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Sorption of Cesium from Aqueous Waste Solution on SuperLig[®] 644 Resin

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The removal of cesium from aqueous waste solution was investigated in a column setup using SuperLig[®] 644 resin. The resin was significantly coarser in size than those used in previous studies because of hydraulic problems encountered during pilot-scale tests. The bed volume (BV = 140) at the onset of breakthrough surpassed the design requirement of 100 BV at 50% breakthrough. The percent of cesium removed by the resin at the onset of breakthrough was 99.96. The elution of cesium with 0.5 M HNO₃ was satisfactory with a peak BV of 2.5. The elution BV for $C/C_0 = 0.01$ was 10, which is less than the target of 15 BV. The percent of sorbed cesium eluted from the resin was 99.88%. In addition, the BV of the various solutions used for the supporting process steps (feed displacement, post-feed displacement rinse, post-elution rinse, and regeneration) of the cesium ion exchange system was sufficient.

Keywords: SuperLig, resin, cesium, column, sorption, breakthrough curve, elution, regeneration.

1. Introduction

The River Protection Project (RPP) is charged with designing and building a high-level nuclear waste treatment plant at the United States Department of Energy's (DOE) Hanford site in Richland, Washington. The waste treatment plant is to process over 53 millions of gallons of radioactive waste are stored in 177 underground tanks at the Hanford site. The waste is the legacy of over 50 years of plutonium production.

The flow sheet of the waste treatment plant comprises various unit operations (ultrafiltration, precipitation, evaporation, ion exchange, vitrification, etc.).¹ The products from the plant operations will be a large volume of low-activity radioactive waste, and a relatively small volume of high-level radioactive waste immobilized into a borosilicate glass matrix. The vitrified wastes are to be deposited in a federal geologic repository. The cesium in the Hanford Site waste is to be removed by ion exchange using a proprietary elutable cation exchange resin (SuperLig[®] 644).

Extensive ion exchange studies have been conducted with small-scale (1.45 cm ID) and medium-scale (2.67 cm ID) columns using both simulants and actual Hanford site waste solutions.¹⁻¹² The principal objective of the studies was to evaluate the ability of the SuperLig[®] 644 resin to remove cesium from Hanford site waste solutions. The studies culminated in pilot-scale (15.2, 30.5, 59.1 cm ID) column tests using AN-105 simulant. The AN-105 simulant is a non-radioactive surrogate of one of the Hanford site wastes. Both the chemical and hydraulic performance of the resin at the small-scale and medium-scale column levels were excellent overall. The pilot-scale tests, however, resulted in serious hydraulic performance problems because of the development of high pressure drops across the resin bed¹³.

The high pressure drop issue was resolved using sieved SuperLig[®] 644 resin with larger particle sizes (600 - 850 μm or 30 - 20 mesh, mean = 766 μm) in a narrow size range.¹³ Note that the previous small-scale, medium-scale and pilot-scale column tests used generally a wide particle size range (63 - 850 μm or 230 - 20 mesh, mean = 460 μm) with the bulk between 300 and 600 μm . The pilot-scale column study using larger particle sizes (30 - 20 mesh) of SuperLig[®] 644 resin focused only on hydraulic performance. The goal of this study was therefore to demonstrate the chemical performance of the ion exchange system in terms of sorption and elution of cesium, and its ancillary process steps using AN-105 simulant solution and SuperLig[®] 644 resin with a larger particle size range (30 - 20 mesh) under a worst-case scenario in cesium concentration (i.e., tenfold higher than normal).

2. Materials and Methods

2.1. Resin. The SuperLig[®] 644 resin (batch # = C-01-11-05-02-35-60, designated as first 250 gallon batch) was received from IBC Advanced Technologies, Inc. (American Fork, Utah). It was received in the sodium form (Na^+ form) in deionized water and was sieved and pretreated before being used.

The resin is a proprietary polymeric organic material that has sequestering ligand agents that are highly selective for cesium in alkaline media containing relatively high concentrations of other competing cations like sodium and potassium. The resin's sorptive ability is based on molecular recognition technology and macrocyclic chemistry¹⁴⁻²¹.

