Optimization of Cesium Removal from Hanford Envelope A Simulant with SuperLig® 639 Ion Exchange Resin

by

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**Optimization of Cesium Removal from Hanford Envelope A Simulant with
SuperLig® 644 Ion Exchange Resin**

April 13, 2000

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SUMMARY

Tests have been completed that provide information on the removal of cesium ions from simulated Hanford tank waste. This work was conducted in support of the Hanford River Protection Project for BNFL, Inc. SuperLig[®] 644 ion exchange resin has been evaluated for the selective removal of cesium cations from Hanford Envelope A simulant. Batch contact and column experiments have been performed using SuperLig[®] 644 resin and 5 M [Na⁺] simulant containing non-radioactive cesium. These tests were highly successful in demonstrating the effective removal of cesium from Hanford tank waste. The results provide a critical link between small-scale radioactive tests and pilot-scale simulant tests. No significant problems were encountered which would prevent use of this resin in the process as planned. The resin pretreatment procedure developed at SRTC was demonstrated to consistently regenerate the column and avoid development of channels leading to early breakthrough. Further testing is needed to evaluate long term chemical and radiation effects on resin performance.

The two batches of SuperLig[®] 644 resin tested (batches 644BZ and 98102mb48-563) had nearly identical cesium capacities at an initial Cs concentration of 7.93 mg/L. The equilibrium adsorption isotherm was determined for resin batch #98102mb48-563 by varying the initial cesium concentrations in the simulant. Cesium distribution coefficients (K_d) ranged from ~500 to 2000 mL/g at feed cesium concentrations ranging from 151 to 0.41 mg/L, respectively. Column experiments were performed with resin batch #98102mb48-563 using two different column diameters and three different superficial velocities chosen to span the range of superficial velocities from small-scale radioactive tests (~0.5 cm/min) to full-scale plant (5.6 to 11.2 cm/min) operation. The kinetics of cesium adsorption by SuperLig[®] 644 were high as indicated by the small impact of superficial velocity and bed geometry on cesium breakthrough profiles. 50% Cs breakthrough occurred at 100 and 240 resin bed volumes in a 2.7 cm ID column ($L/D = 3.3$) at superficial velocities of 10.6 and 0.87 cm/min, respectively. In order to explore the effects of column geometry on resin performance, an additional experiment was performed with the same resin sample in a 4.0 cm ID column ($L/D = 1.0$). At a superficial velocity of 0.83 cm/min, the 50% cesium breakthrough point was observed at 240 BV, which is the same number of bed volumes at which 50% breakthrough was observed for the 2.7 cm ID column at a superficial velocity of 0.87 cm/min. This result indicates that the kinetics of cesium adsorption is sufficiently fast that moderate changes in the L/D ratio do not impact cesium breakthrough at flow rates ≤ 0.87 cm/min. The SuperLig[®] 644 columns were eluted with 0.5 M HNO₃. Peak cesium concentrations were observed in the eluate solutions from 2-6 BV after the start of the elution cycle. The cesium concentration of the eluate met the current design specification of 1% of the feed after approximately 13 BV of eluate had passed through the column. The BNFL Inc. design basis assumes that during the elution the cesium concentration in the eluate reaches less than 1% of the feed concentration after passing 15 to 22.5 bed volumes of eluent through the column⁷. These simulant tests confirm the BNFL Inc. basis of design for the column elution. SRTC is conducting additional column tests with radioactive waste samples to verify the BNFL Inc. design basis for the cesium ion exchange system. During the cesium loading and elution experiments, all solutions were passed through the columns in the downflow direction. However, one additional scoping experiment was

performed to determine whether the resin bed would remain intact during upflow elution conditions.

Several observations of interest were noted during the experiments with SuperLig[®] 644 resin. As previously observed, the resin undergoes volume changes during load/wash/elute cycles. During column experiments with batch #98102mb48-563, the resin bed volume decreased relative to the volume in 0.25 M NaOH pretreatment solution by 15-25% during the loading cycle and by 30-45% during the acid elution cycle. Despite the changes in the bed volume, no channeling, cracks, or gaps were observed in the bed throughout the experiment. The effluent solutions contained no visibly observable fines. Switching from acidic to basic conditions causes the residual solution to become orange or brown in color. In addition, water or caustic solutions used to store SuperLig[®] 644 resin gradually become colored. The cause for discoloration of these solutions is presently unknown. BNFL Inc. has recently received permission from the resin manufacturer to analyze solutions that have contacted the resin. These analyses are the subject of a separate task being conducted at SRTC and will be reported separately. Batch contact tests performed on a mixture of the colored storage solution and freshly-prepared simulant indicated that the compounds contributing to the color of the effluent solution do not affect cesium adsorption by the resin and probably will not impact short-term column performance.

1.0 INTRODUCTION

Hanford Radioactive Waste materials have been categorized into four envelopes labeled A through D as specified in the Tank Waste Remediation Contract between BNFL and DOE.¹ Envelopes A, B and C contain only solubilized species and are specified as Low-Activity Waste (LAW). Each envelope is defined based on compositional maximums of chemical and radioactive constituents. Envelopes A and B contain low concentrations of organic species and the primary form of technetium is pertechnetate (TcO_4^-). Envelope C contains higher levels of organic species and technetium which is primarily in the nonpertechnetate form (presumably complexed TcO_2). Envelope D is sludge which has been separated from the supernate and is referred to as High Activity Waste. The current plant design utilizes SuperLig[®] ion exchange resins to remove cesium and technetium (the primary radioactive constituents) from the Hanford LAW. The process is designed to produce a decontaminated waste stream and a concentrated eluate waste stream for vitrification into low and high activity glasses, respectively.

The conceptualized process for pretreatment of Hanford Low-Activity Waste (LAW) includes the decontamination of radioactive waste solutions by the removal of cesium ions with SuperLig[®] 644 ion exchange resin. SuperLig[®] 644 ion exchange resin is an elutable, organic resin which removes a salt pair (e.g. NaNO_3 , KNO_3 , or CsNO_3) from caustic solutions. Sodium ion concentration in the solid is inversely proportional to cesium ion concentration in the contacting solution. Superlig[®] 644 resin volume is very sensitive to pH. Exposure of the resin to solutions containing high hydroxide concentrations, like caustic, Hanford Waste solutions, causes the resin to swell. Acidic solutions, which are typically used for column elution, result in a considerable decrease in volume. The swelling characteristics of the resin require the implementation of specific pretreatment procedures developed at the Savannah River Technology Center² to avoid channeling of the resin bed upon the introduction of feed solution into the column.

