

## Small-Column Ion Exchange Testing of Spherical Resorcinol-Formaldehyde – 11379

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### ABSTRACT

Ion exchange using the Spherical Resorcinol-Formaldehyde (SRF) resin has been selected by the U.S. Department of Energy's Office of River Protection (DOE-ORP) for use in the Pretreatment Facility (PTF) of the Hanford Tank Waste Treatment and Immobilization Plant (WTP) and for potential application in an at-tank deployment. Numerous studies have shown the SRF resin to be effective for removing Cs-137 from a wide variety of actual and simulated tank waste supernatants. Prior work focused primarily on the loading behavior for 5 M sodium (Na) solutions at 25°C and the eluting behavior of the loaded SRF resin with virgin 0.5 M HNO<sub>3</sub>. Recent proposed changes to the process baseline indicate that loading may include a broader range of sodium molarities (2 to 8 M) and higher temperatures (50°C) to alleviate post-filtration precipitation issues. In addition, elution will likely utilize variable-strength recycled nitric acid containing trace amounts of Cs-137.

Cesium ion exchange loading and elution curves were generated for a 5 M Na, 2.4E-05 M Cs loading solution traced with Cs-134 followed by elution with variable HNO<sub>3</sub> (0.02, 0.07, 0.15, 0.23, and 0.28 M) containing variable CsNO<sub>3</sub> (5.0E-09, 5.0E-08, and 5.0E-07 M) and traced with Cs-137. The ion exchange system consisted of a pump, tubing, process solutions, and a single, small (~15 mL) bed of SRF resin with a water-jacketed column for temperature-control. The columns were loaded with approximately 250 bed volumes (BVs) of feed solution at 45°C and at 1.5 to 12 BV per hour (0.15 to 1.2 cm/min). The columns were then eluted with approximately 25 BVs of HNO<sub>3</sub> processed at 25°C and at 1.4 BV/hr. The two independent tracers allowed analysis of the on-column cesium interaction between the loading and elution solutions. The objective of these tests was to improve the correlation between the spent resin cesium content and cesium leached out of the resin in subsequent loading cycles (cesium bleed) to help establish acid strength and purity requirements.

### INTRODUCTION

Ion exchange using the Spherical Resorcinol-Formaldehyde (SRF) resin has been selected by the U.S. Department of Energy's Office of River Protection (DOE-ORP) for use in the Pretreatment Facility (PTF) of the Hanford Tank Waste Treatment and Immobilization Plant (WTP) and for potential application in at-tank deployment [1]. Numerous studies at Hanford [2-6] and other DOE sites [7-10] have shown the SRF resin to be effective for removing Cs-137 from a wide variety of actual and simulated tank waste supernatants. Much of the prior work focused primarily on the loading behavior for 5 M sodium (Na) solutions at 25°C and the eluting behavior of the loaded SRF resin with virgin 0.5 M HNO<sub>3</sub>. Alternative elution methods and conditions have been reported [11, 12]. Recent proposed changes to the process baseline indicate that loading may include a broader range of sodium molarities (2 to 8 M) and higher temperatures (50°C) to alleviate post-filtration precipitation issues. In addition, elution will likely utilize variable-strength recycled nitric acid containing trace amounts of Cs-137.

## EXPERIMENTAL

The ion exchange column setup is based on prior work [3, 4] at the Pacific Northwest National Laboratory (PNNL). The current system (Figure 1, Figure 2) utilized water-jacketed columns (CHROMAFLEX®, Kimble-Chase, Vineland, NJ) with 2-cm internal diameter, variable-speed pumps (QVG50, Fluid Metering Inc., Syosset, NY), 1/16" i.d. Teflon® tubing, and various fittings, pressure-relief valves, pressure gauges, tube-in-tube heat exchangers constructed in-house, and 3-way valves ([www.swagelok.com](http://www.swagelok.com)). The resin bed was supported inside the column with a 100-mesh, stainless steel, screen tack welded to a stainless steel ring and fitted with a Viton® O-ring. Additional dead space between the screen and the column end fitting was filled with 3-mm glass spheres. The total volume of the system was approximately 42 mL from the solution reservoir to the sample vial. The sodium-form resin bed volume (BV) was ~15.7 mL.

