Removal of Cesium from Savannah River Site Waste with Spherical Resorcinol Formaldehyde Ion Exchange Resin: Experimental Tests

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A principal goal at the Savannah River Site (SRS) is to safely dispose of the large volume of liquid nuclear waste held in many storage tanks. In-tank ion exchange (IX) columns are being considered for cesium removal. The spherical form of resorcinol formaldehyde ion exchange resin (sRF) is being evaluated for decontamination of dissolved saltcake waste at SRS, which is generally lower in potassium and organic components than the Hanford waste. The sRF performance with SRS waste was evaluated in two phases: resin batch contacts and IX column testing with both simulated and actual dissolved salt waste. The tests, equipment, and results are discussed.

INTRODUCTION

Removal of cesium from stored liquid waste at the Savannah River Site (SRS) will be performed on a large scale by solvent extraction at the Salt Waste Processing Facility. To support tank closure requirements at SRS and Hanford, a more immediate need exists to treat salt waste. To address this potential, another separation technology is under investigation that would allow in situ treatment of stored waste called Small Column Ion Exchange (SCIX). The word "small" is relative because a column may be as tall as 6 meters and 0.6 meter in diameter. "Small column" is a column small in comparison with an industrial sized column; therefore, it can completely fit inside the SRS waste storage tanks approximately 11 meters deep.

The resin under study was designed by the Savannah River National Laboratory (SRNL) (1) to remove cesium from highly alkaline wastes, including the radioactive ^{137}Cs, which makes up about 25% of the total cesium. The resin is a resorcinol ($C_6H_6O_2$) formaldehyde (CH_2O) polymer and is referred to as RF. This resin has a strong preference for H^+ and can be eluted by using acid to remove Cs^+ and its competitors. Its relative affinities have

been estimated (2) to be $H^+ > Cs^+ > Rb^+ > K^+ > Na^+$. RF resin can withstand multiple cycles of loading and eluting before its usefulness is exhausted. The original form of RF resin contained ground shards. These sharp-edged and irregular shaped resins resulted in significant flow resistances and inconsistent results as shards cracked and broke down creating fines, as seen with CST (3) and SL-644 resins[1] (4,5). Because of the poor hydraulic performance of the resin in shard-form, the RF resin was improved during work for the Waste Treatment and Immobilization Plant (WTP) of the DOE River Protection Project (RPP) being built at the Hanford Site in the state of Washington. The RF resin was deposited on the surface of microspheres by Microbeads AS, in Skedsmokorset, Norway, leading to much better and consistent flow performance (4–6). In its spherical form the RF resin is referred to as sRF (Fig. 1).

Considerable research has been conducted both computationally and experimentally with sRF on radioactive alkaline wastes; however, most of those studies have been limited to wastes stored at the Hanford Site (4,7–9). At least one significant difference between some of those wastes is the concentration of potassium. As mentioned above, potassium is a competitor of cesium for sites on the sRF resin so its presence will affect loading performance. In general, SRS wastes have lower concentrations of potassium ≤ 0.02 M (Table 1) as compared to some Hanford Site wastes[2]; that is, experimental data of sRF performance with SRS wastes are needed.

To better baseline existing IX models this study chose a combination of experiments to develop the necessary database. The first important selection was the SRS waste to use among the current five tanks under consideration for closure (Table 1). Of those, Tank 2F was chosen based

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[1]CST and SL-644 are two cesium specific IX resins. CST is a Crystalline Silicotitanate resin trademarked as IONSIV® IE-911 by UOP LLC, and SL-644 is trademarked as SupLig®-644 by IBC Advanced Technologies Inc.

[2]The concentration of potassium in seven Hanford wastes of one study (10) indicated an average of 0.2 M while 0.74 M has been reported for Hanford Tank 241-AP-101 (7).
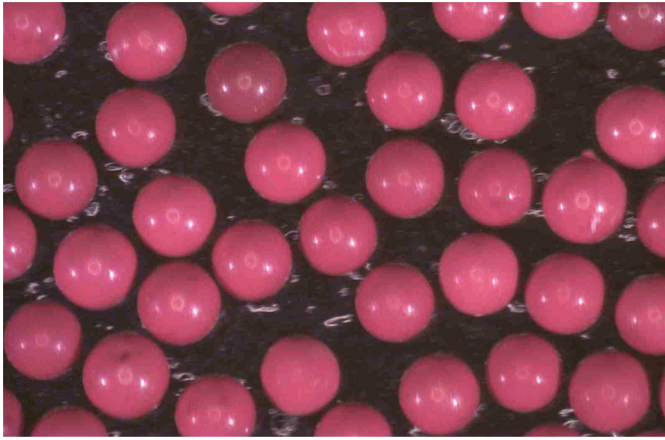
FIG. 1. Spherical resorcinol formaldehyde resin beads in H-form (diameter ~400 microns).

on its low concentration of potassium among other reasons (e.g., the chemical makeup well represented other tanks of concern and the availability of a Tank 2F stimulant). The experiments performed involved batch contacts and small column tests with "small," in this case, meaning a resin bed height of approximately 6.5 cm and diameter of approximately 1.5 cm.

Batch contacts join IX resin, that starts at some known state, with a solution to treat until both come to equilibrium. These tests are used to study a large range of parameters; e.g., temperature, concentrations of Cs, Rb, K, fundamental to benchmark resin models. However, a solution processed through an IX facility generally never comes to an ionic equilibrium with the IX resin; therefore, it is fundamental to have prototypic IX conditions to determine the actual treatment efficiency in IX columns. Moreover, once the resin is fully loaded, it must be eluted and regenerated for further use, meaning the regeneration process must be understood before designing a full-scale unit. The regeneration process with sRF was perfected using Hanford Site wastes (4) and was incorporated into the present IX column tests. To evaluate the flow through resin columns, the models (2) studied the effect of temperatures (i.e., 25°C, 35°C, 45°C) and found that as the temperature increased, cesium loading decreased; therefore, the lower temperature was selected. The models further evaluated waste treatment at flowrates (in terms of resin bed volume [BV]) of 0.7 BV/hr, 1.4 BV/hr, and 2.8 BV/hr. The resin was found to be more effective at the slower rates, but it takes longer to treat equivalent volumes. For this study the middle flowrate of 1.4 BV/hr was chosen.

The other important feature selected for the column tests was the intended lead-lag design where the lead IX column does most of the cesium separation with the lag column, connected in series, capturing cesium that leaves the lead column once the lead column approaches saturation.