As shown in Figure 1, the current phase of the Hanford River Protection Project includes ion exchange testing of actual samples or nonradioactive simulants of each LAW envelope (A, B and C) at the Savannah River Technology Center (SRTC) and the Pacific Northwest National Laboratory. This report describes the intermediate-scale tests performed on simulated Envelope A solutions at SRTC. The principal objective of these intermediate-scale tests (resin bed volume: ~50 mL) was to provide data for computer modeling, allowing comparison of small-scale radioactive tests (resin bed volume: ~6 mL) to pilot-scale simulant tests (resin bed volume: ~1 L). The superficial velocities studied span the range of velocities planned for the radioactive and simulant tests, as well as the design basis for the full-scale waste treatment plant. The column residence time, i.e., time that the liquid is in contact with the resin, is the same for the small-scale radioactive and large-scale simulant tests, as well as the design basis for the full-scale waste treatment plant. The intermediate-scale column tests allow evaluation of the effects of superficial velocity and path length by varying the feed flow rate and resin bed geometry, respectively. In addition, the equilibrium capacities of the resins were determined to evaluate production batch variability. The cesium equilibrium batch contact and column data serve as a technical basis set for the development of an ion

Figure 1. SuperLig[®] Ion Exchange Resin Testing Summary - SRTC = Savannah River Technology Center, Aiken, SC; PNNL = Pacific Northwest National Laboratory, Hanford, WA; BNFL = British Nuclear Fuels Limited, Inc.; IBC = IBC Advanced Technologies, American Fork, UT; VERSE = ion exchange modeling program available from Prof. Linda Wang, Purdue University.

exchange model to predict SuperLig[®] 644 column performance in large-scale plant operations designed for the removal of cesium from actual waste solutions. Results of this modeling will be available in future reports from SRTC.

2.0 EXPERIMENTAL

2.1 Materials

Two batches of SuperLig[®] 644 resin (Batches 644BZ and 98102mb48-563) were received from IBC Advanced Technologies, American Fork, Utah. Some physical data for the resins, which were reported in an earlier document is provided in Table 1.² Both resin samples were composed of dark brownish-red granules. Batch contact tests were conducted with each batch. All column experiments were conducted using batch #98102mb48-563.

Table 1. Physical Characteristics of "As-Received" SuperLig® 644 Resins.²

Batch #	Particle density (g/mL)	Bulk density (g/mL)	Water content (%)	Particle size Range (µm)
644BZ	1.611	0.793	10	212-600
981020mb48-563	1.549	0.758	9.6	62-600

The Envelope A simulant composition given in Table 2 was based on Hanford Tank 241-AN-105.³ The target composition contains approximately 5.0 M Na⁺, 1.3 M NO₃⁻, and 1.6 M free OH⁻. Simulant was prepared in 2 L batches and allowed to sit overnight before being filtered through a 0.45 micron Nalgene® nylon filter. For the column experiments, numerous 2 L batches of simulant were composited in a large carboy. The simulant was periodically inspected and refiltered when solids were observed. The measured simulant density was 1.23 g/mL. In column experiments, the first 750 mL of simulant exiting the column were discarded and the remainder of the solution was reused for subsequent tests after respiking the solution with cesium nitrate. The first portion of simulant was discarded because it contained approximately 1 bed volume of 0.25M sodium hydroxide solution, which, if mixed with the effluent simulant, would have changed the composition and prevented reuse for subsequent experiments. Freshly-prepared 2 L batches of simulant were added to maintain the volume needed to complete subsequent experiments. The composited simulant used for the column tests with SuperLig® 644 resin had been previously used in column tests with SuperLig® 639 resin⁴ and therefore contained residual perrhenate ion (5.9 E-5 M Re). The density of the

Table 2. 241-AN-105 (Env. A) Target Simulant Composition

Chemical	Molarity
NaNO ₃	1.16
KNO ₃	0.09
NaNO ₂	1.13
NaOH	1.62
NaAlO ₂	0.69
NaCl	0.12
Na ₂ CO ₃	0.10
Na ₂ SO ₄	3.8 E-03
Na ₃ PO ₄	0.003
Na ₂ SiO ₃	0.004
K ₂ MoO ₄	4.02 E-4
CsNO ₃	6.2 E-5
H ₃ BO ₃	0.002
NaHCOO	0.03
NaCH ₃ COO	0.02
Na ₂ C ₂ O ₄	0.003
HOCH ₂ COOH	0.01

composited simulant was measured periodically to confirm that the bulk composition had not changed significantly. All solutions were prepared using ACS certified, high-purity reagents from Fisher Scientific, Inc. Analysis of the composited simulant prior to use confirmed the basic composition given in Table 2.

2.2 Equipment and Procedures

2.2.1 Batch Contact Experiments

Batch contact tests were performed in duplicate at ambient temperature using a Thermolyne orbital shaker. In a typical experiment, ion exchange resin (0.12-0.18 g) and simulant (12-18 mL) were transferred to a 21 mL polyethylene vial and placed on the shaker. The ratio of solution volume to exchanger mass was 100 ± 5 . The temperature was measured at the beginning and the end of each experiment (observed range: 22-23°C). After 24 ± 1 hours, samples were removed from the shaker and visually inspected. In all cases the resin appeared to be intact, indicating that agitation of the vials during the test did not lead to significant material degradation. The amounts of resin floating, suspended and sinking were recorded for each sample. The solution was then filtered through a 0.45 micron Nalgene® nylon filter using aspirator vacuum. Portions (2-4 mL) of the filtrate and similarly-treated samples of the feed solutions (blanks) were analyzed for cesium by the Savannah River Technology Center Analytical Development Section using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). Data for the batch contact tests are provided in Attachment 1.

