

PNNL-30142, Rev 0 RPT-DFTP-019, Rev 0

Small to Full Height Scale Comparisons of Cesium Ion Exchange Performance with Crystalline Silicotitanate

September 2020

AM Westesen SK Fiskum TT Trang-Le AM Carney RA Peterson



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

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Summary

The U.S. Department of Energy's (DOE) Hanford Site houses 56 million gallons of radioactive waste generated from plutonium production from 1944 to 1988.¹ The supernatant waste, currently stored in underground tanks, is intended to be vitrified following filtration and ¹³⁷Cs removal at the Hanford Waste Treatment and Immobilization Plant (WTP) Low-Activity Waste (LAW) Vitrification Facility. The WTP Pretreatment Facility will not be operational for several years. The Tank Side Cesium Removal (TSCR) system is a technology demonstration that will remove cesium from tank waste supernate to support directly feeding LAW to the vitrification facility. The ¹³⁷Cs removal is important to meet the WTP LAW contract specification and ultimately for creating a contact-handled waste form. Among other properties, the waste acceptance criteria (WAC) limit for the WTP LAW Facility is <3.18E-5 Ci ¹³⁷Cs per mole Na.²

The TSCR system is skid mounted and employs two key technologies: dead end filtration for solids removal and ion exchange (IX) for cesium removal. Filtration is necessary to protect the functionality of the IX columns. The IX process utilizes sodium form crystalline silicotitanate (CST) IX media produced by UOP Honeywell, LLC (Des Plaines, IL) under the product name IONSIV R9140-B, 18 x 50 mesh, in a lead-lag-polish column configuration. Each column contains a CST bed height of 92 inches and a volume of approximately 157 gallons of CST IX media. The full-scale TSCR operation will run at a residence time of 1.9 bed volumes (BV)/h, which results in a superficial velocity of 7.3 cm/min and a flowrate of ~5 gal/min.

Column testing at small (2.5% of the full bed height), medium (12% of the full bed height), and full-height scales has been previously conducted to evaluate process variables and scale up performance of Cs exchange onto the CST.^{3,4} Cesium load performances from various sieve cuts at the small scale indicated that a 30-mesh sieve cut be tested to determine if it better reflects the 12% and full-height column performances at the small scale. Two process flowrates were tested in the small-column configuration with <30-mesh CST and simulant solutions. These tests were compared to full-height column tests at the same residence times to assess CST particle size effect on column scaling.

Table S.1 summarizes the observed column performance determined for the two flowrates juxtaposed to the previous work with 5.6 M Na simulant at higher scales (used as benchmarks). The WAC breakthroughs between the small and full-height tests at 1.3 BV/h differed by ~59 BVs. The WAC breakthroughs for small, medium, and full-height tests at 1.8 BV/h were consistent at 240 BVs. The 50% Cs breakthroughs were nominally equivalent for all column tests. The common transition zones and onsets of Cs breakthrough at the 1.8 BV/h tests indicated that the Cs mass transfers were equivalent and thus the <30-mesh CST Cs load performance at the small scale successfully modeled that of the full-height system. It is recommended that the <30-mesh CST be used in subsequent 10-mL CST bed tests.

¹ Gerber, M S. Legend and legacy: Fifty years of defense production at the Hanford Site. United States: N. p., 1992. Web. doi:10.2172/10144167.

² From *ICD 30 – Interface Control Document for Direct LAW Feed*, 24590-WTP-ICD-MG-01-030, Rev. 1, 2017, Bechtel National, Inc. (River Protection Project Waste Treatment Plant), Richland, Washington.

³ Fiskum SK, AM Rovira, JR Allred, HA Colburn, MR Smoot, AM Carney, TT Trang-Le, MG Cantaloub, EC Buck, and RA Peterson. 2019a. *Cesium Removal from Tank Waste Simulants Using Crystalline Silicotitanate at 12% and 100% TSCR Bed Heights*. PNNL-28527, Rev. 0; RPT-TCT-001, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

⁴ Fiskum SK, AM Rovira, MG Cantaloub, AM Carney, HA Colburn, RA Peterson, and BD Pierson. 2019b. *Impact of Crystalline Silicotitanate Particle Size on Cesium Removal Efficiency*. PNNL-29237, Rev. 0; RPT-DFTP-017, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Column Test	Flowrate (BV/h)	d_{50} Particle Size $(\mu m)^{(a)}$	WAC Limit Breakthrough (BV)	Maximum Test Cs Breakthrough (% C/C ₀)	Extrapolated 50% Cs Breakthrough (%C/C ₀)
2.5% height, <30 mesh	1.35	542	324	0.5	NA ^(c)
Full height, unsieved ^(b)	1.30	633	277	49.0	960 ^(d)
2.5% height, <30 mesh	1.84	542	239	46.2	1050 ^(d)
12% height, <25 mesh ^(b)	1.83	567	240	47.3	1000 ^(d)
Full height, unsieved ^(b)	1.82	633	240	36.5	1050 ^(d)

Table S.1. Column Performance Summary with CST Lot 2002009604

(a) Cumulative particle undersize fraction, volume basis.

(b) Fiskum SK, AM Rovira, JR Allred, HA Colburn, MR Smoot, AM Carney, TT Trang-Le, MG Cantaloub, EC Buck, and RA Peterson. 2019a. *Cesium Removal from Tank Waste Simulants Using Crystalline Silicotitanate at 12% and 100% TSCR Bed Heights*. PNNL-28527, Rev. 0; RPT-TCT-001, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.
(c) Test terminated after reaching WAC, 50% breakthrough not extrapolated.

(d) Extrapolated values.

Acknowledgments

The authors thank the Analytical Support Operations (ASO) count room staff Mike Cantaloub and Truc Trang-Le for rapid ¹³⁷Cs tracer analysis of the column load samples. We thank Carolyne Burns for particle size analysis of the <30-mesh sieve fraction of crystalline silicotitanate. We thank Susan Asmussen for conducting the technical reviews of the calculation files and test data packages. We also thank Matt Wilburn for technical editing of this report and Bill Dey for the quality reviews of the calculation packages and this report.

Acronyms and Abbreviations

ASO	Analytical Support Operations
BT	breakthrough
BV	bed volume
CST	crystalline silicotitanate
DF	decontamination factor
DI	deionized
FD	feed displacement
GEA	gamma energy analysis
IX	ion exchange
LAW	low-activity waste
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
TSCR	Tank Side Cesium Removal
WAC	waste acceptance criteria
WRPS	Washington River Protection Solutions
WTP	Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

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1.0 Introduction

The U.S. Department of Energy's Hanford Site houses 56 million gallons of radioactive waste generated from plutonium production from 1944 to 1988 (Gerber 1992). The supernatant waste, currently stored in underground tanks, is intended to be vitrified following filtration and ¹³⁷Cs removal at the Hanford Waste Treatment and Immobilization Plant (WTP) Low-Activity Waste (LAW) Vitrification Facility. The WTP Pretreatment Facility will not be operational for several years. The Tank Side Cesium Removal (TSCR) system is a technology demonstration that will remove cesium from tank waste supernate to support directly feeding LAW to the vitrification facility. The removal of ¹³⁷Cs is important to meeting the WTP LAW contract specification and ultimately for creating a contact-handled waste form.

