Alternate Methods for Eluting Cesium From
Spherical Resorcinol-Formaldehyde Resin – 9160

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ABSTRACT

A Small Column Ion Exchange (SCIX) system has been proposed for removing cesium from the supernate and dissolved salt solutions in the high level waste tanks at the Savannah River Site (SRS). The SCIX system could use either crystalline silicotitanate (CST) an inorganic, non-regenerable sorbent or spherical resorcinol-formaldehyde (RF), a new regenerable resin, to remove cesium from the waste solutions. The standard method for eluting the cesium from the RF resin uses 15-20 bed volumes (BV) of 0.5 M nitric acid (HNO_3). The nitric acid eluate, containing the radioactive cesium, would be combined with the sludge from the waste tanks, and would be converted into glass at the Defense Waste Processing Facility (DWPF) at SRS. The amount of nitric acid generated by the standard elution method exceeds the capacity of DWPF to destroy the nitrate ions and maintain the required chemical reducing conditions in the glass melt.

Alternate methods for eluting the resin have been tested, including using lower concentrations of nitric acid, other acids, and changing the flow regimes. About 4 bed volumes of 0.5 M nitric acid are required to remove the sodium (titrate the resin) and most of the cesium from the resin, so the bulk of the acid used for the standard elution method removes a very small quantity of cesium from the resin. The resin was loaded with 9.5 g Cs/L of resin prior to elution, which is the maximum expected loading for RF resin treating the actual dissolved salt waste at SRS.

For the baseline elution method, 465 g of nitrate is used per liter of resin, and >99.9999% of the cesium is removed from the resin. An alternative method that used 4 bed volumes of 0.5 M HNO_3 followed by 11 bed volumes of 0.05 M HNO_3, used 158 g of nitrate per liter of resin (66% less nitrate than used for the standard elution) and removed >99.998% of the cesium. A staccato flow mode using 0.5 M HNO_3 (1 hr on at 1 BV/hr, followed by 3 hrs off) after the resin had been titrated using a continuous flow of acid at 1 BV/hr removed 99.9998% of the cesium while using 12 BV of acid (20% less than the baseline). Formic acid was slightly less efficient than nitric acid for eluting the resin, but 20 BV of 0.5 M HCOOH removed 99.98% of the cesium from the resin.

INTRODUCTION

A Small Column Ion Exchange (SCIX) system has been proposed for removing cesium from the supernate and dissolved salt solutions in the high level waste tanks at the Savannah River Site (SRS). The SCIX system could use either crystalline silicotitanate (CST) an inorganic, non-regenerable sorbent or spherical resorcinol-formaldehyde (RF), a new regenerable resin, to remove cesium from the waste solutions. The RF resin has been studied extensively for possible use at the Hanford Site [1], and more recently for use at SRS [2]. The standard method for eluting the cesium from the RF resin involves 15-20 bed volumes (BV) of 0.5 M nitric acid. The nitric acid eluate, containing the radioactive cesium, would be combined with the sludge from the waste tanks, and would be converted into glass at the Defense

Waste Processing Facility (DWPF) at SRS. The amount of nitric acid that would be used to elute the RF resin, using the current elution protocol, exceeds the capacity of DWPF to destroy the nitrate ions and maintain the required chemical reducing environment in the glass melt. Installing a denitration evaporator at SRS is technically feasible, but would add considerable cost to the project. This work examined methods to elute the RF resin while using lower amounts of nitric acid or alternate acids.

MATERIALS AND METHODS

Either of two small columns, fabricated from 0.5" clear polyvinyl chloride (PVC) pipe, with glued threaded end adapters, was used for these tests. The stainless steel end caps have 100-mesh stainless steel screen tack-welded inside to retain the ion-exchange resin, and 1/16" stainless steel tubing for inlet and outlet flow. The measured I.D. of the columns is 1.51 cm and the total volume is 36 mL. A Masterflex (Cole-Parmer Instrument Company, Vernon Hills, IL) peristaltic pump and 1/32" I.D. PharMed (Saint-Gobain Performance Plastics, Corp., Granville, NY) tubing were used to pump solutions through the columns. The effluent from the columns was collected in 50-mL polypropylene centrifuge tubes, using a Spectra/Chrom CF-1 (Spectrum, Houston, TX) fraction collector to automatically advance the centrifuge tubes at timed intervals. A Mettler AE163 analytical balance (Mettler-Toledo, Inc., Columbus, OH) was used to weigh chemicals and resin samples.

