PNNL-30712, Rev. 0
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January 2021

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Prepared for the U.S. Department of Energy
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Pacific Northwest National Laboratory
Richland, Washington 99354

Executive Summary

The Tank Side Cesium Removal (TSCR) system, under development by Washington River Protection Solutions LLC (WRPS), will send initial low-activity Hanford waste tank supernate feeds to the Hanford Waste Treatment and Immobilization Plant (WTP) Low-Activity Waste (LAW) Facility. In addition to entrained solids removal from the supernate, the primary goal of TSCR is to remove cesium-137 (^{137}Cs) by ion exchange, allowing contact handling of the liquid effluent product at the WTP. Crystalline silicotitanate (CST) ion exchange media, manufactured by Honeywell UOP, LLC (product IONSIV^{TM} R9140-B), was selected as the ion exchange media at TSCR.

CST is a non-elutable inorganic material that has demonstrated robust chemical, physical, and radiation tolerance while maintaining functionality. However, exchange kinetics of Cs onto CST is slow, resulting in low utilization of the CST Cs load capacity before unacceptable Cs breakthrough. Two process flow designs have been tested, as follows.

1. Lead-lag column processing: The lead column was removed after the lag column effluent reached the waste acceptance criteria (WAC) limit,[1] the lag column was moved into the lead position, and a new lag column was installed. This format used ~52% Cs load capacity on the lead column.[2]

2. Lead-lag-polish column processing: The processing was stopped when the polish column effluent reached the WAC limit. This format resulted in 81% Cs load capacity on the lead column.[3]

Testing with diluted feed from Hanford tank AP-105 (AP-105DF) incorporated a nuanced change to the lead-lag-polish column system where the polish column was inserted when the lag column effluent reached WAC limit. A 10.9-L volume of AP-105DF (diluted to 5.6 M Na) was processed through the Direct Feed Test Platform system, established at Pacific Northwest National Laboratory to support small-scale waste qualification efforts. The columns consisted of 10-mL CST beds (CST Lot 2002009604, sieved to screen out >30-mesh particles) placed in 1.5-cm-inner-diameter columns. Feed was processed at 1.83 bed volumes (BV) per hour; the flowrate, in terms of contact time with the CST bed, matched the expected flowrate at TSCR. The <30-mesh CST sieve cut was expected to provide appropriate performance scaling to a full-height column. The installation of the polish column later in processing (after processing 523 BVs) did not appear to fundamentally change the utilization of the lead column for Cs exchange nor did it extend the total feed processing volume when compared to the previous test with AP-107 feed.[3] Table ES.1 and Figure ES.1 summarize the measured AP-105DF Cs load performance.

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[1] From *ICD 30 – Interface Control Document for Direct LAW Feed*, 24590-WTP-ICD-MG-01-030, Rev. 0, 2015, Bechtel National, Inc. (River Protection Project Waste Treatment Plant), Richland, Washington.

[2] 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, RPT-DFTP-011, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

[3] Fiskum SK, AM Rovira, HA Colburn, AM Carney and RA Peterson. 2019. *Cesium Ion Exchange Testing Using a Three-Column System with Crystalline Silicotitanate and Hanford Tank Waste 241-AP-107.* PNNL-28958, Rev. 0, RPT-DFTP-013, Rev. 0. Pacific Northwest National Laboratory. Richland, Washington.

Table ES.1. AP-105DF Column Performance Summary with CST

Column	WAC Limit Breakthrough (BVs)	50% Cs Breakthrough (BVs)	^{137}Cs Loaded (µCi/g)	Cs Loaded (mmoles/g CST)
Lead	187	647	86,580	0.0402
Lag	560	1239[(b)]	41,110	0.0191
Polish	974[(a)]	NA	5,370	0.0025

(a) The polish column was positioned in place after 523 BVs were processed through the lead-lag column system.
(b) Extrapolated value.
BV = bed volume, 10 mL
The time weighted average flowrate was 1.83 BV/h.

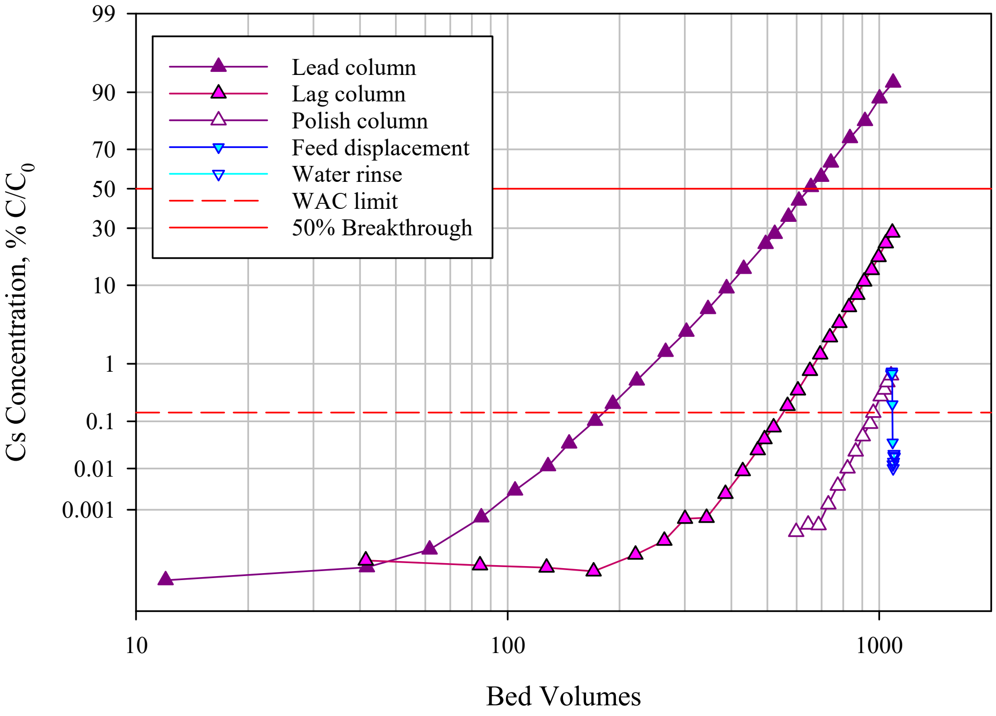

Figure ES.1. Lead, Lag, Polish Column Cs Load Profiles for AP-105DF

Batch contact tests were performed with the AP-105DF tank waste at five Cs concentrations, each at a phase ratio of 200 (liquid volume to dry CST mass). The distribution coefficient (K_d) at the equilibrium condition of 5.66E-5 M Cs (AP-105DF feed condition) was 760 mL AP-105DF/g CST. With a CST bed density of 1.00 g/mL (<30 mesh CST), this K_d corresponded to a predicted 50% Cs breakthrough of 760 BVs. The observed column performance 50% Cs breakthrough (647 BVs) fell ~15% short of the predicted performance (760 BVs). The batch contact testing predicted a Cs load capacity of 0.0420 mmoles Cs/g dry CST at the equilibrium Cs concentration. The Cs breakthrough from the lead column at the end of processing reached 92% C/C$_0$ and resulted in 0.0402 mmoles Cs/ g CST— 95% of the maximum Cs loading at feed condition based on prediction from batch contact testing.

The AP-105DF 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. Large fractions of lead (Pb), neptunium (Np), plutonium (Pu), and strontium (Sr/^{90}Sr) significantly fractionated to the CST.

Table ES.2. Recoveries of Analytes of Interest in the AP-105DF Effluent

	Analyte	Feed Concentration (M)	Effluent Concentration (M)	Fraction in Effluent
Metals / Non-metals	Al	5.26E-01	5.23E-01	99%
	As	<5.5E-04	[9.7E-04]	--
	Ba	<1.06E-06	<1.3E-06	--
	Ca	1.03E-03	1.02E-03	99%
	Cd	[2.4E-05]	[2.0E-05]	--
	Cr	6.43E-03	6.56E-03	101%
	Fe	[2.0E-05]	<1.6E-05	--
	K	1.02E-01	1.02E-01	100%
	Na	5.92E+00	6.00E+00	101%
	Nb	2.74E-07	2.89E-05	NA
	P	1.27E-02	1.44E-02	113%
	Pb	9.00E-05	2.67E-05	29%
	S	4.66E-02	4.65E-02	99%
	Sr	1.82E-06	1.64E-07	9%
	Ti	<5.9E-06	[2.3E-05]	NA
	U	2.46E-05	1.99E-05	80%
	Zn	[4.6E-05]	[4.7E-05]	--
	Zr	<9.4E-06	[4.5E-05]	NA
	Analyte	Feed Concentration (µCi/mL)	Effluent Concentration (µCi/mL)	Fraction in Effluent
Radionuclides[a]	^{90}Sr	6.90E-01	7.23E-04	0.10%
	^{99}Tc	1.13E-01	1.05E-01	93%
	^{137}Cs	1.13E+02	5.36E-02	0.047%
	^{237}Np	6.69E-06	1.22E-06	18%
	^{238}Pu	6.37E-06	2.64E-06	41%
	$^{239+240}$Pu	3.94E-05	1.56E-05	39%
	^{241}Am	2.66E-04	2.30E-04	86%

(a) Reference date is December 2020.

Notes:

"<" values were < method detection limit (MDL), sample-specific MDL provided.

"--" indicates effluent recovery could/should not be calculated; feed and/or effluent result was < estimated quantitation limit (EQL).

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

NA = not applicable; analytes are CST components

The recovered fractions are calculated with values containing more significant figures than shown; using listed values may result in a slight difference due to rounding.

Acknowledgments

The authors thank Shielded Facility Operations staff Hollan Brown, Victor Aguilar, Jarrod Turner, and Mike Rojas for hot cell operations (batch contact and ion exchange column system setup, processing, and sample removal). We thank the Analytical Support Operations (ASO) staff Karl Pool, Lori Darnell, Jenn Carter, Denis Cherkasov, Sam Morrison, and Andrew Carney for the sample analysis, data processing, and reporting. The authors thank Dr. Heather Colburn and Renee Russell for conducting the technical reviews of the calculation files and this report. The authors also thank Bill Dey for the quality review of the calculation files and this report and Matt Wilburn for his technical editing contribution to this report.

Acronyms and Abbreviations

AEA	alpha energy analysis
ASO	Analytical Support Operations
ASR	Analytical Service Request
BV	bed volume
CST	crystalline silicotitanate
DF	decontamination factor
DI	deionized
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
MDL	method detection limit
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
PTFE	polytetrafluoroethylene
QA	quality assurance
R&D	research and development
RPD	relative percent difference
RPL	Radiochemical Processing Laboratory
RSD	relative standard deviation
SV	system volume
TIC	total inorganic carbon
TOC	total organic carbon
TRU	transuranic
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, LLC (WRPS, Richland, WA) 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 the 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 (Ard 2019).

Crystalline silicotitanate (CST) ion exchange media, product IONSIV™ R9140-B, manufactured by Honeywell UOP, LLC (Des Plaines, IL), was selected as the ion exchange media at the TSCR system. CST is a non-elutable inorganic material that has demonstrated robust chemical, physical, and radiation tolerance while maintaining functionality (Pease et al. 2019). Testing of ^{137}Cs/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). Exchange kinetics of Cs onto CST is slow, demonstrated by its long transition zone. The long transition zone challenges full utilization of the CST Cs capacity (Fiskum et al. 2019a). Two column process flow designs have been tested for TSCR on Hanford tank wastes, as follows.

1. **Lead-lag column processing:** The lead column is removed after the lag column effluent reaches the WAC limit and then the lag column is moved up to the lead position and a new lag column is installed (AP-107 tank waste, Rovira et al. 2018, and AW-102 tank waste, Rovira et al. 2019). When processing AP-107 tank waste, 25% Cs breakthrough from the lead column was achieved before it was required to be removed and only partial utilization of the CST bed was achieved. Insufficient volume of AW-102 was available to fully test the Cs loading limits.

2. **Lead-lag-polish column processing:** Feed processing is stopped when the polish column effluent reaches the WAC limit (AP-107 tank waste, Fiskum et al. 2019b). In this case, an extrapolated ~1010 bed volumes (BVs) of feed, corresponding to an estimated 62% Cs breakthrough from the lead column, would have been processed when the WAC limit was reached at the polish column effluent. With the polish column in place, higher lead column utilization was realized.

The primary objective of the work described in this report was to test Cs removal using a hybrid column processing scenario and establish Cs load profiles. In this case, a lead-lag column system was used, and once the lag column effluent reached the WAC limit, a polish column was positioned after the lag column and processing continued. Additional objects of this current study are as follows.

1. Conduct batch contact testing with CST to determine the Cs load capacity of diluted and filtered AP-105 (AP-105DF).

2. Compare the AP-105DF Cs load profile to the previously reported AP-107 load curve (Fiskum et al. 2019b).

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[1] From *ICD 30 – Interface Control Document for Direct LAW Feed*, 24590-WTP-ICD-MG-01-030, Rev. 0, 2015, Bechtel National, Inc. (River Protection Project Waste Treatment Plant), Richland, Washington.

3. Analyze the AP-105DF ion exchange feed and effluent to derive the fates of key analytes (^{90}Sr, ^{99}Tc, ^{137}Cs, $^{239+240}$Pu, ^{237}Np, ^{241}Am, Al, As, Ba, Ca, Cd, Cr, Fe, K, Na, Nb, P, Pb, S, Sr, Ti, U, Zn, Zr).

4. Provide Cs-decontaminated AP-105DF for vitrification (to be conducted later and addressed in a separate report).

5. Provide Cs-loaded CST for follow-on analysis (to be conducted later and addressed in a separate report).

The efficacy of loading higher amounts of Cs onto the lead column CST while maintaining a product below the WAC limit from the lag and then polish columns 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.

WRPS funded Pacific Northwest National Laboratory (PNNL) to conduct testing with AP-105DF tank waste under contract 36437/289.

2.0 Quality Assurance

The work described in this report was conducted with funding from WRPS contract 36437/289, *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-105DF tank waste, batch contact conditions, and column processing 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. This CST production lot was screened by the manufacturer to achieve an 18 × 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 (RPL). The handling and splitting of the CST were previously described (Fiskum et al. 2019a). A 180-g subsample split was passed through a 30-mesh sieve (ASTM E11 specification) as previously described (Fiskum et al. 2019a). Of this starting mass, 65.6 g or 36 wt% passed through the sieve and was collected for batch contact testing and column testing; this was similar to the 32% mass fraction achieved by Westesen et al. (2020). The <30-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 provides the physical properties on <30-mesh sieved CST Lot 2002009604 that had been washed and air dried (Westesen et al. 2020). These properties were expected to apply to the current test because CST processing was essentially identical. The CST particle number across the 1.5-cm column diameter (28) was close to the minimum ideal (≥30) defined by Helfferich (1962) to prevent fluid channeling due to wall effects.

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[1] Fiskum SK. 2019. TP-DFTP-076, Rev. 0.0. *Cesium Ion Exchange Testing with AP-105 Tank Waste with Crystalline Silicotitanate for Tank Side Cesium Removal (TSCR)*. 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 <30 Mesh CST, Washed R9140-B CST Lot 2002009604 (Westesen et al. 2020)

Parameter	Result	Units
Bulk density	1.03	g/mL
CST bed density	1.00	g/mL
Settled bed void volume	68.2	%
Cumulative particle undersize fractions[a]	d_{10}: 398 d_{50}: 541 d_{90}: 738	microns
Column inner diameter	1.5	cm
Particle number across column diameter (based on d_{50})	28	NA

(a) Volume basis, post-sonication

3.2 AP-105DF Tank Waste Sample

Multiple samples (36 each at ~250 mL for a combined ~9 L) were collected in two sets from Hanford tank AP-105 in December 2019. The samples were delivered to PNNL's RPL and placed into the Shielded Analytical Laboratory hot cells. Analytical measurements were conducted by the Analytical Support Operations (ASO) according to two Analytical Service Requests (ASRs); results are provided in Table 3.2. The first sample from the first set, 5AP-19-01, was subsampled and analyzed to confirm Al, K, and Na concentrations by inductively coupled plasma optical emission spectrometry (ICP-OES) (ASR 0957). Subsamples from both the first and last samples from the first set delivered, 5AP-19-01 and 5AP-19-18, were measured for the ^{137}Cs concentration by gamma energy analysis (GEA) (ASR 0957). Following Cs separation, the Cs isotopic ratio was measured by inductively coupled plasma mass spectrometry (ICP-MS) (ASR 0964). The AP-105 densities were measured in-cell using 10-mL volumetric flasks. The results of the duplicate pairs agreed within 4% relative percent difference (RPD), it was assumed that all 36 samples were essentially homogenous, within analytical uncertainty (±10% to 15%).

Table 3.2. Characterization of Samples 5AP-19-01 and 5AP-19-18 Collected from Hanford Tank AP-105 December 2019 (ASR 0957, 0964)

Sample ID>>	5AP-19-01	5AP-19-18	5AP-19-25			
RPL Number>>	20-0321	20-0322	NA			
Analyte				RPD, %	Units	Analysis Method
Al	7.86E-01	--	--	--	M	ICP-OES
K	1.71E-01	--	--	--	M	ICP-OES
Na	8.72E+00	--	--	--	M	ICP-OES
^{137}Cs$^{(a)}$	193	186	--	3.8	µCi/mL	GEA
RPL Number>>	20-0350	20-0351	NA			
^{133}Cs	62.3	61.8	--	0.93	Wt%	ICP-MS
^{134}Cs	19.5	19.5	--	0.08	Wt%	ICP-MS
^{137}Cs$^{(a)}$	18.2	18.7	--	3.0	Wt%	ICP-MS
Density	1.414	--	1.412	0.1	g/mL	Volumetric flask

(a) Reference date is 12/17/19.

The AP-105 tank waste samples were composited and diluted in stages to achieve a 5.92 M Na concentration as previously described (Allred et al. 2020). Nominally three samples were combined into a polyethylene bottle and Columbia River process water was added. The AP-105 and water were mixed and allowed to stand for 3 to 6 months before filtration testing. After filtration, 10 bottles of AP-105 diluted feed (AP-105DF), containing 0.9 to 1.3 L each, were made available for ion exchange testing.

The densities and ^{137}Cs concentrations of each of the 10 bottles of AP-105DF were measured. The density average was 1.285 g/mL [0.38% relative standard deviation (RSD)] and the ^{137}Cs average was 121.7 µCi/mL (1.8% RSD; reference date June 2020). Therefore, AP-105DF feeds in all containers were considered uniform. The total Cs concentration was calculated from the ^{137}Cs concentration (in terms of µg/mL with unit conversion per the specific activity) and ^{137}Cs mass fraction (average 18.5 wt%). The total Cs concentration in the AP-105DF was 7.58 µg/mL or 5.66E-5 M. This value agreed within 5% of the total Cs concentration, 7.92 µg/mL (reference date August 9, 2017), reported previously for AP-105 diluted tank waste (Fiskum et al. 2018a).

3.3 Batch Contact Conditions

The distribution coefficient (K_d) is a quantitative measure of a material’s capability to remove an ion from a specific solution matrix. Specifically, it is the ratio of analyte ion remaining in solution at equilibrium to the amount of analyte ion sorbed on the ion exchange material. The distribution coefficient is determined from batch contact testing.

Batch contact solutions consisted of AP-105DF tank waste samples 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-105DF feed matrix. The preparation and batch contacts were processed in accordance with a test instruction.[1]

Aliquots of Cs spike solutions (133 mg/mL or 16.2 mg/mL) were added to four centrifuge tubes in small volumes. The centrifuge tubes with Cs-spike were transferred to the hot cell and ~30-mL aliquots of AP-

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[1] Fiskum SK. 2019. TI-DFTP-081, *Batch Contact Testing of Diluted and Filtered AP-105 Hanford Tank Waste with Crystalline Silicotitanate*. Pacific Northwest National Laboratory, Richland, Washington. Not publicly available. Implemented July 2020.

105DF were transferred to each container. Exact masses transferred were determined by difference from the measured masses before and after Cs spikes and AP-105DF transfers; the added volumes were calculated from the solution densities and net sample masses. The four vessels of AP-105DF plus added Cs and the unspiked AP-105DF are termed “stock contact solutions.” The stock contact solutions were shaken to mix AP-105DF thoroughly with the Cs spike. Table 3.3 shows the added spiked Cs masses and calculated starting Cs concentrations in the stock contact solutions. The Cs spike solutions were equilibrated with AP-105DF matrix 1 to 2 days.

Table 3.3. Cs Concentrations in Stock Contact Solutions

Solution ID	Added Cs (mg)	Cs Concentration (mg/L)	Cs Concentration (M)
TI081-S0	0	7.58	5.66E-5
TI081-S1	0.808	35.3	2.66E-4
TI081-S2	4.13	150	1.13E-3
TI081-S3	16.11	557	4.19E-3
TI081-S4	58.68	1947	1.47E-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 moisture. 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. This F-factor sample aliquot was dried at ~103 °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 masses to collect for the batch contact samples. The air-dried CST contained ~10% water by mass.

Precisely weighed quantities of the washed and air-dried CST (targeted to be 0.084 g “wet” and 0.075 g dry) were aliquoted into 20-mL liquid scintillation vials, one for each batch contact sample. The air-dried CST mass was determined to an uncertainty of ≤1%.

Two nominal 0.3-g F-factor samples were also collected and precisely weighed, one at the beginning of CST aliquoting process, and one at the end of CST aliquoting process in a tight subsampling time window (≤10 min). The initial F-factor sample masses were designated M_I. The F-factor samples were dried to constant mass at 103 °C. The final F-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, 0.8702 ±0.10% RPD) was used to calculate the dry CST masses contacted with AP-105DF.

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

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-105DF 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 182 and 207 mL/g CST. The actual batch contacted sample solution volumes and CST masses are shown in Table 3.4.

Table 3.4. Dry CST Masses and AP-105DF Tank Waste Volumes for Batch Contacts

Sample ID	Dry CST Mass[(a)] (g)	AP-105DF Volume (mL)	Liquid-to-Solid Phase Ratio (mL/g)
TI081-S0-BC	0.0764	14.9082	195
TI081-S1-BC	0.0768	14.9221	194
TI081-S2-BC	0.0720	14.9076	207
TI081-S3-BC	0.0730	14.8603	204
TI081-S4-BC	0.0752	14.8888	198
TI081-S0-BC-d	0.0728	13.8412	190
TI081-S1-BC-d	0.0768	13.9652	182
TI081-S2-BC-d	0.0742	13.8748	187
TI081-S3-BC-d	0.0722	14.1719	196
TI081-S4-BC-d	0.0745	14.8689	200

(a) Mass-corrected for water loss at 103 °C.

Four 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] set to ~400 revolutions per minute. Agitation continued for 72 h, which had been previously established to reach Cs equilibrium conditions (Fiskum et al. 2019b). The process was repeated for another set of four batch contact vials, and then again for the final two batch contact vials. The average sentinel temperature upon completion of batch contact testing was 29.9 °C with a range of 0.5 °C (Type K thermocouple, accuracy ±2.2 °C). The contact temperature was ~2 °C higher than the ambient cell temperature. No obvious cloudiness was observed in the contact solutions post-processing.

After the batch contact time, the CST was settled and ~ 5 mL of each aqueous fraction was removed from the hot cell. Each sample was filtered through a 0.45-µm pore size nylon-membrane syringe filter. Filtered sample aliquots (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-105DF 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):

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

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)

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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).

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

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

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

The Cs_{IX} value was divided by the Cs formula weight to determine Q, mmoles analyte/g dry CST. In the case of unspiked AP-105DF, the calculated Cs formula weight of 134 g/mole was applied. For the spiked Cs samples, where natural Cs dominated the isotopic composition, the Cs formula weight of 132.9 g/mole was applied.

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. (3.5) (Bray et al. 1993). The CST bed density is the dry CST mass divided by the volume in the column:

$$K_d \times \rho_b = \lambda \tag{3.5}$$

3.4 Ion Exchange Process Testing

This section describes the ion exchange column system and AP-105DF process conditions. The preparations and column testing were conducted in accordance with a test instruction.[1]

3.4.1 Ion Exchange Column System

Figure 3.1 provides a schematic of the lead-lag column ion exchange process system; Figure 3.2 shows the lead-lag-polish column configuration schematic. 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 (back of manifold) with a 10-psi trigger point. The 1/8-inch outside diameter / 1⁄16-inch inside diameter polyethylene tubing was purchased from Polyconn (Plymouth, MN). The 1/8-inch outside diameter / 1/16-inch inside diameter stainless steel tubing was used in conjunction with the manifold.

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[1] Fiskum, SK. 2019. *Cesium Removal from AP-105 Using Crystalline Silicotitanate in a Two and Three-Column Format.* TI-DFTP-082. Pacific Northwest National Laboratory, Richland, Washington. Not publicly available. Implemented July 2020.

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. Multiple quick disconnects were used such that columns could be isolated (required for system install and reserved polish column) or replaced as needed. Also, recovery from upset conditions could be accommodated by allowing access to a column either downflow or upflow.

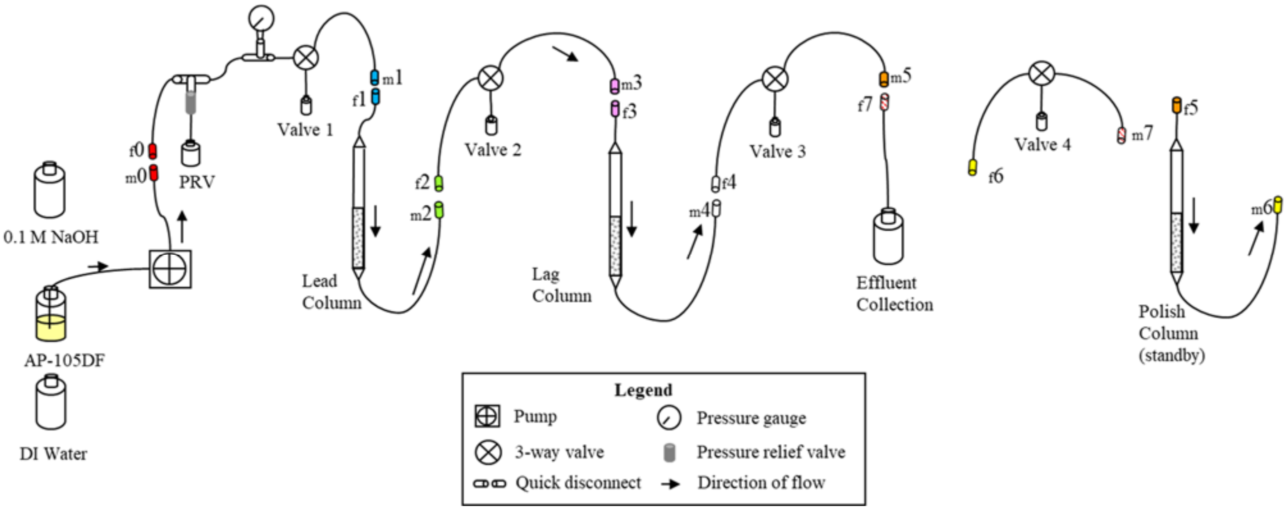

Figure 3.1. Ion Exchange System Schematic (2-Column Configuration)

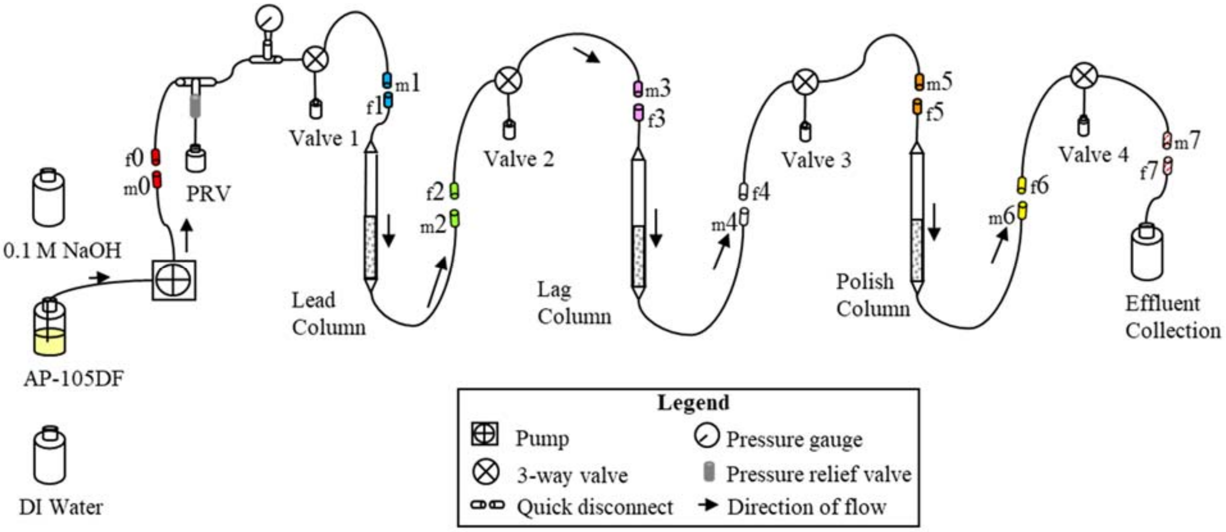

Figure 3.2. Ion Exchange System Schematic (3-Column Configuration)

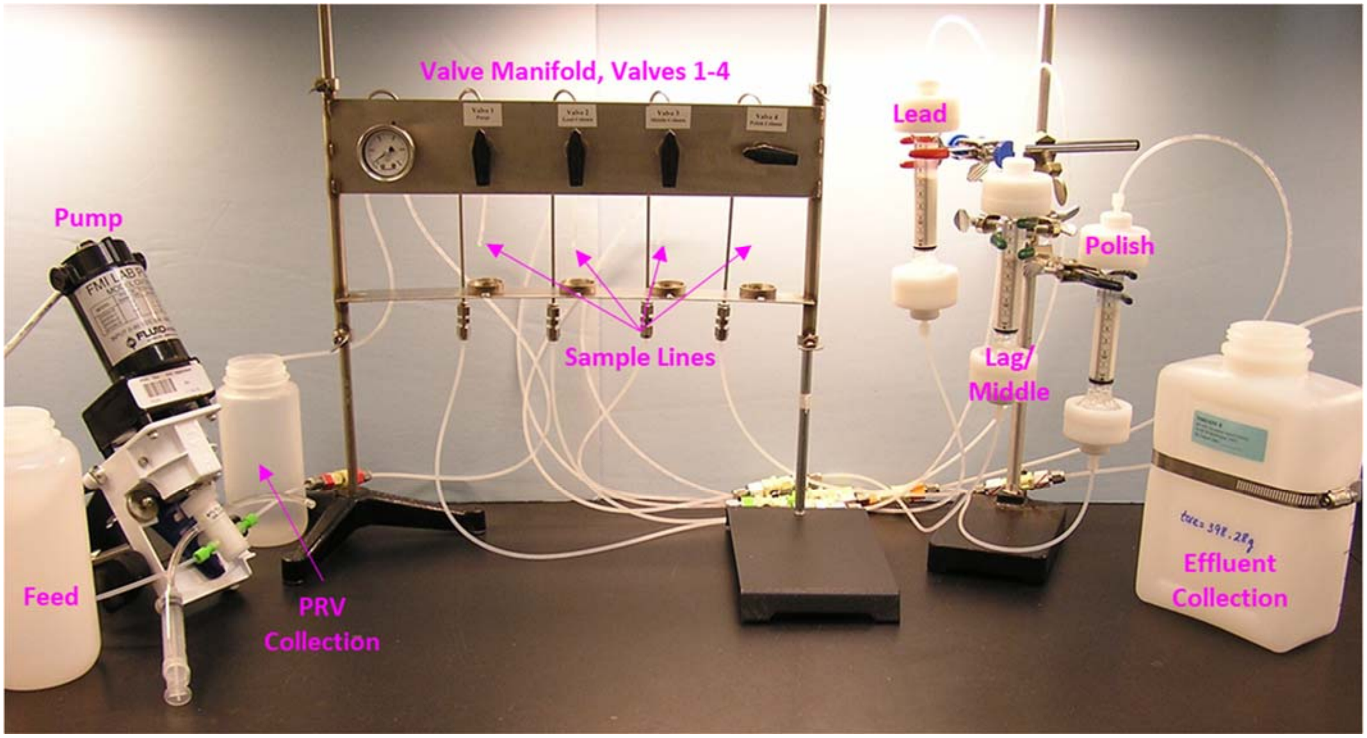

Figure 3.3. Photograph of Ion Exchange System Outside of the Hot Cell

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 1.5-cm inside diameter columns are not commercial-off-the-shelf items. The columns are 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. 2018b). 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. 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 pump (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 lag column samples were collected at valve 3, and the polish column samples were collected at valve 4. The gross AP-105DF effluent, feed displacement (FD), water rinse, and flushed fluid were collected at the effluent line.