The TSCR system is skid mounted and employs two key technologies: dead end filtration for solids removal and ion exchange (IX) for cesium removal. Filtration is necessary to protect the functionality of the IX columns. The IX process uses sodium form crystalline silicotitanate (CST) IX media produced by UOP Honeywell, LLC (Des Plaines, IL) under the product name IONSIV R9140-B, 18 x 50 mesh, in a lead-lag-polish column configuration. Each column contains a CST bed height of 92 inches and a volume of approximately 157 gallons of CST IX media. The full-scale TSCR operation will run at a residence time of 1.9 bed volumes (BV)/h, which results in a superficial velocity of 7.3 cm/min and a flowrate of ~5 gal/min.

Column testing at small (2.5% of the full bed height), medium (12% of the full bed height), and full-height scales has been previously conducted to evaluate process variables and scale up performance of Cs exchange onto the CST. Both the small- and medium-scale tests used <25-mesh CST (60 wt% of the as-received material); this sieve size cut was selected to mitigate wall effects in the small-diameter columns. The medium-scale test compared favorably to the full-height test, but the small-scale test showed earlier breakthrough (Fiskum et al. 2019a). A second small-scale test was conducted with <35-mesh CST, which displayed delayed Cs breakthrough relative to the full-height test condition (Fiskum et al. 2019b). Scaling calculations indicated that a <30-mesh sieve cut supporting the 2.5%-scale (10-mL CST bed volume) would better reflect full-height column performances.

This report describes the testing of small-scale columns using <30-mesh CST. Two process flowrates were tested in the small-column configuration with the same lot of simulant solution used in previous tests. These results were compared to full-height column test results at the comparable residence times to assess CST particle size effect on column scaling. Key parameters were evaluated to determine success: bed volumes required to reach the waste acceptance criteria (WAC),¹ and the general slope of the breakthrough curve.

¹ The WAC for the WTP LAW Vitrification Facility is <3.18E-5 Ci ¹³⁷Cs per mole Na. For a tank waste containing 156 μ Ci/mL ¹³⁷Cs and 5.6 M Na, up to 0.114% of the influent ¹³⁷Cs concentration may be delivered to the WTP (based on ¹³⁷Cs content in AP-107 tank waste), requiring a Cs decontamination factor of 879.

2.0 Quality Assurance

All research and development (R&D) work at Pacific Northwest National Laboratory (PNNL) is performed in accordance with PNNL's Laboratory-Level Quality Management Program, which is based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications* (ASME 2000), to R&D activities. To ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the PNNL's Washington River Protection Solutions (WRPS) Waste Form Testing Program (WWFTP) QA program were also implemented for this work. The WWFTP QA program implements the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications* (ASME 2008), and NQA-1a-2009, *Addenda to ASME NQA-1-2008* (ASME 2009), and consists of the WWFTP Quality Assurance Plan (QA-WWFTP-001) and associated QA-NSLW-numbered procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work.

The work described in this report was assigned the technology level "Applied Research" and was planned, performed, documented, and reported in accordance with procedure QA-NSLW-1102, *Scientific Investigation for Applied Research*. All staff members contributing to the work received proper technical and QA training prior to performing quality-affecting work.

3.0 Test Conditions

This section describes the CST media, 5.6 M Na simulated waste, and column IX conditions. All testing was conducted in accordance with a test plan, prepared by PNNL and approved by Washington River Protection Solutions (WRPS),¹ and a test instruction.²

3.1 CST Media

WRPS purchased ten 5-gallon buckets (149 kg total) of IONSIVTM R9140-B³, lot number 2002009604, material 8056202-999, from UOP Honeywell LLC (Des Plaines, IL). This CST production lot was screened by the manufacturer to achieve an 18 x 50 mesh size product. The product was requested to be delivered to WRPS in a series of 5-gallon buckets (as opposed to a 50-gallon drum) to aid in material distribution, handling, and sampling at PNNL. The CST was transferred from WRPS to PNNL on September 20, 2018, under chain of custody. Once received, the CST was maintained at PNNL in environmentally controlled spaces. One of the 5-gallon buckets of CST was delivered to the PNNL Radiochemical Processing Laboratory. The handling and splitting of the CST were previously described (Fiskum et al. 2019a).

A 231-g subsample was collected for sieving through a 30-mesh sieve (ASTM E11 specification). The CST sample was first divided into thirds for stepwise sieving. Each sieve was shaken by hand until the mass collection on the catch pan was essentially constant. An average mass fraction of 32% (49.7 g) passed through the 30-mesh sieves.

The <30-mesh CST fraction was pretreated by contacting with 100 mL of 0.1 M NaOH five successive times. The 0.1 M NaOH rinse solution and colloidal fines from the CST were decanted. The rinsed CST was maintained with an overburden of 0.1 M NaOH.

A nominal 10-mL fraction of the CST slurry was removed for particle size analysis. The particle size analysis was conducted using a Malvern Mastersizer 2000 coupled with a HydroG dispersion unit. Measurements were collected pre-sonication, during sonication, and post-sonication. It was observed that applied sonication had a marginal impact on the particle size distribution (see Appendix B).

Duplicate 10-mL portions of the <30-mesh sieve fraction were further collected for physical property testing inclusive of bulk density, bed density, and bed void fraction. The CST samples were rinsed once with deionized (DI) water to remove the bulk of the salt solution and were then dried for approximately 6 days in air at room temperature to evaporate interstitial water. The CST was then dried to constant mass at 100 °C. The dried CST was added incrementally to a known volume and mass of DI water in a 25-mL graduated cylinder. Effervescence was observed upon initial contact with water. The CST was gently mixed by turning and slightly tipping the graduated cylinder, allowing free release of the gas. CST addition was paused to allow effervescence to complete before adding the next increment. After all effervescence ceased, the CST was tapped to final constant volume (V_{sl}). The headspace water was removed, the gross mass was measured, and the net slurry mass (M_{sl}) was calculated. The dry mass of

¹ Fiskum SK. 2019. *DFTP Technology Testing and Support: Small Scale Column Tests with Crystalline Silicotitanate and 5.6 M Sodium Simulant*. TP-DFTP-064, Rev. 0.0. Pacific Northwest National Laboratory, Richland Washington. Not publicly available.

² Rovira AM. 2019. *Small Column Crystalline Silicotitanate (CST) Ion Exchange (IX) Using <30 Mesh Sieve*. TI-DFTP-075. Pacific Northwest National Laboratory, Richland, Washington. Not publicly available. Implemented January 2020.

³ R9140-B is provided in the sodium form by the vendor.