The spherical resorcinol-formaldehyde (RF) resin used in these tests was from Microbeads (Skedsmokorset, Norway), Lot Number 5E-370/641, which was produced on 5/24/2005 in a 50-gal production batch. The resin was stored in water, in the hydrogen form, in 1-L glass bottles. The bottle of resin used for these tests was delivered to ORNL from SRS on 6/23/2008.

The resin was weighed in the hydrogen form prior to being added to the column. A sample of the resin was dewatered on a filter paper, under vacuum, and then weighed. Damp resin was transferred into a graduated cylinder containing deionized water to give a resin volume of 14.5 cc. The remaining resin was weighed to determine the weight of damp resin that had been added to the graduated cylinder. A second aliquot of damp resin was weighed, air dried overnight and reweighed to determine the moisture content. The moisture content was used to calculate the dry weight of the resin placed in the column, which averaged 7.2 g of hydrogen-form resin. The resin was regenerated to the sodium-form in the column, by pumping 0.25 M NaOH up through the resin. The height of the sodium-form resin in the column was about 10 cm, which gives an aspect ratio of 6.7 in the 1.5 cm I.D. column, which is the same as proposed for the ion exchange columns in the SCIX system.

Loading and Elution Procedures

Previous modeling work at SRS [3] had predicted maximum cesium loadings of 1.05 to 9.5 g Cs/L of resin on the RF resin used to treat the dissolved salt waste, while producing decontaminated salt waste that would meet the waste acceptance criteria for the Saltstone Facility. The cesium loading procedure used for these tests was designed to load 9.5 g Cs/g resin in about 20 hours. A surrogate dissolved salt solution (see Table I), which represents the average SRS salt waste, but with a much higher cesium concentration of 239 mg/L, was used to load cesium on the RF resin. The surrogate was pumped down through the column containing the RF resin at a flow rate of 0.6 mL/min (2 bed volumes/hr) until 720 mL (36 bed volumes) of surrogate had passed through the column. (Note – all of the bed volume (BV) measurements are referenced to the sodium-form resin volume, even though the resin shrinks significantly when converted to the hydrogen form during elution.) After the loading phase was completed, the surrogate was displaced using 3 BV of 0.25 M NaOH at 2 BV/hr, and then the caustic was displaced by 3 BV of deionized water at 2 BV/hr. The resin was then ready for elution.

Table I. Surrogate Composition

Component	Concentration (M)	
	Target	Measured
NaOH	1.1	NA[*]
$NaNO_3$	2.4	2.4 as NO_3
$NaNO_2$	0.34	0.34 as NO_2
$Al(NO_3)_3$	0.54	0.55 as Al
Na_2SO_4	0.30	0.30 as SO_4
Na_2CO_3	0.55	NA
NaCl	0.035	0.035 as Cl
NaF	0.033	0.006 as F
Na_2HPO_4	0.13	0.02 as PO_4
Na_2SiO_3	0.005	<0.01 as Si
KNO_3	0.006	0.006 as K
CsCl	0.0018	0.0019 as Cs

[*]NA = not analyzed

A summary of the various elution procedures that were tested is listed below. A total of 17 loading and elution tests were performed.

Baseline elution (0.5 M HNO_3 at 1 BV/hr), for comparison
0.5 M HNO_3 to titrate resin (at 1 BV/hr), then either:
    - 0.05 M HNO_3 at 1 BV/hr, or
    - recirculate 0.5 M HNO_3 at 1 BV/hr, or
    - staccato flow with 0.5 M HNO_3 (1 BV/hr for 1 hr then off for 3 hrs)
0.5 M HCOOH (Formic acid) at 1 BV/hr
0.8 M H_3BO_3 (Boric acid) at 1 BV/hr
0.2 M HNO_3 at 1 BV/hr
0.1 M HNO_3 at 1 BV/hr
0.5 M HNO_3 at 0.7 BV/hr
0.5 M HNO_3 at 2 BV/hr

The elution effluent for all of the continuous-flow elution runs was collected in ~30 mL portions using the fraction collector. For the staccato flow and recirculating flow runs, analytical samples were collected manually. All of the loading and elution tests were performed at room temperature, which ranged from 19°C to 22°C. After elution, the acid remaining in the column was displaced with deionized water (3 BV at 1 BV/hr). For the first 14 runs, the resin was sluiced from the column at this point, and a sample of the resin was collected, air dried overnight, and submitted to the ORNL Radioactive Materials Analysis Laboratory for Cs and K analysis. For the last three runs, the resin was left in the column, regenerated using 6 BV of 0.25 M NaOH pumped up through the resin at 2 BV/hr, and then a second cesium-loading cycle was started.

