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Results for the Second Quarter 2013 Tank 50 WAC Slurry Sample

Chemical and Radionuclide Contaminants

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EXECUTIVE SUMMARY

This report details the chemical and radionuclide contaminant results for the characterization of the 2013 Second Quarter sampling of Tank 50 for the Saltstone Waste Acceptance Criteria (WAC) in effect at that time.¹ Information from this characterization will be used by Saltstone Facility Engineering (SFE) to support the transfer of low-level aqueous waste from Tank 50 to the Salt Feed Tank in the Saltstone Facility in Z-Area, where the waste will be immobilized. This information is also used to update the Tank 50 Waste Characterization System.

The following conclusions are drawn from the analytical results provided in this report:

- SRR WAC targets or limits were met for all analyzed chemical and radioactive contaminants unless noted in this section.
- ⁵⁹Ni, ⁹⁴Nb, ²⁴⁷Cm, ²⁴⁹Cf, and ²⁵¹Cf are above the requested SRR target concentrations². However, they are below the detection limits established by SRNL³.
- Norpar 13 and Isopar L have higher detection limits⁴ compared with the Saltstone WAC¹. The data provided in this report is based upon the concentrations in the sub-sample, and due to the limited solubility in aqueous solution, may not represent the concentrations of the analytes in Tank 50.
- The low insoluble solids content increases the measurement uncertainty for insoluble species.

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LIST OF ABBREVIATIONS

AA	Atomic Absorption (spectroscopy)
AD	Analytical Development
ARP/MCU	Actinide Removal Process/Modular CSSX Unit
CLFL	Composite Lower Flammability Limit
CSSX	Caustic Side Solvent Extraction
CVAA	Cold Vapor Atomic Absorption
DDA	Deliquification, Dissolution and Adjustment
EPA	Environmental Protection Agency
ETP	Effluent Treatment Project
GC/MS	Gas Chromatograph/Mass Spectrometer
HDPE	High Density Polyethylene
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
ICP-AES	Inductively coupled plasma – atomic emission spectroscopy
ICP-MS	Inductively coupled plasma – mass spectrometry
L	Liter
LLW	Low Level Waste
LSC	Liquid Scintillation Counting
MDL	Method Detection Limit
MRL	Method Reporting Limit
mg	Milligram
mL	Milliliter
NA	Not Applicable
ND	Not Determined
pCi/mL	Picocurie per milliliter
RSD	Relative Standard Deviation
SC	Shielded Cells (Facility)
SDF	Saltstone Disposal Facility
SFE	Saltstone Facility Engineering
SFT	Salt Feed Tank
SPF	Saltstone Production Facility
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation

SRS	Savannah River Site
SVOA	Semi-volatile Organic Analysis
TCLP/UHC	Toxic Characterization Leaching Procedure/Underlying Hazardous Constituent
TIC	Tentatively Identifiable Compound
TIC/TOC	Total inorganic carbon/total organic carbon
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
VOA	Volatile organic analysis
WAC	Waste Acceptance Criteria
WCS	Waste Characterization System
WT %	Weight percent

1.0 Introduction

The Saltstone Facility is designed and permitted to treat low-level radioactive and hazardous liquid waste (salt solution) remaining from the processing of radioactive material at the Savannah River Site. Low-level waste (LLW) streams from the Effluent Treatment Project (ETP), H-Canyon, and the decontaminated salt solution product from the Actinide Removal Process/Modular Caustic Side Solvent Extraction (CSSX) Unit (ARP/MCU) process are stored in Tank 50 until the LLW can be transferred to the Saltstone Facility for treatment and disposal. The LLW must meet the specified waste acceptance criteria (WAC) before it is processed into saltstone.¹ The specific chemical and radionuclide contaminants and their respective WAC limits are in the current^a Saltstone WAC.

Saltstone Facility Engineering (SFE) requested that the Savannah River National Laboratory (SRNL) perform quarterly analysis on saltstone samples.⁵ The concentrations of chemical and radionuclide contaminants are measured to ensure the saltstone produced during each quarter is in compliance with the current WAC.^{1,5,6} This report documents the concentrations of chemical and radionuclide contaminants and discusses those results for the 2013 Second Quarter samples collected from Tank 50 on April 3, 2013.

