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Cesium Ion Exchange Using Spherical Resorcinol-Formaldehyde Resin in Support of Waste Qualification Testing for LAWPS

September 2017

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MR Smoot
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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Richland, Washington 99352

Executive Summary

The Low-Activity Waste Pretreatment System (LAWPS) facility is planned to pretreat Hanford tank waste supernate by filtering solids and processing through ion exchange columns to remove cesium. The ion exchange media is currently targeted to be spherical resorcinol-formaldehyde resin (SRF). This media has been tested in a wide array of simulants and process scales, but column breakthrough and batch contact testing to date on actual tank waste has been limited to two tank wastes. Washington River Protection Solutions (WRPS) requested a study to determine if a simple batch contact test with SRF can be used to qualify tank waste supernate prior to processing it in the LAWPS. The goal of the batch contact testing would be to determine if there are any issues with the tank waste that would preclude Cs removal by the ion exchanger.

Batch contact and column testing was conducted on SRF provided by Microbeads (Skedsmokorset, Norway, batch number 1F-370/1392), which was manufactured in August 2011. The batch contact testing only varied Cs concentration and tested two process feeds. The column testing was prototypic to the intended LAWPS operations in a lead-lag column format, albeit on a small-scale basis with 10-mL resin beds. In this process, the feed was processed downflow through the lead column and then through the lag column. The feed was displaced with 0.1 M NaOH, and then the columns were rinsed with water sequentially through the lead then lag columns. Elution was conducted downflow from the lag to the lead column with 0.45 M HNO_3. Then the columns were sequentially rinsed with deionized water. The resin was returned to the Na-form by processing 1 M NaOH downflow from the lag to the lead column, unlike the LAWPS intent to implement this step by fluidizing the resin beds.

Testing was conducted with two process feeds: 1) 5.6 M Na simple simulant spiked with 60 µg/mL Cs and 2) actual tank waste from 241-AP-105 diluted to 5.7 M Na (AP-105DF). The initial test with simulant was implemented to ensure that the aged resin still performed as anticipated, and to compare Cs exchange performance with previous testing conducted at a pilot scale and full scale. Characterization of the two feeds was conducted.

Batch contact testing was used to determine the batch equilibrium coefficient at the equilibrium feed condition. In turn, this value was used to calculate the resin bed volumes (BVs) processed to reach 50% Cs breakthrough on an ion exchange column. Batch contact testing was also used to determine Cs load capacity on the ion exchanger at equilibrium conditions. Table ES.1 summarizes the batch contact data obtained for the two test solutions.

Table ES.1. Batch Contact Summary

Feed	Equilibrium K_d (mL/g)	Calculated 50% Cs Breakthrough (BV)	Equilibrium Cs Load Capacity (mg/g)
5.6 M Na Simple Simulant	545	136	31.2
AP-105DF	887	222	7.5

Column testing was used to generate the Cs load and elution profiles from processing both the 5.6 M Na simple simulant and the AP-105DF. From the load profile, the number of bed volumes processed to reach 50% breakthrough was determined along with the number of bed volumes that can be processed before reaching the plant target of 10% of the Hanford Tank Waste Treatment and Immobilization Plant contract limit for receiving waste for vitrification (a function of the Na and ^{137}Cs contents). For AP-105DF, the 10% of the contract limit is set to 0.016% of the influent ^{137}Cs concentration; this requires a Cs decontamination factor of 6160. Table ES.2 summarizes the observed column performance for the two tested feeds.

Table ES.2. Column Performance Summary

Feed	50% Cs Breakthrough (BV)	Cs Load Capacity (mg/g)	Contract Limit Breakthrough (BV)
5.6 M Na Simple Simulant	125	33.4	Not applicable
AP-105DF	206	6.64	275

The batch contact results agreed within 8% of the columns results (capacity and 50% breakthrough calculations). It is not possible to equate the batch contact results to understanding the number of bed volumes that can be processed before reaching the 10% contract limit for Cs from the lag column, as this depends on the slope of the load curve/mass transfer zone.

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The authors thank the ASO count room staff Truc Trang-Le, Bruce Pierson, and Mike Cantaloub for rapid ^{137}Cs analysis for the batch contact and column load/elution sample analysis. We thank the hot cell technician staff, LaWanda Grow, Michael Rojas, Jarrod Turner, Jeff Chenault, Robert Cox, and Jordan Cordray, for sample handling and systems manipulations in-cell. We thank Renee Russell for reviewing the ion exchange calculation files, test data packages, and this technical report.

Acronyms and Abbreviations

ASO	Analytical Support Operations
ASR	Analytical Services Request
BV	bed volume
DF	decontamination factor
DI	deionized
FMI	Fluid Metering, Inc.
GEA	gamma energy analysis
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
LAWPS	Low-Activity Waste Pretreatment System
PNNL	Pacific Northwest National Laboratory
RPL	Radiochemical Processing Laboratory
SRF	spherical resorcinol-formaldehyde
WRPS	Washington River Protection Solutions
WTP	Hanford Tank Waste Treatment and Immobilization Plant

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1.0 Introduction

Decanted tank waste supernatant will be pretreated in the Low-Activity Waste Pretreatment System (LAWPS) to meet the Hanford Tank Waste Treatment and Immobilization Plant (WTP) low-activity waste facility waste acceptance criteria.[1] Specific to ^{137}Cs, this requirement is < 3.18E-5 Ci ^{137}Cs/mole of Na (contract limit). The key process operations for treating the waste include solids filtration and cesium removal. At the LAWPS, cesium removal is planned to be accomplished through the use of spherical resorcinol-formaldehyde (SRF) ion exchange resin in two ~300-gallon resin beds arranged in a lead/lag format, processing feed until the lag column effluent reaches 10% of the contract limit.

The ion exchange performance of filtered supernatant feed has been modeled; however, the model inputs are simplified and may not completely reflect actual tank waste performance. Testing has been conducted at the full scale[2] and 1/9th scale[3] with simplified tank waste simulants that provide good Cs load characteristics under nominal processing conditions. However actual tank waste cannot be precisely simulated because of the concern regarding unknown factors in the feed that may affect Cs load/elute performance and synergistic effects of chemical, radiolytic, and mechanical degradation.

Processing characteristics can be obtained from small-scale column testing with actual tank waste. From the column testing, the transfer zone, 50% Cs breakthrough, and overall process volumes to maintain the desired decontamination factor can be assessed (Nash et al. 2006; Fiskum et al. 2006b; Helfferich 1962; Harland 1994). However, column tests require significant effort; they require about 1 gallon of filtered tank waste supernate diluted to process specification, work in a shielded hot cell facility, and about 2 weeks of actual process time and sample collection, followed by sample analysis.

Washington River Protection Solutions (WRPS) requested an efficacy study of initial batch contact testing to determine if the plant ion exchange resin separates cesium prior to committing a tank waste supernate into the plant for processing. A batch contact test can be performed on a significantly smaller volume of tank waste and at a more rapid pace (nominally 1 week total time inclusive of preparations, contact time, and analysis time), thus reducing time and resources, and ultimately, schedule risk.

This report discusses results of batch contact and column testing studies from testing two feeds: 1) a simple simulant and 2) AP-105 actual tank waste supernatant diluted to 5.7 M Na. The simple simulant was the same composition used for 1/9th-scale and full-scale testing; thus, column test results can be directly compared from small scale (10-mL resin beds) to 1/9th scale and full scale. This report also discusses the results of the batch contact test vis-à-vis the column tests and the efficacy of using batch contacts to determine if the plant ion exchange resin separates cesium and to predict column performance, if needed.

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[1] 24590-WTP-ICD-MG-01-030. 2015. *ICD 30 – Interface Control Document for Direct LAW Feed*. Bechtel National, Inc., Richland, Washington.

[2] Evans B. 2017. 03049-05-RPT-0002. *Full-Scale IX Column Test Report*. AECOM, Richland, Washington.

[3] Evans B. 2017. 03049-05-RPT-0001. *Engineering-Scale Integrated Test Report*. AECOM, Richland, Washington.

2.0 Test Conditions

This section describes the SRF resin, simple simulant, AP-105 tank waste (as-received and diluted), batch contact conditions, and column ion exchange conditions. All testing was conducted in accordance with a test plan prepared by Pacific Northwest National Laboratory (PNNL) and approved by WRPS.[1]

2.1 SRF Resin

The SRF ion exchange resin (Spheromers® RF 380) was provided by Microbeads AS, Skedsmokorset, Norway, batch number 1F-370/1392, which was manufactured in August 2011. The resin and an overburden of water were placed into a Finncont[2] by the manufacturer. The Finncont and contents are flushed with nitrogen and then slightly pressurized with nitrogen, maintaining the slight positive pressure during extended storage periods, thus precluding oxidative attack on the resin. WRPS received the resin from the manufacturer in April 2015 and stored the Finncont in a climate-controlled area until transferring it to PNNL. The Finncont was received at PNNL on September 1, 2015. The resin had been stored as manufactured in the H-form in water under pressurized nitrogen gas (0.26 bar) in the Finncont container. The Finncont had been accessed previously in November 2015 at PNNL to retrieve a resin sample. On March 30, 2017, approximately 500 mL of SRF resin was vacuum-retrieved from the Finncont into a 1-gallon glass jug for the scope of work defined herein. All resin sample retrievals were conducted according to the instructions in GD-LPIST-001, Rev. 0.0.[3] Following sample collection, the Finncont headspace was purged with nitrogen because the resin is known to degrade on contact with oxygen from air. The oxidation-degradation is not a physical hazard, but it will damage active Cs exchange sites and thus reduce effectiveness as a Cs ion exchanger. Likewise, the 500-mL sample fluid and headspace were purged with argon.

The transfer process resulted in a portion of the resin beads floating at the liquid surface. Further, a significant portion of the resin beads did not settle tightly. Figure 2.1a shows the resin sample as retrieved; it appeared diffuse and loosely globular and the aqueous phase appeared cloudy and yellow. The top portion of the poorly settled resin was removed and stored separately based on the thought that it might otherwise be compromised (possibly due to bacterial or fungal growth). Figure 2.1b shows the remaining resin after 4 days of settling; the aqueous portion cleared and the resin appeared to settle more effectively. The removed layer of resin also settled compactly within 4 days. These observations indicated that the nitrogen gas dissolved in the solution (from the positive pressure in the Finncont) and the vacuum movement caused the gas to release within the resin beads themselves, leaving the resin beads more buoyant. With time, the gas released from the resin. Resin subsampled from this bottle was collected from the most compacted layer at the bottom.

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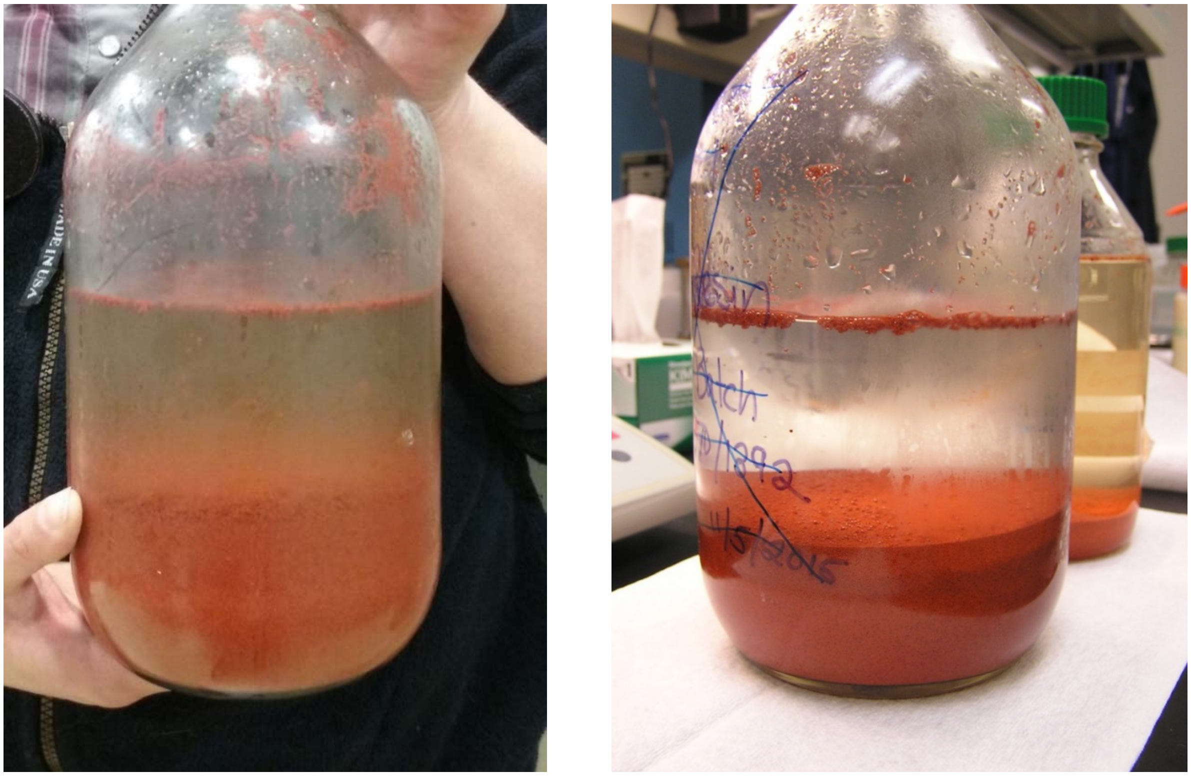
[1] TP-DFTP-001, Rev.0.2. *DFLAW Test Platform Cesium Ion Exchange Testing with AP-105 Tank Waste with Spherical Resorcinol-Formaldehyde Resin*. Pacific Northwest National Laboratory, Richland Washington. 2017.

[2] See http://www.finncont.com/index.php/en/products/tailored-active-container for a description of the vessel manufactured by Finncont Oy, Kiertotie 10-12, PL 44, 34801 Virrat, Finland.

[3] Tran D. 2015. *Sampling and Handling of Spherical Resorcinol-Formaldehyde Resin from Finncont or Smaller Resin Storage Containers*. Internal PNNL technical procedure.



(a) As retrieved (b) After 4 days settling

Figure 2.1. SRF Resin, Lot 1F-370/1392, Sampled on March 30, 2017

On April 12, 2017, a 53-mL subsample of resin was collected (from the 500-mL sample) for use in the batch contact and column testing. It was pretreated in general accordance with the resin pretreatment protocol[1] and previous testing (Russell et al. 2016). The measured resin subsample was transferred to an open beaker and reagents were added and removed from the beaker while trying to minimize resin exposure to air. Pretreatment steps, reagents, reagent volumes, and durations are summarized in Table 2.1. The resin was split into two equal quantities after one full swell/shrink cycle. At this point, half of the resin was removed for column use where the second series of pretreatment steps continued in-column as shown in Table 2.8. The remaining half of the resin, destined for batch contact use, remained in the beaker for continued bulk pretreatment as shown in Table 2.1—subjected to one more swell-shrink cycle.

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[1] Nash CA and CE Duffey. August 17, 2004. *Hanford RPP-WTP Alternate Resin Program - Protocol P1-RF: Spherical Resin Sampling from Containers, Resin Pretreatment, F-Factor, and Resin Loading to Column*. WTP 097893, Savannah River National Laboratory, Aiken, South Carolina.

Table 2.1. Ion Exchange Pretreatment Process Steps

Pretreatment Step	Solution	Volume (mL)	Protocol RV(a)	Test RV	Duration (h)	Mixing(b)
Bulk Pretreatment						
Water rinse	DI Water	300	5	5.7	0.52	Swirl
Resin expansion	1 M NaOH	275	5	5.2	1.53	Swirl
Resin expansion	1 M NaOH	--	--	--	13.65	Soak
Water rinse – 1st	DI Water	300	3	5.7	0.40	Swirl
Water rinse – 2nd	DI Water	300	3	5.7	0.38	Swirl
Water rinse – 3rd	DI Water	300	3	5.7	0.50	Swirl
Resin conversion	0.5 M HNO_3	530	10	10.0	2.00	Swirl
Water rinse – 1st	DI Water	300	3	5.7	0.50	Swirl
Water rinse – 2nd	DI Water	300	3	5.7	0.50	Swirl
Water rinse – 3rd	DI Water	300	3	5.7	0.47	Swirl
Remove half of resin for in-column pretreatment (see Table 2.8); resin for batch contacts continued pretreatment cycling as follows.						
Resin conversion	1 M NaOH	140	5	4.2	1.50	Swirl
Resin expansion	1 M NaOH	--	--	--	2.00	Soak
Water rinse – 1st	DI Water	200	3	5.9	0.50	Swirl
Water rinse – 2nd	DI Water	200	3	5.9	0.50	Swirl
Water rinse – 3rd	DI Water	200	3	5.9	0.50	Swirl
Resin conversion	0.5 M HNO_3	300	10	8.9	0.50	Swirl
Water rinse – 1st	DI Water	200	3	5.9	2.00	Swirl
Water rinse – 2nd	DI Water	200	3	5.9	0.50	Swirl
Water rinse – 3rd	DI Water	200	3	5.9	0.50	Swirl

(a) Resin volume (RV), original volume of resin subsample collected for pretreatment (53 mL); nominal volume expansion to Na-form is 150% (Fiskum et al. 2006a).

(b) Swirling entailed gently swirling with stir rod every 10 min; soaking left resin to soak unmixed for an extended time.

DI = deionized

2.2 Ion Exchange Process Feeds

Two process feed types were tested. One feed was a simplified tank waste simulant at a 5.6 M Na concentration (Russell et al. 2017). The simple simulant feed was used for shakedown testing of the ion exchange system and batch contact testing. The second process feed was collected from Hanford tank 241-AP-105 (AP-105). The AP-105 feed was used to demonstrate ion exchange performance on actual Hanford tank waste and to remove ^{137}Cs to allow for follow-on vitrification studies in a contact-handled environment. This section describes the feed compositions.

