

**Small Column Ion Exchange Testing
of Superlig 644 for Removal of ^{137}Cs
from Hanford Tank Waste Envelope A
(Tank 241-AW-101)**

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June 2000

Prepared for BNFL, Inc.
under Contract W375-LC-98-4168

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Battelle, Pacific Northwest Division
Richland, Washington 99352

SUMMARY

The current BNFL Inc. flow sheet for the pretreatment of the Hanford High-Level tank wastes includes the use of Superlig[®] materials for the removal of ¹³⁷Cs from the aqueous fraction of the waste. The Superlig[®] materials applicable to cesium removal include the cesium selective Superlig[®] 632 and Superlig[®] 644. These materials have been developed and supplied by IBC Advanced Technologies, Inc., American Fork, UT.

The work contained in this report involves testing the Superlig[®] 644 ion exchange material in a small dual column system (15 mL each; L/D = 5.7). The sample processed was approximately 2.5 L of diluted waste ([Na⁺] = 4.6 M) from Tank 241-AW-101 (Envelope A). This waste had been previously clarified in a single tube cross-flow filtration unit. All ion exchange process steps were tested including resin bed preparation, loading, feed displacement, water rinse, elution and resin regeneration. During the initial run, the lag column did not perform as expected so that the ¹³⁷Cs concentration in the effluent composite was above the LAW treatment limits. This required a second column run with the partially decontaminated feed that was conducted at a higher flow rate.

A summary of performance measures for both runs is shown in Table S1. The Cs λ values represent a measure of the effective capacity of the SL-644 resin. The Cs λ of 143 for the lead column in run 1 is very similar to the value obtained by the Savannah River Technology Center during Phase 1A testing. The larger Cs λ value for run 2 reflects a general trend for the effective capacity of the SL-644 material to increase as the cesium concentration decreases. The low value for the lag column during the first run indicates that it did not perform as expected. This may have been due to insufficient conditioning of the bed prior to the start of the loading step or to air in the bed that caused channeling. Equilibrium data obtained with batch contacts using the AW-101 Cs IX feed indicates a range for the Cs λ of 80-97. The maximum decontamination factor (DF) for ¹³⁷Cs is based on analysis of the first samples collected from each column and the concentration in the feed for each run. While the DF's are lower for the second run, this is attributed to the lower ¹³⁷Cs concentration in the feed and the increased flowrate. The overall composite DF for run 2 was quite good since both columns functioned well. The overall DF for both runs was 3000, which provided an effluent with a ¹³⁷Cs concentration of 5.89E-02 Ci/m³ (C/C₀ = 3.31E-04). The ¹³⁷Cs concentration in the effluent composite was 7.3% of the contract limit for ¹³⁷Cs and also below the basis of design limit.

Table S1. Summary of Performance Measures

	Flow rate (BV/hr)	Cs λ		Composite DF	Maximum ¹³⁷ Cs DF	
		Lead column	Lag column		Lead column	Lag column
Run 1	6.0	143	25	8	11,600	47,100
Run 2	8.4	185	NA	355	99	1,130

The elution of the lead column after run 1 proceeded very well with the majority of the ¹³⁷Cs contained in the fourth bed volume of eluant (0.5 M nitric acid). The peak ¹³⁷Cs concentration in this sample was 97 times the ¹³⁷Cs concentration in the feed.

TERMS AND ABBREVIATIONS

BNFL	BNFL, Inc; subsidiary of British Nuclear Fuels, Ltd.
BV	Bed Volume
C/C ₀	analyte concentration in column effluent divided by analyte concentration in feed
DF	decontamination factor
DI	deionized water
DL	detection limit
E	elution
ER	elution rinse
F	feed
FD	feed displacement
GEA	gamma energy analysis
HLW	high-level waste
HLEF	High Level Radiation Facility
IC	ion chromatography
ICP AES	inductively coupled plasma/atomic emission spectrometry
ICP MS	inductively coupled plasma/mass spectrometry
LAW	low-activity waste
L/D	bed length (height) to diameter ratio
MDL	method detection limit
MRQ	minimum reportable quantity
NMRQ	no minimum reportable quantity
R	regeneration
SAL	Shielded Analytical Laboratory
SRTC	Savannah River Technology Center
TIC	total inorganic carbon
TOC	total organic carbon
TRU	transuranic

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1.0 INTRODUCTION

The current BNFL Inc. flow sheet for the pretreatment of the Hanford High-Level tank wastes includes the use of Superlig[®] materials in a dual column system for the removal of ¹³⁷Cs from the aqueous fraction of the waste. The Superlig[®] materials applicable to cesium removal include the cesium selective Superlig[®] 632 and Superlig[®] 644. These materials have been developed and supplied by IBC Advanced Technologies, Inc., American Fork, UT.

The work contained in this report involves the small column testing of the Superlig[®] 644 ion exchange material¹. The sample processed was approximately 2.5 L of diluted waste (@ 4.6 M Na) from Tank 241-AW-101 (the 241 prefix, which is common to all Hanford tanks, will not be used hereafter). This waste had been previously clarified in a single tube cross-flow filtration unit (Brooks et al.). The ion exchange process steps tested include resin bed preparation, loading, feed displacement, water rinse, elution and resin regeneration.

The objectives of this work were to:

- Demonstrate the ¹³⁷Cs decontamination of Envelope A (Tank AW-101) and provide a cesium decontaminated sample for downstream process testing (i.e. ⁹⁹Tc removal, corrosion testing, Low Activity Waste (LAW) melter feed testing and LAW vitrification).
- Demonstrate the effectiveness of all SL-644 ion exchange process steps including loading, feed displacement, DI water washing, elution and resin regeneration.
- Obtain process performance data for SL-644 at conditions different than those previously tested.
- Investigate exchanger/waste chemistry.
- Investigate the potential for exchanger fouling.

¹ The results presented in this report are based on work conducted under test plan TP-29953-3 Rev 0 Ion Exchange Testing for BNFL Inc, December 1998, and test instructions TI-29953-016, Test Instructions for Cesium Removal Column Testing from Envelope A, TI-29953-042 Test Instructions for Cesium Removal Column Testing from Envelope A: Run 2, and BNFL-TP-29953-048, Preparing a Composite Solution of the acid eluant Samples from AW-101 Cs Ion Exchange Column 1 for Analysis. Some data are recorded in Laboratory Record Book BNW 13687. Conditions for conducting these tests were given in the "Ion Exchange Test Specification Rev 1," TSP-W375-99-00013.

2.0 EXPERIMENTAL

2.1 Ion Exchange Column System

A schematic of the ion exchange column system is shown in Figure 2.1. The system consists of two small columns containing the ion exchange material, a small metering pump, four valves, a pressure gauge and a pressure relief valve. Valve 1 is a five-way valve that allows switching between the waste feed and various process solutions. Valves 2,3 and 4 are three-way valves that can be turned to a flow position, a sample position or a no flow position. Valve 2 is placed at the outlet of the pump and is used to eliminate air from the system, purge the initial volume of the system or isolate the columns from the pump. Valves 3 and 4 are primarily used for obtaining samples and may also be used to isolate the columns from the rest of the system. The columns are Kontes Chromaflex chromatography columns made of glass with adjustable plungers on the bottom and the top. The inside diameter of the columns is 1.5 cm which corresponds to a volume of 1.77 mL/cm of length. The connecting tubing is 1/4-in OD (1/8-in ID) polyethylene. The columns are connected in series with the first column referred to as the lead column and the second column referred to as the lag column. The pump is a FMI piston pump with the flow rate controlled from outside of the hot cell with a FMI stroke rate controller. The pump was calibrated with the stroke rate controller and can provide pumping rates from 0-120 mL/hr. The volume actually pumped is determined using the mass of the fluid and the fluid density. The pressure relief valve is set at 40 psi, which is below the maximum operating pressure of 45 psi for the columns. The pressure indicated on the pressure gauge remained below 5 psi during the run. The total holdup volume of the Cs IX system was estimated to be 60 mL (4 BV) with the holdup volume to valve 2 being 30 mL (2 BV).

2.2 SL-644 Resin and Bed Preparation

Some properties of the as-received, hydrogen form of the SL-644 resin (batch # = 644BZ) are shown in Table 2.1. The Battelle values at room temperature and at 85°C are duplicated from Kurath, et al., 1999, while all of the SRTC data is reproduced from (Hassan, et al., 1999). The F factor is the ratio of the dry mass of exchanger to the initial mass of the exchanger. This was obtained by drying approximately 0.5 g in an oven at the temperature of interest until there was no significant change in mass. The as-received bulk density was determined by weighing approximately 10 mL of exchanger in a 50 mL graduated cylinder. The dry bulk densities were obtained by multiplying the as-received bulk density by the appropriate f factor. A particle density of 1.611 g/mL was reported by Hassan, et al., 1999.

Table 2.1. Physical Properties of the As-Received Hydrogen Form of SL-644

	Battelle	SRTC
As-received bulk density (room temperature)	0.86 g/mL	0.88
Dry as received bulk density (85°C)	0.78 g/mL	-
Dry as received bulk density (95°C)	0.69 g/mL	0.793 g/mL
F factor @ 85°C (% water)	0.907 (9.3%)	-
F factor @ 95°C (% water)	0.80 (20%)	0.9 (10%)

The particle size distribution for the as-received SL-644 resin subsample (Kurath, et al., 1999) is compared to the subsample used in column experiments by SRTC (Hassan, et al., 1999) in Table 2.2. It is apparent that the average particle size of the Battelle subsample is smaller than that of the SRTC subsample. The data are not precise enough to allow an accurate estimate of the average particle diameter but the average apparently lies between 210 and 425 microns with a rough estimate of 330 microns.

Table 2.2. Particle Size Distribution of the As-Received, Hydrogen Form of SL-644

Sieve size	Size (μm)	Battelle subsample (wt %)	Size (μm)	SRTC subsample (wt%)
	>600	not measured	>600	14
40	>425	9.9	600-425	44
70	425-210	88	425-210	40
100	210-149	2.1	210-62	0
200	149-74	0		
	<74	0		

The SL-644 resin and bed preparation was performed using a procedure similar to that recommended by Hassan et al. 1999, with the exception that the solution volumes and flow rates were larger. Prior to packing the resin bed, two 7.9 g batches of the as-received SL-644 resin were placed in separate beakers. The resin was soaked in about 70 mL of 1 M NaOH with light agitation for 2.5 hours. The NaOH was decanted and the SL-644 was washed 3 times with 100 mL of DI water per wash. The resin was then slurried into the columns in DI water. The swollen resin volume was about 22 mL and was greater than required. Approximately 32% of the slurried resin volume was removed leaving about 5.4 g of as-received resin per column. The F factor (ratio of the mass of damp resin to dried resin) was determined to be 0.80 at 95°C so the amount of SL-644 in each column was about 4.3 g on a dry basis. Prior to installation of the system into the hot cell, both of the resin beds were cycled through the acid form with the solution amounts shown in Table 2.3. The solution volumes were significantly in excess of those planned for full-scale operation in order to ensure the system was completely flushed and that the resin beds were fully conditioned. The total system hold-up volume was 60 mL.