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. Three 10.0-mL aliquots of settled CST (pretreated, <30 mesh) were measured using a graduated cylinder and then quantitatively transferred, one aliquot each, to 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 nominally 5.6 cm. This small column bed height corresponded to 2.4% of the full height column (234 cm or 92 inches) and the BV corresponded to 0.0017% of the full-scale column (596 L) (Siewert 2019).

Figure 3.4 provides a closeup image of the lag column loaded with CST, the fluid headspace, the CST bed support/O-ring, 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.

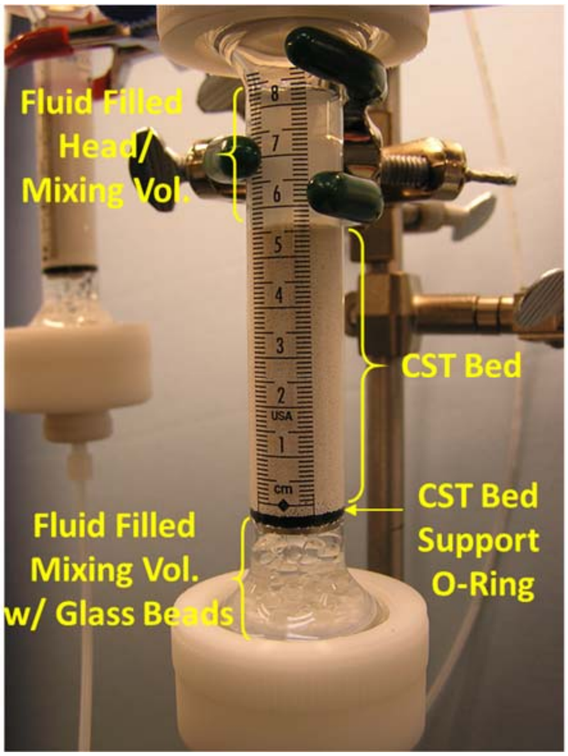

Figure 3.4. Closeup of Lag Chromaflex® Column Loaded with CST

The entire fluid-filled volume of the assembly was calculated for the 2-column system at ~46 mL, and for the 3-column system at ~66 mL. The bed void volume was assigned 66% (Westesen et al. 2020). Therefore, each CST bed held 6.6 mL fluid and the CST beds only comprised ~30% of the fluid-filled volume. The TSCR system platform may have a much larger fluid fraction associated with the CST bed. The fluid-filled mixing space above each CST bed ranged from 3.4 to 4.7 mL. The fluid mixing volume below each CST bed ranged from 2.8 to 3.4 mL. Thus, ~60% of the total fluid holdup volume was unavoidably associated with the geometry of the two and three columns. These scales of 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-105DF processing approximately 1 week after starting the run.

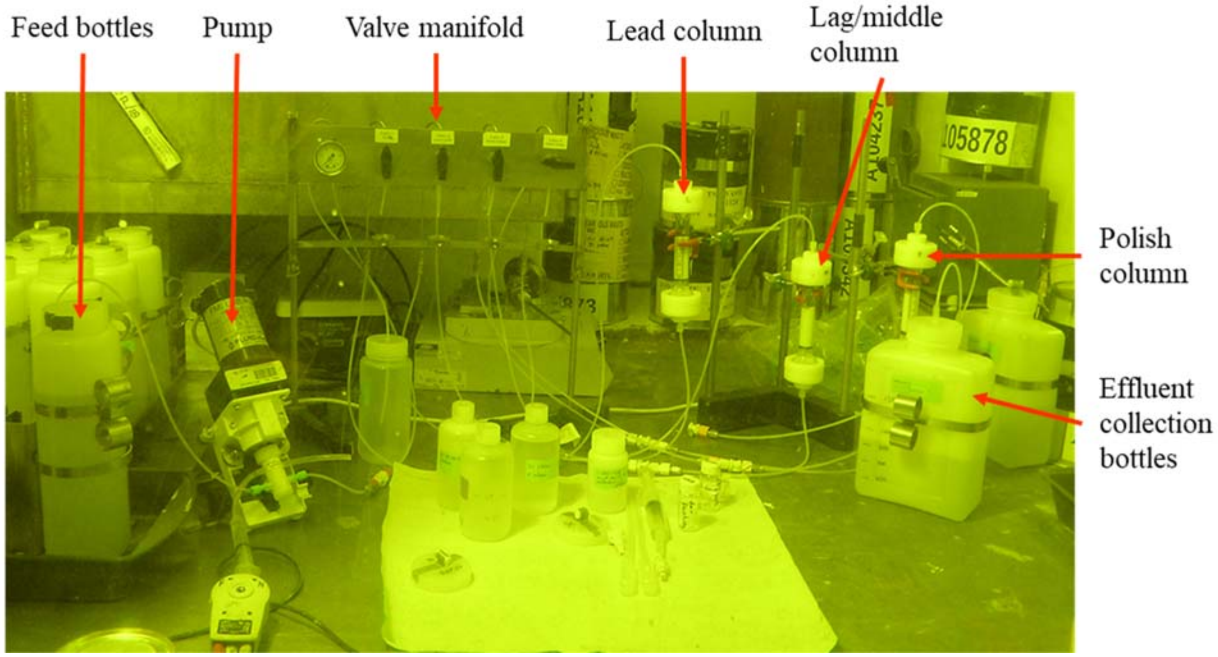

Figure 3.5. Ion Exchange Assembly in the Hot Cell, ~1 Week after Start

3.4.2 AP-105DF Tank Waste Process Conditions

Once the ion exchange assembly was installed in the hot cell, a flow of 0.1 M NaOH was used to verify system integrity and calibrate the pump. The various 1.5-L polyethylene containers from the filtration process (Allred et al. 2020) were used as the ion exchange feed bottles. They were positioned in a bottle stand to provide stability just before the feed line was inserted. When the contents in a feed bottle decreased to ~200 mL, the next bottle in line was moved to the feed position and the residual contents were poured into the new feed bottle. The AP-105DF feed was processed downflow through the ion exchange media beds, lead to lag. Effluent was collected in ~1.0- to 1.3-L increments. The volume limitation allowed for safe transfer out of cell in 1.5-L polyethylene bottles. The lag column effluent Cs concentration was closely monitored. When the WAC limit was reached, the polish column was placed in-line and the run continued.

After the AP-105DF loading was completed, 11 BVs of 0.1 M NaOH FD followed by 11 BVs of DI water were passed downflow through the system to rinse residual feed out of the columns and process lines. The 11 BVs was equivalent to ~1.7 times the fluid-filled system volume (SV).

All processing was conducted at ambient cell temperature, nominally 27 to 29 °C. Test parameters, including process volumes, flowrates, and CST contact times, are summarized in Table 3.5. 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 1.8 and 2.0 BV/h, respectively. Greater fidelity with the stroke rate controller could not be obtained to center on the target 1.83 BV/h. Figure 3.6 shows the achieved flowrate as a function of time.

Table 3.5. Experimental Conditions for AP-105DF Column Processing, July 6 to July 31, 2020

		Volume			Flowrate		Duration
Process Step	Solution	(BV)	(SV)	(mL)	(BV/h)	(mL/min)	(h)
Loading lead column	AP-105DF	1091	NA	10906	1.83	0.305	600
Loading lag column[(a)]	AP-105DF	1085	NA	10850	1.83	0.305	600
Loading polish column[(b)]	AP-105DF	516	NA	5161	1.83	0.305	264
Feed displacement	0.1 M NaOH	10.8	1.63	108	2.93	0.489	3.7
Water rinse	DI water	11.2	1.69	112	2.89	0.482	3.9
Flush with compressed air[(c)]	NA	5.2	0.82	52.3	NA	NA	NA

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

(b) The feed volume through the polish column was lower relative to that of the lead and lag columns because it was placed in position after 523 BVs were processed.

(c) The flush occurred on August 3, 2020, after the system sat in static contact with water rinse for 66 h (over the weekend).

BV = bed volume (10.0 mL as measured in graduated cylinder).
SV = system volume (estimated 66 mL).
NA = not applicable.

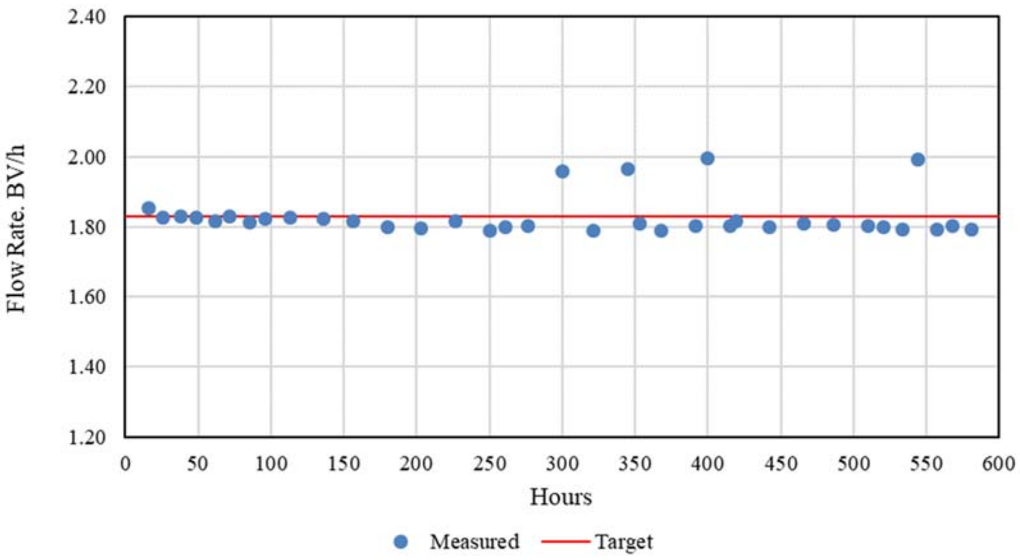

Figure 3.6. AP-105DF Flowrate as a Function of Time

The total cumulative volume of AP-105DF processed was 10.91 L (1091 BVs). The AP-105DF process cycle mimicked, as best as possible, the current process flow anticipated at the TSCR facility in terms of BV/h (i.e., contact time), FD, and water rinse as defined in the test plan. It was understood that the feed linear flow velocity in this small-column configuration (0.17 cm/min) could not begin to match that of the full-height processing configuration (7.3 cm/min, Fiskum et al. 2019a). The point was to match contact time in the bed.

During the loading phase, nominal 2-mL samples were collected from the lead, lag, and polish columns at the sample collection ports (see Figure 3.1, valves 2, 3, and 4). Sampling from the columns necessitated brief (~7-minute) interruptions of flow to the downstream columns. Samples were collected after the first 12 BVs were processed and again at nominal 18- to 93-BV increments. Only brief (~5 min) interruptions were associated with changing the feed bottles.

The FD effluent was collected in a series of 6 vials in ~18-mL increments. The water rinse was similarly collected. The fluid-filled volume was expelled with compressed air connected at the first quick disconnect in the system *f0* (see Figure 3.1) in ~4 min. The collected volume (52.3 mL) did include the interstitial fluid space between the CST beads, but was not expected to include fluid in the CST pore space. Hours of additional gas flow were required to dry the CST enough to be free-flowing such that it would effectively pour out of the columns into specially designed shielded containment for later examination (not addressed in this report). The recovered CST was 10.02 g, 10.28 g, and 10.38 g for the lead, lag, and polish columns, respectively. With a CST bed density is 1.00 g/mL, essentially quantitative recovery of the CST from the columns was estimated.

After setting a couple of days, solids were observed in the flushed solution. The aqueous phase was decanted and removed from the hot cell. The slurry with he settled residual solids was set aside to dry. Some solids were also later found in the decanted solution and are pictured in Figure 3.7. They have the appearance of FeOOH flocculant solids. The dried residue in the parent bottle weighed only 0.026 g; these solids were submitted for acid digestion and ICP-OES analysis per ASR 1109. Solids in gas flushed fluid had not previously been noted; the solids noted herein appeared to be an anomaly.

3.5 Sample Analysis

Cesium load performance was determined from the ^{137}Cs measured in the collected samples relative to the native ^{137}Cs in AP-105DF feed. The collected samples were analyzed directly to determine the ^{137}Cs concentration using GEA. Cesium 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.

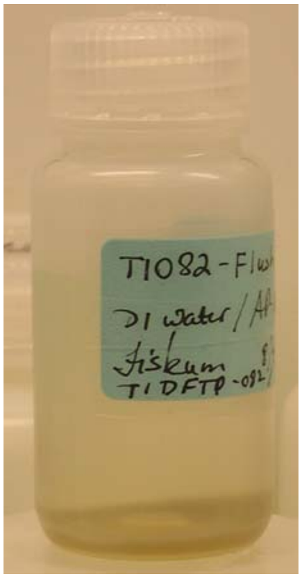

Figure 3.7. Decanted Flushed Solution Post Water Rinse Showing Settled Solids

A composite feed sample was prepared by sampling 1 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 3.6 summarizes the specific sample collections and targeted analytes along with the cross references to the ASO sample identification numbers (IDs).

The feed and effluent samples were submitted to the ASO on ASR 1097. 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, longer count times were used to assess isotopes other than ^{137}Cs.

Table 3.6. Analytical Scope Supporting Column Processing, ASR 1097

Sample ID	ASO Sample ID	Analysis Scope
TI082-COMP-FEED	20-1677	GEA (^{60}Co, ^{137}Cs, ^{154}Eu) ICP-OES (Al, As, Ca, Cd, Cr, Fe, K, Na, P, Si, Ti, Zn, Zr) ICP-MS (Ba, Nb, Pb, Sr, ^{238}U) Radioanalytical (^{90}Sr, ^{99}Tc, ^{237}Np, ^{238}Pu, $^{239+240}$Pu, ^{241}Am)
TI082-COMP-EFF	20-1678	GEA (^{60}Co, ^{137}Cs, ^{154}Eu) IC anions (F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, $C_2O_4^{2-}$, SO_4^{2-}) Furnace oxidation (TOC, TIC) Acid titration (free OH) ICP-OES (Al, As, Ca, Cd, Cr, Fe, K, Na, P, Si, Ti, Zn, Zr) ICP-MS (Ba, Nb, Pb, Sr, ^{238}U) Radioanalytical (^{90}Sr, ^{99}Tc, ^{237}Np, ^{238}Pu, $^{239+240}$Pu, ^{241}Am)
TI082-L-F2-A	20-1679	ICP-OES (Al, Ca, Cd, Fe, K) ICP-MS (Ba, Pb, ^{238}U) Radioanalytical (^{90}Sr, ^{237}Np, $^{239+240}$Pu)
TI082-L-F4-A	20-1680	
TI082-L-F6-A	20-1681	
TI082-L-F8-A	20-1682	
TI082-L-F10-A	20-1683	
TI082-L-F12-A	20-1684	
TI082-L-F14-A	20-1685	
TI082-L-F16-A	20-1686	
TI082-L-F22-A	20-1687	
TI082-L-F26-A	20-1688	

IC = ion chromatography
TIC = total inorganic carbon
TOC = total organic carbon

4.0 Batch Contact Results

This section discusses the batch contact results for the AP-105DF filtered tank waste with <30-mesh CST Lot 2002009604.

Equilibrium Cs concentrations and K_d results for the batch contacted samples are provided in Table 4.1. The K_d values versus Cs concentrations are plotted in Figure 4.1 on a log-log scale; the AP-105DF Cs concentration is shown in a vertical dashed line. Between 1.6 and 35 µg/mL Cs, the K_d values were essentially constant (flattened portion of the curve). The K_d at the feed condition Cs concentration (7.58 µg/mL) is 760 mL/g. At a bed density of 1.00 g CST/mL, the λ value (K_d x bed density) is therefore predicted to be at ~760 BVs. This value was 7% lower than that predicted for AP-107, 814 BVs at a slightly higher Cs feed concentration of 9.19 µg/mL Cs (Fiskum et al. 2019b).

Table 4.1. Equilibrium Results for AP-105DF Batch Contact Samples with CST Lot 2002009604

Sample ID	Final [Cs] (µg/mL)	Final [Cs] (M)	K_d (mL/g)	Q, Equilibrium Cs in CST (mmoles/g)
TI081-S0-BC	1.64	1.22E-5	706	8.65E-3
TI081-S0-BC-d	1.57	1.17E-5	723	8.52E-3
TI081-S1-BC	7.16	5.39E-5	761	4.11E-2
TI081-S1-BC-d	6.77	5.09E-5	763	3.90E-2
TI081-S2-BC	34.7	2.61E-4	689	1.80E-1
TI081-S2-BC-d	30.8	2.31E-4	725	1.68E-1
TI081-S3-BC	214	1.61E-3	325	5.25E-1
TI081-S3-BC-d	215	1.62E-3	311	5.05E-1
TI081-S4-BC	1371	1.03E-2	83	8.59E-1
TI081-S4-BC-d	1420	1.07E-2	74	7.92E-1

Note that the AP-105DF tank waste constituents also included 0.102 M K and 1.24 M free hydroxide.
Contact time = 72 h
Contact temperature = 30 °C
See Table 3.3 for initial Cs concentrations.
See Table 3.4 for CST masses and contact solution volumes.

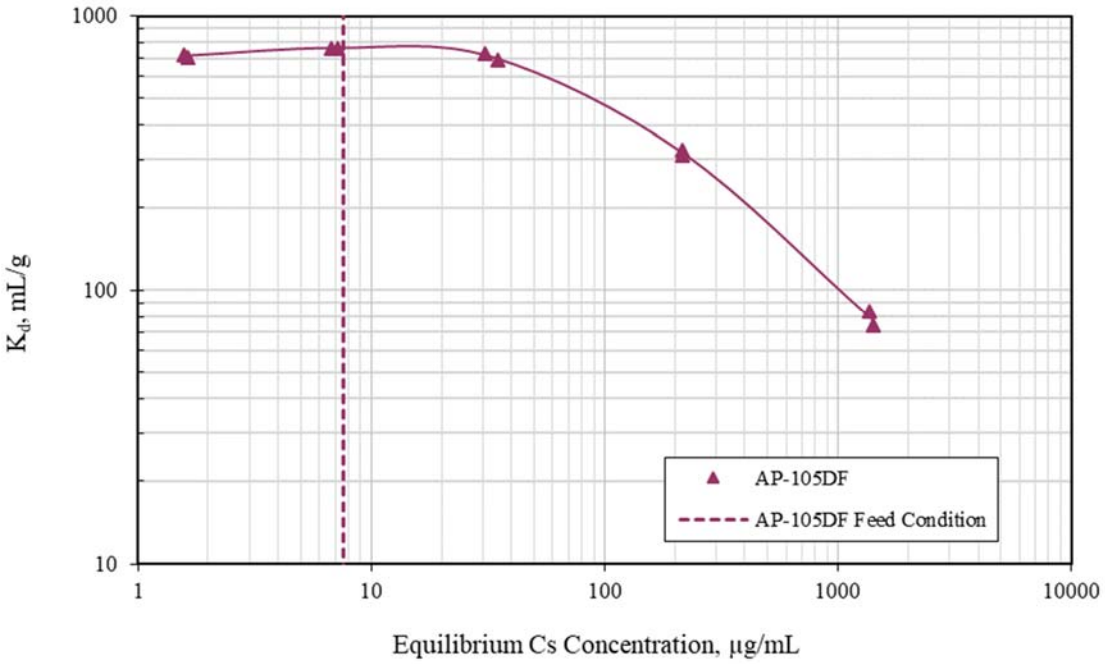

Figure 4.1. Equilibrium Cs K$_d$ Curve for AP-105DF with CST Lot 2002009604

Figure 4.2 provides the isotherms for the AP-105DF batch contact test samples with 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. (4.1). The expected Cs loading onto the CST at a given Cs concentration can be determined from the isotherm.

$$\frac{\alpha_i \times [\mathrm{Cs}]}{(\beta + [\mathrm{Cs}])} = \mathrm{Cs}_{\mathrm{IX}} \qquad (4.1)$$

where:

$[\mathrm{Cs}]$ = equilibrium Cs concentration (mmoles Cs/mL)
$\mathrm{Cs}_{\mathrm{IX}}$ = 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]

---

[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 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).

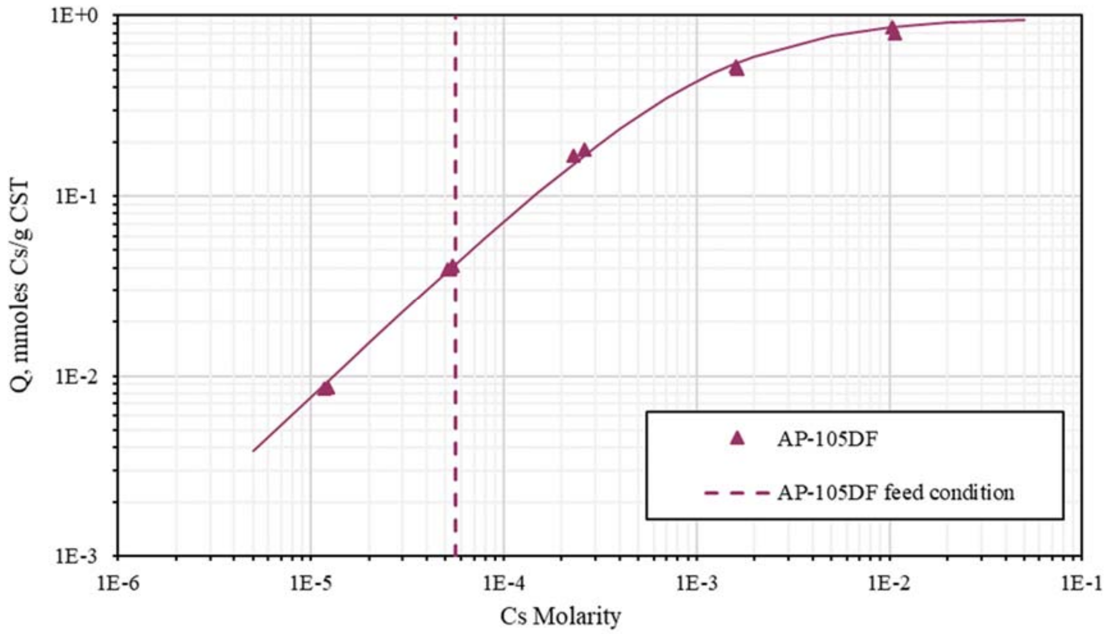

Figure notes: At the equilibrium Cs concentration of 7.58 µg/mL (5.66E-5 M), the equilibrium Cs loading on CST Lot 2002009604 corresponded to 0.0420 mmole Cs per g dry CST (5.63 mg Cs/g CST).

Figure 4.2. Isotherm for AP-105DF Tank Waste with CST Lot 2002009604

The α_i and β parameters for current and past testing are summarized in Table 4.2. As noted previously, 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 AP-105DF Cs capacity α_i parameter conformed to 0.97 mmoles Cs/g CST, which was higher than previously observed. The AP-105DF β parameter conformed to 1.24E-3 M, which was nearly twice as high as other recent tank waste tests. This indicated that the overall Cs capacity in the AP-105DF matrix was high, but specific matrix effects reduced specificity for Cs exchange at the feed condition.

Table 4.2. α_i and β Parameter Summary

Matrix	CST Lot	α_i, (mmoles Cs/g CST)	β, (Cs M)	Reference
AP-105DF	2002009604	0.97	1.24E-3	This report
1.0 M NaOH/4.6 M $NaNO_3$	2002009604	0.55	5.43E-4	Fiskum et al. 2020
AP-107	2002009604	0.72	7.25E-4	Fiskum et al. 2019b
AW-102	2002009604	0.70	5.84E-4	Rovira et al. 2019
AP-107	2081000057	0.50	5.3E-4(a)	Rovira et al. 2018
Envelope A	Not defined	0.3944	2.8552E-4	Hamm et al. 2002

(a) Calculated from reported raw data.

Figure 4.3 compares recent isotherm results with CST Lot 2002009604. The AP-105DF curve fit is offset to the right relative to other curve fits, indicative of lower capacity and concomitant earlier Cs breakthrough in a column run. It is clear, however, that the AP-107 curve fit was not ideal, in that the lowest AP-107 Cs concentration samples appeared to match that of the AP-105DF curve fit. Figure 4.4 examines the same curve in a close-in view around the feed condition. At the AP-105DF feed Cs concentration, the Cs loading for AP-107 is slightly higher than that of AP-105DF and Cs loading from AW-102 is higher than both feeds.

