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**Removal of Cesium from Aluminum
Decladding Wastes Generated in
Irradiated Target Processing
Using a Fixed-Bed Column of
Resorcinol-Formaldehyde Resin**

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DEPARTMENT OF ENERGY**

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Chemical Technology Division

REMOVAL OF CESIUM FROM ALUMINUM DECLADDING WASTES GENERATED IN
IRRADIATED TARGET PROCESSING USING A FIXED-BED COLUMN OF RESORCINOL-
FORMALDEHYDE RESIN

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CONTENTS

	<u>Page</u>
ABSTRACT	v
1. INTRODUCTION	1
2. NATURE OF THE RESIN AND ITS PREVIOUS APPLICATION TO Cs REMOVAL	1
3. PROCESS DEVELOPMENT STUDIES	2
3.1 EXPERIMENTAL METHODS	2
3.2 BENCH-SCALE TESTS	4
4. IN-CELL DEMONSTRATION	8
4.1 COLUMN DESIGN/OPERATION	9
4.2 RESIN BED	10
4.3 CESIUM LOADING AND STRIPPING	10
4.4 BED REGENERATION	13
4.5 MASS TRANSFER	14
7. CONCLUSIONS	17
6. ACKNOWLEDGMENTS	18
7. REFERENCES	18

ABSTRACT

The removal of cesium (Cs) from a low-level liquid waste (LLLW) with a cation-exchange column was demonstrated using a resorcinol-formaldehyde (RF) resin. The RF resin was developed at the Westinghouse Savannah River Laboratory (SRL) and is highly specific for the removal of Cs from an alkaline waste of high sodium content. It was determined that the RF resin would be suitable for removing Cs, the largest gamma radiation contributor, from the LLLW generated at the Radiochemical Engineering Development Center located at the Oak Ridge National Laboratory. Presently, the disposal of the LLLW is limited due to the amount of Cs contained in the waste. Cesium removal from the waste solution offers immediate benefits by conserving valuable tank space and would allow cask shipments of the treated waste should the present Laboratory pipelines become unavailable in the future.

Preliminary laboratory tests of the RF resins, supplied from two different sources, were used to design a full-scale cation-exchange column for the removal of Cs from a Mark 42 SRL fuel element dejacketing waste solution. The in-cell tests reproduced the preliminary bench-scale test results. The initial Cs breakthrough range was 85–92 column volumes (CV). The resin capacity for Cs was found to be ~0.35 meq per gram of resin. A 1.5-L resin bed loaded a combined ~1300 Ci of ^{134}Cs and ^{137}Cs . A distribution coefficient of ~110 CV was determined, based on a 50% Cs breakthrough point. The kinetics of the system was studied by examining the rate parameters; however, it was decided that several more tests would be necessary to define the mass transfer characteristics of the system.

1. INTRODUCTION

This work is a demonstration of cesium (Cs) removal from alkaline waste using a resorcinol-formaldehyde (RF) resin in a cation-exchange column and is aimed at treating the low-level liquid waste (LLW) generated at the Radiochemical Engineering Development Center (REDC) at Oak Ridge National Laboratory (ORNL). Cesium is typically the largest contributor of gamma radiation in the alkaline liquid waste, due to its high solubility. Other gamma emitters are not significantly present in the liquid waste since they have relatively low solubilities.

Removing Cs from the waste meets two short-term objectives. First, it increases the processing capabilities by conserving valuable tank space at REDC. Presently, the waste is held within REDC until a central waste management facility can accommodate the relatively large amount of Cs (~8000 Ci/year) that is generated during the caustic dejacketing operations and the initial fission product separation operations. Second, removing the largest gamma emitter from the liquid waste would permit cask shipments of the LLW to a process waste treatment facility should the present waste disposal line become unavailable in the future.

This demonstration of Cs removal incorporated a resin evaluation study and two bench-scale ion-exchange experiments to determine the feasibility of using an RF resin bed. Based on the bench-scale experiments, a full-scale ion-exchange column was designed and operated in-cell to remove Cs from a Mark 42 dejacketing waste solution.