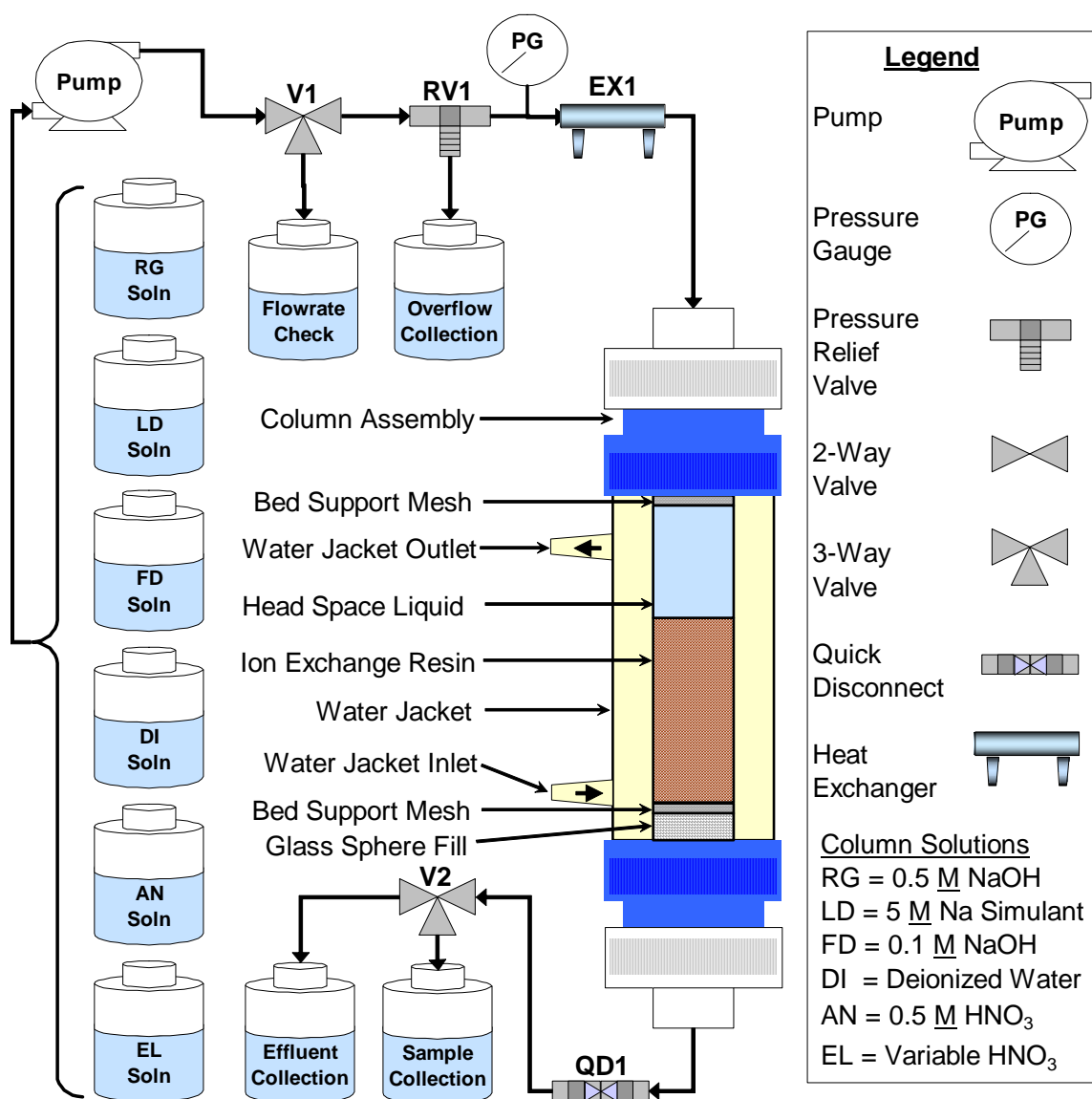


Fig. 1. Schematic of Small-Column Ion Exchange System

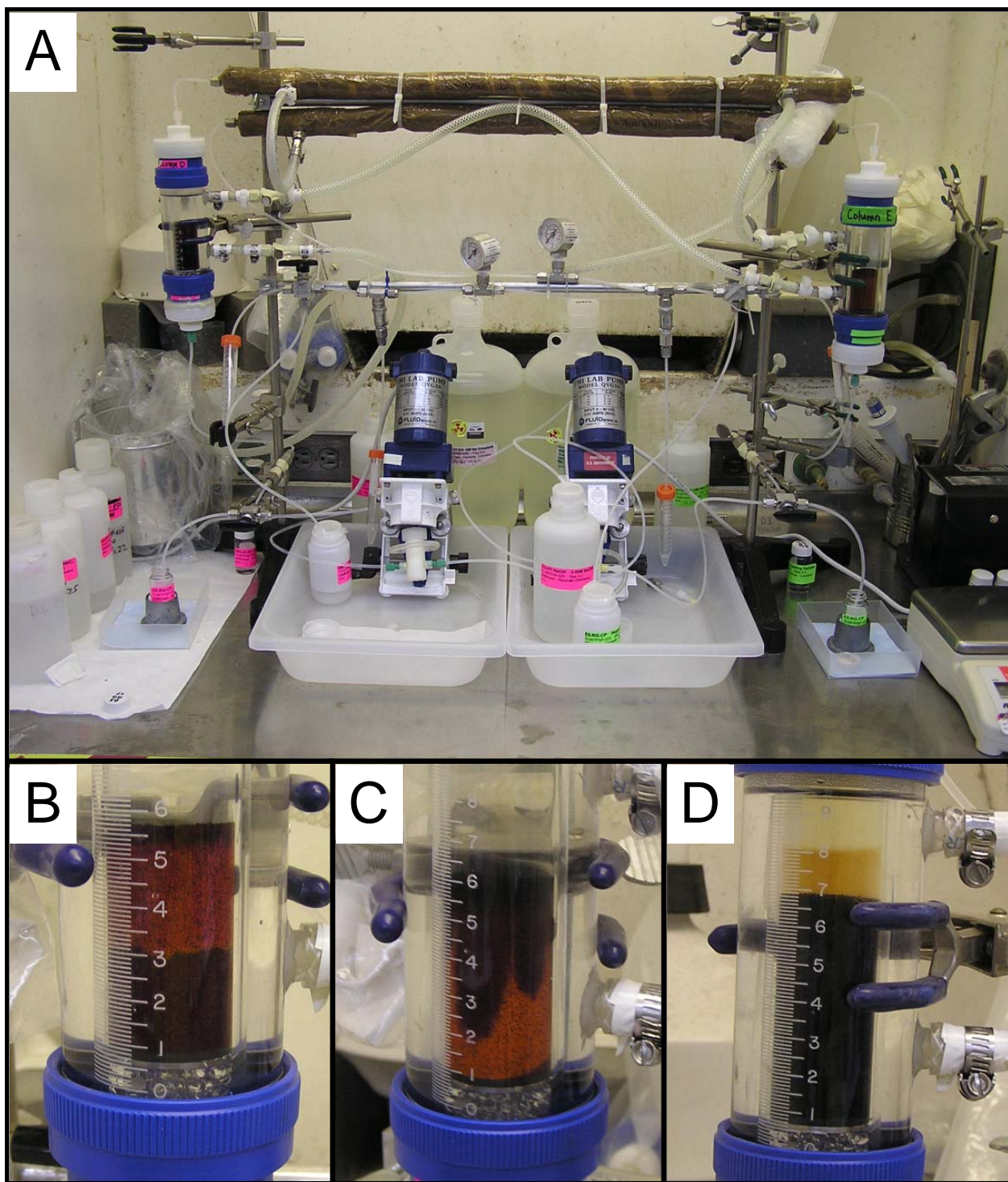


Fig. 2. Photograph of Small-Column Ion Exchange System

The SRF resin used in these tests was from existing stock (Microbeads, Skedsmokorset, Norway, Lot Number 5E-370/641) that had been stored at PNNL for more than 4 years. The resin had been stored in the H-form in water under nitrogen in 2-L plastic bottles. A small (~3 mm) layer of the resin was dark brown, indicating possible oxidative degradation, in contrast to the orange

color of the remaining bulk. Upon opening the container, the top layer of resin was removed by vacuum sluicing and disposed of without use. The remaining resin was thoroughly mixed, and a representative sample was removed for use in the experiment. Approximately 10.7 mL of the resin (H<sup>+</sup>-form) was dispensed into seven, 100-mL, glass beakers. Based on previous reports [3, 4], this volume was estimated to expand to approximately 15 mL in the Na-form. The measured BV was ~15.7 mL in the columns. Three of the samples were used for the column experiment. The remaining samples were oven dried at 50°C, two in the H-form and two in the Na-form.

The resin pretreatment and column processing steps are shown in Table 1. Following the bulk pretreatment steps, the Na-form resin was slurry transferred into the column, rinsed with deionized (DI) water, and converted into the H-form with 0.5 M HNO<sub>3</sub> (Figure 2B). The resin was then re-converted back into the Na-form with 0.5 M NaOH. Because “Fingering” (Figure 2C) was observed during this initial down-flow, in-column, resin expansion, subsequent post-elution regeneration was completed using up-flow NaOH solutions. Figure 2D displays the column after the regeneration process had completely converted the resin to the Na-form. The regeneration process was completed at the end of each weekly processing cycle, with the next cycle typically beginning on the following Monday or Tuesday. The brownish orange discoloration formed over time and was visible in the first several samples collected during the loading phase.