TABLE 1
Characteristics of selected SRS stored waste considered for treatment

Species	Unit	Dissolved saltcake compositions (1)				
		Tank 1F	Tank 2F	Tank 3F	Tank 37H	Tank 41H
Na^{+1}	M	6	6	6	6	6
NO_3^{-1}	M	3.07	4.19	4.60	2.26	2.42
NO_2^{-1}	M	0.30	0.15	0.29	0.74	0.69
OH^{-1}	M	1.41	0.76	0.55	1.97	1.81
AlO_2^{-1}	M	0.30	0.29	0.06	0.35	0.34
CO_3^{-2}	M	0.18	0.13	0.08	0.11	0.13
SO_4^{-2}	M	0.25	0.03	0.10	0.15	0.15
PO_4^{-3}	M	0.003	0.005	0.003	0.01	0.01
Cl^{-1}	M	0.03	0.003	0.01	0.03	0.03
F^{-1}	M	0.06	0.003	0.025	0.03	0.03
K^{+1}	M	0.02	0.007	0.002	0.01	0.01
Cs^{+1}	M	181.0E-6	17.0E-6	63.5E-6	108.0E-6	7.5E-6
Sr^{+1}	M	308.0E-6	308.0E-6	164.0E-6	3.0E-6	3.0E-6
Rb^{+1}	M	21.9E-6	6.3E-6	21.9E-6	11.8E-6	2.6E-6
Physical properties at 25°C (2)						
Density	g/mL	1.240	1.246	1.245	1.232	1.234
Viscosity	cP	2.39	2.14	1.83	2.59	2.54

(1) Values were taken from (11); (Table 4).
(2) Values were calculated with software by OLI Systems, Inc (2).

At some design level of saturation the waste treatment will be stopped, ending one cycle of operation. To begin the next cycle, the lead column is regenerated and then moved to the lag position. The partially loaded lag column is moved to the lead position and the process repeats.

EXPERIMENTAL WORK
Resin History and Handling

The spherical RF ion exchange resin (Fig. 1) was purchased from Microbeads AS and shipped in acid form. The sRF resin has been stored in hydrogen form under deionized water in sealed large metal drums since 2005. This study employed material that had not previously seen pretreatment or use and was procured for large-scale column work (4). Before use the elutable SRF resin needs pretreatment, done to an existing specification (12). That pretreatment includes converting the resin to sodium form and then back to hydrogen form. The process swells, shrinks, and cleans the resin.

Simulant Solution

Before subjecting the IX test rig to radioactive waste, a considerable amount of information can be obtained by testing with a non-radioactive simulant. A simulant test aids in perfecting the test matrix along with understanding and refining the operation of the test equipment and resin performance. Furthermore, radioactive testing is expensive, which could be minimized with effective simulant testing.

A simulant of the waste targeted for testing, Tank 2F, was made to the composition in Table 1 (2). Table 2 shows

that the simulant compared well to the actual waste, especially for the important species; e.g., Na, Cs, K, and OH, which affect loading of the RF resin and test its effectiveness.

All measured values are accurate to $\pm 10\%$ with the exception of ICP-MS, used to determine cesium concentration and estimated at $\pm 20\%$. The cesium in the non-radioactive simulant is all ^{133}Cs. In real waste approximately 25% of the cesium content is made of ^{137}Cs; however, the RF resin does not distinguish between the different isotopes.

Radioactive Dissolved Salt Solution

Two volumes of the dissolved radioactive salt solution were prepared in the course of this work. The first volume was made and all radioactive batch contact work drew from it. After the batch contact work was complete, a larger volume was needed for the radioactive IX column test; therefore, additional stored liquid wastes were added to what remained of the first volume. Because of the additions, the new, larger volume of radioactive solution had a slightly different composition. For both volumes the chemical compositions are shown in Table 2 and the radiochemistry is shown in Table 3. Table 2 also shows that the two radioactive solutions were very similar to each other, as well as to the simulant, which were all similar to the target Tank 2F waste, Table 1.

Spherical Resorcinol Formaldehyde (sRF)

To reiterate, the new sRF resin beads come in acid form (H-form), Fig. 1, ready to be regenerated to sodium form

TABLE 2
Chemical components for waste used for tests

Species	Unit	Tank 2F simulant: Column test	SRS tanks real waste: Batch tests	SRS tanks real waste: Column test
Na^{+1}	M	6.26	6.18	6.05
NO_3^{-1}	M	4.94	3.42	3.53
NO_2^{-1}	M	0.171	0.187	0.174
OH^{-1}	M	0.8	0.714	0.81
Total OH	M	1.39	1.53	1.47
SO_4^{-2}	M	0.033	0.131	0.119
PO_4^{-3}	M	<0.01	NA	0.007
Al	M	0.32	0.382	0.32
F^{-1}	M	<0.013	<0.13	<0.013
K^{+1}	M	0.0076	0.0078	0.0083
Cs^{+1}	M	1.69E-05	2.71E-05	2.51E-05
P	M	0.0053	0.0097	0.011
S	M	0.037	0.164	0.129
pH	–	14	14	14
density (25°C)	g/mL	1.306	NA	1.300

TABLE 3
Radiochemistry for waste used for tests

Isotope	Unit	SRS tanks real waste: Batch tests	Major isotope	SRS tanks real waste: Column test	Major isotope
Cs-137	dpm/mL	1.35E + 08		1.31E + 08	
Sr-90	dpm/mL	1.03E + 04		NA	
Pu-238	dpm/mL	2.90E + 04		2.79E + 04	
Pu-239/240	dpm/mL	2.50E + 02		5.82E + 02	
Pu-241	dpm/mL	<1.95E + 04		<1.62E + 03	
Mass 59	μg/L	NA	NA	246	Stable Co
Mass 95	μg/L	2290	Mo	1690	Mo
Mass 99	μg/L	2330	Tc-99 (1)	1820	Tc-99 (3)
Mass 133	μg/L	2550	Stable Cs	2410	Stable Cs
Mass 137	μg/L	799	Cs-137 (2)	718	Cs-137 (4)
Mass 235	μg/L	<150	U-235	72.5	U-235
Mass 237	μg/L	<100	Np-237	13.8	Np-237
Mass 238	μg/L	<1350	U-238	4590	U-238

(1) This mass would be 8.77E + 04 dpm/mL Tc-99.
(2) Cs-137 gamma activity implies 699 ug/L.
(3) This mass would be 6.85E + 04 dpm/mL Tc-99.
(4) Cs-137 gamma activity implies 678 ug/L.
NA = not available.

(Na-form) in preparation to remove cesium from a waste. The new beads in H-form have a diameter of approximately 388 microns. While in sodium form the beads expand to approximately 450 microns.

For the batch contact tests a small amount of resin was mixed with waste to come to equilibrium, but for the column tests two IX columns were filled with resin that would be employed in series. The target resin bed height,[3] in each column was 6.5 cm to compare to other tests (7,8). Because the columns had an inside diameter of 1.435 cm, leading to a flow area of 1.617 cm^2, the target bed volume was 10.5 mL. The actual resin bed heights turned out to be an average of 10.6 mL for the simulant phase of the test and 11.2 mL for the real waste phase. All column work used the same two resin beds. A slightly taller bed height for the real waste phase resulted from the regeneration process, which causes the resin to shrink and swell. Specifically, sRF shrinks approximately 20% during acid elution and then swells back to its full sodium-form size during alkaline regeneration; however, slight differences in bed height are always present and in fact the height tends to increase with the number of cycles (8) (see section 3.2.4).

