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# January 2022 Semiannual Saltstone Toxicity Characteristic Leaching Procedure (TCLP) Results

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K. A. Hill

July 2022

SRNL-STI-2022-00266, Revision 0

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# January 2022 Semiannual Saltstone Toxicity Characteristic Leaching Procedure (TCLP) Results

K. A. Hill

July 2022



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#### **EXECUTIVE SUMMARY**

The aqueous waste from Tank 50 (salt solution) is sampled semiannually for transfers to the Saltstone Production Facility (SPF). Salt solution is treated at SPF and disposed of in the Saltstone Disposal Facility (SDF). Per request of customer, X-TTR-Z-00025, Revision 0, two SDF waste form (saltstone) samples were prepared in the Savannah River National Laboratory (SRNL) from the Tank 50 Waste Acceptance Criteria (WAC) sample and Z-Area premix material for the January 2022 semiannual Toxicity Characteristic Leaching Procedure (TCLP) samples. One sample contained a Full Premix which included 10:45:45 (by weight) of cement, slag and fly ash. The second sample contained 60:40 (by weight) of slag and fly ash only referred to as the "Cement-Free grout sample." Results from this technical report support Task 2: 'Grout Leaching Analyses' of the Task Technical Request (TTR) prepared by Savannah River Mission Completion (SRMC). After at least 28 days cured, a sample of each of the SDF waste forms was collected and shipped to a certified laboratory for analysis using the Toxicity Characteristic Leaching Procedure (TCLP). The January 2022 semiannual saltstone (Full Premix) and the Cement-Free grout samples met the South Carolina (SC) Code of Regulations for Hazardous Waste Management Regulations (HWMR) 61-79.261.24 and 61-79-268.48 requirements for a non-hazardous waste form with respect to Resource Conservation and Recovery Act (RCRA) metals and Underlying Hazardous Constituents (UHCs), and also met the SPF WAC that was in effect at the time of the tank sampling.

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### LIST OF ABBREVIATIONS

D&S-FE DWPF & Saltstone Facility Engineering

DSS Decontaminated Salt Solution

DSSHT Decontaminated Salt Solution Hold Tank

EC&ACP Environmental Compliance & Area Completion Projects

EPA Environmental Protection Agency

ETF Effluent Treatment Facility

LOD Limit of Detection
LOQ Limit of Quantitation

MCU Modular Caustic Side Solvent Extraction Unit

MRL Minimum Reporting Limit

MS Matrix Spike

MSD Matrix Spike Duplicate

NRC Nuclear Regulatory Commission

RCRA Resource Conservation and Recovery Act

RPD Relative Percent Difference

RL Reporting Limit

SDF Saltstone Disposal Facility
SPF Saltstone Production Facility

SRNL Savannah River National Laboratory
SRNS Savannah River Nuclear Solutions
SRMC Savannah River Mission Completion

SWPF Salt Waste Processing Facility
SwRI® Southwest Research Institute

TCLP Toxicity Characteristic Leaching Procedure
TTQAP Task Technical and Quality Assurance Plan

TTR Technical Task Request

UHC Underlying Hazardous Constituents

WAC Waste Acceptance Criteria

#### 1.0 Introduction

The Saltstone Production Facility (SPF) receives waste from Tank 50 for treatment. The following transfers were selected starting from the last quarterly sampling date when regulatory saltstone samples were prepared third quarter of calendar year 2021 (3QCY21) to the now January semiannual sampling date. Tank 50 accepted the following transfers from July 20, 2021 to January 12, 2022 totaling ~ 1147 kgal<sup>1</sup>:

- ~45.4 kgal from Effluent Treatment Facility (ETF)
- ~1098.3 kgal from the Salt Waste Processing Facility (SWPF)
- ~0.83 kgal from bearing and flush water
- ~3.09 kgal from Modular Caustic Side Solvent Extraction Unit (MCU) / Decontaminated Salt Solution (DSS)

