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Hot Demonstration of Proposed Commercial Cesium Removal Technology

D. D. Lee
J. R. Travis
M. R. Gibson

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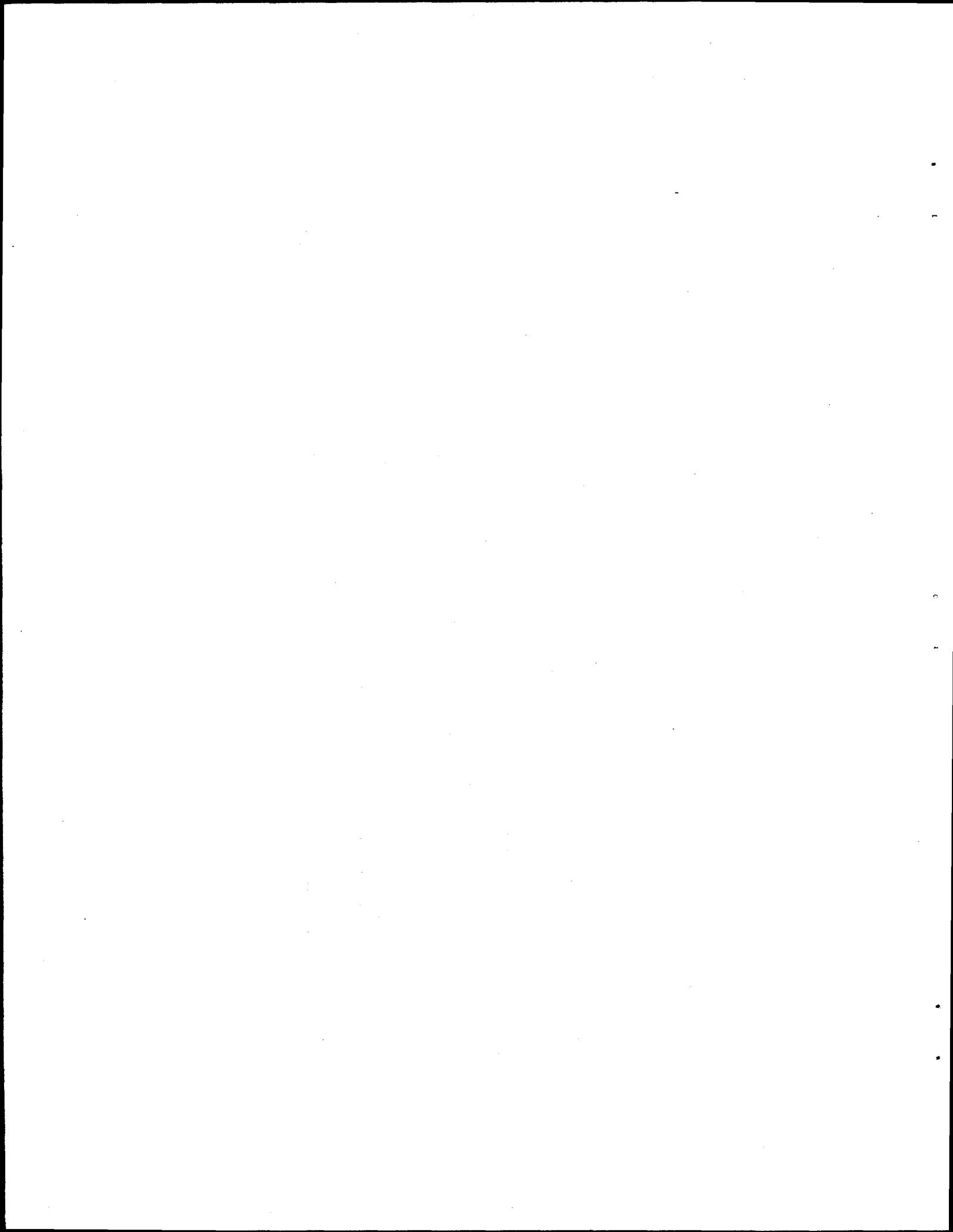
**HOT DEMONSTRATION OF PROPOSED COMMERCIAL
CESIUM REMOVAL TECHNOLOGY**

D. D. Lee, J. R. Travis, and M. R. Gibson

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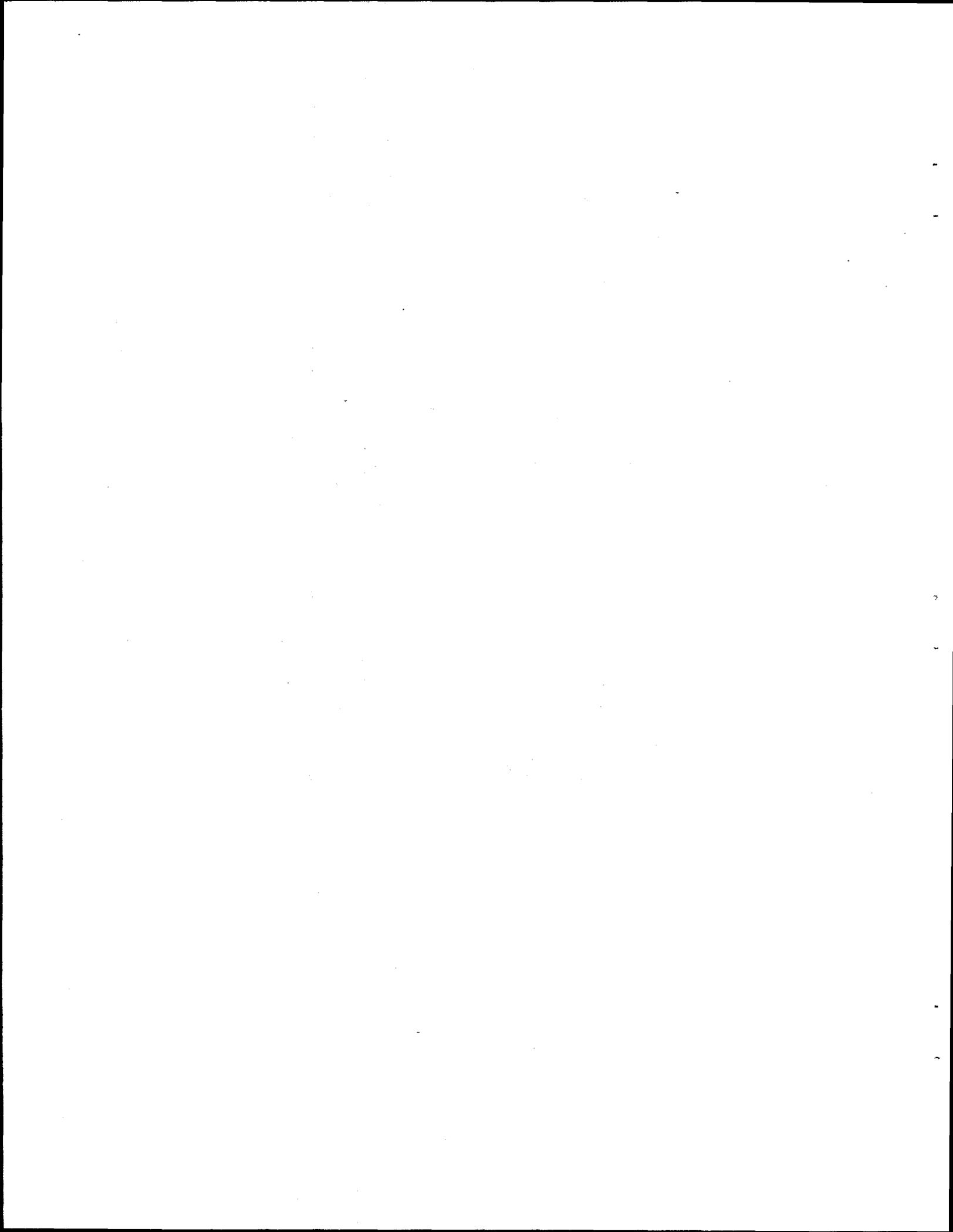
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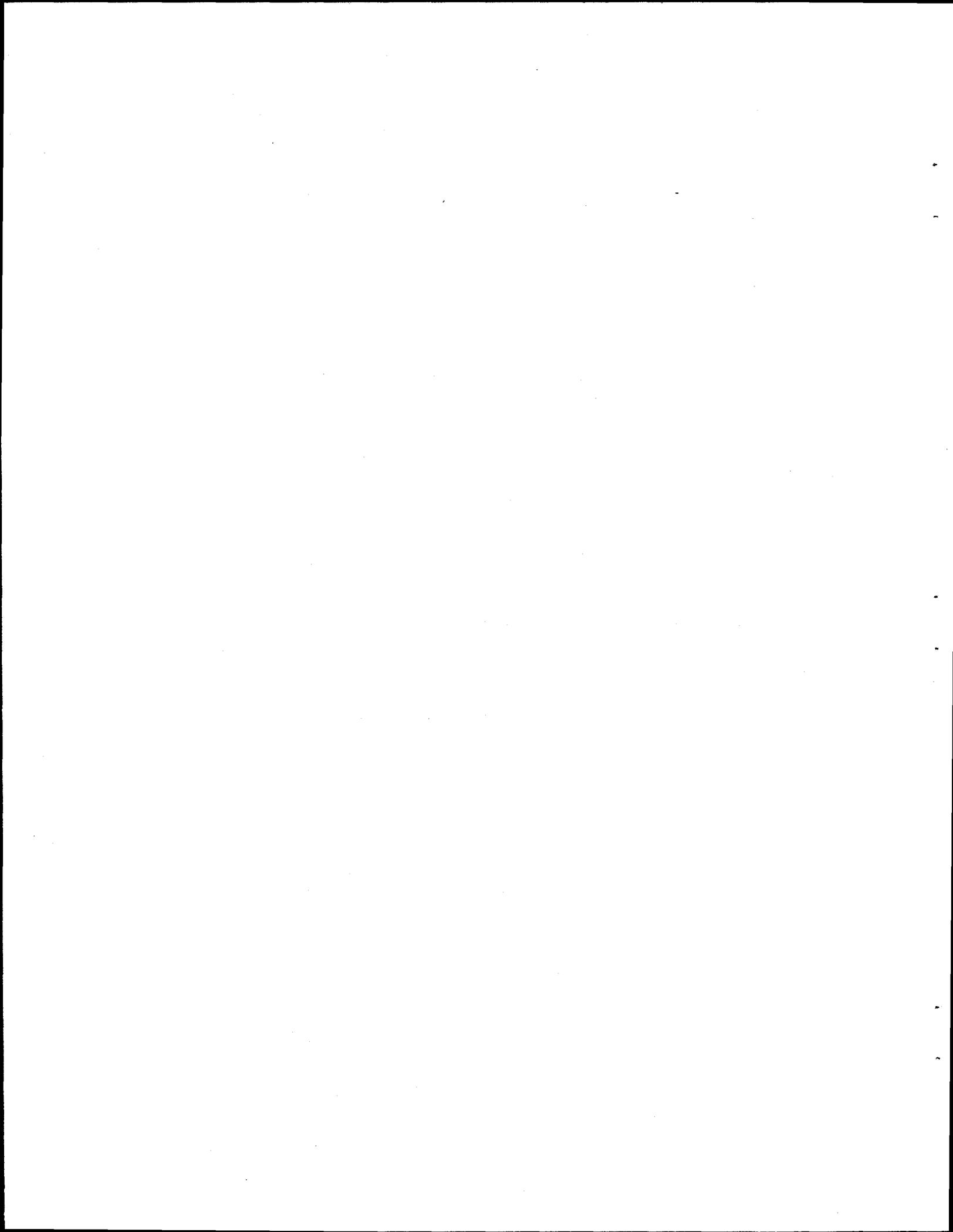


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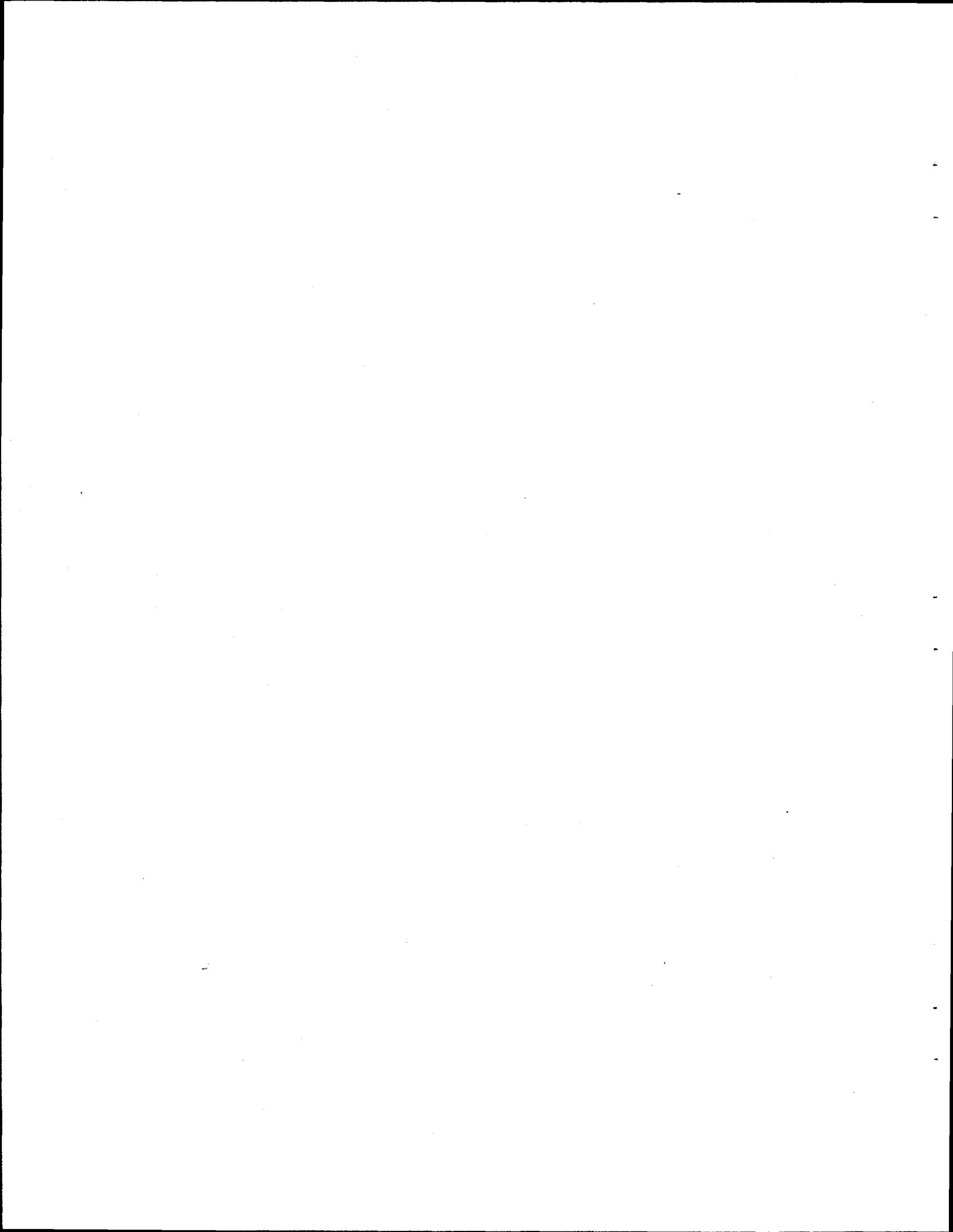
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HOT DEMONSTRATION OF PROPOSED COMMERCIAL CESIUM REMOVAL TECHNOLOGY

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ABSTRACT

This report describes the work done in support of the development of technology for the continuous removal and concentration of radioactive cesium in supernatant from Melton Valley Storage Tanks (MVSTs) at the ORNL site. The primary objective was to test candidate absorbers and ion exchangers under continuous-flow conditions using actual supernatant from the MVSTs. An experimental system contained in a hot-cell facility was constructed to test the materials in columns or modules using the same batch of supernatant to allow comparison on an equal basis.

Resorcinol/formaldehyde (RF) resin was evaluated at three flow rates with 50% breakthrough ranges of 35 to 50 column volumes (CV) and also through a series of five loading/elution/regeneration cycles. SuperLig[®] 644C resin had a 50% breakthrough at 100 CV at 6 CV/h and was evaluated through a complete loading/elution/regeneration cycle. A crystalline silicotitanate (CST) engineered form (IE-911 Lot 07398-38B) was tested at flow rates of 3 and 6 CV/h with 50% breakthrough at 350 and 335 CV, respectively. The 3M SLIG 644 WWL WEB with SuperLig[®] 644 embedded was operated through a complete loading/elution/regeneration cycle with loading at about 49 CV/h and 50% breakthrough at 65 CV. Eichrom KCoFeC sorbent was loaded at 9 CV/h but began to disintegrate after about 250 CV. CS-100 resin was loaded at 3 CV/h and reached 50% breakthrough at about 18 CV. Color bleeding and/or volume changes were observed upon preparation, loading, elution, and regeneration when using the RF, 3M WEB, CS-100, and SuperLig[®] 644 resins. Colored solids were observed in the effluent samples from the RF, 3M WEB, SuperLig[®] 644, and KCoFeC runs. Pumping and other flow problems were noted in the 3M WEB and KCoFeC, as well as in the multiple RF loading, runs.

The results reported here include the cesium loading breakthrough curves, elution curves (when applicable), and operational problems and observations for each material. The comparative evaluations should provide critical data for the selection of the sorbent for the ORNL Cesium Removal Demonstration project. These results will be used to help determine the design parameters for demonstration-scale systems. Such parameters include rates of cesium removal, quantity of resin or sorbent to be used, and elution and regeneration requirements, if applicable.

1. INTRODUCTION

The U.S. Department of Energy (DOE) is faced with remediating millions of gallons of high-level and low-level radioactive waste in underground storage tanks at various sites, including Oak Ridge, Hanford, Savannah River, and Idaho. A large portion of the waste exists as liquid solution (supernatant) that contains the soluble radionuclides, along with high concentrations of sodium and potassium salts. The radioactivity is derived primarily from cesium, strontium, and technetium. Typically, the radionuclides constitute only a small portion (less than 5%) of the waste. If these radioactive components could be removed and concentrated, the volume of waste to be disposed of or stored as HLW could be reduced by a factor of 20 to 100. The objectives of these experiments were to test and select sorbents and commercial cesium removal technologies for removing and concentrating the radioactive cesium, thereby reducing the volume of waste to be stored or disposed of.

The Tanks Focus Area (TFA) is sponsoring a Cesium Removal Demonstration (CsRD) project at ORNL to demonstrate a mobile cesium removal ion-exchange system to process up to 25,000 gal of ORNL liquid low-level waste in fiscal year 1996-97. The sorbents used for this demonstration are to be selected from state-of-the-art ion-exchange materials that are primarily being developed by the DOE Office of Environmental Management's (EM's) Efficient Separations and Processing (ESP) Cross-Cutting Program. The major goals of these experiments were to test and to help select sorbents for the CsRD, using a set of discriminators based on the performance of the sorbents in the hot-cell studies described below. These include applicability of the sorbents to the supernatant, sorbent capacity, sorbent kinetics, decontamination factor, and operability.

This report describes the development and operation of the experimental test unit that is located in Building 4501 (hot cell C) and the results using the sorbent materials evaluated. The experimental equipment has been operated to test radionuclide removal technologies under continuous-flow operation on actual ORNL Melton Valley Storage Tank (MVST) supernatant. The MVST supernatant, as adjusted using sodium hydroxide, contains lower quantities of total cesium and hydroxide but approximately the same amount of sodium as, and more potassium than, many of the Hanford tanks. The technologies evaluated are contained in modules, or columns, that can be

attached to the experimental flow system inside the hot cell and can be continuously fed the test supernatant until the ^{137}Cs exhausts the capacity of the module. Some of the ion-exchange materials were supplied under the other programs sponsored by TFA and ESP.

The tests reported here give direct comparisons of cesium removal operations conducted in the experimental system. A large batch of MVST supernatant was obtained so that all modules were evaluated using the same feed. Ion-exchange materials were tested at a scale that passes from 0.1 to 5 L of MVST supernatant at a prescribed flow rate continuously through the test module until the cesium "breaks through" to the desired end point. The progress was measured with an in-line gamma detector. Depending on the material being tested, this has required from 15 to more than 400 CV of supernatant to pass through the module.