Water and caustic solutions used to store SuperLig® 644 resin gradually become orange or brown in color due to leaching of organic material from the resin. In order to evaluate whether this impacts resin performance, an additional batch contact test was conducted using a mixture of SuperLig® 644 storage solution and simulant. A sample of water which had been used to store a 50 mL sample of SuperLig® 644 resin in column configuration for several months was collected. The solution was orange/brown in color. 1.25 mL of the storage solution was mixed with 25.0 mL of Envelope A salt solution to give a diluted simulant containing 5 volume percent storage solution. A control solution was prepared in a similar manner by mixing 1.25 mL of water with 25.0 mL of simulant. K_d tests were conducted in duplicate following the procedures described above. (Note: 5 volume percent simulant diluted with storage solution was arbitrarily chosen as the test solution with the intent of minimizing dilution effects while still providing sufficient material to potentially impact the batch contact test.)

Cs distribution coefficients and % removal were calculated for each batch contact experiment using the formulas shown in Eqs. 1 and 2, respectively.

$$K_d = [(C_i/C_f) - 1][V/(M \cdot F)] \quad (1)$$

$$\% \text{ removal} = \frac{(100) \cdot (C_i - C_f)}{C_i} \quad (2)$$

C_i = initial Cs in feed (mg/L)
 C_f = final Cs after contact (mg/L)
 V = volume of solution used (mL)
 M = mass of "as-received" resin (g)
 F = resin dry weight correction factor

F factors of 0.90 and 0.904 were used for batches 644BZ and 981020mb48-563, respectively, based on the data in Table 1.

2.2.2 Column Experiments

Figure 2 shows the ion exchange column design. Columns were constructed from 2.7 and 4.0 cm ID sodium borosilicate glass tubing. Decals were affixed to the outer walls of the columns with 1 mm graduations to measure the resin bed height. The columns were coated on the outside with a layer of polyvinylchloride to reduce hazards associated with pressurizing the apparatus. A 3-way, 6 mm bore Teflon[®] stopcock (#1) was attached to the bottom of the columns. The column head was attached to the column using a Rudivis ground-glass joint. Two 2-way, 6 mm bore stopcocks (#2 and #3) were attached on opposite sides of the column head to serve as inlet ports. The column head also contained a pressure gauge, a pressure relief valve, and a fill reservoir that also served as a vent. Stainless steel wire screens (200 mesh) were inserted into the columns to support the ion exchange resin. Colder Products Company polypropylene quick-disconnect couplings were used to connect low-density polyethylene tubing (11/64" ID) to the columns. Solutions were passed through the columns using Fluid Metering Incorporated QG150 positive displacement pumps with 1/4" and 3/8" piston sizes. Samples were collected either manually or using a Spectrum Chromatography IS-95 Interval Sampler. The ion exchange column was prepared by soaking the "as-received" resin overnight in 1 M NaOH and transferring the resin into the column as a suspension. All solutions were pumped into the column in the downflow direction. The resin bed was treated with the following solutions sequentially at a flow rate of 3 BV/hr: 3 BV of fresh deionized water, 6 BV of 0.25 M NaOH, 3 BV of deionized water, 3 BV of 0.5 M HNO₃, 3 BV of deionized water. The bed was pretreated with 6 BV of 0.25 M NaOH over a 2-hour period just prior to beginning each experiment. A single sample of resin from batch #981020mb48-563 was used for all column experiments. The temperature during the column experiments ranged from 20-23 °C. The resin bed volume was determined by multiplying the measured height of the resin bed in 0.25 M NaOH pretreatment solution by the cross-sectional area. The measured resin bed volume at the conclusion of each processing cycle during the experiments is given in Attachment 4. The resin bed volume in 0.25 M NaOH determined the size of 1 BV for the entire experiment despite the fact that the bed volume changed considerably during the experiment. The NaOH liquid level was adjusted prior to the introduction of feed so that the volume of liquid above the resin bed was approximately 50 mL (1 bed volume) before simulant solution was pumped into the column. This experimental arrangement for the test ion exchange column was

selected to emulate the design of the full-scale columns in the BNFL Inc. waste treatment plant.⁵

Simulant (8.0-9.5 mg/L Cs) was pumped into the column and approximately 8 mL samples of effluent were collected every 10-20 bed volumes (Loading cycle). The liquid in the column was then drained to within approximately 1 cm of the top of the resin bed. Sodium hydroxide solution (0.1 M) was pumped into the column until the volume of liquid above the resin bed was approximately 50 mL. 2.5-3.5 bed volumes of 0.1 M NaOH were passed through the column in one hour and samples of the effluent were collected every 20 minutes (NaOH Wash Cycle). 2.5-3.5 bed volumes of deionized water were passed through the column in one hour and samples of the effluent were collected every 20 minutes (Post-Feed Water Wash Cycle). (Note: The water wash cycle served to displace residual sodium hydroxide solution from the column prior to elution.) The columns were eluted with 0.5 M HNO₃ at a flow rate of 1 bed volume per hour and samples were collected approximately every hour (Elution Cycle). Following the elution cycle the liquid in the column was drained to within approximately 1 cm of the top of the resin bed. Deionized water was pumped into the column until the volume of liquid above the resin bed was approximately 50 mL. The column was washed with at least 3 bed volumes of de-ionized water during a 1-hour period (Post-Elution Water Wash). Feed

Figure 2. Ion Exchange Column Design

and effluent samples were analyzed for cesium by the Savannah River Technology Center Analytical Development Section using ICP-MS or Atomic Absorption (AA). Data from the column experiments are provided in Attachment 2.