2.0 Experimental

2.1 Technical

On April 3, 2013, one 3-L sampler (HTF-50-13-54) and one 200-mL sampler (HTF-50-13-53) were collected from Tank 50 for the Second Quarter 2013 (2Q13) WAC analyses and delivered the same day to the SRNL Shielded Cells (SC). The 200 mL sampler is a dip sample taken six inches below the surface and the 3-L sampler was pulled 66 inches from the bottom of the tank with one agitator pump running.

At SRNL, slurry samples (~15 mL each) from HTF-50-13-53 were transferred with glass pipettes to glass vials with Teflon-lined caps. The vials were completely filled to minimize the void space and the volatilization of organics. The aliquots were transferred to the Analytical Development (AD) Organic Analysis Laboratory for semi-volatile and volatile organic analysis (SVOA and VOA, respectively). Two additional 15-mL aliquots were used for SVOA analysis to determine the concentration of Isopar L and Norpar 13, respectively, in the sample.

After the samples for organic analyses were obtained, the slurries in the steel samplers were combined into a 4-L high-density polyethylene (HDPE) bottle. The 200 mL steel sampler was agitated to disperse any solids in the slurry and poured into the 4-L bottle. The transferred slurry was left to settle in the 4-L bottle. Visual inspection of the inside of each sampler indicated there were no visible solids remaining in the samplers, so no clear supernate was returned to either sampler for rinsing. The total weight of the transferred slurry was 4040.39 g.

The 4-L HDPE bottle was agitated to disperse thoroughly the extremely limited solids into the supernate. Aliquots of slurry samples were promptly collected with slurry pipettes to minimize settling effects and placed into HDPE bottles. A three-milliliter sample of the slurry was used to determine the density of the slurry using an Anton-Paar DMA 35n portable density meter.

Slurry samples were submitted in triplicate to SRNL laboratories for the following analyses:

^a This report references the Saltstone WAC revision in effect when the sample is pulled for analysis and/or that which was referenced during initial data reporting. This may or may not be the latest revision when this report receives its final approval signature.

- Six-mL aliquots to the AD Ion Chromatography (IC) Laboratory for soluble anion and cation analyses.
- Three-mL aliquots to the AD Organic Analysis Laboratory for measurement of tetraphenylborate and ethylenediaminetetraacetate by high performance liquid chromatography (HPLC).
- Six-mL aliquots to the AD Wet Chemistry Laboratory for Total Inorganic Carbon/ Total Organic Carbon (TIC/TOC) analyses.
- Two 70-mL aliquots to AD Radiochemistry Laboratory for radiochemical separations and analyses.
- Twelve-mL aliquots of filtered supernate were prepared by filtering aliquots of supernate using a 0.45 micron syringe filter. The filtered supernate samples were then submitted to the AD Wet Chemistry Laboratory for TIC/TOC analyses and Total Base analyses.
- Two 12-mL aliquots were sent to the AD Dissolution Laboratory for digestion using an aqua regia method⁷. Visual inspection of the digested sample by the AD Task Supervisor indicated that all the solids had dissolved. Aliquots of dissolved slurries were analyzed using inductively coupled plasma – atomic emission spectroscopy (ICP-AES), inductively coupled plasma – mass spectrometry (ICP-MS), atomic absorption spectroscopy (AA) for As, K, Na, and Se, and cold vapor atomic absorption spectroscopy (CVAA) for Hg.

Four additional aliquots of supernate were prepared from the combined slurry sample since there was no original surface sample remaining to sample. These samples were submitted for replicate SVOA analyses using two different extraction solvents: the traditional methylene chloride extraction and an additional hexane extraction.

2.2 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

The following tables contain the results for the 2Q13 WAC analyses. Each table provides the analyte of interest, the method used for measuring that analyte, the average concentration of the analyte based on triplicate samples (unless otherwise noted), the standard deviation of the average, and, if applicable, the WAC target or limit for the analyte concentration. Several of the contaminants were either not detected in the slurry samples or detected at values below the method-reporting limit (MRL). For those analytes, the result is preceded by a “<” which indicates the result is an upper limit based on the sensitivity of the method/equipment used to analyze the individual analyte.