The work described in the following sections was conducted on six different exchanger materials, or packages. These were resorcinol-formaldehyde (RF) resin, CS-100 resin, granular potassium cobalt hexacyanoferrate, SuperLig[®] 644, 3M WEB with SuperLig[®] 644 embedded, and an engineered form of crystalline silicotitanate. The last three materials were supplied through the ESP program.

2. EXPERIMENTAL APPARATUS

The experimental equipment for the cesium removal project in hot cell C of Building 4501, the procedures used during the experiment, and results of the initial experiments are described below. The equipment, shown in Fig. 1, consists of tanks, pumps, tubing and fittings, filters, instrumentation, and connections for testing radioactive ion-exchange materials in a continuous-flow system. A photograph of the system in operation inside the cell is shown in Fig. 2. The ion-exchange materials, which are contained in columns as loose resins or in modules supplied by vendors, have been examined for cesium removal only. The columns and modules can be installed and removed remotely. The system can also be serviced in a "hands-on" mode by personnel entering the cell in personal protective equipment. All experimental equipment can be operated remotely in the presence of the MVST supernatant, and more than 7 L of supernatant can be present in the cell at any time.

The module feed tank receives supernatant from the storage tank through a Gelman GWV high-capacity in-line 0.45- μm filter and can store up to 2 L of feed for a run. Two filters are installed

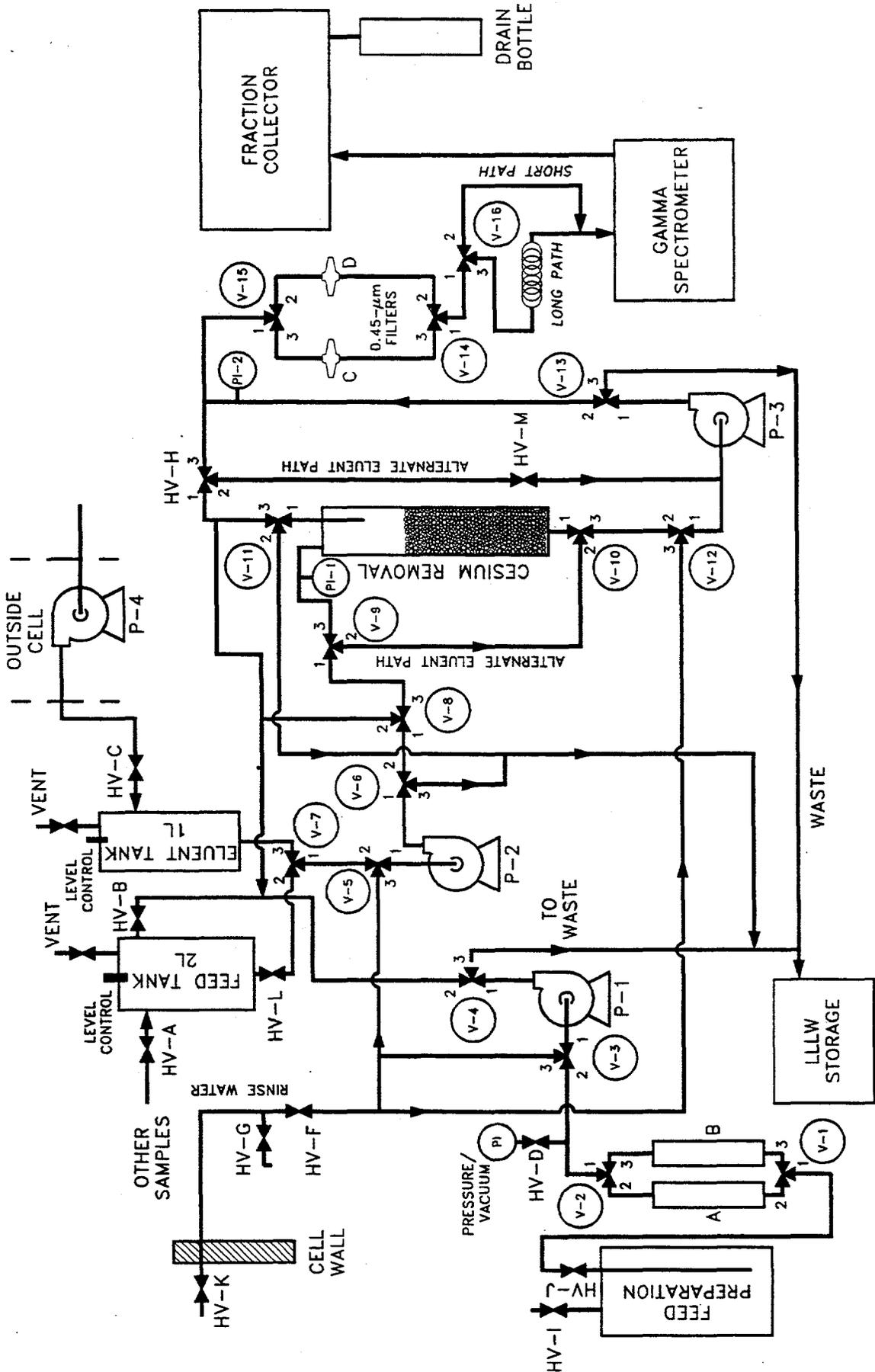


Fig. 1. Equipment diagram for cell system.

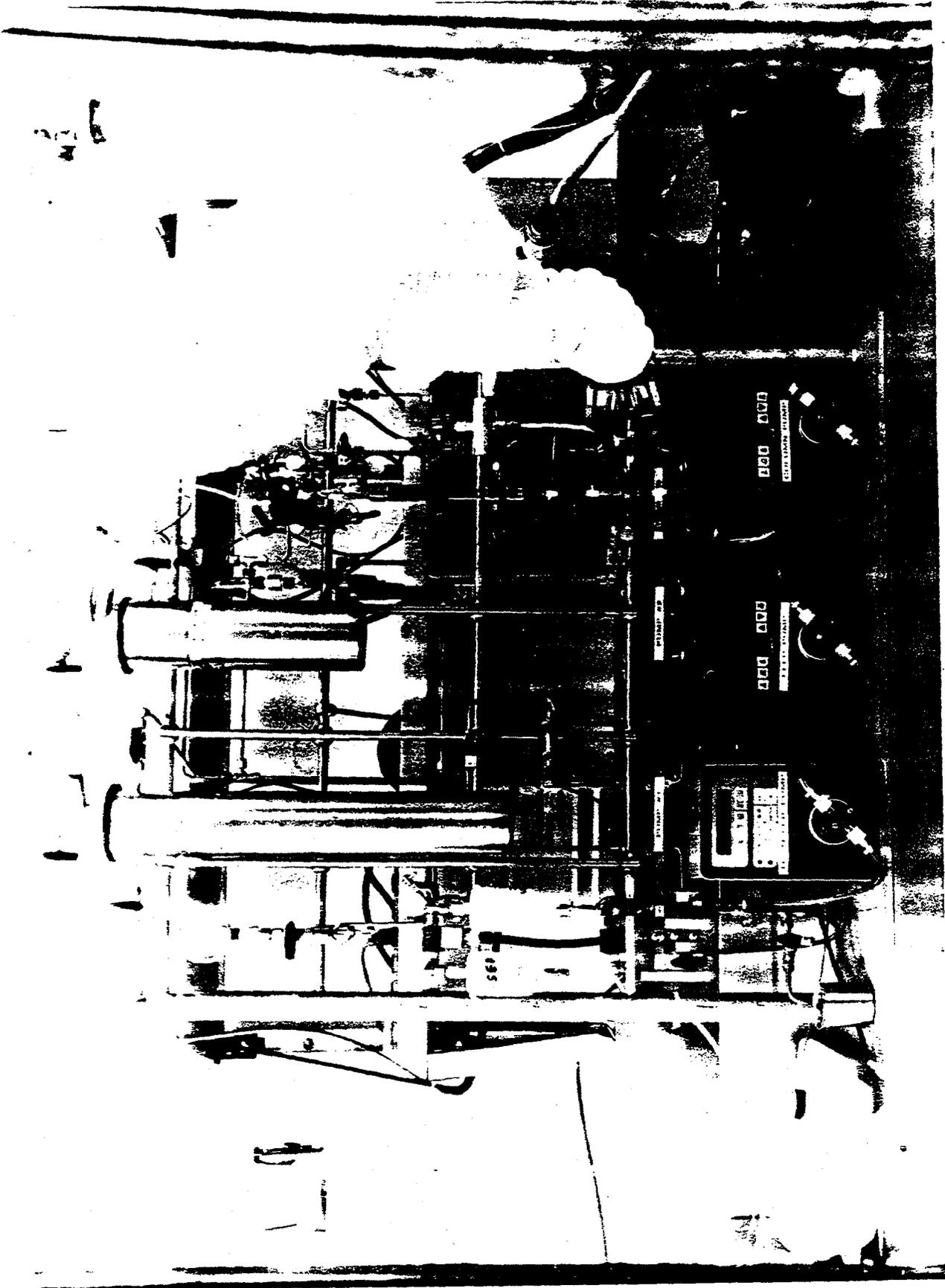


Fig. 2. Photograph of the cell C system in operation.

in parallel, and flow can be switched if one of them becomes clogged. The supernatant transfer pump will deliver feed at rates up to 70 mL/min, if needed. If more than 2 L of supernatant is required during a run, the feed tank can be replenished without the need to temporarily shut down feed to the column. Additional supplies of supernatant feed can be placed in the cell if the feed storage tank is emptied during the experiment.

Flow through the ion-exchange columns can be in either upflow or downflow directions, with loading in downflow and elution in either upflow or downflow. Flow rates can be varied over a 0.2- to 20-mL/min range for both loading and elution; higher or lower rates are also available using alternate pump heads. The liquid from the ion-exchange module passes through a 0.45- μm Gelman AquaPrep-V filter to trap particulates that may come from the module. The system contains two filters in parallel that can be switched if plugging occurs. Filtered effluent then travels to the gamma detector and fraction collector. The first two RF runs and the CS-100 runs used the Gelman GWV filters downstream of the column, but then the smaller AquaPrep-V filters were substituted. (The GWV filters have approximately 90 mL of total wetted volume, and the AquaPrep-V filters have 10 mL of wetted volume.) All pumps, valves, and transfer lines can be rinsed and emptied before and after a run to prevent cross-contamination between runs. Samples collected using the fraction collector are analyzed and can also be used for additional tests with other ion-exchange materials and other ions.

The system is operated continuously with on-line monitoring of the column effluent to detect cesium breakthroughs from the material in the module. The monitor is a sodium iodide detector in a lead-shielded container connected to a power supply, amplifier, and Nuclear Data multichannel analyzer system outside the cell. The module effluent passes by the detector head inside a 6.4-mm-OD by 4.8-mm-ID polyethylene tube that has 5 cm of tubing exposed to the detector head. Flow from the ion-exchange module passes through enough tubing, including the filter system, to ensure that at least 30 min has elapsed between liquid leaving the column and entering the gamma detector. That time allows any $^{137\text{m}}\text{Ba}$, the gamma-emitting decay product of ^{137}Cs , that is present in the feed to the column and in the column to decay [30 min is over 10 half-lives for the $^{137\text{m}}\text{Ba}$ (half-life, 2.5 min), so that only the cesium that passes through the column is detected by the gamma detector]. The detector configuration allows detection of levels of cesium of 10 to 20 counts above background. The feed level for the detector is about 7000 counts/s; thus, the detection limit is about

0.25% of the feed. The counts for the area of the peak for ^{137}Cs were monitored, and the total counts for the selected counting times were recorded by the multichannel analyzer program for later printout.

After being loaded, the column was removed from the experimental system and from the cell to measure the quantity of ^{137}Cs loaded. During repeated cycling of the RF resin, the column was removed and counted before and after each elution and then replaced for further testing. The columns were counted using an ApteC intrinsic germanium detector and a Nuclear Data multichannel analyzer system. This system allows the columns to be placed at distances up to several meters from the detector head for counting, which is necessary for materials that load a high level of cesium. The column product stream is collected in the fraction collector, and samples of these fractions are counted using an LKB Wallac 1282 Compugamma Universal Gamma Counter. The detection limit for this counter is about 0.1% of the feed concentration. Some of the fractions that contain solids, or are suspected to contain solids, can be sampled through 0.2- μm syringe filters.

Regenerable ion-exchange resins in the modules or columns can be treated with any desired eluent (usually 0.5 $N\text{HNO}_3$), regenerant (usually 2 $N\text{NaOH}$), or wash solution; and the effluent can be monitored for removal of cesium from the module using the in-line detector. Eluent is added to the 1-L eluent tank from outside the cell so that any number of chemicals can be added at a given time. The module can be eluted and regenerated in place to allow repeated cycling of the resin between cesium loading and removal; it can be removed for counting after loading and/or elution. Loaded modules can be drained, capped, and placed in storage containers for future testing, transport to other locations, or disposal.

The feed supernatant for the tests was obtained from MVST W-27 in April 1995. Approximately 56 L of the supernatant, enough for the first series of planned tests, was placed in storage vaults in Building 4501. Tank W-27 contains supernatant at pH 7.2 to 7.4 and has the lowest potassium and ^{137}Cs levels of the available tanks. Therefore, this supernatant can be more easily handled because of its lower gamma radiation level. For the cesium absorber tests, this supernatant was adjusted back to the pH levels in other tanks (about pH 12.5-13.0) by adding sodium hydroxide pellets. For tests to simulate conditions at other DOE sites, the pH may be increased to 14 or above; and additional cesium may also be added as cold cesium nitrate or chloride.

3. EXPERIMENTAL PROCEDURES

3.1 PREPARATION OF SUPERNATANT FOR TESTS

Use of the MVST W-27 supernatant received from ORNL Waste Operations in April 1995 required pH adjustment to be appropriate for the tests on the ion-exchange materials that are being considered for the alkaline supernatant tank wastes at ORNL and other DOE sites. The W-27 supernatant has a pH of 7.2, while the pH in the other MVST tanks varies from 10 to 13. To increase the pH, about 0.5 to 0.7 mol of solid NaOH must be added per liter of supernatant. Each container of supernatant contains approximately 2 gal, or 7.5 L, so that a total of 140 to 220 g of NaOH, or about 28 g/L, is required to complete adjustment to the higher pH. Adjusting the pH with NaOH adds 0.5 to 0.7 mol of sodium to the supernatant sodium concentration. The analyses of the W-27 supernatant sample taken in December 1994 (Request 941219-087) and of a sample of the supernatant feed to the ion-exchange column after the pH adjustment and filtration in cell C (Request 950619-053) are shown in Table 1.

The supernatant feed was prepared by adjusting the pH of the solution to 12.85, as measured by two different pH meters, using solid sodium hydroxide pellets to keep dilution to a minimum. Subsequent analysis of the first bottle of feed using titration to the phenolphthalein end point gave a pH of 12.94 instead of the pH meter reading of 12.85. The second and third bottles of feed were adjusted using the same procedure and the same amount of solid sodium hydroxide, but the end points occurred at pH 13.32 and 13.28, respectively, as measured by titrations. As the caustic was added to the yellow supernatant, a fine, slow-settling precipitate began to form. Settling for the two bottles with higher pH levels was slower than for the first bottle.

The supernatant sample obtained in December 1994 from W-27 was analyzed to contain about 3.3×10^5 Bq $^{137}\text{Cs}/\text{mL}$, 2.1×10^{-6} M total cesium, 0.29 M potassium, and 4.14 M sodium. Analyses of the present sample (obtained in April 1995) after pH adjustment, followed by settling and filtration, showed about 3.2×10^5 Bq $^{137}\text{Cs}/\text{mL}$, about 0.26 M potassium, and 4.7 M sodium. The total cesium content was also analyzed by taking a small sample of the supernatant and treating it with excess RF resin to remove all the cesium. The loaded resin was then eluted with 0.1 N HCl after rinsing with water to remove excess salts. The dilute acid solution was analyzed for ^{137}Cs and total cesium, and the ^{137}Cs quantity was used to calculate the concentration of total cesium in the supernatant.

Table 1. Analyses of the MVST W-27 supernatant

Analysis for MVST W-27.				pH adjusted to 12.85		W-27 at pH ~7.2			
Req. No. (950619-053)						Req. No. (941219-087)			
Na/Cs for 7/95 =		7.01E+05	Electrolyte			Na/Cs for 12/94 =		2.28E+06	
K/Cs for 7/95 =		3.74E+04	Balance			K/Cs for 12/94 =		4.11E+04	
Analysis	Jul-95	Jul-95	Anion	Cation	Dec-94	Dec-94	Electrolyte	Electrolyte	
	Bq/ml		Eq./L	Eq./L	Bq/ml		Balance	Balance	
⁶⁰ Co	6.80E+02				2.00E+03		Anion	Cation	
¹³⁷ Cs	3.20E+05				3.30E+05		Eq./L	Eq./L	
¹³⁴ Cs	1.40E+03				1.40E+03				
⁹⁰ Sr	6.50E+04								
	mg/L	mol/L			mg/L	mol/L			
As	8.90E-03				<0.25				
Se	<0.005				<0.5				
Br	288	0.0036	3.60E-03		343	0.0042927	4.29E-03		
Cl	3,180	0.090	8.97E-02		3,800	0.10718	1.07E-01		
F	<7.5				975				
NO ₃	322,000	5.194	5.19E+00		342,000	5.516	5.52E+00		
PO ₄	<30				<10				
SO ₄	1,540	0.016	3.21E-02		1,570	0.01634	3.27E-02		
OH		0.071	7.08E-02						
Hg	0.090	4.49E-07		8.97E-07	0.638				
Ag	0.055	5.10E-07		5.10E-07	<0.069				
Al	0.847	3.14E-05		9.42E-05	<0.32				
Ba	8.040	5.85E-05		1.17E-04	12.7				
Be	<0.0022				<0.003				
Ca	89.100	0.00222		4.45E-03	10,400	0.259481		5.19E-01	
Cd	0.220	1.96E-06		3.91E-06	0.311	7.759E-06		1.55E-05	
Co	<0.12				0.183				
Cr	2.960	5.69E-05		1.71E-04	1.03	2.57E-05		7.71E-05	
Cs ^a	0.935	7.04E-06		7.04E-06	0.28	1.82E-06		1.82E-06	
Cu	<0.0319				0.696	1.737E-05		3.47E-05	
Fe	<0.0352				<0.04				
K	10,300	2.63E-01		2.63E-01	11,500	2.94E-01		2.94E-01	
Mg	<298				1,090	0.0272		5.44E-02	
Mn	<0.055				0.294	7.335E-06		1.47E-05	
Na	113,000	4.935		4.93E+00	95,100	4.153		4.15E+00	
Ni	1.22	2.08E-05		4.16E-05	3.18	7.934E-05		1.59E-04	
Pb	0.009	4.44E-05		4.44E-05	<2.2				
Rb	1.1	1.29E-05		1.29E-05					
Sb	<0.218				<2.8				
Th	<0.440				11.9				
Tl	<0.005				<19				
U	<1.0				503				
V	<0.0561				<0.07				
Zn	0.473	7.23E-06		7.23E-06	1.9				
Totals			5.390	5.203148	Totals			5.660	5.021
Difference			0.187		Difference			0.639	

^aValue for the total cesium for the 7/95 sample was determined for the sample by removing all Cs and then eluting with acid, and then analyzing that sample.

The total cesium in the W-27 supernatant was then calculated to be about 2.7 times the amount expected, based on the ^{137}Cs detected. The total cesium was $7.04 \times 10^{-6} M$ instead of $2.06 \times 10^{-6} M$. The expected amount of total cesium is based on the total cesium fission products from ^{235}U , which include ^{133}Cs , ^{134}Cs , and ^{135}Cs in addition to the ^{137}Cs . Both the ^{133}Cs and the ^{135}Cs are produced at about 35%, and the ^{137}Cs is produced at about 30%, of the total fission product cesium. The ^{134}Cs is only about 0.3% but has about 12% of the total initial activity. Both ^{133}Cs and ^{135}Cs (half-life, 2.5×10^6 years) can be considered constant. The ^{134}Cs has a 2.3-year half-life, so it is almost gone in the MVST supernatants, some of which have cooled for 15 to 20 years. Therefore, an estimate of the total cesium can be taken as about three and one-third times the amount of ^{137}Cs present, based on the total decay time until measurement.¹ It should be noted that the ^{137}Cs level in MVST supernatants is one to two orders of magnitude less than that present in the Hanford tank supernatants.^{2,3} In order to evaluate the data in this report for application at other sites, this fact must be weighed accordingly. Future experiments will include additional cold cesium in the supernatant.