Batch Contact Tests

Most batch contact work was performed in the SRNL Shielded Cells, and the batch bottles had 20 mL of radioactive liquid agitated at 175 rpm. The shaker oven maintained a temperature of $25 \pm 2°C$, but the actual temperature varied less than $25 \pm 0.5°C$. Because adsorption isotherms[4] are a strong function of temperature, this smaller temperature uncertainty is important. Moreover, the total cesium concentration is needed for the isotherm benchmarking; therefore, the predominant cesium isotopes of 133, 135, and 137 were measured. All other isotopes were not large enough to be significant.

At the time the resin was needed, for either a batch contact test or an IX column test, a sufficient quantity was drawn for the test and to determine its F-factor, the ratio of the mass of dry to moist resin. For each test, three aliquots of resin determined the F-factor to obtain an average value, and those aliquots were separate from the test aliquots because the drying process damages the resin, making it no longer usable. The drawn resin would first be put in a filter cup to remove most of the bulk water and then separated into aliquots. For example, Batch Set

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[3]This height is given for the Na-form of resin, which it has while treating waste. Once the resin is saturated with Cs ions, it undergoes elution in acid to remove those ions, which causes the resin to shrink. After elution, the resin undergoes alkaline regeneration during which it returns close to its original height.

[4]Adsorption isotherms are analytical models from chemisorption theory (14) developed to predict the amount of atoms or molecules (e.g., Cs) adsorbed on a surface. For this study that surface is of the sRF resin. Moreover, the word "isotherm" refers to adsorption being a strong function of temperature; therefore, models predict adsorption efficiencies at constant temperature.

1 had eight damp resin aliquots drawn: three were used to determine the F-factor and five were placed in 20 mL bottles to perform the batch contact test. Moist resin in the filter cup was mixed well whenever the aliquots were scooped out, and all aliquots were taken within a period of a few minutes. Batch bottles, sealed after the solution was measured, were purged with argon. The three F-factor aliquots were weighed into tared beakers and then dried to constant weight over several days at 50°C. The drying oven was evacuated to less than 90 torr absolute during drying times (13). The batch contact tests were done in five sets:

- Set 1 used dissolved saltcake, phase ratio of 99 mL/g, and real waste concentration of Cs.
- Set 2a used a mixture of simulant and dissolved saltcake, 24 mL/g phase ratio.
- Set 2b used dissolved saltcake, phase ratio of 23 mL/g, and real waste concentration of Cs.
- Set 2c used very low cesium by recycling liquid from the Set 1 test.
- Set 3 used non-radioactive simulant, phase ratio of 110 mL/g, and a very high concentration of Cs; i.e., more than seven times that of real waste.

Simulant and Real Waste Tests with Small-Scale Columns

Solutions for Regeneration

Resorcinol formaldehyde can be regenerated in situ by stripping (elution) it of cesium with acid, so that it can be reused. The process of cesium separation and then resin regeneration is a six-step process developed for RPP-WTP (4). These steps, collectively called a cycle, are in Table 4.

Six-step process summary:

- After the resin reaches its limit to remove Cs, treatment is terminated to begin regeneration.
- The process begins by flushing the resin bed with 5 BV of inhibited water; i.e., 0.1 M NaOH, which removes the waste and prepares the bed for neutralization by dropping the pH from 14 to approximately 12.
- After the waste is displaced, 5 BV for deionized water is used to further drop the pH in

preparation to receive acid and prevent the precipitation of solids.
- The resin now receives 30 BV of 0.5 M HNO$_3$ to remove Cs and prepare it for regeneration.
- The acid is followed by another 5 BV of deionized water to once again prepare the bed for a change in pH when it returns to sodium form.
- Finally, the resin is regenerated with 6 BV of 0.5 M NaOH.

Test Equipment

For both the simulated and real waste column tests the same equipment was used. The simulant phase was performed to perfect the test apparatus operation and to determine process time to obtain adequate waste treatment, leading to refining the test matrix for the subsequent radioactive phase. For both phases the resin was regenerated and reused. Figure 2 shows the general test setup that highlights the columns and flow logic for each of the two 2-cycle tests.

The columns were set up to operate in series with one column as the lead column and the other as the lag column. The rationale was to start the test with both columns loaded with freshly regenerated resin, ready to separate cesium from waste. Cycle 1 was to operate with Column 1 as the lead column and its effluent would continue on to the lag column, Column 2. Once the cesium concentration in the Column 1 effluent attained a set breakthrough point; e.g., 50%, 75%, or 100% of that of the feed stream cesium concentration, then the process would be stopped to regenerate Column 1. Once the lead column was regenerated, a second cycle would begin by switching the lag column, Column 2, into the lead position, while the lead column, Column 1, would be moved into the lag position. After the column switch, Cycle 2 would be performed, which mimicked the Cycle 1 operation; i.e., when the Column 2 effluent reached the breakthrough point, waste processing would stop so Column 2 could be regenerated, thus ending a 2-cycle test.

The target resin BV was between 10 mL and 11 mL. Since the inside diameter of the columns was 1.435 cm, this leads to a bed height of approximately 6 to 7 cm of

TABLE 4
Six-step cesium separation and resin regeneration

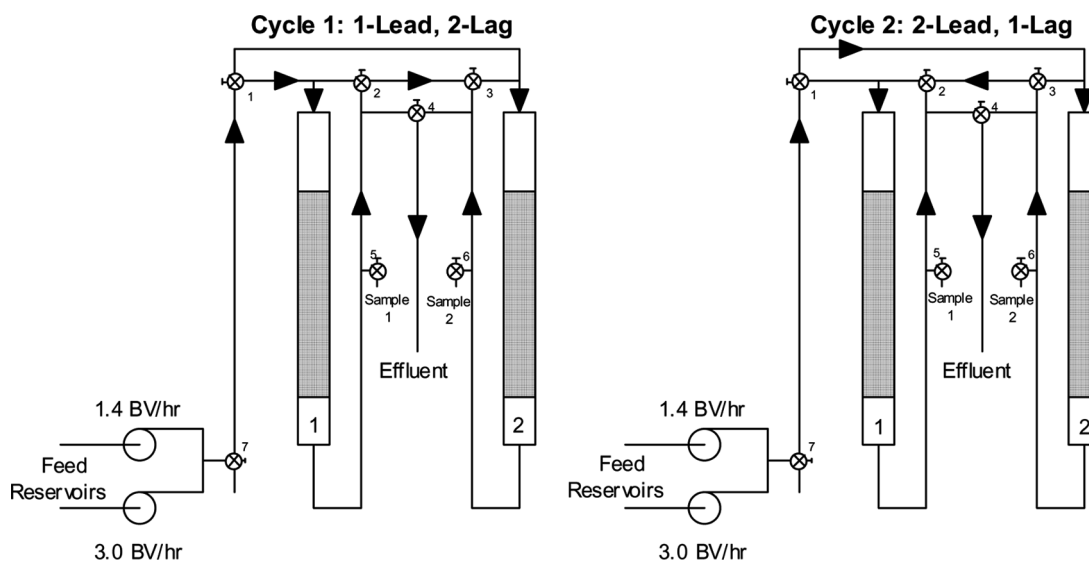| IX cycle step	Solution	Reason
1. Waste Treatment	Alkaline-based waste	Remove Cs
2. Waste Displacement	0.1 M Sodium Hydroxide	Prevent Al precipitation
3. Caustic Displacement	Deionized Water	Prepare for elution
4. Elution	0.5 M Nitric Acid	Strip resin of Cs
5. Acid Displacement	Deionized Water	Prevent Al precipitation
6. Regeneration	0.5 M Sodium Hydroxide	Prepare resin to receive Cs

FIG. 2.   Flow path schematic of two-column test rig in two-column operation.

