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August 2019

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
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Executive Summary

Washington River Protection Solutions (WRPS) is working to support initial production of immobilized low-activity waste by feeding Hanford tank supernate from tank farms to the Hanford Waste Treatment and Immobilization Plant (WTP) Low-Activity Waste (LAW) facility. This goal incorporates the design of a Tank-Side Cesium Removal (TSCR) system, which in effect filters tank waste supernate and processes it through a cesium ion exchange medium to remove ^{137}Cs. The ^{137}Cs-depleted product is sent to the WTP for vitrification. Rovira et al. (2018)[1] reported the successful Cs removal from Hanford tank 241-AP-107 waste (hereafter called AP-107) using crystalline silicotitanate (CST) ion exchange media manufactured by Honeywell UOP, LLC (product IONSIV™ R9140-B, Batch 2081000057)[2] in a lead-lag column system. Since that testing, WRPS has changed the column design to a three-column system. WRPS requested a repeated study with AP-107 tank waste using a different batch of IONSIV™ R9140-B, Lot 2002009604, in a three-column format.

A small-scale test platform was constructed to demonstrate solids filtration, Cs removal, and LAW vitrification and installed at Pacific Northwest National Laboratory. This report describes the small-scale ion exchange testing system component of the test platform and the processing of approximately 8.55 L of filtered AP-107 supernate using CST, Lot 2002009604, that passed through a 25-mesh filter. This report also describes the Cs ion exchange batch contact testing to determine the Cs distribution coefficient and the maximum Cs loading capacity in the AP-107 tank waste matrix.

Batch contact testing helps to evaluate CST performance on tank waste supernate and is often used prior to processing tank waste through ion exchange columns to assess some performance metrics (e.g., 50% Cs breakthrough). Batch contact tests were performed with the filtered AP-107 tank waste at four Cs concentrations at a phase ratio of 200 (liquid volume to exchanger mass). The distribution coefficient (K_d) at the equilibrium condition of 9.2 µg Cs/mL (AP-107 feed condition) was determined to be 806 mL AP-107/g CST. With a CST bed density of 1.01 g/mL (<25 mesh CST), this K_d corresponded to a predicted 50% Cs breakthrough of 814 bed volumes (BVs). The Cs load capacity at the equilibrium feed condition was determined to be 8.3 mg Cs/g dry CST.

The three-column format testing was prototypic to the intended TSCR operations, albeit on a small scale with 10-mL CST beds. Flowrate was adjusted to match the CST contact time expected for the full-scale operation, i.e., matched bed volumes per hour (BV/h) flow rate. The feed was processed downflow through the lead column, then through the middle column, and then through the polish column. Loading continued at an average of 1.88 BV/h (1.83 to 2.04 BV/h range) until the entire available AP-107 feed was processed. The Cs-decontaminated product will be provided for vitrification testing.

The lead column only reached 45% Cs breakthrough after processing 855 BVs of feed. The 50% Cs breakthrough was extrapolated to occur at ~900 BVs. This extrapolated 50% Cs breakthrough value differed from the batch contact estimate (814 BVs) by 11%. Given the extrapolation from column processing and the overall measurement uncertainties, the agreement within 11% was considered reasonable.

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[1] Rovira AM, SK Fiskum, HA Colburn, JR Allred, MR Smoot, and RA Peterson. 2018. *Cesium Ion Exchange Testing Using Crystalline Silicotitanate with Hanford Tank Waste 241-AP-107*. PNNL-27706. Pacific Northwest National Laboratory, Richland, Washington.

[2] The term “Batch” was provided by UOP in paperwork accompanying the CST provided to PNNL February 2018; this term was used on earlier test reports. The term “Batch” and “Lot” may be used interchangeably. For consistency with previous reports, the term “Batch” is used herein.

The waste acceptance criteria (WAC) for the WTP LAW vitrification facility is <3.18E-5 Ci ^{137}Cs per mole Na.[1] For the AP-107 tank waste, only 0.127% of the influent ^{137}Cs concentration may be delivered to the WTP; this required a Cs decontamination factor of 787. The Cs effluent from the middle column reached the WAC after processing 590 BVs. Cs breakthrough from the polish column began at 590 BVs, reaching 6.3E-3 µCi/mL or 4.3E-3% Cs breakthrough after processing 844 BVs of feed. Table ES.1 summarizes the observed column performance and relevant Cs loading characteristics.

Table ES.1. AP-107 Column Performance Summary with CST

Column	WAC Limit Breakthrough (BVs)	Extrapolated 50% Cs Breakthrough (BVs)	^{137}Cs Loaded (µCi)	Cs Loaded (mg/g CST)
Lead	200	900$^{(a)}$	1.08E+6	6.82
Middle	590	NA	1.52E+5	0.96
Polish	1010$^{(a)}$	NA	2.75E+5	0.017

(a) Extrapolated value.
BV = bed volume, 10 mL
The time weighted average flowrate was 1.88 BV/h.

The Cs capacity for IONSIV^{TM} R9140-B Lot 2002009604 was superior to that of Batch 2081000057. Column testing with AP-107 tank waste showed that the Cs breakthrough profile for Lot 2002009604 was delayed about ~100 to 200 BVs (0% to 25% Cs breakthrough range) relative to that of Batch 2081000057. The total Cs load capacity determined from batch contact testing was 44% higher for Lot 2002009604 (0.72 vs. 0.50 mmoles Cs/g CST). The achieved Cs load capacity at the AP-107 feed condition was 9% greater for Lot 2002009604 (0.062 vs. 0.057 mmoles Cs/g CST).

The AP-107 composite feed and composite effluent were characterized to understand the fractionation of selected metals and radionuclides. Concentrations and recoveries of the selected analytes are summarized in Table ES.2; those with low recovery were assumed to be adsorbed onto CST. Six Resource Conservation and Recovery Act (RCRA) elements were in the suite of analytes of interest for this study (Ag, As, Ba, Cd, Cr and Pb). Cd and Cr partitioned mostly to the effluent. Lead (Pb) and barium (Ba) were detected in the feed (with concentration errors likely to exceed 15%) but were below the method detection limit (MDL) in the effluent; this was indicative of uptake by the CST. The Ag and As were not detected in the feed or effluent and their fractionations could not be discerned. In addition to Cs removal, large fractions of calcium (Ca), uranium (U), ^{90}Sr, ^{237}Np, and $^{239\text{-}240}$Pu also significantly fractionated to the CST.

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[1] 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.

Table ES.2. Recoveries of Analytes of Interest in the AP-107 Effluent

	Analyte	Feed Concentration (M)	Effluent Concentration (M)	Fraction in Effluent
Metals / Non-metals	Ag	<4.4E-6	<4.4E-6	--
	Al	3.71E-01	3.61E-01	98%
	As	<1.8E-4	<1.8E-4	--
	Ba	[3.0E-6]	<5.7E-7	--
	Ca	[8.6E-4]	[4.5E-4]	[52%]
	Cd	5.79E-05	[4.7E-5]	[81%]
	Cr	1.01E-02	9.90E-03	98%
	Fe	2.64E-04	[2.2E-4]	[83%]
	K	1.20E-01	1.15E-01	97%
	Na	5.97E+00	5.71E+00	96%
	P	2.82E-02	2.67E-02	95%
	Pb	[3.9E-5]	<1.9E-5	--
	S	6.03E-02	5.75E-02	96%
	Sr	[1.5E-6]	<1.4E-6	--
	Ti	<2.3E-6	[3.9E-6]	--
	U	7.51E-5	4.53E-5	61%
	Zn	<1.6E-5	[2.0E-5]	--
	Zr	<5.2E-6	[2.3E-5]	--

	Analyte	Feed Concentration (µCi/mL)	Effluent Concentration (µCi/mL)	Fraction in Effluent
Radionuclides	^{90}Sr	4.52E-01	<1E-3	<0.2%
	^{99}Tc	1.00E-01	9.82E-02	99%
	^{137}Cs	1.54E+02	5.29E-04	0.00035%
	^{237}Np	4.76E-05	2.02E-05	43%
	^{238}Pu	7.54E-05	2.75E-05	37%
	$^{239+240}$Pu	5.60E-04	2.01E-04	36%

Notes:
"<" values were < MDL, sample-specific MDL provided.
"--" indicates effluent recovery could not be calculated.
Values in brackets [ ] were ≥ MDL but < EQL, with errors likely to exceed 15%.
EQL = estimated quantitation limit.
MDL = method detection limit

Acknowledgments

The authors thank the Shielded Facilities Operations staff Jarrod Turner and Michael Rojas for in-cell sample handling and systems manipulations. We thank the Analytical Support Operations (ASO) count room staff Mike Cantaloub for rapid ^{137}Cs analysis for the column load and batch contact sample analyses. We thank the ASO staff Karl Pool, Lori Darnell, Jenn Carter, Denis Cherkasov, Sam Morrison, Andrew Carney, Crystal Rutherford, and Chuck Soderquist for the sample analysis, data processing, and reporting. We thank Renee Russell for reviewing the calculation files, test data packages, and this technical report. We also thank Matt Wilburn and Bill Dey for technical editing and the quality review, respectively, of this report.

Acronyms and Abbreviations

AEA	alpha energy analysis
ASO	Analytical Support Operations
ASR	Analytical Service Request
AV	apparatus volume
BV	bed volume
CST	crystalline silicotitanate
DF	decontamination factor
DI	deionized (water)
EQL	estimated quantitation limit
FD	feed displacement
GEA	gamma energy analysis
IC	ion chromatography
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
ID	identification (number)
LAW	low-activity waste
LSC	liquid scintillation
MDL	method detection limit
PNNL	Pacific Northwest National Laboratory
PSD	particle size distribution
PTFE	polytetrafluoroethylene
QA	quality assurance
QC	quality control
R&D	research and development
RCRA	Resource Conservation and Recovery Act
SEM	scanning electron microscopy
SV	system volume
TIC	total inorganic carbon
TOC	total organic carbon
TSCR	Tank-Side Cesium Removal
WAC	waste acceptance criteria
WRPS	Washington River Protection Solutions
WTP	Hanford Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

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1.0 Introduction

The U.S. Department of Energy (DOE) is working to expedite processing of Hanford tank waste supernate at the Hanford Waste Treatment and Immobilization Plant (WTP). To support this goal, Washington River Protection Solutions (WRPS) is designing a system for suspended solids and cesium (Cs/^{137}Cs) removal from Hanford tank waste supernate. The effluent will then be sent to the WTP Low-Activity Waste (LAW) facility for vitrification. The Cs removal is critical for eliminating the high dose rate associated with ^{137}Cs and facilitating a contact maintenance philosophy for the LAW Facility. The maximum ^{137}Cs concentration in the LAW sent to the WTP is targeted to be below 3.18E-5 Ci ^{137}Cs/mole of Na waste acceptance criteria (WAC) limit.[1] The filtration and ion exchange systems will be placed near the Hanford tanks and are collectively termed the Tank-Side Cesium Removal (TSCR) system. The ion exchange media selected for Cs removal at TSCR is crystalline silicotitanate (CST) that is manufactured in a nearly spherical form by Honeywell UOP LLC (UOP; Des Plaines, IL) as product IONSIV™
R9140-B.

Recent testing with CST was reported in support of TSCR design inputs with 5.6 M Na simulant using two different CST production lots, Batch[2] 2081000057 and Lot number 2002009604 (Fiskum et al. 2018; 2019, respectively). Fiskum et al. (2018) evaluated CST Batch 2081000057for physical properties, Cs capacity from batch contacts, and processing through lead-lag column systems (10-mL beds) at three different flowrates. The authors found that increasing the flowrate decreased the Cs loading; the Cs capacity and 50% breakthrough predicted by batch contact testing [6.16 mg Cs per gram of CST and 770 bed volumes (BVs), respectively] agreed within 10% of the results of the column tests (~6.3 mg Cs per gram of CST and 800 BVs). Fiskum et al. (2019) also tested CST Lot 2002009604 for CST physical properties, Cs kinetic exchange performance from batch contact testing, and column processing. The column processing evaluated Cs loading at full-height lead/lag columns and individual smaller-scale columns (27-mL beds) at a variety of flow rates and feed conditions. Long Cs exchange transition zones were reported (1120 BVs from 5% to 95% Cs breakthrough), indicating slow Cs kinetic exchange. Additionally, CST Lot 2002009604 was shown to load Cs more effectively during column processing (6.95 mg Cs/g CST and ~1000 BVs at 50% breakthrough) than CST Batch 2081000057. Appendix D provides a summary comparison of the physical properties and ion exchange performances of these two CST production lots.

Testing of cesium (^{137}Cs) removal from defense wastes using CST has been previously reported (King 2007; Walker et al. 1998; Hendrickson et al. 1996; Brown et al. 1996). However, limited data are available on actual Hanford tank wastes processed with more recent CST production lots. Rovira et al. (2018) described testing with CST IONSIV™ R9140-B, Batch 2081000057, on a Hanford tank waste sample collected from 241-AP-107 (hereafter called AP-107). They assessed column loading using a lead/lag column format, processing at 2.2 bed volumes per hour (BV/h). Column testing was conducted such that the lead column was removed after ~25% Cs breakthrough (470 BVs) because the lag column effluent had reached the WAC limit; the lag column was placed in the lead position and a fresh lag column was installed. Processing continued, but the lead column only reached 26% Cs breakthrough before feed was exhausted and lag column effluent again exceeded the WAC. Rovira et al. (2018) also

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[1] 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.

[2] The term “Batch” was provided by UOP in paperwork accompanying the CST provided to PNNL February 2018; this term was used on earlier test reports. The term “Batch” and “Lot” may be used interchangeably. For consistency with previous reports, the term “Batch” is used herein.

reported the effective Cs load capacity at equilibrium feed condition was 7.2 mg Cs per g CST based on batch contact testing.

Rovira et al. (2019) tested Cs loading using the newer CST production Lot 2002009604 with AW-102 tank waste that was diluted to 5.8 M Na. They again used 10-mL CST beds in a lead/lag format. In their tests, only 4.3% Cs breakthrough (451 BVs) was obtained during column testing before depleting the available feed. Batch contact testing with the diluted and filtered AW-102 showed that the effective Cs capacity at the equilibrium feed condition was 6.8 mg Cs per g CST. Matrix effects such as higher K concentration in AW-102 (0.15 M K) relative to AP-107 (0.096 M K) possibly reduced the Cs load capacity (from 7.2 to 6.8 mg Cs per g CST).

WRPS funded Pacific Northwest National Laboratory (PNNL) to conduct additional testing with AP-107 tank waste. The goals of this current study are as follows.

1. Evaluate the effectiveness of Cs removal from AP-107 using a three-column ion exchange system (lead, middle, and polish) with the newer production batch of CST, Lot 2002009604.

2. Determine the Cs load capacity of CST, Lot 2002009604, using batch contact testing with AP-107.

3. Compare the AP-107 Cs load profile to the previously reported AP-107 load curve (Rovira et al. 2018).

4. Analyze the AP-107 effluent to derive the fates of key analytes (^{90}Sr, ^{99}Tc, ^{137}Cs, $^{239+240}$Pu, ^{237}Np, Al, As, Ba, Ca, Cd, Cr, Fe, K, Na, P, Pb, S, Sr, Ti, Zn, Zr).

5. Provide Cs-decontaminated effluent for vitrification studies (to be conducted at a later date).

6. Provide Cs-loaded CST for potential follow-on analysis (to be conducted at a later date).

The efficacy of loading higher amounts of Cs onto the lead column CST while maintaining a product below the WAC limit from the polish column was of prime interest to support the evolving WRPS TSCR design. This test design further exposes the CST to higher feed volume through the individual column beds, allowing for a more representative assessment of the fractionations of analytes of interest.

2.0 Quality Assurance

The work described in this report was conducted with funding from WRPS contract 36437/273, *DFLAW Radioactive Waste Test Platform*. This contract was managed under PNNL Project 73312. All research and development (R&D) work at 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 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, AP-107 tank waste, batch contact conditions, and column ion exchange conditions. All testing was conducted in accordance with a test plan prepared by PNNL and approved by WRPS.[1]

3.1 CST Media

WRPS purchased ten 5-gallon buckets (149 kg total) of IONSIV ™ R9140-B[2], Lot number 2002009604, material number 8056202-999, from Honeywell UOP 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. 2019). A 117-g subsample split was passed through a 25-mesh sieve (ASTM E11 specification) as previously described (Fiskum et al. 2019). Of this starting mass, 61.6 g or 52 wt% passed through the sieve and was collected for batch contact testing and column testing; this was close to the 59 wt% <25 mesh mass fraction reported by Fiskum et al. (2019). The <25 mesh CST fraction was pretreated by contacting with 200 mL of 0.1 M NaOH three 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.

Table 3.1 compares the physical properties measured on the Batch 2081000057 CST (used on the AP-107 two-column test in 2018) and the Lot 2002009604 CST (used on the current three-column test). The physical properties were essentially the same, within experimental uncertainty of a couple of percent, except for the post-sonication particle size distribution (PSD) d_{90}, which was 29 µm larger for the current test batch. Figure 3.1 shows the PSD profiles for the two CST production batches at the indicated sieve cuts. Additional comparisons between the two CST lots are provided in Appendix D.

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[1] Fiskum SK. 2019. TP-DFTP-058, Rev. 0. *DFLAW Cesium Ion Exchange Testing with AP-107 Tank Waste for the Tank Side Cesium Removal (TSCR) Project*. Pacific Northwest National Laboratory, Richland Washington. Not publicly available.

[2] R9140-B is provided in the sodium form by the vendor.

Table 3.1. Physical Properties of <25 Mesh, Washed R9140-B CST (Two Production Batches)

Parameter	Batch 2081000057 (Fiskum et al. 2018)	Lot 2002009604 (Fiskum et al. 2019)
Sieve cut for testing	<25 mesh/+60 mesh	<25 mesh
Bulk density, g/mL	1.00	1.02
CST bed density, g/mL	1.00	1.01
Settled bed void volume, %	65.6	66.2
Cumulative particle undersize fractions, microns[(a)]	d_{10}: 412 d_{50}: 563 d_{90}: 765	d_{10}: 406 d_{50}: 567 d_{90}: 795

(a) Volume basis, post-sonication

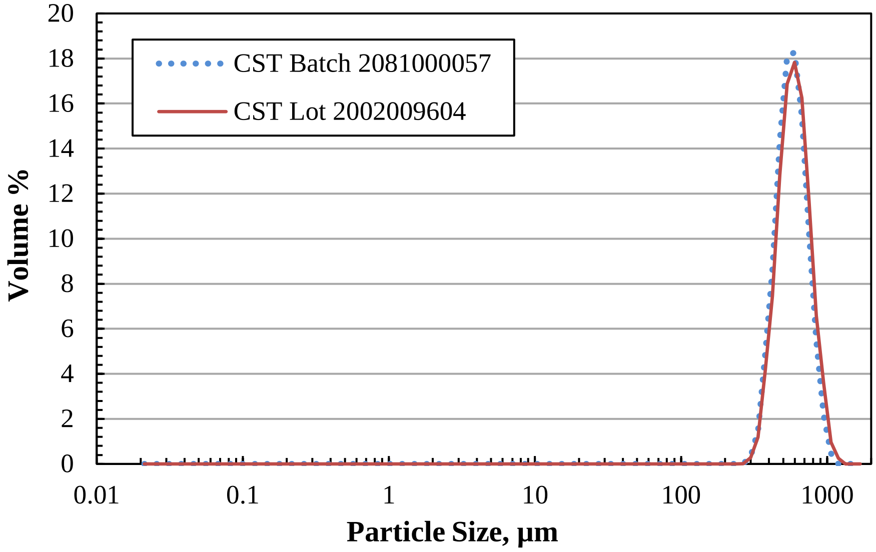

Figure 3.1. PSD Comparison for Two CST Lots

Figure notes: CST Batch 2081000057 <25 mesh/ >60 mesh; Lot 2002009604 <25 mesh, Post-sonication results

3.2 AP-107 Tank Waste Sample

Multiple samples (36 each at nominally 270 mL) were collected from the AP-107 Hanford tank in January 2019. The samples were delivered to PNNL's Radiochemical Processing Laboratory and placed into the Shielded Analytical Laboratory hot cells. The first and last samples collected, 7AP-18-01 and 7AP-18-36, were subsampled for a limited analysis suite to confirm density, Na, K, Cs, ^{133}Cs, and ^{137}Cs concentrations. The densities were measured in-cell using 10-mL volumetric flasks. All other measurements were conducted by the Analytical Support Operations (ASO) according to Analytical Service Request (ASR) 0747; results are provided in Table 3.2. The results of the two samples agreed within 7%, indicating that the 36 samples were essentially homogenous, within analytical uncertainty (±10% to 15%). The results for the AP-107 samples collected in 2017 and used for the two-column test (Rovira et al. 2018) are also shown in Table 3.2 for direct comparison. The average results for the 2017 sample collection agreed within 3% of the average results of the 2019 collection (except for Cs).

Table 3.2. Characterization of Samples 7AP-18-01 and 7AP-18-36 Collected from Hanford Tank AP-107 January 2019 (ASR 0747)

Analyte	AP-107 Average (Rovira et al. 2018)	7AP-18-01 (19-1227)[a]	7AP-18-36 (19-1228)[a]	Units	Analysis Method
Al	0.364	0.361	0.385	M	ICP-OES
K	0.097	0.093	0.099	M	ICP-OES
Na	5.62	5.61	5.98	M	ICP-OES
OH^-	0.92[b]	Not measured	Not measured	M	Titration
^{133}Cs	5.63	5.96	6.14	µg/mL	ICP-MS
^{137}Cs	156[c]	140[d]	141[d]	µCi/mL	GEA
^{137}Cs	1.80[c]	1.61[d]	1.62[d]	µg/mL	GEA
Density	1.266[e]	1.268[f]	1.259[f]	g/mL	Volumetric flask

(a) ASO sample ID, see Appendix E for ASO reports.
(b) Based on first inflection point; assumed to be the free (unbound) hydroxide.
(c) Reference date is 11/27/17.
(d) Reference date is 3/18/19.
(e) Measured at 26.6 °C using a 10-mL volumetric flask.
(f) Measured at 22.8 °C using a 10-mL volumetric flask.
GEA = gamma energy analysis; ICP-MS = inductively coupled plasma mass spectrometry;
ICP-OES = inductively coupled plasma optical emission spectrometry.

The ^{133}Cs results for the 2019 sample collection (average 6.05 µg/mL) were 14% higher than those from the 2017 sample collection (5.30 µg/mL); the 14% difference was within the overall analytical uncertainty. The 2019 ^{137}Cs results were ~5% lower than the 2018 sampling results, accounting for decay correction. The ^{135}Cs isotopic composition of the AP-107 samples was assumed to be equivalent to that of the 2018 measured value of 17.2 wt% (Rovira et al. 2018). The total Cs concentration (from all Cs isotopes) was thus assigned to 9.19 µg/mL (reference date is April 12, 2019) for this report; the Rovira et al. (2018) results were based on 8.57 µg/mL total Cs (7.2 % lower value). This difference was likely driven by analytical uncertainties and will not significantly affect the Cs load profile test conclusions or comparisons between tests. The difference may affect the calculated total Cs load capacity from column processing but not batch contact processing where ^{133}Cs is added.

The AP-107 samples were first processed through either of two dead-end filtration systems (Geeting et al. 2019). The AP-107 samples were filtered in batches and provided in multiple ~0.7- to 1.4-L increments for ion exchange. Each container of material was measured for density using 10-mL volumetric flasks or the Coriolis meter installed in the filtration apparatus. Effluent densities ranged from 1.26 to 1.28 g/mL. It was assumed that, within analytical uncertainty, all samples provided for column ion exchange processing were equivalent and the average density of 1.266 g/mL was applied. Due to the large volume (~8.6 L) of AP-107, the multiple samples were not combined into a 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 weight-lifting limitations of the manipulators in the hot cells.

3.3 Batch Contact Conditions

A primary metric of an ion exchanger's performance is its distribution coefficient (K_d) measured in a batch contact experiment. The distribution coefficient is a quantitative measure of a material's capability to remove an ion from a specific solution matrix and is the ratio of the concentration of the ion remaining in solution at equilibrium to the concentration of the ion sorbed on the ion exchange material.

Batch contact solutions consisted of the AP-107 tank waste plus various amounts of added ^{133}Cs as $CsNO_3$ solution. The equilibrium Cs concentrations were determined after batch contacts to assess the effective Cs loading capacity on the CST and the Cs K_d in the AP-107 feed matrix. The preparation and batch contacts were processed in accordance with a test instruction.[1]

Aliquots of Cs spike solutions (140 mg/mL or 14.0 mg/mL) were added to three centrifuge tubes in small volumes (1.06, 6.97, and 49.1 mg added Cs). The Cs-spiked centrifuge tubes were transferred to the hot cell and ~33-mL aliquots of filtered AP-107 supernate were transferred to each of the Cs spike solution containers. Exact masses transferred were determined by difference from the measured masses before and after Cs spikes and AP-107 transfers; the added volumes were calculated from the solution densities and net sample masses. The three vessels of AP-107 plus added Cs and the unspiked AP-107 are termed "stock contact solutions." The stock contact solutions were shaken to mix AP-107 thoroughly with the Cs spike. Table 3.3 shows the calculated initial Cs concentrations in the stock contact solutions. The Cs spike solutions were equilibrated with AP-107 matrix ~10 days.

Table 3.3. Cs Concentrations in Stock Contact Solutions

Solution ID	Cs Concentration (mg/L)	Cs Concentration (M)
TI062-S0	9.19	6.91E-5
TI062-S1	37.5	2.82E-4
TI062-S2	229	1.73E-3
TI062-S3	1462	1.10E-2

An aliquot of the washed CST, sufficient to apply to all batch contact tests, was allowed to air-dry overnight at ambient temperature to a free-flowing form. However, the air-dried CST still contained water. The F-factor, ratio of dry mass exchanger to sampled mass exchanger, was determined to correct for water content. A small fraction of the air-dried CST was removed for nominal F-factor evaluation. The F-factor sample aliquot was dried at ~100 °C overnight to determine the nominal water content remaining in the air-dried CST. This nominal F-factor was used to determine the target CST aliquot mass to collect for the batch contact samples. This partially dried CST contained ~15% water by mass.

A precisely weighed quantity of the washed and air-dried CST (targeted to be 0.088 g "wet" and 0.075 g dry) was aliquoted into a 20-mL liquid scintillation (LSC) vial for each batch contact sample. The air-dried CST mass was determined to an accuracy of $\leq$1%.

Two F-factor samples were also collected, one at the beginning of CST aliquoting process, one at the end of CST aliquoting process in a tight subsampling time window ($\leq$10 min). The initial F-factor sample masses were designated M_I. The F-factor samples were dried to constant mass at 100 °C. The final F-

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[1] Fiskum SK. 2019. TI-DFTP-062, *Batch Contacts with Crystalline Silicotitanate in AP-107 Tank Waste Matrix—2019*. Pacific Northwest National Laboratory, Richland, Washington. Not publicly available. Implemented April 2019.

factor sample masses were designated M_F. The F-factors were calculated according to Eq. (3.1). The average of the two F-factor samples (first and last from the weighing series, 0.8546 ±0.40% relative percent difference) was used to calculate the dry CST masses contacted with solution.

$$\frac{M_F}{M_I} = F \tag{3.1}$$

The CST aliquots were transferred to the hot cell and then contacted with 15 mL of the various stock contact solutions (see Table 3.3) in duplicate. The AP-107 volume was transferred by pipet, and the actual volume delivered was determined by mass difference and solution density. The targeted phase ratio (liquid volume to dry exchanger mass) was 200 mL/g CST. The obtained ratio varied between 179 and 198 mL/g CST.

The primary batch contact vials along with a temperature sentinel vial (15 mL of deionized [DI] water) were placed upright onto a Thermo LP vortex mixer[1] initially set to ~400 revolutions per minute. Agitation continued for 104 h; the sentinel temperature upon completion was 29.7 °C. After standing in static contact with the CST for 104 h, the duplicate set of batch contact samples were agitated at ~400 revolutions per minute for 71 h; the sentinel temperature was 28.3 °C. In each case, some cloudiness in the contact solution vial was observed, indicating a bit of particle abrasion. However, the CST beads did settle and appeared intact, indicating particle abrasion was minor.

After the batch contact time, the CST was settled and ~2 to 5 mL of the aqueous fraction was removed from the hot cell. The samples were filtered through 0.45-µm pore size nylon-membrane syringe filters. Filtered sample aliquots (0.5 to 2 mL) were collected for gamma counting; the sampled aliquot masses were measured and the exact volumes determined by dividing by the solution density.

Aliquots of the AP-107 stock solutions and batch contacted samples were analyzed by gamma spectrometry to determine ^{137}Cs concentrations. The batch contact Cs K_d value was determined for each sample using the relationship shown in Eq. (3.2):

$$\frac{(C_0 - C_1)}{C_1} \times \frac{V}{M \times F} = K_d \tag{3.2}$$

where:

C_0 = initial ^{137}Cs concentration (µCi/mL) in the stock contact solution
C_1 = final ^{137}Cs concentration (µCi/mL) in the batch contacted solution
V = volume of the batch contact liquid (mL)
M = measured mass CST (g)
F = F-factor, mass of the dried CST divided by the mass of the sampled CST
K_d = batch-distribution coefficient (mL/g)

Final Cs concentrations (Cs_F) were calculated relative to the ^{137}Cs recovered in the batch contacted samples according to Eq. (3.3):

$$Cs_0 \times \left(\frac{C_1}{C_0}\right) = Cs_F \tag{3.3}$$

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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).

where:

Cs_0 = initial Cs concentration in solution (µg/mL or M)
Cs_F = final Cs concentration in solution (µg/mL or M)

The equilibrium Cs concentrations loaded onto the CST (Cs_{IX} in units of mg Cs per g of dry CST mass) were calculated according to Eq. (3.4):

$$\frac{Cs_0 \times V \times \left(1 - \frac{C_1}{C_0}\right)}{M \times F \times 1000} = Cs_{IX} \tag{3.4}$$

where:

Cs_{IX} = equilibrium Cs concentration in the CST (mg Cs/g CST)
1000 = conversion factor to convert µg to mg

3.4 Ion Exchange Process Testing

This section describes the ion exchange column system and AP-107 process conditions. The preparations and column testing were conducted in accordance with a test instruction.[1]

3.4.1 Ion Exchange Column System

Figure 3.2 provides a schematic of the ion exchange process system; Figure 3.3 shows a photograph of the system before installation in the hot cell. Flow through the system was controlled with a Fluid Metering Inc. (FMI) positive displacement pump. Fluid was pumped past an Ashcroft pressure gage and a Swagelok pressure relief valve with a 10-psi trigger point. The ⅛-inch outside diameter / ¹⁄₁₆-inch inside diameter polyethylene tubing was purchased from Polyconn (Plymouth, MN). The ⅛-inch outside diameter / ¹⁄₁₆-inch inside diameter stainless steel tubing was used in conjunction with the manifold. Valved quick disconnects were purchased from Cole Parmer (Vernon Hills, IL). Use of the quick disconnects enabled easy disassembly and re-assembly for installation in the hot cell. The quick disconnects were color-coded to ease correct re-installation.

The quick disconnects had the added advantage of enabling column replacement and accommodating alternate fluid processing options. At the end of the AP-107 feed processing, the lead column fluid height decreased to the top of the CST bed. Fluid replacement was possible by releasing quick disconnects m1/f1 and m2/f2 and using standby quick disconnects at positions m1 and f2 that allowed for fluid backflow into the lead column to replace the lost fluid head and expel the gas void. The original m1 and f2 quick disconnects were re-installed and fluid processing continued.

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[1] Rovira AM. 2019. *Cesium Removal from AP-107 Using Crystalline Silicotitanate in a Three-Column* Format. TI-DFTP-061. Pacific Northwest National Laboratory, Richland, Washington. Not publicly available. Implemented March 2019.

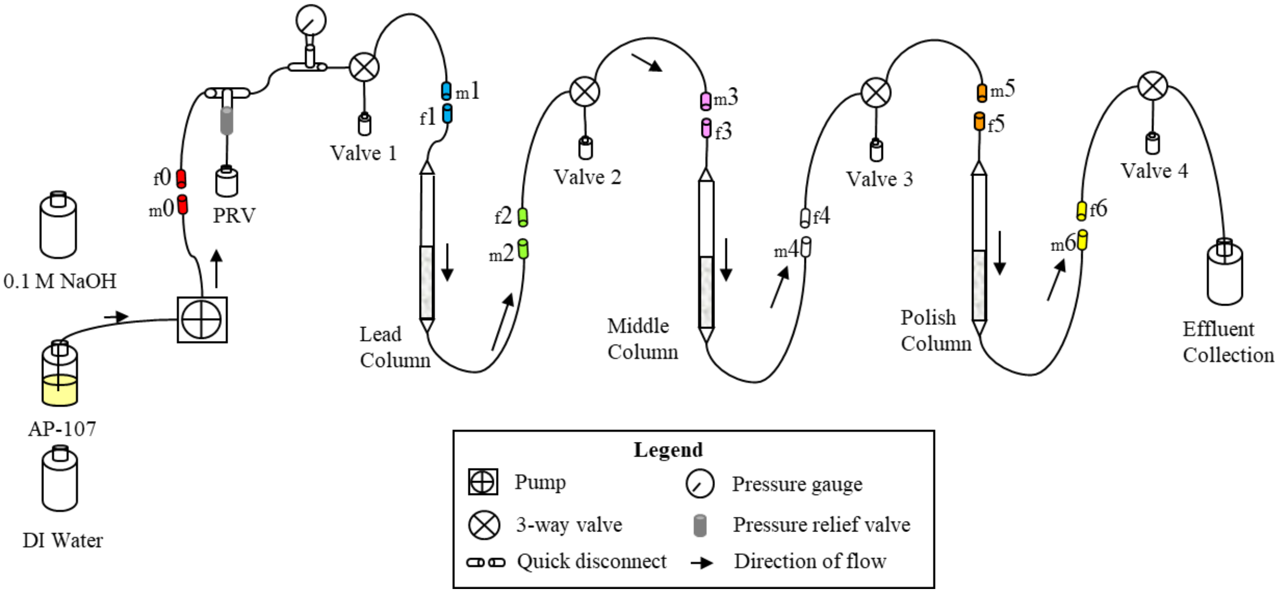

Figure 3.2. Ion Exchange System Schematic

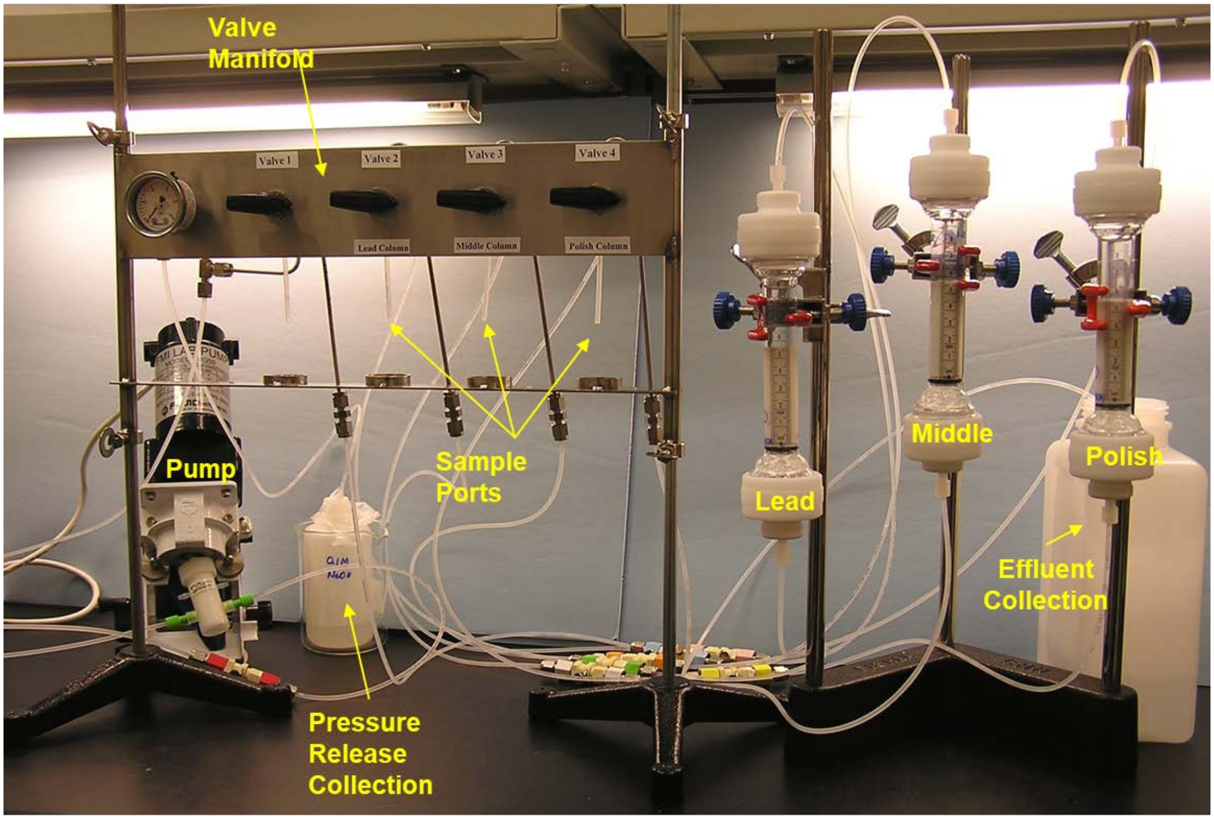

Figure 3.3. Photograph of Ion Exchange System Outside of the Hot Cell

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 (PTFE). The CST was supported by an in-house constructed support consisting of a 200-mesh stainless steel screen tack welded onto a stainless-steel O-ring. With a rubber O-ring, the fitting was snug-fitted into place in the column (as previously described by Fiskum et al. 2018). After packing with CST, a small number of CST particles were observed to have slipped into the narrow gap between the stainless-steel support and glass column barrel; they were blocked from passage by the O-ring. 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 (volume reduction from ~5.6 to ~2.5 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.

