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DISCLAIMER

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Test Plan
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CESIUM ION EXCHANGE USING TANK 241-AN-104 SUPERNATE (U)

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REVIEWS AND APPROVALS

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LIST OF ACRONYMS

BV	bed volume
C/C_o	cesium concentration in column effluent divided by cesium concentration in feed or initial cesium concentration
C_f	final cesium concentration
DF	decontamination factor
DI	deionized water
DL	detection limit
F	F-factor
H-form	hydrogen form
I	I-factor
ID	inside diameter
IC	ion chromatography
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
Kd	sorption partition coefficient
m	mass of damp pretreated Na-form resin
m_d	mass of vacuum-dried Na-form resin
m_H	mass of vacuum-dried H-form resin
MRQ	minimum reportable quantity
Na-form	sodium form
PNNL	Pacific Northwest National Laboratory
PSD	particle size distribution
RPP	River Protection Project
RSD	relative standard deviation
SRTC	Savannah River Technology Center
TC	total carbon
TIC	total inorganic carbon
TOC	total organic carbon
PuTTA	plutonium triphenyltrifluoroacetone
V	volume of solution or resin bed
WTP	waste treatment plant
λ (lambda)	number of bed volumes of solution processed at 50% breakthrough

1.0 SUMMARY OF TESTING

1.1 OBJECTIVES

The objectives of this study were to:

1. Demonstrate SuperLig® 644 ion exchange performance and process steps for the removal of cesium from actual AN-104 tank waste.

2. Pretreat actual AN-104 tank waste to reduce the concentration of cesium-137 in the waste below LAW vitrification limit of 0.087 μCi ^{137}Cs/mL.

3. Produce and characterize cesium eluate solutions for use in eluate evaporation tests.

1.2 CONDUCT OF TESTING

The experiments consisted of batch contact and small-scale column tests.

The batch contact tests measured sorption partition coefficients (Kds). The Kds were used to predict the effective resin capacity. This was achieved through generation of sorption isotherms using three initial concentrations of cesium.

The small-scale column tests, which closely mimic plant conditions, generated loading and elution profile data used to determine whether removal targets and design requirements were met. It involved a two-column system connected in series during loading and parallel during elution.

1.3 RESULTS AND PERFORMANCE AGAINST OBJECTIVES

The actual AN-104 waste column run resulted in cesium-137 removal and overall decontamination factor of 99.6 % (lead column) and 517,000 (lag column) respectively. Also, the concentration of cesium-137 in the lag column effluent (0.000423 μCi ^{137}Cs/mL) was significantly below the LAW vitrification limit of 0.087 μCi ^{137}Cs/mL. The onset-of-breakthrough value of 175 BV shows that the resin surpasses the 100 BV requirement for Envelope A waste.

Cesium-137 elution with 0.5 M HNO_3 was adequate overall with a peak at 3.5 BV. C/C_o = 0.01 occurred at 10 BV of eluting acid. Also, 99.99% of the sorbed cesium-137 was eluted from the resin at 30 BV. Table 1-1 shows a summary of the results.

The concentration of most of the constituents in the eluate was below detection limit because of dilution prior to analysis.

Table 1-1. Summary of Column Performance Characteristics

Loading	
Lead column BV at onset of breakthrough	175
Lead column percent removal	99.6
Lag column total decontamination factor	517,000
Elution	
Lead column elution peak BV	3.5
Lead column BV at $C/C_o = 0.01$	10
Percent of sorbed cesium-137 eluted from the lead column	99.99

1.4 QUALITY REQUIREMENTS

This task was conducted per the requirements of Task Technical & Quality Assurance Plan[1] that was approved by both SRTC and RPP-WTP personnel (Technical and QA personnel). These tests were not HLW form affecting, therefore, the Quality Assurance Requirements and Description (DOE/RW-033P), the principle quality assurance requirements for the Civilian Radioactive Waste Management Program, did not apply to this work. The work was performed to quality assurance requirements NQA-1-1989, and NQA-2a-1990, Part 2.7. All data were recorded in a Laboratory Notebook[6].

The original Technical Specification QA Requirement drivers were to NQA-1-1994, Basic and Supplementary Requirements, and to DOE/RW-0333P Revision 8 (if applicable), which was in effect at the time the specification was issued (6/14/01). The task, however, was conducted in accordance with the newer RPP-WTP QA requirements as specified in DOE IWO MOSRLE60, dated 6/20/2001.

SRTC has provided matrices to WTP demonstrating compliance of the SRTC QA program to the newer requirements as specified by WTP. Specific information regarding the compliance of the SRTC QA program with RW-0333P, Revision 10, NQA-1 1989, Part 1, Basic and Supplementary Requirements and NQA-2a 1990, Part 2.7 is contained in these matrices. The QA requirements specified in the "Task Technical and Quality Assurance Plan for Cesium and Technetium Ion Exchange Using Tank 241-AN-104 Supernate"[1] were to these newer QA requirements. No additional QA requirements were required nor implemented in this work.

1.5 ISSUES

None

2.0 INTRODUCTION

The River Protection Project – Waste Treatment Plant (RPP-WTP) is to design and build a high level nuclear waste treatment facility at the Hanford Site, in Richland Washington. The waste treatment plant (WTP) is to process millions of gallons of radioactive waste stored in tanks at the Hanford Site. The high level nuclear waste treatment process includes various unit operations, such as ultraflitration, precipitation, evaporation, ion exchange, and vitrification. Ion exchange is identified as the optimal treatment method for removal of cesium-137 and Tc-99 from the Hanford waste.

Extensive ion exchange testing was performed at Savannah River Technology Center (SRTC) and Pacific Northwest National Laboratory (PNNL-Battelle) using small-scale columns with actual waste samples. A series of medium-scale and pilot-scale testing with simulants was performed to provide data to a computational model (VERSE) to verify the performance of the ion exchange process for the full-scale plant. To demonstrate the baseline ion exchange resin performance and to define the operating conditions for each of the waste envelopes, batch equilibrium and small-scale ion exchange column testing were performed with actual waste samples to remove cesium and technetium. To date, SRTC has performed ion exchange tests with samples from seven tanks: AN-103, AN-105, AW-101 (Envelope A), AZ-101, AZ-102 (Envelope B), and AN-102 and AN-107 (Envelope C).

The goal of this study was to demonstrate SuperLig® 644 ion exchange performance and process steps for the removal of cesium from actual AN-104 tank waste including reducing the concentration of cesium-137 in the waste below LAW vitrification limit of 8.7E-02 μCi ^{137}Cs/mL, and characterizing cesium eluate solution for use in eluate evaporation tests.

The report deals mainly with batch and column test procedures used for the study followed by a discussion of results. The data not given in the results and discussion section are given in the appendices. The work was done according to the "Task Technical and Quality Assurance Plan for Cesium and Technetium Ion Exchange Using Tank 241-AN-104 Supernate"[1]. The Task Technical and Quality Assurance Plan was also derived from "Test Specification for Cesium and Technetium Ion Exchange Using Tank 241-AN-104 Supernate"[2].

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3.0 EXPERIMENTAL

3.1 MATERIALS

3.1.1 Resin

The SuperLig® 644 resin (First 25 gallon batch, batch # = C-01-05-28-02-35-60) was obtained from IBC Advanced Technologies, Inc. (American Fork, Utah). The resin is a proprietary polymeric organic material resin that is selective for cesium. It was received in the sodium form and was pretreated before being used.

3.1.1.1 Resin Pretreatment

The as-received Na-form resin was pretreated by taking it through caustic-acid-caustic solution treatments. The resin was soaked in 1 M NaOH (1:10 ratio of resin mass to solution volume) for two hours. The resin-NaOH solution mixture was gently shaken periodically, but no stir bar or mechanical agitation of the mixture was used. At the end of the 2-hour soaking period, the resin-NaOH solution mixture was slurried into a 2.67 cm ID glass column. The excess NaOH solution was drained from the column and the column was taken through the following steps:

- 3 bed volumes (BV) of de-ionized water rinse at 3 BV/h
- 15 BV of 0.5 M HNO_3 at 3 BV/h
- 10 BV of de-ionized water rinse at 3 BV/h

After the de-ionized water rinse, the resin was slurried out of the column with deionized water into a 3-liter beaker and allowed to soak overnight in 10 BV of 0.25 M NaOH. Again, the resin-NaOH solution mixture was gently shaken, but no stir bar or mechanical agitation of the mixture was used. This was followed by soaking in 10 BV of deionized water for 30 minutes with periodic gentle shaking. The last step was repeated with 5BVs of deionized water, at which point the pH of the deionized water was about 9. The resin was then filtered 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 pretreated resin was transferred to a tared wide-mouth HDPE bottle and mixed thoroughly using a spatula. Portions of the damp pretreated resin were taken for F-factor, I-factor, and bulk density (in deionized water) measurements. The F-factor is the solids fraction remaining after water loss through vacuum drying. The I-factor is the mass increase after conversion of the H-form resin to the Na-form. Note that the two portions of 12-mL resin in deionized water used for the bulk density measurements were also used for the column runs. The remaining damp pretreated resin was purged with nitrogen and capped tightly.

3.1.1.2 Resin Characterization

For the procedures described below, damp pretreated Na-form SuperLig® 644 resin was used. Damp resin in this report means resin that has been filtered to remove water until several minutes after the water dripping ceased. Vacuuming at 45°C was used to remove all possible moisture for F-factor, and I-factor and determinations.

The bulk density in deionized water was determined by weighing small amounts of damp pretreated resin into a 20-mL graduated cylinder containing deionized water (while simultaneously tapping the cylinder walls to obtain uniform packing) till a resin bed volume of 12 mL was attained.

The F-Factor of damp pretreated resin was determined by weighing in duplicate approximately 0.5 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 $\pm$ 2 °C to constant mass.

The I-Factor was obtained by converting the damp pretreated Na-form resin to H-form. Note that the resin was converted from Na-form to H-form (instead of the other way around) because the resin was already in Na-form. This was achieved by contacting in duplicate about 0.5 g of the damp Na-form resin with 10 mL of 0.5 M HNO_3 solution and equilibrating overnight in an Incubated Benchtop Shaker (model C24, New Brunswick Scientific Company, Edison, New Jersey) at a shaking speed of 275 rpm and temperature of 25 $\pm$ 2 °C. This was followed by filtering the resin-HNO_3 solution mixture with a tared 0.45-µm nylon Nalgene filter unit (Rochester, New York) under vacuum, washing the resin with 20 to 30 ml of deionized water at room temperature, and finally drying the resin for ~24 hours in vacuum oven (< 40 torr absolute pressure) at 45 $\pm$ 2 °C to a constant mass. Note that the resin was converted from Na-form to H-form (instead of the other way around) because the resin was already in Na-form.

Metals content (Na, K, etc.) analysis was performed on damp pretreated unused resin, and damp used resin from the actual AN-104 waste lead column run.

Wet particle size analysis using SRTC Analytical Development Section's Microtrac® SRA150 Particle Size Analyzer (Largo, Florida) was performed on damp pretreated unused resin in deionized water.