The columns were loaded with a simple simulant traced with approximately 1 μCi/g Cs-134 and containing 5.0 M Na<sup>+</sup>, 1.67 M NO<sub>3</sub><sup>-</sup>, 2.4E-05 M Cs<sup>+</sup>, 0.115 M Al(OH)<sub>4</sub><sup>-</sup>, 1.55 M OH<sup>-</sup> (free), and 1.67 M Cl<sup>-</sup>. The columns were loaded with approximately 250 BVs of simulant feed solution at 45°C. The solution was processed at approximately 1.5 BV/h for the first 8 h and at ≥ 12 BV/h for the remaining 16 h.

The columns were eluted with approximately 25 BVs of HNO<sub>3</sub> processed at 25°C and at 1.4 BV/h. As is shown in Table 2, the elution solution was a variable-concentration HNO<sub>3</sub> (0.02, 0.07, 0.15, 0.23, and 0.28 M) containing variable CsNO<sub>3</sub> (5.0E-09, 5.0E-08, and 5.0E-07 M). The elution solutions were individually traced with approximately 0.6 μCi/g Cs-137.

Table 1. Ion Exchanger Pretreatment and Process Steps

Process Step	Solution	Volume	Time	Mixing	Flowrate
<b>Bulk Pretreatment</b>					
Water Rinse	DI Water	5 RV <sup>(a)</sup>	30 min	Swirl <sup>(b)</sup>	NA
Resin Expansion	1 <u>M</u> NaOH	5 RV	1 h	Swirl	NA
Resin Expansion	1 <u>M</u> NaOH	5 RV	>12 h	Soak	NA
Water Rinse – 1 <sup>st</sup>	DI Water	3RV	30 min	Swirl	NA
Water Rinse – 2 <sup>nd</sup>	DI Water	3RV	30 min	Swirl	NA
Water Rinse – 3 <sup>rd</sup>	DI Water	3RV	30 min	Swirl	NA
Resin Conversion	0.5 <u>M</u> HNO <sub>3</sub>	10 RV	2 h	Swirl	NA
Water Rinse – 4 <sup>th</sup>	DI Water	3 RV	1 min	Swirl	NA
Resin Expansion	1 <u>M</u> NaOH	10 RV	1 h	Swirl	NA
Water Rinse – 5 <sup>th</sup>	DI Water	10 RV	1 min	Swirl	NA
<b>Column Pretreatment</b>					
Water Rinse	DI Water	7.5 BV <sup>(c)</sup>	2.5 h	Flow	3 BV/h
Acid Rinse	0.5 <u>M</u> HNO <sub>3</sub>	8 BV	2.7 h	Flow	3 BV/h
Water Rinse	DI Water	3 BV	1 h	Flow	3 BV/h
Feed Prep	0.5 <u>M</u> NaOH	6 BV	2 h	Flow	3 BV/h
<b>Column Loading/Elute</b>					
Simulant <sup>(d)</sup>	Simulant	12 BV	8 h	Flow	1.5 BV/h
Simulant <sup>(d)</sup>	Simulant	≥200 BV	≥16 h	Flow	≥12 BV/h
Feed Displaced	0.1 <u>M</u> NaOH	7.5 BV	2.5 h	Flow	3 BV/h
Water Rinse	DI Water	7.5 BV	2.5 h	Flow	3 BV/h
Neutralization <sup>(e)</sup>	0.5 <u>M</u> HNO <sub>3</sub>	3 BV	2.1 h	Flow	1.4 BV/h
Acid Elution <sup>(f)</sup>	Variable	25 BV	17.9 h	Flow	1.4 BV/h
Water Rinse	DI Water	3 BV	2.1 h	Flow	1.4 BV/h
Regeneration	0.5 <u>M</u> NaOH	6 BV	2.2 h	Flow	1.4 BV/h
<p>(a) Resin volume (RV).  (b) Gently swirling by hand every 10 min.  (c) Bed volume (BV).  (d) Column loading at 1.5 BV/h for the first 8 h and ≥12 BV/h thereafter until solution was exhausted.  (e) Elution with HNO<sub>3</sub> variations commenced after 3 BV 0.5 <u>M</u> HNO<sub>3</sub> was passed through the column.  (f) Elution was continued until at least 25 BV of the eluting acid was processed.</p>					