3.2 MODULE OR COLUMN PREPARATION

Columns (1.5-cm-ID x 15-cm-tall glass columns with polypropylene end fixtures) for ion-exchange resins are prepared for use by first attaching a dimensional tape to the outside surface of the column to allow the observation of the bed depth and liquid level from outside the cell. The resin to be used is treated in a preparation column by the resin-specific procedure recommended by the provider or manufacturer. The measured volume is then added to the column, and the depth of the bed is measured after removal of all air bubbles and settling. Air bubbles are removed by flowing liquid up through the bed to partially fluidize it and allow the air bubbles to rise and escape. A few bubbles may have to be removed by physically agitating the resin with a small stirring rod when the resin forms small clumps and does not easily fluidize with liquid.

The column or module is then installed into the cell system and connected to each of the three quick-connect fittings for the column inside the cell (feed, feed return/column vent, and column effluent). If the bed becomes unsettled or develops air bubbles during installation, it is resettled in place and any trapped air bubbles are removed by introducing liquid in the upflow mode and gently tapping the side of the column. If the bed will be returned to service after elution, the same steps are

completed each time. Finally, the liquid in the column is drained to about 0.5 to 1.0 cm above the bed level before the start of supernatant feeding to minimize dilution of the supernatant.

3.3 OPERATION OF THE CONTINUOUS SYSTEM

Once the feed tank is full and the module is in place, a run is started by preparing the various system components. The fraction collector is set to operate remotely for the desired sample volume or collection time and number of samples. The gamma counter used to monitor the cesium breakthrough from the module is started by initializing the multichannel analyzer program and checking the calibration for the cesium peak. Data for the prerun background count are collected, and the automatic data collection mode is initiated.

The module feed pump is started; and feed is pumped from the feed tank, through the pump, to the column entrance tube above the bed until a liquid level of about 3 to 5 cm above the resin is reached. When all systems have been checked, the column pump is set to the desired rate and turned on. Flow rates through the column are verified by timing the fall of the liquid level in the column through a distance of 2 cm, using the scale on the column. The level is increased by increasing the feed pump rate and then turning off the feed pump for the flow-rate check. If the flow is not at the desired rate, the column pump is adjusted accordingly. The flow rate is checked about once per hour during normal loading tests, and the pump is adjusted to maintain the desired flow rate, if necessary. If the sorbent loading is rapid and only a few column volumes are required, or the flow rate is high, the rate is checked more often. When the rate must be adjusted, it is rechecked immediately after adjustment. Occasionally, when the filter downstream of the pump becomes partially plugged and the pressure drop rises across the filter, the flow rate that the pump delivers can be reduced and is often more difficult to keep constant, so the rate must be checked more often. During most runs, the pump rate was stable for periods of several hours up to several days and did not need frequent adjustment.

The column pump removes liquid from the bottom of the column through the bed support membrane (pore size, 20 μm) and pumps it successively through a 0.45- μm filter and the gamma detector and then to the fraction collector. There is a 30- to 120-min holdup between the column and the detector, depending on the flow rate and whether the short or long path between the filter and

detector is used. The approximate volume of the short path is 35 mL, and the long path is about 90 mL (with the small filter). The course of the run is followed by the in-line sodium iodide detector in the cell. When the desired breakthrough of cesium has been detected, the column shutdown procedure is started. The remaining liquid in the system is pumped to the fraction collector, and then the module is rinsed with distilled/deionized (DI) water or other clean liquid. This liquid rinses the supernatant from the module and prepares it for either removal or elution/regeneration. Rinsing is continued until the cesium in the detector falls to near the initial background level. The module can then be removed from the system and taken to the gamma counter for ^{137}Cs determination. If the module contains regenerable sorbent, it can be returned to the cell and reinstalled in the system for elution, regeneration, and reloading.

The pH levels of some of the fractions are determined by titration with 0.1 N HCl to the phenolphthalein end point, followed by titration to the methyl orange end point to determine the presence of carbonate. The fractions collected during the run are weighed, and the specific gravity of each sample is determined by weighing a known volume of the fraction. The volume of each fraction is calculated, based on its mass and density. The fraction volume and the time for its collection give a check on the average flow rate for that fraction. Small samples are taken from each fraction (~0.5 mL in tared tubes) for gamma-counting of the ^{137}Cs . The results of the sample counts are then used to calibrate the cell cesium detector by correlating the sample counts obtained for each fraction to the cell detector output for the same fraction.

3.4 ION-EXCHANGE MATERIALS USED

In this study, the materials tested were recommended by the TFA and the ESP, based on previous batch tests at Hanford,^{4,5} Sandia,^{6,7} Los Alamos,⁸ Savannah River,⁹ and Oak Ridge^{10,11} that screened many sorbents. Those included for evaluation were the most promising. SuperLig[®] 644C, batch 3695-GM1121, is a polymer resin of the covalently bound SuperLig[®] macrocycle family of sequestering ligands from IBC Advanced Technologies (American Fork, Utah) and was supplied by Lane Bray of Pacific Northwest National Laboratory (PNNL). The resorcinol-formaldehyde (RF) resin developed at the Westinghouse Savannah River Company (WSRC) was made by Boulder Scientific (Mead, Colorado) and was supplied in the potassium form by Jane Bibler of WSRC. The

CS-100 resin, Lot 2-850001, a product of Rohm & Haas, was also supplied by Lane Bray at PNNL. The granular potassium cobalt hexacyanoferrate, Lot JW-40-021, was made and supplied by Eichrom. The 3M SLIG 644 WWL WEB with SuperLig® 644 embedded was supplied by the 3M New Products Department. The engineered form of the crystalline silicotitanate developed by Sandia National Laboratories/Texas A&M was produced and supplied by UOP as IONSIV® IE-911 07398-38B.

4. EXPERIMENTAL RESULTS

4.1 SUPERNATANT PREPARATION AND ANALYSIS

Oak Ridge MVST W-27 supernatant was used as the feed for each experimental run. Once the pH had been adjusted, the container was transferred to the Cell-C feed transfer area for pumping to the module feed tank. The bottles of supernatant were allowed to settle for up to 3 days to allow the calcium and magnesium compounds formed during pH adjustment to settle to the bottom before the solution was pumped to the column feed tank through the 0.45- μ m filter. The feed tank was filled at a flow rate of about 30 mL/min. A level probe in the tank shut off the pump approximately 5 cm from the top. Once the tank was filled, the lines were emptied back to the transfer container, the pump head was rinsed with DI water to prevent salt crystallization in the head, and water was left in the head. When the tank pumping was first started, some solids were observed in the transparent lines to the filters, but the lines were clear during most of the pumping time. The filter retained a slight yellow color, even after rinsing with water, due to the particulates trapped, but was not plugged to the flow of liquid. During subsequent feed tank fillings from the same bottle, the lines remained clear.

The solution in the feed tank after transfer and filtration was clean, slightly yellow, and completely transparent (the bottom of the stainless steel tank was easily visible from the top of the tank through 40 cm of supernatant) for most of the feed tank fills. The exceptions were during the filling from the bottle adjusted to pH 13.32 in which some gray-black, billowy solids formed in the feed tank during and after the CST1 experiment. The solids from the feed tank also passed to the column and formed a layer on the top of the CST bed but did not impact the column operation. Some

of the solids were found on the downstream filter and caused a partial plugging that was eliminated by changing filters. Some of the same solids were also present in a few of the CST sample fractions.

4.2 RF RESIN RUN 1

The first RF resin experiment used the standard 1.5-cm-ID x 15-cm ion-exchange column. The resin was prepared according to the procedures recommended by the developer. Some as-received dry resin was placed in a pretreatment column designed to provide a flow of liquid up through the bed. The resin was wet using water and then acidified from the as-received potassium form to the hydrogen form with 5 CV of 0.5 M HNO₃ and washed with DI water. It was converted from the hydrogen form to the sodium form using 10 CV of 2 M sodium hydroxide solution, and then washed with DI water and sampled. A 12.5-mL tapped volume portion was loaded into the test column for the experiment. The resin had a bulk, tapped dry weight of about 0.690 g/cm³. During the preparation, a dark, brown-colored solution (possibly resin degradation as seen in other studies)¹² passed from the column after the resin had stood in liquid and also after the liquid flowing through the column had changed from acid to base, for example. The volume of the resin changed significantly when base was added to replace acid (e.g., dry resin with a 2-cm bed depth expanded to 4.5 cm after treatment with caustic).

The column was installed in the cell system as described above. A flow rate of 1.25 mL/min was set on the column pump, and the flow rate was checked. The flow rate was chosen to give approximately six to seven column volumes per hour through the column (75 to 84 mL/h). The feed rate during the column loading operation was 1.4 mL/min, giving a rate of about 7 CV/h (7.3 CV/h based on an 11.5-cm³ column volume and 6.7 CV/h based on a 12.5-cm³ column volume.) The original 12.5 cm³ of resin shrank to 11.5 cm³ as supernatant started to flow through the bed and remained at that volume during the remainder of the run. The 11.5-cm³ volume was used for calculations. The results of the loading test showed that 50% breakthrough of the cesium occurred after about 45 CV had been processed through the column. The run was terminated when that point had been reached.

Samples of the prepared resin that were not used in the column were subjected to batch tests using the filtered W-27 feed from the cell feed tank (obtained by pumping directly from the column feed line to a sample bottle) to compare the RF resin used here with other supernatants and RF resins previously batch tested. The tests included RF resin (both as-received and pretreated) from a separate batch used by J. L. Collins (Chemical Technology Division, Oak Ridge National Laboratory) in his experiments. The batch-test results, presented in Table 2, show good agreement between the resin used in the current column tests and the batch of as-received and pretreated RF resins obtained from Collins. Data obtained with the RF resin on W-25 feed show that the D values (D is the distribution ratio of the test species between the sorbent and the test solution after a specified mixing time expressed in volume of supernatant per mass of sorbent) for the W-27 supernatant were about 60% of those for the W-25 feed. The 15-min D values (65 giving a lambda of 17) for the W-27 give a good approximation of what should be obtained in the column under the 7-CV/h conditions, which include a residence time of 8.6 min; however, the D values for 2 h (approximately 200 for a lambda of 56) give a better correlation.

The data from the in-cell flow test were plotted by graphing the value of C/C_0 (column effluent/column feed concentration of the ^{137}Cs as determined by the gamma counting) vs the feed through the column in column volumes. The size of a column volume was taken to be the volume of the resin during most of the run. A plot of the data with the C/C_0 on a probability scale and the column volumes on a log scale is shown in Fig. 3. About 45 CV were required to achieve 50% breakthrough. Based on the analysis of the feed, the fractions collected, and the loaded column, approximately 0.5 L of feed containing 4.42 mCi of ^{137}Cs was fed to the column. Further analyses by titration of the feed and two of the collected fractions showed that the pH of the feed was actually about 12.94. The pH of the first sample from the column was neutral, while that of the sample from the end of the run was 12.96. The neutral pH at the start results from the water in the column used to rinse and prepare the resin at the start of the run. Once the column was loaded and rinsed, it was successively removed from the system and from the cell so it could be counted to determine the ^{137}Cs retained. The column contained 3.2 mCi after loading, based on that count, while the collected samples of the column effluent contained about 1.1 mCi.

Table 2. Batch-test comparison of various RF resins with W-27 feed

Resin	Mass used (g, dry)	Volume of liquid (mL)	Contact time	Removal (%)	D
Column resin batch	0.0501	10.2047 W-27	15 min	23.7	63
	0.0501	9.5959 W-27	15 min	26.0	67
Column resin batch	0.0504	9.6778 W-27	2 h	50.2	193
	0.0491	9.4204 W-27	2 h	53.1	218
Column resin batch	0.0504	9.6069 W-27	24 h	68.8	420
	0.0502	9.3642 W-27	24 h	66.3	366
Other RF/no pretreatment	0.0502	10.0123 W-27	15 min	18.0	44
Other RF/no pretreatment	0.0495	9.9699 W-27	2 h	63.2	346
Other RF/no pretreatment	0.0500	9.9825 W-27	24 h	64.0	354
Other RF on W-25 ^a	0.05	5.0 W-25	24 h	87.3	560

^aFrom J. L. Collins et al., ORNL/TM-12938, April 1995 (see Sect. 7 for complete citation).

4.3 RF RESIN RUN 2

A second experiment was completed using RF resin in which the feed rate through the bed was reduced to about 2.8 to 3.0 CV/h. For this run, 13.9 g of resin (tapped volume, 19 cm³) was treated with 10 CV of 0.5 M HNO₃, followed by 7 CV of DI water. During this treatment, the bed expanded from 19 cm³ to 23 cm³. The bed was then treated with 2 M NaOH for 10 CV at the expanded volume of resin and rinsed with DI water for 3 CV. The resin expanded from 23 cm³ to 50 cm³ during caustic treatment. Approximately 12.5 cm³ of the resin was placed in the 1.5-cm-ID test column and had a bed height of 7.45 cm. The bed volume expansion factor from as-received dry form to wet sodium form was 2.6.

The column was installed as described above. Supernatant feed was started through the bed at 2.6 CV/h. Once feed was started through the bed, the effluent became a brown color that lasted for

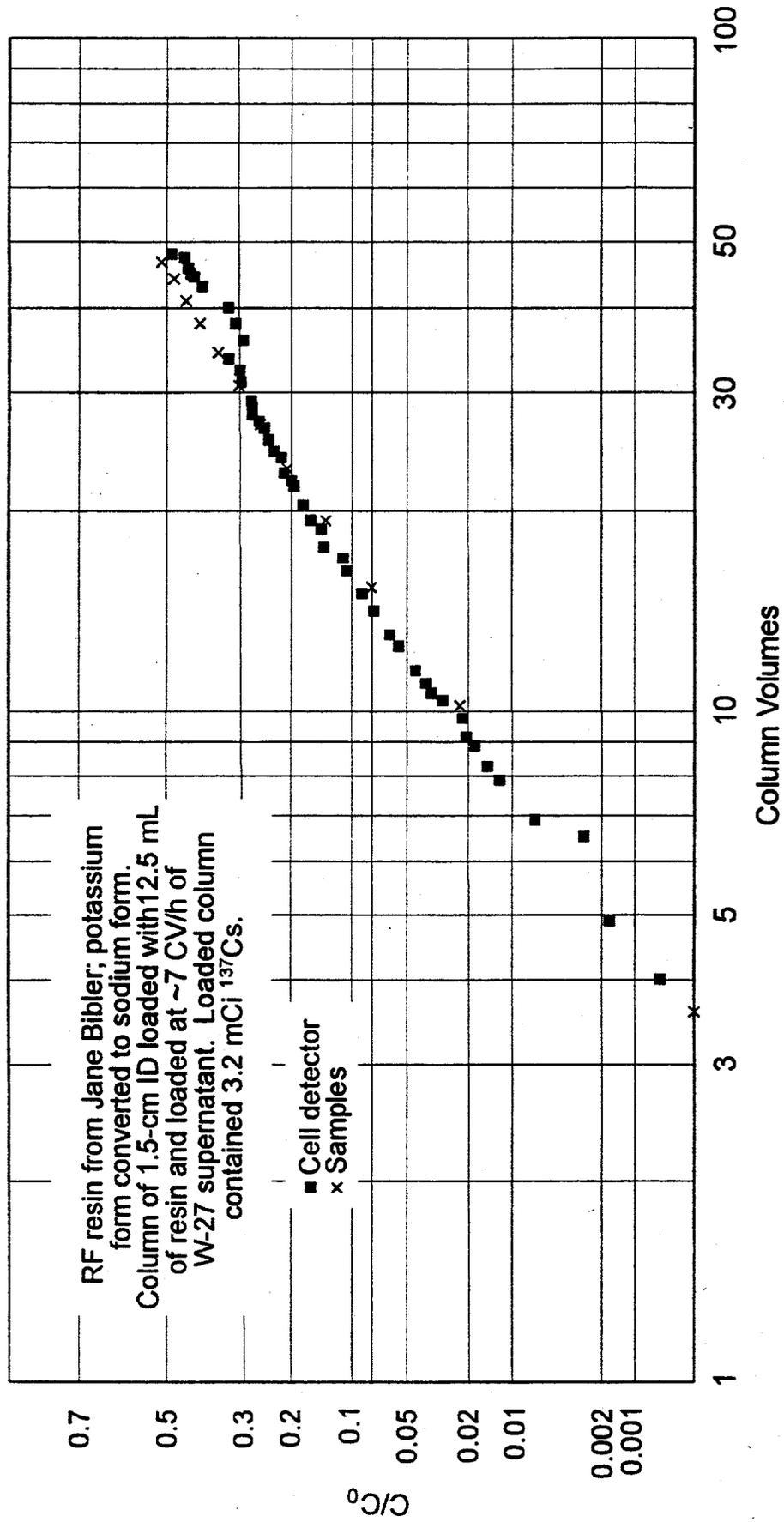


Fig. 3. Loading cycle for the first test of RF resin at 7 CV/h.

2 to 3 CV; the dark color could be seen as it passed through the tubing and filter. During the first 4 CV of feed through the bed, the bed volume decreased from 12.5 cm³ to about 10.55 cm³. The latter value was used for the CV-per-hour rate calculations, which resulted in a feed rate of about 2.9 to 3.0 CV/h. After about 25 CV had been fed, the bed volume had decreased to 10.2 cm³. The final bed volume on completion of the run was 9.9 cm³.

Operation of this experiment was similar to that of the first RF run, except that the flow rate was much slower. This resulted in about a 4-h lag between the time at which the liquid exited the column and the point at which it reached the fraction collector. Again, the behavior of the system was followed using the in-cell detector, and the experiment was terminated at about 50% breakthrough. The results are shown in Fig. 4. The 50% breakthrough occurred at about 36 CV, for both the cell detector and for the samples taken during the run; the shape of the curve was similar to, but steeper than, that in the first RF run. This would be expected for kinetic control of the reaction, but the column volumes to 50% breakthrough were about 25% lower. The reason for the lower value is not known. The effluent sample from the start of the run had a neutral pH, while the pH at the end of the run was approximately that of the feed, 12.98.

4.4 RF RESIN RUN 3 (LOAD-AND-ELUTE MULTIPLE CYCLES)

A third experiment was conducted with RF resin in which the feed rate through the bed was set at about 6.0 CV/h. In each experiment, the column was loaded, eluted, regenerated, and then rinsed — for five cycles. Approximately 10.5 cm³ of RF resin from the second of the two bags of RF resin sent by Jane Bibler and pretreated as described above was placed in the 1.5-cm-ID test column to give a bed height of 6.2 cm. The batch (pH, 12.94) of prepared supernatant used for this test was the same as that used for the first two RF tests.

Supernatant feed was started through the bed at 6 CV/h. Once feed had started to flow through the bed, brown-colored liquid was seen exiting from the bed, and could also be seen going through the tubing and filter. During the first 4 CV of feed through the bed, the bed volume decreased from 10.2 cm³ (the original) to about 9.3 cm³. The value of 9.3 cm³ was used for the CV-per-h rate calculations for the first loading. For each succeeding run, the column volume used for the flow-rate calculations was determined after the initial few column volumes of feed had passed through the bed.

