

PNNL-28780, Rev. 0 RPT-DFTP-015, Rev. 0

Fiscal Year 2019 Filtration of Hanford Tank AP-107 Supernatant

August 2019

JGH Geeting JR Allred

AM Rovira RA Peterson



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

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

PACIFIC NORTHWEST NATIONAL LABORATORY operated by BATTELLE for the UNITED STATES DEPARTMENT OF ENERGY under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062; ph: (865) 576-8401 fax: (865) 576-5728 email: <u>reports@adonis.osti.gov</u>

Available to the public from the National Technical Information Service 5301 Shawnee Rd., Alexandria, VA 22312 ph: (800) 553-NTIS (6847) email: orders@ntis.gov <<u>https://www.ntis.gov/about</u>> Online ordering: <u>http://www.ntis.gov</u>

PNNL-28780, Rev. 0 RPT-DFTP-015, Rev. 0

Fiscal Year 2019 Filtration of Hanford Tank AP-107 Supernatant

August 2019

JGH Geeting JR Allred AM Rovira RA Peterson

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

Pacific Northwest National Laboratory Richland, Washington 99354

Executive Summary

Bench-scale filtration testing of 9 liters of 241-AP-107 supernatant was conducted using two different filters in the hot cells of the Radiochemical Processing Laboratory at Pacific Northwest National Laboratory. The following filters were tested:

- Mott inline filter Model 6480 (media grade 5) (also known as the backpulsed dead-end filter, BDEF)
- Mott 70-mm disc filter (media grade 5) (also known as the dead-end filter, DEF)

The BDEF was used to filter approximately 7 liters of AP-107 at a targeted flux of 0.065 gpm/ft² and exhibited no measurable pressure increase during filtration. The BDEF was backpulsed after 17.5 hours of filtration and no solids were observed in the backpulse concentrate.

The DEF was used to filter 2 liters of AP-107 feed and no increase in filter resistance was measured and no solids were observed on the filter at the conclusion of filtration. Results are in contrast to similar filtration testing of 241-AP-107 supernatant received in fiscal year 2018, where solids were observed and collected and caused a measurable increase in filtration resistance.¹

Both filters used in testing were Mott media grade 5 sintered metal filters, which is the filter manufacturer, type, and grade planned for the tank side cesium removal (TSCR) demonstration. Additionally, for the BDEF testing described in this report, the flux was controlled to 0.065 gpm/ft², which is the targeted TSCR filtration flux. Results indicate that the TSCR filter should perform well when processing AP-107 supernatant.

¹ Geeting JGH, AM Rovira, JR Allred, RW Shimskey, CA Burns, and RA Peterson. 2018. *Filtration of Hanford Tank AP-107 Supernatant*. PNNL-27638, Pacific Northwest National Laboratory, Richland, Washington.

Acknowledgments

The authors gratefully acknowledge the help of hot cell technicians Jarrod Turner and Mike Rojas in conducting this work.

Acronyms and Abbreviations

AOI	analyte(s) of interest
BDEF	backpulsed dead-end filter apparatus
CFF	crossflow filter
CWF	clean water flux
DEF	dead-end filter apparatus
EQL	estimated quantitation limit
GEA	gamma energy analysis
ICP-OES	inductively coupled plasma optical emissions spectroscopy
IX	ion exchange
LAWPS	Low-Activity Waste Pretreatment System
MDL	method detection limit
MFC	mass flow controller
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
RPL	Radiochemical Processing Laboratory
TIC	total inorganic carbon
TMP	transmembrane pressure
TOC	total organic carbon
TSCR	tank side cesium removal
WRPS	Washington River Protection Solutions
WWFTP	WRPS Waste Form Testing Program

Contents

Executi	ve Sum	mary	ii
Acknow	vledgme	ents	iii
Acrony	ms and	Abbreviations	iv
Conten	ts		v
1.0	Introdu	action	1
	1.1	Background	1
	1.2	BDEF	1
	1.3	DEF	
	1.4	Quality Assurance	4
2.0	Test Co	onditions	5
	2.1	BDEF Testing	
	2.2	DEF Testing	6
3.0	Results	5	
	3.1	BDEF Filtration Results	
	3.2	DEF Filtration Results	
	3.3	Sample Analysis	
4.0	Conclu	isions	
5.0	Refere	nces	
Append	lix A – I	Email Describing AP-107 Sample Dates	A.1
Append	lix B – A	Analytical Reports	B.1

Figures

Figure 1.1. BDEF schematic	2
Figure 1.2. Mott 6480 line filter from https://mottcorp.com	3
Figure 1.3. Mott 70-mm disc test filter assembly from https://mottcorp.com	3
Figure 1.4. DEF schematic	4
Figure 3.1. Evolution 2: BDEF filtration	9
Figure 3.2. Evolution 3: BDEF filtration	. 10
Figure 3.3. BDEF resistance during filtration of AP-107	. 10
Figure 3.4. CWF measurements for media grade 5 BDEF at 0.33 liters/hr permeate rate (nominal) before testing	. 11
Figure 3.5. CWF measurements for media grade 5 BDEF at 0.33 liters/hr permeate rate (nominal) after testing and filter cleaning	. 12
Figure 3.6. DEF filtration (AP-107)	. 13
Figure 3.7. Filtration resistance during DEF testing (media grade 5 filter)	. 13

Tables

Table 2.1. Mass Balance – BDEF	7
Table 2.2. Mass Balance – DEF	7
Table 3.1. BDEF Key Events	. 11
Table 3.2. ICP-OES Results for ASR 0780	. 14
Table 3.3. TIC/TOC Results for ASR 0780, mg carbon/liter	. 15
Table 3.4. GEA Results for ASR 0780, $Bq/g \pm 1-\sigma$. 15

1.0 Introduction

1.1 Background

The Low-Activity Waste Pretreatment System (LAWPS) provides for the initial production of immobilized low-activity waste (ILAW) by feeding low-activity waste (LAW) directly from tank farms to the LAW Facility at the Hanford Tank Waste Treatment and Immobilization Plant (WTP) for immobilization. Prior to the transfer of feed to the WTP LAW Facility, tank supernatant waste will be treated in the LAWPS to meet the WTP LAW Facility waste acceptance criteria. The key process operations for treating and immobilizing the waste include solids filtration, cesium removal, and, finally, vitrification of the LAW.