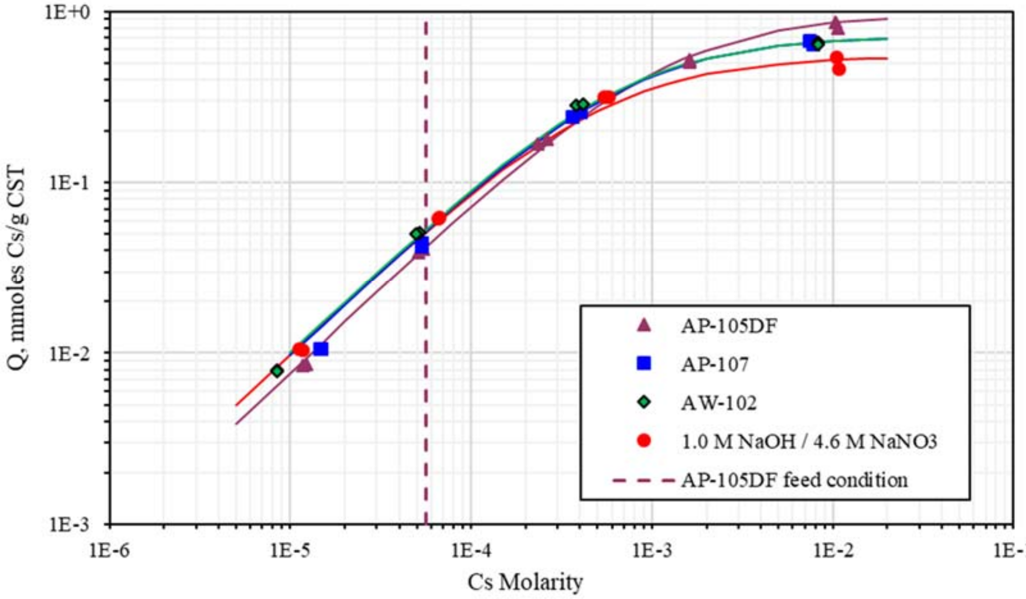

Figure 4.3. Isotherm Comparisons of AP-105DF, AP-107, AW-102, and 1.0 M NaOH/4.6M $NaNO_3$ Simulant with CST Lot 2002009604

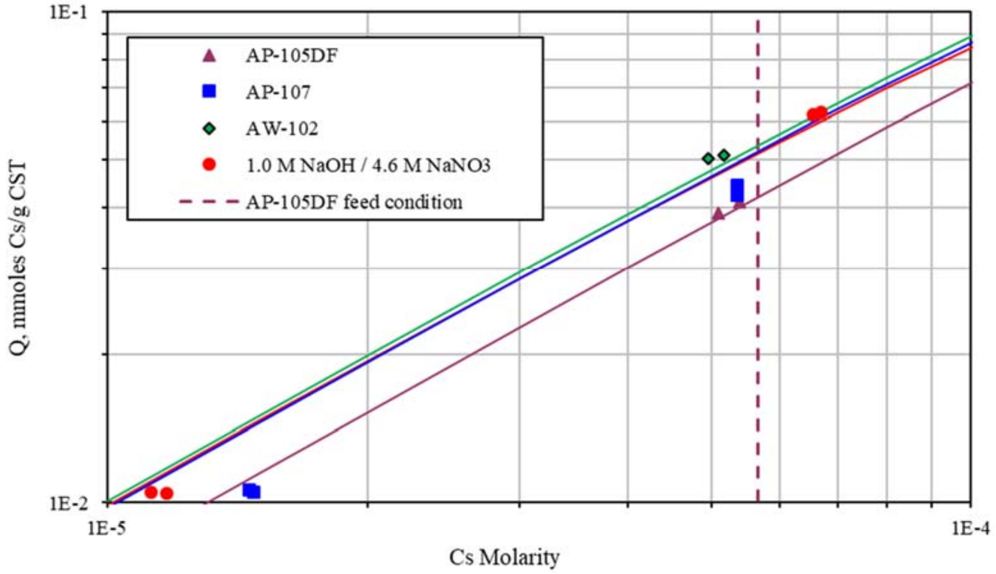

Figure 4.4. Closeup view of the Isotherm Comparisons

Table 4.3 provides the curve-fitted predicted Cs loading at 5.66E-5 M Cs for each feed matrix. The simple simulant result, 1.0 M NaOH / 4.6 M $NaNO_3$, was used as a benchmark (Fiskum et al. 2020). The AP-105DF feed condition Cs loading was ~20% lower than the other matrices. A matrix condition specific to AP-105DF appeared to negatively affect Cs loading relative to other feeds.

Table 4.3. Predicted Cs Loading at 5.66E-5 M Cs Feed Condition with CST Lot 2002009604

Matrix	Predicted Cs Loading (mmole/g CST)	Difference from 1.0 M NaOH / 4.6 M $NaNO_3$ Matrix
1.0 M NaOH/4.6 M $NaNO_3$	0.0516	0%
AP-105DF	0.0420	-19%
AP-107	0.0520[(a)]	+1%[(a)]
AW-102	0.0536	+4%

(a) Likely high bias, see text.

5.0 Column Processing

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

5.1 Cs Loading for AP-105DF, Feed Displacement, and Water Rinse

The AP-105DF feed was processed at nominally 1.83 BV/h through the lead and lag columns for 523 BVs, at which time the lag column effluent reached the WAC limit. The polish column was then placed into position and processing continued. 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 122 µCi/mL (average of all filtered feeds, relative standard deviation of 1.8%). In this graphing layout, the Cs breakthrough from the lead column appeared to start at ~270 BVs and continued to 92% C/C_0 after processing 1091 BVs when the last sample was collected from the lead column. Similarly, the lag column Cs breakthrough appeared to start at ~650 BVs and increased to 28% breakthrough when the last sample was collected from the column. The polish column Cs breakthrough performance was 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 straight-line Cs breakthrough curve and provide greater fidelity of load characteristics at low and high % C/C_0 breakthrough values (Buckingham 1967). In contrast to Figure 5.1, the Cs breakthrough from the lead column was observed to start at ~40 BVs processed and breakthrough from the lag column started just after processing 170 BVs. In addition to the 50% C/C_0 indication line, the WAC limit, set at 0.146% C/C_0, is also apparent (dotted red line).[1]

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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 5.92 M Na and 122 µCi ^{137}Cs/mL in the feed, the WAC limit is 0.155% C/C_0.

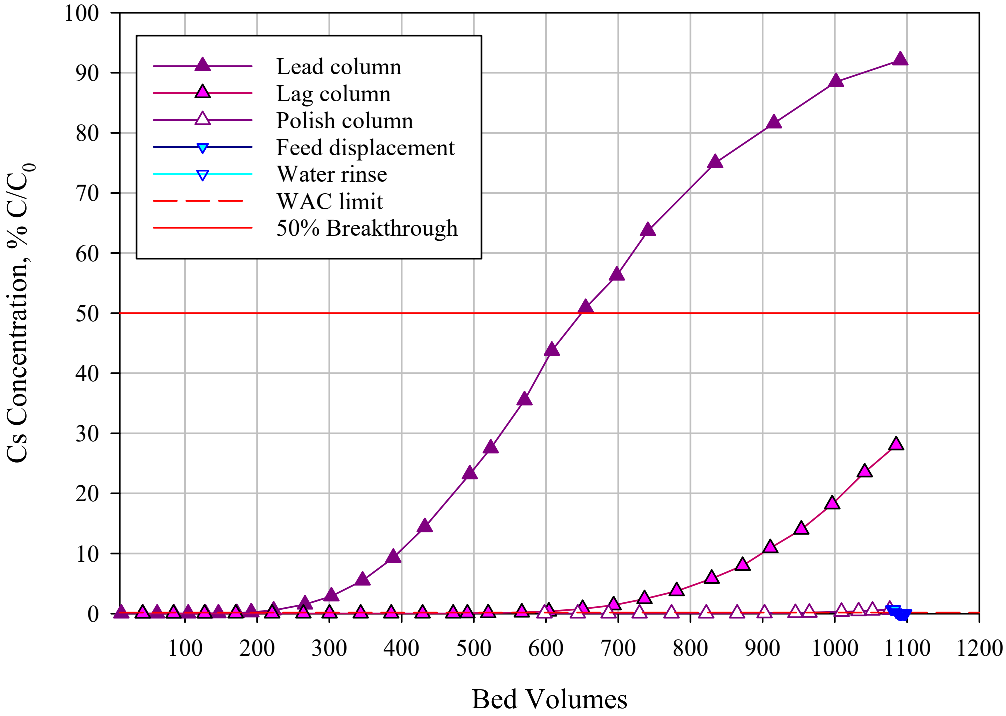

Figure 5.1. Lead, Lag, and Polish Column Cs Load Profiles of AP-105DF at 1.83 BV/h, Linear-Linear Plot

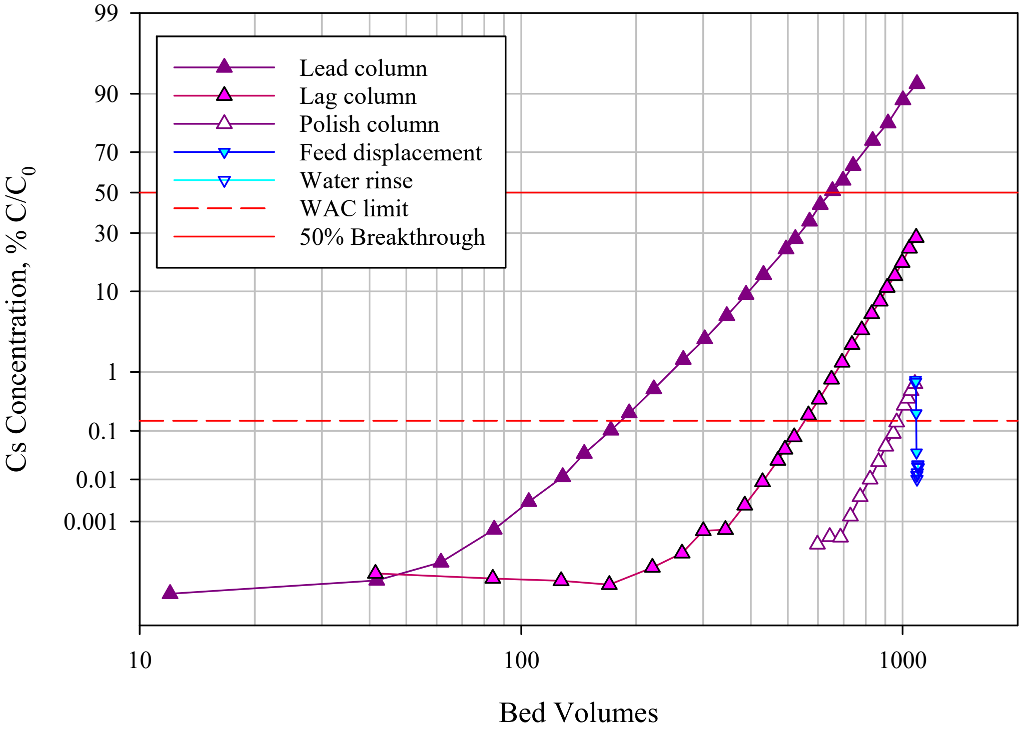

Figure 5.2. Lead, Lag, and Polish Column Cs Load Profiles of AP-105DF at 1.83 BV/h, Probability-Log Plot

The Cs breakthrough curves were modeled by the error function (erf) (Hougen and Marshall 1947; Klinkenberg 1994):

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

where:

k_1 and k_2 = parameters dependent on column conditions and ion exchange media performance
t = time (or BVs processed)
z = column length

Using this model, fits were generated to the lead and lag column experimental data (see Figure 5.3). The lead column breakthrough profile deviated below the model fit starting at ~700 BVs. This indicated non-ideal Cs loading. This is consistent with the differences in capacity seen between the batch contact test and the column test. The batch contact indicates slightly higher capacity than the 50% breakthrough. However, as seen in figure 5.3, the additional cesium is loaded past the 50% breakthrough point (that is, the data fall below the error function fit). These results suggest that the loading kinetics are being retarded in some fashion with this tank waste sample. Potential sources of slower kinetics include the impact of competitor ions (such as calcium) or other constriction to exchange sites. The reader is reminded that significant colloidal solids were found in the solution expelled from the column with compressed air that may be related to occlusion (see Figure 3.7).

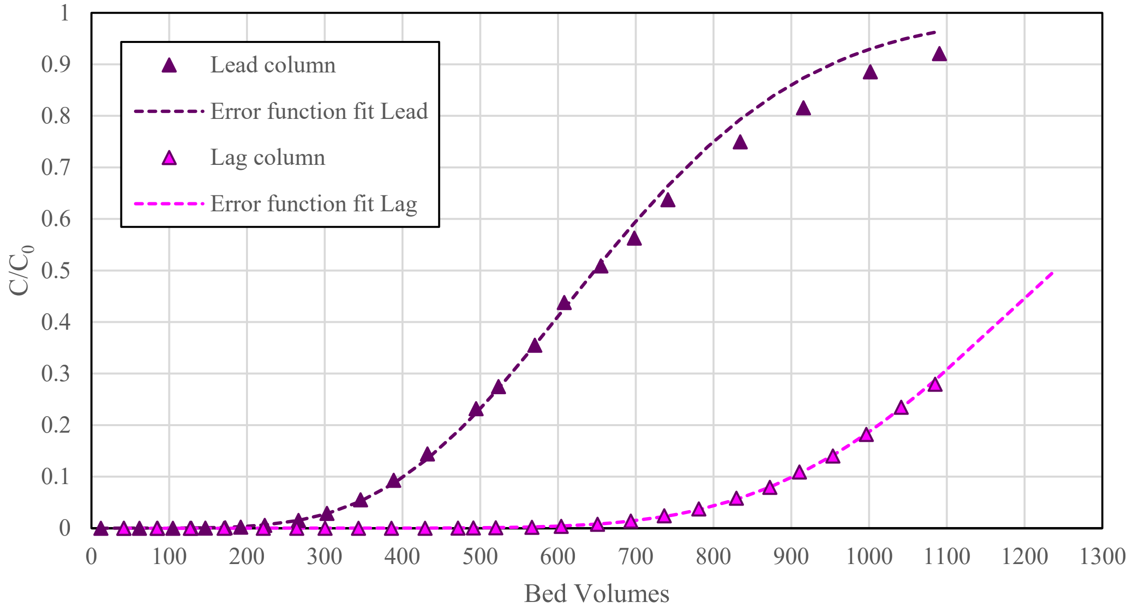

Figure 5.3. Lead and Lag Column Cs Breakthroughs with Error Function Fits

The 50% Cs breakthroughs for the lead and lag columns were estimated from the error function fit at 647 BVs and 1239 BVs, respectively. The lead column 50% Cs breakthrough value was ~15% lower than the 760 BVs Cs λ value predicted from batch-contact studies. The reduced 50% capacity observed during column testing was consistent with the hypothesis that some analyte exchange competition or occlusion was in play during the column run.

The WAC limit Cs breakthroughs were interpolated for each column by curve fitting the BVs processed as a function of the log % C/C_0 values (see Figure 5.4). The curves were fitted to a second-order polynomial function (R^2 = >0.99) and the WAC limits were then easily calculated, resulting in the following:

- Lead column: 187 BVs
- Lag column: 560 BVs
- Polish column: 974 BVs

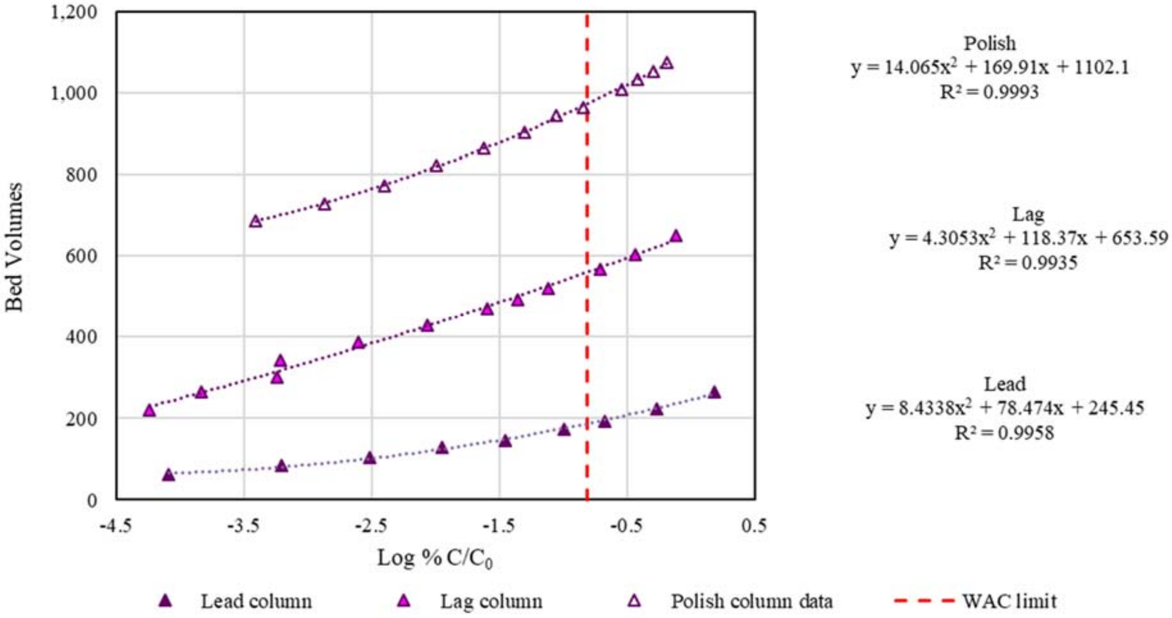

Figure 5.4. Curve Fits to Interpolate WAC Limits from Lead, Lag, and Polish Columns

Figure 5.5 shows the end of the Cs breakthrough profile from the polish column with the FD, water rinse, and the final flushed fluid from the column system on a probability-linear plot. The linear abscissa scale provides better Cs concentration resolution of the various effluent solutions relative to graphing on a log scale. The first 5.4 BVs of the FD simply extended the polish column apparent load curve, consistent with the displacement of residual feed from the system. The Cs concentration began to drop just after processing the seventh BV (one AV), and the effluent Cs concentration continued a downward trajectory. The ensuing water rinse did not result in continued downward Cs concentration; in fact, a slight concentration increase was observed as water rinse progressed. Unlike previous tests with AP-107 and AW-102 where Cs concentrations increased in the water rinse (Fiskum et al. 2019b; Rovira et al. 2019), the Cs concentration in the AP-105DF test water rinse remained relatively static at ~1.6E-2 % C/C_0. As observed previously (Fiskum et al. 2019b; Rovira et al. 2019), the Cs concentration in the solution expelled with compressed air bumped up to the WAC limit. No effort was made to filter this solution prior to ^{137}Cs analysis, so it is not clear if this increased Cs concentration was associated with suspended fines or if a small amount of Cs had exchanged back into solution during the weekend-long contact period with the water rinse.

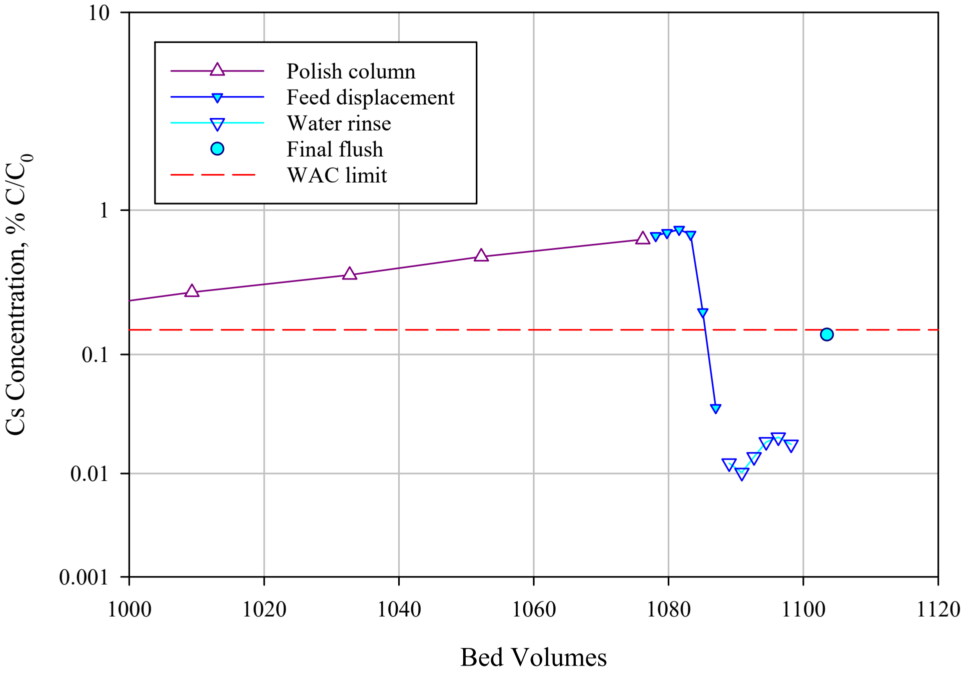

Figure 5.5. AP-105DF Polish Column Cs Load Profile with Feed Displacement, Water Rinse, and Column Flush Solution

Figure 5.6 and Figure 5.7 compare AP-105DF Cs load profiles with AP-107 lead, lag, and polish columns and AW-102 lead and lag columns, respectively. CST Lot 2002009604 was used in all cases; however, the <25-mesh sieve fraction was used for AP-107 and AW102 and the <30-mesh sieve fraction was used for AP-105DF. All else being equal, the smaller sieve fraction would normally result in delayed onset of Cs breakthrough due to higher particle surface area and smaller depth to reach exchange site. The <30-mesh sieve fraction is most prototypic of the full-height column processing (Westesen et al. 2020).

In each case, the AP-105DF Cs breakthrough occurred earlier than those of AP-107 and AW-102, indicative of lower Cs capacity in the AP-105DF matrix at the nominal feed condition. The decreased AP-105DF loading was not kinetically driven, based on the sharper load curve observed with AP-105DF (decreasing kinetic exchange rate corresponds to a lengthening of the load curve). This effect was consistent with the β parameter for AP-105DF being higher than those of AP-107 and 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 in AW-102 diluted feed was 50% higher (0.153 M) than it was in AP-105DF (0.102 M); K is one of the competitors for Cs on CST. Clearly, K competition was not adversely affecting the difference in Cs load profiles. The hydroxide was ~20% higher in AP105DF relative to AP-107 and AW-102; however, this increase was not expected to impact Cs loading.

There was no clear benefit of positioning the polish column in line after the lag column reached the WAC limit. The Cs breakthrough from the polish column used in AP-107 (present for the entire process) began nearly exactly as the Cs breakthrough from the polish column used in AP-105DF processing (employed when lag column reached the WAC limit). The slight offset observed between these two polish columns was similar to the offset trends established in the lead and lag column performances and therefore is likely not associated with the delayed implementation of the AP-105DF polish column.

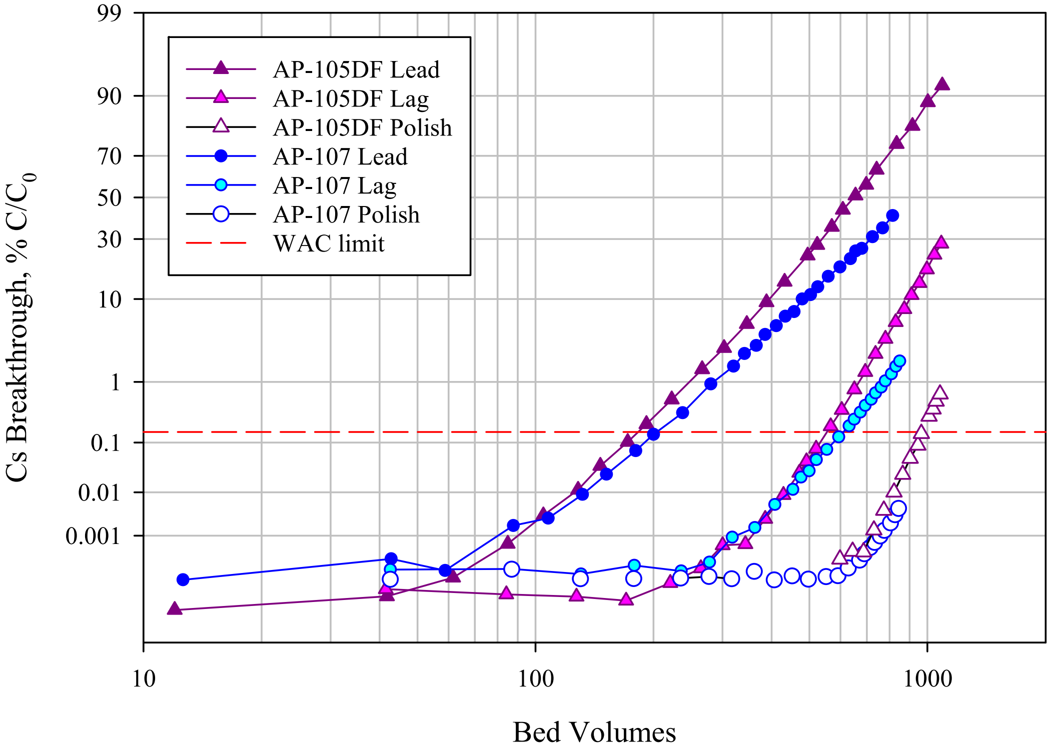

Figure notes:

	AP-105DF	AP-107
Configuration	Lead-lag Lead-lag-polish	Lead-lag-polish
Flowrate, BV/h	1.83	1.88
CST sieve fraction	<30 mesh	<25 mesh
Process Temp. °C	27-29	24-29
Cs, M	5.66E-5	6.91E-5
Na, M	5.92	5.97
K, M	0.102	0.120
OH, M	1.24	0.89
TIC, M	0.472	0.65

Figure 5.6. Load Profile Comparisons: AP-105DF and AP-107 (Fiskum et al. 2019b), CST Lot 2002009604

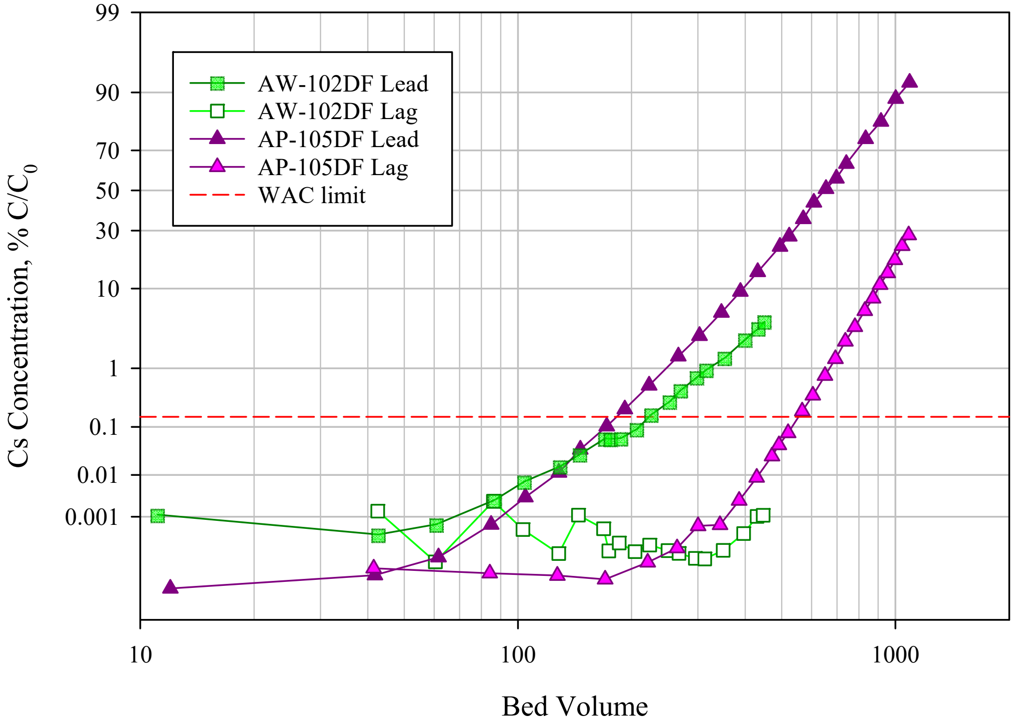

Figure notes:

	AP-105DF	AW-102
Configuration	Lead-lag Lead-lag-polish	Lead-lag
Flowrate, BV/h	1.83	1.81
CST sieve fraction	<30 mesh	<25 mesh
Process Temp. °C	27-29	22
Cs, M	5.66E-5	4.63E-5
Na, M	5.92	5.83
K, M	0.102	0.153
OH, M	1.24	0.98
TIC, M	0.472	0.587

Figure 5.7. Load Profile Comparison: AP-105DF and AW-102 (Rovira et al. 2019), CST Lot 2002009604

5.2 Cesium Activity Balance

The Cs fractionations to the effluents and the columns were determined based on the input ^{137}Cs and the measured ^{137}Cs in the various effluent streams. The quantities of Cs loaded onto the lead, lag, 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 65% of the total Cs loaded onto the lead column (markedly lower than the 87% found with AP-107 processing, Fiskum et al. 2019b), 31% loaded onto the lag column, and 4% loaded onto the polish column. Sample and effluent collection amounted to ~0.2% of the input Cs.

Table 5.1. ^{137}Cs Activity Balance for AP-105DF

Input	µCi	%
Feed sample	1.33E+06	100
Output		
Effluent-1 (0-128 BVs)	0.029	2.17E-06
Effluent-2 (128-223 BVs)	0.020	1.49E-06
Effluent-3 (223-346 BVs)	0.220	1.65E-05
Effluent-4 (346-474 BVs)	12.3	9.20E-04
Effluent-5 (474-570 BVs)	30.5	2.29E-03
Effluent-6 (570-671 BVs)	0.131	9.86E-06
Effluent-7 (671-792 BVs)	1.82	1.36E-04
Effluent-8 (792-916 BVs)	28.6	2.14E-03
Effluent-9 (916-1023 BVs)	188	1.41E-02
Effluent-10 (1023- 1091 BVs)	364	2.73E-02
Load samples	2119	1.59E-01
Feed displacement, water rinse and flush	78.5	5.89E-03
Total ^{137}Cs recovered in effluents	2,823	2.12E-01
Total ^{137}Cs Column Loading		
Lead column Cs loading	8.66E+05	65.0
Lag column Cs loading	4.11E+05	30.8
Polish column Cs loading	5.37E+04	4.03
Column total	1.33E+06	99.8

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 (92% 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 (10.0 g)
C = capacity, mg Cs/g CST

A total of 5.39 mg Cs/g CST (0.0402 mmoles Cs/g CST) was loaded onto the lead column. This represented ~95% of the total capacity found from batch contact testing (see Section 4.0). Given that the breakthrough was 92%, the predicted and obtained capacity values agreed well. The total Cs loading capacity in AP-105DF was markedly lower than observed for AP-107 and the 5.6 M Na simulant (see Table 5.2).