The flow rate was monitored during the column experiments by periodically measuring the time required to collect 10 or 25 mL of effluent. The effluent solution during the loading cycle was collected in 3-4 separate reservoirs. The total volume of effluent in each reservoir was measured and corrected for the volume of samples collected and the flow rate was calculated from the time of collection. The overall flow rate was taken to be the weighted average of the flow rates calculated for each collection bottle. The flow rates for the pretreatment, wash, and elution cycles were calculated from the time of collection and the volume of solution collected (after correction for the total volume of samples collected). Flow rates measured during each experiment for the feed, wash and elution cycles are provided in Attachment 3. The number of bed volumes of solution processed at each sampling period was calculated from the frequency of collection and the flow rate. The column operating procedure was designed to emulate the actual plant operation, where the column is half full of resin and half full of liquid. According to the procedure, the initial simulant that was fed into the ion exchange column during the loading cycle was to be diluted by the 1 BV of 0.25 M NaOH solution which remained above the resin bed following the Pretreatment Cycle. Likewise, the post-feed water wash and the eluting solutions were allowed to mix with the liquid head left above the resin from the previous cycle. No attempt was made to correct for mixing of solutions in the column head-space when calculating the number of bed volumes of feed, wash, or eluate processed. Each cycle was considered to start at the moment that the feed line was transferred to the new feed bottle and the pump was activated. The total volume of solution in the lines between the feed bottle and the column is estimated to be 30-35 mL. The resin bed volume was monitored throughout the experiments by periodically measuring the height of the bed (Attachment 4).

After the completion of all experiments the SuperLig[®] 644 resin (in the acid form) was removed from the columns, filtered, and dried overnight in a desiccator. Duplicate samples of as-received resin and the resin used in the ion exchange column experiments were submitted for analysis. The resin samples were dissolved by acid digestion and the resulting solutions were analyzed by ICP-ES. The results are given in Attachment 6.

3.0 RESULTS AND DISCUSSION

3.1 Batch Contact Experiments

Batch contact tests were conducted for both batches of SuperLig[®] 644 resin at a feed concentration of 7.93 mg/L. Additional tests were performed for batch #98102mb48-563 at feed cesium concentrations ranging from 0.41 to 151 mg/L. This range of feed cesium concentrations brackets the expected cesium concentration for LAW Envelope A type wastes that will be processed at the BNFL Inc. waste treatment facility. The test conducted at a cesium feed concentration of 0.41 mg/L was a recontact test in which the filtrate from earlier contact tests served as the feed solution. Freshly-prepared simulant

solution was used for all other batch contact tests. Inspection of the samples at the conclusion of the batch contact revealed that the resins showed no tendency to float in the simulant solution. The color of the simulant solution was orange/brown at the conclusion of all tests. Freshly-prepared simulant has a faint yellow color.

Distribution coefficients (K_d) provide a quantitative measure of ion exchange resin equilibrium capacity. As shown in Table 3 and Figure 3, at a final cesium concentration of approximately 0.4 mg/L the two batches tested have nearly identical capacities. The shape of the adsorption isotherm for batch #98102mb48-563 in Figure 3 is typical of Langmuir-type adsorption. The distribution coefficients increase sharply as the final cesium concentration decreases from 30 to 0.4 mg/L Cs. A plateau is observed at a K_d value of approximately 2000 mL/g at final cesium concentrations ranging from 0.40 to 0.022 mg/L.

Batch contact tests were also performed using Envelope A simulant, which had been diluted with 5 volume percent of a SuperLig[®] 644 / water storage solution. A control experiment was also performed using a sample of simulant which had been diluted with water. Duplicate tests were performed with each solution. The average K_d for the sample prepared from the storage solution was 2170 mL/g, while the average K_d for the solution diluted with water was 2214 mL/g. The final cesium concentration for each sample was near 0.27 mg/L. The difference between these results is within the measurement accuracy range ($\pm 5\%$). The similar equilibrium capacities measured for the two solutions indicate that the colored organic material that leaches from the resin does not bind cesium in solution leading to decreased cesium uptake by the resin. The K_d values observed for the diluted simulant are also near the expected values based on the equilibrium adsorption isotherm shown in Figure 3.

Table 3. Cesium Distribution Coefficients (K_d) and % Removal Measured for SuperLig[®] 644 Resin Batches.

Batch # 644BZ

Initial [Cs] (mg/L)	Final [Cs] (mg/L)	Cs K_d (mL/g)	% Cs Removal
7.93	0.405	2049	94.9

Batch #98102mb48-563

Initial [Cs] (mg/L)	Final [Cs] (mg/L)	Cs K_d (mL/g)	% Cs Removal
0.408	0.0218	2018	94.7
7.93	0.4005	2070	94.9
25.674	1.64	1612	93.6
63.17	6.905	923	89.1
102.19	14.45	674	85.9
150.95	27.55	488	81.7

Figure 3. SuperLig[®] 644 Batch Comparison - Final [Cs] versus K_d (contact time: 24 hr; soln. vol./resin mass: 100 ± 5; temp.: 22-23 °C)

3.2 Column Experiments

As shown in Table 4, four column experiments were performed with SuperLig[®] 644 resin (batch #981020mb48-563). The experiment number in Table 4 indicates the order in which the experiments were completed. Three experiments were completed using a 2.7 cm ID column at different superficial velocities. In general, the breakthrough profiles for experiments 1, 2, and 3 (Figure 4) follow the expected trends with faster superficial velocities (decreased residence time) resulting in more rapid cesium breakthrough for the fixed column geometry. Decreasing the superficial velocity (and increasing residence time) from 10.6 to 0.87 cm/min increases the 50% breakthrough point by a factor of only 2.4. Such small differences in the 50% Cs breakthrough point across this range of superficial velocities indicates that the kinetics of cesium adsorption is fast.

The current plant design basis assumes a superficial velocity of 5.6 to 11.2 cm/min, a column residence time of 20 to 40 minutes (i.e., flowrate of 1.5 to 3 BV/hr), and 100BV

Table 4. SuperLig[®] 644 Column Cs Breakthrough Summary.

Batch #981020mb48-563, 50 mL Resin Bed

Experiment #	Bed Diameter/Height (cm)	Superficial Velocity (cm/min)	Flow Rate (BV/hr)	50% Breakthrough (BV)
3	2.7/8.8	0.87	5.9	240
1	2.7/8.8	6.0	40.9	135
2	2.7/8.8	10.6	72.3	100
4	4.0/4.1	0.83	12.3	240

for Envelopes A and C and 50BV for Envelope B waste processed at the 50% cesium breakthrough point.⁵ The 50% breakthrough point of 100 BV (Envelope A) observed at the fastest superficial velocity (10.6 cm/min) corresponds approximately to the current plant design target, with the exception that the residence time in test 3 (10.2 minutes) is less than the plant design basis. These results indicate that the process throughput (superficial velocity or bed volumes per hour) could be increased further in the plant operation, although the effect on decontamination factors and pressure drop needs further evaluation. SRTC is conducting modeling of the cesium ion exchange process to assess the effects of process parameters on decontamination factor and column performance. Ion exchange modeling is a subject of a future report.

