Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

- 1) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
- 2) representation that such use or results of such use would not infringe privately owned rights; or
- 3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.



Saltstone Second Quarter Calendar Year 2018 (2QCY18) Toxicity Characteristic Leaching Procedure (TCLP) Results

K. A. Hill November 2018 SRNL-STI-2018-00632, Revision 0

SRNL.DOE.GOV

DISCLAIMER

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

- 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
- 2. representation that such use or results of such use would not infringe privately owned rights; or
- 3. endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Printed in the United States of America

Prepared for U.S. Department of Energy

Keywords: *Tank 50, Regulatory, TCLP, Saltstone*

Retention: Permanent

Saltstone Second Quarter Calendar Year 2018 (2QCY18) Toxicity Characteristic Leaching Procedure (TCLP) Results

K. A. Hill

November 2018



OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

REVIEWS AND APPROVALS

AUTHORS:

K. A. Hill, Immobilization Technology	Date
TECHNICAL REVIEW:	
C. L. Crawford, Chemical Processing Technology, Reviewed per E7 2.60	Date
APPROVAL:	
A. D. Cozzi, Manager Waste Form Processing Technology	Date
S. D. Fink, Director, Chemical Processing Technologies	Date
E. J. Freed, Manager DWPF and Saltstone Facility Engineering	Date
R. E. Edwards, Manager Nuclear Safety and Engineering Integration	Date

EXECUTIVE SUMMARY

The aqueous waste from Tank 50 (salt solution) is sampled quarterly for transfers to the Saltstone Production Facility (SPF). Salt solution is treated at SPF and disposed of in the Saltstone Disposal Facility (SDF). A SDF waste form (saltstone) was prepared in the Savannah River National Laboratory (SRNL) from the Tank 50 Waste Acceptance Criteria (WAC) sample¹ and Z-Area premix material for the second quarter of calendar year 2018 (2QCY18).^{2,3} Results from this memorandum support Task 2: 'Grout Leaching Analyses' of the Task Technical Request (TTR)³ prepared by Savannah River Remediation (SRR). After a 28 day cure, a sample of the SDF waste form was collected and shipped to a certified laboratory for analysis using the Toxicity Characteristic Leaching Procedure (TCLP).⁴ The 2QCY18 saltstone sample 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.⁵⁻⁷

TABLE OF CONTENTS

LIST OF TABLES	vii
LIST OF ABBREVIATIONS	viii
1.0 Introduction	1
2.0 Experimental	1
3.0 Results	2-6
4.0 Conclusions	7
5.0 Reference	8

LIST OF TABLES

Table 3-1. 2QCY18 Saltstone Sample TCLP and Solids Analysis Results	2
Table 3-2. RCRA Metal TCLP Result Concentrations, Limit of Detection, and Limit of Quantitation	3
Table 3-3. TCLP Extraction Fluid Blank	4
Table 3-4. Laboratory Control Sample	5
Table 3-5. TCLP Leachates Matrix Spike and Duplicate Results	6
Table 3-6. Organic UHCs Matrix Spike and Duplicate Results	7

LIST OF ABBREVIATIONS

D&S-FE	DWPF & Saltstone Facility Engineering
EC&ACP	Environmental Compliance & Area Completion Projects
EPA	Environmental Protection Agency
ES	Environmental Stewardship
ETF	Effluent Treatment Facility
LOD	Limit of Detection
LOQ	Limit of Quantitation
MRL	Minimum Reporting Limit
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NRC	Nuclear Regulatory Commission
RCRA	Resource Conservation and Recovery Act
RL	Reporting Limit
SDF	Saltstone Disposal Facility
SPF	Saltstone Production Facility
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
SRR	Savannah River Remediation
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 SPF receives waste from Tank 50 for treatment. The following dates were selected starting from the last quarterly sampling date to the current quarterly sampling date. Tank 50 accepted the following transfers from February 6, 2018 to July 12, 2018:⁸

- ~1.9 kgal from 211-H
- ~4.3 kgal from Effluent Treatment Facility (ETF)
- ~2.7 kgal from 512-S
- ~ 131.6 kgal from the Actinide Removal Process / Modular Caustic Side Solvent Extraction Unit (ARP/MCU) Decontaminated Salt Solution Hold Tank (DSSHT)