A small-scale test platform to demonstrate these processes is located at the Pacific Northwest National Laboratory (PNNL) 325 Building, also known as the Radiochemical Processing Laboratory (RPL). The feed identified for the testing described herein is approximately 9 liters of decanted AP-107 tank waste supernatant. The purpose of this testing was to a) demonstrate dead-end filtration of AP-107 feed to obtain TSCR prototypic flux rates and identify issues that may impact filtration, and b) provide feed to ion exchange (also part of the test platform).

Similar filtration testing was performed on AP-107 supernatant in fiscal year (FY) 2018 (Geeting et al. 2018); however, the current testing campaign was conducted to more closely mimic operations expected for the Tank Side Cesium Removal (TSCR) Demonstration Project. Main differences between testing campaigns described herein and FY18 include:

- Current testing did not include any crossflow filtration.
- Current testing was performed at a targeted flux of 0.065 gpm/ft² planned for TSCR.

Other differences between testing campaigns are manifest in the AP-107 samples received for filtration: The samples received for current testing had no recoverable solids. The samples received for FY18 testing had recoverable solids. This difference in solids content is likely because the FY18 samples were taken within a few weeks of water addition and tank recirculation, while the samples taken for the current work had no recorded tank additions or recirculation for 14 months prior; see email from Washington River Protection Solutions (WRPS), included as Appendix A to this report.

1.2 BDEF

Figure 1.1 shows a schematic of the backpulsed dead-end filter apparatus (BDEF) system installed in the shielded analytical laboratory hot cells located in the RPL. The AP-107 slurry feed was introduced into the system through the slurry reservoir. A rotary lobe pump (powered by an air motor) pumped the slurry through a recirculation loop containing a magnetic flow meter and filter assembly. Adjusting the air motor supply pressure (and thus the pump speed) and the throttle valve controls the slurry velocity and pressure. Note that the two crossflow filters (CFFs) shown in the figure were not used in testing.

The filter differential pressure is measured with a single differential pressure transducer with pressure taps immediately before and after the BDEF. The feed is filtered as it flows through the BDEF and the filtration rate is controlled by a mass flow controller (MFC). The permeate flowrate is measured with the Coriolis flowmeter and/or the glass flow meter. The BDEF may be backpulsed with permeate by using compressed air. The backpulse concentrate is removed from the system and collected at the BDEF sample/flush port. During testing, the slurry temperature was maintained at 25 ± 5 °C by a 1000 W chiller that circulates chilled water through an in-line shell and tube heat exchanger.



Figure 1.1. BDEF schematic

The test filter for the BDEF was a Mott 6480-1/2-6-5, modified¹ to 2.75-in. filter active length. The filter element is fabricated from a seamless sintered stainless steel tube that is closed on one end. The other end is welded to a pipe-reducing bushing. The filter is cylindrical with dimensions of 3/8-in. diameter x 2.75-in. length and has a filtration area of 3.24 in². Figure 1.2 shows a drawing of the Series 6480 filter.

¹ The filter was cut approximately in half and a new non-porous end cap was welded on. The weld was inspected and approved prior to use.



Figure 1.2. Mott 6480 line filter from https://mottcorp.com

1.3 DEF

The test filter for dead-end filtration is a Mott 70-mm disc test filter, which is a commercial off-the-shelf dead-end filter apparatus (DEF) designed for feasibility studies at the laboratory bench scale. Figure 1.3 shows the configuration of the disc filter assembly. The 70-mm disc test filter is a barrier type filter with an available filter area of approximately 4.4 in². The Mott filter media is stainless steel sintered metal and is available in various filter grades (0.1, 0.5, 1, 5, 10 μ m). Grade 5 filter media was used for testing.

Figure 1.4 shows a schematic of the DEF test apparatus. The dilute slurry feed is introduced to the system through the feed reservoir. Compressed air may be supplied to the top of the reservoir to push the feed through the test filter, or if the filter has high permeability, filtrate may pass through the filter due to pressure from its own weight. Filtrate passes through the filter and the transmembrane pressure (TMP) and filtrate mass are measured as a function of time. This filter system has the advantage of having no minimum volume necessary to operate. Therefore, the DEF was used to filter the final 2 liters of AP-107 feed drained from the BDEF system.



Figure 1.3. Mott 70-mm disc test filter assembly from https://mottcorp.com



Figure 1.4. DEF schematic

1.4 Quality Assurance

This work was conducted with funding from WRPS under contract 292592, *DFLAW Feed Qualification Maturation*. The work was conducted as part of PNNL Project 69833.

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 ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the 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.

2.0 Test Conditions

Thirty-six supernatant samples (~250 mL each) were taken from tank AP-107 in December 2018 and transferred to the RPL. Filtration testing occurred in April 2019 and evaluated two sintered metal Mott filters:

- The BDEF is a sintered metal Mott grade 5 in-line filter (model 6480) with a 3/8-in. outside diameter, 1/4-in. internal diameter, 2.75-in. active length,¹ and 3.24-in² (0.023-ft²) filter area. This filter is the same filter used in previous AP-107 testing (Geeting et al. 2018). This filter was acid cleaned and rinsed prior to use.
- 2. The DEF is a sintered metal Mott grade 5 disc filter, 1/16-in. thick, 4.4-in² filter area. This filter was new at the start of testing.

2.1 BDEF Testing

The BDEF system was acid cleaned with 2 M nitric acid and 0.5 M oxalic acid before testing. The evolutions used to test the AP-107 are outlined below.

