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Evaluation of Elution Parameters for Cesium Ion Exchange Resins

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Abstract: Cesium ion exchange is one of the planned processes for treating and disposing of waste at the U.S. Department of Energy Hanford Site. Radioactive supernatant liquids from the waste tanks will undergo ultrafiltration, followed by cesium ion exchange using a regenerable organic ion exchange resin. Two resins, SuperLig®644 and a resorcinol-formaldehyde resin, are being evaluated for cesium removal and cesium elution characteristics. The main purpose of this study is to optimize the cesium elution to provide a resin that, after undergoing elution, would meet the U.S. Department of Energy/Office of River Protection Project-Waste Treatment Plant processing and resin disposal criteria. Columns of each resin type were loaded to greater or equal to 90% breakthrough with a Hanford waste stimulant and eluted with nitric acid. The temperature, flow rate, and nitric acid concentration were varied to determine the optimal elution conditions. Temperature and eluant flow rate were the most important elution parameters. As would be predicted based upon kinetic consideration alone, decreasing the eluant flow rate and increasing the temperature provided the optimal elution conditions. Varying the nitric acid concentration did not have a significant effect on the elution completion; however, elutions performed using both high acid concentration (1 M) and elevated temperature (45°C) resulted in resin degradation, causing gas generation and resin bed disruption.

Keywords: Ion exchange, cesium, elution, resorcinol, formaldehyde, SuperLig®644

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INTRODUCTION

The U.S. Department of Energy's Hanford Site in southeastern Washington State contains 177 large underground storage tanks with approximately 55-million gallons of radioactive waste. Plans are underway to separate the waste into high-level and low-activity waste (LAW) streams at the U.S. Department of Energy/Office of River Protection Project-Waste Treatment Plant (WTP). The primary unit processes of the Hanford waste-treatment flowsheet for LAW feed are cross-flow filtration, Sr/TRU (transuranic) precipitation, cesium ion exchange, evaporation, and vitrification. After solids are removed, the LAW feed will be passed through ion exchange columns to remove cesium. The decontaminated LAW feed will contain the bulk of the waste mass and will be vitrified as a low-activity glass and stored at the Hanford Site. The cesium eluted from the ion exchange columns will be mixed with tank sludge, vitrified as high-level waste, and eventually stored at a federal repository.

The current pretreatment flow sheet for cesium removal includes the use of SuperLig®644, a crown ether ligand attached to an organic substrate. SuperLig®644 has been tested extensively for loading and elution characteristics (1–8). It has demonstrated excellent loading and elution performance with all categories of Hanford Site waste. An alternative resin for cesium removal, resorcinol-formaldehyde (RF) resin, is under consideration as a potential replacement for SuperLig®644 as the baseline ion exchange resin. Other investigators have previously evaluated RF resin for efficacy in cesium removal and elution (9–16). Two forms of the resin, granular (ground-gel) and spherical, are of specific interest. The testing reported here includes column loading and elution studies of each conditioned resin as well as batch distribution measurements of conditioned resin and spent resin from the column testing. While the focus is on producing a resin that has a low final cesium concentration, this must be balanced with the need to meet elution timelines and also to evaluate the impact that elution conditions have on subsequent performance of the resin as each resin bed will undergo multiple load and elute cycles before disposal. The batch distribution measurements provide an indication of the impact the elution conditions will have on subsequent resin performance.

The planned ion exchange processing will use three distinctive resin-bed columns in series, indexed as the lead, the lag, and the polishing columns. Upon exiting the polishing column, the LAW must meet LAW effluent criteria for cesium, which is dependent upon the type of LAW; Envelope A must be $<0.087\,\mu$Ci ^{137}Cs/mL and Envelope B must be $<0.292\,\mu$Ci ^{137}Cs/mL. In subsequent operating cycles, LAW will be fed into the columns using a "carousel" approach to alter the sequence of which resin bed is first contacted with the influent LAW. The performance of the eluted and regenerated lead column placed into the polishing-column position depends upon the amount of residual cesium that remains in the resin after elution. If the cesium concentration on the resin exceeds a pre-determined concentration near to the LAW criteria, the polishing column may "bleed" enough cesium into the LAW to cause the processed LAW to exceed the cesium removal criteria. After a resin bed has been eluted and regenerated 10 times, its performance will have degraded. The resin bed is then designated as spent and made ready for replacement with a fresh resin batch. In the WTP baseline process, the spent resin bed will be eluted to remove residual radiological and hazardous constituents before land disposal. A design goal is to reduce the spent-resin ^{137}Cs concentration to $60\,\mu\text{Ci/g}$ resin (air-dried, H-form SL-644 resin) by a final elution to comply with design assumptions for spent resin disposal equipment.

EXPERIMENTAL SECTION

Waste Tank Simulant

Testing was performed with a Hanford Tank waste simulant that mimics the composition of Tank 241-AN-105. This tank is classified as an Envelope A waste, the more common classification for the Hanford tank wastes. This original simulant has a 5.3 M sodium concentration (1). The composition of the simulant was adjusted during preparation to provide a sodium concentration of 5.0 M, which is typically used for the ion exchange testing and for removing the cesium. Noah Technologies, San Antonio, TX, prepared a 100-L batch of the simulant and provided analysis data confirming the composition. Typical of the AN-105 simulant, black precipitates formed upon aging, presumably silver metal, a photodecomposition product of precipitated silver chloride. The simulant was filtered immediately before use prior to each column loading run. Table 1 shows the composition of the filtered tank waste simulant.