3.1.2 Waste Solutions

3.1.2.1 AN-105 Simulant

A simulant based on tank AN-105 was used in this study for the column shake-down run. The simulant was prepared using the recipe[3] outlined in Appendix D. A total of 5 liters of simulant solution was prepared in three batches (i.e., 1, 2, and 2 liters). The individual batches were filtered under vacuum using 0.45-µm nylon Nalgene filter unit after equilibrating for 2 days with a magnetic stirrer at room temperature. The three batches of filtered solutions were combined into one 5-liter solution and allowed to age for approximately 3 days before being used. No solid particles were visible in the solution at the end of the third day of aging.

3.1.2.2 Actual AN-104 Waste

The actual AN-104 waste solution was received from SRTC High Level Cells after undergoing dilution to 5 M sodium followed by filtration[7] using 0.1 μm sintered metal Mott filter.

3.1.3 Chemicals

Chemicals described in this section are those dealing directly with the batch and column experiments. Chemicals used in the preparation of the simulant are left out for brevity.

All chemicals were reagent grade. 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).

Cesium nitrate (GFS Chemicals, Inc., Columbus, Ohio) was used to spike some of the actual AN-104 waste solutions in the batch contact experiments. A weighed amount was dissolved in the waste solution of interest and allowing to stand overnight with periodic shaking.

3.2 BATCH CONTACT TESTS

Three sets of batch contact runs were conducted as shown in Table 3-1. Batch contact runs were conducted by adding a known volume (100 or 10 mL) of waste solution with a known concentration of cesium to a known mass (about 2.8 g) of damp pretreated Na-form SuperLig® 644 resin in 125-mL polyethylene bottle equipped with Teflon®-lined screw cap. A Mettler-Toledo (Columbus, Ohio) analytical balance (model AG285) with an accuracy of $\pm$ 0.001 g was used to weigh the samples.

Table 3-1. Different Sets of Batch Contact Runs Performed

Set #	Waste	Phase ratio, mL/g dry resin	Initial Concentration	Equilibration Time, hours (days)	Shaker Speed, rpm
1	Simulant	100	Original	120 (5 days)	275
2	Actual AN-104	100	Original, plus two spiked concentrations	72 (3 days)	580
3	Actual AN-104	10	Original	120 (5 days)	580

The bottles were equilibrated in an Incubated Benchtop Shaker (model C24, New Brunswick Scientific Company, Edison, New Jersey) or a Maxi-Mix III Shaker (Type 65800, Barnstead/Thermolyne, Dubuque, Iowa) for predetermined times and shaking speeds at a temperature of 25 $\pm$ 2 ^{o}C. The Incubated Benchtop Shaker was used for the simulant run (set 1), and the Maxi-Mix III Shaker was used for the Actual AN-104 runs (sets 2 and 3). High precision (0.01 ^{o}C) thermometers traceable to the National Institute of Standards and Testing (NIST) were mounted in polyethylene bottles containing deionized water to record the temperature in the Incubated Benchtop Shaker[8].

At the end of the equilibration period, the resin-solution mixtures were separated by filtration. Nalgene (Rochester, New York) 0.45-μm nylon filters connected to a vacuum and trap assembly were used for the filtration. Aliquots (1 - 3 mL) of the filtrate were placed in glass vials with Teflon®-lined screw caps for analyses. The amount of cesium sorbed was determined from the initial and final concentrations of cesium in solution.

Control runs were conducted along with and in the same manner as the batch contact runs previously described. A control is a waste solution containing no resin and is utilized to determine the initial waste solution concentration of the desired constituent.

Three different initial solution concentrations were used for the set 2 run as indicated in Table 3-1. Two of the three initial solution concentrations were obtained by spiking with cesium nitrate. All batch contact runs were conducted in duplicate except the controls for the set 2 run. Single controls were used for the set 2 run in order to have adequate actual AN-104 waste solution for the column run.

The goal of the set 3 batch contact run was to check cesium mass balance. Hence, the following additional steps were carried out after separating the resin-actual waste solution mixtures by filtration as mentioned earlier. The steps below essentially reduced the cesium-137 on the resin to permit its removal from the Intermediate Level Cell for analysis.

1. Using a new filtrate reservoir, the used resin was washed with 20 mL of 0.1 M NaOH (feed displacement).
2. Using a new filtrate reservoir, the used resin was rinsed with 20 mL of deionized water.
3. The used resin was slurried from the filter unit into a 50-mL polyethylene bottle using 20 mL of 0.5 M HNO_3 and allowed to equilibrate in a Maxi-Mix III Shaker (Type 65800, Barnstead/Thermolyne, Dubuque, Iowa) for 120 hours (5 days) at a shaking speed of 580 rpm and a temperature of 25 $\pm$ 2 ^{o}C.
4. Using a new filtrate reservoir, the resin-HNO_3 mixture was filtered.

Note that 0.45 μm nylon Nalgene filter unit under vacuum was used for all the above filtrations. Also, the filtrations were continued till the solution dripping ceased. The individual filtrates and the used resin from step 4 were sent for cesium-137 analysis.

3.3 COLUMN OPERATION

3.3.1 Ion Exchange Column Apparatus

The ion exchange column apparatus consisted of two (designated as lead and lag columns) glass columns, two fraction collectors or two autosamplers, a constant-temperature water circulating bath, and several metering pumps. The column apparatus was set up in a chemical hood and Intermediate Level Cell for simulant and actual waste runs respectively. The pump inlet tubings were manually switched between simulant/actual waste and the other process solutions.

The borosilicate glass columns (Spectrum Chromatography, Houston, Texas) had an inside diameter of 1.45 cm (i.e., 1.65 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 columns were equipped with adjustable polypropylene plungers (model 124108, Spectrum Chromatography, Houston, Texas) at the top and 200 mesh stainless steel screens at the bottom. The plungers were used to control the height of liquid above the resin beds, while the screens were used as supports for the resins. Temperature regulation in the columns was achieved with a constant temperature circulating water bath (Model DC10-P5, ThermoHaake, Newington, New Hampshire) looped with the column glass jackets. The outer walls of the columns and jackets were coated with polyvinyl chloride to help minimize hazard in case of breakage.

Solutions were introduced in down flow through the columns 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[8].

Spectrum Chromatography IS-95 Interval Samplers (for the simulant run) and in-house auto sampler (for the actual AN-104 waste run) located at the outlet of each column were utilized to collect aliquots of samples either manually or automatically. All the individual units (i.e., pumps, columns, fraction collectors) from the solution reservoir bottles to the effluent bottles were connected with polyethylene tubing (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. Figure 3-1 is a picture of the column setup in an Intermediate Level Cell.

3.3.2 Column Tests

The two 12-mL portions of SuperLig® 644 resin in deionized water set aside immediately at the end of the resin pretreatment (see subsection 3.1.1.1) were poured into two glass columns (lead and lag). The walls of the glass columns were simultaneously tapped during the pouring operation to ensure uniform resin bed packing. The quantities of both damp and dry resin for each column are given in Table 3-2.

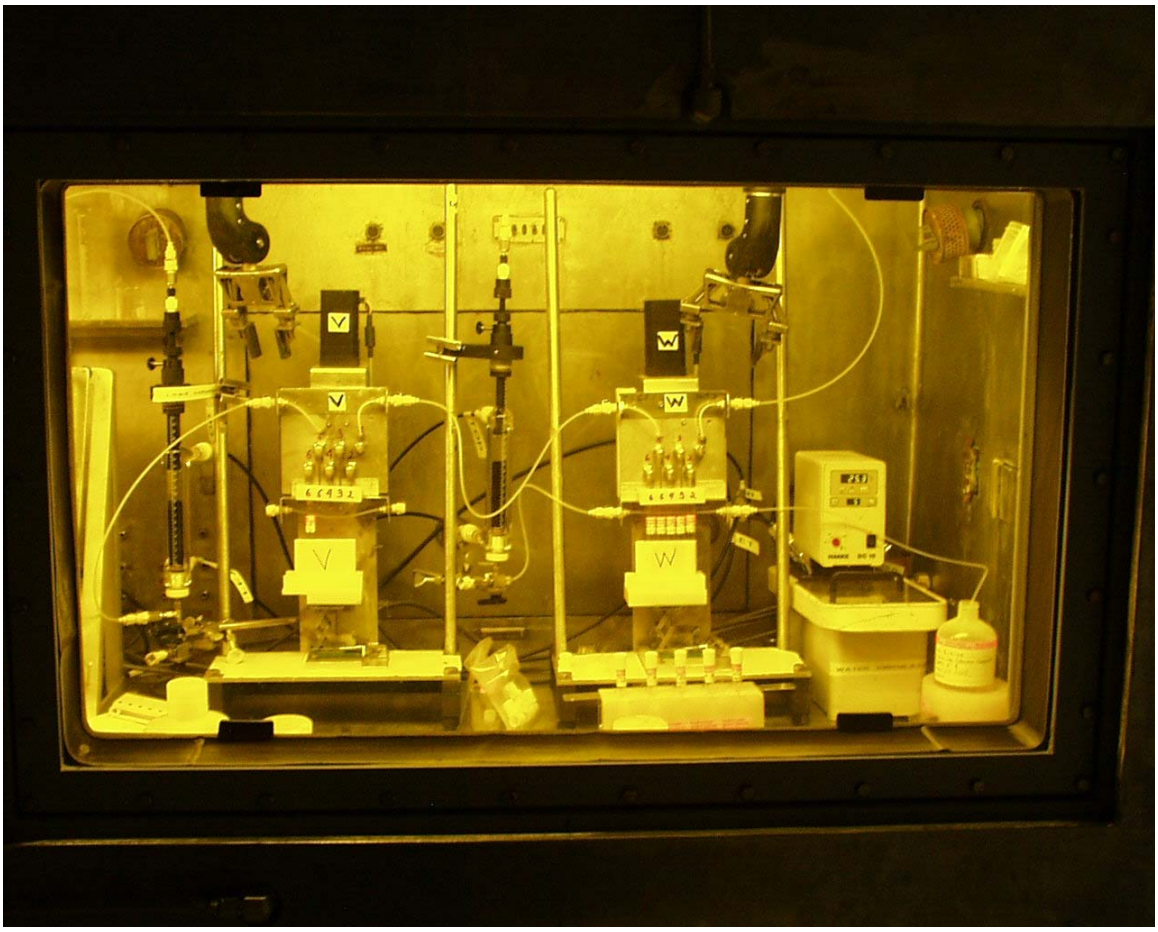

Figure 3-1. Photograph of Column Test Apparatus Inside the Intermediate Level Cell

Two column runs were conducted using the same resins and column setup. The first run used AN-105 simulant, and it was done in a chemical hood. The second run used actual AN-104 waste and was performed in an Intermediate Level Cell. This obviously implies the column setup including the resins were transferred from the chemical hood to the intermediate level cell at the end of the simulant run. The goal of the AN-105 simulant run that preceded the actual AN-104 waste run was to ensure the column setup works properly before proceeding with the actual AN-104 waste run.

Table 3-2. Mass of SuperLig® 644 Used per Column

Column	Damp Na-form Resin Mass, g	Dry Na-form Resin Mass, g
Lead	7.9641	2.8347
Lag	7.9564	2.8319

F-Factor = 0.356

Each column process step (i.e., loading, elution, regeneration, deionized water rinse, 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 columns. 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 ± 2 °C. The volume of liquid above the resin bed during the lead column loading step was 0.87 BV. Table 3-3 and Table 3-4 give details of the experimental conditions including when the lead and lag columns were connected in series or run in parallel for the simulant and actual waste runs respectively.

