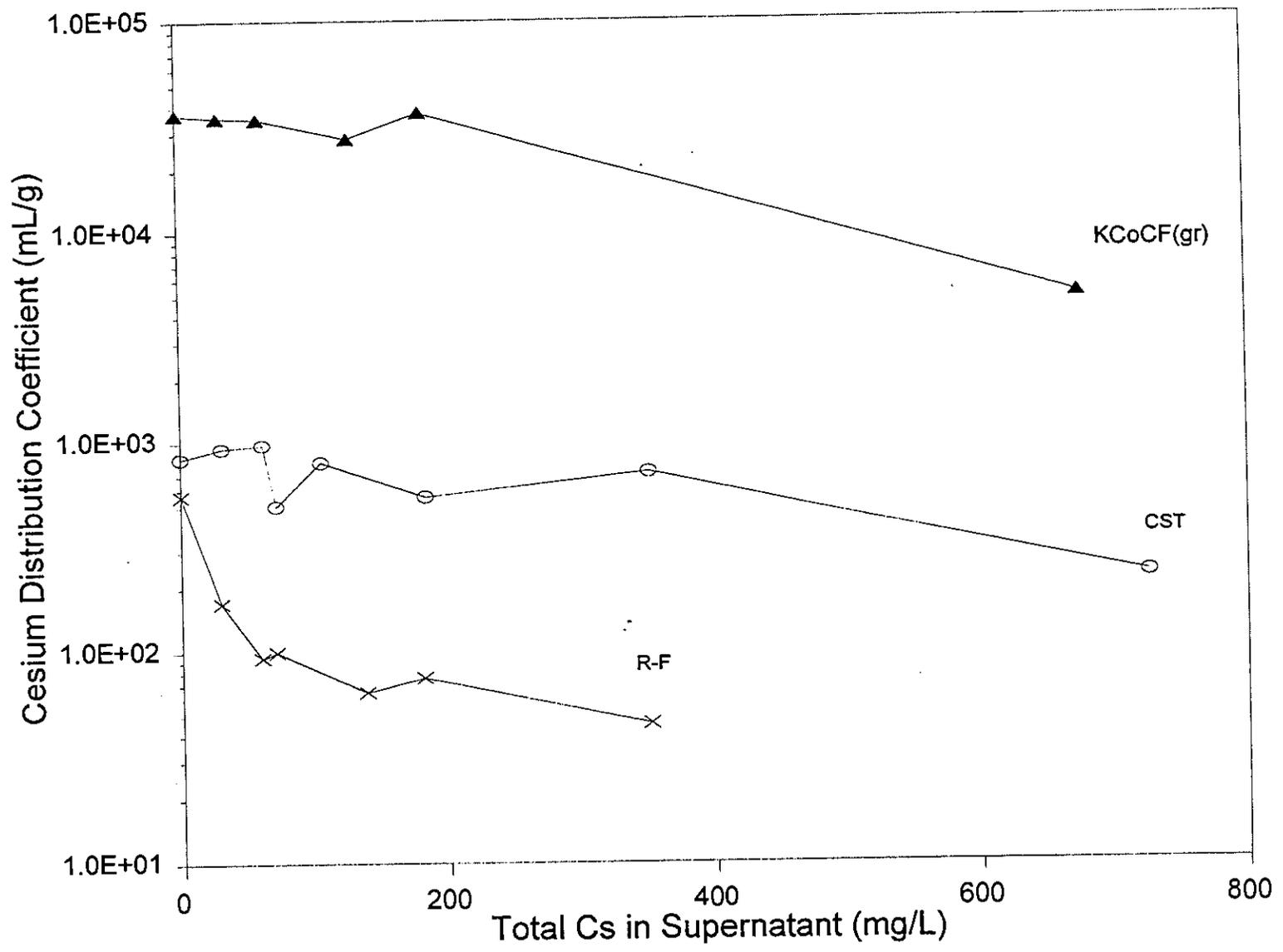


Fig. 3. Effect of total cesium concentration on the cesium distribution coefficient.

that were not treated, the results were as follows: 88 mL/g and 30% for 0.25 h, 220 mL/g and 51% for 2 h, 430 mL/g and 68% for 24 h, 1060 mL/g and 84% for 72 h, and 1250 mL/g and 86% for 144 h. A supernatant-to-sorbent ratio of 200:1 was used in these tests. The values for the 0.25- and 2-h tests in which the resin samples were pretreated were higher. Table 9 compares these data with those obtained for samples of Savannah River resin (R-F resin) that was given no pretreatment.

Duplicate batch tests (24 h) were also conducted with SuperLig<sup>®</sup> 644C resin that was given no pretreatment to examine the effect of varying the supernatant-to-sorbent ratio on cesium removal. The D and %R results were as follows for the indicated ratios: 530 mL/g and 84% (100:1), 430 mL/g and 68% (200:1), 250 mL/g and 41% (400:1), and 230 mL/g and 25% (700:1).

Duplicate batch tests were also conducted with samples of MVST W-27 supernatant using a supernatant-to-SuperLig<sup>®</sup> 644C ratio of 200:1. The samples were pretreated with 2 M NaOH for 4 h before testing. The D and %R results were as follows: 300 mL/g and 60% for 0.25 h, 515 mL/g and 74% for 2 h, 733 mL/g and 81% for 24 h, and 796 mL/g and 79% for 72 h. Two 24-h tests were also conducted using a 400:1 ratio of supernatant to sorbent. The average D and %R values were 840 mL/g and 70. Data for the 200:1 ratio are compared in Table 10 with results obtained for samples of IONSIV IE-911 (the granular engineered form). These batch data showed that these sorbents were very comparable in removing the cesium.

One very interesting observation about the supernatant samples after they were mixed with either the R-F resin or the SuperLig<sup>®</sup> 644C was a pronounced change in color. The pale yellow supernatant changed to a dark amber color. Both resins also underwent volume changes (30–50%) as the ionic strength, pH, and ionic form of the resins were changed (also see Sect. 7.1.1.2).

The effects of organic liquid on cesium distribution behavior were determined by conducting additional batch tests using samples of CST (engineered form #07398-38B), R-F resin, and SuperLig<sup>®</sup> 644C soaked in tributyl phosphate (TBP) before mixing with the supernatant. Approximately 0.025 g of sorbent was soaked in 0.8 mL of TBP for 24 h. The sorbent was then mixed with 5.0 mL of MVST W-29 supernatant. The TBP was not removed from the tubes and floated on top of the supernatant. For comparison, sorbents were mixed with supernatant only. Cesium removal from the supernatant was measured by sampling the solution after mixing with the sorbent samples for 1 or 24 h. The results are given in Table 11 and Fig. 4. The results indicated that soaking the sorbents in TBP decreased the cesium distribution ratios. For the 24-h samples, the average cesium distribution ratio for the R-F resin decreased from 525 to 80 mL/g; for the SuperLig<sup>®</sup> 644C, it decreased from 478 to 327 mL/g; and for the CST, it decreased from 1000 to 569 mL/g. As shown in

**Table 9. Batch adsorption data showing the effect of the mixing time on the removal of cesium from MVST W-29 supernatant with SuperLig® 644C and resorcinol-formaldehyde resin<sup>a</sup>**

Sorbent	Mixing time (h)					
	0.25		2		24	
	D (mL/g)	%R	D (mL/g)	%R	D (mL/g)	%R
R-F <sup>b</sup>	404	66	535	73	528	73
SuperLig® 644C <sup>c</sup>	88	30	220	51	430	68
SuperLig® 644C <sup>d</sup>	160	44	270	57	390	64

<sup>a</sup>Each batch test was conducted by mixing 50 mg of sorbent with 10 mL of MVST W-29 supernatant for the time indicated. The particle size of each sorbent tested was in the range 425–595  $\mu\text{m}$ .

<sup>b</sup>R-F = resorcinol-formaldehyde resin (given no pretreatment).

<sup>c</sup>The sorbent was tested as received.

<sup>d</sup>The sorbent was mixed with 0.1 M NaOH for 4 h before testing.

**Table 10. Batch adsorption data showing the effect of the mixing time on the removal of cesium from MVST W-27 supernatant with IONSIV IE-911 and SuperLig® 644C<sup>a</sup>**

Sorbent	Mixing time (h)					
	0.25		2		24	
	D (mL/g)	%R	D (mL/g)	%R	D (mL/g)	%R
IONSIV IE-911	145	41	357	63	702	77
SuperLig® 644C <sup>b</sup>	300	60	515	74	733	81

<sup>a</sup>Each batch test was conducted by mixing 50 mg of sorbent with 10 mL of MVST W-27 supernatant for the time indicated.

<sup>b</sup>SuperLig® 644C (lot #3695-GM1121). Each sample of sorbent was pretreated for 4 h with 2 M NaOH.

Table 11. Effect of tributyl phosphate fouling on the removal of cesium from MVST W-29 supernatant

Sorbent <sup>a</sup>	Mixing time (h)			
	1		24	
	D (mL/g)	%R	D (mL/g)	%R
CST	179	44.9	944	82.5
CST	135	39.8	1055	83.2
CST <sup>b,c</sup>	86	26.2	574	72.4
CST <sup>b,c</sup>	127	35.9	564	72.9
R-F	85	31.0	535	73.0
R-F	101	33.7	514	76.0
R-F <sup>b</sup>	45	17.9	70	26.9
R-F <sup>b</sup>	48	19.7	89	28.7
SuperLig <sup>®</sup> 644C	230	51.8	479	71.0
SuperLig <sup>®</sup> 644C	226	51.1	477	70.7
SuperLig <sup>®</sup> 644C <sup>b</sup>	143	39.8	330	59.6
SuperLig <sup>®</sup> 644C <sup>b</sup>	131	36.7	323	61.4

<sup>a</sup>Sorbents were used as received.

<sup>b</sup>The sorbent was soaked in tributyl phosphate for 24 h before testing.

