PNWD-3353, Rev. 1
WTP-RPT-089, Rev. 1

Analysis of SuperLig® 644 Resin Used in Hanford Tank Waste Processing

S. K. Fiskum
D. L. Blanchard, Jr
M. J. Steele
J. J. Wagner

February 2004

Prepared for Bechtel National, Inc.
under Contract No. 24590-101-TSA-W000-00004

LEGAL NOTICE

Analysis of SuperLig® 644 Resin Used in Hanford Tank Waste Processing

S. K. Fiskum
D. L. Blanchard, Jr
M. J. Steele
J. J. Wagner

for W. L. Tamosaitis
4/14/04

ACCEPTED FOR
PROJECT USE

February 2004

Test specification: 24590-WTP-TSP-RT-02-004, Rev. 0
Test plan: TP-RPP-WTP-224, Rev. 0
Test exceptions: 24590-WTP-TEF-RT-03-030
R&T focus area: Pretreatment
Test Scoping Statement(s): B-44

Battelle—Pacific Northwest Division
Richland, Washington, 99352

COMPLETENESS OF TESTING

This report describes the results of work and testing specified by Test Specification 24590-WTP-TSP-RT-02-004, Rev. 0 and Test Plan TP-RPP-WTP-224, Rev. 0. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

Gordon H. Beeman

2/24/04

Gordon H. Beeman, Manager
WTP R&T Support Project

Date

History Sheet

Rev	Date	Reason for revision	Revised by
0	October 2003	New Document	SK Fiskum
1	February 2004	Revised pertechnetate results in Table A.13	SK Fiskum

Summary

The U. S. Department of Energy is tasked with the disposition of high-level radioactive waste stored at the Hanford site. The waste is to be vitrified following specific pretreatment processing, separating the waste into a relatively small-volume high-activity waste fraction, and a large-volume low-activity waste (LAW) fraction. To allow for contact handling of the immobilized LAW, and burial at the Hanford site, cesium-137 will need to be removed from the tank waste. Ion exchange is the baseline method for removing ^{137}Cs from Hanford high-level tank waste in the River Protection Project-Waste Treatment Plant (RPP-WTP). The current pretreatment flowsheet includes the use of cesium-selective, elutable, organic ion exchange material, SuperLig® 644 (SL-644), for Cs removal from the aqueous waste fraction. This material has been developed and supplied by IBC Advanced Technologies, Inc., American Fork, UT. After several process cycles, the ion exchanger will be eluted, removed from the columns and disposed.

Battelle—Pacific Northwest Division (PNWD) was contracted to analyze spent ion exchange SL-644 resin after processing eight cycles of waste (one cycle with simulant waste and seven cycles with actual Hanford tank waste) under laboratory-controlled conditions.[a] (PNWD contract number 24590-101-TSA-W000-00004). Appendix C of the *Research and Technology Plan*[b] defines the analysis of spent resin under Technical Scoping Statement B-44. The spent-resin-analysis results will help define residual process-related metals and radionuclide composition expected during actual plant operations.

Objective

The test objective was to analyze the SL-644 resin beds used for actual Hanford tank waste processing. Analysis activities included limited inorganic and radioisotopic determinations. The results will help define the residual, process-related metals and radionuclide compositions in the spent resin that may be expected during RPP-WTP operations. The test objective was met.

Conduct of Test

This report summarizes the testing of spent SL-644 resin generated from processing Hanford tank waste in a dual small-column system in a lead-lag format. The resin beds had been used to process 1.58 L of AW-101 simulant feed (Envelope A waste simulant), 1.19 L of AP-101 diluted feed (an Envelope A waste feed), 0.75 L of AN-102 (an Envelope C waste feed) combined with wash and leachate solutions of C-104 solids (Envelope D waste feed), 1.07 L of AZ-102 concentrated to 4.6 M Na (an Envelope B waste feed), 1.16 L of AZ-101 (Envelope B waste feed), an additional 1.05 L AZ-101, 0.18 L of AP-104/SY-101 (Envelope A waste feed), and an additional 1.90 L of AP-104/SY-101. The lead column was eluted and regenerated after loading with each waste sample, and the lead and lag column positions were switched before processing the next sample. (The columns were designated 1 and 2 for the AW-101 simulant test and retained these designations throughout the testing, regardless of position, to aid in documenting the processing history of each bed.) After processing the AP-104/SY-101 sample, the lead

---

[a] The simulant was processed in a fume hood; the assembly was moved to a shielded facility for actual tank waste processing.

[b] Research and Technology Plan, 24590-WTP-PL-RT-01-002, Rev. 1, April 2002 and Rev. 2, April 2003, S. Barnes, R. Roosa, R. Peterson, Bechtel National, Inc., Richland, WA.

column (Column 1) was eluted with 29.8 bed volumes (BVs) 0.5 M HNO_3, regenerated with 6.5 BVs 0.25 M NaOH, and rinsed with 3.2 BVs deionized water. The lag column (Column 2) had last been exposed to the deionized water rinse following feed displacement, characteristic of a typical run cycle. It still contained Cs from the AP-104/SY-101 processing lead column Cs breakthrough.

The lead column resin bed from the last AP-104/SY-101 processing (Column 1) was removed from the column in the Na-form along with the storage water. The lag column resin bed (Column 2), that had been partially loaded with Cs, was eluted with 16.1 BVs 0.5 M HNO_3 and rinsed with deionized water. Unlike Column 1, the resin in Column 2 was not converted to the Na-form; it was removed in the H-form. The Column 2 transfer water was removed from the resin by filtration. Both resin beds were allowed to air-dry to a free-flowing state. Subsamples were taken for direct gamma energy analysis (GEA) and acid digestion. The dissolved subsamples were measured for selected metals by inductively-coupled plasma-atomic emission spectrometry (ICP-AES), inductively-coupled plasma-mass spectrometry (ICP-MS), uranium by kinetic phosphorescence analysis (KPA), and radionuclides using radiochemical separations followed by counting techniques.

Results and Performance Against Objective

Table S.1 summarizes the analytical results for Column 1 and Column 2. Column 1 contained ^{137}Cs at a factor of 10 higher than Column 2. The difference is most likely due to an intricate combination of the degree of Cs loading, the elution volumes, and the number of regeneration cycles of each column over the last several cycles. Many elements concentrated onto the resin, including, but not limited to, silver, arsenic, barium, chromium, nickel, lead, cobalt, copper, iron, and zirconium. The Cs isotopic distribution, measured by ICP-MS, could only be determined on Column 1 resin (Column 2 resin resulted in undetected ^{133}Cs). The Column 1 Cs isotopic ratio appeared to be primarily a blend of stable Cs (from AW-101 simulant processing) and the Cs isotopic ratio found in the last tank waste processed (AP-104/SY-101).

QA Requirements

PNWD implemented the RPP-WTP quality requirements by performing work in accordance with the quality assurance project plan (QAPjP) approved by the RPP-WTP Quality Assurance (QA) organization. This work was conducted to the quality requirements of NQA-1-1989, Basic and Supplements, and NQA-2a-1990, Part 2.7, as instituted through PNWD's *Waste Treatment Plant Support Project Quality Assurance Requirements and Description* (WTPSP) Manual and to the approved Test Plan, TP-RPP-WTP-224, Rev. 0.

PNWD addressed verification activities by conducting an "independent technical review" of the final data report in accordance with Procedure QA-RPP-WTP-604. This review verified that the reported results were traceable, that inferences and conclusions were soundly based, and that the reported work satisfied the Test Plan objectives. The spent resin analyses reported in this document were to provide the project information about spent resin, but were not intended to be used for permitting purposes.

Issue

The ^{133}Cs isotopic abundance found on Column 1 was 78.4%, higher than any tank waste tested. This indicated that residual Cs from the first simulant process cycle (consisting of 100% ^{133}Cs) was still bound to the resin. If an actual tank waste (containing ^{137}Cs at typical tank waste concentrations) had been first processed through the ion exchanger rather than the simulant containing only a tracer-level of ^{137}Cs, then the residual ^{137}Cs concentration on the spent resin could be expected to be higher than that measured in this test.

Table S.1. Summary of Spent Resin Metals and Radionuclide Concentrations

Targeted Analyte	**Analysis Method**	**Column 1, Na-Form**	**Column 2, H-Form**
Metals	**Digested Aliquot**	**Average μg/g (a, b)**	**Average μg/g (a, b)**
Ag (c)	ICP-AES	49.0 J	46.5 J
As	ICP-AES	[7.6]	[13.5]
Ba	ICP-AES	12.8	1.3
Cd	ICP-AES	[1.5]	[3.1]
Cr	ICP-AES	2,440	3,990
^{133}Cs	ICP-MS	1.80	<0.07
Total Cs	ICP-MS	2.29(d)	NA(e)
Na	ICP-AES	85,550	173
Ni	ICP-AES	[11]	44.0
Pb	ICP-AES	56.2	172
Se	ICP-AES	[4.3]	[6.6]
Th	ICP-AES	< 2.8	< 3.2
U	KPA	< 3.0	4.10
Radionuclides	**Direct Analysis and Digested Aliquot(f)**	**μCi/g (2-σ error)(a)**	**μCi/g (2-σ error)(a)**
^{60}Co	GEA	1.32 E-1 (4%)	1.75 E-1 (4%)
^{106}Ru	GEA	< 2 E-2	1.87 E-2 (8%)
^{113m}Cd	GEA	< 6 E+0	< 4 E-1
^{125}Sb	GEA	< 6 E-3	< 5 E-4
^{126}Sn/Sb	GEA	< 5 E-4	< 4 E-4
^{134}Cs	GEA	1.98 E-3 (14%)	3.51 E-4 (12%)
^{137}Cs	GEA	2.19 E+1 (8%)	1.80 E+0 (6%)
^{152}Eu	GEA	< 4 E-4	< 8 E-5
^{154}Eu	GEA	< 4 E-4	9.13 E-3 (4%)
^{155}Eu	GEA	< 5 E-3	5.75 E-3 (8%)
^{226}Ra	GEA	< 4 E-3	< 4 E-4
^{227}Ac (g)	GEA	< 1E-2	< 6 E-4
^{228}Ra (g)	GEA	< 2 E-2	< 8 E-4
^{231}Pa	GEA	< 6 E-3	< 4 E-3
^{237}Np	GEA	< 4 E-3	7.94 E-4 (16%)
^{241}Am	GEA	< 3 E-2	1.36 E-2 (8%)
Radionuclides	**Digested Aliquot**	**Avg. μCi/g (2-σ error)(a)**	**Avg. μCi/g (2-σ error)(a)**
^{99}Tc	ICP-MS	9.5 E-2 (15%)	8.5 E-2 (15%)
^{238}Pu	Sep. alpha count	1.01 E-3 (9%)	8.01 E-3 (14%)
$^{239+240}$Pu	Sep. alpha count	8.39 E-3 (7%)	7.86 E-2 (5%)
^{241}Am	Sep. alpha count	1.58 E-3 (13%)	1.39 E-2 (28%)
^{242}Cm	Sep. alpha count	< 6 E-5	< 8 E-4
$^{243+244}$Cm	Sep. alpha count	2.36 E-4 (32%)	2.56 E-3 (40%)
Total alpha	Alpha count	1.20 E-2 (20%)	1.12 E-1 (6%)
Total beta	Beta count	2.14 E+1 (6%)	2.70 E+0 (8%)

Table S.1 (Contd)

Targeted Analyte	Analysis Method	Column 1, Na-Form	Column 2, H-Form
Opportunistic Analytes[h]	**Digested Aliquot**	**Average µg/g [(a, b)]**	**Average µg/g [(a, b)]**
Al	ICP-AES	[43]	[48]
B	ICP-AES	328	12.0
Bi	ICP-AES	[12]	[10]
Ca	ICP-AES	[39]	[35]
Co	ICP-AES	8.6	10.6
Cu	ICP-AES	26.2	44.0
Fe	ICP-AES	19.8	52.6
K	ICP-AES	< 114	< 130
Mn	ICP-AES	[0.5]	1.35
Mo	ICP-AES	[1.8]	[1.3]
P	ICP-AES	116	124
Pd	ICP-AES	[117]	[59]
Ru	ICP-AES	[10]	[14]
Sb	ICP-AES	< 3.2	< 3.7
Si	ICP-AES	420	[19]
Sr	ICP-AES	[0.74]	[0.30]
Te	ICP-AES	< 5.7	[7.4]
Ti	ICP-AES	[1.5]	[2.7]
Tl	ICP-AES	[4.8]	[6.6]
V	ICP-AES	< 0.45	[0.72]
Zn	ICP-AES	[2.7]	[4.2]
Zr	ICP-AES	312	364

(a) Dry resin mass basis. To make a direct comparison of the H-form resin results to the Na-form resin results, multiply the H-form resin results by 0.80 (based on H-form to Na-form mass increase factor of 1.25).

(b) Bracketed results are greater than the method detection limit (MDL) but less than the estimated quantitation limit (EQL). The less-than values (<) indicate that the results are less than the MDL; reported values are the instrument detection limits multiplied by the sample dilution factor. Overall errors for values greater than the EQL are estimated to be within 15%. Errors for values less than the EQL but greater than the MDL are likely to exceed 15%.

(c) The Ag results are J-flagged (estimated value) because the matrix spike recovery was low (50%).

(d) Cs isotopic distribution: ^{133}Cs = 78.4%, ^{135}Cs = 9.4%, ^{137}Cs = 12.2%

(e) Not applicable; Cs isotopic distribution could not be measured on Column 2 resin, so total Cs could not be calculated.

(f) Where an analyte was detected, the average concentration is reported. Less-than (<) values are reported from the direct GEA measurement.

(g) The ^{227}Ac and ^{228}Ra detection limits are based on equilibrium daughter emissions. It is possible that ion exchange processing and resin drying upset this equilibrium.

(h) Opportunistic analytes are reported for information only. Results may not have been evaluated relative to quality control criteria.

Terms and Abbreviations

AN-102/C-104	AN-102 tank waste mixed with C-104 wash and leachate solutions, then evaporated to 4.8 M Na
AP-101DF	AP-101 tank waste diluted to 4.97 M Na
AP-104/SY-101	AP-104/SY-101 tank waste diluted to 4.91 M Na
AW-101	AW-101 tank waste simulant diluted to 5.13 M Na
AZ-101	AZ-101 tank waste diluted to nominally 4.85 M Na
AZ-102C	AZ-102 tank waste evaporated to 4.6 M Na
ASR	analytical services request
ASTM	American Society for Testing and Materials
AV	apparatus volume
BS	blank spike
BV	bed volume
CMC	Chemical Measurement Center
DF	decontamination factor
DI	deionized (water)
DOE	U.S. Department of Energy
EQL	estimated quantitation limit
F	furnace
FMI	Fluid Metering, Inc., Syosset, NY
GEA	gamma energy analysis
HB	high blank
HLW	high-level waste
HP	hot persulfate method
IBC	IBC Advanced Technologies, Inc., American Fork, Utah
IC	ion chromatography
ICP-AES	inductively coupled plasma-atomic emission spectrometry
ICP-MS	inductively coupled plasma-mass spectrometry
IDL	instrument detection limit
J	quality control flag indicating the reported value is estimated
KPA	kinetic phosphorescence analysis
LAW	low-activity waste

LCS	laboratory control sample
MDL	method detection limit
MRQ	minimum reportable quantity
MS	matrix spike
M&TE	measuring and test equipment
NA	not applicable
NMRQ	no minimum reportable quantity
NPT	National Pipe Thread
PNWD	Battelle—Pacific Northwest Division
QA	quality assurance
QC	quality control
QAPjP	Quality Assurance Project Plan
RPD	relative percent difference
RPP-WTP	River Protection Project-Waste Treatment Plant
RPL	Radiochemical Processing Laboratory (PNWD facility)
SpA	specific activity
SRTC	Savannah River Technology Center
TC	total carbon
TCLP	Toxicity Characteristic Leach Procedure
TOC	total organic carbon
WTPSP	Waste Treatment Plant Support Project

Terms of Measurement

μCi	microcuries
μg	micrograms
ρ	dry bed density, g/mL
C/C_o	analyte concentration in column effluent divided by analyte concentration in feed, dimensionless
F-factor	ratio of dry resin mass over wet resin mass, dimensionless
g	gram
mL	milliliter
mR/h	dose rate, millirem per hour

Contents

Figures

Tables

1.0 Introduction

The U. S. Department of Energy (DOE) plans to vitrify tank wastes at the Hanford Site in preparation for permanent disposal. Before vitrification, tank wastes will be divided into low-activity waste (LAW) and high-level waste (HLW) fractions through specific pretreatment processes. As part of the pretreatment process, ^{137}Cs will need to be removed to allow for contact handling of the vitrified LAW. The pretreatment flowsheet for the Hanford high-level tank wastes includes the use of SuperLig® 644 (SL-644) for ^{137}Cs removal from the aqueous waste fraction. The SL-644 resin has been developed and supplied by IBC Advanced Technologies, Inc., American Fork, UT (IBC). The SL-644 is a Cs-selective, elutable, organic ion exchanger and has been shown to be effective in removing Cs from a variety of Hanford tank wastes [1-11]. After repeated cycling, the SL-644 will be disposed of as low-level waste.

Battelle—Pacific Northwest Division (PNWD) has conducted several tests with SL-644 on actual Hanford tank wastes [7-11 and Appendix A] in a lead/lag small-column format. After initially processing 1.58 L of AW-101 simulant, actual wastes samples were processed for a total of eight process cycles. The actual waste samples included 1.19 L of AP-101 diluted feed (an Envelope A waste feed), 0.75 L of AN-102 (an Envelope C waste feed) combined with wash and leachate solutions of C-104 solids (Envelope D waste feed), 1.07 L of AZ-102 (concentrated to 4.6 M Na, an Envelope B waste feed), 1.16 L of AZ-101 (Envelope B waste feed), an additional 1.05 L AZ-101, 0.18 L of AP-104/SY-101 (Envelope A waste feed), and an additional 1.90 L AP-104/SY-101. The lead column was eluted and regenerated after loading with each waste sample, and the lead and lag column positions were switched before processing the next sample. After processing the AP-104/SY-101 sample, the lead column was eluted, regenerated and rinsed. The lag column had last been exposed to the deionized water rinse following feed displacement, characteristic of a typical run cycle. It still contained Cs from the AP-104/SY-101 processing lead column Cs breakthrough.

The resins used to process these materials were ideal candidates for analytical testing to identify and quantify residual metals and radionuclides. This report summarizes the spent resin processing and analysis results. The spent resin analyses reported in this document were to provide the project information about spent resin, but were not intended to be used for permitting purposes.

The objectives of this work were to:

- identify and quantify residual metals on the resin beds: silver (Ag), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), cesium (Cs), sodium (Na), nickel (Ni), lead (Pb), selenium (Se), thorium (Th), and uranium (U)

- identify and quantify residual radionuclides on the resin beds: gamma emitters, total alpha and total beta activities, technetium-99 (^{99}Tc), plutonium (Pu), americium (Am), and curium (Cm).

All work was conducted according to Test Specification 24590-PTF-TSP-RT-02-004, Rev. 0,(a) Test Plan TP-RPP-WTP-224, Rev. 0,(b) and Test Exception 24590-WTP-TEF-RT-03-030.

(a) *Analysis of Spent Ion Exchange Resins*. J Toth. River Protection Project-Waste Treatment Plant, Bechtel National Inc., Richland, WA. July 30, 2002.

(b) *Spent Ion Exchange Resin Analysis: SL-644*. S Fiskum. Battelle—Pacific Northwest Division. Richland, WA. March 2003.

2.0 Resin-Bed History

This section summarizes the resin-bed history and test apparatus. All raw data are maintained in the Project File 42365 at PNWD.

2.1 SL-644 Resin

The SL-644 resin was obtained from IBC production batch number 010319SMC-IV-73, prepared at IBC on 3/19/01. This material batch exhibited a black-red appearance peppered with light-brown specks. It was received from the vendor as a dry, granular, free-flowing material in a 1-L polyethylene bottle with an approximately 32% gaseous headspace. There was no indication that this headspace was filled with nitrogen or other inert gas, and no attempt was made to exclude air during storage. The as-received resin form was not identified by the vendor; it was found to contain potassium salts [7]. Before sampling SL-644 from the IBC-supplied plastic bottle, the bulk-resin bottle was turned several times to produce a well-mixed material. Sub-samples were removed immediately after mixing. Table 2.1 reproduces the sieve results of this resin batch that were previously reported [7]. The 212- to 425-µm particle-size dry-sieved fraction was used in the ion exchange columns.[a] This fraction represented 24 wt% of the as-received material.

Table 2.1. Dry Particle-Size Weight-Percent Distribution of As-Received SL-644

Sieve Size[1]	Particle Size, (µm)	010319SMC-IV-73, wt %
18	>1000	0.06
30	600–1000	37.27
40	425–600	38.23
50	300–425	18.01
70	212–300	6.08
100	150–212	0.26
140	106–150	0.06
>140	<106	0.03
(1) U.S. standard sieve size corresponding to ASTM E-11 specification.		

Properties of the 212- to 425-µm 010319SMC-IV-73 SL-644 resin have been previously reported [7]; Table 2.2 reproduces selected properties. The F-factor is the ratio of the dry mass of exchanger to the initial mass of the exchanger and is used to correct for residual water content in the resin. It was determined at the same time the column-resin fractions were weighed by drying approximately 0.5 g resin, under vacuum, at 50°C to constant mass. The L-factor represents the fractional mass remaining after washing the as-received resin form with 0.5 M HNO_3 and deionized (DI) water, and correcting for

---

(a) This particle-size distribution was used successfully in AW-101 simulant testing. The as-received particle-size distribution was shown not to meet the Cs decontamination specification [7].

residual water content as described above. The I_{Na} represents the fractional mass gain upon conversion from the H-form to the Na-form, correcting for water content.[a]

Table 2.2. SL-644 Properties

Property	010319SMC-IV-73
Bulk density, g/mL	0.74
F-factor, as-received	0.877
L, conversion to H-form, fractional mass remaining	0.538
I_{Na}, fractional mass gain from H-form to Na-form	1.25

2.2 Column-Run Experimental Conditions

Figure 2.1 shows a schematic of the ion exchange column system used to process simulant and Hanford tank waste prior to measuring spent resin constituents. The system consisted of two small columns containing the SL-644 ion exchange material, a small metering pump, three valves, a pressure gauge, and a pressure relief valve. Valves 1, 2, and 3 were three-way valves that could be turned to the flow position, sample position, or no-flow position. Valve 1 was placed at the outlet of the pump and was used to eliminate air from the system, purge the initial volume of the system, or isolate the columns from the pump. Valves 2 and 3 were primarily used to obtain samples and could also be used to isolate the columns from the rest of the system. The columns were connected in series with the first column referred to as the lead column and the second column referred to as the lag column.

The columns were prepared at the Savannah River Technology Center (SRTC) Glassblowing Laboratory. Each column consisted of a 15-cm glass column with a 24/40 taper ground-glass fitting on top and a threaded fitting on the bottom. A polyethylene bushing was installed in the glass-threaded fitting to accommodate ¼-in. stainless steel National Pipe Thread (NPT) fitting. The inside diameter of each column was 1.46 cm, which corresponded to a volume of 1.67 mL/cm. A stainless steel, 200-mesh screen supported the resin bed. The height of the resin bed (and thus shrinkage and swelling) was measured with a decal millimeter scale affixed to the column. The upper section contained four entry ports and a taper joint with screw cap that securely fitted the column. The lead column assembly used a pressure relief valve (10 psi trigger), pressure gauge, and sample inlet; the remaining port was plugged. The lag-column assembly used one port for sample entry, and the other three ports were plugged. In both columns, the inlet sample lines extended through the port opening to the top of the column. The connecting tubing was $^{1}/_{8}$-in. OD, $^{1}/_{16}$-in. ID polyethylene. Valved quick-disconnects (Cole Parmer, Vernon Hills, IL) were installed in-line to allow for ease of column switching. A Fluid Metering, Incorporated (FMI) QVG50 pump (Fluid Metering, Inc., Syosset, NY) equipped with a ceramic and

---

(a) The F-factor for the Na-form of the resin was performed differently because of stability problems observed in previous tests on the Na-form of resin [7]. Drying to constant mass under vacuum at ambient temperature was considered adequate for removing water from the Na-form resin. The resin was heated to 50°C after initial drying at ambient temperature under vacuum to constant mass. The heated product appeared (visual inspection) to have degraded, thus potentially nullifying subsequent mass measurements.

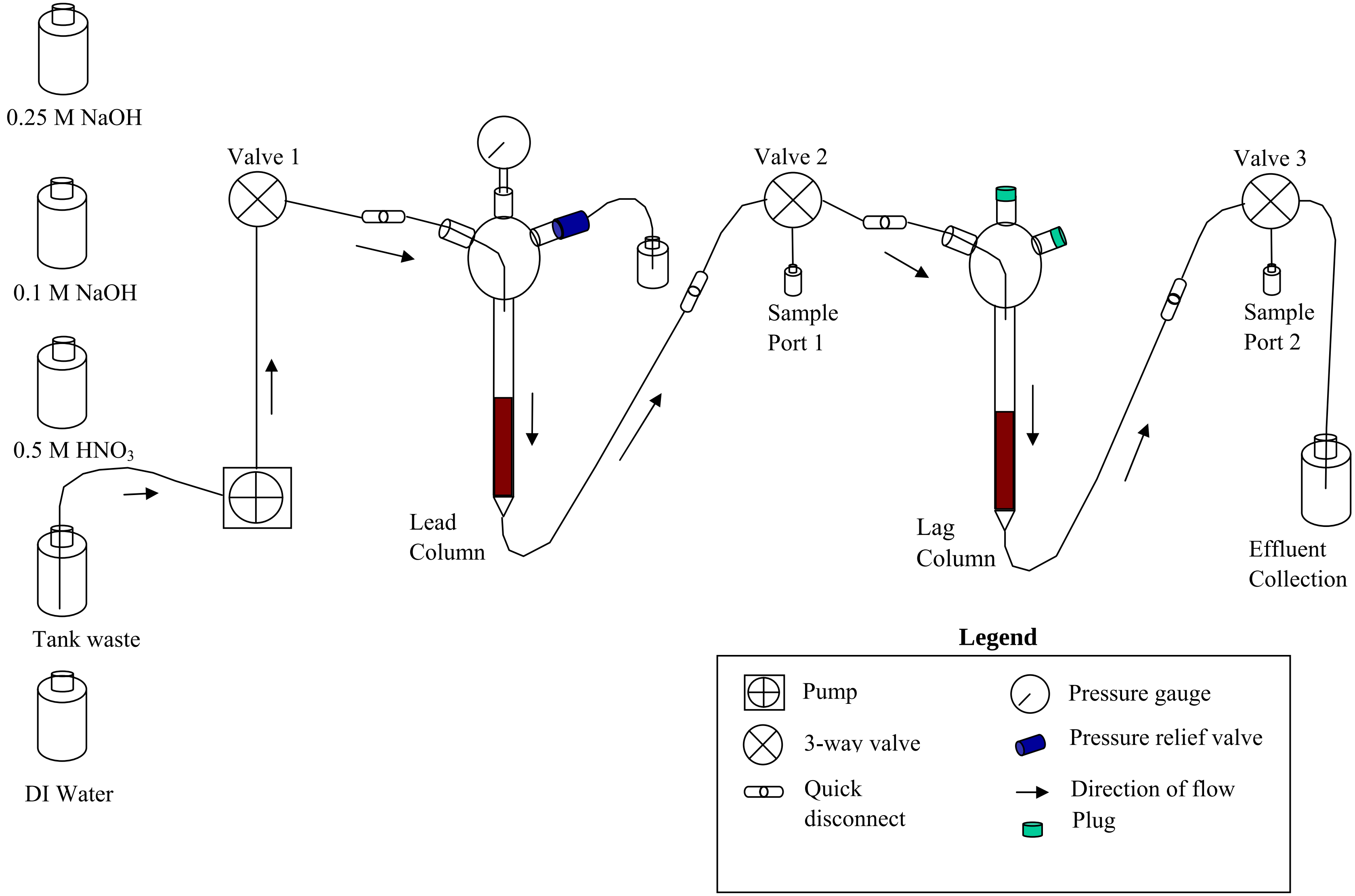


Figure 2.1. Cesium Ion Exchange Column System

Kynar® coated low-flow piston pump head was used to introduce all fluids. The flowrate was controlled with a remotely operated FMI stroke-rate controller. The pump was set up to deliver flowrates from 0.08- to 16-mL/min. The volume actually pumped was determined using the mass of the fluid and the fluid density. The pressure indicated on the pressure gauge remained below 5 psi during all runs. The holdup volume of the entire Cs ion exchange system was the summed volume of all fluid-filled parts and was estimated to be 42 mL; the holdup volume for the lead-column section (feed line through the lead-column sample line) was similarly estimated to be 23 mL.