Table 2.3. Shakedown Testing and Bed Conditioning Parameters

	Solution	Volume	Contact Time
Elution	0.5 M HNO ₃	> 6 BV (>90 mL)	> 1 hr
Eluant rinse	DI water	> 6 BV (>90 mL)	> 1 hr
Regeneration	0.25 M NaOH	> 6 BV (>90 mL)	> 1 hr
DI water wash	DI water	> 6 BV (>90 mL)	> 1 hr

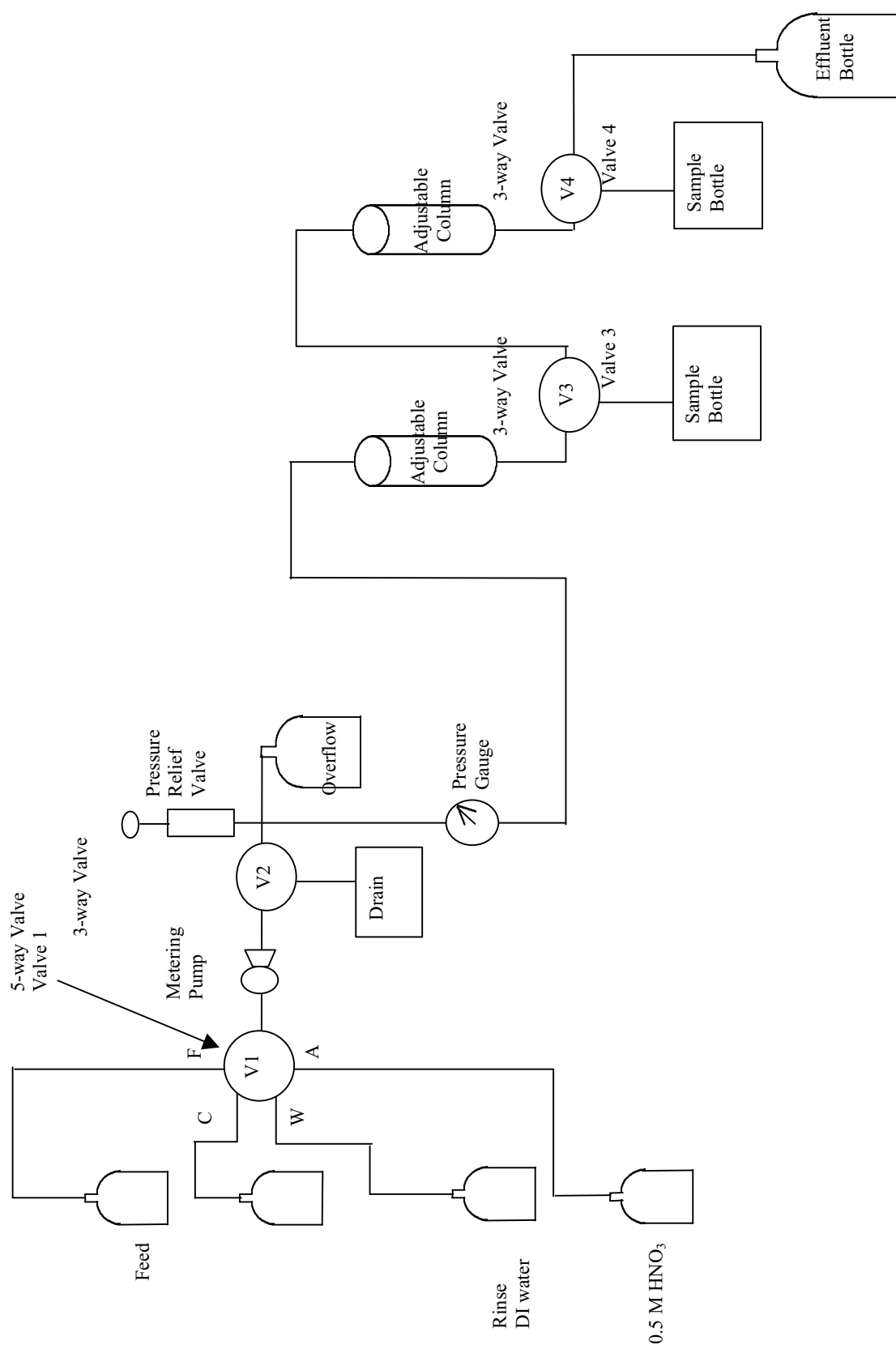


Figure 2.1. Cesium Ion Exchange Column System

A number of the resin bed properties determined during the testing discussed in this report are shown in Table 2.4. The bed volume definition is based on the volume of the SL-644 resin in each column during the loading step. The corresponding bed height and bed length (height) to diameter ratio (L/D) is also given. The expanded particle size diameter was estimated on the basis of the bed volume expansion relative to the as-received bed volume and the initial rough estimate of the average particle size of the resin (330 μm). The average number of resin particles per column diameter is greater than the 20-30 particle diameters commonly assumed necessary to prevent channeling.

Table 2.4. Resin Bed Properties

	Lead and Lag Columns
Bed volume, mL	15
Bed height - cm	8.5
L/D	5.7
Expanded particle size diameter – μm	440
Resin particles per column diameter	34

2.3 Feed Preparation

A sample of the waste from Tank AW-101 (Envelope A) was received in the High Level Radiation Facility (HLRF) during the 4th quarter of 1998. The homogenization, dilution, and subsampling of this sample is described in Urie (1999). The diluted AW-101 sample was then processed in a single tube cross-flow filter to remove entrained solids using a 0.1 micron sintered metal Mott filter (Brooks et al., 1999). The diluted feed added to the filtration unit had a sodium concentration of 6.5 M as determined by ICP-AES (Urie, 1999). Due to dilution from residual water in the filtration unit, the permeate was determined to have a sodium concentration of 6.05 M (Brooks et al. 1999). The clarified AW-101 sample was then transferred in two containers from the HLRF to the shielded analytical laboratory (SAL) hot cells. The total volume transferred was about 2.1 L. The contents of the two transfer containers were combined and homogenized and the sample was diluted with DI water to a target concentration of 4.6 M sodium in preparation for the cesium ion exchange testing. The density of the cesium ion exchange feed was determined with a 25 mL volumetric flask and a 4 place analytical balance.

2.4 Experimental Procedure and Conditions

The experimental conditions for each process step for Run 1 are shown in Table 2.5. In general the flow rates were maintained as close as possible to the recommended values² but in some steps the total volume of the process solutions was increased in an attempt to ensure adequate flushing of the system. In particular, the volume of bed conditioning solutions was increased because the lag column did not appear to be shrinking or swelling as much as the lead column. As will be shown in Section 3.2, the lag column did not perform as expected, possibly because of inadequate bed conditioning. The total lead column eluant volume was also increased in order to achieve the cutoff criteria of $C/C_0 = 0.01$ for elution. The lag column was eluted at higher flow rate since the objective was to remove the cesium from the column to prepare for a second run. Samples were not taken during elution of the lag column. The bed conditioning loading, feed displacement and DI water rinse steps were conducted by passing these solutions through both resin beds connected in series. The elution, elution rinse and the regeneration steps were conducted on each column separately.

² Ion Exchange Testing for BNFL Inc, BNFL-TP-22953-003, December 1998, transmitted to BNFL via letter 29953-023, EV Morrey to ME Johnson.

Table 2.5. Experimental Conditions for Run 1

Process Step	Solution	Total Volume, Bed Volumes (mL)	Flow Rate in Bed Volumes Per Hour (mL/hr)	Time hr
Bed conditioning	0.5 M nitric	6 (90)	4.4 (66)	1.4
Bed conditioning	DI water	8 (120)	8 (120)	1
Bed conditioning	0.25 M NaOH	17.9 (270)	7.8 (117)	2.3
Loading	AW-101 Feed	164 (2455)	6 (90)	27.6
Feed displacement	0.1 M NaOH	3 (45)	3 (45)	1
DI water rinse	DI water	6.7 (100)	3.1 (47)	2.1
Elution of lead column				
Elution (lead col)	0.5 M HNO ₃	13 (195)	1.2 (18)	10.8
Eluant rinse (lead)	DI water	7.1 (106)	3 (45)	2.4
Regeneration (lead)	0.25 M NaOH	6.2 (93)	5.9 (89)	1.1
Elution of lag column				
DI water rinse (lag col)	DI water	4 (60)	8 (120)	0.5
Elution (lag col)	0.5 M HNO ₃	12 (180)	3 (45)	4
Eluant rinse (lag col)	DI water	4 (60)	8 (120)	0.5
Regeneration (lag col)	0.25 M NaOH	6 (90)	8 (120)	0.75

Note: The column volume is based on the volume in the columns at the start of the loading step. The bed volume in both columns was 15 mL with a height of 8.5-cm.

Since insufficient cesium decontamination was obtained during Run 1, a second run utilizing the partially decontaminated AW-101 sample from Run 1 was conducted. The experimental conditions for each process step for Run 2 are shown in Table 2.6. In general the flow rates were higher than those in Run 1 and samples were taken only during the loading phase.

The adjustable plungers at the top of each column were used to minimize the volume of solution above each of the resin beds. The bed volumes changed dramatically from a minimum volume in the acid form during elution (9-10 mL) to a maximum volume of about 21 mL in the sodium form in contact with water. The plungers were moved downward at the end of each process step in which the resin beds shrank and were moved upward periodically as the bed expanded. The plungers did not compress or constrain the resin beds. The height of liquid above the beds was kept to less than 1 cm (about 1.8 mL).

Table 2.6. Experimental Conditions for Run 2

Process Step	Solution	Total Volume, Bed Volumes (mL)	Flow Rate in Bed Volumes Per Hour (mL/hr)	Time hr
Bed conditioning	0.25 M NaOH	7.7 (116)	4.7 (71)	1.6
Loading	AW-101 Feed	152 (2280)	8.4 (126)	18.2
Feed displacement	0.1 M NaOH	6.3 (95)	5.8 (87)	1.1
DI water rinse	DI water	5.4 (80)	5.4 (80)	1
Elution	0.5 M HNO ₃	21 (310)	3-4 (45-60)	5.5
Eluant rinse	DI water	7 (105)	6.4 (96)	1.1
Regeneration	0.25 M NaOH	12.3 (185)	6.5 (98)	1.9

Note: The column volume is based on the volume in the columns at the start of the loading step. The bed volume in both columns was 15 mL with a height of 8.5-cm.