Four Swagelok valves were installed in the valve manifold. Valve 1 was used to isolate the columns from the system (when in the closed position) and purge the tubing from the inlet to valve 1 (when placed in the sampling position). Lead column samples were collected at valve 2, the middle column samples were collected at valve 3, and the polish column samples were collected at valve 4. The gross AP-107, feed displacement (FD), water rinse, and flushed fluid effluents were collected at the effluent line. Samples of FD and water rinse were collected from valve 4.

The system was filled with water and then 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. Triplicate 10.0-mL aliquots of settled CST (pretreated, <25 mesh) were measured using a graduated cylinder and quantitatively transferred to each of the three columns. The CST was allowed to settle through the 0.1 M NaOH solution, thus mitigating gas bubble entrainment. The columns were tapped with a rubber bung until the CST height no longer changed.

The CST BV corresponded to the settled CST media volume as measured in the graduated cylinder prior to transferring the media into the ion exchange column. The reference CST BV was 10.0 mL; each of the three columns contained 10.0 mL CST. The settled CST bed heights in the columns were ~5.6 cm. This CST height corresponded to 2.4% of the full height column (234 cm).

Figure 3.4 provides a closeup image of the lead column loaded with CST, the fluid headspace, the CST bed support, and glass beads filling the void space below the bed. Note that the centimeter scale 0-point is positioned at the CST support screen and some CST particles slipped into the small gap between the column wall and the rubber screen support ring.

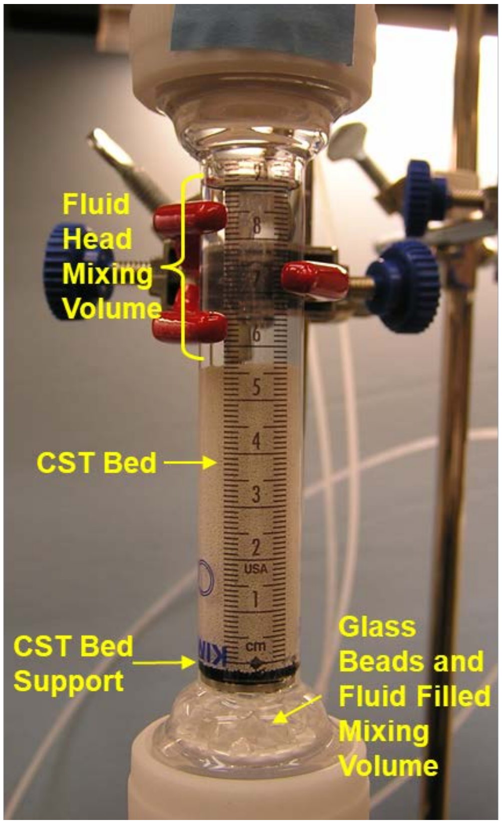

Figure 3.4. Closeup of Lead Chromaflex® Column Loaded with CST

The entire fluid-filled volume of the assembly was ~71 mL, inclusive of fluid in the CST beds. The bed void volume was 66% (Fiskum et al. 2019); therefore, each CST bed held 6.6 mL fluid. The fluid-filled mixing space above each CST bed averaged 5 mL (lead column 4 mL, middle column 6 mL, polish column 5 mL). The fluid mixing volume below each CST bed ranged from 2.1 to 2.6 mL. Thus, ~59% of the total fluid holdup volume was unavoidably associated with the geometry of the three columns. These fluid mixing volume fractions are not likely to be representative of plant-scale operations.

Figure 3.5 is a photograph of the ion exchange system during in-cell AP-107 processing (after processing ~744 BVs of AP-107). Note the lead column has a dark grey appearance whereas the companion columns appear white. The lead column darkening increased over time due to radiolytic damage from the ^{137}Cs on the glass column.

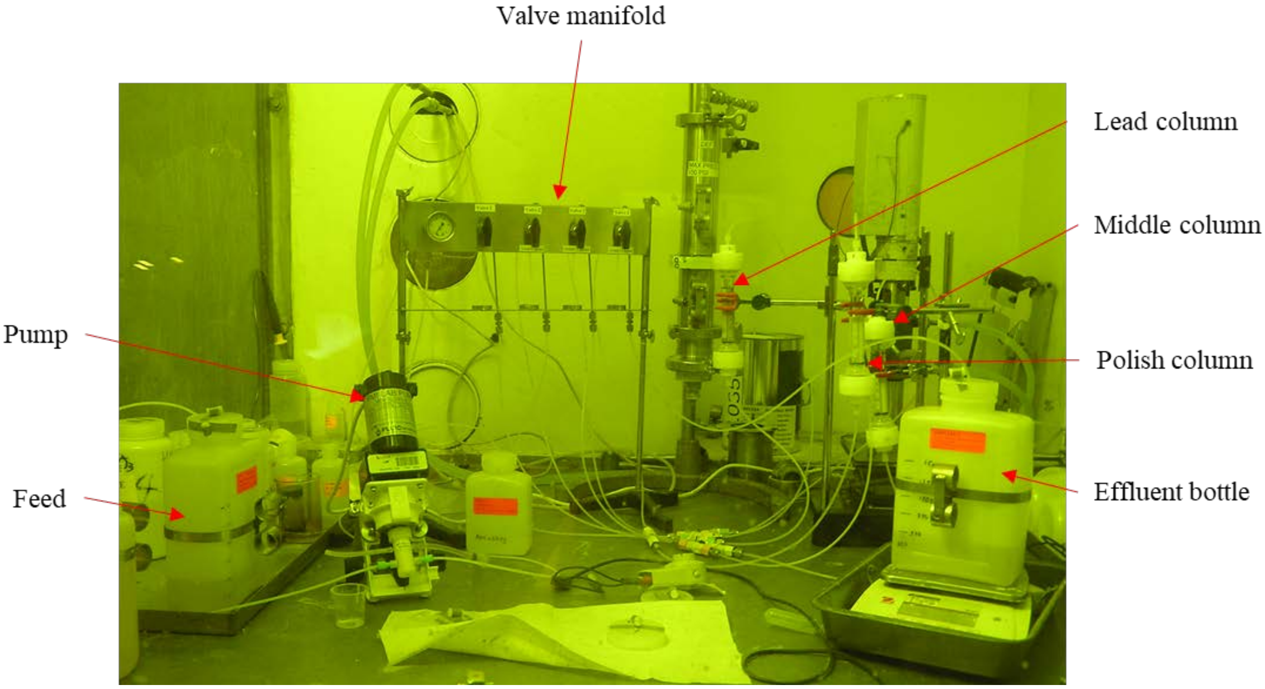

Figure 3.5. Ion Exchange Assembly in the Hot Cell, May 1, 2019, ~744 BVs Processed

3.4.2 AP-107 Tank Waste Process Conditions

Once installed in the hot cell, a flow of 0.1 M NaOH was used to verify the system integrity and calibrate the pump. The various containers from the filtration process (Geeting et al. 2019) were incrementally transferred to a 2-L rectangular polyethylene bottle during the loading phase. The 2-L rectangular bottle was less top-heavy than the tall 1.5-L bottles and offered more volume reserve for unattended operations. The AP-107 feed was processed downflow through the ion exchange media beds, lead to middle to polish. Effluent was collected in ~1.5-L increments. The volume limitation was intended to minimize the impact of potential polish column Cs breakthrough exceeding the WAC and to allow for safe transfer out of cell in 1.5-L polyethylene bottles. After the AP-107 loading was completed, 12 BVs of 0.1 M NaOH FD followed by 12 BVs of DI water rinse were passed downflow through the system to rinse residual feed out of the columns and process lines. The 12 BVs was equivalent to 1.7 times the fluid-filled apparatus volume (AV).

All processing was conducted at ambient cell temperature conditions, nominally 24 to 29 °C. Test parameters, including process volumes, flowrates, and CST contact times, are summarized in Table 3.4. The pump head stroke length was close to the minimum at which it could be set. The stroke rate was toggled between 12.9 and 13.0 (maximum fidelity of 0.1 units) to maintain the flowrate between 1.83 and 2.04 BV/h, respectively. Greater fidelity with the stroke rate controller could not be obtained to center on the target 1.9 BV/h. Figure 3.6 shows the achieved flowrate as a function of time. The 1.88 BV/h flowrate reported in Table 3.4 is a time-weighted average.

Table 3.4. Experimental Conditions for AP-107 Column Processing, April 15 to May 4, 2019

		Volume			Flowrate		Duration
Process Step	Solution	(BV)	(AV)	(mL)	(BV/h)(c)	(mL/min)(c)	(h)
Loading lead column	AP-107	855	NA	8550	1.88	0.313	452
Loading middle column(a)	AP-107	849	NA	8490	1.88	0.313	452
Loading polish column(b)	AP-107	844	NA	8440	1.88	0.313	452
Feed displacement	0.1 M NaOH	12.8	1.79	128	3.66	0.610	3.5
Water rinse	DI water	12.3	1.72	123	4.54	0.757	2.8

(a) The feed volume through the middle column was reduced relative to that of the lead column because samples collected from the lead column did not enter the middle column.

(b) The feed volume through the polish column was reduced relative to that of the middle column because samples from the lead and middle columns did not enter the polish column.

(c) Time-weighted average flowrates.

BV = bed volume (10.0 mL as measured in graduated cylinder).

AV = apparatus volume (nominally 71 mL).

NA = not applicable.

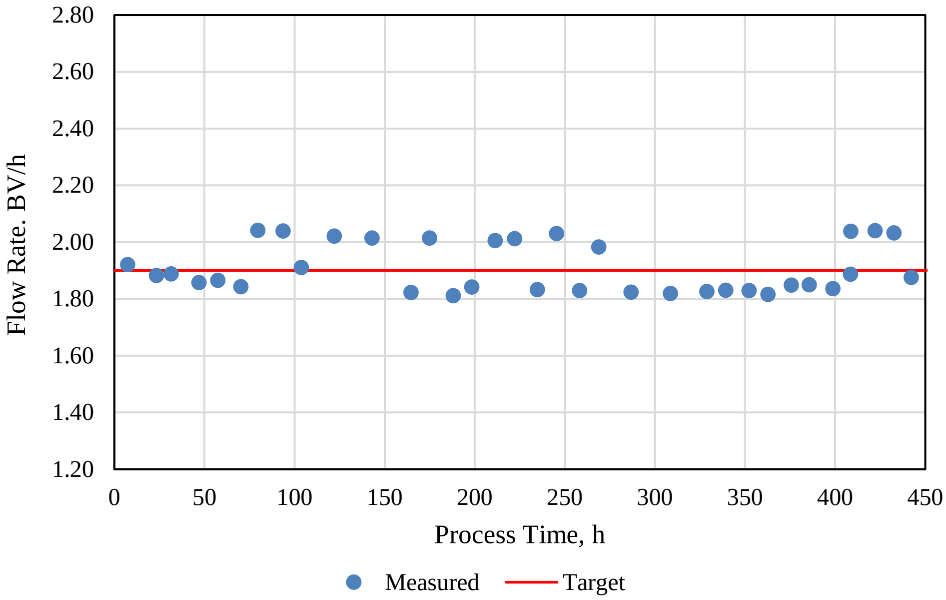

Figure 3.6. AP-107 Flowrate as a Function of Time

The total cumulative volume of AP-107 processed was 8.55 L (855 BVs). The AP-107 process cycle mimicked, as best as possible, the process flow anticipated at the TSCR facility in terms of BV/h (i.e., contact time), FD, and water rinse. It was understood that the feed linear flow velocity in this small-column configuration (0.18 cm/min) could not begin to match that of the full-height processing configuration (7.3 cm/min, Fiskum et al. 2019).

During the loading phase, nominal 2-mL samples were collected from the lead, middle, and polish columns at the sample collection ports (see Figure 3.2, valves 2, 3, and 4). Sampling from the columns necessitated brief (10-minute) interruptions of flow to the downstream columns. Samples were collected after the first ~12 BVs were processed and again at nominal 20- to 57-BV increments. The feed was processed for 452 h nearly continuously. Only brief (~5 min) interruptions were associated with changing the feed bottle near the end of feed processing.

At the end of the AP-107 loading phase, the fluid level in the lead column dropped to the height of the CST bed. Approximately 5 mL of 0.1 M NaOH was back flowed into the lead column from quick disconnect *m2* (see Figure 3.2) to re-establish the headspace fluid such that the CST would not dry as the FD processing began. During backflow processing, brown/black solids were observed at the top of the CST bed. They were briefly suspended with the backflow processing, whereas the CST did not move. Figure 3.7 is an image of the suspended solids observed during the backflow operation. A small sample of the solids was later collected for transmission electron microscopy analysis from the parent bottle where they were found to originate. Results are discussed in Appendix C.

Figure 3.7. Suspended Solids at the Top of the Lead Column During Backflow Processing

The FD effluent was collected in a polyethylene bottle; four samples were collected during the FD process from valve 4 in nominal 3-BV increments. The water rinse was collected similarly to the FD. The fluid-filled volume was expelled with compressed air connected at the first quick disconnect in the system *f0* (see Figure 3.2); the collected volume did include the interstitial fluid space between the CST beads, but did not include fluid in the CST pore space. Hours of additional gas flow were required to dry the CST enough to be free-flowing and effectively pour out of the columns for later use.

Cesium load performance was determined from the ^{137}Cs measured in the collected samples relative to the native ^{137}Cs in AP-107 feed. The collected samples were analyzed directly to determine the ^{137}Cs concentration using GEA. Cesium loading breakthrough curves for both the lead and lag columns were generated based on the feed ^{137}Cs concentration (C_0) and the effluent Cs concentration (C) in terms of % C/C_0.

3.5 Sample Analysis

A composite feed sample was prepared by sampling 2 mL from each filtered sample bottle into one polyethylene vial. An effluent composite sample was generated by collecting a pro-rated volume from each effluent bottle and combining in a polyethylene vial. Selected effluent samples from the lead column were measured for selected radionuclides and cations in an effort to assess the exchange behavior for these analytes. Table 3.5 summarizes the specific sample collections and targeted analytes along with the cross references to the ASO sample identification numbers (IDs).

Samples were submitted to the ASO on ASR 0787. The ASO was responsible for the preparation and analysis of appropriate analytical batch and instrument quality control samples and for providing any additional processing to the sub-samples that might be required (e.g., acid digestion, radiochemical separations, dilutions). All analyses were conducted by the ASO according to standard operating procedures, the ASO QA Plan, and the ASR. Samples were analyzed directly (no preparation) by GEA.

Table 3.5. Analytical Scope for Column Process, ASR 0787

Sample ID	ASO Sample ID	Analysis Scope
TI061-Comp-FEED	19-1773	GEA (^{60}Co, ^{137}Cs, ^{154}Eu) IC anions (F$^-$, Cl$^-$, NO$_2^-$, NO$_3^-$, PO$_4^{3-}$, C$_2$O$_4^{2-}$, SO$_4^{2-}$)$^{(a)}$ TOC/TIC free OH ICP-OES (Ag, Al, As, Ba, Ca, Cd, Cr, Fe, K, Na, Ni, P, Pb, S, Sr, Ti, Zn, Zr) ICP-MS (^{238}U) Radioanalytical (^{90}Sr, ^{99}Tc, ^{237}Np, ^{238}Pu, $^{239+240}$Pu)
TI061-Comp-EFF	19-1774	GEA (^{60}Co, ^{137}Cs, ^{154}Eu) ICP-OES (Ag, Al, As, B, Ba, Ca, Cd, Cr, Fe, K, Li, Mg, Mo, Na, Ni, P, Pb, S, Si, Sr, Ti, W, Zn, Zr) ICP-MS (^{238}U) Radioanalytical (^{90}Sr, ^{99}Tc, ^{237}Np, ^{238}Pu, $^{239+240}$Pu)
TI061-L-F1-A (12.6 BVs)	19-1775	ICP-OES (Al, Ba, Ca, Cd, Cr, Fe, K, Na, Ni, P, Pb, S, Sr, Ti, Zn, Zr), ICP-MS (^{238}U) Radioanalytical (^{90}Sr, ^{237}Np, $^{239+240}$Pu)
TI061-L-F4-A (87.7 BVs)	19-1776	
TI061-L-F8-A (180 BVs)	19-1777	
TI061-L-F11-A (280 BVs)	19-1778	
TI061-L-F14-A (366 BVs)	19-1779	
TI061-L-F18A (457 BVs)	19-1780	
TI061-L-F22-A (558 BVs)	19-1781	
TI061-L-F25-A (656 BVs)	19-1782	
TI061-L-F27-A (724 BVs)	19-1783	
TI061-L-F29-A (815 BVs)	19-1784	

GEA = gamma energy analysis
IC = ion chromatography
ICP-MS = inductively coupled plasma mass spectrometry
ICP-OES = inductively coupled plasma optical emission spectrometry
TIC = total inorganic carbon
TOC = total organic carbon
(a) The IC anion concentrations will be provided in a later report supporting the Cs-decontaminated AP-107 vitrification testing.

4.0 Batch Contact Results

This section discusses the batch contact results for the AP-107 filtered tank waste with <25 mesh CST Lot 2002009604.

Equilibrium Cs concentrations and K_d results for the batch contact samples are provided in Table 4.1. Note that the primary samples were contacted for 104 h and the duplicates were contacted for 71 h. There were no measurable differences in K_d values between the 71- and 104-h contact times, which confirmed that the CST equilibrium condition had been reached by the 71-h contact time.

Table 4.1. Equilibrium Results for AP-107 Batch Contact Samples with CST Lot 2002009604

Sample ID	Initial [Cs] (µg/mL)	Final [Cs] (µg/mL)	Δ Time (h)	K_d (mL/g)	Equilibrium Cs in CST (mg Cs/g)
TI062-S0-CST	9.19	1.94	104	736	1.42
TI062-S1-CST	37.5	7.12	104	793	5.62
TI062-S2-CST	229	53.4	104	642	34.3
TI062-S3-CST	1460	994	104	89	88.6
TI062-S0-CST-d	9.19	1.97	71[(a)]	720	1.41
TI062-S1-CST-d	37.5	7.13	71[(a)]	826	5.89
TI062-S2-CST-d	229	48.4	71[(a)]	668	32.3
TI062-S3-CST-d	1460	1030	71[(a)]	83	85.8

Note that the AP-107 tank waste also contained 0.096 M K and 0.89 M free hydroxide.
(a) The duplicate samples remained in static contact with AP-107 while the primary sample set was agitated 104 h.

The K_d values versus Cs concentrations are plotted in Figure 4.1 on a log-log scale. Also shown are the K_d values from a different lot of CST using AP-107 tank waste (Rovira et al. 2018). In both cases, a curve maximum appeared around 7.1 µg/mL Cs.

The K_d value vs. the log of the Cs equilibrium concentration was fit to a third order polynomial equation to calculate the K_d at the feed concentration. At the feed concentration of 9.19 µg Cs/mL, the curve resulted in 806 mL AP-107/g CST. Rovira et al. (2018) reported the K_d for CST Batch 2081000057 at 670 mL AP-107/g CST. Thus, the current test batch of CST was demonstrated to have higher Cs capacity than that of Batch 2081000057 in the AP-107 feed condition.

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) according to Eq. (4.1). The CST bed density is the dry CST mass divided by the volume in the column. With a CST bed density of 1.01 g/mL (Fiskum et al. 2019), the theoretical 50% breakthrough (λ) for AP-107 with 9.19 µg/mL Cs is predicted to be 814 BVs.

$$K_d \times \rho_b = \lambda \tag{4.1}$$

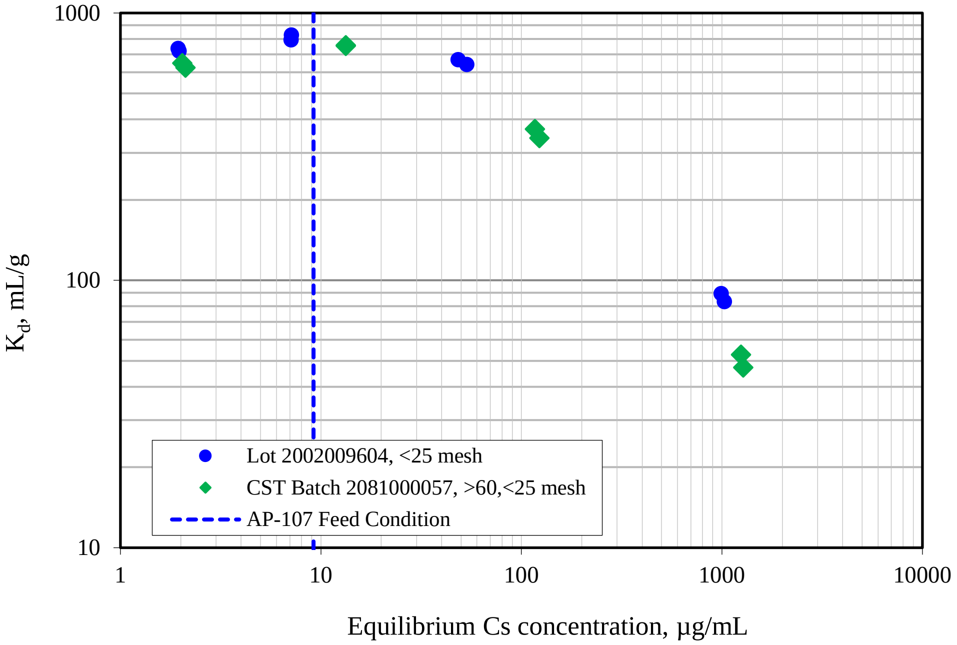

Figure 4.1. Equilibrium Cs K_d Curves for AP-107 with Two Lots of CST

Figure 4.2 provides the isotherms for the AP-107 batch contact test samples with both batches of CST. In this case, the abscissa equilibrium Cs concentration is expressed in terms of molarity and the ordinate is expressed in terms of Q (mmoles Cs/g CST). The isotherm was fit to the Freundlich/Langmuir Hybrid equilibrium isotherm model (see Hamm et al. 2002) according to Eq. (4.2). The expected Cs loading onto the CST at a given Cs concentration can be determined from the isotherm.

$$\frac{\alpha_i \times [Cs]}{(\beta + [Cs])} = Cs_{IX} \qquad (4.2)$$

where:

$[Cs]$ = equilibrium Cs concentration (mmoles Cs/mL)
Cs_{IX} = equilibrium Cs loading on the CST (mmoles Cs per g CST)
α_i = isotherm parameter constant (mmoles Cs/g CST)[1]
β = isotherm parameter constant (mmoles Cs/mL)[2]

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[1] The α_i parameter represents the maximum Cs capacity in the CST (Hamm et al. 2002).

[2] The β parameter incorporates the selectivity coefficients, making it dependent on temperature and liquid composition of all the ionic species in solution; the larger the beta parameter, the less favorable (and lower loadings) an isotherm will be (Hamm et al. 2002).

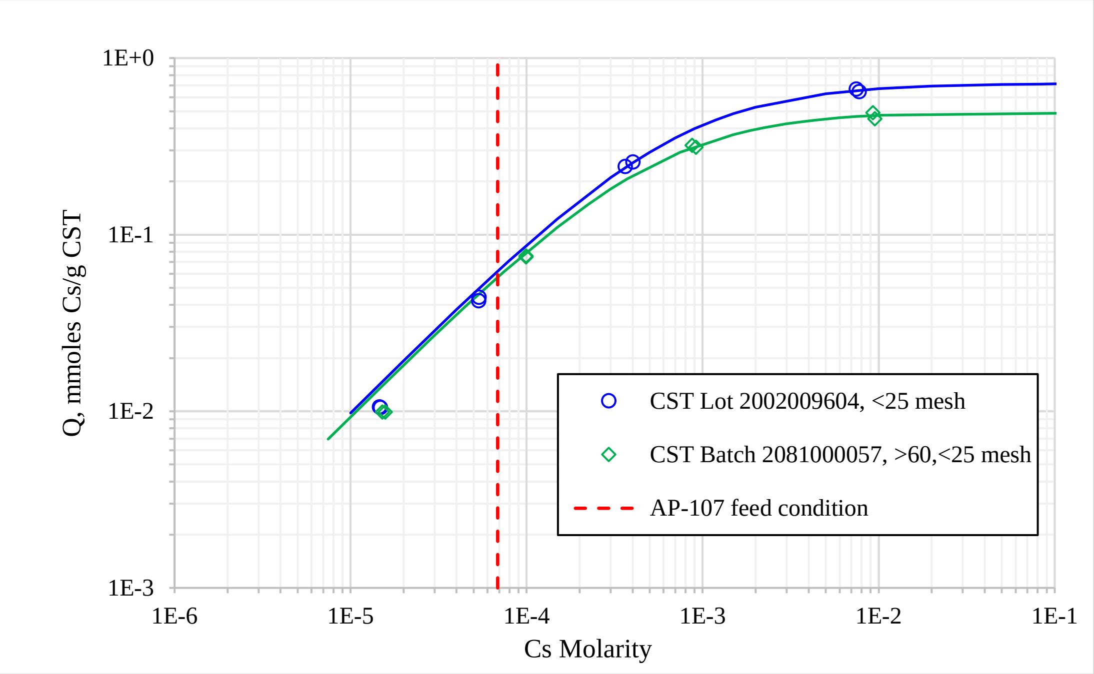

Figure 4.2. Isotherm for AP-107 Tank Waste with Two Lots of CST

Figure notes: At the equilibrium Cs concentration of 9.19 µg Cs/mL (6.85E-5 M), the equilibrium Cs loading on CST Lot 2002009604 corresponded to 0.062 mmole Cs per g dry CST (8.3 mg Cs/g CST).

The α_i and β parameters for current and past testing are summarized in Table 4.2. Both the α_i and the β parameters were significantly higher than those reported by Hamm et al. (2002) (α_i of 0.3944 mmoles Cs/g CST and average β value of 2.8552E-4 M Cs for Envelope A tank waste). The Cs capacity α_i parameter conformed to 0.72 mmoles Cs/g CST, which was consistent with the 0.70 mmoles Cs/g CST capacity measured with AW-102 diluted tank waste (Rovira et al. 2019). The AP-107 β parameter conformed to 7.25E-4 mmoles Cs/mL, which was higher than that of AW-102 test (5.84E-4 mmoles Cs/mL). The CST Lot 2002009604 demonstrated 44% higher total Cs capacity than that of Batch 2081000057 (α_i 0.72 vs 0.50); the β parameters (matrix effect) differed by 36% (7.24E-4 vs 5.3 E-4 M Cs). However, at the equilibrium condition of 6.85E-5 M Cs, Q (Cs loading) values in the AP-107 matrix only differed by 9% between the two different CST lots (0.062 vs. 0.057 mmoles Cs/g CST, Lot 2002009604 and Batch 2081000057, respectively).

Table 4.2. α_i and β Parameter Summary

Matrix	CST Lot or Batch No.	α_i, (mmoles Cs/g CST)	β, (Cs M)	Reference
AP-107	2002009604	0.72	7.25E-4	This report (Fiskum et al.)
AP-107	2081000057	0.50	5.3E-4$^{(a)}$	Rovira et al. 2018
AW-102	2002009604	0.70	5.84E-4	Rovira et al. 2019
Envelope A	Not defined	0.3944	2.8552E-4	Hamm et al. 2002

(a) Calculated from reported raw data.

5.0 Column Processing

This section discusses the Cs exchange behavior during the load, FD, water rinse, and final solution flush from the system. Raw data are provided in Appendix A.

5.1 Cs Loading for AP-107, Feed Displacement, and Water Rinse

The AP-107 feed was processed at nominally 1.88 BV/h through the lead, middle, and polish columns. Figure 5.1 shows a linear-linear plot of the cesium load profile for feed processed through each column. 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 C_0 value for ^{137}Cs was determined to be 145 µCi/mL (average of the seven filtered feeds, relative standard deviation of 2.5%). In this graphing layout, the Cs breakthrough from the lead column appeared to start at ~280 BVs and continued to 41% C/C_0 after processing 815 BVs when the last sample was collected from the lead column. Feed processing continued for 40 BVs past this last sample collection point for a total of 855 BVs. The final feed loading was extrapolated to 44% C/C_0 before FD was initiated. Because the polish column was in place to further remove Cs from the effluent, the system could process well beyond the 25% C/C_0 implemented on the previous AP-107 testing where the two-column system was used (Rovira et al. 2018). It is obvious that the middle and polish column Cs breakthrough performances are not discernable at this linear scale.

Figure 5.2 shows the same Cs load data provided in Figure 5.1, but with the ordinate % C/C_0 on a probability scale and the abscissa BVs processed on a log scale. Under normal load processing conditions, these scales provide a predictable straight-line Cs breakthrough curve and provide greater fidelity of load characteristics at low and high % C/C_0 values (Buckingham 1967). In contrast to Figure 5.1, the Cs breakthrough from the lead column was observed to occur between 60 and 90 BVs processed. In addition to the 50% C/C_0 indication line, the WAC at 0.127% C/C_0 is also apparent (dotted red line).[1] The WAC Cs breakthrough for the lead column occurred at 200 BVs. The middle column WAC Cs breakthrough occurred at ~590 BVs. The polish column did not reach the WAC limit after processing 844 BVs.

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[1] The WAC limit was derived from the allowed curies of ^{137}Cs per mole of Na in the effluent to support contact handling of the final vitrified waste form—3.18E-5 Ci ^{137}Cs/mole Na. At 5.6 M Na and 145 µCi ^{137}Cs/mL in the feed, the WAC limit is 0.127% C/C_0.

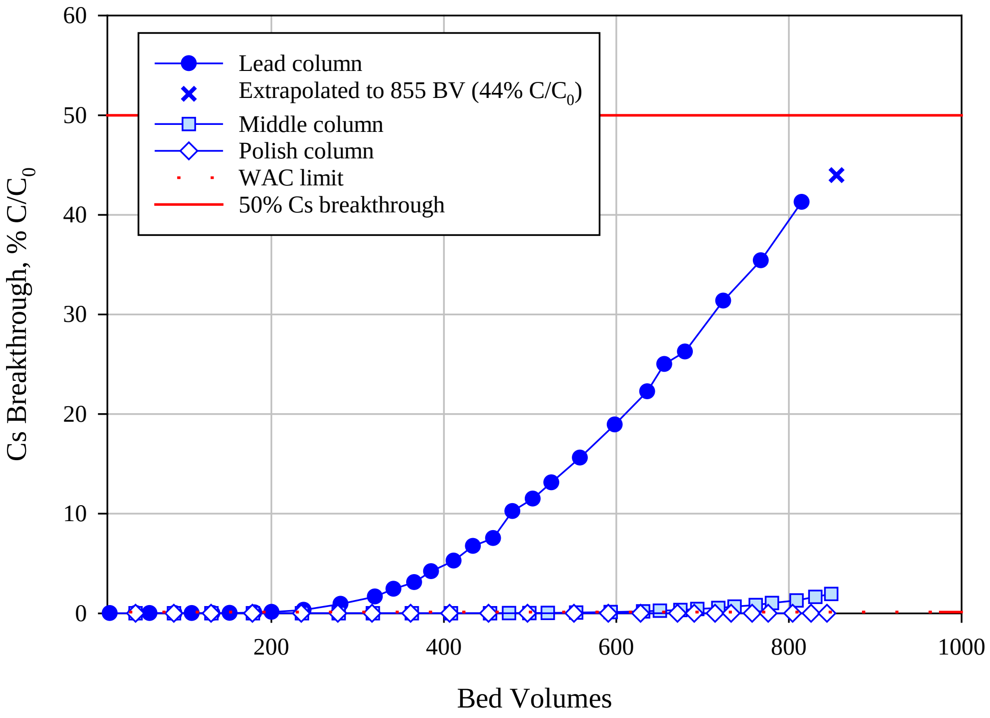

Figure 5.1. Lead, Middle, and Polish Column Cs Load Profiles of AP-107 at 1.88 BV/h, Linear-Linear Plot

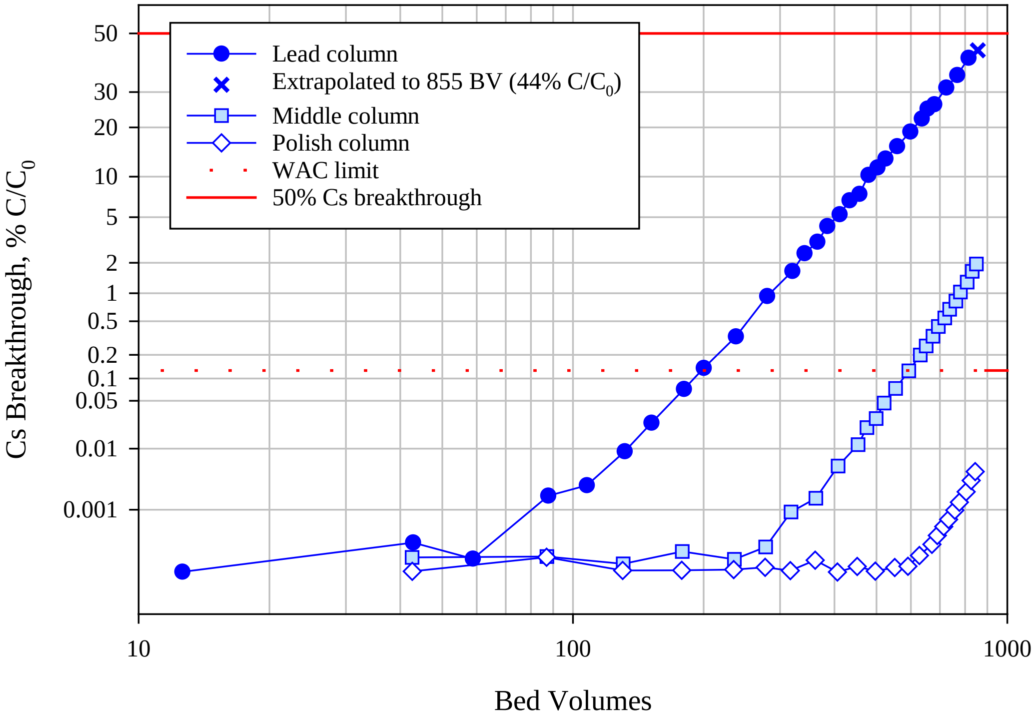

Figure 5.2. Lead, Middle, and Polish Column Cs Load Profiles of AP-107 at 1.88 BV/h, Probability-Log Plot

The 50% Cs breakthrough on the 10.0-mL lead column was not reached because there was insufficient AP-107 feed available at the Radiochemical Processing Laboratory for processing. The lead column data were evaluated to estimate the BVs to 50% breakthrough. The breakthrough curve can be estimated by the error function (erf) (Hougen and Marshall 1947; Klinkenberg 1994):

$$\frac{C}{C_0} = \frac{1}{2}\left(1 + \operatorname{erf}\left(\sqrt{k_1 t} - \sqrt{k_2 z}\right)\right) \tag{5.1}$$

where k_1 and k_2 are parameters dependent on column conditions and ion exchange 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 can then be estimated by multiplication of k_1 and k_2 to give an estimate of 900 BV.

This value was ~11% higher than the 814 BVs Cs λ value predicted from batch-contact studies. Given the extrapolation to 50% breakthrough from column processing and the overall measurement uncertainties, the agreement within 11% was considered reasonable.

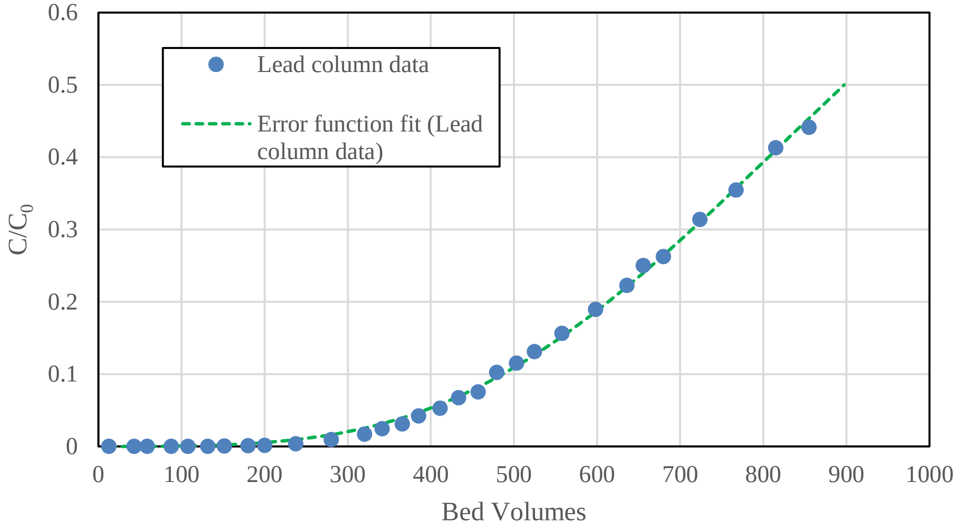

Figure 5.3. Lead Column Extrapolated to 50% Breakthrough

The polish column data from 591 to 844 BVs were evaluated to estimate the BVs processed to WAC limit. The error function fit has some simplifying assumptions that were not valid at these concentrations; therefore, the log of the % C/C_0 values was plotted against the BVs processed (see Figure 5.4). The curve was fitted to a polynomial function ($R^2 = 0.999$), which was then extrapolated to the WAC limit. This evaluation showed that the polish column would reach the WAC limit after processing ~1010 BVs.

