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# Results for the Third Quarter 2013 Tank 50 WAC Slurry Sample

*Chemical and Radionuclide Contaminants*

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November 2013

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## **Results for the Third Quarter 2013 Tank 50 WAC Slurry Sample: Chemical and Radionuclide Contaminants**

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November 2013

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## EXECUTIVE SUMMARY

This report details the chemical and radionuclide contaminant results for the characterization of the 2013 Third Quarter sampling of Tank 50 for the Saltstone Waste Acceptance Criteria (WAC) in effect at that time.<sup>1</sup> Information from this characterization will be used by DWPF & Saltstone Facility Engineering (DSFE) 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.
- <sup>59</sup>Ni, <sup>94</sup>Nb, <sup>247</sup>Cm, <sup>249</sup>Cf, and <sup>251</sup>Cf are above the requested SRR target concentrations.<sup>2</sup> However, they are below the detection limits established by SRNL.<sup>3</sup>
- Norpar 13 and Isopar L have higher detection limits<sup>4</sup> compared with the Saltstone WAC.<sup>1</sup> 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.
- 4-Methyl-3-hexanol was detected in both replicates of the surface dip sample and measured at levels above the detection limit [1.90E+00 mg/L, STDEV = 1.41E-01]. The material is likely formed in situ due to radiolytic hydroxyl radical formation and reaction with trace levels of alkanes.
- 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
DSFE	DWPF & Saltstone Facility Engineering
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
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.<sup>1</sup> The specific chemical and radionuclide contaminants and their respective WAC limits are in the current<sup>a</sup> Saltstone WAC.

Saltstone Facility Engineering (SFE) requested that the Savannah River National Laboratory (SRNL) perform quarterly analysis on saltstone samples.<sup>5</sup> The concentrations of chemical and radionuclide contaminants are measured to ensure the saltstone produced during each quarter complies with the current WAC.<sup>1, 5, 6</sup> This report documents the concentrations of chemical and radionuclide contaminants and discusses those results for the 2013 Third Quarter samples collected from Tank 50 on July 8, 2013.

## 2.0 Experimental

### 2.1 Technical

On July 8, 2013, one 3-L sampler (HTF-50-13-111) and one 200-mL sampler (HTF-50-13-112) were collected from Tank 50 for the Third Quarter 2013 (3Q13) 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-50-13-112 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 3978.19 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 3-mL 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:

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<sup>a</sup> 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 method<sup>7</sup>. 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.

## 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 3Q13 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.<sup>1</sup>

**Table 3-1. Results for the 3rd Quarter 2013 Tank 50 Slurry Samples for Chemical Contaminants Listed in Attachment 8.1 of the Saltstone WAC, Revision 12**

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC Limit (mg/L)</u>
Aluminate (Al(OH) <sub>4</sub> <sup>-</sup> )	ICP-AES	1.43E+04 <sup>f</sup>	2.30E+02	4.08E+05
Ammonium (NH <sub>4</sub> <sup>+</sup> )	IC	<1.00E+02	NA	2.12E+02
Carbonate (CO <sub>3</sub> <sup>2-</sup> )	TIC	1.21E+04 <sup>a</sup>	1.15E+02	1.20E+05
Chloride (Cl <sup>-</sup> )	IC	<5.00E+02	NA	7.95E+03
Fluoride (F <sup>-</sup> )	IC	<5.00E+02	NA	4.07E+03
Free Hydroxide (OH <sup>-</sup> )	Total base	3.29E+04 <sup>a</sup>	2.60E+02	1.58E+05

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC Limit (mg/L)</u>
Nitrate (NO <sub>3</sub> <sup>-</sup> )	IC	1.36E+05	1.73E+03	4.37E+05
Nitrite (NO <sub>2</sub> <sup>-</sup> )	IC	2.13E+04	4.36E+02	2.14E+05
Oxalate (C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> )	IC	<5.00E+02	NA	2.72E+04
Phosphate (PO <sub>4</sub> <sup>3-</sup> )	ICP-ES	4.14E+02	5.79E+00	2.94E+04
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	IC	5.12E+03	1.22E+02	5.69E+04
Arsenic (As)	AA	<1.04E+01	NA	1.50E+02
Barium (Ba)	ICP-ES	<4.99E+01	NA	6.19E+02
Cadmium (Cd)	ICP-ES	<1.32E+00	NA	3.10E+02
Chromium (Cr)	ICP-ES	3.43E+01	6.34E-01	1.24E+03
Lead (Pb)	ICP-MS	<1.05E+00 <sup>e</sup>	NA	6.19E+02
Mercury (Hg)	CVAA	7.29E+01	1.58E+00	3.25E+02
Selenium (Se)	AA	<2.08E-01	NA	4.46E+02
Silver (Ag)	ICP-ES	<9.98E-01	NA	6.19E+02
Aluminum (Al)	ICP-ES	4.05E+03	6.54E+01	1.16E+05
Potassium (K)	AA	2.25E+02	9.35E+00	3.03E+04
Nickel Hydroxide	ICP-ES	<4.00E+00 <sup>d</sup>	NA	1.17E+03
n-Butanol	VOA	<5.00E-01 <sup>b</sup>	NA	7.73E+00
i-Butanol	VOA	<5.00E-01 <sup>b</sup>	NA	7.73E+00
i-Propanol	VOA	<2.50E-01 <sup>b</sup>	NA	1.88E+00
Phenol	SVOA	<1.00E+01 <sup>b</sup>	NA	7.50E+02
Isopar L	SVOA	<2.67E+01 ppm <sup>b,c</sup>	NA	1.10E+01 ppm
Total organic carbon	TOC	4.31E+02 <sup>a</sup>	4.36E+00	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.  
f. Result is calculated from the measured Al concentration assuming all of the Al is present as the hydroxide compound.