RESULTS AND DISCUSSION

The cesium concentration in the surrogate effluent samples from the loading phase of the tests ranged from 0.03 to 0.34 mg/L, with an average of 0.27 mg/L, which gives an average decontamination factor (DF) of 888 from the feed concentration.

The baseline elution procedure of 15 BV of 0.5 M HNO$_3$ at 1 BV/hr, which was used in four tests (runs 2, 5, 12, & 15), produces a very sharp cesium spike at 3 – 4.5 BV, just as the pH of the effluent acid drops (see Fig. 1). The sodium concentration in the eluent was not measured directly, but the drop in pH indicates when most of the sodium on the resin has been displaced. Since the total volume of the column is almost two times the volume of the resin bed, the first 2 BV of effluent are mostly displaced deionized water from the column, although there would be some mixing of the water and acid in the head space of the column above the resin. Run #5 used a lower cesium concentration surrogate over an extended time period to load the resin, to determine if the accelerated loading procedure used for the other tests affected the elution performance. The run #5 eluent samples, using the baseline procedure, contained lower concentrations of cesium, since the amount of cesium loaded on the resin was lower; however, the elution pattern was essentially the same. The peak cesium concentration for run #5 is slightly offset, due to a slight difference in the effluent volumes when the samples were taken; however, there is no evidence that the accelerated loading procedure used for most of the runs changed the elution results. The baseline elution procedure was used for a total of four runs. Analysis of the resin after elution showed that the cesium concentration remaining on the resin was very low, 0.008 – 0.033 ppm (>99.9999% removal).
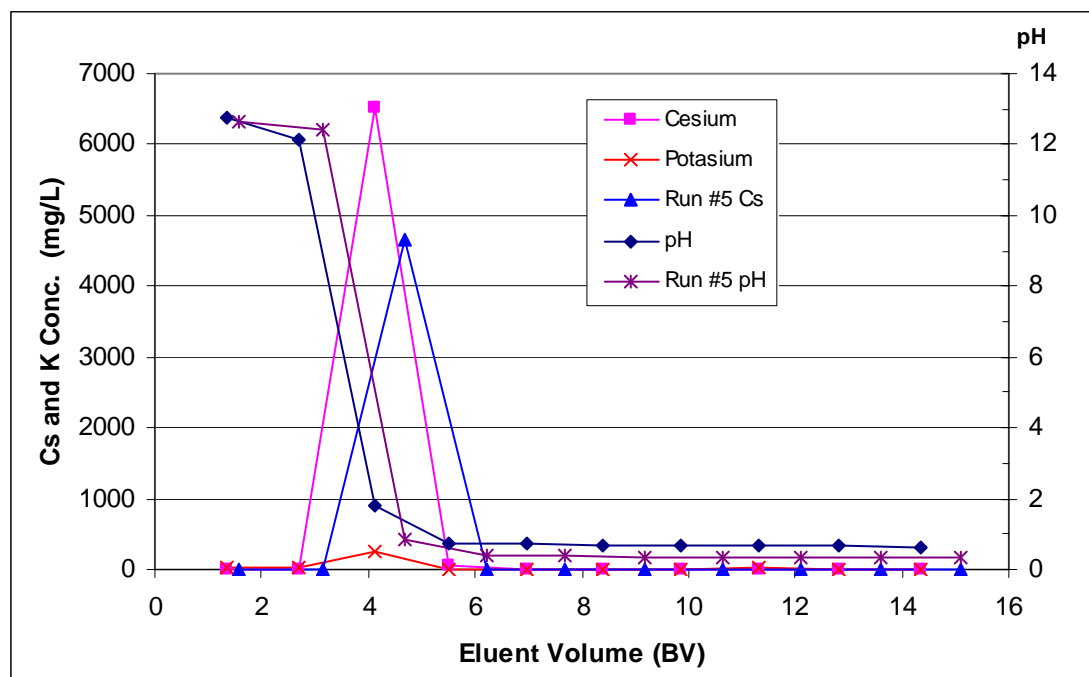

Fig. 1. Results for baseline elution procedure.