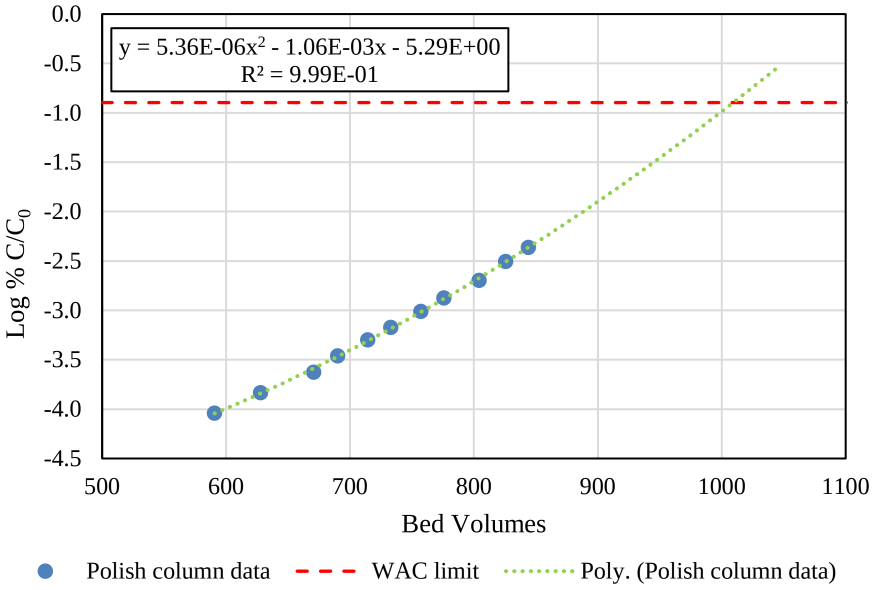

Figure 5.4. Polish Column Extrapolated to WAC Limit

Figure 5.5 shows the Cs breakthrough profile of the polish column with the FD, water rinse, and the final flushed fluid from the column system on a log-linear plot. These scales provide better Cs concentration resolution of the various effluent solutions relative to graphing on a linear-linear scale or probability-log scale. As previously observed, the FD exhibited declining Cs concentration with increased process volume through the first 9.5 BVs (1.3 AVs) processed, then a slight increase in Cs effluent concentration was observed. As water rinsing commenced, the Cs concentration in the effluent continued to increase, approaching the Cs concentration in the last load effluent sample. The Cs concentration in the final flush solution exceeded the last sample Cs concentration collected from the polish column. In all cases, these rinse solutions remained below the WAC limit. If AP-107 processing continued until the polish column reached the WAC limit, it is possible that parts of the water rinse could also approach the WAC limit and the final solution flush could exceed the WAC limit.

The full height column test resulted in a similar Cs leakage characteristic during the water rinsing step (Fiskum et al. 2019). The flowrate was higher (shorter residence time) for the AP-107 test relative to the full height test at 4.54 BV/h (12.3 BVs) and 3.3 BV/h (10.7 BVs), respectively. The corresponding linear flow velocity was much reduced for the AP-107 test relative to the full height test, 0.43 cm/min and 12.3 cm/min, respectively. In the case of the full height test, the Cs leakage appeared to taper after processing 9 BVs (last sample collected). In contrast, the Cs leakage from the AP-107 test showed no signs of tapering after processing 9 BVs. This issue may have ramification for how the rinse water is dispositioned post-ion exchange processing.

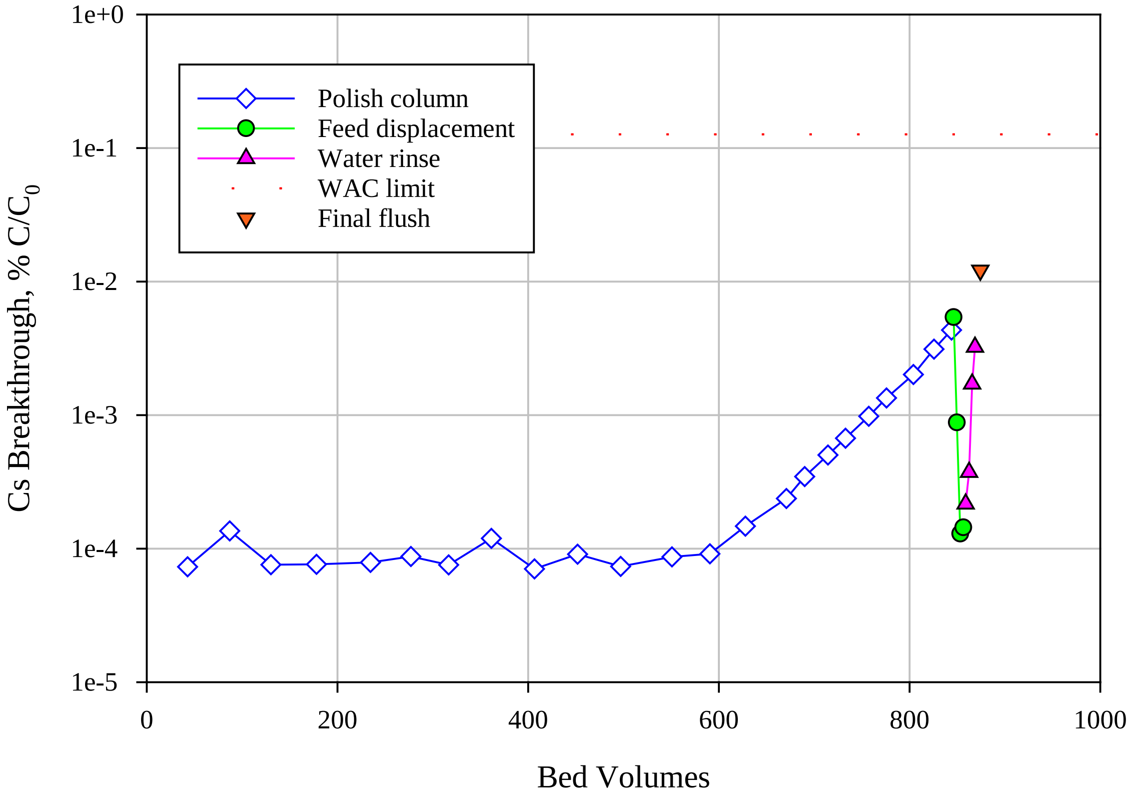

Figure 5.5. Polish Column Cs Load Profile with Feed Displacement, Water Rinse, and Column Flush Solution

Figure 5.6 compares the AP-107 lead and lag/middle column Cs load profiles for two CST materials, Lot 2002009604 (current test data set) and Batch 2081000057 (Rovira et al. 2018). Rovira et al. (2018) Cs load profile results were clearly offset to the left for both the lead and lag columns relative to the current testing lead and middle columns. The CST capacity for CST Lot 2002009604 was shown to be higher than that of Batch 2081000057 from batch contact testing. The Cs loading profile will shift right as the media Cs capacity increases. The kinetic exchange rate was not appreciably different between the two tests based on the similarity in the slopes of Cs loading curves and despite the difference in flowrates (2.2 BV/h compared to 1.9 BV/h).

Figure 5.6 also compares the AP-107 load profiles with the AW-102 load profiles (Rovira et al. 2019) where the same CST Lot 2002009604 was used. The Cs capacities appeared to be similar for these two matrices based on the general congruency of the lead column load profiles. The middle column from the current study and lag column from AW-102 processing were compared. In this case, the Cs load profiles showed a wider gap in performance where the AW-102 Cs load data resulted in a delayed breakthrough (~100 BVs) relative to the AP-107 Cs load data. This effect may be consistent with the higher β parameter for AP-107 than that of AW-102; the β parameter increases with increasing adverse matrix effects on Cs loading (see Section 4.0 of this report and Hamm et al. 2002). It is noted that the K concentration was 58% higher in AW-102 than in AP-107; K is a competitor for Cs on CST.

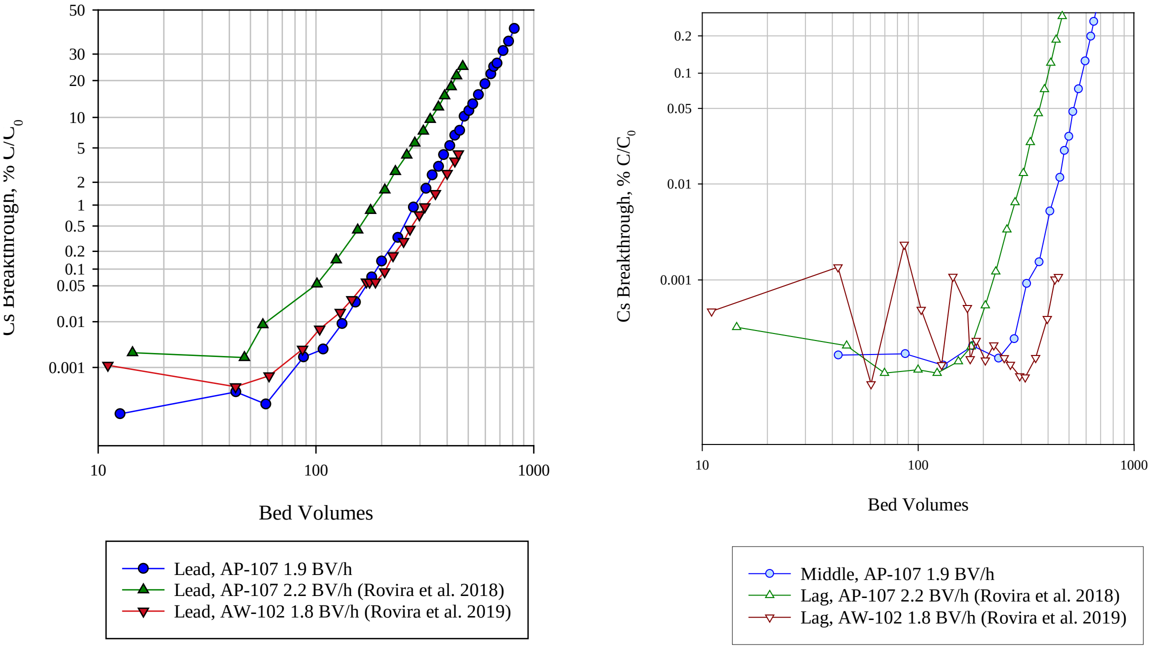

Figure 5.6. AP-107 (Two Tests) and AW-102 Load Profiles Comparisons

Figure notes: Rovira et al. (2018) used CST Batch 2081000057; Rovira et al. (2019) used CST Lot 2002009604

The AP-107 lead column Cs breakthrough data were compared with full-height and medium-height testing of 5.6 M Na simulant previously reported (Fiskum et al. 2018). The CST production lots used in testing were the same, and the residence times in the lead columns were similar at 1.88 BV/h for AP-107 and 1.82 and 1.83 BV/h for the 5.6 M Na simulant tests. The full-height column replicated the anticipated TSCR column height (234 cm); the medium column height was 12% of the full height column (27 cm). At 5.6 cm tall, the CST beds used to process AP-107 were only 2.4% of the full-height column. The efficacy of using the small-scale column (5.6 cm tall/10-mL CST bed) to accurately predict large-scale column performance has not been substantiated. Therefore, the differences in load profiles (i.e., onset of Cs breakthrough and achieved Cs load capacity) cannot be totally separated from column geometry differences. Differences in the feed compositions may also affect the comparative Cs load performances. The feed Cs concentrations differed slightly from 7.9 µg/mL for the simulant to 9.19 µg/mL for AP-107. The AP-107 contained additional components not intentionally added to the simulant (such as Ca, Cr, Fe, U, Pu, and other trace components). The Na concentrations were equivalent within analytical uncertainty.

Figure 5.7 and Figure 5.8 compare the Cs load curves for the 5.6 M Na simulant tests and the AP-107 test. Figure 5.7 shows the lead column Cs load profiles only from AP-107 processing and the Blue (full height) and Red (12% full-height) columns previously described (Fiskum et al. 2018). The AP-107 Cs broke through the lead column sooner than the Cs from simulant tests. Divergence in the load profiles increased from ~50 to ~100 BVs as the processed BVs increased from 160 to 800 BVs.

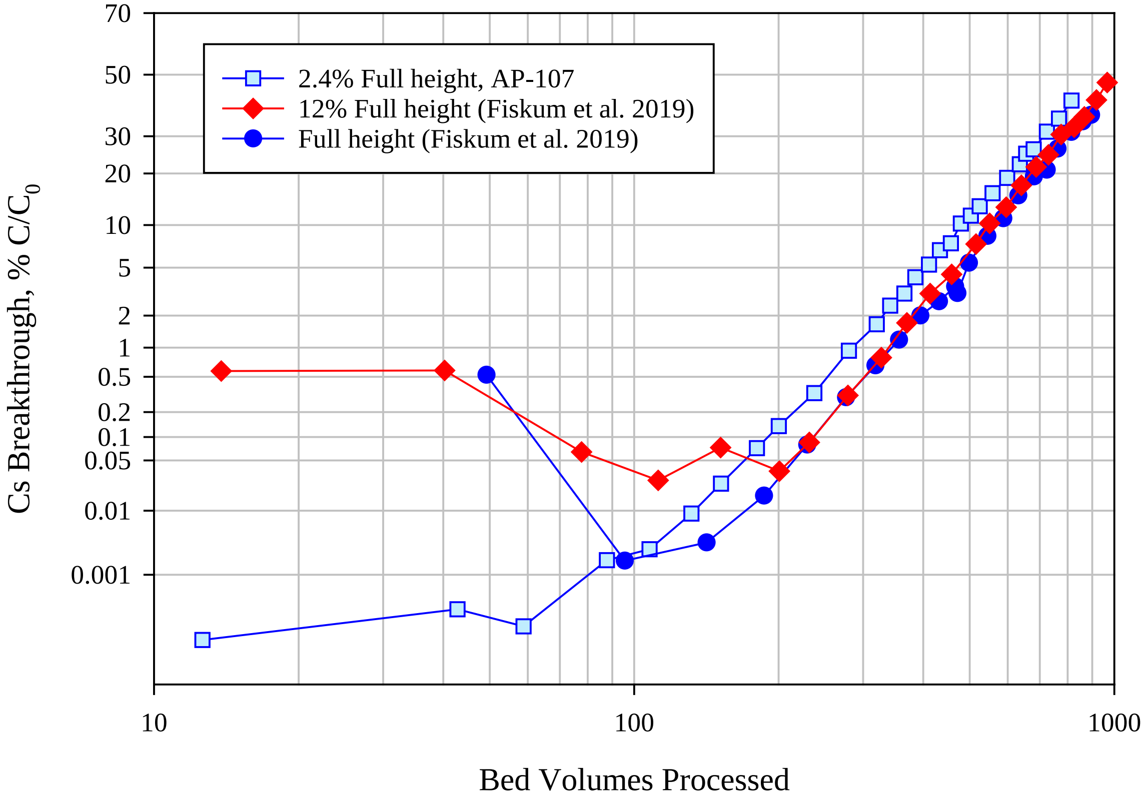

Figure 5.7. Cs Load Profile Comparisons at ~1.85 BV/h

Figure notes:

- AP-107 processed at 1.88 BV/h, 9.19 µg/mL Cs, 0.096 M K, 0.89 M OH; lead column test data
- Fiskum et al. (2018) processed 5.6 M Na simulant at 1.83 BV/h, 7.9 µg/mL Cs, 0.12 M K, 1.4 M OH; lead column test data

Similarly, Figure 5.8 compares the system volumes (SVs) and system flowrates for the Orange (full-height lead plus lag) column (Fiskum et al. 2019) and the small (10.0 mL), combined lead, middle, polish columns from the AP-107 test. The AP107 system BV was 30 mL (3 x 10-mL beds) and flow rate for the system was one third of the baseline flow rate at 0.63 SV/h (1.88 BV/h ÷ 3). Similarly, Fiskum et al. (2018) described the Orange column system of 1.18 L BV (2 x 592-mL beds) at a flow rate for the system one half of the baseline flowrate at 0.65 SV/h (1.13 BV/h ÷ 2). In each case, the system flow rate nominally corresponded to 0.64 SV/h and can be compared based on the common residence times in the system CST beds. The C/C_0 detection limit was much improved for the AP-107 test relative to the Orange column test simply from the increased ^{137}Cs concentration. However, the Cs breakthrough curves join at nominally 0.002% C/C_0, Orange column ^{137}Cs detection limit. At this juncture, the AP-107 Cs breakthrough is shown to precede the Orange column Cs breakthrough by ~43 system BVs, similar to that found for the 1.88 BV/h comparison discussed above.

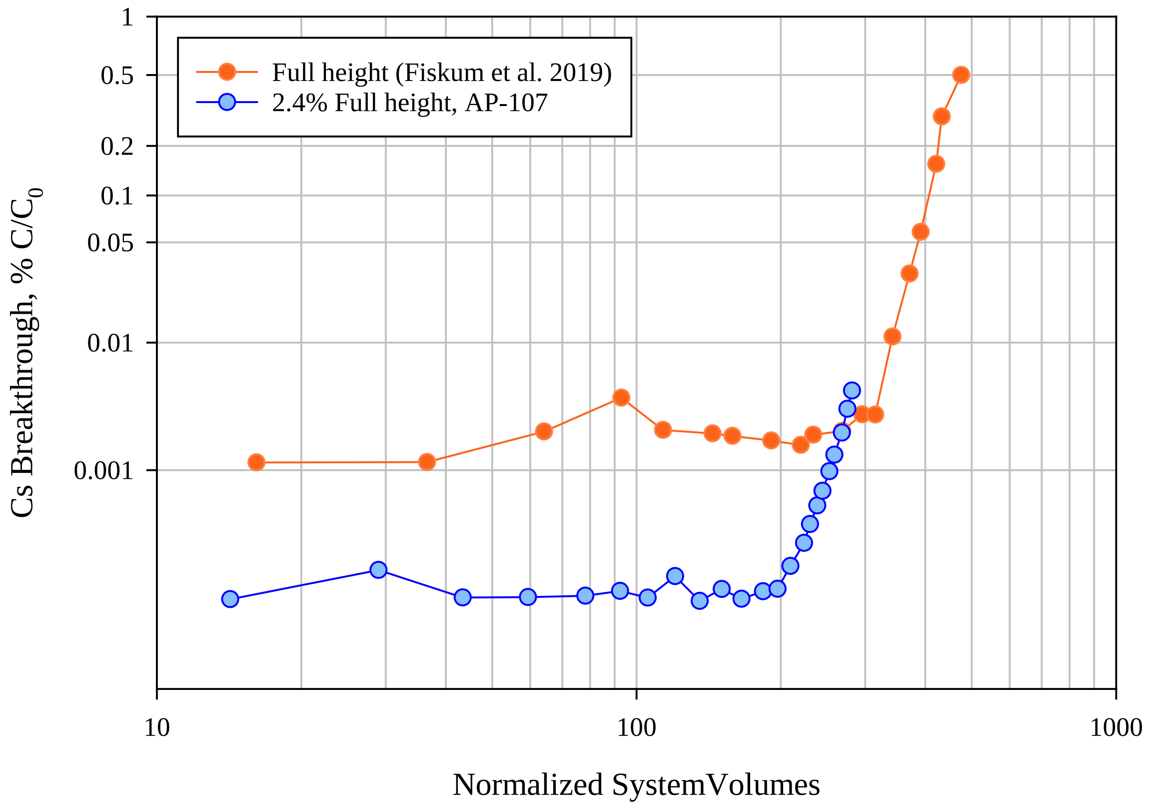

Figure 5.8. Cs Load Comparison at ~0.65 SV/h

Figure notes:

- AP-107 processing through the polish column, normalized to a 30-mL SV (three columns at 10-mL per column), and system flowrate 0.63 SV/h (1.88 BV/h ÷ 3)
- 5.6 M Na simulant processing through the full height system Orange lag column, normalized to a 1.18 L SV (two columns at 0.592 L columns), and system flowrate of 0.65 SV/h (1.30 BV/h ÷ 2)

These results indicated the CST Cs exchange capacity was consumed sooner in AP-107 processing, likely from a combination of factors including slightly higher Cs concentration in AP-107 (9.19 ug/mL vs 7.9 ug/mL); other competitors such as Sr, U, Pu, and Ca; and matrix effects from different K^+ and OH^- concentrations.

In both evaluations (Figure 5.7 and Figure 5.8), load curves were essentially parallel by observation, indicating common Cs exchange kinetics between the different matrices. Thus, despite the Cs breakthrough offset, the 5.6 M Na simulant tests were reasonable predictors of the AP-107 Cs exchange performance.

5.2 Cesium Activity Balance

The Cs fractionations to the effluents and the columns were determined based on the known input ^{137}Cs and the measured ^{137}Cs in the various effluent streams. The quantities of Cs loaded onto the lead, middle, and polish columns were determined by subtracting the Cs recovered in the samples and effluents from the Cs fed to each column. Table 5.1 summarizes the ^{137}Cs fractions found in the various effluents as well as the calculated ^{137}Cs column loadings. About 87% of the total Cs loaded onto the lead column, 12% loaded onto the middle column, and 0.22% loaded onto the polish column. Sample and effluent collection amounted to less than 1% of the input Cs. Although the polish column did not accumulate a significant fraction of the Cs (0.22%), its presence was crucial to preventing the effluent from exceeding the WAC limit while loading over 590 BVs (middle column WAC limit processing volume) of AP-107 feed.

Table 5.1. ^{137}Cs Activity Balance for AP-107

Input	µCi	%
Feed sample	1.23E+06	100
Output		
Effluent-1 (0-131 BVs)	0.136	1.10E-05
Effluent-2 (131-280 BVs)	0.166	1.35E-05
Effluent-3 (280-411 BVs)	0.136	1.10E-05
Effluent-4 (411-558 BVs)	0.155	1.26E-05
Effluent-5 (558-680 BVs)	0.240	1.94E-05
Effluent-6 (680-786 BVs)	0.936	7.58E-05
Effluent-7 (786-855 BVs)	2.59	2.10E-04
Load samples	939	7.61E-02
Feed displacement, water rinse and flush	1.45	1.17E-04
Total ^{137}Cs recovery	945	0.077
Total ^{137}Cs Column Loading		
Lead column Cs loading	1.08E+06	87.4
Middle column Cs loading	1.52E+05	12.3
Polish column Cs loading	2.75E+03	0.22
Column total	1.23E+06	99.9

The total Cs loaded per g CST was calculated from the total Cs loaded onto the lead column, which was nearly fully saturated under these load conditions (estimated 44% Cs breakthrough), and the dry CST mass loaded into the lead column according to Eq. (5.2).

$$\frac{\mathrm{A_{Cs}} \times \mathrm{CF}}{\mathrm{M}} = \mathrm{C} \tag{5.2}$$

where

$\mathrm{A_{Cs}}$ = activity of ^{137}Cs, µCi on the lead column
CF = conversion factor, mg Cs/µCi ^{137}Cs
M = mass of dry CST (10.1 g)
C = capacity, mg Cs/g CST

A total 6.76 mg Cs/g CST (0.0504 mmoles Cs/g CST) was loaded onto the lead column. This represented ~81% of the total capacity found from batch contact testing (see Section 4.0); the lower Cs loading was consistent with the fact that the 50% Cs breakthrough was not quite attained. The total Cs loading onto CST following AP-107 processing at the conclusion of testing was similar to those of the simulant tests (see Table 5.2).

Table 5.2. Cs Loading onto CST Comparison

Test	CST Cs loading (mg Cs/g CST)
AP-107, 2.4% full height	6.76
5.6 M Na simulant, 12% full height	6.95
5.6 M Na simulant, 100% full height	6.60

5.3 WAC Limit

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 flowrate on BVs processed to WAC limit is of special interest. Fiskum et al. (2018, 2019) examined this effect using 5.6 M Na simulant solutions and found the data fit a power curve. In these evaluations, the test column systems were evaluated in segmented units or SVs.

- The first column was evaluated as a unit with the SV defined as the first column BV.
- The first/second columns were evaluated as a unit with the SV defined as the combined CST volume in the two columns.
- The first/second/third columns were evaluated as a unit with the SV defined as the combined CST volume in the three columns, and so on.

The flowrates were calculated based on the residence time in the unit in terms of SV/h. Fiskum et al. (2019) showed that 400 SVs could be processed if the flowrate was reduced to 0.42 SV/h using the 5.6 M Na simulant. In a two-column system, this would equate to 0.84 BV/h, where BV is defined as the lead column CST volume. In a three-column system, the corresponding flowrate would equate to 1.26 BV/h.

The current TSCR approach is to process three columns at 1.9 BV/h, which equates to 0.63 SV/h. Given the simulant results, this was expected to be sufficient for the third column to maintain effluent below the WAC limit. The three columns used to test AP-107 were evaluated in a similar approach. SVs, flowrate, and SVs to WAC limit are provided in Table 5.3. These data are also superimposed on the previously reported graphed data set in Figure 5.9. The AW-102 lead column datum (Rovira et al. 2019) was also incorporated (WAC limit reached at 214 BVs at a flowrate of 1.81 BV/h). The lead column AP-107 and AW-102 data points fall on the curve established from simulant testing. However, the second and third data points for AP-107 define a different trajectory with fewer SVs processed to reach WAC limit than predicted by testing with the 5.6 M Na simulant. This indicated that components in the tank waste were consuming or otherwise affecting exchange sites that were not well modeled by the simulant.

Table 5.3. Bed Volumes Processed to Reach WAC Limit

AP-107 Systems	SV (mL)	Flowrate (SV/h)	SVs to WAC Limit
Lead column	10	1.88	200
Lead/middle column	20	0.94	594
Lead/middle/polish column	30	0.63	337[(a)]

(a) Extrapolated value from 281 BVs and 4.35E-3% C/C_0.

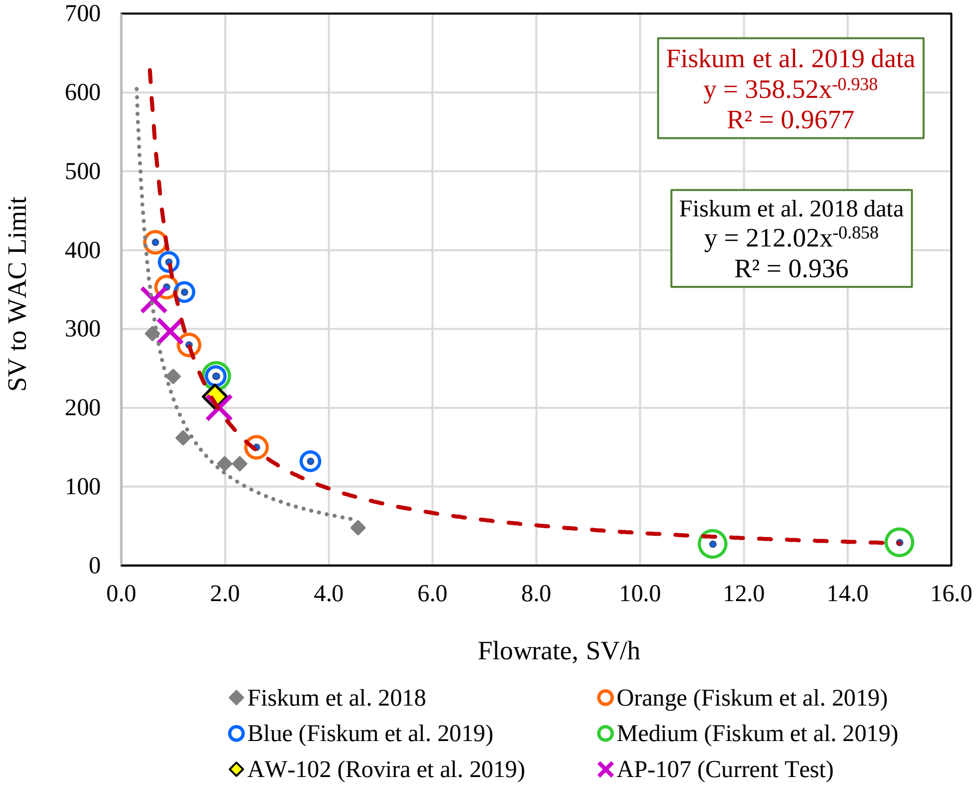

Figure 5.9. System Volume to WAC Limit vs. Flowrate

Figure notes:

- Fiskum et al. 2018, 5.6 M Na simulant test matrix CST Batch 2081000057, two serial 10-mL CST beds.
- Fiskum et al. 2019, 5.6 M Na simulant test matrix, CST Lot 2002009604.
    - Orange and Blue column data collected from four serial ~0.592-L CST beds.
    - Medium column data were collected from single 44-mL CST beds.
- AW-102 datum collected from single 10-mL CST bed (lead column), CST Lot 2002009604 (Rovira et al. 2019).
- The left most data point from AP-107 (current test) was extrapolated, CST Lot 2002009604.

5.4 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% Cs breakthrough point is the inflection point around which the transition zone pivots. In the current study, the lead column was only loaded to 44% Cs breakthrough; the 50% breakthrough was extrapolated to ~919 BVs (see Section 5.1). The number of BVs processed between 20% and 50% Cs breakthrough was calculated from the load curve. This value was doubled to determine the 20% to 80% Cs breakthrough transition zone: 598 BVs. Similarly, the transition zone between 5% and 95% Cs breakthrough was calculated: 1000 BVs. Table 5.4 compares the transition zones for AP-107 to those measured with 5.6 M Na simulant; comparison to Rovira et al. (2018) AP-107 results was not included because Cs loading only resulted in 25% Cs breakthrough. The AP-107 transition zone was ~100 BVs shorter than that determined with the 5.6 M Na simulant (CST Lot 2002009604). The fundamental reason for a decreased transition zone is not understood at this time. It is noted that the simulant hydroxide concentration was ~58% higher than that of AP-107; increased hydroxide concentration improves Cs exchange onto CST supporting the observed delayed Cs breakthrough. Note that the simulant and AP-107 K concentrations were essentially identical (0.122 and 0.120 M, respectively) which minimizes difference from the K competitor effect.

Table 5.4. Transition Zone Comparison

Test	Flowrate (BV/h)	BVs to Cs Breakthrough			Transition Zone, BVs	
		(5%)	(20%)	(50%)	(20-80%)	(5 to 95%)
AP-107[a]	1.88	400	620	~900	~560	~1000
Blue (Fiskum et al. 2019)[a,b]	1.82	492	700	~1050	~700	~1120
Blue (Fiskum et al. 2018)[b,c]	1.99	330	490	1130	640	1600

(a) CST Lot 2002009604
(b) 5.6 M Na simulant matrix
(c) CST Batch 2081000057

5.5 Chemical and Radiochemical Composition

The AP-107 composite feed and composite effluent samples underwent extensive characterization to better define waste characteristics and assess analyte fractionation to the CST. Ten lead column samples were also selected for metal and radionuclide analysis to assess analyte load characteristics (12.6, 87.7, 180, 280, 365, 457, 558, 656, 723, and 815 BVs). Results from the extensive effluent characterization also helped support follow-on vitrification glass formulation.

Table 5.5 summarizes the feed and effluent radioisotope concentrations and fractionations to the effluent. Table 5.6 summarizes the feed and effluent metals concentrations and fractionations to the effluent. The anions, free hydroxide, inorganic carbon, and organic carbon concentrations in the feed are provided in Table 5.7; they were not measured in the effluent because their concentrations were shown not to be affected by the CST processing (Rovira et al. 2018). Analytical reports along with result uncertainties and quality control (QC) discussions are provided in Appendix E.

By inference, the analytes not found in the effluent were assumed to be retained on the CST. Analyte fractionation was calculated as the ratio of the total analyte measured in the feed processed through the columns and the total analyte collected in the Cs-decontaminated effluent according to Eq. (5.3):

$$\frac{C_{Da} \times V_D}{C_{Fa} \times V_F} = F_{Da} \tag{5.3}$$

where:

C_{Da} = concentration of analyte *a* in the Cs-decontaminated effluent
V_D = volume of Cs-decontaminated effluent
C_{Fa} = concentration of analyte *a* in the AP-107 feed
V_F = volume of AP-107 feed
F_{Da} = fraction of analyte *a* in the Cs-decontaminated effluent

Some analyte results are shown in brackets; this indicates that the analytical result was less than the estimated quantitation limit (EQL) but greater than or equal to the method detection limit (MDL) and the associated analytical uncertainty could be higher than ±15%. The fractionation result was placed in brackets where it was calculated with one or more bracketed analytical values to highlight the higher uncertainty. The opportunistic analyte results measured by inductively coupled plasma optical emission spectrometry (ICP-OES) are also shown in Table 5.6; these analytes are part of the ICP-OES data output but have not been fully evaluated for quality control performance. The composite feed sample results in Table 5.5 and Table 5.6 (Al, K, Na, and ^{137}Cs) were compared to the initial characterization sample results (Table 3.2). All results agreed within 10% except for K, which was 20% higher as measured via ASR 0787; this was considered an anomaly.

Table 5.5. AP-107 Feed and Effluent Radionuclide Concentrations and Fractionations (ASR 0787)

Analysis Method	Analyte	TI061-Comp-Feed (µCi/mL)	TI061-Comp-Eff (µCi/mL)	Fraction in Effluent (%)
Gamma energy analysis (GEA)[(a)]	^{60}Co	[5.0E-04]	5.29E-04	107%
	^{126}Sb	<2E-3	1.37E-04	--
	^{137}Cs	1.54E+02	5.29E-04	0.0003%
	^{154}Eu	<2E-3	4.65E-05	--
	^{155}Eu	<3E-2	1.04E-05	--
	^{241}Am	<1E-1	2.45E-04	--
Separations/ Alpha energy analysis (AEA)[(b)]	^{237}Np	4.76E-05	2.02E-05[(c)]	43%
	^{238}Pu	7.54E-05	2.75E-05	37%
	$^{239+240}$Pu	5.60E-04	2.01E-04	36%
Separations/ Beta counting[(b)]	^{90}Sr	4.52E-01	<1E-3	<0.2%
	^{99}Tc	1.00E-01	9.82E-02	99%

(a) Reference date is June 10, 2019.
(b) Reference date is August 2019.
(c) The effluent was analyzed in duplicate and the RPD was 25% exceeding the QC criterion of 20%, see Appendix E.
"--" = not applicable; value not reported or fractionation cannot be calculated with a less-than value.

Table 5.6. AP-107 Feed and Effluent Inorganic Analyte Concentrations and Fractionation (ASR 0787)

Analysis Method	Analyte	TI061-Comp-Feed (M)	TI061-Comp-Eff (M)	Fraction in Effluent
ICP-OES	Ag[(a)]	<4.4E-6	<4.4E-6	--
	Al	3.71E-01	3.61E-01	98%
	As	<1.8E-4	<1.8E-4	--
	Ba	[3.0E-6]	<5.7E-7	--
	Ca	[8.6E-4]	[4.5E-4]	[52%]
	Cd	5.79E-05	[4.7E-5]	[81%]
	Cr	1.01E-02	9.90E-03	98%
	Fe	2.64E-04	[2.2E-4]	[83%]
	K[(b)]	1.20E-01	1.15E-01	97%
	Na	5.97E+00	5.71E+00	96%
	Ni	4.19E-04	3.95E-04	95%
	P	2.82E-02	2.67E-02	95%
	Pb	[3.9E-5]	<1.9E-5	--
	S	6.03E-02	5.75E-02	96%
	Sr	[1.5E-6]	<1.4E-6	--
	Ti	<2.3E-6	[3.9E-6]	--
	Zn	<1.6E-5	[2.0E-5]	--
	Zr	<5.2E-6	[2.3E-5]	--
ICP-MS	^{238}U	7.51E-05	4.53E-05	61%

(a) QC samples recovered only 50% of the Ag.
(b) The K result was ~20% higher in the composite feed analysis than measured in the individual sample aliquots collected from the first and last samples collected from the Hanford tank.

Bracketed results were less than the estimated quantitation limit but greater than or equal to the method detection limit.
"--" indicates the recovery could not be calculated.

Table 5.6 (cont.)