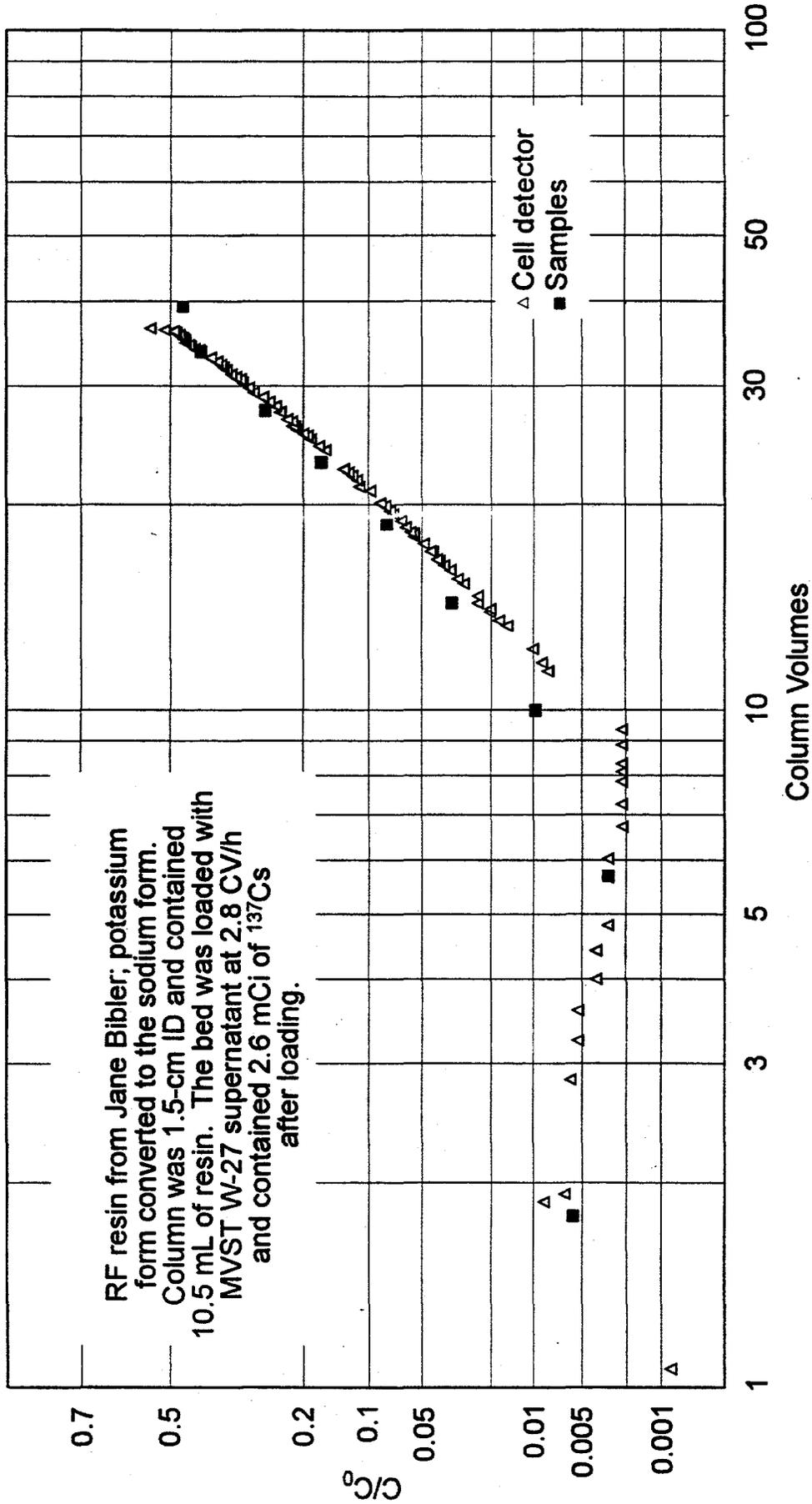


Fig. 4. Loading cycle for the second test of RF resin at 3 CV/h.

Each run was continued until the apparent cesium breakthrough using the cell detector was about 55%, based on the previous calibration.

After the column had been loaded, it was rinsed with DI water and removed from the system. The ends were clamped, and the column was removed from the cell and counted to determine the ^{137}Cs loading on the column. Each of the five loading cycles was completed in the same way, and the column was counted after each cycle. Following each counting, the column was replaced in the cell and eluted with 0.5 M HNO_3 at about 3 CV/h. The first elution was conducted in upward flow through the column, while the last four were conducted in downflow. Samples of the eluent were collected in the fraction collector for later analyses. Progress of the elution was followed during the run using the in-cell gamma detector, and completion was determined as the time that the count rate returned to slightly above background level.

When elution was complete, the column was again rinsed with DI water and removed from the system and cell for gamma counting. Comparison of the counts of the column before and after elution gave an indication of the efficiency of the elution. After being counted, the column was reinstalled and then prepared for regeneration with 2M NaOH. Regeneration was carried out for about 4 to 5 CV; then the column was prepared for the next loading cycle.

Loading of the column was similar to the first RF experiment at 7 CV/h. The behavior of the system was followed using the in-cell detector, with the loading being terminated when the apparent 50% breakthrough occurred. The results are shown in Fig. 5 for the first loading cycle. The five loading-cycle curves are shown in Fig. 6. A plot of the fraction collector sample analyses for the five loadings is shown in Fig. 7; the projection for 50% breakthrough is calculated to be 50 CV. It was determined later, from the analyses of the fractions collected during the five loadings and elutions, that the geometry of the detector had changed since the previous calibration. The 50% loading level indicated by the cell detector was actually only about 35% loading, so the percent breakthroughs for this series were only about 35 to 40% instead of the more than 50% originally planned. The 50% breakthroughs were determined by projecting the data up to that point and were found to occur at about 45 to 50 CV. This compares favorably with the first RF experiment, and the shape of the curve was almost identical to that of the first RF run. As in the previous two RF runs, a significant amount of color was seen in the column effluent at the start of each loading cycle for the first 2 to 4 CV. The

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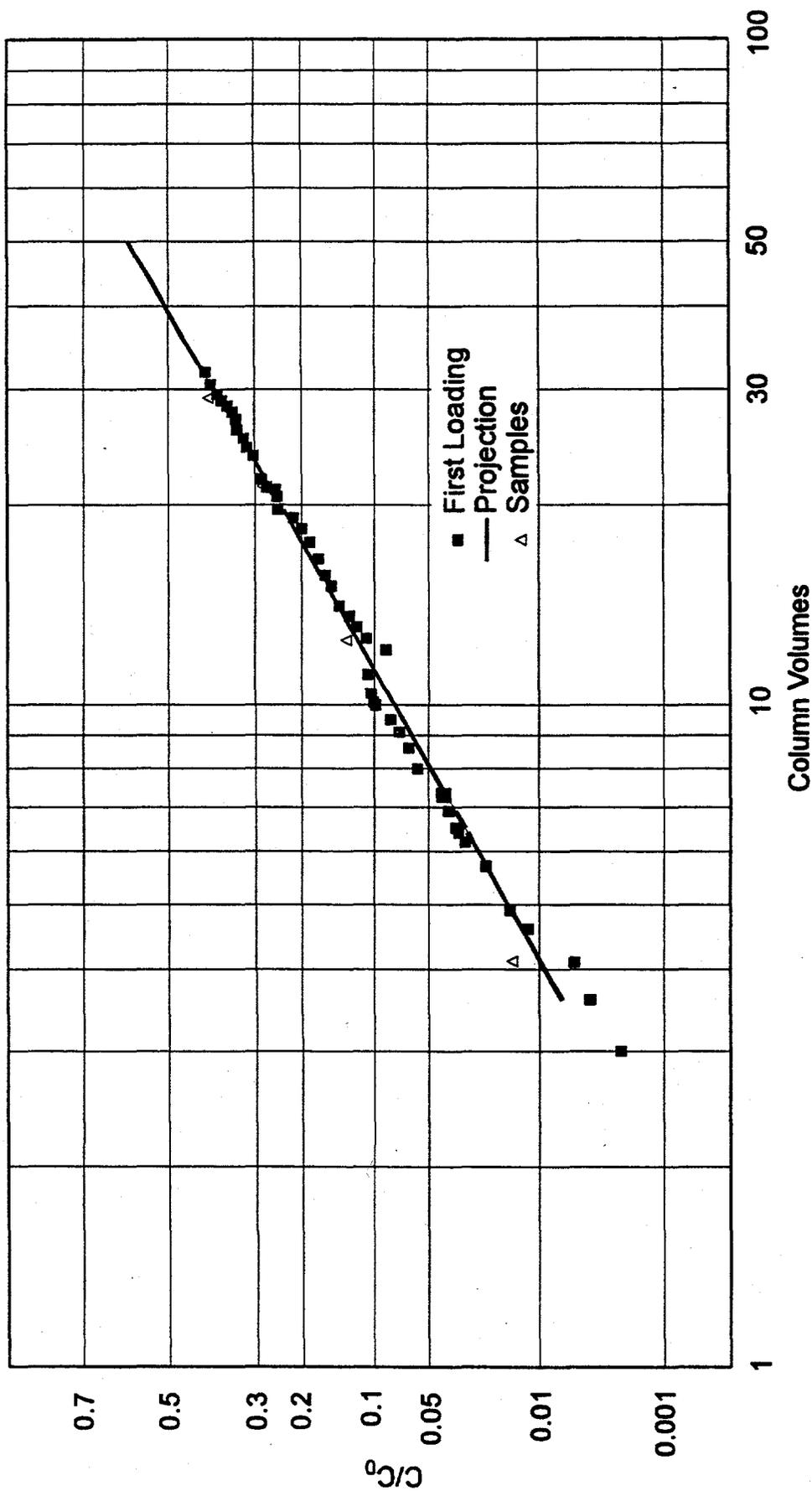


Fig. 5. Loading curve for the first loading cycle for RF resin at 6 CV/h.

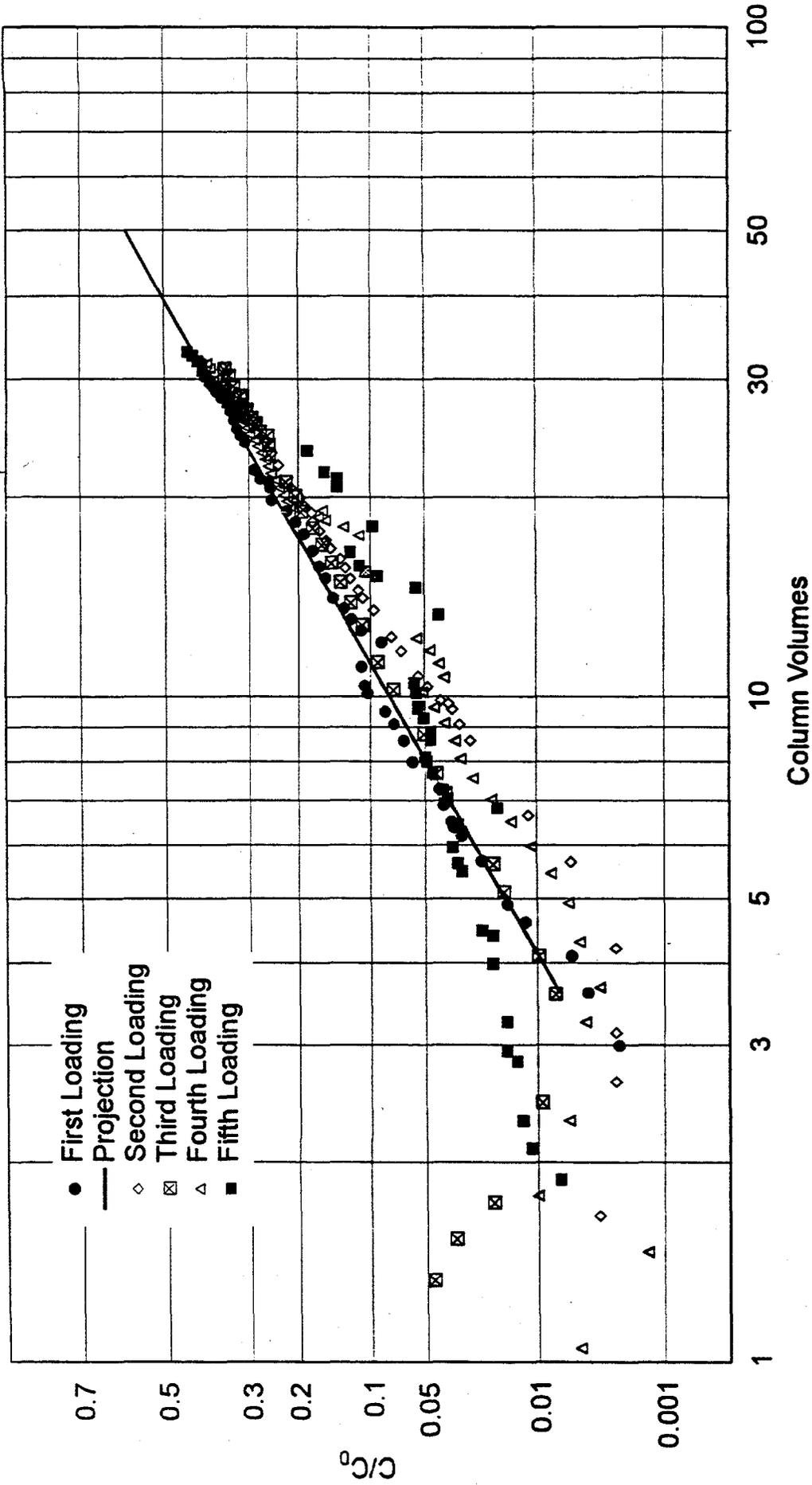


Fig. 6. Loading curves for the five loading cycles for RF resin at 6 CV/h.

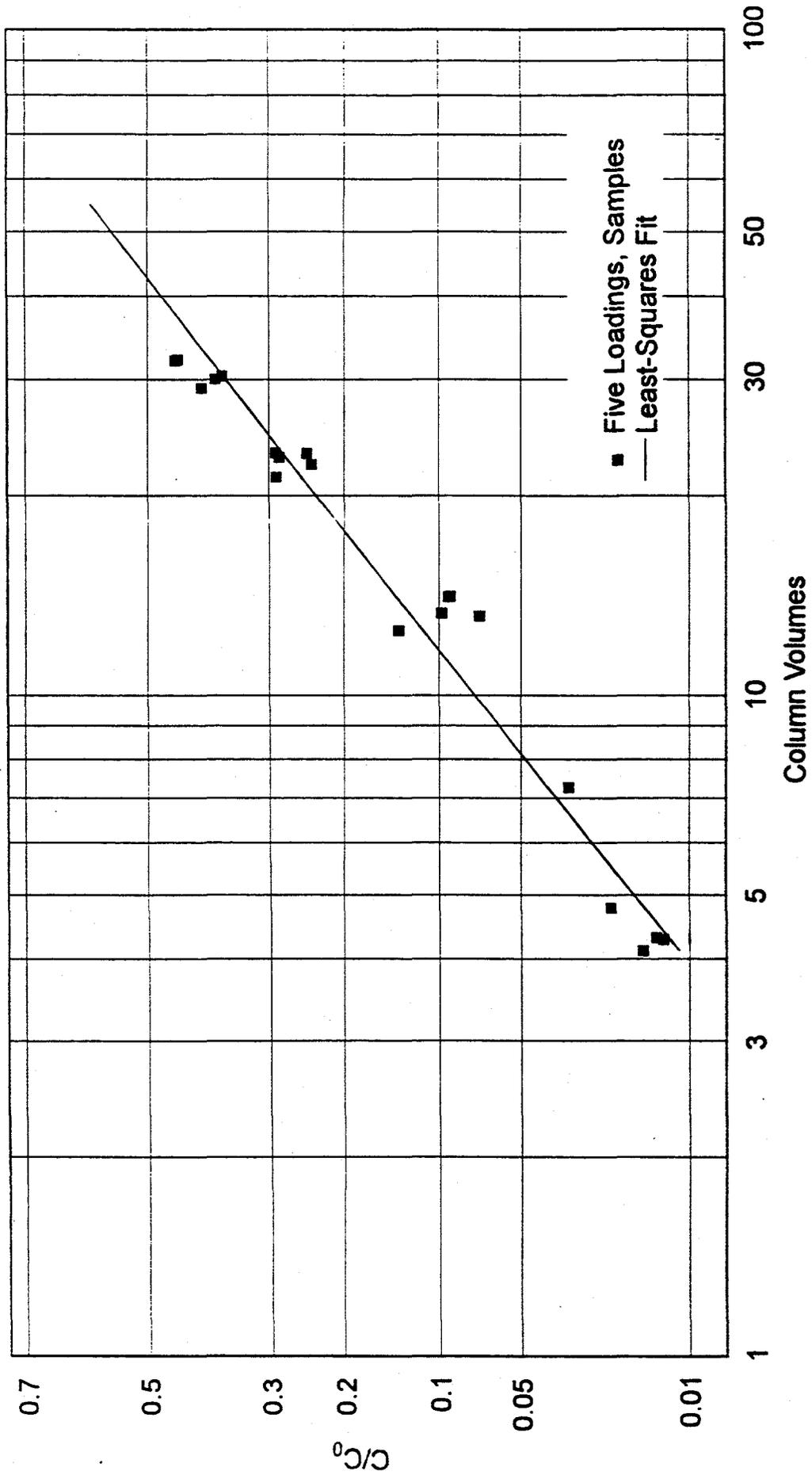


Fig. 7. Loading curves for the five loading cycles, using the sample analyses projected to 50% breakthrough.

amount of color gradually lessened over the course of the five loadings. Also, as in the previous RF runs, the pH of the feed was 12.95 and the pH of the column effluent was 12.95.

The first elution of the resin was conducted in an upflow mode, while the final four elutions were conducted in downflow, as in the loading cycle. During elution, the resin volume shrank from about 10 cm³ to about 5.5 cm³. The elution volumes were determined, using the original column volume of the sodium form for each run, and not the final acid-form volume, as the basis. The results using the in-cell detector showed that approximately 3-CV were required for the cesium to begin to appear at the bottom of the column, and cesium removal was essentially complete at 9 CV. The results for the second through the fifth elutions are shown in Fig. 8. The peak of the cesium level in the eluent was about five times the level in the feed. The elution using the upflow mode was difficult because of the large headspace (about 3 to 4 CV of the acid form of the resin) in the column and the mixing that occurred there. Downflow elutions were straightforward and resulted in good peaks through the detector. Samples of the elutions were normally split into three to four fractions, but the fourth elution was divided into ten fractions to check the samples and the cell detector against each other.

The resin regenerations were conducted in the upflow mode and continued for about five column volumes, during which the bed expanded to about 6 cm³ again. A color band was observed to form and rise through the column and above the bed during regeneration at about the rate that the bed was expanding. The colored band was about 2 cm³ in volume and maintained coherence through the tubing and into the collection bottle. After standing in the collection bottle, it formed a wispy precipitate that was reddish-brown. The size of the band tended to decrease with successive regenerations.

During the series of loadings and elutions, problems with equipment operation increased. The first three cycles were relatively trouble free, except for the change in the volume of the resin during the loading cycle and from one cycle to the next. The loading level of the bed, which was originally 6.2 cm, shrank to 5.7 cm during the first loading. The second cycle started at 6.1 cm and shrank to 5.8 cm; the third cycle started at 5.9 cm and shrank to 5.5 cm; the fourth was 6.3 cm at the start and shrank to 5.3 cm during the loading; and the fifth loading began at 5.9 cm and ended at 5.4 cm. During the elutions, the bed shrank to 3.2 cm after the first, to 2.9 cm after the third, and 3.1 cm after the fourth and fifth.