A total of three elutions (runs 3, 13, & 16) were performed using 0.5 M HNO$_3$ to titrate the resin, and remove most of the cesium from the resin, and then switching to 0.05 M HNO$_3$ to complete the elution. The cesium elution pattern is very similar to that for the baseline procedure; however, it would produce

about 66% less nitrate in the eluent solution. This appears to be one of the more promising methods for reducing the amount of nitrate that would be sent to DWPF from eluting the RF resin. The results for the first test of this procedure are shown in Fig. 2, and the other two tests were similar. Analysis of the resin after elution showed that the cesium concentration remaining on the resin was quite low (0.03 – 0.35 ppm), although slightly higher than for the baseline elutions. The cesium concentration on the resin prior to elution is about 20,000 ppm, so >99.998% of the cesium was removed during the elutions.

Tests were also completed using 0.1 *M* (run #9) and 0.2 *M* (run #10) HNO$_3$ to elute the resin. With the lower concentrations of nitric acid, it takes more volume to titrate the resin and start eluting the cesium, and the cesium peak is lower and broader, as shown in Fig. 2. The amount of cesium left on the resin after elution was very low for both of these tests, with >99.997% removal. If the same volume of acid is used as for the baseline 0.5 *M* HNO$_3$, which was the case for these tests, using 0.2 *M* HNO$_3$ would reduce the nitrate in the eluent stream by 60%, and using 0.1 *M* HNO$_3$ would reduce the nitrate by 80%. With the 0.1 *M* HNO$_3$, the bulk of the cesium is removed shortly before the elution is completed, so there is very little safety factor, unless a larger volume of acid is used.
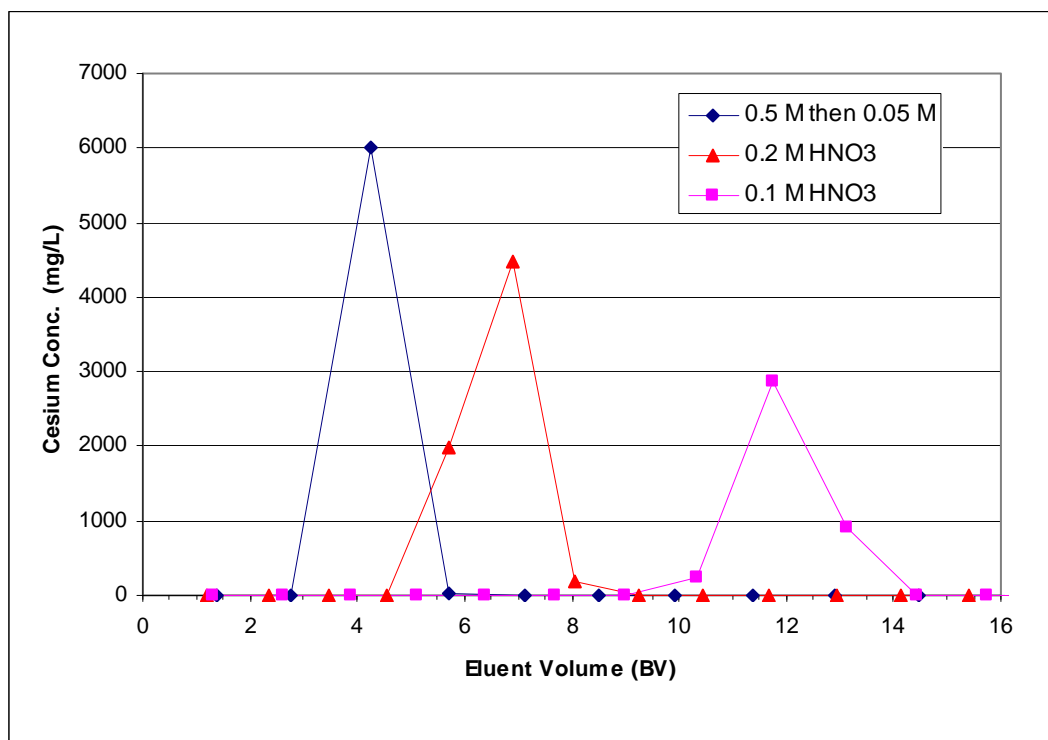

Fig. 2. Results for elutions with lower concentrations of nitric acid.