2. NATURE OF THE RESIN AND ITS PREVIOUS APPLICATION TO Cs REMOVAL

The RF resin was developed at Westinghouse Savannah River Laboratory (SRL) by Bibler and Wallace¹⁻³ and is currently manufactured by the Boulder Scientific Company. This resin was developed because it was highly specific for removing Cs from an alkaline waste of high sodium content. This resin is undergoing study for Cs removal from wastes at the Savannah River Site,¹⁻³ at Hanford,^{4,5} and at ORNL.^{6,7} It is a condensation polymer of resorcinol and formaldehyde and is designated here as RF resin. This resin and modifications of it have received considerable study.¹⁻¹² Like other phenolic resins (such as Duolite CS-100), it can be expected to suffer loss of capacity by oxidation of its phenolic (-OH) groups. The oxidation instability has been the largest objection to both widespread use and large-scale application of phenolic resins. Additional degradation by slow hydrolysis may also occur. In typical usage of Duolite CS-100 at the ORNL wastewater treatment plant, there was extreme capacity loss after 39 cycles. This is not

necessarily an objection at REDC, where waste to be treated is relatively small in volume. Limited operational life (~5 cycles) of RF resins could be accommodated since only a few liters (<10) per annum would be consumed.

The instability of phenol-formaldehyde-based polymers and ion-exchange resins to oxidation has been known and documented by several authors.¹³⁻¹⁷ Phenolics can be oxidized to a variety of higher-molecular-weight materials containing phenolic or quinoid moieties.¹⁴ The oxidation by air, dissolved oxygen, and other chemical oxidants is enhanced by increasing temperature. Early workers noted the phenolic resins were only moderately resistant to dissolved oxygen and alkaline conditions.^{16,17} The polycondensation resins of phenol-formaldehyde dissolve slowly in solutions of alkali, especially at high hydroxide concentration.¹³ It is interesting to note that the earliest commercial ion-exchange resins consisted of a phenol-formaldehyde skeleton to which the exchange groups such as sulfonic acids were attached. These were soon replaced by resins having a styrene-divinylbenzene skeleton because of their greater stability; however, some of the phenolic resins continue to be used in industrial applications where their unique properties give them special advantage.¹⁵

3. PROCESS DEVELOPMENT STUDIES

Process development studies were conducted with simulated waste solutions to determine the bed size of the ion-exchange column that was necessary to treat the caustic decladding wastes generated at REDC. Initial laboratory tests consisted of batch equilibrium contact studies to determine the distribution coefficient (K_d) of Cs for our particular feed concentrations and small-scale resin column experiments to determine Cs loading and elution behavior.

3.1 EXPERIMENTAL METHODS

Three different samples of the SRL RF resin were tested and are designated as SRS-A, SRS-B, and JB-B. The SRS-A sample, which was leftover stock material from a previous study,^{7,8} was obtained from D. D. Lee of ORNL. It originally was obtained from SRL by D. O. Campbell through R. M. Wallace (since deceased). The SRS-B sample was from a stock supply (55-gal drum) for treating waste streams at REDC. This was obtained in August 1991 and was kindly provided by J. P. Bibler of SRL. The resin had been stored at Savannah River since about 1986. The JB-B sample (about 5 L, dry basis) was recently synthesized at Boulder Scientific and was obtained in July 1993. The resins were dry screened on a Tyler portable sieve

shaker, model RX-24. The 60–80 mesh (180–250 μm) fractions of the SRS-A and SRS-B samples were used for tests with those resins, whereas the 40–60 mesh (250–420 μm) fraction of the JB-B sample was employed. The resins were washed batchwise with stirring, using a method adapted from Campbell, Lee, and Dillow.^{6,7} The following reagents were used (a 1 *M* NaOH wash was added to the procedure):

1. Two washes with 1 *M* HCl at a liquid-to-solids volume ratio (L/S) of 10
2. Two washes with demineralized water at a L/S value of 10
3. Five washes with 0.25 *M* NaOH at a L/S value of 6
4. One wash with 1 *M* NaOH at a L/S value of 10
5. Three washes with demineralized water at a L/S value of 10

The washed resin was collected on a Buchner funnel and subsequently placed on dry filter paper to further dry overnight. It was then stored in capped bottles prior to weighing for batch K_d measurements. The SRS-B resin evolved gas and foamed profusely in the initial contact with HCl. Presumably, the gas is CO_2 from carbonate held by the alkaline groups on the resin or excess alkali in the manufacture.