The SuperLig[®] 644 resin removes cesium from solution by exchanging the sodium on the resin with cesium as shown below. The over bars represent solid-phase concentrations. R-Na^+ represents the resin in Na^+ form.



The resin is elutable in acidic media by exchanging the cesium on the resin with hydrogen from solution resulting in a hydrogen-form (H^+ form) resin as given below.



It is also regenerable back to the Na^+ form in alkaline media by exchanging the hydrogen on the resin with sodium from solution as given below.



2.2. Resin Pretreatment. The as-received Na^+ form resin in deionized water was wet-sieved using Gilson wet-vac sieve tester. The 600 - 850 μm (30 - 20 mesh) size range was used for the entire study. The sieved as-received Na^+ form resin was pretreated by taking it through two complete acid-caustic solution treatments.

Each of the pretreatment steps (i) to (v) below began with decanting as much water or solution (from the previous step) from the resin without exposing the resin to air. It was then followed by adding a known volume of water or solution of interest to the resin and letting the resin soak in the water or solution for a predetermined time. The resin-water or solution mixture was gently stirred briefly every ten minutes. The volume of water or solution and soaking time for each of the steps were as follows.

- (i) 5 bed volumes (BV) of 0.5 M HNO₃ for 90 minutes.
- (ii) Three 30-minute rinses using 5 BV of deionized water per rinse.
- (iii) 5 BV of 0.25 M NaOH for 90 minutes.
- (iv) Three 30-minute rinses using 5 BV of deionized water per rinse.
- (v) Repeat of steps (i) to (iv).
- (vi) Resin filtration under vacuum using 0.45 μm nylon Nalgene filter unit (Rochester, New York). The filtration was stopped 5 minutes after the water dripping ceased.

The damp resin was transferred to a wide-mouth HDPE bottle and mixed thoroughly using a spatula. Portions of the damp pretreated resin were immediately taken for F-factor measurements. The F-factor is the solids fraction remaining after water loss through vacuum drying. The F-Factor of the damp pretreated resin was determined by weighing in quadruplicate approximately 0.8 g of resin and drying the resin for ~ 24 hours in a Napco (Winchester, Virginia) model 5851 vacuum oven (< 40 torr absolute pressure) at 45 ± 2 °C to constant mass.

Also, small amounts of the damp pretreated resin were weighed into a 100-mL graduated cylinder containing 0.25 M NaOH solution (while simultaneously tapping the cylinder walls to obtain uniform packing) till a resin bed volume of about 95 mL was attained. Note that this was the resin used for the column run. The remaining damp pretreated resin was stored in 0.01 M NaOH solution for later use.

2.3. Simulant Solution. A simulant solution based on Hanford site waste AN-105 was used in this study. The simulant was prepared using the recipe developed by Eibling et al.²². A total of 27

liters of simulant solution was prepared in one batch. The simulant solution was filtered in two batches under vacuum using 0.45 μm nylon Nalgene filter unit (Rochester, New York) after aging for 32 days. The two batches of filtered solutions were combined into one 27-liter solution a day after the filtration and allowed to age for approximately 6 days before samples were taken for analysis. No solid particles were visible in the solution at the end of the sixth day of aging.

2.4. Chemicals. Chemicals described in this section are those dealing directly with the column experiments. Chemicals used in the preparation of the simulant are left out for brevity. Reagent grade chemicals were used throughout. Nitric acid (Fisher Chemicals, New Jersey) and sodium hydroxide (Fisher Chemicals, New Jersey) were used to prepare the 0.5 M HNO_3 , 0.1 M NaOH, and 0.25 M NaOH solutions. Deionized water was used to prepare the solutions. Deionized water was also used in some of the column process steps (e.g., resin rinsing).