Table 2. Experimental Design for Cesium Ion Exchange Elution

Run ID	Ion Exchange Column Loading Conditions							Column Elution Conditions				
	h (a)	T °C	BV (b)	$\frac{BV}{h}$	Na M	OH M	Initial Cs, M	T °C	BV (c)	$\frac{BV}{h}$	HNO <sub>3</sub> M <sup>(d)</sup>	Cs M in HNO <sub>3</sub>
Test-3-D-1	24	45	250	12	5.0	1.67	2.4E-05	25	25	1.4	0.15	5.00E-08
Test-3-D-2	24	45	250	12	5.0	1.67	2.4E-05	25	25	1.4	0.02	5.00E-08
Test-3-D-3	24	45	250	12	5.0	1.67	2.4E-05	25	25	1.4	0.28	5.00E-08
Test-3-D-4	24	45	250	12	5.0	1.67	2.4E-05	25	25	1.4	0.15	5.00E-07
Test-3-D-5	24	45	250	12	5.0	1.67	2.4E-05	25	25	1.4	0.15	5.00E-09
Test-3-D-6	24	45	250	12	5.0	1.67	2.4E-05	25	25	1.4	0.15	5.00E-07
Test-3-E-1	24	45	250	12	5.0	1.67	2.4E-05	25	25	1.4	0.15	5.00E-08
Test-3-E-2	24	45	250	12	5.0	1.67	2.4E-05	25	25	1.4	0.07	1.40E-07
Test-3-E-3	24	45	250	12	5.0	1.67	2.4E-05	25	25	1.4	0.23	1.90E-08
Test-3-E-4	24	45	250	12	5.0	1.67	2.4E-05	25	25	1.4	0.23	1.40E-07
Test-3-E-5	24	45	250	12	5.0	1.67	2.4E-05	25	25	1.4	0.07	1.90E-08
Test-3-E-6	24	45	250	12	5.0	1.67	2.4E-05	25	25	1.4	0.15	5.00E-08
Test-3-F-1 <sup>(e)</sup>	24	25	250	12	5.0	1.67	2.4E-05	25	25	1.4	0.28	0.00E-00

(a) Column loading proceeded at 1.5 BV/h for the first 8 h and 12 BV/h thereafter until 250 BV were processed. Samples were collected hourly for the first 8 h to define the initial cesium breakthrough curve and at 24 h to confirm loading.

(b) BV = Bed Volume. Approximately 250 BV were processed for each loading cycle.

(c) Approximately 25 BV HNO<sub>3</sub> (variable concentration) were processed for each elution cycle.

(d) Elution with HNO<sub>3</sub> variations was initiated after feed displacement (7.5 BV 0.1 M NaOH), a water rinse (7.5 BV Deionized [D]) Water), and resin neutralization (3BV 0.5 M HNO<sub>3</sub>) solutions were passed through the column. Samples were collected hourly for the first 8 h, every 2 h for the next 4 h and every 3 h thereafter.

(e) The final column (Test 3-F-1) serves as a comparison to prior ion exchange testing at 25°C [3, 4]. The other 12 column tests were loaded at 45°C and eluted at 25°C.

## RESULTS AND DISCUSSION

In all 13 test cycles, the SRF resin was loaded with ~3750 mL (250 BV) of the simple simulant feed solution (5  $\underline{M}$  Na, 2.4E-05  $\underline{M}$  Cs). Columns D and E were each loaded and eluted six times, while Column F was loaded and eluted once. Hourly samples were collected for the first loading cycle on each column as is shown for Column D1 in Figure 3. Similar results were observed for Columns E1 and F1. During subsequent loading cycles, hourly samples were only collected during the first 8 h, followed by a single sample at the end of the loading process (~28 h or 250 BV). This greatly simplified the experiment while still obtaining and confirming the level of cesium breakthrough on subsequent loading cycles.