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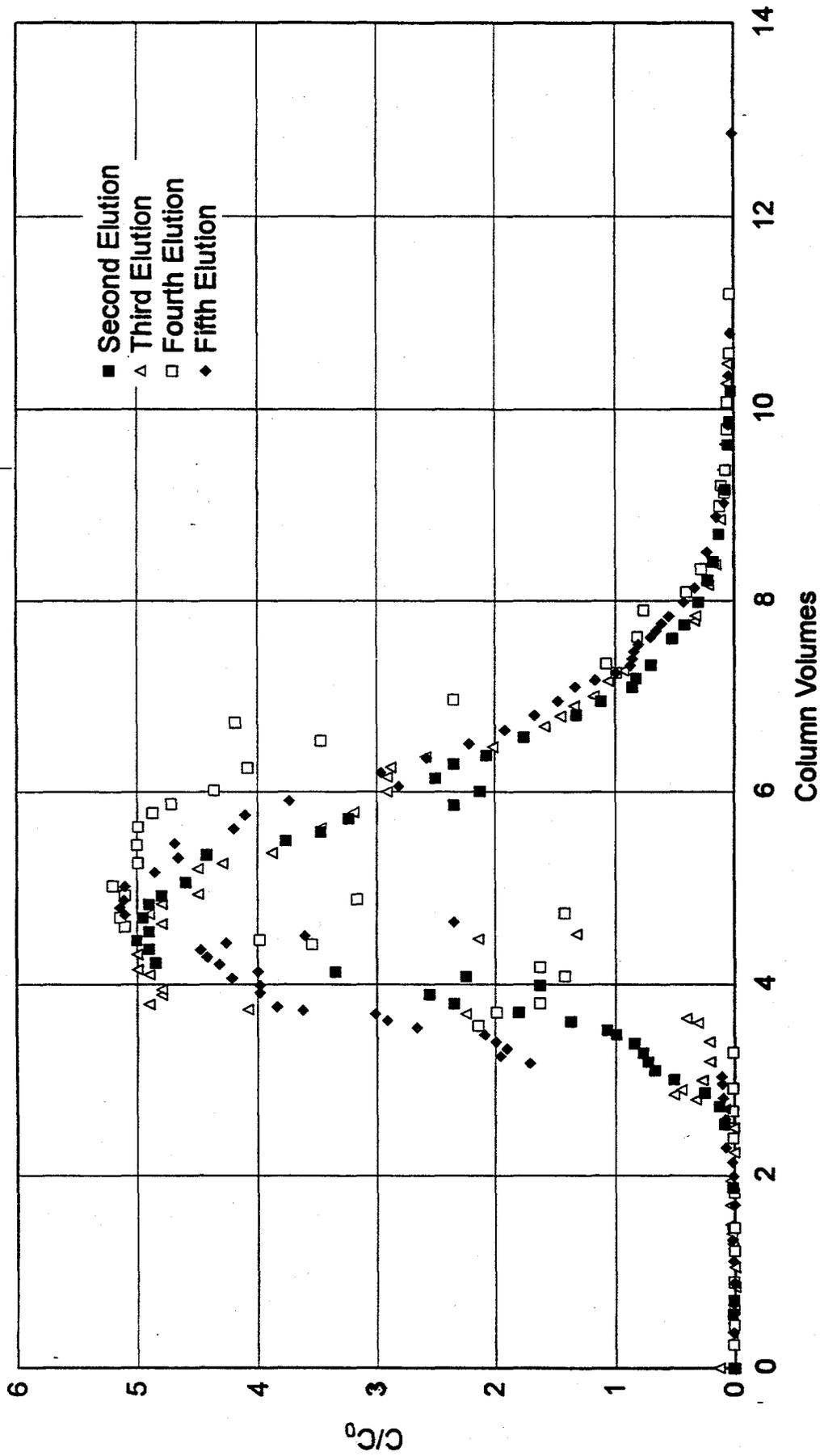


Fig. 8. Elution curves for the RF resin for the second through the fifth elutions. Elution volumes are based on the original column volume of the sodium form for each run.

Other problems included increasing difficulties with formation of a coating on the inside of the lines, which caused air bubbles to stick to the lines instead of moving through the tubes. This was particularly troublesome in the detector and in the inlet to the column. Also, some of the reddish material was found in the first samples of loadings 2 and 4, and black solids were present in the first elution sample from the fourth elution cycle. The column inlet formed a pathway for the liquid that went from the inlet to the vent and, instead of falling to the liquid level in the column, would flow up the vent line. The air bubbles in the system caused problems in the detector, which then gave much lower readings than expected. Normally, the bubbles could be easily removed by tapping the tube or tilting it slightly; however, after the third cycle, they were almost impossible to remove.

The results of the column elution efficiencies are shown in Table 3. This table shows the volume of supernatant fed, the quantity of ^{137}Cs fed, the ^{137}Cs in the fractions collected, the ^{137}Cs loaded on the column, and the ^{137}Cs remaining on the column after elution. The elutions removed an average of more than 99% of the cesium from the column.

Table 3. Results of RF column loadings and elutions

Loading	Supernatant fed (mL)	Cs in feed (μCi)	Cs collected in effluent ^a (μCi)	Cs loaded ^b (μCi)	Cs remaining ^b (μCi)	Removal (%)	Cs accounted for (% fed)
1	330.6	3095	735	2174	9.1	99.6	94.0
2	325.3	3045	575	2251	8.3	99.6	92.8
3	332.3	3111	662	2263	8.4	99.6	94.0
4	318.3	2980	662	2124	7.1	99.7	93.5
5	324.4	3028	681	2205	7.1	99.7	95.3
AVG	326.2	3052	663	2203	8.0	99.6	93.9

^aCalculated based on the sample analyses of the fractions collected.

^bCalculated based on counting of the column before and after elution.

4.5 CS-100 RESIN RUN 1

The second resin used in the continuous-column experiments was CS-100 (obtained from Lane Bray), Lot 2-850001, manufactured by Rohm & Haas. The resin was prepared by first taking a portion from the bag and then measuring the tapped density by placing about 30 cm³ into a graduated

cylinder and tapping until no change was observed. The resin density was 0.56 g/cm^3 (16.92 g for 30 cm^3 of dry, as-received resin). The resin was placed in a 2.5-cm-diam column and hydrated with 2 M NaOH (3 CV) followed by 6 CV of DI water. The wet resin (after removal of excess surface water) weighed 23.125 g . Before treatment, the resin was caramel brown and hygroscopic. After caustic treatment and wash, it was black and appeared like charcoal. Approximately 13.2 cm^3 (13.8 cm^3 settled in the column) of the treated resin was placed in a 1.5-cm-ID glass column (8-cm bed height) and prepared for operation by installing in the cell, removing air bubbles, and checking the flow.

Resin loading was conducted as described above. The feed rate through the column was set at $0.7 \text{ cm}^3/\text{min}$, or about 2.9 to 3.0 bed volumes per hour, and was constant throughout the run. Flow was continued until the in-cell detector showed that more than 60% breakthrough had been achieved. The samples taken and the cell detector results showed that about 17 CV were required to achieve 50% breakthrough of the cesium, and that the run had continued to over 80% breakthrough. A plot of the results is shown in Fig. 9. The column was then rinsed with water and the liquid allowed to drain. Samples from the collected fractions were counted for ^{137}Cs . During operation, the column bed height remained essentially constant and no change in color or appearance was seen. The pH for each sample taken during the run showed that the first sample, as expected when starting with the column rinsed with DI water, had a neutral pH; however, the pH of the later samples was 12.98.

4.6 SUPERLIG® 644C RUN 1

A column loading experiment using SuperLig® 644C from batch 3695-GM1121 was started by pretreating 9.66 g (13.5 mL tapped) of as-received, dry resin in a 1.5-cm-ID column. The resin was prepared by soaking in 0.1 N NaOH . During the soaking, it swelled by well over 100% as compared with the dry volume. A 13.5-mL sample of the swelled resin was placed in the $1.5 \times 15 \text{ cm}$ column and settled. The level in the column was 8.5 cm in 0.1 N NaOH . The column was installed as in previous runs, and the supernatant from the same batch used in the RF and CS-100 runs was fed to the column. The column pump was started at 2.5 to 3 CV/h to pass the supernatant through the bed. The run continued for about 65 CV at a rate of about 2.3 CV/h and resulted in a loading equivalent to about 9 to 10% breakthrough. Samples taken from the fraction collector

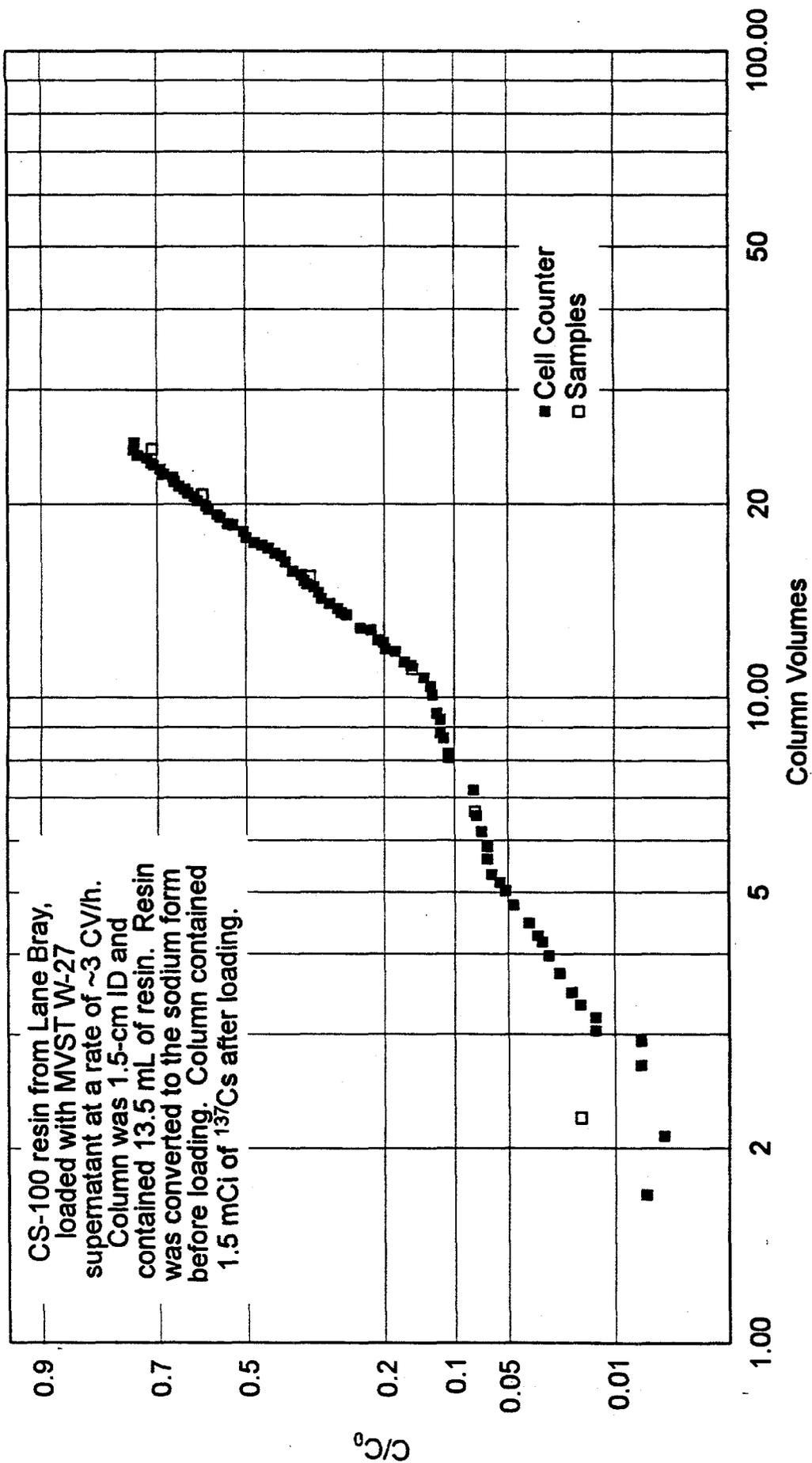


Fig. 9. Loading curve for the CS-100 resin at 3 CV/h.

showed almost immediate breakthrough at the 2 to 3% level, but the rate of increase was very slow. The in-cell detector had an apparent bubble in the line and did not register the correct amount of cesium. The loading was much slower than anticipated, based on limited batch data, and the run was terminated sooner than desired due to lack of appropriate supplies. The samples from the fraction collector showed no problems with solids in any of the samples. The pH levels of the samples by titration were 12.96 to 12.98 for the run.

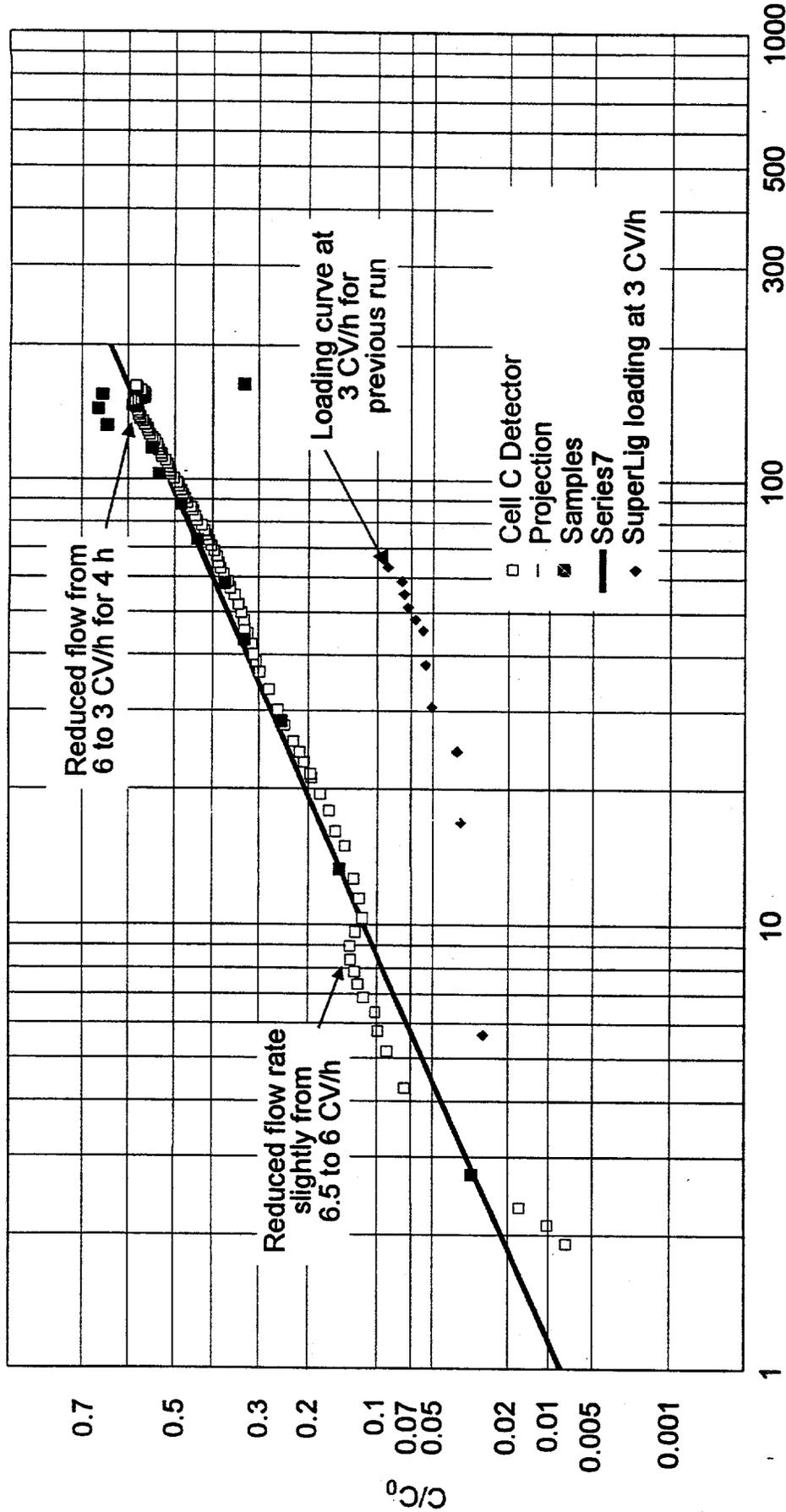
4.7 SUPERLIG® 644C RUN 2

The SuperLig® for this run was prepared by measuring 3.779 g of dry resin into a column and tapping to a no-volume change (5 mL, dry tapped volume). Ron Bruening, of IBC, was consulted about the conditions for the run. The 5 mL of dry resin was added to distilled water and then allowed to wet overnight. Then, 30 mL of 2 *N* NaOH was added by pumping in upflow to fluidize the bed. Some stirring was required to remove air bubbles and break up some clumps to finish swelling and preparing the column for the test. The column with 2 *N* NaOH and resin was allowed to stand for 4 h, after which the volume had increased to 10.5 mL. Another 30 mL of 2 *N* NaOH was pumped through the bed and allowed to stand in the column until startup of the system. The final volume was 11.2 mL. The column was placed in the cell after all but 2 cm of the caustic solution above the bed was removed.

The bed for this run was prepared as in the first run, but it was rinsed with 2.0 *N* NaOH instead of 0.1 *N* NaOH. After feed was started to the column, the level of the bed was at 7 cm, and clumps of bed material formed, the largest of which (about 2 cm by 0.5 cm) floated, sank, and remained at the top of the bed during the rest of the run. The initial rate, 6.4 CV/h, was reduced to 6.0 CV/h soon after the start to coincide with the desired flow rate. Considerable color was noted as the initial feed left the column; however, it became diminished after a few column volumes had passed through.

After the breakthrough had reached over 50%, the flow rate through the column was changed to 3 CV/h to determine whether the lower flow rate would increase the slope of the loading curve. The first SuperLig® 644C run at 3 CV/h had to be terminated before a reliable slope was obtained. Both loading cycles are shown in Fig. 10. The lower rate was continued for 4 h, and an initial decrease in the breakthrough with a slight apparent increase in the slope followed. These data are

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Column Volumes Through Detector

Fig. 10. Loading curve for SuperLig® 644C at 6 CV/h.

not complete enough for a determination of the new slope but give a qualitative indication that it had changed. The feed was then terminated; the column was rinsed with water, and preparations were made for the elution. During the course of the run, the column effluent filter developed a large, dark spot on the upstream side that gradually grew during the run but never plugged the filter to flow. The results of the loading cycle, shown in Fig. 10, include the data from the short loading run at 3 CV/h conducted earlier. Samples of the column effluent fractions were checked; the first had a pH of 13.68, the second was 13.24, and the remainder were 13.13 in each case.

Elution of the loaded cesium was started by removing water from all lines and pumping the 0.5 N HNO₃ to the column at a 3-CV/h flow rate. After the acid started through the column, colored liquid could be seen exiting the column. The elution curve is shown in Fig. 11. The initial bed level, 7.5 cm, decreased to 6.6 cm after the first acid entered the bed. After 2 CV of acid had passed through the bed, the level was 6 cm. It became very difficult to maintain pump flow rates at the desired level as flow rose and fell. The final bed depth was about 5.6 cm. The calculation for the cesium fed and recovered in the column effluent samples showed 17,494 μCi fed ($9.36 \mu\text{Ci/mL} \times 1869 \text{ mL}$) and 7,599 μCi collected in the effluent from the column, giving a calculated column loading of 9,895 μCi . Measurements after the run showed 18.1 μCi left on the column following elution. The eluent samples from the column contained 5,031 μCi .

The results of the run collected in the fraction collector were analyzed, and the physical appearance of the samples was noted. The first fraction collected during loading contained brown liquid but no solids. The last sample contained traces of solids, as did the lines to and from the fraction collector. Elution samples showed traces of solids in the first three sample tubes. The first tube had some (~0.5 mL) solids that were yellowish-brown in color. The second tube had a trace of yellowish-brown solids. The third tube contained almost 1 mL of brown solids in three layers of slightly different looking materials (either puffy or gel-like appearance). No solids were present in the fourth or fifth tubes, but a trace of dark solids was noted in the sixth tube. No other solids were seen.

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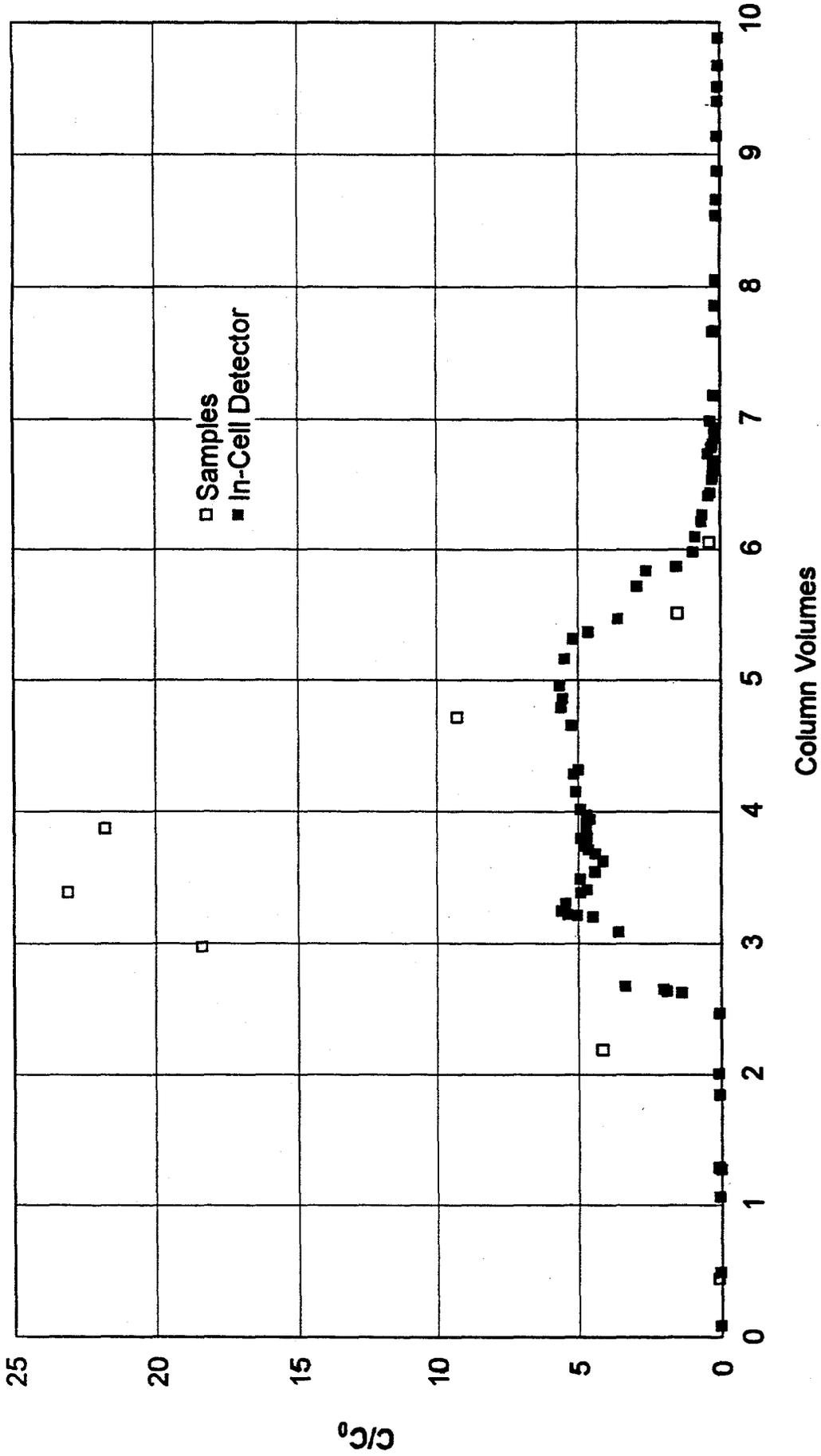


Fig. 11. Elution curve for SuperLig® 644C.