2.2.1 5.6 M Na Simple Simulant

A total of 4 liters of the 5.6 M Na simple simulant was prepared as defined by Russell et al. (2017), with the exception that Cs concentration was increased from 14 to 60 µg/mL. Component salts were American Chemical Society Reagent Grade or similar. The measured component masses and calculated ionic species concentrations are provided in Table 2.2. Nearly all components dissolved; however, complete dissolution of the sodium oxalate was not obtained; the final oxalate concentration is unknown. The simulant was filtered through a 0.45-micron pore size nylon filter housed in a polycarbonate disposable filter apparatus to remove all undissolved salt(s).

Table 2.2. 5.6 M Na Simple Simulant Composition for Shakedown Testing

Component	Component FW (g/mole)	Component Mass (g)	Ionic Species	Target Species Conc. (M)	Calculated Species Conc. (M)	Measured Species Conc. (M)[(b)]
$Al(NO_3)_3•9H_2O$	375.15	249.10	$Al(OH)_4^-$	0.166	0.166	0.171
NaOH (50% w/w)	40.00	663.6	free OH^-	1.41	1.41	1.47
$CsNO_3$	194.91	0.3506	Cs^+	4.51 E-04	4.50E-04	NM
KCl	74.55	36.3927	K^+ and Cl^-	0.122	0.122	0.152
Na_2SO_4	142.05	37.5528	SO_4^{2-}	0.066	0.066	NM
$NaNO_2$	69.00	281.50	NO_2^-	1.020	1.020	NM
$NaNO_3$	85.00	435.8	NO_3^-	1.780	1.282	NM
Na_3PO_4-$12H_2O$	380.13	65.6929	PO_4^{3-}	0.0432	0.0432	NM
Na_2CO_3-H_2O	124.00	231.65	CO_3^{2-}	0.467	0.467	NM
$Na_2C_2O_4$	134.00	6.7995[(a)]	$C_2O_4^{2-}$	0.0127	[(a)]	NM
Deionized water	18.02	2991.6	Na^+	5.60	5.60	5.72

(a) Not all sodium oxalate dissolved; therefore, the final oxalate concentration is unknown. The simulant was filtered, removing the undissolved component(s). The mass of undissolved salt was not determined.
(b) ASR 0262, ASO sample ID 17-0791.
FW = formula weight; NM = not measured

The simulant was analyzed by the PNNL Analytical Support Operations (ASO) for Na, K, and Al by inductively coupled plasma optical emission spectrometry (ICP-OES) and for free hydroxide using acid titration and potentiometric determination of pH according to Analytical Services Request (ASR) 0262. Routine precision and bias was reported to be ±15% or better. All measured analyte concentrations were within 4% of the calculated concentration except for K. The measured K concentration was 25% higher than the calculated concentration. The reason for this discrepancy is not understood at this time. The density of the simple simulant measured was 1.254 g/mL (consistent with 1.26 g/mL reported by Russell et al. [2017]).

A 3-liter aliquot of the simple simulant was spiked with 319 µCi ^{137}Cs tracer (April 13, 2017 reference date) to support both the batch contact and column testing. The total Cs concentration in the tracer (from the carrier Cs and ^{137}Cs) was inconsequential to the prepared 60 µg/mL Cs concentration.

2.2.2 AP-105 Tank Waste

Multiple samples (32 each at nominally 250 mL) were collected at four different depths (91 in., 172 in., 253 in., and 334 in.) from the AP-105 Hanford tank. The samples were received at the PNNL Radiochemical Processing Laboratory (RPL) under chain of custody. The first sample collected, 5AP-16-01, was subsampled for a limited analysis suite. The density was measured in cell using a 10-mL volumetric flask. All other measurements were conducted by the ASO according to ASR 0272; results are provided in Table 2.3.

Table 2.3. Characterization of 5AP-16-01 AP-105 Tank Waste Sample (ASR 0272)

Analyte	Result	Result Units	Analysis Method
Al	1.02	M	ICP-OES
K	0.141	M	ICP-OES
Na	8.53	M	ICP-OES
OH^-	1.75(a)	M	Titration
^{133}Cs	5.7E-5	M	ICP-MS
^{137}Cs	180 ± 2%(b)	µCi/mL	GEA
^{137}Cs	1.51	M	GEA
Density	1.405(c)	g/mL	Volumetric flask

(a) Based on first inflection point; assumed to be the free (unbound) hydroxide.
(b) Reference date is 4/26/17.
(c) Measured at 27.5 °C.
ASR 0272, sample 17-0868
GEA = gamma energy analysis; ICP-MS = inductively coupled plasma mass spectrometry

2.2.3 Diluted AP105 Tank Waste

Samples of the AP-105 tank waste were combined and then diluted to 5.7 M Na with 0.01 M NaOH before filtration through the cross flow filter system. The dilution and filtration were part of the test activities associated with the cross flow filtration task and are reported separately. The diluted and filtered AP-105 tank waste is termed AP-105DF throughout this report. The AP-105DF was provided for ion exchange testing in five vessels (see Table 2.4). All samples were measured for density using 10-mL volumetric flasks. Samples were not combined into one single container for homogenization. Doing so builds risk into the process (should a container leak), and handling the massive composite would be problematic given the lifting weight limitations of the manipulators in the hot cells.

Table 2.4. AP-105DF Samples for Ion Exchange

Sample ID	Density (g/mL)	Volume (mL)	Na (M)	Al (M)	K (M)	^{137}Cs (µCi/mL)[(c)]	Process
IX-E2-1	1.2776	291.1[(a)]					Added to IX-E3-4
IX-E3-1	**1.2730**	**910.2**	**5.70**	**0.505**	**0.092**	**114**	**Batch contacts, column testing**
IX-E3-2	**1.2762**	**898.6**	**5.72**	**0.506**	**0.093**	**112**	**Column testing**
IX-E3-3	1.2924	1013.8[(b)]					Diluted, see IX-E3-3'
IX-E3-3'	**1.2807**	**1064.8**	**5.68**	**0.508**	**0.091**	**111**	**Column testing**
IX-E3-4	1.2467	868.5					Combined with IX-E2-1, see IX-E3-4'
IX-E3-4'	**1.2668**	**1144.3**	**5.43**	**0.484**	**0.087**	**104**	**Column testing**

(a) Sample added to IX-E3-4, new composite called IX-E3-4'.
(b) Sample diluted with water, renamed IX-E3-3'.
(c) Reference date July 19, 2017.
Bolded samples are the final materials and characteristics used for ion exchange testing.
ASR 0316, samples 17-1106, 17-1107, 17-1108, 17-1109.

Because the feed solutions were to be kept in separate containers, it was desired to make the density (and by inference all other chemical/physical properties) the same. To that end, sample IX-E2-1 was transferred to IX-E3-4 in an effort to increase the IX-E3-4 sample density. The combined material was then termed IX-E3-4'. IX-E3-3 sample density was higher than those of the companion samples; therefore, 76 mL of DI water was added to this sample, which was then termed IX-E3-3'. The density decreased enough to proceed with testing. All handling and density analyses were conducted according to test instruction TI-DFTP-014.[1]

A 152-mL aliquot of IX-E3-1 was used for batch contact testing; the remainder was used for column testing. Small volumes of the final constituted IX-E3-1 through -4' samples were collected and analyzed for ^{137}Cs and Na per ASR 0316 (reported in Table 2.4). Two milliliters of each of the final constituted feed samples were combined into one vial for a more comprehensive analysis (sample TI014-FEED). Analyses were conducted by the ASO per ASR 0355. Only the Cs isotopic composition of the composite AP-105DF was determined in time for this report; it is shown in Table 2.5. The Cs isotopic ratio was measured on the peak Cs eluate sample following column loading and elution by ICP-MS per ASR 0329. The advantage of using this sample for the isotopic ratio is that it is relatively free from the AP-105DF high salt matrix and contains the highest Cs concentration and is thus less likely to be affected by isotopic interferences. The total Cs was calculated from the measured ^{137}Cs and the isotopic composition.

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[1] TI-DFTP-014. *Cesium Removal from AP-105 Tank Waste Diluted to 5.6 M Na Using Spherical Resorcinol-Formaldehyde Resin—Test 1*. SK Fiskum, Pacific Northwest National Laboratory, Richland, Washington. Implemented July 2017.

Table 2.5. AP-105DF Cs Isotopic Composition (ASR 0329)

Analyte[(a)]	Analysis Method	Results	Units
Cs isotopic mass ratio[(a)]	ICP-MS	64.0 19.1 16.8	wt% ^{133}Cs wt% ^{135}Cs wt% ^{137}Cs

(a) The peak Cs column eluate sample was analyzed for the Cs isotopic mass distribution by ICP-MS per ASR 0329 sample 17-1224. The quantity of hold-over Cs from the shakedown testing was assumed to result in negligible ^{133}Cs contribution compared to the Cs eluted from AP-105DF processing.

2.3 Batch Contact Conditions

Batch-distribution contact testing is a rapid method for determining relative equilibrium performance of ion exchange materials in a given matrix. Batch contact solutions consist of the target test matrix plus various amounts of added ^{133}Cs. The equilibrium Cs concentrations are determined after batch contacts to assess Cs loading capacity on the resin and the Cs distribution coefficient (K_d) under nominal process conditions. The preparations and batch contacts were processed in accordance with two test instructions: one for 5.6 M Na simple simulant testing in a radiological laboratory and one for AP-105DF testing in the hot cell.[1,2]

2.3.1 5.6 M Na Simple Simulant Batch Contact Testing

The 5.6 M Na simple simulant, containing 60 µg/mL Cs, was initially spiked with ^{137}Cs tracer at 0.107 µCi/mL.[3] Aliquots of this solution were removed for spiking at three different added Cs concentrations. Two Cs spike solutions (140 mg/mL and 21.9 mg/mL) were prepared by dissolving $CsNO_3$ (99.99%, Johnson Matthey) in water. Small volumes of the Cs spike solutions were added to three ~34-mL aliquots of 5.6 M Na simple simulant. (Minimizing the added spike volume minimizes matrix dilution [distortion] such that the batch contact matrix best matches the matrix processed through the ion exchange columns.) All Cs spike transfers and 5.6 M Na simple simulant transfers were tracked by mass and actual volume deliveries calculated based on mass and density. Table 2.6 shows the calculated initial Cs concentrations in the batch contact stock solutions.

Table 2.6. Initial Cs Concentrations Used for the 5.6 M Na Simple Simulant Batch-Contact Tests

Solution ID	Cs Concentration (mg/L)	Cs Concentration Molarity
TI-013-S0	60.0	4.51E-4
TI-013-S1	188	1.41E-3
TI-013-S2	547	4.12E-3
TI-013-S3	1724	1.30E-2

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[1] Fiskum SK. 2017. TI-DFTP-013, *Spherical Resorcinol Formaldehyde Resin Batch Contacts with Simple Simulant Containing 60 mg/L Cs*. Pacific Northwest National Laboratory, Richland, Washington. Implemented May 2017.

[2] Fiskum SK. 2017. TI-DFTP-006, *Spherical Resorcinol Formaldehyde Resin Batch Contacts with AP-105 Hanford Tank Waste*. Pacific Northwest National Laboratory, Richland, Washington. Implemented June 2017.

[3] The ^{137}Cs in the traced 5.6 M Na simple simulant was used to determine the Cs-exchange behavior in each sample using GEA as discussed in Section 2.3.3.

An aliquot of the pretreated H-form resin was collected and placed in a beaker. It was partially dried with argon gas gently blowing over the resin for a couple of hours. The argon gas served to protect the resin from oxidative attack from O_2 in the air. Once the resin was free flowing, it was transferred to a vial and capped. An aliquot of resin was removed for the nominal F-factor evaluation and the vial containing the remaining partially dried resin was flushed with argon. The F-factor sample aliquot was dried at ~48 °C, under vacuum, overnight to determine the nominal water content remaining in the partially dried resin. This nominal F-factor was used to determine the target resin aliquot mass to collect for the batch contact samples. Typically, the partially dried resin contained about 50% water by mass.

A precisely weighed quantity of partially dried H-form resin was aliquoted into a glass liquid scintillation vial for each batch contact sample. The partially dried resin mass was determined to an accuracy of ±1%. The resin mass aliquot was targeted to achieve a phase ratio (volume of liquid to mass of dry resin) of 100. The batch contact tests were prepared in duplicate at each Cs concentration.

Two F-factor samples were also weighed (initial mass, M_I), one at the beginning of resin aliquoting process and one at the end of resin aliquoting process. The F-factor samples were dried to constant mass (final mass, M_F) at 48 °C under vacuum to determine the dry resin mass. The F-factor was calculated according to Eq. (2.1). The average of the two F-factor samples was used to calculate the dry resin mass contacted with solution, as discussed in Section 2.3.3.

$$\frac{M_F}{M_I} = \text{F-Factor} \qquad (2.1)$$

The resin aliquots were then promptly contacted with 10 mL of the various contact solutions (see Table 2.6). The solution volume was transferred by pipet; the actual contact solution volume was determined by mass difference and solution density. The targeted phase ratio (liquid volume to exchanger mass) was 100 mL/g. The obtained ratio varied between 97 and 98 mL/g. Sample-specific volumes and resin masses are given in Appendix A. The headspace above the 5.6 M Na simple simulant was purged with argon gas just before capping; this was easily accommodated in the fume hood space. The resident O_2 in the vial headspace will damage some of the ion exchange sites and reduce Cs exchange capacity. This effect is normally observed as a lower K_d at high Cs concentrations (Russell et al. 2016).

The resin initially floated on contact with the 5.6 M Na simple simulant solution. The resin eventually settled ~1 hour after contact with solution.

The batch contact vials were placed upright in an IKA KS125 orbital shaker with 4-mm shaker diameter set to 400 revolutions per minute. Rigorous mixing was observed for all samples. A vial of water was incorporated with the set to act as a temperature sentinel. The resin materials were contacted for 24 hours; equilibrium for SRF has been confirmed to be reached within 24 hours (Fiskum et al. 2004; Nash et al. 2006). The temperature was not controlled; after mixing for 24 hours, the temperature sentinel was 24 °C, indicating that a very minor temperature increase above ambient was reached during the contact period. After contact, the resins were settled and the aqueous fractions were removed and filtered through 0.45-µm nylon-membrane syringe filters.

2.3.2 AP-105DF Batch Contact Testing

An aliquot of the filtered AP-105DF, sample IX-E3-1, was used for batch contact testing. The AP-105DF solution was treated in a manner similar to the 5.6 M Na simple simulant treatment. The native ^{137}Cs in the AP-105DF was used to determine the Cs-exchange behavior in each sample (using GEA). The Cs spike solutions were similarly added to four additional aliquots of AP-105DF reaching Cs concentration shown in Table 2.7.

Table 2.7. Initial Cs Concentrations Used for the AP-105DF Batch Contact Tests

Solution ID	Cs Concentration (mg/L)	Cs Concentration Molarity
TI-006-S0	7.9	5.96E-5
TI-006-S1	52.2	3.93E-4
TI-006-S2	156	1.17E-3
TI-006-S3[(a)]	570	4.29E-3
TI-006-S4	1716	1.29E-2

(a) The duplicate batch contact sample was dropped and broke during in-cell handling.

A separate aliquot of pretreated H-form resin was collected for processing. It was partially dried and aliquoted as previously described. In this case, the vials of resin to be contacted with AP-105DF were first flushed with argon and then transferred to the hot cell for solution aliquoting and mixing. The radiological dose rate of AP-105DF was too high to work with in the fume hood at the quantities needed for batch contact testing. The AP-105DF solutions were added to the batch contact vials and capped. Purging of the AP-105DF with inert gas was not practical in the hot cell due to logistical constraints with gas handling and manipulator use constraints.

The batch contact vials were placed upright in a Thermo LP vortex mixer[1] equipped with a 25-mm tube holder retrofitted to accommodate five 20-mL liquid scintillation counting vials and a small temperature sentinel vial as shown in Figure 2.2. The mixer has a 4-mm amplitude and was set to 250 revolutions per minute continuous mode during the mixing process. A set of five samples was mixed at one time for 24 hours in the vortex mixer. After mixing, the resin was settled and the aqueous phase was removed from the hot cell for filtration. Unfortunately, one of the duplicate sample containers, TI-006-S3-BC, was broken during processing and could not be recovered.

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[1] The Thermo LP vortex mixer was selected for hot cell use because of its small size (15.4 x 21.0 x 8.3 cm) and small mass (3.1 kg).

Figure 2.2. Thermo LP Vortex Mixer with Retrofitted Vial Holder for In-Cell Sample Batch Contact Shaking

2.3.3 Batch Contact Analysis and Calculations

Filtered 2-mL aliquots were collected for GEA to determine the ^{137}Cs concentrations. Similarly, 2-mL aliquots of the parent Cs-spiked solutions were collected for GEA. The ^{137}Cs tracer concentrations in aliquots of the un-contacted sample solutions were used to define the initial ^{137}Cs concentrations (C_0) for each test matrix. Final (equilibrium) Cs concentrations (Cs_{Eq}) were calculated relative to the ^{137}Cs recovered in the contacted samples (C_1) according to Eq. (2.2):

$$Cs_0 \times \left(\frac{C_1}{C_0}\right) = Cs_{Eq} \tag{2.2}$$

where Cs_0 = initial Cs concentration in solution (μg/mL or M)
C_1 = equilibrium ^{137}Cs concentration in solution (μCi/mL)
C_0 = initial ^{137}Cs concentration in solution (μCi/mL)
Cs_{Eq} = equilibrium Cs concentration in solution (μg/mL or M)

The equilibrium Cs concentrations loaded onto the resins (Cs_R in units of mg Cs per gram of dry resin mass) were calculated according to Eq. (2.3):

$$\frac{Cs_0 \times V \times \left(1 - \frac{C_1}{C_0}\right)}{M \times F \times 1000} = Cs_R \tag{2.3}$$

where Cs_R = equilibrium Cs concentration in the resin (mg Cs/g resin)
Cs_0 = initial Cs concentration in solution (μg/mL)
V = volume of the batch contact liquid (mL)
C_1 = final ^{137}Cs tracer concentration in solution
C_0 = initial ^{137}Cs tracer concentration in solution

M = mass of H-form ion exchanger (g)
F = F-factor, mass of the dried resin divided by the mass of the undried resin
1000 = conversion factor to convert μg to mg

The Cs batch-distribution coefficient (K_d) values were determined according to the standard formula shown in Eq. (2.4).

$$\frac{(C_0 - C_1)}{C_1} \times \frac{V}{M \times F} = K_d \tag{2.4}$$

where C_0 = initial ^{137}Cs concentration (μCi/mL)
C_1 = final (equilibrium) ^{137}Cs concentration (μCi/mL)
V = volume of the batch contact liquid (mL)
M = mass of pretreated H-form ion exchanger (g)
F = F-factor, mass of the dried resin divided by the mass of the undried resin
K_d = batch-distribution coefficient (mL/g)

Errors were kept small because ^{137}Cs tracer was used; samples with low ^{137}Cs concentrations were counted longer to reduce statistical counting error. Sample count errors were less than 1% (1-σ). Mass errors were less than 1%.