CST (M_{CST}) was subtracted from the net slurry mass; the difference was ascribed to the water content in the slurry volume. This water included water in the CST crystalline interstices. The void fraction (VF) was calculated according to Eq. (3.1).

$$VF = \frac{M_{sl} - M_{CST}}{V_{sl}}$$
(3.1)

Table 3.1 provides the physical properties measured on CST Lot 2002009604 for the various sieve cuts tested (Fiskum et al. 2019a, b and current tests). The mass used for the density calculations was based on dried CST at 100 $^{\circ}$ C. With the exception of the particle size distributions, the physical properties were essentially the same, within experimental uncertainty of a couple of percent. The pre-sonication particle diameters were slightly larger than those of the post-sonication measurement (see Appendix B).

		Current Report				
Parameter	Full Height	12% Height	2.5% Height		2.5% Height	
Sieve cut for testing	Unsieved	<25 mesh	<25 mesh	<35 mesh	<30 mesh Sample/duplicate	
Bulk density, g/mL	1.01	1.02	nm	1.04	1.04/1.02	
CST bed density, g/mL	1.00	1.01	nm	1.01	1.00/0.99	
Settled bed void volume, %	67.6	66.2	nm	65.3	70.3/66.0	
Cumulative particle undersize fractions, microns ^(a)	d_{10} : 394 d_{50} : 633 d_{90} : 955	d_{10} : 405 d_{50} : 567 d_{90} : 795	<i>d</i> ₁₀ : 433 <i>d</i> ₅₀ : 593 <i>d</i> ₉₀ : 816	d_{10} : 351 d_{50} : 479 d_{90} : 651	<i>d</i> ₁₀ : 398 <i>d</i> ₅₀ : 541 <i>d</i> ₉₀ : 738	
Column ID, cm	2.54	1.44	1.50	1.50	1.50	
Cross section <i>d</i> ₅₀ particle #	40.1	25.4	25.3	31.3	27.7	

Table 3.1. Physical Properties of Washed R9140-B CST Lot 2002009604

nm = not measured

Table 3.1 also shows the test column ID and the corresponding theoretical cross section of the postsonicated d_{50} size particles. Optimally, at least 30 beads across the column diameter minimizes wall effects and channeling (Helfferich 1962). Testing at the full-height 18 x 50 mesh CST in the 2.5-cm-diameter column and the small scale with <35-mesh CST in the 1.5-cm-diameter column met this threshold. Testing at the small and medium scales with <25-mesh and <30-mesh CST pushed below the lower limit of this goal.

3.2 5.6 M Na Simulant

PNNL contracted the production of 680 gallons of 5.6 M Na simulant to Noah Technologies, Inc. (San Antonio, TX). The simulant preparation was conducted as defined by Russell et al. (2017), with the exception that the Cs concentration was set to 8 μ g/mL (instead of 13.8 μ g/mL). This Cs concentration approximated the Cs concentration in AP-107 Hanford tank waste (Rovira et al. 2018). The sodium oxalate component was omitted to mitigate solids precipitation. The target component masses and calculated ionic species concentrations are provided in Table 3.2. The reagents used to make the simulant were assayed at 99.2% or better. However, the sheer scale of the production process required very large quantities of salts to be used, and a small metal impurity fraction could result in kilogram quantities of

insoluble metal hydroxides. Thus, Noah Technologies was directed to wait at least 24 h after mixing and then filter the simulant through a 0.45-micron pore size filter. The simulant was prepared in one large lot to support full-height and 12% height testing previously described (Fiskum et al. 2019b). A slight overage was requested to support rework (in case it was required) or follow-on work (as described herein).

		Target			_
	Component	Component Mass	Composition,		Target
	Formula Weight	per kg Solution	g Component/	Anion / Cation	Conc.
Component	(g/mole)	(g)	L Solution	Species	(M)
$Al(NO_3)_3 \bullet 9H_2O$	375.13	49.82	62.27	Al as Al(OH)4 ⁻	0.166
NaOH (50%, w/w)	40.00	132.73	165.91	free OH ⁻	1.41
CsNO ₃	194.91	0.0094	0.0117	Cs^+	6.00E-05
KCl	74.55	7.28	9.10	K^+ and Cl^-	0.122
Na_2SO_4	142.04	7.51	9.39	SO_4^{2-}	0.0661
NaNO ₂	69.00	56.30	70.38	NO_2^-	1.02
NaNO ₃	84.99	87.17	108.97	NO ₃ -	1.78
Na ₃ PO ₄ -12H ₂ O	380.12	13.14	16.42	PO4 ³⁻	0.0432
Na ₂ CO ₃	105.99	46.33	57.91	CO3 ²⁻	0.467
DI water	18.02	598.35	747.94	Na ⁺	5.60

Table 3.2. 5.6 M Sodium Simulant Target Composition

A 20-L aliquot of the simulant was collected and spiked with a ¹³⁷Cs tracer to reach a final ¹³⁷Cs concentration of 5.12E-2 μ Ci/mL. A 10-mL sample collection allowed for a calculated decontamination factor of ~100,000 when measured by gamma energy analysis (GEA). The ¹³⁷Cs tracer was mixed into solution using a recirculating pump for a total of 45 min. A simulant sample was collected after 30 min of mixing time and again after an additional 15 min of mixing to verify that the activity concentration was constant. After mixing, the simulant stood for an additional 4 days; this ensured the tracer equilibrated with the simulant Cs. The total Cs mass in the tracer was insignificant relative to the native Cs in the simulant.

3.3 Ion Exchange Process Testing

Two column tests were conducted concurrently. Each column system was given a color code (orange and blue) to better organize samples and paperwork. The color coding served to minimize errors and enhance recognition in sample management and data recording (minimizing the human factor errors). This section describes the IX column system and 5.6 M Na simulant processing conditions.

3.3.1 Ion Exchange Column System

Each test used an independent IX system. Figure 3.1 and Figure 3.2 provide schematics of the two IX process systems. The 1.3-BV/h flowrate test was color coded orange and tested with a single column (Figure 3.1). The 1.8-BV/h flowrate test was color coded blue and tested in a dual-column (lead/lag) format (see Figure 3.2). Except for the addition of the second column, the two IX assemblies were configured as closely as possible to each other.