Tables 3-1, 3-2, 3-3 and 3-4 are based directly on attachments 8.1, 8.2, 8.3, and 8.4, respectively, of the WAC.¹

Table 3-1. Results for the 2nd Quarter 2013 Tank 50 Slurry Samples for Chemical Contaminants Listed in Attachment 8.1 of the Saltstone WAC, Revision 11

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC Limit (mg/L)</u>
Ammonium (NH ₄ ⁺)	IC	<1.00E+02	NA	5.88E+03
Carbonate (CO ₃ ²⁻)	TIC	1.27E+04 ^a	5.00E+01	1.20E+05

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC Limit (mg/L)</u>
Chloride (Cl ⁻)	IC	<5.00E+02	NA	7.95E+03
Fluoride (F ⁻)	IC	<5.00E+02	NA	4.07E+03
Free Hydroxide (OH ⁻)	Total base	3.12E+04 ^a	2.05E+03	1.58E+05
Nitrate (NO ₃ ⁻)	IC	1.30E+05	1.15E+03	4.37E+05
Nitrite (NO ₂ ⁻)	IC	2.01E+04	1.01E+02	2.14E+05
Oxalate (C ₂ O ₄ ²⁻)	IC	5.18E+02	2.31E+00	2.72E+04
Phosphate (PO ₄ ³⁻)	ICP-ES	4.79E+02	1.91E+01	2.94E+04
Sulfate (SO ₄ ²⁻)	IC	4.68E+03	1.41E+02	5.69E+04
Arsenic (As)	AA	<9.54E-02	NA	1.50E+02
Barium (Ba)	ICP-ES	<4.60E-01	NA	6.19E+02
Cadmium (Cd)	ICP-ES	<7.02E-01	NA	3.10E+02
Chromium (Cr)	ICP-ES	3.66E+01	5.14E-01	1.24E+03
Lead (Pb)	ICP-MS	1.40E-00 ^e	1.45E-01	6.19E+02
Mercury (Hg)	CVAA	6.06E+01	1.08E+00	3.25E+02
Selenium (Se)	AA	<1.90E-01	NA	4.46E+02
Silver (Ag)	ICP-ES	<9.71E-01	NA	6.19E+02
Aluminum (Al)	ICP-ES	4.12E+03	3.11E+01	1.16E+05
Potassium (K)	AA	2.45E+02	3.71E+00	3.03E+04
Nickel Hydroxide	ICP-ES	<1.48E+01 ^d	NA	1.17E+03
n-Butanol	VOA	<5.00E-01 ^b	NA	7.73E+00
i-Butanol	VOA	<5.00E-01 ^b	NA	7.73E+00
i-Propanol	VOA	<2.50E-01 ^b	NA	1.88E+00
Phenol	SVOA	<1.00E+01 ^b	NA	7.50E+02
Isopar L	SVOA	<2.67E+01 ppm ^{b,c}	NA	6.56E+01 ppm
Total organic carbon	TOC	3.74E+02 ^a	2.03E+01	5.00E+03
Tetraphenylborate (TPB anion)	HPLC	<5.00E+00	NA	5.00E+00

a. Measurement performed on filtered supernate samples.

b. Measurement performed on duplicate samples rather than triplicate samples.

c. Result is calculated from the reported concentration of < 33 mg/L and the density of the slurry sample listed in Table 3-8.

d. Result is calculated from the measured Ni concentration assuming all of the Ni is present as the hydroxide compound.

e. Blank value was of comparable magnitude indicating that there may be little to no Pb in the sample.

Table 3-2. Results for the 2nd Quarter 2013 Tank 50 Slurry Samples for Chemical Contaminants Listed in Attachment 8.2 of the Saltstone WAC, Revision 11

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC TARGET (mg/L)</u>
Boron (B)	ICP-ES	5.10E+01	7.55E-01	7.43E+02
Cobalt (Co)	ICP-MS	<3.87E-02	NA	7.43E+02
Copper (Cu)	ICP-ES	8.85E-01 ^c	NA	7.43E+02
Iron (Fe)	ICP-ES	6.39E+00	2.17E-01	4.95E+03
Lithium (Li)	ICP-ES	1.18E+01	1.03E-01	7.43E+02
Manganese (Mn)	ICP-ES	2.59E+00	1.43E-02	7.43E+02
Molybdenum (Mo)	ICP-ES	<8.52E+00	NA	7.43E+02
Nickel (Ni)	ICP-ES	<9.40E+00	NA	7.43E+02