2.4 Ion Exchange Process Testing

This section describes the ion exchange column system and the process conditions for the in-column pretreatment, 5.6 M Na simple simulant, and the AP105DF.

2.4.1 Ion Exchange Column System

The ion exchange system was set up as shown schematically in Figure 2.3 (lead to lag solution flow) and Figure 2.4 (lag to lead solution flow). The system consisted of two columns containing ion exchange resin, a small metering pump, three valves, a pressure gauge, and a pressure-relief valve. Valves were three-way valves that could be turned to the flow position (upward) to flow solution through the entire system or a sample position (downward) to collect samples/fluids. Valve 1 was placed at the outlet of the pump and was used to isolate the column from the pump and collect initial fluids and to expel air from the lines at the initial setup. Valves 2 and 3 were primarily used to obtain samples and closed to isolate the system during storage periods.

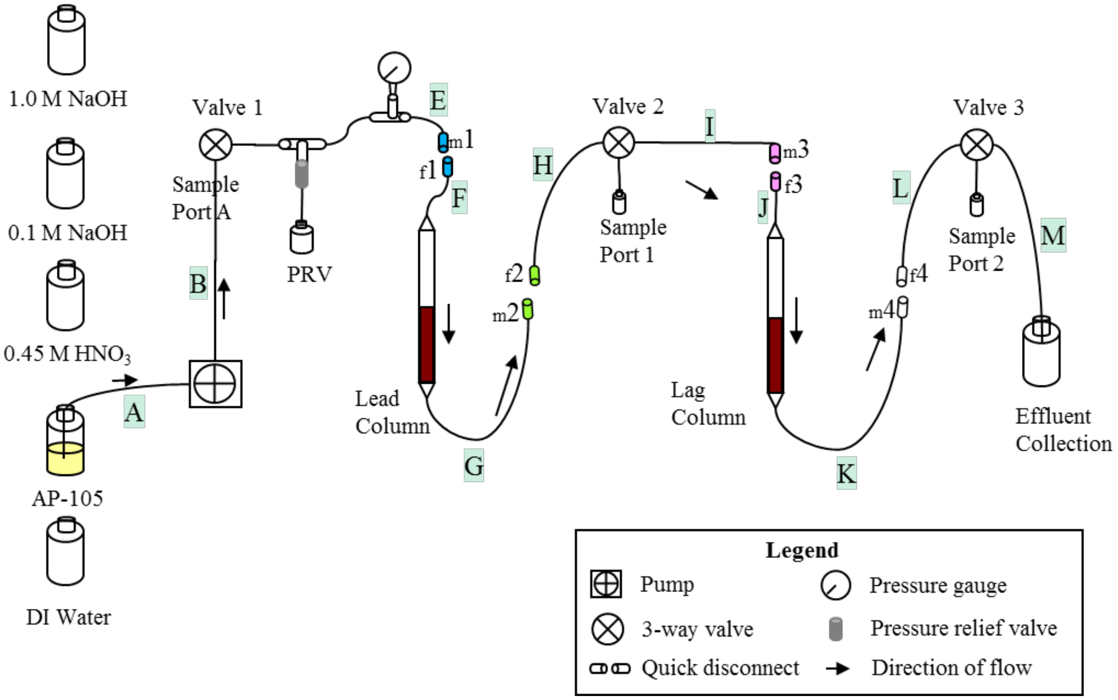

Figure 2.3. Ion Exchange System Schematic (Downflow Direction Lead Column to Lag Column)

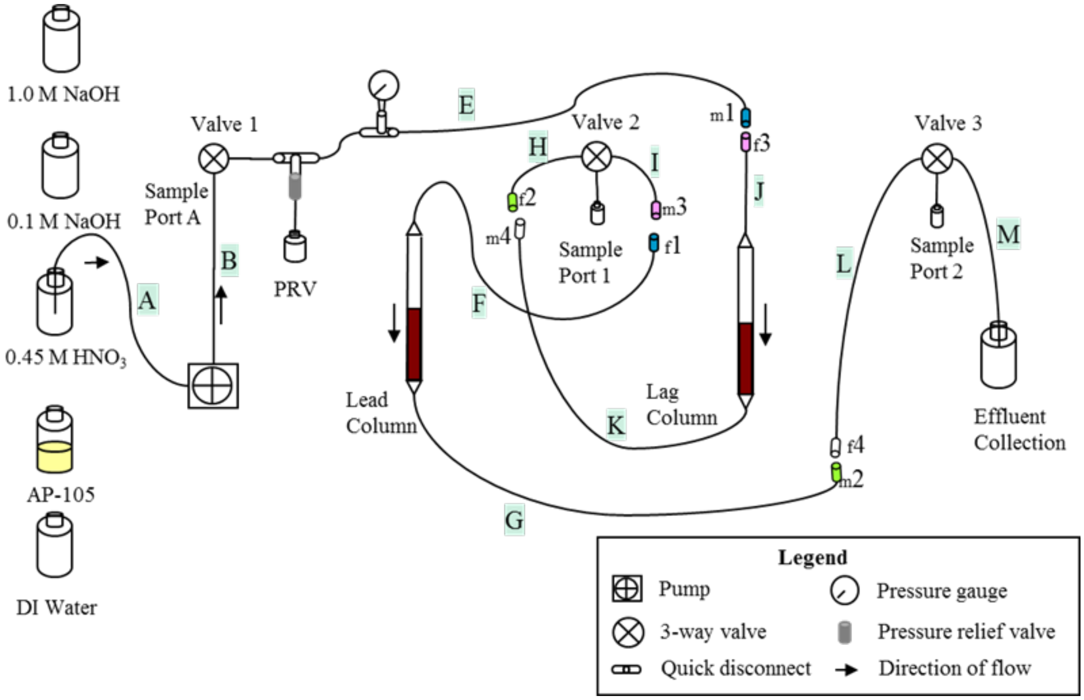

Figure 2.4. Ion Exchange System Schematic (Downflow Direction Lag Column to Lead Column)

Column assemblies were purchased from Spectrum Chromatography (Houston, TX), part number 125009. The column assembly included the column plus the top and bottom end fittings. Each column was made of borosilicate glass and was 20 cm tall with an inside diameter of 1.44 cm (corresponding to a resin volume of 1.6 mL/cm). Column fittings were composed of polytetrafluoroethylene (PTFE) and Teflon endplates and ferrule fittings for 1/8 in. outside diameter tubing.

Resin bed supports were crafted in-house. They were made of stainless steel, 200-mesh screens mounted on stainless steel support rings. The support rings were stabilized with snug-fitting O-rings to remain stationary in the column once seated. Figure 2.5 shows replacement resin bed supports similar to those in the columns along with a centimeter scale. The resin bed supports were positioned just above the site line of the lower column fitting.

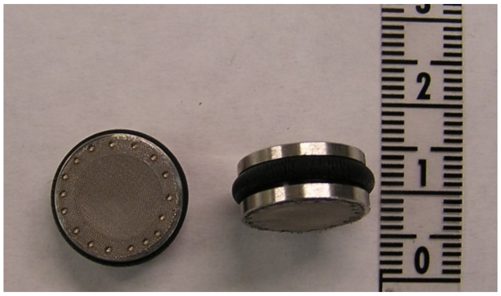

Figure 2.5. Resin Bed Supports with Centimeter Scale

The cavity below the screen support was filled with 4-mm-diameter glass beads, reducing the fluid-filled volume from ~3 to ~1 mL. The height of the resin bed (and thus shrinkage and swelling) was measured with an adhesive millimeter-scale scale affixed to the column with the zero point set to the top of the resin bed support. The associated height measurement error was estimated to be ±2 mm. The fluid level in the column was maintained at nominally the 12-cm height. Depending on whether the resin was expanded in Na-form (nominally 6.4 cm tall) or contracted in H-form (nominally 5 cm tall), fluid volume above the resin bed varied from nominally 8.8 to 11 mL, respectively. (See Section 2.4.5 for change in lag column condition where fluid volume above the lag column resin bed changed to 5.7 mL and 8.0 mL, respectively.)

Most of the connecting tubing was 1/8-in. outside diameter and 1/16-in. inside diameter and was made of polyethylene. The inlet sample line ended at the top column fitting. Tubing between the input of Valve 1 and the exit of the pressure gauge was 1/8-in. outside diameter stainless steel. The column assembly contained an in-line Swagelok Poppet pressure relief check valve with a 10-psi trigger (Solon, OH) and a 15-psi pressure gauge (Swagelok). Valved quick-disconnects (Cole Parmer, Vernon Hills, IL) were installed in-line to ease column removal and switching. Fluid Metering, Inc. (FMI) QVG50 pumps (Syosset, NY) equipped with a ceramic and Kynar® coated low-flow piston pump heads were 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 0.2 to 0.8 mL/min. The actual volume pumped was determined using the mass of the fluid collected divided by the fluid density. The holdup volume of the entire ion exchange system, ~44 mL, was the summed volume of all fluid-filled parts.

The pretreated H-form SRF resin was subdivided into three 8.0-mL settled resin volume aliquots. The first two aliquots were forwarded to column testing for filling the lead and lag columns. The third aliquot was used to determine the dry resin mass. The 8.0-mL volume fraction of H-form resin was transferred to a tared glass beaker. Excess water was removed, and the damp resin was dried under vacuum, at 50 °C to constant mass. Constant mass was defined as a mass change of <1% in a 7-hour period at 50 °C under vacuum. The dry H-form resin mass representing the 8.0-mL wet settled resin BV was 2.4524 g. Thus, the initial H-form resin packing density was 0.31 g/mL.

Figure 2.6 is a photograph of the entire column assembly after processing the 5.6 M Na simple simulant. The lead column is on the left and the lag column on the right. The resin beds are in the H-form and stand 5 cm tall. The black band on the top layer of resin is oxidized resin. The fluid height is at nominally 12 cm (in this case 7 cm above the resin beds).

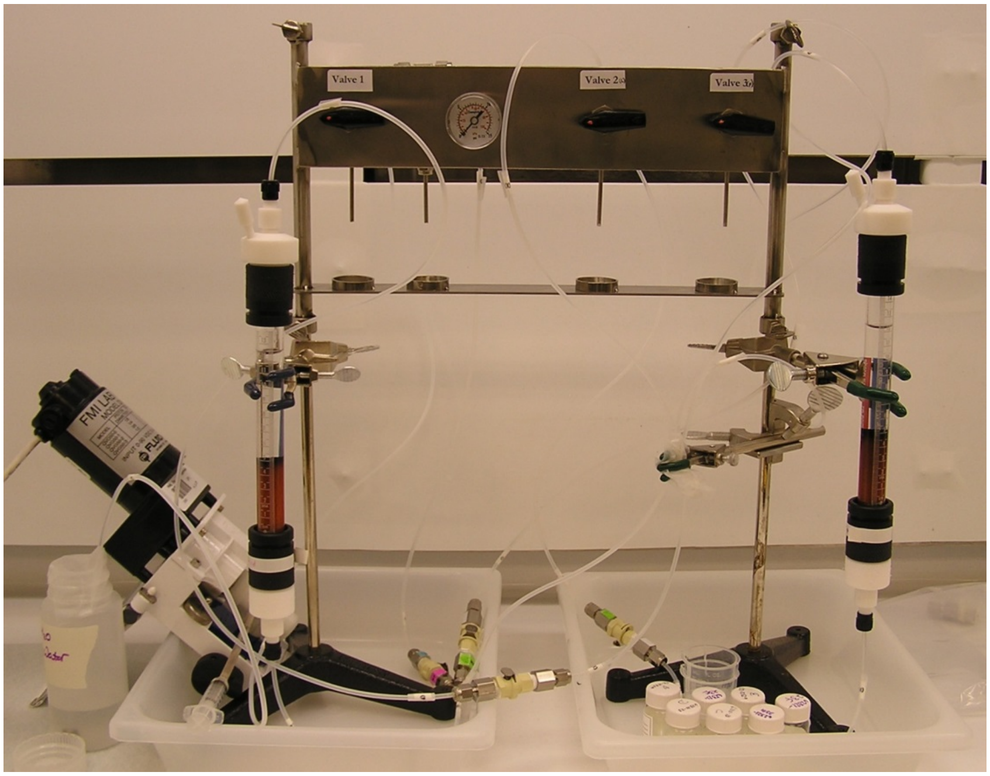

Figure 2.6. Ion Exchange Column Apparatus in the Fume Hood

2.4.2 Bed Volume

The resin BV was defined as the volume of the resin after open-beaker pretreatment and expansion in the 1.0 M NaOH regeneration solution as first loaded into the ion exchange column. The column was tapped with a rubber bung to settle the resin bed to its smallest volume. By this measure, both the lead and lag column BVs were 9.9 mL. It is noted that the resin volume changes with differing feeds. It shrinks about 20% by volume when in the H-form relative to the Na-form. Further, the resin contracts about 3% to 5% from 1.0 M NaOH to the 5.6 M Na simple simulant and expands again when processing the 0.1 M NaOH feed displacement solution. Resin swelling and shrinkage are discussed in Section 4.3. All BVs indicated in this report are on a 9.9-mL, Na-form basis.

2.4.3 Resin Bed Pretreatment

The in-column resin pretreatment was conducted according to test instruction TI-DFTP-007.[1] The two 8-mL H-form resin sub-samples were transferred to separate beakers and contacted with 5× volumes (40 mL each) of 1 M NaOH. The NaOH soak continued for 40 min with agitation every 10 min. The resin slurries were then quantitatively transferred into the columns containing about 10 mL of DI water. The resin beads settled naturally through the fluid layer. Additional DI water was used to aid quantitative resin transfer. The columns were tapped with a rubber bung to further settle the resin to constant volume.

Each resin bed was pretreated in the column by processing sequentially water, 0.5 M HNO_3, water, and then 1.0 M NaOH. Specific in-column pretreatment parameters are provided in Table 2.8. The columns were treated in parallel with individual pumps processing solution; effluents were collected separately. After initial pretreatment, the columns were set up in series as shown in Figure 2.3, at which point additional 1.0 M NaOH was processed through the lead and then through the lag columns.

Table 2.8. Experimental Conditions for Pretreatment and 5.6 M Na Simple Simulant Column Processing

		Total Volume			Flowrate		Time
Process Step	Solution	BV	AV	mL	BV/h	mL/min	h
In-Column Pretreatment, Columns in Parallel, Lead/Lag 4/17/17[(a)]							
Water rinse	DI water	6.5/6.8	1.5/1.6	65/68	4.6/5.0	0.77/0.83	1.4/1.4
Acid wash	0.45 M HNO_3	4.2/4.6	0.96/1.05	42/46	2.1/2.3	0.35/0.38	2.0/2.0
Acid wash	0.45 M HNO_3	3.9/4.1	0.89/0.94	39/41	1.4/1.5	0.23/0.24	2.8/2.7
Water rinse	DI water	5.9/5.8	5.9/5.8	59/58	1.4/1.4	0.23/0.23	4.3/4.2
Regeneration	1.0 M NaOH	6.4/6.3	6.4/6.3	64/63	2.8/2.8	0.47/0.47	2.2/2.2

(a) Two values are provided. The first value indicates the lead column parameter; the second value indicates the lag column parameter.

BV = bed volume (9.9 mL in the Na-form volume as loaded in the column); see Section 2.4.2.

AV = apparatus volume (nominally 44 mL).

2.4.4 5.6 M Na Simple Simulant Process Conditions

The 5.6 M Na simple simulant was processed according to test instruction TI-DFTP-007. The simulant was processed sequentially through the ion exchange resin beds for a full shakedown test. After simulant processing, 0.1 M NaOH feed displacement and water rinse were passed through the system. The flow orientation was then switched by rearranging the quick disconnect connections as shown in Figure 2.4. This allowed elution to occur downflow from the lag column to the lead column. After elution with 0.45 M HNO_3, the columns were rinsed with DI water. All processing was conducted at ambient temperature conditions, ranging from 20 to 22 °C. Test parameters, including process volumes, flowrates, and contact times, are summarized in Table 2.9

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[1] SK Fiskum. 2017. TI-DFTP-007, *Cesium Removal from Simple Simulated Tank Waste (Shakedown Test) Using Spherical Resorcinol-Formaldehyde Resin*. Pacific Northwest National Laboratory, Richland, Washington. Implemented April 2017.

Table 2.9. Experimental Conditions for 5.6 M Na Simple Simulant Column Processing

		Total Volume			Flowrate		Time
Process Step	Solution	BV	AV	mL	BV/h	mL/min	h
5.6 M Na Simple Simulant Test, Columns in Series, 4/24/17 Start							
Regeneration (cont.)	1.0 M NaOH	0.69	0.16	6.9	2.6	0.43	0.27
Loading (lead)	Simulant	168	--	1668	3.0	0.49	56.7
Loading (lag)[(a)]	Simulant	151	--	1502	3.0	0.49	56.7
Feed displacement	0.1 M NaOH	5.3	1.2	52.9	3.1	0.51	1.8
Water rinse	DI water	4.0	0.91	39	3.0	0.49	1.2
Elution	0.45 M HNO_3	16.4	3.7	163	1.4	0.23	12
Water rinse	DI water	5.3	1.2	52	1.4	0.23	3.8
Extended Water Rinse, 5/25/17 Start							
Extended Water Rinse	DI water	8.5	1.9	84	1.4	0.23	6.2

(a) The feed volume through the lag column is reduced because of sampling from the lead column.
BV = bed volume (9.9 mL in the Na-form volume as loaded in the column), see Section 2.4.2.
AV = apparatus volume (nominally 44 mL).