Ion Exchange Material

SuperLig®644 (lot # C-10-05-28-02-35-60) was obtained from IBC Advanced Technologies, American Fork, UT. The RF resin was obtained both as a ground-gel product and a spherical product. The RF resins were supplied from various competing vendors, and the actual producer and lot identification were not available to the experimenters, to protect against potential biases. The resins were rinsed with deionized (DI) water and then converted to the H^+-form using 0.50 M HNO_3, followed by a DI water rinse, then converted to the Na^+-form using 0.25 M NaOH, rinsed again with DI water, and finally converted to the H^+-form using 0.50 M HNO_3 for storage. The resins were dried under nitrogen for three days, sub-aliquotted, and stored in water under a nitrogen head until needed.

Table 1. Composition of filtered AN-105 tank waste simulant

Species	Molarity[a]	Species	Molarity
Ag	5.85E-06	Na	5.00E + 00
Al	6.82E-01	NO_2	1.37E + 00
B	2.53E-03	NO_3	8.52E-01
Ca	4.67E-04	OH	6.25E-01
Cd	1.51E-05	Pb	<1.40E-05
Cl	1.20E-01	PO_4	1.68E-02
CO_3	8.80E-01	Se	1.02E-05
Cr	1.24E-02	Si	4.27E-03
F	1.05E-01	SO_4	1.76E-01
K	8.95E-02	TOC[b]	7.33E-02
Mg	1.04E-04	Zn	2.60E-05
Mo	4.51E-04	—	—

[a] Reported values have an uncertainty of ±10%, for all analytes except B, Cd, F and Se, which have an uncertainty of ±15%.

[b] Total organic carbon is due to the presence of glycolate, acetate, formate, and oxalate.

Column System

Small-scale column testing was performed using a single column containing the sorbent resin, a small metering pump, two valves, a pressure gauge, and a pressure-relief valve. The columns are Spectra Chrom™ chromatography columns made of glass with adjustable plungers on the bottom and the top. The inside diameter of the columns is 1.5 cm, which corresponds to a volume of 1.77 ml per cm of length. The columns are jacketed with a clear plastic to provide temperature regulation and a safety shield. Two water baths (Brinkmann and VWR International) were used to control the temperature during elution. The column connecting tubing is a polyfluorinated plastic with 1/8-in. OD and 1/16-in. ID. An Accu® piston pump (SciLog, Middleton, WI) was used to deliver solutions to the columns. This pump was equipped with a metering pump head (Fluid Metering, Inc., Oyster Bay, NY) and a pump stroke-rate controller (0.025 ml/stroke) or a Fluid Metering, Incorporated (FMI) QVG50 pump (FMI, Syosset, NY) equipped with a ceramic and Kynar® coated low-flow piston pump heads.

Column Processing

Before transfer to the column, the dried, conditioned ion exchange resin was again cycled through the Na^+-form and H^+-form—using 1.0 M NaOH, DI water, 0.50 M HNO_3, and DI water. Once loaded into the column, each column was processed at 3 bed volumes (BV)/h with 3 BV DI water, 3 BV

0.50 M HNO_3, and 3 BV DI water. The resins were then converted to the Na^+-form at a flow of 1 BV/h using either 3 BV of 0.25 M NaOH for SuperLig®644 resin or 6 BV of 1.0 M NaOH for the RF resin.

Column processing was performed at ambient temperature for the loading, feed displacement, and water rinse. The AN-105 feed solution was prepared at 50, 27.5, 10, or 5 μg/ml cesium using a cesium nitrate stock solution and then spiked with a ^{137}Cs tracer. The ^{137}Cs C/C_0 ratio (sample versus feed activity) was determined for each loading sample by counting the gamma emission at 661 KeV with a portable gamma spectrometer equipped with a Ge flat-crystal detector. The elution samples were counted on a portable gamma spectrometer equipped with a well-type, sodium iodide detector.

Each column was loaded with the feed solution until the breakthrough was $\geq 90\%$ C/C_0. The loading rate was varied to balance the feed requirements with the time requirements. The feed flow rate varied from 2 to 7 BV/hr for all the processed columns. The feed was displaced using 3 BV of 0.10 M NaOH; the resin was rinsed with 3 BV of DI water, eluted with the specified concentration of nitric acid, and rinsed again with 3 BV of DI water. The resin was removed from the column, dried under nitrogen air flow, weighed, and aliquotted for batch contact measurements.

Elution Parameters

The SuperLig®644 elution testing used a partial factorial experimental design to examine the effects of elution temperature, elution flowrate, initial cesium feed concentration, and eluant nitric acid concentration on the elution behavior. The temperature ranged from 25°C to 45°C, the elution flowrate ranged from 1 to 2 BV/h, and the nitric acid concentration varied between 0.25 and 1.0 M HNO_3. The RF elution testing was conducted at two temperatures (25° or 45°C), two flow rates (1.2 or 1.4 BV/h) and two HNO_3 concentrations (0.5 or 1.5 M).