4.8 CST RUN 1

Crystalline silicotitanates (CSTs) from UOP, IONSIV IE-911 Lot 07398-38B, were tested in a 1.5-cm-ID column using a volume of 10 cm³, with a bed height of 6 cm. The dry, tapped density of the material was 1.155 g/cm³. This IONSIV was a developmental sample supplied by UOP; improved materials are currently under development by UOP. The column was flushed with 0.1 M NaOH in an upflow mode to wet the packing and remove bubbles. The bed level was 6.0 to 6.1 cm after tapping and settling. The column top was installed, and the column was allowed to stand overnight. The column was operated at 3 CV/h in downflow for a total of over 435 column volumes (over 4.4 L of W27 supernatant was fed). Analytical data for the cesium concentration in the feed and column effluent samples indicated that operation was successful. No problems that could be attributed to the ion exchanger occurred during the continuous run of more than 6 days (24 h/day).

A fresh bottle of feed was prepared for this run using the above procedure, and the pH was adjusted to 12.84 using three different pH meters for analysis. Subsequent analysis using titration showed that the pH was actually 13.32. During the first several hours, the filter downstream from the column plugged with a dark-brown material, and the flow was routed through the second filter when the pressure drop across the filter became greater than 15 psi. The second filter did not plug for the remainder of the run, although the visible obstruction of the filter was about 50 to 60%. Similar solids were later found in the feed tank and also in one of the fractions collected in the fraction collector, after it had stood for several days. The pH levels of the feed and the first fractions from the fraction collector were checked with pH paper and found to be the same, about 12.5 to 12.8, within the precision of the paper. Later, titration showed that the pH levels of the samples were 13.32. This higher value may partially explain the presence of the solids, although the identity of the solids has not been determined.

Figure 12 shows the loading curve plotted on linear coordinates with C/C_0 vs column volumes. The CV was 10 mL, the settled bed volume of the ion exchanger in the column, and did not change during the experiment. As can be seen, the level of ¹³⁷Cs in the column effluent is low (below 1% breakthrough) after 100 CV. Figure 13 shows the same data plotted with C/C_0 on a probability scale vs the log of the CV on the x-axis and indicates a straight line once breakthrough

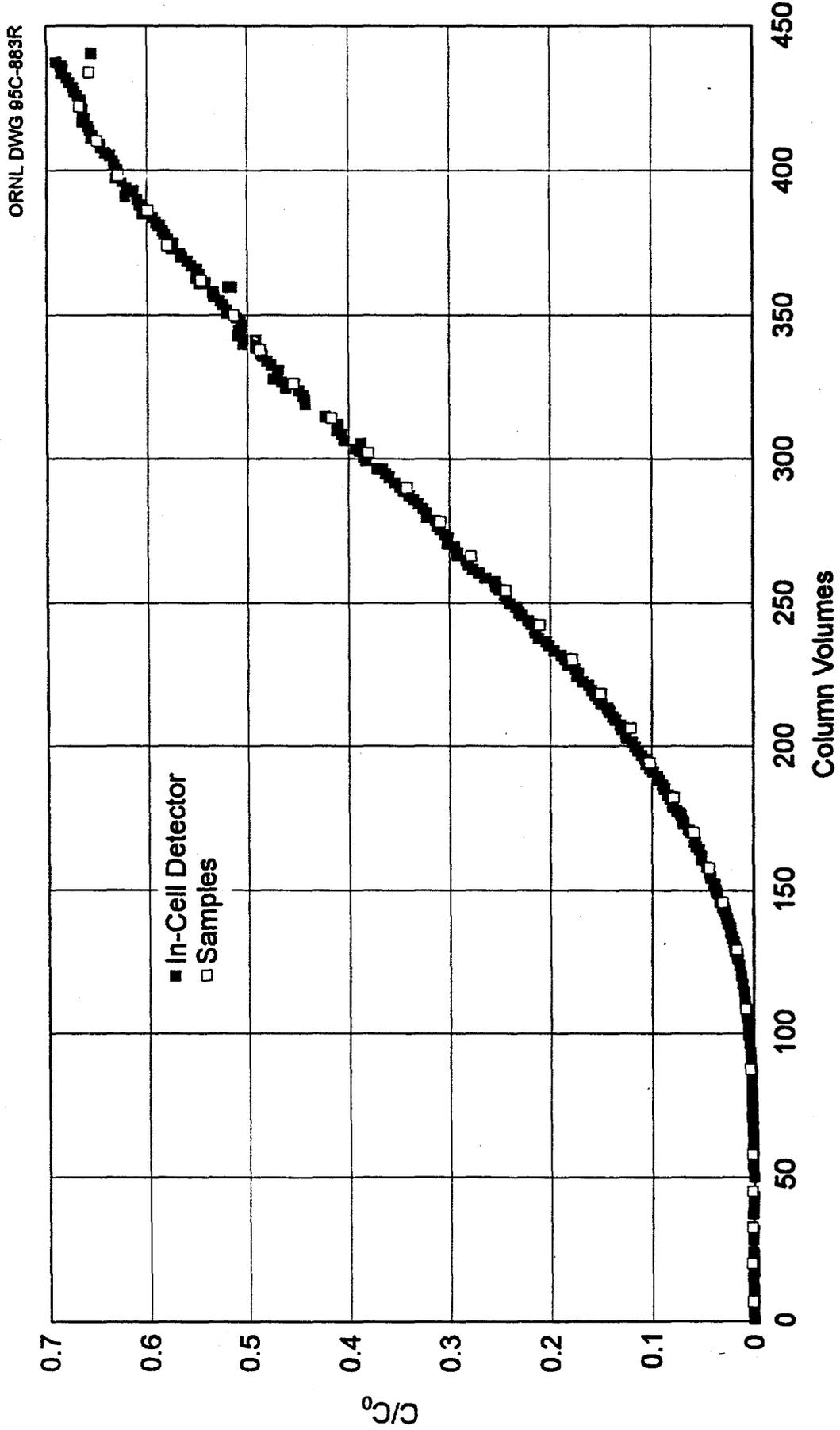
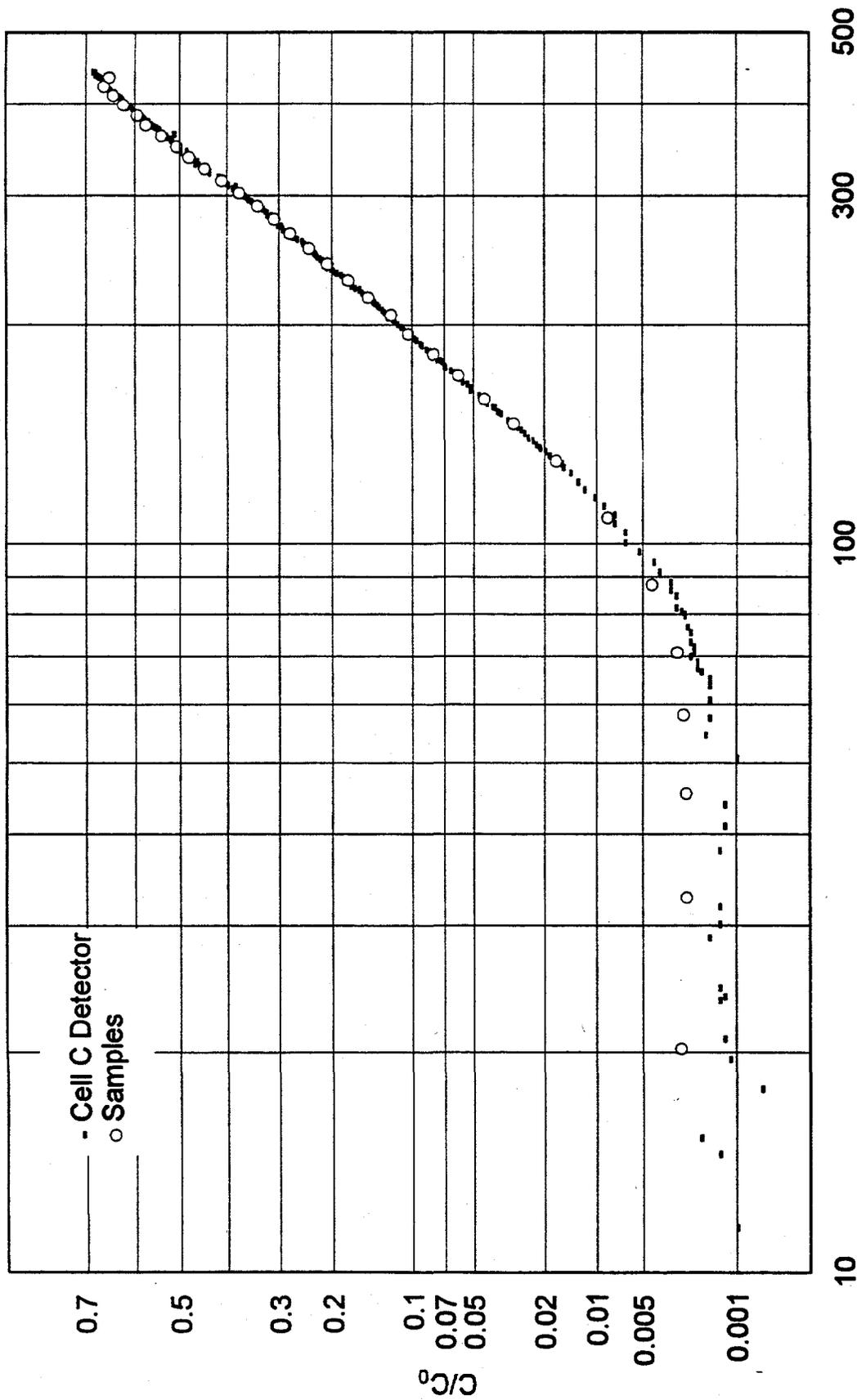


Fig. 12. Loading curve for CST at 3 CV/h (linear coordinates).

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Column Volumes Through Detector
Fig. 13. Loading curve for CST at 3 CV/h.

reached greater than 1%. This plot also shows that 1% breakthrough was at 110 CV and 10% breakthrough at about 190 CV. The test continued through about 65% breakthrough, and in Fig. 12, the standard S-shape ion-exchange loading curve is evident. These results compare favorably with results for W-27 simulant obtained at Sandia and with model calculations.¹³

Further data were obtained, based on the analyses of the samples obtained during the run. Fractions were collected for about 4 h per bottle (~120 mL) or 12 CV per sample bottle. Each bottle was then sampled and counted. The results were subsequently compared with the data obtained using the in-line detector inside the cell (see Fig. 13). The pH levels of some of the samples were obtained by titration to be about 13.32. The column run was started with 0.1 N NaOH present. Calculations for the loading of the column, based on the ¹³⁷Cs in the feed and the volume of feed, gave 41,345 μ Ci fed ($9.34 \mu\text{Ci/mL} \times 4436 \text{ mL}$), and analysis of the effluent from the column showed that 9,917 μ Ci passed through the column. Counting of the column after its removal showed that 26,160 μ Ci was present. These results left about 5,150 μ Ci (12.5% of the cesium fed) unaccounted for.

4.9 CST RUN 2

The cell C experimental system was set up to start run 2 using the UOP Batch 38B CST sample from the same bottle as that used in the first run in September 1995. The column was prepared by using 11.727 g of sorbent measured in a 10-mL graduated cylinder. The CST was placed in the column and tapped to the minimum level (6 cm). Then, 150 mL of DI water was passed through the column in the upflow mode to remove fines and settle the bed. This was followed by 75 mL of 1 N NaOH. About 10 mL of the caustic remained above the bed, and the column was left this way for installation in the cell system. The final volume of the bed before the start of the run was 10.23 mL.

The supernatant bottle used for most of the loading cycles was that used in the previous run at a titrated pH of 13.32. During the run, another bottle of supernatant was prepared to approximately the same pH (pH of 13.28 as measured by titration). This bottle was used for the last 100 CV of feed to the column. Both bottles contained material from the same batch obtained in April 1995 from MVST W-27.

Once the column was installed in the system, feed supernatant was pumped to the column and the flow was started at about 6 CV/h through the column. Flow continued until the effluent showed a ^{137}Cs level greater than 50% of the level in the feed. The column was then washed with water, drained, and prepared for counting and storage. The results of the run are shown in Fig. 14. As expected for kinetic control of the loading of cesium onto the CST, use of the increased flow rate resulted in less cesium being retained in the column as compared with results obtained with the slower flow rate. The breakthrough of cesium at the 50% C/C_0 , however, was very close to that obtained at 3 CV/h. The change in feed after 200+ CV appeared to have no effect on the slope of the curve or other operating parameters.

No difficulties with the system were observed during operation, although the after-column filter showed a dark spot, about 1.5 cm in diameter, which caused no plugging or pressure drop increases. A dark layer, about 1 mm thick, also formed at the top of the bed over the course of the run but did not interfere with operation. The samples obtained from the fraction collector yielded pH levels, by titration, of 13.37 for the first part of the run and 13.29 at the end of the run. The column had 1 *N* NaOH at the start.

Calculations for the loading of the column, based on the ^{137}Cs in the feed and the volume of the feed, gave 36,090 μCi fed ($9.34 \mu\text{Ci} \times 3864 \text{ mL}$), and analysis of the effluent from the column showed that 7,290 μCi passed through the column. Counting of the column after its removal showed that 25,590 μCi was present. This left about 3,210 μCi (8.9% of the cesium fed) unaccounted for.

4.10 3M SLIG 644 WWL WEB MATERIAL WITH SUPERLIG® 644 EMBEDDED

The WEB material was contained in a Gelman 25-mm in-line stainless steel filter holder, provided by 3M, with a design effective filter area of 3.7 cm^2 . The filter was 3.18 mm thick (measured dry) with a density of approximately 0.43 g/cm^3 . The filter volume used for the calculations was 1.29 cm^3 , as given by 3M. The filter holder was attached to an apparatus to interface with the cell system, as shown in Fig. 15. The system used an empty column as a feed reservoir for the filter pump to enable the flow rate to be easily checked. The system was placed in the cell and installed in the system. According to the directions from Lloyd White (3M)

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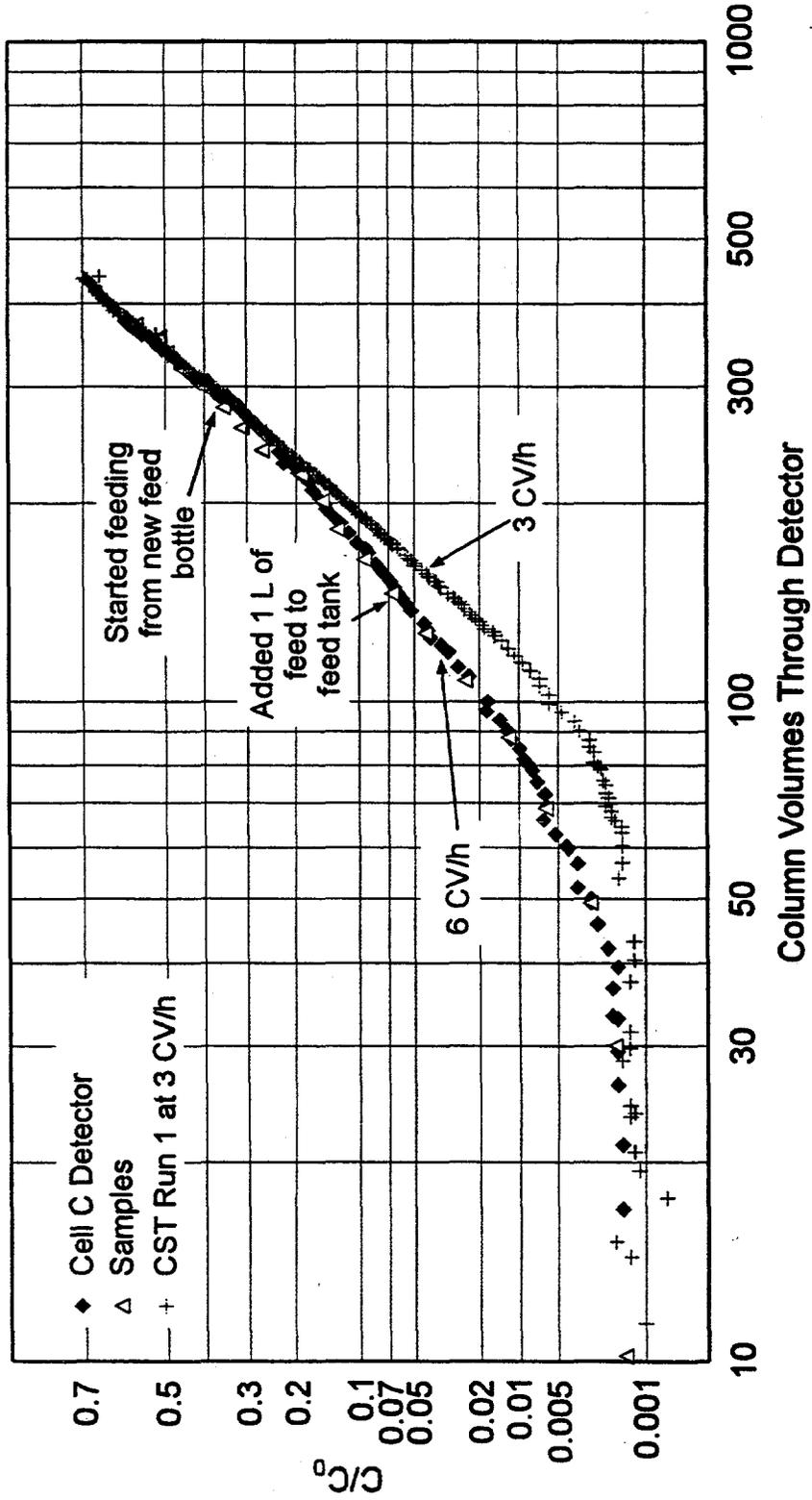


Fig. 14. Loading curve for CST at 6 CV/h.