On July 12, 2018, a salt solution sample was taken from Tank 50¹ and used to prepare a SDF waste form sample, referred to as a saltstone sample.⁹ Once the 2QCY18 saltstone sample cured for 28 days, it was crushed, sieved, packaged, and deemed "collected".¹⁰ The sample was then shipped to Southwest Research Institute (SWRI) to analyze for toxicity per the TCLP method.^{2,4} This saltstone sample determines whether the non-hazardous nature of the grout meets the requirements of the SC Code of Regulations 61-79.261.24⁶ for RCRA metals and 61-79.268.48⁵ for inorganic/organic UHCs (for informational purposes only³).

2.0 Experimental

Saltstone preparation was performed at SRNL. DWPF & Saltstone Facility Engineering (D&S-FE) provided SRNL with the saltstone grout recipe as well as the premix components.^{3,9} The saltstone sample was prepared using the mixing method outlined in SRNL Environmental Stewardship (ES) work instructions.¹¹ The sample was left to cure for at least 28 days. After curing, the sample was crushed and sieved using the method outlines in ES work instructions.¹² Material that passed through the 3/8-inch sieve was subsequently screened through a No. 4 sieve (4.76 mm). The material retained on the No. 4 sieve was packaged and shipped to Southwest Research Institute (SWRI) by Environmental Compliance & Area Completion Projects (EC&ACP).³

3.0 Results

Table 3-1 summarizes the analytical results provided by the vendor, SWRI.¹³ 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.¹³ For comparison, the previous quarter and four quarter average results are shown. The limits are from Table 6 of the WAC⁷ 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. 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.¹⁴ Table 3-2 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, cadmium, lead, silver, beryllium, thallium, benzene and phenol were all less than the detection limit or reporting limit.

				Resu	lts
Analyte	Result ¹³ (mg/L)	Regulatory Limit Toxicity ⁶ (mg/L)	WAC Limit ⁷ (mg/L)	Previous Quarter ¹⁵ (mg/L)	Previous Four Quarter Average ¹⁵⁻¹⁸ (mg/L)
RCRA Metals	•				
Arsenic (As)	$< 0.020^{U}$	5.0	2.5	$< 0.020^{U}$	0.0200^
Barium (Ba)	1.69 ^D	100.0	50	1.84	0.859
Cadmium (Cd)	$< 0.005^{\circ}$	1.0	0.5	$< 0.005^{\text{U}}$	0.005^
Chromium (Cr)	0.0477	5.0	2.5	0.0727	0.0219*
Lead (Pb)	< 0.0075 ^U	5.0	2.5	< 0.0075 ^U	0.00563^{+}
Mercury (Hg)	0.0588	0.2	0.1	0.0593 ^D	0.0215
Selenium (Se)	0.0521	1.0	0.5	0.0417 ^B	0.0294*
Silver (Ag)	< 0.010 ^U	5.0	2.5	< 0.010 ^U	0.01^
Underlying Hazardo	us Constituen	ts (UHCs)			
Antimony (Sb)	<0.025 ^U	-	-	< 0.025 ^U	0.0213+
Beryllium (Be)	< 0.005 ^U	-	-	0.005 ^B	0.005^
Nickel (Ni)	0.0568	-	-	0.0649	0.0201*
Thallium (Tl)	< 0.005 ^{UD}	-	-	< 0.005 ^{UD}	0.005^
Select Solids Analyse	es of Regulato	ry Interest			
	(mg/kg)		(mg/kg)	(mg/kg)	
Benzene	< 0.00095 ^U	-	-	<0.0009 ^U	0.0009^{+}
Amenable Cyanide	0.3 ^J	-	-	<0.211 ^U	2.48*
Total Cyanide	11.0 ^J	-	-	11.0	10.2
Phenol	<0.876 ^{JU}	-	-	1.37 ^J	1.29*

Table 3-1. 2QCY18 Saltstone Sample TCLP and Solids Analysis Results

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

^U Non-detected analyte

^D Results reported from a dilution.