Batch Contacts

The spent-resin contacts were performed with AN-105 simulant prepared at 50 μg/ml cesium (SuperLig®644 resin) or 10 μg/ml cesium (RF resin) with each ion exchange-column resin after column processing was completed, as well as with non-processed, conditioned resin. The batch contacts were conducted using 50 ml of AN-105 simulant contacted with 0.50 g of exchanger in a 60-ml polyethylene bottle for 48 h. The headspace was purged with nitrogen, and the caps were taped shut to retard air infusion. An orbital shaker (Labline 3520) was used to provide agitation at approximately 2300 rpm. The temperature was not controlled, and it varied between 23°C and 25°C over the course of the contacts. All Cs batch-distribution values (K_d) were determined by measuring the relative ^{137}Cs concentration before and after the batch contact. Initial ^{133}Cs concentrations were confirmed by inductively coupled plasma-mass spectrometry.

RESULTS

Column Loading

Eleven columns were processed using SuperLig®644 resin. For this testing, the AN-105 simulant was prepared at three cesium concentrations. Five columns were loaded at 50 μg/ml, two columns at 27.5 μg/ml, and four columns at 5 μg/ml. The flow rate was varied from ~2 to 7 BV/h to facilitate obtaining >90% breakthrough in a timely manner. The loading profile within each subset was internally consistent; Fig. 1 shows a representative SuperLig®644 loading curve for each feed concentration. The column breakthrough (%C/C_0) is plotted as a function of the number of BVs processed through the column.

Four columns were processed using the RF resins—three using the ground-gel RF resin and one using the spherical RF resin. Each column was processed with AN-105 simulant prepared at 10 μg/ml. Tests at

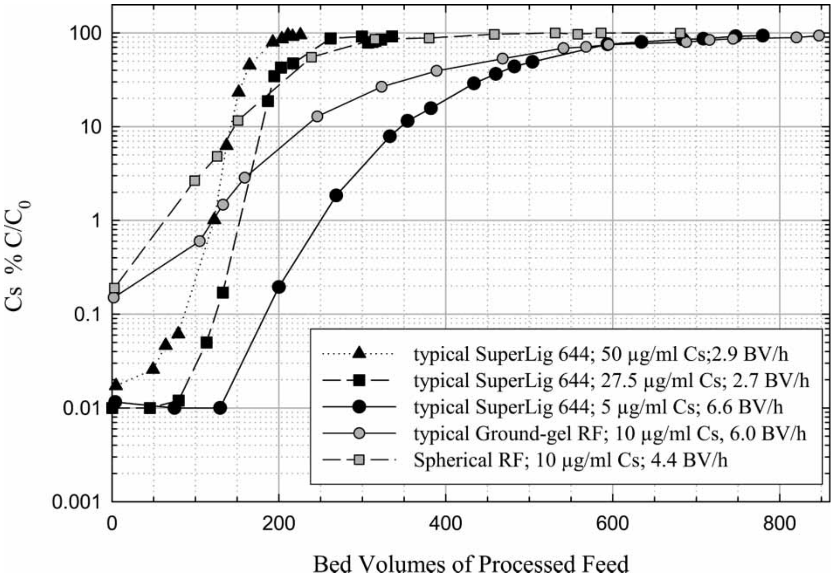

Figure 1. Selected SuperLig®644 and RF loading curves with AN-105 simulant at various initial cesium feed concentrations.

additional cesium concentrations were planned, but due to unforeseen difficulties, were not performed. The flow rate was varied from ~4 to 6 BV/hr to obtain >90% loading in a timely manner. The ground-gel RF resin loading curves were all internally consistent; a representative loading curve is shown in Fig. 1. The spherical RF resin loading curve is also shown in Fig. 1.

The column capacity was calculated for each column run at essentially 100% breakthrough using the following relationship:

$$\text{Capacity} \sum_{i=0}^{i=N} \frac{(C_0 - \bar{C}_i)V_i}{M} \tag{1}$$

where $\bar{C}$ = the average Cs concentration in column effluent sample *i and i-1*, μg/ml, C_0 = the Cs concentration in feed, μg/ml, V*i* = the volume of feed processed between each sample, ml, N = the number of samples collected during loading, and M = the mass of dry resin in column, g.

The column capacity will be dependent upon the feed concentration as well as the extent of the column breakthrough observed in the test. Table 2 shows the column capacities and column run conditions. The column loading was performed at different rates for many of the processed columns; however, the loading capacities were not significantly affected by the load rate. It is evident from Fig. 1 that there is significant difference in the load characteristics of the SuperLig®644 resin and the RF resin. The RF resin exhibits immediate breakthrough followed by moderate slope whereas the SuperLig®644 resin does not exhibit a comparable breakthrough until after processing 120 BVs, but is followed by a much sharper slope. Although there is initial breakthrough of cesium during loading of the RF resin and the RF loading kinetics are poor, the capacity of the ground-gel RF resin is similar to that of the SuperLig®644 resin. The spherical RF resin has a lower cesium capacity than the ground-gel RF resin.