Chemical Name	Method	Average Concentration (mg/L)	Std. Dev.	WAC TARGET (mg/L)
Silicon (Si)	ICP-ES	3.38E+01	3.53E+00	1.07E+04
Strontium (Sr)	ICP-ES	<4.34E-02	NA	7.43E+02
Zinc (Zn)	ICP-ES	6.89E+00	2.00E-01	8.03E+02
Benzene	VOA	<1.50E-01 ^a	NA	3.10E+02
Methanol	VOA	b	NA	1.88E+00
Toluene	VOA	<1.50E-01 ^a	NA	3.10E+02
Dibutylphosphate (DBP)	IC	<2.75E+02	NA	3.47E+02
Tributyl Phosphate (TBP)	SVOA	<7.50E-01 ^a	NA	7.50E+00
EDTA	HPLC	<1.00E+02	NA	3.10E+02
Norpar 13	SVOA	<7.50E-01 ^a	NA	1.00E-01

a. Measurement performed on duplicate samples rather than triplicate samples.

b. Currently, a routine method for detecting this species does not exist in SRNL.

c. Measurement based on a single sample with a value above the detection limit.

As indicated in Tables 3-1 and 3-2, all of the contaminants are within the WAC limits with the exception of Norpar 13. In October 2010, SRNL reviewed the MRL's for the organic constituents in Tank 50. All of the MRL's are at or below the WAC limits for the organics with the exception of Norpar 13, which has an MRL of 0.75 mg/L, which is above the WAC limit.⁵ Isopar L, and Norpar 13 have negligible solubility in aqueous solutions, which makes it difficult to obtain reliable sub-samples of the original sample. The values reported in these tables are the concentrations as detected by the GC/MS but may not necessarily be an accurate representation of the concentrations of these analytes in Tank 50.

Along with phenol and TBP, the initial SVOA analyses of the surface dip sample indicated the presence of chloromethylmercury or methylmercury chloride (CH₃HgCl). This was unexpected because no diphenylmercury was observed in the VOA analyses. In order to determine if the chloromethylmercury observed was a product formed in the GC-MS injection port from reaction of the methylene chloride extractant and the high soluble mercury content of this quarter's sample, another set of samples needed to be tested. There was no remaining surface sample to extract, since it had been combined with the larger 3-L depth sample after the initial organic analysis samples were prepared; therefore, supernate was collected from the full sample and the SVOA extraction was repeated twice using methylene chloride, and twice using hexane as the extractant. When analyzed by GC-MS, the samples extracted with the methylene chloride again indicated the presence of chloromethylmercury, while the hexane extractions showed no measureable chloromethylmercury. We concluded that the chloromethylmercury was a reaction product formed in the 250 °C GC-MS injection port from methylene chloride and extracted Hg, and that it was not a material that was present in the 2Q13 Tank 50 WAC sample. No specific references to this reaction were located in the literature, but the formation of mixed alkylmercury chloride species have been shown to form in a GC-MS during analysis of a mixture of methyl mercury chloride and diphenylmercury, yielding methylphenylmercury which was not in the starting sample⁸.

Table 3-3. Results for 2nd Quarter 2013 Tank 50 Slurry Samples and WAC Limits for Radionuclide Contaminants Listed in Attachment 8.3 of the Saltstone WAC, Revision 11

<u>Radionuclide</u>	<u>Method</u>	<u>Average Concentration (pCi/mL)</u>	<u>Std. Dev.</u>	<u>WAC LIMIT (pCi/mL)</u>
Tritium (³H)	Tritium counting	5.03E+02	4.23E+01	5.63E+05
Carbon-14 (¹⁴C)	C-14 Liquid scintillation	4.80E+02	6.13E+01	1.13E+05
Nickel-63 (⁶³Ni)	Ni-59/63	<1.32E+01	NA	1.13E+05
Strontium-90 (⁹⁰Sr)	Sr-90 Liquid scintillation	4.54E+03	3.64E+02	2.25E+07
Technetium-99 (⁹⁹Tc)	Tc-99 Liquid scintillation	2.13E+04	1.18E+03	2.11E+05
Iodine-129 (¹²⁹I)	I-129 (w/ separation) Liquid scintillation	1.26E+01	1.10E+00	3.80E+02
Cesium-137 (¹³⁷Cs)	Gamma Scan	1.07E+06	1.19E+04	7.13E+06
Uranium-233 (²³³U)	ICP-MS	<1.67E+02	NA	1.13E+04
Uranium-235 (²³⁵U)	ICP-MS	1.66E-01	1.47E-02	1.13E+02
Plutonium-241 (²⁴¹Pu)	Pu238/241 Liquid scintillation	<3.82E+02	NA	8.38E+05
Total Alpha	Liquid Scintillation Counting	<4.82E+03	NA	2.50E+05