Analysis Method	Analyte	TI061-Comp-Feed (M)	TI061-Comp-Eff (M)	Fraction in Effluent
ICP-OES Opportunistic Analytes	B	2.90E-03	2.03E-03	70%
	Be	[1.5E-5]	[1.2E-5]	[82%]
	Bi	<5.9E-5	<5.9E-5	--
	Ce	<1.2E-5	<1.2E-5	--
	Co	<1.5E-5	<1.5E-5	--
	Cu	[1.8E-5]	<6.4E-6	--
	Dy	<4.4E-6	<4.5E-6	--
	Eu	<2.2E-6	<2.2E-6	--
	La	<3.9E-6	<3.9E-6	--
	Li	[3.3E-5]	<3.3E-5	--
	Mg	<6.9E-5	<6.9E-5	--
	Mn	<9.8E-7	<9.8E-7	--
	Mo	4.62E-04	4.33E-04	94%
	Nd	<1.5E-5	<1.5E-5	--
	Pd	<1.8E-5	<1.8E-5	--
	Rh	<4.0E-5	<4.0E-5	--
	Ru	[7.0E-5]	[6.5E-5]	[94%]
	Sb	<1.1E-4	<1.1E-4	--
	Se	<5.0E-4	<5.0E-4	--
	Si	2.53E-03	[1.5E-3]	[58%]
	Sn	[1.2E-4]	[9.4E-5]	[82%]
	Ta	<3.0E-5	<3.0E-5	--
	Te	[6.6E-5]	<6.1E-5	--
	Th	<2.0E-5	<2.0E-5	--
	Tl	<6.5E-5	<6.5E-5	--
	U	[6.4E-5]	<3.8E-5	--
	V	[1.5E-5]	<1.0E-5	--
	W	3.86E-04	3.69E-04	96%
	Y	<3.4E-6	<3.4E-6	--

Bracketed values indicate the associated sample results were less than the EQL but greater than or equal to the MDL. Analytical uncertainty for these analytes is > ±15%.
"--" indicates the recovery could not be calculated.

Table 5.7. AP-107 Feed Free Hydroxide and Carbon Composition (ASR 0787)

Analysis Method	Analyte	TI061-Comp-Feed (µg/mL)	TI061-Comp-Feed (M)
Titration	Free Hydroxide	1.51E4	0.89
Hot persulfate oxidation	Total organic C	2,170	0.18
	Total inorganic C[(a)]	7,749	0.65

(a) Assumed to be carbonate.

In addition to Cs, the CST quantitatively removed ^{90}Sr (Sr) with a decontamination factor of ≥450. The ^{90}Sr removal agreed with previous testing (Rovira et al. 2018 and 2019). About 57% of the Np and 64% of the Pu were also removed. The Np and Pu removal factors were consistent with those reported by Rovira et al. (2018). Assuming the difference in total Np and Pu µCi content between the feed and effluent remained with the CST, the CST would contain 123 nCi/g TRU, exceeding the 100 nCi/g threshold defining TRU waste. The ^{60}Co (Co) and ^{99}Tc were not affected by the CST and reported to the effluent.

The feed composite and effluent composite ICP-OES results showed that the majority of analytes remained in the effluent. (See Table 5.6 and Appendix E for analytical reports.) The Al, Cr, K, Na, Ni, P (phosphate), and S (sulfate) partitioned exclusively to the effluent (>95% recovery). Ba, Pb, and Sr were detected in the feed (with high errors likely exceeding 15%) but were below the MDL in the effluent composite. Ca and U were partially removed by the CST with only ~52% and 61% reporting to the effluent, respectively. By difference, ~3.5 mmoles of Ca were removed from the 8.55 L AP-107 feed, resulting in a loading of ~0.12 mmoles Ca per gram CST (30 g total CST). Similarly, 0.25 mmoles of U were removed from the feed, resulting in a loading of ~0.0084 mmoles U per gram CST.

The load behaviors of selected analytes were examined as a function of BVs processed from the lead column. (Raw data are provided in Appendix B.) Figure 5.10 shows the Al, Ca, Fe, and U breakthrough results. Al breakthrough can serve as an internal standard for the ICP-OES analysis and Fe and Al breakthrough track similarly (notwithstanding the two high flier Fe values). Initially, U is shown to break through slowly on the CST with full recovery occurring starting at about 200 BVs (thus, a 200-BV transition zone). Ca recovery was essentially flat at ~66% breakthrough with no evidence of a breakthrough curve. Both the feed and effluent Ca concentrations were reported with high uncertainty; however, the results were generally similar to those previously reported (Rovira et al. 2018). It is possible that the Ca is present in a multiplicity of chemical forms in the solution such as oxalate, carbonate or sulfate complexes. Additionally, 60-70% of Ca as $Ca(OH)_{2(aq)}$ has been reported in high (e.g., 1 M) NaOH solutions (Kutus et al., 2016). The complexed Ca and $Ca(OH)_{2(aq)}$ would likely not exchange onto CST. It is probable that 34% of the Ca in AP-107 exists in a form amenable to ion exchange or as a suspended colloid form that filters onto the media.

Small concentrations of Ti (0.23 µg/mL) and Zr (1.4 µg/mL) were observed in each of the selected lead column effluent samples (see also Table 5.6 for feed and effluent sample concentrations). Neither Ti nor Zr were detected in the feed; therefore, it was inferred that some small, continuous breakdown of the CST may have occurred during processing. These results were contrary to those reported by Rovira et al. (2018) with AP-107 testing (two columns). However, in that case, a different lot of CST was used and small levels of Ti and Zr were identified in the feed (0.8 and 1.4 µg/mL, respectively) and were equivalent to that of the effluent. Thus, at best, attrition of Ti and Zr should be considered inconclusive.

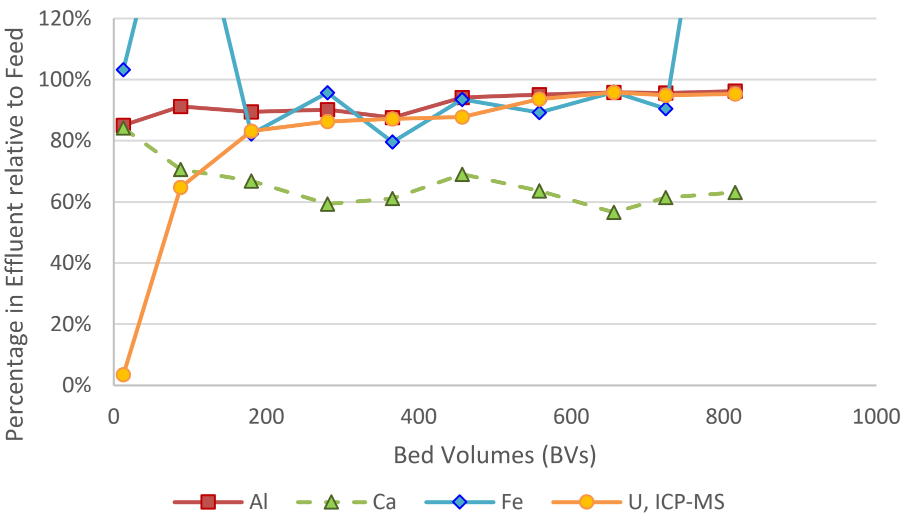

Figure 5.10. Al, Ca, Fe, and U Load Profiles onto the Lead Column

Figure Notes:

- Analytes with dashed lines indicate data were ≥ MDL but < EQL, with errors likely to exceed 15%.
- Two Fe results at 179% and 230% recoveries were likely contaminated in the analysis process.

Resource Conservation and Recovery Act (RCRA) elements were examined and are graphed in Figure 5.11 (Al recovery used as a general recovery marker). Except for the first sample Cd result, there seemed to be relatively no difference in any of the analyte percentage recoveries in the effluent with increased loading. Ba and Pb were detected in the feed (with errors likely to exceed 15%) but were not detected in the lead column effluent samples. Ag and Cd were not detected in the feed or effluent samples. Cr and Ni, like Al, reported solely to the effluent. Data from Figure 5.11 are shown in tabular form in Appendix B.

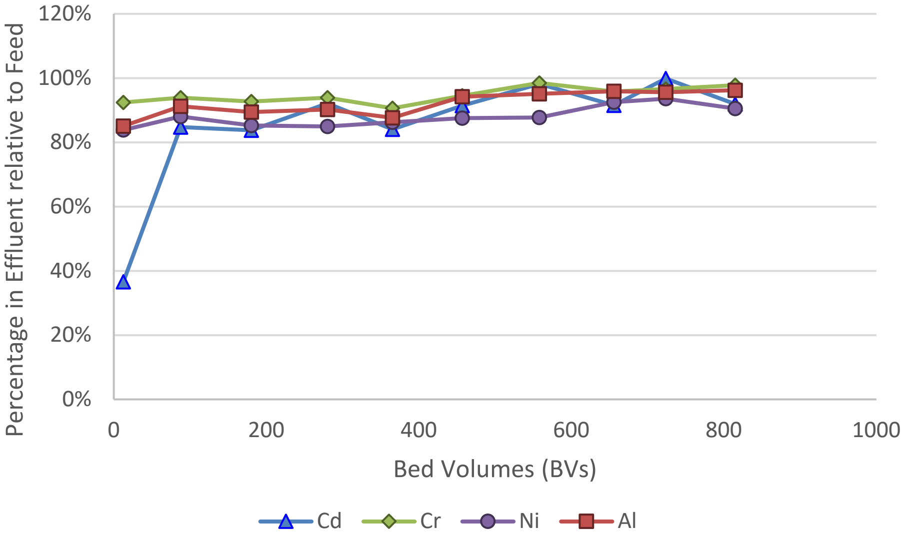

Figure 5.11. RCRA Metal Recoveries during Lead Column Processing; Ag, As, Ba Were Not Detected

Similarly, the selected lead column samples were analyzed for ^{90}Sr, ^{237}Np, ^{238}Pu and $^{239+240}$Pu. Results from both Pu isotopes were equivalent. Figure 5.12 shows the load profiles for these isotopes in comparison with that of ^{137}Cs. The ^{90}Sr clearly did not break through the CST after processing 815 BVs feed. The anomalously high ^{90}Sr result at 280 BVs was likely associated with in-cell contamination. The Np breakthrough profile showed increasing effluent concentration from 10% to 60% in the 12 to 300 BVs range at which point a steady state was reached. It is unclear why the breakthrough profile did not increase in a more normal manner, extending toward 100% breakthrough. The Pu demonstrated an initial 40% breakthrough and very slowly increased to 60% breakthrough to the end of testing. The Pu exchange may be limited by the Pu oxidation state (e.g., mixture of III and IV) and/or the nature and extent of a Pu complexant.

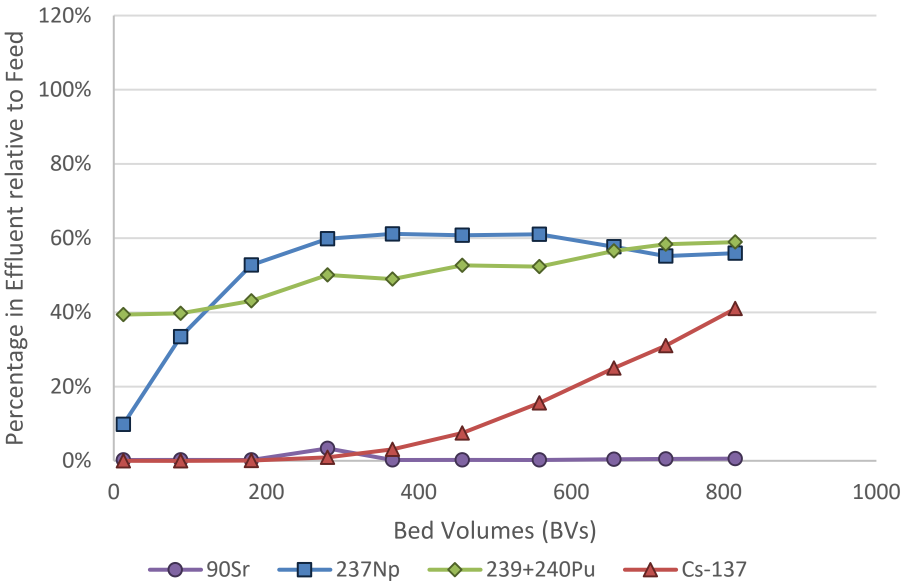

Figure 5.12. ^{90}Sr, ^{137}Cs, ^{237}Np, and $^{239+240}$Pu Load Profiles onto the Lead Column

6.0 Conclusions

Cesium ion exchange batch contact and column testing with CST Lot 2002009604 was conducted to assess Cs exchange performance with AP-107 tank waste. By necessity, testing was conducted at a small scale given the high radiological dose rate of the Hanford tank waste matrix. WRPS established five objective outcomes for this testing; all objectives for CST testing were met.

1. Conduct batch contact testing with CST to determine the Cs load capacity of AP-107.
2. Process filtered AP-107 through a lead-lag-polish column configuration and establish a Cs load profile.
3. Compare the AP-107 Cs load curve results to the previously reported AP-107 load curve results (Rovira et al. 2018).
4. Analyze the feed and effluent to discern the fates of key analytes.
5. Provide the decontaminated AP-107 tank waste (8.55 L) and the Cs-loaded CST for follow-on testing (vitrification and analysis, respectively).

The results summary is provided below.

6.1 Batch Contact Testing

Batch contact testing with CST was conducted to determine the Cs K_d value at equilibrium AP-107 conditions and the total Cs load capacity in the AP-107 matrix. Duplicate tests were conducted; the primary test matrix was mixed for 104 h and the duplicate was mixed for 71 h. The following conclusions were made as a result of this work.

1. Equilibrium was achieved by the 71-h contact time (conditions: orbital shaker at ~400 rpm, 15-mL solution in a glass 20-mL LSC vial, phase ratio ~200). This was consistent with previously reported studies where equilibrium was reached between 46- and 123-h contact time (Fiskum et al. 2019; Rovira et al. 2019).
2. The calculated ^{137}Cs K_d value of 806 mL AP-107/g CST at Cs equilibrium condition of 9.19 µg Cs/mL corresponded to a predicted 50% Cs breakthrough of 814 BVs. Although 50% Cs breakthrough was not achieved with column testing, 50% breakthrough was extrapolated to ~900 BVs. The column test 50% breakthrough was 11% higher than predicted by batch contact. This differed from previously reported data on a different lot of CST where the extrapolated 50% breakthrough agreed within 6% of the batch contact derived value (Rovira et al. 2018).
3. The Cs load capacity at 9.19 µg Cs/mL equilibrium condition was 0.062 mmoles Cs/g CST (8.3 mg Cs/g CST). This value was over 22% higher than measured on the lead column; however, the lead column was not loaded to full capacity (44% Cs breakthrough).

Batch contact testing cannot be used to determine the slope of the Cs load curve. Thus, it cannot predict the WAC limit breakthrough in terms of BVs.

6.2 Column Testing

AP-107 tank waste was processed through three columns sequentially positioned in a lead-middle-polish format; each column was filled with 10.0 mL of CST ion exchanger. A total of 8.55 L of AP-107 tank waste, consisting of 5.6 M Na and 145 µCi/mL ^{137}Cs, was processed through the Cs ion exchange system at 1.88 BV/h. Effluent samples were collected periodically from each column during the load process and measured for ^{137}Cs to establish the Cs load curves. The flowrate was increase to 3.7 BV/h and 4.5 BV/h to process 0.1 M NaOH FD and water rinse, respectively. The following conclusions were made as a result of this work.

1. Testing showed that 855 BVs of AP-107 tank waste, processed at 1.88 BV/h, can be treated before reaching 50% Cs breakthrough on the lead column. The WAC limit was reached on the middle column when 590 BVs of AP-107 feed was processed. The effluent from the polishing column (4.53E-3% C/C_0) was substantially lower than the WAC limit.

2. Extrapolation of Cs effluent concentration data from the polish column showed the WAC limit would be reached after processing 1010 BVs.

3. FD results showed decreasing Cs concentration coming off the polish column, but water rinse resulted in increasing effluent Cs concentration. The change in solution matrix from high salt to 0.1 M NaOH/water mix appeared to result in some Cs leakage from the column system. This Cs leakage was previously observed (Fiskum et al. 2019).

4. AP-107 processing breakthrough profile on the lead column was similar to that observed for AW-102 (Rovira et al. 2019).

5. The higher Cs load capacity of CST Lot 2002009604 relative to CST Batch 2081000057 with AP-107 was clearly demonstrated by comparison of the Cs load profiles. Rovira et al. (2018) tested AP-107 with Batch 2081000057; its Cs load profile was offset (earlier Cs breakthrough) ~100 to 200 BVs relative to the current test using CST Lot 2002009604.

6. The Cs load profile for AP-107 was offset left (earlier Cs breakthrough) of the Cs load profiles generated with 5.6 M Na simulant (Fiskum et al. 2019). This could be due in part to the slightly higher Cs concentration in the AP-107 tank waste (9.2 ug/mL) relative to the simulant (7.9 ug/mL). Additionally, this may indicate that other matrix factors in actual tank waste AP-107 could be limiting Cs loading onto the CST relative to components in the simulant.

7. The total Cs loading onto the lead column (6.76 mg Cs/g CST) was similar to those from the simulant testing (6.60 and 6.95 mg Cs/g CST) at similar processing flowrates.

8. The AP-107 SVs processed to reach the WAC limit as a function of flowrate were evaluated. The curve established with AP-107 veered away from the trajectory established by the simulant testing. This was again indicative that other components may be consuming exchange sites or the matrix is more limiting relative to the simulant.

9. The transition zones for Cs were calculated to be 560 BVs (20% to 80% Cs breakthrough range) and 1000 BVs (5% to 95% Cs breakthrough range).

6.3 Analyte Fractionation

1. Major components Al, Cr, K, Na, P, and S partitioned exclusively to the effluent.

2. Ba, Pb, and Sr were detected in the feed but not in the effluent. This indicated that a major fraction of these analytes exchanged onto the CST.

3. Substantial fractions of Ca and U (52% to 61%, respectively) were found in the effluent composite, indicating they were partially removed by the CST from the feed. The U load curve through the lead column indicated a transition zone of ~200 BVs. The Ca breakthrough curve was essentially flat.

4. Ti and Zr were not detected in the feed. Yet Zr and Ti were measured in the effluent, indicating that potentially a small fraction of CST may be degrading.

5. ^{90}Sr was quantitatively removed by CST; the ^{90}Sr decontamination factor was ≥450 (the decontamination factor was limited by the effluent ^{90}Sr detection limit).

6. Only 40% of the feed Np and Pu were measured in the effluent, demonstrating ~60% of the Np and Pu was retained on the CST. Assuming these isotopes were bound to the CST, the CST would contain 123 nCi/g TRU, exceeding the 100 nCi/g threshold defining TRU waste.

7. ^{99}Tc did not exchange onto the CST.

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Appendix A – Column Load Data

The AP-107 lead, middle, and polish column loading raw data are provided in Table A.1. The feed displacement, water rinse, and final fluid expulsion raw data are provided in Table A.2. The raw data include the processed bed volumes (BVs) and corresponding ^{137}Cs concentration in the collected sample, % C/C_0, and the decontamination factor (DF).

Table A.1. Lead, Middle, and Polish Column Cs Breakthrough Results with AP-107

Lead Column				Middle Column				Polish Column			
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
12.6*	1.04E-4	7.14E-5	1.40E+6	42.6	1.96E-4	1.35E-4	7.39E+5	42.6	1.06E-4	7.30E-5	1.37E+6
42.8	3.73E-4	2.57E-4	3.89E+5	87.1	2.04E-4	1.40E-4	7.12E+5	86.9	1.97E-4	1.36E-4	7.37E+5
58.8	1.85E-4	1.27E-4	7.86E+5	130.5	1.48E-4	1.02E-4	9.81E+5	130.1	1.10E-4	7.58E-5	1.32E+6
87.7*	2.52E-3	1.74E-3	5.76E+4	178.6	2.54E-4	1.75E-4	5.70E+5	178.0	1.11E-4	7.63E-5	1.31E+6
107.7	3.77E-3	2.60E-3	3.85E+4	235.4	1.80E-4	1.24E-4	8.04E+5	234.6	1.14E-4	7.88E-5	1.27E+6
131.6	1.32E-2	9.07E-3	1.10E+4	277.9	3.08E-4	2.12E-4	4.71E+5	277.0	1.27E-4	8.72E-5	1.15E+6
151.7	3.54E-2	2.44E-2	4.10E+3	317.7	1.32E-3	9.13E-4	1.10E+5	316.5	1.09E-4	7.54E-5	1.33E+6
180.2*	1.05E-1	7.21E-2	1.39E+3	362.6	2.28E-3	1.57E-3	6.37E+4	361.3	1.73E-4	1.19E-4	8.39E+5
200.1	1.98E-1	1.36E-1	7.34E+2	408.0	7.77E-3	5.35E-3	1.87E+4	406.5	1.02E-4	7.04E-5	1.42E+6
237.4	4.83E-1	3.33E-1	3.01E+2	453.3	1.67E-2	1.15E-2	8.67E+3	451.6	1.32E-4	9.08E-5	1.10E+6
280.1*	1.35E+0	9.32E-1	1.07E+2	475.4	3.01E-2	2.08E-2	4.81E+3	496.9	1.07E-4	7.36E-5	1.36E+6
320.1	2.42E+0	1.67E+0	6.00E+1	498.9	4.07E-2	2.81E-2	3.56E+3	550.9	1.26E-4	8.66E-5	1.16E+6
341.5	3.56E+0	2.45E+0	4.08E+1	520.6	6.78E-2	4.67E-2	2.14E+3	590.7	1.33E-4	9.13E-5	1.09E+6
365.5*	4.50E+0	3.10E+0	3.22E+1	553.4	1.07E-1	7.36E-2	1.36E+3	628.0	2.14E-4	1.47E-4	6.79E+5
385.2	6.12E+0	4.22E+0	2.37E+1	593.5	1.82E-1	1.26E-1	7.96E+2	670.9	3.44E-4	2.37E-4	4.22E+5
411.2	7.65E+0	5.27E+0	1.90E+1	630.9	2.88E-1	1.98E-1	5.04E+2	690.2	5.03E-4	3.47E-4	2.89E+5
433.5	9.78E+0	6.74E+0	1.48E+1	650.4	3.74E-1	2.57E-1	3.88E+2	714.4	7.30E-4	5.03E-4	1.99E+5
457.0*	1.09E+1	7.53E+0	1.33E+1	674.3	4.87E-1	3.36E-1	2.98E+2	733.0	9.74E-4	6.71E-4	1.49E+5
479.3	1.49E+1	1.02E+1	9.77E+0	693.8	6.32E-1	4.35E-1	2.30E+2	757.4	1.42E-3	9.77E-4	1.02E+5
503.0	1.67E+1	1.15E+1	8.70E+0	718.2	7.89E-1	5.44E-1	1.84E+2	775.9	1.95E-3	1.34E-3	7.46E+4
524.8	1.90E+1	1.31E+1	7.62E+0	736.9	9.85E-1	6.79E-1	1.47E+2	804.2	2.93E-3	2.02E-3	4.95E+4
557.9*	2.27E+1	1.56E+1	6.41E+0	761.6	1.20E+0	8.30E-1	1.20E+2	825.7	4.54E-3	3.13E-3	3.20E+4
598.2	2.75E+1	1.89E+1	5.28E+0	780.3	1.50E+0	1.03E+0	9.70E+1	844.1	6.31E-3	4.35E-3	2.30E+4
635.8	3.23E+1	2.23E+1	4.49E+0	808.8	1.89E+0	1.30E+0	7.68E+1				
655.6*	3.63E+1	2.50E+1	4.00E+0	830.5	2.41E+0	1.66E+0	6.02E+1				
679.6	3.81E+1	2.63E+1	3.81E+0	849.0	2.84E+0	1.95E+0	5.12E+1				
723.8*	4.55E+1	3.14E+1	3.19E+0								
767.4	5.14E+1	3.54E+1	2.82E+0								
814.8*	5.99E+1	4.13E+1	2.42E+0								

BV = bed volume, 10 mL/BV
DF = decontamination factor
C$_0$ = 145 μCi ^{137}Cs/ mL
* = samples submitted for additional analysis

Table A.2. Feed Displacement, Water Rinse, and Final Flush Results Following AP-107 Processing

Feed Displacement				Water Rinse				Final Fluid Flush			
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
2.7	7.85E-3	5.41E-3	1.85E+4	2.5	3.14E-4	2.16E-4	4.62E+5	5.1	1.76E-2	1.21E-2	8.23E+3
5.9	1.28E-3	8.79E-4	1.14E+5	6.0	5.41E-4	3.73E-4	2.68E+5				
9.5	1.88E-4	1.29E-4	7.74E+5	9.3	2.49E-3	1.72E-3	5.83E+4				
12.8	2.09E-4	1.44E-4	6.96E+5	12.3	4.71E-3	3.25E-3	3.08E+4				

BV = bed volume, 10 mL
DF = decontamination factor
C_0 = 145 µCi ^{137}Cs/ mL

Appendix B – Analyte Concentrations As a Function of Loading

The load behaviors of selected analytes in AP-107 were evaluated from selected samples collected from the lead column. Analysis results of these samples are summarized in Table B.1.

Table B.1. Analyte Concentrations of Selected Samples from the Lead Column

BV Processed>	NA	12.6	87.7	180	280	365	457	558	656	724	815
Sample ID>	TI061-Comp-Feed	TI061-L-F1-A	TI061-L-F4-A	TI061-L-F8-A	TI061-L-F11-A	TI061-L-F14-A	TI061-L-F18-A	TI061-L-F22-A	TI061-L-F25-A	TI061-L-F27-A	TI061-L-F28-A
Analyte						µg/mL					
Al	10,014	8,519	9,134	8,960	9,033	8,772	9,432	9,527	9,598	9,577	9,636
Ba	[0.41]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ca	[34]	[29]	[24]	[23]	[20]	[21]	[24]	[22]	[20]	[21]	[22]
Cd	6.51	[2.4]	5.51	[5.4]	6.00	[5.5]	5.95	6.39	5.96	6.50	5.98
Cr	527	487	495	488	495	477	498	519	505	509	515
Fe	14.8	15.3	26.4	[12]	14.1	[12]	13.8	13.2	14.2	13.4	33.9
K	4,685	4,144	4,359	4,187	4,328	4,159	4,512	4,514	4,492	4,459	4,554
Na	137,330	122,716	128,844	126,428	127,623	125,402	128,473	131,486	132,019	130,987	133,132
Ni	24.6	20.6	21.6	21.0	20.9	21.2	21.5	21.6	22.7	23.0	22.2
P	873	775	804	775	804	764	792	824	813	820	822
Pb	[8.1]	<4.0	<4.0	<4.0	<4.0	<4.1	<4.0	<4.0	[4.2]	<4.0	[6.0]
S	1,933	1,761	1,831	1,744	1,852	1,787	1,847	1,906	1,831	1,848	1,855
Sr	[0.13]	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ti	<0.11	[0.30]	[0.26]	[0.23]	[0.29]	[0.21]	[0.18]	[0.24]	[0.14]	[0.21]	[0.21]
^{238}U	17.9	0.623	11.6	14.9	15.4	15.6	15.7	16.7	17.1	17.0	17.0
Zn	<1.1	[1.1]	<1.1	<1.1	[1.3]	<1.1	[1.2]	[1.4]	<1.1	<1.1	<1.1
Zr	<0.48	[1.4]	[1.5]	[1.7]	[1.5]	[1.1]	[1.4]	[1.7]	[1.3]	[1.4]	[1.1]
Analyte						µCi/mL(a)					
^{90}Sr	4.52E-01	<1E-3	1.24E-03	<1E-3	1.51E-02	<1E-3	1.19E-03	<1E-3	1.68E-03	2.14E-03	2.73E-03
^{237}Np	4.76E-05	7.43E-06	2.52E-05	3.98E-05	4.51E-05	4.61E-05	4.58E-05	4.60E-05	4.35E-05	4.16E-05	4.22E-05
^{238}Pu	7.54E-05	2.09E-05	4.05E-05	4.10E-05	4.98E-05	4.56E-05	5.00E-05	4.89E-05	5.10E-05	5.44E-05	5.07E-05
$^{239+240}$Pu	5.60E-04	1.49E-04	2.72E-04	3.07E-04	3.42E-04	3.42E-04	3.77E-04	3.68E-04	3.73E-04	3.96E-04	3.95E-04

(a) Reference date is August 2019.

BV = bed volume, 10 mL

Bracketed values indicate the associated sample results were less than the estimated quantitation limit but greater than or equal to the MDL. Analytical uncertainties for these analytes are > ±15%.

Additional analyte concentrations may be found in Appendix E.

Appendix C – Solids Characterization

Backflow processing was briefly applied to the lead column before loading was completed. Brown/black solids were observed at the top of the crystalline silicotitanate (CST) bed. These solids were briefly suspended in the tank waste fluid with the backflow processing, whereas the CST did not move. Figure 3.7 in the main body of this report is an image of the suspended solids observed during the backflow operation. Small samples of the solids were collected for transmission electron microscopy analysis from the parent bottle where they were found to originate.

The materials removed from the hot cells were examined using a Quanta™ 250FEG (Thermo Fisher Scientific, Inc., Hillsboro, OR) SEM equipped with an EDAX Inc. (Mahwah, NJ) energy dispersive spectrometer (EDS) for detection of major elements. SEM images using backscattered electrons (BSE) were taken from a few of the samples that were prepared. The first sample analyzed had visible white particles on the stub. These were mainly salt-type material. The second sample did not have any clearly visible particles but had significant activity indicating the presence of materials from the hot cell experiments; high contrast particles using BSE imaging were found indicating materials possessing an average higher atomic number than the salt. The SEM images were obtained under low-vacuum conditions (i.e., no conductive coating was used).

Figure C.1 shows a multitude of different morphologies and particle shapes and compositions. There were several areas where spherical particle agglomerates were found. In Figure C.1(C), in the lower left-hand corner of the image, these round particles are visible. Scattered throughout the sample, bright (high-Z) angular particles were observed. Examples of these are shown in both Figure C.2 and Figure C.3.

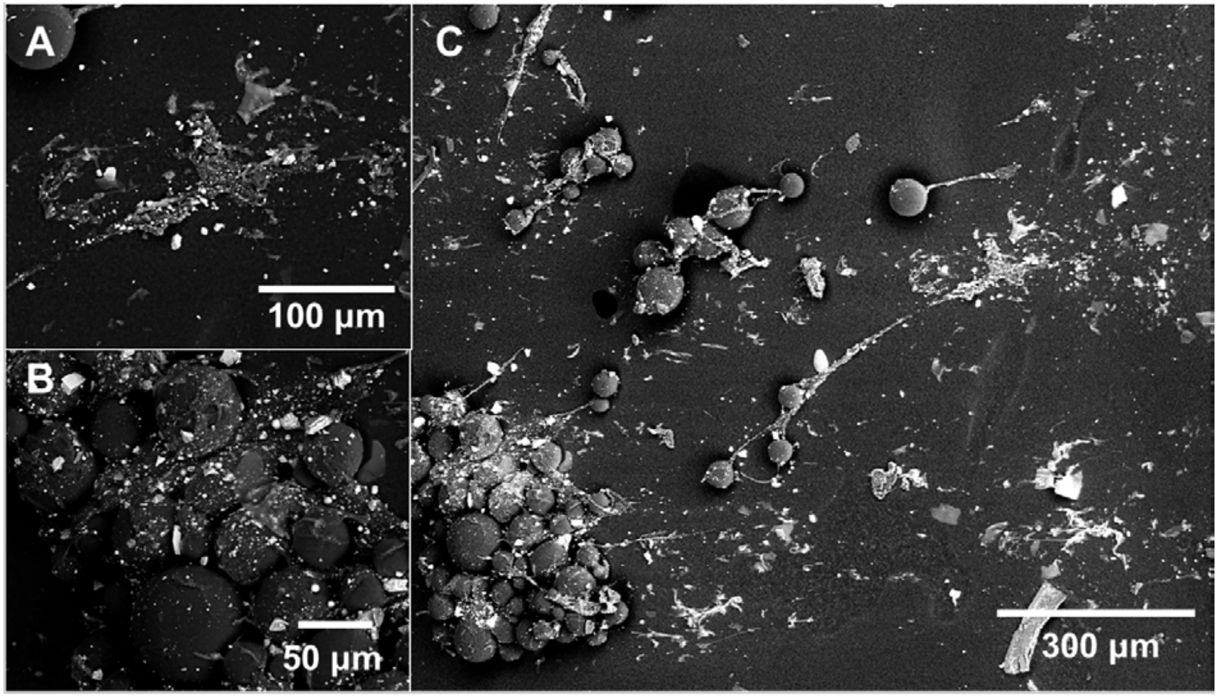

Figure C.1. Low-Magnification Images of the Solids Indicating a Heterogeneous Mixture of Particle Types

Figure Note: The salt-like particles that were visible on other samples were not found on this sample.

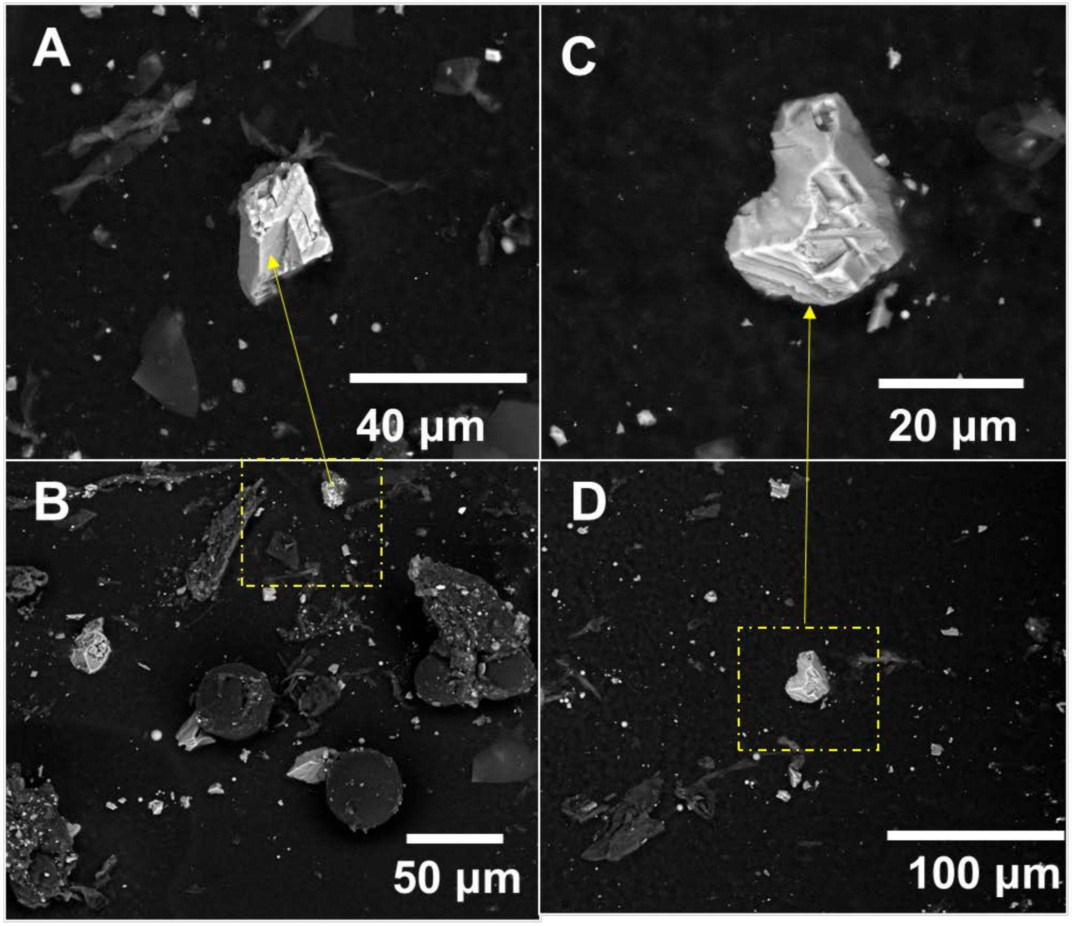

Figure C.2. SEM Images of High-Z Particles in the Specimen with Low-magnification Images (C and D) and High-magnification images (A and B) of Angular Particles

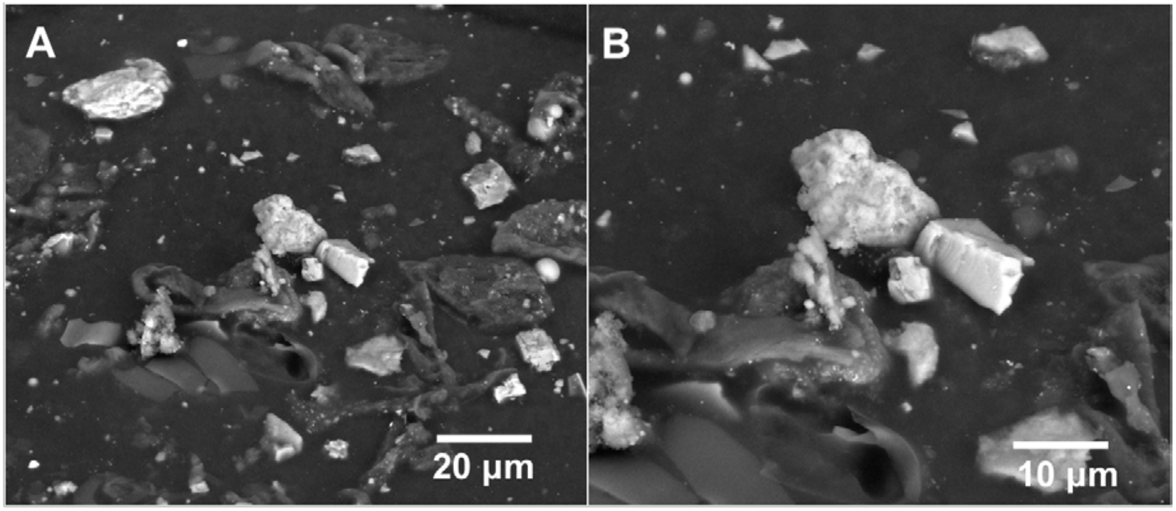

Figure C.3. Low- and High-Magnification SEM Images of High-Z Particles within the Same Region in the Sample

EDS analysis of particles revealed a variety of compositions. Various Ca and Ba-bearing phases were found (see Figure C.4 through C.6). In Figure C.7, an EDS map shows the presence of a tungsten-bearing phase within a matrix of the sodium salt. This was confirmed in Figure C.8 by multi-point EDS analysis.