Before process testing, both of the resin beds were individually cycled through the H-form and back to the Na-form. After the resin cycling, the mass of the Na-form SL-644 (M_c) was calculated, on a dry-weight basis, in each column, according to Equation 2.1.

$$M_c = M * L * F * I_{Na} \tag{2.1}$$

where M_c = dry SL-644 mass in the resin bed
M = SL-644 as-received resin mass
L = fractional mass remaining after washing (0.538)
F = water-loss factor, as-received form (0.877)
I_{Na} = fractional mass gain on conversion from H-form to Na-form (1.25) (this factor was set to 1 when calculating the dry-bed density in the H-form or 0.5 M HNO_3 feed).

The calculated resin masses initially loaded in Column 1 and Column 2 are given in Table 2.3

Table 2.3. Calculated Resin Bed Masses

Resin form	**Column 1**	**Column 2**
As-received form dry resin mass, g	4.17	4.20
H-form dry resin mass, g	1.97	1.98
Na-form dry resin mass, g	2.46	2.48

2.3 Process Cycles

The ion exchange system was cycled eight times with various Hanford tank-waste feeds. The different process cycles and positions of Column 1 and Column 2 during processing are identified in Table 2.4. Also shown are the Cs breakthrough and elution parameters. Table 2.5 summarizes the total Cs loading in terms of moles Cs and Ci ^{137}Cs onto Columns 1 and 2.

Table 2.4. Resin-History Summary

Tank Waste (Process Start Date)	Cycle	Load Volume, mL (BV)	Lead Column ID	Cs Breakthrough % C/C_o [a]	Elution	Eluate Volume, BV	Final Eluate Sample ^{137}Cs Concentration, C/C_o (μCi/mL)	Reference
AW-101 simulant (3/26/01)	1	1576 (143)	Column 1	0.99	Lead and lag columns	12.5	5.5E-3 (trace)	[7]
AP-101 (4/23/01)	2	1189 (112)	Column 1	0.19	Lead column only	19.3	4.2E-3 (0.53)	[8]
AN-102/C-104 (6/25/01)	3	753 (72)	Column 2	1.3E-4 [b]	Lead column only	18.9	6.3E-3 (1.0)	[9]
AZ-102C (11/5/01)	4	1071 (105)	Column 1	78	Lead column only	14.8	6.6E-4 (1.3)	[10]
		Regenerate then re-elute	Column 1	NA	Lead column only	6.5	1.8E-4 (0.37)	[10]
AZ-101 (12/3/01)	5	1261 (122)	Column 2	53	Lead column only	14.3	2.2E-3 (3.7)	[11]
AZ-101 (1/28/02)	6	1046 (95.9)	Column 1	7.2	Lead column only	15.9	1.5E-3 (2.5)	[11]
AP-104/SY-101 (7/15/02)	7	183 (17.4)	Column 2	0.13 [b]	Lead column only	28.4	1.3E-4 (0.021)	Appendix A
AP-104/SY-101 (7/17/02)	8	1903 (182)	Column 1	7.6	Lead column only [c]	29.8	8.3E-5 (0.014)	Appendix A

NA = not applicable

(a) The Cs breakthrough represents the relative Cs concentration in the final load sample.

(b) No breakthrough curve was generated; C/C_o demonstrated a flat-line response as a function of bed volume (BV).

(c) See experimental Section 3.0 for Column 2 processing, that included a baseline elution.

Table 2.5. Total Cs Loading onto Column 1 and Column 2

Tank Waste (Process Start Date)	Cycle	Load Volume, mL (BV)	Lead Column ID	Moles Cs Loaded on Column 1	Moles Cs Loaded on Column 2	Ci of ^{137}Cs Loaded on Column 1	Ci of ^{137}Cs Loaded on Column 2	Reference
AW-101 simulant (3/26/01)	1	1576 (143)	Column 1	1.35E-4	1.76E-7	0.00E+0	0.00E+0	[7]
AP-101 (4/23/01)	2	1189 (112)	Column 1	5.35E-5	1.23E-8	1.53E-1	3.52E-5	[8]
AN-102/C-104 (6/25/01)	3	753 (72)	Column 2	NA(a)	4.51E-5	NA(a)	1.24E-1	[9]
AZ-102C (11/5/01)	4	1071 (105)	Column 1	5.28E-4	3.02E-5	2.03E+0	1.16E-1	[10]
AZ-101 (12/3/01)	5	1261 (122)	Column 2	2.54E-5	5.40E-4	9.47E-2	2.01E+0	[11]
AZ-101 (1/28/02)	6	1046 (95.9)	Column 1	4.67E-4	1.31E-6	1.74E+0	4.89E-3	[11]
AP-104/SY-101 (7/15/02)	7	183 (17.4)	Column 2	NA(a)	1.26E-5	NA(a)	3.12E-2	Appendix A
AP-104/SY-101 (7/17/02)	8	1903 (182)	Column 1	1.21E-4	9.95E-6	3.00E-1	2.47E-2	Appendix A
Total Cs loaded on columns during multiple processing				1.33E-3	6.39E-4	4.32E+0	2.31E+0	--

(a) Not applicable; no significant Cs breakthrough occurred from the lead column (Column 2) onto the lag column (Column 1).

After connecting the columns in series, a typical process cycle began with a system rinse with DI water followed by one apparatus volume (AV) rinse with 0.25 M NaOH, each processed at a flowrate of three bed volumes (BV) per hour. The Hanford tank waste feed was then typically introduced at either 3 BV/h (Envelopes A and C tank waste) or 1.5 BV/h (Envelope B tank waste). The tank waste feed was displaced with two apparatus volumes of 0.1 M NaOH followed by 2 AVs of DI water, each at 3 BV/h. The lead column was then disconnected from the lag column. The lead column was eluted with 0.5 M HNO_3 at 1 BV/h until 1% C/C_o was obtained, then rinsed with 2 AVs DI water. The lead column resin bed was regenerated with 6 BVs 0.25 M NaOH at 1 BV/h, then rinsed again with DI water at 3 BV/h. After processing was completed, the system and resin beds were simply stored with the last matrices processed. In all cases, the resins were stored as the Na-form in DI water. The lag column contained DI water remaining after the DI water rinse (conducted after feed displacement). The lead column contained DI water rinse remaining after the regeneration process. All system valves were closed. In most cases the lead and lag column positions were switched before processing the next waste sample.

Cycle 1. The entire ion exchange system was used for a full shakedown experiment with AW-101 simulant [7]. Both columns were individually eluted, rinsed, and regenerated. The lead column had been eluted to a C/C_o of 7.1E-3 which was equivalent to 6.1E-7 M Cs. The ion exchange system was then transferred to a hot-cell facility and the resin beds were cycled once more through the acid and sodium forms while connected in series. The lead and lag column positions were not switched.

Cycle 2. The system was then used to process 1.19 L of AP-101 (diluted to 5 M Na) tank waste [8]. Only the lead column was eluted to an eluate ^{137}Cs concentration C/C_o of 4.2 E-3, which was equivalent to a ^{137}Cs concentration of 0.53 μCi/mL and 1.5E-7 M total Cs. The lag column contained an estimated 35 μCi ^{137}Cs calculated from integrating the lead-column Cs breakthrough.

Cycle 3. After an 8-week storage period (resin as Na-form in DI water), the lead and lag column positions were switched and 0.75 L of AN-102/C-104 were processed [9]. Again, only the lead column was eluted to an eluate ^{137}Cs concentration C/C_o of 6.3 E-3, which was equivalent to a ^{137}Cs concentration of 1.0 μCi/mL and 3.8E-7 M total Cs. The lag column contained an estimated 0.22 μCi ^{137}Cs calculated from integrating the lead-column Cs breakthrough.

Cycle 4. After a 17-week storage period (Na-form resin in DI water), the lead- and lag-column positions were switched, and 1.07 L of AZ-102 concentrated to 4.6 M Na were processed [10]. The lead column was eluted to a ^{137}Cs concentration C/C_o of 6.6E-4, which was equivalent to a ^{137}Cs concentration of 1.3 μCi/mL and 3.4E-7 M total Cs. The lead column was regenerated and rinsed. After 16 days, the lead column was re-eluted to a C/C_o of 1.8E-4, which was equivalent to 3.7E-1 μCi/mL ^{137}Cs and 9.5E-8 M total Cs. The lag column contained an estimated 1.2E+5 μCi ^{137}Cs calculated from the average of the lead-column integrated Cs breakthrough, integrated Cs recovery in the eluate samples, and Cs recovery in the composite eluate.

Cycle 5. After a 20-day storage period, the lead- and lag-column positions were switched, and 1.26 L AZ-101 were processed [12]. The lead column was eluted with 14.3 BVs 0.5 M HNO_3 to a ^{137}Cs concentration C/C_o of 2.2E-3 (3.7 μCi ^{137}Cs/mL). The lag column contained 9.9E+4 μCi ^{137}Cs calculated from integrating the lead-column breakthrough samples.

Cycle 6. After a 49-day storage period, the lead and lag columns were again switched, and 1.05 L AZ-101 were processed. The lead column was eluted to a ^{137}Cs concentration C/C$_o$ of 1.5E-3 (2.5 μCi ^{137}Cs/mL). The lag column contained 5.2E+3 μCi ^{137}Cs, calculated from integrating the lead-column Cs breakthrough.

Cycle 7. After a 164-day storage period, the lead- and lag-column positions were switched, and processing of AP-104/SY-101 was initiated in two cycles. The first cycle was short (0.18 L) with a flat breakthrough at nominally 0.13% C/C$_o$. The lead- and lag-column Cs-breakthrough profiles were identical so that an equivalent amount of Cs that was loaded on the front of the lag column was also "bled" from the column in the effluent. The lead column was then well eluted with 28 BVs 0.5 M HNO_3 at 1.7 BV/h to a C/C$_o$ of 1.3E-4 (2.1E-2 μCi ^{137}Cs/mL).

Cycle 8. The lead and lag column positions were immediately switched (no storage period). A 1.9-L volume of AP-104/SY-101 was processed through the system, resulting in 7.6% breakthrough. The lag column was loaded with 1.9 mCi ^{137}Cs calculated from integrating the lead-column Cs breakthrough. The lead column was eluted to a C/C$_o$ of 8.3E-5 (1.4E-2 μCi/mL).

The feed compositions are summarized in Table 2.6. Some of the data in Table 2.6 must be used with caution; many analytes were reported by the analytical laboratory on an opportunistic basis and have not been fully evaluated relative to quality control (QC) issues. More analytical detail can be found in the referenced reports. In nearly all cases, Ag, As, B, Se, Si, Sr, Th, and Zn were reported opportunistically. All results (targeted and opportunistic) are summarized to better appreciate the potential influence of the feed composition on the metals found in resins.

Table 2.6. Tank-Waste Feed-Solution Compositions

Analyte	AW-101 Simulant	AP-101 Diluted Feed	AN-102/C-104	AZ-102 Concentrate	AZ-101	AP-104/ SY-101
Density	**g/mL**	**g/mL**	**g/mL**	**g/mL**	**g/mL**	**g/mL**
Density	1.234, T= 24°C	1.256, T= NR	1.244, T= 25°C	1.246, T= 26°C	1.224, T = 24°C	1.225, T = 32°C
Cations	**M**	**M**	**M**	**M**	**M**	**M**
Ag	Not added	<3.1E-5 J	<3.0E-5(a)	<3.1E-5(a)	<6.0E-6(a)	<5.7E-6
As	Not added	<4.5E-4	<3.3E-4(a)	<4.5E-4(a)	[1.2 E-4] (a)	<8.3E-5
B	1.46E-2(a) J	[5.1E-3]	<4.6E-4 HB(a)	7.15E-3(a)	[7.0E-3] (a) J	4.45E-3
Ba	1.32E-4	<1.0E-5	[7.3E-6] HB	<9.6E-6(a)	[2.1 E-6] (a)	<1.8E-6
Ca	<7.8E-4	5.24E-4	[3.7E-3]	<9E-4	<2 E-4	1.69E-3
Cd	Not added	<1.8E-5	2.31E-4	<2E-5	<4 E-6	4.05E-5
Co	Not added	<1.1E-4	<8.5E-5	<1.1E-4(a)	<2 E-5(a)	<2E-5
Cs	8.57E-5	4.5E-5	5.99E-5	5.21E-4	4.48 E-4	6.88E-5
Cu	Not added	<5.3E-5	[1.6E-4]	<5.2E-5(a)	<1 E-5(a)	<1E-5
Fe	[1.6E-4]	[6.8E-5]	[6.6E-5]	<5.9E-5(a)	[4.7 E-5](a)	[6.2E-5]
K	4.17E-1	7.61E-1 J	[2.4E-2]	1.70E-1	1.15 E-1 J	4.64E-2
Mo	[2.61E-4] (a)	[1.5E-4]	[2.3E-4] (a)	1.14E-3(a)	9.75 E-4(a)	5.12E-4
Na	5.15E+0	4.97E+0	4.8E+0 J	4.61E+0	4.85 E+0 J	4.92E+0 J
Ni	[1.2E-4]	[7.5E-5]	3.20E-3	<6.8E-5(a)	<2 E-5(a)	5.76E-4
Pb	Not added	<6.5E-5	[3.2E-4]	<6.3E-5(a)	[1.5 E-5](a)	[4.2E-5]
Se	Not added	<4.3E-4	<3.2E-4(a)	<4.2E-4(a)	<8.1E-5(a)	<7.9E-5
Si	[6.2E-3] (a) J	1.28E-2 HB	[3.95E-2] (a)	[9.1E-3] (a)	[4.0E-3] (a) J	[3.4E-3]
Sr	<2.1E-5(a)	2.32E-5	9.87E-4(a)	<2.3E-5(a)	<4.4E-6(a)	[4.7E-6]
Th	Not added	<5.8E-4	<4.3E-4(a)	<5.7E-4(a)	<1.1E-4(a)	<1.1E-4
U (Uranyl)(b)	Not added	1.7E-4	1.15E-4	6.37E-5 J	9.33 E-5	4.07E-5
W	Not added	1.48E-3	<1.1E-3(a)	<1.4E-3(a)	[3.0 E-4] (a)	[3.8E-4]
Zn	Not added	[1.2E-4] HB	[1.3E-4] (a)	<1.0E-4(a)	[1.6E-4] (a) J	<1.9E-5
Zr	Not added	<7.4E-5	<5.5E-5	<7.2E-5	[2.2E-5]	<1.4E-5
Carbon	**M**	**M**	**M**	**M**	**M**	**M**
CO_3^{2-} (F)	2.47E-1	Not detected	4.75E-1	1.17E-1 J	4.9 E-1	3.7E-1
CO_3^{2-} (HP)	1.15E-1	4.46E-1	6.86E-1	1.25E+0	8.2 E-1	3.5E-1
TOC (F)	2.7E-2	6.58E-1	1.58E+0	1.16E+0	1.2 E-1	2.2E-1
TOC (HP)	1.41E-1	1.36E-1	9.79E-1	8.33E-2	4.2 E-2	3.5E-1
TC (F)	2.73E-1	6.62E-1	1.68E+0	1.24E+0	6.1 E-1	5.9E-1
TC (HP)	2.56E-1	5.82E-1	1.66E+0	1.25E+0	8.7 E-1	7.0E-1

Table 2.6 (Contd)

Analyte	**AW-101 Simulant**	**AP-101 Diluted Feed**	**AN-102/C-104**	**AZ-102 Concentrate**	**AZ-101**	**AP-104/ SY-101**
Anions	**M**	**M**	**M**	**M**	**M**	**M**
AlO_2^- (b)	4.84E-1	2.59E-1	3.04E-1	3.44E-2	2.09 E-1	3.97E-1
F^-	1.63E-2	<1.2E-1	<2.3E-1	9.29E-2	5.79 E-2 J	1.07E-1
Cl^-	7.50E-2	4.1E-2	5.39E-2	<3.9E-3	2.03 E-3	1.51E-1
CrO_4^{-2} (b)	Not added	2.92E-3	2.08E-3	2.90E-2	1.21 E-2	7.84E-3
NO_2^-	8.33E-1	7.1E-1	9.23E-1	1.69E+0	1.54 E+0	1.52E+0
NO_3^-	1.73E+0 J	1.68E+0	1.66E+0	6.08E-1	9.92 E-1	1.76E+0
OH^-	Not measured	1.94E+0	2.0E-1	1.11E+0	6.8 E-1	1.16E+0
PO_4^{-3} (b) (ICP-AES)	[1.9E-3] (a)	1.24E-2	2.41E-2(a)	9.25E-3(a)	1.64 E-2(a)	4.39E-2
PO_4^{-3} (IC)	<2.6E-3	9.55E-3	3.63E-2	1.42E-2	1.68 E-2	4.78E-2
SO_4^{-2}	<2.6E-3	4.8E-2	6.84E-2	3.68E-1	1.75 E-1	2.90E-2
$C_2O_4^{-2}$	Not added	3.06E-4	3.4E-2	1.90E-2 J	1.79 E-2	9.44E-3
Radionuclides	**µCi/mL**	**µCi/mL**	**µCi/mL**	**µCi/mL**	**µCi/mL**	**µCi/mL**
^{60}Co	Not added	2.5E-3	4.06E-2	<3E-2	<7 E-2	<8E-3
^{90}Sr	Not added	7.1E-2	1.70E+0	Not measured	[1.19 E+0]	1.69E+0
^{99}Tc	Not added	3.93E-2	7.71E-2	Not measured	3.27 E-1	1.44E-1
$^{99}TcO_4$	Not added	3.46E-2 J	Not measured	Not measured	3.77 E-1	4.38E-2
^{134}Cs	Not added	2.86E-2	<3E-3	1.26E+0	7.51 E+0	<6E-3
^{137}Cs	trace	1.26E+2	1.61E+2	2.00E+3	1.64 E+3	1.68E+2
^{154}Eu	Not added	<7E-4	<6E-2	<1E-1	<2 E-1	<2E-2
^{238}Pu	Not added	1.4E-5	Not measured	Not measured	3.44 E-4	3.62E-5
$^{239+240}Pu$	Not added	1.1E-4	8.97E-4	Not measured	1.81 E-3	2.59E-4
^{241}Am	Not added	1.38E-4	1.03E-2	Not measured	1.05 E-4	2.81E-3
$^{243+244}Cm$	Not added	2.12E-6	6.8E-4	Not measured	4.18 E-5	5.84E-4
Cs Isotopic Ratio	**%**	**%**	**%**	**%**	**%**	**%**
^{133}Cs	100	60.6	60.3	52.3	51.85	60.5
^{135}Cs	0	15.4	16.7	14.9	16.9	18.7
^{137}Cs	trace	24.0	23.0	32.8	31.25	20.8
Feed Composition Reference	[7]	[8, 12]	[9, 13]	[10]	[11, 14, 15]	[Appendix A, 16]

Table 2.6 (Contd)

(a) Analytes measured opportunistically and results were not fully evaluated relative to quality control (QC) criteria.
(b) Al, Cr, and P were determined by ICP-AES. U was measured by KPA. The ionic forms were assumed on the basis of waste chemistry.

Notes:
Bracketed results indicate that the analyte concentration uncertainty exceeded ±15%. Less-than (<) results indicate that the analyte concentrations were below the instrument detection limit (IDL); the dilution-corrected IDLs are given.
J-flagged results indicate one or more analysis QC failures associated with the analyte (relative percent difference [RPD], matrix spike [MS], and/or blank spike [BS]). Specific information can be found in the referenced reports.
HB = high blank
HP = hot persulfate method
F = furnace method
NR = not recorded
TC = total carbon
TOC= total organic carbon

3.0 Experimental

This section describes resin processing following actual Hanford waste testing. Experimental data were recorded in Test Instruction TI-RPP-WTP-229 and analytical reports generated by the Chemical Measurements Center (CMC). All raw data are maintained in the Project File 42365 at PNWD.

3.1 Column Processing

The ion exchange assembly (Figure 2.1) was stored for 246 days since the end of the AP-104/SY-101 column testing with resin in the Na-form. Both resin beds were black, and the storage water was colored dark brown. Column 1 (in the lead position) had been eluted with 29.8 BVs of 0.5 M HNO_3, regenerated with 6.5 BVs 0.25 M NaOH, and rinsed with 3.2 BVs DI water as part of the AP-104/SY-101 processing. Column 2 (in the lag position) was last rinsed with DI water following the AP-104/SY-101 feed processing and feed displacement.

Column 1 was disconnected and the resin (in the Na-form) was removed using DI water to aid the transfer. All storage fluid (colored deep brown) and water-transfer solution were maintained with the resin. There was no evidence of resin agglomeration during the resin-removal process.

Column 2 was brought to the lead position, and the AV of DI water (dark brown) was displaced with fresh DI water in preparation for elution. The resin was eluted at the nominal plant operating condition of 1 BV/h for 16 BVs, where 1 BV (10.2 mL) is the resin BV in the Na-form in DI water just before elution. The resin bed was then rinsed with DI water. Table 3.1 summarizes the experimental conditions for each process step. The eluate was collected in 1-BV increments, and the DI water rinse was collected in 2-BV increments. All processing was performed in the hot cells at a nominal temperature of 24°C. After the DI water rinse, the resin was removed from the column using DI water to aid the transfer. The individual Cs eluate and rinse samples were measured for ^{137}Cs using gamma energy analysis (GEA).

Table 3.1. Experimental Conditions for Column 2 Elution

Process Step	Solution	Total Volume			Flowrate		Time	T, °C
		BV[a]	AV[b]	mL	BV/h	mL/min	h	
Column 2 Only[c]								
Rinse	DI water	1.4	0.63	14.4	4.2	0.72	0.3	24
Elution	0.5 M HNO_3	16.1	NA	165	1.1	0.19	14.8	24
Rinse	DI water	9.1	4.0	93	2.7	0.45	3.5	24

(a) BV = bed volume (10.2 mL in Na-form)
(b) AV = apparatus volume (23 mL)
(c) Start date = 3/26/03
NA = not applicable

3.2 Resin Handling

Each resin bed was collected as a slurry in its last processing state (Na-form for Column 1 and H-form for Column 2) and maintained separately. The resin-bed slurries were removed from the hot cell. The dose rates were measured with a R03 Eberline ion chamber survey meter and were low enough to allow for contact-handling. The dose rates obtained are summarized in Table 3.2. Because both samples could be contact-handled, they were transferred to a fume hood for subsequent processing.

Table 3.2. Spent-Resin Dose Rates

Column	Contact dose rate mR/h		Correction factors		Corrected contact dose rate, mR/h[(a)]	Dose rate at 30 cm, mR/h
	Open window	Closed window	Beta (β)	Gamma (γ)		
1	5	5	4.5	2	10	0.5
2	1.8	0.8	3	1.5	1.2	<0.5

(a) The corrected contact dose rate is the closed window (γ) dose rate multiplied by the γ correction factor.

The Na-form Column 1 resin was dried in contact with the storage and transfer liquid using a nitrogen purge in order to capture any analytes that may have leached from the resin. Constant mass was obtained in nominally 9 days. The H-form Column 2 resin was stored 6 days in the 35.3-mL DI water used for transfer out of the column. Column 2 resin was then filtered, and the filtrate was submitted for anion analysis. The resin was allowed to air dry in the filter apparatus to constant mass; constant mass was obtained after 8 days.

The resin sample processing and sample splitting are shown in Figure 3.1. Nominally 1.2 g from each resin bed was submitted for direct analysis using GEA. Nominal 0.2-g samples were taken in triplicate (to be used as a sample, sample duplicate, and matrix-spike sample) for acid digestion and subsequent element and radioisotope-specific analyses. Only about 0.3 g remained for F-factor determination, a measure of the residual water content in the resin.

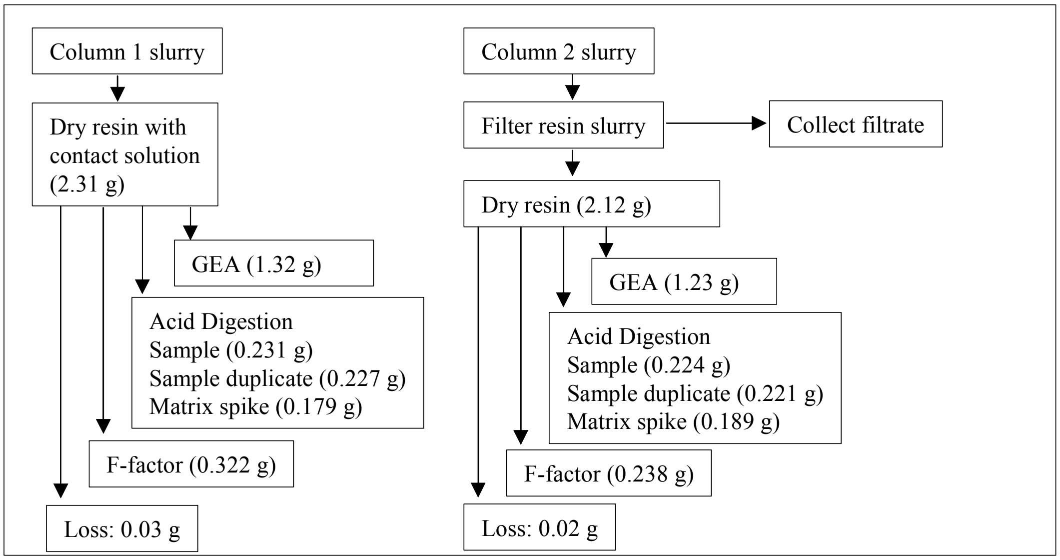


Figure 3.1. Spent-Resin Disposition

3.3 Analysis

The F-factor was determined by drying a known mass of the resin under vacuum at ambient temperature to constant mass.[a] The F-factor (F) was determined according to Equation 3.2,

$$F = \frac{m_i}{m_d} \tag{3.2}$$

where m_i equals the initial resin mass and m_d equals the dried resin mass.