- 1. Clean water flux (CWF) measurement: The CWF measurement serves as a system leak test and provides a baseline measurement of the filter resistance, and was conducted at nominal test conditions 0.33 lph and run for approximately 5 minutes.
- 2. Filtered AP-107 feed with the BDEF at 0.33 liters/hr: The targeted filtration rate is based on scaled flux used during AVANTech testing² [0.306 gpm through 4.7 ft² of Mott sintered metal filter (0.065 gpm/ft²)]. The filtration rate was controlled with an MFC. Permeate was sampled near the beginning and end of Evolution 2 testing.
- 3. Continued the filtration of AP-107 with BDEF at 0.33 liters/hr. Conducted backpulse near end of testing. Filtration continued until 2918 g of feed was left in the BDEF system. The BDEF filter was backpulsed again at the conclusion of filtration.
- 4. Drained BDEF system (drained AP-107 was used for DEF testing).
- 5. Acid cleaned filter: The BDEF filter was cleaned using 2 M HNO₃ cleaning solutions.
- 6. CWF: After cleaning, the BDEF was rinsed and another CWF test was executed on the filter.
- 7. The BDEF was laid up for storage in accordance with the operating procedure.

Table 2.1 provides a mass balance for BDEF testing. A total of 11,645.9 g of AP-107 supernatant was added to the BDEF system during testing. A total of 11,433.5 g was accounted for. The missing mass (212.4 g) is likely due to evaporation and material that wets the inside of the BDEF system and is not recoverable, and represents less than 2% of the initial feed.

¹ The filter was modified from a standard 6-in. length at PNNL. The filter was cut approximately in half and a new end-cap was welded on the filter. The welds were inspected and approved prior to use in the hot cell.

² TSCR Dead End Filter Scoping Test Summary, presentation by AVANTech Inc., presented November 13, 2018, in Richland, Washington.

2.2 DEF Testing

The evolutions used to test the AP-107 in the DEF are outlined below.

- 1. Performed CWF test.
- 2. Added AP-107 (drained from BDEF system) and filtered using static head pressure of feed. A total of three bottles were added to the DEF, so this filtration was repeated a total of three times.
- 3. Inspected filter for solids.
- 4. Rinsed DEF system and performed a CWF test.

Table 2.2 provides a mass balance for DEF testing. A total of 2901.2 g of material was added to the DEF. A total of 2895.3 g was accounted for. That left 5.9 g of material unaccounted for. The missing mass is material that wets the inside of the DEF and is not recoverable, and represents 0.2% of the feed.

		IN (g)	OUT (g)				
			Feed to		Permeate	Slurry	
Evolution	Description	AP-107	DEF	Dewater (to IX)	Sample	Sample	Transfer Loss
2	Composite Feed and BDEF Dewater	7043.0	0	4289.2	17.5	0	0
3	Composite Feed and BDEF Dewater	4602.9	0	3946.3	12.4	250.1	0
4	Drain BDEF SYSTEM	0.0	2918.0	0	0	0	0
	Subtotals	11,645.9	2918.0	8235.5	29.9	250.1	0
	Total	11,645.9			11,433.5		

Table 2.1. Mass Balance – BDEF

Table 2.2. Mass Balance – DEF

		IN (g)	OUT (g)	
			Permeate	a 11 1
		AP-107 Fed	Collected (to	Solids
Evolution	Description	to DEF	IX)	Recovered
2	Filtration of AP-107 (Batch 1)	879.5	870.9	
2	Filtration of AP-107 (Batch 2)	1034.1	1030.0	
2	Filtration of AP-107 (Batch 3)	987.6	994.4	
3	Wet Solids Recovered from Filter			0.0
	Subtotals	2901.2	2895.3	0.0
	Total	2901.2	289	5.3

3.0 Results

3.1 BDEF Filtration Results

Figure 3.1 and Figure 3.2 show the TMP and permeate flowrate during the dewatering of AP-107 with the grade 5 stainless steel filter. Figure 3.1 plots the data from the first day of filtration and Figure 3.2 plots the data from the second day. The filtration rate was controlled with a MFC set at 0.33 liters/hr (0.065 gpm/ft²). The range on the y-axis was selected to be 0-2 psig because during proposed operations for TSCR a backpulse is triggered when the differential pressure rises above 2 psig; thus, 2 psig represents an upper operational bound. The pressure stayed at the low end of the operational range for the entire filtration campaign and averaged 0.045 psig the first day (Figure 3.1) and 0.050 psig the second (Figure 3.2).

The original plan called for backpulsing at the end of day 1; however, because the TMP was not increasing (indicating few to no solids in the feed), the decision was made to delay backpulsing until the second day when more feed had been processed. The first backpulse occurred at approximately hour 8 on the second day (Event i on Figure 3.2). No solids were observed in the concentrate from the backpulse and no decrease in the TMP after backpulsing was observed. A second backpulse was conducted at the conclusion of testing (Event 1 on Figure 3.2), again with no solids observed in the concentrate.

The operation of the BDEF system with the Brooks Quantim MFC produced several discontinuities and deviations as a result of control issues. Table 3.1 highlights the key events and issues that resulted in less than optimal flow rate control. About an hour into AP-107 dewatering on the first day, oscillation of permeate flow rate began to increase (Event a). It was determined that this was a result of the MFC electrical connection cable shaking loose due to of the slurry pump's vibration. This connection was secured more tightly and then monitored periodically throughout the rest of the dewatering (Event b).

After 3 hours of dewatering on the first day of filtration, a sharp rise in permeate flow rate was observed (Event c). This spike was roughly 45% greater than target flow rate of 0.33 liters/hr. The cause of this spike is unknown and the manual needle valve on the permeate side was closed slightly to try to gain control. This did not aid in control. In an effort to bring the permeate flow rate back to the target value, the MFC's power supply was reset (Event d). This did not correct the control problem, but the flow rate did slowly decrease back to the target 0.33 liters/hr. Another spike occurred at 5 hours and 34 minutes of dewater (Event e); again, the cause of this is unknown. The manual needle valve on the permeate side was opened slightly to try to gain control and the again the flow rate did slowly decrease back to the target 0.33 liters/hr.