The sampling and analysis protocol is shown in Tables 2.7 and 2.8 for Run 1 and Run 2, respectively. The ¹³⁷Cs content was determined in all of the samples using a portable GEA instrument. This allowed near real time analysis of the samples. The response time was limited by the rate at which samples could be removed from the hot cell and was often on the order of hours. Due to the dose rate from ¹³⁷Cs, many of the samples required dilution prior to removal from the hot cell. Samples were diluted in either 0.25 M NaOH or 0.5 M HNO₃. The extent of dilution was determined by mass difference on a 4 place analytical balance. The samples that required dilution included the feed sample, the effluent samples from the last half of the loading phase of Run 1 and most of the eluant samples. The ¹³⁷Cs results from the portable GEA instrument were confirmed by analyzing selected samples with the GEA instrument in the analytical laboratory. The sodium and other metal concentrations were determined with ICP-AES. The OH⁻ concentration was determined by titration with hydrochloric acid.

During the loading phase, the treated effluent was collected in one of two effluent bottles except for the small (2 mL) samples that were taken. A composite sample from each of the two effluent bottles was taken for analysis by GEA. The rest of the samples were collected in approximately 1 BV aliquots. Once the GEA results were confirmed for the eluate, all of the eluate samples were composited and a sample of the composite was submitted for GEA, ICP-AES, TOC and ICP-MS for ⁹⁹Tc.

Table 2.7. Sampling Interval and Analyses for Run 1

Process Step	Lead Column BV	Lag Column BV	Approximate Sample Size (mL)	Analyses
Bed conditioning	-	-	-	-
Bed conditioning	-	-	-	-
Bed conditioning	-	-	-	-
Loading	Every 10 BV	Every 20 BV	2	GEA
Feed displacement	-	Every 1 BV	15	ICP, GEA, OH-
DI water rinse	-	Every 1 BV	15	ICP, GEA, OH-
Elution	Every 1 BV	-	15	GEA
Eluant rinse	Every 1 BV	-	15	GEA
Regeneration	1 composite	-	90	ICP, GEA, OH-
Composite Samples				
Effluent – 1			2	GEA
Effluent - 2			2	GEA
Eluate	1 composite	-	7	ICP-AES, GEA, TOC, ICP-MS (Tc)

Table 2.8. Sampling Interval for Run 2

Process Step	Lead Column	Lag Column	Approximate Sample Size (mL)	Analyses
Bed conditioning	-	-	-	-
Loading	Every 20 BV	Every 20 BV	2	GEA
Feed displacement	-	-	-	-
DI water rinse	-	-	-	-
Elution	-	-	-	-
Eluant rinse	-	-	-	-
Regeneration	-	-	-	-

2.5 Batch Contacts

A number of batch contacts between the SL-644 and subsamples of the AW-101 feed were conducted to obtain equilibrium data. Portions of the subsamples were spiked with 0.1 M CsNO₃ stock solutions to obtain additional concentrations of cesium. The initial cesium concentrations in the AW-101 subsamples are given in Table 2.9. The purpose of these spikes was to ensure that the equilibrium composition of the solutions bracketed the cesium feed concentration.

Table 2.9. Initial Cs Concentrations in the AW-101 Solutions Used for the Batch K_d Tests

Solution	Initial Cs Conc. [M]	Initial Na/Cs (a)	Initial K/Cs (a)
Un-spiked	6.14E-05	74,700	6,350
Cs Spike 1	3.67E-04	12,500	1,060
Cs Spike 2	6.17E-04	7,440	632

(a) Na⁺ and K⁺ are the primary cations that compete with Cs⁺ for ion exchange with SL-644. Concentrations of Na⁺ and K⁺ in the AW-101 solution were 4.59M and 0.39M respectively.

The batch K_d tests were performed at a phase ratio of approximately 100 mL/g (liquid volume to exchanger mass). Typically, 0.05 g of exchanger was contacted with 5 mL of solution. The exchanger mass was determined to an accuracy of 0.0001 g. The waste volume was transferred by pipette, and the actual volume was determined by mass difference with an accuracy of 0.0001 g and the solution density. Agitation was provided by an orbital shaker set at 200 rpm for approximately 96 h. The temperature was not controlled, but was generally constant at 24°C during the 4 days of contact.

All K_d measurements were made in duplicate and blank samples (i.e., without the ion exchange resin) were used to determine the initial concentration of the species of interest. All initial and final solutions were analyzed by GEA to determine the ¹³⁷Cs concentration. The initial sodium and potassium concentrations were determined with ICP-AES.

The batch distribution coefficient, K_d (with units of mL/g), was determined using the following relationship:

$$K_d = \frac{(C_0 - C_1)}{C_1} * \frac{V}{M * F} \quad (1)$$

where C₀ and C₁ are the initial and final ¹³⁷Cs concentrations, respectively, V is the volume of the liquid sample (mL), M is the mass of the (as received) ion exchanger (g), and F is the mass of the dried resin divided by the mass of the as-received resin.

3.0 RESULTS AND DISCUSSION

3.1 Feed Composition

The composition of the feed to the cesium ion exchange system is shown in Table 3.1. The concentrations of Na, K, Al, Cr, and P were determined by analysis of a feed sample by ICP-AES. The total cesium concentration is estimated using the GEA results for ^{137}Cs and the isotopic ratios determined with thermal ionization mass spectroscopy and reported in Urie (1999). For the AW-101 sample the ^{137}Cs :total cesium was 0.2465. Some of the anion concentrations are based on an analysis of the Tc IX feed. Some of the component concentrations (generally the anions) are estimated on the basis of the known sample dilution from component concentrations given in the characterization report (Urie, 1999). The feed had a light yellow color that has been attributed to the presence of chromate.

Table 3.1. Composition of Envelope A (AW-101) Cs IX Column Feed ^(c)

Cations, M	
Na^+	4.59
K^+	0.39
Cs^+	6.14E-5
Na/Cs mole ratio	74,700
K/Cs mole ratio	6,350
Anions, M	
AlO_2^- ^(b)	0.411
Cl^-	0.066 ^(a)
CO_3^{2-}	0.13 ^(a)
CrO_4^{-2} ^(b)	8.4E-04
NO_2^-	1.01
NO_3^-	1.50
OH^-	2.17 ^(a)
PO_4^{-3} ^(b)	0.007
SO_4^{-2}	0.0072
Oxalate	<8.6E-3 ^(a)
Radionuclides	
^{134}Cs ($\mu\text{Ci/mL}$)	3.4E-2
^{137}Cs ($\mu\text{Ci/mL}$)	177.5
Solution Density, g/mL	1.228
<p>a) These values have been estimated from the diluted feed characterization data reported in PNWD-2463, BNFL-RPT-003, Rev 0. Unless otherwise noted the results are based on direct analysis of the feed.</p> <p>b) Al, Cr, and P determined by ICP-AES. Anionic form is assumed on the basis of waste chemistry.</p> <p>c) The raw analytical results may be found in the appendix.</p>	

3.2 Loading (^{137}Cs Breakthrough Curves), Feed Displacement and Water Wash

After the resin beds were conditioned, the loading phase was initiated with the diluted AW-101 sample. During the initiation of the loading step, the initial 4 bed volumes^(a) of effluent were not collected. This prevented the estimated holdup of 4 bed volumes of 0.25 M NaOH in the system from being mixed with the AW-101 effluent. Small samples (about 2 mL) were collected from the lead column every 10 BV of feed and from the lag column every 20 BV of feed. Initial samples were collected from both columns soon after loading was initiated in order to obtain a determination of the maximum decontamination factors. The loading phase generally went well except for some leakage of air into the lag column. This was observed by the dropping of the air-liquid interface above the top of the bed. At approximately 45 BV the loading was stopped for slightly over an hour to remove air from the column system. The air did not appear to get into the resin beds and there was no discernable discontinuity in the breakthrough curve.

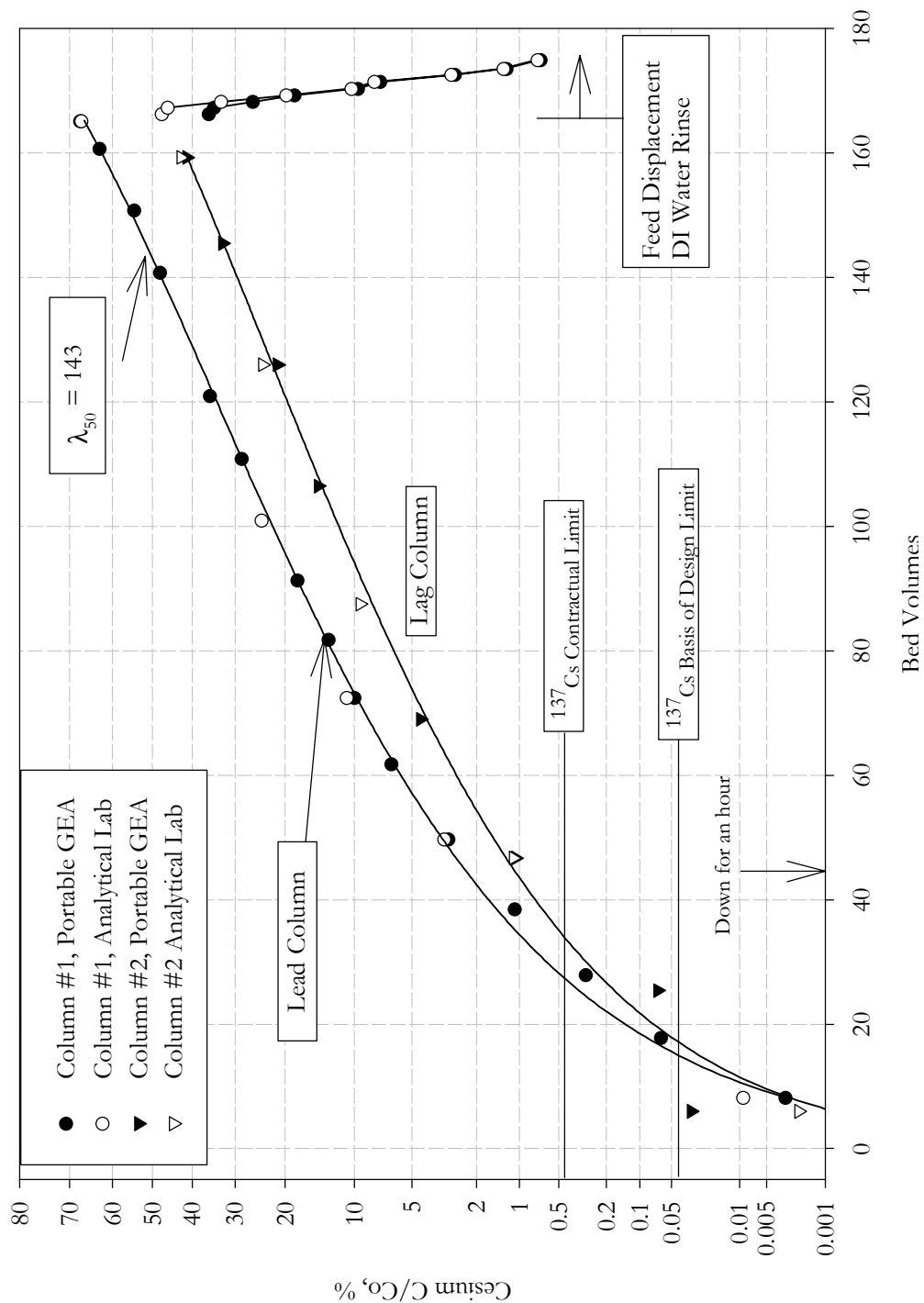
The cesium effluent concentrations from the columns are shown in Figure 3.1 as C/C_o vs the bed volumes of feed processed through each column. The C_o value for ^{137}Cs was determined to be 177.5 $\mu\text{Ci/mL}$. The C/C_o is plotted on a probability scale (i.e. gaussian distribution) since this tends to provide a straight line breakthrough curve. The C/C_o values for the feed displacement (3 BV of 0.1 M NaOH) and DI water rinse (6 BV) are also shown in Figure 3.1. These exhibit a steadily decreasing concentration of ^{137}Cs . Most of the C/C_o values were determined with a portable GEA instrument and selected samples were independently analyzed with a laboratory GEA instrument. The two analyses are generally in good agreement (within 10%). Raw analytical results and calculations may be found in the appendix.