Table 5.2. Cs CST Column Loading Comparison

Test	Sieve fraction	CST Cs loading (mg Cs/g CST)	Reference
AP-105DF, 2.4% full height	<30 mesh	5.39	Current report
AP-107, 2.4% full height	<25 mesh	6.76	Fiskum, et al. 2019b
5.6 M Na simulant, 2.5% full height	<25 mesh	6.87	Fiskum et al. 2019c
5.6 M Na simulant, 2.5% full height	<30 mesh	7.63	Rovira et al. 2020
5.6 M Na simulant, 2.5% full height	<35 mesh	7.04	Fiskum et al. 2019c
5.6 M Na simulant, 12% full height	<25 mesh	6.95	Fiskum et al. 2019a
5.6 M Na simulant, 100% full height	As received	6.60	Fiskum et al. 2019a

See Russell et al. (2017) for the 5.6 M Na simulant formulation.

5.3 WAC Limit

Fiskum et al. (2019a,b) demonstrated that the flowrate through the CST column (in terms of BV/h or contact time) directly influences the volume that can be processed before reaching the WAC limit. The authors were able to evaluate the 1-, 2-, and 3-column systems collectively in terms of SV. The AP-105DF data collected from the lead and lag columns were also evaluated in this manner. The AP-105DF polish column only incorporated the volume associated with its usage interval from 523 BV to 1091 BV and therefore was not fully comparable to a 3-column system where the third column was in position for the test duration.

The SV/h in the lead column was, by definition, equivalent to the BV/h flowrate. The combined lead-lag column, with two sequential 10-mL CST beds, corresponded to half this flowrate. The 3-column system, with three sequential 10-mL CST beds, corresponded to a third of this flowrate. The AP-015DF SVs, adjusted 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 5.8. The AP-105DF data points lie under the curve established for the 5.6 M Na simulant (simulant formulation reported by Russell et al. 2017). Like AP-107, fewer AP-105DF BVs can be processed to reach the WAC limit than predicted by the simulant, indicative that components in the tank wastes 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-105DF Systems	SV (mL)	Flowrate (SV/h)	SVs to WAC Limit
Lead column	10	1.83	187
Lead-lag column	20	0.92	280
Lead-lag-polish column	30	0.61	325(a)

(a) The polish column was only in position during second half of processing interval from 523 BV to 1091 BV and may not be truly representative of the 30-mL CST bed (3-column system) configuration.

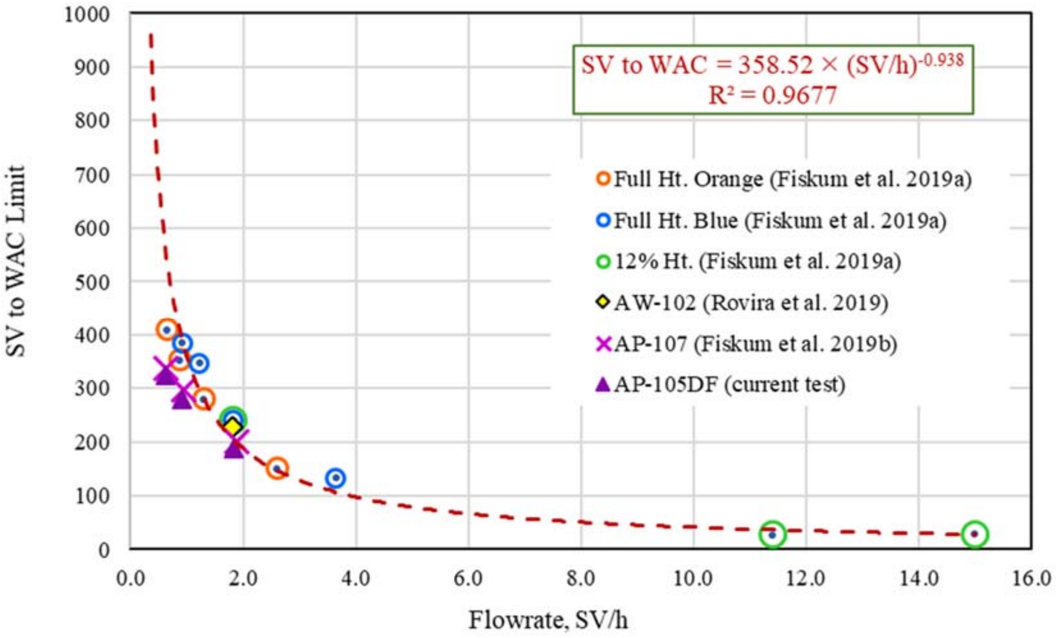

Figure 5.8. System Volume to WAC Limit vs. Flowrate with CST Lot 2002009604

Figure notes:

- Fiskum et al. 2019a, 5.6 M Na simulant test matrix.
  - Orange and Blue column data collected from four serial ~0.592-L CST beds, unsieved CST, 2.54-cm-diameter column.
  - Medium column data were collected from single 44-mL CST beds, <25-mesh CST, 1.5-cm-diameter column.
- AW-102 datum collected from single 10-mL CST bed (lead column), <25-mesh CST, 1.5-cm inside diameter. The WAC limit was re-evaluated to be 226 BVs.
- AP-107 column data were collected from three serial 10-mL CST beds; the left-most data point from the polish column was extrapolated, <25-mesh CST, 1.5-cm-diameter column

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 and the 50% Cs breakthrough point is the inflection point around which the transition zone pivots. In the current study, the lead column was loaded to 92% Cs breakthrough; the 50% breakthrough was interpolated at 647 BVs. 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: 341 BVs. Similarly, the transition zone between 5% and 95% Cs breakthrough was calculated: 626 BVs. Table 5.4 compares the transition zones determined for AP-105DF, AP-107, and 5.6 M Na simulant. The AP-105DF transition zone was hundreds of BVs shorter than those determined with AP-107 and 5.6 M Na simulant. The fundamental reason for a decreased transition zone is not understood at this time.

Table 5.4. Transition Zone Comparison, CST Lot 2002009604

Test	Flowrate (BV/h)	BVs to Cs Breakthrough			Transition Zone (BVs)	
		(5%)	(20%)	(50%)	(20-80%)	(5-95%)
AP-105DF	1.83	334	477	647	341	626
AP-107 (Fiskum et al. 2019b)	1.88	400	620	~900	~560	~1000
Blue (Fiskum et al. 2019a)[a]	1.82	492	700	~1050	~700	~1120

(a) 5.6 M Na simulant matrix

5.5 Chemical and Radiochemical Composition

The AP-105DF 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 (41.8, 84.9, 128, 172, 223, 303, 389, 495, 741, and 1091 BVs).

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 effluent are provided in Table 5.7; they were not measured in the feed because it was shown that their concentrations were not affected by the CST processing (Rovira et al. 2018). Further, bench handling of the effluent was safer for the analysts from a radiological dose perspective. Analytical reports along with result uncertainties and quality control discussions are provided in Appendix C.

By inference, the analytes present in the feed and 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-105DF feed
V_F = volume of AP-105DF feed
F_{Da} = fraction of analyte *a* in the Cs-decontaminated effluent

The analyte results shown in brackets indicate the result was less than the instrument EQL but greater than or equal to the MDL; 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 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.

Table 5.5. AP-105DF Feed and Effluent Radionuclide Concentrations and Fractionations (ASR 1097)

Analysis Method	Analyte	TI082-Comp-Feed (µCi/mL)	TI082-Comp-Eff (µCi/mL)	Fraction in Effluent (%)
Gamma energy analysis (GEA)$^{(a)}$	^{60}Co	<5.8E-04	4.05E-04	--
	^{137}Cs	1.13E+02$^{(b)}$	5.36E-02	0.047
	^{154}Eu	<2.7E-03	7.52E-05	--
Separations/ Alpha energy analysis (AEA)$^{(a)}$	^{237}Np	6.69E-06	1.22E-06	18
	^{238}Pu	6.37E-06	2.64E-06	41
	$^{239+240}$Pu	3.94E-05	1.56E-05	39
	^{241}Am	2.66E-04	2.30E-04	86
Separations/ Beta counting$^{(a)}$	^{90}Sr	6.90E-01	7.23E-04	0.10
	^{99}Tc	1.13E-01	1.05E-01	93

(a) Reference date is December 2020.
(b) ^{137}Cs measured in the individual feed samples was 122 µCi/mL (see Section 3.2); the 113 µCi/mL value was 8% lower and was not considered statistically different given the overall experimental uncertainty and decay correction.
"--" = not applicable; value not reported, or fractionation cannot be calculated with a less-than value.
The recovered fractions are calculated with values containing more significant figures than shown; using listed values may result in a slight difference due to rounding.

Table 5.6. AP-105DF Feed and Effluent Inorganic Analyte Concentrations and Fractionation (ASR 1097)

Analysis Method	Analyte	TI082-Comp-Feed (M)	TI082-Comp-Eff (M)	Percent in Effluent
ICP-OES	Al	5.26E-01	5.23E-01	99%
	As	<5.5E-04	[9.7E-04]	--
	Ca	1.03E-03	1.02E-03	99%
	Cd	[2.4E-05]	[2.0E-05]	--
	Cr	6.43E-03	6.56E-03	101%
	Fe	[2.0E-05]	<1.6E-05	--
	K	1.02E-01	1.02E-01	100%
	Na	5.92E+00	6.00E+00	101%
	P	1.27E-02	1.44E-02	113%
	S	4.66E-02	4.65E-02	99%
	Ti	<5.9E-06	[2.3E-05]	NA
	Zn	[4.6E-05]	[4.7E-05]	--
	Zr	<9.4E-06	[4.5E-05]	NA
ICP-MS	Ba	<1.6E-06	<1.3E-06	--
	Nb	2.74E-07	2.89E-05	NA
	Pb	9.00E-05	2.67E-05	29%
	Sr	1.82E-06	1.64E-07	8.9%
	^{238}U	2.46E-05	1.99E-05	80%

Table 5.6 (cont.)

Analysis Method	Analyte	TI082-Comp-Feed (M)	TI082-Comp-Eff (M)	Fraction in Effluent
ICP-OES Opportunistic Analytes	Ag	<1.2E-05	<1.0E-05	--
	B	5.00E-03	4.56E-03	91%
	Ba	[4.9E-06]	[1.3E-06]	--
	Be	[1.9E-05]	[1.7E-05]	--
	Bi	[1.1E-04]	[7.7E-05]	--
	Ce	[4.9E-05]	[3.8E-05]	--
	Co	<4.1E-05	<3.4E-05	--
	Cu	[4.0E-05]	[2.6E-05]	--
	Dy	<8.8E-06	<7.3E-06	--
	Eu	<3.2E-06	<2.7E-06	--
	La	<8.2E-06	<6.8E-06	--
	Li	<1.3E-04	<1.0E-04	--
	Mg	<4.3E-05	<3.6E-05	--
	Mn	<2.5E-06	<2.0E-06	--
	Mo	4.89E-04	4.98E-04	101%
	Nd	<5.0E-05	<4.1E-05	--
	Ni	4.86E-04	5.35E-04	110%
	Pb	<7.8E-05	<6.5E-05	--
	Pd	<3.0E-05	<2.5E-05	--
	Rh	<8.8E-05	<7.3E-05	--
	Ru	[8.6E-05]	[7.8E-05]	--
	Sb	<3.5E-04	<2.9E-04	--
	Se	[9.1E-04]	<6.5E-04	--
	Si	3.72E-03	3.06E-03	82%
	Sn	<1.4E-04	<1.2E-04	--
	Sr	<1.4E-06	<1.2E-06	--
	Ta	<1.2E-04	<9.6E-05	--
	Te	<9.0E-05	<7.4E-05	--
	Th	<2.1E-05	<1.7E-05	--
	Tl	[3.3E-04]	<7.4E-05	--
	U	[1.4E-04]	<8.3E-05	--
	V	<1.5E-05	<1.2E-05	--
	W	4.26E-04	4.07E-04	95%
	Y	<4.6E-06	<3.8E-06	--

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 was > ±15%.

“--” indicates the recovery could not be calculated.

NA = not applicable; Nb, Ti, and Zr are components of CST

The recovered fractions are calculated with values containing more significant figures than shown; using listed values may result in a slight difference due to rounding.

Table 5.7. AP-105DF Effluent Anions and Carbon Composition (ASR 1097)

Analysis Method	Analyte	TI082-Comp-Feed (M)
Titration	Free Hydroxide	1.24
Ion Chromatography	F^-	<2.6E-04
	Cl^-	1.10E-01
	NO_2^-	1.38E+00
	NO_3^-	1.89E+00
	PO_4^{3-}	8.72E-03
	$C_2O_4^{2-}$	2.84E-03
	SO_4^{2-}	2.44E-02
Hot persulfate oxidation	Total organic C	2.16E-01
	Total inorganic C(a)	4.72E-01

(a) Assumed to be carbonate.

In addition to Cs removal, the CST removed 99.9% of the ^{90}Sr with a ^{90}Sr decontamination factor of 959. The reduced Sr decontamination (91.1%) measured by ICP-MS may have been confounded with Sr isobaric interferences. The radiochemical analysis was considered more reliable with specificity for ^{90}Sr and stable Sr and ^{90}Sr were expected to behave similarly. About 82% of the Np and 60% of the Pu were also removed. The Np and Pu removal factors were consistent with those previously reported (Rovira et al. 2018, Fiskum et al. 2019b). About 14% of Am was calculated to be removed during processing; the chemistry involved in Am removal by CST is not known. Assuming the difference in total Am, Np, and Pu µCi content between the feed and effluent remained with the lead column CST (10 g), the CST would contain 77 nCi/g transuranic (TRU) isotopes, which is under the threshold 100 nCi/g defining TRU waste. Most of ^{99}Tc, 93% (likely present as anionic pertechnetate), was found in the effluent showing minimal Tc interaction with the CST.

The ICP-OES results for the feed composite and effluent composite showed that the majority of analytes remained in the effluent (see Table 5.6 and Appendix C for analytical reports). The Al, Ca, Cr, K, Na, P (phosphate), and S (sulfate) partitioned exclusively to the effluent (>99% recovery). The effluent recoveries of Ca, Pb, and U were higher than expected in the AP-105DF test because previous tests showed much lower analyte recoveries (see analyte recovery summary in Table 5.8). Three possible drivers likely led to the higher analyte recoveries.

1. The AP-105DF process volume was larger than those of previous tests; thus, more analyte would break through into the effluent based on a short breakthrough curve.
2. The analyte concentrations were slightly higher in AP-105DF, and exchange sites may have been consumed more quickly. Table 5.9 compares the feed analyte concentrations.
3. The soluble analytes were complexed differently in AP-105DF, leading to less CST uptake.

Table 5.8. Ca, Pb, Sr, U Effluent Recovery Comparisons

Tank	BVs	Ca	Pb	Sr	U
AW-102(a)	450	[38%]	NA	0.20% (^{90}Sr)	68%
AP-107(b)	855	[52%]	NA	<0.2% (^{90}Sr)	61%
AP-105DF	1091	99%	29%	8.9%	80%

(a) Rovira et al. 2019
(b) Fiskum et al. 2019b
NA = not applicable, the analyte was not detected in the effluent.

Table 5.9. Ba, Ca, Pb, Sr, U Feed Concentration Comparisons

Tank	Ba, M	Ca, M	Pb, M	Sr, M	U, M
AW-102(a)	[3.7E-6]	[6.0E-4]	<3.9E-5	<2.9E-6	7.48E-4
AP-107(b)	[3.0E-6]	[8.6E-4]	[3.9E-5]	[1.5E-6]	7.51E-5
AP-105DF	<1.6E-6	1.03E-3	9.00E-5	1.82E-6	2.46E-5

(a) Rovira et al. 2019
(b) Fiskum et al. 2019b

The Ba, Ca, Sr, and U analyte concentrations differed slightly between the three tank wastes, with just slight elevations in the Ca and Pb concentrations in AP-105DF relative to those measured in AW-102 and AP-107. However, Ca and Pb were not found to have much effect on CST Cs uptake (Fiskum et al. 2020). It is unlikely that these slight elevated concentrations would result in an earlier Cs breakthrough profile with a shorter transition zone.

The load behaviors of selected analytes were examined as a function of BVs processed through the lead column. (Raw data are provided in Appendix B.) Figure 5.9 shows the Al, Ca, Pb, Sr, and U breakthrough results along with the Cs breakthrough profile. The Al breakthrough serves as an “internal standard” for comparison of the ICP-OES analysis results; its breakthrough remained at 99% ±3% throughout the analytical run.

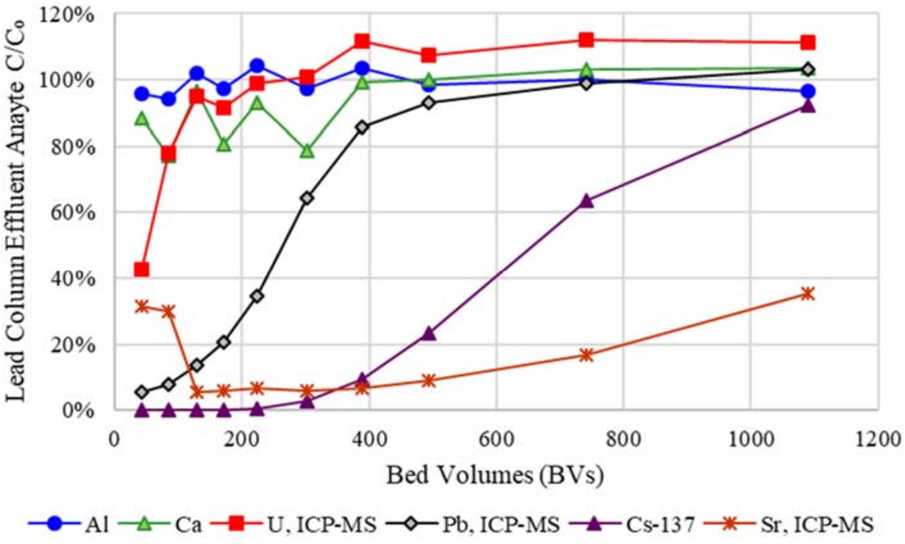

Figure 5.9. Al, Ca, Cs, Pb, Sr, and U Load Profiles from the Lead Column

The Ca results showed somewhat erratic breakthrough behavior (77% to 96% breakthrough) through ~400 BVs processed, at which point it leveled out to 100% breakthrough. The immediate and high Ca breakthrough indicated minimal interaction of Ca occurred on the CST bed. This behavior contrasted with AW-102 and AP-107, where ~40 to 60% Ca breakthroughs were observed (Rovira et al. 2019 and Fiskum et al. 2019b, respectively). Ca may have complexed differently in the AP-105DF by hydroxide, carbonate, and/or organic chelators mitigating CST interaction.

The U broke through rapidly reaching steady state after processing ~390 BVs. The consistent overshoot of 100% breakthrough (390 to 1091 BVs) suggested that the feed U analysis result may have been biased ~10% low or the individual (2-mL) samples may have concentrated slightly from evaporation. The U

50% breakthrough occurred at ~50 BVs, indicating a short transition zone and minimal uptake by CST. These results were generally consistent with Oak Ridge National Laboratory (ORNL) W-27 tank waste (Walker Jr. et al. 1998), where U 50% breakthrough occurred at ~90 BVs, and AP-107 tank waste (Fiskum et al. 2019b), where 50% U breakthrough occurred at ~100 BVs.

The Pb breakthrough occurred intermediate to U and Cs breakthroughs reaching 50% breakthrough after processing ~260 BVs. Comparisons to previous testing of AP-107 and AW-102 tank wastes with this CST lot were not possible because Pb was not measured above the MDL in the column effluent samples. Walker Jr. et al. (1998, Figure 26) reported a Pb breakthrough curve with ORNL W-27 tank waste; in that case 50% Pb breakthrough occurred later at ~400 BVs.

Sr breakthrough measured by ICP-MS was evident, reaching 35% breakthrough after processing 1091 BVs. Sr breakthrough was not detectable in AP-107 or AW-102 processing.

Similarly, the selected lead column effluent samples were analyzed for ^{90}Sr, ^{237}Np, ^{238}Pu and $^{239+240}$Pu. Figure 5.10 shows the load profiles for ^{90}Sr, ^{237}Np, and $^{239+240}$Pu isotopes in comparison with that of ^{137}Cs. The ^{90}Sr breakthrough profile did not show the leading high Sr values at 42 and 85 BVs (as measured by ICP-MS) and it converged with that measured by ICP-MS at ~494 BVs. ^{90}Sr breakthrough was measurable from the first collected sample (see Appendix B). This Sr load behavior was unlike that found in testing with AP-107 where ^{90}Sr concentrations hovered near the detection limit (1.0E-3 µCi/mL) through 558 BVs processed (Fiskum et al. 2019b). The Np breakthrough profile showed increasing effluent concentration from 15% to 77% in the 42 to 1091 BVs range; AP-107 processing resulted in steady-state Np 60% breakthrough once 280 BVs were processed (Fiskum et al. 2019b). The ^{238}Pu results were reported with higher uncertainty and the associated C/C_0 values were more erratic than those of $^{239+240}$Pu. Therefore, the ^{238}Pu values were not further evaluated. The Pu demonstrated an initial 40% breakthrough and very slowly increased to 60% breakthrough to the end of testing. The Pu breakthrough profile was generally consistent with that measured from AP-107 processing (Fiskum et al. 2019b).

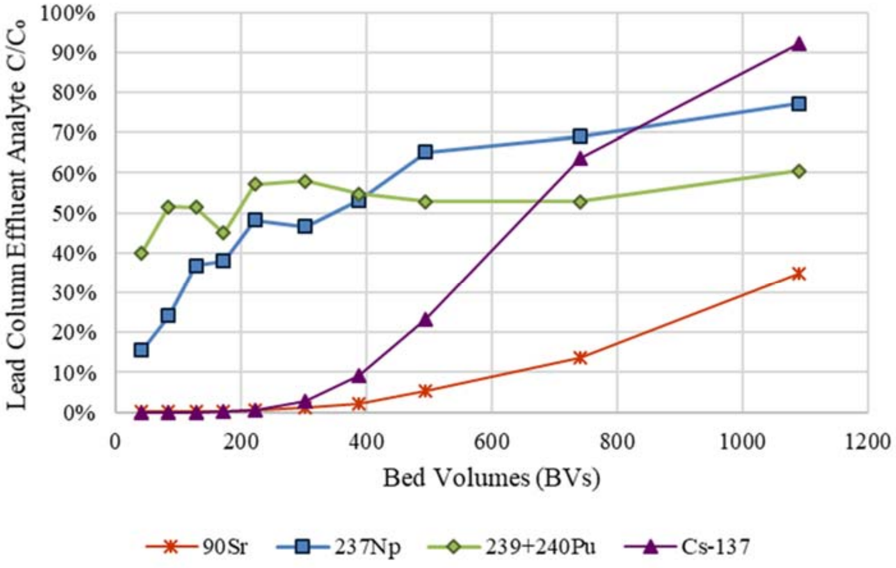

Figure 5.10. ^{90}Sr, ^{137}Cs, ^{237}Np, and $^{239+240}$Pu Load Profiles onto the Lead Column

Figure 5.11 shows the small concentrations of Nb, Ti, and Zr observed in each of the selected lead column effluent samples (see Appendix B for feed and effluent sample concentrations). Neither Ti nor Zr were detected in the feed; only a small amount of Nb was detected in the feed relative to the effluent (2.7E-7 M Nb). Therefore, it was inferred that some small loss of CST components occurred during processing. It is not clear if this loss is due to attrition from extraneous material associated with production or an actual loss of the CST bed. The total Nb, Ti, and Zr masses recovered in the 10.9 L AP-105DF effluent were small and likely would not generate issues with downstream vitrification activities: 0.029 g Nb, ~0.012 g Ti, and ~0.045 g Zr.

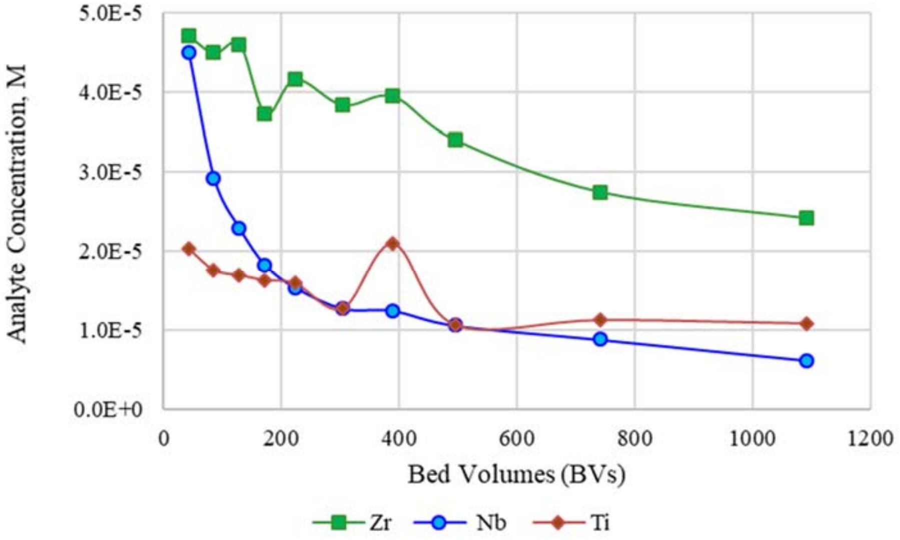

Figure 5.11. Nb, Ti, and Zr Effluent Profiles from the Lead Column

Figure note: The feed analyte concentrations were 2.74E-7 M Nb, <5.9E-6 M Ti, and <9.4E-6 M Zr

5.6 Colloidal Solids Recovered in Flushed Solution

Solids were observed in the final fluid flushed from the column with compressed air. Solids in the flush solution have not been previously observed. The solids were brownish gray and colloidal in nature (see Section 3.4.2). After a settling period, the bulk of the fluid was removed, and the solid residue was evaporated to dryness in the hot cell at cell temperature. The solids were acid digested and analyzed by ICP-OES (per ASR 1109). Table 5.10 provides the result of the targeted analytes along with the opportunistically measured analytes. Collectively, the measured solids represented 35 wt% of the submitted sample; the balance of mass is likely associated with anions (hydroxide, nitrate, nitrite, etc.) and oxides. Figure 5.12 compares the collected solids and AP-105DF tank waste analyte concentrations normalized to Na (molar basis).

Table 5.10. Flushed Solids ICP-OES Analysis (ASR 1109)

Targeted		Opportunistic			
Analyte	TI082-Flush Solids (µg/g)	Analyte	TI082-Flush Solids (µg/g)	Analyte	TI082-Flush Solids (µg/g)
Al	42,200	Ag	[5.3]	Mo	[6.9]
Ca	4,865	As	[123]	Nd	512
Cr	61,800	B	291	Pd	87.4
Fe	8,075	Ba	555	Rh	<15
K	1,890	Be	7.99	Ru	[10]
Na	136,500	Bi	[61]	Sb	[245]
Ni	29,150	Cd	692	Se	<102
P	[220]	Ce	86.3	Sn	[28]
Pb	3,545	Co	[23]	Sr	22.6
S	[500]	Cu	1,090	Ta	<34
Si	5,595	Dy	<2.3	Te	[74]
Ti	5,220	Eu	[5.8]	Th	185
Zn	961	La	116	Tl	<30
Zr	1,910	Li	78.5	U	[69]
		Mg	43,300	W	[9.4]
		Mn	401	Y	<13

Bracketed results were less than the estimated quantitation limit but greater than or equal to the method detection limit.
Opportunistically measured analytes are part of the ICP-OES data output but have not been fully evaluated for quality control performance.

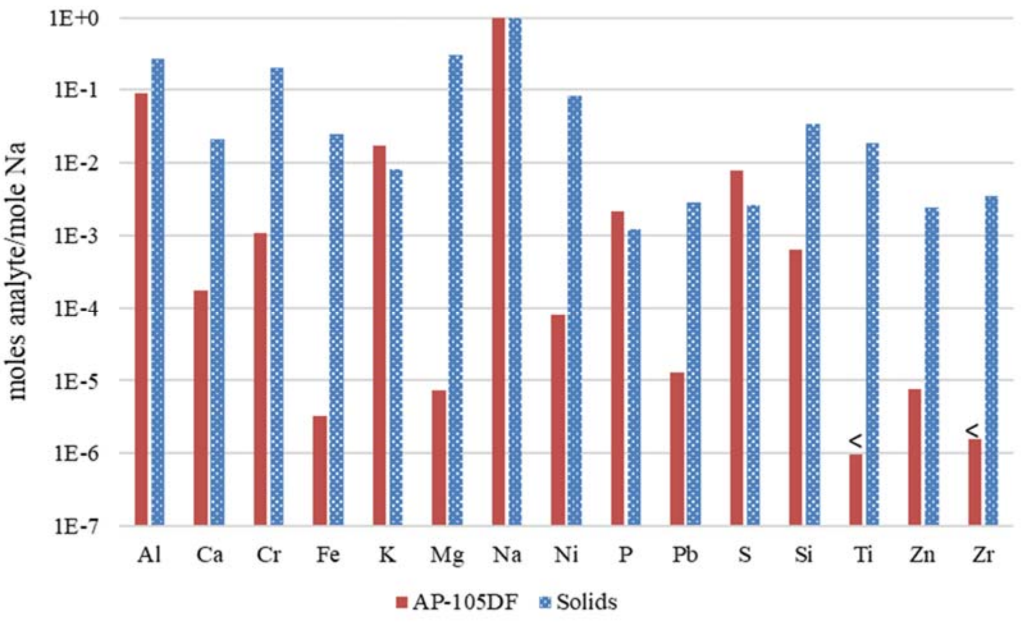

Figure 5.12. Comparison of Solids Flushed from CST Columns and AP-105DF Normalized to Na

Figure Note: Ti and Zr were less-than (<) values in the feed.