<sup>c</sup>An engineered form of CST (#07398-38B).

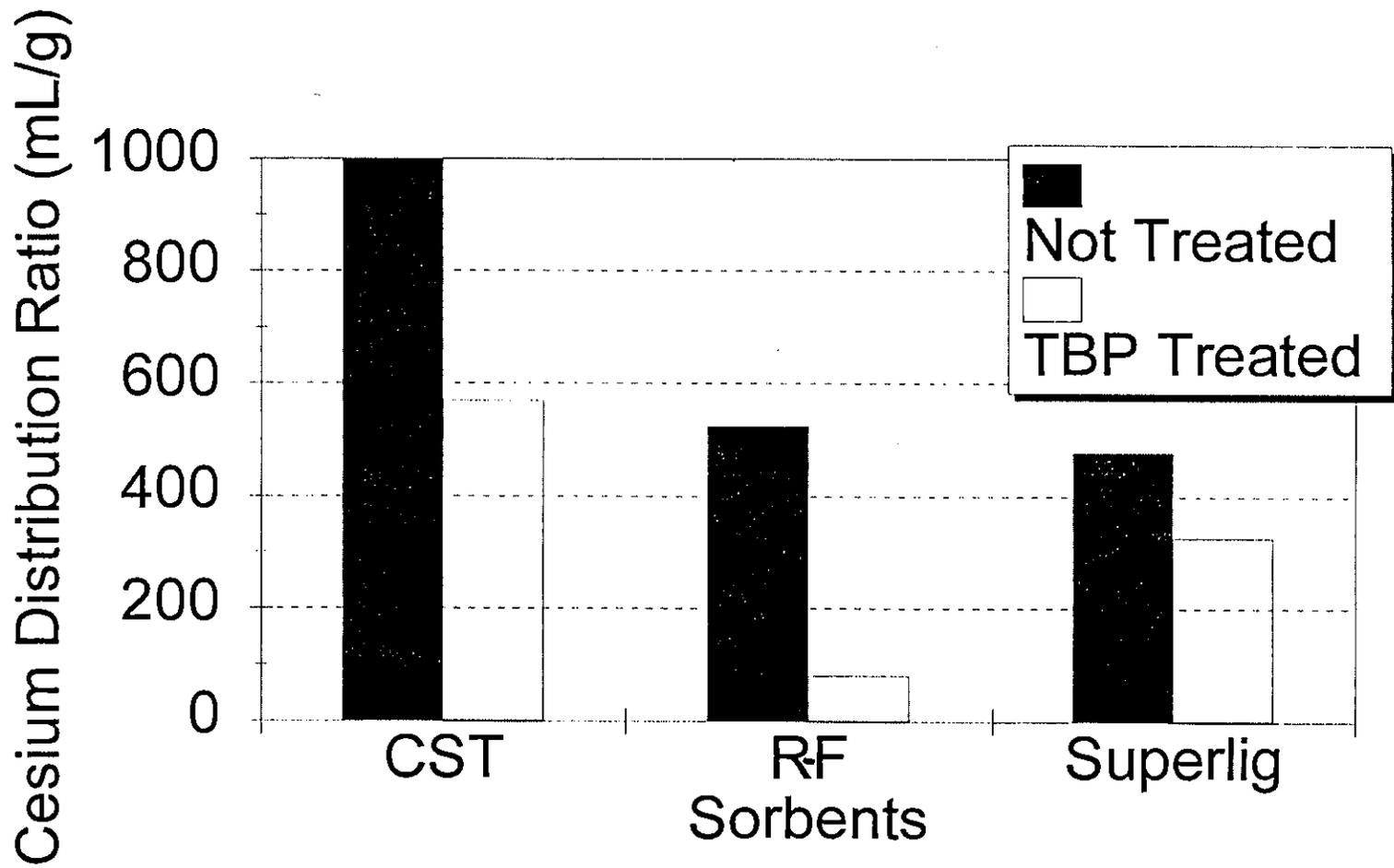


Fig. 4. Effect of tributyl phosphate (TBP) fouling on cesium distribution ratios.

Table 11, the CST and SuperLig® 644C materials were less affected by TBP fouling than was the R-F resin in removing the cesium.

## 6.2 TECHNETIUM

Supernatant from MVST W-29 was treated to remove excess cesium and strontium before use in the technetium batch tests. Technetium was then added as ammonium pertechnetate to give a technetium concentration of  $3 \times 10^{-5} M$ . Sorbents selected for testing included Amberlite IRA-400, Amberlite IRA-904, Eichrom ABEC-5000, Purolite A520E, Reillex 402, Reillex HP, and Reillex HPQ. Some batch experiments consisted of varying the mixing times while maintaining a constant supernatant-to-sorbent ratio. In other tests, a constant contact time was maintained but the supernatant-to-sorbent ratio was varied. The results from these experiments are summarized in Tables 12–14.

For the experiments in which the contact time was varied from 0.25 to 72 h, the results showed that the pertechnetate distribution ratios increased for up to 24-h mixing time (see Fig. 5). For example, using Eichrom ABEC-5000 sorbent, the technetium D values were 243, 391, 780, and 927 mL/g using mixing times of 0.25, 2, 24, and 72 h, respectively (Table 12). However, after 24 h, the D values leveled off. Of the sorbents tested, Eichrom ABEC-5000 was the most effective at separating the pertechnetate ion after a 24-h mixing time, although in many cases Reillex 402, Reillex HP, and Reillex HPQ had D values similar to the ABEC-5000 material. Examination and comparison of the isotherm data indicated a difference in the loading capacity of the sorbents for pertechnetate; the loading capacities were 1980, 2000, 1440, and 1570 mg/kg for the Eichrom ABEC-5000, Reillex 402, Reillex HP, and Reillex HPQ (Tables 13 and 14 and Fig. 6), respectively.

## 6.3 STRONTIUM

Before the strontium nitrate was added to the treated supernatant for the batch tests, the solubility of strontium in the W-29T supernatant was determined. For this determination, enough strontium nitrate, traced with  $^{85}\text{Sr}$ , was added to 200-mL samples of the W-29T supernatant to give a strontium concentration of 70 mg/L. After the solution was mixed for 48 h, a 0.5-mL sample was filtered through 0.45- and 0.2- $\mu\text{m}$  nylon filters and analyzed by gamma counting. The sample was then returned to the original solution. This procedure was repeated several times over a 45-d period. The activity of each sample was measured and

Table 12. Batch data showing the removal of pertechnetate from MVST W-29T supernatant<sup>a</sup>

Sorbent	Mixing time (h)							
	0.25		2		24		72	
	D (mL/g)	%R	D (mL/g)	%R	D (mL/g)	%R	D (mL/g)	%R
Eichrom™ ABEC-5000	243	54	391	66	780	79	927	83
Reillex™ 402	150	43	430	69	786	80	751	79
Reillex™ HP	132	41	458	68	558	71	600	72
Reillex™ HPQ	237	55	317	62	624	76	545	73
Purolite™ A520E	113	37	562	73	694	77	630	75
Amberlite™ IRA-904	80	29	349	66	657	77	636	76
Amberlite™ IRA-400	35	14	88	31	412	68	504	72

<sup>a</sup>Each batch test was conducted by mixing the mass of "as-received" sorbent that was equivalent to 50 mg of the air-dried sorbent with 10 mL of MVST W-29T supernatant for the time indicated.

Table 13. Isotherm data for removing pertechnetate from MVST W-29T supernatant with Eichrom ABEC-5000, Reillex™ 402, and Purolite™ A520E<sup>a</sup>

Sorbent	S/E <sup>b</sup>	Tc loading (mg/kg)	[Tc] (mg/L)	D (mL/g)	%R
Eichrom ABEC-5000	1440	1980	2.5	780	35.1
	780	1470	2.7	750	48.1
	350	1020	1.3	800	66.1
	200	600	0.8	780	78.5
	100	330	0.5	710	87.6
Reillex™ 402	1550	2000	2.5	800	34.0
	780	1320	2.1	620	44.2
	350	860	1.3	660	65.4
	200	580	0.8	750	79.2
	100	320	0.5	730	88.3
Purolite™ A520E	1660	1930	2.6	730	30.7
	840	1430	2.1	680	45.0
	380	944	1.3	712	65.1
	200	553	1.0	580	73.9
	100	350	0.5	730	87.5

<sup>a</sup>Each batch test was conducted by mixing ~10-mL of MVST W-29T supernatant containing  $3 \times 10^{-5} M$  pertechnetate with sorbent for ~24 h.

<sup>b</sup>S/E = ratio of supernatant (milliliters) to mass of air-dried sorbent (grams). The masses of "as-received" sorbents were equivalent to air-dried masses of ~0.1, ~0.05, ~0.025, ~0.012, and ~0.006 g.

Table 14. Isotherm data for removing pertechnetate from MVST W-29T supernatant with Reillex HPQ, Reillex HP, Amberlite IRA-904, and Amberlite 400<sup>a</sup>

Sorbent	S/E <sup>b</sup>	Tc loading (mg/kg)	[Tc] (mg/L)	D (mL/g)	%R
Reillex HPQ	1660	1570	2.8	550	25.0
	880	1360	2.2	610	41.0
	380	890	1.5	610	61.3
	200	580	1.0	610	74.2
	100	330	0.5	610	85.7
Reillex HP	1660	1440	2.9	490	22.9
	870	1100	2.5	440	33.6
	390	810	1.7	480	54.8
	190	500	1.1	460	70.8
	110	320	0.6	530	83.9
Amberlite IRA 904	1670	1480	3.0	500	23.1
	840	1370	2.2	590	41.2
	390	940	1.4	680	63.8
	200	570	0.9	620	75.5
	100	340	0.5	680	87.1
Amberlite 400	1530	1290	3.0	430	21.5
	790	1080	2.4	444	36.1
	390	740	1.9	390	49.8
	200	520	1.2	420	68.0
	100	300	0.8	400	80.2

<sup>a</sup>Each batch test was conducted by mixing ~10-mL of MVST W-29T supernatant containing  $3 \times 10^{-5} M$  pertechnetate with sorbent for ~24 h.