As shown in Table 3-4, none of the radionuclide contaminants exceeds the targets listed in the latest revision of the WAC. In a memo from Savannah River Remediation (SRR), the requested detection limits for several radionuclides were lowered in order to accommodate future inventory reporting requirements.² The reported detection limits of ⁵⁹Ni and ⁹⁴Nb are above the limits requested by SRR (6.59E+00 and 2.00E-03 pCi/mL, respectively)² but below the quantification limits established by SRNL (2.00E+01 and 4.38E-01 pCi/mL, respectively).³

The concentration of ¹³⁵Cs is calculated by assigning all of the mass at 135 to cesium. It is assumed all the mass detected at mass 244 is ²⁴⁴Pu. The Pu alpha Pulse Height Analysis (PHA) method does not resolve the alpha activities of ²³⁹Pu and ²⁴⁰Pu. To determine the maximum concentration of each radionuclide, the total activity is assigned to each radionuclide separately. As shown in Table 3-4, the reported activity is below the WAC target for each radionuclide.

Table 3-4. Results for the 2nd Quarter 2013 Tank 50 Slurry Samples and WAC Targets for Radionuclide Contaminants Listed in Attachment 8.4 of the Saltstone WAC, Revision 11

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.	WAC TARGET (pCi/mL)
Aluminum-26 (²⁶ Al)	Gamma scan (Cs removed)	<1.69E-01	NA	2.88E+03
Cobalt-60 (⁶⁰ Co)	Gamma scan (Cs removed)	3.37E-01	2.89E-02	4.87E+03
Potassium-40 (⁴⁰ K)	Gamma scan (Cs removed)	<1.90E+00	NA	1.00E+02
Nickel-59 (⁵⁹ Ni)	Ni-59/63	<1.35E+01	NA	1.13E+03
Selenium-79 (⁷⁹ Se)	Se-79	1.77E+01	4.70E+00	1.90E+04
Zirconium-93 (⁹³ Zr)	Zr-93 Liquid scintillation	<4.14E+01	NA	1.00E+05
Niobium-94 (⁹⁴ Nb)	Gamma scan (Cs removed)	<3.69E-01	NA	1.53E+02
Ruthenium-106 (¹⁰⁶ Ru)	Gamma scan (Cs removed)	<2.38E+00	NA	1.13E+06
Antimony-125 (¹²⁵ Sb)	Gamma scan (Cs removed)	4.26E+01	1.48E+00	3.99E+04
Tin-126 (¹²⁶ Sn)	Gamma scan (Cs removed)	1.29E+02	2.15E+01	1.80E+04
Cesium-134 (¹³⁴ Cs)	Gamma Scan	<3.12E+01	NA	3.28E+04
Cesium-135 (¹³⁵ Cs)	ICP-MS	<1.99E+01	NA	1.50E+03
Cerium-144 (¹⁴⁴ Ce)	Gamma scan (Cs removed)	<2.45E+00	NA	1.13E+05
Promethium-147 (¹⁴⁷ Pm)	Pm-147/Sm-151 Liquid scintillation	<4.86E+01	NA	5.63E+06
Samarium-151 (¹⁵¹ Sm)	Pm-147/Sm-151 Liquid scintillation	<3.19E+01	NA	2.25E+04
Europium-154 (¹⁵⁴ Eu)	Gamma scan (Cs removed)	2.84E+00	1.66E-01	8.03E+03
Europium-155 (¹⁵⁵ Eu)	Gamma scan (Cs removed)	<1.22E+00	NA	1.13E+04
Radium-226 (²²⁶ Ra)	Ra-226	<8.76E+00	NA	1.00E+03
Radium-228 (²²⁸ Ra)	Gamma scan (Cs removed)	<1.41E+00	NA	1.00E+04
Actinium-227 (²²⁷ Ac)	Th-229/230	<2.10E-02	NA	1.00E+04
Thorium-229 (²²⁹ Th)	Th-229/230	<3.25E-02	NA	1.63E+05
Thorium-230 (²³⁰ Th)	Th-229/230	<2.02E-02	NA	6.26E+03
Thorium-232 (²³² Th)	ICP-MS	<1.90E-03	NA	2.88E+03
Protactinium-231 (²³¹ Pa)	Pa-231	<1.04E+00	NA	1.00E+03
Uranium-232 (²³² U)	U-232	2.59E+00	1.23E+00	1.71E+05
Uranium-234 (²³⁴ U)	ICP-MS	<1.08E+02	NA	1.13E+04
Uranium-236 (²³⁶ U)	ICP-MS	<1.12E+00	NA	1.13E+04
Uranium-238 (²³⁸ U)	ICP-MS	3.90E+00	9.36E-02	1.13E+04
Neptunium-237 (²³⁷ Np)	ICP-MS	<1.22E+01	NA	1.00E+04