Na-form resin or 5 to 6 cm of H-form resin. Once the resin screen was placed in the tubes to support the resin, approximately 2 cm of space was below the resin. A liquid freeboard of 2 cm was left above the bed.

To control the temperature of the resin bed a heating strip was wound around each of the columns to maintain the target temperature of $25°C \pm 2°C$ when ambient temperature was lower. For the simulant test phase the ambient temperature averaged at approximately $21°C$; therefore, the heater was useful. However, during the radioactive waste test phase the average ambient temperature was above $25°C$; therefore, cooling air was used to keep the temperatures of the columns below $27°C$. The temperature of liquid flowing through the columns was measured just under each of the resin bed screens by installed calibrated thermocouples.

Because of the very slow liquid flows through the test rig; i.e., a maximum of 0.55 mL/min, no significant pressure was expected. However, in the event of an accident; e.g., line pluggage, valve left closed, a pressure gauge was installed in the common discharge line of the two pumps. Figure 2 shows two pumps instead of a single pump because of two flowrates, 1.4 BV/hr (~ 0.25 mL/min) and 3.0 BV/hr (~ 0.55 mL/min). It proved much less labor intensive and more accurate having each pump preset with a flowrate.

Figures 3–5 show several aspects of the column test equipment. Testing was performed in a chemical hood because of the chemical hazardous nature of the waste simulant. Any released vapors from the chemicals were safely exhausted from the work area. Figure 3 shows the entire layout of the equipment during the non-radioactive test phase.
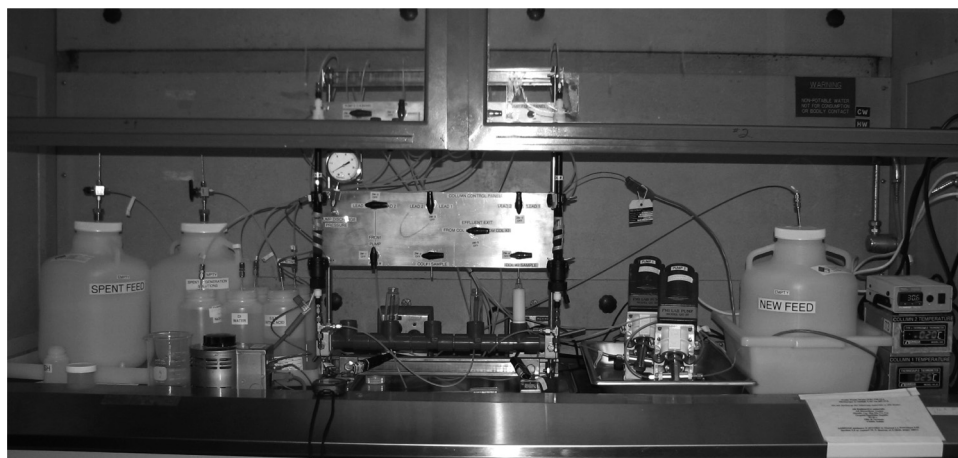

FIG. 3.   Test rig setup for the simulant test (The real waste test setup was similar.)
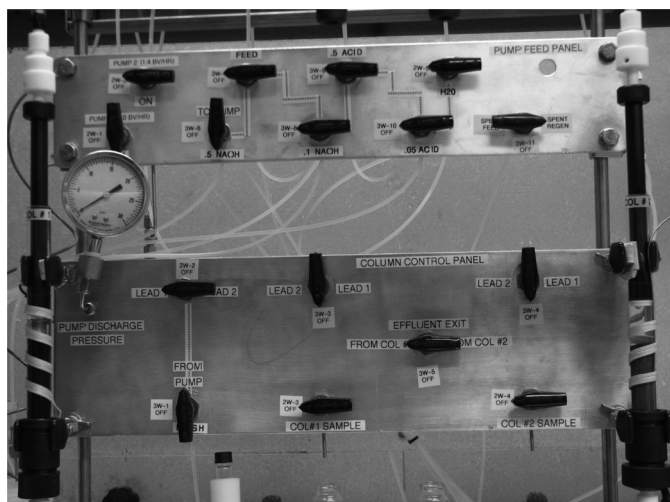
FIG. 4.   Close-up of valve panels with 2-way and 3-way valves.

In Fig. 3, the simulant (shown as NEW FEED) and effluent containers are on both sides of the columns. The pumps are to the right; Column 1 and Column 2 temperature indicators are to the right, above which is an over-temperature control unit to shut power to the strip heater if the temperature became too high. The transformer to control the strip heater is the unit in the forefront to the left of the test rig.

Figure 4 shows a close-up of the valve panels with the sixteen 2-Way and 3-Way valves. Those valves directed the solution through the resin beds and controlled the direction of the flow; i.e., a two-column operation with Column 1 in the lead, a two-column operation with Column 2 in the lead, or single-column operation, needed

FIG. 5.   SCIX test equipment during radioactive waste processing.

when regenerating a specific resin bed. Figure 4 also shows the control panels for the feeds and valves, the discharge pump pressure, and both IX columns. The lighter colored resin to the right had been eluted (i.e., in H-form) while the left column was just starting elution (i.e., still in Na-form and therefore darker in color).

Once simulant testing was completed, the equipment was moved to the SRNL Shielded Cells to begin the radioactive waste processing phase of the test. While the test equipment was exactly the same for this second phase of testing, its protective location made it much harder not only to view, because of the leaded glass, but also to operate, because of the remote manipulators. The valve panels can be seen in Fig. 5 during radioactive operation.

Test Matrix for the Column Tests

The IX Column test operation followed that of previous work (7,8) but in general the matrix was perfected as part of IX process testing for RPP-WTP (4). Plant operation will have many cycles of waste treatment and resin regeneration, but the current column tests had two equal cycles. The operation of one cycle was previously summarized as the six-step process before Table 4. For the current study, the baseline parameters used; e.g., number of BVs before cesium breakthrough, BV/hr, came from computational results of SCIX operation (2) with SRS waste. Prototypic aspects were: the chemical makeup of the waste, the flowrate in BV/hr, and the resin media itself; i.e., sRF. The smaller column size necessitated changing the superficial velocities through the columns and the absolute volumes in BV.