<sup>b</sup>S/E = ratio of supernatant (milliliters) to mass of air-dried sorbent (grams). The masses of "as-received" sorbents were equivalent to air-dried masses of ~0.1, ~0.05, ~0.025, ~0.012, and ~0.006 g.

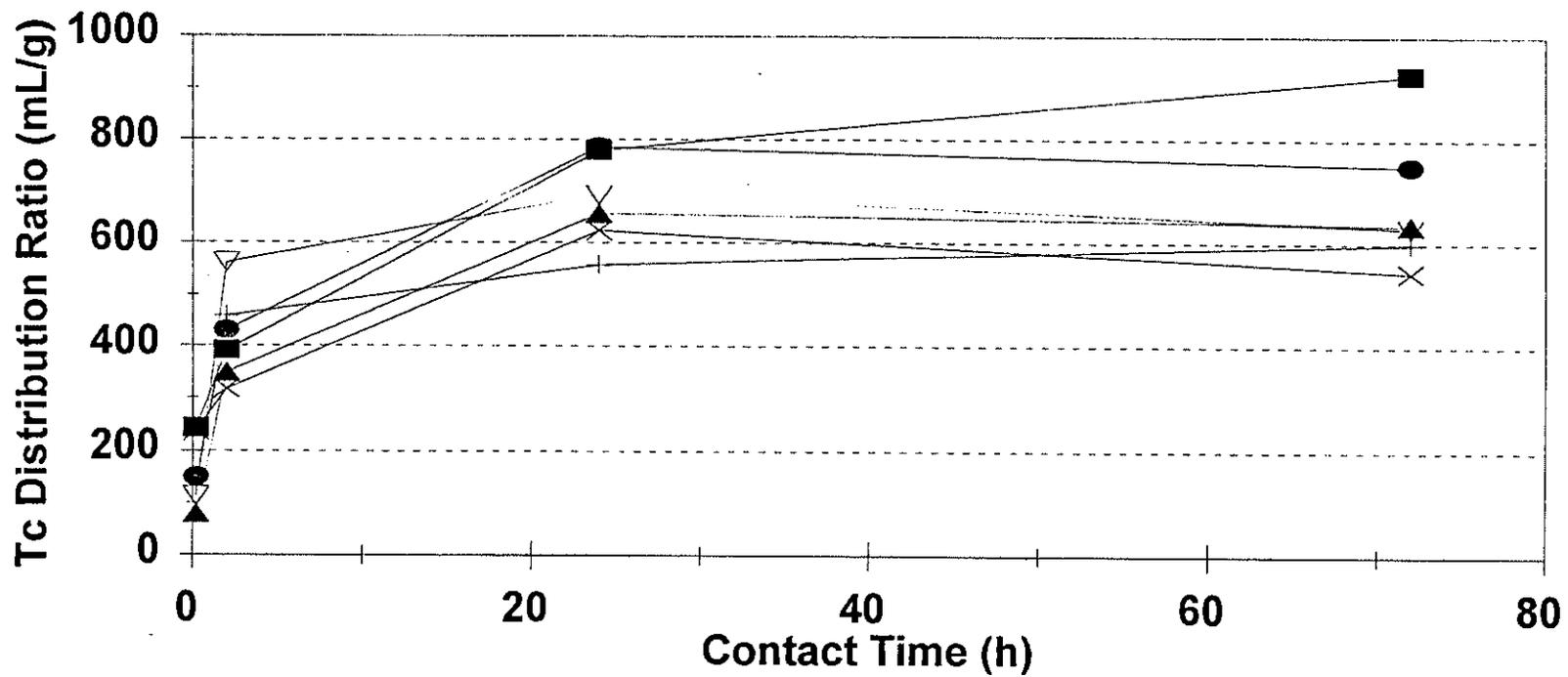


Fig. 5. Batch adsorption of technetium from MVST W-29 supernatant.

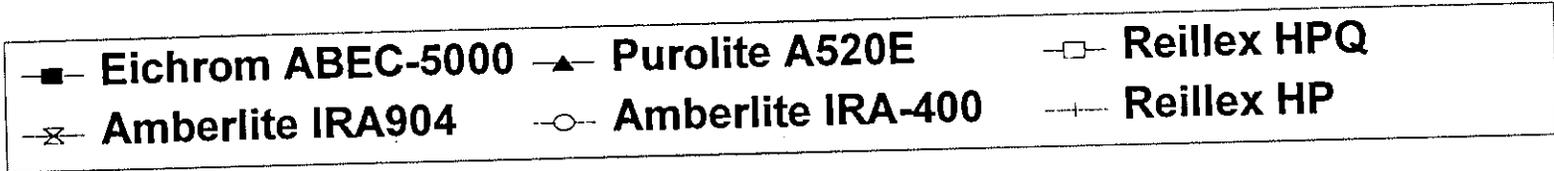
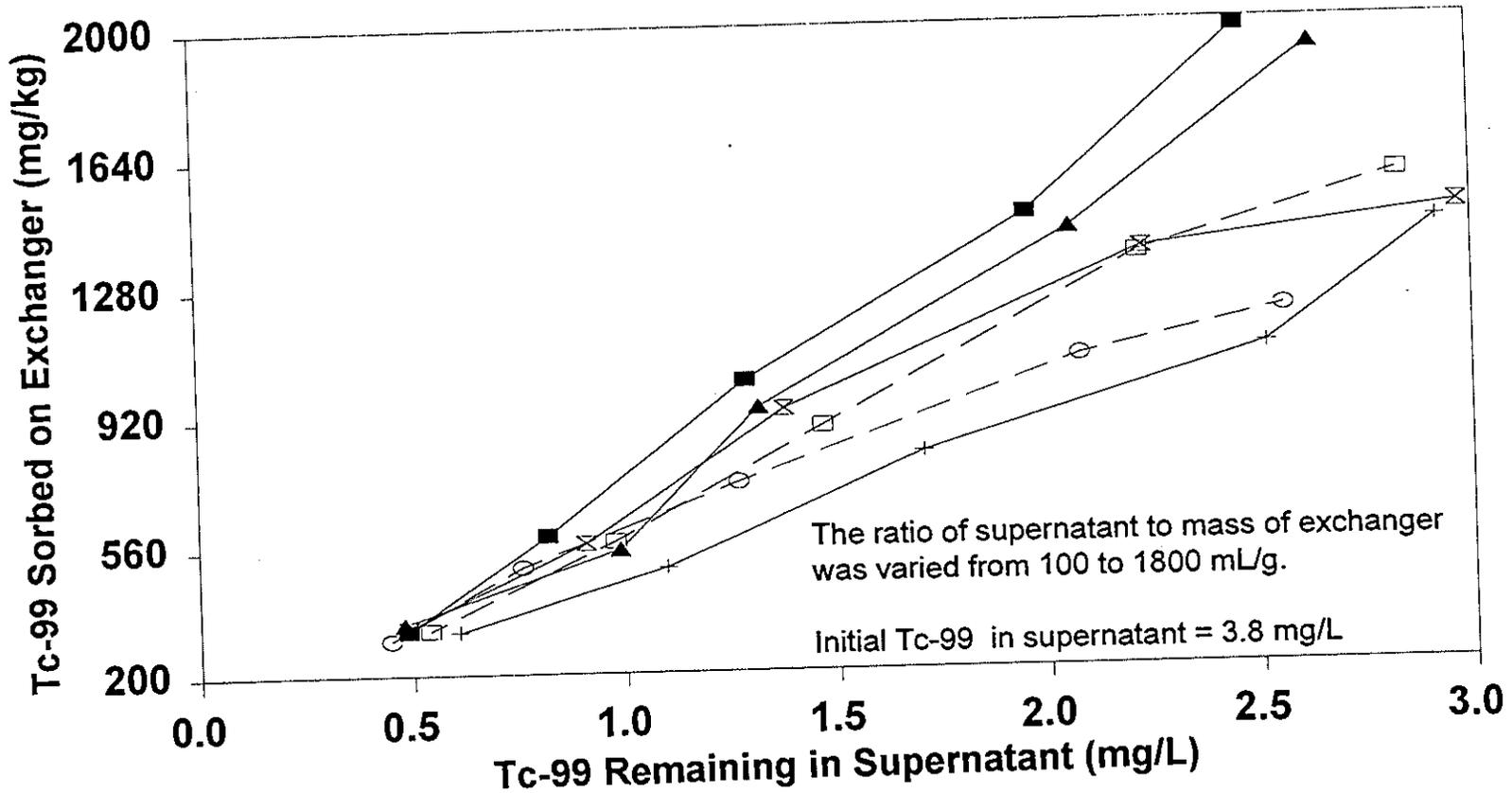


Fig. 6. Sorption isotherms for <sup>99</sup>Tc.

corrected for decay. The strontium concentration gradually decreased. These data, shown in Fig. 7, indicated that the strontium concentration in the W-29T supernatant approached an equilibrium value of  $\sim 1.5$  mg/L. Interestingly, the initial concentration of strontium in the original W-29 supernatant was 1.0 mg/L.

Results from batch tests with nine different sorbents for removing strontium from W-29T supernatant are given in Table 15. The inorganic sorbents outperformed the organic resins in removing the strontium, with the fine powders of NaTiO and CST giving the best results. The largest value for D (31,500 mL/g) was obtained with NaTiO in the 0.25-h test. Of the sorbents with particle sizes suitable for column use, TiHP  $\phi$ , NaTiO-PAN, and TiP-PAN gave the best results and were about equally effective.