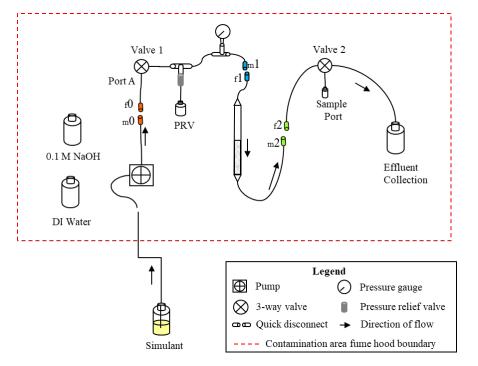


Figure 3.1. Ion Exchange System Schematic 1.3 BV/h (color code orange)

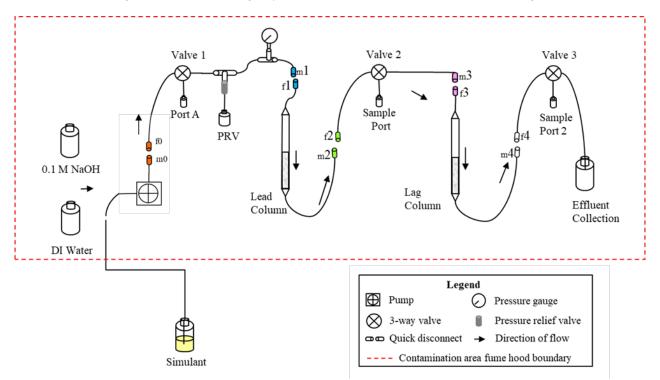


Figure 3.2. Ion Exchange System Schematic 1.8 BV/h (color code blue)

Figure 3.3 and Figure 3.4 show photographs of each system after installation in the fume hood. Fluid flow through the system was controlled with a Fluid Metering Inc. positive displacement pump; flowrate was controlled remotely with the associated stroke rate controller. Fluid was pumped past a Swagelok pressure relief valve with a 10-psi trigger point and an Ashcroft pressure gage. The 1/8-inch outside diameter /

1/16-inch inside diameter polyethylene tubing was purchased from Polyconn (Plymouth, MN). The 1/8inch outside diameter / 1/16-inch inside diameter stainless steel tubing was used in conjunction with the valve manifold and as dip tube in the feed reservoir. Valved quick disconnects were purchased from Cole Parmer (Vernon Hills, IL). Use of the quick disconnects enabled easy flow re-routing, as needed. The quick disconnects were color-coded to ease correct installation.

Chromaflex[®] column assemblies were custom ordered from Kimble Chase (www.kimble-chase.com). Each column assembly included the column plus the standard top and bottom end fittings. Each column was made of borosilicate glass; the straight portion of the column was 9 cm tall with an inside diameter of 1.5 cm (corresponding to a CST volume of 1.77 mL/cm). The columns flared at each end to support the off-the-shelf column fittings and tubing connectors that were composed of polytetrafluoroethylene. The CST was supported by an in-house constructed support consisting of a 200-mesh stainless steel screen tack welded onto a stainless-steel ring. A rubber O-ring was placed on the outside of the stainless-steel support and the fitting was snug fitted into place in the column; see Fiskum et al. (2019b) for more detail. The flared cavity at the bottom of each column was filled to the extent possible with 4-mm-diameter glass beads to minimize the mixing volume below the CST bed (achieved 50% volume reduction, from ~6 mL to ~3 mL). An adhesive centimeter scale with 1-mm divisions (Oregon Rule Co., Oregon City, OR) was affixed to the column with the 0-point coincident with the top of the support screen.

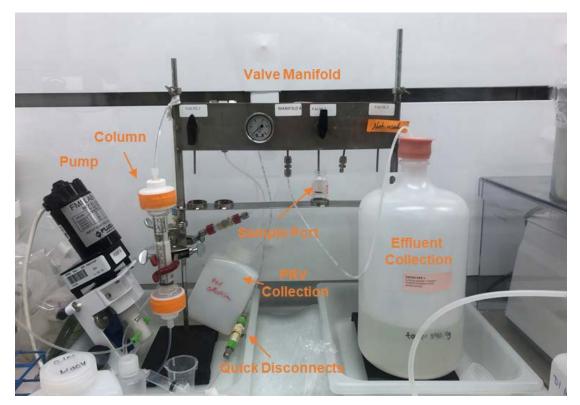


Figure 3.3. Photograph of Ion Exchange System, 1.3 BV/h (color code orange)

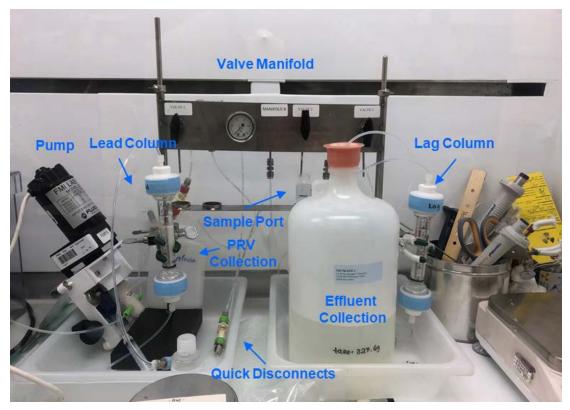


Figure 3.4. Photograph of Ion Exchange System, 1.8 BV/h (color code blue)

Three Swagelok valves were installed in the valve manifold; only the first two valves were used to support the single-column orange test. The third valve was used to support sampling from the lag column on the blue system. Valve 1 was used to isolate the lead column from the system (when in the closed position) and purge the tubing from the inlet to valve 1 (when placed in the sampling position). For the single-column orange system, samples from column loading, feed displacement (FD), and the water rinse were collected at valve 2. The dual-column blue system collected samples from column loading from valves 2 and 3 and collected FD and water rinse samples from valve 3. The gross simulant effluent was collected at the effluent line into a series of 4-L polyethylene bottles. During sample collection, the effluent bottles were capped and weighed to assess the total mass (and hence volume and flowrate) collected between sampling periods.

The systems were filled with water and slightly pressurized to confirm system leak tightness. The pressure relief valve was confirmed to trigger at the manufacturer set point (10 psig). Water was removed from the columns and replaced with 0.1 M NaOH. A 10.0-mL aliquot of settled CST was measured using a 10-mL graduated cylinder and quantitatively transferred to each column. The CST was allowed to settle through the 0.1 M NaOH solution in the column, thus mitigating gas bubble entrainment. The column was tapped with a rubber bung until the CST height no longer changed.

The CST BV corresponded to the settled CST volume as measured in the graduated cylinder prior to transferring it into the IX columns. The reference CST BV was 10.0 mL. The settled CST bed heights in the columns were ~5.6 cm as measured from the adhesive centimeter scale. This CST height corresponded to 2.5% of the full-height column (234 cm). The entire fluid-filled volume of the orange column assembly was ~19.5 mL, inclusive of fluid in the CST beds. The entire fluid filled volume of the blue column assembly was ~36 mL.

3.3.2 Processing Conditions

Once the CST-loaded columns were installed in the manifold system, a flow of 0.1 M NaOH was used to verify the system integrity (leak tightness) and calibrate the pump. The 5.6 M Na simulant was processed through the IX media beds from the feed carboy located below the fume hood. Two different simulant flowrates were tested; the process volumes and flowrates for each test are summarized in Table 3.3 and Table 3.4. During the loading phase, nominal 10-mL samples were collected from each column at the sample collection port. Samples were collected after the first ~11 BVs were processed and again at nominal 35- to 45-BV (~24-h) increments. Flowrate checks and pump stroke rate controller adjustments were made more frequently at the beginning of the process run and as needed throughout run.