<u>Radionuclide</u>	<u>Method</u>	<u>Average Concentration (pCi/mL)</u>	<u>Std. Dev.</u>	<u>WAC TARGET (pCi/mL)</u>
Plutonium-238 (²³⁸ Pu)	Pu238/241 Pu alpha PHA	1.18E+03	7.32E+01	2.50E+05
Plutonium-239 (²³⁹ Pu)	Pu238/241 Pu alpha PHA	1.20E+02	6.92E+00	2.50E+05
Plutonium-240 (²⁴⁰ Pu)	Pu238/241 Pu alpha PHA	1.20E+02	6.92E+00	2.50E+05
Plutonium-242 (²⁴² Pu)	ICP-MS	<6.60E+01	NA	2.50E+05
Plutonium-244 (²⁴⁴ Pu)	ICP-MS	<3.07E-01	NA	7.02E+04
Americium-241 (²⁴¹ Am)	Gamma scan (Cs removed)	9.16E+00	2.19E+00	2.50E+05
Americium-242m (^{242m} Am)	Am/Cm	<6.58E-02	NA	4.50E+05
Americium-243 (²⁴³ Am)	Am/Cm	<9.32E-01	NA	2.50E+05
Curium-242 (²⁴² Cm)	Am/Cm	<5.45E-02	NA	1.13E+04
Curium-244 (²⁴⁴ Cm)	Am/Cm	1.98E+01	8.75E-01	2.50E+05
Curium-245 (²⁴⁵ Cm)	Am/Cm	<2.47E+00	NA	2.25E+05

Tables 3-5 and 3-6 list the chemical contaminants that impact vault flammability. These chemicals must be monitored to ensure flammable gases do not contribute more than 10% of the Composite Lower Flammability Limit (CLFL).¹

Table 3-5. Results for the 2nd Quarter 2013 Tank 50 Slurry Samples for Acceptance Criteria Limits for Chemical Contaminants Impacting Vault Flammability, Listed in Table 3 of the Saltstone WAC, Revision 11

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC Limit</u>
Isopar L	SVOA	<2.67E+01 ppm ^a	NA	1.10E+01 ppm
Tetraphenylborate (TPB anion)	HPLC	<5.00E+00	NA	5.00E+00 mg/L
Ammonium (NH ₄ ⁺)	IC	<1.00E+02	NA	2.12E+02 mg/L

a. Result is calculated from the reported concentration of < 33 mg/L and the density of the slurry sample.

Table 3-6. Results for the 2nd Quarter 2013 Tank 50 Slurry Samples for Concentrations of “Other Organics” Impacting Vault Flammability, Listed in Table 4 of the Saltstone WAC, Revision 11

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC Concentrations (mg/L)</u>
n-Butanol	VOA	<5.00E-01	NA	0.75
Tributylphosphate	SVOA	<7.50E-01	NA	1.0
i-Propanol	VOA	<2.50E-01	NA	0.25
Methanol	a	NA	NA	0.25
Norpar 13	SVOA	<7.50E-01	NA	0.1

a. Currently, a routine method for detecting this species does not exist in SRNL.