The ^{137}Cs concentrations in the Column 1 eluate samples were determined comparatively using a bench-top GEA spectrometer, allowing for rapid sample analysis. Selected sample results were later confirmed by the CMC GEA analysis. The selected eluate samples were submitted to the CMC under Analytical Services Request (ASR) 6768.

The Column 2 water leach solution was submitted to the CMC under ASR 6740. Anions were measured using ion chromatography (IC) according to Procedure PNL-ALO-212, *Determination of Inorganic Anions by Ion Chromatography*.

Resin subsamples were submitted to the CMC under chain-of-custody (see Appendix B) and ASR 6740. Samples from each column were dissolved and acid-digested according to procedure RPG-CMC-137, *Nitric Acid and Hydrogen Peroxide Dissolution of Ion Exchange Resin SL-644*. This entailed contacting a nominally 0.22-g sample with 5 mL of 16 M nitric acid overnight at 105°C in a Teflon vessel until dry. The digestate was dissolved by adding 1.25 mL of 16 M nitric acid plus 2 mL of 50% hydrogen peroxide and heated about 1 hour at 105°C. The reaction with acidic hydrogen peroxide was somewhat more vigorous than test materials conducted with SL-644 resin uncontacted with Hanford tank waste. (The different dissolution behavior may be due to the generally larger particle sizes of the test material, SL-644 from batch C-01-05-28-02-35-60.) Each sample was brought to a known (nominal 25-mL) volume with dilute nitric acid. The digested sample solutions initially were clear and colorless. After setting for nominally 24 hours, a very small amount of dense precipitate was evident. Sample solution aliquots were transferred to polyethylene vials for various analyses by carefully withdrawing solution from the digestion vessels without disturbing the precipitate.

One nominally 1.2-g dry resin aliquot from each column was prepared for GEA in a calibrated 2-mL solution geometry. The samples were counted for an extended time of 60 hours to better detect isotopes of lower counting efficiency. The measurement accuracy of solid SL-644 loaded in this geometry was evaluated relative to ^{137}Cs analysis of aliquots of the acid-digested material.

(a) Normally, a temperature of 50°C is used for F-factor determination. To minimize dispersability, the resin samples were loosely capped during drying. Initially, the resins were dried at ambient temperature. Increasing the temperature to 50°C caused some mass loss from the cap, which interfered with the calculated resin mass loss. Thus, only the ambient drying temperature was used in the F-factor calculation. The calculated F-factor was consistent with other SL-644 F-factors obtained at 50°C.

The acid-digested samples were split and distributed to various workstations for analysis. The metal concentrations were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). Uranium was determined using a kinetic phosphorescence analyzer (KPA). Isotopes of ^{239}Pu, ^{241}Am, and $^{242+243}$Cm were determined, after radiochemical separations, by alpha spectrometry. Total alpha analysis was determined using ZnS scintillation detectors, and total beta was determined using gas-flow proportional counting. Table 3.3 summarizes specific CMC procedures used.

Table 3.3. Analysis Procedure Identification

Analyte	Procedure	Title
Acid digestion	RPG-CMC-137, Rev. 0	Nitric Acid and Hydrogen Peroxide Dissolution of Ion Exchange Resin SL-644
Metals by ICP-AES	RPG-CMC-211, Rev. 0	Determination of Elements by ICP-AES
Tc, Cs, and Cs isotopics by ICP-MS	PNL-SCO1, Rev. 1	ICP-MS Analysis
Gamma emitters	PNL-ALO-450, Rev. 1	GEA and Low Energy Photon Spectrometry
Pu, Am, and Cm	PNNL-ALO-417, Rev. 2	Separation of U, Am/Cm, and Pu and Actinide Screen by Extraction Chromatography
	PNL-ALO-496, Rev. 1	Precipitation Plating of Actinides for High-Resolution Alpha Spectrometry
	RPG-CMC-422, Rev. 1	Solutions Analysis: Alpha Spectrometry
U	RPG-CMC-4014, Rev. 1	Uranium by Kinetic Phosphorescence Analysis
Total alpha and total beta	RPG-CMC-4001, Rev. 0	Source Preparation for Gross Alpha and Gross Beta Analysis
	RPG-CMC-408, Rev. 1	Total Alpha and Beta Analysis

Sample preparations and instrumental calibration and analyses were conducted in a manner consistent with requirements delineated in PNWD's *Conducting Analytical Work in Support of Regulatory Programs*.

4.0 Results and Discussion

The following sections describe final elution from Column 2 and analysis of the Column 1 and 2 spent resin beds.

4.1 Column 2 Elution

Column 2 was calculated to contain 1910 µCi ^{137}Cs based on the integrated ^{137}Cs breakthrough from AP-104/SY-101 processing [Appendix A]. Table 4.1 summarizes the elution and water-rinse results, and the elution profile is shown in Figure 4.1. The ordinate in Figure 4.1 shows ^{137}Cs concentration values on a logarithmic scale to clearly delineate the large range of concentrations obtained. The abscissa is given in BVs relative to the expanded condition just before elution, where 1 BV is equal to 10.2 mL. Most of the ^{137}Cs was contained in elution BVs 3 through 6. The peak Cs concentration was found to be 127 µCi/mL. Integrating the elution peak resulted in 104% ^{137}Cs recovery in the eluate.(a) The final eluate sample contained 0.0127 µCi/mL ^{137}Cs.(b) The ^{137}Cs concentration in the water rinse significantly tailed off, indicating that the water matrix reduced Cs elution.

4.2 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 [17]. Table 4.2 shows the historical and current resin BV change history. The relative BVs did not change appreciably for similar feed conditions during the eight process cycles and during the current Column 2 elution processing. The BV in 0.5 M HNO_3 was relatively constant at 7.8 ± 0.3 mL. The BV in 0.25 M NaOH was relatively constant at 10.5 ± 0.3 mL.

Figure 4.2 shows the variation in BV as a function of the process step for both columns and all process testing. Each process step is denoted with a number corresponding to the number in Table 4.2. The volume contraction after the initial 0.5 M HNO_3 conditioning step and AW-101 processing became more pronounced with cycling as evidenced by comparing the AW-101 simulant run with the AP-101 run. After this initial cycling, however, the resin beds appeared to remain fairly consistent with respect to the shrink/swell characteristic.

The regeneration volume expansion at steps 72 and 73 appear to be suspect. However, the resin bed was regenerated with a larger volume of 0.25 M NaOH, 2.9 AVs or 6.5 BVs, as opposed to previous cycles where 2 AVs or 4.5 BVs were processed. The resin bed may also be experiencing greater shrink-swell characteristics with repeated processing and associated chemical degradation. By the time the resin was ready for removal from the column, the bed had packed down to the more typical 10.5-mL volume.

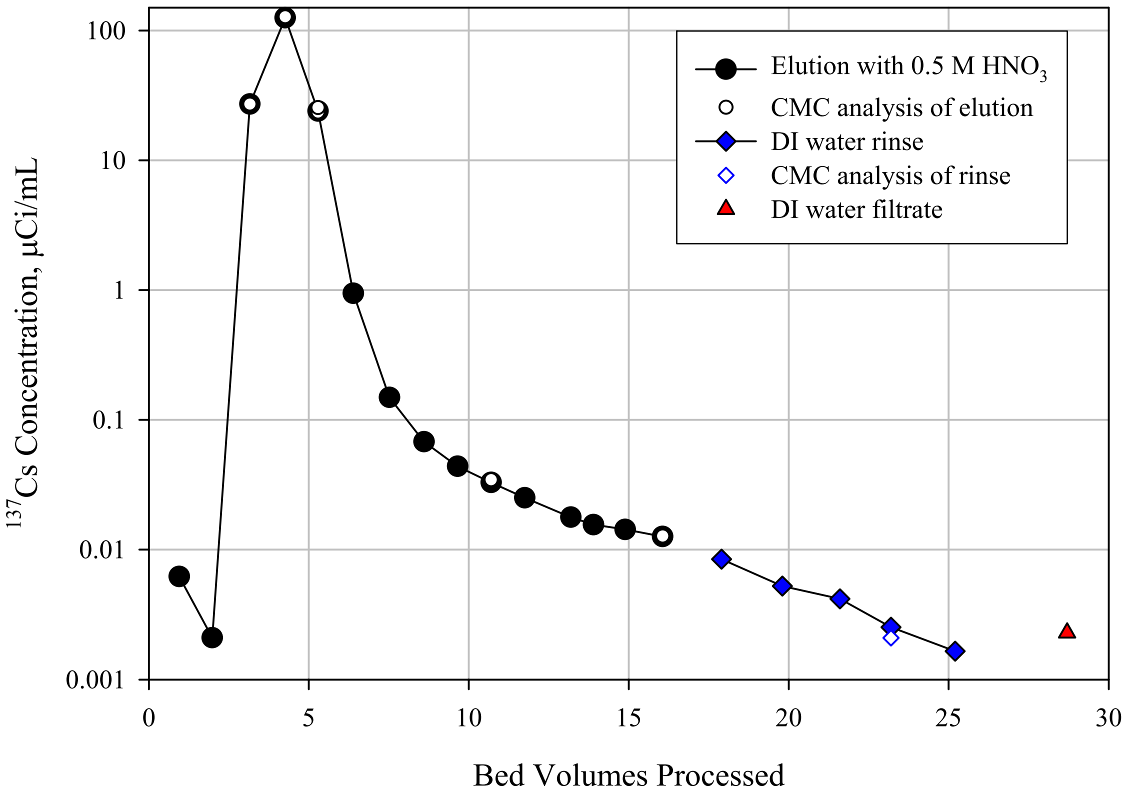
(a) The overall uncertainty in ^{137}Cs measurement is nominally 6% (2-σ) per sample. The calculated recovery at 104% ± 6% is within statistical uncertainty of 100% recovery.

(b) For comparison, the final elution sample ^{137}Cs concentration from Column 1 was 0.014 µCi/mL.

Table 4.1. ^{137}Cs Elution and Rinse Sample Results from Column 2

Column Feed	Cumulative BV	^{137}Cs, µCi/mL	CMC-measured ^{137}Cs, µCi/mL
0.5 M HNO_3	0.95	6.22E-3	--
	1.98	2.10E-3	--
	3.16	2.71E+1	2.70E+1
	4.26	1.25E+2	1.27E+2
	5.29	2.39E+1	2.44E+1
	6.39	9.44E-1	--
	7.52	1.49E-1	--
	8.60	6.78E-2	--
	9.65	4.39E-2	--
	10.7	3.30E-2	3.46E-2
	11.8	2.51E-2	--
	13.2	1.78E-2	--
	13.9	1.56E-2	--
	14.9	1.43E-2	--
	16.1	1.26E-2	1.27E-2
DI Water Rinse	17.9	8.45E-3	--
	19.8	5.23E-3	--
	21.6	4.19E-3	--
	23.2	2.53E-3	2.09E-3
	25.2	1.65E-3	--
DI Water Filtrate	28.7	2.29E-3	1.95E-3

BV = bed volume, 10.2 mL
“--” no data taken
CMC measurements from ASR 6768



Conditions:	SL-644 batch # 010319SMC-IV-73 212- to 425-µm dry particle size	
	Process temperature = 24°C	BV = 10.2 mL
	Flowrate = 1.1 BV/h	Eluant = 0.5 M HNO_3
	Total Cs loading = 1.9 mCi	

Figure 4.1. ^{137}Cs Elution and Eluant Rinse of Column 2

Table 4.2. SL-644 Bed Volumes

Feed	Process Step	010319SMC-IV-73 212-425 μm particle size	
		Column 1(a)	**Column 2(b)**
Initial Column Positions		**Lead Column, mL**	**Lag Column, mL**
Initial packing	1	10.9	10.9
0.5 M HNO_3	2	9.2	8.9
DI water	3	9.2	8.9
0.25 M NaOH	4	11.2	10.8
AW-101 simulant	5	10.2	10.0
0.1 M NaOH	6	10.9	10.7
DI water	7	10.9	10.9
0.5 M HNO_3	8	8.9	8.9
DI water	9	8.9	8.7
Re-fluidize bed	10	7.5	7.5
Place Columns in Hot Cell		**Lead Column, mL**	**Lag Column, mL**
0.25 M NaOH	11	11.0	10.9
DI water	12	10.5	11.0
0.5 M HNO_3	13	7.9	7.7
DI water	14	7.9	7.7
0.25 M NaOH	15	10.7	10.5
AP-101DF	16	9.7	9.7
0.1 M NaOH	17	10.5	10.4
DI water	18	10.4	10.5
0.5 M HNO_3	19	7.7	—
DI water	20	7.7	—
0.25 M NaOH	21	10.5	—
DI water	22	10.2	—
Switch Column Positions		**Lag Column, mL**	**Lead Column, mL**
0.25 M NaOH	23	10.5	10.4
AN-102/C-104	24	9.9	9.9
0.1 M NaOH	25	10.7	10.4
DI water	26	10.7	10.4
0.5 M HNO_3	27	—	7.7
DI water	28	—	7.5
0.25 M NaOH	29	—	10.2
DI water	30	—	10.4
Switch Column Positions		**Lead Column, mL**	**Lag Column, mL**
0.25 M NaOH	31	10.2	10.0
AZ-102C	32	9.5 (jumped to 10.4)	9.4
0.1 M NaOH	33	10.7	10.0
DI water	34	10.9	10.3
0.5 M HNO_3	35	8.1	—
DI water	36	8.2	—
0.25 M NaOH	37	10.4	—
DI water	38	10.7	—
0.5 M HNO_3	39	7.9	—
DI water	40	7.8	—
0.25 M NaOH	41	10.5	—
DI water	42	10.7	—

Table 4.2 (Contd)

Feed	Process Step	010319SMC-IV-73 212-425 μm particle size Column 1[a]	 Column 2[b]
Switch Column Positions		**Lag Column, mL**	**Lead Column, mL**
0.25 M NaOH	43	10.9	10.3
AZ-101, first test	44	10.2	9.5
0.1 M NaOH	45	10.9	10.5
DI water	46	10.9	10.7
0.5 M HNO_3	47	—	7.7
DI water	48	—	7.9
0.25 M NaOH	49	—	10.4
DI water	50	—	10.9
Switch Column Positions		**Lead Column, mL**	**Lag Column, mL**
0.25 M NaOH	51	10.9	10.5
AZ-101, second test	52	10.2	9.7
0.1 M NaOH	53	10.9	10.5
DI water	54	10.9	10.5
0.5 M HNO_3	55	8.4	—
DI water	56	8.5	—
0.25 M NaOH	57	11.0	—
DI water	58	11.0	—
Switch Column Positions		**Lag Column, mL**	**Lead Column, mL**
0.25 M NaOH	59	10.5	10.5
AP-104/SY-101, 1st test	60	9.9	10.0
0.1 M NaOH	61	10.5	10.7
DI water	62	10.7	10.5
0.5 M HNO_3	63	—	7.9
DI water	64	—	7.7
0.25 M NaOH	65	—	10.7
DI water	—	—	Not performed[c]
Switch Column Positions		**Lead Column, mL**	**Lag Column, mL**
0.25 M NaOH	66	10.4	10.9
AP-104/SY-101, 2nd test	67	9.7	9.9
0.1 M NaOH	68	10.4	10.7
DI water	69	10.4	10.7
0.5 M HNO_3	70	7.9	—
DI water	71	7.9	—
0.25 M NaOH	72	11.2	—
DI water	73	11.6	—
Place Lag Column in Lead Position		**Lead Column Removed**	**Lead Column, mL**
DI water	74	10.5	10.2
0.5 M HNO_3	75	—	7.5
DI water	76	—	7.4

(a) Calculated resin mass after washing, dry Na-form: 2.46 g.
(b) Calculated resin mass after washing, dry Na-form: 2.48 g.
(c) AP-104/SY-101 feed started immediately.
"—" not applicable

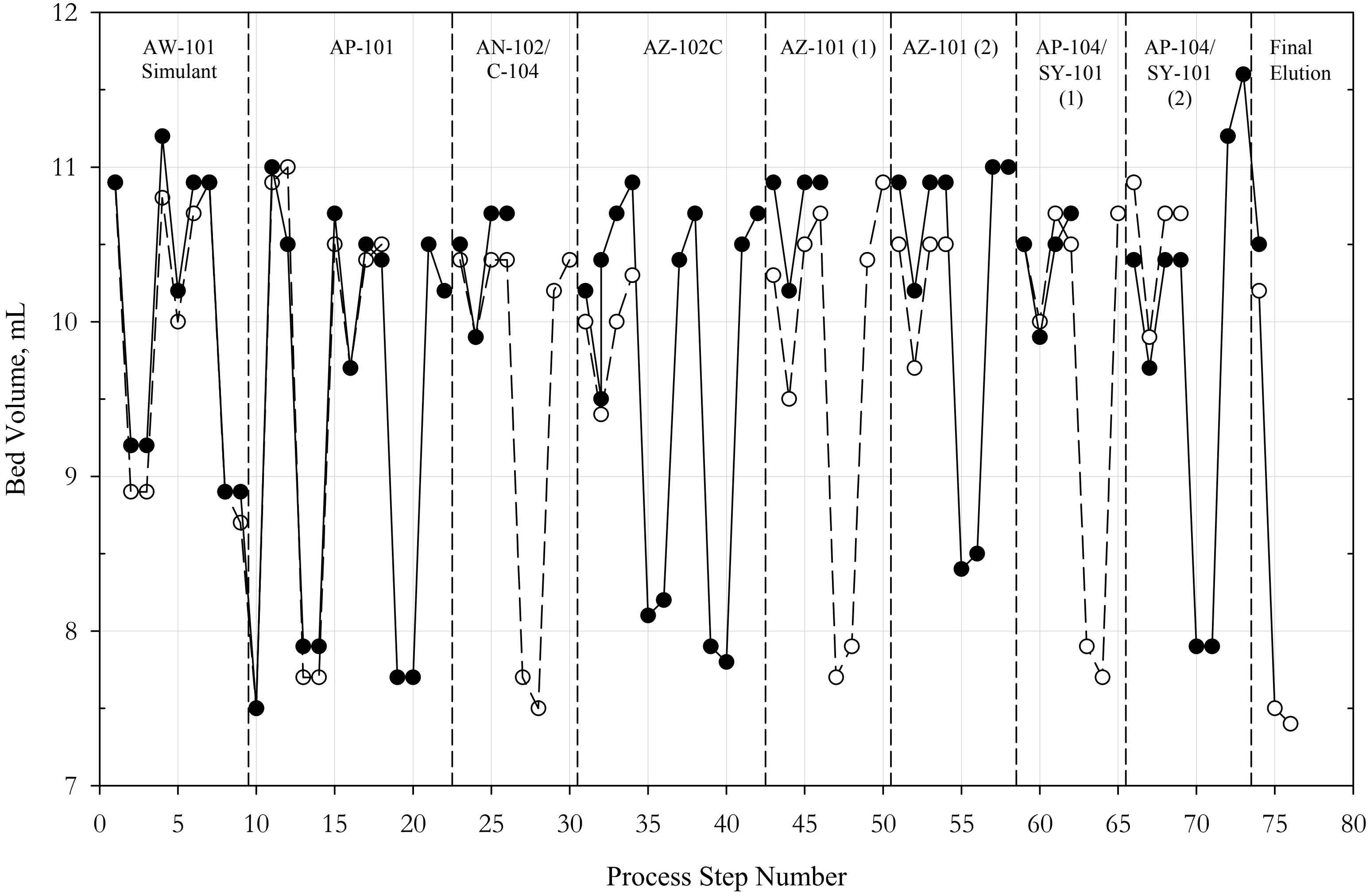


Figure 4.2. Comparison of BVs of the Lead and Lag Columns for all Test Cycles (SL-644 Batch 010319SMC-IV-73, 212- to 425-µm; Solid Points Indicate Column 1, Hollow Points Indicate Column 2)

4.3 Resin Recovery

The dry resin masses recovered from each column were determined from the mass of air-dried free-flowing resin obtained multiplied by its F-factor. The resin mass fraction (mass of dry recovered resin to mass of dry resin added to column) were calculated for each column according to Equation 4.1

$$M_l = \frac{M_i - M_f}{M_i} * 100 \tag{4.1}$$

where M_l is the mass loss fraction, M_i is the initial mass, and M_f is the final mass.

Results are shown in Table 4.3. The average mass loss was 9.6%. Given a total of 8 process cycles, the mass loss corresponds to 1.2% per cycle. This is consistent with what Arm et al. reported (1.4% mass loss per process cycle) during a chemical degradation study (based on a 25-cycle test) [18].

Table 4.3. Recovered Resin Masses

Column	Initial dry resin mass, g[a]	Recovered net mass, g[c]	F-factor	Recovered dry resin mass, g	Calculated mass loss, %
Column 1 (Na-form)	2.46[b]	2.314	0.950	2.20	10.6
Column 2 (H-form)	1.98	2.117	0.854	1.81	8.6

(a) Both resin beds were slurried into their columns in the Na form, but each aliquot was weighed in the as-received form before conversion. The initial resin masses were calculated by multiplying the weighed as-received form resin (4.17 g and 4.20 g, respectively) by the F-factor (0.877), the mass loss on washing factor (0.538) and, in the case of Na-form resin, the mass increase factor on conversion to Na-form (1.25) as shown in Equation 2.1.

(b) Possible high bias where $I_{Na} = 1.25$. The potential high bias relates to the Na-form F-factor determination where drying was conducted at ambient temperature under vacuum.

(c) Air-dried, free-flowing state.

4.4 Resin-Bed Density

The SL-644 dry-bed resin densities were determined from the ion exchange processing test. It was calculated from the column dry-bed resin mass (M_c) and the resin BV according to Equation 4.2.

$$\rho = \frac{M_c}{BV} \tag{4.2}$$

where M_c is the dry SL-644 mass in the resin bed (discussed in Section 2.2), and BV is the resin BV in the feed (discussed in Section 4.2).

The calculated dry-bed densities are summarized in Table 4.4. The dry-bed densities were also calculated relative to the recovered resin masses and are shown parenthetically.

Table 4.4. Dry Bed Density

Property	010319SMC-IV-73, Column 1	010319SMC-IV-73, Column 2
Column resin mass, g, as-received	4.17	4.20
Corrected resin mass, M_c, in column, g (Na-form)	2.46 (2.20)	2.48
Corrected resin mass, M_c, in column, g (H-form)	1.97	1.98 (1.81)
Bed volume, Na-form in DI water, mL	10.5	10.2
Bed volume, 0.5 M HNO_3, mL	Not performed	7.5
Dry Bed Density, ρ		
Na-form in DI water, g/mL (Na-form mass basis)	0.234 (0.210)	0.243
0.5 M HNO_3, g/mL (H-form mass basis)	Not performed	0.264 (0.241)
Parenthetical values are based on the recovered resin from the columns after eight process cycles.		

4.5 Column 2 Filtrate Analysis

The water contacted for 6 days with the Column 2 spent resin was analyzed using IC to determine if corrosive anions leached from the resin. The anion results are reported in Table 4.5. The analyte results reported on a volume basis were converted to a dry resin mass basis according to Equation 4.3.

$$C_R = \frac{C_L * V_L}{m} \tag{4.3}$$

where C_R = analyte concentration in dry resin, µg/g
C_L = average analyte concentration in water leach solution, µg/mL
V_L = leach solution volume, 35.3 mL
m = dry resin mass for Column 2, 1.81 g.

Nitrate was present in the highest concentration and was probably left over from residual eluant (0.5 M HNO_3) on the column. Trace amounts of chloride and sulfate were also present.

4.6 Spent Resin Analysis

The inorganic analysis results for Column 1 and Column 2 are summarized in Table 4.6. The results are based on the dry-resin mass.[a] The process blank (reagents only, no resin), sample, sample duplicate, and average results are provided along with the calculated µmoles analyte per gram of dry resin. The metals analysis by ICP-AES targeted Ag, As, Ba, Cd, Cr Cs, Na, Ni, Pb, Se, Th, and U. Because the ICP-AES measures a much larger suite of metals (and some non-metals), their concentrations are reported opportunistically; their results, however, were not evaluated with respect to QC.

(a) Spent resin generated in the plant will probably contain residual water. The residual water would effectively increase the sample mass and result in a corresponding decreased metal concentration.

Table 4.5. Anion Analysis of Column 2 Water Leach Solution

Analyte	Sample	Sample Duplicate	Average	Concentration relative to dry resin mass
	µg/mL	µg/mL	µg/mL	µg/g[(a)]
Bromide	<0.013	<0.013	<0.013	<0.25
Chloride	0.41 J[(b)]	0.31 J[(b)]	0.36 J[(b)]	7.0 J[(b)]
Fluoride	<0.013	<0.013	<0.013	<0.25
Nitrite	<0.025	<0.025	<0.025	<0.49
Nitrate[(c)]	13.0	12.9	13.0	253
Phosphate	<0.025	<0.025	<0.025	<0.49
Sulfate	0.72	0.72	0.72	14
Oxalate	<0.025	0.038 J[(d)]	0.038 J[(d)]	0.74 J[(d)]

(a) Based on a dry resin mass basis.

(b) Chloride results are J-flagged because the RPD of the duplicate results (28%) exceeded the QC criterion of <20%.

(c) Nitrate is most probably from residual eluant (0.5 M HNO_3).

(d) The oxalate concentration was calculated from the one detected value, 0.038 µg/mL, which is J-flagged as estimated because the result was greater than the method detection limit (MDL) but less than the estimated quantitation limit (EQL).

The Ag analysis result must be used with caution because the Ag matrix spike only recovered 50% of the added Ag. The blank spike and post spikes recovered at 104%. It must be assumed that the low Ag matrix-spike recovery was due to a matrix effect. Silver is normally difficult to maintain in solution because it easily forms insoluble compounds and easily reduces to the insoluble ground state. Chloride and sulfate were shown to be present in the water leach solution of Column 2 resin material. Silver easily forms insoluble complexes with these anions. The slight amount of precipitate noted during the digestion preparation may be related to the loss of Ag from solution.

Sodium was the most abundant metal in Column 1 because it was removed in the Na-form. Cr was the second most abundant metal in Column 1 resin and the most abundant metal in Column 2 resin. Zr, Pd, Pb, and Ag were also present. Generally the concentrations of common analytes of interest (including Ag, Ba, Cd, Cr, and Pb) were higher, the Na and Ni concentrations were consistent, and Cu concentrations were lower than those previously reported by Kurath and Wagner [18].

To ascertain that the metals concentrations were not due to residual AP-104/SY-101 tank waste in the system, the relative mole ratios of metals to Na were calculated for each column and the tank waste. These results are provided in Table 4.7. In most cases, the spent resin analyte to Na mole ratios were greater than those of the last tank waste processed. This indicated that the analyte was concentrated on the resin. This concentration effect was especially apparent with respect to Column 2 where the resin was removed in the H-form as opposed to the Na-form.