During the second day of filtration, an error code on the MFC was noted 6 minutes into dewatering and the instrument was reset (Event f). After fully opening the manual permeate side needle valve and placing the set point controller back to 0.33 liters/hr, the flow rate returned to equilibrium (Event g). A quick battery swap for the MFC set point controller occurred at 4 hours and 14 minutes into dewatering and is noted as Event h.

The first backpulse occurred 7 hours and 32 minutes into dewatering on the second day after 7350.9 g of AP-107 feed had been dewatered (Event i). An error code was again displayed on the MFC after dewatering resumed (Event j) and troubleshooting again led to the MFC power supply reset (Event k). This corrected the control problem and permeate flow resumed at 0.33 liters/hr. A second backpulse occurred at the end of dewatering after filtering another 1223.1 g of AP-107 feed (Event l).

Because of the difficulties in controlling the feed rate, the average and standard deviation was examined during times when the MFC was providing good control. During the last 2 hours shown in Figure 3.1, the average TMP was 0.041 psi with a standard deviation of 0.024.

Darcy's law relates the flow rate through a porous media to the pressure drop causing that flow:

$$J = \Delta P / (\mu * R)$$

Where J=filtration flow rate, m/s

 ΔP = filtration pressure, Pa=kg/(m*s²)

μ=liquid viscosity, kg/(m*s)

R=total filtration resistance, m⁻¹

Rearranging

$$R = \Delta P / (\mu * J)$$

Figure 3.3 shows the total filter resistance over the 2-day test. The filter resistance was basically unchanged over testing and averaged 1.54 E9 m⁻¹ during day 1 (Evolution 2) and 1.46 E9 m⁻¹ during day 2 (Evolution 3). The backpulse occurred at 2.83 m³/m² volume filtered. The backpulse had little to no measurable effect on the resistance.



Figure 3.1. Evolution 2: BDEF filtration



Figure 3.2. Evolution 3: BDEF filtration



Figure 3.3. BDEF resistance during filtration of AP-107

		Time on Figure	
	Event	(hr:min)	Figure
a)	Control Issue: MFC cable shaking loose	~ 01:00	3.1
b)	Tightening connections on MFC cable	1:52	3.1
c)	Control Issue: no known cause. Permeate side needle valve closed slightly to try and rectify.	3:10	3.1
d)	Control Issue: no known cause. Reset MFC power supply to rectify.	3:32	3.1
e)	Control Issue: no known cause. Permeate side needle valve opened slightly to try and rectify.	5:34	3.1
f)	Reset MFC, increased its set point to troubleshoot	0:06	3.2
g)	Fully opened permeate side needle valve & set MFC back to 0.33 liters/hr.	0:15	3.2
h)	Battery replaced on MFC set point controller	4:14	3.2
i)	Backpulse	7:32-7:47	3.2
j)	Error code displayed by MFC	8:05	3.2
k)	MFC power supply reset	8:31	3.2
l)	Second backpulse and end of test	9:24	3.2

Table 3.1. BDEF Key Events

Figure 3.4 and Figure 3.5 show the CWF of the media grade 5 BDEF filter before testing and after testing. In both cases, the filter was acid cleaned and rinsed just prior to the CWF test. The CWF tests were conducted at a nominal 0.33 liters/hr permeate rate controlled by the MFC. The TMP averaged 0.030 and 0.015 psi (with standard deviations of 0.03 and 0.006) in the pre- and post-CWF tests, respectively. The standard deviation in the first CWF test is comparable to the average pressure and suggests that the averages reported here are not significantly different than zero (i.e., outside the ability to quantify).



Figure 3.4. CWF measurements for media grade 5 BDEF at 0.33 liters/hr permeate rate (nominal) before testing



Figure 3.5. CWF measurements for media grade 5 BDEF at 0.33 liters/hr permeate rate (nominal) after testing and filter cleaning

3.2 DEF Filtration Results

AP-107 drained from the BDEF system was filtered through the DEF (grade 5 filter). No solids were observed on the filter at the completion of filtration. The AP-107 was filtered in three batches, with no external pressure applied to the filter assembly.¹ That is, the pressure for filtration was due to the static pressure head of the feed inside the DEF. Figure 3.6 shows the volume of feed filtered as a function of time for the three batches of AP-107 feed and the CWF data for this testing.

Figure 3.7 shows the average filter resistance of the three batches of AP-107. The three batches show only a very minor increase in resistance during testing, within the experimental uncertainty. The average resistances for the three batches were 6.4 E8, 6.8 E8, and 6.8 E8 m⁻¹, respectively. The DEF filter exhibited virtually no flux decay and the measured resistances were consistent with a clean filter.

¹ Air pressure was only applied to the DEF at the very end of Batch 3 to clear filter of AP-107 feed. Data from clearing the filter is not shown in Figure 3.6 or 3.7.



Figure 3.6. DEF filtration (AP-107)



Figure 3.7. Filtration resistance during DEF testing (media grade 5 filter)

3.3 Sample Analysis

Three permeate samples (TI-059-E2-P1-A, TI-059-E2-P2-A, TI-059-E2-P3-A) were collected at the approximate beginning, middle, and end of filtration testing, respectively. These samples were submitted for the following analysis:

- Inductively coupled plasma atomic emission spectrometry (analytes of interest [AOI]: Na, K, Mg, Ca, Fe, Al, Si, P, S, Cr)
- Total inorganic carbon and total organic carbon (TIC/TOC)
- Gamma energy analysis (AOI: ¹³⁷Cs, ⁶⁰Co, Eu isotopes, ²⁴¹Am, ²³⁹Pu)

The first permeate sample (TI-059-E2-P1-A) has analyte concentrations approximately 75% of the latter two permeate samples. This first permeate sample was inadvertently diluted with residual water; analytical results for this sample are not included in this section but can be found in Appendix B.

The BDEF was backpulsed twice during testing and each flush from the backpulse was sampled. Because there were no solids observed, the backpulse samples were combined and centrifuged in an attempt to concentrate and collect any solids. No solids were visible in the combined, centrifuged sample. The top $\sim 2/3$ of the sample supernatant was removed by transfer pipette. The bottom fraction was submitted for the same analysis as the permeate to see if there were any measurable differences between the permeate and backpulse samples (TI-059-BDEF-S-A).