During the loading phase, nominal 10-mL samples were collected from both the lead and lag columns at the sample collection ports (Valves 2 and 3). The solution in the lag column remained static during the lead column sampling time of about 20 min. Samples were collected after the first 5 BVs were processed and again at nominal 10-BV increments. The simulant feed was processed for nearly 57 hours continuously. Feed displacement, water rinse, elution, and water rinse following elution samples were collected in nominal 1-BV increments.

Cesium load and elution performance was determined from the ^{137}Cs tracer concentration in the collected samples relative to the ^{137}Cs tracer in the 5.6 M Na simple simulant feed. The collected samples were analyzed directly to determine the ^{137}Cs concentration using GEA. Cesium loading breakthrough and elution curves were generated based on the feed ^{137}Cs concentration (C_0) and the effluent Cs concentration (C) in terms of %C/C_0 and C/C_0, respectively.

The last water rinse sample following elution was further measured for pH using intermediate-range pH paper (0 - 6 pH units, EMD Millipore) for indication only. Because the solution measured pH 0 and the system was to be stored for several weeks before regeneration and use with tank waste, it was desired to displace the residual acidic solution in contact with the resin with additional water. The extended water rinse was started 4 weeks later. The water rinse volume extended well beyond proposed baseline plant operations, with an additional 8.5 BVs processed before effluent reached pH 4.5. The sample pH was simplistically tested, again using intermediate-range pH 0 - 6 paper for indication only.

2.4.5 AP-105DF Process Conditions

The ion exchange assembly was disconnected to allow for transfer into the hot cell. It was reconnected in the Shielded Analytical Laboratory hot cell. Figure 2.7 shows an image of the reconnected ion exchange system while processing AP-105DF.

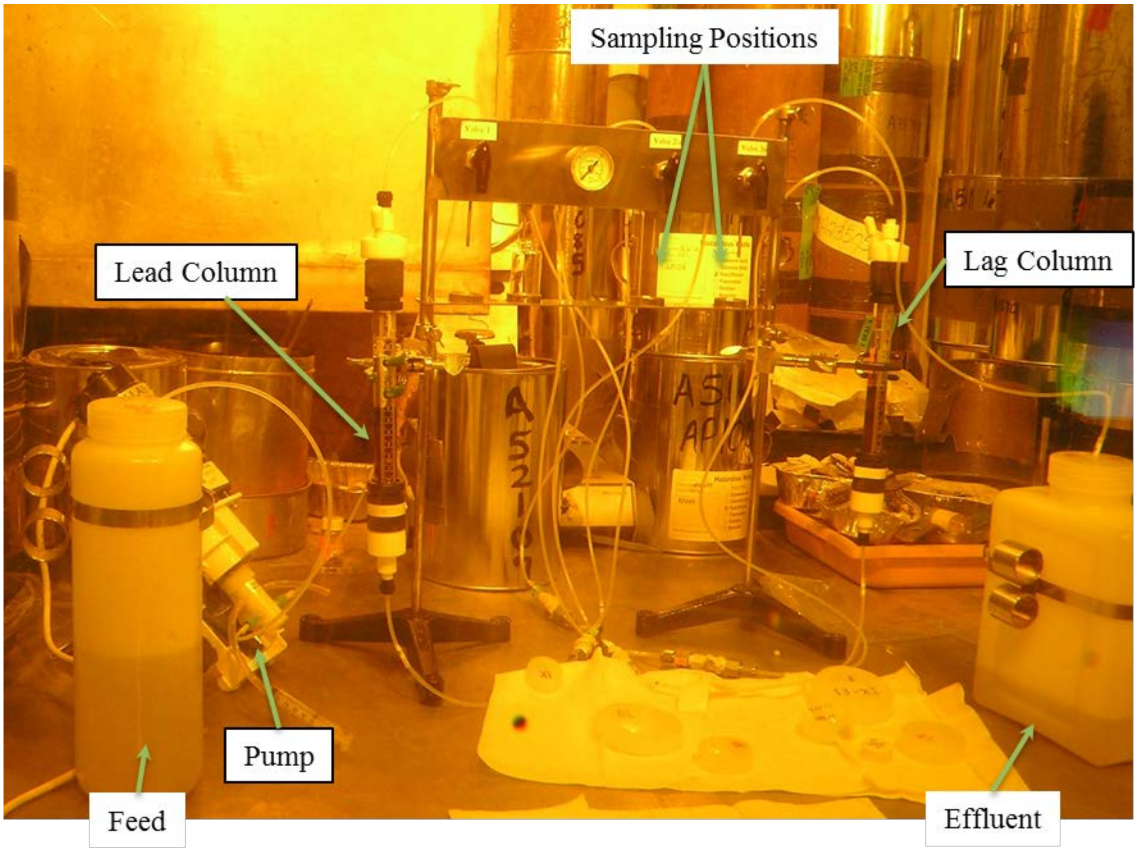


Figure 2.7. Column Assembly in the Hot Cell

The ion exchange resin was in the H-form when transferred to the hot cell. The resin was converted to the Na-form using 1 M NaOH from the lag column to the lead column, prototypic of the LAWPS operation. The system was then reconfigured to process lead to lag by reconfiguring the tubing at the quick disconnects.

The AP-105DF was processed according to test instruction TI-DFTP-014 sequentially through the ion exchange resin beds, lead to lag. The AP-105DF column feeds were strategically processed in the following order: IX-E3-3', IX-E3-1, IX-E3-4', and IX-E3-2; this allowed optimal feed volume management supporting unattended off-shift work. Feed bottles were changed during day shift. Effluent was collected in two different containers so that if unacceptable breakthrough from the lag column occurred later in the load cycle, it could be maintained separately from the acceptable product. After tank waste processing, 0.1 M NaOH feed displacement and water rinse were passed through the system in the same lead to lag configuration. The flow orientation was switched by rearranging the quick disconnect connections as shown in Figure 2.4, allowing elution to occur downflow from the lag column to the lead column. The columns were then rinsed with DI water. All processing was conducted at ambient cell temperature conditions, nominally 30 °C. Test parameters, including process volumes, flowrates, and contact times, are summarized in Table 2.10.

During the loading phase, nominal 2-mL samples were collected from both the lead and lag columns at the sample collection ports. The solution in the lag column remained static during the lead column sampling time of about 7 min. Samples were collected after the first ~4 BVs were processed and again at nominal 10- to 20-BV increments. After processing ~144 BVs of feed, one polyethylene line between the lead and lag columns broke. The break occurred off-shift and was not found until the next morning, after an estimated 147 mL of feed was calculated to have leaked from the system (passing through the lead column but not through the lag column). The broken line was replaced; the air in the replacement line displaced 3.7 mL of the fluid above the lag column. The replacement also broke after processing another ~12 BVs of AP-105DF. At this point, the system was placed in standby mode (all valves closed) over the weekend (Friday, July 14, at 5:00 p.m. until the following Monday, July 17, at 1:30 p.m.). The broken line was then replaced with stainless steel tubing before resuming feed processing. The AP-105DF was in contact with resin for 239 hours, including the weekend standby period. Feed displacement, water rinse, elution, and water rinse following elution were collected sequentially in nominal 1.1-BV increments. Aliquots of solution were removed for GEA analysis.

Cesium load and elution performance was determined from the native ^{137}Cs in the collected samples relative to the native ^{137}Cs in AP-105DF feed. The collected samples were analyzed directly to determine the ^{137}Cs concentration using GEA. Cesium breakthrough and elution curves were generated as previously described (Section 2.4.4).

Table 2.10. Experimental Conditions for AP-105DF Column Processing

		Total Volume			Flowrate		Time
Process Step	Solution	BV	AV	mL	BV/h	mL/min	h
Dual Column Actual AP-105DF Waste Test, 7/10/17							
Regeneration	1.0 M NaOH	9.6	2.4	95	4.77	0.789	2.0
Loading (lead)	AP-105DF	294	NA	2921	1.80	0.298	239(b)
Loading (lag)(a)	AP-105DF	274	NA	2724	1.80	0.298	239(b)
Feed displacement	0.1 M NaOH	6.65	1.7	66.0	3.05	0.505	2.2
Water rinse	DI water	4.17	1.04	41.4	3.08	0.511	1.4
Elution	0.45 M HNO_3	15.9	3.98	158	1.40	0.231	11.7
Water rinse	DI water	5.79	1.44	57.5	1.47	0.243	4.0
Extended water rinse	DI water	8.74	2.18	86.8	3.14	0.520	2.8

(a) The feed volume through the lag column is reduced because of sampling from the lead column.

(b) Time includes the standby time over the weekend; see discussion in text.

BV = bed volume (nominally 9.9 mL in the Na-form volume as loaded in the column).

AV = apparatus volume (nominally 40 mL).

NA = not applicable.

2.5 Comparison to Large-Scale Testing

The 5.6 M Na simple simulant (also called the nominal 5.6 M Na simulant) was processed at the 1/9th scale in a lead/lag column format and the full scale in a single-column format. The 1/9th-scale testing was conducted by Mid Columbia Engineering, Inc. and AECOM staff per direction from WRPS at a test stand located in Richland, Washington. The 1/9th-scale tests were conducted in a 14-inch-diameter column with 34.4-gallon resin beds (full column was approximately 56 gallons). The full-scale testing was conducted by AVANTech, Inc. in Columbia, South Carolina. The full-scale tests were conducted in a single 42-inch-diameter column with a 297-gallon resin bed (full column was approximately 506 gallons). Loading, displacement, water rinse, elution, and final water rinse steps were conducted downflow. Only conversion to the Na-form resin with 1 M NaOH was conducted while fluidizing the resin beds in the upflow direction. Although feed flowrates in the 1/9th-scale varied, two tests (Phase 1 Test 3 and Phase 3 Test 1) were conducted at 1.9 BV/h and at nearly the same Cs concentration (54.9 and 56.9 µg/mL Cs, respectively); these conditions were nearly equivalent to the small-scale test. Full-scale testing was conducted at 2.4 BV/hr, slightly faster than the small column test. The superficial velocity of the feed flowrate for the 1/9th-scale and full-scale tests was much higher. Higher superficial velocity improves film diffusion (transfer of Cs from the fluid film around the resin bead onto the bead structure). The results of small-scale feed Cs load and elution will provide interesting comparisons to the 1/9th-scale and full-scale tests. Note that the full-scale and 1/9th-scale test data received at the time this report was prepared were considered preliminary.

2.6 Sample Analysis

A summary of the sample collections and analyses from the various tests and process steps is provided in this section along with the cross reference to ASR and RPL sample IDs.

2.6.1 Batch Contact Sample Analysis

The post-contacted batch contact samples were only analyzed by GEA for ^{137}Cs. Table 2.11 summarizes the sample types and analyses for batch contact samples. The samples were aliquoted using a pipet into tared scintillation vials, then weighed. The net mass transferred was determined by mass difference and the volume calculated from dividing the net mass by the solution density. Attempts were made to conform the sample to the standard GEA calibration geometry (2 mL in the scintillation vials). However, the dose rates for the AP-105DF were high; thus, smaller sample volumes were pulled for the batch-contacted samples. These smaller samples were backed away from the detector to minimize the error in geometry differences.

Table 2.11. Batch Contact Samples ASRs and Sample IDs

Sample Type	Sample Size	ASR	Sample IDs
5.6 M Na Simple Simulant			
Pre-contacted samples	2 mL	0290	17-1023 to 17-1026
Post-contacted samples	2 mL	0290	17-1027 to 17-1034
AP-105DF			
Pre-contacted samples	2 mL	0310	17-1084 to 17-1088
Post-contacted samples	1 mL	0310	17-1089 to 17-1097

2.6.2 Column Sample Analysis

The feed, effluent, and elution sample ^{137}Cs concentrations were determined by the ASO. To support this analysis, all samples and sub-samples were collected and packaged in 10-mL and/or 2-mL volumes to accommodate the calibrated detector geometries. Exact effluent volumes were calculated from the measured net mass and solution densities. Densities were measured using volumetric flasks and net weight or by measured mass of a known pipetted volume. Because of the high dose rate from ^{137}Cs, eluate samples required dilution before removal from the hot cell. The peak eluate samples were diluted 10,000x. These eluate samples were diluted with 0.45 M HNO_3. The GEA count time was adjusted to accommodate the specific sample ^{137}Cs concentration to obtain ≤1% count uncertainty. An aliquot of the peak elution sample was submitted for ICP-MS for Cs isotopic distribution analysis. Table 2.12 provides the sampling and analysis summary.

Table 2.12. Column Samples ASRs and Sample IDs

Process Step	Approximate Sample Size (mL)	Process Sample Analyses	ASO Sample Analysis	ASR	Sample IDs
5.6 M Na Simple Simulant Test, April 2017					
Loading	10	^{137}Cs	GEA	0270	17-0804 to 17-0880
Effluent composite 0-90 BV	10	^{137}Cs	GEA	↓	↓
Effluent composite 90-168 BV	10	^{137}Cs	GEA	↓	↓
Feed displacement	10	^{137}Cs	GEA	↓	↓
Water rinse	10	^{137}Cs	GEA	↓	↓
Elution	0.1 to 10	^{137}Cs	GEA	↓	↓
Water rinse	2	^{137}Cs, pH	GEA	↓	↓
Extended rinse	10	pH	--	--	--
AP-105DF Test, July 2017					
Feeds (four individually)	0.2	^{137}Cs, Na, Al	GEA, ICP-OES	0316	17-1106 to 17-1109
Loading	2	^{137}Cs	GEA	0370	17-1110 to 17-1178
AP-105DF effluent composite 0–144 BV	2	^{137}Cs	GEA	↓	↓
AP-105DF effluent composite 144-294 BV	2	^{137}Cs	GEA	↓	↓
Feed displacement	2	^{137}Cs	GEA	↓	↓
Water rinse	2	^{137}Cs	GEA	↓	↓
Elution	0.02 to 1.9E-4	^{137}Cs	GEA	↓	↓
Water rinse	0.02	^{137}Cs	GEA	↓	↓
Peak Cs eluate sample	1.9E-4	Cs isotopic distribution	TIMS	0329	17-1224

TIMS = thermal ionization mass spectrometry

2.6.3 Analytical Services

All analyses were conducted by the ASO according to standard operating procedures, the ASO QA Plan, and the ASR. The ASO was responsible for the preparation and analysis of appropriate analytical batch and instrument quality control samples and to provide any additional processing to the sub-samples that might be required (e.g., acid digestion). Preparation by direct dilution (e.g., Na-only by ICP-OES) did not require preparative blanks and matrix spikes.

3.0 Batch Contact Results

This section discusses the batch contact results for the 5.6 M Na simulant and the AP-105DF tank waste.

3.1 5.6 M Na Simulant Batch Contact Results

The K_d values versus Cs concentrations are provided in Table 3.1 and plotted in Figure 3.1 on a linear-log scale. The duplicate values compared well with each other (within 4% relative percent difference), except for the S2 test solutions (with a 11% relative percent difference). The K_d vs. the log of the Cs equilibrium concentration was curve-fitted to a second order polynomial equation to calculate the K_d at the feed concentration of 60 µg/mL: 545 mL/g. The theoretical 50% Cs breakthrough on the ion exchange column (λ) can be predicted from the product of the K_d value and the ion exchanger bed density (ρ_b) (see Eq. (3.1)). The resin bed density is the dry resin mass divided by the expanded volume in the column. For this assessment, the resin bed density was calculated from the ion exchange column run (Section 4.0), 0.25 g/mL (based on a 2.45 g dry H-form resin mass and a Na-form resin bed volume of 9.9 mL). The theoretical 50% breakthrough (λ) for 5.6 M simple simulant with 60 µg/mL Cs is 136 BVs.

$$K_d \times \rho_b = \lambda \tag{3.1}$$

Table 3.1. Equilibrium Results for Batch Contact Samples in 5.6 M Na Simple Simulant

Sample ID	Initial [Cs] (µg/mL)	Final [Cs] (µg/mL)	K_d (mL/g)	Equilibrium Cs in Resin (mg Cs/g)
TI-013-S0-BC	60.0	4.07	1358	5.48
TI-013-S1-BC	188.0	21.50	763	16.3
TI-013-S2-BC	546.9	89.58	507	44.9
TI-013-S3-BC	1724	640.8	167	106
TI-013-S0-BC-d	60.0	4.23	1308	5.47
TI-013-S1-BC-d	188.0	21.21	779	16.4
TI-013-S2-BC-d	546.9	97.52	454	43.7
TI-013-S3-BC-d	1724	652.4	161	104

Note that the 5.6 M Na simple simulant also contains 0.122 M K.