Treated supernatant from the MVST W-27 (W-27T) was used in additional batch studies to evaluate sorbents for strontium removal. Removal of strontium from the supernatant was measured using a supernatant-to-sorbent ratio of 200:1. Results for Amberlite IRC-718, Chelex 100, Duolite C-467, IONSIV IE-911, NaTiO, and NaTiO-PAN sorbents using a mixing time of 24 h are shown in Table 16 and compared with results obtained using MVST W-29T supernatant. With NaTiO sorbent, the distribution ratios for strontium were 3170 mL/g in the MVST W-27T supernatant and 24,200 mL/g in the MVST W-29T supernatant. Batch sorption studies using CST resulted in a strontium D value of 24,900 mL/g using MVST W-29T supernatant. The organic sorbents exhibited lower strontium distribution ratios. It is interesting that some sorbents removed strontium better from MVST W-29T supernatant, while others were more effective with the MVST W-27T supernatant. The two top-performing organic sorbents were Duolite C-467 and Amberlite IRC-718. The distribution ratios obtained for the MVST W-29T supernatant using these materials were 1120 and 857 mL/g for Duolite C-467 and Amberlite IRC-718, respectively. However, Amberlite IRC-718 was more effective at removing strontium from the MVST W-27T supernatant; these distribution ratios were 1260 and 920 mL/g for Amberlite IRC-718 and Duolite C-467, respectively.

#### 6.4 SUMMARY OF BATCH TESTS

In summary, batch tests conducted at ORNL identified the sorbents that were effective in removing cesium, technetium (as pertechnetate), and strontium from the MVST supernatants. Based on the results from the batch studies, sorbents were selected for potential use in column studies. The primary candidates were KCoCF, R-F resin, CST, and SuperLig<sup>®</sup> 644C for removing cesium; several sorbents, particularly Eichrom ABEC-5000 and Reillex HPQ, for removing pertechnetate; and NaTiO, CST, and Amberlite IRC-718 for

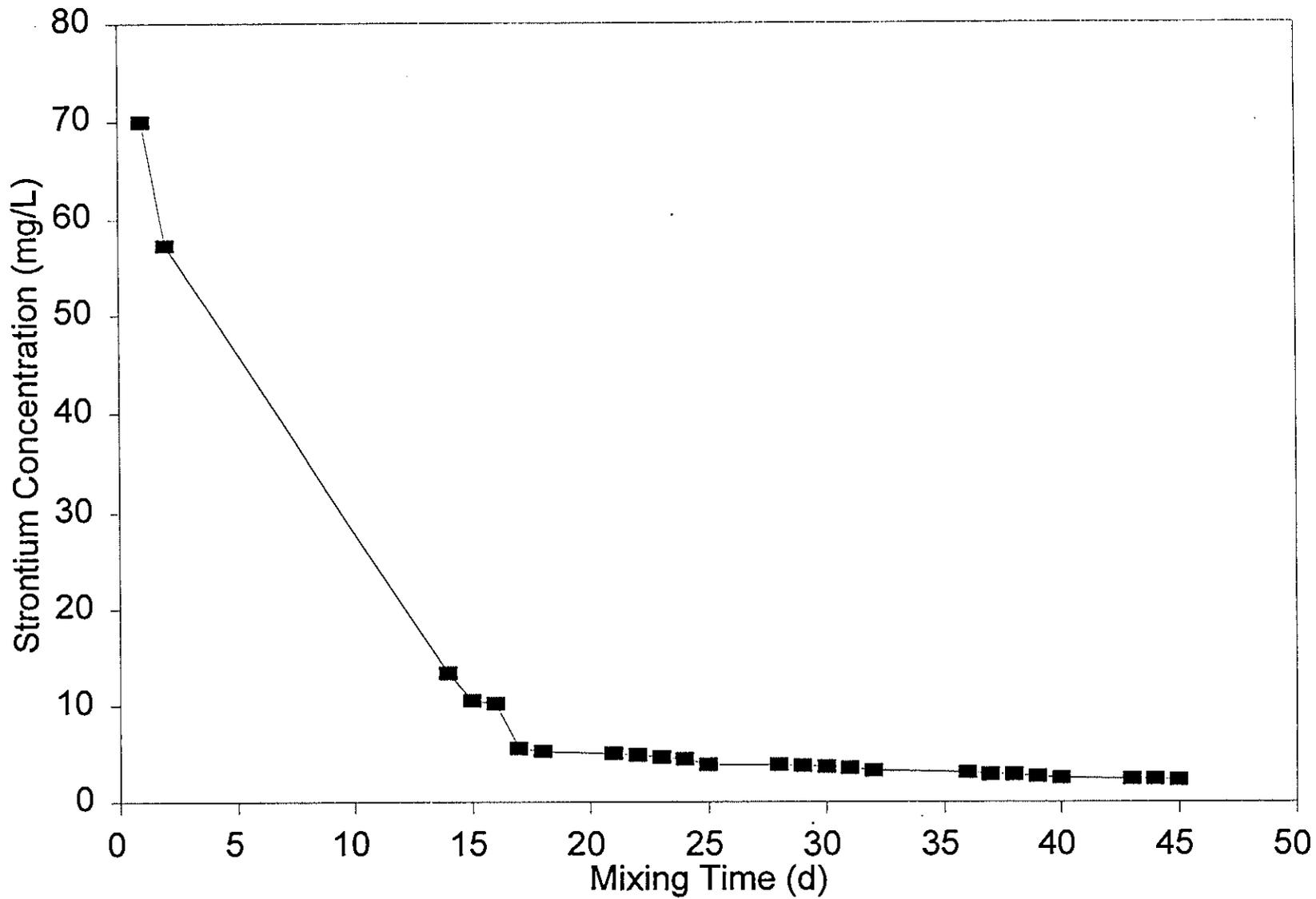


Fig. 7. Results of the experiment to determine the solubility of strontium in MVST W-29 supernatant.

Table 15. Batch adsorption data showing the effect of mixing time on the removal of strontium from MVST W-29T supernatant<sup>a</sup>

Sorbent	Mixing time (h)							
	0.25		2		24		144	
	D (mL/g)	%R	D (mL/g)	%R	D (mL/g)	%R	D (mL/g)	%R
NaTiO	31,500	99.3	30,500	99.4	24,200	99.2	25,200	99.2
CST	684	78.1	24,000	99.2	24,900	99.2	21,700	99.1
TiHP $\phi^b$	1,130	84.8	4,500	95.8	5,630	96.6	5,190	96.3
TiP-PAN	505	74.6	2,770	93.7	2,900	94.4	3,030	94.2
NaTiO-PAN	394	66.7	2,830	93.6	3,069	94.0	4,360	95.8
Duolite™ C-467	323	62.6	992	83.1	1,120	84.4	1,290	86.9
Chelex™ 100	245	54.5	611	76.4	673	74.0	1,500	88.3
Amberlite™ IRC-718	161	44.2	589	75.4	857	80.4	1,240	85.9
R-F resin	97	32.7	210	52.7	321	62.2	320	62.8

<sup>a</sup>The W-29T supernatant characterization is given in Table 5. The strontium concentration in the supernatant was 1.5 mg/L ( $1.7 \times 10^{-5} M$ ).

<sup>b</sup> $\phi$  = microspheres.

Table 16. Typical results from batch tests for removing strontium from MVST supernatants  
(Solution/sorbent = 200:1, mixing time = 24 h)

Sorbent	D (mL/g)	
	MVST W-29T	MVST W-27T
NaTiO (fp) <sup>a</sup>	24,200	3,170
CST (fp)	24,900	NM <sup>b</sup>
IONSIV IE-911	NM	2,790
TiHP $\phi$ <sup>c</sup>	5,630	NM
TiHP/PAN	2,900	NM
NaTiO-PAN	3,070	3,200
Duolite C-467	1,120	920
Amberlite IRC-718	857	1,260
Chelex 100	673	300
MERSORB-S	436	NM
R-F	321	NM

<sup>a</sup>(fp) = fine powder.

<sup>b</sup>NM = not measured.

<sup>c</sup> $\phi$  = microspheres.

removing strontium. (Samples of SuperLig<sup>®</sup> 644C were not received until late in the program, and a complete batch test evaluation could not be made.)

## 7. COLUMN RESULTS

Several of the sorbents were selected for evaluation in column tests for removing cesium, technetium (pertechnetate), and strontium. Sorbents evaluated for cesium removal included IONSIV IE-911, SuperLig<sup>®</sup> 644C, R-F resin, Duolite CS-100, and Eichrom KCoCF granular sorbent. Because of the high radioactivity associated with the cesium, all of the cesium column runs were conducted in a hot cell. These tests were used for verification of batch data and to establish parameters for use in the ORNL CsRD. The removal of the pertechnetate was tested in column runs using Eichrom ABEC-5000 and Reillex-HPQ sorbents. NaTiO, CST, and Amberlite IRC-718 were identified as candidates to remove strontium, and IRC-718 was chosen for a column test.

### 7.1 CESIUM

Several sorbents were tested in column runs to evaluate their effectiveness for cesium removal from MVST W-27 and supernatant from MVST W-27 blended with W-29 supernatant (W-27/W-29). These supernatants were tested "as received" and after pH adjustment. All of the column tests were conducted in a hot cell at ORNL by Lee, Travis, and Gibson.<sup>24,25</sup>

#### 7.1.1 Hot Cell Tests

##### 7.1.1.1 Crystalline Silicotitanates

Several runs were made using IONSIV IE-911, the engineered form of CST sorbent. Three runs involved using a developmental sample of CST supplied by UOP, labeled IONSIV IE-911 #07398-38B (CST-38B). An additional two runs used production-engineered forms of CST from UOP: IONSIV IE-911 from lot #999096810001 (CST-0001) or #999096810003 (CST-0003). For runs using CST-38B, the MVST W-27 supernatant was adjusted to a pH of 12.84 before use in two experiments. In the third column run using CST-38B and in the runs using CST-0001 or CST-0003, the W-27 supernatant was adjusted to pH 14 by adding solid NaOH (MVST W-27pH). The resulting solution contained 1 M OH<sup>-</sup> and  $7.5 \times 10^{-5}$  M cesium. The sorbent volume was approximately 10 cm<sup>3</sup> in a 1.5-cm-ID column. The dry tapped density for the CST-38B was measured and estimated to be 1.155 g/cm<sup>3</sup>. Density of the CST-0001 was about 10–20% less

than that for the CST-38B material. The average mass of the sorbent in the columns was 11.4 g. The sorbent was pretreated by flushing the column with 0.1 M NaOH for one column run or 1 M NaOH solution for three runs to wet the packing and remove bubbles. The longest time the sorbent was in caustic solution was about 3 d.