¹⁰ Results reported from a dilution.
 ¹ Matrix spike and/or matrix spike duplicate criteria was not met.
 ¹⁸ Analyte was detected at the instrument at or above Limits of Detection (LOD), but less than Limit of Quantitation (LOQ).
 * 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).
 ^ Contains qualifier of "U" in all quarters with same RL or LOD.

Analyte	Methods	LOD (µg/L)	LOQ (µg/L)	Sample Results (µg/L)	Qualifiers
Antimony (Sb)	6010D	25.0	50.0	<25.0	U
Arsenic (As)	6010D	20.0	40.0	<20.0	U
Barium (Ba)	6010D	50.0	10.0	1690	D
Beryllium (Be)	6010D	5.00	10.0	<5.00	U
Cadmium (Cd)	6010D	5.00	10.0	<5.00	U
Chromium (Cr)	6010D	5.00	10.0	47.7	-
Lead (Pb)	6010D	7.50	15.0	<7.50	U
Mercury (Hg)	7470A	1.00	2.00	58.8	-
Nickel (Ni)	6010D	5.00	10.0	56.8	-
Selenium (Se)	6010D	25.0	50.0	52.1	-
Silver (Ag)	6010D	10.0	20.0	<10.0	U
Thallium (Tl)	6020B	5.00	10.0	< 5.00	UD
-	-	-	RL (mg/kg)	(mg/kg)	-
Benzene	8260C	-	-	< 0.00095	U
Amenable Cyanide	Amenable cyanide 9012B	-	0.212	0.300	J
Total Cyanide	Cyanide 9012B	-	0.212	11.0	J
Phenol	Phenol 9065	-	0.876	< 0.876	UJ

Table 3-2. RCRA Metal TCLP Result Concentrations, Limit of Detection, and Limit of Quantitation¹³

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

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

^D Result is reported from a dilution.

^J Matrix spike and/or matrix spike duplicate criteria was not met.

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.¹³

Table 3-3 shows all TCLP Extraction Fluid Blank concentrations. In the TCLP Blank, barium was present at levels above the detection limit of 5 μ g/L but below the limit of quantitation of 10 μ g/L. Antimony, arsenic, beryllium, cadmium, chromium, lead, mercury, nickel, selenium, silver, thallium, benzene, amenable cyanide, total cyanide, and phenol were all less than detection limit or reporting limit.

Analyte	TCLP Blank (µg/L)	Qualifiers
Antimony (Sb)	<25.0	U
Arsenic (As)	<20.0	U
Barium (Ba)	7.69	В
Beryllium (Be)	<5.00	U
Cadmium (Cd)	<5.00	U
Chromium (Cr)	<5.00	U
Lead (Pb)	<7.50	U
Mercury (Hg)	< 0.100	U
Nickel (Ni)	<5.00	U
Selenium (Se)	<25.0	U
Silver (Ag)	<10.0	U
Thallium (Tl)	<5.00	UD
Benzene	< 0.50	U
Amenable Cyanide	<0.240	U
Total Cyanide	<0.249	U
Phenol	< 0.997	U

Table 3-3. TCLP Extraction Fluid Blank¹³

^UResult is less than the Limit of Detection (LOD) and/or Reporting Limit (RL). ^BResult is greater than or equal to the Limit of Detection (LOD) and less than the Limit of Quantization (LOQ). ^DResult is reported from a dilution.

Table 3-4 shows all LCS recoveries meet SWRI's acceptance limit in the range of 80% to 120% for metals and phenol, 70% to 130% for benzene and 90% to 110% for total cyanide. The laboratory control samples are clean aqueous solutions analyzed to assure integrity of the analytical technique exclusive of matrix effects.