The SRS-A and SRS-B resins seem to contain one or more species that are much more soluble in NaOH washing than in HCl washing. An intense yellow-brown solution is always obtained in initial NaOH washing. Although the color diminishes on prolonged washing, it never disappears entirely. The soluble species show light absorption in both the ultraviolet and infrared regions of the spectrum. No identification of species has been made, although it appears that some may contain carbonyl moieties. (It was also noted, by visual inspection of the soluble yellow-brown species, that CS-100 resin was more NaOH soluble than the RF resin.)

Batch K_d determinations were made using tracer amounts ($\sim 100 \mu\text{Ci/L}$) of Cs^{134} - Cs^{137} obtained from very small aliquots of actual Mark 42 de jacketing solution. Weighed samples of the resin were equilibrated with test solutions on a laboratory shaker apparatus for 19 to 36 h.

Simulated Mark 42 decladding solutions were prepared with the following compositions:

<u>Constituent</u>	<u>Concentration, mol/L</u>
NaAlO_2	1.14
NaOH	2.0
NaNO_3	0.85
NaNO_2	0.13
CsNO_3	1.50 E-3
RbNO_3	1.85 E-4
$\text{Sr}(\text{NO}_3)_2$	4.20 E-5
$\text{Ba}(\text{NO}_3)_2$	1.38 E-4

The dissolved aluminum was prepared by dissolving aluminum metal pellets using a procedure identical to that employed in Mark 42 target de jacketing. The quantities of the Cs, Sr, Rb, and Ba nitrates were added in accordance with those calculated by the ORIGEN code^{18,19} and the solubilities of the elements in the caustic decladding solution. In high-burnup Pu targets, about 90% of the Cs and Rb is solubilized, and about 10% of the Sr and Ba is estimated to be soluble. The concentrations of Cs and Sr in Mark 42 decladding waste are greater than those in decladding waste associated with Cm targets by factors of 9 and 7, respectively. REDC has traditionally processed Cm targets as a mainline process which produces transplutonium elements. Typically, less resin capacity will be needed for the decladding wastes from Cm targets.

In experiments with laboratory columns, the resin was always conditioned with about 5 column volumes (CV) of 2 M NaOH prior to addition of feed to avoid precipitation of aluminum hydroxide. The term CV designates the volume of a conditioned resin bed where the resin is the Na⁺ form. After column loading was completed, the feed solution was also displaced using 5 CV of a 2 M NaOH wash solution to avoid the precipitation. The NaOH solution was then washed from the column by about 5 CV of demineralized water. Peristaltic pumps were used to meter feed and eluant solutions to the column. The laboratory columns were constructed of glass.

3.2 BENCH-SCALE TESTS

In the initial studies, samples of the SRS resins from two different sources were evaluated in batch equilibrium experiments using simulated Mark 42 decladding waste and compared with CS-100 (Table 1). For reference purposes, similar measurements using simulated SRL and ORNL Melton Valley waste solutions were also performed. The K_d values for CS-100 were relatively low, as was expected. The SRS-A resin, which previously^{7,8} had a high K_d value ($\sim 10^4$ at trace Cs), had lost most of its capacity for Cs. The loss in resin capacity may be due to degradation mechanisms discussed in the previous section. Two laboratory column runs confirmed this loss of capacity at higher Cs loading.

The two fixed-bed column tests were carried out using bed residence times of 4.3 and 36 min (Table 2). Neither test indicated any promise for satisfactory Cs removal. Cesium breakthrough was almost immediate at the shorter residence time of Run 1 and was about 4% after 7.5 CV in Run 2, which had a rather large residence time (36 min). The results are consistent with the recent sorption isotherm results of W. D. Arnold²⁰ in that this resin (SRS-A) appears to have a very limited capacity.