Results are summarized below, with full analytical reports provided in Appendix B.

ICP-OES

ICP-OES analyses are provided in Table 3.2 on a mass per unit volume basis ($\mu g/mL$). The top three components measured were Na, Al, and K. The concentrations of the backpulse sample match the two permeate samples, with the exception of Ca and Si. The reason for these differences is not known.

					Relative
					Percent
					Difference
	Permeate	Permeate	Average	Backpulse	(average
	TI-059-E2-P2-A	TI-059-E3-P3-A	Permeate	TI-059-E2-BDEF-S-A	permeate vs.
Analyte	$(\mu g/mL)$	(µg/mL)	(µg/mL)	$(\mu g/mL)$	backpulse)
Al	9,550	10,100	9,825	9,870	0%
Ca	[28]	[32]	[30]	46.2	35%
Cr	513	535	524	521	-1%
Fe	15.4	14.8	15	16.7	10%
Κ	4,710	4,790	4,750	4,630	-3%
Mg					N/A
Na	129,000	138,000	133,500	131,000	-2%
Р	831	866	849	840	-1%
S	1,840	1,950	1,895	1,820	-4%
Si	140	124	132	82.9	-59%
Dash ()	indicates the value is	s <mdl (method="" det<="" td=""><td>ection limit).</td><td></td><td></td></mdl>	ection limit).		
Values in	brackets [] are ≥ME	DL, but < EQL (estim	ated quantitati	on limit).	

Table	32	ICP_OES	Reculte	for	ΔSR	0780
rable	3.2.	ICP-OES	Results	101	ASK	0/00

TIC/TOC

TIC and TOC measurements are provided in Table 3.3 and are relatively consistent. For comparison, TOC of a backflush from previous AP-107 filtration testing (Geeting et al. 2018), was 17,963 mg carbon/liter, but the sample did have visible solids. This result is consistent with the conclusion made in 2018 that the solids found in AP-107 are high in organic carbon.

Comparison of TOC levels of TI-059-BDEF-S-A with results from previous testing indicates little to no solids in the backflush sample, which is consistent with other measurements and observations in this report.

Analysis	TI-059-E2-P2-A	TI-059-E3-P3-A	TI-059-BDEF-S-A
TIC	8088	7687	7762
TOC	2481	2520	2526
Total TIC+TOC	10,569	10,207	10,288

Table 3.3	TIC/TOC	Results f	for ASR	0780	mg carb	on/liter
1 4010 5.5.	110/100	itesuits i	IOI TIDIC	0700,	ing care	/on/ mon

<u>GEA</u>

Gamma activity detected are shown in Table 3.4. As expected, the predominant gamma activity was from ¹³⁷Cs, which is soluble and expected in all samples. Plutonium and americium, which are generally insoluble in tank waste, are below the detection limit for all samples. This result is consistent with no solids in the backpulse sample.

Isotope	TI-059-E2-P2-A	TI-059-E2-P3-A	TI-059-BDEF-S-A
⁶⁰ Co	<1.1E+02	<1.3E+01	<7.0E+01
317 C a	5.50E+06	5.53E+06	5.80E+06
Cs	+/-2%	+/-2%	+/-2%
¹⁵⁴ Eu	<7.3E+01	<1.0E+02	<2.0E+02
¹⁵⁵ Eu	<1.2E+03	<1.8E+03	<3.0E+03
²⁴¹ Am	<4.8E+03	<7.0E+03	<1.0E+04
²³⁹ Pu	<4.1E+06	<5.9E+06	<1.0E+07

Table 3.4. GEA Results for ASR 0780, $Bq/g \pm 1-\sigma$

4.0 Conclusions

Based on the results of filtration experiments on AP-107, the following observations and conclusions were made:

- The media grade 5 BDEF filter was run at the TSCR targeted flux of 0.065 gpm/ft² and the filter exhibited no measurable increase in resistance over almost 20 hours of testing (and ~3 m³ of permeate produced per m² of filter area).
- There were no observable solids in the AP-107 sample received [in contrast to sample received and filtered in FY18 (Geeting et al. 2018)]. The BDEF filter was backpulsed after approximately 18 hours of filtration with no observable solids in the backflush concentrate. The conclusion of no observable solids is supported by comparison of the chemical analyses of the permeate and backflush samples.
- Both filters used in testing were Mott media grade 5 sintered metal filters, which is the filter manufacturer, type, and grade planned for the TSCR demonstration. Results indicate that the TSCR filter should perform well when processing AP-107 supernatant.

AP-107 drained from the BDEF system was filtered through a media grade 5 70-mm disc filter (DEF) and no solids were observed on the filter at the completion of testing. The DEF filter exhibited virtually no flux decay and the measured resistances were consistent with a clean filter.

5.0 References

ASME. 2000. NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*. American Society of Mechanical Engineers, New York, New York.

ASME. 2008. NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*. American Society of Mechanical Engineers, New York, New York.

ASME. 2009. NQA-1a-2009, *Addenda to ASME NQA-1-2008*. American Society of Mechanical Engineers, New York, New York.

Chen W. 1996. *Solid/Liquid Separation Fundamentals and Practices*. Dow Chemical Company, Freeport, Texas.

Geeting JGH, AM Rovira, JR Allred, RW Shimskey, CA Burns, and RA Peterson. 2018. *Filtration of Hanford Tank AP-107 Supernatant*. PNNL-27638, Pacific Northwest National Laboratory, Richland, Washington.

Reynolds JG, MD Britton, and RM Orme. 2018. *Solids Removal Requirements in the Direct Feed Low Activity Waste Process*. RPP-RPT-60670, Rev. 0, Washington River Protection Solutions, Richland, Washington.