The Na is presumed to be largely associated with carryover from residual tank waste and 0.1 M NaOH flush solution. The solids S/Na, P/Na, Al/Na, and K/Na mole ratios are similar to those of the feed and are thus likely associated primarily with the residual salts from tank waste. The Ca/Na and Si/Na are higher in the solids; in combination with the slightly higher mole ratio observed for Al/Na in the solids, these may be associated with cancrinite. Of the remaining metals, the mole ratio differences between the solids and the AP-105DF decrease in the following order: Mg/Na > Cr/Na > Ni/Na > Fe/Na > Pb/Na >Zn/Na. It is not clear where the relatively large fractions of Mg, Cr, Ni, Fe, Pb, and Zn arise. Ba and Sr were detected in the solids (see Table 5.10). Ba, Pb, and Sr exchange onto CST and may be associated with CST fines blown from the columns. Ti and Zr were also present in the solids, again indicative of some amount of CST fines in these solids (Nb was not measured).

6.0 Conclusions

Cesium ion exchange batch contact testing and column testing were conducted with CST Lot 2002009604 sieved to <30 mesh to assess Cs exchange performance with AP-105DF tank waste. Column testing was conducted at a small scale in the RPL hot cells to accommodate the high radiological dose rate of the Hanford tank waste matrix. The results summary is provided below.

6.1 Batch Contact Testing

Batch contact testing with five Cs concentrations in the AP-105DF matrix was conducted to develop Cs K_d and isotherm curves. Duplicate tests were conducted, each mixed for 72 h at nominally 30 °C cell temperature. The following conclusions were made as a result of this work.

1. The calculated ^{137}Cs K_d value of 760 mL AP-105DF/g CST at Cs equilibrium condition of 7.58 µg Cs/mL (5.66E-5 M Cs) corresponded to a predicted 50% Cs breakthrough of 760 BVs. The measured 50% Cs breakthrough in the column testing was 15% lower (647 BVs) than predicted, indicating that a competitor or other matrix condition was challenging Cs exchange in the dynamic column system.

2. The Cs load capacity at 7.58 µg Cs/mL (5.66E-5 M Cs) equilibrium condition was 0.0420 mmoles Cs/g CST (5.63 mg Cs/g CST). Column testing resulted in lower achieved Cs loading on the lead column, 0.0402 mmoles Cs/g CST or 95% of the predicted capacity measured by batch contacts (the lead column Cs breakthrough reached 92%).

3. The maximum Cs load capacity was measured at 0.966 mmoles Cs/g CST based on a Freundlich/Langmuir hybrid equilibrium fit. This was a higher total capacity than previously measured with AW-102 (0.719 mmoles Cs/g CST) and AP-107 (0.718 mmole Cs/g CST).

4. The Cs capacity in the AP-105DF matrix was about 20% less than found with AP-107, AW-102, and 1.0 M NaOH/4.6M $NaNO_3$ simulant at the AP-105DF feed Cs concentration (5.66E-5 M Cs) even though the total Cs capacity was higher in the AP-105DF matrix.

6.2 Column Testing

AP-105DF tank waste was processed through two columns sequentially positioned in a lead-lag format; after processing 523 BVs, a polish column was placed in line. Each column was filled with 10.0 mL of CST ion exchanger. A total of 10.9 L of AP-105DF tank waste, containing 5.92 M Na and 122 µCi/mL ^{137}Cs, was processed through the Cs ion exchange system at 1.83 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 2.9 BV/h to process 11 BVs each of 0.1 M NaOH FD and water rinse. The following conclusions were made as a result of the column test.

1. A total of 647 BVs of AP-105DF tank waste, processed at 1.83 BV/h, can be treated before reaching 50% Cs breakthrough on the lead column.

2. The lag column reached the WAC limit when 560 BVs of AP-105DF feed was processed. The effluent from the polishing column reached the WAC limit after processing 974 BVs.

3. FD resulted in decreasing Cs concentration coming off the polish column once the SV was removed, but the subsequent water rinse resulted in slightly increased effluent Cs concentration that remained well below the WAC limit.

4. The AP-105DF Cs breakthrough profile was compared with those of AP-107 (Fiskum et al. 2019b) and AW-102 (Rovira et al. 2019). Although onsets of Cs breakthroughs were similar, the AP-105DF Cs breakthrough was steeper from all three columns relative to those found with AP-107. Similar observations were found relative to AW-102. The steeper AP-105DF Cs breakthrough load curve (shorter transition zone) indicated that a matrix effect was challenging the Cs loading.

5. There was no substantive improvement in the Cs breakthrough from the polish column with its late placement in line to the exchange system relative to results from AP-107 processing. The BVs processed to reach the WAC limit from the polish column with AP-105DF was interpolated to 974 BVs; the BVs processed to reach the WAC limit with AP-107 was extrapolated to 1010 BVs.

6. The total Cs loaded onto the lead column (0.0402 mmoles Cs/g CST) was about 20% less than those from the simulant testing (0.0497 and 0.0523 mmoles Cs/g CST, Fiskum et al. 2019a) and AP-107 processing (0.0509 mmoles Cs/g CST, Fiskum et al. 2019b) despite the higher number of BVs processed with AP-105DF.

7. The AP-105DF SVs processed to reach the WAC limit as a function of flowrate were evaluated. The AP-105DF generally matched the curve established with AP-107, both veered to lower SVs processed to reach the WAC when compared to the trajectory established by the simulant testing (Fiskum et al. 2019a). This was indicative that other components may be consuming exchange sites, the tank waste matrix itself was limiting Cs loading, or occlusion was occurring.

8. The transition zones for Cs breakthrough were calculated to be 341 BVs (20% to 80% Cs breakthrough range) and 626 BVs (5% to 95% Cs breakthrough range).

6.3 Analyte Fractionation

1. Major components Al, K, Na, P, and S partitioned exclusively to the effluent. Minor component Ca also portioned to the effluent (99% recovery).

2. Approximately 29% of the Pb was found in the effluent; a Pb breakthrough curve was obtained with 50% C/C_0 reached at 260 BVs.

3. Based on stable Sr analysis, 8.9% Sr was recovered in the effluent. Based on ^{90}Sr analysis, only 0.10 % was in the effluent. The ^{90}Sr decontamination factor was 959. A Sr breakthrough curve was measured showing 35% C/C_0 from the lead column after processing 1091 BVs.

4. Most of the U (89%) was found in the effluent composite, indicating partial U removal by the CST from the feed. The U load curve through the lead column indicated a 50% U breakthrough at ~50 BVs.

5. Nb, Ti, and Zr, components of CST (near or below MDL in the feed) were detected in the composite effluent and the selected lead column effluent samples, indicating that CST components were leached into solution. Concentrations of these analytes decreased with

increasing process BVs. Total masses recovered in the 10.9 L composite effluent were small: 0.029 g Nb, ~0.012 g Ti, and ~0.045 g Zr.

6. The effluent contained 18% of the feed Np, 40% of the feed Pu, and 86% of the feed Am. The balances of these isotopes were assumed to remain with the CST. Assuming the retained isotopes were bound only to the lead column CST bed, the CST would contain 77 nCi/g TRU, which is lower than the 100 nCi/g threshold defining TRU waste.
7. The ^{99}Tc (likely anionic pertechnetate) did not significantly exchange onto the CST (93% was recovered in the effluent).

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Appendix A – Column Load Data

The AP-105DF lead, lag, 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, Lag, and Polish Column Cs Breakthrough Results with AP-105DF

Lead Column				Lag 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	1.20E-5	9.86E-6	1.01E+7	42	4.77E-5	3.92E-5	2.55E+6	598	3.11E-4	2.56E-4	3.91E+5
42*	2.97E-5	2.44E-5	4.09E+6	84	3.41E-5	2.80E-5	3.57E+6	644	4.91E-4	4.03E-4	2.48E+5
62	9.98E-5	8.20E-5	1.22E+6	127	2.89E-5	2.38E-5	4.21E+6	687	4.78E-4	3.93E-4	2.55E+5
85*	7.60E-4	6.24E-4	1.60E+5	170	2.24E-5	1.84E-5	5.43E+6	730	1.66E-3	1.36E-3	7.35E+4
105	3.70E-3	3.04E-3	3.29E+4	221	7.07E-5	5.81E-5	1.72E+6	774	4.84E-3	3.97E-3	2.52E+4
128*	1.37E-2	1.13E-2	8.88E+3	264	1.78E-4	1.46E-4	6.84E+5	822	1.23E-2	1.01E-2	9.88E+3
146	4.33E-2	3.55E-2	2.81E+3	300	7.04E-4	5.78E-4	1.73E+5	865	2.92E-2	2.40E-2	4.16E+3
172*	1.24E-1	1.02E-1	9.79E+2	343	7.50E-4	6.16E-4	1.62E+5	903	6.06E-2	4.98E-2	2.01E+3
192	2.58E-1	2.12E-1	4.73E+2	386	3.05E-3	2.50E-3	3.99E+4	945	1.08E-1	8.88E-2	1.13E+3
223*	6.59E-1	5.41E-1	1.85E+2	429	1.06E-2	8.74E-3	1.14E+4	965	1.77E-1	1.45E-1	6.90E+2
266	1.85E+0	1.52E+0	6.59E+1	471	3.11E-2	2.56E-2	3.91E+3	1009	3.52E-1	2.89E-1	3.46E+2
303*	3.50E+0	2.88E+0	3.48E+1	491	5.32E-2	4.37E-2	2.29E+3	1033	4.64E-1	3.81E-1	2.63E+2
346	6.71E+0	5.51E+0	1.81E+1	520	9.25E-2	7.60E-2	1.32E+3	1052	6.14E-1	5.05E-1	1.98E+2
389*	1.13E+1	9.31E+0	1.07E+1	566	2.36E-1	1.94E-1	5.17E+2	1076	7.96E-1	6.54E-1	1.53E+2
432	1.76E+1	1.44E+1	6.93E+0	604	4.48E-1	3.68E-1	2.72E+2				
495*	2.82E+1	2.32E+1	4.31E+0	651	9.40E-1	7.72E-1	1.30E+2				
523	3.35E+1	2.75E+1	3.64E+0	694	1.69E+0	1.39E+0	7.21E+1				
570	4.32E+1	3.55E+1	2.82E+0	737	2.95E+0	2.42E+0	4.13E+1				
608	5.33E+1	4.38E+1	2.28E+0	781	4.55E+0	3.74E+0	2.67E+1				
655	6.20E+1	5.09E+1	1.96E+0	829	7.08E+0	5.81E+0	1.72E+1				
698	6.86E+1	5.63E+1	1.78E+0	872	9.67E+0	7.95E+0	1.26E+1				
741*	7.76E+1	6.37E+1	1.57E+0	911	1.33E+1	1.09E+1	9.17E+0				
834	9.13E+1	7.50E+1	1.33E+0	954	1.71E+1	1.40E+1	7.13E+0				
916	9.93E+1	8.16E+1	1.23E+0	996	2.22E+1	1.82E+1	5.49E+0				
1002	1.08E+2	8.85E+1	1.13E+0	1041	2.86E+1	2.35E+1	4.26E+0				
1091*	1.12E+2	9.21E+1	1.09E+0	1085	3.40E+1	2.80E+1	3.58E+0				

BV = bed volume, 10 mL/BV

DF = decontamination factor

C_0 = 122 μCi ^{137}Cs/ mL (reference date June 2020)

* = samples submitted for additional analysis to assess selected constituent breakthrough profiles

Table A.2. Feed Displacement, Water Rinse, and Final Flush Results Following AP-105DF Processing

Feed Displacement					Water Rinse				Final Fluid Flush			
BV	Density (g/mL)	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
1.8	1.29	8.42E-1	6.91E-1	1.45E+2	2.0	1.51E-2	1.24E-2	8.06E+3	5.2	1.73E-1	1.42E-1	7.03E+2
3.6	1.29	8.80E-1	7.23E-1	1.38E+2	3.9	1.25E-2	1.02E-2	9.77E+3				
5.4	1.30	9.22E-1	7.58E-1	1.32E+2	5.7	1.72E-2	1.41E-2	7.09E+3				
7.1	1.28	8.57E-1	7.04E-1	1.42E+2	7.5	2.32E-2	1.91E-2	5.24E+3				
8.9	1.13	2.54E-1	2.09E-1	4.79E+2	9.3	2.55E-2	2.10E-2	4.77E+3				
10.8	1.05	4.55E-2	3.74E-2	2.68E+3	11.2	2.22E-2	1.82E-2	5.49E+3				

BV = bed volume, 10 mL

DF = decontamination factor

C$_0$ = 122 µCi ^{137}Cs/ mL (reference date June 2020)

Densities of water rinse samples and final fluid flush were ~1.02 g/mL

Appendix B – Analyte Concentrations as a Function of Loading

The load behaviors of selected analytes in AP-105DF 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 During AP-105DF Processing

BV Processed>	NA	42	85	128	172	223	303	389	495	741	1091
Sample ID>	TI082-Comp-Feed	TI082-L-F2-A	TI082-L-F4-A	TI082-L-F6-A	TI082-L-F8-A	TI082-L-F10-A	TI082-L-F12-A	TI082-L-F14-A	TI082-L-F16-A	TI082-L-F22-A	TI082-L-F26-A
Analyte	ICP-OES, M										
Al	5.26E-1	5.04E-1	4.97E-1	5.37E-1	5.11E-1	5.49E-1	5.11E-1	5.45E-1	5.19E-1	5.26E-1	5.08E-1
Ca	1.03E-3	9.08E-4	7.93E-4	9.91E-4	8.28E-4	9.56E-4	8.08E-4	1.02E-3	1.03E-3	1.06E-3	1.06E-3
Cd	[2.4E-5]	[1.4E-5]	[2.2E-5]	[2.0E-5]	[1.4E-5]	[2.2E-5]	[2.4E-5]	[3.7E-5]	[2.5E-5]	[2.1E-5]	[2.1E-5]
Fe	[2.0E-5]	<1.6E-5	<1.6E-5	[2.9E-5]	<1.6E-5	[1.7E-5]	[2.1E-5]	[3.6E-5]	[2.0E-5]	[3.2E-5]	[1.8E-5]
K	1.02E-1	1.01E-1	9.90E-2	1.03E-1	1.02E-1	1.06E-1	9.82E-2	1.05E-1	1.01E-1	1.02E-1	9.80E-2
Ti	<5.9E-6	[2.0E-5]	[1.8E-5]	[1.7E-5]	[1.6E-5]	[1.6E-5]	[1.3E-5]	[2.1E-5]	[1.1E-5]	[1.1E-5]	[1.1E-5]
Zr	<9.4E-6	[4.7E-5]	[4.5E-5]	[4.6E-5]	[3.7E-5]	[4.2E-5]	[3.8E-5]	[3.9E-5]	[3.4E-5]	[2.7E-5]	[2.4E-5]
Analyte	ICP-MS, M										
Ba	<1.6E-6	<2.6E-6	<1.4E-6	<1.4E-6	<1.4E-6	<1.8E-6	<1.5E-6	<1.3E-6	<1.9E-6	<2.0E-6	<3.4E-6
Nb	2.74E-7	4.50E-5	2.92E-5	2.29E-5	1.82E-5	1.54E-5	1.27E-5	1.24E-5	1.06E-5	8.77E-6	6.16E-6
Pb	9.00E-5	5.12E-6	7.05E-6	1.24E-5	1.86E-5	3.12E-5	5.80E-5	7.73E-5	8.37E-5	8.91E-5	9.30E-5
Sr	1.82E-6	6.85E-7	6.54E-7	2.15E-7	2.21E-7	2.32E-7	2.17E-7	2.32E-7	2.78E-7	4.15E-7	7.59E-7
^{238}U	2.46E-5	1.05E-5	1.92E-5	2.34E-5	2.26E-5	2.43E-5	2.48E-5	2.75E-5	2.64E-5	2.76E-5	2.74E-5
Analyte	Radiochemistry, µCi/mL(a)										
^{90}Sr	6.90E-01	3.91E-04	5.24E-04	1.14E-03	2.03E-03	3.98E-03	8.72E-03	1.58E-02	3.62E-02	9.34E-02	2.41E-01
^{237}Np	6.69E-06	1.04E-06	1.62E-06	2.46E-06	2.54E-06	3.22E-06	3.12E-06	3.56E-06	4.36E-06	4.62E-06	5.16E-06
^{238}Pu	6.37E-06	4.13E-06	4.56E-06	6.25E-06	3.96E-06	4.67E-06	5.81E-06	4.20E-06	3.27E-06	2.47E-06	3.87E-06
$^{239+240}$Pu	3.94E-05	1.58E-05	2.03E-05	2.03E-05	1.77E-05	2.25E-05	2.28E-05	2.16E-05	2.08E-05	2.08E-05	2.38E-05

(a) Reference date is December 2020.

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 C, ASR 1097.

Appendix C – Analytical Reports

Analytical reports provided by the Analytical Support Operations (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 3.6).

Appendix C Table of Contents

ASR 0957, Initial Characterization of AP-105, As-Received

ASR 0964, Isotopic Characterization of AP-105, As-Received

ASR 1097, AP-105DF Ion Exchange Feed, Effluent, and Selected Lead Column Samples

ASR 1109, Metals Analysis of Final Flush Solution

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 A. Rovira
Print Name A. Rovira
Phone 371-7908 MSIN P7-25

Project Number: 75433
Work Package: NE4452

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)

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 X Return

QA/Special Requirements

- **QA Plan:**
  X ASO-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

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**
  ☐ ASO-QAP-001 (Equivalent to HASQARD).
  X 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:**
  12/20/19
  (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: ____________
  or, Previous RPL Number: ____________

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

Send Report To: A. Rovira **MSIN** P7-25
MSIN ____________

Additional or Special Instructions ____________

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

Date Delivered: 12/16/19
Delivered By (optional) ____________
Time Delivered: 3:00 pm
Group ID (optional) ____________
CMC Waste Sample? X No ☐ Yes

Received By: T Trang-Le

ASR Number: **0957** Rev.: **00**
RPL Numbers: 20-0321 and 20-0322
(first and last)

ASO Work Accepted By: KN Pool **Signature/Date:** Karl N. Pool 12/17/19

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**	**Library**
20-0321	5AP-19-01	AP-105 Tank Supernate	1) GEA 2) ICP/OES - Na, Al, K		
20-0322	5-AP-19-18	AP-105 Tank Supernate	1) GEA		

ASR # 0957 Rev: 00

Page 1 of 1

ASR 0957.00 Request Page

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

PO Box 999, Richland, Washington 99352

Project / WP#:	75433 / NE4452
ASR#:	0957.00
Client:	A. Rovira
Total Samples:	1 (Aqueous)

ASO Sample ID	Client Sample ID	Client Sample Description	Sample Weight (g)
20-0321	5AP-19-01	AP-105 Tank Supernate	NA

Sample Preparation: Simple dilution of "as received" samples in 5% v/v HNO_3 performed by J. Carter on 12/17/19.

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:**	12/17/19	**ICP File:**	C0839

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

M&TE:			
☒	PerkinElmer 5300DV ICP-OES	SN: 077N5122002	RPL 405 Bench
☐	Sartorius ME414S Balance	SN: 22406373	RPL 405 Bench
☒	Ohaus Pioneer PA224C	SN: B725287790	RPL 405 Bench
☐	Mettler AT400 Balance	SN: 192720-92	RPL 405 FH #3
☐	Mettler AT400 Balance	SN: 1113292667	RPL 420 FH #13
☐	Sartorius R200D Balance	SN: 39080058	RPL 525 FH #9

Report Preparer

12/18/19
Date

Review and Concurrence

12/20/19
Date

Page 1 of 1

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

		Run Date >	12/17/2019	12/17/2019	12/17/2019
		Process Factor >	1.0	250.0	250.0
			405 diluent	20-0321 @ 250x	
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Lab Diluent	5AP-19-01	
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)
0.0048	0.048	Al	--	20,700	21,700
0.0134	0.134	K	--	6,480	6,880
0.0072	0.072	Na	--	196,000	205,000
Other Analytes					
0.0021	0.021	Ag	--	--	--
0.0647	0.647	As	--	--	--
0.0048	0.048	B	[0.032]	[45]	[47]
0.0001	0.001	Ba	--	[0.58]	[0.62]
0.0001	0.001	Be	--	[0.21]	[0.21]
0.0215	0.215	Bi	--	--	--
0.0052	0.052	Ca	--	[55]	[58]
0.0013	0.013	Cd	--	--	--
0.0082	0.082	Ce	--	--	--
0.0038	0.038	Co	--	--	--
0.0021	0.021	Cr	--	458	481
0.0021	0.021	Cu	--	[4.2]	[4.2]
0.0023	0.023	Dy	--	--	--
0.0008	0.008	Eu	--	--	--
0.0017	0.017	Fe	[0.014]	--	--
0.0018	0.018	La	--	--	--
0.0014	0.014	Li	--	--	--
0.0017	0.017	Mg	--	--	--
0.0002	0.002	Mn	--	--	--
0.0056	0.056	Mo	--	[70]	[74]
0.0114	0.114	Nd	--	--	--
0.0041	0.041	Ni	--	[39]	[42]
0.0371	0.371	P	--	580	626
0.0257	0.257	Pb	--	--	--
0.0050	0.050	Pd	--	--	--
0.0143	0.143	Rh	--	--	--
0.0070	0.070	Ru	--	--	[11]
0.1089	1.089	S	--	1,650	1,730
0.0671	0.671	Sb	--	--	--
0.0987	0.987	Se	--	--	--
0.0072	0.072	Si	--	[17]	[16]
0.0267	0.267	Sn	--	--	--
0.0002	0.002	Sr	--	--	--
0.0331	0.331	Ta	--	--	--
0.0181	0.181	Te	--	--	--
0.0076	0.076	Th	--	--	--
0.0004	0.004	Ti	--	--	--
0.0291	0.291	Tl	--	--	--
0.0376	0.376	U	--	--	--
0.0012	0.012	V	--	--	--
0.0128	0.128	W	--	[120]	[120]
0.0006	0.006	Y	--	--	--
0.0027	0.027	Zn	--	--	--
0.0013	0.013	Zr	--	--	--

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "
near the top of each column. The estimated sample quantitation limit = EQL (in Column .
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-0957 Results from C0839 ASR-0957 Rovira

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

Page 2 of 2

QC Performance 12/17/2019

Criteria >	≤ 20%	80%-120%	80%-120%	≤ 10%
QC ID >	20-0321 Dup	LCS/BS	20-0321 + PS-A	20-0321 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Diff
Al	4.6	101	nr	7.1
K	5.9	98	98	3.1
Na	4.3	99	nr	8.1
Other Analytes				
Ag		91	80	
As		99	84	
B		97	83	
Ba		99	89	
Be		98	84	
Bi		107	96	
Ca		101	93	
Cd		99	84	
Ce		97		
Co		97	82	
Cr	5.0	96	84	7.9
Cu		99	89	
Dy		95		
Eu		93		
Fe		95	82	
La		92		
Li		105	100	
Mg		99	87	
Mn		97	84	
Mo		96	82	
Nd		96		
Ni		96	80	
P	7.7	97	82	
Pb		97	83	
Pd		87		
Rh		93		
Ru		85		
S	4.5	94		
Sb		94	83	
Se				
Si		91	86	
Sn		94	80	
Sr		100	91	
Ta				
Te		80		
Th		90		
Ti		98	85	
Tl		91	75	
U		101		
V		95	82	
W		95	82	
Y		97	86	
Zn		93	80	
Zr		99	87	

Shaded results are outside the acceptance criteria.

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

ASR-0957 Results from C0839 ASR-0957 Rovira

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

filename: 20-0321 Rovira
12/17/2019

Client: Rovira
ASR 0957

Project: 75433
NE4452

Prepared by: T Trang-le 12/17/19

Technical Reviewer: LRGreenwood 12/17/19

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

M&TE: Gamma detectors T
Reference dates: 12/17/2019 @ 7:10 am

Measured Activity, µCi per Sample ± 1s

RPL ID: Sample ID: **Isotope**	20-0321 5AP-19-01		20-0322 5AP-19-18	
Cs-137	**1.89E+01**	**± 1%**	**1.82E+01**	**± 1%**

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: Sandra Fisk
Print Name: SANDRA FISKUM
Phone: ______ MSIN: ______

Project Number: 75433
Work Package: NE4456

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)

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

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

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:** 1/20/2020
  (Note: Priority rate charge for < 10 business day turn-around time)
- **Negotiated Commitment Date:** 1/20/20
  (*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: SK Fiskum **MSIN** ______
______ **MSIN** ______

Additional or Special Instructions ______

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

Date Delivered: 12/19/19
Delivered By (optional): ______
Time Delivered: 9:50 am
Group ID (optional): ______
CMC Waste Sample? ☒ No ☐ Yes

Received By: T Trang-le
ASR Number: 0964 Rev.: 00
RPL Numbers: 20-0350 → 20-0352
(first and last)

ASO Work Accepted By: KN Pool **Signature/Date:** 12/19/19

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**
20-0350	5AP-19-01-Cs	0.45M HNO3 w/ Cs fraction	ICP-MS : Cs isotopic ratio		
20-0351	5AP-19-18-Cs	from AP-105	↓		
20-0352	BL-Cs	0.45M HNO3 process blank			

ASR # 0964 Rev.: 00

Page 1 of 1

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

PO Box 999, Richland, Washington 99352

Project / WP#:	75433 / NE4456
ASR#:	0964.00
Client:	S. Fiskum
Total Samples:	3 (liquids)

ASO Sample ID	Client Sample ID	Client Sample Description	Sample Weight (g)
20-0350	5AP-19-01-Cs	0.45 M HNO_3/ Cs Fraction	NA
20-0351	5AP-19-18-Cs	From AP-105	NA
20-0352	BL-Cs	0.45 M HNO_3 process blank	NA

Sample Preparation: Simple dilution of "as received" samples in 2% v/v HNO_3 performed by D. E. Cherkasov on 01/06/2020.

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

Analyst:	D. Cherkasov	**Analysis Date:**	01/07/2020	**ICP File:**	M2042

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

M&TE:	☒	PerkinElmer NexION^{TM} 350X ICP-MS	SN: 85VN4070702
	☐	Sartorius ME414S Balance	SN: 22406373
	☒	Mettler AT400 Balance	SN: M19445
	☐	Sartorius R200D Balance	SN: 39080042
	☐	Mettler AT201 Balance	SN: 192720-92
	☒	Ohaus Pioneer PA224C	SN: B725287790
	☐	SAL Cell 2 Balance	SN: 8033311209
	☐	Lab 309 Balance	SN: 10803210

Samuel S Morrison
Report Preparer

01/09/2020
Date

Dennis Cherkasov
Review and Concurrence

01/13/2020
Date

Three samples were submitted under Analytical Service Request (ASR) 0964.00 were analyzed by ICP-MS. The samples and one blank were processed through dissolution prior to analysis. All solutions were diluted in 2% HNO_3 prior to analysis. None of the solutions were filtered.

All results are reported on a mass per unit mass 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. Because the ICP-MS cannot distinguish between isobaric interferences, the AOI are displayed as m/z 133, 135, and 137. 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 (natural abundance) 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 curves and for initial and continuing calibration verification (ICV/CCV). The data have been corrected from the natural abundance calibration solutions to report total isobaric results (ng/mL) at m/z 133. The results for m/z 135 and m/z 137 were determined by using the raw intensity isotope ratio of 135/133 and 137/133 to determine the quantity of 135 and 137 present in the samples respectively.

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 Bi-209 as the internal standard (IS). The AOI data for all m/z were normalized to the Bi-209 IS. The Bi-209 IS recoveries ranged from 98.6% to 109.8% for the entire analysis sequence, with the acceptance criterion of 30% to 120% recovery.

Preparation Blank (PB):

An ICP-MS laboratory prep blank was prepared and analyzed for this sample set, blank #8. The concentrations of all AOI in the process blank 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 single blank spike (BS) samples prepared from a dilution of the 2% HNO_3 blank with an equivalent volume of each 2 ppb standard CCV 71A (1:1 ratio). The recovery for the all AOI were within the acceptance criteria of 80% to 120% recovery.

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

A duplicate of sample 20-0350 and 20-0351 were analyzed. RPD are listed for all analytes that were below the EQL and were not reported.

Matrix-Spike (MS) Sample:

A matrix spike was not used in the MS analysis. Instead of a MS sample, post-digestion spikes (PS-71A) was conducted on samples 20-0350 and 20-0351 as is discussed later in this report.

Initial/Continuing Calibration Verification (ICV/CCV):

ICV/CCV solutions (71A) 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):

ICB/CCB solutions (2% v/v HNO_3) were analyzed immediately after each ICV solution and after each respective CCV solution (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.

DEC 07/8/20

Post-Digestion Spike (PS)/Analytical Spike (AS) - Sample (71A, ~~71B~~ & ~~71C~~ Components):

Instead of a MS sample, post-digestion spikes (PS-71A) were conducted on sample 20-0350 and 20-0351. 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 were all within the acceptance criteria, 75%-125%.

Low-Level Standard (LLS):

The LLS solution (71A) 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):

ICS solution (71A) 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 samples 20-0350 and 20-0351. Percent differences (%D) are listed for all analytes that had a concentration at or above the 10xEQL in the diluted sample. The %Ds for the AOI were not reported since the sample samples were below EQL.

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.