2.5. Column Apparatus. The ion exchange column apparatus consisted of a glass column, a fraction collector, a constant temperature circulating water bath, and several metering pumps. The column apparatus was setup in a chemical hood. The pump inlet tubings were manually switched between the simulant and the other process solutions.

The borosilicate glass column (Spectrum Chromatography, Houston, Texas) had an inside diameter (ID) of 2.67 cm (i.e. 5.60 mL/cm of height) and graduations on the walls to facilitate measurement of resin bed height and height of liquid above resin bed. The glass column was equipped with adjustable polypropylene plunger (model 124122, Spectrum Chromatography, Houston, Texas) at the top and 200 mesh stainless steel screen at the bottom. The plunger was used to control the height of liquid above the resin bed, while the screen was

used as support for the resin. Temperature regulation in the column was achieved with a constant temperature circulating water bath (Model DC10-P5, ThermoHaake, Newington, New Hampshire) connected to the column glass jacket. The outer walls of the column and jacket were coated with polyvinyl chloride to help minimize hazard in case of breakage.

Solutions were introduced down flow through the column using a Fluid Metering Incorporated (FMI, Syosset, New York) positive displacement pump (model RP-P) equipped with Scilog Inc. (Middletown, Wisconsin) piston pump head (model RH00). The piston pump head (1/8-in ID) was made of stainless steel and was rotated by a 450-rpm optically encoded servo-controlled motor. The maximum flow rate for the pump was 23 mL/min.

Spectrum Chromatography IS-95 Interval Sampler located at the outlet of the column was utilized to collect aliquots of samples either manually or automatically. All the individual units (i.e. pump, column, fraction collector) from the solution reservoir bottles to the effluent bottles were connected with polyethylene tubings (1/16-in ID X 1/8-in OD) supplied with Teflon quick-disconnect fittings (Cole-Palmer Instrument Company, Vernon Hills, Illinois) at the ends.

2.6. Column Experiments. The SuperLig[®] 644 resin in 0.25 NaOH solution set aside at the end of the resin pretreatment was poured into the glass column. The wall of the glass column was simultaneously tapped during the pouring operation to ensure uniform resin bed packing. The mass of damp Na⁺ form resin put in the column was 66.2 g (equivalent to 28.0 g of dry Na⁺ form resin).

Each column process step (i.e., sorption, feed displacement, elution, water rinse, regeneration, etc.) was considered to begin when the liquid being processed reached the top of the liquid above the resin bed. As mentioned in the previous subsection, liquid was passed

downward through the column. The height of the resin bed, the height of the liquid above the resin bed, flow rate, and temperature of water in the circulating bath were measured periodically. The temperature for all the column process steps was 25 ± 1 °C. The volume of liquid above the resin bed during the loading step was 0.4 BV. Table 1 gives details of the experimental conditions for the column run.

Samples of the effluent were collected periodically for analysis (cesium, potassium, sodium and pH) during the column run. Cesium was analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), and potassium and sodium were analyzed by Inductively Coupled Plasma-Emission Spectrometry (ICP-ES). At the end of the last process step (i.e post-regeneration rinse), the used resin was removed from the column and filtered till the water dripping ceased, followed by drying the resin in vacuum oven (< 40 torr absolute pressure) at 45 ± 2 °C to a constant mass. A portion of the dried used resin was then sent for cesium analysis.

The column run proceeded as expected except the column inadvertently ran out of feed solution after the 260th BV of the sorption step for a couple of hours. As a result, air was entrapped in the resin bed. The resin tends to degrade in air. The resin bed was therefore refilled with simulant feed solution while simultaneously tapping the wall of the column to remove the air. This was followed by the 0.1 M NaOH feed displacement process step.

3. Results and Discussion

3.1. Resin Properties. Table 2 shows properties of the SuperLig[®] 644 resin. The F-factor is given by Eq (4).

$$F = m_d/m \tag{4}$$

where m_d is the mass of vacuum-dried Na^+ form resin (g), and m is the mass of damp pretreated Na^+ form resin (g). The Na^+ form dry basis resin bed density in AN-105 simulant is given by Eq (5).

$$\text{Na}^+ \text{ form dry basis resin bed density} = (mF)/V \quad (5)$$

where V (mL) is the resin bed volume.