During this same time period there was a total of 1306 kgal of Tank 50 material transferred out to SPF.<sup>1</sup> On January 12, 2022, a salt solution sample was taken from Tank 50<sup>2</sup>. DWPF & Saltstone Facility Engineering (D&S-FE) requested the Savannah River National Laboratory (SRNL) prepare two SDF waste form samples, referred to as a Full Premix saltstone sample and Cement-Free grout sample.<sup>3</sup> The Full Premix sample is the historical formulation for saltstone and the Cement-Free sample represents the current recipe for saltstone processing. The Cement-Free sample is the sample used to determine that saltstone produced by the SPF is a non-hazardous waste form. The January 2022 semiannual Full Premix and Cement-Free saltstone samples were prepared on February 8, 2022.<sup>4</sup> The samples cured for 42 days, they were crushed, sieved, packaged, and deemed "collected".<sup>4,5</sup> The samples were then shipped to Southwest Research Institute (SwRI®) to analyze for toxicity per the TCLP method.<sup>3,6</sup> The Cement-Free saltstone sample determines whether the non-hazardous nature of the grout meets the requirements of the SC Code of Regulations 61-79.261.24<sup>7</sup> for RCRA metals and 61-79.268.48<sup>8</sup> for inorganic/organic UHCs (for informational purposes only<sup>3</sup>).

#### 2.0 Experimental

Saltstone preparation was performed at SRNL. D&S-FE provided SRNL with the saltstone grout recipe as well as the premix components.<sup>3</sup> Table 2-1 shows the premix components obtained for the last quarterly TCLP sample (3QCY21) including specific LOT numbers.<sup>9</sup> Premix components used for 3QCY21 were used for the January 2022 semiannual TCLP, per SRMC.<sup>4</sup> SRMC provided SRNL personnel with the premix formulation for the January 2022 semiannual saltstone samples.<sup>4</sup>

Table 2-1. Premix Components for 3QCY21 and January 2022 Semiannual TCLP Sample.

Premix Component	Date SRNL Received	LOT#
Holcim Cement 3QCY21/ January 2022 semiannual	8/6/2021	2021-IR-05-0683
Lehigh Slag 3QCY21/ January 2022 semiannual	8/6/2021	2021-IR-05-1480
SE Fly Ash 3QCY21/ January 2022 semiannual	8/6/2021	2021-IR-05-0695

The January 2022 semiannual salt solution had been stored since collection in a zero-headspace Teflon® bottle refrigerated at <10 °C to preserve the mercury species present in the sample. The saltstone samples were prepared using the mixing method outlined in SRNL work instructions¹⁰ and the January 2022 semiannual premix components in Table 2-1.⁴ One sample contained a Full Premix which included 10:45:45 (by weight) of cement, slag and fly ash. The second sample contained 60:40 (by weight) of slag and fly ash only referred to as the "Cement-Free grout sample". The samples cured in a Ziploc® sealed plastic bag for 42 days. After curing, the samples were crushed and sieved using the method outlined in SRNL work instructions.¹¹ Material that passed through the 3/8-inch (0.375") sieve (9.252 mm) was subsequently screened through a No. 4 sieve (4.76 mm). The material retained on the No. 4 sieve was packaged in a primary container (250 mL High Density Polyethylene (HDPE) bottle) and shipped on the same day that it was prepared to SwRI® by Environmental Compliance & Area Completion Projects (EC&ACP).

#### 3.0 Results

Table 3-1 summarizes the analytical results provided by the vendor, SwRI.<sup>12</sup> The first eight rows show data for the RCRA metals and the next four rows show data for the UHC metals from the TCLP leachates. The last four rows show results from solids analyses of the saltstone for benzene, phenol, total and amenable cyanide. The entire vendor report is documented and included as a reference. 12 Some of the data values are flagged with qualifier letters (U, L, D, J, B) that are shown as footnotes to the table. Further explanation for these qualifiers can be found in the vendor report.<sup>12</sup> For comparison to the current Full Premix results, the previous quarter and four previous quarter average results for the Full Premix sample are shown in the final two columns. The four-quarter average values contain a qualifier (\*, +, ^) if past values have been reported as a non-detectable analyte ('U'). The Regulatory Toxicity<sup>7</sup> values and the WAC Limits are from Table 6 of the WAC<sup>13</sup> and reflect the requirements in the applicable version of the document. Note that the vendor used a "modified" Method 1311 where sample mass was restricted due to the elevated activity of the sample.<sup>12</sup> This methodology is consistent with the joint guidance from the Nuclear Regulatory Commission (NRC) and Environmental Protection Agency (EPA) for mixed radioactive and hazardous waste. For the January 2022 semiannual saltstone samples, the TCLP extraction was performed on the Full Premix and the Cement-Free samples using extraction fluid #2.12 Extraction fluid #2 is an aqueous acetic acid solution with pH=  $2.88 \pm 0.05$  prepared by diluting 5.7 mL of glacial acetic acid into reagent water for a total volume of 1 Liter. Extraction fluid #1 is an aqueous acetic acid solution with pH=  $4.93 \pm 0.05$ prepared by diluting 5.7 mL of glacial acetic acid into 500 mL of reagent water, then adding 64.3 mL of sodium hydroxide and diluting with reagent water for a total volume of 1 Liter.<sup>6</sup> Determination of the extract fluid used in the TCLP uses Section 7.1.4 'Determination of Appropriate Extraction Fluid' of the TCLP method.<sup>6</sup> A size reduced portion of the solid is mixed with water and if the resulting pH of the contacted water is below pH 5.0, then extraction fluid #1 is used. However, if the resulting pH is above 5.0, then an additional step using HCl is performed. Both samples resulted in high pH slightly above 12 of the contacted