Analyte	Laboratory Co	ontrol (µg/L)	Recovery (%)
	True	Found	
Antimony (Sb)	1000	970	97.0%
Arsenic (As)	4000	3840	96.0%
Barium (Ba)	4000	3770	94.2%
Beryllium (Be)	100	108	108.0%
Cadmium (Cd)	100	94.7	94.7%
Chromium (Cr)	400	372	93.0%
Lead (Pb)	1000	903	90.3%
Mercury (Hg)	1	0.988	98.8%
Nickel (Ni)	1000	900	90.0%
Selenium (Se)	4000	3650	91.2%
Silver (Ag)	100	92.1	92.1%
Thallium (Tl)	4000	3830	95.8%
Benzene	10	10	100%
Amenable Cyanide	-	-	-
Total Cyanide	0.500	0.462	92.4%
Phenol	0.500	0.487	97.4%

Table 3-4. Laboratory Control Sample¹³

- 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 3-5 and Table 3-6. These results shown in Table 3-5 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%) except for mercury. In Table 3-6, results show benzene met the recommended quality control acceptance criteria for MS, MSD and RPDs. In Table 3-6, results show total cyanide and phenol did not meet the recommended quality control acceptance criteria for MS, MSD, and RPDs.

	Initial Concentrations (µg/L)			-	ed Sample µg/L)	Reco	very (%)		
Analyte	SWRI ID: W- 18078 - 00001	Qualifiers	Spike Added	Spike	Spike Duplicate	Spike	Spike Duplicate	RPD (%)	
Antimony (Sb)	<25.0	U	5000	4930	5070	98.6	101.4	2.8	
Arsenic (As)	<20.0	U	2500	2500	2580	100.0	103.2	3.1	
Barium (Ba)	1690	D	5000	6380	6440	93.8	95.0	1.3	
Beryllium (Be)	<5.00	U	500	498	509	99.6	101.8	2.2	
Cadmium (Cd)	<5.00	U	500	431	446	86.2	89.2	3.4	
Chromiu m (Cr)	47.7	-	1000	874	907	82.6	85.9	3.9	
Lead (Pb)	<7.50	U	2500	2000	2070	80.0	82.8	3.4	
Mercury (Hg)	58.8	-	4.00	58.8	58.4	0.0	-10.0	200*	
Nickel (Ni)	56.8	-	2500	2080	2140	80.9	83.3	2.9	
Selenium (Se)	52.1	-	2500	2470	2550	96.7	99.9	3.3	
Silver (Ag)	<10.0	U	500	414	424	82.8	84.8	2.4	
Thallium (Tl)	<5.00	UD	2500	2280	2290	91.2	91.6	0.4	

Table 3-5. TCLP Leachates Matrix Spike and Duplicate Results¹³

* Parent value exceeded 4 times the spike added; therefore, MS/MSD %Recovery and %RPD are not required for evaluation. - Indicates a location in the table for which an entry would not be appropriate.

Amelute	Initial Concentrations (mg/kg)					ed Sample ng/kg)	Reco	very (%)	
Analyte	SWRI ID: W- 18078-00001	Qualifiers	MS- Spike Added	MSD- Spike Added	Spike	Spike Duplicate	Spike	Spike Duplicate	RPD (%)
Benzene	0.0	U	20	19	20	19	100	100	0.0
Amenable Cyanide	-	-	-	-	-	-	-	-	-
Total Cyanide	11.0	J	1.98	1.82	11.8	15.8	40.4	263.7	150.0*
Phenol	0.876	UJ	22.1	24.1	0.884	0.965	0.0	0.0	0.0

Table 3-6. Organic UHCs Matrix Spike and Duplicate Results¹³

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

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

4.0 Conclusions

Analyses of the SDF waste form prepared from the 2QCY18 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 non-hazardous waste form.⁶
- 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.⁵
- The measured concentrations of the TCLP RCRA metals met the SPF WAC.⁷