Two ^{137}Cs -removal limits are also shown in Figure 3.1. The higher C/C_o value of 0.45% corresponds to the contractual limit of 3 Ci/m^3 for ^{137}Cs in the low-activity waste (LAW) glass, and the lower C/C_o value of 4.5E-02% corresponds to the basis of design target of 0.3 Ci/m^3 for ^{137}Cs in the LAW glass, which is 10 times less than the contractual limit. The C/C_o values corresponding to these limits are determined using the sodium concentration of 4.59 M in the AW-101 sample, the ^{137}Cs feed concentration of 177.5 $\mu\text{Ci/mL}$, a 20 wt% total Na_2O loading in the glass, and a glass product density of 2.66 g/mL .

Volume corrections have been made in the analysis of the data so that the indicated data points correspond to the bed volumes that have actually passed through each column at the time of sampling. These volumes are different from the amount of feed pumped from the feed container because of the holdup volume. The bed volumes actually pumped from the feed vessel can be estimated by adding 2 bed volumes for the lead column and 4 bed volumes for the lag column.

The $\text{Cs } \lambda$ value is 143 for the lead column and an estimated (by extrapolation) 25 for the lag column. The $\text{Cs } \lambda$ value is the point at which the C/C_o value is 50% (0.5) and is a direct indicator of the effective capacity of the resin. The $\text{Cs } \lambda$ value of 143 for the lead column is consistent with the estimated $\text{Cs } \lambda$ of 145-150 obtained during Phase IA testing (Hassan and McCabe, 1997). The very low value for the lag column indicates that this resin bed was not functioning properly.

^(a) Many solution volumes given as bed volumes are based on the 15.0-mL BV for both columns.



Conditions: Temperature = 26°C, Feed Rate = 6 BV/hr, Bed Volume = 15.0 mL, SL-644 Batch Number = 644BZ,
 ^{137}Cs C_0 = 177.5 uCi/mL, Tank AW-101 Na Concentration = 4.6 M.

Figure 3.1. ^{137}Cs Breakthrough Curve (Run 1), Feed Displacement and Water Washing

The cause of the relatively poor performance of the lag column could have been due to channeling due to air in the resin bed or due to incomplete bed conditioning. Air is probably not the cause of the poor bed performance because the initial C/C_0 values for the lag column indicate the bed was not performing well prior to the leakage of air into the column system. Furthermore, air was not observed in the lag column resin bed during subsequent process steps. The cause may be incomplete bed conditioning even though the recommended or greater volumes of conditioning solutions were used. As discussed in section 3.4, the second resin bed did not change volume as much as the lead column during the shakedown testing and the resin bed preconditioning prior to introduction of the feed. This could have been due to partial consumption of the bed conditioning solutions by the resin in the lead column. The SL-644 resin has been shown to be sensitive to the bed conditioning prior to initiating the loading (McCabe et al. 1997).

The maximum decontamination factors measured were 11,600 for the lead column and 47,100 for the lag column. These values are based on ^{137}Cs concentrations of $1.54\text{E-}2 \mu\text{Ci/mL}$ for the lead column and $3.8\text{E-}3 \mu\text{Ci/mL}$ for the lag column. The overall DF was only 8.5 and is low due to the poor performance of the lag column.

The concentrations of sodium, potassium, Al and hydroxide in the feed displacement and DI water rinse solutions from run 1 are shown in Figure 3.2. The concentrations of the sodium, potassium, and Al are indicated on the left hand axis while the hydroxide concentration is shown on the right hand axis. Both Y axes are logarithmic scales in order to clearly show the roughly 100 fold decrease in concentrations. The samples were taken from the effluent line after the lag column, after the solutions had passed sequentially through both columns. Analytical results and calculations may be found in the appendix.

Due to the holdup volume in the system there was a delay between the introduction of the feed displacement and DI water wash solutions and the collection of these samples from the effluent line. In switching from the feed to the feed displacement step, valve 2 (Figure 2.1) was switched to the drain position and the initial part of the system was flushed. The valve was then switched to the flow position and sampling was initiated from the effluent line after the lag column. The holdup in the system between valve 2 and the effluent line was estimated to be about 40 mL so it is likely that the first 2 samples and much of the third sample consisted largely of AW-101 feed. This is supported by the component concentrations that are similar to the feed concentrations in the first two samples and by the visual observation of the sample color. The first two samples had a light yellow color that looked like the AW-101 feed and the third sample had a slight pink tinge to it. The source of the pink color is probably the SL-644 resin. In switching to the DI water rinse step, valve 1 was turned to the water supply container and the initial part of the system was not flushed. The total holdup in the system is estimated at 60 mL (4 BV) so the first four samples in the DI water rinse step, probably contained decreasing amounts of feed and caustic. The component concentrations indicate that washing was nearing completion at the fifth and sixth samples. The first four samples collected during the water rinse step had a distinct pink tinge to them while the last two were nearly clear. The required volume of feed displacement and DI water rinse solutions could be significantly reduced with a smaller holdup volume in the system and may not reflect the performance of a large-scale system.

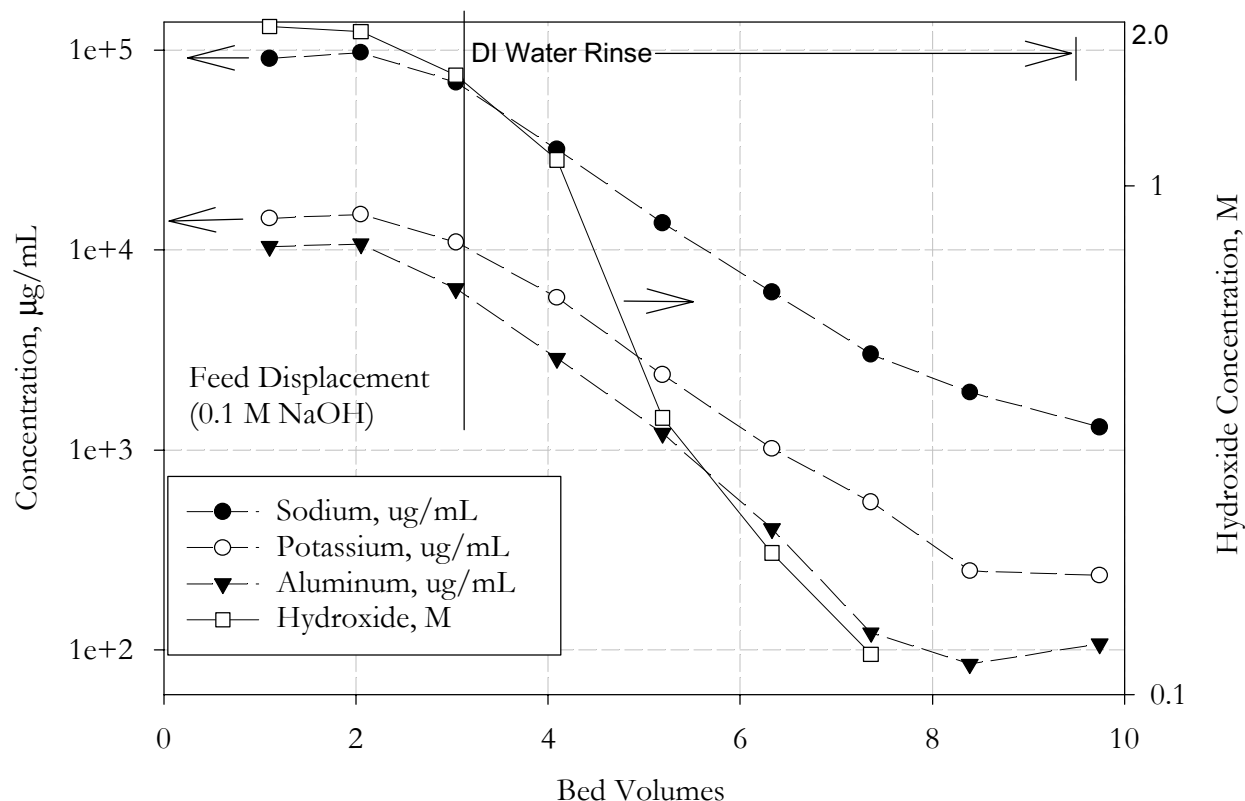


Figure 3.2. Component Concentrations in Feed Displacement and DI Water Rinse Solutions

Since the lag column did not perform as expected, the overall decontamination factor was only about 8 and the level of ^{137}Cs in the effluent. Consequently a second column run was conducted with the partially treated AW-101 sample. This breakthrough curve is shown in Figure 3.3. A reduced sample set was collected only for the loading step. Two ^{137}Cs -removal limits are also shown in Figure 3.3. The higher C/C_0 value of 3.9% corresponds to the contractual limit for ^{137}Cs in the low-activity waste (LAW) glass, and the lower C/C_0 value of 0.39% corresponds to the basis of design target for ^{137}Cs in the LAW glass, which is 10 times less than the contractual limit. The C/C_0 values corresponding to these limits are determined using the sodium concentration of 4.59 M in the AW-101 sample, the ^{137}Cs feed concentration of 20.9 $\mu\text{Ci/mL}$, a 20 wt% total Na_2O loading in the glass, and a glass product density of 2.66 g/mL.