Table 2. SuperLig®644 and RF column cesium capacity

	Feed concentration			
	50 μg/ml	27.5 μg/ml	10 μg/ml	5 μg/ml
Resin, type	Capacity in mg Cs/g resin			
SuperLig®644	44.2 ± 3.0	29.9 ± 0.8	—	13.2 ± 1.9
RF, ground-gel	—	—	15.7 ± 0.3	—
RF, spherical	—	—	9.5[a]	—

[a] There is only a single measurement for cesium capacity.

SuperLig®644 Elution

The SuperLig®644 elution testing used a partial factorial experimental design to examine the effects of elution temperature, elution flowrate, initial cesium feed concentration, and eluant nitric acid concentration on the elution behavior. Table 3 identifies the parameters for each SuperLig®644 elution test. Figure 2 shows the elution profile for each run, with the exception of Run 11, which was stopped after processing 8 BV of 1.0 M nitric acid. Regardless of the initial feed concentration or the elution conditions, 99% of the cesium was removed from each column in ≤13 BV. The elution testing included two elution runs that were performed at both high acid strength (1.0 M HNO_3) and high temperature (45°C). This particular combination of temperature and acid concentration results in significant gas generation (i.e., resin degradation) during processing.

After elution was completed, the spent resin was analyzed for the final cesium content. Using this value and the calculated amount of cesium present in each elution sample, the amount of Cs remaining on the resin during elution was calculated using Equation 2. Equation 2 accounts for all of the cesium eluted from the column, as all of the eluant was collected and analyzed in each sample.

$$\mathrm{Cs}_{\mathrm{Resin}} = \mathrm{Cs}_{\mathrm{End}} + \sum_{i=0}^{i-N} (C/C_0) * Cs_{133} * \Delta V \tag{2}$$

Table 3. Experimental details of SuperLig®644 elution testing

Column ID	Feed [Cs], μg/ml	Elution temp, °C	HNO_3, M[a]	Elution flow rate, BV/h	Elution volume, BV[b]	μg Cs/g spent resin @ 40 BV
1	27.5	45	0.25	1	41	1.8
2	50	25	0.50	2	64	2.0
3	5.0	25	0.50	1	41	2.4
4	50	45	0.50	1	52	0.7
5	5.0	45	0.50	2	52	1.0
6	50	35	0.75	1.5	45	3.1
7	50	35	0.75	1.5	44	3.0
8	50	25	1.0	1	45	1.6
9	5.0	25	1.0	2	49	1.5
10[c]	5.0	45	1.0	1	28	24.3
11[c]	27.5	45	1.0	2	8	—

[a] Target concentrations were 1.0, 0.75, 0.50, and 0.25 M HNO_3, titration results are: 0.986 M, 0.732 M, 0.488 and 0.252 M.

[b] BV determined in 0.25 M NaOH is 11.3 ml.

[c] A large amount of gas generation occurred; elution stopped during processing.