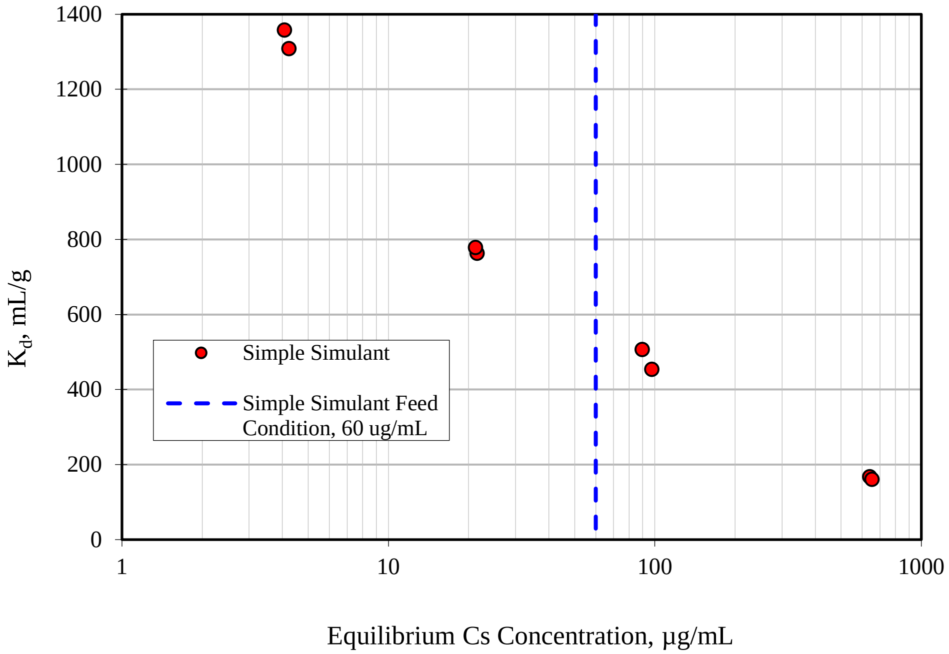


Figure 3.1. Equilibrium Cs K_d Curve for 5.6 M Na Simple Simulant with SRF

Figure 3.2 provides the isotherm for the 5.6 M Na simple simulant batch contact test samples. In this case, the equilibrium Cs concentration is expressed in terms of mg/mL (as opposed to µg/mL in Figure 3.1). The isotherm was fitted to the Langmuir adsorption equation according to Eq. (3.2). The expected Cs loading onto the resin at a given Cs concentration can be determined from the isotherm.

$$\frac{740.1 \times [\mathrm{Cs}]}{(5.516 \times [\mathrm{Cs}]+1)} = \mathrm{Cs_R} \tag{3.2}$$

where [Cs] = equilibrium Cs concentration in solution, mg Cs per mL solution

$\mathrm{Cs_R}$ = equilibrium Cs loading on the resin, mg Cs per g H-form resin

At the equilibrium Cs concentration of 60 µg/mL (0.06 mg/mL), the equilibrium Cs loading corresponds to 33.4 mg Cs per g dry H-form resin.

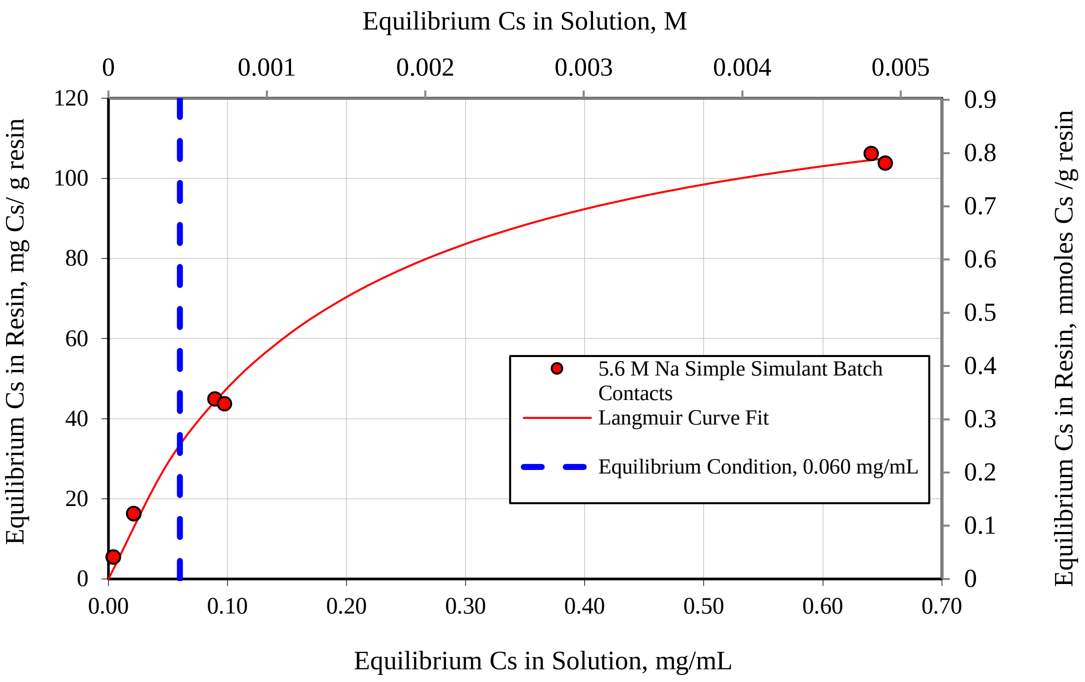


Figure 3.2. Isotherm for the 5.6 M Na Simple Simulant with SRF

3.2 AP-105DF Batch Contact Results

The AP-105DF was evaluated similarly to the 5.6 M Na simple simulant. Table 3.2 and Figure 3.3 provide the batch contact results for the test samples. The duplicate values compared well with each other (within 10% relative percent difference). The K_d vs. the log of the equilibrium Cs concentration was curve-fitted to a second order polynomial equation to calculate the K_d at the feed concentration of 7.92 µg/mL: 887 mL/g. The λ value was calculated to be 222 BVs based on Eq. (3.1).

Table 3.2. Equilibrium Results for Batch Contact Samples in AP-105DF

Sample ID	Initial [Cs] (µg/mL)	Final [Cs] (µg/mL)	K_d (mL/g)	Equilibrium Cs in Resin (mg Cs/g)
TI-006-S0-BC	7.92	0.36	1605	0.591
TI-006-S1-BC	52.24	3.13	1197	3.81
TI-006-S2-BC	156.1	14.26	748	10.83
TI-006-S3-BC(a)	569.8	--	--	--
TI-006-S4-BC	1716	582.5	147	86.97
TI-006-S0-BC-d	7.92	0.37	1541	0.586
TI-006-S1-BC-d	52.24	3.39	1084	3.73
TI-006-S2-BC-d	156.1	15.03	715	10.89
TI-006-S3-BC-d	569.8	105.9	334	35.69
TI-006-S4-BC-d	1716	544.9	162	89.39

(a) Sample was broken and lost in cell.

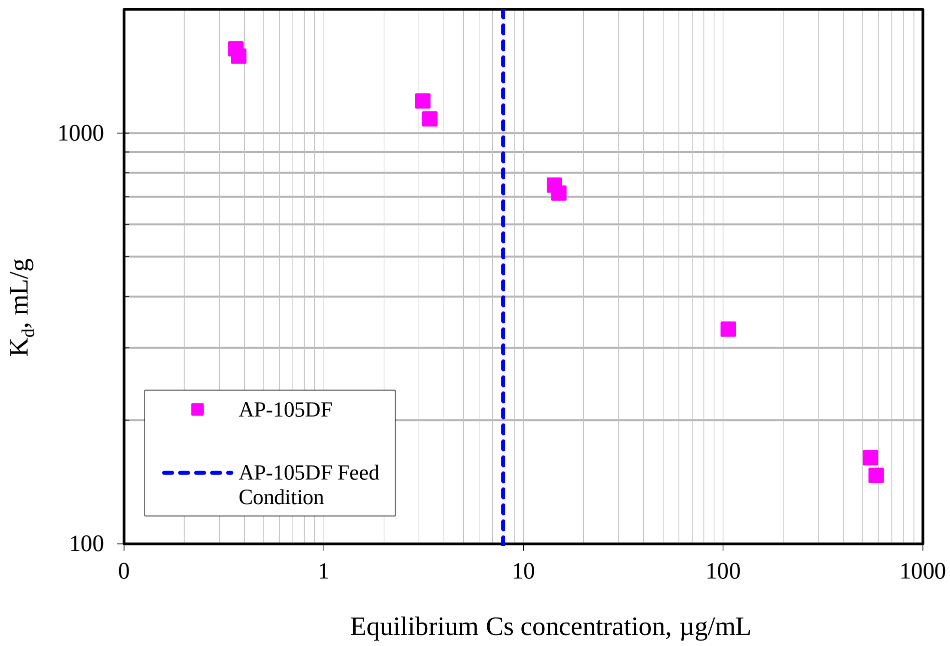
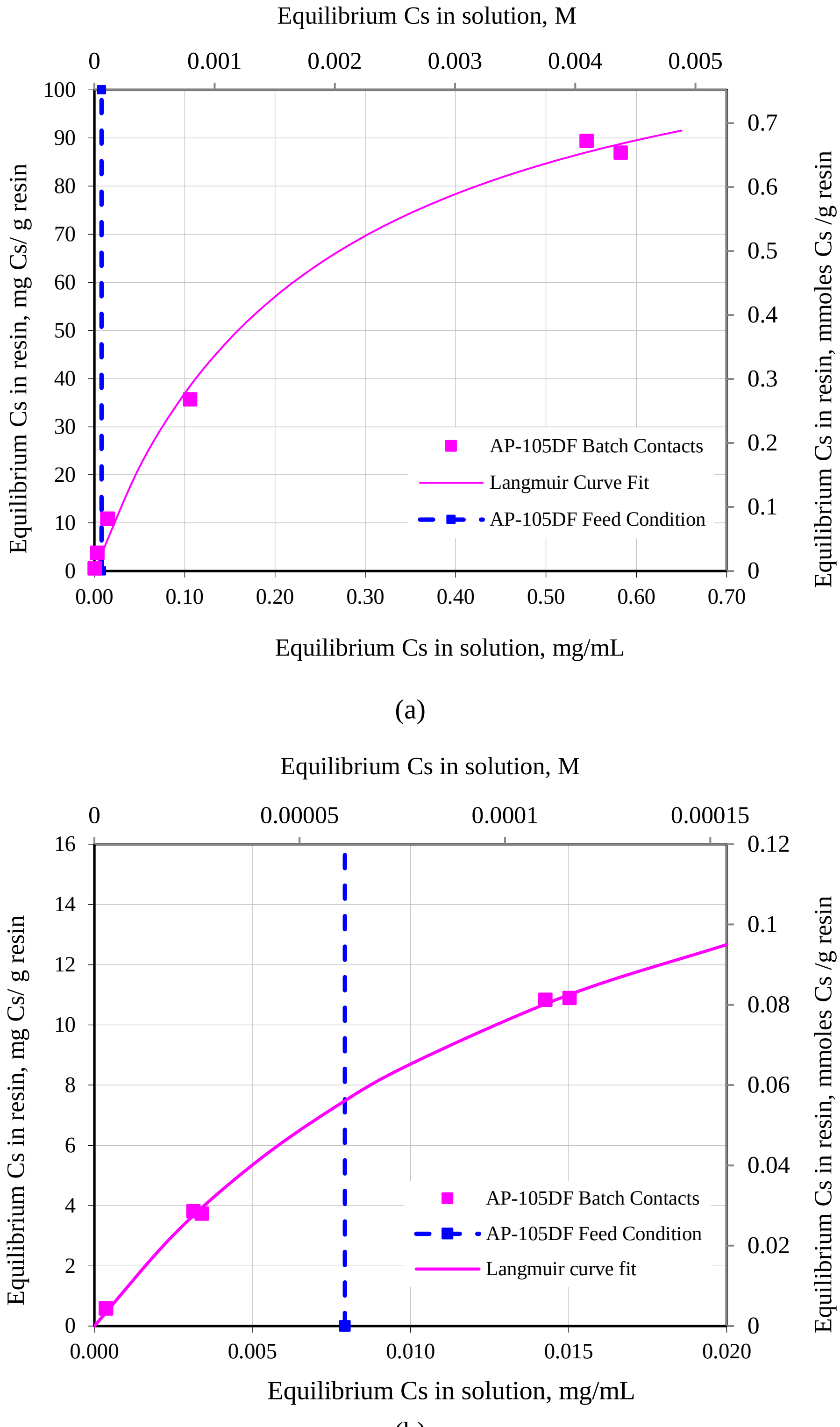


Figure 3.3. Equilibrium Cs K_d Curve for AP-105DF with SRF

The data were also plotted to show the isotherm (Figure 3.4a). The data generally appeared to fit the Langmuir adsorption equation. However, the low Cs concentration data (<0.02 mg/mL) were not well modeled in this fit; the calculated Cs load capacity at the AP-105DF equilibrium load condition was estimated to be 4.0 mg/g. The reduced data set (0.54 to 10.84 mg/mL equilibrium Cs concentration) was plotted and refitted to the Langmuir adsorption equation as shown in Figure 3.4b. In this scenario, the calculated Cs load capacity at the AP-105DF equilibrium load condition was estimated to be 7.5 mg/g.



(a)

(b)

Figure 3.4. Isotherm for AP-105DF with SRF: (a) Full Data Set, (b) Re-fitted with Low Concentration Data Set

4.0 Column Test Results

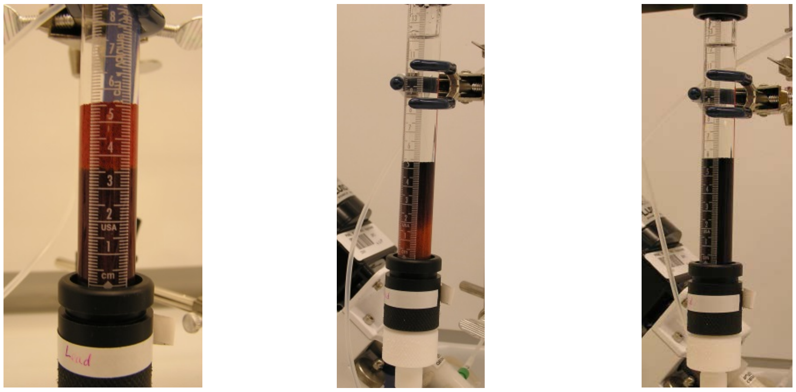
The Cs load and elution behavior was evaluated on the both the 5.6 M Na simple simulant and the AP-105DF tank waste. The same resin beds were used for both tests. The simple simulant was processed in the fume hood, and then the system was moved to the hot cell for use on AP-105DF. This section discusses the load and elution results for both tests. Raw data are provided in Appendix B.

4.1 5.6 M Na Simple Simulant Column Testing

This section discusses the Cs loading, feed displacement, water rinse, elution, and Cs mass balance when processing the 5.6 M Na simple simulant spiked at 60 µg/mL Cs.

4.1.1 Cs Load, Feed Displacement, and Water Rinse Results

Figure 4.1 shows prototypic images of the conversion fronts during the conditioning period of fresh resin. The conversion from the Na-form to the H-form was generally sharp and the conversion front from H-form to Na-form was generally diffuse. No major channeling was observed.



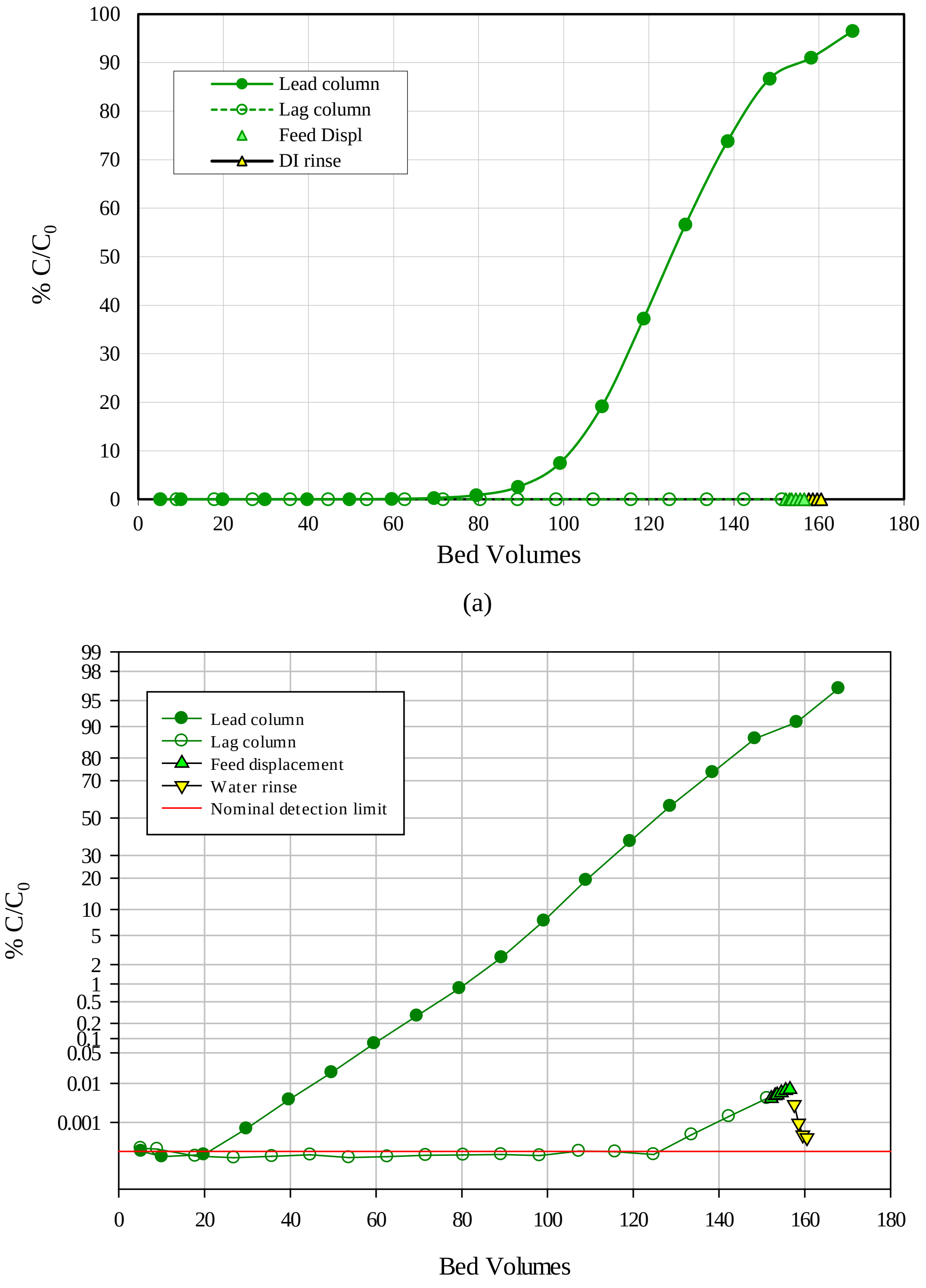
Lead column conversion
Na- to H-form
(conditioning)

Lead column conversion
H- to Na-form
(conditioning)

Lead column with
5.6 M Na simple simulant

Figure 4.1. Conversion Fronts in Resin Beds

Figure 4.2a shows the Cs load profiles for the lead and lag columns on a linear-linear plot. The x-axis shows the BVs processed and the y-axis shows the effluent Cs concentration (C) relative to the feed concentration (C_0) in terms of % C/C_0. The AECOM studies presented Cs breakthrough profiles on a similar plot format (y-axis as C/C_0); thus, this format provides for a direct comparison between the data sets. In this graphing format, the Cs breakthrough from the lead column starts at 80 BVs and continues to 168 BVs (a range of 88 BVs). The lead column 50% breakthrough was at 125 BVs. The lag column Cs breakthrough was not observable at this scale. Figure 4.2b shows the same Cs load data provided in Figure 4.2a on a probability-linear scale plot. Under ideal conditions, the Cs load profile will appear linear on the probability plot. Further, the probability plots show much more detail for the performances of the lead and lag columns at low % C/C_0 values—further enabled by the low detection limits achievable with the ^{137}Cs tracer.