The $\text{Cs } \lambda$ value for the lead column in run 2 is estimated by extrapolation, to be 185. Insufficient breakthrough of ^{137}Cs prevents the determination of a $\text{Cs } \lambda$ for the lag column. The uniformly low level of ^{137}Cs in the effluent from the lag column indicates that the performance of the resin bed was much improved over the first run. The relatively good performance may be due to the additional cycle of the resin bed through the acid form during the elution of the lag column. The maximum decontamination factor measured was 99 for the lead column and at least 1130 for the lag column. These values are based on the ^{137}Cs concentrations determined by the analytical laboratory in the first sample from each column. While these DF's appear to be lower than those for run 1, it should be noted that roughly 88% of the ^{137}Cs was removed from the waste during the first run. A comparison of the ^{137}Cs concentrations and decontamination factors for both runs is shown in Table 3.2.

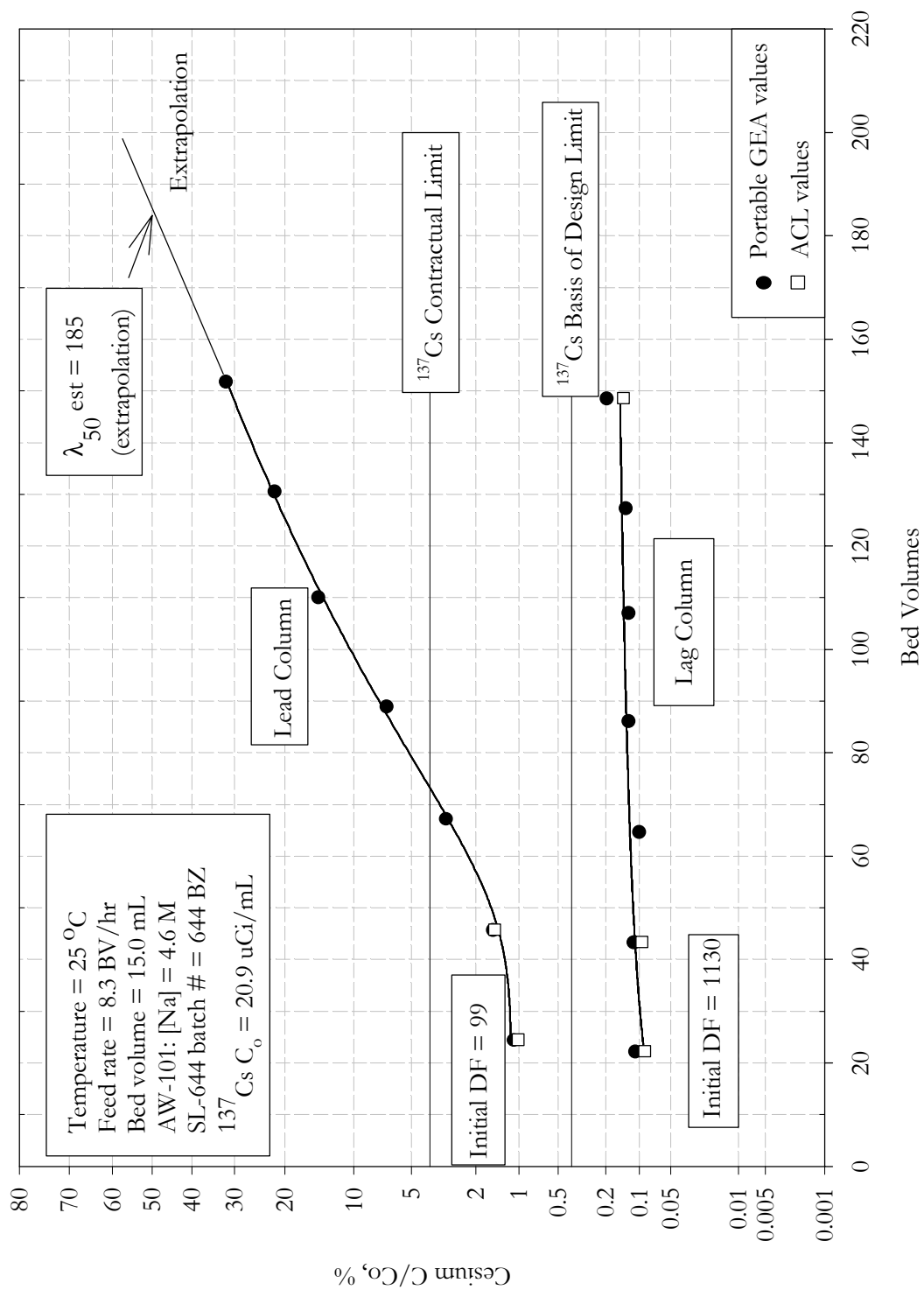


Figure 3.3. ^{137}Cs Breakthrough Curve (Run 2)

Table 3. 2. Decontamination Factors for ^{137}Cs

	Processed Volume ^(a) , BV (mL)	^{137}Cs Concentration $\mu\text{Ci/mL}$	C/C_0 , %	DF
Run 1				
First sample from Lead Column	8.2 (123)	1.54E-02	8.6E-03	11,600
First sample from lag column	6 (90)	3.8E-03	2.1E-03	47,100
Effluent bottle-1	127 (1905)	10.9	6.2	16.3
Effluent bottle-2	37 (550)	56.1	31.6	
Composite effluent	164 (2455)	20.9	11.8	8.5
Run 2				
First sample from lead column	25 (375)	0.21	1.0	99
First sample from lag column	22 (330)	1.85E-02	0.089	1130
Composite effluent	152 (2280)	5.89E-02	0.28	355
Overall (both runs)	-	5.89E-02	3.3E-02	3000

(a) Processed volume is the volume collected in the effluent bottles adjusted for sampling and column system holdup.

3.3 Elution, Eluant Rinse and Regeneration

At the completion of the DI water wash, elution of the lead column was initiated by pumping 0.5 M nitric acid into the lead column at 1.2 BV/hr. Samples of the eluate and the eluant rinse were collected in approximately 1 BV increments while the regeneration solution was collected as a single composite. The ^{137}Cs content of these samples was determined with the portable GEA instrument and confirmed with analysis in the laboratory instrument. Due to holdup in the system, the first couple of bed volumes probably contained a substantial amount of the DI water rinse that preceded the elution.

The elution generally went well except for two instances when the top portion of the bed started to float due to air bubbles in the resin bed. The source of this air is thought to be in-leakage around the upper column plunger and not due to gas generation in the bed. The air was removed from the bed by tapping the column until the bubble migrated to the top of the resin and into the headspace above the bed and the elution was resumed. Eluate sample #3 was observed to contain solids. Although the solids were not analyzed they were light in color and very fluffy and are suspected of being precipitated NaAlO_2 . The source of this is likely residual waste that was not washed out of the column system.

The C/C_0 ^(a) values for ^{137}Cs are shown in Figure 3.4 for the elution, the eluant rinse and the regeneration steps. The Y axis is a logarithmic scale to clearly show the large range of C/C_0 values. The majority of the ^{137}Cs came off in just one sample (#4) which had a C/C_0 value of 97. The elution was continued until a C/C_0 of 0.01 was reached. The C/C_0 values for the eluant rinse are below the elution

^(a) The C_0 refers to the ^{137}Cs concentration in the AW-101 sample fed to the lead column. For elution, the C/C_0 value is an indication of the extent to which ^{137}Cs is concentrated relative to the feed. It is an indirect measure of the extent to which the resin is actually eluted.

cutoff of $C/C_0 = 0.01$. The ^{137}Cs concentration in the eluant rinse ranges from 0.12 - 5 uCi/mL. The last DI water rinse sample shows an unexpected spike in C/C_0 . The results of an analysis of the regeneration composite sample are shown in Table 3.3. For the ICP-AES results, the component determined is shown along with the assumed form in the regeneration solution.

Table 3.3. Composition of Regeneration Solution

	Concentration, $\mu\text{g/mL}$	BNFL MRQ, $\mu\text{g/mL}$	Concentration, M
Al	29	-	1.1E-03
B	23	-	2.2E-03
Ba	[0.1]	-	8.0E-07
Cr	[0.5]	-	9.8E-06
Fe	[0.8]	-	1.5E-05
Mn	[0.02]	-	4.2E-07
Mo	[0.37]	-	3.9E-06
Na^+	1800	75	7.8E-02
P	[0.65]	-	2.1E-05
Si	45.7	-	1.6E-03
Ti	[0.07]	-	1.6E-03
Zr	0.31	-	3.4E-06
OH-	1,100	17	0.065
^{137}Cs	6.9E-2 uCi/mL	9	-
Total Cs	-	-	2.4E-08
Density, g/mL	-	-	1.004

Notes: MRQ is minimum reportable quantity. The overall error is estimated to be within $\pm 15\%$. Values in brackets are within 10 times the detection limit, and errors are likely to exceed $\pm 15\%$.

Samples of the eluate composites from runs 1 and 2 were submitted to the analytical laboratory for analysis with ICP-AES, GEA, total alpha, TOC and ICP-MS to determine the ^{99}Tc content. The results are shown in Tables 3.4, 3.5 and 3.6. Sodium was the dominant component detected with ICP-AES, although a number of other metals were also detected. Many of these same metals were also found in the eluate from the AN-107 testing (Kurath et al., 2000) and include Ca, Cr, Cu, Fe, Na Ni, Pb, U and Zn. Many of these same components were also detected during the analysis of the spent resin (Kurath and Wagner 2000) and include Ca, Cr, Cu, Fe, K, Na, Ni, Pb and Zn. A relatively high concentration of Al was found in the lead column eluate (Table 3.3) and this is attributed to the solids observed in sample # 3. As expected, the cesium isotopes are the dominant radionuclides. The only anion detected was nitrate, which is not surprising since the eluant was 0.5 M nitric acid. A small amount of total organic carbon was detected, but it is not known if this is from residual waste in the column system or from organic materials leaching from the resin.

Most of the BNFL-specified minimum reportable quantity (MRQ) levels were met with some exceptions. The large amount of ^{137}Cs prevented the detection limits for ^{241}Am , ^{154}Eu , and ^{155}Eu from meeting the MRQ levels. Relatively high ^{137}Cs activity increases the gamma background level in the detectors due to Compton scattering, thereby making it difficult to detect lower concentrations of other gamma emitters. The large amount of nitrate prevented the detection limit for Cl and F (Table 3.3 only) from meeting the MRQ levels. The large concentration of nitrate requires large sample dilutions and increases the method detection limit (MDL) for the other components. In any case, the anion concentrations other than nitrate are expected to be small. This is somewhat confirmed by the fact that no P was detected with the ICP-AES analysis. The total inorganic carbon (TIC) analysis was not completed because carbonate is known to evolve as CO_2 in acidic solutions.