Table 4.6. Metals Analysis Summary for Spent Resin

	Analysis	Process Blank	Column 1, Na-form(a, b)				Column 2, H-form(a, b)			
			Sample	**Duplicate**	**Average**	**Average**	**Sample**	**Duplicate**	**Average**	**Average**
Analyte	**Method**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µmole/g**	**µg/g**	**µg/g**	**µg/g**	**µmole/g**
Ag(c)	ICP-AES	<0.60	47.4 J	50.5 J	49.0 J	0.45 J	42.2 J	50.8 J	46.5 J	0.43 J
As	ICP-AES	<4.3	[6.7]	[8.4]	[7.6]	[0.10]	[13]	[14]	[14]	[0.18]
Ba	ICP-AES	<0.13	12.6	13.0	12.8	0.093	[1.2]	1.4	1.3	0.0095
Cd	ICP-AES	<0.45	[1.4]	[1.5]	[1.5]	[0.013]	[3.1]	[3.1]	[3.1]	[0.028]
Cr	ICP-AES	<0.72	2,420	2,460	2,440	46.9	3,930	4,050	3,990	76.7
^{133}Cs	ICP-MS	<6E-4	1.83	1.76	1.80	0.0135	<0.070	<0.072	<0.071	<5E-4
Total Cs	ICP-MS	NA	2.34(d)	2.24(d)	2.29(d)	0.0172(d)	NA(d)	NA(d)	NA(d)	NA(d)
Na	ICP-AES	[32]	82,500	88,600	85,550	3,720	179	167	173	7.52
Ni	ICP-AES	<1.5	[10]	[11]	[11]	[0.18]	43.2	44.9	44.0	0.75
Pb	ICP-AES	[3.1]	54.9	57.4	56.2	0.27	169	174	172	0.83
Se	ICP-AES	<4.3	<4.0	[4.3]	[4.3]	[0.054]	[5.5]	[7.8]	[6.6]	[0.084]
Th	ICP-AES	<3.0	<2.8	<2.9	<2.8	<0.012	<3.2	<3.3	<3.2	<0.014
U	ICP-AES	<64	<60	<62	<60	<0.25	<69	<71	<69	<0.29
U	KPA	<3.0	<3.0	<3.0	<3.0	<0.013	3.86	4.33	4.10	0.0172
Opportunistic Analytes(e)										
Al	ICP-AES	<3.7	[41]	[45]	[43]	[1.6]	[47]	[49]	[48]	[1.8]
B	ICP-AES	<1.2	316	339	328	30.3	11.9	12.1	12.0	1.11
Bi	ICP-AES	<3.0	[11]	[12]	[12]	[0.055]	[9.3]	[10]	[10]	[0.046]
Ca	ICP-AES	<5.4	[39]	[38]	[39]	[0.96]	[27]	[43]	[35]	[0.87]
Co	ICP-AES	<0.60	8.51	8.69	8.60	0.15	10.5	10.7	10.6	0.18
Cu	ICP-AES	<0.83	26.9	25.5	26.2	0.41	42.5	45.6	44.0	0.69
Fe	ICP-AES	<1.2	20.5	19.2	19.8	0.36	52.6	52.5	52.6	0.94
K	ICP-AES	<119	<112	<116	<114	<2.9	<128	<132	<130	<3.3
Mn	ICP-AES	<0.074	[0.5]	[0.5]	[0.5]	[0.009]	[1.4]	[1.3]	[1.4]	[0.025]
Mo	ICP-AES	<0.68	[1.5]	[2.1]	[1.8]	[0.019]	[1.2]	[1.4]	[1.3]	[0.014]

Table 4.6 (Contd)

Analyte	Analysis Method	Process Blank µg/g	Column 1, Na-form[a, b]				Column 2, H-form[a, b]			
			Sample µg/g	Duplicate µg/g	Average µg/g	Average µmole/g	Sample µg/g	Duplicate µg/g	Average µg/g	Average µmole/g
Opportunistic Analytes[e]										
P	ICP-AES	76	114	118	116	3.75	125	123	124	4.00
Pd	ICP-AES	<15	189	[44]	[117]	[1.1]	[57]	[61]	[59]	[0.55]
Ru	ICP-AES	<2.4	[10]	[9.4]	[10]	[0.10]	[13]	[14]	[14]	[0.13]
Sb	ICP-AES	<3.3	<3.1	<3.2	<3.2	<0.026	<3.6	<3.7	<3.7	<0.030
Si	ICP-AES	<3.6	559	281	420	15.0	[14]	[23]	[19]	[0.66]
Sr	ICP-AES	<0.18	[0.71]	[0.76]	[0.74]	[0.0084]	[0.31]	[0.29]	[0.30]	[0.0034]
Te	ICP-AES	<6.0	<5.6	<5.8	<5.7	<0.045	[6.8]	[7.9]	[7.4]	[0.058]
Ti	ICP-AES	<0.30	[1.5]	[1.5]	[1.5]	[0.031]	[2.6]	[2.7]	[2.7]	[0.055]
Tl	ICP-AES	<2.5	[4.0]	[5.5]	[4.8]	[0.023]	[6.0]	[7.1]	[6.6]	[0.032]
V	ICP-AES	<0.46	<0.44	<0.45	<0.45	<0.0087	[0.69]	[0.75]	[0.72]	[0.014]
Zn	ICP-AES	<0.83	[2.6]	[2.7]	[2.7]	[0.041]	[3.6]	[4.7]	[4.2]	[0.063]
Zr	ICP-AES	<0.51	312	312	312	3.42	370	357	363.5	3.98

(a) Results are presented on a dry resin mass basis.

(b) Bracketed results were greater than the MDL but less than the EQL. The less-than values (<) indicate that the results were less than the MDL: reported values are the instrument detection limits multiplied by the sample dilution factor. Overall errors for values greater than the EQL were estimated to be within 15%. Errors for values less than the EQL but greater than the MDL were likely to exceed 15%.

(c) The Ag results are J-flagged (estimated value) because the matrix-spike recovery was low (50%). The blank spike and post spike recovered at 104%. It must be assumed that the low Ag matrix-spike recovery was due to a matrix effect.

(d) Based on ^{133}Cs isotopic abundance of 78.2% and 78.6% for the Column 1 sample and sample duplicate, respectively. Column 2 sample total Cs could not be estimated because the ^{133}Cs concentration was less than the MDL.

(e) Opportunistic analytes are reported as a courtesy. Results were not fully evaluated relative to QC criteria.

NA = not applicable

Data are from ASR 6740 RPL Sample ID = 03-0858 and 03-0859 (Na-form sample and duplicate) and 03-0860 and 03-0861 (H-form sample and duplicate).

Table 4.7. Relative Mole Ratios of Metals in Spent Resin

	AP-104/SY-101 Mole ratios	**Column 1**	**Mole ratios**	**Column 2**	**Mole ratios**
Analyte	**Analyte: Na(b)**	**µmoles/g(a, b)**	**Analyte: Na(b)**	**µmoles/g(a, b)**	**Analyte: Na(b)**
Ag(c)	<1.2E-6	0.45 J(c)	1.2E-4 J(c)	0.43 J(c)	5.7E-2 J(c)
As	<1.7E-5	[0.10]	[2.7E-5]	[0.18]	[2.4E-2]
Ba	<3.7E-7	0.093	2.5E-5	0.0095	1.3E-3
Cd	8.23E-6	[0.013]	[3.5E-6]	[0.028]	[3.7E-3]
Cr	1.59E-3	46.9	1.3E-2	76.7	1.0E+1
Cs (total)	1.40E-5	0.0172	4.6E-6	(d)	(d)
Na	1.0E+0	3720	1.0E+0	7.52	1.0E+0
Ni	1.17E-4	[0.18]	[4.8E-5]	0.75	1.0E-1
Pb	[8.5E-6]	0.27	7.3E-5	0.83	1.1E-1
Se	<1.6E-5	[0.054]	[1.5E-5]	[0.084]	[1.1E-2]
Th	<2.2E-5	<0.012	<3.2E-6	<0.014	<1.8E-3
U (ICP-AES)	<4.2E-5	<0.25	<6.8E-5	<0.29	<3.9E-2
U (KPA)	8.27E-6	<0.013	<3.5E-6	0.0172	2.3E-3
Opportunistic Analytes(e)					
Al	8.07E-2	[1.6]	[4.3E-4]	[1.8]	[2.4E-1]
B	9.05E-4	30.3	8.15E-3	1.11	1.5E-1
Bi	<2.4E-6	[0.055]	[1.5E-5]	[0.046]	[6.1E-3]
Ca	3.43E-4	[0.96]	[2.6E-4]	[0.87]	[1.2E-1]
Co	<4.1E-6	0.15	3.92E-5	0.18	2.4E-2
Cu	<2.0E-6	0.41	1.11E-4	0.69	9.2E-2
Fe	[1.3E-5]	0.36	9.56E-5	0.94	1.3E-1
K	9.43E-3	<2.9	<7.8E-4	<3.3	<4.4E-1
Mn	<4.6E-6	[0.0087]	[2.3E-6]	[0.025]	[3.3E-3]
Mo	1.04E-4	[0.019]	[5.0E-6]	[0.014]	[1.8E-3]
P	8.92E-3	3.75	1.01E-3	4.00	5.3E-1
Pd	<3.6E-5	[1.1]	[2.9E-4]	[0.55]	[7.4E-2]
Ru	<5.5E-5	[0.10]	[2.6E-5]	[0.13]	[1.8E-2]
Sb	<2.1E-5	<0.026	<7.0E-6	<0.030	<4.0E-3
Si	[6.9E-4]	15.0	4.02E-3	[0.66]	[8.8E-2]
Sr	[9.6E-7]	[0.0084]	[2.3E-6]	[0.0034]	[4.6E-4]
Te	<2.0E-5	<0.045	<1.2E-5	[0.058]	[7.7E-3]
Ti	2.6E-6	[0.031]	[8.4E-6]	[0.055]	[7.4E-3]
Tl	<1.2E-5	[0.023]	[6.2E-6]	[0.032]	[4.3E-3]
V	<6.1E-6	<0.0087	<2.3E-6	[0.014]	[1.9E-3]
Zn	<3.9E-6	[0.041]	[1.1E-5]	[0.063]	[8.4E-3]
Zr	<2.8E-6	3.42	9.20E-4	3.98	5.3E-1

Table 4.7 (Contd)

(a) Results are presented on a dry-resin-mass basis.
(b) Bracketed results were greater than the MDL but less than the EQL. The less-than values (<) indicate that the results were less than the MDL: reported values were the instrument detection limits multiplied by the sample dilution factor. Overall errors for values greater than the EQL were estimated to be within 15%. Errors for values less than the EQL but greater than the MDL were likely to exceed 15%.
(c) The Ag results are J-flagged (estimated value) because the matrix-spike recovery was low (50%). The blank spike and post spike recovered at 104%. It must be assumed that the low Ag matrix spike recovery was due to a matrix effect.
(d) The Cs isotopic ratio was not known, and total Cs could not be estimated.
(e) Opportunistic analytes are reported as a courtesy. Results were not fully evaluated relative to QC criteria.

The total metals analysis should not be confused with metals solubilized during a toxicity characteristics leach procedure (TCLP). A TCLP and analysis study using bounding analyte concentrations has been previously reported by Arm et al. [19]. In Arm's study, all leached toxicity characteristic metals (Ag, As, Ba, Cd, Cr, Hg Pb, and Se) were below the regulatory threshold. If all toxicity characteristic metals found in the Column 1 and 2 spent resins were successfully solubilized in a TCLP, then the waste form could be compared to the regulatory thresholds. This comparison is given in Table 4.8 where a 20X dilution was applied to each analyte concentration converting from the solid phase concentration to the projected liquid phase concentration. For both columns, the Cr concentration would have exceeded the regulatory threshold. The Pb concentration in Column 2 would have exceeded the regulatory threshold. Because the reported Ag concentration could be biased 50% low, the worst-case TCLP Ag concentration could closely approach the regulatory level. Otherwise, all toxic metals would be below the regulatory threshold if fully solubilized, consistent with results reported by Arm et al. [19].

Table 4.8. Projected Worst-Case Toxicity Characteristic

Toxic metal	Regulatory threshold, mg/L	Column 1[(a)] Analyte conc., µg/g[(b)]	Column 1[(a)] Analyte diluted to 20X, mg/L	Column 1[(a)] Ratio diluted analyte to threshold	Column 2[(a)] Analyte conc., µg/g[(b)]	Column 2[(a)] Analyte diluted to 20X, mg/L	Column 2[(a)] Ratio diluted analyte to threshold
Ag[(c)]	5.0	49.0 J	2.45 J	0.49 J	46.5 J	2.33 J	0.46 J
As	5.0	[7.6]	[0.38]	[0.076]	[14]	[0.70]	[0.14]
Ba	100	12.8	0.640	0.00064	1.3	0.065	0.00065
Cd	1.0	[1.5]	[0.075]	[0.075]	[3.1]	[0.16]	[0.16]
Cr	5.0	2440	122	**24.4**	3990	200	**39.9**
Pb	5.0	56.2	2.81	0.562	172	8.6	**1.72**
Se	1.0	[4.3]	[0.22]	[0.22]	[6.6]	[0.33]	[0.33]

(a) Bracketed results were greater than the MDL but less than the EQL. The less-than values (<) indicate that the results were less than the MDL: reported values were the instrument detection limits multiplied by the sample dilution factor. Overall errors for values greater than the EQL were estimated to be within 15%. Errors for values less than the EQL but greater than the MDL were likely to exceed 15%.
(b) Results are presented on a dry-resin-mass basis.
(c) The Ag results are J-flagged (estimated value) because the matrix-spike recovery was low (50%). It must be assumed that the low Ag matrix spike recovery was due to a matrix effect.
Note: Bold values indicate exceedance of regulatory threshold.

Radioisotopic constituents were measured directly on nominally 1.2 g resin sub-samples (i.e., no processing) and on acid-digested aliquots. Results are listed in Table 4.9. Direct analysis of Column 1 resulted in lower concentrations of ^{60}Co and ^{137}Cs relative to the acid-digested samples. Direct analysis of Column 2 resulted in comparable ^{60}Co and ^{137}Cs concentrations relative to acid-digested subsamples. Sample heterogeneity was assumed to be the main contributor to the difference in Column 1 results. The average ^{137}Cs concentrations were calculated by averaging the direct resin analysis result with the duplicate acid-digested analysis results.

The major radioisotopic constituent was ^{137}Cs averaging 21.9 µCi/g for Column 1 (Na-form) and 1.80 µCi/g for Column 2 (H-form). Because of the lower ^{137}Cs concentration on Column 2, lower concentrations of other gamma-emitting isotopes could be detected, including ^{60}Co, ^{154}Eu, ^{155}Eu, ^{237}Np, and ^{241}Am. The Column 1 resin average ^{137}Cs concentration determined by GEA (21.9 µCi/g) was in good agreement with the ICP-MS ^{137}Cs concentration (24.4 µCi/g) calculated from the measured ^{133}Cs concentration and isotopic distribution. The total beta activity measured on Column 1 (21.4 µCi/g) was approximately equal to the sum of ^{137}Cs and ^{60}Co (22.0 µCi/g), indicating that all beta-activity sources could be identified.(a) The total beta activity measured on Column 2 (2.7 µCi/g) was significantly higher than the sum of identified beta emitters, ^{60}Co, ^{99}Tc, ^{134}Cs, and ^{137}Cs (2.0 µCi/g), indicating that 26% of the total beta activity source(s) was not identified.

In contrast to the relative Cs concentrations, the total alpha activity found on Column 1 was nearly an order of magnitude less than that found on Column 2. The total alpha activities on both resin beds were largely accounted for by the sum of Pu, Am, and Cm isotopes. Column 1 sum of Pu, Am, and Cm (1.12E-2 µCi/g) resulted in 94% ± 7% of the total alpha activity; Column 2 sum of Pu, Am, and Cm (1.03E-1 µCi/g) resulted in 92% ± 4% of the total alpha activity. The U contribution to the total alpha activity was calculated based on the AP-104 U isotopic ratios and the measured Column 2 U concentration and was found to be negligible.

The ^{137}Cs concentrations on both resin beds were lower than results reported by Arm (37 µCi/g projected for Envelope A and 50 µCi/g projected for Envelope B) [19], and Column 1 results were equivalent to results reported by Kurath (21.3 µCi/g) [18]. The relatively lower Cs concentration determined for Column 2 (in spite of a shorter final elution than for Column 1) was most likely due to the differences in processing conditions during the last three cycles..

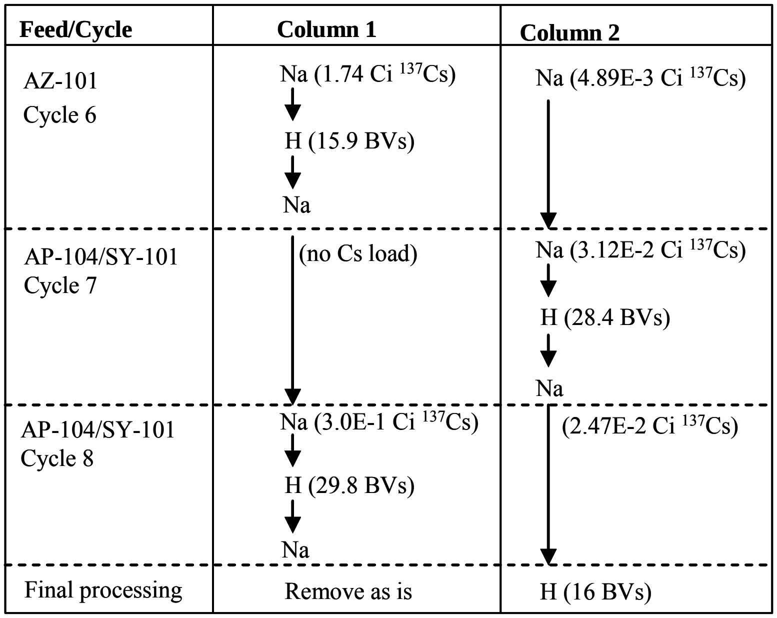
Column 1 was loaded with over 33 times more ^{137}Cs (2.04 Ci) than Column 2 (6.08E-2 Ci) during the last three process cycles (see Table 2.5). Column 2 was the lag column for the second AZ-101 processing (Cycle 6) so was not heavily loaded with Cs during this cycle; Column 2 was then moved to the lead position and loaded very briefly with AP-104/SY-101 feed, resulting in a very small ^{137}Cs load. It was then eluted with a larger volume than normal (28 BV; see Sec. 2.3, Cycle 7 discussion) and moved to the lag position for the second AP-104/SY-101 processing (Cycle 8). During this cycle, it again received only a small ^{137}Cs loading.

Another mechanism aiding Cs removal from Column 2 may be associated with resin cycling between the Na-form and H-form. Column 2 had been cycled repeatedly between the H-form and the Na-form

---

(a) Total beta sources were measured as dry preparations using gas-flow proportional counting. Thus volatile and low-energy beta sources are excluded from this comparison.

with correspondingly minimal Cs loading. The expansion and contraction may help remove Cs from exchange sites deep in the resin particle. Column 1 experienced minimal form changes while exchanging a large quantity of Cs. The resin form changes as a function of process cycle (last three cycles) and Cs loading are summarized in Figure 4.3.



Feed/Cycle	**Column 1**	**Column 2**
AZ-101 Cycle 6	Na (1.74 Ci ^{137}Cs) ↓ H (15.9 BVs) ↓ Na	Na (4.89E-3 Ci ^{137}Cs) ↓
AP-104/SY-101 Cycle 7	↓ (no Cs load)	Na (3.12E-2 Ci ^{137}Cs) ↓ H (28.4 BVs) ↓ Na
AP-104/SY-101 Cycle 8	Na (3.0E-1 Ci ^{137}Cs) ↓ H (29.8 BVs) ↓ Na	↓ (2.47E-2 Ci ^{137}Cs)
Final processing	Remove as is	H (16 BVs)

Figure 4.3. Final Three Process Cycles Summarizing Cs Load and Resin Forms.

Table 4.9. Radioisotopic Analysis of Spent Resin

Radionuclide	Analysis Method	Column 1, Na-form(a)				Column 2, H-form(a)			
		Direct Analysis µCi/g (2-σ error)	Acid Digest µCi/g (2-σ error)	Acid digest duplicate µCi/g (2-σ error)	Average µCi/g (2-σ error)	Direct Analysis µCi/g (2-σ error)	Acid Digest µCi/g (2-σ error)	Acid digest Duplicate µCi/g (2-σ error)	Average µCi/g (2-σ error)
^{60}Co	GEA	1.05E-1 (4%)	1.45E-1 (2%)	1.42E-1 (2%)	1.31E-1 (2%)	1.77E-1 (4%)	1.72E-1 (4%)	1.76E-1 (4%)	1.75E-1 (4%)
^{99}Tc	ICP-MS	NA	9.61E-2 (15%)	9.42E-2 (15%)	9.52E-2 (15%)	NA	8.40E-2 (15%)	8.57E-2 (15%)	8.48E-2 (15%)
^{106}Ru	GEA	< 2E-2	<8E-2	<5E-2	<2E-2	1.87E-2 (8%)	<3E-2	<2E-2	1.87E-2 (8%)
^{113m}Cd	GEA	< 6E+0	<4E+1	<2E+1	<6E+0	<4E-1	<2E+1	<7E+0	<4 E-1
^{125}Sb	GEA	< 6E-3	<5E-2	<3E-2	<6E-3	<5E-4	<2E-2	<8E-3	<5E-4
^{126}Sn/Sb	GEA	< 5E-4	<3E-2	<2E-2	<5E-4	<4E-4	<2E-2	<1E-2	<4E-4
^{134}Cs	GEA	1.98E-3 (14%)	<3E-3	<2E-3	1.98E-3	3.51E-4 (12%)	<3E-3	<2E-3	3.51E-4 (12%)
^{137}Cs	GEA	1.68E+1 (8%)	2.49E+1 (8%)	2.40E+1 (8%)	2.19E+1 (8%)	1.87E+0 (6%)	1.76E+0 (6%)	1.78E+0 (6%)	1.80E+0 (6%)
^{152}Eu	GEA	<4E-4	<5E-3	<3E-3	<4E-4	<8E-5	<5E-3	<3E-3	<8E-5
^{154}Eu	GEA	<4E-4	<3E-3	<3E-3	<4E-4	9.13E-3 (4%)	<5E-3	<3E-3	9.13E-3 (4%)
^{155}Eu	GEA	<5E-3	<3E-2	<2E-2	<5E-3	5.75E-3 (8%)	<2E-2	<7E-3	5.75E-3 (8%)
^{226}Ra	GEA	<4E-3	<3E-2	<2E-2	<4E-3	< 4E-4	<9E-3	<5E-3	<4E-4
^{227}Ac(b)	GEA	<1E-2	<6E-2	<4E-2	<1E-2	<6E-4	<2E-2	<2E-2	<6E-4
^{228}Ra(b)	GEA	<2E-1	<8E-2	<5E-2	<2E-1	<8E-4	<3E-2	<2E-2	<8E-4
^{231}Pa	GEA	<6E-3	<4E-1	<2E-1	<6E-3	<4E-3	<2E-1	<7E-2	<4E-3
^{237}Np	GEA	<4E-3	<3E-2	<2E-2	<4E-3	7.94E-4 (16%)	<8E-3	<5E-3	7.94E-4 (16%)
^{241}Am	GEA	<3E-2	<4E-2	<3E-2	<3E-2	1.36E-2 (8%)	<2E-2	<1E-2	1.36E-2 (8%)
^{241}Am	Separations and α spec.	NA	1.56E-3 (16%)	1.60E-3 (20%)	1.58E-3 (13%)	NA	1.33E-2 (40%)	1.44E-2 (40%)	1.39E-2 (28%)
^{238}Pu	Separations and α spec.	NA	9.75E-4 (12%)	1.04E-3 (14%)	1.01E-3 (9%)	NA	8.82E-3 (16%)	7.20E-3 (24%)	8.01E-3 (14%)
$^{239+240}$Pu	Separations and α spec.	NA	8.28E-3 (12%)	8.51E-3 (6%)	8.39E-3 (7%)	NA	7.95E-2 (6%)	7.77E-2 (8%)	7.86E-2 (5%)
^{242}Cm	Separations and α spec.	NA	<6E-5	<9E-5	<6E-5	NA	<1E-3	<8E-4	<8E-4

Table 4.9 (Contd)

		Column 1, Na-form[a]				**Column 2, H-form**[a]			
		Direct analysis	**Acid digest**	**Acid digest duplicate**	**Average**	**Direct analysis**	**Acid digest**	**Acid digest duplicate**	**Average**
Radionuclide	**Analysis Method**	**µCi/g (2-σ error)**	**µCi/g (2-σ error)**	**µCi/g (2-σ error)**	**µCi/g (2-σ error)**	**µCi/g (2-σ error)**	**µCi/g (2-σ error)**	**µCi/g (2-σ error)**	**µCi/g (2-σ error)**
$^{243+244}$Cm	Separations and α spec.	NA	1.94E-4 (42%)	2.77E-4 (48%)	2.36E-4 (32%)	NA	3.01E-3 (50%)	2.10E-3 (62%)	2.56E-3 (40%)
Total alpha	Scintillation count	NA	1.13E-2 (22%)	1.28E-2 (20%)	1.20E-2 (20%)	NA	1.15E-1 (6%)	1.09E-1 (6%)	1.12E-1 (6%)
Total beta	Gas-flow prop. count	NA	2.14E+1 (8%)	2.13E+1 (6%)	2.14E+1 (6%)	NA	2.63E+0 (8%)	2.77E+0 (8%)	2.70E+0 (8%)

(a) Results are presented on a dry-resin mass basis.

(b) Detection limits for ^{227}Ac and ^{228}Ra were based on equilibrium daughter emissions. Neither ^{227}Ac nor ^{228}Ra can be seen directly by GEA. The ^{227}Ac (half-life = 21.8 y) decays to ^{223}Ra (half-life = 11.4 days), and the MDA is based on the 269-keV gamma from ^{223}Ra. The ^{228}Ra (half-life = 5.75 y) decays to ^{228}Ac (half-life = 6.1 h), and the MDA is based on the 338 keV gamma from ^{228}Ac.

Data are from ASR 6740 RPL Sample ID 03-0854 (direct analysis Na-form), 03-0856 (direct analysis H-form), 03-0858 and 03-0859 (Na-form acid digest sample and duplicate), and 03-0860 and 03-0861 (H-form acid digest sample and duplicate).

To ascertain that the radionuclide content was not due to residual AP-104/SY-101 tank waste in the system, the relative microcurie concentrations of radionuclides to Na concentration (µmoles/g) were calculated for each column and the tank waste. These results are provided in Table 4.10. As with the metals, the Column 2 ^{60}Co, ^{99}Tc, ^{241}Am, and $^{239+240}$Pu analyte (µCi/g) to Na (mmoles/g) ratios were greater than those of the last tank waste processed. This indicated the analytes were concentrated on Column 2. Because Column 1 was removed in the Na-form, the analyte concentration relative to Na concentration is not pronounced.

Table 4.10. Relative Radioisotopic Concentrations

Analyte	AP-104/SY-101	Column 1		Column 2	
Radionuclide	µCi analyte: mmole Na	µCi/g$^{(1)}$	µCi analyte: mmole Na	µCi/g$^{(1)}$	µCi analyte: mmole Na
^{60}Co	<1.6E-3	1.1E-1	2.96E-2	1.77E-1	2.35E+1
^{99}Tc	2.93E-2	9.52E-2	2.56E-2	8.48E-2	1.13E+1
^{134}Cs	<1.2E-3	1.98E-3	5.32E-4	3.51E-4	4.67E-2
^{137}Cs	3.41E+1	2.19E+1	5.89E+0	1.80E+0	2.39E+2
^{154}Eu	<4.1E-3	<4E-4	<1E-4	9.13E-3	1.21E+0
^{155}Eu	Not reported	<5E-3	<1E-3	5.75E-3	7.64E-1
^{237}Np	Not reported	<4E-3	<1E-3	7.94E-4	1.06E-1
^{241}Am (GEA)	5.71E-4	<3E-2	<8E-3	1.36E-2	1.81E+0
$^{239+240}$Pu	5.26E-5	8.39E-3	2.26E-3	7.86E-2	1.04E+1

(1) Results are presented on a dry-resin mass basis.