The 50% Cs breakthrough point of 240 BV observed at a feed superficial velocity of 0.87 cm/min is less than the value predicted based on the batch contact data. At a final cesium concentration near 8 mg/L (approximately the feed cesium concentration in the column experiments) the K_d of SuperLig[®] 644 resin was approximately 850 mL/g. The measured wet bulk resin density for SuperLig[®] 644 resin is 0.4 g/mL.² The theoretical 50% breakthrough point (λ) can be predicted from K_d data and the swollen bulk resin density

Figure 4. SuperLig[®] 644 Cesium Breakthrough Profiles – Flow Rate Dependence (resin bed: 50 mL, 2.7 cm ID, batch #981020mb48-563)

using Eqn. 3.

$$\lambda = (K_d) \times (\text{bulk resin density}) = (850) \times (0.4) \quad (3)$$

The calculated λ value is 340 BV. The observed 50% Cs breakthrough point of 240 BV at the slowest superficial velocity is 71% of the λ value. Early breakthrough has been observed previously with SuperLig[®] 644 resin and Hanford waste samples. McCabe and Hassan reported 50% cesium breakthrough at approximately 37% of the λ value (column ID: 0.95 cm; flow rate: 0.38 cm/min) for a Hanford Envelope A sample from Tank AW-101.⁶ Similar results were reported for Envelope B⁷ and C⁸ waste samples. These results indicate that the simplified λ approximation does not accurately predict SuperLig[®] 644 column performance. Efforts are currently underway to model the SuperLig[®] 644 column experiments based on the data reported herein. This work should provide more insight regarding the apparent discrepancy between the predicted and observed column performance.

Cesium elution profiles for the three experiments in the 2.7 cm ID column are shown in Figure 5. All columns were eluted with 0.5 M HNO₃. The peaks of the elution profiles were observed from 2 to 6 BV after the start of the elution cycle. The shapes of the elution curves varied considerably, possibly due to differences in the cesium loading profile and small variations in the sampling increments. In experiments 1 and 3, after 9 BV of eluate had been collected, the concentration of cesium in grab samples of the

Figure 5. SuperLig[®] 644 Acid Elution Profiles – 2.7 cm ID Column (resin bed: 50 mL, 2.7 cm ID, batch #981020mb48-563; superficial velocity: app. 0.15 cm/min; eluting solution: 0.5 M HNO₃)

eluate was 0.31 and 4.8 mg/L, respectively. This difference can be attributed to greater loading of the column in experiment 3 due to the slower superficial velocity used for the loading cycle. (The area above the breakthrough profile in Figure 4 for each experiment indicates the amount of cesium loaded onto the resin.) For experiment 3, the area under the elution curve is considerably smaller than the area under the curves for experiments 1 and 2. In addition, the peak of the elution profile in experiment 3 is not observed until 6 BV after the start of the elution, whereas the peaks in experiments 1 and 2 occurred at 2 and 4 BV, respectively. This result was surprising since the column was more fully loaded in experiment 3. This discrepancy is likely due to experimental or analytical error. (Note: It is clear that cesium was removed during the elution in Experiment 3, as the resin was reused for Experiment 4, after transferring it into a larger diameter column. The breakthrough profile in Experiment 4 is consistent with use of a resin that is not pre-loaded with cesium, as this would likely have rapid breakthrough or a continuous passage of a low concentration of cesium.) In experiment 2, the column was eluted with only 8 BV of 0.5M nitric acid and the cesium concentration only decreased to 9.3% of the feed. However, the amount of cesium remaining on the column should have a minimal effect upon the subsequent reloading of the column in experiment 3. Approximately 13 BV of acid were required to decrease the cesium concentration in the eluate to 1% of the feed concentration. (The current design specification assumes that 15 to 22.5 BV of eluate are required to reach 1% of the feed Cs concentration.) In general, however, the elution tail was longer than expected based on earlier data³ and further work may be needed to minimize the volume of acid required for elution.

After completing three column experiments in the 2.7 cm ID column, the resin was transferred to a 4.0 cm diameter column. A column experiment was performed at a feed superficial velocity of 0.83 cm/min, which is near the slowest velocity used in the smaller diameter column (Exp. 3). In order to obtain the same superficial velocity in the 4.0 cm ID column as was used in experiment 3, it was necessary to increase the volumetric flow rate from 4.9 mL/min to 10.3 mL/min. Figure 6 compares the cesium breakthrough profiles observed for the experiments performed in the 2.7 and 4.0 cm ID columns at comparable superficial velocities. Despite the decrease in the path length from 8.8 to 4.1 cm in going from the 2.7 to 4.0 cm ID column, the cesium breakthrough profiles for the two experiments are nearly identical. This indicates that the kinetics of cesium adsorption is high relative to the residence time of cesium ions in the resin bed in experiments 3 (10.2 min.) and 4 (4.8 min.). This data may also indicate that film phase diffusion is not the controlling kinetic mechanism when superficial velocity is above 0.83 cm/min, since the slower superficial velocity tests yielded the higher cesium loading results.

The 4.0 cm diameter column was eluted downflow with 0.5 M nitric acid at a flow rate of approximately 1 BV/hr (Figure 7). The maximum cesium concentration in the eluate was observed near 2 BV after the start of the elution cycle, which is in the range observed for the experiments in the 2.7 cm ID column. Initially the column was not fully eluted. After 11 BV of eluate were collected the cesium concentration had decreased to only

Figure 6. SuperLig® 644 Cesium Breakthrough Profiles – Column L/D Comparison (resin bed: 50 mL, batch #981020mb48-563; superficial velocity: app. 0.85 cm/min).