Table 3-3. Experimental Conditions for AN-105 Simulant Column Run

Process Step	Solution	Bed Volumes of Solution Processed	Flow Rate, BV/hr	Time per Process Step, hr
Lead and Lag Columns in Parallel				
Resin Preconditioning	0.25 M NaOH	6	3	2
Lead and Lag Columns in Series				
Loading	AN-105 simulant	340	3	113.3
Feed Displacement	0.10 M NaOH	6	3	2
Post-Feed Water Rinse	Deionized water	4	3	1.3
Lead and Lag Column in Parallel				
Elution	0.5 M HNO_3	25	1	25
Post-Elution Water Rinse	Deionized water	6	1	6
Temperature of each process step = 25 ± 2 °C Bed volume (BV) of each column = 12 mL (in simulant solution)				

Table 3-4. Experimental Conditions for Actual AN-104 Waste Column Run

Process Step	Solution	Bed Volumes of Solution Processed	Flow Rate, BV/hr	Time per Process Step, hr
Lead and Lag Columns in Parallel				
Regeneration	0.25 M NaOH	12	3	4
Lead and Lag Columns in Series				
Loading	Actual AN-104 waste	267	3	89
Feed Displacement	0.10 M NaOH	6	3	2
Post-Feed Water Rinse	Deionized water	6	3	2
Lead and Lag Column in Parallel				
Elution	0.5 M HNO_3	30	1	30
Post-Elution Water Rinse	Deionized water	6	1	6
Regeneration	0.25 M NaOH	6	3	2
Post-Regeneration Water Rinse	Deionized water	15	3	5
Temperature of each process step = 25 $\pm$ 2 ^{o}C Bed volume (BV) of each column = 12 mL (in simulant solution)				

Samples of the effluent were collected periodically per the sampling and analysis scheme given in Table 3-5 and Table 3-6 for the simulant and actual waste runs respectively. The overall error for all the analyses is within $\pm$ 20%. At the end of the last process step (i.e., post-regeneration water rinse) for the actual AN-104 waste column run, the lead column used resin was removed from the column and filtered till the water dripping ceased. A portion of the damp used resin was the sent for metals content (Na, K, etc. and cesium-137) analysis. The column runs proceeded as expected except the top 1 cm of the lead and lag columns turned gray during the simulant loading process step. The gray 1-cm top remained throughout the simulant and actual waste column runs.

Table 3-5. Sampling and Analysis Scheme for AN-105 Simulant Column Run

Process Step	Lead Column Sampling Events	Lag Column Sampling Events	Analytical Sample Volume, mL	Analysis
0.25 M NaOH Preconditioning	Not sampled	Not sampled	n/a	n/a
Loading	* 5th BV and 10 BV increments thereafter	** Every 40 BV	4	Cs using ICP-MS
Loading Composite	n/a	Composite	n/a	Not analyzed
Feed Displacement	n/a	Every 1 BV	n/a	Not analyzed
Post-Feed Water Rinse	n/a	Every 1 BV	10	Cs using ICP-MS, Na , K using ICP-AES, & pH
Elution	1 BV increments for first 6 BV and 2 BV increments thereafter	Not sampled	6	Cs using ICP-MS, and pH
Elution Composite	Composite	Composite	n/a	Not analyzed
Post-Elution Water Rinse Composite	Composite	Composite	n/a	Not analyzed

n/a = not applicable
ICP-MS = Inductively coupled plasma mass spectrometry
ICP-AES = Inductively coupled plasma atomic emission spectrometry
* Only selected samples were analyzed
** Samples were not analyzed

Table 3-6. Sampling and Analysis Scheme for Actual AN-104 Waste Column Run

Process Step	Lead Column Sampling Events	Lag Column Sampling Events	Analytical Sample Volume, mL	Analysis
0.25 M NaOH Preconditioning	Every 3 BV	Every 3 BV	10	pH
Loading	*Every 10 BV	Every 20 BV	3	Cs using GEA
Loading Composite	n/a	Composite	30	Cs using GEA & ICP-MS, other metals using ICP-AES, nitrate, nitrite, chloride, fluoride, sulfate, phosphate using IC, TIC/TOC using furnace oxidation, and hydroxide using titration
Feed Displacement	n/a	Every 1 BV	3	Na & K using ICP-AES,& pH
Post-Feed Water Rinse	n/a	Every 1 BV	10	pH
Elution	Every 1 BV	Not sampled	3	Cs using GEA, Na using ICP-AES, & pH
Elution Composite	Composite	Not sampled	4	Cs using GEA, &other metals using ICP-AES
Post-Elution Water Rinse	Every 1 BV	Not sampled	10	Cs using GEA & pH
Regeneration	Every 1 BV	Not sampled	10	Cs using GEA & pH
Regeneration Composite	Composite	Not sampled	4	Cs using GEA
Post-Regeneration Water Rinse Composite	Not sampled	Not sampled	n/a	n/a
Used Resin at the end of run	1 gram in duplicate	Not sampled	n/a	Cs using GEA, & other metals using ICP-AES

n/a = not applicable
GEA Gamma energy analysis
ICP-MS = Inductively coupled plasma mass spectrometry
ICP-AES = Inductively coupled plasma atomic emission spectrometry
IC = Ion chromatography
TOC = Total organic carbon
TIC = Total inorganic carbon
* Only selected samples were analyzed

4.0 RESULTS AND DISCUSSION

4.1 RESIN CHARACTERIZATION

Wet particle size distribution of pretreated Na-form SuperLig® 644 resins is given in Table 4-1. The bulk of the resin was between 249 and 704 μm, i.e., 91 volume %. The relative standard deviation for duplicate measurements per particle size range was below 8% except for the smallest particle size range. The high relative standard deviation for the smallest size range is due to the low or small volume of resin in that size range.

Table 4-1. Wet Particle Size Distribution Data of Pretreated Na-Form SuperLig® 644 Resin

U.S. Mesh Size	Particle Size, μm	Volume Percent	Percent RSD*
35 - 25	498 - 704	43.305	1.7
45 - 35	352 - 498	31.98	3.1
60 - 45	249 - 352	15.69	0.5
80 - 60	176 - 249	5.92	1.4
120 - 80	125 - 176	2.125	6.3
170 - 120	88 - 125	0.865	7.4
230 - 170	62 - 88	0.115	43.0
Total	n/a	100	n/a

* RSD of duplicate measurements
n/a = not applicable

Table 4-2 shows various properties of the SuperLig® 644 resin. The F-factor is solid fraction of the resin remaining after vacuum-drying the damp Na-form resin. It is given by Equation 4-1:

Equation 4-1 $$F = m_d/m$$

where:
m_d is the mass of vacuum-dried Na-form resin
m is the mass of damp pretreated Na-form

The I-factor is the mass increase upon conversion from H-form to Na-form as given by Equation 4-2:

Equation 4-2 $\mathbf{I = (m * F)/m_H}$

where:

m_H is the mass of vacuum-dried H-form resin
m and F have same meanings as before

The Na-form and H-form dry basis resin bed densities are given by Equation 4-3 and Equation 4-4:

Equation 4-3 **Na-form dry basis resin bed density = (m * F)/V**

Equation 4-4 **H-form dry basis resin bed density = (m * F/I)/V**

where V is the resin bed volume

Table 4-2. SuperLig® 644 Resin Characterization Data

Property	SuperLig® 644
F-factor	0.356[a] (0.355 - 0.357)
I-factor	1.469[b] (1.209 - 1.646)
Bed Density (Dry basis)	g dry resin/mL
Deionized Water	0.236[a,c] (0.2362 - 0.2360)
AN-104 Waste	0.244[c]
0.25 M NaOH	0.207[c]
0.5 M HNO_3	0.224[d]

[a] Average of duplicate measurements - range of measured values are in parenthesis
[b] Average of quadruplicate measurements - range of measured values are in parenthesis
[c] Calculated using Equation 4-3
[d] Calculated using Equation 4-4

4.2 AN-105 SIMULANT AND ACTUAL AN-104 WASTE CHARACTERIZATION

Table 4-3 gives the compositions of the AN-105 simulant and the actual AN-104 waste solutions. The analytical results for the AN-105 simulant generally compare favorably with the amounts used to prepare the solution. For example, the cesium concentration in simulant based on the amount actually put in solution is 7.71 μg/mL versus the measured concentration of 7.73 μg/mL.

The actual AN-104 waste data also agree roughly with the AN-104 filtrate data from an ultrafiltration study[7]. Recall the actual AN-104 waste solution came from the ultrafiltration work. The amount of cesium-137 in the actual AN-104 waste was 20.6% of the total cesium in the waste. The total cesium comprises the following isotopes: cesium-133, cesium-135, cesium-137, and cesium-138.

Table 4-3. Composition of AN-105 Simulant and Actual AN-104 Waste Solutions

Analyte	AN-105 Simulant, µg/mL	Actual AN-104 Waste, µg/mL	Analyte	AN-105 Simulant, µg/mL	Actual AN-104 Waste, µg/mL
Ag	13.6	1.26	F^-	< 20	66
Al	9,040	13,019	$(HCOO)^-$	1,450	nm
B	23.7	36.8	Cl^-	3,370	3,170
Ba	0.12	< 2.15	NO_2^-	48,850	43,300
Ca	0.72	3.40	NO_3^-	73,700	75,300
Cd	0.55	< 0.475	PO_4^-	186	1,490
Ce	< 0.154	15.1	SO_4^-	103	2,810
Co	< 0.088	nm	$(C_2O_4)^{2-}$	219	nm
Cr	610	142			
Cs	7.73	See below	TIC	2,785	3,330
Cu	0.145	1.73	TOC	1,155	2,710
Fe	1.4	2.89	TC	3,940	6,040
Gd	nm	< 2.65			
K	3,480 (0.089 M)	3,800 (0.097 M)	Total Base, M	2.31	2.478
La	< 1.4	1.27	Free OH^-, M	1.79	1.334
Li	< 0.2	5.51	Other Base excluding $(CO_3)^{2-}$, M	0.386	0.859
Mg	< 0.168	< 0.600	$(CO_3)^{2-}$, M	0.107	0.285
Mn	< 0.018	< 0.091	pH	14	nm
Mo	39.7	38.9	Dissolved solids, wt %	26.96	nm
Na	104,102 (4.5 M)	106,813 (4.6 M)	Density, g/mL	1.22	1.22
Nb	< 1	nm			
Nd	< 0.52	nm	**Radionuclides**	**µg/mL (µCi/mL**	**µg/mL (µCi/mL)**
Ni	< 0.124	1.53	^{137}Cs	n/a	2.51 (218.7)
P	73.42	432	^{133}Cs	n/a	7.60
Pb	29.6	12.9	^{135}Cs	n/a	1.91
Re	11.3	n/a	^{138}Cs	n/a	0.091
S	54.3	1,211	Total Cs	n/a	12.091
Sb	nm	47.4	^{137}Cs /Total Cs	n/a	0.206
Si	210	177	^{60}Co	n/a	(0.000293)
Sn	0.54	20.5	^{154}Eu	n/a	(0.00465)
Sr	0.17	0.781	^{90}Sr	n/a	(0.0955)
Ti	< 0.28	< 0.872	^{99}Tc	n/a	(0.0919)
U	nm	35.2	^{235}U	n/a	0.0504
V	< 0.26	5.07	^{238}U	n/a	3.66
Zn	335	2.67	Alpha	n/a	(0.131)
Zr	0.123	< 2.58	Beta	n/a	(289)

Each data point is an average of duplicate measurements.
Data with "<" symbols are detection limits.
n/a = not applicable
nm = not measured

4.3 CESIUM BATCH CONTACT TESTS

The sorption capacity of the resin was evaluated using the batch contact approach. Table 4-4 is a summary of cesium batch contact data for both AN-105 simulant and actual AN-104 waste with SuperLig® 644 resin for various initial cesium concentrations, equilibration times, and phase ratios. The top and bottom portions of the table are exclusively for AN-105 simulant and actual AN-104 waste, respectively.