The first test of recirculating 0.5 *M* HNO$_3$ following 3 BV of once-through 0.5 *M* HNO$_3$ (run #6) started the recirculation too soon, before the cesium concentration of the effluent was low, so a relatively high cesium concentration was present in the recirculating acid. For this test, a total of 5.7 BV of acid was used, and only 95% of the cesium originally loaded on the resin was eluted. This test was repeated (run #14), using 4.7 BV of acid before the recirculation was started and a total of 7.0 BV of acid. The acid was recirculated through the column for 15 hrs, with small samples removed from the feed container after 1, 2, 4, 6, 9, 12, and 15 hrs. The cesium concentration in the recirculating solution remained low, increasing from 0.6 mg/L to 1.2 mg/L, as a small amount of cesium continued to be eluted from the resin.

The cesium concentration left on the resin after elution was 3.98 ppm (99.98% removal), which is significantly higher than for most of the other elution methods tested.

One test (run #1) was conducted using 0.5 M HNO_3 at twice the normal flow rate (2 BV/hr). The cesium peak occurred in the sample from 3.2 – 4.8 BV, which is later than for the baseline flow rate of 1 BV/hr. The amount of cesium left on the resin after elution was 0.275 ppm (99.999% removal). This elution method would require less time to complete the elution, but uses the nitric acid less efficiently.

One test (run #11) was conducted using 0.5 M HNO_3 at a lower flow rate, which averaged   0.56 BV/hr, with a range of 0.47 to 0.64 BV/hr (0.16 – 0.22 mL/min). The pump speed for this test was at the lower range of the pump's ability to control, so there was more variation than for the other tests. The cesium elution peak was sharper than for the higher flow rate, but it was similar to the baseline flow rate of 1 BV/hr. The amount of cesium left on the resin after elution was   0.076 ppm (99.9997% removal). A total of 224 mL (11 BV) of acid was used in the elution, which is 27% less than for the baseline elution method.

One test (run #4) used 0.5 M HNO_3 in a staccato flow mode (1 hr on at 1 BV/hr, followed by 3 hrs off) after the resin had been titrated using a continuous flow of 5.7 BV of acid at 1 BV/hr. This procedure displaces the acid that is in contact with the resin and then lets the new acid soak for 3 hrs before displacing that acid with fresh acid. The amount of cesium left on the resin after elution was 0.044 ppm (99.9998% removal). A total of 240 mL (12 BV) of acid was used in the elution, which is 20% less than for the baseline elution method. We did not try a test using 240 mL of 0.5 M HNO_3 at 1 BV/hr (baseline elution procedure with a lower volume of acid); however, analytical results are available for the concentration of cesium in the elution samples from 12 BV through 15 BV. The average cesium concentration was 0.07 mg/L, which would represent a concentration of 0.56 ppm Cs on the resin that was removed by the last three bed volumes of acid. Since this concentration is significantly higher than the cesium concentration left on the resin by the staccato flow procedure using 12 BV of acid, the staccato flow method uses the acid more efficiently.

Two potential alternative acids (formic acid and boric acid) were identified based on their likely compatibility with DWPF and the SRS tank farm. Formic acid (HCOOH) is currently used at DWPF to control the redox potential of the feed stream to the glass melter. Formic acid is the simplest and most acidic (pKa = 3.74) of the carboxylic acids, and is completely miscible with water [4]. A 0.5 M formic acid solution was tested for eluting the RF resin. This solution would have a free hydrogen ion concentration of 0.0095 M; however, when in contact with the high pH, sodium form resin, the formic acid would supply a higher amount of hydrogen ions, as the resin exchanges the hydrogen ions from the solution for sodium ions initially on the resin. After the resin is converted to mostly the hydrogen form (titrated), the amount of hydrogen ions supplied by the formic acid solution would drop to about 0.0095 M. The amount of solution required to titrate the resin and elute most of the cesium was only slightly higher than for the baseline (0.5 M HNO_3) solution. The amount of cesium remaining on the resin (5.7 ppm, 99.98% removal) was significantly higher than for the baseline elution method, although still relatively low. SRS personnel have not determined the maximum amount of formic acid that could be accommodated at DWPF. A higher concentration of formic acid could potentially be used, which should improve the elution results.

Boric acid does not dissociate in aqueous solution but it is slightly acidic (pKa of 9.24) due to its interaction with water molecules: $B(OH)_3 + H_2O \rightarrow B(OH)_4^- + H^+$. Boric acid has a maximum solubility in water of 0.9 M [5]. Since the cesium-loaded RF resin has a very high pH, contact between a boric acid solution and the resin would increase the amount of hydrogen ions supplied by the solution. A solution of 0.8 M boric acid, which has a free hydrogen ion concentration of 2.2E-5 M, was tested for eluting the resin. About 8 BV of boric acid solution was required to titrate the resin and start eluting the cesium.