Table 1. Cesium distribution coefficients (K_d) for the SRS and Duolite CS-100 resins with simulated waste

		K_d (mL/g)		Cesium concentration in liquid phase (M)		
Resin	Feed	Cs-134	Cs-137	Initial	Final	Cs resin loading (meq/g)
SRS-A	2	40	45	2.40E-04	1.84E-04	8.3E-03
	3	462	475	Trace	Trace	Trace
SRS-B	1	781	765	1.52E-03	2.49E-04	1.9E-01
	2	1433	1475	2.40E-04	2.22E-05	3.3E-02
	3	10195	9225	Trace	Trace	Trace
CS-100	1	66	58	1.52E-03	1.09E-03	6.4E-02
	2	54	47	2.40E-04	1.83E-04	8.6E-03
	3	156	167	Trace	Trace	Trace

Feed 1 = Simulated Mark 42 caustic dissolver solution: 1.14 M NaAlO₂, 2 M NaOH, 0.85 M NaNO₃, and 0.13 M NaNO₂; Cs = 1.5E-3 M

Feed 2 = Simulated SRL supernate: 0.38 M AlCl₃, 2.9 M NaOH, 2.7 M NaNO₃, and 0.015 M KI; Cs = 2.4E-4 M

Feed 3 = Modified Melton Valley supernate: 4.34 M NaNO₃ and 0.24 M NaOH; Cs = tracer level

Two follow-up fixed-bed tests were then conducted using a 4.45-mL bed (2.01 g of resin) of SRS-B resin having a cross-sectional area of 0.50 cm² using the same column described in Run SRS-A-2 of Table 2.

Flow conditions for the two tests with SRS-B were as follows:

	<u>Loading, CV/h</u>	<u>Elution, CV/h</u>
Test SRS-B-1	2.7	7
Test SRS-B-2	3.7	7

In Test SRS-B-1, breakthrough occurred sooner than anticipated between 76 (0.01% Cs breakthrough) and 125 CV (100% Cs breakthrough) when the column was unattended. The SRS-B resin, therefore, had much greater capacity than the previously tested SRS-A resin, which showed Cs breakthrough at <7.5 CV (Table 2). The bed was completely eluted with about 16 CV of 2 M HCl as indicated by a gamma probe

scan of the column. Therefore, elution with the 2 M HCl is very efficient. The bed shrinkage on elution was approximately 50 vol %. In Test SRS-B-2 (Figs. 1 and 2), the loading and elution profiles for the column were obtained. Test 2 confirmed that the resin was satisfactory for in-cell use for treating caustic decladding waste. The 50% breakthrough point (C/C_0) was about 110 CV, which corresponds to a K_d of 240 mL/g. The density of the swollen bed was 0.465 g/mL. Based on the total Cs eluted in the tests, the column capacity is 0.35 meq/g (0.36 in Test 1 and 0.33 in Test 2). These loading results indicated that a resin volume of only about 2–3 L would be sufficient for treating each batch (150–200 L) of Mark 42 decladding waste.

Table 2. Fixed-bed tests of SRS-A resin for Cs removal from simulated Mark 42 decladding waste

Run number	SRS-A-1	SRS-A-2
Bed diameter, cm	1.18	0.79
Bed length, cm	4.3	9.4
Bed aspect ratio	3.7	11.9
Bed volume, mL	4.7	4.7
Feed rate, mL/min	1.1	0.13
Superficial velocity, cm/min	1.0	0.26
Superficial residence time, min	4.3	36
% Cs breakthrough at CV = 1.7	45%	---
CV = 3.9	63%	---
CV = 7.5	---	3.7%
CV = 30	---	96.2%
CV = 40	---	100.0%
Note: CV = Volume of resin bed		

The bench-scale tests were completed about 1 year before (September 1992) the in-cell tests could be scheduled. During this time a new series of batch shake tests was conducted with the SRS-B resin and a newly synthesized RF (JB-B) resin. The tests employed the previously described simulated feed. A summary of the results along with previous test results is provided in Table 3.

Fig.1. Loading profile of Cs on resin SRS-B in a laboratory fixed-bed column.

Fig. 2. Elution profile of Cs on resin SRS-B in a laboratory fixed-bed column.

The SRS-B sample had not changed within experimental reproducibility within 1 year. The K_d value for the JB-B sample was about 20% lower than that for the SRS-B resin. The JB-B resin was selected for the in-cell test since, unlike the SRS-B resin, it had not yet experienced extensive aging and would better demonstrate the effects of aging. Controlling the amount of air exposure would also be easier with the newly synthesized JB-B resin.