(a)

(b)

Figure 4.2. Cs Load Profiles of 5.6 M Na Simple Simulant with 60 µg/mL Cs in the Small Column Geometry: (a) Linear-Linear Plot, (b) Probability-Linear Plot

Figure 4.3 juxtaposes the small column test with 9.9-mL ion exchange resin beds, the 1/9th-scale Phase 3 Test 1 (34.4-gallon resin beds), and full-scale Test 2 (297-gallon resin bed). The 1/9th-scale and full-scale data are preliminary. For reference, the flowrates were 1.9 BV/h for the 1/9th-scale test, 2.4 BV/h for the full-scale test, and 3.0 BV/h for the small column test; the feed superficial flow velocity was orders of magnitude higher in the 1/9th-scale and full-scale relative to the small-scale columns. The 50% Cs breakthrough for the small-scale (125 BVs) was delayed significantly relative to the 50% breakthrough point for the 1/9th-scale test (93 BVs) and the full-scale test (105 BVs). It should be understood that the resin in the 1/9th-scale Phase 3 Test 1 may have lost some Cs capacity with multiple process cycles that could diminish the 50% Cs breakthrough point; Phase 1 Test 1 50% Cs breakthrough point occurred at about 100 BVs. It is also interesting to note that the full-scale test Cs breakthrough profile appears to have two segments of different slopes. Between 63 and 88 BVs, the Cs load breakthrough appears similar to the small-scale test; at ~88 BVs, the slope changes and diverges from the small-scale test.

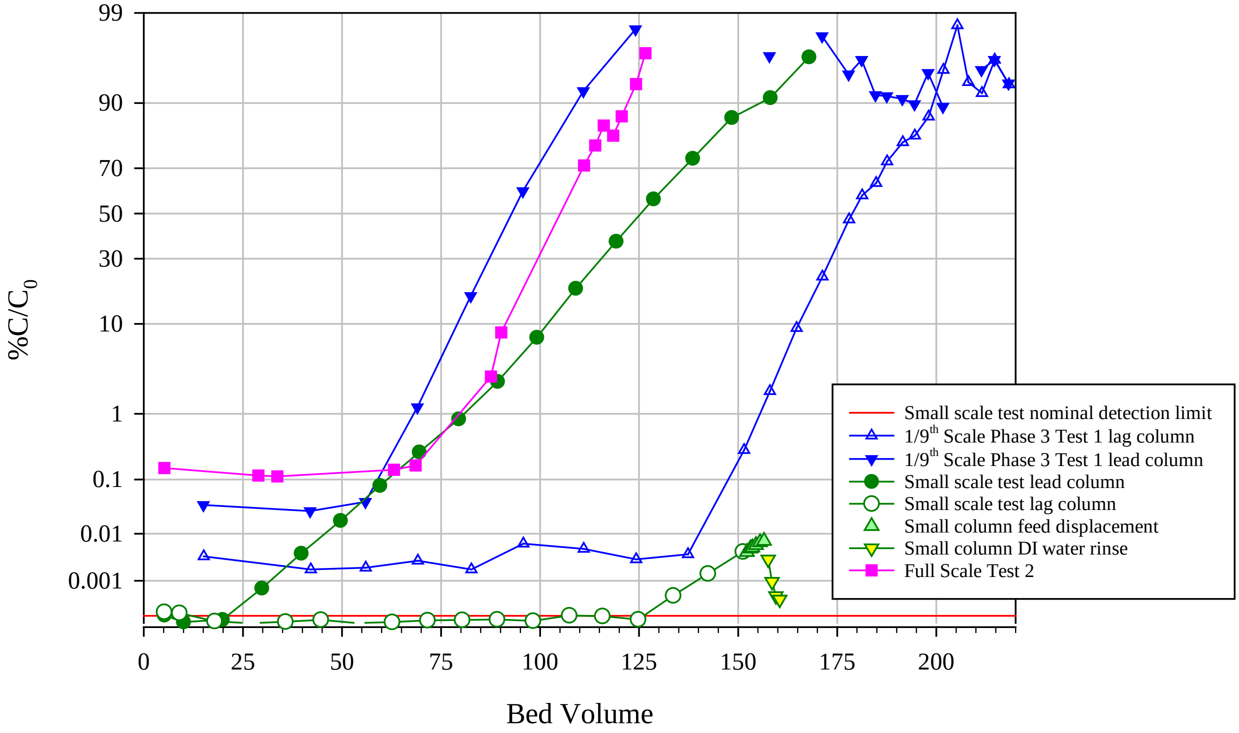


Figure 4.3. Cs Loading Profile from 5.6 M Na Simple Simulant and Small Column, 1/9th-Scale Phase 3 Test 1 (Preliminary Data), and Full-Scale Test 2 (Preliminary Data) (Probability Plot)

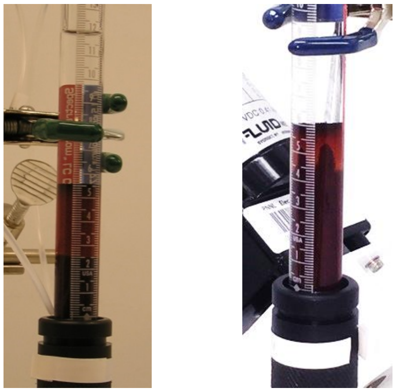
Figure Notes:

Test	Flowrate, BV/h	BV
1/9th-scale Phase 3 Test 1	1.9	34.4 gal
Full-scale Test 2	2.4	297 gal
Small scale	3.0	9.9 mL

The feed displacement following 5.6 M Na simple simulant feed was shown to simply extend the lag column Cs breakthrough profile, as would be expected because the feed displacement simply pushes out the 5.6 M Na simple simulant feed existing in the system. Of greater interest is the effect of the water rinse that followed the feed displacement. The effluent collection of the water rinse would be mostly composed of the feed displacement solution (0.1 M NaOH). As the contact solution changed from 5.6 M Na simple simulant to 0.1 M NaOH, Cs leakage from the lag column noticeably dropped off. This indicates that the Cs remained locked into the resin while the ionic strength of the solution decreased. This drop in Cs concentration may affect the WRPS approach to handling this solution.

4.1.2 Column Cs Elution Results

The elution flow through the ion exchange system was adjusted to flow sequentially downflow from the lag column to the lead column. Figure 4.4 shows images of the conversion fronts of these two columns. The conversion front for the lag column was sharp, showing a level front in color change from the dark-colored Na-form to the light-colored H-form. The conversion front for the lead column showed some channeling with nearly 1 cm amplitude between high and low ends of the conversion front. Both the lead column and lag column showed an oxidized resin layer at the top of the resin beds. The lead column would have been more affected as it was first to be contacted with feed, feed displacement, and water rinse before elution began. It is possible that this oxidized layer resulted in a bit of channeling of the eluting solution, leading to channeling.


Lag column elution

Lead column elution

Figure 4.4. Elution Conversion Fronts

Figure 4.5 provides the elution profile generated from samples collected from the lead column in 1-BV increments. In this configuration, Cs elution from the lead column did not occur until 10 BVs had been pumped through the system. Virtually all of the Cs was removed in the elution step. The subsequent water rinse continued the elution process as the DI water displaced a large portion of the 0.45 M HNO_3.

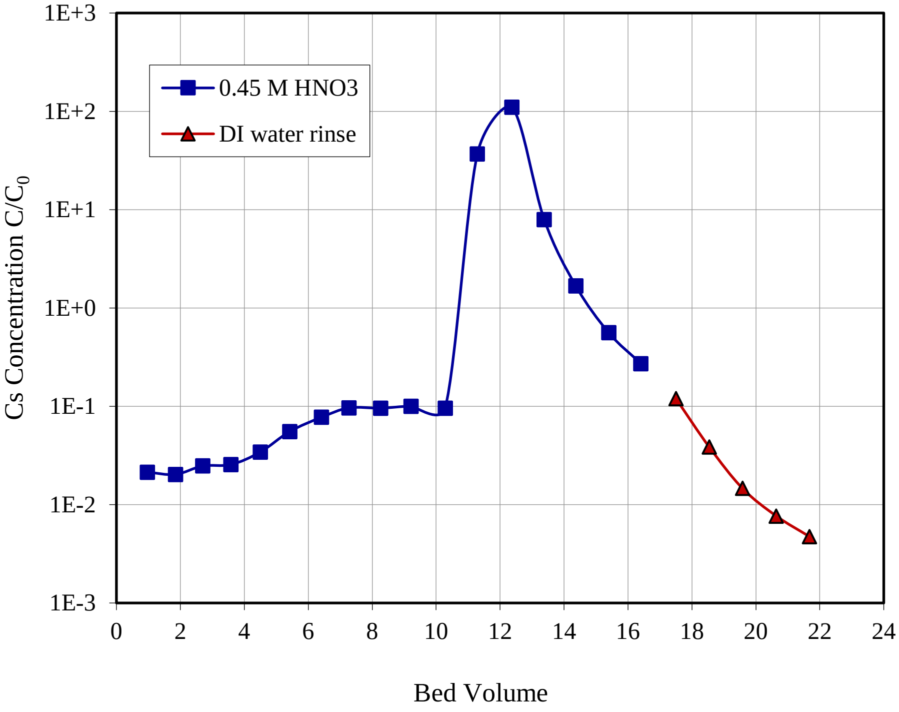


Figure 4.5. Elution Profile Following 5.6 M Na Simple Simulant Loading (Log-Linear Plot)

The pH of the final water rinse solution was determined 1 month after processing; it was still very acidic (pH 0), indicating that the water rinse did not effectively remove acid from the ion exchange system. Because the system was not to be used for several weeks, the columns were further rinsed sequentially with DI water to flush out the remaining acid. An additional 8.5 BVs of DI water flush were required to bring the effluent pH to 4.5. The initial two BVs of water rinse effluents were tinged yellow, indicating possible reaction between the low-pH solution and the resin.

4.1.3 Cesium Recovery from 5.6 M Na Simple Simulant Processing

Table 4.1 summarizes the ^{137}Cs fractionation between the effluents (collected in two different collection bottles), samples collected during the load processing, feed displacement, water rinse, elution, and the final water rinse associated with the first 5.3 BVs processed; ^{137}Cs analysis was not conducted on samples from the extended water rinse. The total Cs fractionation is the same as the ^{137}Cs fractionation. The 60 µg/mL Cs in the feed corresponds to 0.107 µCi/mL ^{137}Cs tracer in the feed. A total of 181.8 µCi of ^{137}Cs was input into the ion exchanger. Seventy-five percent of the Cs loaded onto the lead column and twenty-two percent loaded onto the lag column. Sample collection amounted to 2.7% of the input Cs. The remaining Cs was collected in the eluate. About 70% of the total Cs loaded into the system was collected in the peak Cs sample at the 11- to 12-BV increment.

Table 4.1. ^{137}Cs Activity Balance for the 5.6 M Na Simple Simulant Test

Input	µCi ^{137}Cs	%
Feed Sample	181.8	100
Output	µCi ^{137}Cs	%
Effluent-1 (0-89 BVs)	<8.9E-5	<4.9E-5
Effluent-2 (90-168 BVs)	3.94E-04	2.17E-04
Load samples	4.89	2.69
Feed displacement	3.13E-04	1.72E-04
Water rinse	5.12E-05	2.82E-05
Elution	178.3	98.1
Water rinse	0.21	0.12
Total ^{137}Cs recovery	183.4	101
Lead column Cs loading	136.8	75.3
Lag column Cs loading	40.1	22.0

The Cs load capacity was calculated from the total Cs loaded onto the lead column, which was assumed to be fully saturated under these load conditions, and the dry H-form resin mass loaded into the lead column according to Eq. (4.1).

$$\frac{\mathrm{A_{Cs}} \times \mathrm{CF}}{\mathrm{M_R}} = \mathrm{C} \tag{4.1}$$

where A_{Cs} = activity of ^{137}Cs, µCi on the lead column

CF = conversion factor, 0.559 mg Cs/µCi ^{137}Cs, specific to the Cs and ^{137}Cs spike conditions of this test

M_R = mass of dry, H-form resin

C = capacity, mg Cs/g H-form resin

A total of 76.4 mg Cs was loaded on the lead column, which contained 2.45 g dry H-form resin. The capacity was thus 31.2 mg Cs/g H-form resin. Batch contact testing resulted in a capacity 33.4 mg Cs/g H-form resin at 60 mg/mL Cs equilibrium condition, approximately 7% higher than the column result. The lead column resin was likely not fully saturated as it reached 96.5% C/C_0 breakthrough, indicating some minor exchange capacity was left after the test run was stopped. However, the 7% difference cannot be excluded from overall experimental uncertainty.

4.2 AP-105DF Column Testing

This section discusses the Cs loading, feed displacement, water rinse, elution, and Cs mass balance when processing the AP-105DF tank waste in the hot cell.

4.2.1 Cs Load, Feed Displacement, and Water Rinse Results

Figure 4.6 shows the Cs load profiles for the lead and lag columns on a probability-linear plot. Also shown is the contract limit. For the AP-105DF, this limit is 0.016% C/C_0 based on the feed composition of 5.7 M Na and 112 µCi/mL ^{137}Cs. The line break occurred after processing 144 BVs of AP-105DF through the lead column and 134 BVs through the lag column (see Section 2.4.5). The transitory increase in Cs effluent concentration from the lag column at this point is not understood; it is possible the sample was contaminated from the emerging leak. After processing 172 BVs through the lead column and 154 BVs through the lag column, the system was placed in standby mode over the weekend (see Section 2.4.5). This extended stop-flow condition did not appear to cause any perturbations in the load curve. The lead column 50% breakthrough was reached at 206 BVs. The lag column Cs breakthrough exceeded the 10% contract limit at 255 BVs. As with the 5.6 M Na simple simulant shakedown test, the ^{137}Cs concentrations in the feed displacement and water rinse effluents quickly dropped once AP-105DF feed was flushed out of the system. It is noted that the last feed displacement sample dropped in Cs content, unlike the shakedown test with 5.6 M Na simple simulant. This is attributed to the decreased fluid volume in the system where 3.7 mL above the lag column resin bed was displaced with air associated with replacement of the broken process line (see Section 2.4.5).

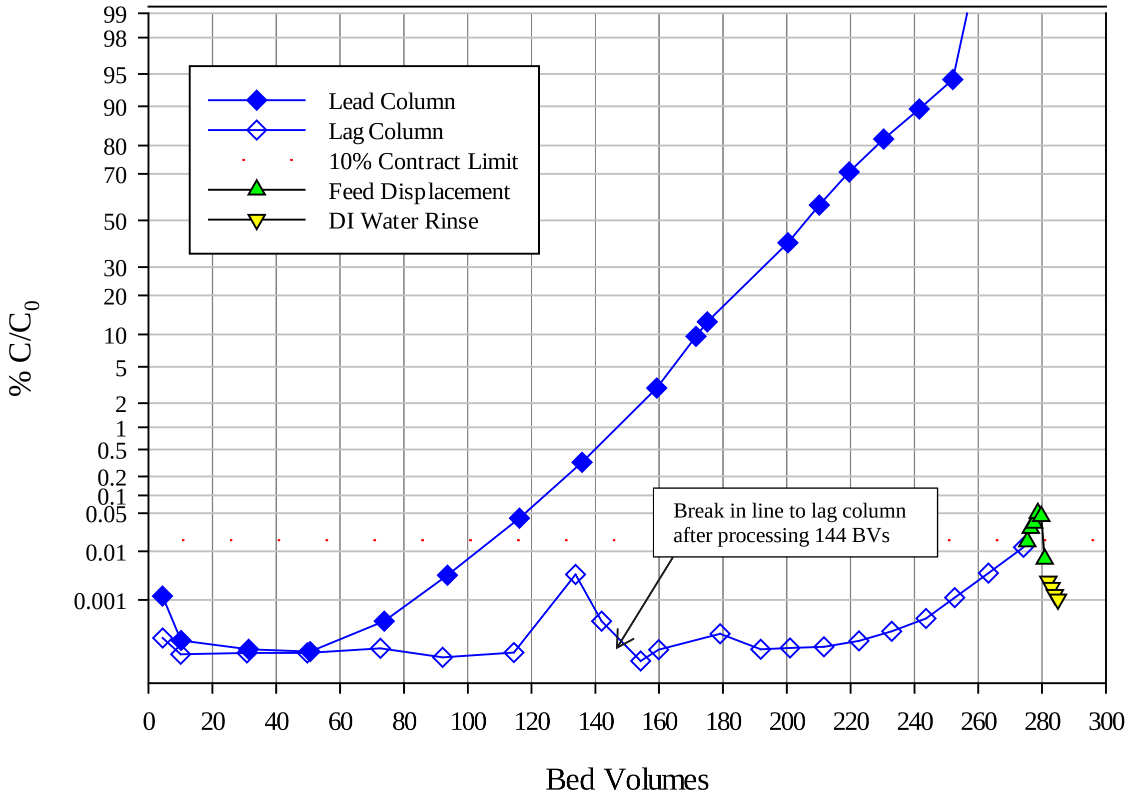


Figure 4.6. AP-105DF Cesium Load Profile, Probability-Linear Plot

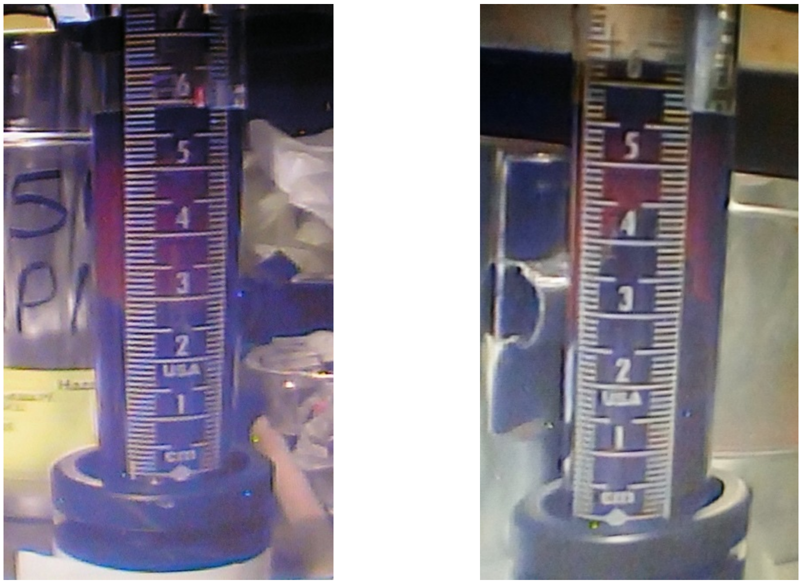
Table 4.2 provides the two Cs-decontaminated effluent composite results in terms of ^{137}Cs concentration and overall decontamination factor (DF). Excellent Cs decontamination was obtained.