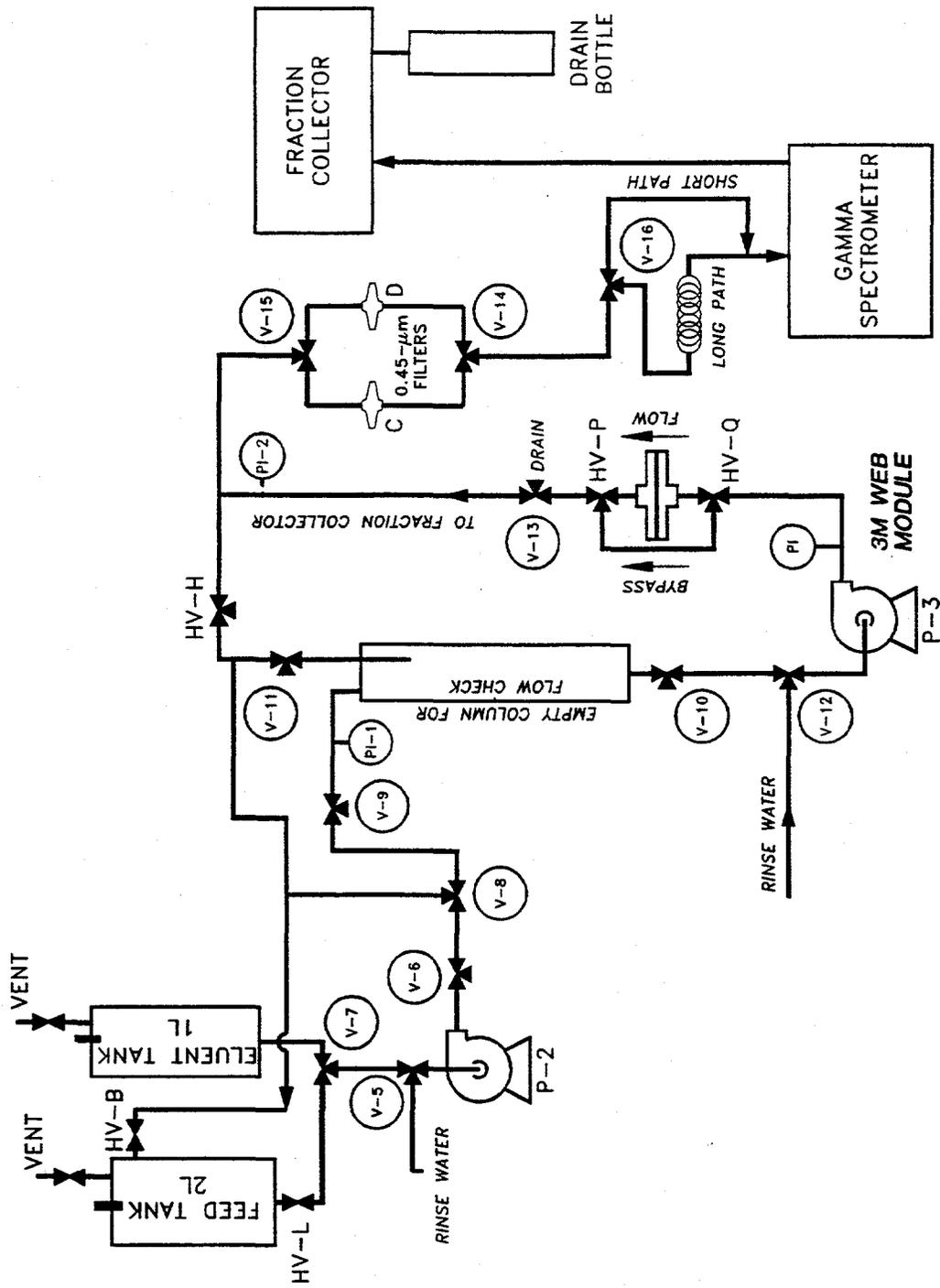


Fig. 15. Apparatus diagram for the 3M SLIG 644 WWL WEB material system.

concerning preparation before the run, orientation of the filter, and flow-rate requirements, the filter was prepared by running water and 2 M caustic successively through the filter with the filter in an upflow orientation. Fifteen milliliters of the NaOH was passed through the filter, and some was left in the filter. Considerable color from the filter passed through and was sent to the system drain. During the caustic treatment, a significant pressure increase on the pump was noticed (loss of flow rate resulted); therefore, it was necessary to install a pressure gauge in the line between the pump and the filter to more closely monitor the operations.

The SLIG 644 WWL WEB material from 3M was operated through a loading/elution/regeneration cycle. After the feed had been started and supernatant reached the filter, the pressure was 4 psi on the gauge. The feed rate was initially less than desired, about 0.71 mL/min, so the pump rate was increased. Brown color was seen leaving the WEB filter after the supernatant began passing through. The pressure drop across the filter caused the flow rate through the pump to be lower than that normally observed for the pump setting. This lower flow rate caused increases in the setting on the pump rate to compensate. After the rate had been stabilized at about 1 mL/min, the run continued at that rate for the remainder of the loading cycle. The pressure upstream of the filter increased to 14 psi before finally stabilizing at about 7 psi. After several filter volumes of feed had flowed through the filter, the color in the filtrate gradually lightened until it almost disappeared. The average flow rate for the loading was 1.07 mL/min. The filter volume provided by 3M for the run, 1.29 mL, is roughly equivalent to the column volume of an ion-exchange column. This flow rate and filter volume gave a flow rate, in filter volumes per hour, of 49.78.

The loading curve for the SLIG 644 WWL WEB material is shown in Fig. 16. When loading was complete, the supernatant feed to the column was stopped and the feed lines were emptied. The filter feed pump was shut off, and about 15 mL of distilled water was passed through the filter. Then about 15 mL of 0.5 M HNO₃ was added to the feed column to run through the filter for elution. Some backflow of water through the pump diluted the acid about 20%. When the acid flow through the filter was complete, an additional 12 mL of water rinse was passed through the filter. Following the water rinse, the feed column was filled with 15 mL of 2 M caustic for regeneration of the filter.

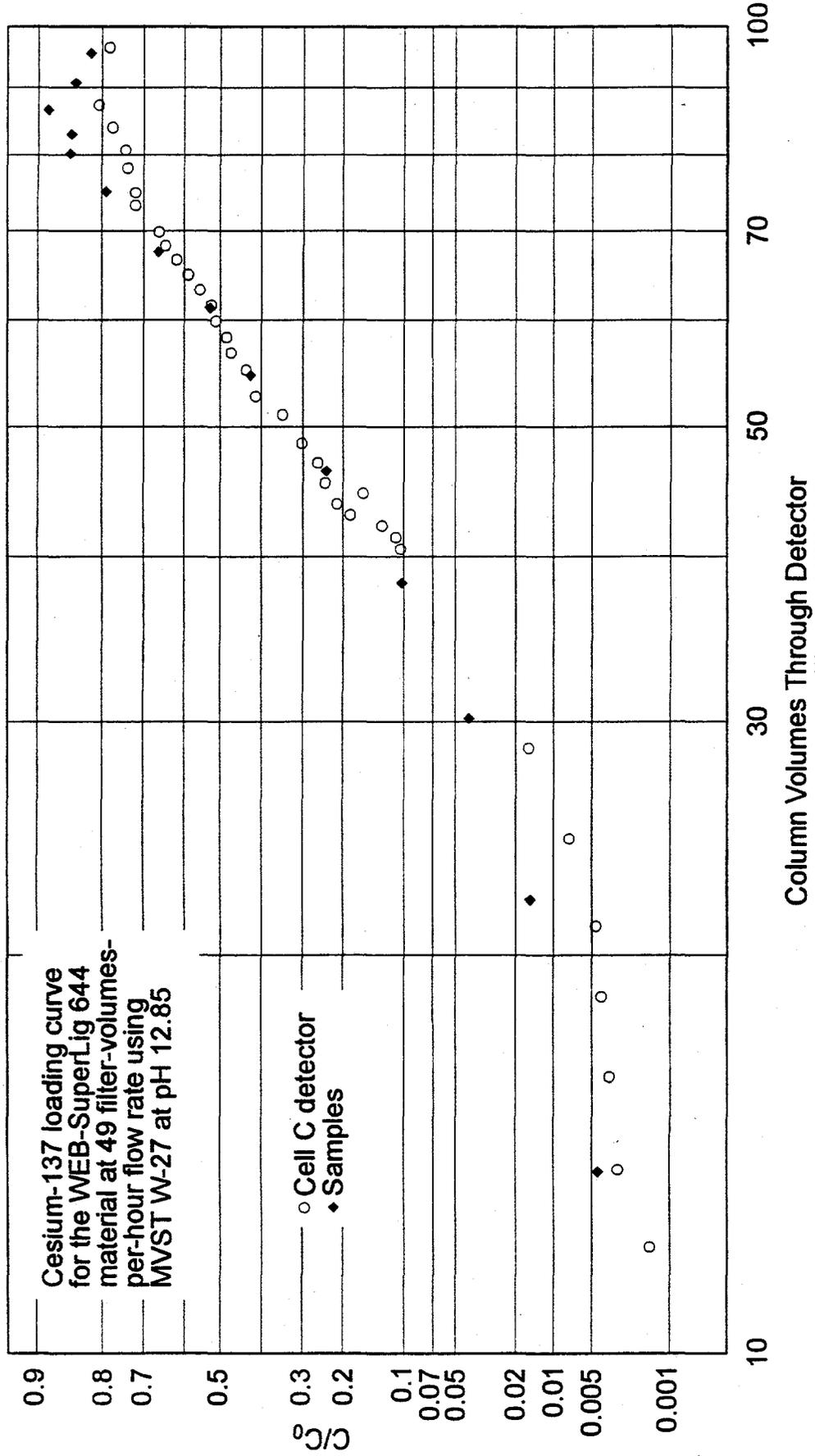


Fig. 16. Loading curve for 3M SLIG 644 WWL WEB with SuperLig® 644C embedded, at about 49 CV/h.

After the caustic had started through the filter, a significant volume of colored effluent was, again, observed coming from the filter, and the pressure drop across the filter was causing pumping problems. When the caustic flow was finished, water rinse was passed through the filter. Pressure drop was still high, with attendant pumping problems. The system was drained after bypassing the filter and leaving it full of DI water. Figure 17 is a curve showing the loading, elution, and regeneration of the WEB material on a linear plot. After shutdown, the fractions were removed from the fraction collector and submitted for ^{137}Cs analysis.

The pH of the feed used for the run was 13.30. The second sample taken after starting the supernatant feed had a pH of 13.79, which was expected since the filter was prepared with 2 N NaOH. The last sample from the loading had a pH of 13.32. Several observations of solids in the samples were noted during analyses of the collected fractions. The first fraction, 1.8 mL, contained a trace amount of brownish-black solids on the bottom of the tube. The second fraction, 8.9 mL, contained a small amount of black solids. Loose, greenish solids (volume, about 1 mL) were seen in the first eluent sample. Solids were also seen as traces of brownish-red solids in the first, about 0.5 mL of tan solids in the second, and just a trace of dark solids in the third of the three tubes of regenerant samples. Whether the solids are part of the SLIG 644 WWL WEB material or the SuperLig[®] 644 embedded in it is not known, but the different colors of solids seen here were not observed in the SuperLig[®] 644 loading or elution. The filter holder was not removed from the cell and disassembled to examine the WWL WEB. A ^{137}Cs balance for the run showed that a total of 1070 μCi was contained in the feed, and about 350 μCi was recovered in the effluent during loading plus 746 μCi in the eluent and rinses, for a 102% recovery of the ^{137}Cs .

4.11 EICHROM KCoFeC GRANULAR SORBENT

The granular sorbent used in this run was a sample of KCoFeC, lot JW-40-021, obtained from Eichrom. It was prepared for use by filling a 10-mL graduated cylinder with 7.272 g (tapped volume, 10 mL) of material and transferring this to the column to be used in the test. Next, 150 mL of DI water was pumped through the column in the upflow mode to remove fines and settle the bed. A small amount (lightly covering the bottom of a 50-mL beaker) of fines material was carried out of the column and collected in a beaker. After being rinsed, the bed was settled and had a 6-cm depth

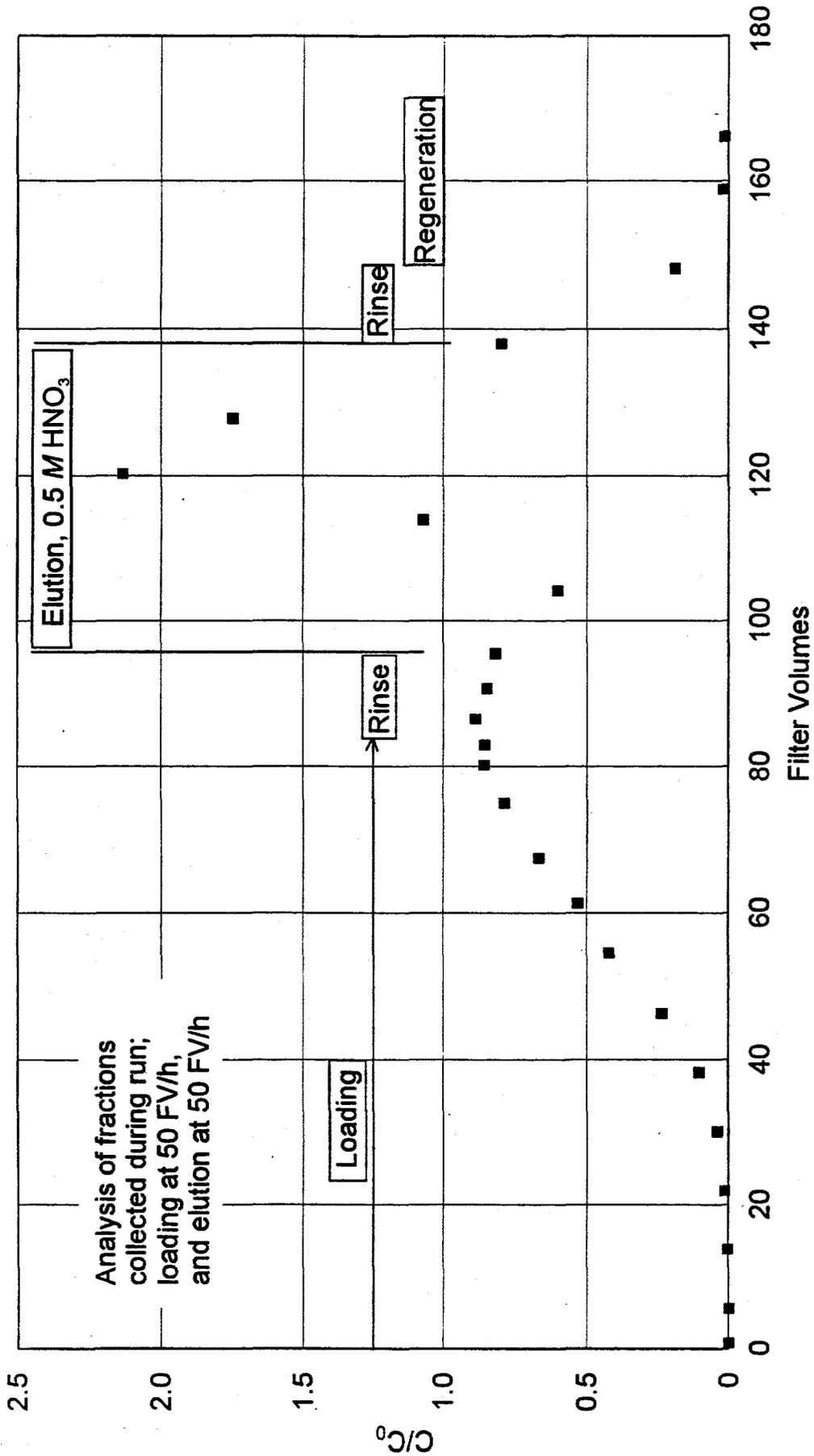


Fig. 17. Linear plot of the loading, elution, and regeneration of 3M SLIG 644 WWL WEB with SuperLig® 644. FV = filter volumes.

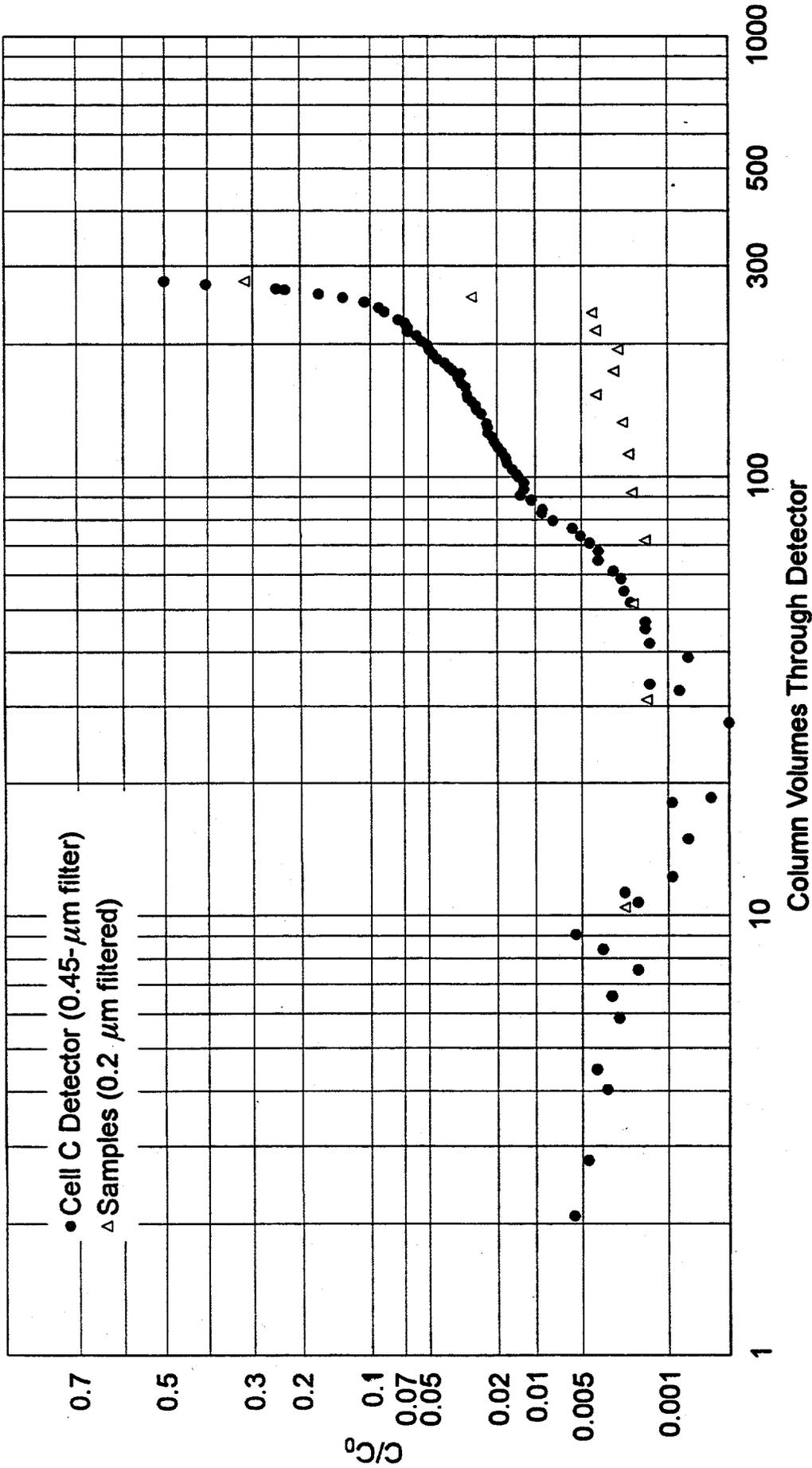
(10 mL) before installation in the cell. A 1.5-cm layer of water was left in the column above the bed, and the column was prepared for placement in the cell system. Following installation of the column, the remainder of the system was readied for operation. The feed was from the same bottle of W-27 supernatant that was used in the previous SuperLig[®] run at 6 CV/h.

The run was made at 9 CV/h using supernatant at pH 13.32 (the same pH level as used in previous tests on the CST and SuperLig[®] 644C). Immediately upon starting to feed supernatant to the column, a precipitate formed on the top of the bed. A blue-colored, gel-like material was also noted in the feed above the bed after feed had entered the column. After a few minutes, the solids at the top of the bed had grown to what appeared to be a lump, about 1 cm thick, of cloudy material. No solids were present in the feed tank or in the lines to the column from the feed tank or pump.

After supernatant had been pumped through the column for about 12 min, the indicator for pressure drop across the product filter (downstream of the column and upstream of the filter) read 47 psi, indicating a completely plugged filter. The pump was shut off, and the filter valve was then switched so that the alternate filter could be used and the plugged one could be replaced. Use of the alternate filter decreased the pressure drop to normal, and the pump was restarted with no further blockages. During the next 30 min, however, the second filter became about 80% covered with a grayish-brown precipitate. However, this material was not enough to plug the filter and stop the flow. After an hour, the coverage appeared to be almost 100% but no appreciable pressure drop was seen.