water so the HCl step was applied. The resulting pH from the HCl step showed a pH of 9.91 for the Full Premix sample and a pH of 5.44 for the Cement-Free sample. Thus the extraction fluid #2 was applied for the Full Premix and for the Cement-Free. The final extract pH values resulting from the TCLP extraction using fluid #2 showed a pH of 7.10 for the Full Premix and a pH of 7.25 for the Cement-Free Sample.

#### Full-Premix Saltstone

Table 3-1 shows the reported value for Se of 0.036~mg/L is above the Limit of Detection (LOD) of 0.025~mg/L and below the Limit of Quantitation (LOQ), similar to the previous quarter (3QCY21) in which a quarterly full-premix saltstone sample was analyzed. Lead has remained as less than detectable at <0.0075~mg/L in comparison to the previous quarter. The analyzed value for Be of <0.005~mg/L is below the quantitation limit, which is the same as the previous quarter. The reported value for Cr for this quarter was measured at <0.005~mg/L and is similar to the previous quarter. The reported TCLP value for Ba of 0.491~mg/L is higher than the previous quarter (0.367~mg/L), but is comparable to the previous four quarter average of 0.521~mg/L.

The mercury TCLP value for the January 2022 semiannual sample of 0.0048 mg/L is lower than the previous TCLP regulatory quarterly (3QCY21) sample which measured 0.0092 mg/L and the past four quarters that generated saltstone samples with an average of 0.005 mg/L. Table 3-2 shows the total mercury and methyl Hg expressed as mg Hg/L for the current January 2022 sample and the previous four quarters that generated saltstone samples. The associated TCLP values are also shown in the final column. The past five quarters, saltstone samples have been made with total mercury in the range of 46 to 68 mg/L and methyl mercury to total mercury ratios in the range of 0.22 to 0.46. This indicates that the TCLP value for mercury has remained below 0.010 mg/L, which is 5% of the regulatory toxicity limit of 0.200 mg/L.

### Cement-Free Saltstone

All of the RCRA metals and UHCs shown in Table 3-1 for the Full Premix and Cement-Free samples are comparable, i.e., within 50% of the value. The amenable and total cyanide and phenol for the Cement-Free sample are higher than for the Full Premix sample. The Cement-Free values for total cyanide and phenol are also higher than the four-quarter average of the Full Premix.

Table 3-1. January 2022 Semiannual Saltstone Sample TCLP and Solids Analysis Results