Ideally each pair of IX cycles, Cycles 1 and 2 for simulant and Cycles 1 and 2 for real waste, should have treated the same volume of waste before cesium breakthrough, but the ability of the resin to load cesium from a target waste was a principal variable under study. Computational modeling (2) indicated for waste contained in Tank 2F at SRS that a volume of 250 BV would be needed for the effluent of the lead column to reach a cesium concentration of 75% of the untreated waste. As such, 250 BV was the initial target volume to process but after stopping Cycle 1 at 276 BV to prepare for Cycle 2, the cesium concentration was slightly less than 5% of the untreated feed. Because the cesium concentration did not reach its intended target, the amount of simulant to treat with the Cycle 2 lead column, Column 2, was increased to more than 500 BV. Subsequently, the 525 BV actually processed was found to be more than sufficient to fully load the Cycle 2 lead column, Column 2. This information was useful to fine tune the amount of radioactive waste to be treated in the next phase of testing. For plant operation, the amount of waste to process for each cycle differs because after Cycle 1, Column 1 is regenerated while Column 2 is not. For Cycle 2, Column

2 becomes the new lead column and should reach saturation sooner because it starts with some cesium already preloaded from Cycle 1. For this study during the radioactive test phase, Cycle 1 was targeted to process 483 BV of feed and Cycle 2 lead column, 315 BV of feed. The actual amounts processed were slightly different as will be discussed.

RESULTS AND DISCUSSION
Batch Contact Results

Batch contact tests were performed in five sets to ensure that the experimental techniques were correct and to demonstrate equilibrium adsorption performance of the sRF resin under different conditions. Set 1, Table 5, examined only the batch contact time as a variable. Results did compare favorably with an improved SRNL "isotherm"[5] model.

Sets 2a, 2b, and 2c, Table 6, varied phase ratio and initial cesium level to provide additional points for comparison with model isotherms.

Set 3, Table 7, examined the effect of a high concentration cesium; i.e., 27 mg/L using the Tank 2F simulant at relatively high cesium and a constant phase ratio of 110 mL/g.

In Tables 5–7, the letters A and B in the first columns refer to replicates, and Q_{final} was calculated from dry hydrogen-form resin mass and the decrease in cesium concentration in the liquid phase. Post-contact resin was not analyzed because of the inability to separate residual solution and un-adsorbed cesium on the beads and in resin pores. The following calculation was used:

Q_{final} = (Batch liquid volume) ∗

(Initial − Final Cs batch concentrations)/resin mass

When volume is in mL, cesium concentrations are in molar (M), resin mass is in grams, and the units of Q_{final} are in mmol/g. The tables of batch contact results also provide resin loadings in units of mg (Cs)/g (dry hydrogen-form resin). Average cesium atomic weights, accounting for the mix of mass 133, 135, and 137 isotopes, were used for the interconversion between mass and moles.

Figure 6 shows the batch contact data appear linear on a log-log plot. In correlating those data, a prediction at the feed cesium level of 2.51E-05 M would be the resin can load to 4.0E-02 mmol/g of cesium. The mass resin on a dry hydrogen-form basis was determined to be 2.9061 g; therefore, the predicted adsorption capacity of the radioactive column test is 15.2 mg in the lead column of Cycle 1 and

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[5]"Isotherm" refers to a chemisorption model of ion adsorption and the improvement was to an existing model to better predict adsorption at low concentrations of cesium (2).

TABLE 5
Batch contacts with real dissolved saltcake: Set 1

Batch	Phase ratio mL/g	Initial Cs mg/L	Kd mL/g	Final Cs total, M	Q_{final} mg/g	Q_{final} mmol/g
24 hr	99.6	3.62	2850.	9.15E-07	0.348	2.60E-03
48 hr, A	99.1	3.62	3000.	8.65E-07	0.348	2.60E-03
48 hr, B	99.1	3.62	3240.	8.03E-07	0.348	2.60E-03
72 hr, A	99.2	3.62	3230.	8.07E-07	0.349	2.60E-03
72 hr, B	99.3	3.62	2650.	9.76E-07	0.347	2.59E-03

TABLE 6
Batch contacts with a mixture of real waste and simulant: Sets 2a, 2b, and 2c

Batch	Phase ratio mL/g	Initial Cs mg/L	Kd mL/g	Final Cs total Cs, M	Q_{final} mg/g	Q_{final} mmol/g
Set 2a:						
48 hr	23.6	2.56	3720	1.21E-07	0.0600	4.51E-04
Set 2b						
48 hr, A	23.0	3.62	4700	1.31E-07	0.0827	6.18E-04
48 hr, B	23.4	3.62	4810	1.31E-07	0.0845	6.31E-04
72 hr	23.3	3.62	5110	1.23E-07	0.0838	6.26E-04
Set 2c						
48 hr, A	66.5	0.1189	5370	1.09E-08	0.00781	5.83E-05
48 hr, B	64.4	0.1189	5370	1.05E-08	0.00757	5.65E-05
72 hr	63.9	0.1189	6480	8.67E-09	0.00752	5.61E-05

TABLE 7
Non-radioactive batch contacts: Set 3

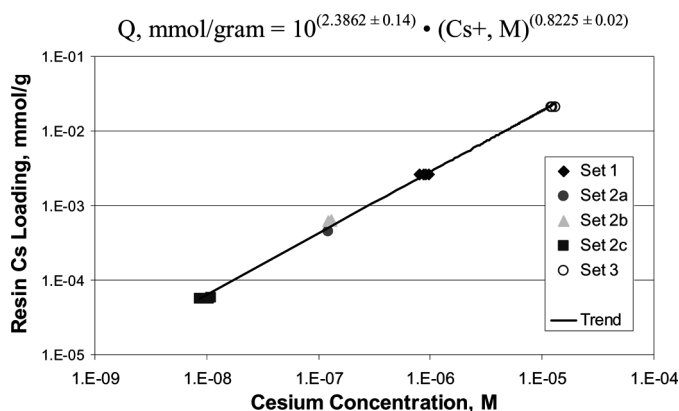| Batch	Phase ratio mL/g	Initial Cs mg/L	Kd mL/g	Final Cs total Cs, M	Q_{final} mg/g	Q_{final} mmol/g
48 hr	110	26.9	1710	1.2172E-05	2.7872	2.10E-02
72 hr, A	110	26.9	1679	1.2397E-05	2.7868	2.10E-02
72 hr, B	110	26.9	1563	1.3218E-05	2.7659	2.08E-02

FIG. 6. Batch contact data and a power law fit.

is 12.0 mg in Cycle 2, where the lead column had a preload of 3 mg of cesium. As will be seen from the column test results these values are close to the measured quantities. From Cycle 1, the measured adsorption was 12.5 mg of cesium or the measured desorption was 15.1 mg of cesium. From Cycle 2, the measured adsorption was 9.4 mg of cesium or the measured desorption was (16.1 mg − 3 mg) = 13.1 mg or cesium. The predictions are within the cesium measurement uncertainty of 20% (by ICP-MS) and compared well (<5%) to the desorption results.

A simple power law fit of the batch contact data provides the following equation.

$$Q, \text{ mmol/gram} = 10^{(2.3862 \pm 0.14)} \bullet (Cs+, M)^{(0.8225 \pm 0.02)}$$

Ion Exchange Column Work

Cesium Results with Simulated Waste

Approximately 2.9 liters (275 BV) for Cycle 1 and 5.6 liters (525 BV) for Cycle 2 of simulated Tank 2F feed were used to test the sRF resin performance during the non-radioactive phase of testing. Figure 7 shows both Cycles 1 and 2 treatment of SRS Tank 2F simulated waste.