Table 4.2. AP-105DF Effluent Composites ^{137}Cs Content and Decontamination Factor

	^{137}Cs (µCi/mL)	DF
Effluent-1 (0-159 BVs)	7.07E-5	1.58E+06
Effluent-2 (160-294 BVs)	7.25E-4	1.54E+05

4.2.2 AP-105DF Column Cs Elution Results

The conversion fronts for the elution were fairly sharp for the lag column. The lead column displayed more significant channeling than was observed during the shakedown test; channeling had amplitude of 2 cm. Figure 4.7 shows the elution fronts for both columns.



Lag column elution front, 2.9 BVs processed

Lead column elution front, 8.8 BVs processed

Figure 4.7. Lag and Lead Column Elution Fronts

Figure 4.8 provides the Cs elution profile following the AP-105DF loading. The elution profile from the shakedown test is juxtaposed to the tank waste test for direct comparison. The peak Cs was similar at nominally 100 times the feed composition. The AP-105DF test peak Cs elution eluted slightly sooner (1.5 BVs) than that of the shakedown test. This is attributed to the 3.7-mL decrease in the fluid holdup volume above the lag column resin bed and the fidelity at which elution samples were collected (1-BV increments for the shakedown test and ~1.5-BV increments for the AP-105DF test).

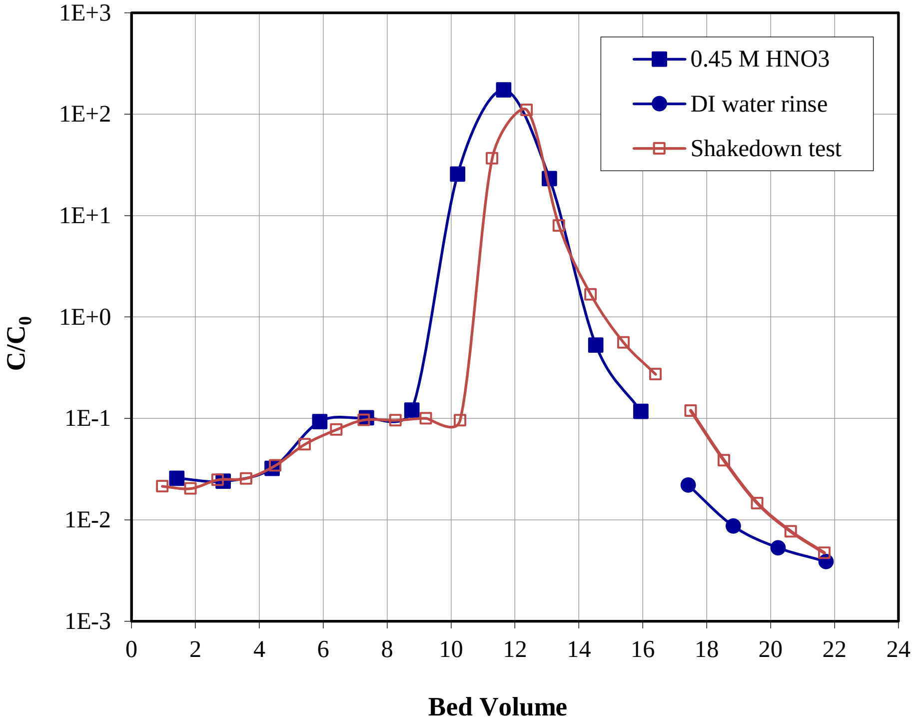


Figure 4.8. Cs Elution Profile Following AP-105DF Loading Compared to Shakedown Test

4.2.3 Cesium Recovery from AP-105DF Processing

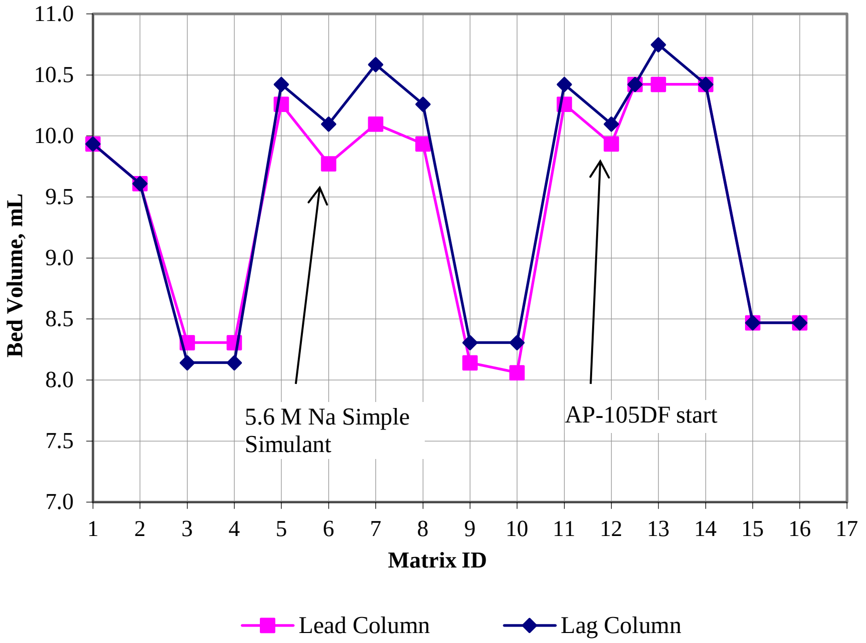
Table 4.3 summarizes the ^{137}Cs fractionation between the effluents (collected in two different collection bottles), samples collected during the load processing, feed displacement, water rinse, elution, and the final water rinse associated with the first 5.8 BVs processed; ^{137}Cs analysis was not conducted on samples from the extended water rinse. A total of 0.325 Ci of ^{137}Cs was input into the ion exchange system. Sixty-nine percent of the Cs loaded onto the lead column and thirty percent loaded onto the lag column. Sample collection amounted to 0.51% of the input Cs. The spill amounted to a very minor loss of ~0.08% ^{137}Cs. The remaining Cs was collected in the eluate. Nominally 78% of the total Cs loaded into the system was collected in the peak Cs sample at the 10- to 12-BV increment.

Table 4.3. ^{137}Cs Activity Balance for the AP-105DF Test

Input	µCi	%
Feed Sample	3.29E+05	100
Output		
Effluent-1 (0-159 BVs)	1.08E-01	3.29E-05
Effluent-2 (160-294 BVs)	9.38E-01	2.85E-04
Load samples	1.74E+03	0.529
Loss (spill)	2.71E+02	0.082
Feed displacement	2.16E+00	6.58E-04
Water rinse	7.75E-02	2.36E-05
Elution	3.52E+05	107
Water rinse	4.40E+00	1.34E-03
Total ^{137}Cs Recovery	3.54E+05	108

4.3 Resin Bed Physical Properties

The ion exchange resin bed contracts as it converts to H-form and expands when it converts to Na-form. Figure 4.9 shows the in-column contraction/expansion history starting with the in-column pretreatment operations and continuing through the final water rinse following AP-105DF processing. Typical 20% shrink/swell behavior was observed. The H-form resin BV following AP-105DF processing appeared to increase a little bit where the final H-form BV was at 8.5 mL and initially it was at 8.1 to 8.2 mL.



Matrix ID	Matrix
1	1.0 M NaOH soak
2	DI water rinse
3	0.45M HNO_3
4	DI water rinse
5	1.0 M NaOH
6	Feed, simple simulant
7	0.1 M NaOH FD
8	DI water rinse
9	0.45 M HNO_3
10	DI water rinse
11	1.0 M NaOH
12	AP-105DF start
12.5	AP-105DF end
13	0.1 M NaOH FD
14	DI water rinse
15	0.45 M HNO_3
16	DI water rinse

Figure 4.9. Resin Bed Expansion and Contraction History

The dark layer, indicative of oxidative attack, at the top surface of the ion exchange resin bed expanded relative to its pretreatment form. Figure 4.10 provides pictures of the lead and lag columns following feed processing, elution, and water rinse. Images collected after shakedown testing with the 5.6 M Na simple simulant were collected in the fume hood with a standard digital camera. Images collected after AP-105DF processing, elution, and water rinse were taken with the in-cell camera. The depth of the black band on the top resin bed surface increased after the second feed processing. As these resin beds are exposed to more process cycles, the black band is expected to continue to increase in depth.

Lead column, post 5.6 M Na simple simulant processing and elution

Lead column, post AP-105DF processing and elution

Lag column, post 5.6 M Na simple simulant processing and elution

Lag column, post AP-105DF processing and elution

Figure 4.10. Post-Eluted Resin Beds Showing Black Band of Resin Oxidation

4.4 Comparison of 50% Breakthrough from Batch Contact and Column Test

The K_d determination from the batch contact test is used to estimate the 50% breakthrough according to Eq. (4.2), where ρ_b is the resin bed density and λ is the bed volumes at 50% Cs breakthrough.

$$K_d \times \rho_b = \lambda \tag{4.2}$$

The 5.6 M Na simple simulant 50% C/C_0 breakthrough occurred at 125 BVs for the small column test; this value is about 8% lower than predicted from the batch contact K_d evaluation (136 BVs). In contrast, the 50% breakthrough was ~93 BVs in the 1/9th scale (Phase 3 Test 1) and 105 BVs in the full-scale test (Test 2). The batch contact appeared to more successfully predict the small column test Cs breakthrough than those of the full-scale and 1/9th-scale tests. The Phase 3 Test 1 used resin that had been processed several times before, and total capacity may be reduced from chemical and oxidative attack. Earlier tests on the 1/9th-scale resin bed, however, resulted in a 50% breakthrough at about 105 BVs, equivalent to the full-scale test.

The AP-105DF 50% C/C_0 breakthrough occurred at 206 BVs. The predicted λ value based on batch contact testing was 222 BVs. The difference between the two values is about 7%, similar to the difference noted for the 5.6 M Na simple simulant; within experimental uncertainty, this represents good agreement. The slight negative bias may be associated with decreased capacity from oxidative chemical attack on the ion exchanger from the shakedown process cycle.

Table 4.4 summarizes the results for the predicted 50% Cs breakthrough from batch contact testing and measured 50% Cs breakthroughs from column tests. Based on this one comparative result, the batch contact testing appears to over-predict the 50% Cs breakthrough in the large-scale test format.

Table 4.4. Summary of 50% Breakthrough: Predicted vs Measured

Matrix	Predicted BVs at 50% C/C_0	Test Geometry	Measured BVs at 50% C/C_0	% Difference
5.6 M Na simple simulant	136	Small column	125	8
		1/9th scale	93	32
		Full scale	105	23
AP-105DF	222	Small column	206	7

4.5 Transition Zone

The transition (or exchange) zone is defined as the volume processed from the onset of Cs breakthrough to the full saturation of the ion exchanger where the effluent Cs concentration equals the influent Cs concentration. The 50% breakthrough point is the inflection point around which the transition zone pivots.

The transition zones were estimated from data obtained from the probability plot (Figure 4.3). For the 1/9th-scale Phase 3 Test 1, the transition zone for the lead column was calculated to be 68 BVs (56 BVs onset of breakthrough subtracted from 124 BVs at 96% Cs breakthrough); the lag column transition zone was similarly calculated to be 67 BVs (205 BVs - 138 BVs). The full-scale Test 2 transition zone was 58 BVs (126 BVs – 68 BVs). The small column test transition zone was estimated to be 148 BVs (168 BVs – 20 BVs). Clearly, the achievable Cs detection limit and/or Cs leakage from the previous load cycle affects how the transition zone can be measured as follows:

1. as Cs detection limit improves, one can observe Cs exiting the column as part of the breakthrough profile sooner, and
2. as the Cs leakage from the previous test increases (observed as constant Cs leakage concentration), the onset of the observed breakthrough profile will be delayed.

The 1/9th-scale test transition zone was sharper (higher slope) than that of the small-scale test. This is likely attributable in part to the film diffusion constraint where faster superficial velocity solution flowrate improves film diffusion, which in turn improves the Cs exchange rate. The full-scale breakthrough profile consisted of two segments of differing slopes (see Figure 4.3); the second segment (BVs 88 to 125) had a higher slope than that of the 1/9th-scale test.

The differences in Cs breakthrough slope (and thus transition zone) can be traced to ion exchange dynamics. In general, there are three steps to the absorption of material on ion exchange media such as SRF (Harland 1994):

1. Transfer of the cesium from the bulk solution to the surface of the resin bead through the mass transfer layer (film diffusion)
2. Diffusion of the cesium within the SRF bead from the surface to the ion exchange site (particle/pore diffusion)
3. Exchange of the cesium atom for a sodium atom at the ion exchange site (chemical reaction/ion exchange)

These process steps are shown graphically in Figure 4.11 (adapted from Harland 1994 and Hardy et al. 2004).

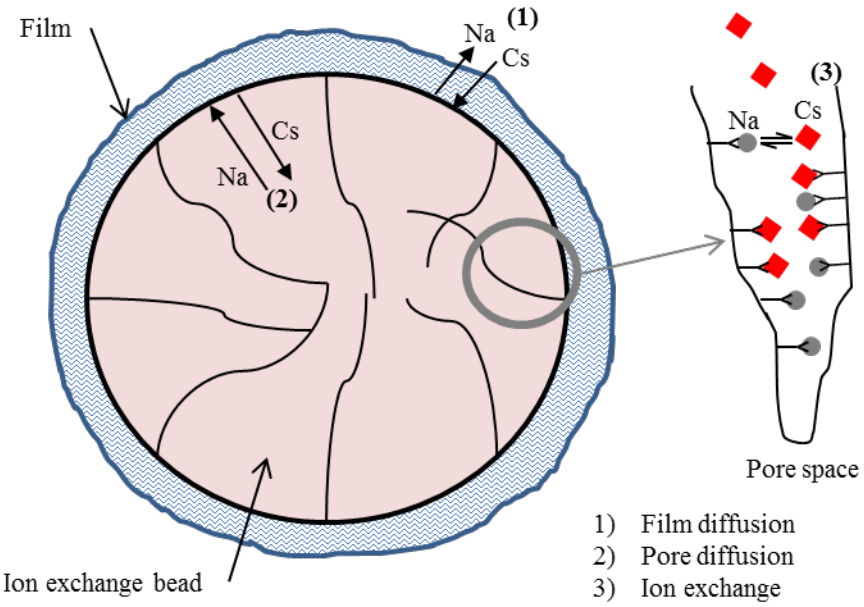


Figure 4.11. Schematic of the Three Processes Limiting Ion Exchange onto SRF

Any one of these three steps can be the rate-limiting step. At very low superficial velocities, the mass transfer rate of cesium from the bulk to the resin bead surface will be low, and as such, the film diffusion in the ion exchange process will be the rate-limiting step (Helfferich 1962). Under this regime, increasing the superficial velocity, and thus increasing the BV/h processed, will improve the film diffusion and will sharpen the load curve, thus decreasing the transition zone.

As the superficial velocity increases, there will be a point at which the mass transfer rate is balanced by either the diffusion rate and/or ion exchange rate. Beyond this point, further increasing the superficial velocity will not control the Cs exchange rate limiting step, and thus beyond this point, the transition zone will continue to get larger because the flowrate will increase without a concomitant improvement in loading kinetics (see also Hardy et al. 2004).

Figure 4.12 is a representation of this phenomenon. The data shown indicate the effective transition zone of Cs on the lead column using the lower and upper Cs breakthrough limits provided for the 1/9th-scale and full-scale testing (normalized to ~0.5 to 82 % C/C_0 for comparability). As indicated, the transition zone decreases with decreasing superficial velocity (and decreasing BV/h) for the pilot-scale test. However, one would expect that, at the much lower superficial velocities for the lab-scale tests, the mass transfer would cause an increase in the transition zone length. Note that curve shown is only a visualization of the impact, and is not a prediction of the behavior between the two testing scales. Thus, the small lab-scale columns are operated at a fundamentally different rate-limiting step (mass transfer limited) than the full-size columns (which are operated with diffusion limiting). As such, the small-scale columns provide only a bounding assessment of the expected transition zone length.