		Cement-			Results Fu	ll Premix
Analyte	Full Premix Result (mg/L) <sup>12</sup>	Free Result (mg/L) <sup>12</sup>	Regulatory Toxicity <sup>7</sup> (mg/L)	WAC Limit <sup>13</sup> (mg/L)	Previous Quarter (mg/L) <sup>9</sup>	Previous Four Quarter Average <sup>9,14-16</sup> (mg/L)
RCRA	Metals					
Arsenic (As)	< 0.025 <sup>U</sup>	< 0.025 <sup>U</sup>	5.0	2.5	< 0.025 <sup>U</sup>	$0.027^{*}$
Barium (Ba)	0.491	0.656	100.0	50	0.367	0.521
Cadmium (Cd)	< 0.005 <sup>U</sup>	< 0.005 <sup>U</sup>	1.0	0.5	< 0.005 <sup>U</sup>	0.005^
Chromium (Cr)	< 0.005 <sup>U</sup>	< 0.005 <sup>U</sup>	5.0	2.5	< 0.005 <sup>U</sup>	0.005^
Lead (Pb)	< 0.0075 <sup>U</sup>	< 0.0075 <sup>U</sup>	5.0	2.5	< 0.0075 <sup>U</sup>	0.008^
Mercury (Hg)	0.0048	0.0061	0.2	0.1	0.0092	0.005
Selenium (Se)	$0.036^{B}$	$0.037^{\mathrm{B}}$	1.0	0.5	$0.042^{B}$	0.034*
Silver (Ag)	< 0.010 <sup>U</sup>	< 0.010 <sup>U</sup>	5.0	2.5	< 0.010 <sup>U</sup>	$0.010^{^{\wedge}}$
Under	lying Hazardo	us Constituen	ts (UHCs)			
Antimony (Sb)	< 0.025 <sup>U</sup>	< 0.025 <sup>U</sup>	-	1	< 0.025 <sup>U</sup>	0.0250^
Beryllium (Be)	< 0.005 <sup>U</sup>	< 0.005 <sup>U</sup>	=	ı	< 0.005 <sup>U</sup>	0.005^
Nickel (Ni)	$0.005^{B}$	$0.006^{B}$	-	ı	< 0.005 <sup>U</sup>	0.009+
Thallium (Tl)	< 0.075 <sup>U</sup>	< 0.075 <sup>U</sup>	-	1	< 0.075 <sup>U</sup>	0.019+
Select	Solids Analyse	es of Regulato	ry Interest			
	(mg/kg)	(mg/kg)			(mg/kg)	(mg/kg)
Benzene	<0.001 <sup>U</sup>	<0.001 <sup>U</sup>	-	-	<0.001 <sup>U</sup>	$0.00098^{+}$
Amenable Cyanide	< 0.321 <sup>U</sup>	0.400	-	-	<0.384 <sup>U</sup>	1.26*
Total Cyanide	12.5 <sup>D</sup>	19.8 <sup>D</sup>	-	-	15.1	15.3
Phenol	< 0.833 <sup>UJ</sup>	< 0.836 <sup>UJ</sup>	-	-	<0.800 <sup>UJ</sup>	0.852+

<sup>-</sup>Indicates a location in the table for which an entry would not be appropriate.

Table 3-2. Mercury Speciation Data from Current and Past Tank 50 Salt Solutions

Tank 50 Sample	Total Hg (mg/L)	Methyl Hg (mg/L) as Hg	Ratio Methyl Hg as Hg /Total Hg	TCLP (mg/L) <sup>a</sup>
2QCY19 a	63.0	19.3	0.306	0.0036
3QCY19 a	67.6	19.9	0.294	0.0016
1QCY21 a	59.0	13.1	0.222	0.0045
3QCY21 a	62.2	24.6	0.395	0.0092
Jan. 2022	45.9	20.9	0.455	0.0048

<sup>&</sup>quot;a" Past four quarter average TCLP =  $0.0047 \text{ mg/L} \pm 0.0032 \text{ mg/L}$ 

Table 3-3 provides comparison between analytical results for each analyte to SwRI®'s Limit of Detection (LOD) and Limit of Quantitation (LOQ) for the TCLP leachates and to the Reporting Limits (RL) for the solids analyses. Antimony, arsenic, beryllium, cadmium, chromium, lead, silver and thallium were all less

U Non-detected analyte

D Results reported from a dilution.

<sup>&</sup>lt;sup>J</sup> Matrix spike and/or matrix spike duplicate criteria was not met.

<sup>&</sup>lt;sup>B</sup> Analyte was detected at the instrument at or above Limits of Detection (LOD), but less than Limit of Quantitation (LOQ).

<sup>\*</sup> Contains qualifier of "U" in at least one quarter.

+ Contains qualifier of "U" in all quarters with multiple Reporting Limits (RL) or Limits of Detection (LOD).

<sup>^</sup> Contains qualifier of "U" in all quarters with same RL or LOD.

than the detection limit or reporting limit for the Full Premix sample. The same was true for the Cement-Free. Appendix A includes summaries of results from blanks, laboratory control samples, matrix spikes, and matrix spike duplicates.