As previously explained, Cycle 1 was stopped when the lead column effluent cesium concentration only reaching 4.4% of the feed concentration. However, the data in Fig. 7 do show that cesium began showing up in the effluent stream of the lead column just after 200 BV. Because of the minimum cesium breakthrough during Cycle 1, the Cycle 2 lead column, the lag column during Cycle 1, was basically a column of freshly regenerated sRF; therefore, the Cycle 1 lag column had an insignificant amount of cesium loading. Indeed, the cesium concentration in the effluent of the Cycle 2 lead column began showing measurable cesium after treating approximately the same volume

of feed; i.e., just before 250 BV. The transition from no cesium in the lead column effluent to a concentration equal to the feed was rapid and occurred within a span of approximately 150 BV. The steep breakthrough slope differed from the modeled behavior (2), which indicated that cesium should begin to show up in the lead column effluent at approximately 400 BV and reach a concentration maximum after 1000 BV. The data should be very useful to better benchmark the model.

After each cycle the resin in the lead column was regenerated. The regeneration process included resin elution by flowing 30 BV of 0.5 M nitric acid at 1.4 BV/hr. Figure 8 shows the overall results for both cycles of elution of the lead columns. The 30 BV of acid was used expecting a more spread out cesium desorption; however, for sRF resin with SRS wastes it appears the brunt of desorption starts at around 2 BV and is basically complete at around 6 BV.

To check on the mass balance of the cesium adsorbed to the cesium eluted, the elution masses were roughly estimated from the area under the curves in Fig. 8. For Cycle 1 the cesium recovered was 6.9 ± 0.7 mg and for Cycle 2, 6.7 ± 0.7 mg. Now, to obtain the cesium adsorbed, Table 2 shows the simulant cesium concentration, 2.25 mg/L (i.e., 1.69E-05 M). With the breakthrough curves data shown in Fig. 7, the cesium adsorbed can be estimated, and for the lead column during Cycle 1, it was 6.2 ± 0.7 mg and for Cycle 2, 7.6 ± 0.8 mg. Within measurement uncertainty, the masses balance.

Cesium Results with SRS Real Waste

Similar to the simulant test, the real waste test performed two complete IX cycles with the lead-lag column design previously explained. During the simulant test both cycles began with the lead column having freshly regenerated resin. This is not how the plant is designed to operate. However, the real waste test was conducted in the manner following the plant design. That is, the Cycle 2 lead column resin is not regenerated so that it would have a certain pre-load of cesium. This means, for the radioactive test phase, Cycle 1 began with same two columns of regenerated resin; i.e., using the same resin that was used for the
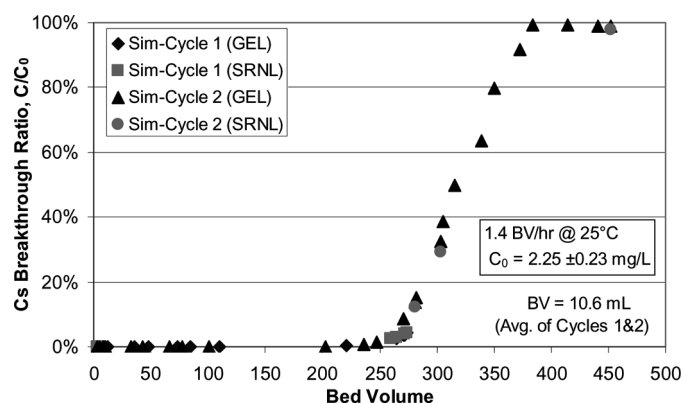

FIG. 7. Lead column effluent Cs for Cycles 1 and 2 with SRS Tank 2F simulant feed [GEL = GEL laboratories LLC and SRNL = data measured at the at SRNL].
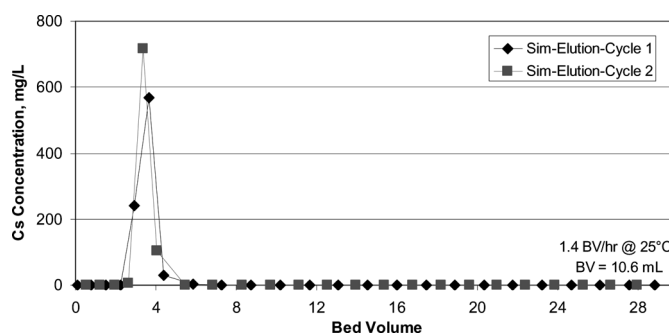

FIG. 8. Lead column Cs elution during Cycles 1 & 2 of the simulant test.

simulant phase, but for Cycle 2, once the lead and lag columns were switched, the new lead column, Column 2, would begin partially loaded.

Approximately 4.8 liters (~432 BV) for Cycle 1 and 3.7 liters (~329 BV) for Cycle 2 of actual SRS waste were used to test the sRF resin performance during the radioactive phase of testing.

Figure 9 shows the lead column results from both waste treatment cycles. The figure indicates the resin BV was 11.2 mL, slightly larger than the BV for the simulant test of 10.6 mL. The sRF resin beds were the same for both tests but after undergoing the bed shrinking and swelling which occurs during the regeneration process, the BV changed slightly.

Because the resin in the lead column of Cycle 2 had a pre-load of cesium, the breakthrough curve initiated earlier; i.e., just after 100 BV. This breakthrough volume is about 100 BV sooner than if the resin in the lead column had started a newly regenerated resin from Cycle 1. Once cesium is detected in the effluent, the slope of the breakthrough curve is identical to the curve for a freshly regenerated column of resin. That is, in Cycle 2, the cesium began to show up in the effluent at approximately 100 BV and attained 100% breakthrough at just before 250 BV. For Cycle 1, cesium began at 200 BV and ended at around 340 BV, resulting in a similar BV range of 140 BV to transition.

Before checking the mass balance of cesium adsorbed to cesium eluted, as was done for the simulant data, the difference between the two test phases need highlighting. Figure 9 shows for both cycles the lead column; i.e., Column 1 for Cycle 1 and Column 2 for Cycle 2, the effluent stream reached 100% breakthrough. Furthermore, the planned SCIX operation for Cycle 2 will not regenerate the new lead column. To estimate the cesium loading on the Cycle 1 lead column, the concentration of the cesium in the feed waste, 3.36 mg/L (i.e., 2.51E-05 M), was used. With the total Cs concentration and the data in Fig. 9, the cesium

adsorbed is estimated at 11.3 ± 1.4 mg. For the lead column of Cycle 2, the estimate is 8.6 ± 1.1 mg. In both cases, when a resin bed is taken to 100% breakthrough, approximately 85% of the cesium is adsorbed before showing up in the column effluent, and the remaining 15% is loaded onto the bed as it reaches saturation.