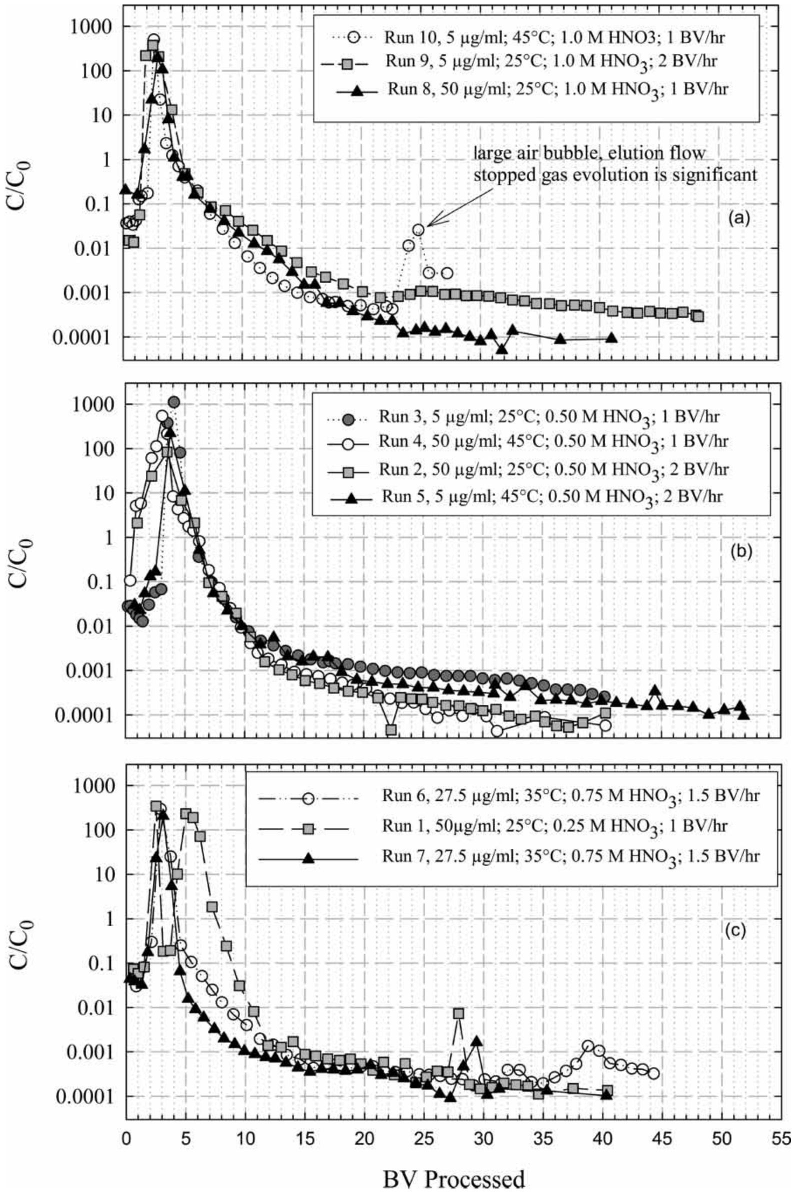

Figure 2. SuperLig$^{®}$644 elution curves at (a) 1.0 M HNO_3, (b) 0.50 M HNO_3 and (c) 0.25 or 0.75 M HNO_3.

where Cs_{Resin} = amount of cesium remaining on the resin at each data point, μg, Cs_{End} = amount of residual cesium on the resin at the end of elution, μg, C = ^{137}Cs counts in each elution sample, C_0 = ^{137}Cs counts in the initial feed, C_{133} = initial feed ^{133}Cs concentration, μg/ml, ΔV = volume of feed processed between each sample (including sample volume), ml, and N = number of samples collected during elution.

The data were divided by the final, dried mass of spent resin and are shown in Fig. 3. The μg Cs/mass dry resin is plotted as a function of the number of BVs of eluant processed.

The intent of the parametric design was to determine the relative effects of temperature, eluant concentration, flow rate, and Cs load concentration on the eluant behavior. The values of each parameter and the μg of Cs present on the resin after elution with 40 BVs were entered into a commercial statistical software package (JMP^{TM}, Statistical Analysis System Institute Inc, Cary NC) to facilitate analysis. The data were fitted to the correlation,

$$\mathrm{Cs_R} = 2.685 - 0.519[H^+] - 0.0400\mathrm{T} + 0.835\mathrm{F_R} + 0.00947[\mathrm{Cs}] \quad (3)$$

where $\mathrm{Cs_R}$ = residual Cs on the resin, μg per total spent resin sample (average spent resin mass is 2.232 g), $[H^+]$ = HNO_3 concentration, M, T = elution temperature, °C, F_R = flow rate of eluant, BV/h, and [Cs] = Cs concentration of feed, μg/ml.

The applicable range for $[H^+]$ in the Equation is 0.50 to 1.0 M, the temperature range is 25°C to 45°C, the flowrate range is 1.0 to 2.0 BV/h, and the feed cesium range is 5 to 50 μg/ml. The reasonably good statistical fit of the data appears to show that all significant parameters are accounted for in the correlation shown in Table 4. The statistical fit of the data identifies two of the four factors as significant to the determination of the residual Cs on the resin; the feed cesium concentration and the nitric acid concentration do not contribute significantly to the residual cesium. The statistical significance factor “p-value” identifies temperature and flow rate as the most statistically significant factors in the fit.

The modeling equation was used to calculate the residual cesium as a function of each parameter. Table 5 tabulates the spent resin cesium concentration based upon modifying one variable at a time. The model predicts that an elution performed at high temperature (45°C) and low flow rate (1 BV/hr) will provide a resin that has the least residual cesium. The acid concentration (0.25 to 1.0 M) and initial feed concentration (5 to 50 μg/ml) have only a minimal effect on residual cesium levels. The acid concentration impacts the location and shape of the maximum elution profile, but this does not correlate to a more complete elution.

Resorcinol-formaldehyde Elution

The RF elution testing was conducted at two temperatures and two HNO_3 concentrations as shown in Table 6. A total of three ground-gel RF columns were