**Table 3-3. RCRA Metal TCLP Result Concentrations, Limit of Detection, and Limit of Quantitation**<sup>12</sup>

Analyte	Methods	LOD	LOQ	Full premix Sample Results	Cement Free Sample Results
		(µg/L)	(µg/L)	(µg/L)	(µg/L)
Antimony (Sb)	6010D	25.0	50.0	<25.0 <sup>U</sup>	<25.0 <sup>U</sup>
Arsenic (As)	6010D	25.0	50.0	<25.0 <sup>U</sup>	<25.0 <sup>U</sup>
Barium (Ba)	6010D	5.0	10.0	491	656
Beryllium (Be)	6010D	5.00	10.0	< 5.00 <sup>U</sup>	< 5.00 <sup>U</sup>
Cadmium (Cd)	6010D	5.00	10.0	< 5.00 <sup>U</sup>	< 5.00 <sup>U</sup>
Chromium (Cr)	6010D	5.00	10.0	<5.00 <sup>U</sup>	< 5.00 <sup>U</sup>
Lead (Pb)	6010D	7.50	15.0	<7.50 <sup>U</sup>	<7.50 <sup>U</sup>
Mercury (Hg)	7470A	0.05	0.100	4.89	6.08
Nickel (Ni)	6010D	5.0	10.0	5.25 <sup>B</sup>	$6.38^{B}$
Selenium (Se)	6010D	25.0	50.0	$36.9^{B}$	37.6 <sup>B</sup>
Silver (Ag)	6010D	10.0	20.0	<10.0 <sup>U</sup>	<10.0 <sup>U</sup>
Thallium (Tl)	6010D	75.00	150.0	<75.0 <sup>U</sup>	<75.0 <sup>U</sup>
-	-	-	RL (mg/kg)	(mg/kg)	(mg/kg)
Benzene	8260D	-	0.00091 & 0.00097	<0.001 <sup>U</sup>	<0.001 <sup>U</sup>
Amenable Cyanide	9012C	-	0.321 & 0.380	<0.321 <sup>U</sup>	0.400
Total Cyanide	9012C		0.321 & 0.949	12.5 <sup>D</sup>	19.8 <sup>D</sup>
Phenol	9065	-	0.833 & 0.836	< 0.833 <sup>UJ</sup>	< 0.836 <sup>UJ</sup>

<sup>-</sup> Indicates a location in the table for which an entry would not be appropriate.

#### 4.0 Conclusions

Analyses of the SDF Full Premix and Cement-Free waste forms prepared from the January 2022 semiannual Tank 50 salt solution sample and premix material resulted in the following findings.

- The RCRA metal TCLP result concentrations met the SC Code of Regulations 61-79.261.24 requirements for a nonhazardous waste form.<sup>7</sup>
- The measured concentrations of the TCLP RCRA metals and additional inorganic/organic UHCs met the SC Code of Regulations 61-79.268.48 non-wastewater standards.<sup>8</sup>
- The measured concentrations of the TCLP RCRA metals met the SPF WAC.<sup>13</sup>

<sup>&</sup>lt;sup>U</sup> Result is less than the Limit of Detection (LOD) and/or Reporting Limit (RL).

<sup>&</sup>lt;sup>D</sup> Result is reported from a dilution.

<sup>&</sup>lt;sup>J</sup> Matrix spike and/or matrix spike duplicate criteria was not met.

<sup>&</sup>lt;sup>B</sup> Analyte was detected at the instrument at or above Limits of Detection (LOD), but less than Limit of Quantitation (LOQ).