Now, assuming that both Columns 1 and 2 have the same capacity of cesium loading when starting from the same state of regeneration and as was estimated for the simulant test, then this assumption should be correct. Specifically, if the Cycle 2 lead column started with freshly regenerated resin, then it should be able to adsorb approximately 11.3 mg when operated under the same flow conditions. If so, the Cycle 2 lead column started with a cesium loading of $11.3–8.6 = 2.7 \pm 2.5$ mg or, in other words, was 24% preloaded. This preloaded value depends on when feed treatment stops after a certain level of breakthrough is realized. For the current test, after the Cycle 1 lead column effluent reached 100% breakthrough, the feed continued for another approximate 80 BV through the lag column. This means the lag column received another 3.36 mg/L $\times 80$ BV $\times 11.2$ mL/BV/1000 mL/L $= 3.0$ mg of cesium, which, when considering uncertainty, is the entire amount shown to be preloaded on the resin bed in the Cycle 1 lag column; i.e., 2.7 mg. This implies that if the treatment of the feed is stopped at, or slightly before, the point when the lead column effluent is at 100% breakthrough, then the lag column still has most of its capacity to adsorb cesium.

Once again, a mass balance can be made by determining the amount of cesium that was eluted from the resin during the regeneration process. The results are very similar to those seen in the preceding simulant phase of the test; that is, the majority, if not all, of the cesium elution occurred between 2 BV and 6 BV with a steep peak (Fig. 10).

For Cycle 1, the peak of cesium concentration occurred at approximately 3.5 BV. By 5.6 BV the effluent of Column
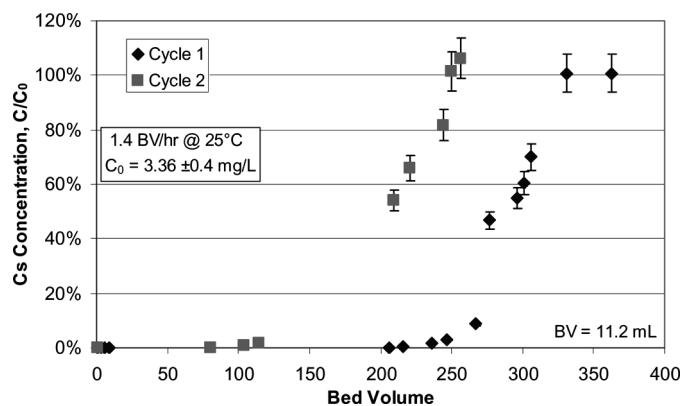

FIG. 9. Lead column effluent Cs for Cycle 2 with SRS real waste feed.
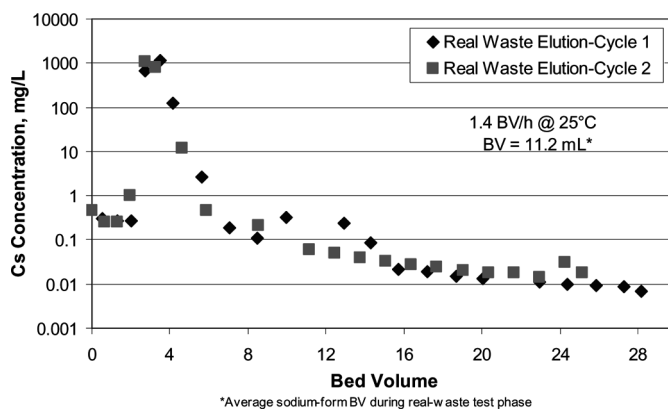

FIG. 10. Lead column Cs elution during Cycles 1 & 2 from the real waste test.

1; i.e., the Cycle 1 lead column that was regenerated, no longer had a significant cesium concentration. By roughly estimating the area under the curve, the cesium released during Cycle 1 elution was 15.2 ± 2.3 mg. The cesium recovered from Cycle 2 elution was estimated to be 16.1 ± 2.4 mg. While both estimates of the cesium recovered during elution are similar to each other, they are considerably higher than the Cycle 1 loading of 11.3 mg, even when considering the stated uncertainty of 1.4 mg. This discrepancy between the mass separated, and then recovered, indicates the difficulty in accurately estimating the cesium during adsorption, desorption, or both.

Not only was cesium recovered similar from both the Cycle 1 and Cycle 2 elutions, but also the overall elution results shown in Fig. 10 were similar. Both cycles began releasing cesium at 2 BV and nothing significant was detected after 6 BV. Further, both elutions showed similar peak concentrations; i.e., 1155 mg/L for Cycle 1 and 1102 mg/L for Cycle 2, well within the measurement uncertainty of $\pm 15\%$.

Figure 10 is shown in a semi-log format to illustrate the lower concentrations of cesium more easily detectable with the radioactive feed.

Comparison of Cesium Results: SRS Simulant versus Real Waste Tests

By utilizing a simulant strongly representative of the real waste in both its chemical and mechanical properties (Table 2), useful data were obtained for sRF resin performance. Figure 11 shows the three sets of data where the lead column started with freshly regenerated sRF; the data for Cycle 2 of the real waste test were not included because the resin was not regenerated before use. The results indicate that the simulant data represent the real waste data well and serve as a good substitute to radioactive waste testing.

As a reminder, no lag column data are shown because cesium was not detected from the lag columns for either cycle or test. This is even true for the lag column of Cycle 1 of the real waste test which received more than 80 BV of feed after the lead column effluent reached 100% breakthrough at 340 BV.

Cesium elution was similar for both tests as seen in the comparison in Fig. 12. The eluted cesium in the column effluent stream was normalized with the maximum cesium concentration of each respective stream. Since waste treatment through the lead column in Cycle 1 of the simulant test was stopped after reaching less than 5% breakthough, the sRF resin in the column was not fully saturated[6] and, therefore, is not shown in Fig. 12.

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[6]Saturation is a function of many variables; i.e., temperature, flow rate of feed, regenerated state of resin, life of resin, etc. Because this test maintained these parameters constant, a comparison can be made.
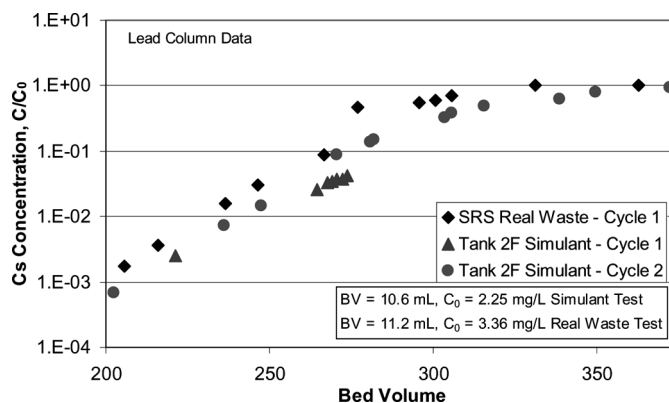

FIG. 11.   Cs loading for both the simulant and real waste tests.