The batch distribution coefficient, Kd, was determined with Equation 4-5.

Equation 4-5 $$Kd = [(C_o - C_f)*V]/[C_f * m * F]$$

where:
C_o is initial cesium concentration
C_f is final cesium concentration
V is the volume of solution
m in the mass of damp pretreated resin
F is the F-factor of the resin

The data in Table 4-4 is consistent overall, with Kd decreasing with increasing initial cesium concentration. The Kd values for the first two sets of batch contact tests under actual AN-104 waste agree closely, even though the tests were conducted at different equilibration times (72 and 120 hours) and phase ratios (101 and 10). The deduction here is that equilibrium is reached in 72 hours.

Figure 4-1 shows log–log plot of Kd versus final total cesium concentration for actual AN-104 waste with linear regression line through the data points. Extrapolation (vertical dashed line) using an initial total cesium concentration of 12.1 μg/mL gives Kd of 1648 mL/g.

The λ value, which is a prediction of the number of bed volumes required to reach 50% breakthrough in a column operation, is given by Equation 4-6.

Equation 4-6 $$\lambda = Kd * \text{dry basis resin bed density}$$

Hence, based on the initial total cesium concentration of 12.1 μg/mL, λ for actual AN-104 waste = 402. The above λ value surpasses 100 BV at 50% breakthrough.

Table 4-4. Cesium Batch Contact Data for AN-105 Simulant and Actual AN-104 Waste Using SuperLig® 644 Resin at 25 °C

Batch Contact Test	Initial Cesium Conc.	Final Cesium Conc.	Phase Ratio	Time	Cesium Sorbed	Cesium Kd	Average Cesium Kd	% RSD
AN-105 Simulant								
	^{133}Cs, μg/mL	**^{133}Cs, μg/mL**	**mL/g**	**hours**	**μg/g**	**mL/g**	**mL/g**	**% RSD**
Unspiked	7.65	0.192	100	120	743	3,870	3,640	8.9
Unspiked duplicate	7.54	0.214	100	120	730	3,410	-	-
Actual AN-104 Waste								
	^{137}Cs, μCi/mL	**^{137}Cs, μCi/mL**	**mL/g**	**hours**	**μCi/g**	**mL/g**	**mL/g**	**% RSD**
Unspiked	225.5	4.05	101	72	22,309	5,504	5,496	0.2
Unspiked duplicate	nm	4.07	101	72	22,329	5,487	-	-
Unspiked	222.2	0.419	10	120	2,281	5,447	5,616	4.3
Unspiked duplicate	223.2	0.397	10	120	2,297	5,786	-	-
	^{133}Cs, μg/mL	**^{133}Cs, μg/mL**	**mL/g**	**hours**	**μg/g**	**mL/g**	**mL/g**	**% RSD**
Cs Spike 1	95.4	3.39	101	72	9,265	2,731	2,698	1.7
Cs Spike 1 duplicate	nm	3.48	101	72	9,268	2,665	-	-
Cs Spike 2	139.2	7.51	101	72	13,271	1,768	1,736	2.6
Cs Spike 2 duplicate	nm	7.78	101	72	13,242	1,703	-	-

F-factor = 0.36
Kds are based on mass of Na-form resin
225.5 μCi/mL = 12.6 μg/mL total cesium
222.2 μCi/mL = 12.4 μg/mL total cesium
223.2 μCi/mL = 12.5 μg/mL total cesium
4.05 μCi/mL = 0.23 μg/mL total cesium
0.419 μCi/mL = 0.02 μg/mL total cesium
Dash denotes not applicable because average of two data points is given
nm = not measured
Resin mass and solution volume are given in Table A- 2 of Appendix A

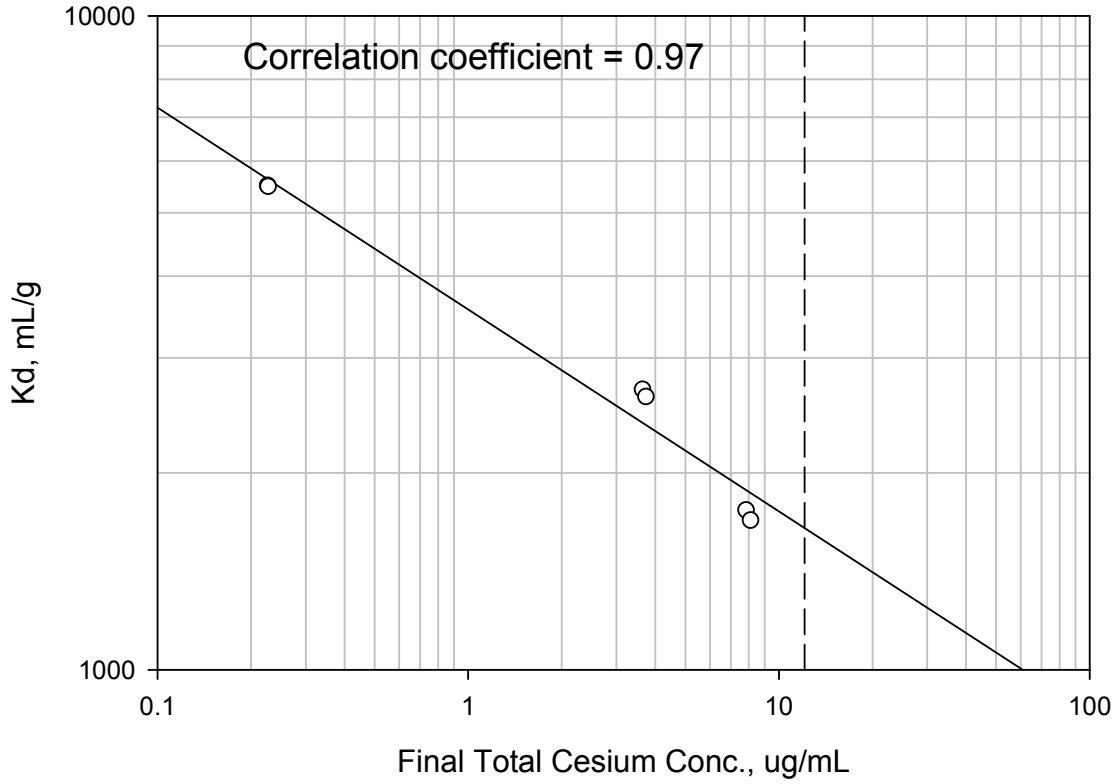

Figure 4-1. Cesium Batch Distribution Coefficients for Actual AN-104 Waste and SuperLig® 644 Resin at 25 °C

Recall in the experimental section (section 3.2) it was mentioned that the second set of actual AN-104 waste batch contact tests (i.e., equilibration time = 120 hours and phase ratio = 10) in Table 4-4 was evaluated for cesium mass balance. Table 4-5 gives batch contact data and data for each of the cesium recovery operations. The upper portion of the table is essentially the same as the second set of data under actual AN-104 waste in Table 4-4. The data in the upper portion of Table 4-5 shows the amount of cesium sorbed determined by difference in the initial and final cesium concentrations.

The approach here was to analyze the resin for cesium-137 at the end of the batch contact tests. Since the cesium-137 on the resin at the end of the batch contact tests was anticipated to be fairly high to permit removal from the Intermediate Level Cell for direct analysis, some of the cesium-137 on the resin was removed by eluting with 0.5 M HNO_3. The above implies the amount of cesium-137 sorbed by the resin (calculated by concentration difference in the upper portion of the Table 4-5) should be equal to cesium-137 eluted from the resin plus cesium-137 remaining on resin after elution (i.e., lower portion of the Table 4-5).

Table 4-5. Cesium Batch Contact Data for AN-104 Waste with SuperLig® 644 Resin Along with Mass Balance Data at 25 °C

Calculation of Cesium Sorbed Based on Initial and Final Solution Concentrations							
Batch Contact Test	**Initial Cesium Conc.**	**Final Cesium Conc.**	**Phase Ratio**	**Time**	**Cesium Sorbed**	**Average Cesium Sorbed**	**% RSD**
	^{137}Cs, µCi/mL	**^{137}Cs, µCi/mL**	**mL/g dry resin**	**hours**	**µCi/g dry resin**	**µCi/g dry resin**	**% RSD**
Unspiked	222.2	0.419	10	120	2,281	2,289	0.5
Unspiked duplicate	223.2	0.397	10	120	2,297	-	-
F-factor = 0.36							

Cesium Recovery Operations to Check Mass Balance				
Batch Contact Test	**^{137}Cs Conc. in Solution µCi/mL**	**Volume of Solution mL**	**^{137}Cs in Solution µCi**	**^{137}Cs in Resin µCi/g dry resin**
0.1 M NaOH Feed Displacement*				
Unspiked	0.099	20	1.99	n/a
Unspiked duplicate	0.092	20	1.83	n/a
Deionized Water Rinse*				
Unspiked	0.072	20	1.44	n/a
Unspiked duplicate	0.062	20	1.25	n/a
0.5 M HNO_3 Elution**				
Unspiked	91.7	20	1,833	1,833
Unspiked duplicate	76.9	20	1,537	1,537
Resin				
Unspiked	n/a	n/a	n/a	548
Unspiked duplicate	n/a	n/a	n/a	465
Total ^{137}Cs in Resin = ^{137}C s in HNO_3 Eluate and ^{137}Cs Left on Resin				
Unspiked	n/a	n/a	n/a	2,381
Unspiked duplicate	n/a	n/a	n/a	2,002
			Average	2,192
			% RSD	12.2

* Contact time = ~20 minutes
** Contact time = 120 hours
n/a = not applicable
Dash denotes not applicable because average of two data points is given

The data in Table 4-5 shows good agreement between the upper and lower portions of the table in terms of amount of cesium-137 sorbed on the resin. The difference between the average cesium-137 sorbed in the upper and lower portions of the table is 4%. This indicates good overall mass balance for cesium. Note that the cesium-137 that went into the feed displacement solution (0.1 M NaOH) and the deionized water rinse solution was very small.

4.4 COLUMN TESTS

4.4.1 AN-105 Simulant Column Run - Cesium Loading

Lead column loading data for cesium-133 is shown in Figure 4-2. (See Table B- 1 in the Appendix for the data.) The onset of breakthrough was at 280 BV. At the time of run termination of 340 BV, 1.7% breakthrough had been attained, an indication of the relatively large sorption capacity of this batch (first 25 gallon batch) of SuperLig® 644 resin. Due to the low breakthrough reached at the time of termination of the run, the λ value (the number of bed volumes processed at $C/C_o = 0.5$) is unknown. However, it is certainly greater than 100 BV.