#### 5.0 References

- 1. "Electronic Morning Report: Tank Addition Data," Savannah River Remediation, Aiken, SC, January 2022, Available at <a href="http://pceweb.srs.gov/emr/default.aspx">http://pceweb.srs.gov/emr/default.aspx</a>.
- 2. C.L. Crawford, "Results for the January 2022 Semiannual Tank 50 Salt Solution Sample," Savannah River National Laboratory Aiken, SC, SRNL-STI-2022-00137, Revision 0, May 2022.
- 3. M. Brown, "Routine Saltstone Support for Salt Solution and Grout Analyses," Savannah River Mission Completion, Aiken, SC, X-TTR-Z-00025, Revision 0, August 2021.
- 4. K.A. Hill, "January 2022 Semiannual TCLP," Savannah River National Laboratory Aiken, SC, i7557-00151-33, SRNL E-Notebook (Production), January 2022.
- 5. D.H. Miller, "Definition of TCLP Sample Term Collected," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2015-00081, Revision. 0, April 2015.
- 6. "Toxicity Characteristic Leaching Procedure," Environmental Protection Agency, SW-846 Test Method 1311, 1992.
- 7. "Toxicity Characteristics," South Carolina Code of Regulations, 61-79.261.24, amended by State Register Volume 27, Issue No. 6 Part 1, eff June 27, 2003, available at <a href="http://www.scstatehouse.gov/codregs/Ch%2061-79%20part%201.pdf">http://www.scstatehouse.gov/codregs/Ch%2061-79%20part%201.pdf</a>.
- 8. "Universal Treatment Standards," South Carolina Code of Regulations, 61-79.268.48, amended by State Register Volume 39, Issue No. 6, Doc. No. 4541, eff June 26, 2015, available at <a href="http://www.scstatehouse.gov/coderegs/Ch%2061-79%20part%202.pdf">http://www.scstatehouse.gov/coderegs/Ch%2061-79%20part%202.pdf</a>.
- 9. K.A. Hill, "Saltstone Third Quarter Calendar Year 2021 (3QCY21) Toxicity Characteristic Leaching Procedure (TCLP) Results," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2021-00681, Revision 0, February 2022.
- 10. "Preparation of Grout in a CA Hood," Savannah River National Laboratory, Work Instruction, L33-WI-0065, Latest Revision,
- 11. "Crushing and Screening of Saltstone TCLP Sample in a CA Hood," Savannah River National Laboratory Work Instruction, L33-WI-0066, Latest Revision,
- 12. K.A. Hill, "Data Package from Vendor for January 2022 Semiannual TCLP Analysis," Savannah River National Laboratory Aiken, SC, SRNL-L3310-2022-00008, Revision 0, May 2022.
- 13. S.J. Harrington, "Waste Acceptance Criteria for Transfers to the Z-Area Saltstone Production Facility During Salt Disposition Integration" Savannah River Remediation, Aiken, SC, X-SD-Z-00004, Revision 4, March 2021.
- 14. K.A. Hill, "Saltstone First Quarter Calendar Year 2021 (1QCY21) Toxicity Characteristic Leaching Procedure (TCLP) Results," Savannah River National Laboratory Aiken, SC, SRNL-STI-2021-00325 Revision 0, August 2021.

- 15. K.A. Hill, "Saltstone Third Quarter Calendar Year 2019 (3QCY19) Toxicity Characteristic Leaching Procedure (TCLP) Results," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2019-00702, Revision 0, February 2020.
- 16. K.A. Hill, "Saltstone First Quarter Calendar Year 2019 (1QCY19) Toxicity Characteristic Leaching Procedure (TCLP) Results," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2019-00306, Revision 0, August 2019

## Appendix A. Quality Assurance

The following subsections include summaries of results from blanks, laboratory control samples, matrix spikes, and matrix spike duplicates. The data package also includes data for calibration verifications, interference checks and serial dilutions.<sup>12</sup>

Table A-1 shows all TCLP extraction fluid blank concentrations and the solid matrix blank concentrations. In the extraction fluid blank, antimony, arsenic, barium, cadmium, chromium, lead, mercury, nickel, selenium, silver and thallium were all less than detection limit or reporting limit. Thallium and beryllium were detected at the instrument at or above the LOD, but less than the LOQ. Benzene, amenable cyanide, total cyanide and phenol were all less than detection limit or reporting limit.

Table A-1. TCLP Extraction Fluid Blank and Solid Matrix Blank<sup>12</sup>

Analyte	TCLP Blank (µg/L)	Qualifiers
Antimony (Sb)	<25.0	U
Arsenic (As)	<25.00	U
Barium (Ba)	< 5.00	U
Beryllium (Be)	< 5.00	U
Cadmium (Cd)	< 5.00	U
Chromium (Cr)	< 5.00	U
Lead (Pb)	<7.50	U
Mercury (Hg)	< 0.500	U
Nickel (Ni)	<5.0	U
Selenium (Se)	<25.0	U
Silver (Ag)	<10.0	U
Thallium (Tl)	<75.00	U
Analyte	Solid Matrix Blank (mg/Kg)	Qualifiers
Benzene	< 0.00050	U
Amenable Cyanide	< 0.300	U
Total Cyanide	< 0.300	U
Phenol	< 0.987	Ū

UResult is less than the Limit of Detection (LOD) and/or Reporting Limit (RL).

Table A- 2 shows all Laboratory Control Sample (LCS) recoveries meet the SwRI®'s acceptance limit in the range of 80% to 120% for metals and phenol, 70% to 130% for benzene and 87.8% for total cyanide, which was within the manufacturers acceptance limit.<sup>17</sup> The laboratory control samples are clean aqueous solutions analyzed to assure integrity of the analytical technique exclusive of matrix effects.