Figure 7. SuperLig® 644 Acid Elution Profile – 4.0 cm ID Column (resin bed: 50 mL, 4.0 cm ID, batch #981020mb48-563; superficial velocity: app. 0.13 cm/min; eluting solution: 0.5 M HNO_3)

16% of the feed cesium concentration used for the column loading cycle. This is consistent with the elution profile observed in experiment 3, where the cesium concentrations after 9 and 13 BV of eluate had been collected were 51% and 1.1% of the feed cesium concentration, respectively. Attachment 4 shows the resin swelling data recorded for SuperLig® 644 (Batch 981020mb48-563) during the column experiments. The maximum resin volume was typically observed in the 0.25 M NaOH pretreatment solution and the minimum volume was typically observed during the elution with 0.5 M HNO₃. The resin bed reduced in volume relative to the volume in the pretreatment solution by 15-25% in 5 M [Na⁺] simulant solution and by 30-45% in 0.5 M HNO₃. The volume of the SuperLig® 644 resin bed in 0.25 M NaOH pretreatment solution was observed to increase with each successive caustic loading and acid elution cycle. The bed volume in experiment 1 was 50.3 mL and the volume in experiment 4 was 55.4 mL. Despite the gradual increase observed in the resin bed volume throughout the experiments, the original volume of 50 mL measured for experiment 1 was considered to be 1 BV for all experiments.

After the completion of experiment 4, a portion (~50 %) of the resin was transferred back to a 2.7 cm ID column to determine whether the bed would remain intact under upflow elution conditions. (Note: The resin was eluted with an additional 8 BV of acid in the 2.7 cm ID column before conducting the upflow elution tests.) The BNFL Inc. basis of design for the waste treatment plant columns assumes downflow elution at a superficial velocity of ~2.3cm/min (1 BV/hr). However, BNFL Inc. is evaluating eluting the column in the countercurrent direction to the load. Countercurrent elution (i.e., upflow) results in the cleanest resin near the column exit during the subsequent loading cycle, which should favor reduced cesium concentration in the treated waste solution. Upflow elution would also be a more efficient way to elute the resin since the upper region of the bed, which is more highly loaded, is eluted out the top of the column rather than having to pass through the entire column length. It should be emphasized that the resin in this test was in the more dense acid form at the beginning of the test. This differs from an actual column elution in which the resin would be in the less dense sodium form at the beginning of the elution. The data for the upflow elution test is provided in Attachment 5. At superficial velocities up to 2.21 cm/min, virtually no movement was observed in the resin bed and no expansion of the resin bed was observed. At a superficial velocity of 6.58 cm/min, <5% of the resin particles were suspended in the solution and the bed had expanded by approximately 18% from the original volume. At a superficial velocity of 8.97 cm/min, <10% of the resin particles were suspended in the solution and the bed had expanded by approximately 32%. For comparison, the superficial velocity used for the downflow elution in the experiments with the 2.7 cm ID column was 0.15 cm/min. This test indicates that upflow elution may be feasible, and further testing is warranted.

Following the upflow elution test, the resin was removed from the column and dried by vacuum filtration for several minutes. After being dried in a desiccator overnight, two samples of the resin were dissolved by acid digestion and submitted for analysis by ICP-ES along with two samples of the as-received resin. Results are shown in Attachment 6. For one of the as-received resin samples a much higher analysis result (16,731 ug/g resin) was reported for aluminum than was observed for any other samples. The aluminum concentration reported for this sample is higher by a factor of 70 than the value reported

for the duplicate sample of the as-received resin. Presumably the high aluminum analysis result is due to sample preparation, as repeated analysis of the solution yielded similar results.

4.0 CONCLUSIONS

Simulant batch contact and column optimization tests have been completed on two batches of SuperLig[®] 644 ion exchange resin. The equilibrium cesium capacities of the resin batches are virtually identical at a feed cesium concentration of 7.93 mg/L. The relatively small impact of the feed flow rate and the column geometry on the cesium breakthrough profile indicates that the kinetics of cesium adsorption by SuperLig[®] 644 is fast. The 50% cesium breakthrough point of 240 BV observed at the slowest superficial velocity (0.87 cm/min) is 71% of the λ value predicted from the batch contact data. This discrepancy appears not to be a result of slow kinetics of adsorption. Computer modeling is needed to further evaluate this discrepancy. Despite the lower than expected column performance of the resin, the capacity is more than adequate to meet the current design specifications. Even at the fastest superficial velocity tested (10.6 cm/min), the 50% cesium breakthrough point of 100 BV satisfies the current design criteria for the BNFL Inc. waste treatment plant. Although large-scale tests are needed to determine the impact on decontamination factors and pressure drop, these results do suggest that even faster flow rates might be considered for the plant operation. The elution of SuperLig[®] 644 resin required more eluate than expected but the eluate still meets the design specification (1% of the feed concentration) within 13 BV of the start of the elution cycle. Preliminary scoping tests indicate that upflow elution might be considered as an alternate to downflow. Additional tests are recommended to further evaluate countercurrent elution of the cesium ion exchange column and optimize the eluate volume. In many ion exchange systems, increasing the temperature of the eluate solution reduces the volume of eluate needed to remove the target analyte from the resin. The effect of temperature on cesium elution should also be evaluated to determine if the eluate volume can be reduced.

5.0 DESIGN CHECK

M.C. Thompson
M. C. Thompson

4/19/00
Date

6.0 APPROVALS

Hanford Tank Waste Ion Exchange Column Optimization Task Technical and Quality Assurance Plan (U), BNF-003-98-0032, Rev. 0.