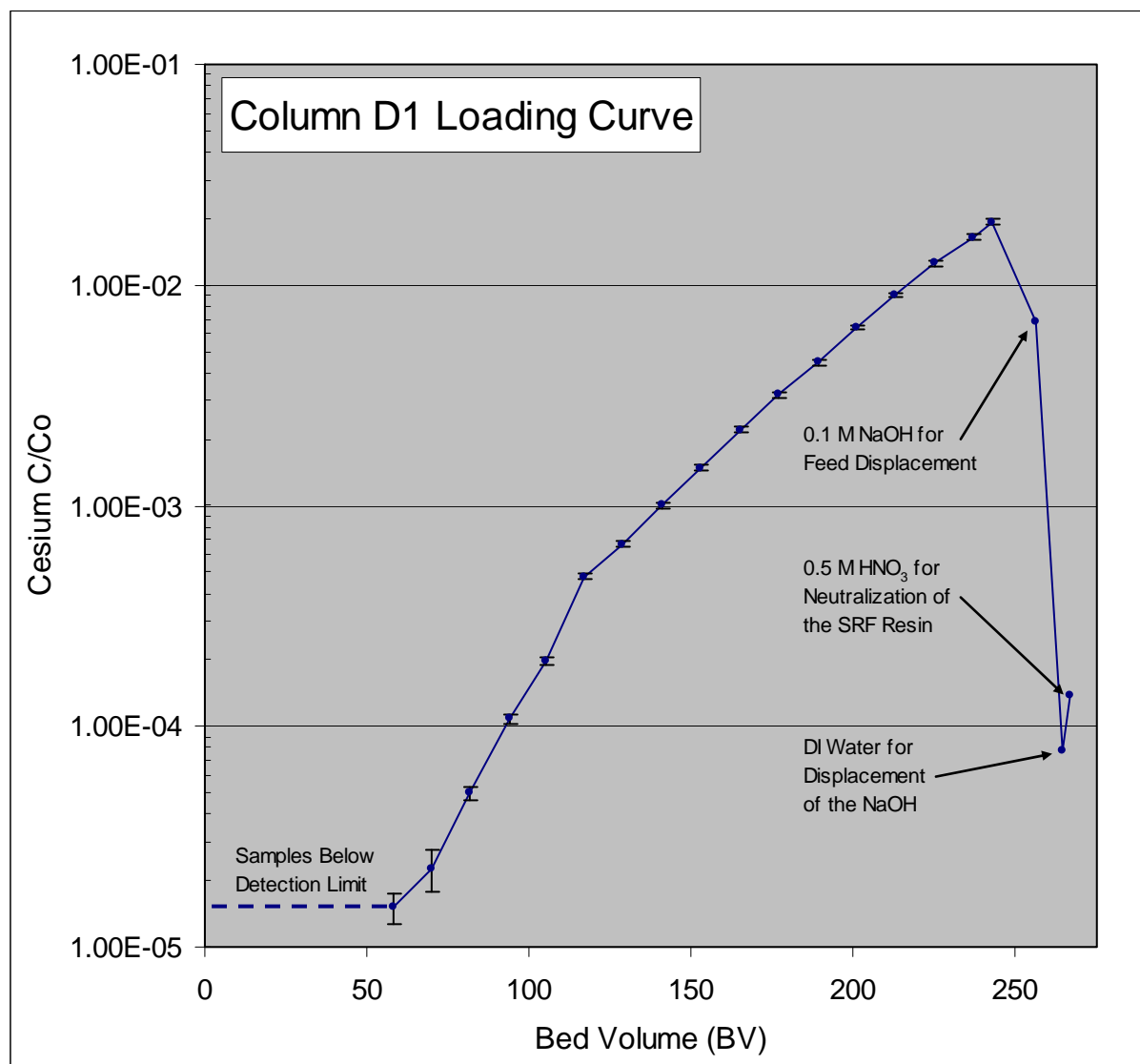


Fig. 3. Column D1 Cesium Loading Profile



All SRF columns were loaded to approximately 2% C/C<sub>0</sub> Cs-134 breakthrough. The original experimental design called for achieving a minimum of 50% breakthrough (e.g., full loading). Preliminary loading calculations were based on previous experimental results for Hanford Tank AN-105 [11]. Unfortunately, the simple simulant did not contain potassium while the AN-105 waste contained ~0.1 M K<sup>+</sup>. Apparently, the difference in K<sup>+</sup> concentration was enough to increase the 50% breakthrough point from an estimated 220 BV (AN-105) to more than 350 BV (simple simulant). It is anticipated that the lower Cs<sup>+</sup> loading of the SRF resin should not have a significant impact on the corresponding elution results reported herein.