Appendix A – Email Describing AP-107 Sample Dates

From: Landon, Matthew R <<u>matthew r landon@rl.gov</u>>
Sent: Wednesday, April 10, 2019 2:38 PM
To: Colosi, Kristin A (WRPS) <<u>kristin a colosi@rl.gov</u>>; Peterson, Reid A
<<u>Reid.Peterson@pnnl.gov</u>>
Subject: RE: sample dates

After some research it looks like the following for the AP107 samples.

September 2017 – Pump out of AP-107 approx. 161" of waste and add 138" of water October 2017 (early) – Recirculate for approximately 1 tank turnover October 13th and 20th 2017 – Pull waste samples send to PNNL, samples taken 50" below surface

December 13, 2018 and January 3, 2019 – Pull samples and send to PNNL, samples taken 50" below surface.

Note: overall loss from October 2017 to April 2019 looks like approximately 6" (evaporation)

I am still working on if the tank has been recirculated since 2017 but information to date indicates no recirculation has taken place.

Thanks,

Matt Landon

Technology Maturation & Analysis 509-373-1379 Washington River Protection Solutions, Contractor to the U. S. Department of Energy

Appendix B – Analytical Reports

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

73312 / NC4185
0780
J. Geeting
4 (Aqueous)

ASO Sample ID	ASO Client Imple ID Sample ID Client Sample Description		Sample Weight (g)
19-1720	TI-059-E2-P1-A	CUF Permiate Solution	NA
19-1721	TI-059-E2-P2-A	CUF Permiate Solution	NA
19-1722	TI-059-E3-P3-A	CUF Permiate Solution	NA
19-1723	TI-059-BDEF-S-A	Combined Back Pulse Solution	NA

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

Procedure	<u>RPG-CMC-21</u> Inductively Co Spectrometry (<u>1, Rev. 4</u> , "Determi upled Argon Plasma ICP-OES)".	nation of Elemen Optical Emission	tal Compositior n	n by
Analyst:	J. Carter	Analysis Date:	07-03-2019	ICP File:	C0804
See Chemi	cal Measurement	Center 98620 file:	ICP-325-405-3 (Calibration an	d Maintenance	Records)
M&TE:	PerkinElmer	5300DV ICP-OES	SN: 077N512	2002	
	Sartorius ME	414S Balance	SN: 21308482	2	
	Ohaus PA224	4C Balance	SN: B725287	790	
	Mettler AT40	00 Balance	SN: 11132920	667	
	Sartorius R20	00D Balance	SN: 3908005	8	

Report Preparer

Review and Concurrence

7/11/19 Date 07/17/19

Page 1 of 1

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

Initial/Continuing Calibration Verification (ICV/CCV):

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

Initial/Continuing Calibration Blank (ICB/CCB):

The ICB/CCB solution (5% v/v HNO₃) 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 \leq EQL.

Low-Level Standard (LLS):

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

Interference Check Standard (ICS/SST):

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

Serial Dilution (SD):

Five-fold serial dilution was conducted on sample 19-1723. 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 0.2% to 25.3% and were within the acceptance criterion of $\leq 10\%$, with the exception of potassium (25.3%).

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

In addition to the BS sample, a post-digestion spike (A Component) was conducted on sample 19-1720. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration \geq 25% of that in the sample. Recovery values for the AOI meeting this requirement ranged from 106% to 169% and were within the acceptance criterion of 80% to 120% except for Al at 122% and Na at 169%.

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

In addition to the BS sample, a post-digestion spike (B Component) was conducted on sample 19-1720. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration \geq 25% of that in the sample. Recovery values for the AOI meeting this requirement ranged was 97% and was 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.

Page 3 of 4

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

Comments:

- 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 HNO₃ 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%.</p>
- 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.

Page 4 of 4

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

Page 1 of 2

		Run Date >	7/3/2019	7/3/2019	7/3/2019	7/3/2019	7/3/2019	7/3/2019
		Process						
		Factor >	1.0	24.7	199.6	198.7	248.4	248.7
					19-1720@	19-1721@	19-1722 @	19-1723 @
			405 diluent	BLK-1720	4x	4x	5x	5x
Instr. Det.	Est. Quant.			Reagent	TI-059-E2-	TI-059-E2-	TI-059-E3-	<u>T1-059-</u>
Limit (IDL)	Limit (EQL)	Client ID >	Lab Diluent	Blank	<u>P1-A</u>	<u>P2-A</u>	<u>P3-A</u>	BDEF-S-A
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
0.0122	0.122	AI		[0.35]	7,620	9,550	10,100	9,870
0.0177	0.177	Ca		[2.1]	[18]	[28]	[32]	46.2
0.0025	0.025	Cr			404	513	535	521
0.0052	0.052	Fe		[0.34]	11.8	15.4	14.8	16.7
0.0240	0.240	к	-	-	3,540	4,710	4,790	4,630
0.0068	0.068	Mg		[0.24]	-		-	-
0.0246	0.246	Na			104,000	129,000	138,000	131,000
0.0554	0.554	Р			651	831	866	840
0.1186	1,186	S			1,420	1.840	1,950	1,820
0.0237	0.237	Si		[0.86]	112	140	124	82.9
Other Analyt	es			[c.c.c]				
0.0019	0.019	An			-			
0.0529	0.579	As						
0.0067	0.067	B	10 0431	[1.0]	EE 2	67.4	45.7	36.3
0.0007	0.007	Ba	[0.045]	[1.0]	10.241	10.351	40.7	10 421
0.0003	0.003	Da			[0.21]	[0.35]	[0.37]	[0.44]
0.0001	0.001	Be			[0.094]	0.130	[0.13]	[0.14]
0.0494	0.494	Bi				-		
0.0022	0.022	Cd			4.71	6.84	6.92	6.42
0.0069	0.069	Ce						
0.0035	0.035	Co			-	-	-	
0.0016	0.016	Cu		[0.068]	[1.7]	[1.5]	[1.3]	[1.2]
0.0029	0.029	Dy						
0.0013	0.013	Eu				-		
0.0022	0.022	La				-	-	-
0.0009	0.009	Li				-	-	
0.0002	0.002	Mn		-				[0.19]
0.0045	0.045	Mo	-		34.3	42.5	44.1	43.1
0.0086	0.086	Nd						
0.0049	0.049	Ni			18.2	22.6	22.8	24.1
0.0162	0.162	Pb			[4.0]	[4.8]	[10]	[6.5]
0.0077	0.077	Pd			[1.6]	[1.8]	[2.9]	
0.0165	0.165	Rh			-		-	
0.0097	0.097	Ru			[4.8]	[6.7]	[6.2]	[7.4]
0.0518	0.518	Sb				[13]		
0.1595	1.595	Se						
0.0313	0 313	Sn		10 801	[1 2]	[12]	[15]	[24]
0.0005	0.005	6. 6.		[0.00]	[14]	10 441	[10]	[21]
0.0003	0.005	Ta				[0.11]	-	-
0.0217	0.217	Ta						
0.0311	0.311	Te	-			-		-
0.0189	0.189	in Ti					-	
0.0004	0.004	11			-	-	-	
0.0530	0.530	n			-			
0.0360	0.360	U	-	-		[15]	[10]	-
0.0021	0.021	v	-		[0.46]	[0.63]	[0.73]	[0.57]
0.0216	0.216	w			54.9	67.4	75.4	66.9
0.0012	0.012	Y					-	-
0.0043	0.043	Zn	-	[0.52]	[1.3]	[1.2]	[1.6]	
0.0019	0.019	Zr						