Final Report

		Run Date >	1/7/2020	1/7/2020	1/7/2020	1/7/2020	1/7/2020	1/7/2020
		Process Factor >		891.6	891.6	890.5	890.5	887.8
		RPL/LAB >	Lab Blank	20-0350	20-0350 Rep	20-0351	20-0351 Rep	20-0352
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	2% HNO3 Lab Blank	5AP-19-01-Cs		5AP-19-18-Cs		BL-CS
(ng/mL)	(ng/mL)	(Analyte)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)	(ng/mL)
7.76E-05	7.76E-04	m/z 133	--	6.83E+02	7.03E+02	1.05E+03	1.07E+03	4.51E+00
8.29E-05	8.29E-04	m/z 135	--	2.12E+02	2.21E+02	3.28E+02	3.41E+02	8.38E-01
1.17E-04	1.17E-03	m/z 137	--	2.03E+02	2.01E+02	3.14E+02	3.29E+02	1.40E+00

Internal Standard % Recovery

Bi 209 (IS)	104%	109%	100%	106%	102%	107%

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 red 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 01/07/2020

Criteria >	≤ 20%	≤ 20%	80%-120%	75%-125%	75%-125%	≤ 10%	≤ 10%
QC ID >	20-0350 DUP	20-0351 DUP	BS-71A	20-0350 PSA	20-0351 PSA	20-0350 5-fold Serial Dil	20-0351 5-fold Serial Dil
Analytes	RPD (%)	RPD (%)	%Rec	%Rec	%Rec	%Diff	%Diff
m/z 133	3%	2%	98%	99%	97%	1%	1%
m/z 135	4%	4%	98%	101%	103%	1%	2%
m/z 137	1%	5%	97%	95%	100%	1%	3%

Internal Standard % Recovery

Bi 209 (IS)	100%	102%	104%	103%	106%	107%	104%

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.

M0242 ASR-0964 S. Fiskum Cs DEC200107.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 SK Fiskum
Print Name SK Fiskum
Phone 375-5677 MSIN

Project Number: 75433
Work Package: NE4456

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:** 9/15/20
(Note: Priority rate charge for < 10 business day turn-around time)

◆ **Negotiated Commitment Date:** All but radchem by 9/30/20
(*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: 1017
or, Previous RPL Number:

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

Send Report To: SK Fiskum **MSIN**
AM Westesen **MSIN**

Additional or Special Instructions

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

Date Delivered: 8/3/20
Delivered By (optional)
Time Delivered:
Group ID (optional)
CMC Waste Sample? ☒ No ☐ Yes

Received By: T Trang-le

ASR Number: 1097 Rev.: 0
RPL Numbers: 20-1677 thru 20-1682
(first and last)

ASO Work Accepted By: KN Pool **Signature/Date:** Karl N Pool 8/6/20

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**
20-1677	TI082-COMP-FEED	AP-105 Diluted Feed	1) GEA - All samples (Cs-137, Co-60 and Eu-154 and any other observed gamma emitting isotopes) 2) Tc-99 3) Sr-90 4) Np-AEA, Np-237 5) Pu-AEA, Pu-238, Pu-239/240 6) Am-AEA, Am-241 7) Acid Digestion- 128 - Prep Lab a) ICP/OES - Al, As, Ca, Cd, Cr, Fe K, Na, P, S, Ti, Zn, Zr b) ICP/MS - Ba, Nb, Pb, Sr, U-238		
20-1678	TI082-COMP-EFF	AP-105 Tank Waste - Cs Removed	1) GEA - All samples (Cs-137, Co-60 and Eu-154 and any other observed gamma emitting isotopes) 2) IC-Anions - F, Cl, NO_2, NO_3, PO_4, C_2O_4 and SO_4 3) TOC/TIC - Hot Pursulfate 4) OH 5) Sr-90 6) Tc-99 7) Np-AEA, Np-237 8) Pu-AEA, Pu-238, Pu-239/240 9) Am-AEA, Am-241 10) Acid Digestion- 128 - Prep Lab a) ICP/OES - Al, As, Ca, Cd, Cr, Fe K, Na, P, S, Ti, Zn, Zr b) ICP/MS - Ba, Nb, Pb, Sr, U-238		

ASR: 1097______ Rev: 00

ASR 1097.00 Request Page

Page 1 of 2

Analytical Services Request (ASR)

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

ASO Staff Use Only RPL Number	Provide Analytes of Interest and Required Detection limits - ☐ Below ☐ Attached Client Sample ID	Sample Description (& Matrix if varies)	Analyses Requested	ASO Staff Use Only Test	Library
20-1679	TI082-L-F2-A	AP-105 Tank Waste - Cs Removed	1) Sr-90 2) Pu-AEA, Pu-238, Pu-239/240 3) Np-AEA, Np-237 4) Acid Digest - 128 - Prep Lab a) ICP/OES - Al, Ca, Cd, Fe, K b) ICP/MS - Ba, Pb, U-238		
20-1680	TI082-L-F4-A				
20-1681	TI082-L-F6-A				
20-1682	TI082-L-F8-A				
20-1683	TI082-L-F10-A				
20-1684	TI082-L-F12-A				
20-1685	TI082-L-F14-A				
20-1686	TI082-L-F16-A				
20-1687	TI082-L-F22-A				
20-1688	TI082-L-F26-A				

ASR: 1097______ Rev: 00

ASR 1097.00 Request Page

Page 2 of 2

Special Instructions for ASR 1097

Analysis of AP-105 diluted feed composite, effluent composite, and selected samples from column processing. All samples are caustic and are ~5.6 M Na.

Use the ASO QA Plan, ASO-QAP-001, current revision to apply batch processing and instrument QC.

Client ID	**ASO Sample ID**	**Analysis**
TI082-COMP-FEED	20-1677	Table 1
TI082-COMP-EFF	20-1678	Table 2
TI082-L-F2-A	20-1679	Table 3
TI082-L-F4-A	20-1680	
TI082-L-F6-A	20-1681	
TI082-L-F8-A	20-1682	
TI082-L-F10-A	20-1683	
TI082-L-F12-A	20-1684	
TI082-L-F14-A	20-1685	
TI082-L-F16-A	20-1686	
TI082-L-F22-A	20-1687	
TI082-L-F26-A	20-1688	

The high salt samples are assumed to require acid digestion for most analytes. However, if the preparative technique sufficiently dilutes the sample into required acid matrix, then acid digestion may be omitted. Note that several MDLs listed in Tables 1-3 should generally not pose an issue as the analytes are anticipated to be in relative high concentrations.

Preparative QC samples per preparative batch expected for this suite include:

1. Process blank (digestion blank or diluent blank); not applicable to GEA
2. Duplicate (one duplicate per analytical batch; if dilution is the only preparation, please prepare a diluent duplicate); not applicable to GEA
3. Blank spike (BS), laboratory control sample (LCS), or reagent spike (RS); not applicable to GEA
4. Matrix spike
    a. Not needed for major analytes (e.g., Na and NO_3^- in the TI082-COMP-FEED and TI082-COMP-EFF samples). In the cases where analyte spikes are not used, measure post spikes instead, per the ASO QA Plan.
    b. Not applicable to GEA.

ASR 0787

Table 1. Column Feed Composite Analyte List

Analyte	Target MDL	Analyte	Target MDL
GEA		**Acid Digestion / ICP-OES**	
^{60}Co	1E-5 μCi/mL	Al	1000 μg/mL
^{137}Cs	1E-5 μCi/mL	As	100 μg/mL
^{154}Eu	1E-5 μCi/mL	Ca	10 μg/mL
Acid Digestion / Radiochemical Separations/AEA		Cd Cr	10 μg/mL 10 μg/mL
^{90}Sr	1E-4 μCi/mL	Fe	10 μg/mL
^{99}Tc	1E-4 μCi/mL	K	100 μg/mL
^{237}Np	1E-6 μCi/mL	Na	1000 μg/mL
^{238}Pu	1E-6 μCi/mL	P	10 μg/mL
$^{239+240}$Pu	1E-6 μCi/mL	S	100 μg/mL
^{241}Am	1E-6 μCi/mL	Ti	10 μg/mL
Acid Digestion / ICP-MS		Zn	10 μg/mL
^{238}U	0.5 μg/mL	Zr	10 μg/mL
Ba	1 μg/mL		
Nb	1 μg/mL		
Pb	1 μg/mL		
Sr	1 μg/mL		

ASR 0787

Table 2. Column Effluent Composite Analyte List

Analyte	Target MDL	Analyte	Target MDL
GEA		**Acid Digestion / ICP-MS**	
^{60}Co	1E-5 µCi/mL	^{238}U	0.5 µg/mL
^{137}Cs	1E-5 µCi/mL	Ba	1 µg/mL
^{154}Eu	1E-5 µCi/mL	Nb	1 µg/mL
Dilution / Ion Chromatography (IC)		Pb	1 µg/mL
F^-	200 µg/mL	Sr	1 µg/mL
Cl^-	200 µg/mL	**Acid Digestion / ICP-OES**	
NO_2^-	200 µg/mL	Al	1000 µg/mL
NO_3^-	200 µg/mL	As	100 µg/mL
PO_4^{3-}	200 µg/mL	Ca	10 µg/mL
$C_2O_4^{2-}$	200 µg/mL	Cd	10 µg/mL
SO_4^{2-}	200 µg/mL	Cr	10 µg/mL
Hot Persulfate Oxidation		Fe	10 µg/mL
Total organic carbon (TOC)	200 µg/mL	K	100 µg/mL
Total inorganic carbon (TIC)	200 µg/mL	Na	1000 µg/mL
Titration		P	10 µg/mL
Free Hydroxide	0.1 M	S	100 µg/mL
Acid Digestion / Radiochemical Separations/AEA		Ti	10 µg/mL
		Zn	10 µg/mL
^{90}Sr	1E-4 µCi/mL	Zr	10 µg/mL
^{99}Tc	1E-4 µCi/mL		
^{237}Np	1E-6 µCi/mL		
^{238}Pu	1E-6 µCi/mL		
$^{239+240}$Pu	1E-6 µCi/mL		
^{241}Am	1E-6 µCi/mL		

Table 3. Lead Column Sample Analyte List

Analyte	Target MDL
Acid Digestion Radiochemical Separations/counting	
$^{239+240}$Pu	1E-6 µCi/mL
^{237}Np	1E-6 µCi/mL
^{90}Sr	1E-4 µCi/mL
Acid Digestion / ICP-MS	
^{238}U	0.5 µg/mL
Ba	1 µg/mL
Pb	1 µg/mL
Acid Digestion / ICP OES	
Al	0.01 M
Ca	10 µg/mL
Cd	10 µg/mL
Fe	10 µg/mL
K	0.01 M

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

PO Box 999, Richland, Washington 99352

Project / WP#: 75433 / NE4456
ASR#: 1097.00
Client: S. Fiskum
Total Samples: 12 (liquids)
Sample Description: AP-105

ASO Sample ID	Client Sample ID	ASO Sample ID	Client Sample ID
20-1677	TI082-COMP-FEED	20-1683	TI082-L-F10-A
20-1678	TI082-COMP-EFF	20-1684	TI082-L-F12-A
20-1679	TI082-L-F2-A	20-1685	TI082-L-F14-A
20-1680	TI082-L-F4-A	20-1686	TI082-L-F16-A
20-1681	TI082-L-F6-A	20-1687	TI082-L-F22-A
20-1682	TI082-L-F8-A	20-1688	TI082-L-F26-A

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 09/17/20. Simple dilution of "as received" samples in 5% v/v HNO_3 performed by J. Carter on 09/22/20.

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:**	09/22/20	**ICP File:**	C0859

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: 1113162654
	☒	Ohaus PA224C Balance	SN: B725287790
	☒	Sartorius ME414S Balance	SN: 21308482
	☐	SAL Cell 2 Balance	SN: 8033311209

Report Preparer

9/23/2020
Date

Denis Cherkasov
Review and Concurrence

09/24/2020
Date

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

Twelve liquid samples submitted under Analytical Service Request (ASR) 1097 were analyzed by ICP-OES. The samples were prepared following RPG-CMC-128, Rev. 1. "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater". The samples were then diluted 21x-25x. 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 except Zinc (Zn) were within the acceptance criteria of <EQL (estimated quantitation level), ≤50% regulatory decision level, or ≤10% of the concentration in the samples. There was 1.25ppm Zn in the preparation blank, which is above the EQL of 0.0267ppm. Since all samples were below EQL for Zn they are not affected by this failure.

Reagent Spike (RS):

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 were within the acceptance criterion of 94% to 102%.

Duplicate Relative Percent Difference (RPD):

A duplicate of sample 20-1678 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 0.3% to 17.2% and meets the acceptance criterion of ≤20% for liquid samples.

Matrix-Spike (MS) Sample:

A matrix spike (MS) of sample 20-1678 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 86% to 96% and were within the acceptance criterion of 75% to 125%.

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, except for the final MCVAs. Calcium (Ca) failed low at 90%, and it was analyzed a second time during which Ca failed at 89%, Cadmium at 90% and Zinc at 89%.

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 meeting the acceptance criteria of <EQL. A CCB was not analyzed at the end of the run.

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 20-1677. Percent differences (%Ds) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. The %D for the AOI meeting this requirement were 0.3% to 9.1% and meet the acceptance criterion of ≤10%.

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

In addition to the MS sample, a post-digestion spike (A Component) was conducted on sample 20-1677. 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 95% to 104% 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 20-1677. 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 value for the AOI meeting this requirement was 96%, 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

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		Run Date >	9/22/2020	9/22/2020	9/22/2020	9/22/2020	9/22/2020	9/22/2020	9/22/2020	9/22/2020
		Process Factor >	1.0	25.4	633.3	633.3	523.1	532.4	534.7	532.1
			405 diluent	BLK-1677	20-1677 @ 25x		20-1678 @ 21x	20-1679 @ 21x	20-1680 @ 21x	20-1681 @ 21x
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Lab Diluent	Reagent Blank	TI082-Comp-Feed		TI082-Comp-EFF	TI082 L-F2-A	TI082 L-F4-A	TI082 L-F6-A
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
0.0048	0.048	Al	--	1.29	14,200	14,200	14,100	13,600	13,400	14,500
0.0647	0.647	As	--	--	--	--	[73]	[37]	--	--
0.0052	0.052	Ca	--	[0.29]	42.8	39.5	41.0	36.4	31.8	39.7
0.0013	0.013	Cd	[0.0026]	--	[2.4]	[2.9]	[2.3]	[1.6]	[2.5]	[2.3]
0.0021	0.021	Cr	--	--	338	331	341	335	332	346
0.0017	0.017	Fe	--	[0.19]	[1.1]	--	--	--	--	[1.6]
0.0134	0.134	K	--	[1.5]	3,980	3,960	3,970	3,940	3,870	4,040
0.0072	0.072	Na	--	--	136,000	136,000	138,000	137,000	135,000	143,000
0.0371	0.371	P	--	--	427	360	445	417	379	433
0.1089	1.089	S	--	[18]	1,660	1,330	1,490	1,410	1,080	1,630
0.0004	0.004	Ti	[0.0005]	[0.014]	--	--	[1.1]	[0.97]	[0.84]	[0.81]
0.0027	0.027	Zn	--	1.25	--	[3.0]	[3.1]	--	[4.0]	--
0.0013	0.013	Zr	--	--	--	--	[4.1]	[4.3]	[4.1]	[4.2]
Other Analytes										
0.0021	0.021	Ag	--	--	--	--	--	--	--	--
0.0048	0.048	B	[0.010]	[0.62]	57.2	50.9	49.3	114	132	93.4
0.0001	0.001	Ba	[0.0002]	0.212	[0.66]	[0.68]	[0.18]	[0.28]	[0.37]	[0.27]
0.0001	0.001	Be	--	--	[0.16]	[0.18]	[0.15]	[0.13]	[0.13]	[0.13]
0.0215	0.215	Bi	[0.032]	--	[22]	--	[16]	--	--	--
0.0082	0.082	Ce	--	--	[6.9]	--	[5.3]	[6.3]	[6.6]	[5.3]
0.0038	0.038	Co	--	--	--	--	--	--	--	--
0.0021	0.021	Cu	--	--	[2.6]	--	[1.7]	--	[3.2]	[1.5]
0.0023	0.023	Dy	--	--	--	--	--	--	--	--
0.0008	0.008	Eu	--	--	--	--	--	--	--	--
0.0018	0.018	La	--	--	--	--	--	--	--	--
0.0014	0.014	Li	--	--	--	--	--	--	--	--
0.0017	0.017	Mg	--	[0.19]	--	--	--	--	[1.4]	--
0.0002	0.002	Mn	--	[0.0080]	--	--	--	[0.28]	--	--
0.0056	0.056	Mo	--	--	47.2	46.6	47.8	47.6	48.0	47.1
0.0114	0.114	Nd	--	--	--	--	--	[7.8]	--	--
0.0041	0.041	Ni	--	--	28.1	28.9	31.4	29.7	30.1	29.6
0.0257	0.257	Pb	--	--	--	--	--	--	--	--
0.0050	0.050	Pd	--	--	--	--	--	--	--	--
0.0143	0.143	Rh	--	--	--	--	--	--	--	--
0.0070	0.070	Ru	[0.0081]	[0.20]	[7.4]	[9.9]	[7.9]	[11]	[10]	[9.3]
0.0671	0.671	Sb	--	--	--	--	--	--	--	--
0.0987	0.987	Se	[0.12]	--	[72]	--	--	--	--	--
0.0072	0.072	Si	--	[1.1]	108	101	86.0	183	160	181
0.0267	0.267	Sn	--	--	--	--	--	--	--	--
0.0002	0.002	Sr	--	[0.0061]	--	--	--	--	--	--
0.0331	0.331	Ta	--	--	--	--	--	--	--	--
0.0181	0.181	Te	--	--	--	--	--	--	--	--
0.0076	0.076	Th	--	--	--	--	--	--	--	--
0.0291	0.291	Tl	--	[1.1]	--	[68]	--	[33]	[39]	[24]
0.0376	0.376	U	--	--	--	[34]	--	--	--	--
0.0012	0.012	V	[0.0026]	[0.053]	--	--	--	[0.73]	[1.0]	--
0.0128	0.128	W	--	--	89.7	[67]	74.8	70.6	87.8	68.5
0.0006	0.006	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%.

Results from C0859 ASR-1097 (AP-105) Fiskum.xlsm

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

		Run Date >	9/22/2020	9/22/2020	9/22/2020	9/22/2020	9/22/2020	9/22/2020	9/22/2020
		Process Factor >	534.0	531.3	530.5	531.5	541.2	528.6	537.0
			20-1682 @ 21x	20-1683 @ 21x	20-1684 @ 21x	20-1685 @ 21x	20-1686 @ 21x	20-1687 @ 21x	20-1688 @ 21x
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	TI082 L-F8-A	TI082 L-F10-A	TI082 L-F12-A	TI082 L-F14-A	TI082 L-F16-A	TI082 L-F22-A	TI082 L-F26-A
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
0.0048	0.048	Al	13,800	14,800	13,800	14,700	14,000	14,200	13,700
0.0647	0.647	As	--	[53]	[49]	--	--	--	[44]
0.0052	0.052	Ca	33.2	38.3	32.4	40.9	41.2	42.5	42.6
0.0013	0.013	Cd	[1.6]	[2.5]	[2.7]	[4.2]	[2.8]	[2.4]	[2.4]
0.0021	0.021	Cr	331	357	332	352	336	334	324
0.0017	0.017	Fe	--	[0.96]	[1.2]	[2.0]	[1.1]	[1.8]	[1.0]
0.0134	0.134	K	3,970	4,150	3,840	4,110	3,940	3,970	3,830
0.0072	0.072	Na	137,000	146,000	138,000	144,000	138,000	138,000	134,000
0.0371	0.371	P	376	466	379	435	402	406	408
0.1089	1.089	S	1,320	1,370	1,160	1,530	1,520	1,450	1,570
0.0004	0.004	Ti	[0.78]	[0.76]	[0.61]	[1.0]	[0.51]	[0.54]	[0.52]
0.0027	0.027	Zn	--	--	[2.9]	[2.0]	--	[3.5]	[2.2]
0.0013	0.013	Zr	[3.4]	[3.8]	[3.5]	[3.6]	[3.1]	[2.5]	[2.2]
Other Analytes									
0.0021	0.021	Ag	--	--	--	--	--	--	--
0.0048	0.048	B	105	107	87.6	86.3	86.7	79.6	58.1
0.0001	0.001	Ba	[0.22]	[0.30]	[0.21]	[0.21]	[0.31]	[0.28]	[0.26]
0.0001	0.001	Be	[0.13]	[0.15]	[0.15]	[0.15]	[0.13]	[0.11]	[0.13]
0.0215	0.215	Bi	--	--	--	[25]	[13]	[15]	[15]
0.0082	0.082	Ce	--	[6.5]	[6.2]	--	--	[4.6]	--
0.0038	0.038	Co	--	--	--	--	--	--	--
0.0021	0.021	Cu	[2.9]	[2.0]	--	[2.1]	[1.2]	[1.3]	[1.5]
0.0023	0.023	Dy	--	--	--	--	--	--	--
0.0008	0.008	Eu	--	--	--	--	--	--	--
0.0018	0.018	La	--	--	--	--	--	--	--
0.0014	0.014	Li	--	--	--	--	--	--	--
0.0017	0.017	Mg	--	--	--	--	[0.93]	[1.1]	[1.2]
0.0002	0.002	Mn	--	--	--	--	--	--	[0.19]
0.0056	0.056	Mo	48.1	52.7	48.9	50.1	54.2	48.4	45.6
0.0114	0.114	Nd	[11]	--	--	--	[9.5]	--	--
0.0041	0.041	Ni	28.7	32.5	28.8	29.7	30.6	29.1	26.0
0.0257	0.257	Pb	--	--	--	--	--	--	--
0.0050	0.050	Pd	--	--	--	--	--	--	--
0.0143	0.143	Rh	[8.6]	--	[12]	--	[8.9]	--	--
0.0070	0.070	Ru	[4.9]	[5.8]	[12]	[13]	[7.3]	[9.3]	[9.6]
0.0671	0.671	Sb	--	--	--	--	--	--	--
0.0987	0.987	Se	[55]	--	--	[120]	[140]	[61]	[160]
0.0072	0.072	Si	184	200	186	160	174	158	113
0.0267	0.267	Sn	--	--	--	--	[24]	--	--
0.0002	0.002	Sr	--	--	--	--	--	--	--
0.0331	0.331	Ta	--	--	--	--	--	--	--
0.0181	0.181	Te	--	--	--	--	--	--	--
0.0076	0.076	Th	--	--	--	--	--	--	--
0.0291	0.291	Tl	[33]	[41]	[26]	[21]	[26]	[29]	--
0.0376	0.376	U	--	--	--	--	--	--	--
0.0012	0.012	V	--	--	[0.98]	[0.97]	[1.1]	--	--
0.0128	0.128	W	81.9	74.4	68.3	87.9	72.5	71.6	[62]
0.0006	0.006	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%.

Results from C0859 ASR-1097 (AP-105) Fiskum.xlsm

QC Performance 9/22/2020

Criteria >	≤ 20%	80%-120%	75%-125%	80%-120%	80%-120%	≤ 10%
QC ID >	20-1678 Dup	Reagent Spike	20-1678 MS	20-1677 + PS-A	20-1677 + PS-B	20-1677 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Al	0.9	100	nr	95		0.4
As				104		
Ca	17.2	101	93	97		
Cd		97	93	96		
Cr	1.5	95	nr	98		0.3
Fe		99	96	98		
K	4.0	99	93	97		9.1
Na	0.3	101	nr	100		1.6
P	3.4	97	86	96		
S	11.8	95	93		96	
Ti		100	93	96		
Zn		94	93	97		
Zr		102	96	97		
Other Analytes						
Ag				91		
B	10.5	100	88	94		
Ba		100	93	97		
Be		102	97	98		
Bi		72		94		
Ce		98	88		97	
Co				96		
Cu		100	98	101		
Dy					99	
Eu					96	
La		99	93		96	
Li		108	97	100		
Mg		102	93	97		
Mn		99	96	96		
Mo	1.6	94	93	96		
Nd		100	95		97	
Ni	15.5	97	95	98		
Pb		96	95	94		
Pd					92	
Rh					95	
Ru					95	
Sb				101		
Se				101		
Si	8.8	82	103	101		
Sn				95		
Sr		98	94	97		
Ta				97		
Te					97	
Th		99	94		97	
Tl				92		
U		102	96		99	
V		99	95	95		
W		94	65	96		
Y				95		

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.

Results from C0859 ASR-1097 (AP-105) Fiskum.xlsm

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

Project / WP#: 75433 / NE4456
ASR#: 1097.00
Client: S. Fiskum
Total Samples: 12 (liquids)
Sample Description: AP-105

ASO Sample ID	Client Sample ID	ASO Sample ID	Client Sample ID
20-1677	TI082-COMP-FEED	20-1683	TI082-L-F10-A
20-1678	TI082-COMP-EFF	20-1684	TI082-L-F12-A
20-1679	TI082-L-F2-A	20-1685	TI082-L-F14-A
20-1680	TI082-L-F4-A	20-1686	TI082-L-F16-A
20-1681	TI082-L-F6-A	20-1687	TI082-L-F22-A
20-1682	TI082-L-F8-A	20-1688	TI082-L-F26-A

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 09/17/20. Simple dilution of "as received" samples in 2% v/v HNO_3 performed by J. Carter on 09/25/20.

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

Analyst:	D. Cherkasov	**Analysis Date:**	09/28/20	**ICP File:**	M0299

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

M&TE:		
☒	PerkinElmer NexION^{TM} 350X ICP-MS	SN: 85VN4070702
☒	Ohaus PA224C Balance	SN: B725287790
☒	Mettler AT400 Balance	SN: M19445
☒	Mettler AT400 Balance	SN: 1113162654
☐	Mettler AT400 Balance	SN: 1113292667

Denis Cherkasov
Denis E Cherkasov
Digitally signed by Denis E Cherkasov
Date: 2020.10.08 10:10:32 -07'00'
10/06/2020

Report Preparer — Date

Samuel S Morrison
2020-1009

Review and Concurrence — Date

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

Twelve liquid samples submitted under Analytical Service Request (ASR) 1097.00 were analyzed by ICP-MS. The samples were prepared following RPG-CMC-128, Rev. 1. "HNO3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater". The samples and one blank were diluted in 2% HNO_3 prior to analysis. 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. The analyte list requested was as follows: strontium (Sr), niobium (Nb), barium (Ba), lead (Pb) and uranium (U-238). 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 (natural abundance) 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 curves 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 each of Tb-159 and Bi-209 as the internal standard (IS). The AOI data for strontium (Sr), niobium (Nb) and barium (Ba) were normalized to the Tb-159 IS and lead (Pb) and uranium (U-238) AOI's were normalized to Bi-209 IS. The Tb-159 and Bi-209 IS recoveries ranged from 89.0% to 105.6% and 79.0% to 102.6% respectively for the entire analysis sequence, with the acceptance criterion of 30% to 120% recovery.

Preparation Blank (PB):

A process reagent blank (BLK-1677) was prepared and analyzed for this sample set. Process blank solution (BLK-1677) had recoveries for Sr at 5.7x EQL (EQL=0.0135 ng/mL), Ba at 98.5x EQL (EQL=0.0080 ng/mL), Pb at 8.5x EQL (EQL=0.0081 ng/mL), and U at 28.4x EQL (EQL=0.0008 ng/mL). The eight samples affected by elevated PB concentrations were 20-1678 through 20-1685. The concentrations of all other AOI's in the batch process blank 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):

Three blank spike (BS) samples (BS71A, BS71B, and BS71C) were prepared by separately spiking the 2% HNO_3 blank with an equivalent volume of each 2 ppb standard (1:1 ratio). The recovery for the all AOI ranged from 93.6% to 96.7%, 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 DUP-1678 was prepared and analyzed. RPD are listed for all analytes that were measured at or above the EQL. RPD for the AOI meeting this requirement ranged from 0.1% to 2.6% and were within the acceptance criterion of ≤20% for liquid samples.

Matrix-Spike (MS) Sample:

Instead of a MS sample, post-digestion spikes (PS-71A, PS-71B, PS-71C) were conducted on sample 20-1678 as is discussed later in this report.

Initial/Continuing Calibration Verification (ICV/CCV):

The ICV/CCV solutions ((71A, 71B, 71C) 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 that bracket the reported results were within the acceptance criteria of 90% to 110% recovery.

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solutions (2% v/v HNO_3) were analyzed immediately after each respective ICV solution and after each respective CCV solution (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 exception of lead (Pb) recoveries at around 1.2x EQL (EQL=0.0081 ng/mL) for all CCB solutions and niobium (Nb) recoveries at 1.72x EQL and 1.04x EQL (EQL=0.0025 ng/mL) for the last two closing continuing calibration blanks (CCB).

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

Instead of a MS sample, post-digestion spikes (PS-71A, PS-71B, PS-71C) were conducted on sample 20-1678. 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 95.8% to 102.9% and were within the acceptance criterion of 75% to 125%.

Low-Level Standard (LLS):

The LLS solutions (71A, 71B, 71C) were 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):

Three different ICS solutions (71A, 71B, 71C) were 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 20-1678. Percent differences (%D) 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 1.6% to 3.8% and were within the acceptance criterion of ≤10%.

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. Analyte included in the spike Hg component is Hg.
5) Isotopic abundances values were obtained from Nuclides and Isotopes: Chart of the Nuclides. 16th Edition, Revised 2002. Ed Baum, Harold Knox, Tom Miller
6) Analytes included in P1 solution are Ag, Cd, In, Mo, Nb, Pd, Rh, Ru, Sn, Zr.