Cesium isotopic distribution was evaluated on the duplicate acid-digested samples from Column 1 resin. These results are presented in Table 4.11. Column 2 resin Cs results were less than the instrument quantitation limit so an isotopic analysis was not conducted on it. The ^{137}Cs abundance of 12.2% was about half of a typical Envelope A actual tank waste. This result was contrary to the expectation that the abundance would be equal to that of the AP-104/SY-101 tank waste that the resins last processed (20.8% ^{137}Cs) [16].

Table 4.11. Cs Isotopic Distribution in Column 1 Resin

	Atomic Abundance		
Isotope	Sample	Duplicate	Average
^{133}Cs	0.782	0.786	0.784
^{135}Cs	0.095	0.093	0.094
^{137}Cs	0.124	0.121	0.122

The higher abundance of stable Cs (^{133}Cs) appears to be a holdover from initial processing with AW-101 simulant, the first material processed by the resin beds.[a] The measured isotopic composition in the spent resin is consistent with the combined feeds weighted heavily with the first and last waste compositions as shown in Table 4.12. The weighting takes into consideration the total moles of Cs (from Table 2.5) and the Cs isotopic distribution (Table 2.6) loaded onto Column 1 for each feed processed.

Table 4.12. Feed Impact on Cs in Spent Resin

Column 1 Feed	Cycle Number	Weighting Factor, %
AW-101 Simulant	1	51
AP-101	2	<0.1
AN-102/C-104	3	0(a)
AZ-102C	4	<0.1
AZ-101	5	<0.1
AZ-101	6	4
AP-104/SY-101	7	0(a)
AP-104/SY-101	8	44
(a) No significant Cs loading from process cycle.		

If the low ^{137}Cs isotopic concentration is a result of initial processing with the simulant, then the final isotopic Cs concentrations can be expected to be driven in part by the first waste type processed on the resin. Thus, if actual tank waste had been processed first on the SL-644 (as opposed to a simulant), the spent resin would likely have contained a higher ^{137}Cs concentration. Depending on the actual waste first processed on a resin bed, the ^{137}Cs concentration could have been closer to 31% (Envelope B) or 22% (Envelope A) of the total Cs. Thus, based on the worst-case scenario of Column 1 at a ^{137}Cs concentration of 21.9 µCi/g, initial processing with Envelope A waste may have resulted in a factor of 1.8 increase (22% divided by 12.2%) in spent resin ^{137}Cs concentration or 39 µCi/g; initial processing with Envelope B waste may have resulted in a factor of 2.5 increase (31% divided by 12.2%) or 56 µCi/g. These results are consistent with previously reported values by Arm et al. [18] where an estimated 37 µCi/g and 50 µCi/g ^{137}Cs would remain on the resin following Envelope A and Envelope B processing, respectively.

A large suite of generally expensive radioisotopic analyses may be required for waste designation purposes. However, upper-bound radioisotopic activity concentrations can be estimated from the inorganic metal concentrations. This calculation leverages information obtained from the large array of elemental analyses offered by ICP-AES and/or ICP-MS. The conversion from inorganic metal

---

(a) Another possibility for the elevated ^{133}Cs concentration is the presence of Cs in the regenerating solution. The American Chemical Society reagent grade NaOH reagent did not explicitly list Cs as an impurity. Taken at the maximum possible concentration where heavy metals ≤ 0.002%, the maximum Cs concentration that could be found in the resin from processing 67 mL of 0.25 M NaOH regeneration solution was 6.1 µg/g. Analysis of a separate NaOH solution by ICP-MS resulted in a concentration of 9.2E-3 µg Cs per g of NaOH (based on preliminary/unverified data). Using this result, the maximum ^{133}Cs concentration from the regeneration solution on the resin would be 2.8E-3 µg/g or 0.15% of the ^{133}Cs found on the resin bed.

concentration to radioisotopic concentration was calculated for selected radioisotopes according to Equation 4.4.

$$C_i = C_m * SpA \tag{4.4}$$

where C_i is the isotope concentration in the resin, µCi/g, C_m is the metal concentration in the resin, µg/g, and *SpA* is the specific activity for the isotope, µCi/µg. The calculation assumes 100% of the metal concentration is attributed to the radionuclide. The calculated upper-bound concentrations for selected radioisotopes in the spent resin are reported in Table 4.13. These upper-bound limits can be compared to waste disposal criteria to determine if a radioisotope-specific analyses should be pursued.

Table 4.13. Upper-Bound Radioisotopic Concentrations in Spent Resin

Analyte		Specific Activity[(a)]	Column 1, Na-form		Column 2, H-form	
			Analyte Concentration	Maximum Activity	Analyte Concentration	Maximum Activity
Metal	**Radioisotope**	**µCi/µg**	**µg/g[(b, c)]**	**µCi/g[(b, c)]**	**µg/g[(b, c)]**	**µCi/g[(b, c)]**
Cd	^{113m}Cd	2.31E+2	[1.5]	[3.4E+2]	[3.1]	[7.2E+2]
Ni	^{59}Ni	8.1E-2	[11]	[8.5E-1]	44.1	3.57E+0
Ni	^{63}Ni	5.67E+1	[11]	[6.0E+2]	44.1	2.50E+3
Se	^{79}Se	1.53E-2	[4.3]	[6.6E-2]	[6.7]	[1.0E-1]
Th	^{229}Th	2.13E-1	<2.9	<6.2E-1	<3.2	<6.8E-1
Th	^{232}Th	1.10E-7	<2.9	<3.2E-7	<3.2	<3.5E-7
U	^{232}U	2.24E+1	<3.0	<6.7E+1	4.10	9.18E+1
U	^{233}U	9.64E-3	<3.0	<2.9E-2	4.10	3.95E-2
U	^{234}U	6.22E-3	<3.0	<1.9E-2	4.10	2.55E-2
U	^{235}U	2.16E-6	<3.0	<6.5E-6	4.10	8.86E-6
U	^{236}U	6.51E-6	<3.0	<2.0E-5	4.10	2.67E-5
U	^{238}U	3.36E-7	<3.0	<1.0E-6	4.10	1.38E-6
Opportunistic Analytes						
Sr	^{90}Sr	1.39E+2	[0.74]	[1.0E+2]	[0.30]	[4.2E+1]
Zr	^{93}Zr	2.51E-3	312	7.83E-01	364	9.12E-01

(a) E. Browne and R. Firestone, *Table of Radioactive Isotopes*, John Wiley and Sons, New York, 1986.
(b) Results are presented on a dry-resin mass basis.
(c) Bracketed results were greater than the method detection limit (MDL) but less than the estimated quantitation limit (EQL). The less-than values (<) indicate that the results were less than the MDL: reported values are the instrument detection limits multiplied by the sample dilution factor. Overall errors for values greater than the EQL were estimated to be within 15%. Errors for values less than the EQL but greater than the MDL were likely to exceed 15%.

If the elemental isotopic ratios are known (from the tank waste feed composition, for example), the isotopic concentration estimates may be further refined according to Equation 4.5.

$$C_i = C_m * SpA * A_i \tag{4.5}$$

where A_i equals the isotopic abundance of the isotope of interest. Application of the isotopic abundance factor would reduce the upper bound activity concentration estimate. Again, if calculated radioisotopic threshold limits are approached, additional targeted radionuclide analyses can be conducted.

5.0 Quality Control

The following sections describe the quality assurance (QA) and QC requirements and implementation.

5.1 Quality-Assurance Requirements

PNWD implemented the River Protection Project-Waste Treatment Plant (RPP-WTP) quality requirements by performing work in accordance with the PNWD Waste Treatment Plant Support Project quality assurance project plan (QAPjP) approved by the RPP-WTP QA organization. This work was performed to the quality requirements of NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Subpart 2.7. These quality requirements were implemented through PNWD's *Waste Treatment Plant Support Project (WTPSP) Quality Assurance Requirements and Description Manual* and to the approved Test Plan, TP-RPP-WTP-224, Rev. 0 and Test Exception 24590-WTP-TEF-RT-03-030. The analytical requirements were implemented through PNWD's *Conducting Analytical Work in Support of Regulatory Programs* requirements document.

Experiments that were not method-specific were performed in accordance with PNWD's procedures QA-RPP-WTP-1101 "Scientific Investigations" and QA-RPP-WTP-1201 "Calibration Control System," assuring that sufficient data were taken with properly calibrated measuring and test equipment (M&TE) to obtain quality results.

As specified in Test Specification 24590-PTF-TSP-RT-02-004, Rev. 0, *Analysis of Spent Ion Exchange Resins*, BNI's QAPjP, 24590-QA-0001, was not applicable since the work was not performed in support of environmental/regulatory testing, and the data should not be used as such.

PNWD addressed internal verification and validation activities by conducting an independent technical review of the final data report in accordance with PNWD's procedure QA-RPP-WTP-604. This review verified that the reported results were traceable, that inferences and conclusions were soundly based, and that the reported work satisfied the test-plan objectives. This review procedure is part of PNWD's *WTPSP Quality Assurance Requirements and Description Manual*.

5.2 Analytical Results

A discussion of data quality and QC is discussed for each analytical method. Analytical results and batch QC results are summarized in Table 5.1 through Table 5.3. All raw and reduced data are maintained in data files under Project 42365 at PNWD.

5.2.1 Inductively-Coupled Plasma-Atomic Emission Spectrometry

The ICP-AES spent-resin analysis was conducted using the acid-digested sample aliquots. All batch and instrument QC requirements were met except the Ag MS that recovered low at 50%. The Ag BS recovery was acceptable at 104%, and the post-matrix spike resulted in 104% recovery. These results indicated that there was a significant matrix effect causing low Ag recovery in the samples. The solution did contain chloride and sulfate, and both of these anions form insoluble precipitates with Ag.

5.2.2 Inductively Coupled Plasma-Mass Spectrometry

The ICP-MS spent resin analysis for Cs and Tc was conducted using the acid-digested sample aliquots. All batch QC requirements were met except the Tc MS that recovered high at 164%. The reason for the high recovery was not clear. The BS recovered at 100%, and the post matrix spike recovered at 96%. All instrument QC requirements were met except the calibration and calibration verification standards were prepared from the same parent stock of NIST-traceable material. The ICP-MS was used to measure ^{133}Cs (stable Cs) as well as the Cs isotopic distribution for Column 1. Using these values, the ^{137}Cs concentration could be calculated. The ^{137}Cs sample results calculated from ICP-MS analyses were within 2% of the ^{137}Cs measured by GEA.

5.2.3 Uranium by Kinetic Phosphorescence Analysis

The KPA spent resin analysis was conducted using the acid-digested sample aliquots. All batch and instrument QC requirements were met.

5.2.4 Gamma Energy Analysis

Gamma energy analysis was conducted directly on samples (solutions from ion exchange processing and solid spent resin). Therefore, laboratory control samples (LCSs), blank spike (BS), and matrix spike (MS) QC samples were not required. Duplicate samples were tested for spent-resin digestions, and the relative percent differences were found to be within the acceptance criterion of <20%.

5.2.5 Americium, Curium, and Plutonium

Isotopes of Am, Cm, and Pu were measured on aliquots of acid-digested spent-resin samples. All batch and instrument QC requirements were met except for sporadic spectral energy resolution problems. Column 1 Pu spectra, Column 2 Am/Cm spectra, and the Am BS spectrum resulted in peaks that were not well defined. The problem appeared to be associated with high solids loading on the precipitation plate mounts. The source of the problem is under investigation. Peak integrations were corrected for tailing effects from adjacent peaks to minimize bias associated with the poor energy resolution. The $^{239+240}$Pu RPD for Column 1 exceeded 20%. Therefore the mean difference (MD, an alternate method for evaluating precision of radioanalytical results) was calculated and it met the acceptance criterion of <1.96.

5.2.6 Total Alpha and Total Beta

Total alpha and total beta were measured on aliquots of acid-digested spent-resin samples. All batch and instrument QC requirements were met. The sum of alpha isotopes (Pu, Am, and Cm) equaled the total alpha measurements for each resin bed within the errors of the methods. The Column 1 total beta measurement equaled the sum of GEA-measured beta emitters (^{137}Cs and ^{60}Co). The Column 2 total beta measurement exceeded the sum of GEA-measured beta-emitters indicating other beta emitting isotopes were present.

5.2.7 Ion Chromatography

Anions were measured on Column 2 water-leach samples. All batch and instrument QC requirements were met except precision for chloride. The chloride duplicate samples resulted in an RPD of 28%, exceeding the acceptance criteria of <20%. Since the chloride results were only at three to four times the EQL, the poor RPD can be attributed to the higher measurement uncertainty at the EQL. Because the sample was analyzed directly, no preparation was required and thus no preparation blank was prepared.

Table 5.1. QC Results of Metals Analysis in Spent Resin

		Process Blank 1		Column 1 Average			Column 2 Average					
	MRQ	EQL	03-0858-PB	EQL	03-0858 and 03-0859	RPD	EQL	03-0860 and 03-0861	RPD	BS Recovery	MS Recovery	Serial Dilution
Analyte	µg/g	µg/g	µg/g(a)	µg/g	µg/g(a)	%	µg/g	µg/g(a)	%	%	%	%
Criteria:						<20			<20	80 - 120	75 - 125	<10
Ag	1.4E+1	8.2	<0.60	8.0	49.0	6.4	9.1	46.5	18.4	104	**50(b)**	3.8
As	7.2E+1	43	<4.3	42	[0.10]	—	47	[14]	—	105	109	—
Ba	7.8E+1	1.2	<0.13	1.2	12.8	2.9	1.4	1.3	13	102	105	1.0
Cd	7.5E+0	4.5	<0.45	4.4	[1.5]	—	5.0	[3.1]	—	108	111	—
Cr	1.5E+1	7.2	<0.72	6.9	2,440	1.8	7.9	3,990	3.1	105	100	0.5
^{133}Cs	NA	5.5E-4	<5E-4	0.061	1.80	2.5	0.071	<0.071	—	100	107	7.9
Total Cs	1.0E+1	NA	NM	NA	2.29	4.4	NA	NM	—	—	—	—
Na	1.8E+2	104	[32]	100	85,550	7.2	114	173	7.0	102	106	0.8
Ni	3.0E+1	15	<1.5	15	[11]	—	17	44.0	3.8	108	110	—
Pb	3.0E+2	31	[3.1]	31	56.2	4.4	35	172	2.6	103	105	—
Se	5.0E+1	43	<4.3	42	[4.3]	—	47	[6.6]	—	106	105	—
Th	5.0E+2	33	<3.0	32	<2.8	—	37	<3.2	—	103	90	—
U	1.0E+3	590	<64	570	<60	—	650	<69	—	100	102	—
U (KPA)	5.0E+1	3.0	<3.0	3.0	<3.0	—	3.0	4.1	11	101	90	—
Opportunistic Analytes(c)												
Al	NA	53	<3.7	52	[43]	—	59	[48]	—	—	—	—
B	NA	3.7	<1.2	3.6	328	6.9	4.1	12.0	1.4	—	—	2.0
Bi	NA	30	<3.0	29	[12]	—	33	[10]	—	—	—	—
Ca	NA	54	<5.4	52	[39]	—	59	[35]	—	—	—	—
Co	NA	6.0	<0.60	5.8	8.60	2.1	6.6	10.6	1.8	—	—	—
Cu	NA	8.3	<0.83	8.1	26.2	5.1	9.2	44.0	7.1	—	—	—
Fe	NA	12	<1.2	12	19.8	6.6	13	52.6	0.3	—	—	—
K	NA	1200	<119	1200	<114	—	1300	<130	—	—	—	—
Mn	NA	1.4	<0.074	1.4	[0.5]	—	1.6	1.35	—	—	—	—
Mo	NA	6.8	<0.68	6.6	[1.8]	—	7.5	[1.3]	—	—	—	—
P	NA	28	76	27	116	3.4	31	124	1.6	—	—	—
Pd	NA	150	<15	140	[117]	—	160	[59]	—	—	—	—

Table 5.1 (Contd)

		Process Blank 1		Column 1 Average			Column 2 Average					
	MRQ	**EQL**	**03-0858-PB**	**EQL**	**03-0858 and 03-0859**	**RPD**	**EQL**	**03-0860 and 03-0861**	**RPD**	**BS Recovery**	**MS Recovery**	**Serial Dilution**
Analyte	**µg/g**	**µg/g**	**µg/g(a)**	**µg/g**	**µg/g(a)**	**%**	**µg/g**	**µg/g(a)**	**%**	**%**	**%**	**%**
Criteria:						<20(b)			<20(b)	80 - 120	75 - 125	<10
Ru	na	24	<2.4	23	[10]	—	26	[14]	—	—	—	—
Sb	na	33	<3.3	32	<3.2	—	37	<3.7	—	—	—	—
Si	na	36	<3.6	34	420	66.2	39	[19]	—	—	—	—
Sr	na	1.8	<0.18	1.7	[0.74]	—	2.0	[0.30]	—	—	—	—
Te	na	60	<6.0	58	<5.7	—	66	[7.4]	—	—	—	—
Ti	na	3.0	<0.30	2.9	[1.5]	—	3.3	[2.7]	—	—	—	—
Tl	na	25	<2.5	24	[4.8]	—	28	[6.6]	106	109	—	—
V	na	4.8	<0.46	4.6	<0.45	—	5.3	[0.72]	99	101	—	—
Zn	na	8.3	<0.83	8.1	[2.7]	—	9.2	[4.2]	105	110	—	—
Zr	na	5.1	<0.51	5.0	312	0.0	5.6	364	3.7	—	—	1.6

(a) The overall error for values without brackets was estimated to be within ±15% (analytes greater than the EQL). Bracketed values identify sample concentrations that were <EQL but >MDL, and errors likely exceeded 15%. The MDL was typically a factor of 10 lower than the EQL.

(b) The MS Ag recovery was low, see discussion.

(c) Opportunistic analytes are reported for information only; QC requirements did not apply to these analytes.

BS = blank spike
EQL = estimated quantitation limit
MRQ = minimum reportable quantity
MS = matrix spike
na = not applicable
nm = not measured
RPD = relative percent difference
"—" indicates calculation was not required
The bolded and shaded result indicates non-compliance with BNI acceptance criteria; see discussion.

Data are from ASR 6740, RPL Sample ID = 03-0858 through 03-0861

Table 5.2. Radionuclide QC Results for Spent Resin Analysis

		Process Blank 1		Column 1 Average			Column 2 Average					
Analyte	**MRQ µCi/g**	**EQL µCi/g**	**03-0858-PB µCi/g**	**EQL µCi/g**	**03-0858 and -0859 µCi/g**	**RPD** %	**EQL µCi/g**	**03-0860 and 03-0861 µCi/g**	**RPD** %	**BS Recovery %**	**MS Recovery %**	**Serial Dilution %**
Criteria:						*<20*			*<20*	*80 - 120*	*75 - 125*	*<10*
^{60}Co	0.50	—	—	—	1.44E-1(a)	2.1	—	1.74E-1(b)	2.3	—	—	—
^{99}Tc	0.40	7.2E-6	<7.2E-6	8.2E-4	9.5E-2	2.1	9.4E-4	8.5E-2	2.0	100	**164(c)**	7.4
^{137}Cs	0.050	—	—	—	2.44E+1(d)	3.7	—	1.77E+0(e)	1.1	—	—	—
^{241}Am	0.010	—	<2E-5	—	1.58E-3	2.5	—	1.39E-2	7.9	83	97	—
$^{239/240}$Pu	0.010	—	<2E-5	—	8.39E-3	2.8	—	7.86E-2	2.3	85	84	—
Total alpha	0.010	2E-3	<2.1E-3	—	1.20E-2	12.5	—	1.12E-1	0.70	105	89	—
Total beta	0.0010	—	5.95E-4	—	2.14E+1	5.4	—	2.70E+0	5.2	88	83	—

(a) Direct analysis on the resin resulted in 1.05E-1 µCi/g (RPL ID: 03-0854).

(b) Direct analysis on the resin resulted in 1.51E-1 µCi/g (RPL ID: 03-0856).

(c) The post matrix spike recovery was 96%.

(d) Direct analysis on the resin resulted in 1.68E+1 µCi/g (RPL ID: 03-0854).

(e) Direct analysis on the resin resulted in 1.87E+0 µCi/g (RPL ID: 03-0856).

Notes:
"—" indicates calculation was not required
BS = blank spike
EQL = estimated quantitation limit
MRQ = minimum reportable quantity
MS = matrix spike
RPD = relative percent difference
RSD = relative standard deviation

The bolded and shaded result indicates non-compliance with BNI acceptance criteria; see discussion.
EQLs for radiochemical counting techniques are driven by counting times and vary as necessary to meet MRQs. Therefore, method-specific EQLs are not listed.
Data are from ASR 6740, RPL Sample ID = 03-0858 through 03-0861

Table 5.3. Anion Analysis of Column 2 Water Leach

		Sample		Duplicate			LCS	MS
	MRQ	EQL	03-0862	EQL	03-0862-DUP	RPD	Recovery	Recovery
Analyte	µg/mL	µg/mL[a]		µg/mL[a]		%	%	%
					Criteria:	*<20*	*80 - 120*	*75 - 125*
Test Specification Analytes								
Cl^-	0.3	0.13	0.41	0.13	0.31	**28[b]**	106	97
F^-	0.15	0.13	<0.013	0.13	<0.013	—	108	107
NO_2^-	3.0	0.25	<0.025	0.25	<0.025	—	110	104
NO_3^-	3.0	0.25	13.0	0.25	12.9	1	104	102
PO_4^{3-}	2.5	0.25	<0.025	0.25	<0.025	—	106	103
SO_4^{2-}	2.3	0.25	0.72	0.25	0.72	0	106	102
Opportunistic Analytes[c]								
Br^-	NA	0.13	<0.013	0.13	<0.013	—	100	101
$C_2O_4^{2-}$	NA	0.25	<0.025	0.25	0.038	—	106	103

(a) The overall error is estimated to be within ±15% or better for non-complex aqueous samples that are free of interference.

(b) The RPD acceptance criterion for chloride was exceeded; therefore, the results are qualified as estimated.

(c) Opportunistic analytes are reported for information only; QC requirements do not apply to these analytes.

Notes:
EQL = estimated quantitation limit
LCS = laboratory control spike
MDL = minimum detection limit (note: the MDL is a factor of ten less than the EQL)
MRQ = minimum reportable quantity
MS = matrix spike
NA = not applicable
RPD = relative percent difference
"—" indicates calculation was not required.
The bolded and shaded result indicates non-compliance with BNI acceptance criteria; see discussion.
Data are from ASR 6740, RPL Sample ID = 03-0862.

6.0 Conclusions

The spent SL-644 resin has been characterized with respect to residual metals and radionuclides. Results were generally consistent with previously-reported results.

- The ^{137}Cs concentrations were measured at 21.9 and 1.80 µCi/g for Column 1 and Column 2, respectively. The difference may be due to a higher total Cs loading on Column 1 over the course of the seven actual waste tests, and on other processing characteristics of the last several waste tests (Cs loaded relative to elution volume and contraction/expansion steps). The measured isotopic fraction for ^{137}Cs on Column 1 was low (12%) with respect to typical tank waste. This indicated that the measured results for residual ^{137}Cs on spent resin may be biased low if actual waste had initially been processed on the ion exchanger. Correcting for the bias by applying typical tank waste ^{137}Cs isotopic fractions would result in residual ^{137}Cs equal to 39 µCi/g (Envelope A waste with 22% ^{137}Cs) and 56 µCi/g (Envelope B waste with 31% ^{137}Cs).

- The Column 2 ^{137}Cs concentration was an order of magnitude lower than the Column 1 ^{137}Cs concentration, indicating the resin can be better eluted with respect to Cs. The specific conditions resulting in the lower ^{137}Cs concentration on Column 2 were not determined; they were most likely an intricate combination of the degree of Cs loading, the elution volumes, and the number of regeneration cycles of each column over the last several cycles.

- The following metals concentrated to some extent on the resin: Ag, As, Ba, Cd, Cr, Ni, Pb, Se, and U (analytes of interest) and Bi, Ca, Co, Cu, Fe, Mn, and Zr (opportunistic analytes).

- The following radionuclides concentrated to some extent on the resin: ^{60}Co, ^{99}Tc, ^{241}Am, and $^{239+240}$Pu.

- A total of 12.0 nCi/g total alpha activity and 2.14E+4 nCi/g total beta activity were found on the Column 1 resin; 94% (±7%) of the total alpha and 97% (±10%) of the total beta activities sources were identified.

- A total of 112 nCi/g total alpha activity and 2.70E+3 nCi/g total beta activity were found on the Column 2 resin; 92% (±4%) of total alpha activity and 74% (±10%) of the total beta activity sources were identified.

- The total resin mass losses over the eight process cycles were 11% and 9% for the Column 1 and Column 2 resin beds, respectively.

7.0 References

1. NM Hassan, DJ McCabe, and WD King. 2000. *Small-Scale Ion Exchange Removal of Cesium and Technetium from Hanford Tank 241-AN-103, Revision 1*, April, 2000, BNF-003-98-0146, Savannah River Technology Center, Westinghouse Savannah River Co. Aiken, SC.

2. NM Hassan, DJ McCabe, WD King, and ML Crowder. 2000. *Small-Scale Ion Exchange Removal of Cesium and Technetium from Hanford Tank 241-AN-102*, March 2000, BNF-003-98-0219, Savannah River Technology Center, Westinghouse Savannah River Co. Aiken, SC.

3. NM Hassan, WD King, DJ McCabe, and ML Crowder. 2001. *Small-Scale Ion Exchange Removal of Cesium and Technetium from Envelope B Hanford Tank 241-AZ-101*, January, 2001, WSRC-TR-2000-00419, SRT-RPP-2000-00036, Savannah River Technology Center, Westinghouse Savannah River Co. Aiken, SC.

4. WD King, NM Hassan, and DJ McCabe. 2001. *Intermediate-Scale Ion Exchange Removal of Cesium and Technetium from Hanford Tanks 241-AN-102*, August, 2001, WSRC-TR-2000-00420, SRT-RPP-2000-00014, Savannah River Technology Center, Westinghouse Savannah River Co. Aiken, SC.

5. DE Kurath, DL Blanchard, Jr., and JR. Bontha. 2000a. *Small Column Ion Exchange Testing of Superlig 644 for Removal of 137Cs from Hanford Tank Waste Envelope C (Tank 241-AN-107)*, June 2000, PNWD-3039, Battelle Pacific Northwest Division, Richland, WA.

6. DE Kurath, DL Blanchard, Jr., and JR Bontha. 2000b. *Small Column Ion Exchange Testing of Superlig 644 for Removal of* ^{137}*Cs from Hanford Tank Waste Envelope A (Tank 241-AW-101)*, June 2000, PNWD-3001, Battelle Pacific Northwest Division, Richland, WA.

7. SK Fiskum, DL Blanchard, and ST Arm. 2002a. *Aging Study and Small Column Ion Exchange Testing of SuperLig® 644 for Removal of* ^{137}*Cs from Simulated AW-101 Hanford Tank Waste*, September 2002, PNWD-3195, Battelle Pacific Northwest Division, Richland, WA.