1) "-" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier"

near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

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

ASR-0780 Results from C0804 ASR-0780 Geeting

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

Page 2 of 2

Criteria >	≤ 20%	80%-120%	75%-125%	80%-120%	80%-120%	≤ 10%
QC ID >	19-1774 Dup	BS	19-1774 MS	19-1720 + AS-A	19-1720 + AS-B	19-1723 5-fold Serial Di
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
AI	1.6	98	88	122		3.2
Ca		105	111	109		1.00
Cr	4.2	101	nr	118		1.0
Fe		101	97	106		
к	0.8	93	121	108		25.3
Mg		103	102	106		
Na	3.2	111	nr	189		2.9
Р	4.4	99	88	106		0.2
S	2.0	98	93		97	6.9
Si		91	100	107		
ther Analy	tes					
Ag		84	49	98		
As				104		
B	11.9	102	95	103		
Ba		101	98	104		
Be		100	99	106		
Bi		85	00	98		
Cd		99	96	103		
Ce		92	88	100	95	
Co		32	00	104		
Cu		101	102	109		
Du		101	103	109	102	_
Eu					102	
La		100	07		100	
La		110	97	112	100	
Ma		100	123	102		
Ma	2.0	100	96	102		
MO	3.6	99	94	103	400	
NO	2.0	100	90	107	102	_
NI	3.8	100	97	107		
PD		102	98	104		
Pa					96	
Rn					102	
Ru					99	
Sb				102		
Se				107		
Sn				102		
Sr		103	97	102		
Та				101		
Te		-			101	_
Th		100	97		100	
Ti		101	99	104		
TI				97		
U		101	96		105	
v		96	92	99		
w	14.6	100	90	106		
Y		-		101		
Zn		99	95	105		
Zr	1.1.1	101	97	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.

ASR-0780 Results from C0804 ASR-0780 Geeting xlsm

Project Number:	73312
Charge Code:	NC4185
ASR Number:	0780
Client:	J. Geeting
	A. Rovira
Total Samples:	4 liquid

	RPL Numbers	Client IDs
	19-1720	TI-059-E2-P1-A
	19-1721	TI-059-E2-P2-A
Samples	19-1722	TI-059-E3-P3-A
	19-1723	TI-059-BDEF-S-A

Analysis Procedure	RPG-CMC-386 Rev. 1, "Carbon Measured in Solids, Sludge, and Liquid Matrices"
Prep Procedure	None
Analyst	A. Carney
Analysis Date	June 18, 2019
CCV Standards	TIC/TOC CMS # 543144 and 543143
BS/LCS/MS Standards	TIC/TOC CMS # 542973 and 543145
Excel Data File	ASR-0780-Geeting.xlsx
M&TE Numbers	Carbon System (WD36639, RPL/701)
Contraction (Contraction)	Balance : Sartorius R200D, S/N 30809774
All Analysis Records	5015_06-18-2019-083737.CSV

6/20/19 Date Andrew Cary Prepared By

Reviewed By

6/21/19 Date

Page 1 of 4

Table 1: TOC/TIC Results for ASR 0780

TIC in Sample 19-1720 (mg C/L):	7267.28	TIC in Sample 19-1721 (mg C/L):	8087.95	TIC in Sample 19-1723 (mg C/L):	7761.79
MDL (mg C/L):	206	MDL (mg C/L):	206	MDL (mg C/L):	206
EQL (mg C/L):	1028	EQL (mg C/L):	1028	EQL (mg C/L):	1028
TOC in Sample 19-1720 (mg C/L):	2002.22	TOC in Sample 19-1721 (mg C/L):	2480.75	TOC in Sample 19-1723 (mg C/L):	2526.46
MDL (mg C/L):	206	MDL (mg C/L):	206	MDL (mg C/L):	206
EQL (mg C/L):	1028	EQL (mg C/L):	1028	EQL (mg C/L):	1028
TIC in Sample 19-1720-Dup:	7356.71	TIC in Sample 19-1722 (mg C/L):	7686.72		
MDL (mg C/L):	206	MDL (mg C/L):	206		
EQL (mg C/L):	1028	EQL (mg C/L):	1028		
TOC in Sample 19-1720-Dup:	2102.75	TOC in sample 19-1722 (mg C/L):	2520.43		
MDL (mg C/L):	206	MDL (mg C/L):	206		
EQL (mg C/L):	1028	EQL (mg C/L):	1028		
19-1720 TIC RPD:	1.2%				
19-1720 TOC RPD:	4.9%				