After processing 232 BVs, a backpressure of 6 psi was observed in the orange column system. Pressure relief could not be obtained from cycling the valves between flow and sample position. The system was shut down for 20 h until further evaluations could be made. After the 20-h shutdown, the pressure in the system had subsided. It was determined the plugging could be attributed to foam filter inserts manufactured at the top and bottom of the column. The top inset was removed, and processing continued without further evidence of backpressure buildup. After 172 more BVs were processed, the effluent exceeded the WAC and the test was terminated. The system was flushed with 10 BVs of 0.1 M NaOH and 10 BVs of DI water. The total processing time for the orange column test was 14 days.

After processing ~590 BVs of feed through the blue system, a backpressure of 3 psi was observed. The flow was stopped for 3 h, allowing the top foam inserts from both the lead and lag columns to be removed. Removal of the inserts did not remedy the pressure. After isolating the effluent line from the rest of the system, a plug in the line (potentially due to salt buildup) was determined to be the cause of the backpressure. The lower ~4 inches of the line were removed, the pressure subsided, and processing continued.

After simulant loading in the blue system was completed, ~6 BVs of 0.1 M NaOH FD was passed downflow through the system to rinse residual feed out of the column and process lines through valve 3. The 6 BVs was equivalent to ~2 times the fluid-filled apparatus volume through valve 3. The system was then rinsed with ~12 BVs of DI water and collected through valve 3. The blue column test lasted 24 days.

Both the blue system and the orange system were connected to an argon gas source plugging into quick disconnect 0. A slight pressure of argon was applied to purge the systems of drainable fluid; purging continued until no more fluid was collected. The collected volume did include the interstitial fluid space between the CST beads, but did not include fluid in the CST pore space.

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0.17

0.24

0.25

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Step	Feed Material	Volume (BV)	Flowrate (BV/h)	Superficial Velocity (cm/min)
Shakedown testing	0.1 M NaOH	As needed	Variable	
Feed processing	5.6 M Na simulant	380	1.34	0.126
Feed displacement	0.1 M NaOH	10	(a)	
Water rinse	DI water	10	(a)	
Fluid displacement	Compressed gas	NA	(a)	
BV = bed volume, 10 mL. (a) The test was terminated	ed after Cs breakthrough reache	d the WAC.		

Table 3.3. Orange System Flow Description Summary, 1.3 BV/h

-	Fable 3.4. Blue System Flo	w Description Sur	nmary, 1.8 BV/h	
				Superficial
		Volume	Flowrate	Velocity
Step	Feed Material	(BV)	(BV/h)	(cm/min)

0.1 M NaOH

5.6 M Na simulant

0.1 M NaOH

DI water

Compressed gas

As needed

1013

5.2

11.8

NA

Variable

1.84

2.6

2.8

NA

The blue simulant process cycle emulated the flows anticipated during small-scale testing in the hot cell with actual tank waste as well as the TSCR facility in terms of BV/h (i.e., residence time), FD, and water rinse. Both the blue test and the orange test mimicked the residence time from full-height column testing reported by Fiskum et al. (2019a) in order to assess the efficacy of relating small-column testing, as required in hot cells on actual wank waste, to the full-height column testing.

3.4 Sample Gamma Energy Analysis

Shakedown testing

Feed displacement

Fluid displacement

BV = bed volume, 10 mL

Feed processing

Water rinse

Two 10-mL samples of the feed solution were collected and analyzed by GEA to determine the baseline feed ¹³⁷Cs concentration. Blue and orange column systems collected 10-mL loading samples off each column daily. Feed displacement, water rinse, and fluid flush samples associated with the blue column processing were individually bulk collected. The collected 10-mL samples were analyzed directly to determine the ¹³⁷Cs concentration using GEA. Cesium loading breakthrough curves were generated based on the feed ¹³⁷Cs concentration (C_0) and the effluent Cs concentration (C) in terms of % C/C₀.

Samples were submitted to the Analytical Support Operations (ASO) and were analyzed directly (no preparation) by GEA. Each sample was counted long enough to provide a nominal 1% count uncertainty or 24 h, whichever came sooner. All analyses were conducted by the ASO according to a standard operating procedure, the ASO QA Plan, and the Analytical Service Request.

3.5 CST Digestion and Analysis

The digestion protocol described by Campbell et al. (2019) was used for the digestion of a CST aliquot collected from the blue lead column. Digestion of the CST from this column allowed for analysis of trace contaminants in the 5.6 M Na simulant, such as Ca, Sr, Ba, and Pb, that have previously been shown to have some affinity for CST and contribute to total measured capacity of the IX media (Rovira et al. 2018, 2019; Fiskum et al. 2019c; Walker Jr. et al. 1998).

Weighed aliquots (targeting 0.5 g) of CST from the blue lead column (in duplicate) were transferred to 40-mL glass vials containing a stir bar. The aliquots of spent CST were not corrected to dry mass using an F-factor. Digestion of spent CST was accomplished by transferring 25 mL of 5 M HNO₃ to the glass vial and placing the vial on a stir plate/hot plate with the vial loosely capped to minimize evaporation. The stir speed was adjusted to medium with the heat set to "high." The HNO₃ was brought just to a boil and removed from heat, and 2.5 mL of 30% H₂O₂ was added. The hot plate temperature was turned off and the digestate solution was placed back on the hot plate/stir plate with vigorous stirring. Vigorous bubbling of the HNO₃/H₂O₂ solution was observed for ~10 min after addition of H₂O₂. The solution turned a deep red color and was removed from stirring and allowed to cool. After cooling, the post-digestion solution mass was determined. A process blank of pre-treated <30-mesh CST underwent the same digestion protocol in parallel with the two sample digestions to assess contamination from processing conditions.

The digested solution was submitted to the ASO for analysis by inductively coupled plasma optical emission spectrometry. The concentration of analyte recovered (mg/g CST) in the digestion solution was calculated according to Eq. (3.2).

$$\frac{(C_D \times D) \times M_d}{d \times M_{CST}} = C_{CSTa}$$
(3.2)

where:

 C_{CSTa} = concentration of analyte *a* per gram of dry CST

D = ratio of diluted digestate (g) per gram of digestate solution (dilution factor)

- C_D = concentration of analyte in diluted digestate solution
- M_d = mass of digestate solution
- d = density of the diluted digestate solution
- M_{CST} = free-flowing mass of CST digested

4.0 Column Processing Results

The Cs load behavior was evaluated at two different flowrates and superficial velocities in the small-column configuration with the 5.6 M Na simulant: 1.35 BV/h and 0.126 cm/min for the orange (single-column) test and 1.84 BV/h and 0.168 cm/min for the blue (dual-column) test. This section discusses the Cs load, FD, water rinse, and final solution flush from the systems. Direct comparisons to the full-height column are also provided. Raw data are provided in Appendix A.