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

Page 1 of 3

		Run Date >	09/28/20	09/28/20	09/28/20	09/28/20	09/28/20	09/28/20	09/28/20	09/28/20	09/28/20	09/28/20
		Process Factor >	1.00	127.2	756.7 22608.2	745.9 22335.5	745.9 22335.5	759.8 22773.8	761.9 22799.8	761.1 22860.6	759.5 22686.9	758.1 22717.7
		RPL/LAB >	Blank-8	BLK-1677	20-1677	20-1678	20-1678 rep	20-1679	20-1680	20-1681	20-1682	20-1683
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	2% HNO3 Lab Blank	Reagent Blank	TI082-Comp-Feed	TI082-Comp-EFF		TI082 L-F2-A	TI082 L-F4-A	TI082 L-F6-A	TI082 L-F8-A	TI082 L-F10-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)
0.0013	0.0135	Sr	--	9.8	169.6	13.6	13.2	60.1	57.3	18.9	19.3	20.3
0.0002	0.0025	Nb	--	0.1	25.5	2657.1	2595.6	4181.6	2714.3	2125.1	1691.5	1427.4
0.0008	0.0080	Ba	--	207.6	216.4	129.3	133.3	260.5	359.9	188.8	189.8	246.8
0.0008	0.0081	Pb	--	8.7	18661.9	5555.8	5449.8	1061.0	1461.0	2565.0	3854.2	6470.7
0.0001	0.0008	U-238	--	2.9	5860.1	4750.4	4654.8	2505.8	4576.7	5561.4	5372.1	5784.4

Internal Standard % Recovery

Tb 159 (IS)	103%	96%	90%	90%	90%	91%	92%	91%	90%	92%
Bi 209 (IS)	100%	90%	90%	81%	82%	81%	80%	80%	81%	80%

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.

ASR-1097 Final rev01 from F:\Inorganic Analyses\ICP-MS NexION 350\Analysis Data\M0200-M0299\M0299 ASR-1097 Fiskum 71A,B,C DEC20200928.xlsx

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

		Run Date >	**09/28/20**	**09/28/20**	**09/28/20**	**09/28/20**	**09/28/20**	**09/28/20**
		Process Factor >	**752.8 22437.3**	**757.8 22688.7**	**771.8 23113.0**	**758.2 22838.4**	**766.6 22985.4**	**767.5 23047.4**
		RPL/LAB >	**20-1684**	**20-1685**	**20-1686**	**20-1687**	**20-1688**	**DUP-1678**
Instr. Det. Limit (IDL)	**Est. Quant. Limit (EQL)**	**Client ID >**	**TI082 L-F12-A**	**TI082 L-F14-A**	**TI082 L-F16-A**	**TI082 L-F22-A**	**TI082 L-F26-A**	**TI082-Comp-EFF**
(ng/mL)	**(ng/mL)**	**(Analyte)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**
0.0013	**0.0135**	**Sr**	**19.0**	**20.3**	**24.4**	**36.3**	**66.5**	**34.9**
0.0002	**0.0025**	**Nb**	**1182.6**	**1155.5**	**981.3**	**815.0**	**572.5**	**2737.6**
0.0008	**0.0080**	**Ba**	**211.0**	**175.8**	**257.8**	**270.6**	**464.5**	**217.4**
0.0008	**0.0081**	**Pb**	**12022.6**	**16012.5**	**17334.8**	**18464.3**	**19261.2**	**5563.7**
0.0001	**0.0008**	**U-238**	**5906.6**	**6546.6**	**6282.6**	**6563.6**	**6528.6**	**4759.7**

Internal Standard % Recovery

Tb 159 (IS)	90%	90%	89%	91%	89%	90%
Bi 209 (IS)	81%	80%	79%	80%	80%	79%

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.

ASR-1097 Final rev01 from F:\Inorganic Analyses\ICP-MS NexION 350\Analysis Data\M0200-M0299\M0299 ASR-1097 Fiskum 71A,B,C DEC20200928.xlsx

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

QC Performance 09/28/2020

Criteria >	≤ 20%	80%-120%	80%-120%	75%-125%	75%-125%	75%-125%	≤ 10%
QC ID >	**20-1678 Dup**	**BS71A**	**BS71B**	**MS (None)**	**20-1678 + CCV71A**	**20.1678 + CCV71B**	**20-1678 5-fold Serial Dil**
Analytes	**RPD (%)**	**%Rec**	**%Rec**	**%Rec**	**%Rec**	**%Rec**	**%Diff**
Sr	--	93.6%			102.9%		--
Nb	0.1%		91%			82.1%	3.8%
Ba	--	92.3%			102.0%		--
Pb	1.4%	96.3%			101.2%		--
U-238	2.6%	96.7%			95.8%		1.6%

Internal Standard % Recovery

Tb 159 (IS)	104%	104%	106%		93.2%	94%	90%
Bi 209 (IS)	98%	98%	101%		85.2%	86%	81%

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.

ASR-1097 Final rev01 from F:\Inorganic Analyses\ICP-MS NexION 350\Analysis Data\M0200-M0299\M0299 ASR-1097 Fiskum 71A,B,C DEC20200928.xlsx

Pacific Northwest
NATIONAL LABORATORY

Client:	S. Fiskum	Report Date:	9/23/2020
		Analysis Date:	9/23/2020
Subject:	Hydroxide Analyses for:		**Aqueous Samples**
Project:	75433	WP #	NE4456
ASR:	**1097** Rev-0	Procedure:	RPG-CMC-228-Rev 0.1
Sample ID.	20-1678		

One diluted aqueous sample aliquots (see above assigned RPL Sample #), provided on ASR's 1097 was analyzed by manual titration for the base constituents content following procedure RPG-CMC-228. The sample was diluted prior to titration to allow sufficient volume of water/sample mixture to contact the pH probe. The sample aliquot used was 0.1 mL. The titrant used was 0.0925 M HCl (Standardized HCl was prepared and documented on Chem Rec 240, prepared on 9/23/20). pH measurements were obtained using a Beckman Coulter 560 pH meter, 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 initial diluted pH is reported on attached Report Summary along with the free hydroxide molarity (the 1st inflection point at pH of 10.9) was very weak but discernable. A 2nd inflection point was pH 7.6. The third inflection point (at pH 5.3) was very weak but identified and reportable.

Following is the 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.

Prepared by: Date: 9/25/20

Reviewed by: Date: 9/25/2020

Battelle Pacific Northwest Laboratory Nuclear Chemistry and Engineering Group Chemical Measurements Center	ASR # 1097 WP# NE4456

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

Equip # Beckman Coulter 560, SN#110650046

Report Summary for ASR # -- 1097
Revision # **Rev-0**

Report Date: 9/23/2020
Analysis Date: 9/23/2020

				Concentration, moles / Liter		
				First Point	Second Point	Third Point
RPG #	Client ID	Diluted Initial pH	OH conc ug/mL	Molarity	Molarity	Molarity
20-1678	TI082-COMP-EFF	12.32	2.11E+04	1.24	1.19	0.43

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, 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 9/25/20
Reviewer: Karl N. Pool 9/25/20

Battelle Pacific Northwest Laboratory
Nuclear Chemistry and Engineering Group

ASR # and Rev #	1097.00	Rev-0
Client:	S. Fiskum	
Project: 75433	WP#	NE4456
75433		NE4456

Report Date: 9/23/2020
Analysis Date: 9/23/2020

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 9/25/2020

Titrant	Molarity	Chem Rec#
HCl	**0.0925**	**240**

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
20-1678	TI082-COMP-EFF		NA	0.100	NA	NA	NA	12.320	1.340	10.9	0.124	1.240

Instrument Calibration

Buffer	Vendor	Lot Number	Expire Date
4	Inorganic Ventures	N2-WCS673492	30-Jun-21
7	Inorganic Ventures	N2-WCS674708	30-Jun-21
10	Inorganic Ventures	P2-WCS675599	30-Jun-21

2-nd Verif	Vendor	Lot Number	Expire Date
7	Inorganic Ventures	P2-WCS680595	31-Aug-21

Slope
96.7%

Battelle Pacific Northwest Laboratory
Nuclear Chemistry and Engineering Group

ASR # and Rev # 1097.00

WP# NE4456
NE4456

Procedure:
Alkalinity of Aqueous Solutions, Leachates and Supernates

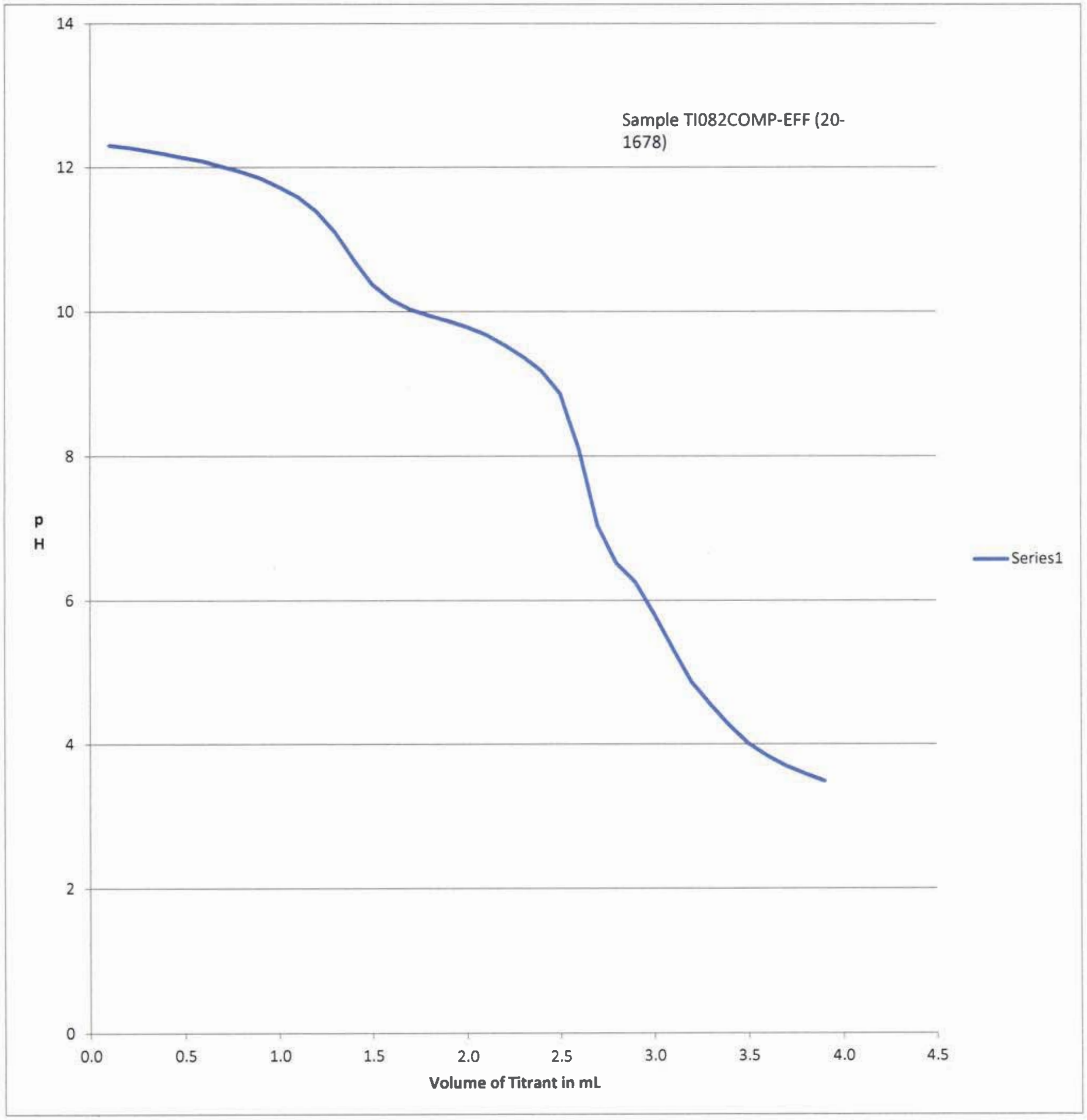
By Manual Titration

Equip # Beckman Coulter 560, SN#110650046

Titrant	Molarity
HCl	0.0925

RPG #		Sample Vol. (mL)	2nd Equivalence Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base
20-1678		0.100	2.630	7.60	0.119	1.193

3rd Equivalence Point Titrant Vol. (mL)	pH	Found millimoles base	Molarity base
3.100	5.300	0.043	0.435


Sample TI082COMP-EFF (20-1678)
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 in mL
Series1

Project Number:	75433
Charge Code:	NE4456
ASR Number:	1097
Client:	S. Fiskum A. Westesen
Total Samples:	1 liquid

	RPL Numbers	Client IDs
Samples	20-1678	TI082-COMP-EFF

Analysis Procedure	RPG-CMC-386 Rev. 1, "Carbon Measured in Solids, Sludge, and Liquid Matrices"
Prep Procedure	None
Analyst	A. Carney
Analysis Date	September 9, 2020
CCV Standards	TIC/TOC CMS # 556337 and 556338
BS/LCS/MS Standards	TIC/TOC CMS # 556313 and 556496
Excel Data File	ASR-1097-Fiskum.xlsx
M&TE Numbers	Carbon System (WD36639, RPL/701)
	Balance : Sartorius R200D, S/N 30809774
All Analysis Records	5015_09-09-2020-103401.CSV

Andrew Carney 9/17/2020
Prepared By Date

Karl N Pool 9/21/20
Reviewed By Date

Table 1: TIC/TOC Results for ASR 1097

TIC in Sample **20-1678** (mg C/L):	5667
MDL (mg C/L):	113
EQL (mg C/L):	567
TOC in Sample **20-1678** (mg C/L):	2550
MDL (mg C/L):	113
EQL (mg C/L):	567
TIC in Sample **20-1678-Dup**:	5666
MDL (mg C/L):	113
EQL (mg C/L):	567
TOC in Sample **20-1678-Dup**:	2648
MDL (mg C/L):	113
EQL (mg C/L):	567
20-1678 TIC RPD:	0.01%
20-1678 TOC RPD:	3.74%

Sample Analysis/Results Discussion

One liquid sample was submitted under Analytical Service Request (ASR) 1097 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 determined first by acidifying with heated sulfuric acid, converting inorganic carbonates to CO_2 (i.e., TIC analysis), then the persulfate solids and silver-catalyst solution are added and the remaining organic carbon converted to CO_2 (i.e., TOC analysis). 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 all <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 94.9% and 95.1% recovery, and for the two TIC ICVs the results were 98.9% and 99.2% recovery, within the acceptance criterion of 90% to 110%. The TOC result for the CCV was 96.2% recovery and the TIC CCV was 90.5% 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 101.1% recovery and the TOC LCS/BS result was 96.7% 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 20-1678 TIC RPD was 0.01% and TOC was 3.74%. Both TIC and TOC 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 100.5% recovery and for the TOC, 93.9% recovery. The AS recovery for the TOC and TIC results meets the acceptance criterion of 75% to 125%.

Deviation from Procedure:

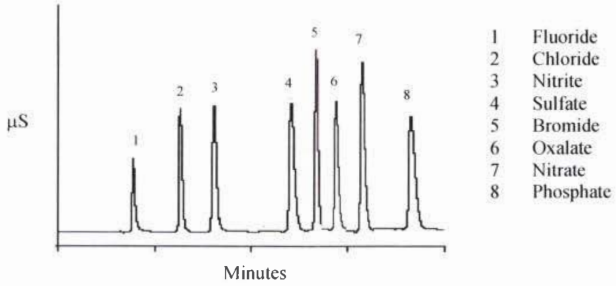
None

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 - Pacific Northwest National Laboratory
Analytical Support Operations – IC Report
PO Box 999, Richland, Washington 99352

Common Inorganic Anions
Dionex AS18 Column; Hydroxide Gradient



Client:	S Fiskum	***ASR #:***	1097
Project #:	75433	***# Samples:***	1 liquid
Charge Code:	NE4456		

Revision 1

*** RPL Number: 20-1678 ***

Procedure, Analysis, System, and Records Information

Analysis Procedure	RPG-CMC-212 Rev.2, "Determination of Common Anions by Ion Chromatography"
Prep Procedure	None
Analyst	JC Carter
Analysis Dates	08/20/2020-08/24/20
Calibration Date	08/19/2020
Cal/Ver Stds Prep Date	Cal 08/18/20 and Ver 08/18/20
Excel Data File	IC-0248 Fiskum.xls
M&TE Numbers	IC System (M&TE) WD81129 Balance: B725287790
All Analysis Records	Chemical Measurement Center 98620: RIDS IC System File (IC-0248)

Prepared By 9/28/20 Date

Reviewed By 9/28/20 Date

IC Report

Sample Results

See Attachment: Sample Results ASR 1097

Revision 1

The report has been revised to include the sample and duplicate results for oxalate in the portion of the results report where the sample and duplicate results are presented.

Sample Analysis/Results Discussion

One liquid sample was submitted to the Analytical Support Operations (ASO) laboratory for ion chromatography analysis under ASR 1097. The results are discussed in this report. The analytes of interest for the sample includes fluoride, chloride, nitrite, sulphate, nitrate, oxalate and phosphate. Multiple sample dilutions were required. The best result for each anion was chosen based on that which yielded the best quality control (QC) results and were still within the IC System QC Sample requirements listed below. The sample results are reported in µg/mL.

The estimated method detection limits (MDL) are provided for each analyte of interest measured and the MDLs have been adjusted for all analytical dilutions and processing factors. The MDLs are set at one-tenth the lowest calibration standard, which is defined as the estimated quantitation limit (EQL).

Data Limitations

There are no limitations regarding this data. All QC requirements were met.

Quality Control Discussion

The method performance is evaluated against the acceptance criteria established by Analytical Support Operations QA Plan ASO-QAP-001.

IC Workstation QC Results

The method performance is evaluated against the acceptance criteria established by Analytical Support Operations QA Plan ASO-QAP-001.

Process Blank (Dilution Blank): No analytes of interested were detected, thus meeting the ASO's QA Plan acceptance criteria of all analytes being <EQL.

Duplicate: The sample was analyzed in duplicate. The relative percent difference (RPD) is reported for all analytes which were measured at or above the EQL. The reported RPDs for analytes meeting this requirement were between 0% - 13%, meeting the ASO's QA Plan acceptance criteria of <20% for liquid samples.

Laboratory Control Sample (LCS): A routine instrument LCS was analyzed with recoveries ranging from 83.3% to 100.5%, meeting the acceptance criteria of 80% to 120%.

IC Report

Analytical Spike (AS) (Accuracy): Analytical spikes were prepared using all of the prepared dilutions of the two liquid samples by adding a known concentration of mid-range multi-mix standard, "CCV 081820". Where the spiking concentration exceeds 20% of the sample concentration, the AS recoveries ranged from 83% to 101% meeting the QA Plan acceptance criteria of 75% to 125%.

IC System QC Samples: Numerous calibration verification standards and calibration verification blanks were analyzed with each run. The results for the IC System QC samples (that bound the reported results for each analyte of interest) are within acceptance criteria of the ASO's QA Plan (i.e., verification standard recoveries from 90% to 110% and verification blank results <EQL or <5% of reported sample result).

Deviations from Procedure

None

General Comments

- The reported "Final Results" have been corrected for all dilutions performed on the sample during processing or analysis.
- For each anion, the instrument EQL is defined as the concentration of the lowest calibration standard and the instrument MDL is set at one-tenth of the EQL. The MDLs and EQLs reported for each sample are adjusted for the sample dilution factors (processing and analysis) and assume non-complex aqueous matrices. Matrix-specific MDLs or EQLs may be determined, when requested.
- Routine precision and bias are typically ±15% or better for non-complex aqueous samples that are free of interference.

Sample Results ASR 1097

			F			Cl			NO_2			SO_4		
RPL Number	Client Sample ID	Ext. Dil.	MDL µg/mL	Result µg/mL	DF	MDL µg/mL	Result µg/mL	DF	MDL µg/mL	Result µg/mL	DF	MDL µg/mL	Result µg/mL	DF
Dilution Blank	Dilution Blank		0.062	0.062	U	0.075	0.075	U	0.1	0.1	U	0.15	0.15	U
20-1678	TI082-COMP-EFF		5	5	U	390	3,900		2,100	63,600		97	2,190	

			C_2O_4			NO_3			PO_4		
RPL Number	Client Sample ID	Ext. Dil.	MDL µg/mL	Result µg/mL	DF	MDL µg/mL	Result µg/mL	DF	MDL µg/mL	Result µg/mL	DF
Dilution Blank	Dilution Blank		0.1	0.1	U	0.2	0.2	U	0.12	0.12	U
20-1678	TI082-COMP-EFF		65	230	J	4,200	117,000		9.7	838	

Sample QC Results ASR 1097

Sample/Replicate Precision Results

		F		Cl		NO_2		SO_4		C_2O_4		NO_3		PO_4	
RPL Number	Sample ID	µg/mL	RPD	µg/mL	RPD	µg/mL	RPD	µg/mL	RPD	µg/mL	RPD	µg/mL	RPD	µg/mL	RPD
20-1678	Sample	U	--	3,900	--	63,600	--	2,190	--	230	--	117,000	--	838	--
	Duplicate	U	N/A	3,900	0	63,800	0	2,500	13	270	N/A	117,000	0	818	2

Sample Spike Results - At IC Workstation

		F		Cl		NO_2		SO_4		C_2O_4		NO_3		PO_4	
RPL Number	Sample ID	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec
20-1678	Sample	U	--	3,900	--	63,600	--	2,190	--	230	--	117,000	--	838	--
	AS Sample	1.08	86	1.81	96	3.51	99	4.71	101	2.05	94	6.24	98	7.25	83

LCS/Blank Spike Results

Run ID	Sample ID	F % Rec	Cl % Rec	NO_2 % Rec	SO_4 % Rec	C_2O_4 % Rec	NO_3 % Rec	PO4 % Rec
8/20/2020 11:57	LCS	100.5	95.6	92.1	89.7	87.5	83.3	90.0

AS = Analytical Spike: Spike performed at IC Workstation on Liquid Samples.
LCS = Laboratory Control Sample (or Blank Spike)
RPD = Relative Percent Difference
%Rec = Percent Recovery
DF = Data Quality Flag

U = Not Detected Above Method Detection Limit (MDL)
J = Detected, Result are Qualitative: Result >MDL but <EQL (Estimated Quantitation Limit)
-- = Value Not Calculated or Place Holder for Blank Cell

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

Gamma Energy Analysis (GEA)

Project / WP#:	75433/NE4456
ASR#:	1097.00
Client:	SK Fiskum
Total Samples:	2

RPL ID	Client Sample ID
20-1677	TI082-COMP-FEED
20-1678	TI082-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:	November 5-6, 2020
Technician/Analyst:	T Trang-Le
Rad Chem Electronic Data File:	*20-1677 Fiskum.xlsx*
ASO Project 98620 File:	*File Plan 5872, T4.4 Technical (Radiochemistry), Gamma Calibration, daily checks, and maintenance records; and T3 standard certificates and preparation. Also, balance calibration and performance check records.*
M&TE Number(s):	*Detectors E,T*

Truc Trang-Le Digitally signed by Truc Trang-Le Date: 2020.11.19 10:25:05 -08'00' /

Prepare **Date**

Lawrence R Greenwood Digitally signed by Lawrence R Greenwood Date: 2020.11.20 09:51:00 -08'00' /

Reviewer **Date**

Page 1 of 3

SAMPLE RESULTS

Activities for all gamma emitters detected in this sample are presented in an attached Excel spreadsheet for ASR 1097.00. All sample results for target isotopes are reported in units of µCi/mL with estimates of the total propagated uncertainty reported at the 1-sigma level.

ASO Project File, ASR 1097.00 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

2 mL samples were sent to the counting room for GEA.

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 by ASO for gamma counting.

Required Detection Limits

There are no required detection limits for these samples.

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.

Battelle PNNL/NCE/ASO Radiochemistry Analysis Report

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. 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.

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 10 cm or more 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 1097.00.

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

filename 20-1677 Fiskum
11/18/2020

Client: SK Fiskum Project: 75433
ASR: 1097 WP: NE4456

Prepared by: Truc Trang-Le Digitally signed by Truc Trang-Le Date: 2020.11.19 08:54:50 -08'00'

Technical Reviewer: Lawrence R Greenwood Digitally signed by Lawrence R Greenwood Date: 2020.11.19 09:24:39 -08'00'

Procedure: RPG-CMC-450 Rev3, Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS)
Count date: November 5-6, 2020
M & TE: E, T

	Lab	Measured Gamma Emitters, µCi per mL ± 1s counting error							
Sample	ID	**Co-60**		**Cs-137**		**Eu-154**		**Am-241**	
TI082-COMP-FEED	20-1677	< 5.8E-4		**1.13E+2**	**± 2%**	< 2.7E-3		< 9.5E-2	
TI082-COMP-EFF	20-1678	**4.05E-4**	**± 2%**	**5.36E-2**	**± 2%**	**7.52E-5**	**± 3%**	**2.57E-4**	**± 26%**

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#:	75433 / NE4456
ASR#:	1097.00
Client:	S. Fiskum
Total # of Samples:	12

RPL ID	Client Sample ID	RPL ID	Client Sample ID
20-1677	TI082-COMP-FEED	20-1683	TI082-L-F10-A
20-1678	TI082-COMP-EFF	20-1684	TI082-L-F12-A
20-1679	TI082-L-F2-A	20-1685	TI082-L-F14-A
20-1680	TI082-L-F4-A	20-1686	TI082-L-F16-A
20-1681	TI082-L-F6-A	20-1687	TI082-L-F22-A
20-1682	TI082-L-F8-A	20-1688	TI082-L-F26-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-19 (Sr-90)
Separation Date:	012/11/20 @ 08:15
Technician/Analyst:	L. Darnell
Analysis Procedure:	RPG-CMC-474, Rev. 1, *Measurement of Alpha and Beta Activity by Liquid Scintillation Spectrometry*
Reference Date:	12/11/20
Analysis Date or Date Range:	12/11/20 (first count), 12/14/20 (second count)
Technician/Analyst:	LP Darnell & T. Trang-Le
Rad Chem Electronic Data File:	RPG-RC\PNL\Projects\Backup files\Backup 20\20-1677 Fiskum.xls
ASO Project 98620 File:	File Plan 5872: T 75433: 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.

Karl N Pool Digitally signed by Karl N Pool Date: 2020.12.16 11:15:14 -08'00' /

Preparer **Date**

Truc Trang-Le Digitally signed by Truc Trang-Le Date: 2020.12.16 11:18:32 -08'00' /

Reviewer **Date**

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report

SAMPLE RESULTS

See attached data report, Sample Results for ASR 1097.00. All sample data are reported in µCi/mL with a 1-σ uncertainty (see Comments).

Sample preparation, separation, mounting, and counting

The 12 samples submitted on the ASR were all diluted with acid from direct sample and analyzed for Sr-90 by chemical separation and liquid scintillation counting. All the samples were prepared in RPL/420. 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.

<u>Laboratory Preparation Blank (PB):</u>

> The activity level of Sr-90 present in the laboratory separation blank (2.67 E-7 µCi/mL) is both below the lowest activity present in the samples (2.10 E-4 µCi/mL or higher) and less than sample MDC (2.3 E-6 µCi/mL) meeting the acceptance criteria of less than 5% of the sample activity or less than the sample MDC.

<u>Blank Spike (BS) – Reagent Spike (RS):</u>

> The RS recovery of 99% meets the procedure acceptance criteria of 80% to 120% recovery.

<u>Matrix Spike (MS):</u>

> The MS recovery of 100% 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 20-1678 (TI082-COMP-EFF).

<u>Duplicate -- Relative Percent Difference (RPD):</u>

> Duplicate results 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 3.3% RPD; thus meeting the ≤ 20% requirement.

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 1097.00

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

Tc-99 Analysis

Project / WP#:	75433/NE4456
ASR#:	1097
Client:	S. Fiskum
Total # of Samples:	2

RPL ID	Client Sample ID
20-1677	TI082-COMP-FEED
20-1678	TI082-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* ☐ Other: Soil Leaching using equal volumes of 30% H_2O_2 and concentrated ammonium hydroxide.
Pre-dilution Prior to Radiochemical Processing?	☒ No ☐ Yes -- *example 2 mL to 100 mL; 50x dilution*
Total Alpha and Beta Preparation Procedure:	RPG-CMC-4001, Rev. 1, Source Preparation For Gross Alpha and Gross Beta analyses.
Technician/Analyst:	LP Darnell, (11/12/2020)
Spike Standard ID's	R-687-a-11 (Pu-239), R693-b-16 (Sr-90)
Analysis Procedure	RPG-CMC-408, Rev. 2, *Total Alpha and Beta Analysis*
Technician/Analyst:	LP Darnell, CZ Soderquist and T. Trang-Le
RadioChemical Preparation Procedure:	RPG-CMC-432, Rev. 0, *Technicium-99 Analysis*
Technician/Analyst:	LP Darnell, 12/15/20
Spike and Tracer Standard ID's:	R-714-a-3 (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:	December 16 and 17, 2020
Technician/Analyst:	LPDarnell
Analysis Data (File):	RPG-RC\PNL\Projects\Backup files\Backup 20\20-1677 Fiskum.xls
CMC Project 98620 File:	File Plan 5872: 75433: 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
Digitally signed by Karl N Pool
Date: 2020.12.18 14:17:44 -08'00' /

Preparer **Date**

Truc Trang-Le
Digitally signed by Truc Trang-Le
Date: 2020.12.18 14:22:56 -08'00' /

Reviewer **Date**

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Sample Results

See attached data report, Sample Results for ASR 1097. All data are reported in units of µCi/mL with a 1-σ uncertainty (see comments).