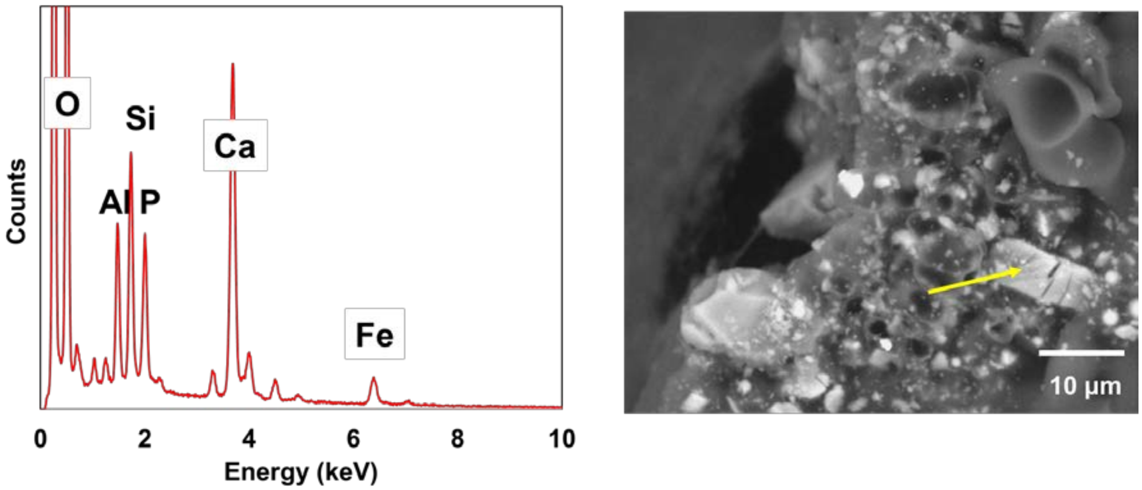

Figure C.4. EDS Analysis and SEM Image of High Z Particles Indicating the Presence of a Ca-rich Phase Containing P and Si

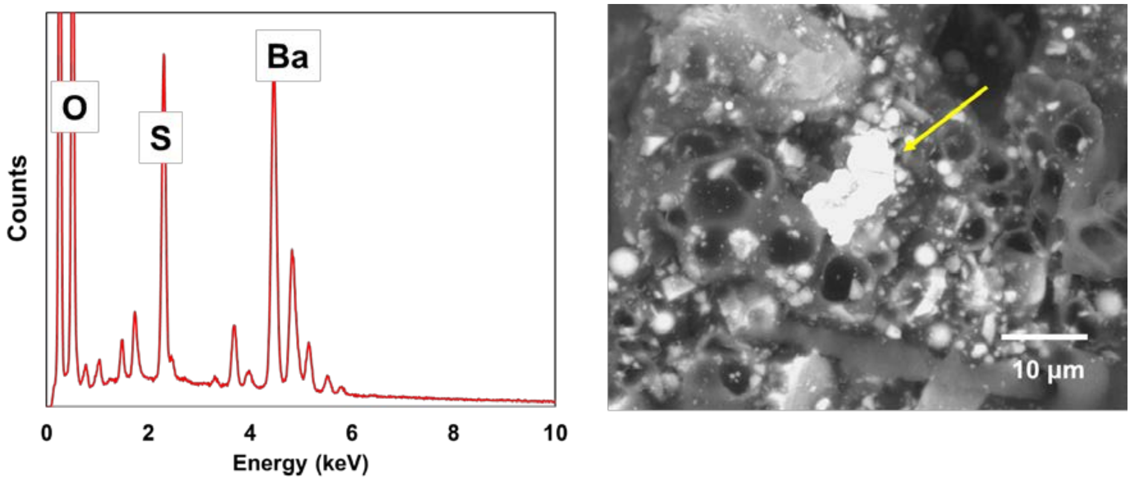

Figure C.5. EDS Analysis and SEM Image of High Z Particles Indicating the Presence of a Ba Sulfate Phase

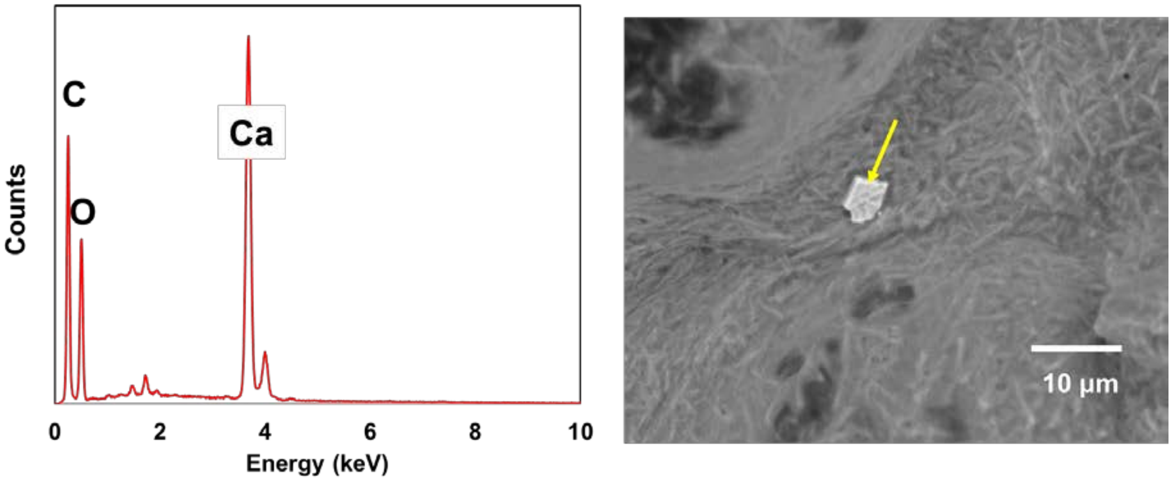

Figure C.6. EDS Analysis and SEM Image of High Z Particles Indicating the Presence of a Ca-rich Phase, Possibly Calcite

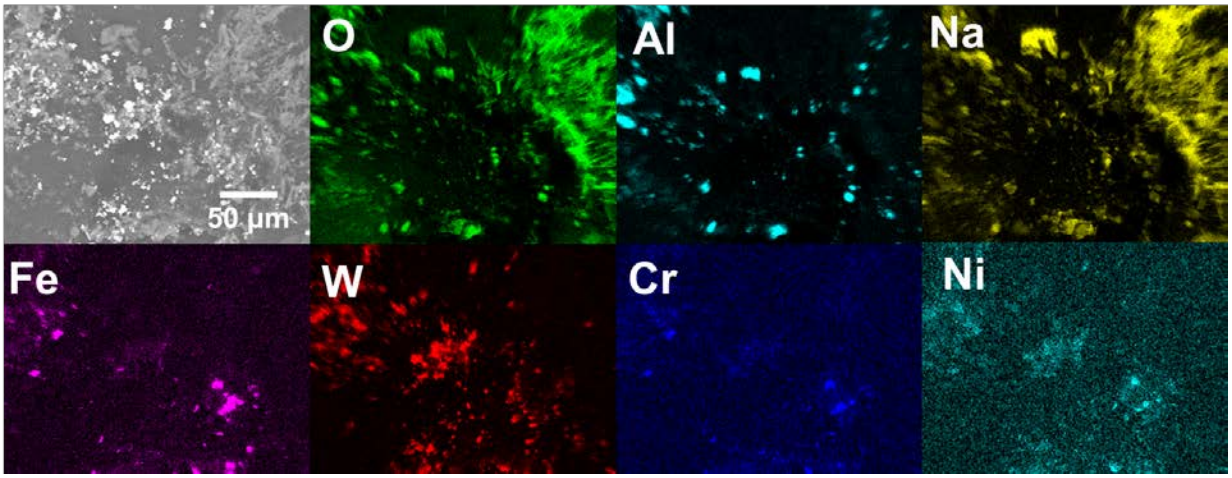

Figure C.7. EDS Mapping Showing the Presence of Na-phase and a W-containing Phase, Together with Particles of Fe and Cr

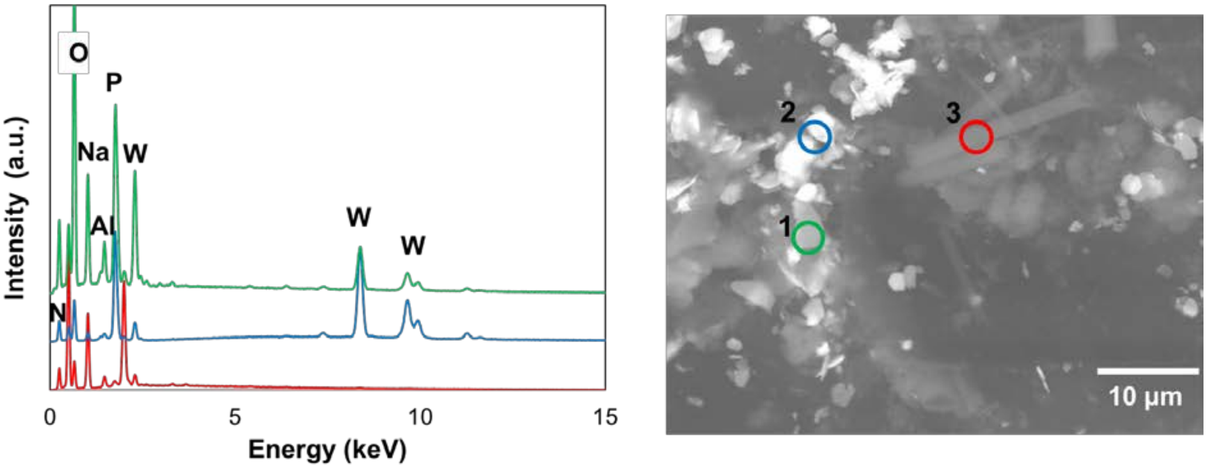

Figure C.8. Multi-point EDS Analysis and SEM Image of High Z Particles Indicating the Presence of W-rich Phases (1 and 2) and Na-P Bearing Phases (3)

Appendix D – CST Lot Comparison

Crystalline silicotitanate (CST) is manufactured by Honeywell UOP, LLC (UOP); product IONSIV^{TM} R9140-B is provided by UOP already converted to the sodium form. Pacific Northwest National Laboratory recently tested both CST production lots with 5.6 M Na simulant (Russell et al. 2017) and Hanford tank waste collected from tank AP-107. The two CST production lots were identified as:

- Batch 2081000057
- Lot number 2002009604, material number 8056202-999

Summaries of the key characterization attributes are provided in the following data tables and figures for the two CST production lots. A sample of Batch 2081000057 CST was passed through a 25-mesh sieve and collected on a 60-mesh sieve to support batch contact testing and small-scale column processing in 1.44 cm inside diameter ion exchange columns. A sample of Lot 2002009604 was passed through a 25-mesh sieve to support batch contact testing and small-scale column processing. This sieving process removed large particles that could potentially lead to wall effects and flow maldistribution in the ion exchange column. Most characterizations were conducted on the sieved product materials. Results are also reported where characterization was conducted on unsieved material.

Table D.1 summarizes the CST chemical properties as measured by Campbell et al. (2019). The Nb concentration in Lot 2002009604 was notably higher (27 wt%) compared to that of Batch 2081000057. Chitra et al. (2013) demonstrated significant Cs uptake differences in CST as a function of the Nb content. The corresponding Si concentration in Lot 2002009604 was significantly lower than that of Batch 2081000057. The other analyte concentrations were essentially equal within analytical uncertainty.

Table D.1. Chemical Composition (Campbell et al. 2019)

Analyte	Batch 2081000057, >60/<25 mesh	Lot 2002009604, <25 mesh	% difference between lots
Na, wt%	9.76	9.38	-4%
Nb, wt%	9.86	12.5	+27%
Si, wt%	3.0	2.1	-30%
Ti, wt%	18.9	17.9	-5%
Zr, wt%	12.0	11.4	-5%

Per UOP product information, Si content should be 7.8 to 8.2 wt% and Nb content be 12 to 15 wt%.

Table D.2 provides an overview of physical properties. Lot 2002009604 underwent more physical property testing than Batch 2081000057. Batch 2081000057 appeared to be provided as a 25 x 40 mesh sieve cut whereas Lot 2002009604 was more consistent with an 18 x 40 mesh sieve cut. Figure D.1 shows the volume percent particle size distribution (PSD) for two sieved samples. There were no appreciable differences in the sieved material PSDs.

Table D.2. Physical Properties

	Batch 2081000057		Lot 2002009604	
Physical Properties	>60/<25 mesh	As-received	<25 mesh	As-received
wt% >25 mesh(a)	0	7.7	0	59
Particle density, g/mL	nm	nm	3.77	3.33
Pre-sonication cumulative particle undersize fractions, volume basis, microns	d_{10} 418 d_{50} 571 d_{90} 775	d_{10} 419 d_{50} 573 d_{90} 779	d_{10} 428 d_{50} 589 d_{90} 809	d_{10} 467 d_{50} 708 d_{90} 1098
Post-sonication cumulative particle undersize fractions, volume basis, microns	d_{10} 412 d_{50} 563 d_{90} 765	d_{10} 412 d_{50} 563 d_{90} 765	d_{10} 406 d_{50} 567 d_{90} 795	d_{10} 394 d_{50} 633 d_{90} 954
Surface area, m^2/g(b)	nm	nm	108	104
Bulk density, g/mL(c)	1.00	nm	1.02	1.01
CST bed density, g/mL(c)	1.00	nm	1.01	1.00
Settled bed void volume, %	65.6	nm	66.2	67.6

(a) 1.7 wt% passed through the 60-mesh sieve.
(b) Samples were dried to 105 °C prior to conducting measurement.
(c) Mass based on dry weight at 105 °C.
nm = not measured

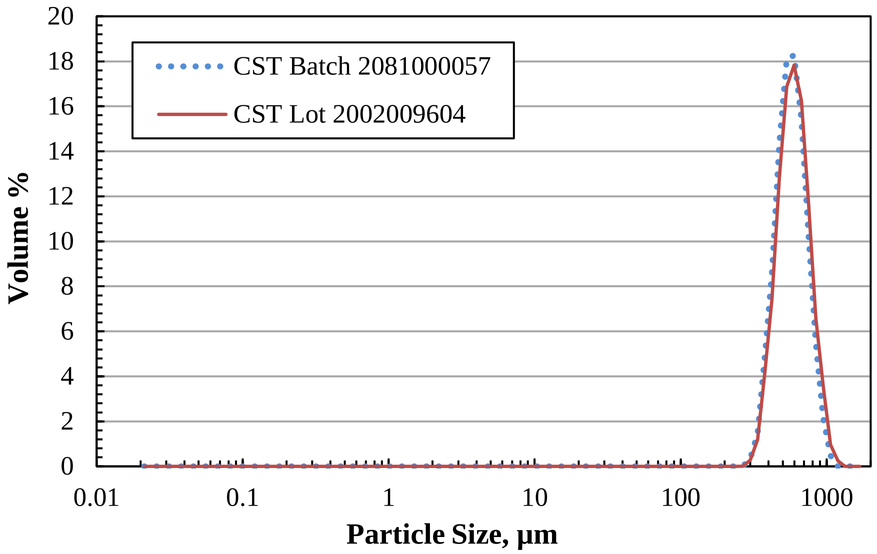

Figure D.1. PSD Comparison for Two CST Lots

Figure notes: CST Batch 2081000057 <25 mesh/ >60 mesh; Lot 2002009604 <25 mesh, Post-sonication results

The thermal gravimetric analysis was completed in duplicate for both lots of CST. Figure D.2 provides a comparison of the two CST lots tested. Rapid mass loss to 100 °C was observed and was associated directly with water loss. Per King et al. (2018), $Zr(OH)_4$ loses mass with the reorganization of $Zr(OH)_4$ to ZrO_2 and two H_2O when heated to 250 °C. Soliz et al. (2016) describe the mass losses of $Zr(OH)_4$ in phases where the initial mass loss up to 100 °C is associated with water loss and peaks "around 175 °C and between 400 to 475 °C in the derivative weight loss plot correlate to the loss of strongly bound hydroxyls and the formation of bridging oxygens, respectively, as the material begins to crystallize into ZrO_2." Thus, the extra mass loss associated with the peak around 200 °C is likely water associated with the decomposition of the $Zr(OH)_4$ binder to ZrO_2 and two waters. Given the CST formulation proposed by

Nyman et al. (2001), $H_2NaSi_2(Nb_{0.30}Ti_{0.7}O)_4O_{13}(OH)\cdot 4H_2O + 0.93Zr(OH)_4$, (FW 840.6 g/mole), an extra 4.3 wt% loss would be expected when the $Zr(OH)_4$ converts to water (loss of 36 g/mole) and ZrO_2.

Both lots of CST were measured in duplicate for mass loss by thermogravimetric analysis. The temperature ramp was 10 °C/min from 20 to 800 °C under an Ar cover gas. Sample analysis size ranged from 20 to 30 mg. Figure D.2 provides the mass loss as a function of temperature along with the derivative of the mass loss for both lots of CST. Each lot was analyzed in duplicate and the thermogravimetric analysis scans for the duplicate measures were essentially identical. Three exotherms were found in equivalent positions for each production batch. The major exotherm occurred at 100 °C, a secondary exotherm at ~230 °C and a small, sharp exotherm at ~350 °C. The first exotherm was considered water loss from entrained water easily evaporated from the CST. The origins of the second exotherm may be associated with the destruction of $Zr(OH)_4$ binder. The genesis of the final exotherm is not understood at this time.

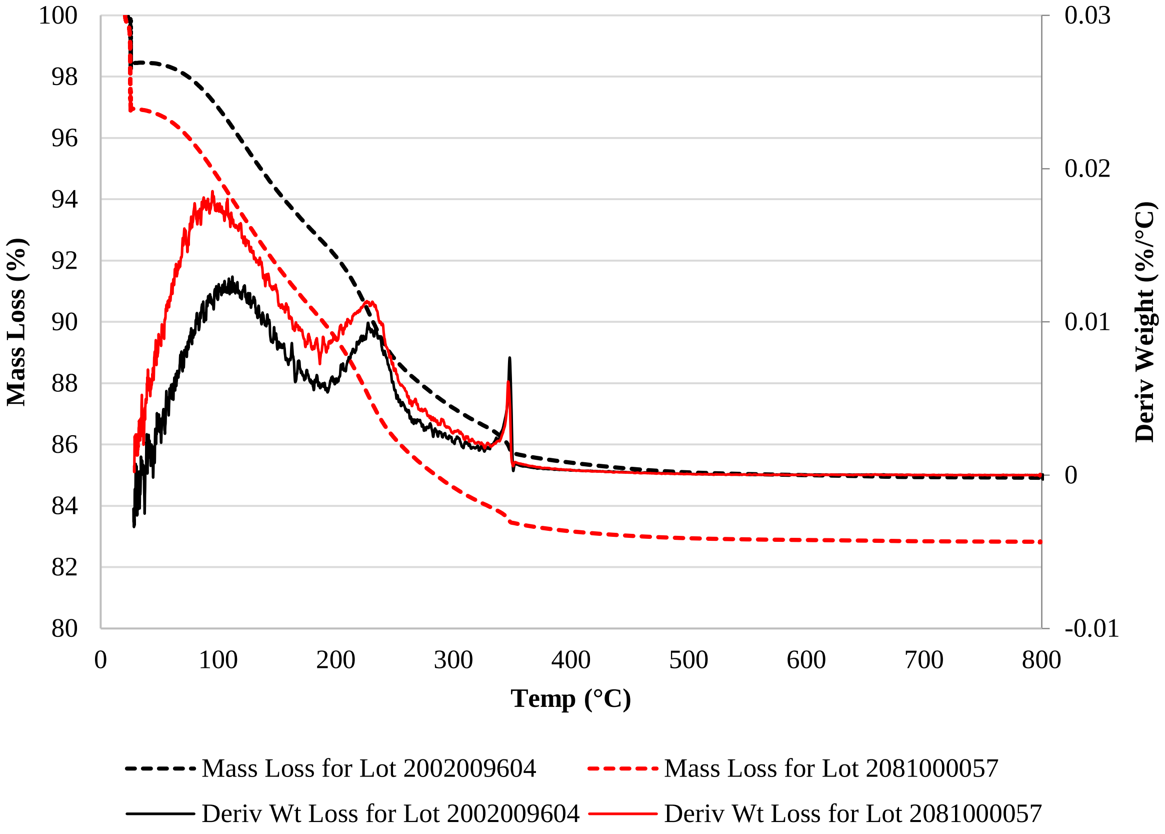

Figure D.2. Thermal Gravimetric Analysis of CST

The batch contact performances with a 5.6 M Na simulant [produced according to formulation provided by Russell et al. (2017)] and AP-107 tank waste were used to compare Cs load performance. Kinetic testing was not conducted with Batch 2081000057; however, >24 h was shown to be needed at low Cs concentrations to reach equilibrium. Lot 2002009604 was tested for kinetic exchange in batch contacts but not capacity testing. Direct comparison with the AP-107 tank waste matrix could be made between the two CST lots. At the equilibrium AP-107 tank waste matrix, the achieved capacity for Lot 2002009604 was shown to be 10% higher than that of Batch 2081000057. Table D.3 summarizes the batch contact performances.

Table D.3. Batch Contact Summary

Parameter	Batch 2081000057 >60/<25 mesh	Reference	Lot 2002009604 <25 mesh	Reference
5.6 M Na Simulant				
Time to equilibrium	Estimated 45 h	Fiskum et al. 2018	Between 45 and 123 h	Fiskum et al. 2019
K_d at feed condition, mL/g	770 (45 h contact)		nm	
Achieved Cs load capacity at feed conditions, mg/g	6.2		nm	
AP-107 Tank Waste				
Time to equilibrium	Estimated 48 h	Rovira et al. 2018	Reached by 71 h	This report
K_d at feed condition, mL/g	669 (48-91 h)		806 (71 h)	This report
Achieved Cs load capacity at feed conditions, mL/g	7.5		8.3	This report
Dry mass basis for CST is 100 °C.				

Column testing was conducted with both CST production lots in two matrix test solutions: 5.6 M Na simulant and AP-107 tank waste. Table D.4 provides a summary of the salient column performance parameters with effort to match general flow rate or residence time in terms of bed volumes per hour (BV/h).

Table D.4. Column Performance Summary

Parameter	Batch 2081000057 >60/<25 mesh	Reference	Lot 2002009604 <25 mesh	Unseived	Reference
5.6 M Na Simulant					
Flowrate, BV/h	1.99	Fiskum et al. 2018	1.83	1.82	Fiskum et al. 2019
WAC limit breakthrough, BV	162		240	240	
50% Cs breakthrough, BV	800		~1000	~1050	
Cs loading, mg/g	6.38		6.95	6.60	
AP-107 Tank Waste					
Flowrate, BV/h	2.20	Rovira et al. 2018	1.88	Not tested	In this report
WAC limit breakthrough, BV	120		200	Not tested	
50% Cs breakthrough, BV	~615		900	Not tested	
Cs loading, mg/g	Not comparable		6.76	Not tested	
Values containing "~" are extrapolated values.					

Radiolytic gas generation testing was recently conducted on the two CST lots in a side-by-side test (Colburn et al. 2019). The CST production lots were pretreated as follows:

- Wet CST: CST was soaked in 0.1 M NaOH for 1 h, soaked in 3 M NaOH overnight followed by a 1-h 0.1 M NaOH soak, and then soaked in deionized water for 1 h. The excess liquid was drained from the CST and the CST was sealed in a jar until the vessels were loaded for testing.
- Dry CST: The CST received the same treatment as the wet, free-drained CST, after which it was air-dried on the lab bench until it reached a free-flowing state.

Nominal 30-mL aliquots of the CST samples were exposed to 588 krad/h for 549 h with an estimated total accumulated dose of 323 Mrad. Samples were maintained at 25 °C during the exposure period. Table D.5 provides the cumulative G-values (molecules/100 eV) for the two CST lots. It was not expected that differences in PSD (sieved vs. unsieved) would alter gas production rates. Clearly, the CST Batch 2081000057 resulted in much higher H_2 and O_2 production rates than that of Lot 2002009604.

Table D.5. G Values, Molecules/100 eV (Colburn et al. 2019)

Parameter	Batch 2081000057 Unsieved	Lot 2002009604 Unsieved	Parameter Ratio Batch 2081000057 / Lot 2002009604
Wet CST			
Moisture, wt % (105 °C)	38.38	39.57	0.97
G(H_2)	0.1259	0.0191	6.59
G(CH_4)	No CH_4 observed	9.47×10^{-6}	--
G(O_2)	0.0194	0.004	4.85
G(N_2O)	No N_2O observed	No N_2O observed	--
Dry CST			
Moisture, wt % (160 °C)	22.45	11.12	2.02
G(H_2)	0.3291	0.0894	3.68
G(CH_4)	No CH_4 observed	0.0003	--
G(O_2)	0.0689	No O_2 observed	--
G(N_2O)	0.0004	9.1×10^{-5}	4.40

D.1 References

Chitra S, R Sudha, S Kalavathi, AGS Mani, SVS Rao, and PK. Sinha. 2013. “Optimization of Nb-substitution and Cs+/Sr+2 ion exchange in crystalline silicotitanates (CST).” *J. Radioanal. Nucl. Chem.* 295:607-613.

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Russell RL, PP Schonewill, and CA Burns. 2017. *Simulant Development for LAWPS Testing*. RPT-LPIST-001, Rev. 0; PNNL-26165, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Soliz JR, AD Klevitch, CR Harris, JA Rossin, A Ng, RM Stroud, AJ Hauser and GW Peterson. 2016. “Structural Impact on Dielectric Properties of Zirconia.” *J. Phys. Chem. C* 120:26834-26840.

Appendix E – Analytical Reports

Analytical reports provided by the Analytical Support Operation (ASO) are included in this appendix. In addition to the analyte results, they define the procedures used for chemical separations and analysis, as well as quality control sample results, observations during analysis, and overall estimated uncertainties. The analyses are grouped according to Analytical Service Request (ASR) number. Cross reference of ASO sample IDs to test description are provided in the body of the report (see Table 3.2 and Table 3.5).

Appendix E Table of Contents

ASR 0747, Initial Characterization of AP-107, As-Received

ASR 0787, AP-107 Filtered Feed, Effluent, and Selected Lead Column Samples

Analytical Service Request (ASR)

(Information on this COVER PAGE is applicable to all samples submitted under this ASR)

Requestor --- Complete all fields on this COVER PAGE, unless specified as optional or ASR is a revision

Requestor:
Signature amyRovira
Print Name Amy ROVIRA
Phone 371-7908 MSIN

Project Number: 73312
Work Package: NC4186

Matrix Type Information

◆ **Liquids:** ☒ Aqueous ☐ Organic ☐ Multi-phase
◆ **Solids:** ☐ Soil ☐ Sludge ☐ Sediment
☐ Glass ☐ Filter ☐ Metal
☐ Smear ☐ Organic ☐ Other

◆ **Other:** ☐ Solid/Liquid Mixture, Slurry
☐ Gas ☐ Biological Specimen

(If sample matrices vary, specify on Request Page)

Disposal Information

◆ **Disposition of Virgin Samples:**

Virgin samples are returned to requestor unless archiving provisions are made with receiving group!

If archiving, provide:
Archiving Reference Doc: ____________

◆ **Disposition of Treated Samples:**
☒ Dispose ☐ Return

QA/Special Requirements

◆ **QA Plan:**
☒ ASO-QAP-001 (Equivalent to HASQARD)
☐ Additional QA Requirements, List Document Below:
Reference Doc Number: ____________

◆ **Field COC Submitted?** ☒ No ☐ Yes
◆ **Lab COC Required?** ☒ No ☐ Yes
◆ **Sample/Container Inspection Documentation Required?**
☒ No ☐ Yes

◆ **Hold Time:** ☒ No ☐ *Yes*

If *Yes*, Contact ASO Lead before submitting Samples
☐ Use SW 846 (PNL-ASO-071, identify analytes/methods where holding times apply)
☐ Other? Specify: ____________

◆ **Special Storage Requirements:**
☒ None ☐ Refrigerate ☐ Other, Specify: ____________

◆ **Data Requires ASO Quality Engineer Review?** ☐ No ☒ Yes

Data Reporting Information

◆ **Is Work Associated with a Fee-Based Milestone?** ☒ No ☐ Yes
If yes, milestone due date: ____________

◆ **Preliminary Results Requested, As Available?** ☐ No ☒ Yes

◆ **Data Reporting Level**
☒ ASO-QAP-001 (Equivalent to HASQARD).
☐ Minimum data report.
☐ Project Specific Requirements: Contact ASO Lead or List Reference Document: ____________

◆ **Requested Analytical Work Completion Date:** ____________
(Note: Priority rate charge for < 10 business day turn-around time)

◆ **Negotiated Commitment Date:** 4/15/19
(To be completed by ASO Lead)

Waste Designation Information

◆ **ASO Sample Information Check List Attached?** ☒ No ☐ Yes
If no, Reference Doc Attached: ____________
or, Previous ASR Number: ____________
or, Previous RPL Number: ____________

Does the Waste Designation Documentation Indicate Presence of PCBs?
☒ **No** ☐ **Yes**

Send Report To: A. ROVIRA, S. FISKUM **MSIN** ____________
J. Geeting **MSIN** ____________
Additional or Special Instructions ____________

Receiving and Login Information *(to be completed by ASO staff)*

Date Delivered: 3/18/19
Delivered By (optional): ____________
Time Delivered: 1:00 pm
Group ID (optional): ____________
CMC Waste Sample? ☒ No ☐ Yes

Received By: T Trang-le
ASR Number: 0747 Rev.: 00
RPL Numbers: (19-1227) → (19-1228)
(first and last)

ASO Work Accepted By: KN Pool **Signature/Date:** N. Pool 3/18/19

Analytical Service Request (ASR)

(REQUEST PAGE ----- Information Specific to Individual Samples)

Provide Analytes of Interest and Required Detection limits - ☐ Below ☐ Attached

ASO Staff Use Only				ASO Staff Use Only	
RPL Number	**Customer Sample ID**	**Sample Description** (& Matrix, if it varies)	**Analysis Requested**	**Test**	**Library**
19-1227	7AP-18-19 TTL 3/18/19	AP-107 tank supernate	1) GEA-as received solutions		
19-1228	7AP-18-36	AP-107 tank supernate	(CS-137, Am-241)		
			2) acid digestion-128		
			a) ICP/OES-Al, K, and Na		
			b) ICP/MS-Cs-133 (isotopes)		

~~Project expectations for ASO to maintain hard copy records showing evidence of Analyst sign-off and Technical Reviewer signature approval have been suspended for this ASR. ASO is relieved from meeting these requirements and the project assumes responsibility for the records.~~

XMP 3/18/19

ASR # 0747 Rev.: 00

Page 1 of 1

Battelle PNNL/RPL/Inorganic Analysis ... ICP-OES Analysis Report
PO Box 999, Richland, Washington 99352

Project / WP#: 73312 / NC4186
ASR#: 0747
Client: A. Rovira
Total Samples: 2 (liquids)
Sample Description AP-107 Tank Waste

ASO Sample ID	Client Sample ID	Sample Weight (g)
19-1227	7AP-18-1	NA
19-1228	7AP-18-36	NA

Sample Preparation: RPG-CMC-128, Rev. 1. "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater", performed by L. Darnell on 04/17/19. Simple dilution of "as received" samples in 5% v/v HNO_3 performed by J. Carter on 04/25/19.

Procedure: RPG-CMC-211, Rev. 4, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)."

Analyst:	J. Carter	**Analysis Date:**	04/25/19	**ICP File:**	C0789

See Chemical Measurement Center 98620 file: ICP-325-405-3 (Calibration and Maintenance Records)

M&TE:			
	☒	PerkinElmer 5300DV ICP-OES	SN: 077N5122002
	☐	Mettler AT400 Balance	SN: 1113292667
	☒	Ohaus PA224C Balance	SN: B725287790
	☐	Sartorius ME414S Balance	SN: 21308482
	☐	SAL Cell 2 Balance	SN: 8033311209

J. Carter
Report Preparer

5/1/19
Date

Denis Chelman
Review and Concurrence

05/01/19
Date

Two aqueous samples submitted under Analytical Service Request (ASR) 0747 were analyzed by ICP-OES. The samples were prepared following RPL procedure RPG-CMC-128, Rev. 1, "*HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater*". All samples were diluted in 5% HNO_3 prior to analysis. None of the samples were filtered.

All sample results are reported on a mass per unit volume basis (µg/mL) for each detected analyte. The data have been adjusted for instrument dilutions.

Analytes of interest (AOI) were specified in the ASR and are listed in the upper section of the attached ICP-OES Data Report. There were two analyte lists requested. Samples were divided between those two lists and a separate data report is provided for each. The quality control (QC) results for the AOI have been evaluated and are presented below. Analytes other than the AOI are reported in the bottom section of the report but have not been fully evaluated for QC performance.

Calibration of the ICP-OES was done following the manufacturer's recommended calibration procedure using multi-analyte custom standard solutions traceable to the National Institute of Standards and Technology (NIST). Midrange calibration verification standards (MCVA and MCVB) were used to verify acceptance of the two-point calibration curves obtained for each analyte and for continuing calibration verification.

The controlling documents were procedures RPG-CMC-211, Rev. 4, *Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)*, and ASO-QAP-001, Rev. 11, *Analytical Support Operations (ASO) Quality Assurance Plan.* Instrument calibrations, QC checks and blanks (e.g., ICV/ICB, CCV/CCB, LLS, ICS), matrix spike, post-digestion spikes, duplicate, reagent spike, blank spike, and serial dilution were conducted during the analysis run.

Preparation Blank (PB):

A preparation blank (reagents only) was prepared for the extraction process. All analytes were within the acceptance criteria of <EQL (estimated quantitation level), ≤50% regulatory decision level, or ≤10% of the concentration in the samples.

Blank Spike (BS)/Laboratory Control Sample (LCS):

A reagent spike (RS) sample (reagents and spikes) was prepared for the extraction process. Recovery values are listed for all analytes included in the RS that were measured at or above the EQL. Recovery values for the AOI meeting this requirement and within the acceptance criterion of 80% to 120%, ranged from 99% to 104%.

Duplicate/Replicate Relative Percent Difference (RPD)/Relative Standard Deviation (RSD):

A duplicate of sample 19-1227 was prepared and analyzed. RPD's are listed for all analytes that were measured at or above the EQL. RPDs for the AOI meeting this requirement ranged from 2.5% to 4.1% and were within the acceptance criterion of ≤20% for liquid samples.

Matrix-Spike (MS) Sample:

A matrix spike (MS) of sample 19-1228 was prepared for the extraction process. Recovery values are listed for all analytes included in the MS that were measured at or above the EQL. Recovery values for the AOI meeting this requirement was 107%, within the acceptance criterion of 75% to 125%, except for K (144%). The recovery for Na is not reported (nr) as the spike concentration was less than 25% of the sample.

Initial/Continuing Calibration Verification (ICV/CCV):

MCVA and MCVB solutions were analyzed immediately after calibration, after each group of not more than ten samples, and at the end of the analytical run. The concentrations of all AOI were within the acceptance criteria of 90% to 110% recovery.

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solution (5% v/v HNO_3) was analyzed immediately after the ICV solutions and after the CCV solutions (after each group of not more than ten samples and at the end of the analytical run). The concentration of all AOI were within the acceptance criteria of <EQL.

Low-Level Standard (LLS):

The LLS solution was analyzed immediately after the first CCB solution. The concentrations of all AOI were within the acceptance criteria of 70% to 130% recovery.

Interference Check Standard (ICS/SST):

The ICS solution was analyzed immediately after the first LLS solution and immediately prior to analyzing the final CCV solutions. The concentrations of all AOI were within the acceptance criteria of 80% to 120% recovery.

Serial Dilution (SD):

Five-fold serial dilution was conducted on sample 19-1227. Percent differences (%Ds) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. The %Ds for the AOI meeting this requirement ranged from 1.4% to 9.5% and were within the acceptance criterion of ≤10%.

Post-Digestion Spike (PS-A) - Sample (A Component):

In addition to the BS sample, a post-digestion spike (A Component) was conducted on sample 19-1227. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. Recovery values for the AOI meeting this requirement ranged from 109% to 112% and were within the acceptance criterion of 80% to 120%.

Post-Digestion Spike (PS-B) - Sample (B Component):

In addition to the MS sample, a post-digestion spike (B Component) was conducted on sample 19-1227. No AOIs are present in this spike.

Other QC:

All other instrument-related QC tests for the AOI passed within their respective acceptance criteria.