The particle size range and mean particle size of the resin are also given in Table 2.

3.2. Simulant Solution Characterization. Table 3 gives the composition of the major constituents in the AN-105 simulant solution. The analytical results for the AN-105 simulant generally compare favorably with the amounts used to prepare the solution. For example, the cesium, sodium, and potassium concentrations in the simulant based on the amount actually put in solution are 78.0 $\mu\text{g}/\text{mL}$, 4.74 M, and 0.090 M versus the measured concentrations of 77.5 $\mu\text{g}/\text{mL}$, 4.96 M, and 0.094 M respectively.

3.3. Cesium Sorption. The column sorption data for cesium is shown in Figure 1. The ordinate is the relative concentration expressed as the ratio of the column effluent concentration (C) to the initial or column influent concentration (C_o). The onset of breakthrough was at 140 bed volumes (BV). At the time of run termination of 260 BV, 94.3% breakthrough had been attained. The BV at the onset of breakthrough obtained in this study is consistent with that (280 BV) of an earlier

study¹² using AN-105 simulant and unsieved (particle size range = 63 - 850 μm) SuperLig[®] 644 resin at an initial cesium concentration of 7.7 $\mu\text{g}/\text{mL}$, flow rate of 3 BV/hr, and a temperature of 25 °C.

The number of bed volumes processed at 50% breakthrough (λ value) is 205. It must be noted that the λ value is remarkably greater than the design requirement of 100 BV at 50% breakthrough even for the fairly high initial cesium concentration of 77.5 $\mu\text{g}/\text{mL}$.²³ Note also that this concentration is tenfold higher than normal for AN-105 waste. This is an indication of the relatively large sorption capacity of the SuperLig[®] 644 resin. The λ value of 205 agrees closely with the value of 215 predicted from batch sorption tests using the same resin.²⁴

Table 4 provides a summary of the cesium sorption data for BV of feed simulant processed, percent cesium removed, and amount of cesium sorbed at various stages of breakthrough. The percent cesium removed and the amount of cesium sorbed are based on estimate of the area above the breakthrough curve. Again, the amount of cesium sorbed (411 $\mu\text{mole}/\text{g}$ or 55,000 $\mu\text{g}/\text{g}$ dry Na^+ form resin) at 94.3% breakthrough is roughly close to the amount sorbed at equilibrium (432 $\mu\text{mole}/\text{g}$ or 57,000 $\mu\text{g}/\text{g}$ dry Na^+ form resin) predicted from batch sorption tests using the same resin.²⁴

3.3. Feed Displacement and Post-Feed Displacement Rinse. Figure 2 shows the relative effluent concentration (C/C_0) of cesium, potassium, and sodium during the feed displacement (with 0.1 M NaOH) and post-feed displacement water rinse steps. The vertical dashed line demarcates the feed displacement and the post-feed displacement rinse portions of the curves. In other words, 6 BV of feed displacement was followed by 6 BV of post-feed displacement rinse.

The concentrations of cesium, potassium, and sodium decreased with increasing effluent BV. The decrease in concentration was more drastic in the feed displacement step. At the start of feed displacement, the concentrations of cesium, potassium, and sodium were roughly the same as the feed simulant concentration ($C/C_o \sim 1$). At the end of the post-feed displacement rinse step, the concentrations of cesium, potassium, and sodium were all three orders of magnitude lower than their respective initial concentrations. The above indicates 6 BV of 0.1 M NaOH solution and 6 BV of water are adequate for the feed displacement and post-feed displacement rinse steps respectively.