As shown in Table 3, subsequent loading cycles (after Column D and Column E cycles 1 through 5) typically exhibited less than 0.006% C/C<sub>0</sub> Cs-134 and 0.2% C/C<sub>0</sub> Cs-137 average “leakage” or breakthrough during the first 8-h period (12 BV). The test following elution with 0.02 M HNO<sub>3</sub>, displayed nearly 0.2% Cs-134 and 0.8% Cs-137 breakthrough, indicating insufficient cesium removal during the previous elution cycle. These results (except column test D2) indicate sufficient acid strength to elute cesium from the SRF resin and reduce carryover (breakthrough) to subsequent process cycles. Table 3 also displays the approximate amount of residual Cs-134 and Cs-137 left on the column post elution. Prior researchers [4] have estimated that ≤0.1% C/C<sub>0</sub> (decontamination factor [DF] ≥ 1000) will be required to meet waste loading criteria for similar Hanford tank wastes. The results from this test indicate that all conditions (except Column D2) were sufficient to achieve a DF greater than 1000 (e.g., <1.0E-03 Cs-134 C/C<sub>0</sub>).

Table 3. Summary of Cesium Elution Results

Column ID	Elution Content		Next-Load Cycle Leakage		Post-Elute Column Residue	
	[Cs], M	[H <sup>+</sup> ], M	Cs-134 C/C <sub>0</sub>	Cs-137 C/C <sub>0</sub>	Cs-134 C/C <sub>0</sub>	Cs-137 C/C <sub>0</sub>
D1	5.00E-08	1.50E-01	4.43E-05	1.45E-03	1.53E-04	9.40E-02
D2	5.00E-08	2.00E-02	1.43E-03	7.85E-03	4.88E-03	1.91E+00
D3	5.00E-08	2.80E-01	1.76E-05	7.66E-04	5.73E-05	3.51E-02
D4	5.00E-07	1.50E-01	5.06E-05	1.41E-03	7.42E-05	7.84E-02
D5	5.00E-09	1.50E-01	5.92E-05	1.44E-03	7.35E-05	6.05E-02
D6	5.00E-07	1.50E-01	NA	NA	7.22E-05	5.09E-02
E1	5.00E-08	1.50E-01	4.46E-05	1.26E-03	1.22E-04	9.08E-02
E2	1.40E-07	7.00E-02	3.93E-05	1.20E-03	1.47E-04	1.39E-01
E3	1.90E-08	2.30E-01	4.23E-05	1.22E-03	7.20E-05	5.07E-02
E4	1.40E-07	2.30E-01	2.87E-05	1.06E-03	6.57E-05	5.81E-02
E5	1.90E-08	7.00E-02	7.25E-05	1.79E-03	7.76E-05	1.05E-01
E6	5.00E-08	1.50E-01	NA	NA	7.16E-05	5.40E-02
F1	0.00E+00	2.80E-01	NA	NA	1.59E-04	6.43E-02

Figure 4 shows the Cs-134 and Cs-137 concentration profiles for the first three Column D elution cycles. The solid colored labels represent the Cs-134 data while the white colored labels represent the Cs-137 data. The Cs-134 data clearly show the effect of acid concentration on the elution profile. After a similar peak concentration (sample nn-EL-02), the 0.28 M HNO<sub>3</sub> is capable of reducing the Cs-134 concentration more quickly than the 0.15 or 0.02 M HNO<sub>3</sub>. After 21 BV (sample nn-EL-15), the highest strength acid generates ~0.1% C/C<sub>0</sub> while the



0.15 M HNO<sub>3</sub> generates an acceptable level of less than 1% C/C<sub>0</sub>. Eluting with 0.02 M HNO<sub>3</sub>, however, does not achieve an acceptable level even after 40 BV (sample nn-EL-30).

The Cs-137 data shown in Figure 4 indicate that the cesium impurity in eluting acids may be concentrated initially on the SRF resin, but eventually returns to the initial concentration in the eluting acid. Fortunately, the Cs-137 concentration is reduced during the DI water rinse (sample nn-EDI-CP) and NaOH regeneration (sample nn-RG-CP) in preparation for subsequent loading.