Table 3. Comparison of Cs sorption on the newly synthesized RF resin (JB-B) with the aged RF resin (SRS-B)

Sample code	Date of test	Equilibration time (h)	Initial ^{137}Cs conc. (Bq/mL)	Final ^{137}Cs conc. (Bq/mL)	K_d (mL/g)	Cesium loading (meq/g)
SRS-B	09/01/92	19	2500	410	765	0.191
SRS-B	09/01/92	19	360	58	781	0.191
SRS-B	11/29/92	19	1853	332	687	0.187
SRS-B	11/29/92	19	241	43	691	0.187
SRS-B	09/20/93	24	990	180	720	0.199
SRS-B	09/20/93	24	990	150	861	0.198
JB-B	09/20/93	24	990	200	583	0.179
JB-B	09/20/93	24	990	190	626	0.183
SRS-B	09/20/93	36	1044	170	771	0.191
SRS-B	09/20/93	36	1046	170	743	0.184
JB-B	09/20/93	36	1043	200	582	0.17
JB-B	09/20/93	36	1043	190	626	0.173

4. IN-CELL DEMONSTRATION

Two in-cell ion-exchange experiments were conducted using the JB-B resin to remove Cs from a typical caustic de jacketing waste solution generated at REDC. The first experiment did not reveal a fully developed breakthrough curve due to an excess of resin; however, in the second experiment a double batch of feed was used and exhibited a fully developed breakthrough curve.

4.1 COLUMN DESIGN/OPERATION

An in-cell cation-exchange column was designed and built at ORNL. Figure 3 is a representative drawing of the column. The detailed drawings of the column are identified as drawing numbers N3E017049051 and N3E017049052. The ion-exchange column consisted of a 36-in. length of ~3-in.-ID Pyrex pipe. The column flanges, tubing, and valves were constructed of Zircalloy. A 100 mesh Hastelloy-C screen, sandwiched between perforated Zircalloy plates, served as the resin support.

Loading and unloading the resin was done via the 3/4-in. tube located on the top flange. The 3/8-in. tubes located on the top flange were the feed solution input line and the column vent line. The treated solution exited the bottom of the column via the 3/8-in. line and was sampled via a tee in the output line, before being discharged to the tank pit.

A separate diaphragm pump was used to pressure solution through the column. The column was designed to run with the liquid level just above the resin bed, but air leaks allowed solution to siphon out of the column to the collection tank located in a lower pit area. Overcoming the effects of siphoning and controlling the flow rate were done by setting a pumping rate and then restricting the column exit valve until the proper inlet and outlet flow rates were roughly equal. The column was overdesigned for these particular experiments, resulting in a considerable void volume above the resin bed. The large plenum above the resin required "sweetening on" and "sweetening off" in between the conditioning, loading, and elution streams in order to prevent mixing in the plenum.*

Fig. 3. In-cell ion exchange column.

*The "sweetening" process is a standard practice in the industry and refers to the drawdown of the plenum volume to the resin bed level before introducing a new stream.

4.2 RESIN BED

The resin bed used in-cell was initially classified using 40–60 mesh sieves, which resulted in a dry particle size range of 250–420 μm . The resin bed consisted of 580 g of air-dried RF resin. The density of the swollen resin was measured as 0.387 g/mL.

The resin bed was treated with a series of column washes to condition the resin. The resin was first converted to the H^+ form by acid washing with 20 CV of 1 M HCl. Next, a 20-CV water wash was used to sweep away any remaining acid. A series of caustic washes was then performed to convert the resin to an Na^+ form. The caustic washes consisted of 10 CV of 0.25 M NaOH followed by 5 CV of 1 M NaOH. Due to considerable degassing during the 1 M NaOH solution wash, the resin remained in the 1 M NaOH overnight (~18 h) to allow for complete degassing. The degassing was believed to have been air leaving the pores of the resin. After ~18 h, the resin was washed with another 6 CV of 1 M NaOH solution and then washed with 10 CV of water. The ion-exchange column was then placed in the cell bank for operation. Before introducing the dejacketing waste feed solution to the column, the resin bed was subjected to a final conditioning wash of ~12 CV of 2 M NaOH. This final conditioning wash ensured that the resin was in the Na^+ form and that the residual liquid in the resin bed would not precipitate aluminum from the feed.

4.3 CESIUM LOADING AND STRIPPING

Two in-cell demonstrations of Cs removal using the RF resin in an ion-exchange column were conducted in the fall of 1993. The results consist of the standard breakthrough curves for loading performance and elution profiles for the Cs stripping performance. The bench-scale tests correctly predicted the initial breakthrough point and the K_d range (50% breakthrough point).