The flow rate for the column runs was 6 CV/h, except for the first one, which was 3 CV/h. Using these flow rates, the columns were operated until more than 435, 384, 272, 294, and 560 CV of supernatant was passed through five different columns. The 50% cesium breakthrough occurred at about 350, 340, 272, 294, and 504 to 546 CV (as a result of the different sample analyses for  $^{137}\text{Cs}$ ). A dark brown material plugged the filter downstream from the column in the system operated at 3 CV/h, resulting in a pressure drop across the filter. The effluent was routed through a second filter when the pressure drop across the filter reached more than 15 psi. For the remainder of the run, the second filter did not plug, although the filter appeared to have 50–60% of the surface area covered again. However, using a flow rate of 6 CV/h, no difficulties were observed, although a 1.5-cm-diam dark spot appeared on the after-column filter. In addition, a dark layer about 1 mm thick was noted at the top of the bed during the second run.

The results comparing the effect of flow rate on cesium removal are shown in Fig. 8. As expected, increasing the flow rate from 3 to 6 CV/h resulted in less cesium being retained on the column. However, the 50% cesium breakthrough for the column run using the flow rate of 6 CV/h and half of the original cesium concentration was very close to that obtained at 3 CV/h.

Based on the  $^{137}\text{Cs}$  passed through the column [41,430  $\mu\text{Ci}$  and 36,090  $\mu\text{Ci}$  (9.34  $\mu\text{Ci}/\text{mL}$  in the feed  $\times$  4436 mL for the column run using the flow rate of 3 CV/h and  $9.34 \times 3864$  mL at a flow rate of 6 CV/h, respectively)] and the analysis of the effluent (9920  $\mu\text{Ci}$  for 3 CV/h and 7290  $\mu\text{Ci}$  for 6 CV/h), the  $^{137}\text{Cs}$  loading was calculated. From this calculation, the cesium activity expected on the column was 31,510 and 28,800  $\mu\text{Ci}$  for the experiments using flow rates of 3 and 6 CV/h, respectively. Analysis of the sorbent in the column showed 26,160 and 25,590  $\mu\text{Ci}$  were loaded on the column, corresponding to 87 and 91% of the cesium in the feed sorbed on the column.

#### 7.1.1.2 SuperLig<sup>®</sup> 644C

Three runs were conducted using SuperLig sorbent materials.<sup>24,25</sup> The sorbent preparation included soaking it in 0.1 M NaOH for the first column run and wetting it with water followed by 2 M NaOH solution for the second and third runs. The pretreatment resulted in a 100% increase in sorbent volume compared with the dry volume. After the material settled, the initial CVs were 8.5 mL for the first run, 10.5 mL for the second one, and 10.2 mL for the last run. The supernatant used for the runs was from MVST W-27. For the third

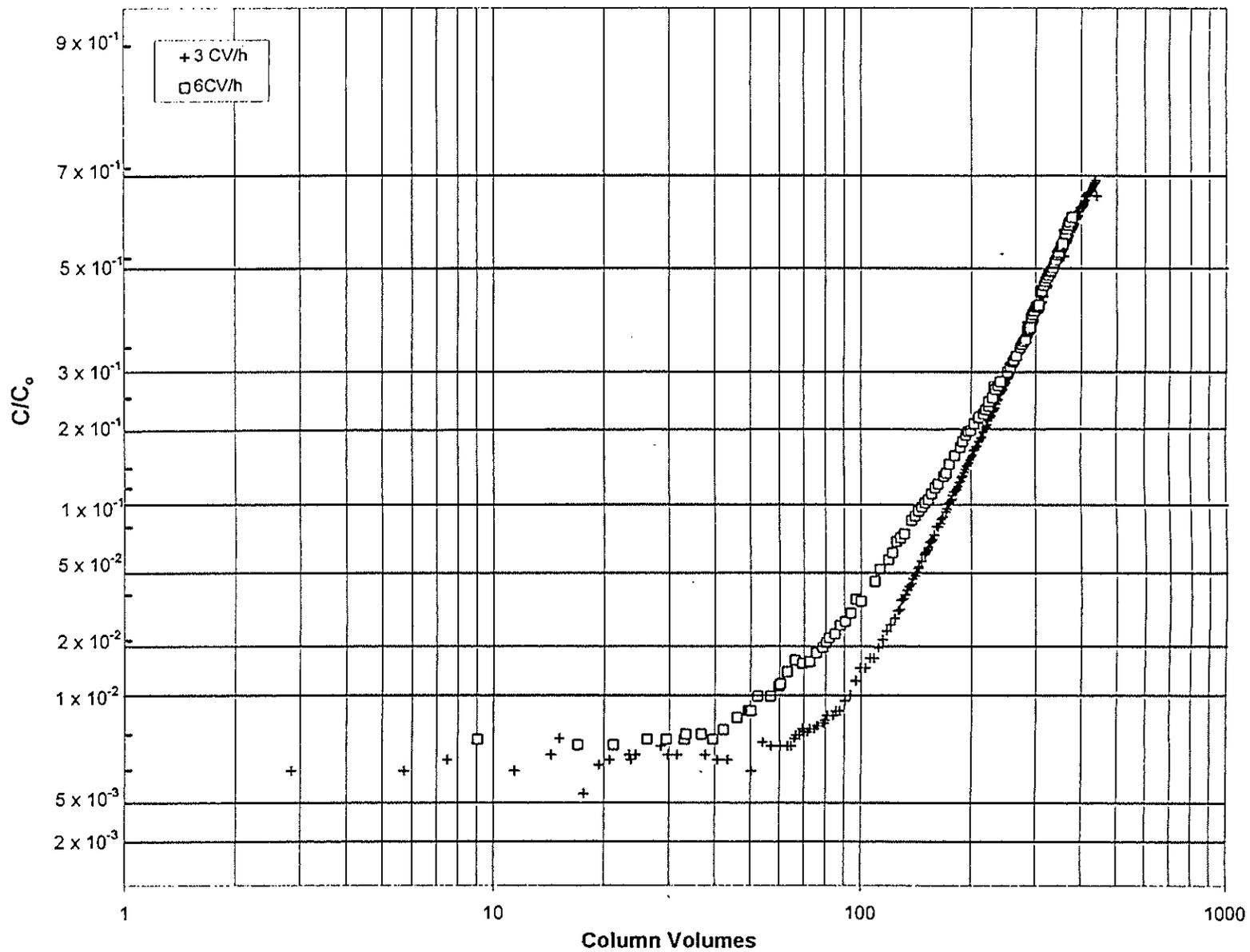


Fig. 8. The effect of flow rate on cesium removal from MVST supernatant by CST.

column run, the supernatant pH was adjusted to 14 (MVST W-27pH). Flow rates for the three column runs were about 2.5–3, 6.0–6.4, and 3.5 CV/h, respectively. For the second column run, the flow rate of 6.0 CV/h was slowed to 3 CV/h after reaching the 50% cesium breakthrough.

The first column run resulted in almost an immediate breakthrough at the 2–3% cesium level. Due to problems in the detection system, the run was stopped before reaching 50% cesium breakthrough. For the second column run, 50% cesium breakthrough was reached after about 138 CV. The third column was loaded, eluted using 0.5 M HNO<sub>3</sub>, regenerated with 2 M NaOH, and reloaded. For the initial loading cycle on the third column, the supernatant contained  $1.1 \times 10^{-5}$  M cesium. However, in the three subsequent loadings approximately seven times more cesium was added to the MVST W-27 supernatant as cold cesium nitrate and measured to contain  $7.5 \times 10^{-5}$  M in the feed. In order of loading, the 50% cesium breakthroughs occurred at 167, 77, 65, and 50 CV for these cycles.

A total of 9895  $\mu$ Ci of cesium was loaded onto the second column. The cesium was eluted from the column by pumping 0.5 M HNO<sub>3</sub> through the column at a flow rate of 3 CV/h. After elution, only 18.1  $\mu$ Ci of cesium remained on the column. However, the effluent solution from the acid elution was brown. The bed height changed from 7.5 cm to a final height of 5.6 cm, making it difficult to maintain a constant flow rate.

During the loading and elution of cesium, sorbent degradation apparently occurred. The initial fractions that were collected during the loading of the sorbent contained brown liquids but no solids. The last fractions contained some solids, as did the lines to the fraction collector. Most of the first six fractions collected during the elution, and in the lines to and from the fraction collector, showed trace amounts of solids. This behavior was noted when supernatants at pH 14 were used. Another problem with the SuperLig<sup>®</sup> 644C sorbent was its low density. During the first column run, a large clump of the resin separated and rose to the top of the solution above the bed. A custom-designed device which was developed by J. L. Collins was used in the third run that maintained a packed bed without applying undue force on the bed.

#### 7.1.1.3 Resorcinol-Formaldehyde Resin

Lee et al.<sup>24,25</sup> conducted five column runs using R-F resin to remove cesium from MVST W-27 supernatant. The bulk, tapped dry weight of the resin was about 0.69 g/cm<sup>3</sup>. The resin was pretreated by wetting with water, converting the as-received potassium form to the hydrogen form by washing with 5 or 10 CV of 0.5 M HNO<sub>3</sub>, and then washing with distilled/deionized (DI) water. All the resin samples were treated with 10 CVs of 2 M NaOH to convert the material from the hydrogen form to the sodium form. The resin was then washed with DI water. Once the resin pretreatment was completed, the test columns were loaded with the resin. Because column volumes changed throughout the runs, the values used for calculations were

based on the volume just after the run was started. For the loading/elution/regeneration column run, the column volume continually changed; as a result, the value for the column volume was adjusted at the beginning of each cycle. The supernatant used in the fourth column run was adjusted to pH 14 (MVST W-27pH).