8. SK Fiskum, ST Arm, DL Blanchard, and BM Rapko. 2002. *Small Column Ion Exchange Testing of Superlig® 644 for Removal of* ^{137}*Cs from Hanford Waste Tank 241-AP-101 Diluted Feed (Envelope A),* September 2002, PNWD-3196, Battelle Pacific Northwest Division, Richland, WA.

9. SK Fiskum, DL Blanchard, and ST Arm. 2002b. *Small Column Ion Exchange Testing of SuperLig® 644 for Removing* ^{137}*Cs from Hanford Waste Tank 241-AN-102 Supernate (Envelope C) Mixed with Tank 241-C-104 Solids (Envelope D) Wash and Permeate Solutions,* January 2003, PNWD-3240 Battelle Pacific Northwest Division, Richland, WA.

10. SK Fiskum, DL Blanchard, and ST Arm. 2002c. *Small Column Ion Exchange Testing of SuperLig® 644 for Removal of* ^{137}*Cs from Hanford Waste Tank 241-AZ-102 Concentrate (Envelope B),* April 2003, PNWD-3267 Battelle Pacific Northwest Division, Richland, WA.

11. SK Fiskum, ST Arm, DL Blanchard, Jr. 2003. *Small Column Ion Exchange Testing of SuperLig® 644 for Removal of ^{137}Cs from Hanford Waste Tank 241-AZ-101 (Envelope B)*, April 2003, PNWD-3266, Rev. 0, Battelle, Pacific Northwest Division, Richland, WA.

12. SC Goheen, PR Bredt, OT Farmer, III, SK Fiskum, KA Gaither, LR Greenwood, LK Jagoda, AP Poloski, RD Scheele, CZ Soderquist, RG Swoboda, MP Thomas, MW Urie, and JJ Wagner. 2002. *Chemical Analysis and Physical Property Testing of Diluted 241-AP-101 Tank Waste*, June 2002, PNWD-3174, Battelle, Pacific Northwest Division, Richland, WA.

13. MW Urie, PR Bredt, JA Campbell, OT Farmer, LR Greenwood, LK Jagoda, GM Mong, AP Poloski, LL Reed, RD Scheele, CZ Soderquist, RG Swoboda, MP Thomas, JJ Wagner. 2002. *Chemical and Physical Property Testing of 241-AN-102 Tank Waste Blended with 241-C-104 Wash/Leachate Solutions*, December 2002, PNWD-3228, Battelle Pacific Northwest Division, Richland, WA.

14. MW Urie, PR Bredt, JA Campbell, OT Farmer, SK Fiskum, LR Greenwood, EW Hoppe, GM Mong, AP Poloski, RD Scheele, CZ Soderquist, RG Swoboda, MP Thomas, JJ Wagner. 2002. *Chemical Analysis and Physical Property Testing of 241-AZ-101 Tank Waste—Supernatant and Centrifuged Solids*, November 2002, PNWD-3215, WTP-RPT-048, Rev. 0, Battelle Pacific Northwest Division, Richland, WA.

15. JGH Geeting, KP Brooks, RT Hallen, LK Jagoda, AP Poloski, DR Weier, RD Scheele. 2002. *Filtration, Washing, and Caustic Leaching of Hanford Tank AZ-101 Sludge,* October 2002, PNWD-3206, Battelle Pacific Northwest Division, Richland, WA.

16. DL Baldwin, PR Bredt, JA Campbell, OT Farmer, SK Fiskum, LR Greenwood, GM Mong, AP Poloski, RD Scheele, CZ Soderquist, MR Smith, LA Snow, RG Swoboda, MP Thomas, MW Urie, JJ Wagner. 2003. *Chemical Analysis and Physical Property Testing of 241-AP-104 Tank Waste, Revision 0*, February 2003, WTP-RPT-069, Battelle Pacific Northwest Division, Richland, WA.

17. NM Hassan, WD King, and DJ McCabe. 1999. *Superlig® Ion Exchange Resin Swelling and Buoyancy Study (U)*, March 1999, Savannah River Technology Center, Westinghouse Savannah River Co., Aiken, SC.

18. DE Kurath, JJ Wagner. 2000. *Analysis of Spent Ion Exchange Media: SuperLig 639 and SuperLig 644*, May 2000, PNWD-3037. Battelle Pacific Northwest Division, Richland, WA.

19. ST Arm, SK Fiskum, and DL Blanchard. 2003. *Chemical Degradation of SuperLig-644 Ion Exchange Resin*, July 2003, PNWD-3315, Battelle, Pacific Northwest Division, Richland, WA.

Appendix A

AP-104/SY101 Processing

Appendix A: AP-104/SY-101 Processing

A.1.0 Introduction

The RPP-WTP vitrification task required the preparation and study of immobilized low-activity waste (ILAW) glass made from processing Hanford waste from Tank 241-AP-104 (abbreviated AP-104/SY-101).(a) Battelle—Pacific Northwest Division (PNWD) was contracted to perform vitrification studies under Contract 24590-101-TSA-W000-00004. The ILAW glass-testing activities are defined in Appendix C of the *Research and Technology Plan*(b) under Technical Scoping Statement B-15. The vitrification activity required pretreatment of the waste according to normal unit operations expected to be conducted at the WTP. Removal of Sr and transuranics was not required; however, Cs and Tc removal were required.(c)

The pretreatment flowsheet for the Hanford high-level tank wastes includes the use of SuperLig® 644 (SL-644) material for ^{137}Cs removal from the aqueous waste fraction. The SL-644 is a Cs-selective, elutable, organic ion exchanger and has been shown to be effective in removing Cs from a variety of Hanford tank wastes. The SL-644 resin is a proprietary product developed and supplied by IBC Advanced Technologies, Inc., American Fork, UT (IBC). An ion exchange test system containing SL-644 was already set up in the PNWD Radiochemical Processing Laboratory (RPL) shielded facilities and was used for ion exchange processing of AP-104/SY-101. This ion exchange system had already been used successfully on a waste tank simulant and four actual tank wastes. [1-5]

This appendix reports the Cs ion exchange test results obtained from the AP-104/SY-101 processing run. All work was conducted according to Test Specification 24590-LAW-TSP-RT-02-003, Rev. 0(d) and Test Plan TP-RPP-WTP-175, Rev. 0.(e) The objectives of this work were to:

- remove Cs from AP-104/SY-101
- characterize the Cs eluate
- provide Cs-decontaminated AP-104/SY-101 for follow-on testing, including Tc removal and vitrification studies.(f)

All test objectives were met. Many useful observations were made during Cs ion exchange processing of the AP-104/SY-101 tank waste. The processing information and results are reported herein so that they will not be lost to the WTP project.

(a) Waste from tank 241-SY-101 had been transferred to tank 241-AP-104. The sample represents a mixture of the two wastes, hence the combined name, AP-104/SY-101.

(b) Research and Technology Plan, 24590-WTP-PL-RT-01-002, Rev. 1, April 2002 and Rev. 2, April 2003, S. Barnes, R. Roosa, R. Peterson, Bechtel National, Inc., Richland, WA.

(c) At the processing time, Tc removal was still included in the plant design and operation.

(d) Sidibe, Aissata. *AP 104/SY 101 (Envelope A) LAW Pretreatment, Vitrification, Product Testing, and Regulatory Analyses*, April 26, 2002, Bechtel National Inc., Richland, WA.

(e) Fiskum, SK. *AP 104/SY 101 (Envelope A) LAW Pretreatment, Vitrification, Product Testing, and Regulatory Analyses*. July 2002. Battelle, Pacific Northwest Division, Richland WA.

(f) The AP-104/SY-101 vitrification task was cancelled after Cs ion exchange processing was completed.

A.2.0 Experimental

This section describes the experimental parameters for processing AP-104/SY-101 through the SL-644 ion exchange system. It includes a description of materials, experimental approach to column tests, and sample analyses. Experimental data were recorded in specific test instructions and analytical reports (as identified). All raw data are maintained in the Project File 42365 at Battelle—Pacific Northwest Division (PNWD).

A.2.1 AP-104/SY-101 Feed

The AP-104/SY-101 sample receipt, mixing, sub-sampling, analyses, and filtration were reported separately [6]. The AP-104/SY-101 composite was split into eight subsamples (AP-104ARA through AP-104-ARH). Four sub-samples were mixed to produce feed for Cs ion exchange: AP-104ARA, AP-104ARC, AP-104ARE, and AP-104ARH. The combined sample volume of AP-104/SY-101 was 1.82 L. The density of this material (1.263 g/mL at $T = 32^{o}C$) was slightly higher than required for ion exchange processing (acceptable range 1.21 to 1.25 g/mL). A 283-mL volume of 0.01 M NaOH was added to the AP-104/SY-101 sample to reduce the density (1.225 g/mL at $T = 32\ ^{o}C$). The final diluted volume available for Cs ion exchange processing was therefore 2.09 L. Table A.1 summarizes the AP-104/SY-101 diluted feed composition. Most analytical results were reported from Analytical Services Request (ASR) 6515, RPL sample number 02-3061 taken immediately before ion exchange processing. Some results presented in Table A.1 were calculated based on the results reported by Baldwin et al. [6] and the applied dilution factor required for density reduction.

A.2.2 SL-644 Resin

The SL-644 resin was obtained from IBC production batch number 010319SMC-IV-73, prepared at IBC on 3/19/01. This material has been previously described [1]. The 212- to 425-µm particle size dry-sieved fraction was used in the ion exchange columns.(a)

A.2.3 Apparatus

The ion exchange apparatus has been previously described [1]. It consisted of two glass columns in a lead and lag format. The inside diameter of each column was 1.46 cm. Each column contained 2.4 g Na-form SL-644 resin providing a resin BV of nominally 10-mL in 0.25 M NaOH. A stainless steel, 200-mesh screen supported the resin bed. The total apparatus volume (AV) was nominally 42 mL. The connecting tubing was $^{1}/_{8}$-in. OD, $^{1}/_{16}$-in. ID polyethylene. Valved quick-disconnects (Cole Parmer, Vernon Hills, IL) were installed in-line to allow for ease of column switching. An FMI QVG50 pump (Fluid Metering, Inc., Syosset, NY) equipped with a ceramic and Kynar® coated low-flow piston pump head was used to introduce all fluids.

(a) This particle-size distribution was used successfully in AW-101 simulant testing.

Table A.1. Composition of AP-104/SY-101 (Envelope A)

Cations	**M**	**Anions**	**M**
Na	4.92 E+0	AlO_2^{-} (c)	3.97 E-1
K	4.64 E-2	F^{-}	1.07 E-1
Cs	6.88 E-5(a, b, d)	Cl^{-}	1.51 E-1
As	<8.3 E-5	CrO_4^{-2} (c)	7.84 E-3
Ba	<1.8 E-6	NO_2^{-}	1.52 E+0
Ca	1.69 E-3	NO_3^{-}	1.76 E+0
Cd	4.05 E-5	OH^{-}	1.16 E+0
Co	<2 E-5	PO_4^{-3} (c) (ICP-AES)	4.39 E-2
Cu	<1 E-5	PO_4^{-3} (IC)	4.78 E-2
Fe	[6.2 E-5]	SO_4^{-2}	2.90 E-2
Li	<1.1 E-4	$C_2O_4^{-2}$	9.44 E-3
Mo	5.12 E-4	**Radionuclides**	**(µCi/mL)**
Ni	5.76 E-4	^{60}Co	<8 E-3
Pb	[4.2 E-5]	^{90}Sr	1.69 E+0(b)
Si	[3.4E-3]	^{99}Tc	1.44 E-1(b)
Sn	<1 E-4	$^{99}TcO_4$	4.38 E-2(b)
Sr	[4.7E-6]	^{134}Cs	<6. E-3
U (Uranyl)(c)	4.07 E-5	^{137}Cs	1.68 E+2
V	<3 E-5	^{154}Eu	<2 E-2
W	[3.8 E-4]	^{155}Eu	<2 E-1
Cations	**Mole ratio**	^{238}Pu	3.62 E-5
Na/Cs	7.15 E+4	$^{239+240}$Pu	2.59 E-4
K/Cs	6.74 E+2	^{241}Am	2.81 E-3
Density	**g/mL**	$^{243+244}$Cm	5.84 E-4
Density	1.225 T = 32°C	Sum of alpha	3.69 E-3
Carbon	**M**	**Carbon**	**M**
CO_3^{2-} (F)	3.7 E-1(b)	CO_3^{2-} (HP)	3.5 E-1(b)
TOC (F)	2.2 E-1(b)	TOC (HP)	3.5 E-1(b)
TC (F)	5.9 E-1(b)	TC (HP)	7.0 E-1(b)

(a) Cs isotopic analysis resulted in 60.5 wt% ^{133}Cs, 18.7 wt% ^{135}Cs, 20.8 wt% ^{137}Cs.

(b) Reported in ASR 6378, supernatant characterization results, corrected for dilution.

(c) Al, Cr, and P determined by ICP-AES. U measured by kinetic phosphorescence analysis (KPA). The ionic form was assumed on the basis of waste chemistry.

(d) The total Cs concentration calculated from the ^{137}Cs and the isotopic ratio is 6.90E-5 M.

HP = hot persulfate method; F = furnace method

Bracketed results indicate that the analyte concentration uncertainty exceeded 15%. Less-than (<) results indicate that the analyte concentration was below the instrument detection limit (IDL); the dilution-corrected IDL is given.

ASR 6515 RPL # = 02-3061; ASR 6378 RPL # = 02-1832 [6].

A.2.4 Resin Bed History

The ion exchange system was used for a full shakedown experiment with AW-101 simulant [1] before installation in the hot cell facility. Both columns were individually eluted, rinsed, and regenerated. The ion exchange system was then transferred to the hot cell and used to process diluted AP-101 tank waste [2]. Only the lead column was eluted to a ^{137}Cs concentration C/C$_o$[(a)] of 4.2 E-3, (0.53 µCi ^{137}Cs/mL and 1.5E-7 M total Cs). The lead column was then rinsed with DI water, regenerated with 0.25 M NaOH, and again rinsed with DI water. The lag column contained an estimated 35 µCi ^{137}Cs calculated from integrating the lead-column Cs breakthrough. After an 8-week storage period (resin as Na-form in DI water), the lead and lag column positions were switched, and 0.75 L of AN-102/C-104 were processed [3]. Again, only the lead column was eluted to a ^{137}Cs concentration C/C$_o$ of 6.3 E-3 (1.0 µCi ^{137}Cs/mL and 3.8E-7 M total Cs). The lead column was then rinsed with DI water, regenerated with 0.25 M NaOH, and again rinsed with DI water. The lag column contained an estimated 0.22 µCi ^{137}Cs calculated from integrating the lead-column Cs breakthrough. After a 17-week storage period (Na-form resin in DI water), the lead- and lag-column positions were switched, and 1.07 L of AZ-102 concentrated to 4.6 M Na were processed [4]. The lead column was eluted to a ^{137}Cs concentration C/C$_o$ of 6.6E-4 (1.3 µCi ^{137}Cs /mL and 3.4E-7 M total Cs). The lead column was regenerated, rinsed, and re-eluted to a C/C$_o$ of 1.83E-4 (3.7E-1 µCi ^{137}Cs/mL and 9.5E-8 M total Cs). The lag column contained an estimated 1.2E+5 µCi ^{137}Cs calculated from the average of the lead-column Cs-breakthrough integration, integrated Cs recovery in the eluate samples, and Cs recovery in the composite eluate. After a 20-day storage period, the lead and lag column positions were switched, and 1.26 L AZ-101 were processed [5]. The lead column was eluted with 14.3 BVs 0.5 M HNO_3 to a ^{137}Cs concentration C/C$_o$ of 2.2E-3 (3.7 µCi ^{137}Cs/mL). The lag column contained 9.9E+4 µCi ^{137}Cs calculated from integrating the lead column breakthrough samples. After a 49-day storage period, the lead and lag columns were again switched, and 1.05 L AZ-101 were processed. The lead column was eluted with 15.9 BVs 0.5 M HNO_3 to a ^{137}Cs concentration C/C$_o$ of 1.5E-3 (2.5 µCi ^{137}Cs/mL). The lag column contained 5.2E+3 µCi ^{137}Cs, calculated from integrating the lead-column Cs breakthrough. The system was regenerated and rinsed again with DI water for storage. The resin bed history is summarized in Table A.2.

(a) C$_o$ refers to the ^{137}Cs concentration in the respective tank waste feed; C refers to the ^{137}Cs concentration in the column effluent sample.

Table A.2. Resin Bed History Summary

Tank Waste (Process start date)	Cycle	Load volume, mL (BV)	Lead column	Lead Cs breakthrough % C/C$_o$	Lead column Cs load, Ci	Lag column Cs load, µCi	Elution	Eluate volume, BV	Final eluate sample ^{137}Cs concentration C/C$_o$ (µCi/mL)	Ref.
AW-101 simulant (3/26/01)	1	1576 (143)	Column 1	0.99	trace	trace	Lead and lag columns	12.5	5.5E-3 (trace)	[1]
AP-101 (4/23/01)	2	1189 (112)	Column 1	0.19	0.15	35	Lead column	19.3	4.2E-3 (0.53)	[2]
AN-102/ C-104 (6/25/01)	3	753 (72)	Column 2	1.3E-4(a)	0.12	0.22	Lead column	18.9	6.3E-3 (1.0)	[3]
AZ-102C (11/5/01)	4	1071 (105)	Column 1	78	2.2	1.2E+5	Lead column	14.8	6.6E-4 (1.3)	[4]
		Regenerate then re-elute	Column 1	NA	NA	NA	Lead column	6.5	1.8E-4 (0.37)	[4]
AZ-101 (A) (12/3/01)	5	1261 (122)	Column 2	53	2.1	9.9E+4	Lead column	14.3	2.2E-3 (3.7)	[5]
AZ-101 (B) (1/28/02)	6	1046 (95.9)	Column 1	7.2	1.8	5.2E+3	Lead column	15.9	1.5E-3 (2.5)	[5]

(a) No breakthrough curve was generated; C/C$_o$ demonstrated a flat-line response as a function of bed volume (BV).
NA = not applicable

A.2.5 Column Operation

The AP-104/SY-101 was processed in two complete column cycles. The first cycle processed a small amount of AP-104/SY-101 followed by extensive elution of the lead column. The second cycle processed a large tank waste volume. All experimental data were recorded in applicable test instructions.[a]

A.2.5.1 First (Short) AP-104/SY-101 Ion Exchange Column Test

The ion exchange assembly was stored for 164 days in the Na-form in DI water since the end of AZ-101 column testing. The lead and lag columns were switched and the AV of DI water was displaced with 0.25 M NaOH before introducing AP-104/SY-101 feed. All subsequent processing was performed in the hot cells at a nominal temperature of 34°C. Table A.3 shows the experimental conditions for each process step. One BV is the lead resin BV in 0.25 M NaOH (10.5 mL) just before loading AP-104/SY-101. The bed conditioning, AP-104/SY-101 loading, feed displacement, and DI water-rinse steps were conducted by passing these solutions through both resin beds connected in series. The AP-104/SY-101 effluent was collected in two effluent bottles. The first bottle collected 42 mL, nominally one AV, and consisted primarily of the displaced regeneration solution. The remaining 124 mL effluent was collected in one fraction. The feed displacement and DI water rinse solutions were collected and sampled as composites. The elution was conducted on the lead column only, continuing until 28.5 BVs had been processed through the column. The resin bed was then rinsed with water and regenerated with 0.25 M NaOH.

Table A.3. Experimental Conditions for AP-104/SY-101 Ion Exchange Short Test

Process step	**Solution**	**Total Volume**			**Flowrate**		**Time, h**	**T, °C**
		BV[(a)]	**AV[(b)]**	**mL**	**BV/h**	**mL/min**		
Two Columns in Series								
DI water displacement	0.25 M NaOH	8.0	2.0	84	2.6	0.45	3.1	31
Loading lead column[(c)]	AP-104/SY-101 Feed	17.5	NA	183	2.5	0.44	6.4	33-35
Loading lag column[(d)]	AP-104/SY-101 Feed	16.7	NA	175	2.5	0.44	6.4	33-35
Feed displacement	0.1 M NaOH	7.9	2.0	83	3.9	0.68	2.0	35
Rinse	DI water	9.0	2.2	94	3.4	0.60	2.6	35
Lead Column Only								
Elution	0.5 M HNO_3	28.4	NA	298	1.7	0.30	17.0	33-34
Rinse	DI water	4.3	1.9	45	2.5	0.44	1.8	34
Regeneration	0.25 M NaOH	5.6	2.6	59	1.0	0.18	5.9	34

(a) BV = bed volume (10.5 mL in 0.25 M NaOH regeneration condition)
(b) AV = apparatus volume (42 mL for columns in series; 23 mL for lead column and 21 mL for lag column)
(c) Start date = 7/15/02
(d) The feed volume through the lag column was reduced because of sampling from the lead column.
NA = not applicable

---

[a] The ion exchange processing of the AP-104/SY-101 actual waste was conducted according to Test Instruction TI-PNNL-WTP-185, Rev. 0, *Separation of Cesium from Hanford Tank Waste 241-AP-104/SY-101 Using the Dual Small-Column SuperLig® 644 Cesium Ion Exchange System*, SK Fiskum, July 2002.

A.2.5.2 Second (Full) AP-104/SY-101 Ion Exchange Column Test

Immediately following the first process test, the lead and lag columns were switched, and the residual DI water in the lead column was displaced with 0.25 M NaOH from the lead into the lag column. All subsequent processing was performed in the hot cells at a nominal temperature of 34°C. Table A.4 shows the experimental conditions for each process step where one BV is the lead resin BV in 0.25 M NaOH, 10.4 mL, just before loading AP-104/SY-101. The bed conditioning, AP-104/SY-101 loading, feed displacement, and DI water rinse steps were conducted by passing these solutions through both resin beds connected in series. The AP-104/SY-101 effluent was collected in six effluent bottles. The first bottle collected 48 mL, nominally one AV, and consisted primarily of the displaced 0.25 M NaOH. The next 146 mL of AP-104/SY-101 were processed at the nominal baseline feed condition of 2.6 BV/h. The remaining effluent was collected at a faster flowrate of 3.9 BV/h and was collected in five nominal 360-mL fractions. Sampling of the feed displacement and DI water rinse solutions began immediately after switching the feed line into the respective feed solution. The elution was conducted on the lead column only in two stages until 29 BVs had been processed through the column. (The elution was paused after processing 21 BVs 0.5 M HNO_3 and rinsed with water to allow the resin to store safely over the weekend [58.5 h]). The resin bed was then rinsed, regenerated, and rinsed again.

Table A.4. Experimental Conditions for AP-104/SY-101 Ion Exchange Second Test

Process step	Solution	Total Volume			Flowrate		Time,	T, °C
		BV[(a)]	AV[(b)]	mL	BV/h	mL/min	h	
Two Columns in Series, Baseline Load Condition								
DI water displacement	0.25 M NaOH	4.6	1.1	47.5	3.2	0.56	1.4	34
Loading Lead column[(c)]	AP-104/SY-101 Feed	18.5	NA	193	2.6	0.45	6.7	33
Loading Lag column[(d)]	AP-104/SY-101 Feed	17.1	NA	187	2.6	0.45	6.7	33
Two Columns in Series, Rapid Load Condition								
Loading Lead column[(c)]	AP-104/SY-101 Feed	164.4	NA	1710	3.9	0.68	41.3	33 - 34
Loading Lag column[(d)]	AP-104/SY-101 Feed	152.1	NA	1657	3.9	0.68	41.3	33 - 34
Feed displacement	0.1 M NaOH	9.2	2.3	96	2.7	0.46	3.7	33
Rinse	DI water	8.8	2.2	92	2.9	0.51	3.2	32 - 33
Lead Column Only								
Elution	0.5 M HNO_3	21.1	NA	219	2.0	0.34	10.7	32
Rinse	DI water	4.1	1.9	43	2.5	0.44	1.7	32
Elution, continued	0.5 M HNO_3	8.7	NA	91	1.9	0.33	4.5	31
Rinse	DI water	4.9	2.2	51	2.9	0.50	1.7	31
Regeneration	0.25 M NaOH	6.5	2.9	67	0.87	0.15	7.5	31
Rinse	DI water	3.2	1.4	33	2.2	0.38	1.5	31

(a) BV = bed volume (10.4 mL in 0.25 M NaOH regeneration condition)
(b) AV = apparatus volume (42 mL for columns in series; 23 mL for lead column and 21 mL for lag column)
(c) Start date = 7/17/02
(d) The feed volume through the lag column was reduced because of sampling from the lead column.
NA = not applicable

A.2.6 Sampling and Analysis

During the loading phase of both the short and long tests, small samples (about 2 mL) were collected from the lead and lag columns at nominal 10-BV increments. The feed displacement, DI water rinse, elution, and elution rinse samples were taken at 1- to 2-BV increments.

The ^{137}Cs concentrations were determined comparatively using a bench-top gamma-energy analysis (GEA) spectrometer, allowing for rapid sample analysis. Selected sample results were later confirmed by GEA analysis in the Chemical Measurements Center (CMC) analytical laboratory. The effluent composite sample was submitted to the CMC for various analyses: GEA, ICP-AES, IC, U, and hydroxide. The eluate samples required dilution before removal from the hot cell to reduce the dose rate from ^{137}Cs. The extent of dilution was determined by mass difference. Once the GEA results were confirmed for the eluate samples, the eluate samples from the full test were composited,(a) and a sample of the composite was submitted to the CMC (ASR 6544, # 02-3250) for various analyses: GEA, ICP-AES, ICP-MS, TOC, IC, U, Pu, Am, and various other radionuclides.

The Na and other metal concentrations were determined with ICP-AES. The OH^- concentration was determined by potentiometric titration with standardized HCl. The OH^- concentration was based on the first inflection point of the titration curve. Uranium was determined using kinetic phosphorescence analysis (KPA). The pertechnetate concentration was determined using radiochemical separations specific for pertechnetate followed by beta counting. Anions were determined using IC. TOC was determined by silver-catalyzed hot-persulfate oxidation and furnace oxidation methods. Pu, Am, and Cm were determined, after separations, by alpha spectrometry. Following element-specific separations, ^{14}C, ^{63}Ni, ^{79}Se, and ^{151}Sm were determined by liquid scintillation counting.

(a) The Cs eluate samples were composited according to Test Instruction TI-RPP-WTP-204, Rev. 0, *Preparing a Composite Solution of the Acid Eluate Samples from AP-104 Cs Ion Exchange Lead Column,* SK Fiskum, August 2002.

A.3.0 Cs Ion Exchange Results

Cesium ion exchange processing load and elution results and profiles are summarized in this section. Chemical and radiochemical analysis results of the effluent and eluate are also presented.

A.3.1 Loading, Feed Displacement, and Rinse

The AP-104/SY101 was tested twice to evaluate the effect of extended column elution on the product Cs decontamination. Results of both tests are discussed.

A.3.1.1 First (Short) Ion Exchange Column Test

The lead column (Column 2) for this test had last been used as the lag column for the second AZ-101 processing. During this processing, it had been partially loaded with Cs (5.2 E+3 μCi ^{137}Cs) from the lead-column Cs breakthrough. The lag column (Column 1) for this test had last been used as the lead AZ-101 column that was eluted with 15.9 BVs 0.5 M HNO_3 at nominally 2 BV/h (twice the baseline flowrate). These parameters are summarized in Table A.5.