Bed Changes Occurring during sRF Resin Elution

One of the well-known (6) aspects of elutable RF resin is its change in volume and color when undergoing the process of regeneration. When removing cesium with acid, the pH of the resin drops from 14 to 1 and its volume decreases. When the resin is regenerated with sodium, the pH returns to 14 and the volume returns to its full working size. This volume change has been between 20 to 25%. In the present study, the same results were elicited. At a flow-rate of 1.4 BV/hr, or, for this small scale, at a superficial velocity through the column of 0.15 cm/min, the total change in volume from the beginning to the end of the elution process was approximately 20% during the simulant test and 23% during the real waste test (Fig. 13). The elution time was just over 21 hours, but most of the volume change; i.e., greater than 90%, occurred during the first four hours, during which about 6 BV of acid passed through the resin bed. The "negative" BVs shown in the figure are the volumes processed in the beginning of elution, which is actually showing the tail end of the pre-elution rinse with deionized water. That is, when acid feed is initiated, the tubing leading to the column is still
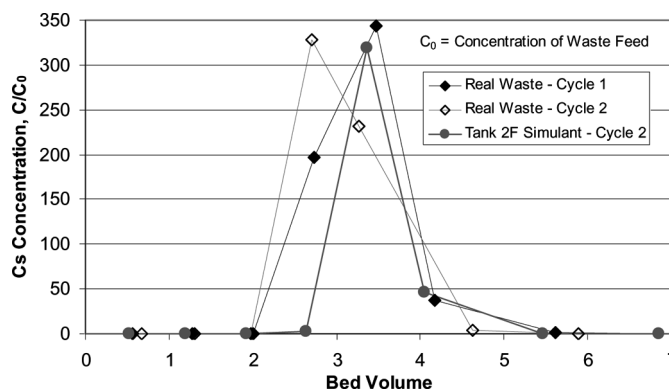

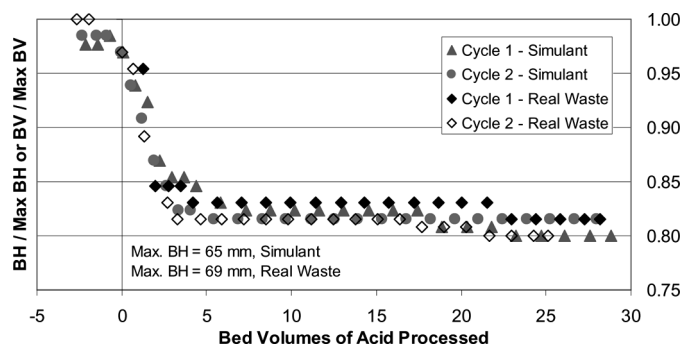FIG. 12.   Cs elution for both the simulant and real waste tests.

FIG. 13. Cs elution for both the simulant and real waste tests.

filled with the deionized water used to rinse out traces of any waste feed still present to prevent precipitation. Several BVs of acid are needed to clear out the tubing, thus between −5 and 0 BV in Fig. 13 are BVs of deionized water initially traveling through the resin bed. Even with water, the process of resin shrinkage begins as the pH drops from its value of 14. However, once the acid arrives, the bed height takes a precipitous drop.

The other sRF resin feature that changes during elution is its color. In sodium form the sRF resin has a dark burnt orange coloring, stable throughout waste treatment, but on elution the color changes. Once the acid reaches the resin, not only does it begin to shrink but also its stable burnt orange color begins to change to a bright orange. Figure 14 shows the color changing at several stages.

Most of this color change occurs sooner than the 6 BV during which cesium is removed concurrent with height changes. During the simulant phase of the test the speed of the color change was measured. Once the first few resin beads turned to bright orange, the rest of the column only took approximately 70 minutes to completely change. Since
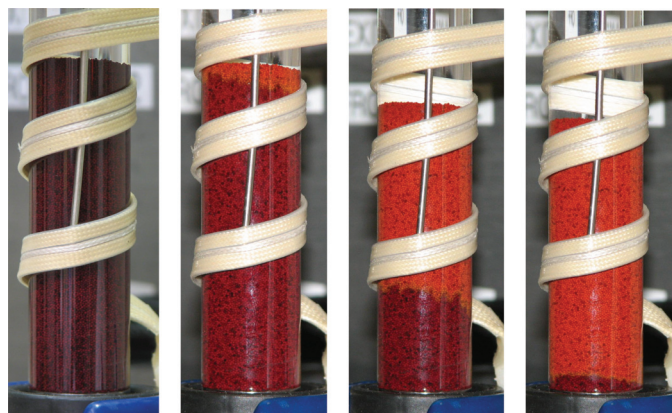
the resin bed with simulant started with a height[7] of 6.5 cm, this implies a velocity of 0.09 cm/min from the leading edge of the color wave. This velocity was slightly slower than the superficial velocity of the acid traveling through the resin bed, as was mentioned above to be 0.15 cm/min. This velocity difference is likely impacted by the kinetics of the proton exchange reaction.

CONCLUSIONS
Batch Contact Tests

- The sRF used for this work was shown to effectively adsorb cesium.
- The data were shown to be linear on a log-log scale.
- The sRF resin adsorption was predicted to be 15.2 mg of cesium as compared to 12.5 mg measured during adsorption or to the 15.1 mg during desorption in Cycle 1 of the column test with actual waste.
- The sRF resin adsorption was predicted to be 12.0 mg of cesium as compared to 9.4 mg measured during adsorption or to the 13.1 mg during desorption in Cycle 2 of the column test with actual waste. (This comparison considers the 3 mg of cesium preloaded onto the Cycle 2 lead column resin.)

Column Tests

For the sRF resin performance to remove cesium from SRS waste with a flowrate of 1.4 BV/hr at 25°C, the following were observed:

- The simulant and the actual waste results were equivalent demonstrating that resin performance can be accurately obtained with non-radioactive dissolved salt wastes.
- For the regenerated resin, breakthrough begins after processing between 200 and 250 BV and reaches 100% at around 400 BV. The slope of the data is approximately linear from about 5% to 100%.
- At initial breakthrough the sRF resin is at approximately 85% of its load capacity.
- Even when a lag column with some level of cesium pre-loading is put in the lead position, its breakthrough curve has approximately the same slope as the regenerated resin bed.

FIG. 14. sRF resin color and height shrinkage during elution as it changes from pH = 14 to pH = 1 [Approximate time progression from left to right: 0, 12, 45, 64 min].

[7]As noted in Fig. 14 and explained in the preceding paragraph, not only the color is changing, but the bed volume or bed height is changing, too. As the color interface moves along the resin bed, the bed's initial 6.5-cm height concurrently drops 80% to its final height of 5.2 cm by the time the color is completely changed.

- Most cesium desorption from the resin using 0.5 M nitric acid occurs from 2 to 6 BV and most, if not all, of the cesium adsorbed onto the resin is released during acid elution.
- During the sRF resin elution, the resin shrinks to about 80% of its fully working bed volume, or bed height, in sodium form as 0.5 M nitric acid is used to elute cesium that changes the pH from 14 to 1. Approximately 90% of the bed height shrinkage occurs during the first 6 BV of acid and stops completely at approximately 22 BV.
- During elution the resin changes color, from a burnt orange color, stable while it is sodium form, to a bright orange in hydrogen form. This color change occurs during the first 2 BV of acid processing. The color wave moves along the height of the resin bed at approximately 60% of the superficial velocity of the acid moving through the column.

ACKNOWLEDGEMENTS

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