A brown effluent solution was observed during the preparation of the resin for the first run. For the second run, the appearance of the dark solution was observed within the first 3–4 CV that was collected. The resin volume changed significantly when the acid was replaced by the caustic. Color was noted in the effluent during the loading phase during some column runs. The bed height changed from 2 cm for the dry resin to 4.5 cm after caustic was added.

The five columns contained 11.5, 10.6, 9.3, 11.1, and 10.3 mL of R-F material. The R-F used in column 5 was from a different source and batch. The flow rates were measured at 7, 2.9, 6.0, 3.5, and 6.0 CV/h, respectively. The 50% cesium breakthrough was reached at about 45, 36, 50, and 18 CV for the first through fourth columns and at greater than 75 CV at about 1.2% breakthrough for the fifth column. For the column containing 11.5 mL, 3.2 mCi of  $^{137}\text{Cs}$  was removed from 0.5 L of the feed containing a total of 4.42 mCi.

The column containing 9.3 mL of material was loaded/eluted/regenerated for five cycles. An average of 72.2% of the cesium in the supernatant was removed for the loading cycles (Table 17). Elution of the cesium from the column was very effective, with an average elution of 99.6%. However, a characteristic of the R-F resin was the apparent material degradation noted during the loading and elution cycles. The bed shrank from 6.2 cm for the first loading to 5.3 cm at the start of the fourth and fifth runs.

Table 17. Results of R-F column loadings and elutions

Loading	Supernatant fed (mL)	Cs in feed ( $\mu\text{Ci}$ )	Cs loaded <sup>a</sup> ( $\mu\text{Ci}$ )	Cs loaded (%)	Cs remaining <sup>b</sup> , ( $\mu\text{Ci}$ )	Cs stripped from resin (%)
1	330.6	3095	2174	70.2	9.1	99.6
2	325.3	3045	2251	73.9	8.3	99.6
3	332.3	3111	2263	72.7	8.4	99.6
4	318.3	2980	2124	71.3	7.1	99.7
5	324.4	3028	2205	72.8	7.1	99.7
Avg	326.2	3052	2203	72.2	8.0	99.6

<sup>a</sup>Calculated based on the sample analyses of the fractions collected.

<sup>b</sup>Calculated based on counting the cesium on the column before and after elution.

#### 7.1.1.4 Duolite CS-100

One column run was completed using Duolite CS-100. For this test, 13.2 mL of CS-100 sorbent was used in a 1.5-cm-ID column. The sorbent was pretreated with 3 CV of 2 M NaOH and 6 CV of distilled water. The pretreatment converted the color of the resin from caramel brown to black. Using a column flow rate of 2.9–3.0 CV/h with the MVST supernatant, 50% cesium breakthrough occurred at 17 CV.

#### 7.1.1.5 Potassium Cobalt Hexacyanoferrate

One column run using KCoCF obtained from Eichrom Industries, Inc., was completed. The KCoCF was prepared by adding 10 mL of sorbent (equivalent to 7.3 g) to the column. About 150 mL of distilled water was pumped in upflow mode through the sorbent to remove fines and pack the bed. When the supernatant was pumped down through the column at 9 CV/h, precipitation occurred at the top of the bed. In the feed solution above the bed, a blue-colored, gel-like material was noted. In addition, the solids in the column formed a lump of cloudy material about 1 cm thick. An inspection of the supernatant did not indicate any solids either in the feed tank or in the lines to the column from the feed tank or pump.

The column run was continued for more than 250 CV. During the run, two post-column filters plugged, resulting in a pressure increase. The bed height decreased from an initial height of the wet sorbent of 6.3 to 5.2 cm, apparently due to degradation of the sorbent. Solids were filtered from some of the effluent samples using a 0.2- $\mu$ m filter. Parts of the system had to be replaced after the system was shut down because of the solids in the system. Therefore, cesium breakthroughs reported using these materials were inaccurate because of the degraded sorbent in the effluent. The results were not unexpected.

#### 7.1.1.6 Summary of Hot Cell Column Studies on Cesium Removal

Several materials were tested in column runs for cesium removal from MVST W-27 supernatant. These materials included CST, SuperLig<sup>®</sup> 644C, R-F resin, Duolite CS-100, and KCoCF. Duolite CS-100 served as a benchmark for comparison. Multiple runs were conducted using different flow rates and sorbent pretreatment methods. The regenerable sorbents, SuperLig<sup>®</sup> 644C and R-F resin, were eluted with nitric acid. CST is not considered regenerable, so no attempts were made to elute the cesium. The KCoCF material was not eluted because it degraded during the loading phase. All the materials except the CST had stability problems, either during cesium loading or elution. The KCoCF was the most unstable with the chosen supernatant because the pH was too high (>12).

### 7.1.2 Cesium Removal Demonstration

The batch and column studies resulted in the selection of the CST ion-exchange material, IONSIV IE-911 (CST-0003), for use in the CsRD, a project designed to treat 100,000 L of supernatant from an MVST at ORNL.<sup>26</sup> During the operation of the CsRD, four runs were made: a minimal-loading run and three full-loading runs were completed. For these runs, 38-L columns were used. The minimal-loading run was to test the system and verify procedures before starting the full-loading runs. The supernatant was prepared by adding 50% caustic solution to tank W-27 to adjust the pH and allow it to settle for 2 weeks. Then approximately 83,000 L was pumped to tank W-29 and mixed with supernatant remaining in the tank. The mixed supernatant in W-29 was allowed to settle for 1 month.

The first run was completed after loading ~23 Ci of <sup>137</sup>Cs onto the sorbent. The second run (i.e., the first full run) was operated at 3 CV/h using a single-column system. Approximately 18,000 L of MVST supernatant was processed before reaching the 50% breakthrough of <sup>137</sup>Cs. A total of ~154 Ci of <sup>137</sup>Cs was loaded onto the sorbent. Two columns were operated in series for the third run at a flow rate of 6 CV/h. The volume of supernatant processed, 39,000 L, was a little more than double that of the single-column system. The first column reached ~80% <sup>137</sup>Cs breakthrough, representing ~222 Ci of <sup>137</sup>Cs, and the second column was loaded to ~47% cesium breakthrough, equaling a total <sup>137</sup>Cs activity of ~112 Ci on the sorbent. For the fourth run, a three-column series was used. Column 1 processed ~28,000 L of supernatant before reaching 55% <sup>137</sup>Cs breakthrough and loading ~253 Ci of <sup>137</sup>Cs. Initial analyses of columns 2 and 3 showed that ~266 Ci of <sup>137</sup>Cs was loaded onto column 2 and ~112 Ci of <sup>137</sup>Cs was loaded onto column 3, giving a total <sup>137</sup>Cs removal during this run of ~631 Ci.

A total of ~116 m<sup>3</sup> ( $1.16 \times 10^5$  L) of supernatant was processed, and ~1142 Ci of <sup>137</sup>Cs was loaded onto 0.266 m<sup>3</sup> (266 L) of sorbent. These values compare very well with the hot cell tests. For the demonstration system, 50% cesium breakthrough occurred after about 500 CV was processed. For the hot cell tests using W-29 waste, ~500 CV was also required to reach the 50% cesium breakthrough.

## 7.2 TECHNETIUM

Reillex HPQ was selected as the sorbent for the first column run to measure the removal of pertechnetate from ORNL MVST W-27 supernatant. This sorbent has been tested at Los Alamos National Laboratory,<sup>7</sup> and further tests were completed at PNNL<sup>22</sup> for technetium removal from Hanford tank supernatants. The supernatant used in the ORNL tests was column effluent generated from column

chromatography using IONSIV IE-911 to remove cesium from MVST W-27. Further treatment of this supernatant has been described. After the additional treatment, the supernatant was filtered through a 0.45- $\mu\text{m}$  filter and ammonium pertechnetate solution was added. Analyses of the supernatant showed that the concentrations of the primary constituents of the supernatant were 5.4 *M* sodium, 0.30 *M* potassium, 5.1 *M* nitrate, and 0.1 *M* chloride. The pH was measured at 12.86. After addition of ammonium pertechnetate, the technetium concentration was 2.9 mg/L.

The particle size of the sieved Reillex HPQ resin was between 249 and 595  $\mu\text{m}$ . Before the resin was added to the column, 6.97 g of "as-received" resin (hydroxide form) was contacted for about 24 h with 0.16 *M* NaOH. After pretreatment, the resin was transferred to the 1.45-cm-ID by 15-cm ion-exchange column. The resin bed was conditioned by using a solution containing 5.0 *M* sodium nitrate and 0.16 *M* sodium hydroxide. The effluent had a dark amber color that faded as additional solution passed through the bed. The height of the preconditioned bed was 6.3 cm, providing a packed bed of about 10.4  $\text{cm}^3$ .

About 1300 mL of supernatant was passed through the column at a rate of about 6 CV/h. Eluate fractions were collected in 15-mL polypropylene centrifuge tubes to better define the loading profile with time; selected samples were submitted for analysis by ICP-MS. Filtered and unfiltered samples of these fractions were analyzed to determine the technetium concentrations. The 50% technetium breakthrough occurred at approximately 45 CV (see Fig. 9). This corresponds to approximately 1.4 mg of technetium loaded on the 6.97 g of the resin at 50% technetium breakthrough.