Sample Preparation, Separation, Mounting and Counting Methods

Two liquid samples submitted under ASR 1097 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 December 16 and 17, 2020; no decay corrections were made.

Although not formally requested by the ASR, gross beta analyses were performed on each sample to obtain information to estimate aliquot sizes for other analyses and for checking the internal consistency of the Tc-99 data. The gross beta results are included in the data tables as supplemental information only. The Gross beta activity was measured by evaporating small aliquots of the acid digestion leachate onto counting planchets per procedure RPG-CMC-4001 and counting per procedure RPG-CMC-408.

QUALITY CONTROL RESULTS

Quality control (QC) samples prepared in laboratory 420 include a process blank (PB) and sample duplicates. Additional QC samples were prepared prior to alpha counting including a laboratory blank, a reagent blank spike (RS, Tc-99), and addition of Tc-99 standard to a separate aliquot of one of the samples was selected as the matrix spike (MS).

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:

Tracers are not used for Tc-99 analysis.

Laboratory Preparation Blank (PB):

The activity level of Tc-99 present in the laboratory separation blank (2.8E-5 µCi/mL) is both below the activity present in the samples (1.09E-1 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.

Reagent Spike (RS):

The RS recovery of 98% (Tc-99) meets the acceptance criteria of 80% to 120% recovery.

Matrix Spike (MS):

A matrix spike sample was prepared using sample 20-1678 (TI082-COMP-EFF). The sample activity was significantly higher (~10x) 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 20-1678 (TI082-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 7% 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.

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

Attachment: Data Report -- Sample Results for ASR 1097.

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

Neptunium 237 Analysis

Project / WP#:	75433/NE4456
ASR#:	1097.00
Client:	S. Fiskum
Total # of Samples:	12

RPL ID	Client Sample ID	RPL ID	Client Sample ID
20-1677	**TI082-COMP-FEED**	**20-1683**	**TI082-L-F10-A**
20-1678	**TI082-COMP-EFF**	**20-1684**	**TI082-L-F12-A**
20-1679	**TI082-L-F2-A**	**20-1685**	**TI082-L-F14-A**
20-1680	**TI082-L-F4-A**	**20-1686**	**TI082-L-F16-A**
20-1681	**TI082-L-F6-A**	**20-1687**	**TI082-L-F22-A**
20-1682	**TI082-L-F8-A**	**20-1688**	**TI082-L-F26-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-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*
Total Alpha and Beta Preparation Procedure:	RPG-CMC-4001, Rev. 1, *Source Preparation For Gross Alpha and Gross Beta analyses.*
Technician/Analyst:	LP Darnell, (11/12/2020)
Spike Standard ID's	R-687-a-11 (Pu-239), R693-b-16 (Sr-90)
Analysis Procedure	RPG-CMC-408, Rev. 2, *Total Alpha and Beta Analysis*
Technician/Analyst:	LP Darnell, CZ Soderquist and T. Trang-Le
Neptunium Separation Procedure:	RPG-CMC-4017, Rev. 0, *Analysis of Environmental Water Samples for Actinides and Strontium- 90*
Technician/Analyst:	LP Darnell, (12/10/2020)
Spike Standard ID's:	R-686-a-4 (Np-237)
Co-Precipitation Procedure:	RPG-CMC-496, Rev. 1, *Coprecipitation Mounting of Actinides for Alpha Spectroscopy*
Technician/Analyst:	LP Darnell, (12/10/2020)
Analysis Procedure:	RPG-CMC-422, Rev. 2, *Solutions Analysis: Alpha Spectrometry*
Reference Date:	Same as counting dates
Analysis Date or Date Range:	December 11-14,2020
Technician/Analyst:	CS Soderquist & TL Trang-Le
	RPG-RC\PNL\Projects\Backup files\Backup 20\20-1677 Fiskum.xls
CMC Project 98620 File:	File Plan 5872: 75433: 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 – A26, A27, A28, A31, A32 – See attached M&TE list

Truc Trang-Le Digitally signed by Truc Trang-Le Date: 2020.12.16 14:16:09 -08'00' /
Preparer **Date**

Karl N Pool Digitally signed by Karl N Pool Date: 2020.12.16 14:20:11 -08'00' /
Reviewer **Date**

Page 1 of 3

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report

Sample Results

See attached data report, Sample Results for ASR 1097.00. 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

Twelve samples submitted under Analytical Service Request (ASR) 1097 were analyzed for neptunium by Alpha Spectrometry. All the samples were prepared in RPL/420, only Np-AEA is presented in this report.

The Np was separated from the "as received" 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 December 11-14, 2020; 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 (-1.21E-8 µCi/mL) is below the activity present in the samples and less than lowest sample MDC (2.6E-7 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 89% meets the acceptance criteria of 80% to 120% recovery.

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report

Matrix Spike (MS):

The MS recovery of 84% meets the acceptance criterion of 75% to 125% recovery. The matrix spike samples was prepared by adding a known Np-237 standard quantity to an aliquot of the diluted sample. Sample number 20-1678 (TI082-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%. In this case, both sample results are less than 5x the MDA. The duplicate RPD is not calculated when one or both results are less than 5x the MDA.

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 1097.00.

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

Plutonium 238, 239+240 Analysis

Project / WP#:	75433/NE4456
ASR#:	1097.00
Client:	SK Fiskum
Total # of Samples:	12

RPL ID	Client Sample ID	RPL ID	Client Sample ID
20-1677	TI082-COMP-FEED	20-1683	TI082-L-F10-A
20-1678	TI082-COMP-EFF	20-1684	TI082-L-F12-A
20-1679	TI082-L-F2-A	20-1685	TI082-L-F14-A
20-1680	TI082-L-F4-A	20-1686	TI082-L-F16-A
20-1681	TI082-L-F6-A	20-1687	TI082-L-F22-A
20-1682	TI082-L-F8-A	20-1688	TI082-L-F26-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 (12/07/20)
Co-Precipitation Procedure:	RPG-CMC-496, Rev. 1, Coprecipitation Mounting of Actinides for Alpha Spectroscopy
Technician/Analyst:	LP Darnell (12/07/20)
Spike and Tracer Standard ID's:	R-687-a-11 (Pu-239), R-719-2 (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:	December 07-10, 2020
Technician/Analyst:	T. Trang-Le & CZ Soderquist
Analysis Data (File):	RPG-RC\PNL\Projects\Backup files\Backup 20\20-1677 Fiskum.xls
CMC Project 98620 File:	File Plan 5872: T 75433: 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: A26, A27, A28, A31, and A32

Truc Trang-Le Digitally signed by Truc Trang-Le Date: 2020.12.16 13:02:54 -08'00' /
Preparer **Date**

Karl N Pool Digitally signed by Karl N Pool Date: 2020.12.16 13:07:38 -08'00' /
Reviewer **Date**

Page 1 of 3

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report

Sample Results

See attached data report, Sample Results for ASR 1097.00. 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) 1097.00 were analyzed for plutonium isotopes by Alpha Spectrometry. All the samples were prepared in RPL/420, only Pu-AEA is presented in this report.

The Pu was separated from the "as received" 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 December 07-10, 2020 ; 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 77% to 102%.

Laboratory Preparation Blank (PB):

The activity levels of Pu-239/240 and Pu-238 present in the laboratory preparation blank (8.5E-7 μCi/mL, Pu-239/240 and -3.4E-7 μCi/mL, Pu-238) are both below the activities present in the samples (1.50E-5 μCi/mL Pu-239/240 and 2.47E-6 μCi/mL Pu-238 or higher). The blank results for Pu-239/240 is above 5% of the sample activity for samples; TI082-COMP-EFF (5.6%) and TI082-L-F2-A (5.4%) and greater than the MDA of 7.7E-7 μCi/mL for both samples. The remainder the Pu-239/240 and Pu-238 the blank activities are less than 5% the activity present in the samples and less than the sample MDA's thus meeting the blank acceptance criteria.

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

The RS recovery of 94% meets the acceptance criteria of 80% to 120% recovery.

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report

Matrix Spike (MS):

The MS recovery of 97% meets the acceptance criterion of 75% to 125% recovery. Note: the MS sample was prepared by adding a known Pu-239 standard quantity to an aliquot of the diluted sample. Sample number 20-1678 (TI082-COMP-EFF) was selected as the matrix spike sample.

Duplicate -- Relative Percent Difference (RPD):

Sample 20-1678 (TI082-COMP-EFF) was selected as the duplicate sample. The Pu-238 sample and duplicate RPD of 7% and the Pu-239/240 sample and duplicate RPD of 8% is within the acceptance limit of $\leq$ 20% RPD.

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 1097.00.

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

Am-241 Analysis

Project / WP#: 75433/NE4456
ASR#: 1097.00
Client: S. Fiskum
Total # of Samples: 2

RPL ID	Client Sample ID
20-1677	**TI082-COMP-FEED**
20-1678	**TI082-COMP-EFF**

Analysis Type:	AEA – Am-241
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* ☐ Other:
Pre-dilution Prior to Radiochemical Processing?	☐ No
	☒ Yes -- *example 2 mL to 100 mL; 50x dilution*
Americium Separation Procedure:	RPG-CMC-4017, Rev. 0, *Analysis of Environmental Water Samples for Actinides and Strontium-90*
Spike and Tracer Standard ID's:	R-542-a-8 (Am-241), R-718-3 (Am-243 tracer)
Co-Precipitation Procedure:	RPG-CMC-496, Rev. 1, *Coprecipitation Mounting of Actinides for Alpha Spectroscopy*
Technician/Analyst:	LP Darnell (12/07/2020)
Analysis Procedure:	RPG-CMC-422, Rev. 2, *Solutions Analysis: Alpha Spectrometry*
Reference Date:	Same as analyses dates
Analysis Date or Date Range:	December 10-11, 2020
Technician/Analyst:	T. Trang-Le & CZ Soderquist
Analysis Data (File):	RPG-RC\PNL\Projects\Backup files\Backup20\ 20-1677 Fiskum.xlsx
CMC Project 98620 File:	File Plan 5872: 75433 Sample preparation and analysis records; Alpha Detector calibration, calibration verification checks, and maintenance records; and standard certificates and preparation. Also balance calibration and instrument performance checks.
M&TE Number(s):	Ortec AEA detectors; 32 counters, see attached M&TE list; A26, A27, A28, A31, and A32

Truc Trang-Le Digitally signed by Truc Trang-Le Date: 2020.12.16 13:09:04 -08'00' /
Preparer **Date**

Karl N Pool Digitally signed by Karl N Pool Date: 2020.12.16 13:16:44 -08'00' /
Reviewer **Date**

Sample Results

Sample activity concentrations for Am-241 samples are presented in an attached data report for ASR 1097.00. Results are reported in units of µCi/mL with estimates of the total propagated uncertainty reported at the 1-sigma level.

Sample Preparation, Separation, Mounting and Counting Methods

Americium was chemically separated from the solutions as received, mounted for alpha spectrometry by coprecipitation, and measured by alpha spectrometry against Am-243 tracers. Uncertainty is one standard deviation of propagated uncertainty. The americium data shown on this report were measured using an accurate counting geometry and are not affected by other radionuclides in the sample.

The americium blank was calculated using the same dilutions used for the accompanying samples, so that the blanks would be directly comparable to the samples.

Reagent spike (RS) samples and preparation blank (PB) samples were also prepared. After the addition of appropriate tracers, the samples were chemically adjusted for anion exchange separations.

Samples were processed as a single batch. The Am was separated from the leachate by anion exchange using procedure RPG-CMC-4017. The separated Am fractions were then mounted for alpha spectrometry by co-precipitation using procedure RPG-CMC-496, and then counted using alpha spectrometry using procedure RPC-CMC-422. The samples were counted on December 10-11, 2020; no decay corrections were made. Sample digestion, separations and sample mounting were conducted in RPL/420 laboratory.

QUALITY CONTROL RESULTS

Quality control (QC) samples prepared in the RPL/420 laboratory included blank (BLK) sample, reagent blank spike (RS) sample, and matrix spike (MS) sample. The QC sample results for Am-241 have been evaluated and are discussed below. A summary of the analysis results, including QC sample performance, is given in the attached data report.

<u>Tracer:</u>

> The Am-243 tracer is added to every sample prior to acid digestion and Am separation. The Am-243 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 Am-243 tracer counting statistics were acceptable for all samples. The tracer recoveries ranged from 83% to 96%.

Laboratory Preparation Blank (PB):

The activity level of Am-241 present in the laboratory preparation blank (9.2E-7 µCi/mL, Am-241) is less than 5% of the activity present in the samples, meeting the criteria of less than 5% of the sample activity or less than the sample MDC.

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

The RS recovery for Am-241 was 100%, and these results meet 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. The matrix spike samples was prepared by adding a known Np-237 standard quantity to an aliquot of the diluted sample. Sample number 20-1678 (TI082-COMP-EFF) was selected as the matrix spike sample.

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

Sample 20-1678 (TI082-COMP-EFF) was selected as the duplicate sample. The Am-241 sample and duplicate RPD of 11% are within the acceptance limit of ≤ 20% RPD.

Instrument Quality Control

Alpha counters are initially calibrated 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.

Assumption and Limitations of the Data

None

Attachment: Data Report – ASR 1097.00.

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

filename 20-1677 Fiskum
12/18/2020

Client: SK Fiskum Project: 75433
ASR: 1097 WP: NE4456

Prepared by: C Soderquist 12-18-2020

Technical Reviewer: T Trang-le 12/18/20

Procedures:	RPG-CMC-4001 Rev. 1 Source Preparation For Gross Alpha and Gross Beta Analysis
	RPG-CMC-408 Rev 2, Total Alpha and Total Beta Analysis
	RPG-CMC-496 Rev 1, Coprecipitation Mounting of Actinides for Alpha Spectrometry
	RPG-CMC-422 Rev 2, Solutions Analysis: Alpha Spectrometry
	RPG-CMC-432 Rev 0, Technicium-99 Analysis
M&TE:	LB4100 gas proportional counters
	Perkin Elmer TriCarb model 3100TR liquid scintillation spectrometer

		Measured Activity, µCi/mL ± 1s							
		Gross Beta		Sr-90		Tc-99		Cs-137	
TI082-COMP-FEED	20-1677	1.26E+2	± 4%	6.90E-1	± 1%	1.13E-1	± 3%	1.13E+2	± 2%
TI082-COMP-EFF	20-1678	1.68E-1	± 4%	7.35E-4	± 7%	1.09E-1	± 3%	5.36E-2	± 2%
	20-1678 Dup	1.68E-1	± 4%	7.11E-4	± 7%	1.01E-1	± 3%		
		0.1%		3.3%		7%			
TI082-L-F2-A	20-1679	1.15E-1	± 4%	3.91E-4	± 12%	--			
TI082-L-F4-A	20-1680	1.10E-1	± 4%	5.24E-4	± 9%	--			
TI082-L-F6-A	20-1681	1.39E-1	± 4%	1.14E-3	± 5%	--			
TI082-L-F8-A	20-1682	2.37E-1	± 4%	2.03E-3	± 3%	--			
TI082-L-F10-A	20-1683	7.38E-1	± 4%	3.98E-3	± 2%	--			
TI082-L-F12-A	20-1684	4.06E+0	± 4%	8.72E-3	± 11%	--			
TI082-L-F14-A	20-1685	1.36E+1	± 4%	1.58E-2	± 7%	--			
TI082-L-F16-A	20-1686	3.11E+1	± 4%	3.62E-2	± 13%	--			
TI082-L-F22-A	20-1687	8.70E+1	± 4%	9.34E-2	± 6%	--			
TI082-L-F26-A	20-1688	1.24E+2	± 4%	2.41E-1	± 19%	--			
	Lab blank	-1.4E-4	± 76%	2.6E-7	± 166%	2.8E-5	± 23%		
	Reagent spike	98%		99%		98%			
	Matrix spike	127%		100%		[spike was too small for the sample activity]			

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

filename 20-1677 Fiskum
12/11/2020

Client: SK Fiskum
ASR: 1097

Project: 75433
WP: NE4456

Prepared by: C. Soderquist 12-15-2020

Technical Reviewer: T Trang-Le 12/15/20

Procedures:
RPG-CMC-4001, Rev. 1 Source Preparation For Gross Alpha and Gross Beta Analysis
RPG-CMC-408 Rev 2, Total Alpha and Total Beta Analysis
RPG-CMC-496, Rev 1, Coprecipitation Mounting of Actinides for Alpha Spectrometry
RPG-CMC-422, Rev 2, Solutions Analysis: Alpha Spectrometry

M&TE: Ludlum, Alpha AEA

		Measured Activity, µCi/mL ± 1s							
Sample	ID	**Gross Alpha**		**Np-237**		**Pu-238**		**Pu-239+240**	
TI082-COMP-FEED	20-1677	1.39E-3	± 394%	6.69E-6	± 7%	6.37E-6	± 11%	3.94E-5	± 4%
TI082-COMP-EFF	20-1678	1.10E-4	± 64%	9.73E-7	± 22%	2.54E-6	± 22%	1.50E-5	± 8%
	20-1678 Dup	1.48E-4	± 47%	1.46E-6	± 16%	2.73E-6	± 18%	1.62E-5	± 7%
	RPD	--		--		7%		8%	
TI082-L-F2-A	20-1679	2.54E-4	± 32%	1.04E-6	± 18%	4.13E-6	± 14%	1.58E-5	± 7%
TI082-L-F4-A	20-1680	2.65E-4	± 33%	1.62E-6	± 14%	4.56E-6	± 13%	2.03E-5	± 6%
TI082-L-F6-A	20-1681	2.24E-4	± 38%	2.46E-6	± 12%	6.25E-6	± 11%	2.03E-5	± 6%
TI082-L-F8-A	20-1682	2.72E-4	± 32%	2.54E-6	± 12%	3.96E-6	± 16%	1.77E-5	± 7%
TI082-L-F10-A	20-1683	3.05E-4	± 30%	3.22E-6	± 11%	4.67E-6	± 13%	2.25E-5	± 6%
TI082-L-F12-A	20-1684	6.59E-5	± 802%	3.12E-6	± 10%	5.81E-6	± 11%	2.28E-5	± 6%
TI082-L-F14-A	20-1685	-3.13E-4	± 163%	3.56E-6	± 10%	4.20E-6	± 13%	2.16E-5	± 6%
TI082-L-F16-A	20-1686	-1.52E-4	± 386%	4.36E-6	± 9%	3.27E-6	± 17%	2.08E-5	± 6%
TI082-L-F22-A	20-1687	-4.23E-3	± 104%	4.62E-6	± 8%	2.47E-6	± 22%	2.08E-5	± 6%
TI082-L-F26-A	20-1688	3.24E-4	± 1720%	5.16E-6	± 8%	3.87E-6	± 14%	2.38E-5	± 5%
	Lab blank	5.0E-5	± 118%	-1.2E-8	± 524%	-3.4E-7	± 82%	8.5E-7	± 43%
	Reagent spike	97%		89%				94%	
	Matrix spike	72%		84%				97%	

Sample	lab ID	Am-241		Cm-242		Cm-243+244	
TI082-COMP-FEED	20-1677	2.66E-4	± 2%	7.60E-7	± 34%	6.41E-6	± 11%
TI082-COMP-EFF	20-1678	2.17E-4	± 3%	5.31E-7	± 46%	4.80E-6	± 13%
	20-1678 Dup	2.42E-4	± 2%	1.23E-6	± 25%	6.90E-6	± 10%
	RPD	11%		--		36%	
TI082-L-F2-A	20-1679	--		--		--	
TI082-L-F4-A	20-1680	--		--		--	
TI082-L-F6-A	20-1681	--		--		--	
TI082-L-F8-A	20-1682	--		--		--	
TI082-L-F10-A	20-1683	--		--		--	
TI082-L-F12-A	20-1684	--		--		--	
TI082-L-F14-A	20-1685	--		--		--	
TI082-L-F16-A	20-1686	--		--		--	
TI082-L-F22-A	20-1687	--		--		--	
TI082-L-F26-A	20-1688	--		--		--	
	Lab blank	9.2E-7	± 42%	3.0E-8	± 474%	-7.4E-8	± 173%
	Reagent spike	100%		--		--	
	Matrix spike	102%		--		--	

Page 2 of 2

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 Sandra k. Fisk
Print Name Sandra K Fiskum
Phone ______ MSIN ______

Project Number: 75433
Work Package: NE445G

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)

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

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

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:** 8/21/2020
(Note: Priority rate charge for < 10 business day turn-around time)
- **Negotiated Commitment Date:** 9/30/20
(*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: 1097
or, Previous RPL Number: ______

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

Send Report To: SK Fiskum **MSIN** ______
AM Westesen **MSIN** ______
Additional or Special Instructions ______

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

Date Delivered: 8/11/20
Delivered By (optional) ______
Time Delivered: ______
Group ID (optional) ______
CMC Waste Sample? ☒ No ☐ Yes

Received By: T Trang-Le
ASR Number: 1109 Rev.: 00
RPL Numbers: (20-1803)
(first and last)

ASO Work Accepted By: KN Pool **Signature/Date:** Karl N Pool 8/12/20

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 RPL Number	Customer Sample ID	Sample Description (& Matrix, if it varies)	Analysis Requested	ASO Staff Use Only Test	ASO Staff Use Only Library
20-1803	TI082-Flush-solids	solids from flushing fluid	acid digest		
		from CST columns	ICP-OES (Al, Ca, Cr,		
			Fe, K, Na, Ni, P, Pb, S,		
			Sr, Ti, Zn, Zr)		

ASR # 1109 Rev.: 00

Page 1 of 1

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

Project / WP#:	75433 / NE4456
ASR#:	1109
Client:	S. Fiskum
Total Samples:	1 (solid)

ASO Sample ID	Client Sample ID	Sample Description
20-1803	TI082-Flush Solids	Solids from flushing fluid from CST columns

Sample Preparation: RPG-CMC-129, Rev. 0. "HNO3-HCl Acid Extraction of Solids Using a Dry-Block Heater", performed by L. Darnell on 09/17/20. Simple dilution of the dissolved sample in 5% v/v HNO_3 performed by J. Carter on 09/18/20.

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:**	09/18/2020	**ICP File:**	C0858

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

Jake Carter
Report Preparer

09/23/2020
Date

Denis Cherkasov
Review and Concurrence

09/23/2020
Date

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

One solid sample was submitted under Analytical Service Request (ASR) 1109 and analyzed by ICP-OES. The samples were prepared following RPL procedure RPG-CMC-129, Rev. 0. "HNO3-HCl Acid Extraction of Solids Using a Dry-Block Heater". All samples were then diluted in 5% HNO3 prior to analysis. Neither the sample nor any of the dilutions were filtered.

All sample results are reported on a mass per unit volume basis (μg/g) 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. 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 also passed these criteria.

Blank Spike (BS):

A 50:50 mixture of the MCVA and MCVB solutions was analyzed as the blank spike. Recovery values are listed for all analytes included in the BS that were measured at or above the EQL. Recovery values for the AOI meeting this requirement were within the acceptance criterion of 80% to 120%.

Laboratory Control Sample (LCS):

A reagent spike (RS) sample (reagents and spikes) was prepared as an LCS 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 91% to 105% and were within the acceptance criterion of 80% to 120%.

Replicate Relative Percent Difference (RPD):

A replicate of sample 20-1803 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 0.2% to 2.4% and were within the acceptance criterion of ≤35% for solid samples.

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, with exception of closing CCB where Sulfur (S) recovery was at 86%.

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.

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

An analytical spike (A Component) was conducted on sample 20-1803. 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 were 93% to 101% meeting the acceptance criterion of 80% to 120%. Silicon (Si), did not meet the acceptance criterion with a recovery of 127%.

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

An analytical spike (B Component) was conducted on sample 20-1803. 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 value for the AOI meeting this requirement was 88% and within the acceptance criterion of 80% to 120%.

Matrix-Spike (MS) Sample:

No matrix spike sample was required to be prepared for the samples.

Serial Dilution (SD):

Five-fold serial dilution was conducted on sample 20-1803. 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 0.5% to 8.7% and were within the acceptance criterion of ≤10%.

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.

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		Run Date >	9/18/2020	9/18/2020	9/18/2020	9/18/2020
		Process Factor >	1.0	1032.6	1032.6	1032.6
			405 diluent	BLK-1803	20-1803	
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Lab Diluent	Reagent Blank	TI082-Flush Solids	TI082-Flush Solids
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/g)	(µg/g)	(µg/g)
0.0048	0.048	Al	--	[32]	41,800	42,600
0.0052	0.052	Ca	[0.0076]	[20]	4,820	4,910
0.0021	0.021	Cr	--	--	61,100	62,500
0.0017	0.017	Fe	--	[2.6]	8,000	8,150
0.0134	0.134	K	[0.017]	[110]	1,890	1,890
0.0072	0.072	Na	--	--	135,000	138,000
0.0041	0.041	Ni	--	[5.4]	28,900	29,400
0.0371	0.371	P	--	--	[250]	[190]
0.0257	0.257	Pb	--	--	3,550	3,540
0.1089	1.089	S	--	--	[500]	--
0.0072	0.072	Si	[0.012]	[31]	5,600	5,590
0.0004	0.004	Ti	--	--	5,170	5,270
0.0027	0.027	Zn	--	36.7	952	969
0.0013	0.013	Zr	--	--	1,890	1,930
Other Analytes						
0.0021	0.021	Ag	--	[4.0]	[5.0]	[5.5]
0.0647	0.647	As	--	--	[160]	[86]
0.0048	0.048	B	[0.0087]	[15]	293	289
0.0001	0.001	Ba	[0.0002]	11.1	549	561
0.0001	0.001	Be	--	--	7.96	8.01
0.0215	0.215	Bi	[0.048]	[49]	[36]	[85]
0.0013	0.013	Cd	--	--	689	694
0.0082	0.082	Ce	[0.013]	[12]	[83]	89.5
0.0038	0.038	Co	--	--	[20]	[25]
0.0021	0.021	Cu	--	--	1,090	1,090
0.0023	0.023	Dy	--	[2.6]	--	--
0.0008	0.008	Eu	--	--	[6.0]	[5.6]
0.0018	0.018	La	--	--	116	116
0.0014	0.014	Li	--	--	76.2	80.7
0.0017	0.017	Mg	--	[5.9]	42,800	43,800
0.0002	0.002	Mn	--	--	398	404
0.0056	0.056	Mo	--	[7.6]	--	[6.9]
0.0114	0.114	Nd	--	--	510	514
0.0050	0.050	Pd	--	--	89.7	85.1
0.0143	0.143	Rh	--	--	--	--
0.0070	0.070	Ru	--	--	[9.6]	[11]
0.0671	0.671	Sb	--	--	[270]	[220]
0.0987	0.987	Se	--	--	--	--
0.0267	0.267	Sn	--	--	--	[28]
0.0002	0.002	Sr	--	[0.30]	22.1	23.0
0.0331	0.331	Ta	--	--	--	--
0.0181	0.181	Te	--	[20]	[57]	[90]
0.0076	0.076	Th	--	--	185	185
0.0291	0.291	Tl	[0.049]	--	--	--
0.0376	0.376	U	--	--	[73]	[65]
0.0012	0.012	V	--	[3.3]	[9.2]	[9.5]
0.0128	0.128	W	[0.014]	--	--	--
0.0006	0.006	Y	--	--	30.8	31.0

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%.

Results from C0858 ASR-1109 Fiskum.xlsm

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QC Performance 9/18/2020

Criteria >	≤ 35%	80%-120%	80%-120%	80%-120%	80%-120%	≤ 10%
QC ID >	20-1803 Rep	BS	LCS	20-1803 + PS-A	20/1803 + PS-B	20/1803 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Al	1.9	99	104	100		0.5
Ca	1.9	100	101	99		1.8
Cr	2.4	97	100	nr		1.2
Fe	1.8	101	103	100		0.5
K	0.2	96	100	100		3.3
Na	2.0	100	101	98		0.1
Ni	1.9	99	102	nr		1.4
P		98	101	98		
Pb	0.4	98	103	93		8.7
S		96	91		88	
Si	0.2	98	91	127		1.2
Ti	2.0	100	104	98		1.1
Zn	1.7	97	101	95		7.8
Zr	2.0	99	105	101		1.2
Other Analytes						
Ag		97		98		
As		106		98		
B	1.3	97	103	96		1.7
Ba	2.1	100	103	99		0.3
Be	0.6	99	104	101		0.5
Bi		89	75	90		
Cd	0.7	95	102	95		0.8
Ce		97	99		97	
Co		99		97		
Cu	0.2	99	102	102		2.0
Dy		104			105	
Eu		102			101	
La	0.2	101	106		102	2.8
Li	5.8	103	106	106		1.6
Mg	2.4	100	107	101		0.9
Mn	1.6	100	104	98		1.2
Mo		97	99	96		
Nd	0.7	103	105		102	
Pd	5.2	94			92	
Rh		96			99	
Ru		98			98	
Sb		101		101		
Se		98		101		
Sn		94		92		
Sr	3.8	96	107	104		0.7
Ta		99		97		
Te		98			97	
Th	0.3	103	105		101	
Tl		91		94		
U		102	103		101	
V		98	103	98		
W		94	97	95		
Y	0.3	98		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.

Results from C0858 ASR-1109 Fiskum.xlsm

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