Table A.5. First Process Cycle Initial Column Conditions

Column	Column ID	^{137}Cs on column, μCi	Last elution volume, BV	Elution flowrate, BV/h
Lead	2	5.2E+3$^{(a)}$	14.3$^{(b)}$	1.0$^{(b)}$
Lag	1	Nil$^{(c)}$	15.9	1.8

(a) AZ-101 processing, second cycle.
(b) AZ-101 processing, first cycle.
(c) This column had been eluted following AZ-101 processing.

The first processing test results are summarized in Table A.6. For the short processing time, both the lead- and lag-column effluent ^{137}Cs concentrations were virtually identical at nominally 0.22 and 0.26 μCi/mL, respectively ($C/C_o \approx 0.14\%$), equivalent to a decontamination factor (DF) of nominally 700. Neither the lead-column nor the lag-column effluents met the minimum ^{137}Cs removal limit for the Envelope A waste ($C/C_o = 0.0726\%$; DF = 1380). This behavior, attributed to Cs bleed from incompletely eluted resin from previous ion exchange processing activities, was expected, and the ion exchange run was terminated after processing 17.5 BVs AP-104/SY-101.

Table A.6. Results of Short Process Test

Column Feed	Lead column			Lag column		
	Cumulative BV	^{137}Cs, % C/C_o	Calculated ^{137}Cs, μCi/mL	Cumulative BV	^{137}Cs, % C/C_o	Calculated ^{137}Cs, μCi/mL
AP-104/ SY-101	5.2	1.18E-1	1.97E-1	4.9	1.22E-1	2.04E-1
	12.6	1.32E-1	2.22E-1	12.0	1.60E-1	2.69E-1
	17.5	1.33E-1	2.23E-1	16.7	1.57E-1	2.64E-1

BV = bed volume, 10.5 mL
C_o = 168 μCi/mL ^{137}Cs

After the feed displacement and DI water rinse, the lead column was eluted with 28.4 BVs (nearly twice the baseline condition of 15 BVs) 0.5 M HNO_3 at an average 1.7 BV/h. The long and fast elution was intended to better remove residual Cs from the resin before starting the next ion exchange processing. The lead column was then regenerated.

A.3.1.2 Second (Full) Ion Exchange Column Test

The lead- and lag-column positions were switched for the second Cs ion exchange processing. The lead column for this test was thus the lag column for the short test AP-104/SY-101 processing. The ^{137}Cs remaining on the lead column was essentially residual Cs from the second AZ-101 processing and elution. The lag column for this test was last used as the lead column for the short AP-104/SY-101 test (minimal Cs loading) that had been subsequently well-eluted (beyond baseline conditions) and regenerated. Initial column conditions are summarized in Table A.7.

Table A.7. Second Process Cycle Initial Column Conditions

Column	Column ID	^{137}Cs on column, µCi	Last elution volume, BV	Elution flowrate, BV/h
Lead	1	Nil[(a)]	15.9	1.8
Lag	2	Nil[(b)]	28.4	1.7

(a) This column had been eluted after AZ-101 processing and used as lag column for 17 BV AP-104/SY-101 load.

(b) This column had been well eluted after processing 17 BVs of AP-104/SY-101 and regenerated.

The measured ^{137}Cs in the load samples from both the lead and lag columns are summarized in Table A.8. The %C/C$_o$ values, determined using the bench-top GEA spectrometer, were generally in good agreement with selected samples independently analyzed by the CMC analytical laboratory. It is evident that the lead column initial Cs effluent concentration was virtually unchanged from the first processing run (when it was located in the lag position) at ~0.1% C/C$_o$ (nominally 0.2 µCi/mL).

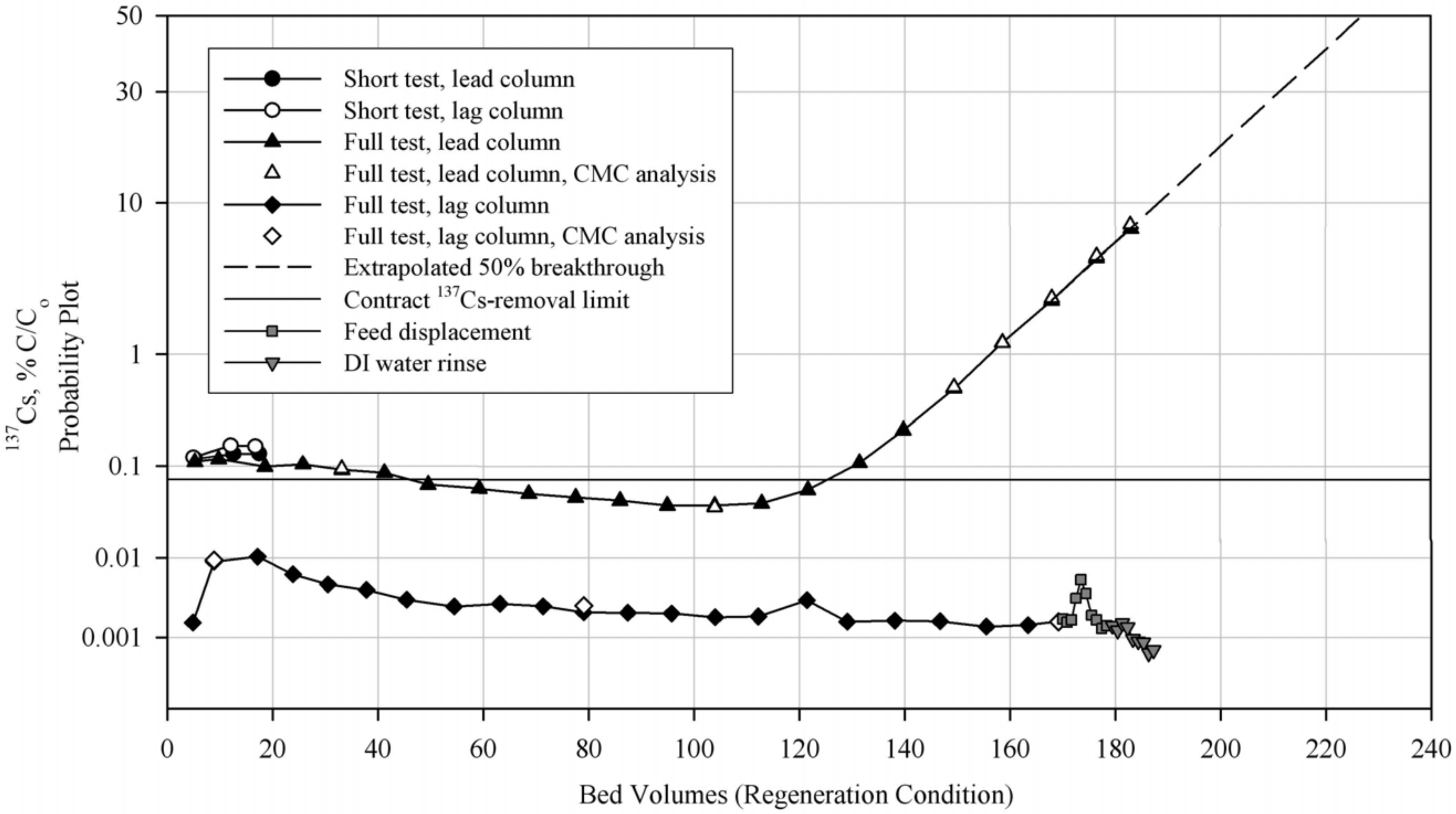
The first 18.5 BVs were processed at the nominal load flowrate of 2.6 BV/h. The flowrate increased to nominally 3.9 BV/h after processing 18.5 BVs AP-104/SY-101. The lack of significant change in C/C$_o$ as the flowrate increased indicated the Cs ion exchange behavior was primarily particle-diffusion limited.

Figure A.1 shows the ^{137}Cs effluent concentrations from the lead and lag columns graphically as % C/C$_o$ vs. the BVs of feed processed through each column, both short and long tests. The abscissa reflects BVs as a function of the resin in the expanded regeneration condition. The C$_o$ value for ^{137}Cs was determined to be 168 µCi/mL. The C/C$_o$ is plotted on a probability scale to show better definition of Cs load behavior.

Table A.8. Results of Long Process Test

Column Feed	Lead Column				Lag Column			
	Cumulative BV	^{137}Cs, % C/C$_o$	^{137}Cs, µCi/mL (a)	CMC ^{137}Cs, µCi/mL	Cumulative BV	^{137}Cs, % C/C$_o$	^{137}Cs, µCi/mL (a)	CMC ^{137}Cs, µCi/mL
AP-104/ SY-101 2.6 BV/h	5.2	1.10E-1	1.84E-1	--	4.8	1.57E-3	2.65E-3	--
	9.7	1.17E-1	1.96E-1	--	8.8	8.94E-3	1.50E-2	1.58E-2
	18.5	9.84E-2	1.65E-1	--	17.1	1.03E-2	1.74E-2	--
AP-104/ SY-101 3.9 BV/h	25.7	1.04E-1	1.74E-1	--	23.8	6.32E-3	1.06E-2	--
	33.1	9.15E-2	1.54E-1	1.58E-1	30.5	4.78E-3	8.04E-3	--
	41.2	8.51E-2	1.43E-1	--	37.8	4.07E-3	6.83E-3	--
	49.4	6.45E-2	1.08E-1	--	45.4	3.06E-3	5.14E-3	--
	59.2	5.91E-2	9.93E-2	--	54.4	2.52E-3	4.23E-3	--
	68.6	5.21E-2	8.75E-2	--	63.1	2.74E-3	4.61E-3	--
	77.4	4.76E-2	8.00E-2	--	71.3	2.54E-3	4.28E-3	--
	85.9	4.42E-2	7.42E-2	--	79.0	2.13E-3	3.59E-3	4.36E-3
	94.9	3.91E-2	6.57E-2	--	87.4	2.09E-3	3.51E-3	--
	103.9	3.92E-2	6.59E-2	6.28E-2	95.7	2.05E-3	3.44E-3	--
	112.8	4.12E-2	6.93E-2	--	104.0	1.83E-3	3.08E-3	--
	121.6	5.73E-2	9.62E-2	--	112.2	1.88E-3	3.16E-3	--
	131.4	1.08E-1	1.81E-1	--	121.4	3.02E-3	5.08E-3	--
	139.7	2.23E-1	3.75E-1	--	129.1	1.61E-3	2.71E-3	--
	149.3	5.23E-1	8.79E-1	9.03E-1	138.1	1.66E-3	2.78E-3	--
	158.5	1.24E+0	2.08E+0	2.07E+0	146.7	1.63E-3	2.74E-3	--
	167.9	2.51E+0	4.22E+0	4.38E+0	155.5	1.39E-3	2.34E-3	--
	176.4	4.77E+0	8.01E+0	8.26E+0	163.4	1.45E-3	2.44E-3	--
	182.9	7.14E+0	1.20E+1	1.27E+1	169.2	1.62E-3	2.73E-3	2.71E-3
0.1 M NaOH	Not applicable				170.0	1.73E-3	2.90E-3	--
					170.8	1.58E-3	2.65E-3	--
					171.6	1.70E-3	2.86E-3	--
					172.5	3.19E-3	5.36E-3	--
					173.4	5.47E-3	9.20E-3	--
					174.4	3.67E-3	6.16E-3	--
					175.5	1.94E-3	3.26E-3	--
					176.4	1.68E-3	2.82E-3	--
					177.4	1.30E-3	2.19E-3	--
					178.4	1.42E-3	2.38E-3	--
DI water	Not applicable				179.4	1.42E-3	2.39E-3	--
					180.4	1.23E-3	2.06E-3	--
					181.3	1.53E-3	2.58E-3	--
					182.3	1.35E-3	2.26E-3	--
					183.3	9.51E-4	1.60E-3	--
					184.3	8.75E-4	1.47E-3	--
					185.3	8.51E-4	1.43E-3	--
					186.3	6.08E-4	1.02E-3	--
					187.2	6.71E-4	1.13E-3	--

(a) Calculated from relative measure of bench-top GEA.
BV = bed volume, 10.4 mL
C$_o$ = 168 µCi/mL ^{137}Cs
"--" no data
CMC data from ASR 6515



Conditions:	SL-644 batch number 010319SMC-IV-73 212- to 425-µm dry particle size	Process temperature = 33 - 34°C
	Flow rate = 2.6 BV/h for first 20 BVs, then 3.9 BV/h	BV = 10.4 mL
	^{137}Cs C_o = 168 µCi/mL	Na concentration = 4.92 M

Figure A.1. **^{137}Cs Breakthrough Curves for AP-104/SY-101 Tank Waste, Probability Plot**

The Cs breakthrough from AP-104/SY-101 processing on the lead column began at nominally 120 BVs and was nearly linear on the probability scale, culminating in 7.6 % C/C_o at approximately 183 BVs, at which point the feed was exhausted. The 50% C/C_o breakthrough was extrapolated to be 227 BVs, assuming continuation of the linear load profile on the probability scale.

The ^{137}Cs concentrations in the lag-column samples were about a factor of 20 *lower* in ^{137}Cs concentration than those obtained from the lead column through the first 100 BVs processed. This observation was opposite to that observed with the AN-102/C-104 processing and AZ-101 processing where ^{137}Cs concentrations in the lag-column samples were higher than the lead-column samples, a result of ^{137}Cs bleed-off from previous waste processing [2, 4]. The processing conditions, including extended elution of the lead column during the previous short AP-104/SY-101 test (now moved to the lag position), removed sufficient Cs such that subsequent processing allowed the effluent to meet the required Cs decontamination.[a] The entire lag-column effluent met the minimum ^{137}Cs removal limit for this Envelope A waste (required: 0.0726 % C/C_o, DF = 1380; measured: 0.00319 % C/C_o, DF = 31,300).

A slight rise in effluent Cs concentration occurred during feed displacement after processing 4.2 BVs (173 cumulative BVs), followed by ^{137}Cs tailing. The slight rise in % C/C_o during feed displacement may have been caused by the decrease in ionic strength and/or the decrease of hydroxide concentration of the processing solution. The subsequent drop in Cs bleed-off was most likely related to the drop in Na concentration in the rinse solution, where Na acted as a competitor to Cs on the ion exchanger. Introducing water did not significantly change the effluent Cs concentration.

The total quantity of AP-104/SY-101 ^{137}Cs processed through the second test ion exchange system was 0.319 Ci. The ^{137}Cs breakthrough from the lead column was integrated. The lag-column ^{137}Cs loading was assumed to be 100% of the lead-column breakthrough and was calculated at 1.91E-3 Ci, corresponding to 0.6 % of the total ^{137}Cs in the feed. The lead column ^{137}Cs loading was calculated to be 0.317 Ci by subtracting the ^{137}Cs breakthrough onto the lag column (0.0019 Ci), and assuming residual Cs remaining on the lead column from the previous processing was nil (i.e., 0.319 Ci - 0.00191 Ci).

Figure A.1 also shows the minimum contract ^{137}Cs removal limit for AP-104/SY-101. The C/C_o value of 0.0726% (0.122 μCi/mL) corresponds to the contract limit of 0.3 Ci/m^3 for ^{137}Cs in the LAW glass. The C/C_o value corresponding to this limit was determined using the Na concentration of 4.9 M in the AP-104/SY-101 waste, the ^{137}Cs feed concentration of 168 μCi/mL, a 14 wt% waste Na_2O loading, and a glass-product density of 2.66 g/mL. The second test lag-column effluent remained below the contract limit; at the highest concentration (17 BVs), the lag column effluent was 14 % of the contract limit (C/C_o = 1.03E-2%). The composite lag-column effluent contained 0.00536 μCi/mL, corresponding to a DF of 3.13 E+4 (9.9 μCi ^{137}Cs), or 0.0031% of the total Cs processed through the columns.

---

[a] This testing did not rule out the possibility that resin-bed expansion, followed by re-elution, aided Cs removal from the resin. This resin bed was eluted with 14.3 BVs 0.5 M HNO_3 (first AZ-101 processing), regenerated, loaded with nominally 17.5 BVs AP-104/SY-101 (minimal Cs loading), then eluted with 28.5 BVs HNO_3.

The Cs-decontaminated effluent from the second full test was characterized, and results are summarized in Table A.9. Most analyte concentrations were equivalent to the feed concentration within the experimental error of the method (typically ±15%). The losses of U, Ni, Pb, and Pu were consistent with previous test results and the corresponding recoveries in the current test eluate results. The negative change indicated for the anions measured by IC were probably a result of bias associated with sample dilutions and not an indicator of removal by SL-644.

Table A.9. AP-104/SY-101 Cs-Decontaminated Product

Cations	**M**	**% Change**	**Radionuclides**	**µCi/mL**	**% Change**
Na	4.78 E+0	-2.7	^{60}Co	7.38 E-3	NA
K	4.39 E-2	-5.0	^{126}Sn/Sb	5.64 E-4	NA
Cs	2.2E-9	-99.997	^{134}Cs	<2 E-4	NA
Ca	1.75 E-3	+3.6	^{137}Cs	5.36 E-3	-99.997
Cd	3.81 E-5	-5.9	^{154}Eu	2.85 E-3	NA
Fe	[6.1 E-5]	[-1.3]	^{155}Eu	1.69E-3	NA
Mo	5.14 E-4	+0.4	$^{239+240}$Pu	2.21 E-4	-15
Ni	4.73 E-4	-18	^{241}Am (GEA)	2.25 E-3	NA
Pb	[2.0 E-5]	[-53]	^{241}Am (AEA)	1.97 E-3	-30
Sr	[4.9 E-6]	[+4.7]	$^{234+244}$Cm	4.07 E-4	-30
U (Uranyl)(a)	5.08 E-7	-98.8	**Solution Density**	**g/mL**	**% Change**
W	[3.8 E-4]	[-0.8]	Density	1.232 (25°C)	+0.5(b)
Anions	**M**	**% Change**	**Anions**	**M**	**% Change**
AlO_2^- (a)	3.91 E-1	-1.5	NO_3^-	1.51 E+0	-14
Cl^-	1.37 E-1	-9.2	OH^-	1.13 E+0	-2.6
CrO_4^{-2} (a)	7.70 E-3	-1.8	PO_4^{-3} (a) (ICP-AES)	4.28 E-2	-2.5
F^-	9.58 E-2	-10	PO_4^{-3} (IC)	4.16 E-2	-13
NO_2^-	1.23 E+0	-19	SO_4^{-2}	2.59 E-2	-11
			Oxalate	7.55 E-3	-20

ASR 6515 RPL # = 02-3062
NA = not applicable; analyte was not detected in the feed.
The IC and ICP-AES result uncertainties are expected to be ±15% (2-σ). Bracketed results indicate that the analyte concentration uncertainties exceeded 15%. Less-than (<) results indicate that the analyte concentrations were below the instrument detection limits (IDLs); the dilution-corrected IDLs are given.
(a) Al, Cr, and P determined by ICP-AES. U measured by KPA. The ionic form was assumed on the basis of waste chemistry.
(b) The change in density is probably driven by the temperature difference between the two measurements.

The ^{137}Cs concentration for the combined short and full test AP-104/SY-101 effluents was calculated (2.87E-2 µCi/mL) and found to be acceptable for LAW vitrification activities. Therefore, the short-test and full-test ion exchange effluents were combined into one composite for follow-on processing through Tc ion exchange.

A.3.2 Elution and Eluant Rinse

The lead column elution was tested at twice the baseline flowrate, 1.7 BV/h and 2.0 BV/h, for the first and second processing runs, respectively. Discussions of both tests follow.

A.3.2.1 First (Short) Ion Exchange Processing

Most of the eluted ^{137}Cs was contained in elution BVs 3 through 6. The peak C/C$_o$ value was found to be 16 (2.66E+3 µCi/mL). Integrating the elution peak resulted in 108 % ^{137}Cs recovery. The baseline elution cutoff of C/C$_o$ = 0.01 was reached within 9 BVs. Elution was continued well beyond 1% C/C$_o$ to 1.26E-4 C/C$_o$ (0.0212 µCi/mL). Results are tabulated in Table A.10.

Table A.10. Elution Data for Short Process Cycle of AP-104/SY-101

Column Feed	Cumulative BV	^{137}Cs, C/C$_o$	Calculated ^{137}Cs, µCi/mL	CMC-measured ^{137}Cs, µCi/mL
0.5 M HNO$_3$	1.2	3.92E-5	6.59E-3	--
	2.6	1.01E-4	1.70E-2	--
	3.8	1.59E+1	2.66E+3	--
	4.9	5.24E+0	8.80E+2	9.11E+2
	6.0	1.47E-1	2.47E+1	2.61E+1
	7.1	3.11E-2	5.23E+0	--
	8.2	1.19E-2	2.00E+0	--
	9.4	5.90E-3	9.92E-1	--
	10.4	3.37E-3	5.67E-1	--
	11.5	1.61E-3	2.70E-1	--
	12.9	1.18E-3	1.98E-1	--
	14.2	9.66E-4	1.62E-1	--
	15.5	6.26E-4	1.05E-1	--
	16.8	4.26E-4	7.15E-2	--
	18.2	3.47E-4	5.82E-2	--
	19.5	2.77E-4	4.65E-2	--
	20.9	2.22E-4	3.72E-2	--
	22.6	1.92E-4	3.22E-2	--
	23.9	1.75E-4	2.94E-2	--
	25.4	1.55E-4	2.60E-2	3.36E-2
	26.9	1.44E-4	2.42E-2	--
	28.4	1.26E-4	2.12E-2	--

BV = bed volume, 10.5 mL
"--" no data taken
CMC measurements from ASR 6515

A.3.2.2 Second (Full) Ion Exchange Processing

The elution data are tabulated in Table A.11.Figure A.2 shows the lead column elution and water-rinse profiles. The ordinate shows the ^{137}Cs C/C$_o$[(a)] values on a logarithmic scale to clearly show the large range of C/C$_o$ values obtained. The abscissa is given in BVs relative to the regeneration condition just before the AP-104/SY-101 load.

A total activity of 3.19 E+5 µCi ^{137}Cs was loaded on the lead column (based on total ^{137}Cs processed and subtraction of integrated Cs breakthrough). The peak elution C/C$_o$ was found to be 117 (1.96E+4 µCi/mL). Integration of the elution peak resulted in 101% Cs recovery. The baseline cutoff of C/C$_o$ = 0.01 was reached in 11 BVs. Elution was continued beyond 1% C/C$_o$ to prepare the columns for follow-on testing. The elution was stopped after processing 21 BVs eluant and then rinsed with water (endpoint on Figure A.2 is at 25 BVs) to allow the columns to store safely over the weekend. Elution was resumed after 58.5 hours with the first re-elution sample shown at 26.7 BVs. At this point, the C/C$_o$ was clearly higher than the last elution sample at 21 BVs. This indicated that Cs continued diffusing out of the resin particles into the contact solution during storage. At the onset of continued flow/elution, the eluate Cs concentration increased, then dropped rapidly as the storage solution was flushed from the resin bed.

The eluate samples from the full ion exchange processing run were composited and analyzed. Tables A.12 and A.13 summarize the analytical results. The specified minimum reportable quantities (MRQ) and the percent mass recovered relative to the mass in the feed are also provided. In cases where a result was below the IDL, the dilution-corrected IDL was provided as a “less-than” value.

The Ni, U, Pb, and Pu losses observed in the effluent were confirmed by their recoveries in the eluate. Copper was below the detection limit in both the feed and effluent (<0.6 µg/mL). The high recovery may be associated with Cu remaining on the lead column from previous processing test runs.

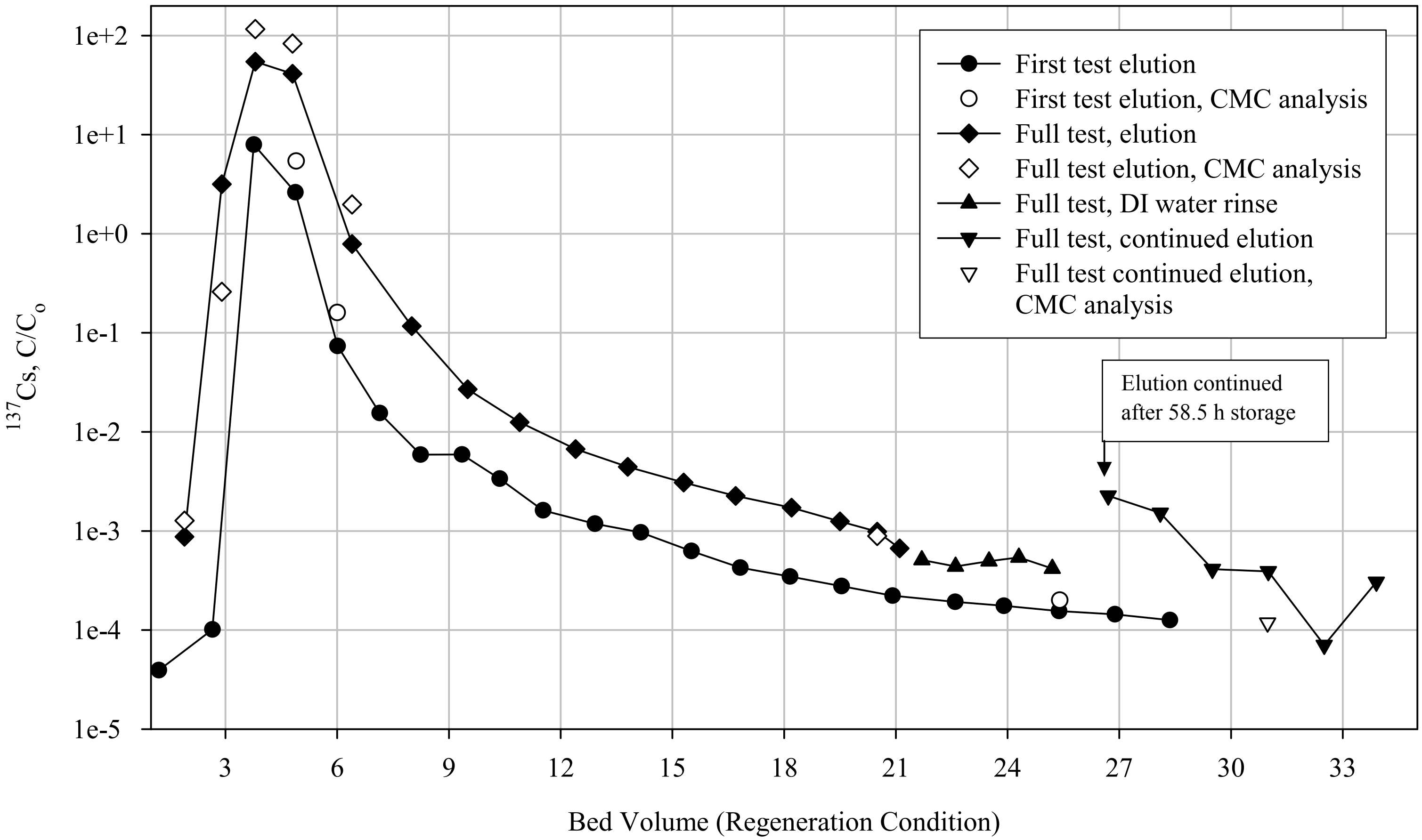
The TOC results for the two methods, hot persulfate and furnace oxidation, were similar and below 60 µg/mL. This indicated that minimal resin degradation products were present in the eluate. Because the TOC concentration was <60 µg/mL, individual organic analytes were not measured (per the test plan governing this work).