3.4. Cesium Elution. The elution of cesium from the resin using 0.5 M HNO₃ solution is shown in Figure 3 along with pH data. The elution curve displays a peak at approximately 2.5 BV. The BV value at $C/C_o = 0.01$ is about 10 (between 9 and 11.3). Note that the $C/C_o = 0.01$ value of 10 is lower than the target of 15.²³ The peak and $C/C_o = 0.01$ BV values generally agree with past cesium-SuperLig[®] 644 resin elution data.^{5-8,10-12}

Based on residual cesium on the used resin at the end of the column run (see Table 7), the percent of sorbed cesium eluted is 99.88. Also, based on an estimate of the area below the elution curve, the percent of sorbed cesium eluted is 95.52. The above two estimates are reasonably close.

The pH profile is consistent with the elution profile in that it drops from 11 to 0.9 at the elution peak and remains fairly constant at 0.9 thereafter. It is unclear why the cesium concentration increased after the 23rd BV. The air entrapment at the end of the sorption step does not seem to have affected the resin.

3.5. Post-Elution Rinse. The relative effluent concentrations (C/C_o) of cesium, potassium, and sodium during the post-elution water rinse step are given in Table 5. As observed in the feed displacement and post-feed displacement rinse steps, each of the concentrations continues to decrease with increasing effluent bed volume. In fact, all the C/C_o values are at least an order of magnitude below their respective post-feed displacement rinse step values. Note that the potassium concentration is below detection limit throughout. A clear indication that the post-elution rinse step proceeded well, and that 6 BV of water are enough for the rinsing of the resin.

3.6. Resin Regeneration. Table 6 gives data on relative effluent concentrations (C/C_o) of cesium and potassium along with sodium concentration during the regeneration of SuperLig[®] 644 resin with 0.25 M (nominal) NaOH following the post-elution rinse step. Cesium is virtually an order of magnitude below the corresponding values for the post-elution rinse step. Even though the cesium concentration seems to be increasing with increasing effluent bed volume, the values are still fairly low and roughly close to each other. The potassium C/C_o values are still below detection limit just as the previous post-elution rinse step.

The sodium concentration increases as effluent bed volume increases. Initially, the sodium in solution is exchanged with the hydrogen on the resin. Hence, the low concentration of sodium in solution. At 12 BV, the sodium concentration has increased to close to the nominal value of the regenerating solution (i.e., 0.25 M NaOH). This indicates elution is complete and that 12 BV of 0.25 M NaOH solution is sufficient for the regeneration.

3.7. Post-Column Run Resin Mass and Analysis. Table 7 gives the pre- and post-column run dry masses of the Na⁺ form SuperLig[®] 644 resin and the residual cesium on the used Na⁺ form

SuperLig[®] 644 resin at the end of the column run. Note that the used resin was regenerated to the Na⁺ form with 0.25 M NaOH solution followed by deionized water rinse and vacuum drying before being sent for analysis. The pre- and post-column run dry masses of the resin are close (relative standard deviation = 2.3%). This implies there was virtually no resin loss or degradation during the column run considering the fact that the resin was inadvertently exposed to air towards the end of the sorption step. The cesium analysis involved microwave dissolution of the resin in aqua regia followed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) of the resulting solution.

4. Conclusions

On the whole, the chemical and hydraulic performance of the medium-scale column test using SuperLig[®] 644 resin with larger particle sizes (600 - 850 μm or 30 - 20 mesh) in a narrow size range was outstanding even under a worst-case scenario of a tenfold higher than typical cesium concentration. The specifics are as follows.

The sorption step of the column run resulted in cesium percent removal of 99.96 at the onset of breakthrough. The BV (140) at the onset of breakthrough exceeded the requirement of 100 BV at 50% breakthrough even for the relatively high initial cesium concentration.

Cesium elution with 0.5 M HNO₃ was efficient with a peak BV of 2.5, and a BV at $C/C_0 = 0.01$ of ~10. This BV at $C/C_0 = 0.01$ value is below the target of 15 BV. Also, 99.88% of sorbed cesium was eluted from the resin.

Aside from the above two main process steps (sorption and elution), the ancillary process steps (feed displacement, post-feed displacement water rinse, post-elution water rinse, and

regeneration) for the cesium ion exchange system all proceeded well with the stipulated BV of the respective solutions used.