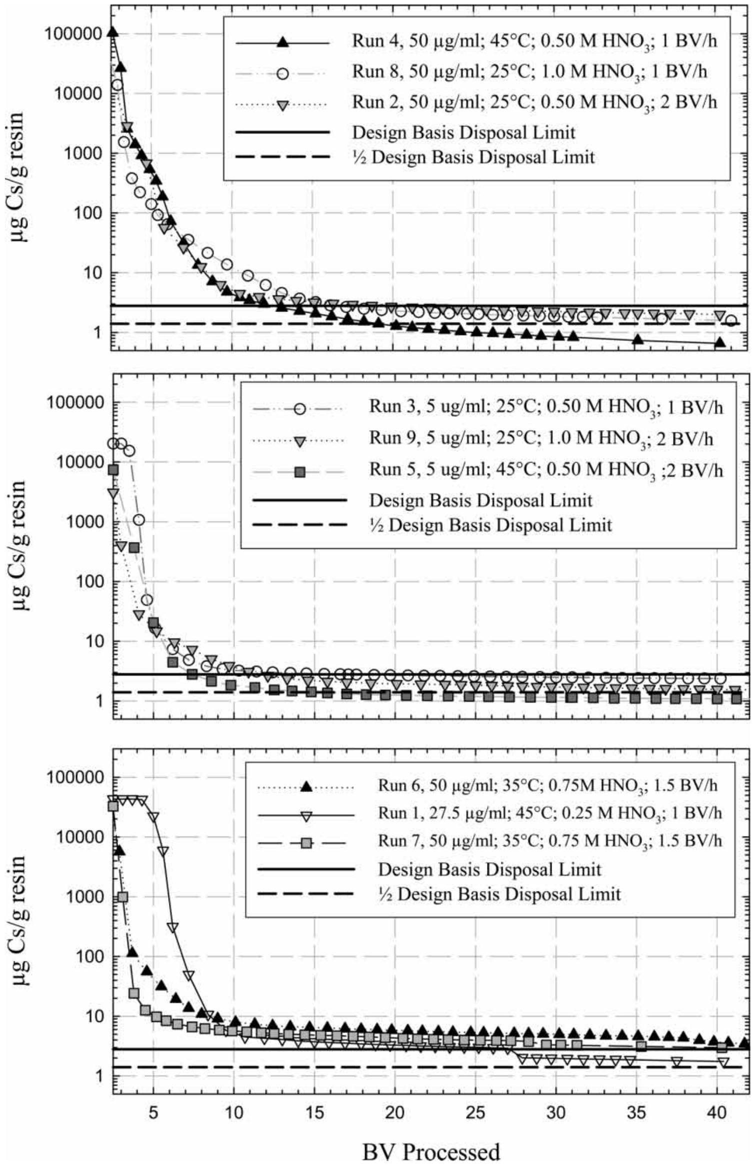

Figure 3. Comparison of SL-644 elution curves depicting residual cesium during processing.

loaded and eluted under conditions that systematically varied the elution temperature, the nitric acid concentration, and the eluant flow rate. One column of the spherical RF resin was also processed. The elution parameters matched a set of the ground-gel RF elution tests, allowing a direct comparison

Table 4. Statistical modeling data for SuperLig®644 residual cesium prediction

$R^2 = 0.8321$	
Parameter	Prob > |t |
Temperature	0.0878
Acid concentration	0.4769
Elution flow rate	0.0602
Cesium concentration	0.1953

of the elution performance of the two RF resin forms. Figure 4 shows the elution profile for each RF elution test.

The spherical RF resin shows excellent elution characteristics, providing for a more complete elution than the ground-gel RF resin under any combination of acid concentration and temperature. Cesium elution initially occurs more quickly with higher acid concentration; however, as with the SuperLig®644 testing, this does not correlate to more complete elution. Increasing the temperature allows a more complete elution of the RF resin.

The elution performance of the ground-gel RF resin is not quite as good as that of the SuperLig®644 resin. Regardless of the temperature and acid concentration, 99% of the cesium was removed from each column in 14 to 16 BV. The spherical RF resin out performed the ground-gel RF resin and in

Table 5. Model residual cesium values for SuperLig®644 resin at 40 BVs of processed eluant

$[HNO_3]$, M	Temp, °C	Flow rate, BV/h	Feed [Cs], μg/ml	Resin residual cesium, μg/g resin	Trend of residual cesium within modeling set	Variable
0.5	25	1	5	1.09		Flow rate
0.5	25	1.5	5	1.29	+37%	
0.5	25	2	5	1.49		
0.5	25	1	5	1.09		
0.75	25	1	5	1.03	−11%	H^+
1	25	1	5	0.97		
0.5	25	1	5	1.09		
0.5	25	1	27.5	1.19	+19%	[Cs]
0.5	25	1	50	1.30		
0.5	25	1	5	1.09		
0.5	35	1	5	0.91	−34%	Temp
0.5	45	1	5	0.72		

general performed better than the SuperLig®644 resin, achieving 99% cesium removal within 7 BV.

The amount of cesium present on the resin during processing was calculated using Equation 1. The μg Cs was divided by the final, dried mass of spent resin and plotted against the number of BVs, as shown in Fig. 5. The spherical RF resin demonstrated the greatest removal of cesium, removing 99.99% of the cesium after processing with 25 BV. The ground-gel RF could not achieve this performance, and the SuperLig®644 could only achieve this performance in a few of the 12 column tests after processing 30 BV.

Residual Cesium on Resin

The WTP design basis for spent resin is 60 μCi/g resin. This value is based upon the air-dried, H-form SL-644 resin. This value, based on processing with SL-644 resin with a bulk density of 0.66 g/ml and processing a waste that would contain nominally 25% ^{137}Cs, corresponds to a mass-basis limit for total Cs on spent SuperLig®644 resin of 2.8 μg/g. The corresponding limit for spherical RF resin is 4.2 μg/g, and for ground-gel RF resin it is 2.4 μg/g. Figures 3 and 5 show these values as well as one-half of these values.

The SuperLig®644 resin elution was generally capable of meeting the WTP design basis disposal limit, as was the spherical RF resin elution. The ground-gel RF resin was only able to meet the WTP design basis disposal limit when eluted at 45°C and 0.50 M HNO_3. A more conservative disposal level, one-half of the WTP design basis, could only be met by the SuperLig®644 elution performed at 45°C and 0.50 M HNO_3 and the spherical RF resin elution.