Isopar L and Norpar 13 are the only species considered in Tables 3-5 or 3-6 with reported values above the WAC limit. Although the reported detection limit for Isopar L is greater than the WAC limit for vault flammability, it is below the WAC limits for accident analysis as shown in Table 3-1. It should be noted that the detection limit for Isopar L was expected based on current SRNL capabilities.⁴ The reported detection limit for Norpar is above the WAC limit for both accident analysis (Table 3-2) and vault flammability (Table 3-6), but it is the lowest achievable MRL for this analyte.⁴ As previously discussed, the insolubility of Isopar L and Norpar 13 makes sub-sampling difficult, therefore the reported results are not necessarily representative of the concentration of these analytes in the Tank 50 sample received by SRNL.

Table 3-7 provides results for the processing criteria for transfers into the Saltstone Facility. All of the results contained in Table 3-7 fall within the general processing criteria. The pH was calculated using the free base concentration (OH⁻). The low insoluble solids content makes subsampling difficult.

Table 3-7. Results for the 2nd Quarter 2013 Tank 50 Slurry Samples for Saltstone Processing Criteria WAC Limits, Listed in Table 5 of the Saltstone WAC, Revision 11

<u>Processing Criterion</u>	<u>Method</u>	<u>Value</u>	<u>Std. Dev.</u>
pH > 10	Calculated	>13	NA
2.5 M < [Na⁺] < 7.0 M	ICP-ES	5.27 M	0.0203
Total Insoluble Solids <15 wt. %	Calculated	0.165 wt. %	0.500

Table 3-8 provides constituents listed in the Technical Task Request but not contained in the WAC.

Table 3-8. Requests for Constituents for TCLP/UHC Support as well as from the TTR for the 2nd Quarter 2013 Tank 50 Slurry Samples; Results Not Contained in Previous Tables

<u>Constituent</u>	<u>Method</u>	<u>Average Value (mg/L, unless stated otherwise)</u>	<u>Std. Dev.</u>
Antimony (Sb)	ICP-ES	<2.99E+01	NA
Beryllium (Be)	ICP-ES	<1.04E-01	NA
Cyanide (CN)	a	NA	NA
Thallium (Tl)	ICP-MS	<1.00E-01 ^b	NA
Density (slurry)	Measured (22.5°C)	1.2354 g/mL	0.0016
Total Beta	LSC	1.14E+06 pCi/mL	2.60E+03
Total Solids	Measured	28.61 wt. %	0.221

a. Currently, a routine method for detecting this species does not exist in SRNL.

b. Blank value was of comparable magnitude indicating that there may be little to no Tl in the sample.

The results from Table 3-8 are used to support TCLP/UHC testing by a certified laboratory.⁹ The density of the slurry was measured at 22.5 °C. Natural Tl is composed of two isotopes, ²⁰³Tl and ²⁰⁵Tl with

fractional abundances of 0.295 and 0.705, respectively. The concentration of each isotope was divided by its fractional abundance, and the reported concentration of Tl is that determined from averaging the six values determined from the three replicates for each isotope.

What was unusual was that for these Tl masses, as well as those for Pb (206 – 208), the blank showed a signal of the same magnitude. The samples were analyzed a second time, but the same result was found. The digestion acids, both nitric acid and hydrochloric acid, used to perform the aqua regia digestions of the replicates were examined. The nitric acid gave no measurable signal for masses 203, 205 – 208. The hydrochloric acid (HCl) did give measurable signal at these masses; see Table 3-9. The HCl would be expected to contribute about 1/5th of the signal measured for the blank at each mass due to the use of 9 mL of HCl diluted to a 50 mL final volume. For masses 203 and 205, the observed blank signal could be due to Tl in the HCl, though it is a bit lower than anticipated. However, for masses 206 – 208, the blank gave roughly 5x the signal expected if the only contribution to these masses was coming from trace Pb in the HCl. It should be noted that the sample is around 300 parts per trillion at the instrument. The concentrated nature of these samples, which are diluted to 1:4, versus a more typical 1:100 or even 1:400 dilution, is allowing these small values to be above the detection limit of the instrument. The entire digestion was repeated on three replicates of Tank 50 material and a blank a second time, but collected essentially the same results. In light of this, the values for both Pb (Table 3-1) and Tl are given as detection limit values since there is likely little or no Pb or Tl in these samples.