Table A- 2 Laboratory Control Sample<sup>12</sup>

Analyte	Laboratory Control (µg/L)		Recovery (%)
	True	Found	1
Antimony (Sb)	500	538	107.6%
Arsenic (As)	2000	2150	107.5%
Barium (Ba)	2000	2120	106.0%
Beryllium (Be)	50.0	52.6	105.2%
Cadmium (Cd)	50.0	52.4	104.8%
Chromium (Cr)	200	208	104.0%
Lead (Pb)	500	505	101.0%
Mercury (Hg)	1.00	0.951	95.1%
Nickel (Ni)	500	503	100.6%
Selenium (Se)	2000	1960	98.0%
Silver (Ag)	50.0	53.2	106.4%
Thallium (Tl)	2000	2210	110.5%
Analyte	Laboratory Co	ontrol (mg/Kg)	Recovery (%)
	True	Found	7
Benzene	0.020	0.021	105%
Amenable Cyanide	-	-	-
Total Cyanide	58.1	51.0	87.8%
Phenol	25.0	23.1	92.4%

<sup>-</sup> Indicates a location in the table for which an entry would not be appropriate.

Results from analysis of the matrix spike (MS) and the matrix spike duplicate (MSD) are given in Table A-3 and Table A-4. The results shown in Table A-3 indicate all analytes met the recommended quality control acceptance criteria for MS and MSD percent recoveries (75-125%) and the Relative Percent Difference (RPD) acceptance limits (0-20%). In Table A-4, results show benzene met the recommended quality control acceptance criteria for MS, MSD and RPDs. In Table A-4, results show phenol did not meet the recommended quality control acceptance criteria for MS, MSD and RPDs. However, a post-digestion spike recovery sample showed a phenol recovery  $\geq 75\%$  within the control limit of 60% to 120%.

Table A-3 TCLP Leachates Matrix Spike and Duplicate Results<sup>12</sup>

Amaluta	Initial C	Concentrations	s (µg/L)	Spiked Sample** (µg/L)		Reco	very (%)	RPD (%)
Analyte	Parent Sample Result	Qualifiers	Spike Added	Spike	Spike Duplicate	Spike	Spike Duplicate	KI D (70)
Antimony (Sb)	<25.0	U	500	552	555	110.4	111.0	0.5
Arsenic (As)	<25.0	U	500	549	564	109.8	112.8	2.7
Barium (Ba)	491	-	500	987	988	99.2	99.4	0.2
Beryllium (Be)	< 5.00	U	500	478	482	95.6	96.4	0.8
Cadmium (Cd)	< 5.00	U	500	482	490	96.4	98.0	1.6
Chromium (Cr)	< 5.00	U	500	478	482	95.6	96.4	0.8
Lead (Pb)	<7.50	U	500	447	452	89.4	90.4	1.1
Mercury (Hg)	4.89	-	500	436	433	86.2	85.6	0.7
Nickel (Ni)	5.25	В	500	481	486	95.2	96.2	1.0
Selenium (Se)	36.9	В	500	564	564	105.4	105.4	0.0
Silver (Ag)	<10.0	U	500	517	517	103.4	103.4	0.0
Thallium (Tl)	<75.00	U	500	524	543	104.8	108.6	3.6

<sup>&</sup>lt;sup>U</sup> Result is less than the Limit of Detection (LOD) and/or Reporting Limit (RL).

Table A-4. Organic UHCs Matrix Spike and Duplicate Results<sup>12</sup>

Analota	Initial Concentrations (mg/kg)					Initial Concentrations (mg/kg)  Spiked Sample (mg/kg)			Reco	RPD
Analyte	Result	Qualifiers	MS- Spike Added	MSD- Spike Added	Spike	Spike Duplicate	Spike	Spike Duplicate	(%)	
Benzene*	0.0	-	0.039	0.039	0.039	0.038	100	97	3.0	
Amenable Cyanide	-	-	-	-	-	-	-	-	-	
Total Cyanide***	12.5**	D	0.629	0.683	14.4	14.0	302.1	219.6	32.0	
Phenol	0.833	UJ	20.2	22.4	0.808	0.895	0.0	0.0	0.0	

UResult is less than the Limit of Detection (LOD) and/or Reporting Limit (RL).

<sup>&</sup>lt;sup>B</sup> Analyte was detected at the instrument at or above Limits of Detection (LOD), but less than Limit of Quantitation (LOQ).

<sup>&</sup>quot;-" No Qualifier

<sup>\*\*</sup> SwRI<sup>®</sup> Sample ID = W-18489-00001 MS/MSD

<sup>&</sup>lt;sup>J</sup> Matrix spike and/or matrix spike duplicate criteria was not met.