The column was washed with about 7 CV of water. The resin bed was eluted at a flow rate of about 4 CV/h using an eluant solution containing 0.017 *M* stannous chloride, 0.1 *M* ethylenediamine, and 0.075 *M* sodium hydroxide. This eluant was developed and used successfully by N. C. Schroeder<sup>7,8</sup> of Los Alamos National Laboratory for eluting technetium from Reillex HPQ. The technetium was readily removed from the column using this eluant. Approximately 1.2 mg of technetium was eluted in 7 CV of eluant. In one fraction, the technetium concentration was more than 40 times the concentration in the supernatant feed.

An additional small-column test was completed for removal of the pertechnetate from MVST W-27 supernatant using Eichrom ABEC-5000. This supernatant was D. D. Lee's column effluent from column chromatography on SuperLig<sup>®</sup> 644C to remove the cesium.<sup>24,25</sup> After removal of the cesium, the treated supernatant was filtered through a 0.2- $\mu\text{m}$  filter. Additional technetium was added to 2 L of the treated supernatant to increase the concentration from 0.43 to 3.0 mg/L.

A Kontes glass column with an inside diameter of 1.45 cm was used. The resin, slurried in water, was added to give a bed height of 10.5 cm, corresponding to a bed volume of 17.3 mL. The resin was then washed

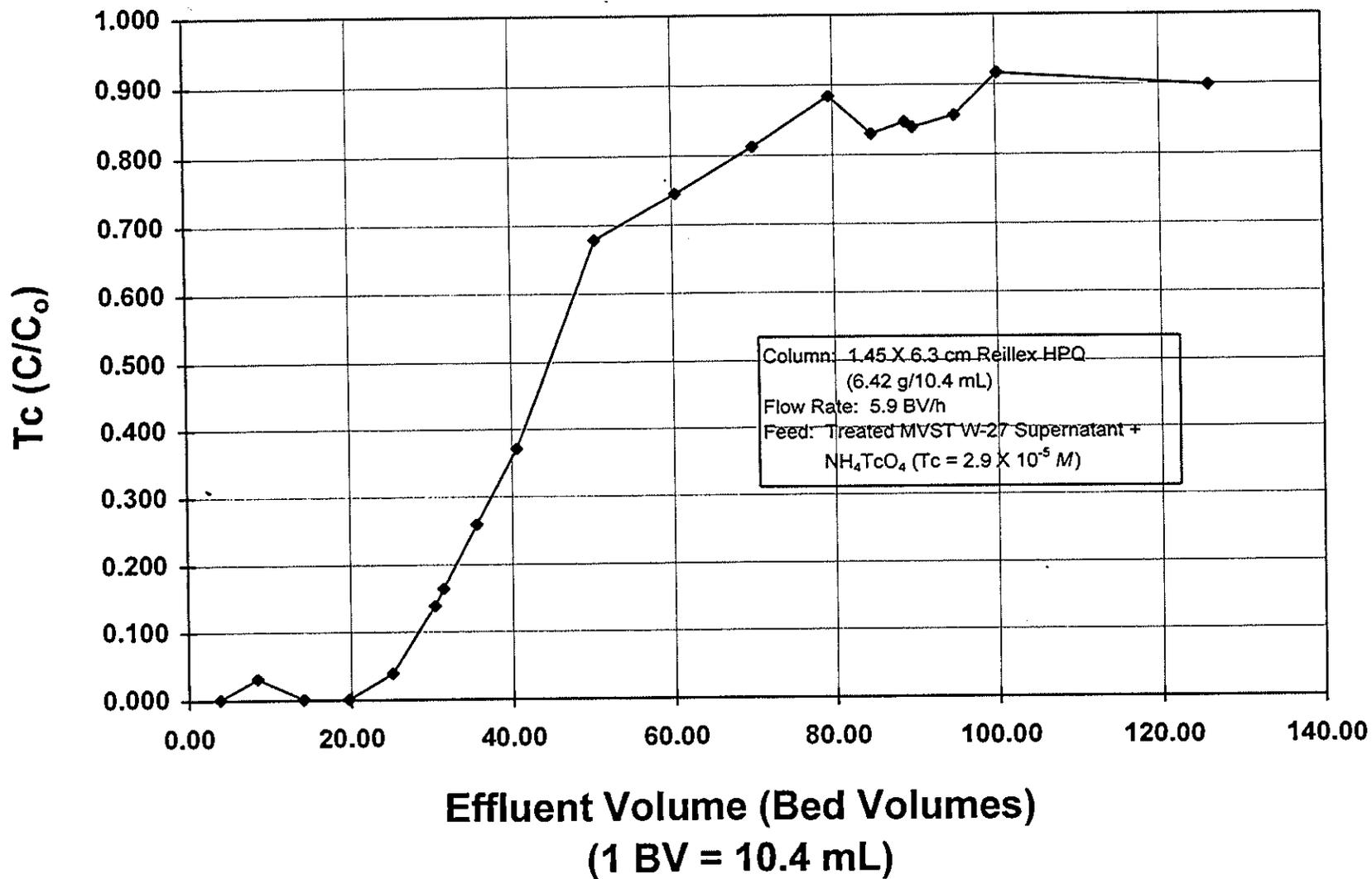


Fig. 9. Pertchnetate removal from MVST W-27 supernatant.

with 3 CV of 4 M NaOH. This caused the bed height to shrink to 5.1 cm. A simulant solution containing 0.16 M NaOH and 4.5 M NaNO<sub>3</sub> was added to the column, resulting in an increase in the bed height to 8.6 cm. Once the treated MVST W-27 supernatant was added to the resin bed, the final bed height was 6.2 cm, providing a packed bed of about 10.4 cm<sup>3</sup>. Supernatant solution was passed through the column at a rate of about 6.8 CV/h. The ABEC-5000 resin floated in all of the solutions except water. A special apparatus designed by J. L. Collins was used to maintain a packed bed to allow for swelling and shrinkage of the bed during the run.

About 1200 mL of supernatant was passed through the column, and 120 fractions were collected. The column was then washed with about 3 CV of 2 M NaOH. To elute the technetium from the column, about 100 mL of water was passed through the column at an average flow rate of 5 CV/h. Eluate fractions were collected, and selected fractions were analyzed by ICP-MS to measure the technetium concentration.

Analysis of the eluate fractions indicated that the resin did not remove appreciable amounts of the pertechnetate, with technetium breakthrough occurring after less than 5 CV was collected. This was much earlier than expected based on previous batch tests with a similar supernatant solution (see Sect. 6.2).

Additional batch tests were conducted to learn whether the differences were due to sorbent pretreatment, differences in the supernatants, or analytical procedures. The resin was pretreated before contact with the supernatant by several methods: (1) washing with a solution consisting of 4.5 M NaNO<sub>3</sub> and 0.16 M NaOH; (2) washing with the same solution, followed by mixing with 4 M NaOH; (3) treating with 4 M NaOH only; and (4) no pretreatment. Also, a sample of the Eichrom resin from a different batch was tested "as received," with no pretreatment. The ratio of supernatant to sorbent was 200:1, with a contact time of 24 h. Test results showed no significant differences in the technetium removed by the samples subjected to the different pretreatments; very little technetium was sorbed.

Several tests were also designed to examine whether the counting procedure, particularly the liquid scintillation cocktail, was the limiting factor in the analysis. For these tests the pertechnetate distribution on three sorbents, Purolite A520E, Reillex HPQ, and Eichrom ABEC-5000, was measured. Solutions were analyzed using three different scintillation fluids. Results from these tests were inconclusive; little technetium was sorbed. It is suspected that the low technetium removal from this supernatant is related to the previous column chromatography on SuperLig<sup>®</sup> 644C. Perhaps some SuperLig<sup>®</sup> 644C degradation products in the supernatant effluent changed the species of technetium in the feed. A search of the literature showed that numerous reducing agents such as certain ion-exchange resins, hydrochloric acid, stannous ion, thiocyanate ion, hydrazine, ascorbic acid, and some organic solvents are known to reduce technetium(VII) to lower-valence states.<sup>30</sup> The only known difference in the two supernatants feeds used in the technetium removal column tests

was their exposure to IONSIV IE-911 and SuperLig<sup>®</sup> 644C. Another reason may be the change in technetium speciation with the pertechnetate being reduced in the highly alkaline environment. The ABEC-5000 has since been tested successfully at PNNL.<sup>22,23</sup>

### 7.3 STRONTIUM

Batch studies identified several commercially available sorbents that could be effective for strontium removal. These included NaTiO, CST, NaTiO-PAN, TiHP, Amberlite IRC-718, Chelex 100, and Duolite C467. From these batch tests, sieved Amberlite IRC-718 (300–710  $\mu\text{m}$ ) was selected for a column test. The sieved sorbent was soaked in deionized water and then added to a 1-cm-ID column to a bed height of 4 cm. A solution consisting of 4.5  $M$   $\text{NaNO}_3$  and 0.16  $M$   $\text{NaOH}$  was passed through the column to simulate the supernatant. No significant change in bed volume occurred. Subsequently, the sorbent was washed with a 0.1  $M$   $\text{HNO}_3$  solution and the bed height decreased to about 3.6 cm. The salt solution was passed through the column again, resulting in a final bed height of 4 cm, corresponding to a column volume of 3.2  $\text{cm}^3$  (approximately 0.7 g of sorbent). Treated MVST W-27 supernatant (treated as described previously to remove cesium), containing 1.5 ppm strontium, was passed through the column at a flow rate of 8 CV/h. The collected fractions were analyzed by gamma spectroscopy. One percent strontium breakthrough occurred at approximately 213 CV, and at the termination of the run, about 25% strontium breakthrough was reached after 719 CV (2.3 L). Strontium loading on the sorbent, calculated using a ratio of initial counts corresponding to 1.5 ppm strontium, indicated that a total of 2.85 mg of strontium was removed from the supernatant and loaded on the column.