Comments:

1) The "Final Results" have been corrected for all laboratory dilutions performed on the samples during processing and analysis, unless specifically noted.
2) Instrument detection limits (IDL) and estimated quantitation limits (EQL) shown are for acidified water and/or fusion flux matrices as applicable. Method detection limits (MDL) for individual samples can be estimated by multiplying the IDL by the "Process Factor" for that individual sample. The estimated quantitation limit (EQL) for each concentration value can be obtained by multiplying the EQL by the "Process Factor".
3) Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g. 5% v/v HNO_3 or less) at analyte concentrations > EQL up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000 µg/mL (0.5 per cent by weight). Note that bracketed values listed in the data report are within the MDL and the EQL, and have potential uncertainties greater than 15%. Concentration values < MDL are listed as "- -". Note, that calibration and QC standard samples are validated to a precision of ±10%.
4) Analytes included in the spike A component (for the AS/PS) are; Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ta, Ti, Tl, V, W, Y, Zn, and Zr. Analytes included in the spike B component are; Ce, Dy, Eu, La, Nd, Pd, Rh, Ru, S, Te, Th, and U.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

		Run Date >	4/25/2019	4/25/2019	4/25/2019	4/25/2019	4/25/2019
		Process Factor >	1.0	49.2	1230.0	1227.5	1226.0
			405 diluent	BLK-1227	19-1227 @ 25x	19-1228 @ 25x	Dup-1228 @ 25x
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Lab Diluent	Process Blank	7AP-18-1	7AP-18-36	
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
0.0122	0.122	Al	--	[5.0]	9,730	10,200	10,600
0.0240	0.240	K	--	[5.9]	3,620	3,820	3,920
0.0246	0.246	Na	--	--	129,000	135,000	140,000
Other Analytes							
0.0019	0.019	Ag	--	[0.10]	--	--	[2.6]
0.0529	0.529	As	--	--	[110]	[68]	--
0.0067	0.067	B	[0.036]	[2.1]	[60]	[54]	[56]
0.0003	0.003	Ba	--	[0.15]	[0.90]	[0.80]	[0.65]
0.0001	0.001	Be	--	--	[0.19]	[0.13]	[0.16]
0.0494	0.494	Bi	--	--	--	--	--
0.0177	0.177	Ca	--	[1.1]	[36]	--	--
0.0022	0.022	Cd	--	--	[7.6]	[5.5]	[8.9]
0.0069	0.069	Ce	[0.0080]	--	--	[11]	--
0.0035	0.035	Co	--	--	--	--	--
0.0025	0.025	Cr	--	--	502	517	532
0.0016	0.016	Cu	--	[0.28]	[2.3]	[3.8]	[2.7]
0.0029	0.029	Dy	--	--	--	--	--
0.0013	0.013	Eu	--	--	--	--	--
0.0052	0.052	Fe	--	[0.48]	[13]	[14]	[13]
0.0022	0.022	La	--	--	--	--	--
0.0009	0.009	Li	--	[0.28]	[1.4]	--	--
0.0068	0.068	Mg	--	[0.46]	--	--	--
0.0002	0.002	Mn	--	[0.031]	--	--	[0.33]
0.0045	0.045	Mo	--	--	[43]	[39]	[40]
0.0086	0.086	Nd	--	--	--	--	--
0.0049	0.049	Ni	--	--	[21]	[20]	[24]
0.0554	0.554	P	--	--	800	866	825
0.0162	0.162	Pb	--	--	--	--	--
0.0077	0.077	Pd	--	[0.41]	--	--	--
0.0165	0.165	Rh	--	--	--	--	--
0.0097	0.097	Ru	--	--	--	--	--
0.1186	1.186	S	--	--	1,730	1,880	1,900
0.0518	0.518	Sb	--	--	--	--	--
0.1595	1.595	Se	--	--	--	--	--
0.0237	0.237	Si	--	--	[84]	[94]	[100]
0.0313	0.313	Sn	--	--	--	--	--
0.0005	0.005	Sr	--	--	--	--	--
0.0217	0.217	Ta	--	--	--	--	--
0.0311	0.311	Te	--	--	--	--	--
0.0189	0.189	Th	--	--	--	--	--
0.0004	0.004	Ti	--	--	--	--	--
0.0530	0.530	Tl	--	--	--	--	--
0.0360	0.360	U	--	--	--	--	--
0.0021	0.021	V	--	--	--	--	[2.7]
0.0216	0.216	W	--	--	[61]	[60]	[66]
0.0012	0.012	Y	--	--	--	--	--
0.0043	0.043	Zn	--	3.81	--	--	--
0.0019	0.019	Zr	--	--	--	--	--

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

ASR-0747 Results from C0789 ASR-0747 Rovira .xlsm

QC Performance 4/25/2019

Criteria >	≤ 20%	80%-120%	75%-125%	80%-120%	80%-120%	≤ 10%
QC ID >	19-1227 Dup	BS	19-1227 MS	19-1227 + AS-A	19-1227 + AS-B	19-1227 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Al	2.5	104	107	109		2.1
K	4.1	99	144	112		9.5
Na	2.6	104	nr	112		1.4
Other Analytes						
Ag				92		
As				103		
B				111		
Ba		101	102	104		
Be		103	105	106		
Bi		84		97		
Ca		107	123	111		
Cd		103	107	105		
Ce		97	96		104	
Co				101		
Cr	0.4	95	96	104		3.3
Cu		100	102	106		
Dy					103	
Eu					103	
Fe		94	107	105		
La		97	101		101	
Li		117	136	121		
Mg		101	105	106		
Mn		101	106	108		
Mo				101		
Nd		97	100		102	
Ni		97	103	103		
P	3.2			104		
Pb		100	104	101		
Pd					98	
Rh					103	
Ru					100	
S	2.1				101	
Sb				104		
Se				102		
Si				108		
Sn				104		
Sr		105	106	107		
Ta				102		
Te					105	
Th					101	
Ti				105		
Tl				95		
U		99	102		106	
V		94	99	101		
W				105		
Y				102		
Zn		98	107	105		
Zr				106		

Shaded results are outside the acceptance criteria.

nr = spike concentration less than 25% of sample concentration. Matrix effects can be assessed from the serial dilution.

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report
P.O. Box 999, 902 Battelle Blvd., Richland, Washington 99352

Gamma Energy Analysis (GEA)

Project / WP#: 73312/ NC4186
ASR#: 0747.00
Client: A Rovira
Total Samples: 2

RPL ID	Client Sample ID
19-1227	**7AP-18-1**
19-1228	**7AP-18-36**

Analysis Type:	GEA- for all positively measured or non-detected isotopes
Sample Processing Prior to Radiochemical Processing/Analysis	☒ None ☐ Digested as per RPG-CMC-129, Rev. 0 *HNO_3-HCl Acid Extraction of Solids Using a Dry Block Heater* ☐ Fusion as per RPG-CMC-115, *Solubilization of Metals from Solids Using a KOH-KNO_3 Fusion* ☐ Other: Preparation may also involve attaining a GEA geometry that is compatible with the calibration geometry.
Analysis Procedure:	RPG-CMC-450, Rev. 3 *Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS)*
Reference Date:	3/18/2019
Analysis Date or Date Range:	March 18, 2019
Technician/Analyst:	T Trang-Le
Rad Chem Electronic Data File:	*19-1227 Rovira.xls*
ASO Project 98620 File:	*File Plan 5872, Technical (Radiochemistry), Gamma Calibration, daily checks, and maintenance records; and standard certificates and preparation. Also, balance calibration and performance check records.*
M&TE Number(s):	*Detectors T*

T Trang-le / 3/21/19
Prepare **Date**

LRGreenwood / 3/21/19
Reviewer **Date**

Page 1 of 3

SAMPLE RESULTS

Activities for all gamma emitters detected in these samples are presented in an attached Excel spreadsheet for 0747.00. Cs-137 was the main activities for these samples.

ASO Project File, ASR 0747.00 has been created for this report including all appropriate supporting records which may include the Pipette Performance Check Worksheet form, standard certificates, laboratory bench records, Shielded Analytical Laboratory Bench Sheet, and Gamma Energy Analysis printouts. Detector calibration records, control charts and balance calibration records can be found in the ASO Records.

Sample Preparation, Separation, Mounting and Counting Methods

The quality control (QC) sample results for each of the isotopes measured above background have been evaluated and are discussed below. A summary of the GEA analysis results, including QC sample performance, is given in the attached Data Report.

QUALITY CONTROL RESULTS

Tracer:

Tracers are not used for ASO Gamma Energy Analysis (GEA) methods.

Process Blank (PB):

No process blank was prepared for gamma counting.

Required Detection Limits

There are no required detection limit requirements for these samples.

Blank Spike (BS)/Laboratory Control Sample (LCS)/ Matrix Spike (MS):

There are no BS, LCS or MS QC samples analyzed for ASO GEA analyses. Instrument performance is assessed by the analyses of daily control counts and weekly background counts, as discussed below.

Duplicate Relative Percent Difference (RPD):

No duplicate samples were provided for gamma counting.

Instrument Calibration and Quality Control

Gamma detectors are calibrated using multi-isotope standards that are NIST-traceable and prepared in the identical counting geometry to all samples and detectors, if possible. Counter control sources containing Am-241, Cs-137 and Co-60 are analyzed daily before the use of each detector. Procedure RPG-CMC-450 requires that a counter control source is checked daily and must be within ±3 sigma or ±3% of the control value, whichever is greater. Gamma counting was not performed unless the control counts were within the required limits. Background counts are performed on all gamma detectors at least weekly for either an overnight or weekend count within operational limits, and/or when system background is thought to have changed. The most recent background is subtracted from all sample counts.

The samples were prepared in a 2 mL geometry from client.

Assumptions and Limitations of the Data

None

Interferences/Resolution

None.

Uncertainty

For gamma counting, the uncertainty in the counting data, photon abundance and the nuclear half-life, and efficiency are included in the calculation of the total uncertainty along with a systematic uncertainty for sample prep. The Canberra Genie software includes both random and systematic uncertainties in the calculation of the total uncertainties which are listed on the report. We conservatively estimate that 2% is the lowest uncertainty possible for our GEA measurements taking into account systematic uncertainties in gamma calibration standards. This uncertainty assumes the sample geometry matches the calibration geometry, and is undoubtedly larger when the sample geometry does not match a calibration geometry.

Comments

None.

Attachment: Data Report Sample Results for ASR 0747.00.

Pacific Northwest National Laboratory
PO Box 999, Richland, WA
Radiochemical Sciences and Engineering Group

filename: 19-1227 Rovira
3/20/2019

Client: Rovira
ASR 0747

Project: 73312
NC4186

Prepared by: T Trang-le 3/20/19

Technical Reviewer: LRGreenwood 3/20/19

Procedures: RPG-CMC-450, Rev. 3 Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS) Spectrometry

M&TE: Gamma detectors T
Reference dates: 3/18/2019 @ 1:00 pm

Measured Activity, µCi per Sample ± 1s

RPL ID: Sample ID: **Isotope**	19-1227 7AP-18-1		19-1228 7AP-18-36	
Cs-137	2.80E+02	± 2%	2.82E+02	± 2%

Battelle PNNL/RPL/Inorganic Analysis … ICP-MS Analysis Report

PO Box 999, Richland, Washington 99352

Project / WP#:	73312 / NC4186
ASR#:	0747.00
Client:	A. Rovira
Total Samples:	2 (Aqueous)

ASO Sample ID	**Client Sample ID**	**Client Sample Description**	**Sample Weight (g)**
19-1227	7AP-18-1	AP-107 Tank Supernate	NA
19-1228	7AP-18-36	AP-107 Tank Supernate	NA

Sample Preparation: Acid digestion was performed according to RPG-CMC-128, "HNO_3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater", performed by L. Darnell between 04/16/19. Sample were diluted prior to ICP-MS analysis in 2% v/v HNO_3 performed by S.S. Morrison on 04/19/19.

Procedure: RPG-CMC-292, Rev. 1, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Mass Spectrometry (ICP-MS)."

Analyst:	S.S. Morrison	**Analysis Date:**	04/19/2019	**ICP File:**	M0154

See Chemical Measurement Center 98620 file: ICP-325-405-3 (Calibration and Maintenance Records)

M&TE:				
	☒	PerkinElmer NexION^{TM} 350X ICP-MS	SN: 85VN4070702	RPL 405
	☒	Ohaus PA224C	SN: B725287790	RPL 405
	☒	Mettler AT400 Balance	SN: M19445	RPL 405 FH
	☐	Mettler AT400 Balance	SN: 1113292667	RPL 420 FH
	☐	Ohaus EX324 Balance	SN: 8033311209	SAL Cell 2
	☐	Sartorius BA3105 Balance	SN: 10803210	RPL 309
	☐	Sartorius R200D Balance	SN: 39080058	RPL 525 FH

S S

Report Preparer

04/26/2019

Date

Denis Cherkasov

Review and Concurrence

04/26/2019

Date

Two aqueous samples submitted under Analytical Service Request (ASR) 0747.00 were analyzed by ICP-MS. Prior to analysis all samples were diluted in 2% HNO_3. None of the samples were filtered.

All results are reported on a mass per unit volume basis (ng/mL) for each detected analyte. The data have been adjusted for instrument dilutions.

Analytes of interest (AOI) were specified in the ASR and are listed in the upper section of the attached ICP-MS Data Report. Cesium-133, Cesium-135, and Cesium-137 were the AOI. The quality control (QC) results for the AOI have been evaluated and are presented below.

Calibration of the ICP-MS was done following the manufacturer's recommended calibration procedure using multi-analyte custom standard solutions traceable to the National Institute of Standards and Technology (NIST). Midrange calibration verification standards were used to verify acceptance of the five-point calibration curve and for initial and continuing calibration verification (ICV/CCV).

The controlling document was procedure RPG-CMC-292, Rev 1, *Determination of Elemental Composition by Inductively Coupled Argon Plasma Mass Spectrometry (ICP-MS.* Instrument calibrations, QC checks and blanks (e.g., ICV/ICB, CCV/CCB, LLS, ICS), post-digestion spike, duplicate, blank spike, and serial dilution were conducted during the analysis run.

Internal Standard (IS):

All solutions (blanks, standards, QC checks, and samples) were mixed in-line with a solution containing 10 ppb of Bi-209 as the internal standard (IS). The AOI (m/z 133, 135, and 137) data were normalized using the data for the IS Bi-209). The Bi-209 IS recoveries ranged from 91.0% to 110.4% for the entire analysis sequence, which were within the acceptance criterion of 30% to 120%.

Preparation Blank (PB):

A preparation blank was prepared according to RPG-CMC-128, and labeled as BLK-1227 and diluted in 2% HNO_3, this solution was analyzed as a preparation blank. Results for the diluent blank were within the acceptance criteria of less than ≤10% of the concentration in the samples.

Blank Spike (BS)/Laboratory Control Sample (LCS):

A blank spike (BS) sample was prepared by spiking the preparation blank (BLK-1227) with an equivalent volume of the CCV-71A-2ppb standard (1:1 ratio). The recovery for the m/z 133 (98%), 135 (95%), 137 (95%) were within the acceptance criteria of 80% to 120% recovery.

Duplicate/Replicate Relative Percent Difference (RPD)/Relative Standard Deviation (RSD):

Duplicate of sample 19-1228 was prepared during dissolution according to RPG-CMC-128, the solution was diluted and analyzed. RPD are listed for all analytes that were measured at or above the EQL. RPD for the m/z 133, 135, and 137 were 4%, 2%, and 4%, respectively; which were within the acceptance criterion of ≤20% for liquid samples.

Matrix-Spike (MS) Sample:

The sample was not analyzed because there is no Cs tracer in the matrix spike solution and the analysis would not speak to matrix effects within the sample. Instead, a post spike sample was prepared and analyzed results reported in the post digestion spike section.

Initial/Continuing Calibration Verification (ICV/CCV):

The ICV/CCV solution was analyzed immediately after calibration, after each group of not more than ten samples, and at the end of the analytical run. The concentrations of all AOI were within the acceptance criteria of 90% to 110% recovery.

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solution (2% v/v HNO_3) was analyzed immediately after the ICV solutions and after the CCV solutions (after each group of not more than ten samples and at the end of the analytical run). The concentration of all AOI were within the acceptance criteria of <5% of sample.

Low-Level Standard (LLS):

The LLS solution was analyzed immediately after the first CCB. The recovery for m/z 133, 135, and 137 were 103%, 102%, and 99% respectfully; all were within the acceptance criteria of 75% to 125%.

Interference Check Standard (ICS):

The ICS solution was analyzed immediately after the LLS solution and immediately after the final CCV solution. The recoveries for m/z 133 (105%, 105%), m/z 135 (102%, 102%), and m/z 137 (100%, 101%) which were within the acceptance criteria of 80% to 120%.

Serial Dilution (SD):

Five-fold serial dilution was conducted on samples 19-1228. Percent differences (%D) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. The %D for the AOI m/z 133 (6%), m/z 135 (2%), and m/z 137 (9%) were within the acceptance criterion of ≤10%, when analytes were at >10xEQL.

Post-Digestion Spike (PS-71A)/Analytical Spike (AS-71A) - Sample (71A Component):

Because no MS sample was analyzed, a post-digestion spike (PS-71A) was conducted on samples 19-1228. The recovery is listed for all analytes in the spike that was measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. Recovery values for m/z 133, 135 and 137 were 102%, 106%, and 104% respectively, and were within the acceptance criterion of 75% to 125%.

Other QC:

All other instrument-related QC tests for the AOI passed within their respective acceptance criteria.

Comments:

1) The "Final Results" have been corrected for all laboratory dilutions performed on the samples during processing and analysis, unless specifically noted.
2) Instrument detection limits (IDL) and estimated quantitation limits (EQL) shown are for acidified water and/or fusion flux matrices as applicable. Method detection limits (MDL) for individual samples can be estimated by multiplying the IDL by the "Process Factor" for that individual sample. The estimated quantitation limit (EQL) for each concentration value can be obtained by multiplying the EQL by the "Process Factor".
3) Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g. 2% v/v HNO_3 or less) at analyte concentrations > EQL up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000 µg/mL (0.5 per cent by weight). Note that bracketed values listed in the data report are within the MDL and the EQL, and have potential uncertainties greater than 15%. Concentration values < MDL are listed as "- -". Note, that calibration and QC standard samples are validated to a precision of ±10%.
4) Analytes included in the spike 71A component (for the AS/PS) are; Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ho, K, La, Lu, Mg, Mn, Na, Nd, Ni, P, Pb, Pr, Rb, S, Se, Sm, Sr, Th, Tl, Tm, U, V, Yb, and Zn. Analytes included in the spike 71B component are; Ge, Hf, Mo, Nb, Sb, Si, Sn, Ta, Te, Ti, W, and Zr. Analytes included in the spike 71C component are; Ir, Os, Pd, Pt, Re, Rh, and Ru. Analytes included in the spike 71D component are; Bi, In, Li, Sc, Tb, and Y. Analytes included in the spike Hg component are; Hg.

Battelle PNNL/RPG/Inorganic Analysis ... ICP-MS Data Report

		Run Date >	04/19/19	04/19/19	04/19/19	04/19/19
		Process Factor >	43207	42808	42660	42346
		RPL/LAB >	BLK-1227	19-1227	19-1228	DUP-1228
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Process Reagent Blank	7AP-18-1	7AP-18-36	7AP-18-36
(ng/mL)	(ng/mL)	(Analyte)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)
2.35E-04	2.35E-03	Cs 133	1.45E+01	5.96E+03	6.04E+03	6.21E+03
6.41E-05	6.41E-04	Cs 135	4.74E+01	1.71E+03	1.76E+03	1.78E+03
7.56E-05	7.56E-04	Cs 137	7.67E+01	1.96E+03	2.03E+03	2.09E+03

Internal Standard % Recovery

Bi 209 (IS)	95%	102%	99%	97%

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

IS = Internal Standard. The concentration of certain elements cannot be determined due to the presence of the IS in all solutions.

QC Performance 04/19/2019

Criteria >	≤ 20%	80%-120%	75%-125%	75%-125%	≤ 10%
QC ID >	DUP-1228	BS/LCS	MS (None)	19-1228 PSA	19-1228 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Diff
Cs 133	3.7%	98%	NA	102%	5.7%
Cs 135	2.0%	95%	NA	106%	2.2%
Cs 137	3.4%	95%	NA	104%	9.3%

Standard % Recovery

Bi 209 (IS)	97%	101%	NA	102%	99%

Shaded results are outside the acceptance criteria.

nr = spike concentration less than 25% of sample concentration. Matrix effects can be assessed from the serial dilution.

na = not applicable; KOH flux and Ni crucible or Na2O2 flux and Zr crucible for fusion preparations, or Si for HF assisted digests.

IS = Internal Standard. The concentration of certain elements cannot be determined due to the presence of the IS in all solutions.

NM = Not measured. The isotope was not measure due to method or molecular interference limitations.

N:\Inorganic Analyses\ICP-MS NexION 350\Analysis Data\M0100-M0199\M0154 ASR-0747 Rovira Cs SSM20190419.xlsx

Analytical Service Request (ASR)

(Information on this COVER PAGE is applicable to all samples submitted under this ASR)

Requestor --- Complete all fields on this COVER PAGE, unless specified as optional or ASR is a revision

Requestor:
Signature Karl N. Pool For S. Fiskum
Print Name S. Fiskum
Phone 375-5677 MSIN P7-25

Project Number: 73312
Work Package: NC4189

Matrix Type Information

◆ **Liquids:** X Aqueous ☐ Organic ☐ Multi-phase
◆ **Solids:** ☐ Soil ☐ Sludge ☐ Sediment
☐ Glass ☐ Filter ☐ Metal
☐ Smear ☐ Organic ☐ Other

◆ **Other:** ☐ Solid/Liquid Mixture, Slurry
☐ Gas ☐ Biological Specimen

(If sample matrices vary, specify on Request Page)

QA/Special Requirements

◆ **QA Plan:**
XASO-QAP-001 (Equivalent to HASQARD)
☐ Additional QA Requirements, List Document Below:
Reference Doc Number:

◆ **Field COC Submitted?** X No ☐ Yes
◆ **Lab COC Required?** X No ☐ Yes
◆ **Sample/Container Inspection Documentation Required?**
X No ☐ Yes

◆ **Hold Time:** X No ☐ *Yes*
***If Yes,* Contact ASO Lead before submitting Samples**
☐ Use SW 846 (PNL-ASO-071, identify analytes/methods where holding times apply)
☐ Other? Specify:

◆ **Special Storage Requirements:**
X None ☐ Refrigerate ☐ Other, Specify:

◆ **Data Requires ASO Quality Engineer Review?** X No ☐ Yes

Disposal Information

◆ **Disposition of Virgin Samples:**
Virgin samples are returned to requestor unless archiving provisions are made with receiving group!
If archiving, provide:
Archiving Reference Doc:

◆ **Disposition of Treated Samples:**
X Dispose ☐ Return

Data Reporting Information

◆ **Is Work Associated with a Fee-Based Milestone?** ☐ No X Yes
If yes, milestone due date:

◆ **Preliminary Results Requested, As Available?** ☐ No X Yes

◆ **Data Reporting Level**
X ASO-QAP-001 (Equivalent to HASQARD).
☐ Minimum data report.
☐ Project Specific Requirements: Contact ASO Lead or List Reference Document:

◆ **Requested Analytical Work Completion Date:**

(Note: **Priority rate charge for < 10 business day turn-around time)**

◆ **Negotiated Commitment Date:**
7/23/19
(To be completed by ASO Lead)

Waste Designation Information

◆ **ASO Sample Information Check List Attached?** X No ☐ Yes
If no, Reference Doc Attached:
or, Previous ASR Number: 0521
or, Previous RPL Number:

Does the Waste Designation Documentation Indicate Presence of PCBs?
X No ☐ Yes

Send Report To: **S. Fiskum** **MSIN** **P7-25**
A. Rovira **MSIN** P7-25
Additional or Special Instructions

Receiving and Login Information *(to be completed by ASO staff)*

Date Delivered: 5/7/19
Delivered By (optional) S. Fiskum
Time Delivered:
Group ID (optional)
CMC Waste Sample? X No ☐ Yes

Received By: K. Pool 5/7/19
ASR Number: **0787** Rev.: **02**
RPL Numbers: 19-1773 thru 19-1784
(first and last)

ASO Work Accepted By: KN Pool **Signature/Date:** Karl N. Pool 6/26/19

Analytical Services Request (ASR)

(REQUEST PAGE ---- Information Specific to Individual Samples)

Provide Analytes of Interest and Required Detection limits - ☐ **Below** ☐ **Attached**

ASO Staff Use Only **RPL Number**	Client Sample ID	Sample Description (& Matrix if varies)	Analyses Requested	ASO Staff Use Only **Test**	ASO Staff Use Only **Library**
Revision 1 - ASR revised to add F to the IC analyses on sample 19-1773 and add Si, B, Li, Mg, Mo and W to sample 19-1774 ICP/OES analyses					
Revison 2 - ASR revised to remove the requirement for QE Review					
19-1773	TI061-COMP-FEED	AP-107 Tank Waste	1) GEA - All samples (Cs-137, Co-60 and Eu-154 and any other observed gamma emitting isotopes) 2) Tc-99 3) IC-Anions - **F**, Cl, NO$_2$, NO$_3$, PO$_4$, C$_2$O$_4$ and SO$_4$ 4) TOC/TIC - Hot Pursulfate 5) OH 6) Acid Digestion- 128 - Prep Lab a) ICP/OES - Ag, Al, As, Ba, Ca, Cd, Cr, Fe, K, Na, Ni, P, Pb, S, Sr, Ti, Zn, Zr b) ICP/MS - U-238 c) Sr-90 d) Np-AEA, Np-237 e) Pu-AEA, Pu-238, Pu-239/240		
19-1774	TI061-COMP-EFF	AP-107 Tank Waste - Cs Removed	1) GEA - All samples (Cs-137, Co-60 and Eu-154 and any other observed gamma emitting isotopes) 2) Tc-99 3) Acid Digestion- 128 - Prep Lab a) ICP/OES - Ag, Al, As, **B** Ba, Ca, Cd, Cr, Fe, K,**Li**, **Mg**, **Mo**, Na, Ni, P, Pb, S, **Si**, Sr, Ti, **W**, Zn, Zr b) ICP/MS - U-238 c) Sr-90 d) Pu-AEA, Pu-238, Pu-239/240 e) Np-AEA, Np-237		

ASR: 0787______ Rev: 02

ASR 0787.02 Request Page

Analytical Services Request (ASR)

(REQUEST PAGE ---- Information Specific to Individual Samples)

ASO Staff Use Only	**Provide Analytes of Interest and Required Detection limits** - ☐ **Below** ☐ **Attached**			ASO Staff Use Only	
RPL Number	Client Sample ID	Sample Description (& Matrix if varies)	Analyses Requested	**Test**	**Library**
19-1775	TI061-L-F1-A	AP-107 Tank Waste - Cs Removed	1) Acid Digest - 128 - Prep Lab a) ICP/OES - Ba, Ca, Cd, Cr, Fe, K, Ni, Pb, Ti, Zn, Zr b) ICP/MS - U-238 c) Sr-90 c) Pu-AEA, Pu-238, Pu-239/240 d) Np-AEA, Np-237		
19-1776	TI061-L-F4-A				
19-1777	TI061-L-F8-A				
19-1778	TI061-L-F11-A				
19-1779	TI061-L-F14-A				
19-1780	TI061-L-F18-A				
19-1781	TI061-L-F22-A				
19-1782	TI061-L-F25-A				
19-1783	TI061-L-F27-A				
19-1784	TI061-L-F29-A				

Battelle PNNL/RPL/Inorganic Analysis … ICP-OES Analysis Report

PO Box 999, Richland, Washington 99352

Project / WP#: 73312 / NC4189
ASR#: 0787
Client: S. Fiskum
Total Samples: 12 (liquids)
Sample Description AP-107 Tank Waste

ASO Sample ID	Client Sample ID	Sample Weight (g)	ASO Sample ID	Client Sample ID	Sample Weight (g)
19-1773	TI061-COMP-FEED	NA	19-1779	TI061-L-F14-A	NA
19-1774	TI061-COMP-EFF	NA	19-1780	TI061-L-F18-A	NA
19-1775	TI061-L-F1-A	NA	19-1781	TI061-L-F22-A	NA
19-1776	TI061-L-F4-A	NA	19-1782	TI061-L-F25-A	NA
19-1777	TI061-L-F8-A	NA	19-1783	TI061-L-F27-A	NA
19-1778	TI061-L-F11-A	NA	19-1784	TI061-L-F29-A	NA

Sample Preparation: RPG-CMC-128, Rev. 1. "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater" using Nitric Acid only, performed by L. Darnell on 07/02/19. Simple dilution of "as received" samples in 5% v/v HNO_3 performed by J. Carter on 07/03/19.

Procedure: RPG-CMC-211, Rev. 4, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)."

Analyst:	J. Carter	**Analysis Date:**	07/03/19	**ICP File:**	C0804

See Chemical Measurement Center 98620 file: ICP-325-405-3
(Calibration and Maintenance Records)

M&TE:

☒	PerkinElmer 5300DV ICP-OES	SN: 077N5122002
☐	Mettler AT400 Balance	SN: 1113292667
☒	Ohaus PA224C Balance	SN: B725287790
☒	Sartorius ME414S Balance	SN: 21308482
☐	SAL Cell 2 Balance	SN: 8033311209

7/10/19

Report Preparer — Date

Denis Cherkasov — 7/12/19

Review and Concurrence — Date

Twelve aqueous samples submitted under Analytical Service Request (ASR) 0787 were analyzed by ICP-OES. The samples were prepared following RPL procedure RPG-CMC-128, Rev. 1, "*HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater*". This process was conducted without the use of HCl. All samples were diluted in 5% HNO_3 prior to analysis. None of the samples were filtered.

All sample results are reported on a mass per unit volume basis (µg/mL) for each detected analyte. The data have been adjusted for instrument dilutions.

Analytes of interest (AOI) were specified in the ASR and are listed in the upper section of the attached ICP-OES Data Report. There were two analyte lists requested, one being a shortened version. Samples were reported using the most extensive analyte list. The quality control (QC) results for the AOI have been evaluated and are presented below. Analytes other than the AOI are reported in the bottom section of the report but have not been fully evaluated for QC performance.

Calibration of the ICP-OES was done following the manufacturer's recommended calibration procedure using multi-analyte custom standard solutions traceable to the National Institute of Standards and Technology (NIST). Midrange calibration verification standards (MCVA and MCVB) were used to verify acceptance of the two-point calibration curves obtained for each analyte and for continuing calibration verification.

The controlling documents were procedures RPG-CMC-211, Rev. 4, *Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)*, and ASO-QAP-001, Rev. 11, *Analytical Support Operations (ASO) Quality Assurance Plan.* Instrument calibrations, QC checks and blanks (e.g., ICV/ICB, CCV/CCB, LLS, ICS), matrix spike, post-digestion spikes, duplicate, reagent spike, blank spike, and serial dilution were conducted during the analysis run.

Preparation Blank (PB):

A preparation blank (reagents only) was prepared for the extraction process. All analytes were within the acceptance criteria of <EQL (estimated quantitation level), ≤50% regulatory decision level, or ≤10% of the concentration in the samples. The lab diluent passed these criteria.

Blank Spike (BS)/Laboratory Control Sample (LCS):

A reagent spike (BS) sample (reagents and spikes) was prepared for the extraction process. Recovery values are listed for all analytes included in the RS that were measured at or above the EQL. Recovery values for the AOI meeting this requirement ranged from 83% to 109% and were within the acceptance criterion of 80% to 120%.

Duplicate/Replicate Relative Percent Difference (RPD)/Relative Standard Deviation (RSD):

A duplicate of sample 19-1774 was prepared and analyzed. RPDs are listed for all analytes that were measured at or above the EQL. RPDs for the AOI meeting this requirement ranged from 0.8% to 4.4% and were within the acceptance criterion of ≤20% for liquid samples.

Matrix-Spike (MS) Sample:

A matrix spike (MS) of sample 19-1774 was prepared for the extraction process. Recovery values are listed for all analytes included in the MS that were measured at or above the EQL. Recovery values for the AOI meeting this requirement ranged from 50% to 122% and were within the acceptance criterion of 75% to 125%, with the exception of Ag (50%).

Initial/Continuing Calibration Verification (ICV/CCV):

MCVA and MCVB solutions were analyzed immediately after calibration, after each group of not more than ten samples, and at the end of the analytical run. The concentrations of all AOI were within the acceptance criteria of 90% to 110% recovery.

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solution (5% v/v HNO_3) was analyzed immediately after the ICV solutions and after the CCV solutions (after each group of not more than ten samples and at the end of the analytical run). The concentration of all AOI were within the acceptance criteria of <EQL, with the exception of sodium in the final CCB solution (0.372ppm). Associated samples are greater than 10x the EQL.

Low-Level Standard (LLS):

The LLS solution was analyzed immediately after the first CCB solution. The concentrations of all AOI were within the acceptance criteria of 70% to 130% recovery.

Interference Check Standard (ICS/SST):

The ICS solution was analyzed immediately after the first LLS solution and immediately prior to analyzing the final CCV solutions. The concentrations of all AOI were within the acceptance criteria of 80% to 120% recovery.

Serial Dilution (SD):

Five-fold serial dilution was conducted on sample 19-1773. Percent differences (%Ds) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. The %Ds for the AOI meeting this requirement ranged from 0.3% to 24.3% and were within the acceptance criterion of ≤10% except for potassium which had a %D of 24.3%.

Post-Digestion Spike (PS-A) - Sample (A Component):

In addition to the BS sample, a post-digestion spike (A Component) was conducted on sample 19-1775. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. Recovery values for the AOI meeting this requirement ranged from 96% to 117%, and were within the acceptance criterion of 80% to 120%.

Post-Digestion Spike (PS-B) - Sample (B Component):

In addition to the MS sample, a post-digestion spike (B Component) was conducted on sample 19-1775. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. Recovery values for the AOI meeting this requirement was 99% and within the acceptance criterion of 80% to 120%.

Other QC:

All other instrument-related QC tests for the AOI passed within their respective acceptance criteria.