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8.0 APPENDIX

8.1 Attachment 1. SuperLig® 644 Batch Contact Data.

Batch # 644BZ

Sample #	BNF-SSIX-26-2	BNF-SSIX-26-2-D
LIMS #	300128810	300128811
Solution Mass (g)	22.0648	22.0408
Resin Mass (g)	0.182	0.1815
Solution Volume (mL)	17.98	17.96
Initial Cs (mg/L)	7.93	7.93
Final Cs (mg/L)	0.396	0.414
solution volume/exchanger mass	98.8	99.0
Temperature (C)	23	23
Shake Time (hr)	23.1	23.1
K _d (mL/g)	2095.7	2003.1
Duplicate Average K _d	2049.4	
Duplicate Average Final Cs (mg/L)	0.405	

Measured Cs in Feed (mg/L)	7.93
Sample #	BNF-SSIX-7-S
LIMS #	300128812

Batch #981020mb48-563

Sample #	BNF-SSIX-31-1	BNF-SSIX-31-1-D	BNF-SSIX-26-1	BNF-SSIX-26-1-D
LIMS #	300129753	300129754	300128808	300128809
Solution Mass (g)	17.4841	17.5118	22.0272	22.0075
Resin Mass (g)	0.1394	0.1399	0.1831	0.1803
Solution Volume (mL)	14.25	14.27	17.95	17.94
Initial Conc. (mg/L)	0.404	0.412	7.93	7.93
Final Conc. (mg/L)	0.02	0.0213	0.400	0.401
solution volume/exchanger mass	102.2	102.0	98.1	99.5
Temperature (C)	22	22	23	23
Shake Time (hr)	24.0 hr recontact	24.0 hr recontact	23.1	23.1
K _d (mL/g)	1950.6	2086.1	2057.6	2082.2
Duplicate Average K _d	2018.3		2069.9	
Duplicate Average Final Cs (mg/L)	0.022		0.401	

Measured Cs in Feed (mg/L)	0.404	0.412	7.93
Sample #	BNF-SSIX-26-1	BNF-SSIX-26-1-D	BNF-SSIX-7-S
LIMS #	300128808	300128809	300128812

Attachment 1. SuperLig® 644 Batch Contact Data (cont.).

Batch #981020mb48-563

Sample #	BNF-SSIX-32-1	BNF-SSIX-32-1-D	BNF-SSIX-32-1	BNF-SSIX-32-1-D
LIMS #	3001299941	3001299942	300129757	300129758
Solution Mass (g)	14.7185	14.7163	17.5608	17.5315
Resin Mass (g)	0.1224	0.1217	0.1405	0.141
Solution Volume (mL)	12.00	11.99	14.31	14.29
Initial Cs (mg/L)	25.67	25.67	63.17	63.17
Final Cs (mg/L)	1.60	1.67	6.92	6.89
solution volume/exchanger mass	98.0	98.6	101.9	101.3
Temperature (C)	23	23	23	23
Shake Time (hr)	24	24	24	24
K _d (mL/g)	1643.9	1579.2	923.1	922.7
Duplicate Average K _d	1611.5		922.9	
Duplicate Average Final Cs (mg/L)	1.64		6.91	

Measured Cs in Feed (mg/L)	25.67
Sample #	BNF-SSIX-7-VP-1
LIMS #	300129987

63.17
BNF-SSIX-7-C-2
300122420

Batch #981020mb48-563

Sample #	BNF-SSIX-32-2	BNF-SSIX-32-2-D	BNF-SSIX-32-3	BNF-SSIX-32-3-D
LIMS #	300129943	300129944	300129945	300129946
Solution Mass (g)	14.7468	14.7436	14.738	14.7128
Resin Mass (g)	0.1203	0.1216	0.1232	0.1222
Solution Volume (mL)	12.02	12.02	12.01	11.99
Initial Cs (mg/L)	102.19	102.19	150.95	150.95
Final Cs (mg/L)	13.90	15.00	27.40	27.70
solution volume/exchanger mass	99.9	98.8	97.5	98.1
Temperature (C)	23	23	23	23
Shake Time (hr)	24.0	24.0	24.0	24.0
K _d (mL/g)	707.4	640.3	490.1	486.7
Duplicate Average K _d	673.9		488.4	
Duplicate Average Final Cs (mg/L)	14.45		27.55	

Measured Cs in Feed (mg/L)	102.19
Sample #	BNF-SSIX-7-P-2
LIMS #	300129988

150.95
BNF-SSIX-7-P-3
300129989

Attachment 1. SuperLig® 644 Batch Contact Data (cont.).

Batch #981020mb48-563

Sample #	BNF-SSIX-15-1	BNF-SSIX-15-1-D	BNF-SSIX-15-2	BNF-SSIX-15-2-D
LIMS #	300126559	300126560	300126561	300126562
Solution Mass (g)	13.4097	13.3368	13.5003	13.5059
Resin Mass (g)	0.122	0.1221	0.1214	0.121
Solution Volume (mL)	11.97	11.91	12.06	12.06
Initial Cs (mg/L)	5.66	5.66	5.66	5.66
Final Cs (mg/L)	0.267	0.275	0.268	0.272
solution volume/exchanger mass	98.15	97.54	99.30	99.67
Temperature (C)	22	22	22	22
Shake Time (hr)	24.0	24.0	24.0	24.0
K _d (mL/g)	2210.2	2129.3	2227.3	2201.1
Duplicate Average K _d	2169.7		2214.2	
Duplicate Average Final Cs (mg/L)	0.271		0.270	

Measured Cs in Feed (mg/L)	102.19	150.95
Sample #	BNF-SSIX-7-P-2	BNF-SSIX-7-P-3
LIMS #	300129988	300129989
Comment	Simulant + water storage solution	Simulant + water

8.2 Attachment 2. SuperLig® 644 Column Data.

SuperLig® 644 Batch 980624001DC**Cs Breakthrough and Elution Profiles****0.87 cm/min (5.9BV/hr), 2.69 cm ID****Column****Load Cycle****0.5M Nitric Acid****Elution****Feed 9.32 mg/L****Cs****# BV C/Co****# BV Cs (mg/L)**

3.7	0.049
7.8	0.062
22.6	0.061
37.4	0.066
52.3	0.078
67.1	0.097
81.9	0.108
96.7	0.133
111.5	0.172
125.6	0.212
153.9	0.291
182.2	0.349
211.5	0.431
245.3	0.524
279.0	0.601
312.8	0.670
346.6	0.715
388.8	0.755
422.3	0.809

1	0.65
3	0.805
4	1.04
5	2.535
6	130.305
7	17.085
9	4.775
13	0.1

6.0 cm/min (40.9BV/hr), 2.69 cm ID**Column****Load Cycle****0.5M Nitric Acid****Elution****Feed 7.96 mg/L****Cs****# BV C/Co****# BV Cs (mg/L)**

2.6	0.002
6.6	0.007
22.0	0.101
36.4	0.213
46.0	0.246
74.8	0.366
83.9	0.382
125.5	0.460
200.2	0.562
274.9	0.633
321.3	0.653
339.6	0.673

2.7	434.945
3.9	632.1
5.0	171.36
5.9	7.865
6.8	1.62
7.5	0.78
9.4	0.31
11.3	0.115

Attachment 2. SuperLig® 644 Column Data (cont.)