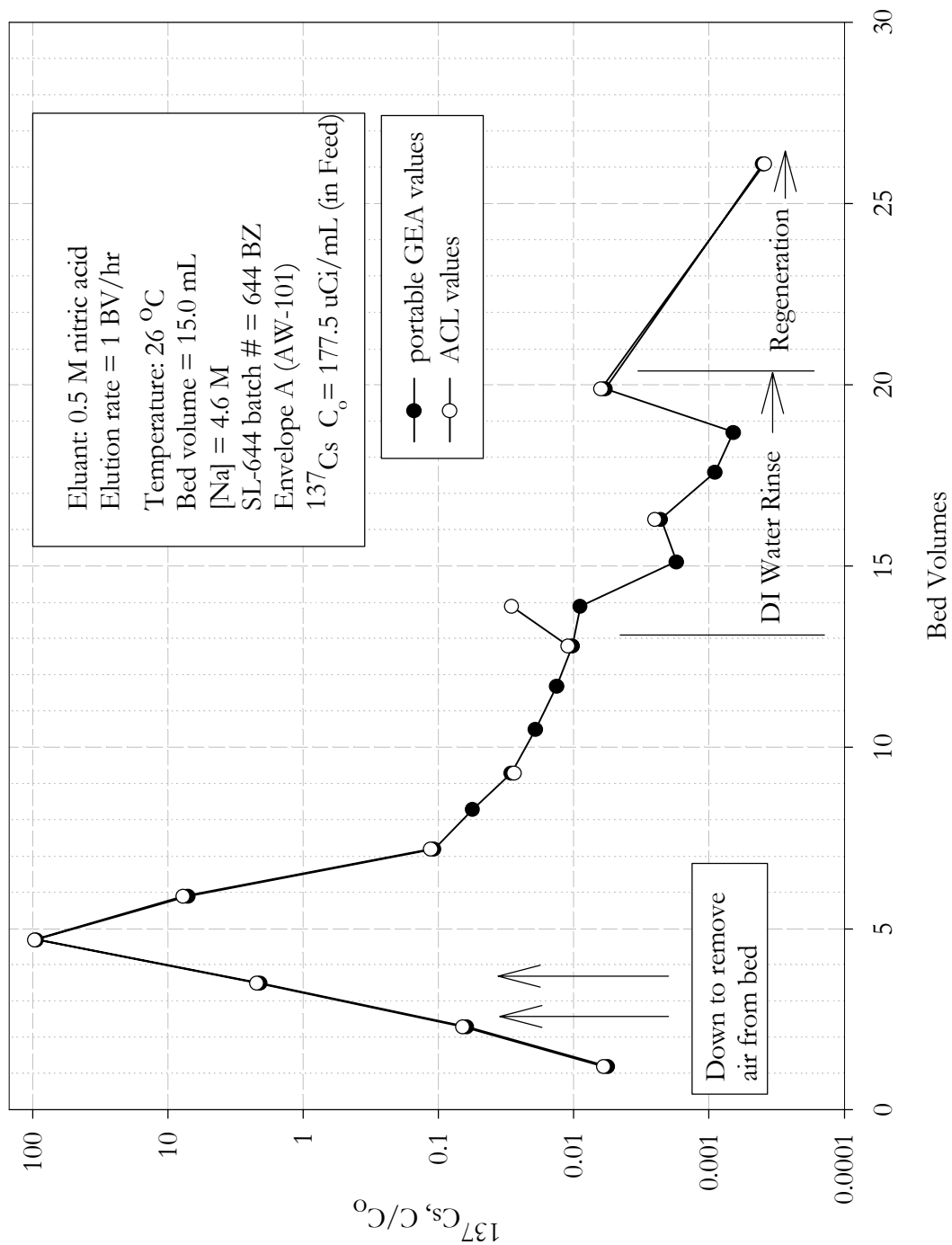


Figure 3.4. Elution, Eluant Rinse and Regeneration of Lead Column

Table 3.4. Analysis of the Lead Column Eluate Composite from Run 1 and Minimum Reportable Quantities

ICP-AES Components		BNFL MRQ	Anions		BNFL MRQ
	µg/mL	µg/mL		µg/mL	µg/mL
Al	141	7.50E+01	TOC	[119]	1.50E+03
Ba	[0.42]	7.80E+01	TIC	NA	1.5E+02
Ca	[2.1]	1.50E+02	Br	<500	NMRQ
Cd	[0.31]	7.50E+00	Cl	<500	3.0E+00
Co	< 0.27	3.00E+01	F	<500	1.5E+02
Cr	3.48	1.50E+01	NO2	<1000	NMRQ
Cu	50.6	1.70E+01	NO3	33,000	3.0E+03
Fe	12.3	1.50E+02	PO4	[8.9]	2.5E+03
K	382	7.50E+01	SO4	<1000	2.3E+03
La	< 0.27	3.50E+01	oxalate	<1000	NMRQ
Mg	< 1.07	1.50E+02			
Mn	0.67	1.50E+02	Radionuclides		MRQ
Mo	< 0.32	9.00E+01		µCi/mL	µCi/mL
Na	2230	7.50E+01	Cs-134	3.36E-01	NMRQ
Ni	5.89	3.00E+01	Cs-137	1.61E+03	9.00E+00
Pb	15.6	3.00E+02	Sr-90	<5E-2	1.50E-01
Si	51.4	1.70E+02	Tc-99	9.05E-04 (5.3E-2 ug/mL)	1.50E-03
Sn	< 10.7	1.50E+03	Am-241	<1E+0	7.20E-04
Ti	< 0.05	1.70E+01	Eu-154	<6E-2	2.00E-03
U	[48]	6.00E+02	Eu-155	<1E+0	9.00E-02
Zn	12	1.65E+01	Total alpha	<4E-2	2.30E-01
B	72.6	NMRQ	Total volume = 195 mL		
P	[2.9]	NMRQ	Total mass = 198 g		
			Density = 1.015 g/mL		

Notes: MRQ is minimum reportable quantity. NMRQ is no minimum reportable quantity. NA = not analyzed. < indicates detection limit; component not detected. Overall error is estimated to be within +/-15%. Values in brackets are within 10-times the detection limit and errors are likely to exceed +/-15%.

Table 3.5. Analysis of the Lag Column Eluate Composite from Run 1 and Minimum Reportable Quantities

ICP-AES Components		BNFL MRQ	Anions		BNFL MRQ
	µg/mL	µg/mL		µg/mL	µg/mL
Al	[1.3]	7.50E+01	TOC	<18	1.50E+03
Ba	[0.23]	7.80E+01	TIC	NA	1.5E+02
Ca	[3.3]	1.50E+02	Br	<100	NMRQ
Cd	[0.34]	7.50E+00	Cl	<100	3.0E+00
Co	< 0.52	3.00E+01	F	<100	1.5E+02
Cr	6.54	1.50E+01	NO2	<200	NMRQ
Cu	12.7	1.70E+01	NO3	31,500	3.0E+03
Fe	12.8	1.50E+02	PO4	<3	2.5E+03
K	[190]	7.50E+01	SO4	<200	2.3E+03
La	< 0.52	3.50E+01	oxalate	<200	NMRQ
Mg	< 1.1	1.50E+02			
Mn	< 0.52	1.50E+02	Radionuclides		MRQ
Mo	< 0.52	9.00E+01		µCi/mL	µCi/mL
Na	698	7.50E+01	Cs-134	4.05E-02	NMRQ
Ni	[2.8]	3.00E+01	Cs-137	2.42E+02	9.00E+00
Pb	12.8	3.00E+02	Sr-90	2.44E-01	1.50E-01
Si	[6.5]	1.70E+02	Tc-99	4.66E-04 (2.74E-02 ug/mL)	1.50E-03
Sn	< 15.5	1.50E+03	Am-241	<2E-01	7.20E-04
Ti	< 0.26	1.70E+01	Eu-154	<7E-03	2.00E-03
U	[48]	6.00E+02	Eu-155	<2E-01	9.00E-02
Zn	6.2	1.65E+01	Total alpha	<2E-5	2.30E-01
B	7.8	NMRQ	Total volume = 182 mL		
P	< 1.0	NMRQ	Total mass = 185 g		
			Density = 1.015 g/mL		

Notes: MRQ is minimum reportable quantity. NMRQ is no minimum reportable quantity. NA = not analyzed. < indicates detection limit; component not detected. Overall error is estimated to be within +/-15%. Values in brackets are within 10-times the detection limit and errors are likely to exceed +/-15%.

Table 3.6. Analysis of the Eluate Composite for Both Columns, Run 2 and Minimum Reportable Quantities

ICP-AES Components		BNFL MRQ	Anions		BNFL MRQ
	µg/mL	µg/mL		µg/mL	µg/mL
Al	[6.1]	7.50E+01	TOC	< 18	1.50E+03
Ba	< 0.1	7.80E+01	TIC	NA	1.5E+02
Ca	[2.9]	1.50E+02	Br	< 100	NMRQ
Cd	[0.23]	7.50E+00	Cl	< 100	3.0E+00
Co	< 0.52	3.00E+01	F	1500	1.5E+02
Cr	3.25	1.50E+01	NO ₂	< 200	NMRQ
Cu	7.13	1.70E+01	NO ₃	26,500	3.0E+03
Fe	8.1	1.50E+02	PO ₄	< 3	2.5E+03
K	[210]	7.50E+01	SO ₄	< 200	2.3E+03
La	< 0.52	3.50E+01	oxalate	< 200	NMRQ
Mg	< 1.04	1.50E+02			
Mn	< 0.52	1.50E+02	Radionuclides		MRQ
Mo	< 0.52	9.00E+01		µCi/mL	µCi/mL
Na	1150	7.50E+01	Cs-134	2.43E-02	NMRQ
Ni	5.69	3.00E+01	Cs-137	1.47E+02	9.00E+00
Pb	[9.9]	3.00E+02	Sr-90	8.56E-02	1.50E-01
Si	[6.3]	1.70E+02	Tc-99	2.59E-04 (1.52E-02 ug/mL)	1.50E-03
Sn	< 15.5	1.50E+03	Am-241	<9E-02	7.20E-04
Ti	< 0.26	1.70E+01	Eu-154	<6E-3	2.00E-03
U	< 20.6	6.00E+02	Eu-155	<9E-02	9.00E-02
Zn	< 0.52	1.65E+01	Total alpha	1.64E-05	2.30E-01
B	7.42	NMRQ	Total volume = 305 mL		
P	< 1.03	NMRQ	Total mass = 310 g		
			Density = 1.015 g/mL		

Notes: MRQ is minimum reportable quantity. NMRQ is no minimum reportable quantity. NA = not analyzed. < indicates detection limit; component not detected. Overall error is estimated to be within +/-15%. Values in brackets are within 10-times the detection limit and errors are likely to exceed +/-15%.