Comments:

1) The "Final Results" have been corrected for all laboratory dilutions performed on the samples during processing and analysis, unless specifically noted.
2) Instrument detection limits (IDL) and estimated quantitation limits (EQL) shown are for acidified water and/or fusion flux matrices as applicable. Method detection limits (MDL) for individual samples can be estimated by multiplying the IDL by the "Process Factor" for that individual sample. The estimated quantitation limit (EQL) for each concentration value can be obtained by multiplying the EQL by the "Process Factor".
3) Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g. 5% v/v HNO_3 or less) at analyte concentrations > EQL up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000 µg/mL (0.5 per cent by weight). Note that bracketed values listed in the data report are within the MDL and the EQL, and have potential uncertainties greater than 15%. Concentration values < MDL are listed as "- -". Note, that calibration and QC standard samples are validated to a precision of ±10%.
4) Analytes included in the spike A component (for the AS/PS) are; Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ta, Ti, Tl, V, W, Y, Zn, and Zr. Analytes included in the spike B component are; Ce, Dy, Eu, La, Nd, Pd, Rh, Ru, S, Te, Th, and U.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

		Run Date >	7/3/2019	7/3/2019	7/3/2019	7/3/2019	7/3/2019	7/3/2019	7/3/2019	7/3/2019
		Process Factor >	1.0	1.0	248.9	249.6		247.0	246.6	248.9
					19-1773 @ 5x	19-1774 @ 5x	DUP-1774 @ 5x	19-1775 @ 5x	19-1776 @ 5x	19-1777 @ 5x
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Lab Diluent	Reagent Blank	TI061-COMP-FEED	TI061-COMP-EFF		TI061-L-F1-A	TI061-L-F4-A	TI061-L-F8-A
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
0.0019	0.019	Ag	--	--	--	--	--	--	--	--
0.0122	0.122	Al	--	[0.35]	10014.22	9829.47	9676.03	8519.36	9134.23	8959.56
0.0529	0.529	As	--	--	--	--	--	--	--	--
0.0003	0.003	Ba	--	--	[0.41]	--	--	--	--	--
0.0177	0.177	Ca	--	[2.13]	[34.48]	[23.09]	[12.60]	[29.03]	[24.36]	[23.05]
0.0022	0.022	Cd	--	--	6.51	[5.11]	5.43	[2.38]	5.51	[5.45]
0.0025	0.025	Cr	--	--	526.82	525.56	503.84	486.89	494.73	488.30
0.0052	0.052	Fe	--	[0.34]	14.77	[12.48]	[11.79]	15.26	26.42	[12.14]
0.0240	0.240	K	--	--	4684.88	4518.87	4484.80	4143.80	4359.04	4187.15
0.0246	0.246	Na	--	--	137330.45	133410.93	129259.79	122715.68	128843.96	126427.90
0.0049	0.049	Ni	--	--	24.58	23.60	22.72	20.61	21.64	20.96
0.0554	0.554	P	--	--	873.09	845.57	808.90	774.90	804.26	774.71
0.0162	0.162	Pb	--	--	[8.12]	--	--	--	--	--
0.1186	1.186	S	--	--	1932.77	1862.85	1826.32	1761.04	1831.36	1743.59
0.0005	0.005	Sr	--	--	[0.13]	--	--	--	--	--
0.0004	0.004	Ti	--	--	--	[0.19]	[0.18]	[0.30]	[0.26]	[0.23]
0.0043	0.043	Zn	--	[0.52]	--	[1.53]	[1.08]	[1.11]	--	--
0.0019	0.019	Zr	--	--	--	[2.09]	[2.09]	[1.37]	[1.52]	[1.66]
Other Analytes										
0.0067	0.067	B	[0.04]	[1.01]	31.35	23.21	20.59	107.27	99.41	87.96
0.0001	0.001	Be	--	--	[0.14]	[0.11]	[0.12]	--	[0.09]	[0.10]
0.0494	0.494	Bi	--	--	--	--	--	--	--	--
0.0069	0.069	Ce	--	--	--	--	--	--	--	--
0.0035	0.035	Co	--	--	--	--	[1.40]	--	[1.07]	--
0.0016	0.016	Cu	--	[0.07]	[1.14]	[0.55]	--	--	--	[0.62]
0.0029	0.029	Dy	--	--	--	--	--	--	--	--
0.0013	0.013	Eu	--	--	--	--	--	--	--	--
0.0022	0.022	La	--	--	--	--	--	--	--	--
0.0009	0.009	Li	--	--	[0.23]	--	--	--	--	--
0.0068	0.068	Mg	--	[0.24]	--	--	--	--	--	--
0.0002	0.002	Mn	--	--	--	--	--	--	--	--
0.0045	0.045	Mo	--	--	44.28	42.27	40.76	39.66	40.59	40.54
0.0086	0.086	Nd	--	--	--	--	--	--	--	--
0.0077	0.077	Pd	--	--	--	--	--	--	--	--
0.0165	0.165	Rh	--	--	--	--	--	--	--	--
0.0097	0.097	Ru	--	--	[7.06]	[7.54]	[5.67]	[7.92]	[7.29]	[6.03]
0.0518	0.518	Sb	--	--	--	--	--	--	--	--
0.1595	1.595	Se	--	--	--	--	--	--	--	--
0.0237	0.237	Si	--	[0.86]	70.96	[41.84]	[40.66]	122.87	105.73	108.96
0.0313	0.313	Sn	--	[0.80]	[13.68]	[8.24]	[13.99]	[16.39]	[16.96]	--
0.0217	0.217	Ta	--	--	--	--	--	--	--	--
0.0311	0.311	Te	--	--	[8.45]	--	--	--	--	--
0.0189	0.189	Th	--	--	--	--	--	--	--	--
0.0530	0.530	Tl	--	--	--	--	--	--	--	--
0.0360	0.360	U	--	--	[15.24]	--	[10.10]	--	--	[9.00]
0.0021	0.021	V	--	--	[0.78]	--	--	--	--	--
0.0216	0.216	W	--	--	70.89	72.72	62.83	65.68	62.41	60.32
0.0012	0.012	Y	--	--	--	--	--	--	--	--

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

ASR-0787 Results from C0804 ASR-0787 Fiskum (128)

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

		Run Date >	7/3/2019	7/3/2019	7/3/2019	7/3/2019	7/3/2019	7/3/2019	7/3/2019
		Process Factor >	250.2	250.7	247.0	248.5	251.9	248.3	246.8
			19-1778 @ 5x	19-1779 @ 5x	19-1780 @ 5x	19-1781 @ 5x	19-1782 @ 5x	19-1783 @ 5x	19-1784 @ 5x
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	TI061-L-F11-A	TI061-L-F14-A	TI061-L-F18-A	TI061-L-F22-A	TI061-L-F25-A	TI061-L-F27-A	TI061-L-F29-A
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
0.0019	0.019	Ag	--	--	--	--	--	--	--
0.0122	0.122	Al	9032.73	8772.12	9431.78	9526.53	9598.06	9576.94	9636.19
0.0529	0.529	As	--	--	--	--	--	--	--
0.0003	0.003	Ba	--	--	--	--	--	--	--
0.0177	0.177	Ca	[20.47]	[21.08]	[23.83]	[21.94]	[19.51]	[21.19]	[21.77]
0.0022	0.022	Cd	6.00	[5.47]	5.95	6.39	5.96	6.50	5.98
0.0025	0.025	Cr	494.77	477.32	497.64	518.84	504.67	508.87	515.21
0.0052	0.052	Fe	14.13	[11.75]	13.81	13.19	14.18	13.37	33.90
0.0240	0.240	K	4328.35	4159.06	4512.37	4514.00	4492.38	4459.46	4554.30
0.0246	0.246	Na	127623.19	125402.26	128473.07	131485.59	132018.56	130987.29	133132.27
0.0049	0.049	Ni	20.89	21.20	21.51	21.58	22.75	23.01	22.25
0.0554	0.554	P	803.51	764.11	791.91	823.87	812.99	819.64	821.55
0.0162	0.162	Pb	--	--	--	--	[4.23]	--	[5.99]
0.1186	1.186	S	1851.86	1786.69	1846.62	1906.33	1831.28	1847.77	1855.36
0.0005	0.005	Sr	--	--	--	--	--	--	--
0.0004	0.004	Ti	[0.29]	[0.21]	[0.18]	[0.24]	[0.14]	[0.21]	[0.21]
0.0043	0.043	Zn	[1.34]	--	[1.16]	[1.37]	--	--	--
0.0019	0.019	Zr	[1.51]	[1.13]	[1.38]	[1.68]	[1.28]	[1.39]	[1.10]
Other Analytes									
0.0067	0.067	B	106.90	96.55	83.88	83.78	74.02	62.54	77.17
0.0001	0.001	Be	[0.12]	[0.11]	[0.12]	[0.12]	[0.13]	[0.12]	[0.12]
0.0494	0.494	Bi	--	--	--	--	--	--	--
0.0069	0.069	Ce	--	--	--	--	--	--	--
0.0035	0.035	Co	--	--	--	--	[1.12]	--	[0.98]
0.0016	0.016	Cu	[1.30]	[0.78]	[0.86]	[1.25]	[1.23]	[1.05]	[1.05]
0.0029	0.029	Dy	--	--	--	--	--	--	--
0.0013	0.013	Eu	--	--	--	--	--	--	--
0.0022	0.022	La	--	--	--	--	--	--	--
0.0009	0.009	Li	--	--	--	--	--	--	--
0.0068	0.068	Mg	--	--	--	--	--	--	--
0.0002	0.002	Mn	--	--	--	--	--	--	--
0.0045	0.045	Mo	42.41	40.52	41.87	43.87	41.49	42.31	42.89
0.0086	0.086	Nd	--	--	--	--	--	--	--
0.0077	0.077	Pd	--	[2.39]	--	[2.80]	--	--	--
0.0165	0.165	Rh	--	--	[4.79]	--	--	--	--
0.0097	0.097	Ru	[7.40]	[6.07]	[8.41]	[5.29]	[6.17]	[7.37]	[5.61]
0.0518	0.518	Sb	--	--	[15.65]	[17.18]	[13.10]	--	--
0.1595	1.595	Se	--	--	--	--	--	--	--
0.0237	0.237	Si	135.56	137.68	176.52	166.97	150.31	162.13	146.35
0.0313	0.313	Sn	[11.49]	[16.61]	[16.51]	[9.26]	[14.51]	[14.84]	[9.56]
0.0217	0.217	Ta	--	--	--	--	--	--	--
0.0311	0.311	Te	[8.77]	--	--	--	--	--	--
0.0189	0.189	Th	--	--	--	--	--	--	--
0.0530	0.530	Tl	--	--	--	--	--	--	--
0.0360	0.360	U	--	--	[9.40]	--	[10.20]	--	--
0.0021	0.021	V	--	--	--	--	--	--	--
0.0216	0.216	W	67.88	64.92	67.48	74.50	70.61	73.16	67.19
0.0012	0.012	Y	--	--	--	--	--	--	--

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

ASR-0787 Results from C0804 ASR-0787 Fiskum (128)

QC Performance 7/3/2019

Criteria >	≤ 20%	80%-120%	75%-125%	80%-120%	80%-120%	≤ 10%
QC ID >	19-1774 Dup	BS-1720	19-1774 MS	19-1775 + AS-A	19-1775 + AS-B	19-1773 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Ag		83	50	96		
Al	1.6	97	89	105		0.3
As				102		
Ba		100	99	104		
Ca		104	111	113		
Cd		97	96	101		
Cr	4.2	100	nr	102		1.7
Fe		100	98	105		
K	0.8	92	122	117		24.3
Na	3.2	109	nr	nr		1.6
Ni	3.8	99	98	104		
P	4.4	98	89	98		1.2
Pb		100	99	100		
S	2.0	96	94		99	3.9
Sr		101	97	101		
Ti		100	99	103		
Zn		97	95	102		
Zr		99	97	104		
Other Analytes						
B	11.9	101	96	101		
Be		99	100	105		
Bi		83		96		
Ce		91	89		93	
Co				101		
Cu		100	103	107		
Dy					100	
Eu					99	
La		98	97		98	
Li		111	123	120		
Mg		101	103	107		
Mn		98	96	101		
Mo	3.6	98	94	99		
Nd		98	97		100	
Pd					96	
Rh					102	
Ru					96	
Sb				101		
Se				103		
Si		90	101	106		
Sn				99		
Ta				100		
Te					100	
Th		99	98		99	
Tl				91		
U		100	97		103	
V		95	93	99		
W	14.6	98	90	101		
Y				100		

Shaded results are outside the acceptance criteria.

nr = spike concentration less than 25% of sample concentration. Matrix effects can be assessed from the serial dilution.

Battelle PNNL/RPL/Inorganic Analysis … ICP-MS Analysis Report

PO Box 999, Richland, Washington 99352

Project / WP#:	73312 / NC4189
ASR#:	0787
Client:	S. Fiskum
Total Samples:	12 (Aqueous)
Sample Description	AP-107 Tank Waste

ASO Sample ID	Client Sample ID	Client Sample Description	Sample Weight (g)
19-1773	TI061-COMP-FEED	AP-107 Tank Waste	NA
19-1774	TI061-COMP-EFF	AP-107 Tank Waste Cs Removed	NA
19-1775	TI061-L-F1-A	AP-107 Tank Waste Cs Removed	NA
19-1776	TI061-L-F4-A		NA
19-1777	TI061-L-F8-A		NA
19-1778	TI061-L-F11-A		NA
19-1779	TI061-L-F14-A		NA
19-1780	TI061-L-F18-A		NA
19-1781	TI061-L-F22-A		NA
19-1782	TI061-L-F25-A		NA
19-1783	TI061-L-F27-A		NA
19-1784	TI061-L-F29-A		NA

Sample Preparation: RPG-CMC-128, Rev. 1. "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater" performed by L. Darnell on 07/02/19; ICP-MS bench dilution in 2% v/v HNO_3 performed by D. Cherkasov on 07/09/19.

Procedure: RPG-CMC-292, Rev. 1, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Mass Spectrometry (ICP-MS)."

Analyst:	D.E.Cherkasov	**Analysis Date:**	07/09/2019	**ICP File:**	M0181

See Chemical Measurement Center 98620 file: ICP-325-405-3 (Calibration and Maintenance Records)

M&TE:	☒	PerkinElmer NexION™ 350X ICP-MS	SN: 85VN4070702	RPL 405
	☒	Sartorius R200D Balance	SN: 39080042	RPL 405
	☒	Mettler AT400 Balance	SN: M19445	RPL 405 FH
	☒	Sartorius ME414S Balance	SN: 21308482	RPL 420
	☐	Ohaus EX324 Balance	SN: 8033311209	SAL Cell 2

Denis Cherkasov — 07/15/2019

Report Preparer — Date

07/18/2019

Review and Concurrence — Date

Twelve aqueous samples submitted under Analytical Service Request (ASR) 0787 were analyzed by ICP-MS. Sample 19-1774 was prepared in duplicate following RPL procedure RPG-CMC-128 by diluting 1 mL to approximately 25 mL. Prior to analysis all samples were further diluted in 2% HNO_3. None of the samples were filtered.

All results are reported on a mass per unit volume basis (ng/mL) for each detected analyte. The data have been adjusted for instrument dilutions.

Analyte of interest (AOI) was specified in the ASR and is listed in the upper section of the attached ICP-MS Data Report. The U-238 was the only analyte of interest for samples 19-1773 to 19-17844. The quality control (QC) results for the AOI have been evaluated and are presented below.

Calibration of the ICP-MS was done following the manufacturer's recommended calibration procedure using multi-analyte custom standard solutions traceable to the National Institute of Standards and Technology (NIST). Midrange calibration verification standards were used to verify acceptance of the six-point calibration curve and for initial and continuing calibration verification (ICV/CCV).

The controlling document was procedure RPG-CMC-292, Rev 0, *Determination of Elemental Composition by Inductively Coupled Argon Plasma Mass Spectrometry (ICP-MS)* and ASO-QAP-001, Rev. 11, *Analytical Support Operations (ASO) Quality Assurance Plan*. Instrument calibrations, QC checks and blanks (e.g., ICV/ICB, CCV/CCB, LLS, ICS), post-digestion spike, duplicate, blank spike, and serial dilution were conducted during the analysis run.

Internal Standard (IS):

All solutions (blanks, standards, QC checks, and samples) were mixed in-line with a solution containing 10 ppb each of Tb-159, and Bi-209 as the internal standard (IS). The AOI data were normalized using the IS mass (e.g., Bi-209). The Bi-209 IS recoveries ranged from 95.3% to 113.7%, which were within the acceptance criterion of 30% to 120%.

Preparation Blank (PB):

A preparation blank (reagents only) was prepared for the dissolution process. The concentration of U was within the acceptance criteria of <EQL (estimated quantitation level), <50% regulatory decision level, or less than ≤10% of the concentration in the samples.

Blank Spike (BS)/Laboratory Control Sample (LCS):

A blank spike (BS) sample was prepared by spiking a 2% HNO3 blank with an equivalent volume of the CCV-71A-2ppb standard (1:1 ratio). The recovery for the AOI was 99.7%, which is within the acceptance criteria of 80% to 120% recovery.

Duplicate/Replicate Relative Percent Difference (RPD)/Relative Standard Deviation (RSD):

A duplicate of sample 19-1774 was prepared. The RPD% for Uranium was 2.3% which is within the acceptance criterion of ≤20% RPD for liquid samples.

Matrix-Spike (MS) Sample:

Post digestion spike sample (PS-A) was run on the samples 19-1775 as an alternative and the results are discussed later in this report.

Initial/Continuing Calibration Verification (ICV/CCV):

The ICV/CCV solution was analyzed immediately after calibration, after each group of not more than ten samples, and at the end of the analytical run. The concentrations of all AOI were within the acceptance criteria of 90% to 110% recovery.

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solution (2% HNO_3) was analyzed immediately after the ICV solutions and after the CCV solutions (after each group of not more than ten samples and at the end of the analytical run). The concentration of all AOI were within the acceptance criteria of <EQL.

Low-Level Standard (LLS):

The LLS solution was analyzed immediately after the first CCB solution. The concentrations of all AOI were within the acceptance criteria of 70% to 130% recovery.

Interference Check Standard (ICS):

The ICS solution was analyzed immediately after the first LLS solution and immediately prior to analyzing the final CCV solutions. The concentrations of all AOI were within the acceptance criteria of 80% to 120% recovery.

Serial Dilution (SD):

Five-fold serial dilution was conducted on sample 19-1775. Percent differences (%D) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. The Uranium result was below the EQL and was not evaluated.

Post-Digestion Spike (PS-71A)/Analytical Spike):

A post spike sample was prepared for sample 19-1775 with the addition of CCV-71A. The recovery of U was 96.8, which met the acceptance criterion of 80% to 120%.

Other QC:

All other instrument-related QC tests for the AOI passed within their respective acceptance criteria.

Comments:

1) The "Final Results" have been corrected for all laboratory dilutions performed on the samples during processing and analysis, unless specifically noted.
2) Instrument detection limits (IDL) and estimated quantitation limits (EQL) shown are for acidified water and/or fusion flux matrices as applicable. Method detection limits (MDL) for individual samples can be estimated by multiplying the IDL by the "Process Factor" for that individual sample. The estimated quantitation limit (EQL) for each concentration value can be obtained by multiplying the EQL by the "Process Factor".
3) Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g. 2% v/v HNO_3 or less) at analyte concentrations > EQL up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 50 µg/mL (0.005 per cent by weight). Note that bracketed values listed in the data report are within the MDL and the EQL, and have potential uncertainties greater than 15%. Concentration values < MDL are listed as "- -". Note, that calibration and QC standard samples are validated to a precision of ±10%.
4) Analytes included in the spike 71A component (for the AS/PS) are; Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ho, K, La, Lu, Mg, Mn, Na, Nd, Ni, P, Pb, Pr, Rb, S, Se, Sm, Sr, Th, Tl, Tm, U, V, Yb, and Zn. Analytes included in the spike 71B component are; Ge, Hf, Mo, Nb, Sb, Si, Sn, Ta, Te, Ti, W, and Zr. Analytes included in the spike 71C component are; Ir, Os, Pd, Pt, Re, Rh, and Ru. Analytes included in the spike 71D component are; Bi, In, Li, Sc, Tb, and Y. Analytes included in the spike Hg component are; Hg.

Battelle PNNL/RPG/Inorganic Analysis ... ICP-MS Data Report

		Run Date >	7/9/2019	7/9/2019	7/9/2019	7/9/2019	7/9/2019	7/9/2019	7/9/2019	7/9/2019	7/9/2019	7/9/2019	7/9/2019	7/9/2019	7/9/2019	7/9/2019	7/9/2019	7/9/2019
		Process Factor >	1.00	43488.1	44525.6	44743.1	43460.4	44148.5	44065.0	44036.6	44492.4	44710.5	44802.6	44123.6	44423.3	44958.0	44266.7	44022.9
		RPL/LAB >	2% HNO3 Lab Blank	(900x) BLK-1720	(900x) 19-1773	(900x) 19-1774	(900x) DUP-1774	(900x) 19-1775	(900x) 19-1775 Rep	(900x) 19-1776	(900x) 19-1777	(900x) 19-1778	(900x) 19-1779	(900x) 19-1780	(900x) 19-1781	(900x) 19-1782	(900x) 19-1783	(900x) 19-1784
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	2% HNO3 Lab Blank	Process Blank	TI061-COMP-FEED	TI061-COMP-EFF		TI061-L-F1-A		TI061-L-F4-A	TI061-L-F8-A	TI061-L-F11-A	TI061-L-F14-A	TI061-L-F18-A	TI061-L-F22-A	TI061-L-F25-A	TI061-L-F27-A	TI061-L-F29-A
(ng/mL)	(ng/mL)	(Analyte)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)
0.00004	0.00039	U-238	--	[3.3E+00]	17878	10819	10752	617	628	11580	14884	15432	15576	15685	16738	17130	16959	17045

Internal Standard % Recovery

Bi 209 (IS)	104%	106%	107%	108%	106%	102%	105%	103%	109%	102%	103%	106%	105%	103%	101%	104%

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.
2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.
IS = Internal Standard. The concentration of certain elements cannot be determined due to the presence of the IS in all solutions.

QC Performance7/18/2018

Criteria >	≤ 20%	≤ 20%	80%-120%	75%-125%	≤ 10%
QC ID >	19-1774 DUP	19-1775 Rep	BS/LCS	19-1775 + PSA	19-1775 5-fold Serial Dil
Analytes	RPD (%)	RPD (%)	%Rec	%Rec	%Diff
U-238	2.3%	2.0%	99.7%	96.8%	--

Internal Standard % Recovery

Bi 209 (IS)	106%	105%	105%	110%	102%

Shaded results are outside the acceptance criteria.
nr = spike concentration less than 25% of sample concentration. Matrix effects can be assessed from the serial dilution.
na = not applicable; KOH flux and Ni crucible or Na2O2 flux and Zr crucible for fusion preparations, or Si for HF assisted digests.
IS = Internal Standard. The concentration of certain elements cannot be determined due to the presence of the IS in all solutions.
NM = Not measured. The isotope was not measure due to method or molecular interference limitations.

Battelle PNNL/RPL/ASO Hydroxide Analysis Report
P.O. Box 999, 902 Battelle Blvd., Richland, Washington 99352

Hydroxide Analysis by Titration

Project / WP#:	73325/NC2504 73312/NC4189
ASR#:	0731.00 & 0787.01
Client:	SK Fiskum
Total # of Samples:	2

RPL ID	Client Sample ID
19-1107	TCT008-COMP-FEED
19-1773	TI061-COMP-FEED

Analysis Type:	Hydroxide
Sample Processing Prior to Radiochemical Processing/Analysis	☒ None ☐ Digested as per RPG-CMC-128, Rev.1, *HNO_3-HCL Acid extraction of Liquids for Metals Analysis Using a Dry-Block Heater* ☐ Fusion as per RPG-CMC-115, *Solubilization of Metals from Solids Using a KOH-KNO_3 Fusion* ☐ Other:
Pre-dilution Prior to Radiochemical Processing?	☒ No ☐ Yes
Analysis Procedure:	RPG-CMC-228, Rev. 0.1, *Determination of Hydroxyl (OH^-) and Alkalinity of Aqueous Solutions, Leachates & Supernates*
Analysis Date or Date Range:	5/30/19
Technician/Analyst:	KN Pool & AM Carney
Electronic Data File:	ASR 0731 & 0787.01_Fiskum.xls
ASO Project 98620 File:	File Plan 5872: Sample preparation and analysis records; LSC 3100 TR calibration, daily checks, and maintenance records; and standard certificates and preparation. Also, balance calibration and performance check records.
M&TE Number(s):	Beckman Coulter pH Meter, SN: 110650046

Karl N. Pool / 6/2/19
Preparer **Date**

Andrew Carney / 6/4/19
Reviewer **Date**

SAMPLE RESULTS

See attached data report, Sample Results for ASR's 0731.00 and 0787.01. All sample data are molarity of hydroxide at each end point.

ASO Project Files, ASR 0731.00 and 0787.01 have been created for this report including all appropriate supporting records which may include the Pipette Performance Check Worksheet form and laboratory bench records, and records associated with hydroxide analysis. Standard certificates and balance calibration records can be found in the ASO Records.

Sample preparation and analysis

Hydroxide analysis was performed for diluted sample aliquots of 2 aqueous samples (19-1107 and 19-1773). Samples were analyzed by manual titration for the base constituents content following procedure RPG-CMC-228, Rev. 0.1, *Determination of Hydroxyl (OH^-) and Alkalinity of Aqueous Solutions, Leachates & Supernates*.

A sample size of 0.100 mL was added to 2.5 mL of DI water. The titrant used was 0.0887 M HCl. Standardized HCl was prepared on 5/6/19 and documented on Chem_Rec 238. Titration pH measurements were obtained using a Beckman Coulter 560 pH meter with serial number (SN) 110650046. The pH meter was calibrated using 3 buffers, pH 4, 7 and 10 and the calibration verified using an independent pH 7 buffer.

The customer requested target MDL of 0.1M was achieved for all samples. The titrant used for the sample analyses is 0.0887M HCl along with a pH meter accurate to within 0.05 pH units. The low concentration of the titrant along with the sensitivity of the pH meter provides the detection capability to meet this requirement.

The initial diluted pH is reported on the attached Report Summary along with the free hydroxide molarity. pH measured at each inflection point are provided below.

Sample ID	1st Inflection point	2nd Inflection point	3rd Inflection point
19-1107	10.9	8.3	4.8
19-1773	10.9	7.9	4.8

Included in the data package is a report summary and the sample results calculated from the raw data. A copy of the titration curve data for each sample is also included with this report.

Battelle PNNL/RPL/ASO Hydroxide Analysis Report

QUALITY CONTROL RESULTS

This analysis has limited quality control (QC) samples that are prepared. There are no laboratory blanks (LB), matrix spikes or reagent spikes analyzed.

Instrument Calibration Control

The pH meter was calibrated using 3 buffers, pH 4, 7 and 10 and the calibration verified using an independent pH 7 buffer.

Assumption and Limitations of the Data

Generally ASO analysis methods are associated with reported uncertainty. Titrations are not amenable to calculations of uncertainty.

Comments

1. The results have been corrected for all dilution factors resulting from sample processing.

Attachment: Data Report -- Sample Results for ASR 0731.00 and 0787.01

Battelle Pacific Northwest Laboratory
Nuclear Chemistry and Engineering Group
Chemical Measurements Center

ASR # 731.00 & 0787.01

WP# NC2504 & NC4189

Hydroxide and Alkalinity Determination
Procedure: RPG-CMC-228, Rev 0.1

Equip # Beckman Coulter 560, SN#110650046

Report Summary for ASR # -- 731.00 & 0787.01
Revision # **Rev-00 & 01**

Report Date: 6/2/2019
Analysis Date: 5/30/2019

				Concentration, moles / Liter		
		Diluted Initial	OH conc	First Point	Second Point	Third Point
RPG #	**Client ID**	**pH**	**ug/mL**	**Molarity**	**Molarity**	**Molarity**
19-1107	**TCT008-COMP-FEED**	**12.39**	1.66E+04	**0.98**	**1.24**	**0.71**
19-1773	**TI061-COMP-FEED**	**12.42**	1.51E+04	**0.89**	**1.15**	**0.71**

OH conc (mg/L) = M (g/L) * 17,000

Note: Results are presented for the first, second, and third inflection points on the titration curves for the hydroxide titration, as applicable. The first inflection point is generally associated with the free hydroxide concentration. The second inflection point generally represents total hydroxide, or carbonate or a combination of aluminate and carbonate. The third inflection point is usually indicative of bicarbonate or other weak acids or possibly the continued protonation of alumina.

Analyst: Andrew Carey 6/4/19

Reviewer: Karl N. Pool 6/2/19

Battelle Pacific Northwest Laboratory
Nuclear Chemistry and Engineering Group

ASR # and Rev # 731.00 & 0787.0 Rev-00 & 01
Client: S. Fiskum
Project: 71274 WP# NC2504 NC4189

Report Date: **6/2/2019**
Analysis Date: **5/30/2019**

Procedure: **RPG-CMC-228, Rev 0.1** Determination of Hydroxyl (OH-) and Alkalinity of Aqueous Solutions, Leachates and Supernates

Spreadsheet: OH-TemplateLocked07.xls 4/1/2007

By Manual Titration

Equip # 110650046 Lab Loc. 420

Analyst: andrew Carey

Titrant	Molarity	Chem Rec#
HCl	**0.0887**	**238**

RPG #	Sample ID		Dilution Factor	Sample Vol. (mL)	Sample Wt. (g)	Density g/mL	Titrator Routine #	**Diluted** Initial pH reading	**OH** **1st Equivalence** Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base
19-1107	TCT008-COMP-FEED		NA	0.105	NA	NA	NA	12.39	1.15	10.86	0.102	0.976
19-1773	TI061-COMP-FEED		NA	0.105	NA	NA	NA	12.42	1.05	10.89	0.093	0.887

Instrument Calibration

Buffer	Vendor	Lot Number	Expire Date
4	Inorganic Ventures	N2-WCS673492	30-May-20
7	Inorganic Ventures	N2-WCS674708	30-May-20
10	Inorganic Ventures	P2-WCS675599	30-May-19

2-nd Verif	Vendor	Lot Number	Expire Date
7	Spex	1-53MJX	23-May-20

Slope
NA

Battelle Pacific Northwest Laboratory
Nuclear Chemistry and Engineering Group

ASR # and Rev #	31.00 & 0787.0	Rev-00 & 01
WP#	NC2504 NC4189	

Procedure:

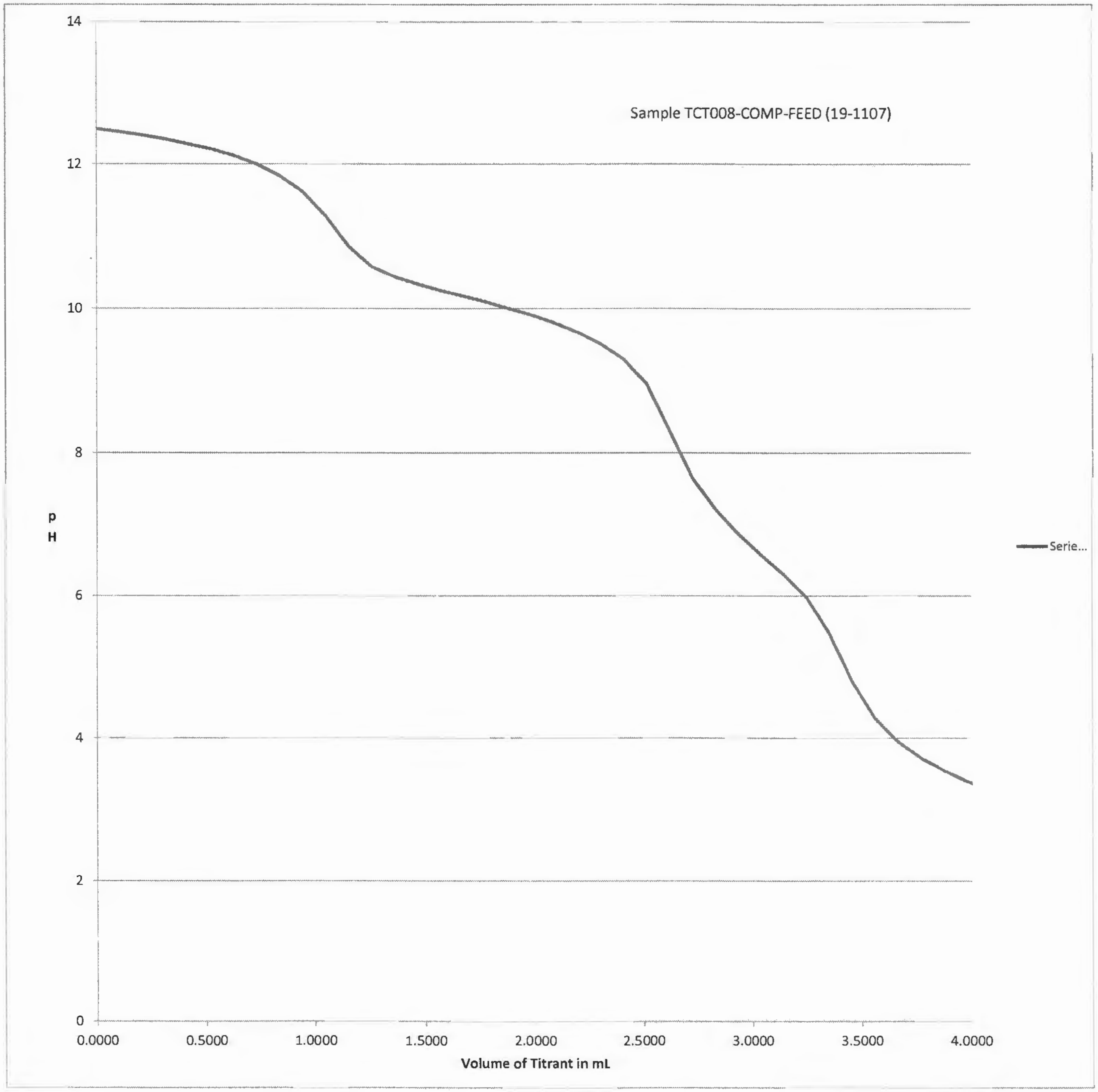
Alkalinity of Aqueous Solutions, Leachates and Supernates

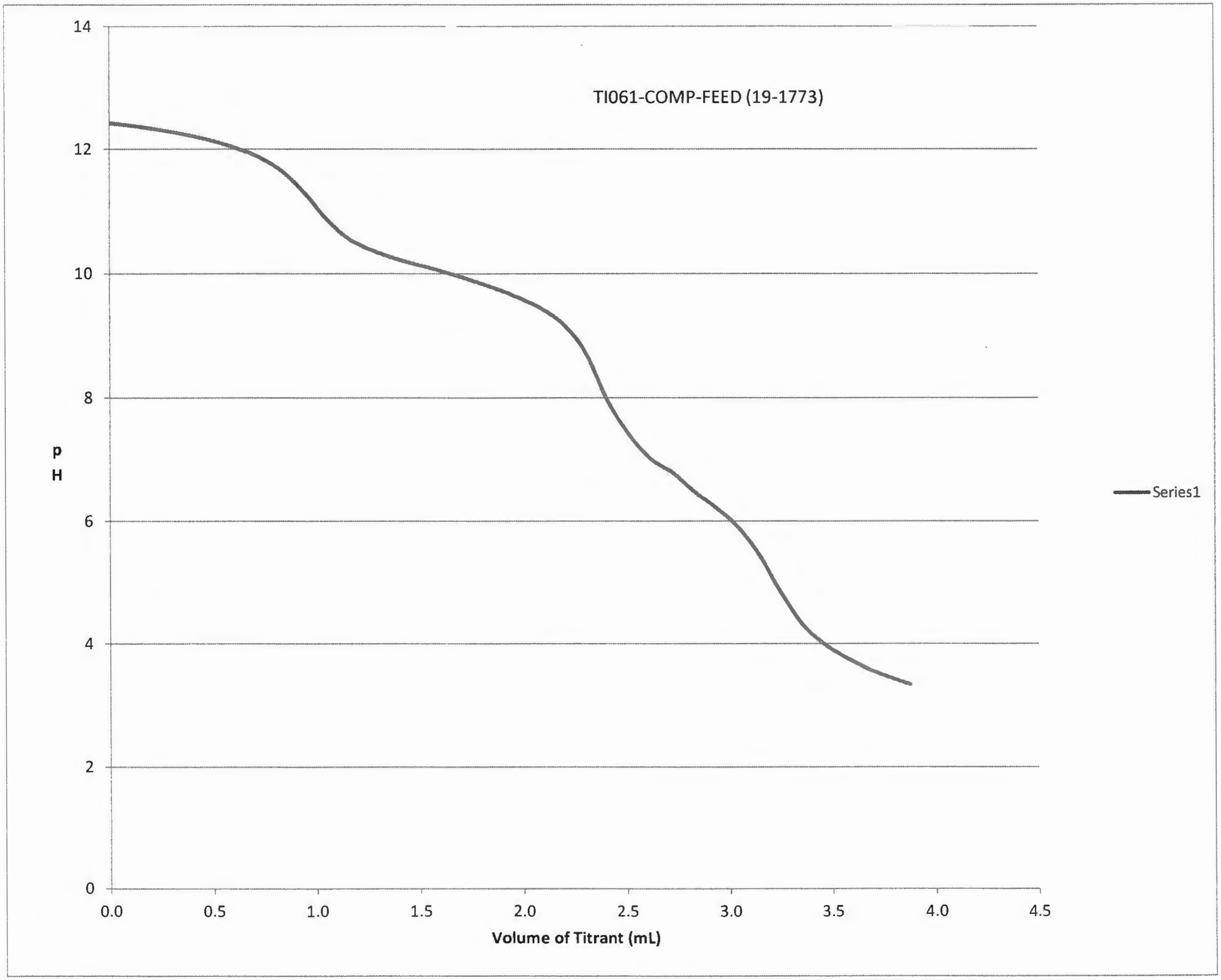
By Manual Titration

Equip # Beckman Coulter 560, SN#110650046

Titrant	Molarity
HCl	0.0887

RPG #		Sample Vol. (mL)	2nd Equivalence Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base	3rd Equivalence Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base
19-1107		0.105	2.618	8.310	0.130	1.242	3.455	4.790	0.074	0.710
19-1773		0.105	2.408	7.940	0.121	1.153	3.246	4.840	0.074	0.710


Sample TCT008-COMP-FEED (19-1107)
14
12
10
8
6
4
2
0
pH
0.0000
0.5000
1.0000
1.5000
2.0000
2.5000
3.0000
3.5000
4.0000
Volume of Titrant in mL
Serie...


TI061-COMP-FEED (19-1773)
pH
14
12
10
8
6
4
2
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Volume of Titrant (mL)
Series1

Project Number:	73312
Charge Code:	NC4189
ASR Number:	0787
Client:	S. Fiskum A. Rovira
Total Samples:	1 liquid

	RPL Numbers	**Client IDs**
Samples	19-1773	TI061-COMP-FEED

Analysis Procedure	RPG-CMC-386 Rev. 1, "Carbon Measured in Solids, Sludge, and Liquid Matrices"
Prep Procedure	None
Analyst	A. Carney
Analysis Date	June 10, 2019
CCV Standards	TIC/TOC CMS # 543144 and 543143
BS/LCS/MS Standards	TIC/TOC CMS # 542973 and 543145
Excel Data File	ASR-0787-Fiskum.xlsx
M&TE Numbers	Carbon System (WD36639, RPL/701)
	Balance : Sartorius R200D, S/N 30809774
All Analysis Records	5015_06-10-2019-131336.CSV

Andrew Carney 6/20/19
Prepared By Date

Karl N. Pool 6/21/19
Reviewed By Date

Table 1: TOC/TIC Results for ASR 0787

TIC in Sample **19-1773** (mg C/L):	7776.69
MDL (mg C/L):	194
EQL (mg C/L):	970
TOC in Sample **19-1773** (mg C/L):	2154.96
MDL (mg C/L):	194
EQL (mg C/L):	970
TIC in Sample **19-1773-Dup**:	7720.46
MDL (mg C/L):	194
EQL (mg C/L):	970
TOC in Sample **19-1773-Dup**:	2184.46
MDL (mg C/L):	194
EQL (mg C/L):	970
19-1773 TIC RPD:	0.7%
19-1773 TOC RPD:	1.4%

Sample Analysis/Results Discussion

One liquid sample was submitted under Analytical Service Request (ASR) 0787 for total inorganic and total organic carbon analysis. The analysis was performed by the hot persulfate wet oxidation method, with the results summarized in Table 1. The TIC is measured first with additions of heated sulfuric acid followed by the addition of a silver catalyzed acidic potassium persulfate solution for oxidation at 92-95 °C for TOC. The analyses were performed following procedure RPG-CMC-386, Rev. 1, *Carbon Analyses in Solids, Sludge and Liquid Matrices*.

The sample was analyzed with one duplicate for each TIC and TOC. An analytical spike was also run for TIC and TOC on the sample. The sample results are corrected for the contribution from the system blank, as per procedure RPG-CMC-386, Rev. 1. All data are reported as mg C/L of sample.