4.1 Cs Loading, Feed Displacement, and Water Rinse

The Cs load profiles for blue and orange column testing are shown in Figure 4.1 through Figure 4.3. The Cs breakthrough is plotted on both a linear-linear and probability-log plot for blue, where ¹³⁷Cs concentration (C) is normalized to the feed concentration (C₀). The C₀ value for ¹³⁷Cs was 5.10E-2 μ Ci/mL and the total Cs was 8.0 μ g/mL. Under normal load processing conditions, the probability-log plot provides a predictable straight-line Cs breakthrough curve and provides greater fidelity of load characteristics at low and high % C/C₀ values (Buckingham 1967). In addition to the 50% C/C₀ indication line, the WAC limit at 0.114% C/C₀ is also apparent (dotted red line).¹

In Figure 4.1 for the blue system, the Cs breakthrough appears to start at ~300 BVs. Figure 4.2 shows the same Cs load data provided in Figure 4.1 on the probability-log plot. Clearly, the Cs breakthrough started much earlier, at ~100 BVs. The 50% Cs breakthrough was nearly reached for the 1.8-BV/h test; the final Cs concentration occurred after processing 1009 BVs (45% C/C₀). The column data was evaluated to estimate the BVs to 50% breakthrough. The breakthrough curves were estimated by the error function (erf) (Hougen and Marshall 1947; Klinkenberg 1994):

$$\frac{C}{C_0} = \frac{1}{2} \left(1 + \operatorname{erf}(\sqrt{k_1 t} - \sqrt{k_2 z}) \right)$$
(4.1)

where k_1 and k_2 are parameters dependent on column conditions and IX media performance, *t* is time (or BVs processed), and *z* is the length of the column. Using this model, a fit was generated to the experimental data. The 50% breakthrough was estimated by multiplication of k_1 and k_2 . Figure 4.2 shows the experimental data points with the curve fitted data. The 50% Cs breakthrough is estimated to occur at 1048 BVs; however, this cannot be obtained before Cs breakthrough above the WAC from the lag column occurs. The WAC limit Cs breakthrough occurred at 239 BVs for the lead column and 812 BVs for the lag.

Figure 4.3 shows the breakthrough data for the orange system. The amount of feed that can be processed before the effluent reaches the WAC limit is directly affected by the contact time the feed has with the CST bed. Thus, the effect of the lower flowrate for the orange system on BVs processed to the WAC limit is significantly higher than that of the blue system. The WAC limit Cs breakthrough occurred at 323 BVs, almost 100 BVs later than the blue lead column. The 50% Cs breakthrough was not achieved for the 1.3-BV/h test because the test was terminated after the WAC was reached. The extra contact time during the 20-h stop flow condition appears in Figure 4.3 within the black circled area. Following the stop flow condition, a jump in Cs concentration is seen in the Cs effluent concentration. This is likely associated with plumbing the lines around the column during filter removal and potentially contaminating the effluent side of the tubing with raw feed.

¹ The WAC limit was derived from the allowed curies of ¹³⁷Cs per mole of Na in the effluent to support contact handling of the final vitrified waste form—3.18E-5 Ci ¹³⁷Cs/mole Na. At 5.6 M Na and 156 μ Ci ¹³⁷Cs/mL (from AP-107, Rovira et al. [2018]) in the feed, the WAC limit is 0.114% C/C₀.

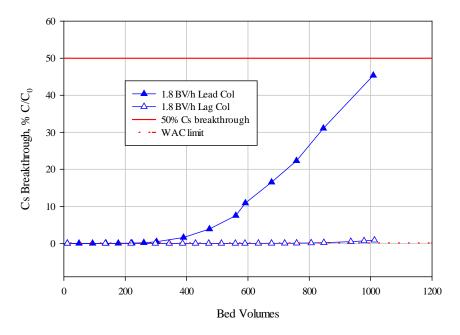


Figure 4.1. 5.6 M Na Simulant at 1.8 BV/h, Blue System, Linear-Linear Plot

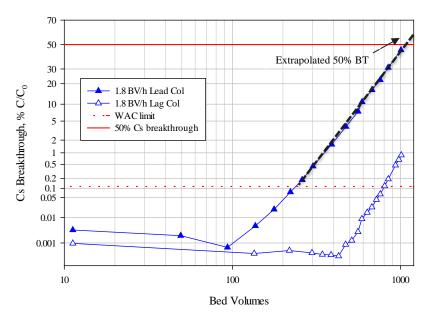


Figure 4.2. 5.6 M Na Simulant at 1.8 BV/h, Blue System, Probability-Log Plot

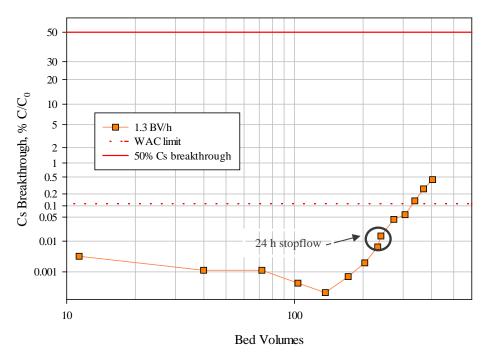


Figure 4.3. 5.6 M Na Simulant at 1.3 BV/h, Probability-Log Plot

The bulk FD and bulk water rinse ¹³⁷Cs (Cs) concentrations from the blue system declined (see Appendix A). The final flushed fluid ¹³⁷Cs (Cs) concentration from the column system was slightly higher than that of the water rinse sample; this increase may be associated with residual contamination in valve 3. Orange system FD, water rinse, and final flushed fluid were not counted for GEA.

4.2 Cs Load Performance Comparisons

The small-column Cs breakthrough data was compared (Figure 4.4 and Figure 4.5) with full-height lead column testing with 5.6 M Na simulant previously reported (Fiskum et al. 2019a). The 1.8-BV/h flowrate is also compared to 5.6 M Na simulant 12% height column testing. All significant parameters were held constant between the scaled tests: CST production lot (Lot 2002009604), simulant production lot and associated chemical impurities, and the residence times in the CST bed (1.3 and 1.8 BV/h). The full-height column replicated the anticipated TSCR column height (234 cm). The 12% height column was 27 cm tall. At 5.8 cm tall, the CST beds used to process small-scale tests were only 2.5% of the full-height TSCR column.

The tall column processing at 1.3 BV/h reached the WAC ~50 BVs earlier than the small column at the same flowrate, 280 BVs vs. 330 BVs. Stop flow conditions have a slightly positive effect on Cs exchange into the CST and could be attributed to the later WAC breakthrough on the small-column system. In contrast, the lead column 1.8-BV/h processing scales crossed the WAC consistently at 240 BVs.