3.4 Mass Balance for ¹³⁷Cs

A mass balance for ¹³⁷Cs was completed for runs 1 and 2 in order to compare the ¹³⁷Cs recovered in various process streams to the ¹³⁷Cs present in the feed sample (Table 3.7 and 3.8). As expected, the majority of the ¹³⁷Cs was found in the eluate streams. Most of the ¹³⁷Cs present in the feed sample was accounted for in the samples and process streams, indicating that the integrity of the experiment was fairly good.

Table 3.7. Mass Balance for ^{137}Cs , Run 1

	^{137}Cs , μCi	% of ^{137}Cs in Feed Sample
Feed sample	435,900	100
Effluent-1	20,200	4.63
Effluent-2	29,100	6.67
Load samples	3,100	0.71
Feed displacement	3,500	0.80
DI water rinse	2,500	0.57
Column #1 eluate	313,800	71.98
Column #1 DI water rinse	120	0.03
Column #1 regeneration	6	0.00
Column #2 eluate	44,000	10.10
Total ^{137}Cs recovery	416,300	95.5

Table 3.8. Mass Balance for ^{137}Cs , Run 2

	^{137}Cs , μCi	% of ^{137}Cs in Feed Sample
Feed sample	47,700	100
Effluent	132	0.28
Load samples	47	0.10
Eluate-both columns	45,900	96.26
Total ^{137}Cs recovery	46,100	96.6

3.5 SL-644 Resin Volume Changes

The SL-644 resin is known to change in volume as a function of the solution pH and ionic strength (Hassan et al., 1999). The variation in bed volume as a function of the process steps for both columns is shown in Figures 3.5 and 3.6 as a ratio of bed volume to the baseline value of 15 mL. In this case the baseline value was chosen as the volume of the beds shortly after the loading step was initiated. This is the same volume as the bed volume in 0.25 M NaOH when the column system was loaded into the hot cell. The bed volume ratios can be converted to an as-received resin bed volume basis by multiplying the values given in Figures 3.5 and 3.6 by 2.4. This value is the ratio of the 15 mL bed volume used in the figures to the as-received resin volume of 6.2 mL.

Together, the two figures show the bed volume changes of each bed as they are cycled 4 times through the acid and sodium form. The first three cycles are shown in Figure 3.4. The first cycle was performed outside of the hot cell during shakedown testing. A second cycle was performed in order to condition the resin bed just prior to initiating run 1. The third cycle was run 1 with the AW-101 waste sample and the fourth run was the second run with the AW-101 sample. Each process step is denoted with a letter defined as follows: W (DI water), E (elution with 0.5 M nitric acid), ER (elution rinse with DI water), R (regeneration with 0.25 M NaOH), F (feed), and FD (feed displacement with 0.1 M NaOH).

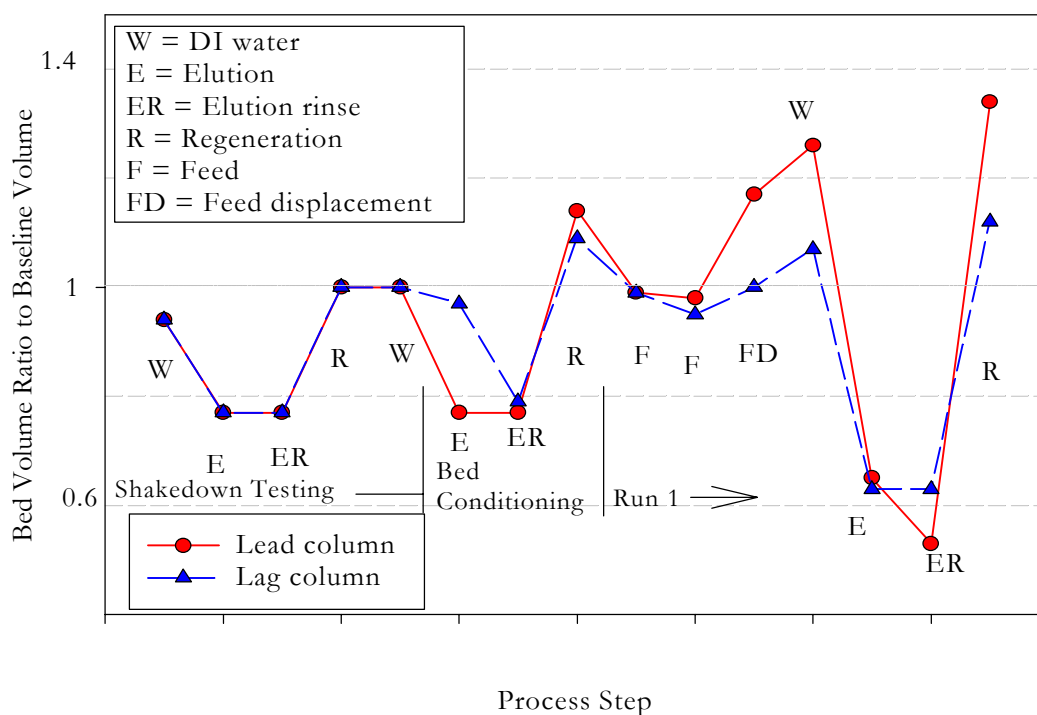


Figure 3.5. Comparison of Bed Volumes of the Lead and Lag Columns for the First Run (SL-644 Batch # 644BZ; Baseline Bed Volume = 15 mL)

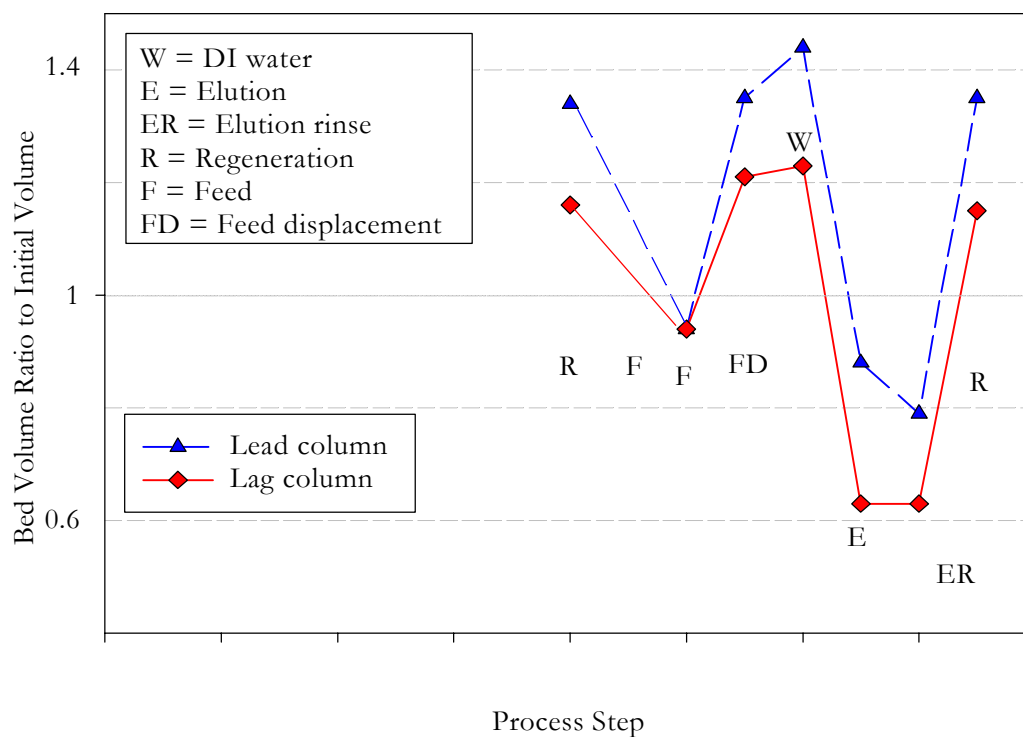


Figure 3.6. Comparison of Bed Volumes of the lead and Lag Columns for the Second Run (SL-644 Batch # 644BZ; Baseline Bed Volume = 15 mL)

The following observations are qualitatively similar to the resin volume changes reported in Hassan et al., 1999.

- Both columns reached minimum volumes in the hydrogen form (after elution) and maximum volumes in the sodium form after contact with dilute caustic and water.
- The amplitude of the swelling and shrinking increased for both resin beds as the resin was successively cycled through the hydrogen and sodium forms,

A close comparison of the volume changes in the two beds indicates the following:

- By the end of the 4th cycle, the resin bed in the lead column appears to be about 10% larger than the resin bed in the lag column.
- Both columns had nearly the same volume during the loading step when in contact with the waste sample.
- During the bed conditioning steps prior to the initiation of run 1, the volume change of the lag column did not occur as quickly as the lead column and the lag column may not have been as fully conditioned as the lead column. This could have been due to partial consumption of the bed conditioning chemicals in the lead column. Since adequate conditioning of the resin beds has been found to be important to the SL-644 performance this could explain the relatively poor loading performance of the lag column. In future testing, the bed conditioning solutions will be pumped through the beds until the volume changes of both columns are complete and the columns may be conditioned separately instead of together in series.

3.6 Batch Contact Results

The distribution coefficients (Kds) are shown in Figure 3.7 for the SL-644 resin in contact with the AW-101 column feed. The Kd values were calculated using Equation 1 and are based on the ¹³⁴Cs and ¹³⁷Cs concentrations as measured by GEA. The Na/Cs ratio is calculated from the individual sodium and cesium concentrations. The sodium concentrations are based on an analysis of the initial feed as prepared for the column run and is assumed to be constant for the batch contacts. Since the quantity of H⁺ added with the resins is small relative to the moles of Na⁺ and OH⁻ (phase ratio of 100 mL of solution: gram of exchanger), this is a reasonable assumption. In these experiments, the waste solutions were estimated to have 10.9 meq of OH⁻ and 23 meq of Na⁺, while the resin had 0.005 meq of H⁺. The total cesium was based on the ¹³⁷Cs concentrations, and the ratio of ¹³⁷Cs:total cesium was determined for the unspiked and spiked solutions. There appears to be considerable scatter in the data since the results are expected to lie on a reasonably smooth curve.

The K_d at the AW-101 feed conditions can be estimated to range from 280-340 mL/g from the point at which the K_d plot crosses the Na/Cs mole ratio (74,700) for the AW-101 sample. The column distribution ratio can be determined from the K_d and the appropriate bed density using the following relationship

$$C_s \lambda = K_d * \rho_b \quad (2)$$

where $C_s \lambda$ is the column distribution ratio, and ρ_b is the dry bed density.