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Figures

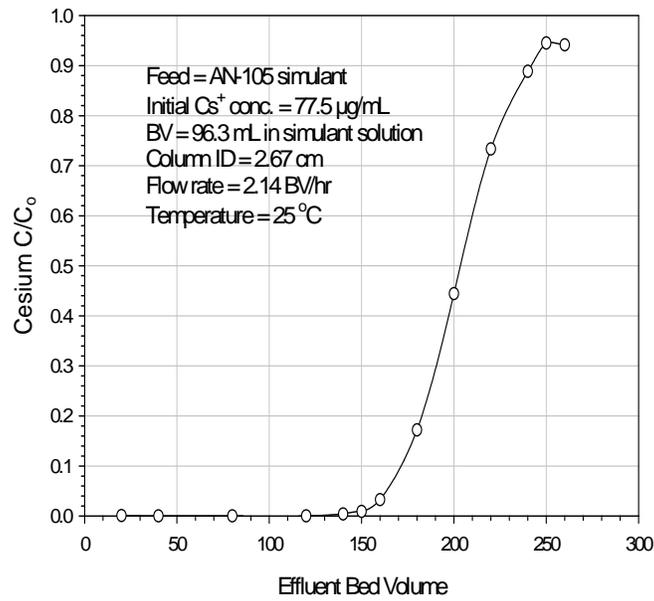


Figure 1. Cesium breakthrough curve for AN-105 simulant and SuperLig[®] 644 resin.

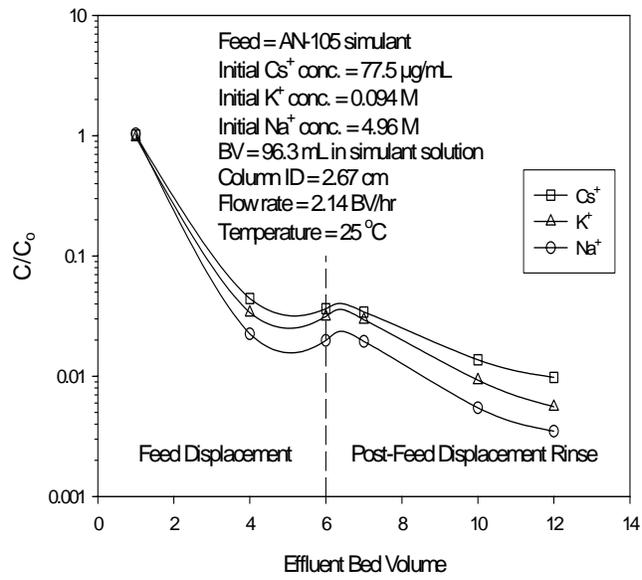


Figure 2. Effluent concentrations during feed displacement and post-feed displacement rinse steps.

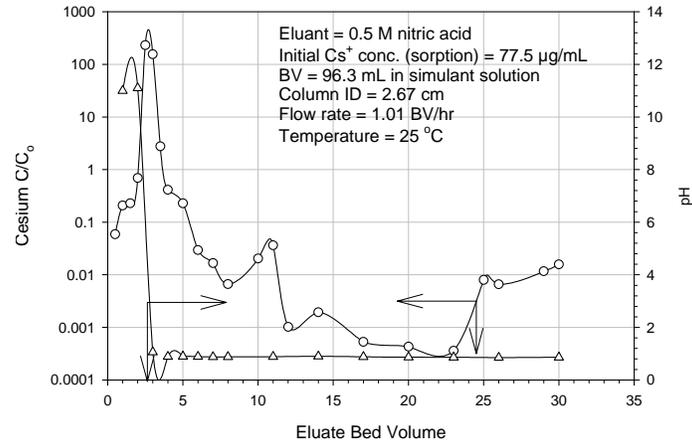


Figure 3. Cesium elution and pH profiles for AN-105 simulant and SuperLig[®] 644 resin.