Using an estimate of the area above the breakthrough curve (Figure 4-2), the amount of cesium-133 in the feed removed by the lead column at run termination (i.e., 1.7% breakthrough) equals 11,000 μg/g dry Na-form resin. This translates to a percent removal of 99.8, which also implies the remaining 0.2% of cesium-133 was retained by the lag column.

As mentioned earlier in the experimental section, the AN-105 simulant run was a shakedown run for the subsequent radioactive AN-104 waste run. As a result, minimal analysis was conducted. For instance, the effluent from lag column was not analyzed because cesium-133 was expected to be low. Hence, the overall or total decontamination factor (DF) for the lead and lag system could not be calculated.

4.4.2 AN-105 Simulant Column Run - Cesium Elution

The lead column elution profile for AN-105 simulant column run is shown in Figure 4-3 for cesium-133 along with pH data. (See Table B- 3 in the Appendix for the data.) The graph displays a peak at approximately 12 BV. As of 20 BV, $C/C_o = 0.01$ was yet to be reached.

Generally, past work[4, 9] on cesium elution from SuperLig® 644 resin has typically reported peak at 3 - 4 BV. Nevertheless, the pH trend is consistent with the elution profile. Elution truly occurred when the pH dropped below was 8. The known cause for the shift or delay in the elution is that during the first four hours of the elution step the flow rate was inadvertently set at 0.5 BV/hr instead of 1.0 BV/hr.

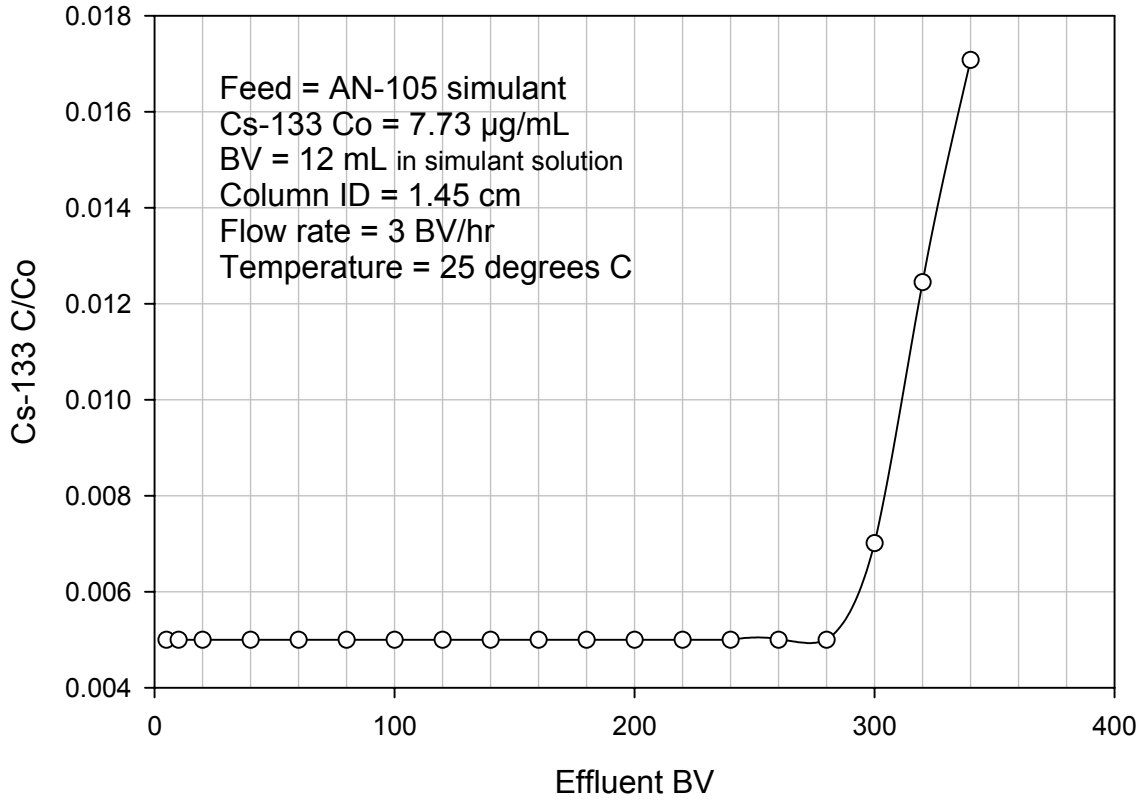

Figure 4-2. Cesium Lead Column Loading Profile for AN-105 Simulant and SuperLig® 644 Resin

The resin bed began shrinking six hours after the start of elution. Assuming this is roughly the time the nitric acid reached the top of the resin bed, and that it took another 3 - 4 hours (or BV) to attain the typical elution peak, it would have resulted in a peak at 7 - 8 BV. The remaining 4 or 5 BV not accounted for may be the result of the low diffusion or mixing rates that most likely occurred due to the low flow rate of 0.5 BV/hr at the beginning of elution. This is supported by the fact that the pH was between 11 and 8.5 during the first 8 BV. This further indicates the resin was clearly still in the Na-form (i.e., in caustic solution) up to 8 BV, and that elution did not occur during the first 8 BV.

Note also that the concentration of nitric acid used for the elution was verified to be 0.44 M. Other than the previous explanation, the only other speculation that comes to mind is some buffering action at the initial phase of the elution. Remember the top 1 cm of the resin bed was gray during the loading process step.

In view of the above, the lead column was eluted with additional 5 BV of 0.5 M HNO_3. The cesium-133 concentration at the 5th BV was 0.0195 µg/mL (i.e., C/Co = 0.0025). Note that the lag column was eluted, but no analysis was performed on the eluate. Although the lead column elution profile issue was not fully resolved in terms of the cause, a decision was made to proceed with the actual radioactive AN-104 waste column run.

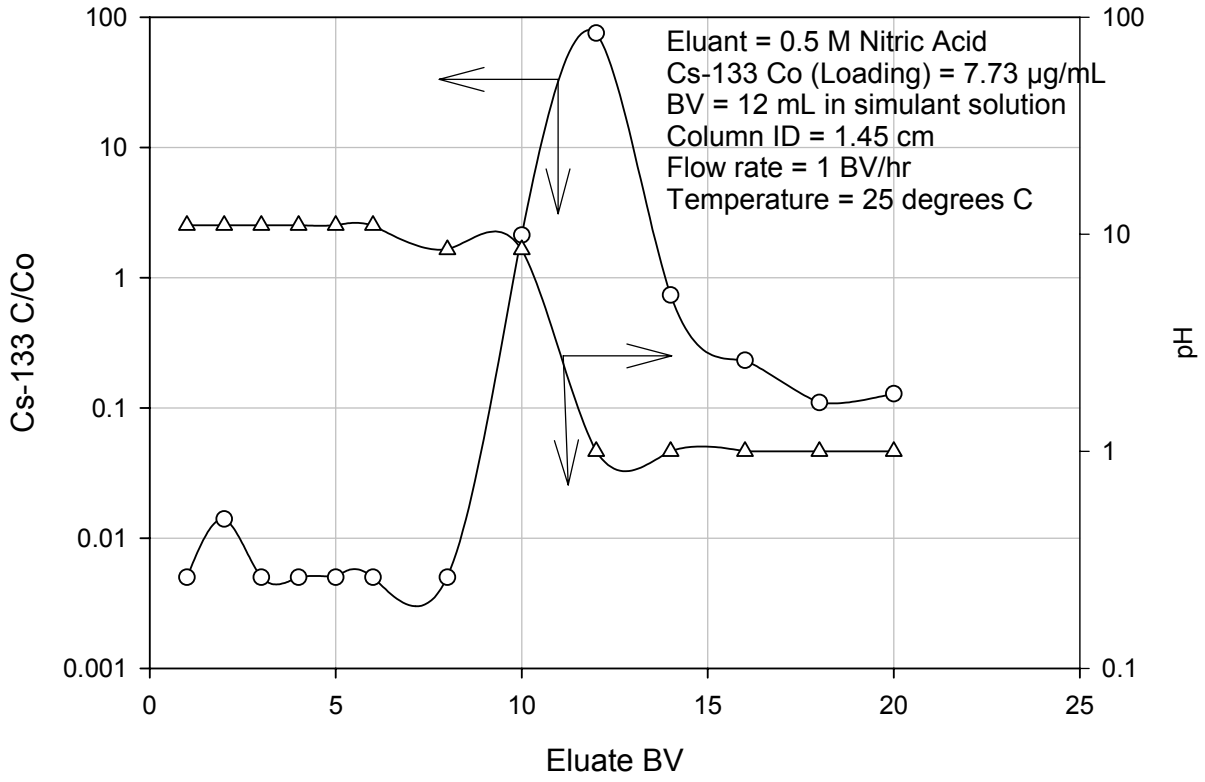

Figure 4-3. Cesium Lead Column Elution and pH Profiles for AN-105 Simulant and SuperLig® 644 Resin

4.4.3 Actual AN-104 Waste Column Run - Cesium Loading

The lead column loading breakthrough curve for cesium-137 using SuperLig® 644 resin for actual AN-104 waste is shown in Figure 4-4. (See Table C- 2 in the Appendix for the data.) The onset of breakthrough occurred at 175 BV. As of 267 BV when the run was terminated, 4.1% breakthrough had been attained.

Note that the BV at the onset of breakthrough for the AN-105 simulant run is higher (280 BV). This is because the total initial cesium concentration in the actual AN-104 waste is higher (12.1 versus 7.7 µg/mL) than that of the AN-105 simulant. Even though the λ value (the number of bed volumes processed at $C/C_o = 0.5$) is not known, it definitely exceeds 100 BV.

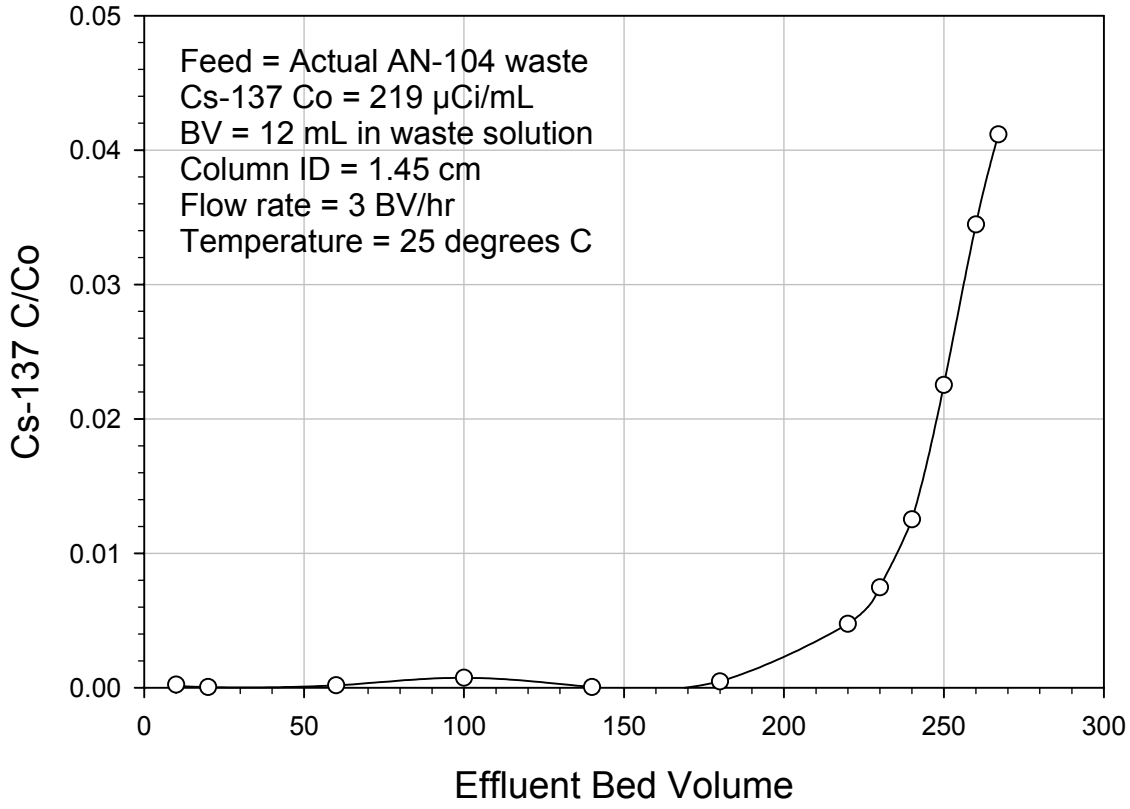

Figure 4-4. Cesium Lead Column Loading Profile for Actual AN-104 Waste and SuperLig® 644 Resin

Based on an estimate of the area above the breakthrough curve (Figure 4-4), the amount of cesium-137 in the feed removed in the lead column at run termination (i.e., 4.1% breakthrough) equals 243,000 µCi/g dry Na-form resin or 2,800 µg/g dry Na-form resin. This translates to a percent removal of 99.6, which also implies the remaining 0.4% of cesium-137 was retained by the lag column.