Page 2 of 4

Sample Analysis/Results Discussion

Four liquid samples were submitted under Analytical Service Request (ASR) 0780 for total inorganic and total organic carbon analysis. The analysis was performed by the hot persulfate wet oxidation method, with the results summarized in Table 1. The TIC is measured first with additions of heated sulfuric acid followed by the addition of a silver catalyzed acidic potassium persulfate solution for oxidation at 92-95 °C for TOC. The analyses were performed following procedure RPG-CMC-386, Rev. 1, *Carbon Analyses in Solids, Sludge and Liquid Matrices*

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

Data Limitations

None

Quality Control Discussion

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

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

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

Page 3 of 4

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 96.9% and 96.6% recovery, and for the two TIC ICVs the results were 99.0% and 99.8% recovery, within the acceptance criterion of 90% to 110%. The TOC result for the CCV was 97.9% recovery and the TIC CCV was 100.8% 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 101.8% recovery and the TOC LCS/BS result was 98.7% recovery, meeting the acceptance criteria of 75% to 125%.
- <u>Duplicate/Replicate</u>: Precision of the carbon measurements is demonstrated by the relative percent difference (RPD) between sample and duplicate/replicate. Sample 19-1720 TIC RPD was 1.2% and TOC was 4.9%. Both samples meet the acceptance criteria of ≤20%.
- <u>Analytical Spike (AS)</u>: The accuracy of the carbon measurements can be estimated by the recovery from the AS. The results for the analytical spike for TIC is 100.1% recovery and for the TOC, 98.7% 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.</p>
- 3) Where applicable, the reported "Final Results" have been corrected for any dilution performed on the sample prior to analysis.

Page 4 of 4

Pacific Northwo PO Box 999, Ri Radiochemical	est National La chland, WA Sciences and E	aboratory Engineering	Group				filename	19-1720 Geeting 6/14/2019
Client: Geeting ASR 0780	Project: 73312 NC4185	1	Pr	repared by: Reviewer:	T.R.	Trang	-le envere	6/14/19
Procedures:	RPG-CMC-45 Spectrometry	0, Rev. 3 Ga	mma Energy A	nalysis (G	EA) and Low-	Energy Ph	oton Spectron	netry (LEPS)
Count dates:	June 11-12, 20	019	Measured	Activity	Baper mI +	10		
RPL ID: Sample ID: Isotope	19-1 T1-059-E	720 E2-P1-A	19-17 T1-059-E	721 2-P2-A	19-17 TI-059-E	722 3-P3-A	19-1 TI-059-BI	723 DEF-S-A
Co-60	<1.1E+02	+ 2%	<1.1E+01	+ 2%	<1.3E+01	+ 2%	<7.0E+01	+ 2%
Eu-154 Eu-155	<3.1E+02	- 2 70	<7.3E+01 <1.2E+03	± 2 70	<1.0E+02 <1.8E+03	- 270	<2.0E+02 <3.0E+03	
	5.6ET03		4.05.02				1.00.04	

Page 1 of 1

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

Gamma Energy Analysis (GEA)

Project / WP#:	73312/NC4185
ASR#:	0780.00
Client:	J. Geeting
Total Samples:	4

	RPL ID		Client Sample ID			
	19-1720		TI-059-E2-P1-A			
	19-1721		TI-059-E2-P2-A			
	19-1722		TI-059-E3-P3-A			
	19-1723		TI-059-BDEF-S-A			
Analysis Type:		GEA- f	or all positively measured or non-detected	isotopes		
Sample Processing Prior Processing/Analysis	to Radiochemical	 None Digested as per RPG-CMC-129, Rev. 0 HNO₃-HCl Acid Extraction of Solids Using a Dry Block Heater Fusion as per RPG-CMC-115, Solubilization of Metals from Solids Using a KOH-KNO₃ Fusion Other: Preparation may also involve attaining a GEA geometry that is compatible with the solbter the solution of the solution. 				
Analysis Procedure:		RPG-CMC-450, Rev. 3 Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS)				
Reference Date:		None				
Analysis Date or Date Ra	ange:	June 11	-12, 2019			
Technician/Analyst:		M Cantaloub				
Rad Chem Electronic Da	ita File:	19-172) Geeting.xls			
ASO Project 98620 File:		File Plan 5872, Technical (Radiochemistry), Gamma Calibration, daily checks, and maintenance records; and standard certificates and preparation. Also, balance calibration and performance check records.				
M&TE Number(s):		Detecto	r T			

7/8/19 Date 1 IRang-le Prepare

FR Jicemand 1-Reviewer 7/8/19 Date

Page 1 of 3

Battelle PNNL/RSE/ASO Radiochemistry Analysis Report

SAMPLE RESULTS

The client requested measurement of Cs-137, Co-60 and Eu, Am-241, and Pu-239 and all detected isotopes in these samples.

ASO Project File, ASR 0780.00 has been created for this report including all appropriate supporting records which may include the Pipette Performance Check Worksheet form, standard certificates, laboratory bench records, Sample Preparation Laboratory Bench Sheets, and Gamma Energy Analysis printouts. Detector calibration records, control charts and balance calibration records can be found in the ASO Records.

Sample Preparation, Separation, Mounting and Counting Methods

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

QUALITY CONTROL RESULTS

Tracer:

Tracers are not used for ASO GEA methods.

Process Blank (PB):

No process blank was prepared for gamma counting.

Required Detection Limits

There is no 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.

Instrument Calibration and Quality Control

Page 2 of 3

Battelle PNNL/RSE/ASO Radiochemistry Analysis Report

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

Assumptions and Limitations of the Data

For these samples, the sample geometry was not the same as our calibrated geometries. Consequently, we used calibration geometries that were as close as possible to the sample geometries. This introduces some additional uncertainty above what is listed in our report. However, this additional uncertainty is thought to be small since all samples were counted at distances of more than 53 cm from the detector face.

Interferences/Resolution

None.

Uncertainty

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

Comments

None.

Attachment: Data Report Sample Results for ASR 0780.00.

Page 3 of 3

Pacific Northwest National Laboratory

902 Battelle Boulevard P.O. Box 999 Richland, WA 99354 1-888-375-PNNL (7665)

www.pnnl.gov