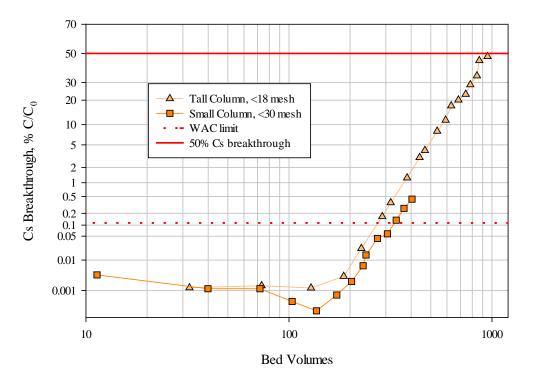


Figure 4.4. Cs Load Profile Comparisons, 5.6 M Na Simulant, 1.3 BV/h

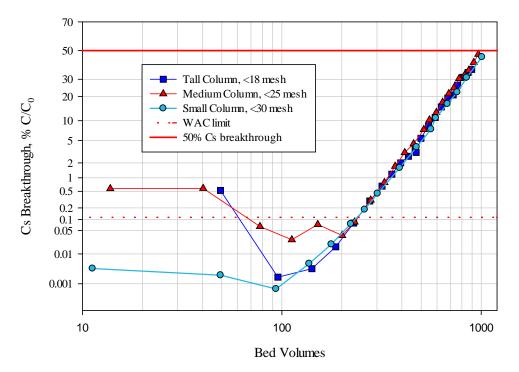


Figure 4.5. Cs Load Profile Comparisons, 5.6 M Na Simulant, 1.8 BV/h

As the size of the column is decreased from full height to 2.5% height, the CST particle size needs to be adjusted to balance the system performance. To maintain constant residence time, the superficial velocity is decreased, which results in a lower film mass transfer coefficient. For CST, the dominant resistance is the diffusion resistance inside the bead; however, film diffusion contributes to the overall mass transfer.

As such, the CST particle size adjustment was essential in scaling the column dynamics down from full scale (2.54-cm-diameter column) to medium (1.44-cm-diameter column) and small (1.5-cm-diameter column) scales. The mean (d_{50}) CST particle size needed to be reduced from 633 microns to 567 (<25 mesh) and 542 microns (<30 mesh), respectively, to achieve appropriately scaled results.

Small and tall lag column breakthrough curves are shown in Figure 4.6. A slight lengthening of the transition zone in the small-column system relative to the tall column may be evident. The tall lag column reached the WAC slightly earlier than the small lag column (770 BVs vs. 800 BVs). However, the onset of Cs breakthrough was slightly earlier at 513 BVs for small system compared with 540 BVs for tall system (at the detection limit driven by the tall column results). Overall, the lag column performance reasonably replicated the full-height lag column performance. It is inferred that performance of a polish column would be similarly replicated.

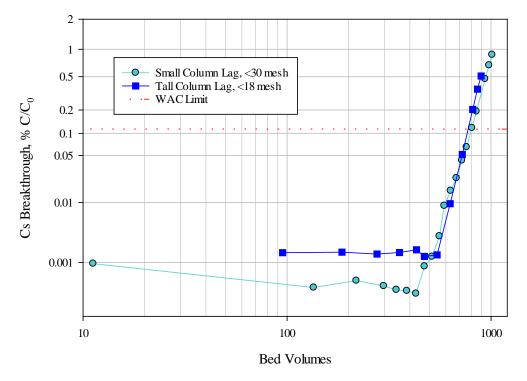


Figure 4.6. Cs Load Profile Lag Column Comparisons, 5.6 M Na Simulant, 1.8 BV/h

4.3 Digested CST Characterization

Analytical results for the digestion of CST used in the blue lead column are shown in Table 4.1. The reported analytical uncertainty is $\pm 15\%$; therefore, any analyte exceeding 15% of the native CST concentration was considered to have had some concentration effect.

				Process	
		Loaded CST		Blank	
	Loaded CST	(mmole/g	Process Blank	(mmole/g	Concentration
Analyte	(mg/g CST)	CST)	(mg/g CST)	CST)	Factor
Pb	0.77	3.71E-03	0.002	1.12E-05	331
K ^(a)	10.5	2.68E-01	[0.51]	1.30E-02	21
Fe	0.79	1.42E-02	0.11	2.05E-03	6.9
Ba	0.08	5.83E-04	0.02	1.64E-04	3.5
Sr	0.04	4.97E-04	0.01	1.46E-04	3.4
Al ^(a)	0.79	2.93E-02	0.30	1.12E-02	2.6
Ca	3.04	7.58E-02	2.38	5.95E-02	1.3
Si ^(b)	52.8	1.88E+00	44.8	1.59E+00	1.2
Mg	0.27	1.09E-02	0.23	9.45E-03	1.2
Cu	1.60	2.52E-02	1.44	2.27E-02	1.1
Ti ^(b)	151.5	3.16E+00	139.4	2.91E+00	1.1
Zr ^(b)	96.7	1.06E+00	92.5	1.01E+00	1.0
Na ^(a,b)	77	3.35E+00	85.3	3.71E+00	0.90
Cs ^(a,c)	7.63	5.74E-02	nm	nm	

Table 4.1. Chemical Composition of CST Digestate Post-processing from Blue Lead Column

(a) These analytes were explicitly added to the simulant.

(b) These analytes are intrinsic to CST.

(c) This value was calculated from the load curve.

nm = not measured, assumed 0.

Bracketed value indicates the associated sample result were less than the estimated quantitation limit but greater than the method detection limit. Analytical uncertainty for this analyte is $> \pm 15\%$.

Several analytes concentrated on the lead column, none of which were intentionally added to the feed solution but were assumed to exist as trace impurities in one or more feed reagents. Pb concentrated 331x higher than the uncontacted CST, and slightly elevated levels of Sr, Ba, Ca, and Mg were measured; all were likely associated with exchange onto CST. This is consistent with results previously reported (Campbell et al. 2019). K was found about 20x higher than uncontacted CST; CST has exchange capacity for K but is much less selective than for Cs, Pb, Ba, Sr, and Ca. Increased Al and Si may be associated with precipitation of alumino-silicates on the CST bed (such as cancrinite) (Taylor and Mattis 2001; Fiskum et al. 2019a). Additionally, a small amount of Fe was retained by the CST. The mechanism for Fe retention may be the CST bed itself filtering out iron oxyhydroxides (e.g., FeOOH or Fe(OH)₃) rather than an IX. The sum of exchanged analytes (Ba, Cs, Ca, K, Mg, Pb, and Sr) of 0.34 mmoles/g CST agreed well with the reduction in Na of 0.36 mmoles/g CST.

Compositional integrity of the CST following processing can be determined using concentrations of the main CST components. Ti and Zr concentrations in the blank and the lead column samples were equivalent within analytical error. This indicated that no major chemical destruction of the CST occurred after processing 1000 BVs of corrosive simulant over 578 hours.