SuperLig® 644 Batch 980624001DC**Cs Breakthrough and Elution Profiles**

10.6 cm/min (72.3BV/hr), 2.69 cm

ID Column

Load Cycle

Feed 8.099 mg/L

# BV	C/Co
4.4	0.009
8.9	0.066
17.9	0.141
37.3	0.258
95.4	0.471
153.6	0.569
231.2	0.684
307.7	0.727
362.4	0.777

0.5M Nitric Acid
Elution
Cs

# BV	Cs (mg/L)
0.4	0.78
1.5	0.895
2.4	1080.59
3.3	871.395
4.1	480.095
5.0	49.49
5.8	3.61
7.6	0.75

0.83 cm/min (12.3BV/hr), 4 cm ID Column

Load Cycle

Feed 8.55 mg/L

# BV	C/Co
90.5	0.157
109.6	0.204
128.8	0.263
147.9	0.295
186.1	0.391
280.8	0.571
374.8	0.727
384.3	0.730

0.5M Nitric Acid
Elution
Cs

# BV	Cs (mg/L)
0.9	0.19
1.8	551.905
2.7	499.055
3.6	485.465
4.5	385.805
5.4	309.55
6.3	87.58
8.1	17.28
10.8	1.44

8.3 Attachment 3. Flow Rate Conditions for SuperLig[®] 644 Column Feed and Elution Cycles.

Experiment #	Bed Diameter (cm)	Feed cm/min (BV/hr)	Feed Range (cm/min)	Elution cm/min (BV/hr)
3	2.7	0.87 (5.9)	0.78 - 0.93	0.14 (0.95)
1	2.7	6.0 (40.9)	5.8 - 6.2	0.14 (0.94)
2	2.7	10.6 (72.3)	9.8 - 10.7	0.12 (0.85)
4	4.0	0.83 (12.3)	0.81 - 0.84	0.13 (0.90)

8.4 Attachment 4. SuperLig® 644 Batch 981020mb48-563 Resin Swelling Data

Bed Height (cm) Volume (mL)

Experiment #1 (2.7 cm ID column)

0.25 M NaOH	8.85	50.3
Simulant	7.45	42.3
0.1 M NaOH/water wash	9.15	52.0
Elution	5.55	31.5

Experiment #2 (2.7 cm ID column)

0.25 M NaOH	9.45	53.7
Simulant	7.45	42.3
0.1 M NaOH/water wash	9.25	52.5
Elution	6.35	36.1

Experiment #3 (2.7 cm ID column)

0.25 M NaOH	9.55	54.2
Simulant	8.15	46.3
0.1 M NaOH/water wash	9.25	52.5
Elution	6.3	35.8

Experiment #4 (4.0 cm ID column)

0.25 M NaOH	4.5	55.4
Simulant	3.5	43.1
0.1 M NaOH/water wash	4.8	59.1
Elution	2.7	33.2

8.5 Attachment 5. SuperLig® 644 Upflow Elution Scoping Tests

Experimental Details

Resin: SuperLig® 644 Batch 98102mb48-563 in acid form

Column ID: 2.7 cm

Column Design: columns used for intermediate-scale simulant tests

Flow Rate (BV ¹ /hr)	Flow Rate (mL/min)	Flow Rate (cm/min)	Resin Height (cm)	% resin expansion	Observations
2.3	1.9	0.38	2.8	0	no movement of resin particles
5.1	4.3	0.84	2.8	0	
7.5	6.3	1.24	2.8	0	
13.4	11.2	2.21	2.8	0	
17.7	14.7	2.90	2.9	3.6	initial movement of a few resin particles
21.4	17.9	3.52	2.9	3.6	
24.0	20.0	3.95	3.0	7.1	bed surface slightly disturbed
28.6	23.8	4.70	3.2	14.3	
32.1	26.8	5.29	3.2	14.3	resin bed observed to pulsate slightly with the pump motion
36.7	30.6	6.04	3.3	17.9	
40.0	33.3	6.58	3.3	17.9	
47.4	39.5	7.79	3.5	25.0	
51.4	42.9	8.46	3.5	25.0	<5% of resin particles suspended in solution
54.5	45.5	8.97	3.5	25.0	
60.0	50.0	9.87	3.7	32.1	

1 BV is defined as the volume of resin in the 2.7cm ID column after contracting with 0.25M NaOH.

8.6 Attachment 6. ICP-ES Analysis of as-received SuperLig® 644 resin and resin used for column experiments (Resin Batch: #981020mb48-563; Units: µg/g resin)

	as-received resin		resin used for column exp.	
	Sample 1	Sample 1D (duplicate)	Sample 2	Sample 2D (duplicate)
Al	16731	241	114	<50
B	<50	<50	<50	<50
Ba	11	198	430	93
Ca	131	72	118	33
Cd	<5	<5	<5	<5
Co	<5	<5	<5	<5
Cr	70	59	<10	<10
Cu	<5	<5	<5	<5
Fe	151	95	381	52
La	<14	<14	<14	<14
Li	<70	<70	<70	<70
Mg	11	<5	15	<5
Mn	20	<4	<4	<4
Mo	<5	<5	<5	<5
Na	7178	2306	7310	7844
Ni	<6	<6	<6	<6
P	235	80	112	91
Pb	<50	<50	<50	<50
Si	99	45	76	51
Sn	<40	<40	<40	<40
Sr	15	7.0	5.3	4.8
Ti	24	46	9.6	14
V	<12	<12	<12	<12
Zn	13	5.3	13	9.7
Zr	<15	<15	<15	<15

Note: Dissolution of the resins was accomplished using a high-pressure, sealed vessel (Parr bomb) and concentrated nitric acid. 0.1 g of SuperLig® 644 resin was added to the vessel with 3 ml of concentrated (16 M) HNO₃. The temperature was raised to 150° C and maintained for 1.5 hours. Then the vessel was cooled and the sample was diluted with water to a final volume of 10 mL and analyzed by ICP-ES.