In this case, the dry-bed density is 0.287 g/mL, which is determined from the dry (@ 95°C) mass of exchanger (4.3 g) divided by the expanded BV in the columns of 15 mL. The $C_s \lambda$ is then estimated to range from 80-97. This value should correspond fairly closely to the $C_s \lambda$ of 143 determined from the breakthrough curve for the lead column (see Figure 3.1). The reason for the considerable difference is not known.

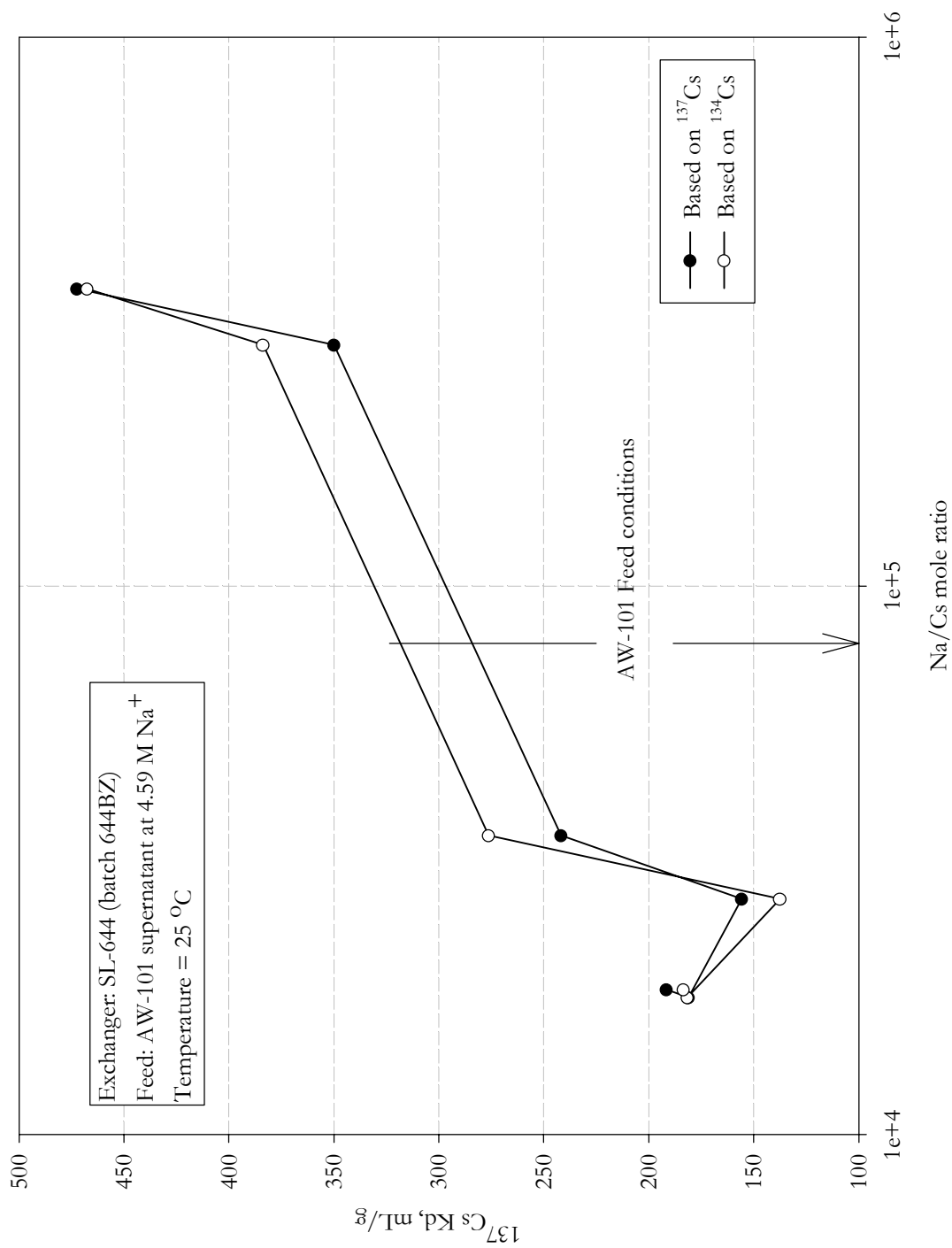


Figure 3.7. ¹³⁷Cs Distribution Coefficients (Kd) for AW-101 Feed

4.0 CONCLUSIONS AND RECOMENDATIONS

- Small-column testing with SL-644 indicates that sufficient decontamination of ^{137}Cs can be obtained with waste from Tank 241-AW-101 (Envelope A) to allow the LAW glass product to meet the basis of design limit for ^{137}Cs removal, which is a factor of 10 less than the contractual limit. An overall decontamination factor of 3000 was obtained providing a cesium-decontaminated effluent with a ^{137}Cs concentration of $5.89\text{E-}02\text{ Ci/m}^3$. This is 7.3% of the contract limit.
- While two separate runs were required to achieve the necessary decontamination, this is not expected to be normally required. During the first run the lag column did not function as expected and an unexpectedly large amount of cesium passed through the system. During the second run both columns functioned well and good decontamination factors were obtained.
- The poor performance of the lag column is thought to have been caused by inadequate bed conditioning prior to the introduction of the waste into the columns. This could have caused channeling or slow uptake of cesium. Channeling could also have resulted from air in the bed due to air leakage into the system. Although air did get into the system it was never observed in the bed in the lag column.
- Batch contacts were conducted to obtain equilibrium data in the form of batch distribution coefficients (Kds). These equilibrium data predict a range for the Cs λ of 80-97.
- The feed displacement (0.1 M NaOH) volume of 3 BV followed by 6 BV of DI water rinse appeared to leave some residual waste in the column system since a small amount of solids were observed in the third eluate sample. An increase in the volume of feed displacement solutions is recommended.
- The cesium loaded columns are efficiently eluted with 0.5 M nitric acid. The majority of the ^{137}Cs elutes from the column in 1 bed volume of eluate although a total of 12 bed volumes of eluant was necessary to reach the elution end point of a $C/C_o = 0.01$.
- The SL-644 was adequately regenerated with 6 bed volumes of 0.25 M NaOH. The average ^{137}Cs concentration in the regeneration solution was $6.9\text{E-}2\text{ }\mu\text{Ci/mL}$ with a C/C_o of $3.89\text{E-}04$.
- Fouling of the resin bed or exchanger was not observed.

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APPENDIX A

Appendix A: Sample Identification for AW-101 Cs IX Runs

Sample ID	Description
A1-Cs-0	Initial feed sample for run 1 – AW-101
A1-Cs-ICP	Initial feed sample for run 1 – AW-101
A1-Cs-L1 through L17	Loading samples from lead column, run 1 – AW-101
A1-Cs-P1 through P9	Loading samples from lag column, run 1 – AW-101
Eff – 1	Effluent composite container 1, run 1 – AW-101
Eff – 2	Effluent composite container 2, run 1 – AW-101
A1-Cs-PW1 through PW3	Feed displacement samples, run 1 – AW-101
A1-Cs-PR1 through PR6	DI water rinse samples, run 1 – AW-101
A1-Cs-E1-1 through E1-12	Eluate samples from run 1, lead column – AW-101
A1-Cs-E1-R1 through R6	Eluant rinse samples from run 1, lead column – AW-101
Regeneration solution	Regeneration composite, run 1, lead column – AW-101
A1R-Cs-0	Feed sample for run 2 – AW-101
A1R-Cs-L1 through L17	Loading samples from lead column, run 2 – AW-101
A1R-Cs-P1 through P9	Loading samples from lag column, run 2 – AW-101
A1-Cs-E1-composite	Eluate composite, lead column, run 1 – AW-101
A1-Cs-E2-Comp and A1-Cs-E2-CO	Eluate composite, lag column, run 1 – AW-101
A1R-Cs-E-comp	Eluate composite, both columns, run 2 – AW-101
A1-Tc-LC	AW-101 Tc IX Feed which is the same as the Cs IX effluent composite from run 2.
A1-Tc-0	Tc IX Feed which is the same as the Cs IX effluent composite from run 2

Notes: 1) The letter A, B, C or D after the sample ID indicates that the original sample was diluted and/or transferred to a new, uncontaminated vial for loading out from the hot cell.

Sample Identification Continued

The following sample results are included in the appendix since they were reported with some of the AW-101 Cs IX samples. Samples from other work were batched to reduce cost and duration (schedule). These results are discussed in other reports.

C1-Cs-0AR	Initial feed sample – AN-107 Cs IX
C1-Cs-ICP	Additional feed sample – AN-107 Cs IX
C1-Cs-L1 through L12	Loading samples from lead column – AN-107 Cs IX
C1-Cs-P1 through P6	Loading samples from lag column – AN-107 Cs IX
Effluent – 1D	Effluent composite container 1 – AN-107 Cs IX
Effluent – 2D	Effluent composite container 2 - AN-107 Cs IX
AN-107-TcIX	Cs IX effluent which is also the Tc IX feed
C1-Cs-FD1 through FD7	Feed displacement samples - AN-107 Cs IX
C1-Cs-PR1 through PR6	DI water rinse samples - AN-107 Cs IX
C1-Cs-E1-1 through E1-13	Eluate samples from lead column - AN-107 Cs IX
C1-Cs-E1-R1 through R6	Eluant rinse samples from lead column - AN-107 Cs IX
Regeneration	Regeneration composite for lead column - AN-107 Cs IX
C1-Cs-E2-1 through E2-13	Eluate samples from lag column - AN-107 Cs IX
C1-CA	AN-107 feed control for batch contacts
C1-S1A	AN-107 spike 1 feed control for batch contacts
C1-S2A	AN-107 spike 2 feed control for batch contacts
C1-44A, C1-44-D-A	Batch contact with unspiked AN-107 sample
C1-44-S1-A, C1-44-S1-D-A	Batch contact with spike 1 AN-107 sample
C1-44-S2-A, C1-44-S2-D-A	Batch contact with spike 2 AN-107 sample
C1-Cs-E1-composite	Eluate composite from column 1, AN-107 run
C1-Cs-E2-composite	Eluate composite from column 2, AN-107 run
N7-Tc-0	Tc IX feed which is also Cs IX effluent composite
AN-107-TcIX	AN-107 Tc IX feed sample
A1-Tc-EC1	Eluate composite from Tc IX/AW-101
N7-Tc-Elu-Comp	Tc IX eluant composite from elution of lead column loaded with AN-107 sample
N7-Tc-PW1 – PW7	Feed displacement samples from Tc IX, AN-107 run
N7-Tc-PR1 –PR2	Rinse samples from Tc IX, AN-107 run

AW-101 Column Run Analytical Results

Eluate Composite Analytical Results

APPENDIX B

Appendix B: Spreadsheet Calculations

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