The feed solutions for the demonstrations were alkaline dejacketing solutions created during the dissolution of Mark 42 target segments. The feed solutions typically had a $[\text{OH}^-]$ range from 1 to 2 M. The feed solution for the first run (M5-RC-EXP1) was ~160 L of dejacketing waste containing ^{137}Cs and ^{134}Cs activity levels of 2.6×10^8 and 3.4×10^7 Bq/mL, respectively. The second run involved 245 L of dejacketing waste with ^{137}Cs and ^{134}Cs activity levels of 2.7×10^8 and 3.3×10^7 Bq/mL, respectively.

The characteristics of the in-cell tests are revealed in Fig. 4, where the ratio of the ^{137}Cs effluent concentration (C) to ^{137}Cs feed concentration (C_0) is profiled with the dejacketing solution throughput.

A summary of the breakthrough results from column runs with effective RF resin is displayed in Table 4.

Fig. 4. Cesium loading profiles of the two in-cell runs and the bench-scale test.

The initial breakthrough point for the three runs is in the range of 85–92 CV. The first in-cell run (M5-RC-EXP1) reached only a 17.7% breakthrough point due to an excess of resin. The second in-cell run (M5-RC-EXP2) used a larger volume of feed material and exhibited a fully developed breakthrough curve similar to that in the bench-scale run (SRS-B-2). The SRS-B-2 and M5-RC-EXP2 runs reached the 50% breakthrough point at ~110 CV. The K_d values for the M5-RC-EXP2 in-cell run and the SRS-B-2 bench-scale run were based on the 50% breakthrough point and found to be 283 and 237 mL/g, respectively. The resin capacities for SRS-B-2, M5-RC-EXP1, and M5-RC-EXP2, based on the amount of Cs eluted from the column, were found to be 0.33, 0.35, and 0.36 meq/g, respectively. The resin capacity for the SRS-B-2 and M5-RC-EXP2 runs was also calculated based on the 50% breakthrough point run and resulted in similar values of 0.35 and 0.32 meq/g, respectively.

Table 4. Summary of the Cs breakthrough results for the bench-scale and in-cell tests

Run no.	^{137}Cs feed conc. (Bq/mL)	Superficial velocity (cm/min)	Residence time (min)	Initial break-through (CV)	50% break-through (CV)	K_d (mL/g)	Resin capacity for Cs (meq/g)
SRS-B-2	1.8×10^3	0.6	16.5	~85	109.8	237	0.35
M5-RC-EXP1	2.6×10^8	2.1	17.3	~88			0.35
M5-RC-EXP2	3.3×10^7	1.8	20	~92	109.2	283	0.36

Figure 5 profiles the stripping data from the in-cell runs M5-RC-EXP1 and M5-RC-EXP2. The resin was stripped with a 2 M HCl solution. Samples were pulled as the strip solution exited the column. Due to an erratic flow, caused by siphoning at the start of the M5-RC-EXP1 run, the Cs elution peak went undetected; however, a complete elution profile was obtained during the M5-RC-EXP2 run. The highest Cs concentrations were found as 1–2.5 CV of the strip solution passed through the resin bed, indicating that the vast majority of the material is actually removed from the resin in less than 3 CV. The stripping operation was completed after 15–16 CV of strip solution passed through the column.

Fig. 5. Cesium concentration profiles during the elution process.

The Cs stripping data revealed that the 1.5-L resin bed was loaded with 1130 Ci of ^{137}Cs and 146.9 Ci of ^{134}Cs during M5-RC-EXP1 and 1160 Ci of ^{137}Cs and 141 Ci of ^{134}Cs during the M5-RC-EXP2 run. Based on the stripping data, the resin loaded 27.6 g of Cs during M5-RC-EXP1 and 28.4 g of Cs during M5-RC-EXP2. Mass loadings of Cs were calculated using a specific activity value for ^{137}Cs of 40.9 Ci/g that was obtained from ORIGEN code calculations. The material balance for the M5-RC-EXP1 run resulted in an output-to-input ratio of 105% and 104% for ^{137}Cs and ^{134}Cs , respectively. The material balance for the M5-RC-EXP2 run revealed an output-to-input ratio of 102% and 101% for ^{137}Cs and ^{134}Cs , respectively.