Data Limitations

None

Quality Control Discussion

The calibration and QC sample standards for the TOC initial/continuing calibration verification check (ICV/CCV) sample is a 1000 µg/mL solution of total organic carbon standard. The calibration and QC sample standards for the TIC initial/continuing calibration verification check (ICV/CCV) sample is a 1000 µg/mL total inorganic standard. The identification of the standards and their Chemical Management System (CMS) numbers are included on the raw data bench sheets for traceability.

The QC samples analyzed as part of the method include initial and continuing calibration verification samples (ICV/CCV), initial and continuing calibration blanks (ICB/CCB), laboratory duplicate for the sample, a laboratory control sample/blank spike (LCS/BS), and an analytical spike (AS). The work was performed in one batch.

Two blanks are run at the beginning of each batch and a blank is run after ICV/CCV. The blanks must be <EQL. The blanks run in the batch are <EQL.

Initial Calibration Check and Continuing Calibration Verification Standards:

The calibration of the coulometer analysis system was checked by calibration verification standards analyzed at the beginning and end of the analysis run. TOC results for the two ICVs were 100.2% and 97.5% recovery, and for the two TIC ICVs the results were 98.0% and 99.4% recovery, within the acceptance criterion of 90% to 110%. The TOC result for the CCV was 98.6% recovery and the TIC CCV was 99.0% recovery, within the acceptance criterion of 85% to 115%.

Laboratory Control Sample/Blank Spike: One TIC and TOC LCS/BS was analyzed. The TIC LCS/BS result was 100.9% recovery and the TOC LCS/BS result was 99.9% recovery, meeting the acceptance criteria of 75% to 125%.

Duplicate/Replicate: Precision of the carbon measurements is demonstrated by the relative percent difference (RPD) between sample and duplicate/replicate. Sample 19-1773 TIC RPD was 0.7% and TOC was 1.4%. Both samples meet the acceptance criteria of ≤20%.

Analytical Spike (AS): The accuracy of the carbon measurements can be estimated by the recovery from the AS. The results for the analytical spike for TIC is 99.4% recovery and for the TOC, 93.3% recovery. The AS recovery for the TOC and TIC results meets the acceptance criterion of 75% to 125%.

Deviation from Procedure:

None

General Comments

1) Routine precision and bias are typically ±15% or better for non-complex samples that are free of interferences.
2) For the TIC/TOC, the analysis MDL is calculated by dividing the batch IDL by the sample mass and is therefore dependent on sample size. The estimated quantitation limit (EQL) is defined as 5x the MDL. Results <5x MDL have higher uncertainties and RPDs are not calculated if the results are <5x MDL.
3) Where applicable, the reported "Final Results" have been corrected for any dilution performed on the sample prior to analysis.

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report
P.O. Box 999, 902 Battelle Blvd., Richland, Washington 99352

Gamma Energy Analysis (GEA)

Project / WP#:	73312/NC4189
ASR#:	0787.00
Client:	SK Fiskum
Total Samples:	2

RPL ID	Client Sample ID
19-1773	TI061-COMP-FEED
19-1774	TI061-COMP-EFF

Analysis Type:	GEA- for all positively measured or non-detected isotopes
Sample Processing Prior to Radiochemical Processing/Analysis	☒ None ☐ Digested as per RPG-CMC-129, Rev. 0 *HNO_3-HCl Acid Extraction of Solids Using a Dry Block Heater* ☐ Fusion as per RPG-CMC-115, *Solubilization of Metals from Solids Using a KOH-KNO_3 Fusion* ☐ Other: Preparation may also involve attaining a GEA geometry that is compatible with the calibration geometry.
Analysis Procedure:	RPG-CMC-450, Rev. 3 *Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS)*
Reference Date:	None
Analysis Date or Date Range:	June 10, 2019
Technician/Analyst:	M Cantaloub
Rad Chem Electronic Data File:	*19-1773 Fiskum.xls*
ASO Project 98620 File:	*File Plan 5872, Technical (Radiochemistry), Gamma Calibration, daily checks, and maintenance records; and standard certificates and preparation. Also, balance calibration and performance check records.*
M&TE Number(s):	*Detector T,Z*

T Trang-Le / 6/19/19
Prepare **Date**

/ 19 Jun 2019
Reviewer **Date**

Page 1 of 3

SAMPLE RESULTS

The client requested measurement of Cs-137, Co-60 and Eu-154 and all detected isotopes in these samples.

ASO Project File, ASR 0787.00 has been created for this report including all appropriate supporting records which may include the Pipette Performance Check Worksheet form, standard certificates, laboratory bench records, Sample Preparation Laboratory Bench Sheets, and Gamma Energy Analysis printouts. Detector calibration records, control charts and balance calibration records can be found in the ASO Records.

Sample Preparation, Separation, Mounting and Counting Methods

The quality control (QC) steps for direct GEA are discussed below.

QUALITY CONTROL RESULTS

Tracer:

Tracers are not used for ASO GEA methods.

Process Blank (PB):

No process blank was prepared for gamma counting.

Required Detection Limits

There are required detection limits for these samples. MDL for Eu-154 of 1.0E-5 uCi/mL not achieved on COMP FEED sample due to high Cs-137 activity.

Blank Spike (BS)/Laboratory Control Sample (LCS)/ Matrix Spike (MS):

There are no BS, LCS or MS samples analyzed for ASO GEA analyses. Instrument performance is assessed by the analyses of daily control counts and weekly background counts, as discussed below.

Duplicate Relative Percent Difference (RPD):

No duplicate samples were provided for gamma counting.

Instrument Calibration and Quality Control

Gamma detectors are calibrated using multi-isotope standards that are NIST-traceable and prepared in the identical counting geometry to all samples and detectors, if possible. Counter control sources containing Am-241, Cs-137 and Co-60 are analyzed daily before the use of each detector. Procedure RPG-CMC-450 requires that a counter control source is checked daily and must be within ±3 sigma or ±3% of the control value, whichever is greater. Gamma counting was not performed unless the control counts were within the required limits. Background counts are performed on all gamma detectors at least weekly for either an overnight or weekend count. The most recent background is subtracted from all sample counts.

Assumptions and Limitations of the Data

For these samples, the sample geometry was not the same as our calibrated geometries. Consequently, we used calibration geometries that were as close as possible to the sample geometries. This introduces some additional uncertainty above what is listed in our report. However, this additional uncertainty is thought to be small since all samples were counted at distances of about 10 cm from the detector face.

Interferences/Resolution

None.

Uncertainty

For gamma counting, the uncertainty in the counting data, photon abundance and the nuclear half-life, and efficiency are included in the calculation of the total uncertainty along with a systematic uncertainty for sample prep. The Canberra Genie software includes both random and systematic uncertainties in the calculation of the total uncertainties which are listed on the report. We conservatively estimate that 2% is the lowest uncertainty possible for our GEA measurements taking into account systematic uncertainties in gamma calibration standards.

Comments

None.

Attachment: Data Report Sample Results for ASR 0787.00.

Pacific Northwest National Laboratory
PO Box 999, Richland, WA
Radiochemical Sciences and Engineering Group

filename 19-1773
8/22/2019
Revision 1

Client: Fiskum
ASR 0787

Project: 73312
NC4189

Prepared by: 8/22/19
Mike Cantaloub

Technical Reviewer: T Trang-Le 8/22/19

Procedures: RPG-CMC-450, Rev. 3 Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS) Spectrometry
M&TE: Gamma detectors T, Z
Count dates: 10-Jun-19

Measured Activity, µCi/mL ± 1s

RPL ID:	19-1773		19-1774	
Sample ID:	TI061-COMP-FEED		TI061-COMP-EFF	
Isotope				
Co-60	**4.96E-04**	± 34%	**5.29E-04**	± 2%
Sb-126	< 2E-3		**1.37E-04**	± 2%
Sn-126	**1.36E-01**	± 6%	**3.19E-04**	± 3%
Cs-137	**1.54E+02**	± 1%	**5.29E-04**	± 2%
Eu-154	< 2E-3		**4.65E-05**	± 2%
Eu-155	< 3E-2		**1.04E-05**	± 15%
Am-241	< 1E-1		**2.45E-04**	± 3%

Notes: MDL for Eu-154 of 1.0E-5 uCi/mL not achieved on COMP FEED sample due to high Cs-137 activity
Revision 1 COMP-FEED Sn-126 result impacted by gamma-induced Pb x-ry fluencence interference with the primary Sn-126 line.
Revision 1 COMP-FEED Sn-126 results should be considered an upper limit. MDA is 2E-2.
Revision 1 Sb-126 is decay daughter of Sn-126
Closest matching geometry used for COMP FEED sample analysis - PSV10mlw at 20 inches from detector.

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report
P.O. Box 999, 902 Battelle Blvd., Richland, Washington 99352

Sr-90 by Liquid Scintillation Spectrometry

Project / WP#:	73312 / NC4189
ASR#:	0787.02
Client:	S. Fiskum
Total # of Samples:	12

RPL ID	Client Sample ID	RPL ID	Client Sample ID
19-1773	TI061-COMP-FEED	19-1779	TI061-L-F14-A
19-1774	TI061-COMP-EFF	19-1780	TI061-L-F18-A
19-1775	TI061-L-F1-A	19-1781	TI061-L-F22-A
19-1776	TI061-L-F4-A	19-1782	TI061-L-F25-A
19-1777	TI061-L-F8-A	19-1783	TI061-L-F27-A
19-1778	TI061-L-F11-A	19-1784	TI061-L-F29-A

Analysis Type:	Sr-90
Sample Processing Prior to Radiochemical Processing/Analysis	☒ None ☐ Digested as per RPG-CMC-128, Rev.1, *HNO_3-HCL Acid extraction of Liquids for Metals Analysis Using a Dry-Block Heater* ☐ Fusion as per RPG-CMC-115, *Solubilization of Metals from Solids Using a KOH-KNO_3 Fusion* ☐ Other:
Pre-dilution Prior to Radiochemical Processing?	☐ No ☐ Yes
Separation Procedure:	RPG-CMC-476, Rev. 0, *Strontium Separation Using Eichrom Strontium Resin*
Spike Standard ID:	R-693-b-10 (Sr-90)
Separation Date:	08/06/2019 @ 11:00
Technician/Analyst:	L. Darnell
Analysis Procedure:	RPG-CMC-474, Rev. 1, *Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry*
Reference Date:	08/6/19
Analysis Date or Date Range:	08/07/19 (first count), 08/11/19 (second count)
Technician/Analyst:	LP Darnell & T. Trang-Le
Rad Chem Electronic Data File:	RPG-RC\PNL\Projects\Backup files\Backup 19\19-1773 Fiskum.xls
ASO Project 98620 File:	File Plan 5872: T 73312: Sample preparation and analysis records; T-4.4 LSC 3100 calibration, daily checks, and maintenance records; and T3 standard certificates and preparation. Also, balance calibration and performance check records.
M&TE Number(s):	Perkin Elmer Tri-Carb 3100, Serial # DG08061340, RPL 425, Tri-Carb 2700TR software version 1.04 dated 9/99.

/ 8/12/19
Preparer **Date**

T Trang-le / 8/12/19
Reviewer **Date**

Page 1 of 3

SAMPLE RESULTS

See attached data report, Sample Results for ASR 0787.02. All sample data are reported in µCi/mL with a 1-σ uncertainty (see Comments).

Sample preparation, separation, mounting, and counting

All twelve samples submitted under Analytical Service Request (ASR) 0787.02 were analyzed for Sr-90 by chemical separation and liquid scintillation counting. All the samples were prepared in RPL/420. Aliquots of the as received samples were used for radioanalytical analyses; only Sr-90 data are presented in this report.

QUALITY CONTROL RESULTS

Quality control (QC) samples include a laboratory preparation blank (PB) and sample duplicate. Additional laboratory QC samples were prepared prior to separations; these include a reagent blank spike (RS), and a matrix spike (MS), each made with the addition of Sr-90 standard to an aliquot of the samples.

Laboratory Preparation Blank (PB):

The activity level of Sr-90 present in the laboratory separation blank (1.55E-5 µCi/mL) is both below the activity present in the samples (1.19 E-3 µCi/mL or higher) and less than sample MDC (2.2 E-5 µCi/mL) meeting the acceptance criteria of less than 5% of the sample activity or less than the sample MDC.

Blank Spike (BS) – Reagent Spike (RS):

The RS recovery of 97% meets the procedure acceptance criteria of 80% to 120% recovery.

Matrix Spike (MS):

The MS recovery of 102% meets the acceptance criterion of 75% to 125% recovery. Note: the MS sample was prepared "after" digestion (see comments), by adding a known Sr-90 standard quantity to an aliquot of 19-1774 (TI061-COMP-EFF).

Duplicate -- Relative Percent Difference (RPD):

Duplicate results are required to agree within ≤20% RPD. The ASO QAP further specifies that the two results need to be >5 times the MDA or have individual uncertainties <20%. The sample and duplicate result were both less than 5 times MDA. The RPD is not calculated when one or both of the results used to calculate the RPD is less than 5 times MDA.

Instrument Quality Control

The liquid scintillation counter is calibrated for tritium and C-14 using quenched standard sets that are purchased from the vendor. Daily control counts are then performed using a tritium, C-14, and a background count sample. The instrument software assesses the performance of the control counts and provides control charts to ensure the continuing calibration of the instrument. If the daily performance check fails, then the instrument is not used. Preventative maintenance and repairs are performed by the vendor under our service contract. The counting efficiency for Sr-90 is assumed to be 100%; therefore, no specific Sr-90 calibration is performed. The LSC system calibration and performance is verified by assessing the recovery of a reagent spike and a matrix spike that are included in every batch of samples. A preparation blank (i.e., digestion blank) and a laboratory separations blank are also included with every batch of samples; the instrument background is subtracted from all results and the preparation and separation blanks are used to assess sample contamination during sample processing steps.

Assumption and Limitations of the Data

None

Comments

1. The results have been corrected for all dilution factors resulting from sample processing.

2. The stated 1-σ uncertainty represents the total propagated error associated with processing and counting operations and includes weighing errors, volume uncertainties, and counting error. Generally, errors are set at 2% to provide a more realistic estimate of the uncertainty in view of the systematic uncertainties that are not fully accounted for in the uncertainty calculations.

Attachment: Data Report -- Sample Results for ASR 0787.02

Pacific Northwest National Laboratory
PO Box 999, Richland, WA
Radiochemical Sciences and Engineering Group

filename 19-1773
8/12/2019

Client: Fiskum
ASR 0787.02

Project: 73312
NC4189

Prepared by: T Trang-le 8/12/19
Technical Reviewer: 8/12/19

Procedures: RPG-CMC-474, Rev 1, Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry
M&TE: Perkin Elmer TriCarb model 3100TR liquid scintillation spectrometer
Count dates: August 7 & 11, 2019

Sample	Lab ID	**Sr-90 Concentration, µCi/mL ± 1s uncertainty**	
TI061-COMP-FEED	19-1773	**4.52E-1**	**± 2%**
TI061-COMP-EFF	19-1774	<1.E-3	
	DUP-1774	<1.E-3	
	RPD	-	
TI061-L-F1-A	19-1775	<1.E-3	
TI061-L-F4-A	19-1776	**1.24E-3**	**± 16%**
TI061-L-F8-A	19-1777	<1.E-3	
TI061-L-F11-A	19-1778	**1.51E-2**	**± 2%**
TI061-L-F14-A	19-1779	<1.E-3	
TI061-L-F18-A	19-1780	**1.19E-3**	**± 17%**
TI061-L-F22-A	19-1781	<1.E-3	
TI061-L-F25-A	19-1782	**1.68E-3**	**± 12%**
TI061-L-F27-A	19-1783	**2.14E-3**	**± 10%**
TI061-L-F29-A	19-1784	**2.73E-3**	**± 8%**
	Reagent Spike	97%	
	Matrix Spike	102%	
	Blank	**1.55E-5**	**± 25%**

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report
P.O. Box 999, 902 Battelle Blvd., Richland, Washington 99352

Tc-99 Analysis

Project / WP#:	73312/NC4189
ASR#:	0787.02
Client:	SK Fiskum
Total # of Samples:	2

RPL ID	Client Sample ID
19-1773	TI061-COMP-FEED
19-1774	TI061-COMP-EFF

Analysis Type:	Tc-99
Sample Processing Prior to Radiochemical Processing/Analysis	☒ None ☐ Digested as per PNL-ALO-106, Rev. 1, *Acid Digestion of Waters, Soils, and Sludges for Subsequent Radiochemical Sample Analyses* ☐ Fusion as per RPG-CMC-115 Rev. 0, *Solubilization of Metals from Solids Using a KOH-KNO$_3$ Fusion* ☐ Digested as per RPG-CMC-128, Rev.1, *HNO$_3$-HCL Acid extraction of Liquids for Metals Analysis Using a Dry-Block Heater*
Pre-dilution Prior to Radiochemical Processing?	☐ No ☐ Yes
RadioChemical Preparation Procedure:	RPG-CMC-432, Rev. 0, *Technicium-99 Analysis*
Technician/Analyst:	LP Darnell, (8/7/19)
Spike and Tracer Standard ID's:	R-714-b-1 (10/25/19) (Tc-99)
Analysis Procedure:	RPG-CMC-474, Rev. 1, *Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry*
Reference Date:	Not applicable
Analysis Date(s) or Date Range:	8/13/19
Technician/Analyst:	LP Darnell
Analysis Data (File):	RPG-RC\PNL\Projects\Backup files\Backup 19\19-1773 Fiskum.xls
CMC Project 98620 File:	File Plan 5872: T 73312: Sample preparation and analysis records; T-4.4 Alpha Detector calibration, calibration verification checks, and maintenance records; and T3 Standard certificates and preparation. Also balance calibration and instrument performance checks
M&TE Number(s):	Perkin Elmer 3100 TR Liquid scintillation spectrometer– See attached M&TE list

Karl N. Pool / 8/16/19
Preparer **Date**

T Trang-le / 8/16/19
Reviewer **Date**

Sample Results

See attached data report, Sample Results for ASR 0787.02. All data are reported in units of µCi/mL with a 1-σ uncertainty (see comments).

Sample Preparation, Separation, Mounting and Counting Methods

Two samples submitted under ASR 0787.02 were analyzed for Tc-99. All the samples were prepared in Laboratory 420. A direct aliquot of each of the parent samples was processed using procedure RPG-CMC-432, Rev. 0, *Technicium-99 Analysis*.

The samples were counted on August 13, 2019; no decay corrections were made.

QUALITY CONTROL RESULTS

Quality control (QC) samples prepared in laboratory 420 include a laboratory blank and sample duplicate, matrix spike sample and reagent spike sample.

The QC sample results for Tc-99 have been evaluated and are discussed below. A summary of the Tc-99 analysis results, including QC sample performance, is given in the attached data report.

Tracer:

There is no tracer for Tc-99 analysis.

Laboratory Separation Blank (LB):

The activity level of Tc-99 present in the laboratory separation blank (1.3E-6 µCi/mL) is both below the activity present in the samples (9.79E-2 µCi/mL or higher) and less than sample MDC (4.0 E-5 µCi/mL) meeting the acceptance criteria of less than 5% of the sample activity or less than the sample MDC.

Reagent Spike (RS):

The RS recovery of 101% (Tc-99) meets the acceptance criteria of 80% to 120% recovery.

Matrix Spike (MS):

A matrix spike sample was prepared using sample 19-1774 (TI061-COMP-EFF). The sample activity was significantly higher (~200x) than the activity of spike added for the matrix spike. The matrix spike is not calculated in this case.

Laboratory Duplicate - Relative Percent Difference (RPD):

> Duplicate results for 19-1774 (TI061-COMP-EFF) are required to agree within ≤20% RPD. The ASO QAP further specifies that the two results need to be > 5 times the MDC or have individual uncertainties < 20%. Duplicate results were 1% RPD, thus meeting the ≤ 20% requirement.

Instrument Quality Control

LSC counters receive initial calibration with NIST traceable sources to determine the counter efficiency. When internal tracers are not used, the counter efficiency is used in calculation of final results.

The liquid scintillation counter (LSC) is calibrated for tritium and C-14 using quenched standard sets that are purchased from the vendor. Daily control counts are then performed using a tritium, C-14, and a background count sample. The instrument software assesses the performance of the control counts and provides control charts to ensure the continuing calibration of the instrument. If the daily performance check fails, then the instrument is not used. Preventative maintenance and repairs are performed by the vendor under our service contract. The counting efficiency for Tc-99 is assumed to be 100%; therefore no specific Tc-99 calibration is performed. The LSC system calibration and performance is verified by assessing the recovery of a reagent spike and a matrix spike that are included in every batch of samples. A laboratory separation blank is also included with every batch of samples; the instrument background is subtracted from all results and separation blanks are used to assess sample contamination during sample processing steps.

Assumption and Limitations of the Data

None

Attachment: Data Report -- Sample Results for ASR 0787.02.

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report
P.O. Box 999, 902 Battelle Blvd., Richland, Washington 99352

Neptunium 237 Analysis

Project / WP#:	73312/NC4189
ASR#:	0787.02
Client:	SK Fiskum
Total # of Samples:	12

RPL ID	Client Sample ID	RPL ID	Client Sample ID
19-1773	TI061-COMP-FEED	19-1779	TI061-L-F14-A
19-1774	TI061-COMP-EFF	19-1780	TI061-L-F18-A
19-1775	TI061-L-F1-A	19-1781	TI061-L-F22-A
19-1776	TI061-L-F4-A	19-1782	TI061-L-F25-A
19-1777	TI061-L-F8-A	19-1783	TI061-L-F27-A
19-1778	TI061-L-F11-A	19-1784	TI061-L-F29-A

Analysis Type:	AEA – Np-237
Sample Processing Prior to Radiochemical Processing/Analysis	☐ None ☐ Digested as per PNL-ALO-106, Rev. 1, *Acid Digestion of Waters, Soils, and Sludges for Subsequent Radiochemical Sample Analyses* ☐ Fusion as per RPG-CMC-115, Rev0, *Solubilization of Metals from Solids Using a KOH-KNO₃ Fusion* ☒ Digested as per RPG-CMC-128, Rev.1, *HNO₃-HCL Acid extraction of Liquids for Metals Analysis Using a Dry-Block Heater*
Pre-dilution Prior to Radiochemical Processing?	☐ No ☐ Yes -- *example 2 mL to 100 mL; 50x dilution*
Neptunium Separation Procedure:	RPG-CMC-4017, Rev. 0, *Analysis of Environmental Water Samples for Actinides and Strontium- 90*
Technician/Analyst:	LP Darnell, (08/01/2019)
Spike Standard ID's:	R-686-a-2 (Np-237)
Co-Precipitation Procedure:	RPG-CMC-496, Rev. 1, *Coprecipitation Mounting of Actinides for Alpha Spectroscopy*
Technician/Analyst:	LP Darnell, (08/01/2019)
Analysis Procedure:	RPG-CMC-422, Rev. 2, *Solutions Analysis: Alpha Spectrometry*
Reference Date:	Same as counting dates
Analysis Date or Date Range:	August 5-8, 2019
Technician/Analyst:	T. Trang-Le
Analysis Data (File):	RPG-RC\PNL\Projects\Backup files\Backup 19\19-1773 Fiskum.xls
CMC Project 98620 File:	File Plan 5871: T 73312: Sample preparation and analysis records; T-4.4 Alpha Detector calibration, calibration verification checks, and maintenance records; and T3 Standard certificates and preparation. Also balance calibration and instrument performance checks.
M&TE Number(s):	Ortec AEA counters – 32 counters – See attached M&TE list

/ 8/16/19 T Trang-le / 8/16/19

Preparer **Date** **Reviewer** **Date**

Sample Results

See attached data report, Sample Results for ASR 0787.02. All data are reported in units of µCi per mL with a 1-σ uncertainty unless noted otherwise (see Comments).

Sample Preparation, Separation, Mounting and Counting Methods

All twelve samples submitted under Analytical Service Request (ASR) 0787.02 were analyzed for neptunium by Alpha Spectrometry. All the samples were prepared in RPL/420, only Np-AEA is presented in this report.

Following the digestion process of samples, the Np was separated from the aqueous samples using anion exchange chromatography using procedure RPG-CMC-4017. The separated Np fraction was mounted for alpha spectrometry by co-precipitation using procedure RPG-CMC-496, and then counted by alpha spectrometry using procedure RPC-CMC-422. The samples were counted on August 5-8, 2019; no decay corrections were made.

Alpha and beta analyses were performed on each sample to determine appropriate aliquot sizes for the chemical separations needed for the alpha and beta emitters of interest. Gross alpha and gross beta activity were measured by evaporating small aliquots of leachate onto counting planchets per procedure RPG-CMC-4001 and counting per procedure RPG-CMC-408.

QUALITY CONTROL RESULTS

Quality control (QC) samples include a laboratory preparation blank and sample duplicate. Additional QC samples were prepared prior to separations; these include a reagent spike (RS), and a matrix spike (MS) made by adding Np-237 standard to a diluted sample.

Tracer:

Tracer is not used for analyses of Np.

Laboratory Preparation Blank (PB)):

The activity level of Np-237 present in the laboratory preparation blank (-6.1E-9 µCi/mL) is both below the activity present in the samples (7.43E-6 µCi/mL or higher) and less than lowest sample MDC (3.4 E-8 µCi/mL) meeting the acceptance criteria of less than 5% of the sample activity or less than the sample MDC.

Blank Spike (BS) – Reagent Spike (RS):

The RS recovery of 93% meets the acceptance criteria of 80% to 120% recovery.

Matrix Spike (MS):

The MS recovery of 87% meets the acceptance criterion of 75% to 125% recovery. Note: the MS sample was prepared "after" digestion, by adding a known Np-237 standard quantity to an aliquot of the leachate. Sample number 19-1774 (TI061-COMP-EFF) was selected as the matrix spike sample.

Duplicate -- Relative Percent Difference (RPD):

Duplicate results are required to agree within ≤20% RPD. The ASO QAP further specifies that the two results need to be >5 times the MDA or have individual uncertainties <20%. The duplicate result was 25% RPD; exceeding the ≤20% requirement.

Instrument Quality Control

Alpha counters undergo calibration annually to determine the counter's efficiency over the normal calibration range of 3 to 6 MeV. The vendor software determines a constant detector efficiency for this energy range. Np samples are counted and results calculated using the established detector efficiency.

Detector backgrounds are determined every 4 weeks or after the last analytical run, whichever is longer. Detector background counts are subtracted from all subsequent sample counts. A process blank is analyzed with each analytical batch to evaluate for contamination in the sample preparation process.

Assumption and Limitations of the Data

None.

Comments

1. The results have been corrected for all dilution factors resulting from sample processing.
2. The 1-sigma uncertainty represents the total propagated error associated with processing and counting operations and include; weighing errors, volume uncertainties, and counting error.

Attachment: Data Report -- Sample Results for ASR 0787.02.

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report
P.O. Box 999, 902 Battelle Blvd., Richland, Washington 99352

Plutonium 238, 239+240 Analysis

Project / WP#:	73312/NC4189
ASR#:	0787.02
Client:	SK Fiskum
Total # of Samples:	12

RPL ID	Client Sample ID	RPL ID	Client Sample ID
19-1773	TI061-COMP-FEED	19-1779	TI061-L-F14-A
19-1774	TI061-COMP-EFF	19-1780	TI061-L-F18-A
19-1775	TI061-L-F1-A	19-1781	TI061-L-F22-A
19-1776	TI061-L-F4-A	19-1782	TI061-L-F25-A
19-1777	TI061-L-F8-A	19-1783	TI061-L-F27-A
19-1778	TI061-L-F11-A	19-1784	TI061-L-F29-A

Analysis Type:	AEA – Pu-238, Pu-239+240
Sample Processing Prior to Radiochemical Processing/Analysis	☐ None ☐ Digested as per PNL-ALO-106, Rev. 1, *Acid Digestion of Waters, Soils, and Sludges for Subsequent Radiochemical Sample Analyses* ☐ Fusion as per RPG-CMC-115, Rev0, *Solubilization of Metals from Solids Using a KOH-KNO$_3$ Fusion* ☒ Digested as per RPG-CMC-128, Rev.1, *HNO$_3$-HCL Acid extraction of Liquids for Metals Analysis Using a Dry-Block Heater*
Pre-dilution Prior to Radiochemical Processing?	☐ No ☒ Yes -- *example 2 mL to 100 mL; 50x dilution*
Plutonium Separation Procedure:	RPG-CMC-4017, Rev. 0, Analysis of Environmental Water Samples for Actinides and Strontium-90
Technician/Analyst:	LP Darnell, (07/25/2019)
Co-Precipitation Procedure:	RPG-CMC-496, Rev. 1, Coprecipitation Mounting of Actinides for Alpha Spectroscopy
Technician/Analyst:	LP Darnell, (07/25/2019)
Spike and Tracer Standard ID's:	R-687-a-7 (Pu-239), R-719-1 (Pu-242 tracer)
Analysis Procedure:	RPG-CMC-422, Rev. 2, *Solutions Analysis: Alpha Spectrometry*
Reference Date:	Same as counting dates
Analysis Date or Date Range:	July 29 - August 1, 2019
Technician/Analyst:	T. Trang-Le
Analysis Data (File):	RPG-RC\PNL\Projects\Backup files\Backup 19\19-1773 Fiskum.xls
CMC Project 98620 File:	File Plan 5871: T 73312: Sample preparation and analysis records; T-4.4 Alpha Detector calibration, calibration verification checks, and maintenance records; and T3 Standard certificates and preparation. Also balance calibration and instrument performance checks.
M&TE Number(s):	Ortec AEA counters – 32 counters – See attached M&TE list

	8/16/19	T Trang-le	8/16/19
Preparer	**Date**	**Reviewer**	**Date**

Sample Results

See attached data report, Sample Results for ASR 0787.02. All data are reported in units of µCi per mL with a 1-σ uncertainty unless noted otherwise (see Comments).

Sample Preparation, Separation, Mounting and Counting Methods

All twelve samples submitted under Analytical Service Request (ASR) 0787.02 were analyzed for plutonium isotopes by Alpha Spectrometry. All the samples were prepared in RPL/420, only Pu-AEA is presented in this report.

Following the digestion process of the samples, the Pu was separated from the aqueous samples by anion exchange chromatography using procedure RPG-CMC-4017. The separated Pu fraction was mounted for alpha spectrometry by co-precipitation using procedure RPG-CMC-496, and then counted by alpha spectrometry using procedure RPC-CMC-422. The samples were counted on July 29-August 1, 2019; no decay corrections were made.

QUALITY CONTROL RESULTS

Quality control (QC) samples include a laboratory preparation blank and sample duplicate. Additional QC samples were prepared prior to separations; these included a reagent spike (RS) and a matrix spike (MS) made by adding Pu-239 standard to a diluted sample.

Tracer:

The Pu-242 tracer is added to every sample after appropriate dilution and prior to plutonium separations. The use of a Pu-242 tracer corrects for radiochemical yield and mathematically removes the detector counting efficiency from the results calculations. Tracer recovery is required to be high enough to provide acceptable counting statistics. The Pu-242 tracer counting statistics were acceptable for all samples. The tracer recoveries ranged from 37% to 106%.

Laboratory Preparation Blank (PB):

The activity levels of Pu-239/240 and Pu-238 present in the laboratory preparation blank (9.59E-6 µCi/mL, Pu-239/240 and 1.08E-6 µCi/mL, Pu-238) are both below the activities present in the samples (1.49E-4 µCi/mL Pu-239/240 and 2.09E-5 µCi/mL Pu-238 or higher). The blank result for the Pu-239/240 is 6.4% of the activity present in the lowest activity sample, thus not meeting the less than 5% of the activity present in the samples criteria. The blank result for the Pu-238 is 5.1% of the activity present in the lowest activity sample, thus not meeting the less than 5% of the activity present in the samples criteria. Sample TI061-L-F1-A is the only sample in the group of 12 where the activity present in the blank is greater than 5% or the activity present in the samples.

Blank Spike (BS) – Reagent Spike (RS):

The RS recovery of 98% meets the acceptance criteria of 80% to 120% recovery.

Matrix Spike (MS):

The MS recovery of 102% meets the acceptance criterion of 75% to 125% recovery. Note: the MS sample was prepared "after" digestion, by adding a known Pu-239 standard quantity to an aliquot of the leachate. Sample number 19-1774 (TI061-COMP-EFF) was selected as the matrix spike sample.

Duplicate -- Relative Percent Difference (RPD):

Duplicate results are required to agree within ≤20% RPD. The ASO QAP further specifies that the two results need to be >5 times the MDA or have individual uncertainties <20%. The duplicate results were ≤2% RPD for Pu-238 and Pu-239/240; thus meeting the ≤20% requirement.

Instrument Quality Control

Alpha counters receive initial calibration with NIST traceable sources to determine the counter efficiency. When internal tracers are not used, the counter efficiency is used in calculation of final results.

Detector backgrounds are determined every 4 weeks or after the last analytical run, whichever is longer. Detector background counts are subtracted from all subsequent sample counts. A process blank is analyzed with each analytical batch to evaluate for contamination in the sample preparation process.

Assumption and Limitations of the Data

None

Comments

1. The results have been corrected for all dilution factors resulting from sample processing.
2. The 1-sigma uncertainty represents the total propagated error associated with processing and counting operations and include; weighing errors, volume uncertainties, and counting error.

Attachment: Data Report -- Sample Results for ASR 0787.02.

Pacific Northwest National Laboratory
PO Box 999, Richland, WA
Radiochemical Sciences and Engineering Group

filename 19-1773 Fiskum
8/15/2019

Client: Fiskum
ASR 0787.02

Project: 73312
NC4189

Prepared by: Chuck Soderquist 8-16-19

Technical Reviewer: T Trang-le 8/16/19

Procedures:
RPG-CMC-474, Rev 1, Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry
RPG-CMC-432, Rev 0, Technetium-99 Analysis
RPG-CMC-4017, Rev 0, Analysis of Environmental Water Samples for Actinides and Strontium-90
RPG-CMC-422, Rev 2, Solutions Analysis: Alpha Spectrometry (Np, Pu, Am, Cm)
RPG-CMC-496, Rev 1, Coprecipitation Mounting of Actinides for Alpha Spectrometry

M&TE:
Perkin Elmer TriCarb model 3100TR liquid scintillation spectrometer
Alpha spectrometry counting system

Count dates: July 31-August 11, 2019

	Lab	Measured Concentration, µCi/mL ± 1s uncertainty									
Sample	ID	**Sr-90**		Tc-99		Np-237		Pu-238		Pu-239+240	
TI061-COMP-FEED	19-1773	**4.52E-1**	**± 2%**	**1.00E-1**	**± 5%**	**4.76E-5**	**± 2%**	**7.54E-5**	**± 4%**	**5.60E-4**	**± 2%**
TI061-COMP-EFF	19-1774	<1.E-3		**9.84E-2**	**± 5%**	**1.77E-5**	**± 3%**	**2.78E-5**	**± 5%**	**2.01E-4**	**± 2%**
	DUP-1774	<1.E-3		**9.79E-2**	**± 5%**	**2.28E-5**	**± 3%**	**2.71E-5**	**± 5%**	**2.01E-4**	**± 2%**
	RPD	-		1%		25%		2%		0.3%	
TI061-L-F1-A	19-1775	<1.E-3		--		**7.43E-6**	**± 4%**	**2.09E-5**	**± 6%**	**1.49E-4**	**± 3%**
TI061-L-F4-A	19-1776	**1.24E-3**	**± 16%**	--		**2.52E-5**	**± 3%**	**4.05E-5**	**± 4%**	**2.72E-4**	**± 2%**
TI061-L-F8-A	19-1777	<1.E-3		--		**3.98E-5**	**± 2%**	**4.10E-5**	**± 4%**	**3.07E-4**	**± 2%**
TI061-L-F11-A	19-1778	**1.51E-2**	**± 2%**	--		**4.51E-5**	**± 2%**	**4.98E-5**	**± 4%**	**3.42E-4**	**± 2%**
TI061-L-F14-A	19-1779	<1.E-3		--		**4.61E-5**	**± 2%**	**4.56E-5**	**± 4%**	**3.42E-4**	**± 2%**
TI061-L-F18-A	19-1780	**1.19E-3**	**± 17%**	--		**4.58E-5**	**± 2%**	**5.00E-5**	**± 4%**	**3.77E-4**	**± 2%**
TI061-L-F22-A	19-1781	<1.E-3		--		**4.60E-5**	**± 2%**	**4.89E-5**	**± 4%**	**3.68E-4**	**± 2%**
TI061-L-F25-A	19-1782	**1.68E-3**	**± 12%**	--		**4.35E-5**	**± 2%**	**5.10E-5**	**± 4%**	**3.73E-4**	**± 2%**
TI061-L-F27-A	19-1783	**2.14E-3**	**± 10%**	--		**4.16E-5**	**± 2%**	**5.44E-5**	**± 4%**	**3.96E-4**	**± 2%**
TI061-L-F29-A	19-1784	**2.73E-3**	**± 8%**	--		**4.22E-5**	**± 2%**	**5.07E-5**	**± 6%**	**3.95E-4**	**± 3%**
	Reagent Spike	97%		101%		93%		--		98%	
	Matrix Spike	102%		--		87%		--		102%	
	Lab Blank	**1.55E-5**	**± 25%**	1.3E-6	± 952%	-6.1E-9	± 173%	1.08E-6	± 31%	9.59E-6	± 8%

[Tc-99 spike was too small for the sample activity]

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