Cesium-137 in the actual AN-104 waste is 20.6% of the total cesium in the waste. Hence, the amount of total cesium sorbed at run termination (i.e., 4.1% breakthrough) equals 13,600 µg/g dry Na-form resin (i.e., 2,800/0.206). This value is approximately close to the corresponding value for the AN-105 simulant lead column run.

The lag column loading data for cesium-137 is shown in Table 4-6. A table is provided instead of a breakthrough curve because the C/C_o values are all close to zero. As of 267 BV when the run was terminated, no sign of breakthrough was apparent. All lag column effluent cesium-137 concentrations are below the LAW vitrification limit requirement of 0.087 µci/mL.

The overall or total decontamination factor (DF) for the lead and lag system based on loading effluent composite concentration (0.000423 μCi/mL) is 517,000. This DF value corresponds to cesium-137 removal of 100%. Virtually all the cesium-137 was removed by the lead and lag columns. The target cesium-137 removal of 98% for Envelope A waste is surpassed[10, 11].

Table 4-6. Cesium Lag Column Loading for Actual AN-104 Waste using SuperLig® 644 Resin at 25 °C

Effluent BV*	[^{137}Cs], μCi/mL**	^{137}Cs C/Co
0-20	7.49E-04	3.43E-06
20-40	3.98E-04	1.82E-06
40-80	2.90E-04	1.33E-06
80-100	3.77E-04	1.73E-06
100-140	4.48E-04	2.05E-06
140-160	3.33E-04	1.52E-06
160-180	3.71E-04	1.70E-06
180-220	4.44E-04	2.03E-06
220-240	5.41E-04	2.47E-06
240-267	3.09E-04	1.41E-06
Composite	4.23E-04	n/a
DF	5.17E+05	n/a
% Removal	1.00E+02	n/a

* Based on lead column BV count
** LAW vitrification contract limit = 8.7E-02 μCi/mL = 8.7E-05 Ci/L
Cesium-137 C_o = 219 μCi/mL
Resin BV in waste solution = 12 mL
Flow rate = 3.0 BV/hr
n/a = not applicable

4.4.4 Actual AN-104 Waste Column Run - Cesium Elution

The lead column elution profile for cesium-137 from SuperLig® 644 resin using 0.5 M HNO_3 at 25 ^oC is shown in Figure 4-5 as a semi-log plot. (See Table C- 5 in the Appendix for the data.) The plot displays a peak at about 3.5 BV. The BV value at $C/C_o = 0.01$ is 10.

Based on residual cesium-137 in the used resin at the end of the column run (Table 4-9), the percent of sorbed cesium-137 eluted is 99.99. The pH and sodium concentration for the 13th to the 23rd BV were measured (Table C- 5). The pH was 1.2 in the entire range, while the sodium concentration decreased from 4.83E-04 to 2.20E-04 M.

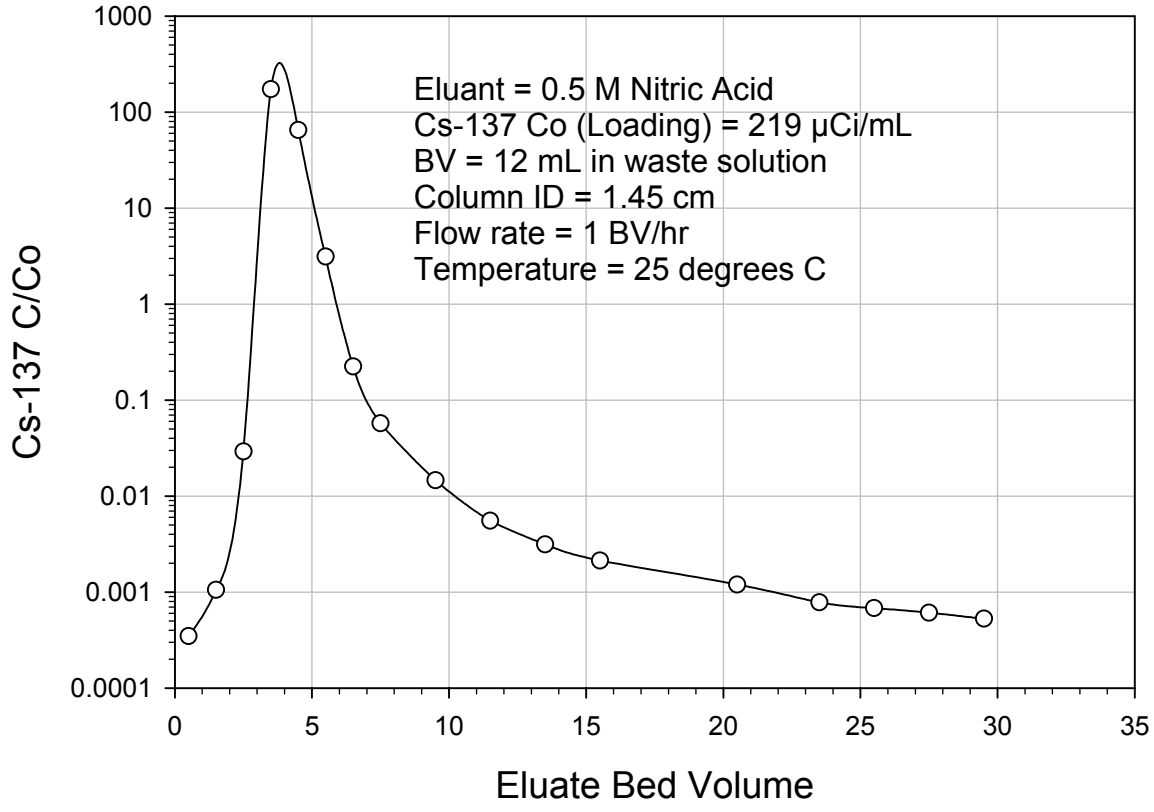

Figure 4-5. Cesium Lead Column Elution Profile for Actual AN-104 Waste and SuperLig® 644 Resin

A tabulation of lead column eluate composite concentrations is shown in Table 4-7 along with the minimum reportable quantity. The composite is a combination of all the individual fractions of samples collected minus the aliquots sent for analysis. The concentration of cesium-137 in the eluate has to be diluted before the eluate can be removed from the Intermediate Level Cell for analysis. The dilution reduces the concentration of most of the other constituents to below detection limits. It also leads to high detection limits for most of the other constituents. The concentration of most of the metals in Table 4-7 is below detection limits except sodium and cesium-137. Due to these factors, the other analyses were not performed. Also due to above, Cd and K did not meet the specified minimum reportable quantity levels.

4.4.5 Actual AN-104 Waste Column Run - Resin Bed Volume Changes

The swelling/shrinking behavior of SuperLig® 644 resin as a function of process solution is shown in Table 4-8 for the Actual AN-104 Waste Column Run. The resin swells in NaOH solution and shrinks in HNO_3 solution. The swelling/shrinking behavior of the resin in water is relatively small. The resin swells about 60 vol% from 0.5 M HNO_3 solution (H-form) to 0.25 M NaOH solution (Na-form).

4.5 USED RESIN ANALYSIS

Table 4-9 gives data on residual radionuclides in the used Na-form SuperLig® 644 resin at the end of the actual AN-104 lead column run. Note that the used resin was regenerated to Na-form with 0.25 M NaOH solution followed by deionized water rinse before being sent for analysis. The analysis was done in two ways. The first involved microwave dissolution of the resin followed by analysis of the resulting solution. The second, on the other hand, directly measured radionuclide in the resin.

The cesium-137 content in the used resin is virtually the same irrespective of the analytical approach. The data are in close agreement with those reported by Hassan et al.[4] (20 μCi/g dry resin), and Kurath and Wagner[5] (21.3 μCi/g dry resin) for used SuperLig® 644 resin contacted with actual Hanford AW-101 waste solutions.

The metals content analyses of unused Na-form resin and the used Na-form resin at the end of actual AN-104 lead column run are compared in Table 4-10. The metals content of Al, Cr, Cu, Fe, Mg, Ni, and Zr increased in the used resin. The increase may be the result of small amounts of the above metals getting sorbed from the simulant and actual waste solutions during the loading process step. For example, Cr and Fe are known to sorb on the resin during the loading step[8].

The amount of Ca, La, Na, Si, and Zn decreased in the used resin, which is probably an indication of removal by, for example desorption, dissolution, etc. The Na content in the used resin implies the resin regeneration may have been incomplete. It is hard to comment on Si because of its potential leaching from glass. It is not clear from the data of the remaining constituents whether their contents decreased or increased.

The amount of Ag in the used resin seems high. Since Ag was not measured in the unused resin, no comparison can be made.