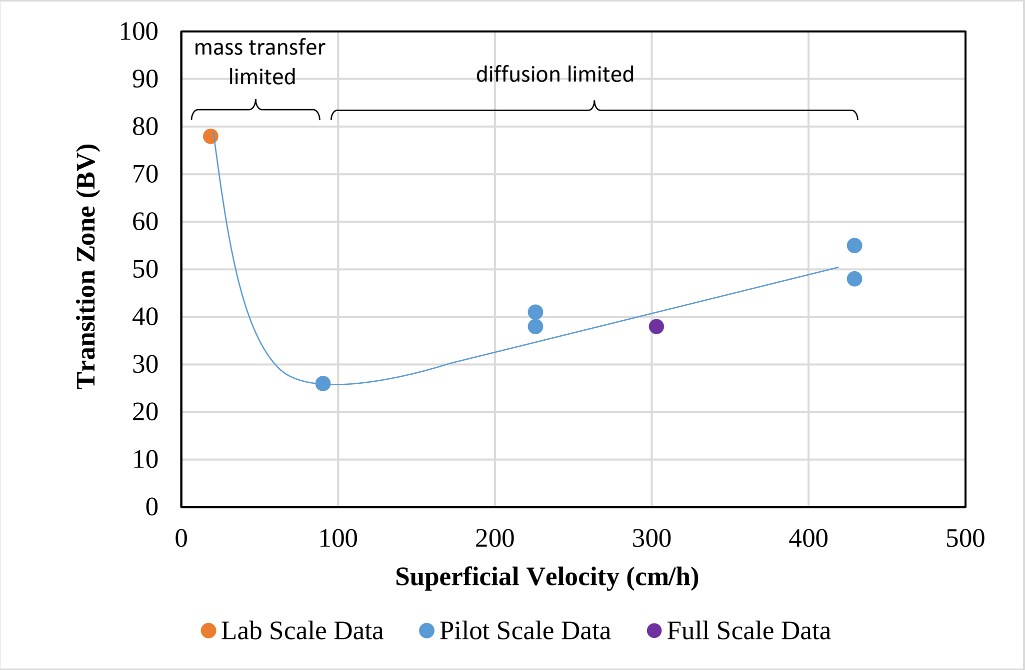


Figure 4.12. Transition Zone as a Function of the Superficial Velocity

Batch contact test results may infer the 50% Cs breakthrough, i.e., the inflection point of the load curve/transition zone; however, they cannot be used to discern the slope of the load curve/transition zone. The slope of the Cs breakthrough profile determines how quickly Cs breakthrough will challenge the effluent ^{137}Cs contract limit. This in turn dictates the volume of feed that can be processed before regeneration is required. Further, batch contact testing will not infer in-column conditions whereby some of the resin may have been exhausted from oxidative, chemical, and radiolytic attack.

5.0 Qualification Testing Conclusions

The goal of qualification testing was to demonstrate Cs decontamination using SRF resin through the use of simple, rapid, batch contact testing. The batch contact testing is used to 1) determine the equilibrium distribution coefficient (K_d), 2) predict the 50% Cs breakthrough on an ion exchange column, and 3) determine the Cs loading capacity under equilibrium conditions (isotherm). These values were compared to measured values on small column tests. Two conditions were tested: 5.6 M Na simple simulant and the AP-105DF tank waste. Results are as summarized in Table 5.1. Overall comparisons between the batch contact predicted values and the small column tests measured values were good (within 10%).

Table 5.1. Batch Contact Parameter Comparison to Small Column Test

Parameter	5.6 M Na Simple Simulant	AP-105DF
Cs concentration	60 µg/mL	7.9 µg/mL
50% Cs breakthrough estimated from batch contact	136 BVs	222 BVs
50% Cs breakthrough measured from column test	125 BVs	206 BVs
% difference	8	7
Capacity batch contact	$33.4\ \frac{\text{mg Cs}}{\text{g H-form resin}}$	$7.5\ \frac{\text{mg Cs}}{\text{g H-form resin}}$
Capacity column test	$31.2\ \frac{\text{mg Cs}}{\text{g H-form resin}}$	$6.6\ \frac{\text{mg Cs}}{\text{g H-form resin}}$
% difference	7	12

The batch contact testing successfully predicted the 50% Cs breakthrough point (within 8%) in a small column format. The 50% Cs breakthrough point was over-predicted on the 1/9th-scale and full-scale column runs by 32% and 23%, respectively, based on a suite of tests with 5.6 M Na simple simulant. Batch contact testing cannot be used to predict the transition zone and how many BVs can be processed before the Cs effluent target limit is reached and regeneration is required.

6.0 References

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Appendix A

Batch Contact Raw Data

Appendix A

Batch Contact Raw Data

The batch contact raw data are provided in Table A.1 for the 5.6 M Na simple simulant matrix and in Table A.2 for the AP-105DF tank waste.

Table A.1. 5.6 M Simple Simulant Batch Contact Data

Sample ID	Initial [Cs] (µg/mL)	Net Resin Mass (g)	F-factor, Water Loss	Corrected Net Resin Mass (g)	Simulant Volume (mL)	Liquid Volume to Solid Mass Ratio	Equilibrium (µCi ^{137}Cs/mL)	Equilibrium [Cs] (mg/mL)	K_d (mL/g)	Equilibrium Cs Molarity	Equilibrium Cs in Resin (mg Cs/g)	Equilibrium Cs in Resin (mmoles Cs/g)
TI-013-S0	60.0	--	--	--	--	--	0.1149	--	--	--	--	--
TI-013-S1	188	--	--	--	--	--	0.1088	--	--	--	--	--
TI-013-S2	547	--	--	--	--	--	0.1188	--	--	--	--	--
TI-013-S3	1724	--	--	--	--	--	0.1031	--	--	--	--	--
TI-013-S0-BC	60.0	0.2128	0.4817	0.1025	10.0404	97.9	0.0078	0.00407	1358	3.06E-05	5.48	4.12E-02
TI-013-S1-BC	188	0.2131	0.4817	0.1027	10.0198	97.6	0.0124	0.0215	763	1.62E-04	16.3	1.22E-01
TI-013-S2-BC	547	0.2113	0.4817	0.1018	10.0022	98.3	0.0195	0.0896	507	6.74E-04	44.9	3.38E-01
TI-013-S3-BC	1724	0.2117	0.4817	0.1020	10.0039	98.1	0.0383	0.641	167	4.82E-03	106	7.99E-01
TI-013-S0-BC-d	60.0	0.2118	0.4817	0.1020	10.0057	98.1	0.0081	0.00423	1308	3.18E-05	5.47	4.12E-02
TI-013-S1-BC-d	188	0.2116	0.4817	0.1019	10.0106	98.2	0.0123	0.0212	779	1.60E-04	16.4	1.23E-01
TI-013-S2-BC-d	547	0.2122	0.4817	0.1022	9.9508	97.3	0.0212	0.0975	454	7.34E-04	43.7	3.29E-01
TI-013-S3-BC-d	1724	0.2128	0.4817	0.1025	9.9342	96.9	0.0390	0.652	161	4.91E-03	104	7.81E-01

Table A.2. AP-105DF Batch Contact Data

Sample ID	Initial [Cs] (µg/mL)	Net Resin Mass (g)	F-factor, Water Loss	Corrected Net Resin Mass (g)	AP-105DF Volume (mL)	Liquid volume to solid mass ratio	Equilibrium µCi ^{137}Cs/mL	Equilibrium [Cs] (mg/mL)	Kd (mL/g)	Equilibrium Cs Molarity	Equil. Cs in Resin (mg Cs/g)	Equil. Cs in Resin (mmoles Cs/g)
TI-006-S0	7.92	--	--	--	--	--	122.7	--	--	--	--	--
TI-006-S1	52.24	--	--	--	--	--	122.7	--	--	--	--	--
TI-006-S2	156.1	--	--	--	--	--	123.8	--	--	--	--	--
TI-006-S3	569.8	--	--	--	--	--	122.0	--	--	--	--	--
TI-006-S4	1716	--	--	--	--	--	122.3	--	--	--	--	--
TI-006-S0-BC	7.92	0.2462	0.5274	0.1279	9.9936	78.1	5.616	0.000363	1605	2.73E-06	0.591	4.45E-03
TI-006-S1-BC	52.2	0.2472	0.5274	0.1283	9.9596	77.6	7.361	0.00313	1197	2.36E-05	3.81	2.87E-02
TI-006-S2-BC	156.1	0.2501	0.5274	0.1298	9.9163	76.4	11.31	0.0143	748	1.07E-04	10.83	8.15E-02
TI-006-S3-BC	569.8	0.2510	0.5274	0.1305	9.9279	76.1	--	--	--	--	--	--
TI-006-S4-BC	1716	0.2479	0.5274	0.1286	9.8629	76.7	41.50	0.583	147	4.38E-03	86.97	6.54E-01
TI-006-S0-BC-d	7.92	0.2486	0.5274	0.1290	10.0178	77.6	5.798	0.000374	1541	2.82E-06	0.586	4.41E-03
TI-006-S1-BC-d	52.2	0.2513	0.5274	0.1306	9.9770	76.4	7.971	0.00339	1084	2.55E-05	3.73	2.81E-02
TI-006-S2-BC-d	156.1	0.2480	0.5274	0.1290	9.9589	77.2	11.91	0.0150	715	1.13E-04	10.89	8.19E-02
TI-006-S3-BC-d	569.8	0.2471	0.5274	0.1290	9.9229	76.9	22.67	0.106	334	7.97E-04	35.69	2.69E-01
TI-006-S4-BC-d	1716	0.2486	0.5274	0.1296	9.8878	76.3	38.82	0.545	162	4.10E-03	89.39	6.73E-01

Appendix B

Column Loading Raw Data

Appendix B

Column Loading Raw Data

The 5.6 M Na simple simulant column loading raw data are provided in Table B.1 and elution raw data are provided in Table B.2. The AP-105DF tank waste column loading raw data are provided in Table B.3 and elution raw data are provided in Table B.4.

Table B.1. 5.6 M Na Simple Simulant Cs Load, Feed Displacement, and Water Rinse Results

Lead Column				Lag Column				Feed Displacement and Water Rinse			
BV	μCi ^{137}Cs/ mL	% C/C$_0$	DF	BV	μCi ^{137}Cs/ mL	% C/C$_0$	DF	BV	μCi ^{137}Cs/ mL	% C/C$_0$	DF
5.2	<1.65E-7	<1.53E-4	>652,513	**5.1**	<1.99E-7	<1.85E-4	>539,240	FD			
10.0	<1.12E-7	<1.05E-4	>955,461	**9.0**	<1.88E-7	<1.75E-4	>571,161	**152.2**	4.55E-6	4.24E-3	23,587
19.8	1.29E-7	1.20E-4	833,564	**17.8**	<1.18E-7	<1.10E-4	>912,787	**153.1**	5.37E-6	5.00E-3	19,993
29.8	7.23E-7	6.73E-4	148,576	**26.8**	<1.04E-7	<9.71E-5	>1,029,350	**153.6**	5.63E-6	5.24E-3	19,081
39.7	4.26E-6	0.00	25,223	**35.7**	<1.15E-7	<1.07E-4	>932,543	**154.5**	6.30E-6	5.87E-3	17,038
49.6	2.02E-5	0.02	5,323	**44.6**	<1.28E-7	<1.19E-4	>841,061	**155.6**	7.25E-6	6.75E-3	14,813
59.6	8.48E-5	0.08	1,267	**53.7**	<1.06E-7	<9.84E-5	>1,016,135	**156.6**	7.69E-6	7.16E-3	13,966
69.5	2.98E-4	0.28	360	**62.6**	<1.13E-7	<1.05E-4	>952,493	Water rinse			
79.4	9.10E-4	0.85	118	**71.6**	<1.24E-7	<1.16E-4	>865,702	**157.6**	3.19E-6	2.97E-3	33,662
89.3	2.73E-3	2.54	39	**80.3**	<1.26E-7	<1.18E-4	>850,066	**158.6**	1.02E-6	9.54E-4	104,825
99.1	8.05E-3	7.50	13	**89.1**	<1.30E-7	<1.21E-4	>825,941	**159.6**	4.82E-7	4.49E-4	222,897
109.0	2.06E-2	19.20	5.2	**98.2**	<1.21E-7	<1.13E-4	>887,559	**160.5**	4.00E-7	3.72E-4	268,751
118.8	4.00E-2	37.24	2.7	**106.9**	<1.64E-7	<1.52E-4	>656,672				
128.6	6.08E-2	56.63	1.8	**115.8**	<1.58E-7	<1.47E-4	>679,374				
138.5	7.93E-2	73.87	1.4	**124.8**	<1.31E-7	<1.22E-4	>822,873				
148.4	9.31E-2	86.69	1.2	**133.6**	4.91E-7	4.57E-4	218,779				
158.1	9.77E-2	91.01	1.1	**142.4**	1.55E-6	1.45E-3	69,175				
167.9	1.04E-1	96.53	1.0	**151.2**	4.61E-6	4.29E-3	23,291				

BV = bed volume; DF = decontamination factor; FD = feed displacement; C$_0$ = 0.107 μCi ^{137}Cs/ mL

Table B.2. Elution and Water Rinse Results Following 5.6 M Na Simple Simulant Processing

Elution			Water Rinse		
BV	µCi ^{137}Cs/ mL	% C/C_0	BV	µCi ^{137}Cs/ mL	% C/C_0
0.96	2.30E-3	2.14E-2	**17.50**	1.28E-2	1.20E-1
1.85	2.18E-3	2.03E-2	**18.54**	4.15E-3	3.87E-2
2.70	2.66E-3	2.47E-2	**19.58**	1.57E-3	1.46E-2
3.58	2.75E-3	2.56E-2	**20.64**	8.23E-4	7.67E-3
4.50	3.68E-3	3.43E-2	**21.68**	5.08E-4	4.73E-3
5.42	5.95E-3	5.54E-2			
6.41	8.31E-3	7.74E-2			
7.27	1.04E-2	9.65E-2			
8.26	1.03E-2	9.58E-2			
9.22	1.08E-2	1.00E-1			
10.28	1.03E-2	9.59E-2			
11.29	3.95E+0	3.68E+1			
12.37	1.18E+1	1.10E+2			
13.38	8.53E-1	7.94E+0			
14.37	1.80E-1	1.67E+0			
15.40	6.01E-2	5.59E-1			
16.40	2.92E-2	2.72E-1			

BV = bed volume; C_0 = 0.107 µCi ^{137}Cs/ mL

Table B.3. AP-105DF Cs Load, Feed Displacement, and Water Rinse Results

Lead Column				Lag Column				Feed Displacement and Water Rinse			
BV	µCi ^{137}Cs/ mL	% C/C_0	DF	BV	µCi ^{137}Cs/ mL	% C/C_0	DF	BV	µCi ^{137}Cs/ mL	% C/C_0	DF
4.4	1.36E-3	1.22E-3	82,238	4.4	1.50E-4	1.34E-4	743,720	FD			
10.2	1.30E-4	1.17E-4	856,213	10.0	6.05E-5	5.43E-5	1,843,199	275.3	1.71E-2	1.54E-2	6,507
31.4	8.05E-5	7.21E-5	1,386,420	30.8	6.53E-5	5.86E-5	1,707,607	276.4	3.03E-2	2.72E-2	3,682
50.6	7.04E-5	6.32E-5	1,583,472	49.7	6.50E-5	5.83E-5	1,716,546	277.6	3.74E-2	3.35E-2	2,985
73.9	3.71E-4	3.33E-4	300,640	72.6	8.41E-5	7.54E-5	1,325,798	278.7	5.55E-2	4.97E-2	2,010
93.6	3.72E-3	3.34E-3	29,978	92.1	5.09E-5	4.56E-5	2,192,986	279.7	4.91E-2	4.40E-2	2,273
116.2	4.56E-2	4.09E-2	2,446	114.5	6.65E-5	5.96E-5	1,676,868	280.8	7.95E-3	7.12E-3	14,040
135.8	3.65E-1	3.28E-1	305	133.8	3.85E-3	3.45E-3	28,946	DI rinse			
159.3	3.32E+0	2.98	34	141.9	3.72E-4	3.34E-4	299,567	281.9	2.77E-3	2.48E-3	40,332
171.6	1.07E+1	9.63	10	154.2	4.13E-5	3.70E-5	2,702,566	283.0	2.04E-3	1.83E-3	54,722
175.1	1.42E+1	12.73	7.9	159.9	7.80E-5	7.00E-5	1,429,522	284.0	1.44E-3	1.29E-3	77,221
200.4	4.47E+1	40.07	2.5	179.2	1.90E-4	1.70E-4	587,351	285.0	1.15E-3	1.03E-3	97,250
210.2	6.34E+1	56.8	1.8	191.9	8.02E-5	7.19E-5	1,390,128				
219.6	7.89E+1	70.7	1.41	201.0	8.63E-5	7.73E-5	1,293,150				
230.4	9.14E+1	82.0	1.22	211.7	9.25E-5	8.30E-5	1,205,396				
241.5	9.98E+1	89.5	1.12	222.6	1.28E-4	1.15E-4	870,556				
252.1	1.05E+2	94.3	1.06	232.9	2.17E-4	1.95E-4	513,854				
262.9	1.12E+2	100	1.00	243.6	4.30E-4	3.85E-4	259,499				
272.1	1.17E+2	105	0.95	252.6	1.25E-3	1.12E-3	89,109				
282.9	1.20E+2	107	0.93	263.2	4.11E-3	3.68E-3	27,169				
294.0	1.19E+2	107	0.93	274.2	1.33E-2	1.19E-2	8,382				

BV = bed volume; DF = decontamination factor; FD = feed displacement; C_0 = 112 µCi ^{137}Cs/ mL

Table B.4. Elution and Water Rinse Results Following AP-105DF Processing

Elution			Water Rinse		
BV	µCi ^{137}Cs/ mL	C/C$_0$	BV	µCi ^{137}Cs/ mL	C/C$_0$
1.42	2.84E+0	2.54E-2	17.42	2.43E+0	2.18E-2
2.87	2.65E+0	2.37E-2	18.84	9.56E-1	8.57E-3
4.40	3.55E+0	3.18E-2	20.23	5.85E-1	5.25E-3
5.89	1.03E+1	9.21E-2	21.73	4.28E-1	3.84E-3
7.35	1.12E+1	1.01E-1			
8.77	1.33E+1	1.20E-1			
10.21	2.83E+3	2.54E+1			
11.64	1.92E+4	1.72E+2			
13.08	2.56E+3	2.29E+1			
14.53	5.84E+1	5.24E-1			
15.94	1.29E+1	1.16E-1			

BV = bed volume; C$_0$ = 112 µCi ^{137}Cs/ mL

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