Evaluating the efficiency of the stripping operation was done by examining how much Cs was left on the resin after the M5-RC-EXP2 stripping operation had been completed. Two ~1-g resin samples were pulled from the column, air dried, and then dissolved in ~100 mL of 6 M HNO_3 . Analyses of the samples are listed in Table 5.

Table 5. Residual radioactivity remaining on the resin column after stripping with HCl

ID no.	Resin weight	^{137}Cs	^{134}Cs
MS-76	0.87 g	4.45 E+6 Bq/g	5.29 E+5 Bq/g
MS-76	0.88 g	4.66 E+6 Bq/g	5.65 E+5 Bq/g
Avg.	0.875 g	4.56 E+6 Bq/g	5.47 E+5 Bq/g
In-cell resin bed	580 g	7.45 E+10 Bq/g	8.95 E+9 Bq/g

The data from the two resin samples indicate that very little Cs was left on the bed after stripping. The percentage of ^{137}Cs and ^{134}Cs remaining on the resin was found to be 0.006% of the material loaded on the resin bed, based on the amount of Cs stripped from the resin bed and the residual Cs remaining on the resin after stripping. This analysis indicates that essentially all the Cs was removed during the stripping operation.

Sample analysis of the column loading samples also indicated that ^{90}Sr was initially loading on the resin. Figure 6 is the loading profile for ^{90}Sr . The initial ^{90}Sr breakthrough point is located at ~20 CV. Additional ^{90}Sr did not significantly load on the resin after the 50% Cs breakthrough point was reached at 110 CV.

4.4 BED REGENERATION

After stripping Cs from the column, which converts the resin back to an H^+ form, the resin was stored in the column under water until it was regenerated back to a Na^+ form. Regenerating the resin was always performed just prior to resin reuse in subsequent Cs loadings using an upflow path through the column. The regeneration process consisted of washing the resin bed with 4 CV of water to sweep away any remaining strip solution and to fluidize the resin for maximum liquid-to-surface contact. The resin was then converted to the Na^+ form by passing ~12 CV of 2 M NaOH through the resin bed. The last 3 CV of the caustic wash

Fig. 6. Loading profile of ^{90}Sr on resin bed during in-cell run.

was introduced using downflow. The resin remained in the caustic wash for ~18 h before loading to ensure that the resin was fully converted to the Na^+ form. During the stripping process the resin underwent a 45% decrease. Converting the resin back to the Na^+ form resulted in the resin bed returning to its original 1.5-L volume.

4.5 MASS TRANSFER

Rigorous treatment of this system must account for the nonlinear sorption of Cs under the experimental conditions. This requires both extensive equilibrium data and a numerical solution of the defining differential equations. A more empirical approach was employed that strictly compared rate parameters of the three tests and then used the parameters to estimate the mass transfer coefficient (k) and the height of a transfer unit (HTU).

First, the slope at 50% breakthrough was calculated based on dimensionless coordinates:

$$\text{Slope @ 50\% breakthrough (BT)} = \left(\frac{\partial x}{\partial T} \right)_{C/C_0 = 0.5},$$

where x is the concentration ratio of the input to output at 50% breakthrough, and T is the throughput parameter, given as the ratio of resin bed volume to the number of bed volumes of solution passed through the resin bed at the 50% breakthrough point as shown in the following equations:

$$x = C/C_0,$$

$$T = \frac{CV}{CV @ 50\% BT}.$$

The number of theoretical transfer units is calculated based on the shape of the breakthrough curve at 15.9% and 50%. The method gives the total number of transfer units in the column as described by Glueckauf and shown in the following equation:

$$N = \frac{(V_{0.5})(V_{0.159})}{(V_{0.5} - V_{0.159})^2},$$

where $V_{0.5}$ = throughput (number of CV at 50%) and $V_{0.159}$ = throughput (number of CV at 15.9%).