Table 4-7. Compositions of Lead Column Eluate Composite for Actual AN-104 Waste Run Resin

Analyte	Eluate, µg/mL	Minimum Reportable Quantity[1,2], µg/mL	Analyte	Eluate, µg/mL	Minimum Reportable Quantity[1,2], µg/mL
Ag	< 8.0	Not specified	F^-	nm	1.5E+02
Al	< 82.6	7.5E+01	$(HCOO)^-$	nm	1.5E+03
B	< 863.1	Not specified	Cl^-	nm	3.0E+02
Ba	< 8.0	2.3E+00	NO_2^-	nm	3.0E+03
Ca	< 2.1	1.5E+02	NO_3^-	nm	3.0E+03
Cd	< 241.3	7.5E+00	PO_4^-	nm	2.5E+03
Ce	< 10.7	Not specified	SO_4^-	nm	2.3E+03
Co	< 132.1	Not specified	$(C_2O_4)^{2-}$	nm	1.5E+03
Cr	< 9.1	1.5E+01			
Cu	< 16.5	1.5E+00	TIC	nm	1.5E+02
Fe	< 11.7	1.5E+02	TOC	nm	1.5E+03
Gd	< 14.4	Not specified	TC	nm	Not specified
K	< 5,071.9	7.5E+01			
La	< 10.7	3.5E+01	Density, g/mL	1.022	Not specified
Li	< 45.3	Not specified			
Mg	< 33.0	3.0E+02			
Mn	< 11.7	Not specified	**Radionuclides**	**µg/mL (µCi/mL)**	**µg/mL (µCi/mL)**
Mo	< 108.7	Not specified	^{137}Cs	3,200	(1.0E-02)
Na	1,142.4	7.5E+01	^{133}Cs	nm	1.5E+00
Ni	< 40.0	3.0E+01	^{135}Cs	nm	Not specified
P	< 258.4	6.0E+02	^{138}Cs	nm	Not specified
Pb	< 131.1	3.0E+02	Total Cs	nm	Not specified
S	< 203.5	3.0E+01	^{137}Cs /Total Cs	nm	n/a
Sb	< 80.4	Not specified	^{60}Co	nm	Not specified
Si	< 19.7	Not specified	^{154}Eu	nm	2.0E-03
Sn	< 130.5	Not specified	^{90}Sr	nm	(1.5E-01)
Sr	< 53.3	Not specified	^{99}Tc	nm	(3.0E-03)
Ti	< 3.2	Not specified	Alpha	nm	(2.3E-01)
U	< 402.2	6.0E+02			
V	< 5.9	Not specified			
Zn	< 29.3	Not specified			
Zr	< 6.4	Not specified			

Each data point is an average of duplicate measurements.
Data with "<" symbols are detection limits.
n/a = not applicable
nm = not measured

Table 4-8. Bed Volume of SuperLig® 644 Resin in Various Column Process Solutions for the Actual AN-104 Waste Run

Process Step	Solution	Lead Column Bed Volume, mL
Preconditioning	0.25 M NaOH	13.9
Loading	AN-104 waste	11.6
Feed displacement	0.1 M NaOH	13.2
Rinse	Deionized water	12.9
Elution	0.5 M HNO_3	8.6
Rinse	Deionized water	8.6
Regeneration	0.25 M NaOH	13.5
Rinse	Deionized water	12.9

Table 4-9. Amount of Residual Radionuclides in Used Na-Form SuperLig® 644 Resin at the End of the Actual AN-104 Waste Lead Column Run

Radionuclide	Analytical Method	Radionuclide Content in Used Resin[a]	
		µCi/g dry resin[b]	µCi/g dry resin[c]
^{137}Cs	GEA	2.30E+01	2.30E+01
^{135}Cs	ICP-MS	< 8.19E-01	nm
^{133}Cs	ICP-MS	3.17E+00	nm
^{60}Co	GEA	5.18E-02	5.19E-02
Total α[d]	Gross Proportional Counting	< 1.10E-02	nm
Total α[d]	Rad Screen	< 5.87E-02	nm
Total β	Rad Screen	2.66E+01	nm
^{238}Pu	PuTTA	3.55E-03	nm
$^{239/240}Pu$	PuTTA	2.58E-03	nm

[a] Used resin means resin at the end of the actual AN-104 waste lead column run
[b] Microwave dissolution of resin followed by analysis of resulting solution
[c] Direct analysis of resin
nm = not measured
[d] Rad Screen is supposed to be more accurate than Gross Proportional Counting

Table 4-10. Metals Content Analysis of Unused and Used Na-form SuperLig® 644 Resins

Constituent	*Unused Resin, μg/g dry resin	*Used Resin**, μg/g dry resin
Ag	nm	110.3
Al	< 119.5	516.7
B	190.08	< 89.91
Ba	< 3.89	< 60.95
Be	nm	< 12.41
Ca	129.5	< 74.00
Cd	< 4.55	< 13.50
Ce	nm	< 99.72
Co	< 16.21	nm
Cr	< 16.22	842.0
Cu	< 16.22	47.47
Fe	118.6	167.3
Gd	nm	< 75.08
K	907.2	< 3,907
La	227.3	< 23.15
Li	< 32.47	< 138.2
Mg	< 27.27	174.0
Mn	< 2.93	< 2.57
Mo	< 32.47	< 170.2
Na	185,444	58,276
Nb	162.3	nm
Ni	24.98	90.73
P	< 220.8	< 227.4
Pb	< 222.5	< 102.6
Re	17.14	nm
S	162.3	< 439.7
Sb	nm	< 1216
Si	267.4	< 91.24
Sn	< 84.37	< 144.6
Sr	0.88	< 24.42
Ti	< 45.45	< 24.74
U	nm	< 729.3
V	< 42.20	< 19.27
Zn	< 120.11	54.07
Zr	< 15.58	304.6

* Microwave dissolution of resin followed by ICP-AES of resulting solution
** Used resin means resin at the end of the actual AN-104 waste lead column run
nm = not measured
Each data point is an average of duplicate measurements
Data with "<" symbols are detection limits

5.0 CONCLUSIONS

Conclusions of this study are as follows.

The batch contact work showed the SuperLig® 644 resin (first 25 gallon batch) has a relatively high sorption capacity with a predicted λ of 402 based on an initial total cesium concentration of 12.1 μg/mL.

The cesium column run for actual AN-104 waste resulted in percent removal and overall DF of 99.6 (lead column) and 517,000 (lag column) respectively. Also, the concentration of cesium in the column effluent was two orders of magnitude below the LAW vitrification limit of 0.087 μCi ^{137}Cs/mL.

The performance of the lead column was excellent. The BV (175) at the onset of breakthrough exceeds the 100 BV requirement[11] for envelope A waste.

Cesium elution with 0.5 M HNO_3 was efficient with a peak BV of 3.5, and a BV at $C/C_o = 0.01$ of 10. Also, 99.99 % of sorbed cesium was eluted from the resin using 30 BV of eluant.

The concentration of most of the constituents in the eluate was below detection limit because of dilution prior to analysis.

Residual cesium-137 in the resin after the column operation was 23 μCi/g dry Na-form resin. This was after eluting the resin with 30 BV of eluant at 1 BV/hr, and regenerating the resin with 6 BV of 0.25 M NaOH solution at 3 BV/hr.

No column bed fouling was observed in any of the column process steps.

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6.0 REFERENCES

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APPENDIX A.
ACTUAL AN-104 WASTE BATCH CONTACT RUN DATA

Table A- 1. Cesium Batch Contact Data Based on Total Cesium for Actual AN-104 Waste Using SuperLig® 644 Resin at 25 °C

Batch Contact Test	Initial Total Cesium Conc.	Final Total Cesium Conc.	Phase Ratio	Time	Total Cesium Sorbed	Cesium Kd	Average Cesium Kd	% RSD
	µg/mL	µg/mL	mL/g	hours	µg/g	mL/g	mL/g	% RSD
Unspiked	12.6*	0.226*	101	72	1,243	5,504	5,496	0.2
Unspiked duplicate	nm	0.227*	101	72	1,245	5,487	-	-
Cs Spike 1	100.5	3.64	101	72	9,758	2,684	2,650	1.8
Cs Spike 1 duplicate	nm	3.73	101	72	9,760	2,617	-	-
Cs Spike 2	144.4	7.83	101	72	13,735	1,754	1,723	2.5
Cs Spike 2 duplicate	nm	8.10	101	72	13,707	1,693	-	-

* Based on cesium-137:total cesium ratio of 0.206
F-factor = 0.36
Kds are based on mass of Na-form resin
Dash denotes not applicable because average of two data points is given

Table A- 2. Cesium Batch Contact Data for AN-105 Simulant and Actual AN-104 Waste Using SuperLig® 644 Resin at 25 °C

Batch Contact Test	Initial Cesium Conc.	Final Cesium Conc.	Phase Ratio	Time	Resin Mass	Solution Volume
	^{133}Cs, µg/mL	^{133}Cs, µg/mL	mL/g	hours	g	mL
Unspiked	7.65	0.192	100	120	2.8092	99.6061
Unspiked duplicate	7.54	0.214	100	120	2.8093	99.6149
	^{137}Cs, µCi/mL	^{137}Cs, µCi/mL	mL/g	hours	g	mL
Unspiked	225.5	4.05	101	72	2.8098	100.7377
Unspiked duplicate	nm	4.07	101	72	2.8093	100.8197
Unspiked	222.2	0.419	10	120	2.8094	10.2820
Unspiked duplicate	223.2	0.397	10	120	2.8096	10.3107
	^{133}Cs, µg/mL	^{133}Cs, µg/mL	mL/g	hours	g	mL
Cs Spike 1	95.4	3.39	101	72	2.8101	100.7377
Cs Spike 1 duplicate	nm	3.48	101	72	2.8090	100.8197
Cs Spike 2	139.2	7.51	101	72	2.8101	100.8197
Cs Spike 2 duplicate	nm	7.78	101	72	2.8104	100.8197

F-factor = 0.36
225.5 µCi/mL = 12.6 µg/mL total cesium
222.2 µCi/mL = 12.4 µg/mL total cesium
223.2 µCi/mL = 12.5 µg/mL total cesium
4.05 µCi/mL = 0.23 µg/mL total cesium
0.419 µCi/mL = 0.02 µg/mL total cesium
nm = not measured

APPENDIX B.
AN-105 SIMULANT COLUMN RUN DATA

Table B- 1 Lead Column Loading of AN-105 Simulant on SuperLig® 644 Resin at 25 °C

Effluent BV	[^{133}Cs], µg/mL	^{133}Cs C/Co
5	< 0.04	< 0.005
10	< 0.04	< 0.005
20	< 0.04	< 0.005
40	< 0.04	< 0.005
60	< 0.04	< 0.005
80	< 0.04	< 0.005
100	< 0.04	< 0.005
120	< 0.04	< 0.005
140	< 0.04	< 0.005
160	< 0.04	< 0.005
180	< 0.04	< 0.005
200	< 0.04	< 0.005
220	< 0.04	< 0.005
240	< 0.04	< 0.005
260	< 0.04	< 0.005
280	< 0.04	< 0.005
300	0.054	0.007
320	0.096	0.012
340	0.132	0.017

Data with "<" symbols are detection limits
Cesium-133 C_o = 7.73 µg/mL
Resin BV in simulant solution = 12 mL
Flow rate = 3 BV/hr

Table B- 2. Lead and Lag Column Post Feed Water Rinse at 25 °C for the AN-105 Simulant Run

Effluent BV	[^{133}Cs], µg/mL	^{133}Cs C/Co	[Na^+], M	[K^+], M
1	0.403	0.052	1.01E-03	6.49E-05
2	0.276	0.036	9.27E-04	< 2.56E-05
3	0.233	0.030	7.87E-04	< 2.56E-05
4	0.188	0.024	4.66E-04	< 2.56E-05

Data with "<" symbols are detection limits
Flow rate = 3 BV/hr

Table B- 3. Lead Column Elution from SuperLig® 644 Resin using 0.5 M HNO^3 at 25 °C for the AN-105 Simulant Column Run

Eluate BV	[^{133}Cs], µg/mL	^{133}Cs C/Co	pH
1	< 0.040	< 0.005	11
2	0.112	0.014	11
3	< 0.040	< 0.005	11
4	< 0.040	< 0.005	11
5	< 0.040	< 0.005	11
6	< 0.040	< 0.005	11
8	< 0.040	< 0.005	8.5
10	16.40	2.122	8.5
12	584.0	75.550	1
14	5.680	0.735	1
16	1.790	0.232	1
18	0.853	0.110	1
20	0.992	0.128	1
25*	0.0195	0.0025	nm