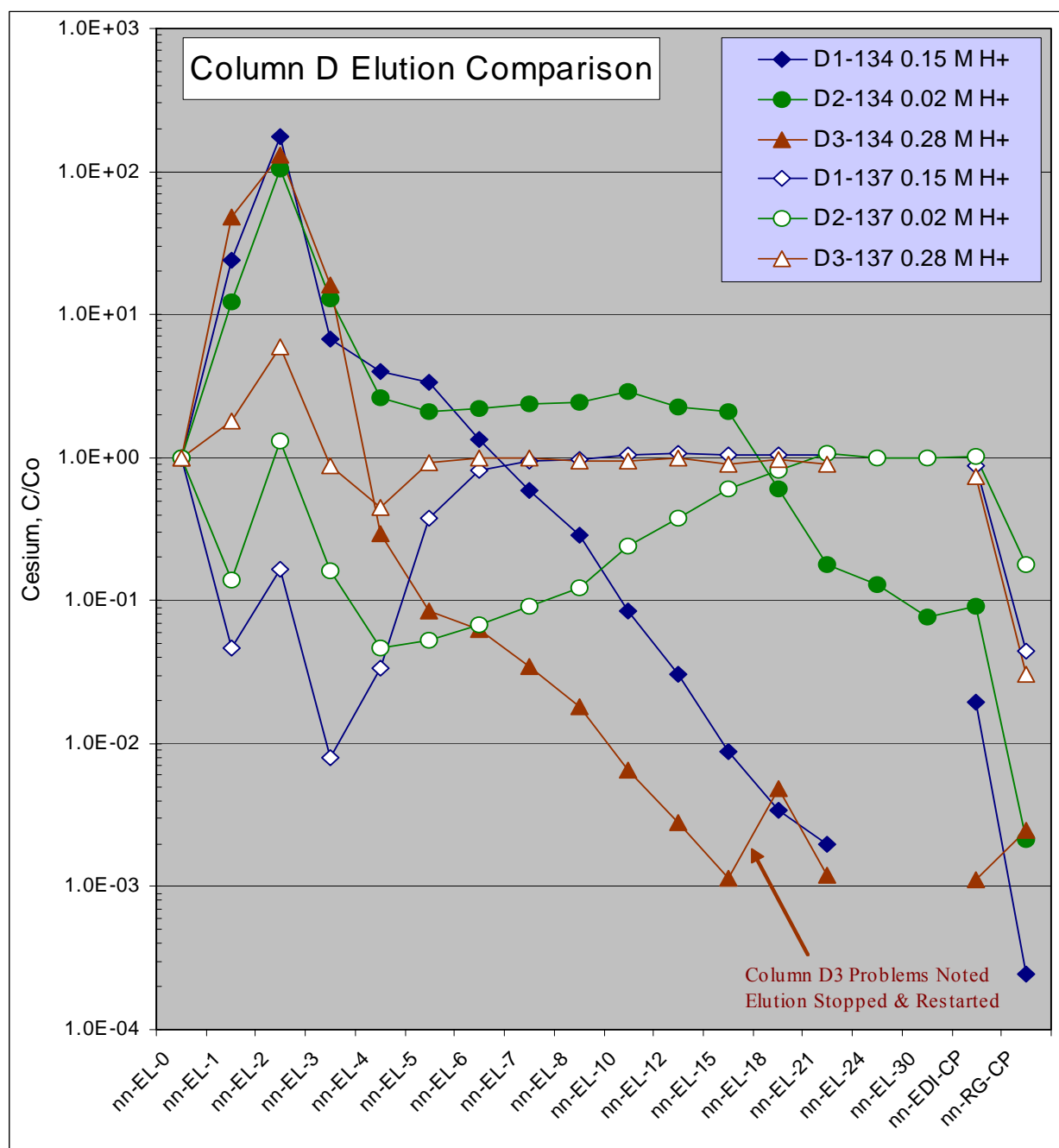


Fig. 4. Column D1, D2 and D3 Cesium Elution Profile vs. Sample Number

## CONCLUSIONS

Effective removal of cesium from the SRF resin has been demonstrated using 3 BV of 0.5 M HNO<sub>3</sub> followed by less than 25 BV of dilute HNO<sub>3</sub> (e.g., 0.07 to 0.28 M). As expected from previous work [11, 12], the higher acid concentration was more effective at eluting the SRF resin. However, effective elution to 0.001 C/C<sub>0</sub> (DF=1000) was still observed after 20 BV of 0.07 M HNO<sub>3</sub>. In contrast, the WTP baseline pretreatment process calls for 25 BV of 0.5 M HNO<sub>3</sub>. The use of more dilute nitric acid may facilitate the use of acid streams recycled from the evaporator. Under the conditions evaluated during this test (5.00E-09 M to 5.00E-07 M Cs), residual Cs impurity in the eluting acid does not affect the elution process (e.g., the amount of residual Cs remaining in the column post elution or the amount of Cs leakage during subsequent loading cycles).

Approximately 3–4 BV of 0.5 M HNO<sub>3</sub> are required to acid neutralize (titrate) the SRF resin, thereby exchanging protons for sodium, cesium and other cations. For this work, the lower 3 BV value was used, thereby minimizing the possibility of removing cesium during the titration step and allowing observation of the cesium elution profile peak. The results for the 0.07 M HNO<sub>3</sub> test compare favorably to the previously reported [12], stepped elution method on the basis of total acid consumption.

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