Batch Contacts

The impact of the elution conditions on the resin capacity was assessed by performing batch contacts on both spent resin and conditioned-only resin.

Table 6. Experimental details of RF elution testing

Column ID	RF resin type	Elution temp, °C	HNO_3, M	Elution flow rate, BV/h	Elution volume, BV	μg Cs/g spent resin @ 40 BV
1	Ground-gel	45	0.50	1.4	68	2.1
2	Ground-gel	25	0.50	1.4	67	4.9
3	Spherical	25	0.50	1.4	51	0.2
4	Ground-gel	45	1.5	1.2	57	3.8

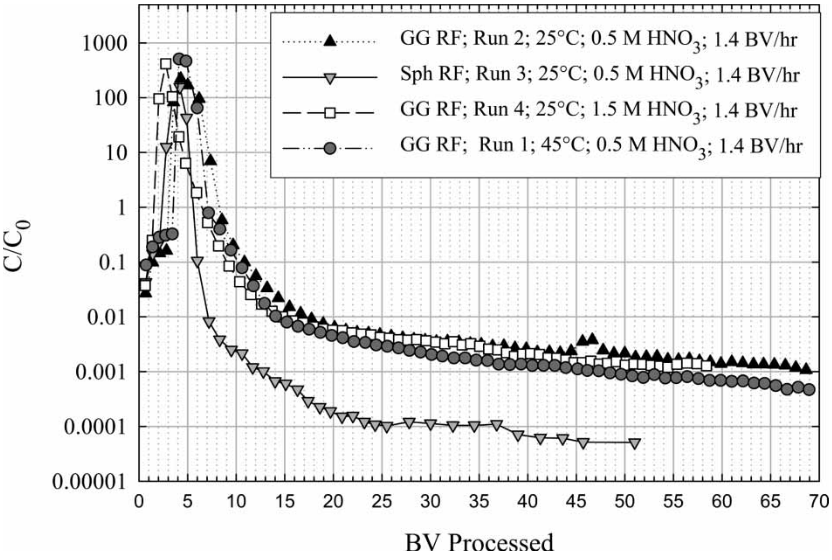

Figure 4. Elution of spherical and ground-gel RF resin.

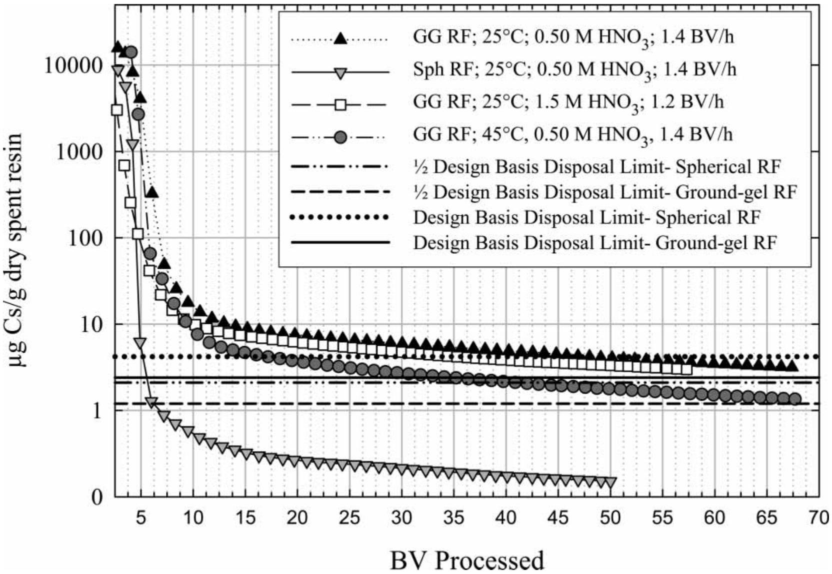

Figure 5. Comparison of RF elution curves depicting residual cesium during processing.

The spent resin duplicate contacts were compared to those of the conditioned resin, which had not been processed for Cs removal. Table 7 shows the results of the SuperLig®644 batch contacts; Table 8 shows the results of the RF resin.

As either the temperature or nitric acid concentration is increased, there is a significant negative impact on the cesium capacity of the SuperLig®644 resin. When both the acid concentration and temperature are increased, the resin degradation is very severe, and the cesium capacity is lost. The RF resin does not appear to be as sensitive to temperature and acid concentration variations. Increasing the temperature did not significantly affect the cesium capacity. Increasing the nitric acid concentration to 1.5 M produced a 25% reduction in the cesium capacity.