Table 3-9. Signal Observed For Masses 203 and 205 – 208 in Digestion Acid and the Tank 50 Sample Blank Showing the Contribution to the Sample Signal Expected from the Digestion Acid

<u>Mass</u>	<u>Concentrated HCl</u> µg/g	<u>Sample Blank</u> µg/g	<u>Acid Contribution</u> <u>Expected in Blank</u> µg/g
203	2.22E-01	2.60E-02	4.00E-02
205	6.08E-01	6.50E-02	10.9E-02
206	3.32E-01	25.5E-02	5.98E-02
207	3.12E-01	24.0E-02	5.62E-02
208	6.01E-01	59.0E-02	10.8E-02

The tank corrosion species listed in Table 3-10 were requested by SFE.¹⁰ Specific gravity was calculated by dividing the measured density of the slurry (given in Table 3-8 at 22.5 °C) by the density of water at the same temperature.¹¹

Table 3-10. Requests from the SFE for Corrosion Species from the 2nd Quarter 2013 Tank 50 Slurry Samples (Results Not Contained in Previous Tables)

<u>Constituent</u>	<u>Method</u>	<u>Average Value</u>	<u>Std. Dev.</u>
Specific Gravity	a	1.2383	0.0016
Ba-137m	b	1.01E+06 pCi/mL	1.13E+04
Total Gamma	c	1.01E+06 pCi/mL	6.51E+03

- a. Calculated from the measured density of slurry and density of water at 22.5 °C¹¹.
b. Calculated from the measured concentration of Cs-137.
c. Calculated from the sum of measured gamma emitters.

The radionuclide ^{137m}Ba is the radioactive daughter of 94.6% of the beta decay of ^{137}Cs . 5.3% of the ^{137}Cs decays to stable ^{137}Ba . The half-life of the parent radionuclide, ^{137}Cs , is five times longer than its daughter, ^{137m}Ba , therefore the two radionuclides are in secular equilibrium. Radionuclides in secular equilibrium have the same activity associated with their decay. Thus, the activity of ^{137m}Ba is 94.6% of the activity of the ^{137}Cs or $1.01\text{E}+06$ pCi/mL. The activities calculated for total gamma and ^{137m}Ba are expected to be close for this sample because the total gamma activity is dominated by ^{137m}Ba , the radioactive daughter of ^{137}Cs . The total gamma activity was calculated by summing the measured gamma activity of the major gamma emitters: ^{60}Co , ^{125}Sb , ^{126}Sb , ^{126}Sn , ^{137}Cs (via ^{137m}Ba), ^{154}Eu , and ^{241}Am .

Table 3-11 provides results for additional radionuclides not listed in the WAC but which now require quantification in order to support inventory-reporting requirements.

Table 3-11. Additional Radionuclides Requested for Inventory Reporting Requirements

<u>Radionuclide</u>	<u>Method</u>	<u>Average Concentration (pCi/mL)</u>	<u>Std. Dev.</u>
Niobium-93m (^{93m}Nb)	ICP-MS	<4.24E+01	NA
Silver-108m (^{108m}Ag)	Gamma scan (Cs removed)	<4.21E-01	NA
Barium-133 (^{133}Ba)	Gamma scan (Cs removed)	<6.44E-01	NA
Bismuth-207 (^{207}Bi)	Gamma scan (Cs removed)	<4.12E-01	NA
Thorium-228 (^{228}Th)	Gamma scan (Cs removed)	<8.47E+00	NA
Curium-247 (^{247}Cm)	Am/Cm	<5.18E+00	NA
Californium-249 (^{249}Cf)	Am/Cm	<5.41E+00	NA
Californium-251 (^{251}Cf)	Am/Cm	<4.00E+00	NA

4.0 Conclusions

The following conclusions are drawn from the analytical results provided in this report:

- SRR WAC targets or limits were met for all analyzed chemical and radioactive contaminants unless noted in this section.
- ^{59}Ni , ^{94}Nb , ^{247}Cm , ^{249}Cf , and ^{251}Cf are above the requested SRR target concentrations². However, they are below the detection limits established by SRNL³.
- Norpar 13 and Isopar L have higher detection limits⁴ compared with the Saltstone WAC¹. The data provided in this report is based upon the concentrations in the sub-sample, and due to the limited solubility in aqueous solution, may not represent the concentrations of the analytes in Tank 50.
- The low insoluble solids content increases the measurement uncertainty for insoluble species.

5.0 References

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