* 2nd elution run of additional 5 BV
Cesium-133 Co in AN-105 simulant solution = 7.73 µg/mL
Resin BV in AN-105 simulant solution = 12 mL
Flow rate = 1 BV/hr
nm = not measured
Data with "<" symbols are detection limits

APPENDIX C.
ACTUAL AN-104 WASTE COLUMN RUN DATA

Table C- 1. Lead Column SuperLig® 644 Resin Preconditioning or Regeneration with 0.25 M NaOH at 25 °C Prior to Actual AN-104 Waste Loading

Effluent Bed Volume	pH
0 - 3	2.64
3 - 6	11.9
6 - 9	12.1
9 - 12	12.2

Flow rate = 3 BV/hr

Table C- 2. Lead Column Loading of Actual AN-104 Waste on SuperLig® 644 Resin at 25 °C

Effluent Bed Volume	[^{137}Cs], µCi/mL	^{137}Cs C/Co
10	4.94E-02	2.26E-04
20	1.06E-02	4.84E-05
60	3.76E-02	1.72E-04
100	1.61E-01	7.35E-04
140	1.04E-02	4.73E-05
180	1.03E-01	4.71E-04
220	1.04E+00	4.75E-03
230	1.63E+00	7.46E-03
240	2.74E+00	1.25E-02
250	4.92E+00	2.25E-02
260	7.54E+00	3.45E-02
267	9.00E+00	4.12E-02

Cesium-137 C_o = 219 µCi/mL
Resin BV in waste solution = 12 mL
Flow rate = 3 BV/hr

Table C- 3. Lead and Lag Column Feed Displacement with 0.1 M NaOH After Actual AN-104 Waste Loading at 25 ^{o}C

Effluent BV	pH	$[Na^{+}]$, M	$[K^{+}]$, M
0 - 1	11.8	4.74	0.12
1 - 2	11.9	nm	nm
2 - 3	12.0	4.57	0.12
3 - 4	12.0	nm	nm
4 - 5	12.0	nm	nm
5 - 6	12.1	3.42	0.10

Flow rate = 3 BV/hr
nm = not measured

Table C- 4. Lead and Lag Column Post Feed Water Rinse at 25 oC for the Actual AN-104 Waste Run

Effluent BV	pH
0 - 1	12.3
1 - 2	12.2
2 - 3	12.2
3 - 4	12.0
4 - 5	11.9
5 - 6	11.9

Flow rate = 3 BV/hr

Table C- 5. Lead Column Elution From SuperLig® 644 Resin Using 0.5 M HNO^3 at 25 °C for the Actual AN-104 Waste Run

Eluate BV	[^{137}Cs], µCi/mL	^{137}Cs C/Co	pH	[Na^+], M
0 - 1	7.59E-02	3.47E-04	nm	nm
1 - 2	2.31E-01	1.06E-03	nm	nm
2 - 3	6.39E+00	2.92E-02	nm	nm
3 - 4	3.80E+04	1.74E+02	nm	nm
4 - 5	1.42E+04	6.51E+01	nm	nm
5 - 6	6.82E+02	3.12E+00	nm	nm
6 - 7	4.91E+01	2.25E-01	nm	nm
7- 8	1.25E+01	5.73E-02	nm	nm
9 - 10	3.20E+00	1.46E-02	nm	nm
11 - 12	1.21E+00	5.54E-03	nm	nm
13 - 14	6.86E-01	3.14E-03	1.17	4.83E-04
15 - 16	4.66E-01	2.13E-03	1.18	4.33E-04
18 - 23	2.63E-01	1.20E-03	1.18	2.20E-04
23 - 24	1.71E-01	7.81E-04	nm	nm
25 - 26	1.49E-01	6.80E-04	nm	nm
27 - 28	1.33E-01	6.10E-04	nm	nm
29 - 30	1.15E-01	5.27E-04	nm	nm

Cesium-137 Co in AN-104 waste solution = 219 µCi/mL
Resin BV in AN-104 waste solution = 12 mL
Flow rate = 1 BV/hr
nm = not measured

Table C- 6. Lead Column Post Elution Water Rinse at 25 °C for the Actual AN-104 Waste Run

Effluent BV	[^{137}Cs], µCi/mL	^{137}Cs C/Co	pH
0 - 1	nm	nm	nm
1 - 2	nm	nm	nm
2 - 3	nm	nm	nm
3 - 4	8.96E-02	4.10E-04	1.46
4 - 5	nm	nm	nm
5 - 6	< 2.78E-02	< 1.27E-04	2.02

Flow rate = 1 BV/hr
nm = not measured
Data with "<" symbols are detection limits

Table C- 7. Lead Column SuperLig® 644 Resin Regeneration with 0.25 M NaOH at 25 °C After Post Elution Water Rinse for the Actual AN-104 Waste Run

Effluent BV	[^{137}Cs], µCi/mL	^{137}Cs C/Co	pH
0 - 1	nm	nm	2.75
1 - 2	nm	nm	nm
2 - 3	nm	nm	2.45
3 - 4	nm	nm	nm
4 - 5	nm	nm	2.58
5 - 6	6.19E-03	2.83E-05	10.2
Composite	2.64E-02	1.21E-04	nm

Flow rate = 3 BV/hr
nm = not measured

Table C- 8. Comparison of Compositions of Original Actual AN-104 Waste with Column Loading Effluent Composite

Constituent	Original Actual AN-104 Waste, µg/mL	Loading Effluent Composite, µg/mL	Constituent	Original Actual AN-104 Waste, µg/mL	Loading Effluent Composite, µg/mL
Ag	1.26	0.171	F^-	66	35
Al	13,019	13,250	$(HCOO)^-$	nm	638
B	36.8	22.9	Cl^-	3,170	2,850
Ba	< 2.15	0.563	NO_2^-	43,300	37,350
Be	nm	0.180	NO_3^-	75,300	67,050
Ca	3.40	1.08	PO_4^-	1,490	1,265
Cd	< 0.475	0.276	SO_4^-	2,810	2,700
Ce	15.1	4.67	$(C_2O_4)^{2-}$	nm	721
Cr	142	151			
Cs	See below	See below	TIC	3,330	4,010
Cu	1.73	0.496	TOC	2,710	1,750
Fe	2.89	0.863	TC	6,040	5,760
Gd	< 2.65	0.621			
K	3,800 (0.097 M)	3,030 (0.078)	Total Base, M	2.478	2.43
La	1.27	0.664	Free OH^-, M	1.334	1.41
Li	5.51	< 0.860	Other Base excluding $(CO_3)^{2-}$, M	0.859	0.663
Mg	< 0.600	< 0.106	$(CO_3)^{2-}$, M	0.285	0.284
Mn	< 0.091	< 0.016	pH	2.478	nm
Mo	38.9	43.4	Dissolved solids, wt %	nm	25.78
Na	106,813 (4.6 M)	109,000 (4.7 M)	Density, g/mL	1.22	1.22
Ni	1.53	3.24			
P	432	492	**Radionuclides**	**µg/mL (µCi/mL)**	**µg/mL (µCi/mL)**
Pb	12.9	12.5	^{137}Cs	2.51 (218.7)	(0.000423)
S	1,211	1,435	^{133}Cs	7.60	nm
Sb	47.4	40.5	^{135}Cs	1.91	nm
Si	177	111	^{138}Cs	0.091	nm
Sn	20.5	22.1	Total Cs	12.091	nm
Sr	0.781	1.63	^{137}Cs /Total Cs	0.206	nm
Ti	< 0.872	< 0.154	^{60}Co	(0.000293)	nm
U	35.2	12.8	^{154}Eu	(0.00465)	nm
V	5.07	4.80	^{90}Sr	(0.0955)	nm
Zn	2.67	2.44	^{99}Tc	(0.0919)	nm
Zr	< 2.58	1.18	^{235}U	0.0504	0.00364
			^{238}U	3.66	1.29
			Alpha	(0.131)	(< 0.000204)
			Beta	(289)	(0.163)

nm = not measured
Data with "<" symbols are detection limits

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APPENDIX D.
AN-105 SIMULANT RECIPE

Table D- 1. AN-105 Simulant Recipe

Volume of Feed = 5,000 mL			
In a tared 5,000 mL volumetric flask add			
	Formula	**Mass Needed, grams**	**Actual Mass, grams**
Water	H_2O	1,000	1,000.00
Transition Metals and Complexing agents			
Compounds	**Formula**	**Mass Needed, grams**	**Actual Mass, grams**
Boric Acid	H_3BO_3	0.68182	0.681
Cadmium Nitrate	$Cd(NO3)_2.4H2O$	0.021015	0.0213
Calcium Nitrate	$Ca(NO3)_2.4H2O$	0.55106	0.5506
Cesium Nitrate	CsNO3	0.05604	0.0565
Lead nitrate	$Pb(NO3)_2$	0.198475	0.2018
Magnesium Nitrate	$Mg(NO3)_2.6H2O$	0.133095	0.1319
Potassium Nitrate	KNO3	44.881035	44.88
Silver Nitrate	AgNO3	0.06071	0.00607
Zinc Nitrate	$Zn(NO3)_2.6H2O$	8.1725	8.1748
Glycolic Acid	$HOCH_2COOH$, 70 wt%	3.887775	3.8914
Sodium Chloride	NaCl	34.98764	34.9922
Sodium Fluoride	NaF	0.9807	0.9822
Sodium Chromate	Na_2CrO_4	9.818675	9.8205
Sodium Perrhenate	$NaReO_4$	0.094	0.0943
Sodium Sulfate	Na_2SO_4	2.6619	2.1816
Potassium Molybdate	K_2MoO_4	0.47634	0.4768
Ammonium Acetate	CH_3COONH_4	1.197855	1.2013

Table D-1. AN-105 Simulant Recipe – page 2 of 2

In a separate container mix the following			
Compounds	**Formula**	**Mass Needed, grams**	**Actual Mass, grams**
Aluminum Trihydroxide	$Al(OH)_3$	267.98795	268.0089
Sodium Hydroxide	NaOH	459.2478	459.2738
Selenium dioxide	SeO_2	0.002335	-
Sodium meta-silicate	$Na_2SiO_3.9H2O$	4.985225	4.9845
Sodium Acetate	$NaCH_3COO.3H2O$	9.024775	9.0286
Sodium Formate	HCOONa	10.159585	10.1615
Sodium Oxalate	$Na_2C_2O_4$	2.169215	2.1715
Sodium Phosphate	$Na_3PO4.12H2O$	5.326135	5.327
Add	**Formula**	**Mass Needed, grams**	**Actual Mass, grams**
Water	H_2O	1,500	1,500.00
Mix thoroughly. Then add this solution to the volumetric flask.			
Add	**Formula**	**Mass Needed, grams**	**Actual Mass, grams**
Sodium Carbonate	Na_2CO_3	51.7	51.7018
Mix thoroughly.			
Add	**Formula**	**Mass Needed, grams**	**Actual Mass, grams**
Sodium Nitrate	$NaNO_3$	489.65	489.6506
Sodium Nitrite	$NaNO_2$	388.75	388.7563
Mix thoroughly.			
Add water to the mark and mix thoroughly.			