DISCUSSION

This paper describes the result of load and elution testing on SuperLig®644 and two forms of RF resin. Multiple single-column load and elution tests were performed with both types of resin. The RF exhibits an initial cesium breakthrough during loading whereas the SuperLig®644 did not show appreciable breakthrough until processing 120 BV of feed. However, the slope of the breakthrough profile is much steeper for SuperLig®644 resin. These observations are consistent with other studies using similar feeds reported in the literature (1–3, 7, 10), although both the ground-gel RF resin and the SuperLig®644 resin processed more feed to reach $>50\%$ breakthrough than estimated from extrapolation of previous breakthrough curves. The loading capacity of each processed column was determined at essentially 100% breakthrough. Although the ground-gel RF resin demonstrated a high initial cesium breakthrough and had poor loading kinetics, the cesium capacity was similar to the SuperLig®644 resin. The capacity of the ground-gel RF resin was ~16 mg Cs/g dry resin, and for SuperLig®644 resin it was ~13 mg Cs/g dry resin. These results are consistent with similar studies (3, 6). The spherical RF resin unexpectedly had a much lower cesium capacity than either SuperLig®644 resin or ground-gel RF resin.

Complete elution, $\geq 99\%$ cesium removal, was reached within 13 BV for all the SuperLig®644 elution conditions, within 17 BV for the ground-gel elution conditions, and within 7 BV for the spherical RF resin. Typically the SuperLig®644 elution was complete, $<1\%$ Cs remaining, after processing with 14 BV of eluant (1–3, 6). The ground-gel RF resin typically required 18 or more BV to reach this level (10). The rapid elution of the spherical RF resin was unexpected. The batch distribution measurements of the spent resin from the column tests indicate that the SuperLig®644 resin undergoes significant loss of cesium capacity at either high temperature or high acid concentration. If both high temperature and high acid strength are used, the resin loses all capacity to exchange cesium. The RF resin did not exhibit any loss of

Table 7. SuperLig®644 Control and spent resin batch contact results in AN-105 simulant

Column ID	K_d value, ml/g	Change from control[a], %	Elution Conditions Temp, °C	[HNO$_3$], M	Flow rate, BV/h
Run 1	3,370 ± 210	−21	45	0.25	1.0
Run 2	5,290 ± 900	25	25	0.50	2.0
Run 3	2,930 ± 70	−31	25	1.0	2.0
Run 4	3,490 ± 70	−18	45	0.50	1.0
Run 5	3,770 ± 80	−11	45	0.50	2.0
Run 6	5,440 ± 310	−8	35	0.75	1.5
Run 7	2,930 ± 40	−31	35	0.75	1.5
Run 8	2,990 ± 150	−29	25	1.0	1.0
Run 9	4,390 ± 40	4	25	1.0	2.0
Run 10	110 ± 12	−97	45	1.0	1.0
Run 11	5 ± 4	−100	45	1.0	2.0

[a] Control K_d value for runs 6 and 7 is 5,940 ± 190 ml/g. The K_d control value for the other runs is 4,240 ± 180 ml/g.

capacity as a result of eluting at high temperature (45°C). The RF resin is not as sensitive to acid concentration as the SuperLig®644 resin. Increasing the acid concentration from 0.50 to 1.5 M reduces the effectiveness of cesium removal by 25%.

The temperature, flow rate, and nitric acid concentration were varied to determine the optimal elution conditions with respect to minimizing the amount of residual cesium after processing. The SuperLig®644 residual cesium values were most strongly affected by changes in the elution tempera-

Table 8. RF control and spent resin batch contact results in AN-105 simulant

Column ID	Resin type	K_d Value, ml/g	Elution conditions Change from control, %	Temp, °C	[HNO$_3$], M	Flow rate, BV/h
Run 1	Ground-gel[a]	3,790 ± 100	4	45	0.50	1.4
Run 2	Ground-gel	3,830 ± 120	5	25	0.50	1.4
Run 3	Spherical[b]	1,030 ± 50	23	25	0.50	1.4
Run 4	Ground-gel	2,830 ± 130	−23	25	1.5	1.2

[a] Ground-gel control Kd value is 3,660 ± 130 ml/g.
[b] Spherical control Kd value is 840 ± 40 ml/g.

ture and eluant flow rate. As would be predicted based upon kinetic consideration alone, decreasing the eluant flow rate and increasing the temperature provides the best elution. Varying the nitric acid concentration did not have a significant effect on the residual cesium for either SuperLig®644 or RF resins (when compared at 40 BV processed eluant). The acid concentration impacts the location and shape of the maximum elution profile, but this does not correlate to a more complete elution.

The SuperLig®644 resin elution was generally able to comply with design assumptions for spent resin disposal equipment, as was the spherical RF resin elution. The mass-basis limit for total Cs on the spent SuperLig®644 resin is 2.8 μg/g and for spherical RF resin it is 4.2 μg/g. The ground-gel RF resin did not reach the mass-basis limit of 2.4 μg/g unless the elution was performed at slightly elevated temperature. The elution required for spent resin disposal is more stringent than the elution necessary to ensure the cesium will not bleed from the lead column when it is rotated into the polishing column position. For Envelope A effluents, an eluted-resin residual cesium concentration of 14.6 μg/g would provide an effluent which is less than one-third of the LAW disposal limits. The SuperLig®644 resin would generally reach this level after elution with 14 BV, and the spherical resin clearly would be able to meet this level within 10 BVs. The ground-gel RF would also be able to meet this level. Future work will need to be performed to determine the residual cesium level needed for the ground-gel and spherical RF resins to be rotated into the polishing column position. Additional testing of the RF resins is currently underway.

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