Another method of calculating the number of theoretical plates based on the midheight slopes is suggested by Thomas, Gilliland, and Baddour.²¹ The equation, which follows, is based on the constant-pattern region of a favorable isotherm:

$$\left(\frac{\partial x}{\partial T} \right)_{0.5} = \frac{(1 - R)N}{4} .$$

Rearranging the equation allows N to be calculated as

$$N = 4 \frac{\left(\frac{\partial x}{\partial T} \right)_{0.5}}{(1 - R)} ,$$

where the variable R is a scaled separation factor for component A at trace levels ($x_A \ll 0.1$). The variable R is calculated as follows:

$$R = \frac{1}{1 + (x_A)_0 (1/r - 1)} .$$

The variable r is a normal separation factor based on the fluid and solid concentrations as shown in the following equation:

$$r = \frac{x_A (1 - y_A)}{y_A (1 - x_A)} ,$$

where x is the concentration of A in fluid and y is the concentration of A on resin.

The following equation was then used to determine the mass transfer coefficient based on the average number of theoretical transfer units:

$$N \equiv k \cdot K_d \cdot \left(\frac{v}{f} \right) ,$$

where k is the mass transfer coefficient and the residence time (v/f) is the ratio of the resin bed volume to the volumetric flow rate. Rearranging this equation allows the transfer coefficient to be determined as follows:

$$k = \frac{N}{K_d \cdot \left(\frac{v}{f} \right)} .$$

The rate parameters and the resulting mass transfer coefficient are shown in Table 6. The various methods for estimating N all gave about the same result (within a 16% difference), so an average N was reported and used to determine the mass transfer coefficient (k).

Table 6. Mass transfer coefficient estimates for the laboratory column and the in-cell column

Experiment	Feed [Cs] (mM)	Superficial velocity (cm/min)	K_d (CV)	Slope at 50% breakthrough	Average N	HTU (mm)	k (h^{-1})
SRS-B-2 Bench-scale	1.5	0.6	109.8	7	218.3	0.5	7.2
M5-RC-EXP2 In-cell	1.3	1.8	109.2	4.6	158.8	2.9	4.4

The superficial velocity of M5-RC-EXP2 was based on an average loading rate of ~ 3 CV/h; however, controlling problems associated with siphoning and sampling would not allow a constant loading rate to be sustained over the loading period. The values of dx/dT , N , and k seem reasonable given the difference between laboratory and cell conditions. The derived HTU values are suspect and likely reflect the asymptotic nature of constant-pattern sorption behavior.

The one in-cell demonstration along with a bench-scale test does not offer enough data to study the kinetics of the system. Several system tests, in which a fully developed breakthrough curve is established, would be needed to gain a better understanding of the system's kinetics.

5. CONCLUSIONS

Preliminary batch shake tests and bench-scale column tests were used to design an in-cell cation-exchange column. The in-cell column used a resorcinol-formaldehyde resin to remove Cs from the de jacketing waste solutions generated during the processing of Mark 42 targets at the REDC. The resin proved to be highly Cs selective in the alkaline waste solutions.

A 1.5-L RF resin bed (wet) averaged loading ~ 1300 Ci of radioactive Cs and ~ 30 g of total Cs isotopes. An initial Cs breakthrough occurred as 85–92 CV of alkaline waste passed through the resin bed. The 50%

breakthrough point was 110 CV and resulted in a distribution coefficient (K_d) of 283 mL/g. A Cs loading capacity of 0.35 meq/g was achieved with the $1.5\text{E-}03\text{ M}$ Cs concentration in the dejacketing solution.

The Cs was stripped from the resin bed using 15 CV of 2 M HCl solution with the majority of the Cs being removed as the first 5 CV of strip solution passes through the column. Analysis of the resin bed after stripping revealed that greater than 99.9% of the Cs was removed after 15 CV of strip solution passed through the resin bed.

Based on the in-cell demonstrations, the goal of conserving tank space and enhancing the operational capability of the facility could be achieved by employing a 3- to 3.5-L RF resin bed. Conservatively, 2-3 Mark 42 target segments could be processed before needing to strip the Cs from the resin. The Cs could then be concentrated into ~15 CV (ideally) by stripping the resin bed. The concentrated Cs solution could then be held for further processing or delivered to a storage/waste facility as time permitted.

Trucking of waste from REDC requires that the radiation levels of the main REDC waste be lowered. Since ^{134}Cs and ^{137}Cs are the largest gamma emitters in the alkaline waste, using the cation-exchange column to remove Cs will help make it possible to truck the waste from REDC should it become necessary.

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