(a) The C$_o$ refers to the ^{137}Cs concentration in the AP-104/SY-101 feed sample. For elution, the C/C$_o$ value was an indication of the extent to which ^{137}Cs was concentrated relative to the feed. It was an indirect measure of the extent to which the resin is actually eluted.

Table A.11. Elution Data for Full Process Cycle of AP-104/SY-101

Column Feed	Cumulative BV	^{137}Cs, C/C$_o$	Calculated ^{137}Cs, µCi/mL	CMC-measured C/C$_o$	CMC-measured ^{137}Cs, µCi/mL
0.5 M HNO$_3$	1.9	8.75E-4	1.47E-1	1.27E-3	2.14E-1
	2.9	3.16E+0	5.30E+2	2.62E-1	4.40E+1
	3.8	5.46E+1	9.17E+3	1.17E+2	1.96E+4
	4.8	4.12E+1	6.93E+3	8.33E+1	1.40E+4
	6.4	7.88E-1	1.32E+2	1.98E+0	3.33E+2
	8.0	1.17E-1	1.96E+1	--	--
	9.5	2.69E-2	4.52E+0	--	--
	10.9	1.25E-2	2.10E+0	1.22E-2	2.05E+0
	12.4	6.71E-3	1.13E+0	--	--
	13.8	4.45E-3	7.48E-1	--	--
	15.3	3.08E-3	5.18E-1	--	--
	16.7	2.26E-3	3.80E-1	2.26E-3	3.79E-1
	18.2	1.72E-3	2.89E-1	--	--
	19.5	1.25E-3	2.09E-1	--	--
	20.5	9.81E-4	1.65E-1	8.87E-4	1.49E-1
	21.1	6.68E-4	1.12E-1	--	--
DI water	21.7	5.10E-4	8.56E-2	--	--
	22.6	4.39E-4	7.37E-2	--	--
	23.5	4.95E-4	8.31E-2	--	--
	24.3	5.40E-4	9.07E-2	--	--
	25.2	4.17E-4	7.01E-2	--	--
0.5 M HNO$_3$	26.7	2.27E-3	3.81E-1	2.60E-3	4.36E-1
	28.1	1.52E-3	2.55E-1	--	--
	29.5	4.11E-4	6.90E-2	--	--
	31.0	3.90E-4	6.56E-2	1.18E-4	1.98E-2
	32.5	7.05E-5	1.18E-2	--	--
	33.9	3.06E-4	5.13E-2	8.27E-5	1.39E-2
DI water	38.8	--	--	--	--

BV = bed volume, 10.4 mL
"--" no data taken
CMC measurements from ASR 6515



Conditions: SL-644 batch # 010319SMC-IV-73 212- to 425-µm dry particle size
BV = 10.4 mL
Eluant = 0.5 M HNO_3
Flow rate = 1.7 BV/h first test; 2.0 BV/h full test
Process temperature = 32°C
^{137}Cs C$_o$ = 168 µCi/mL

Figure A.2. ^{137}Cs Elution and Eluant Rinse of the Lead Column Short and Long Ion Exchange Processing

Table A.12. Inorganic and Organic Analytes in the Lead Column Eluate Composite

Analyte	Method	MRQ(a) μg/mL	Cs eluate μg/mL	% recovered	Analyte	Method	MRQ(a) μg/mL	Cs eluate μg/mL	% recovered
Ag	ICP-AES	NMRQ	< 0.6	ND	P	ICP-AES	NMRQ	< 3	< 0.02
Al	ICP-AES	75	[1.6]	[1.8E-3]	Pb	ICP-AES	300	[12]	[17]
As	ICP-AES	NMRQ	< 7	ND	Pd	ICP-MS	NMRQ	2.0	ND
B	ICP-AES	NMRQ	[7.5]	[1.9]	PO_4^{-3}	IC	2500	< 5	< 0.02
Ba	ICP-AES	2.3	[0.33]	[> 16]	Pr	ICP-MS	NMRQ	4.86E-2	NM
Be	ICP-AES	NMRQ	< 0.3	ND	Pt	ICP-MS	NMRQ	< 6E-2	NM
Bi	ICP-AES	NMRQ	< 3	ND	Rh	ICP-MS	NMRQ	1.45E-2	ND
Ca	ICP-AES	150	< 6	< 2	Ru(c)	ICP-MS	NMRQ	< 2E-2	ND
Br^-	IC	NMRQ	< 25	ND	Sb	ICP-AES	NMRQ	< 13	ND
Cd	ICP-AES	7.5	[0.99]	[2.7]	Se	ICP-AES	NMRQ	< 7	ND
Ce	ICP-AES	NMRQ	< 5	ND	Si	ICP-AES	170	[14]	[1.8]
Co	ICP-AES	30	< 2	ND	Sn	ICP-AES	1500	< 13	ND
Cl^-	IC	300	[22]	[0.051]	SO_4^{-2}	IC	2300	[7.8]	[0.035]
Cr	ICP-AES	15	19.4	0.59	Sr	ICP-AES	NMRQ	< 0.4	< 12
Cs(b)	GEA	NMRQ	72.4	97	Ta(d)	ICP-MS	NMRQ	< 6E-3	NM
Cu	ICP-AES	17	9.8	> 195	Te	ICP-AES	NMRQ	< 13	ND
Dy	ICP-AES	NMRQ	< 2	ND	Th	ICP-AES	NMRQ	< 26	ND
Eu	ICP-AES	NMRQ	< 3	ND	Ti	ICP-AES	17	< 0.7	ND
F^-	IC	150	[10]	[0.061]	Tl	ICP-AES	NMRQ	< 13	NM
Fe	ICP-AES	150	[2.0]	[7.0]	TOC	Hot Pers.	1500	[26]	[0.09]
Hg	CVAA	NMRQ	< 0.006	< 65	TOC	Furnace	1500	[45]	[0.2]
K	ICP-AES	75	< 52	< 0.4	U	ICP-AES	600	< 51	ND
La	ICP-AES	35	< 2	ND	U	KPA	600	56.9	72

Table A.12 (Contd)

Analyte	Method	MRQ[a] µg/mL	Cs eluate µg/mL	% recovered	Analyte	Method	MRQ[a] µg/mL	Cs eluate µg/mL	% recovered
Li	ICP-AES	NMRQ	< 0.8	ND	U	ICP-MS	NMRQ	54.1	82
Mg	ICP-AES	300	< 3	ND	V	ICP-AES	NMRQ	< 2	ND
Mn	ICP-AES	150	< 2	ND	W	ICP-AES	NMRQ	< 13	< 3
Mo	ICP-AES	150	< 2	< 0.3	Y	ICP-AES	NMRQ	< 2	ND
Na	ICP-AES	75	531	0.058	Zn	ICP-AES	16.5	< 2	ND
Nd	ICP-AES	NMRQ	< 3	ND	Zr	ICP-AES	NMRQ	< 2	ND
Ni	ICP-AES	30	28	10	**Physical Properties**				
NO_2^-	IC	3000	57	0.01	Wt% dried solids		0.1	0.276	NA
NO_3^-	IC	3000	35,600	NA	Wt% oxides		NMRQ	0.123	NA
Oxalate	IC	NMRQ	< 5	< 0.07	Density, g/mL		NMRQ	1.012	NA

(a) MRQ is minimum reportable quantity. NMRQ indicates no minimum reportable quantity was requested.
(b) Calculated based on ^{137}Cs concentration in the eluate and applied eluate Cs isotopic distribution ratio (^{133}Cs 60.5 wt%, ^{135}Cs 18.7 wt%, ^{137}Cs 20.8 wt%).
(c) Total Ru based on ^{102}Ru concentration and isotopic abundance of 31.6%.
(d) The Ta analysis QC sample blank spike and matrix spike recoveries were low, 76% and 66%, respectively.

Notes:
The overall error was estimated to be within ±15%. Values in brackets were within 10-times the detection limit, and errors were likely to exceed ±15%. Less-than (<) values indicate the analytes were not detected by the instrument, and the reported values represent the IDLs multiplied by the sample dilution factors.
NA = not applicable; ND = analyte not detected in the feed; NM = analyte not measured in the feed
ASR 6544 and 6544.01, Sample ID 02-3250

Table A.13. Radionuclides in the Combined Lead Column Eluate Composite

Analyte	Method	MRQ$^{(a)}$ µCi/mL	Cs eluate µCi/mL	Error % (1-σ)	% recovered	Analyte	Method	MRQ$^{(a)}$ µCi/mL	Cs eluate µCi/mL	Error % (1–σ)	% recovered
^{14}C	Radchem	NMRQ	< 2E-5	–	< 0.39	^{232}Th	GEA	NMRQ	< 2 E+0	–	NM
^{51}Cr	GEA	NMRQ	< 6 E+0	–	NM	^{233}U	ICP-MS	NMRQ	< 7 E-05	–	< 180$^{(b)}$
^{59}Fe	GEA	NMRQ	< 8 E-2	–	NM	^{234}U	ICP-MS	NMRQ	< 4 E-5	–	< 130$^{(b)}$
^{60}Co	GEA	NMRQ	< 5 E-2	–	< 76	^{235}U	ICP-MS	NMRQ	1.01 E-6	0.8	79$^{(b)}$
^{63}Ni	Radchem	NMRQ	3.24E-2	3	NM	^{236}U	ICP-MS	NMRQ	1.94 E-6	2	86$^{(b)}$
^{79}Se	Radchem	NMRQ	< 3E-5	–	< 0.48	^{238}U	ICP-MS	NMRQ	1.80 E-5	0.6	81$^{(b)}$
^{88}Y	GEA	NMRQ	< 6 E-2	–	NM	^{236}Pu	Radchem	NMRQ	< 9 E-6	–	ND
^{90}Sr	Radchem	1.50 E-1	1.12E-1	3	0.82	^{237}Np	ICP-MS	NMRQ	3.03 E-6$^{(c)}$	15	11
^{95}Nb	GEA	NMRQ	< 6 E-2	–	NM	^{238}Pu	Radchem	NMRQ	3.95 E-5	14	14
^{99}Tc (+7)	Radchem	NMRQ	1.04E-4	10	0.03	$^{239+240}$Pu	Radchem	NMRQ	1.59 E-4	6	7.7
^{99}Tc	ICP-MS	3.00 E-3	<4E-4$^{(c)}$	–	< 0.03	^{239}Pu	ICP-MS	NMRQ	< 2 E-3$^{(c)}$	–	< 27
^{103}Ru	GEA	NMRQ	< 9 E-1	–	NM	^{240}Pu	ICP-MS	NMRQ	< 2 E-4$^{(c)}$	–	ND
^{106}Ru	GEA	NMRQ	< 5 E+0	–	NM	^{241}Pu	Radchem	NMRQ	2.81 E-3	16	NM
^{113}Sn	GEA	NMRQ	< 2 E+0	–	NM	^{241}Am	Radchem	3.0 E-2	1.25 E-3	3	5.5
^{125}Sb	GEA	NMRQ	< 3 E+0	–	ND	^{241}Pu, ^{241}Am	ICP-MS	NMRQ	4.18 E-4 µg/mL$^{(d)}$	10	3.4
^{126}Sn/Sb	GEA	NMRQ	< 2 E+0	–	ND	^{242m}Am	Radchem	NMRQ	< 7 E-6	–	NM
^{134}Cs	GEA	NMRQ	< 5 E-1	–	ND	^{242}Cm	Radchem	NMRQ	< 7 E-6	–	< 9
^{137}Cs	GEA	5.00 E-2	1.31 E+3	3	96$^{(e)}$	^{242}Pu	ICP-MS	NMRQ	< 2 E-6$^{(c)}$	–	NM
^{144}Ce	GEA	NMRQ	< 4 E+0	–	NM	$^{243+244}$Cm	Radchem	NMRQ	3.56 E-4	6	7.5
^{151}Sm	Radchem	NMRQ	3.84 E-2	5	NM	Alpha sum$^{(f)}$	Radchem	NMRQ	1.81 E-3	3	6.0
^{152}Eu	GEA	NMRQ	< 2 E-1	–	NM	Total alpha	Radchem	2.30 E-1	< 6 E-2	–	ND
^{154}Eu	GEA	2.00 E-3	< 2 E-1	–	ND	Total beta	Radchem	NMRQ	1.10 E+3	4	76
^{155}Eu	GEA	9.00 E-2	< 2 E+0	–	ND						

ASR 6544 and 6544.01, RPL # 02-3250, reference date = September 2002 through January 2003.

NM = not measured in the feed; ND = not detected in feed or eluate; "—" = error not applicable to less-than (<) values

(a) MRQ is minimum reportable quantity. NMRQ indicates no minimum reportable quantity requested.

(b) The total eluate U recovery was measured by ICP-MS at 82%.

(c) Analysis may be affected by calibration QC issues; see QC discussion.

(d) The AMU-241 is reported in units of µg/mL. Applying the specific activity of ^{241}Pu (103 Ci/g,) the sample activity is 4.3E-2 µCi/mL; applying the specific activity of ^{241}Am (3.428 Ci/g), the sample activity is 1.4E-3 µCi/mL.

(e) The remaining 4% Cs was apportioned to analytical samples submitted to the CMC. The integrated eluate Cs recovery resulted in 101%.

(f) The alpha sum (total of individually-measured Pu, Am, and Cm alpha emitters) provides the best estimate of the total alpha activity in the sample.

Table A.14 presents a condensed summary of the analyte masses and millimoles recovered in the eluate. The millimoles recovered in the eluate may be related to the active sites available on the resin. Milliequivalents were not estimated because the ionic form exchanging onto the resin was not always known. The major cation was Na. The total millimoles recovered were consistent with previous testing [1-5]. The Cu recovery was >195%. The additional Cu may have remained on the lead column to some extent after AZ-101 processing.

Table A.14. Select Analyte Recoveries in Eluate

Analyte	AP-104/SY-101 feed, total mg	Amount Recovered in Eluate		
		mg	mmoles	%
U (by KPA)	18.4	13.3	0.0556	72.5
Ba	< 0.5	[0.077]	[0.00056]	[>16]
Ca	129	< 1.5	<0.04	< 2
Cd	8.67	[0.23]	[0.0020]	[2.7]
Cr	776	4.55	0.0875	0.59
Cs	17.6	17.0	0.126	96.7
Cu	< 1.2	2.30	0.0362	>195
Fe	[6.7]	[0.47]	[0.0084]	[7.0]
Na	215,000	125	5.43	0.058
Ni	64.3	6.57	0.112	10.2
Pb	[16.7]	2.81	0.014	[17]
Sum	NA	NA	5.87	NA

Values in brackets were based on results reported within 10 times the detection limit, and errors were likely to exceed ±15%. Less-than (<) values indicate that the analytes were not detected by the instrument, and the reported values represent the IDLs multiplied by the sample dilution factors. The greater-than (>) value for % Ba and Ca recoveries indicates that the analyte was not detected in the feed, and the recovery is based on a maximum feed value.
NA = not applicable

A.4.0 Quality Control

The following sections describe the quality assurance (QC) and quality control (QC) requirements and implementation.

A.4.1 Quality-Assurance Requirements

PNWD implemented the River Protection Project-Waste Treatment Plant (RPP-WTP) quality requirements by performing work in accordance with the PNWD Waste Treatment Plant Support Project quality assurance project plan (QAPjP) approved by the RPP-WTP QA organization. This work was performed to the quality requirements of NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Subpart 2.7. These quality requirements were implemented through PNWD's *Waste Treatment Plant Support Project (WTPSP) Quality Assurance Requirements and Description Manual* and to the approved Test Plan, TP-RPP-WTP-175, Rev. 0. The analytical requirements were implemented through PNWD's *Conducting Analytical Work in Support of Regulatory Programs* requirements document.

Experiments that were not method-specific were performed in accordance with PNWD's procedures QA-RPP-WTP-1101 "Scientific Investigations" and QA-RPP-WTP-1201 "Calibration Control System," assuring that sufficient data were taken with properly calibrated measuring and test equipment (M&TE) to obtain quality results.

As specified in Test Specification 24590-LAW-TSP-RT-02-003, Rev. 0, *AP-104/SY-101 (Envelope A) LAW Pretreatment, Vitrification, Product Testing, and Regulatory Analyses*, BNI's QAPjP, 24590-QA-0001, was not applicable since the work was not performed in support of environmental/regulatory testing, and the data should not be used as such. (Only the vitrified product was to be tested in support of environmental/regulatory testing.)

PNWD addressed internal verification and validation activities by conducting an independent technical review of the final data report in accordance with PNWD's procedure QA-RPP-WTP-604. This review verified that the reported results were traceable, that inferences and conclusions were soundly based, and that the reported work satisfied the test-plan objectives. This review procedure is part of PNWD's *WTPSP Quality Assurance Requirements and Description Manual*.

A.4.2 Analytical Results

The data quality and QC are discussed for each analytical method. No analytes of interest or QC criteria were delineated for the feed and composite effluent analyses. Method-specific acceptance criteria were established by PNWD's *Conducting Analytical Work in Support of Regulatory Programs* requirements document where the RPD acceptance criterion is <20%, laboratory control sample/blank spike (LCS/BS) acceptance criteria are 80 to 120% recovery and matrix spike (MS) acceptance criteria are 75 to 125% recovery. The composite Cs eluate analysis was to meet BNI-directed MRQ and QC requirements. The precision acceptance criterion was set to <15% RPD. The LCS/BS was to recover typically at 80 to 120% (^{90}Sr was set to 75 to 125%; total alpha and total beta were set to 70 to 130%). The MS acceptance criteria were set at 75 to 125% or 70 to 130% recovery, as defined in the test plan.

All defined MRQs were met. All raw and reduced data, including actual QC results, are maintained in data files under Project 42365 at PNWD under ASR 6515 and ASR 6544.

A.4.2.1 Gamma Energy Analysis

GEA was conducted directly on ion exchange process samples. Therefore, LCSs, BS, and MS QC samples were not required. Sample results demonstrated good agreement with the bench-top counter results. Sample duplicate results met the acceptance RPD criterion.

A.4.2.2 Inductively Coupled Plasma-Atomic Emission Spectrometry

The ICP-AES spent resin analysis was conducted on acid-digested sample aliquots. All batch and instrument QC requirements were met except as indicted.

AP-104/SY-101 feed analysis: The Na BS that recovered high at 185% and was attributed to low-level Na contamination during initial preparation. The Zr MS recovered low at 72%.

AP-104/SY-101 composite effluent analysis: Si recovered high at 169% in the LCS, indicating it may have been contaminated during preparation. The Si MS recovery was within the acceptance criteria.

Cs eluate composite analysis: No QC issues.

A.4.2.3 Inductively-Coupled Plasma-Mass Spectrometry

The ICP-MS spent-resin analysis was conducted on an aliquot of the Cs eluate composite only. All batch and instrument QC requirements were met except as indicted. Neither a BS nor MS was prepared containing ^{99}Tc, ^{237}Np, ^{239}Pu, ^{240}Pu, ^{241}Am, or ^{242}Pu; matrix effects were evaluated relative to post-matrix spiking. Both the Ta BS and MS recovered low at 76% and 66%, respectively. The low recovery may be indicative that the preparation method was not satisfactory for the matrix. Direct analysis of the spiking standard also indicated low recovery, indicating that the standard may have deteriorated. The Np and Pu calibration and calibration verification solutions were taken from the same parent stock of material. The Tc standard was later shown to have a 24% high bias. For these reason, the Ta, ^{99}Tc, ^{237}Np, ^{239}Pu, ^{240}Pu, and ^{242}Pu are flagged as having a QC issue. The Ta, ^{99}Tc, ^{239}Pu, ^{240}Pu, and ^{242}Pu were non-detectable by ICP-MS so results should not be impacted. A detectable amount of ^{237}Np was measured; however the calibration issue was not anticipated to affect the accuracy of the result within the reported 15% relative error.

A.4.2.4 Uranium by Kinetic Phosphorescence Analysis

The U KPA spent-resin analysis was conducted on acid-digested aliquots of feed, effluent composite, and Cs eluate composite. All batch and instrument QC requirements were met.

A.4.2.5 Americium, Curium, and Plutonium

Isotopes of Am, Cm, and Pu were measured on aliquots of acid-digested feed, effluent composite, and eluate composite samples. All batch and instrument QC requirements were met.

A.4.2.6 Total Alpha and Total Beta

Total alpha and total beta were measured on the Cs eluate composite only. All batch and instrument QC requirements were met with the following exception. The added MS beta spike activity was too low to be measured relative to the total beta concentration.

A.4.2.7 Low-Energy Beta Emitters

The isotopes of ^{14}C, ^{63}Ni, ^{79}Se, ^{90}Sr, ^{99}Tc (as pertechnetate), ^{241}Pu, and ^{151}Sm, were measured on aliquots of the Cs eluate composite after radiochemical separations using beta-counting techniques. All batch and instrument QC requirements were met.

A.4.2.8 Ion Chromatography

Anions were measured on sample dilutions of the feed, effluent composite, and Cs eluate composite. All batch and instrument QC requirements were met. Peaks were present in the IC system chromatograms of the feed and effluent near the fluoride and chloride peaks that potentially affected peak integration.

A.4.2.9 Hydroxide

Hydroxide was measured on the feed and effluent composite. All batch and instrument QC requirements were met.

A.4.2.10 Weight Percent Solids and Oxides

The weight percent solids and oxides were measured on the Cs eluate composite only. All batch and instrument QC requirements were met.

A.4.2.11 Total Organic Carbon

Total organic carbon was measured on the composite Cs eluate only by both the hot persulfate method and the furnace oxidation method. All batch and instrument QC requirements were met.

A.4.2.12 Mercury

Mercury was measured on the Cs eluate composite only. All batch and instrument QC requirements were met, except the low-level instrument calibration standard recovered at only 72%. The sample results were not affected because they were below the EQL.

A.5.0 References

1. SK Fiskum, DL Blanchard, and ST Arm. 2002a. *Aging Study and Small Column Ion Exchange Testing of SuperLig® 644 for Removal of* ^{137}*Cs from Simulated AW-101 Hanford Tank Waste*, WTP-RPT-015, Battelle Pacific Northwest Division, Richland, WA.

2. SK Fiskum, ST Arm, DL Blanchard, and BM Rapko. 2002. *Small Column Ion Exchange Testing of Superlig® 644 for Removal of* ^{137}*Cs from Hanford Waste Tank 241-AP-101 Diluted Feed (Envelope A),* WTP-RPT-016, Battelle Pacific Northwest Division, Richland, WA.

3. SK Fiskum, DL Blanchard, and ST Arm. 2002b. *Small Column Ion Exchange Testing of SuperLig® 644 for Removing* ^{137}*Cs from Hanford Waste Tank 241-AN-102 Supernate (Envelope C) Mixed with Tank 241-C-104 Solids (Envelope D) Wash and Permeate Solutions,* WTP-RPT-033, Battelle Pacific Northwest Division, Richland, WA.

4. SK Fiskum, DL Blanchard, and ST Arm. 2002c. *Small Column Ion Exchange Testing of SuperLig® 644 for Removal of* ^{137}*Cs from Hanford Waste Tank 241-AZ-102 Concentrate (Envelope B),* WTP-RPT-041, Battelle Pacific Northwest Division, Richland, WA.

5. SK Fiskum, ST Arm, and DL Blanchard. 2003. *Small Column Ion Exchange Testing of SuperLig® 644 for Removal of* ^{137}*Cs from Hanford Waste Tank 241-AZ-101 (Envelope B)*, WTP-RPT-054, Battelle Pacific Northwest Division, Richland, WA.

6. DL Baldwin, PR Bredt, JA Campbell, OT Farmer, SK Fiskum, LR Greenwood, GM Mong, AP Poloski, RD Scheele, CZ Soderquist, MR Smith, LA Snow, RG Swoboda, MP Thomas, MW Urie, JJ Wagner. 2003. *Chemical Analysis and Physical Property Testing of 241-AP-104 Tank Waste, Revision 0*, February 2003, WTP-RPT-069, Battelle Pacific Northwest Division, Richland, WA.

Appendix B

Chains of Custody

Battelle - Pacific Northwest Division
Chain of Custody (COC) Form

Chain of Custody No.	Project No./Title	Analyses	Project Point of Contact	Phone Number
WTP-COC-013	42365/Spent Resin Samples		SK Fiskum	376-7015
			Scope of Work Document(s): TI-RPP-WTP-229	

Date	Time	Sample Identification	# of Containers	Acid digest	ICP-AES	ICP-Ms	Radiochemistry			Matrix	Comments
4/8/03	11:30	229-C1-AD	1	√	√	√	√			SL-644	
4/8/03	11:30	229-C1-AD-Dup	1	√	√	√	√			SL-644	
4/11/03	09:30	229-C2-AD-MSAES	1	√	√					SL-644	
4/8/03	11:30	229-C1-AD-MSMS	1	√		√				SL-644	
4/11/03	09:30	229-C2-AD	1	√	√	√	√			SL-644	
4/11/03	09:30	229-C2-AD-D	1	√	√	√	√			SL-644	

Samples Preserved? Yes* [✓ No]

Date 4/11/03	Time 9:30	Relinquished by S.K. Fiskum	Date 4/11/03	Time 09:50	Received by MJ Steele
Date	Time	Relinquished by	Date	Time	Received by
Date	Time	Relinquished by	Date	Time	Received by

* If yes, then note preservation in Comments section.

Battelle - Pacific Northwest Division
Chain of Custody (COC) Form

Chain of Custody No.		Project No./Title		Analyses						Project Point of Contact	Phone Number
WTP-COC-014		42365/Spent Resin Samples								SK Fiskum	376-7015
										Scope of Work Document(s): TI-RPP-WTP-229	
Date	Time	Sample Identification	# of Containers	GEA						Matrix	Comments
4/8/03	11:15	229-C1-GEA	1	√						SL-644	2-mL geometry
insufficient sample		229-C1-GEA-Dup	1	√						SL-644	2-mL geometry
4/11/03	09:30	229-C2-GEA	1	√						SL-644	2-mL geometry
insufficient sample		229-C2-GEA-Dup	1	√						SL-644	2-mL geometry

Samples Preserved? Yes* [✓ No]

Date 4/11/03	Time 09:50	Relinquished by S.K. Fiskum	Date 4/11/03	Time 09:50	Received by MJ Steele
Date	Time	Relinquished by	Date	Time	Received by
Date	Time	Relinquished by	Date	Time	Received by

* If yes, then note preservation in Comments section.

Distribution

No. of Copies

OFFSITE

6 Savannah River Technology Center
Larry Hamm
PO Box 616, Road 1
Building 773-42A
Aiken, South Carolina 29808

Neguib Hassan
PO Box 616, Road 1
Building 773-A
Aiken, South Carolina 29808

Jim Marra
PO Box 616, Road 1
Building 773-43A
Aiken, South Carolina 29808

Charles Nash
PO Box 616, Road 1
Building 773-42A
Aiken, South Carolina 29808

Robert Pierce
PO Box 616, Road 1
Building 773-A
Aiken, South Carolina 29808

Harold Sturm
PO Box 616, Road 1
Building 773-A
Aiken, South Carolina 29808

No. of Copies

ONSITE

11	Battelle - Pacific Northwest Division	
	S. T. Arm	P7-28
	D. L. Blanchard	P7-25
	S. K. Fiskum (3)	P7-22
	D. E. Kurath	P7-28
	M. J. Steele	P7-22
	Project File (2)	P7-28
	Information Release (2)	K1-06
3	Bechtel National, Inc.	
	J. F. Doyle	H4-02
	R. A. Peterson	H4-02
	M. R. Thorson	H4-02