The cesium in the column effluent, which was at a low level during the start of the experiment, gradually increased as the first 100 CV of supernatant passed through the column. Following the collection of samples in the fraction collector, a sample of each fraction was passed through a 0.2- μ m filter and this step showed that, in fact, the increase in cesium was almost entirely due to particles of KCoFeC leaving the column, passing through the 0.45- μ m filter, and entering the rest of the system. The first fraction from the fraction collector also contained visible solids that coated the bottom of the bottle. The normal column operation continued for over 250 CV in this manner, but then apparently the material in the column began to disintegrate because the cesium level in the effluent rose rapidly and could not be filtered out using the 0.2- μ m filters. Figure 18 shows the loading curve, along with the sample data for the 0.2- μ m-filtered samples. The cesium level in the samples increased

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until it was greater than the concentration in the feed. These results are shown in Fig. 19, which is a linear plot of the loading cycle.

The column bed also lost volume during this time, and the bed level decreased from about 6.3 cm to 5.7, and then finally to 5.2 cm, during about 6 h of continued operation following the initial evidence of breakdown. Following the shutdown of feed to the column, the column was rinsed with DI water, drained, and removed from the system. After the system was drained following the column rinse, the column pump piston seized in the cylinder because of the many solids in the pump head. Thus, the pump had to be removed from service and the pump head replaced.

During cleanup of the experimental system, the flow path was first rinsed with 4 M NaOH, which was allowed to remain in the system for 16 h and then rinsed with water. Following the water rinse, the system was rinsed with 2 M HNO₃. All of the color that had coated the lines disappeared, and visible parts of the flow path were immediately cleared of residue. However, the solids that exited the system plugged several valves when the system was drained.

5. DISCUSSION OF CELL COLUMN RUNS

5.1 COMPARISON OF THE CONTINUOUS RUNS WITH BATCH EXPERIMENTS

Many of the materials tested in the continuous system had been examined in batch studies using both actual supernatant and surrogate materials. Some of these tests were mentioned above during the discussion of the results for the RF runs. Batch studies were done on SuperLig[®] 644, RF, and CS-100 ion-exchange materials for comparison with the same materials in column tests.⁵ Based on the batch studies, the SuperLig[®] 644, RF, and CS-100 materials had K_d values of 644, 1340, 620, and 99, respectively. The simulated feed had 5 M sodium, 0.12 M potassium, 5×10^{-4} M cesium, and 1.68 M free hydroxide concentrations.

Other batch tests were conducted to compare CS-100, RF, SuperLig[®] 644, and CST (-38B).⁴ In these tests, both DSSF simulant composite and actual DSSF composite were compared in batch distribution tests using sodium concentrations of 0.2, 1, 3, and 5 M and sodium/cesium ratios of 50, 500, 5000, 50,000, and 500,000. Results were given for time-dependent cesium uptake for simulant at 5 M sodium and a sodium/cesium ratio of 50,000, indicating that up to 10 h was required for

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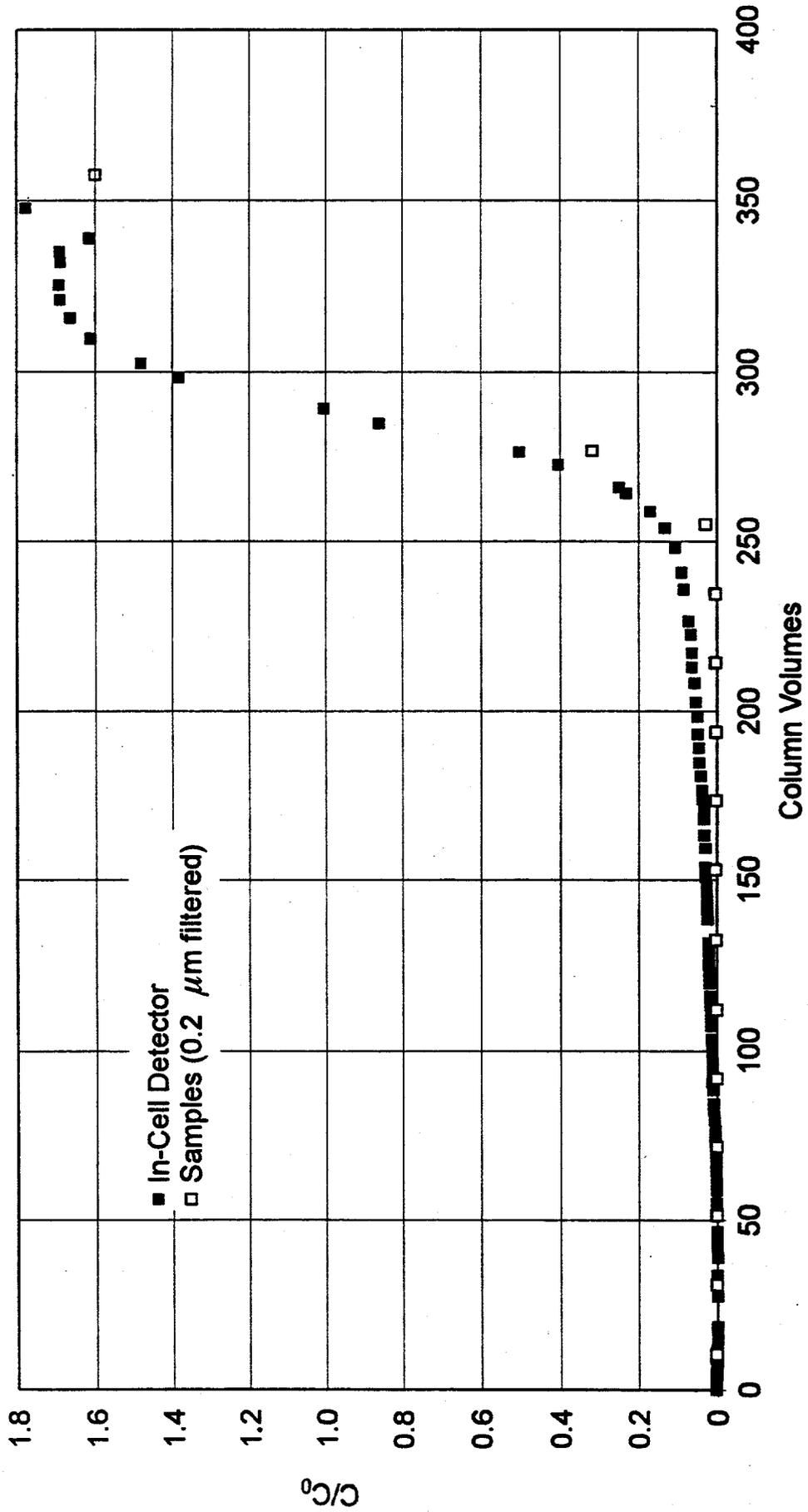


Fig. 19. Linear plot of the loading curve for Eichrom KCoFeC.

equilibrium to be reached for the RF, SuperLig® 644, and CST, while the CS-100 required only about 1 h. Equilibrium results for the RF showed a range of λ ($K_d \times$ resin density) from 100 to 2000, depending on the sodium concentration at the same sodium/cesium ratio. Over the same range for SuperLig® 644, the λ also varied from 100 to 2000, and the CST-38B ranged from 1000 to >20,000. When the exchanger results were compared with those using actual waste, the greatest deviation in performance was noted for the RF resin, which had about 25 to 50% lower values across the range, and for the CST-38B at the highest sodium/cesium ratios, where the actual supernatant resulted in a 35% drop in performance (although all exchangers showed decreased performance).

The predictions for operation of a column for the W-27 supernatant, based on the above batch tests, gave column volumes greater than were seen in the experiments. The batch distribution coefficients give an equilibrium measure of the overall ability of the solid-phase ion-exchange material to remove an ion from solution under the particular experimental conditions that exist during the contact. When simplified by using analyte concentrations in solution, the K_d represents the theoretical volume of solution at equilibrium that can be processed per mass of exchanger, and multiplying by the bed density results in the theoretical number of bed volumes of solution that can be processed per volume of exchanger.² For example, the RF batch results cited above suggest that approximately 185 CV should be achieved, SuperLig® 644 should be about 110 CV, CS-100 should be about 21 CV, and CST-38B about 800 CV. Results for the W-27 showed the actual values to be: 45 to 50 CV for RF, 100 CV for SuperLig® 644, 17.5 CV for CS-100, and 350 CV for CST-38B. These results compare very favorably except for the predictions for the CST-38-B, which is affected by other ions present in the W-27.

5.2 COMPARISON WITH OTHER CONTINUOUS COLUMN EXPERIMENTS

Experiments were conducted using actual supernatant from tanks 101-SY and 103-SY with CS-100 as the ion exchanger at PNNL.² These supernatants were diluted to about 5 M sodium with 2 M NaOH and had a ¹³⁷Cs concentration of about 140 to 160 μ Ci/mL after dilution. The concentration of hydroxide was approximately 3 M; the total cesium concentration was about 5×10^{-5} M. Simulants were also prepared with these concentrations for comparison. The results showed breakthroughs at 0.5 C/C₀, of 36 to 41 CV, at a flow rate of 6 CV/h. (The actual and

simulated supernatant results were almost identical.) The present work gave a cesium breakthrough of about 17 CV for the CS-100, less than half of the value for the PNNL study. The supernatants tested here and at PNNL had about the same sodium concentrations, but the PNNL samples had approximately nine times as much total cesium. The difference in the hydroxide concentration was significant (3 *M* at PNNL vs 0.3 *M* in W-27), as was the difference in the concentration of the potassium, which also competes with cesium for loading.^{10,11} The potassium concentration in the PNNL supernatants was 0.03 *M*, while the potassium concentration of the W-27 is 0.26 *M*.

SuperLig® 644, RF, and CS-100 ion-exchange materials were compared in tests using simulated alkaline supernatant solutions.⁵ The simulant in this series was 5 *M* in sodium, 0.12 *M* in potassium, 5×10^{-4} *M* in cesium, and 1.68 *M* in free hydroxide. Columns that were 2.54 cm in diameter and 41.9 cm tall and contained 200 mL of ion-exchange resin were used in the tests. The flow rate through the columns was set at 9 CV/h. The results for the SuperLig® 644 showed almost immediate cesium breakthrough as compared with the RF resin; and 50% breakthrough occurred at about 100 CV, while the breakthrough for the RF resin was observed at 140 CV. The SuperLig® 644 used in these tests was the low-density material (density, about one-half that of the RF resin). The CS-100 gave a 50% breakthrough at 22 CV. Both the CS-100 and the SuperLig® 644 results are comparable to those reported for the current series of W-27 tests. The RF results on the PNNL simulant are almost three times higher, but that discrepancy is partially explained by the higher capacity for cesium as the hydroxide concentration exceeds 1 *M* and opens more sites in the resin for exchange, as well as the higher concentration of potassium in the W-27 supernatant. The elution of the RF and SuperLig® 644 PNNL simulant-loaded resins showed the same patterns as reported here for W-27. The SuperLig® 644C elution from the W-27 loaded column produced a very sharp peak using a comparatively small volume of eluent (~6 CV), while the RF resin required a much larger volume of eluent to achieve the same eluent cesium concentration from the column (10 to 15 CV).

Additional considerations for these studies include the effects of the resin or particle density on the performance during the column testing. Very light resin can almost float and result in an unpacked column that resembles a fluidized bed in its removal capabilities. This situation would result in very early breakthrough of the cesium due to the dispersion throughout the bed. The columns in this study used a bed depth/bed diameter ratio of about 4; thus, for the light organic resins, especially SuperLig® 644C, not very much material was present to create a long, packed depth. The

PNNL studies⁵ used columns with length/diameter ratios of ~16 and still had very early breakthroughs with the SuperLig[®] 644. These results can be compared with the CST results with -38B in which the initial breakthrough is at almost 100 CV. The CST is almost five times as dense as the SuperLig[®] 644C resin. Evidence for these density and bed height effects was also observed with RF resin in several experiments and modeling efforts.¹⁴ It was shown that in the case of RF resin, a bed length/bed diameter ratio of 15 was required before behavior similar to a fixed bed with a constant pattern was observed. Other possibilities for poor breakthrough curves are improper preconditioning of the bed and mismatching of bed presaturant and the column feed relative to salt concentration or density. Some of these conditions could have had a negative effect on the runs using W-27 for the organic resins. Also, in some of the RF and the CS-100 runs, water was used as the preconditioner after conversion to the sodium form with 1 or 2 M NaOH.

5.3 PROBLEMS ASSOCIATED WITH THE RUNS

In RF run 3, some reddish solid material was found in the first samples of loadings 2 and 4, and black solids were found in the first elution sample from the fourth elution. The buildup of material inside the lines and column caused flow problems with the pumps, the detector, and column operation. The materials that presented problems were apparently soluble and did not collect on the filters. Each filter was used for only one loading or elution.

During the SuperLig[®] 644 run 2, the column effluent filter developed a large, dark spot on the upstream side that gradually grew during the run but never plugged the filter. The results of the run collected in the fraction collector were analyzed, and the physical appearance of the samples was noted. The first fraction collected during loading contained a brown liquid but no solids. The last sample contained traces of solids, as did the lines to and from the fraction collector. Elution samples showed traces of solids in the first three sample tubes. The first tube had some (~ 0.5 mL) solids that were yellowish-brown. The second tube had a trace of yellowish-brown solids. The third tube contained almost 1 mL of brown solids in three layers of slightly different looking materials (either puffy or gel-like appearance). No solids were present in the fourth or fifth tubes, but a trace of dark solids was noted again in the sixth tube. No other solids were seen.

In the 3M WEB run, analyses of the collected fractions revealed solids in several of the samples. The first fraction, 1.8 mL, contained a trace amount of brownish-black solids on the bottom of the tube. The second tube, 8.9 mL of liquid, contained a small amount of black solids. Loose, greenish solids (volume, about 1 mL) were seen in the first eluent sample. Solids were also observed as traces of brownish-red material in the first, about 0.5 mL of tan solids in the second, and just a trace of dark solids in the third of the three tubes of regenerant samples.

During the KCoFeC experiment, the first fraction from the fraction collector contained visible solids that coated the bottom of the bottle. The later samples also contained solids with cesium attached that escaped the 0.45- μm filter but were trapped by the 0.2- μm filter used for sampling. Once the material in the column began to disintegrate, more solids were present in the samples; however, a significant portion could not be filtered out, and much of the cesium that had been removed was resolubilized. The solids exiting the column became lodged in the column pump and caused the piston to seize, which required that the pump head be changed.

6. CONCLUSIONS

In order to compare all of the tested materials, the breakthrough curves for the materials were plotted on the same graph (see Fig. 20). As can be readily seen, the CST-38B material showed overall better performance than any of the other materials when the column volumes to 50% breakthrough were compared at either a 3- or a 6-CV/h flow rate using the W-27 feed at pH 12.95-13.32; the best kinetic performance was at 3 CV/h. Also, the CST was able to maintain the cesium in the column effluent at less than 1% breakthrough for a much longer time than the other materials. Thus, the effluent through the CST columns contained lower levels of cesium (e.g., if C/C_0 was 0.01, then 99% of the cesium was removed from the supernatant) as compared with the SuperLig[®] or 3M SLIG 644 WWL WEB materials, which showed almost immediate breakthrough at more than 1 to 5% breakthrough in less than 10 CV. The KCoFeC supplied by Eichrom showed good cesium removal for over 200 CV as long as the samples were filtered through 0.2- μm filters prior to ¹³⁷Cs analysis; however, after 250 CV, the effluent contained more cesium than the feed because of the chemical breakdown of the sorbent.

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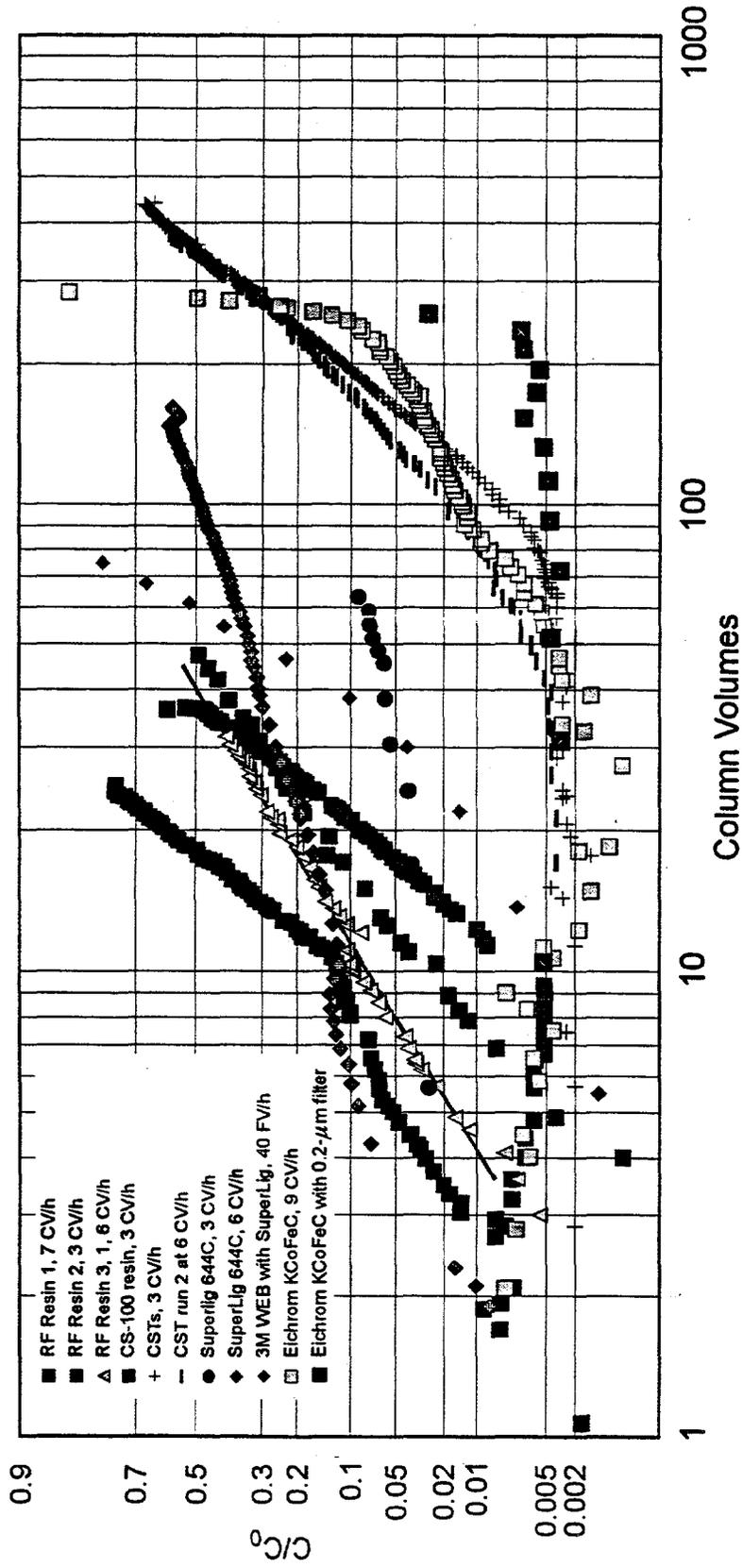


Fig. 20. Comparison of the cesium removal technologies tested in cell C, using MVST W-27 supernatant.

Comparison of the column data with the W-27 results obtained using simulant and actual supernatants at other sites showed good agreement and predictability from batch equilibrium to column testing. There were exceptions, and the comparisons must consider not only the cesium concentration, but also the hydroxide concentration, the other cations in the supernatant, and the ratios of the other cations to the cesium concentration.

The comparative evaluations shown here should provide critical data for the selection of the sorbent for the CsRD, as well as data applicable to other DOE sites, taking into account variations and differences in the supernatant compositions. In addition to the cesium removal capacity of the materials tested, the operational characteristics during continuous loading experiments were monitored. As described above, the organic sorbents RF, SuperLig[®], and the 3M SLIG 644 WWL WEB yielded colored products upon the first introduction of feed or during regeneration after elution. They, plus the CS-100, also exhibited volume changes during various stages of the preparation, loading, elution, and regeneration. The high pH of the feed supernatant to the KCoFeC material supplied by Eichrom resulted in its chemical breakdown and loss in the column effluent.

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