The cesium concentration in the eluate samples was much lower than for the other elution methods, and the elution was not complete after 18 BV. The concentration of cesium left on the resin was 9450 ppm (73% removal). Boric acid is not recommended for eluting cesium from the RF resin.

Figure 3 shows the elution results for the baseline, staccato flow, 0.5 M HNO$_3$ followed by 0.05 M HNO$_3$, and 0.5 M formic acid elution methods on a semi-log scale, which emphasizes the small differences in the cesium concentration at the end of the elution cycles. The cesium concentrations in the solutions at the end of the elution cycles correlate well with the amount of cesium left on the resin after the elution (see Table II and Fig 3). For the staccato flow method, the high cesium peak was split between two samples, so the peak is lower and broader than for the other elution methods.

Table II. Cesium Concentrations Left On Resin After Elutions

Elution Method	Cesium Conc. on Resin (ppm)
0.5 M HNO$_3$ - Baseline	0.013
0.5 M HNO$_3$ – Staccato Flow	0.044
0.5 M HNO$_3$ then 0.05 M HNO$_3$	0.348
0.5 M Formic Acid	5.70

The last three tests used (1) the baseline procedure (run #15), (2) 0.05 M HNO$_3$ following the initial titration by 0.5 M HNO$_3$ (run #16), and (3) 0.5 M formic acid (run #17) for eluting the cesium from the resin. For each of these tests, a second loading cycle, using a lower cesium concentration surrogate, was performed to measure any impact of the first elution on the initial phase of the next loading cycle. After the elution step, the acid was displaced by deionized water (3 BV downflow at 1 BV/hr), and then the resin was converted to the sodium form (regenerated) by 6 BV of 0.25 M NaOH pumped upflow at 2 BV/hr. The second loading cycle used a surrogate salt solution with 55 mg/L Cs, which was pumped down through the column at 2 BV/hr. The fraction collector was used to collect composite samples of the effluent surrogate every hour.
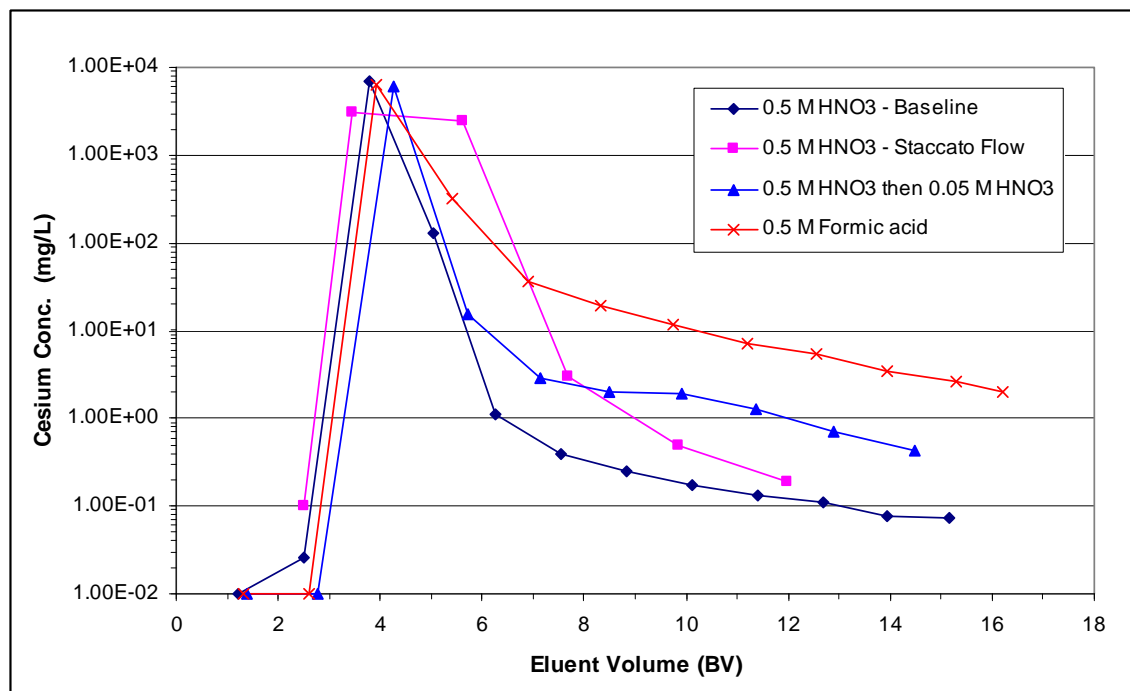
Fig. 3. Results of various elution methods