5.0 Conclusions

Cesium IX column testing with CST Lot 2002009604 was conducted to assess Cs exchange performance with 5.6 M Na simulated tank waste at the small (10-mL) column scale at two different flowrates. This testing was conducted to determine the CST sieve cut needed for Cs exchange performance scale-down from full-height to small-scale column testing applications, as required in hot cells on actual tank waste.

The column tests evaluated two flowrates (1.35 BV/h and 1.84 BV/h; 0.126 cm/min and 0.168 cm/min, respectively). A 5.6 M Na simulant, traced with ¹³⁷Cs, was passed through each system. The Cs load profile, WAC limit breakthrough, and 50% Cs concentration breakthrough were determined. The following were observed.

- The mean CST d₅₀ particle size needed to be reduced from 633 microns (18 x 50 mesh) at full scale to 542 microns (<30 mesh) to achieve appropriately scaled results at the small scale (10-mL CST bed).
- 2. The number of BVs processed to reach the WAC limit was ~50 BVs less for tall column testing than small column at 1.3 BV/h. The WAC limit for 1.8 BV/h matched those of the medium- and tall-scale tests perfectly at 240 BVs. Extrapolation beyond the small 1.84 BV/h flowrate system lead column breakthrough indicated that a 50% breakthrough of 1050 BVs would have been obtained with continuous loading.
- 3. The amount of feed that can be processed before the effluent reaches the WAC limit is directly affected by the contact time the feed has with the CST bed. The 1.3-BV/h flowrate processed nearly 100 more BVs when reaching the WAC limit compared to the 1.8-BV/h flowrate.
- 4. Digestion of the 1.84 BV/h flowrate lead column CST for the purpose of quantifying trace analytes retained by the CST indicated that various fractions of Ba, Ca, K, Mg, Pb, and Sr (in addition to Cs) partitioned to the CST during processing. All but K were present as impurities in the simulant.

Successful scale down at the small column height with 5.6 M Na simulant was achieved using a minus 30-mesh sieve cut. Actual waste testing is recommended to be done with a minus 30-mesh sieve cut in small scale columns to best predict Cs breakthrough behavior at the full scale. Previous actual waste tests with a larger sieve cut may be slightly underrepresenting full-height performance in reaching the WAC limit.

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Appendix A – Column Load Data

The raw Cs breakthrough data for processing 5.6 M Na simulant at 1.35 bed volumes (BV)/h (orange column) and 1.84 BV/h (blue columns) are provided in Table A.1 and Table A.2, respectively. The blue column feed displacement, water rinse, and final fluid expulsion raw data are also provided in Table A.2. The raw data include the processed BVs and corresponding ¹³⁷Cs concentrations in the collected samples, % C/C₀, and the decontamination factors (DFs).

	0	(lead only)	
	¹³⁷ Cs		
BV	(µCi/ mL)	% C/C ₀	DF
11.3	1.71E-6	3.35E-3	2.99E+4
39.9	5.80E-7	1.14E-3	8.79E+4
71.9	<2.04E-7	<4.01E-4	>2.49E+5
103.6	9.13E-8	1.79E-4	5.58E+5
136.6	<3.48E-7	<6.83E-4	>1.46E+5
172.0	1.03E-6	2.03E-3	4.93E+4
203.5	3.37E-6	6.62E-3	1.51E+4
231.9	7.29E-6	1.43E-2	6.99E+3
239.5	2.21E-5	4.33E-2	2.31E+3
273.0	2.96E-5	5.82E-2	1.72E+3
305.6	6.82E-5	1.34E-1	7.47E+2
337.7	1.35E-4	2.64E-1	3.78E+2
368.7	2.21E-4	4.34E-1	2.30E+2
403.8	4.11E-4	8.07E-1	1.24E+2
BV = bed volDF = deconta	lume, 10 mL amination factor		

Table A.1. Cs Breakthrough Results with 1.35 BV/h, <30 mesh CST

 $C_0 = 5.12E-2 \ \mu Ci^{137}Cs/mL$, 6.00E-5 M Cs

	Blue	Lead			Blue I	Lag	
	¹³⁷ Cs				¹³⁷ Cs		
BV	$(\mu Ci/mL)$	% C/C ₀	DF	BV	(µCi/ mL)	% C/C ₀	DF
11.2	1.72E-6	3.36E-3	2.98E+4	11.2	4.90E-7	9.57E-4	1.04E+
49.2	1.02E-6	1.99E-3	5.02E+4	135.0	1.81E-7	3.53E-4	2.83E+
93.5	3.32E-7	6.48E-4	1.54E+5	218.5	2.43E-7	4.74E-4	2.11E+
137.1	2.48E-6	4.85E-3	2.06E+4	297.9	1.93E-7	3.77E-4	2.65E+
177.3	1.01E-5	1.98E-2	5.06E+3	343.4	1.64E-7	3.21E-4	3.12E+
221.7	3.89E-5	7.60E-2	1.32E+3	386.7	1.57E-7	3.07E-4	3.25E+
260.5	9.30E-5	1.82E-1	5.50E+2	429.0	1.39E-7	2.72E-4	3.68E+
302.1	2.27E-4	4.44E-1	2.25E+2	472.2	4.40E-7	8.59E-4	1.16E+
389.9	8.17E-4	1.60E+0	6.26E+1	513.3	6.49E-7	1.27E-3	7.88E+
474.4	1.99E-3	3.88E+0	2.57E+1	558.9	1.46E-6	2.85E-3	3.51E+
560.3	3.84E-3	7.51E+0	1.33E+1	590.1	4.54E-6	8.88E-3	1.13E+
591.4	5.57E-3	1.09E+1	9.19E+0	634.2	7.79E-6	1.52E-2	6.57E+
677.1	8.45E-3	1.65E+1	6.06E+0	676.8	1.21E-5	2.36E-2	4.24E+
758.2	1.14E-2	2.23E+1	4.48E+0	719.8	2.18E-5	4.25E-2	2.35E+
845.9	1.59E-2	3.11E+1	3.22E+0	758.9	3.33E-5	6.52E-2	1.53E+
1008.7	2.32E-2	4.54E+1	2.20E+0	806.1	6.03E-5	1.18E-1	8.49E+
				847.7	9.81E-5	1.92E-1	5.22E+
				935.4	2.42E-4	4.72E-1	2.12E+
				978.6	3.45E-4	6.73E-1	1.48E+
				1012.5	4.49E-4	8.76E-1	1.14E+
					Feed Displ	acement	
				1017.7	4.25E-4	8.30E-1	1.20E+
				Water Rinse			
				1029.5	1.87E-5	3.66E-2	2.73E+
					Final Argo	on Flush	
				1033.0	3.40E-5	6.64E-2	1.50E+

Table A.2. Cs Breakthrough, Feed Displacement,	Water Rinse, and Final Flush, Results with 1.84 BV/h,
<30 mesh CST	

DF = decontamination factor $C_0 = 5.12E-2 \ \mu Ci^{-137}Cs/mL$, 6.00E-5 M Cs