Tables

Table 1. Experimental Conditions for the AN-105 Simulant Column Run

Process step	Solution	Bed volumes of solution processed	Flow rate, BV/hr	Time per process step, hr
Resin preconditioning	0.25 M NaOH	5	5.00	1.0
Sorption	AN-105 simulant	260	2.14	121.5
Feed displacement	0.10 M NaOH	6	2.14	2.8
Post-feed displacement rinse	Deionized water	6	2.14	2.8
Elution	0.5 M HNO ₃	30	1.01	29.7
Post-elution rinse	Deionized water	6	1.01	5.9
Regeneration	0.25 M NaOH	12	2.14	5.6
Post-regeneration rinse	Deionized water	6	2.14	2.8

Temperature of each process step = 25 ± 1 °C
Bed volume (BV) of column = 96.3 mL (in simulant solution)

Table 2. Properties of SuperLig[®] 644 Resin

F-factor	0.423
Particle size range	600 - 850 μm or 30 - 20 mesh
Mean particle size	766 ²⁴ μm
Bed density (dry basis)	
AN-105 Simulant	0.290 ^{a, b} g dry Na ⁺ form resin/mL

^a Based on resin bed volume during column run sorption step

^b Calculated using Eq 5

Table 3. Composition of AN-105 Simulant

Constituent	μg/mL	Constituent	μg/mL
Al	17,100	F ⁻	< 20
Cr	570	Cl ⁻	4,120
Cs	77.5	NO ₂ ⁻	53,300
K	3,665 (0.094 M)	NO ₃ ⁻	77,850
Na	114,000 (4.96 M)	PO ₄ ³⁻	163
P	75.0	SO ₄ ²⁻	409
Pb	50.0	TIC ^a	1,105
S	150	TOC ^b	< 10
Free OH ⁻ , M	1.34	TC ^c	1,105
Density, g/mL	1.23		

^a TIC = Total inorganic carbon

^b TOC = Total organic carbon

^c TC = Total carbon

Data with “<” symbols are detection limits

Table 4. BV of Feed Solution Processed Along With Percent and Amount of Cesium Sorbed at Various Stages of Breakthrough

Percent Breakthrough	BV	Percent Cs ⁺ Sorbed	Cs ⁺ Sorbed, $\mu\text{g/g}$ ($\mu\text{mole/g}$)
Onset	140	99.96	37,000 (281)
50	205	94.89	52,000 (388)
94.3	260	78.80	55,000 (411)

Table 5. Post-Elution Water Rinse at 25 °C

Effluent BV	Cs ⁺ C/C ₀	K ⁺ C/C ₀	Na ⁺ C/C ₀
1	3.02E-04	< 2.72E-04	7.72E-05
4	1.23E-04	< 2.72E-04	6.19E-05
5	1.21E-04	< 2.72E-04	6.70E-05

Initial Cs⁺ concentration (sorption) = 77.5 µg/mL

Initial K⁺ concentration (sorption) = 0.094 M

Initial Na⁺ concentration (sorption) = 4.96 M

Flow rate = 1.01 BV/hr

Table 6. SuperLig® 644 Resin Regeneration at 25 °C After the Post-Elution Rinse Step

Effluent BV	Cs ⁺ C/C ₀	K ⁺ C/C ₀	[Na ⁺], M
4	7.53E-05	< 2.72E-04	2.91E-02
8	9.46E-05	< 2.72E-04	2.13E-01
12	1.13E-04	< 2.72E-04	2.33E-01

Initial Cs⁺ concentration (sorption) = 77.5 µg/mL

Initial K⁺ concentration (sorption) = 0.094 M

Flow rate = 2.14 BV/hr

Table 7. Pre- and Post-Column Run Masses of SuperLig[®] 644 Resin Along with Post-Column Run Residual Cesium on Resin

Pre-column run mass	28.0 g dry Na ⁺ form resin
Post-column run mass	28.9 g dry Na ⁺ form resin
Post-column run residual cesium on resin	64.4 μg/g dry Na ⁺ form resin