Direct measurement of the surrogate effluent samples using the most sensitive method available gave non-detects (<5 μg/L) for the cesium concentration in all of the samples from runs 15 and 16. The detection limit for these samples is mostly driven by the high sodium concentration (~6 M) in the surrogate solution. In order to improve the detection limit for cesium, the effluent samples were composited into early (0 – 7 BV), middle (7 – 18 BV), and late (18 – 28 BV) samples. Each of the composite samples (~55 mL) was batch-contacted for 24 hrs with about 0.3 g of RF resin. Each resin sample was rinsed with 1 M NaOH, and then with deionized water, and the resin was then eluted with 25 mL of 1 M HNO$_3$ (24-hr batch contact). This treatment approximately doubled the cesium concentration from the surrogate effluent samples and greatly reduced the sodium concentration. After applying the concentration factor (surrogate volume / acid volume) for each sample, the cesium concentrations in the surrogate effluent composites were calculated to range from 3.3 – 5.0 μg/L with no systematic trend for the early, middle and late samples from either run. For the run #17 samples, the calculated cesium concentration in the original surrogate effluent samples ranged from 15.1 – 24.0 μg/L with no systematic trend for the early, middle and late samples. The average cesium concentration for the run #15 samples was 4.2 μg/L, and the average for the run #16 samples was 4.1 μg/L. A t-test analysis of variance shows that there is a 46% probability that this difference in cesium concentrations is caused by random variation, rather than any real difference caused by the elution methods. Therefore, the baseline elution procedure and the procedure using 0.05 M HNO$_3$ following the initial titration by 0.5 M HNO$_3$ show the same performance for the subsequent cesium-loading cycle. The average cesium concentration for run #17 was 18.5 μg/L, which is significantly higher than the run #15 and #16 results. The average cesium decontamination factor (DF) for runs #15 and #16 (up through 28 BV of surrogate treated) was 13,400 and the DF for run #17 was 3000. The average DF for the first loading cycle, using 36 BV of surrogate containing 239 mg/L of cesium, was 1030. It is not known why the second loading cycle showed a much higher DF than the first loading cycle for these tests. The cesium concentration in the feed solution was different for the first and second loading cycles; however, the DF for the first 60 BV of run #5, which used a cesium feed concentration (26 mg/L) even lower than for the second loading cycle in these tests,

showed a DF of only 248. The resin used in these tests had been cycled twice through the hydrogen and sodium forms prior to starting the first cesium loading, so it does not seem likely that one more cycle during the elution and regeneration steps would cause a large improvement in the cesium sorption.

CONCLUSIONS

The standard method for eluting cesium from the RF resin uses 15-20 bed volumes (BV) of 0.5 M nitric acid (HNO_3). Alternate methods for eluting the resin have been tested, including using lower concentrations of nitric acid, other acids, and changing the flow regimes. About 4 bed volumes of 0.5 M nitric acid are required to remove the sodium (titrate the resin) and most of the cesium from the resin, so the bulk of the acid used for the standard elution method removes a very small quantity of cesium from the resin. The resin was loaded with 9.5 g Cs/L of resin prior to elution, which is the maximum expected loading for RF resin treating the actual dissolved salt waste at SRS.

For the baseline elution method, 465 g of nitrate is used per liter of resin, and >99.9999% of the cesium is removed from the resin. An alternative method that used 4 bed volumes of 0.5 M HNO_3 followed by 11 bed volumes of 0.05 M HNO_3, used 158 g of nitrate per liter of resin (66% less nitrate than used for the standard elution) and removed >99.998% of the cesium. A staccato flow mode using 0.5 M HNO_3 (1 hr on at 1 BV/hr, followed by 3 hrs off) after the resin had been titrated using a continuous flow of acid at 1 BV/hr removed 99.9998% of the cesium while using 12 BV of acid (20% less than the baseline). Formic acid was slightly less efficient than nitric acid for eluting the resin, but 20 BV of 0.5 M HCOOH removed 99.98% of the cesium from the resin.

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