D Result is reported from a Dilution

<sup>\*</sup>  $SwRI^{\text{(R)}}$  Sample ID = W-18489-00001

<sup>\*\*</sup>Parent value exceeded 4 times the spike added; therefore, MS/MSD %Recovery and %RPD are not required for evaluation

<sup>-</sup> Indicates a location in the table for which an entry would not be appropriate.

<sup>\*\*\*</sup>  $SwRI^{\text{(R)}}$  Sample ID = W-18489-00001 MS/MSD

## **Distribution:**

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H. M. Hunter	
J. F. Iaukea	
V. Jain	
R. C. Jolly	
A. W. Jung	
D. E. Kucab	

#### 6.0 References

- 1. "Electronic Morning Report: Tank Addition Data," Savannah River Remediation, Aiken, SC, January 2022, Available at <a href="http://pceweb.srs.gov/emr/default.aspx">http://pceweb.srs.gov/emr/default.aspx</a>.
- 2. C.L. Crawford, "Results for the January 2022 Semiannual Tank 50 Salt Solution Sample," Savannah River National Laboratory Aiken, SC, SRNL-STI-2022-00137, Revision 0, May 2022.
- 3. M. Brown, "Routine Saltstone Support for Salt Solution and Grout Analyses," Savannah River Mission Completion, Aiken, SC, X-TTR-Z-00025, Revision 0, August 2021.
- 4. K.A. Hill, "January 2022 Semiannual TCLP," Savannah River National Laboratory Aiken, SC, i7557-00151-33, SRNL E-Notebook (Production), January 2022.
- 5. D.H. Miller, "Definition of TCLP Sample Term Collected," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2015-00081, Revision. 0, April 2015.
- 6. "Toxicity Characteristic Leaching Procedure," Environmental Protection Agency, SW-846 Test Method 1311, 1992.
- 7. "Toxicity Characteristics," South Carolina Code of Regulations, 61-79.261.24, amended by State Register Volume 27, Issue No. 6 Part 1, eff June 27, 2003, available at <a href="http://www.scstatehouse.gov/codregs/Ch%2061-79%20part%201.pdf">http://www.scstatehouse.gov/codregs/Ch%2061-79%20part%201.pdf</a>.
- 8. "Universal Treatment Standards," South Carolina Code of Regulations, 61-79.268.48, amended by State Register Volume 39, Issue No. 6, Doc. No. 4541, eff June 26, 2015, available at <a href="http://www.scstatehouse.gov/coderegs/Ch%2061-79%20part%202.pdf">http://www.scstatehouse.gov/coderegs/Ch%2061-79%20part%202.pdf</a>.
- 9. K.A. Hill, "Saltstone Third Quarter Calendar Year 2021 (3QCY21) Toxicity Characteristic Leaching Procedure (TCLP) Results," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2021-00681, Revision 0, February 2022.
- 10. "Preparation of Grout in a CA Hood," Savannah River National Laboratory, Work Instruction, L33-WI-0065, Latest Revision,
- 11. "Crushing and Screening of Saltstone TCLP Sample in a CA Hood," Savannah River National Laboratory Work Instruction, L33-WI-0066, Latest Revision,
- 12. K.A. Hill, "Data Package from Vendor for January 2022 Semiannual TCLP Analysis," Savannah River National Laboratory Aiken, SC, SRNL-L3310-2022-00008, Revision 0, May 2022.
- 13. S.J. Harrington, "Waste Acceptance Criteria for Transfers to the Z-Area Saltstone Production Facility During Salt Disposition Integration" Savannah River Remediation, Aiken, SC, X-SD-Z-00004, Revision 4, March 2021.
- 14. K.A. Hill, "Saltstone First Quarter Calendar Year 2021 (1QCY21) Toxicity Characteristic Leaching Procedure (TCLP) Results," Savannah River National Laboratory Aiken, SC, SRNL-STI-2021-00325 Revision 0, August 2021.

- 15. K.A. Hill, "Saltstone Third Quarter Calendar Year 2019 (3QCY19) Toxicity Characteristic Leaching Procedure (TCLP) Results," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2019-00702, Revision 0, February 2020.
- 16. K.A. Hill, "Saltstone First Quarter Calendar Year 2019 (1QCY19) Toxicity Characteristic Leaching Procedure (TCLP) Results," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2019-00306, Revision 0, August 2019.