Elution of the strontium from the loaded column was initially attempted using 0.1  $M$   $\text{HNO}_3$  and a flow rate of approximately 2.3 CV/h. A salt solution composed of 4.5  $M$   $\text{NaNO}_3$  and 0.16  $M$   $\text{NaOH}$  was first pumped through the column to remove strontium in the interstitial liquid. A total of 6 CV was collected before the 0.1  $M$   $\text{HNO}_3$  solution was added. About 6 CV of the 0.1  $M$   $\text{HNO}_3$  eluate was collected and analyzed. Since all of the strontium was not eluted at this point, a 1  $M$   $\text{HNO}_3$  solution was added to elute the strontium remaining on the column. A total of 11 CV was collected using this eluate. Elution of the strontium appeared to reach a maximum with the collection of 1.3 CV of the eluant. Analysis indicated that only about 15% of the strontium on the column was eluted.

The difficulty in eluting the strontium from the column resulted in additional batch studies being conducted to find a method for complete elution. For these tests, 50 mg of the sieved sorbent (sieve size

300–710  $\mu\text{m}$ ) was added to preweighed centrifuge tubes. To each tube, 5 mL of MVST supernatant from tank W-27 was added and weighed. These samples were then mixed for 24 h using a wrist-action shaker. The solutions were pipetted from the initial centrifuge tube to a second centrifuge tube for sampling for analyses.

The centrifuge tubes were weighed after removal of the aqueous phase. Five-milliliter samples of 1, 2, 3, and 6  $M \text{HNO}_3$  were added to the separate sorbents in the tubes. After weighing the tubes, they were placed on a wrist-action shaker overnight. Before the aqueous phase was sampled, it was centrifuged. The results indicate that the bulk of the strontium could be removed from the sorbent more efficiently using a 2 or 3  $M \text{HNO}_3$  strip (80% for 1  $M \text{HNO}_3$  and 95% for 3  $M \text{HNO}_3$ ).

Finally, to elute the strontium from the column, a flow rate of 2.3 CV/h was established using deionized water; then about 6 CV of 6  $M \text{HNO}_3$  was pumped through the column using a downward flow. The sorbent was monitored, and triplicate samples were transferred into preweighed tubes for analysis. Analysis of the sorbent showed that little or no strontium remained on the column. Therefore, stripping with higher acid concentrations, though undesirable due to potential chemical reactivity with the sorbent, was effective for removing strontium from the sorbent.

## 8. SUMMARY AND CONCLUSIONS

Over 25 sorbents have been evaluated in batch tests for removing cesium, technetium, and strontium from MVST supernatants. Several sorbents were selected for hot cell column tests on cesium removal conducted by D. D. Lee.<sup>24,25</sup> Based on the hot cell tests, IONSIV IE-911 was chosen for a cesium removal demonstration in which over 100,000 L of MVST supernatant was treated. In addition, sorbents were also selected, based on the batch tests, for column runs to remove technetium (as pertechnetate) and strontium, which were added to the supernatants after the cesium had been removed. The greatest effort has been directed toward cesium removal since  $^{137}\text{Cs}$  is responsible for a large fraction of the radioactivity in the supernatants. From these tests, several potential sorbents have been identified for use in treatment of supernatants from underground storage tanks. The technetium and strontium concentrations in MVST supernatants are much lower than they are in the Hanford supernatants, so their removal is not as important. However, adding technetium and strontium to the MVST supernatants could make the results from our studies more applicable to the Hanford supernatants.

When evaluating sorbents for radionuclide removal, it is important to remember that the batch-distribution-ratio data as frequently reported are compared on the basis of mass of sorbent (milliliters per gram)

rather than the volume of sorbent. The different swelling properties of the sorbents are a significant factor that must be taken into account in designing column processes. Depending upon the sorbent, the mass in a given volume can differ by factors ranging from 1 to 7. Swelling can also change for a given sorbent, depending on the acidity, ionic strength, etc.

Knowledge of the total concentration of the element to be removed by ion exchange is important because all of the isotopes of the element are sorbed equally well by ion-exchange materials (although some isotopic separation by ion exchange has been reported). The amount of "cold" material adsorbed has a significant effect on the radionuclide removal. Codes are available for calculating fission product yields, but other sources of "cold" material have been added to many of the waste tanks. And, of course, the amount of radioactive material changes with time.

The "best" sorbent for a particular application depends on several considerations. Different sorbents are more stable and usable in different pH ranges and acid and base concentrations. Some of the sorbents are more easily eluted, allowing recovery and concentration of the radionuclide, while the radionuclides cannot be readily removed from other sorbents. Some of the sorbents are more adaptable to storage in final waste forms. Therefore, the sorbent of choice depends on the ultimate objective as well as the characteristics of the feed supernatant.

## 8.1 CESIUM

Several sorbents were evaluated for removing cesium from underground storage tank supernatants in the MVSTs and were effective in removing the cesium. Most of the sorbents were stable in the batch tests, where relatively small solution/sorbent ratios were used and any sorbent dissolution was limited by equilibrium or steady state. However, in the column tests, the larger volumes of solutions resulted in degradation or dissolution of some of the sorbents (SuperLig<sup>®</sup> 644C and R-F).

CST, R-F, KCoCF, and SuperLig<sup>®</sup> 644C effectively removed cesium from supernatants. The engineered commercial form of CST, IONSIV IE-911, gave the most-favorable all-around behavior in batch and column tests for cesium removal. It is effective over a wide range of pH values and has good physical properties. It is also a reasonably good sorbent for strontium. This sorbent has also been demonstrated successfully for removing cesium from Hanford tank supernatant. The cesium is not readily recoverable from the CST. Some studies have been conducted on the feasibility of incorporating the loaded CST in glass for final disposal.

Potassium cobalt hexacyanoferrate had the highest cesium distribution coefficient in the batch tests, but it is most stable below pH 12. In the column runs with supernatant at pH > 12, the KCoCF was unstable, resulting in dissolution of the sorbent and formation of fines in the effluent. The use of KCoCF to remove cesium from alkaline supernatant has been demonstrated on an industrial scale at the Loviisa Nuclear Power Station in Finland.<sup>27,28</sup> The pH of the feed stream was adjusted to < 12 before treatment. The stainless steel columns were 60 cm long by 14 cm diam with a bed volume of 8 L. The loaded columns were washed and dried and placed in concrete blocks for disposal. While cesium was readily removed from supernatant by either the CST or the KCoCF, it cannot be readily eluted from either of these sorbents.

The R-F resin showed some inconsistency in loading and elution. Potassium has a greater effect on cesium removal with the R-F resin than with CST. Fouling by liquid organics such as TBP can significantly reduce the cesium removal by the sorbents, especially R-F resin. The effects of dissolved organics on the sorbent behavior were not measured. However, any dissolved organics that could act as complexants for any of the radionuclides would be expected to reduce the radionuclide sorption. In contrast to the CST and KCoCF, the cesium can be eluted from the R-F and SuperLig<sup>®</sup> 644C resins and recovered. To maintain a fixed bed and prevent the SuperLig<sup>®</sup> 644C from floating in the column tests, a self-adjusting, fixed bed support system was used that was designed by J. L. Collins. It also maintained a fixed bed during the swelling and shrinking phases of the resin that occurred during elution and loading.

## 8.2 TECHNETIUM

Technetium removal is very dependent on technetium speciation. In all tests, technetium was added to the supernatant solutions as ammonium pertechnetate. Several anion exchangers were effective in removing the pertechnetate anion. However, a significant fraction of technetium in the Hanford tanks exists as non-pertechnetate. Consequently, anion exchangers would not be expected to be effective for removing all of the technetium from the Hanford supernatants. One approach to improving the technetium removal in this case would be to oxidize the technetium to pertechnetate to facilitate anion exchange. Studies are under way at Los Alamos National Laboratory to evaluate this approach.<sup>29</sup> An alternative would be to reduce the technetium and precipitate it as the hydrous oxide, which would then become part of the tank sludge and treated accordingly.

Both Reillex HPQ and Eichrom ABEC-5000 were effective in removing pertechnetate from supernatants. Elution of the technetium from Reillex HPQ requires reduction with stannous chloride and

complexation with ethylenediamine. Technetium can be eluted from ABEC-5000 with water, which is a great advantage. However, both sorbents exhibit volume changes during loading and elution. The volume of the ABEC-5000 can change by a factor of two when switching from feed to eluant. Also, the densities of these sorbents are similar to those of some of the supernatants and eluants. Consequently, the sorbents may float and require bed stabilization. The problems described previously about the low loading of technetium by the ABEC-5000 column are believed to be due to the presence of SuperLig<sup>®</sup> 644C degradation products in the supernatant that was used as feed. The technetium was apparently reduced to a nonloading form. There was no apparent reduction of the pertechnetate that was added to MVST W-27 supernatant effluent from D. D. Lee's column tests in which IONSIV IE-911 was used. This supernatant was used in the column test in which technetium was removed by Reillex HPQ anion resin, which was previously described in Sect. 7.2. ABEC-5000 has been successfully used at PNNL to remove pertechnetate from Hanford tank supernatant.

### 8.3 STRONTIUM

In general, strontium removal is not as significant a problem as cesium removal, either at ORNL or Hanford. Significant amounts of strontium may be in particulate form and therefore removable by filtration. The presence of carbonate can significantly reduce the strontium solubility. On the other hand, complexing agents in the supernatant can increase strontium solubility and reduce removal by ion exchange. In fact, if the strontium concentration is much higher than expected from solubility considerations, organic complexes may be indicated.

In batch tests, Amberlite IRC-718, Duolite C-467, CST, sodium titanate, TiP-PAN, NaTiO-PAN, and TiHP microspheres were effective in removing strontium from MVST supernatant solutions. In addition to removing cesium, both CST and R-F resin have some capacity for strontium removal. However, in a column run using Amberlite IRC-718, it was difficult to elute the strontium from the resin, requiring 6 M HNO<sub>3</sub>. Generally, the inorganic sorbents were more effective than the resins for removing strontium from the supernatants. J. L. Collins has developed an engineered form of sodium titanate as microspheres that can be used in column processes.

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