5.0 Reference

- 1. C.L. Crawford, "Results for the Second Quarter Calendar Year 2018 Tank 50 Salt Solution Sample," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2018-00499, Rev. 0, December 2018.
- 2. K.A. Hill, "Task Technical and Quality Assurance Plan for SRNL Support of Salt Solution Analyses and Grout Sample Preparation and Analyses – FY2018," Savannah River National Laboratory, Aiken, SC, SRNL-RP-2017-00658, Rev. 0, December 2017.
- 3. J.W. Ray, "Routine Saltstone Support for Salt Solution and Grout Analyses FY2018," Savannah River Remediation, Aiken, SC, X-TTR-Z-00012, Rev. 1, June 2018.
- 4. "Toxicity Characteristic Leaching Procedure," Environmental Protection Agency, SW-846 Test Method 1311, 1992.
- 5. "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 http://www.scstatehouse.gov/coderegs/Ch%2061-79%20part%202.pdf.
- 6. "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 http://www.scstatehouse.gov/codregs/Ch%2061-79%20part%201.pdf.
- 7. J.W. Ray, "Waste Acceptance Criteria for Aqueous Waste Sent to the Z-Area Saltstone Production Facility," Savannah River Remediation, Aiken, SC, X-SD-Z-00001, Rev. 18, November 2018.
- 8. "Electronic Morning Report: Tank Addition Data," Savannah River Remediation, Aiken, SC, September 2018, Available at <u>http://pceweb.srs.gov/emr/default.aspx</u>.
- 9. K.A. Hill, "3Q18 Quarterly TCLP," Savannah River National Laboratory, Aiken, SC, i7557-00151-16, SRNL E-Notebook (Production), November 2018.
- 10. D.H. Miller, "Definition of TCLP Sample Term Collected," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2015-00081, Rev. 0, April 2015.
- 11. "Preparation of Grout in a CA Hood," Savannah River National Laboratory, Aiken, SC, ITS-WI-0065, Rev. 0, February 2015.
- 12. "Crushing and Screening of Saltstone TCLP Sample in a CA Hood," Savannah River National Laboratory Aiken, SC, ITS-WI-0066, Rev. 0, February 2015.
- 13. K.A. Hill, "Data Package from Vendor for 2QCY18 Saltstone TCLP Analysis," Savannah River National Laboratory, Aiken, SC, SRNL-L3300-2018-00062, Rev. 0, November 2018.
- 14. "Joint NRC EPA Guidance on Testing Requirements for Mixed Radioactive and Hazardous Waste," Nuclear Regulatory Commission, Washington, DC, 1997, Available at <u>https://www.nrc.gov/docs/ML0330/ML033000328.pdf</u>.

- 15. K.A. Hill, "Saltstone First Quarter Calendar Year 2018 (1QCY18) Toxicity Characteristic Leaching Procedure (TCLP) Results," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2018-00321, Rev. 0, June 2018.
- 16. K.A. Hill, "Saltstone Third Quarter Calendar Year (3QCY17) Toxicity Characteristic Leaching Procedure (TCLP) Results," Savannah River National Laboratory, Aiken, SC, SRNL-L3300-2017-00046, Rev. 0, December 2017.
- 17. K.A. Hill, "Saltstone Second Quarter Calendar Year 2017 (2QCY17) Toxicity Characteristic Leaching Procedure (TCLP) Results," Savannah River National Laboratory, Aiken, SC, SRNL-L3300-2017-00031, Rev. 0, September 2017.
- 18. F.C. Johnson, "Saltstone 1QCY17 TCLP Toxicity Results," Savannah River National Laboratory, Aiken, SC, SRNL-L3300-2017-00011, Rev. 0, June 2017.

Distribution:

P. M. Almond	C. A. Langton
J. P. Arnold	K. R. Liner
C. J. Bannochie	M. J. Mahoney
T. R. Ball	K. B. Martin
C. J. Bannochie	M. W. McCoy
M. J. Barnes	R. T. McNew
M. N. Borders	P. W. Norris
J. M. Bricker	J. E. Occhipinti
K. M. Brotherton	F. M. Pennebaker
L. W. Brown	R. C. Player
T. B. Brown	M. M. Potvin
N. F. Chapman	J. W. Ray
J. H. Christian	S. H. Reboul
W. A. Condon	C. Ridgeway
A. D. Cozzi	L. B. Romanowski
C. L. Crawford	K. H. Rosenberger
C. C. DiPrete	A. Samadi-Dezfouli
K. D. Dixon	D. C. Sherburne
R. E. Edwards	F. M. Smith
S. D. Fink	A. V. Staub
E. J. Freed	J. Stevens
E. W. Harrison	C. B. Sudduth
C. C. Herman	B. J. Wiedenman
K. A. Hill	T. L. White
P. J. Hill	A. W. Wiggins
J. F. Iaukea	L. A. Wooten
V. Jain	R. H. Young
V. M. Kmiec	Records Administration (EDWS)