**Table 3-2. Results for the 3rd Quarter 2013 Tank 50 Slurry Samples for Chemical Contaminants Listed in Attachment 8.2 of the Saltstone WAC, Revision 12**

<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	4.28E+01	8.68E-01	7.43E+02
Cobalt (Co)	ICP-MS	<8.38E-01	NA	7.43E+02
Copper (Cu)	ICP-ES	<2.59E+00	NA	7.43E+02
Iron (Fe)	ICP-ES	5.01E+00	8.15E-01	4.95E+03
Lithium (Li)	ICP-ES	1.01E+01	1.24E-01	7.43E+02
Manganese (Mn)	ICP-ES	9.12E-01	2.01E-02	7.43E+02
Molybdenum (Mo)	ICP-ES	<7.81E+00	NA	7.43E+02
Nickel (Ni)	ICP-ES	<2.53E+00	NA	7.43E+02
Silicon (Si)	ICP-ES	2.88E+01	6.88E-01	1.07E+04
Strontium (Sr)	ICP-ES	<9.41E-02	NA	7.43E+02

<u>Chemical Name</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC TARGET (mg/L)</u>
Zinc (Zn)	ICP-ES	6.18E+00	2.36E-01	8.03E+02
Benzene	VOA	<1.50E-01 <sup>a</sup>	NA	3.10E+02
Methanol	VOA	b	NA	1.88E+00
Toluene	VOA	<1.50E-01 <sup>a</sup>	NA	3.10E+02
Dibutylphosphate (DBP)	IC	<2.75E+02	NA	3.47E+02
Tributyl Phosphate (TBP)	SVOA	<7.50E-01 <sup>a</sup>	NA	7.50E+00
EDTA	HPLC	<1.00E+02	NA	3.10E+02
Norpar 13	SVOA	<7.50E-01 <sup>a</sup>	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.

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.<sup>1</sup> 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.

**Table 3-3. Results for 3rd Quarter 2013 Tank 50 Slurry Samples and WAC Limits for Radionuclide Contaminants Listed in Attachment 8.3 of the Saltstone WAC, Revision 12**

<u>Radionuclide</u>	<u>Method</u>	<u>Average Concentration (pCi/mL)</u>	<u>Std. Dev.</u>	<u>WAC LIMIT (pCi/mL)</u>
Tritium ( <sup>3</sup> H)	Tritium counting	6.07E+02	2.15E+01	5.63E+05
Carbon-14 ( <sup>14</sup> C)	C-14 Liquid scintillation	4.70E+02	3.59E+01	1.13E+05
Nickel-63 ( <sup>63</sup> Ni)	Ni-59/63	<8.92E+00	NA	1.13E+05
Strontium-90 ( <sup>90</sup> Sr)	Sr-90 Liquid scintillation	1.93E+03	6.90E+01	3.15E+06
Technetium-99 ( <sup>99</sup> Tc)	Tc-99 Liquid scintillation	1.93E+04	7.94E+02	NA
Iodine-129 ( <sup>129</sup> I)	I-129 (w/ separation) Liquid scintillation	1.43E+01	8.79E-01	3.80E+02
Cesium-137 ( <sup>137</sup> Cs)	Gamma Scan	1.21E+06	1.82E+04	3.96E+06
Uranium-233 ( <sup>233</sup> U)	ICP-MS	<1.82E+02	NA	1.13E+04
Uranium-235 ( <sup>235</sup> U)	ICP-MS	1.66E-01 <sup>a</sup>	1.51E-02	1.13E+02
Plutonium-241 ( <sup>241</sup> Pu)	Pu238/241 Liquid scintillation	<2.89E+02	NA	8.38E+05
Total Alpha	Liquid Scintillation Counting	<3.50E+02	NA	2.13E+05

a Measurement derived from duplicate samples rather than triplicate samples.

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.<sup>2</sup> The reported detection limits of <sup>59</sup>Ni and <sup>94</sup>Nb are above the limits requested by SRR (6.59E+00 and 2.00E-03 pCi/mL, respectively)<sup>2</sup> but below the quantification limits established by SRNL (2.00E+01 and 4.38E-01 pCi/mL, respectively).<sup>3</sup>

The radionuclide  $^{137m}\text{Ba}$  is the radioactive daughter of 94.6% of the beta decay of  $^{137}\text{Cs}$ . 5.3% of the  $^{137}\text{Cs}$  decays to stable  $^{137}\text{Ba}$ . The half-life of the parent radionuclide,  $^{137}\text{Cs}$ , is five times longer than its daughter,  $^{137m}\text{Ba}$ , therefore the two radionuclides are in secular equilibrium. Radionuclides in secular equilibrium have the same activity associated with their decay. Thus, the activity of  $^{137m}\text{Ba}$  is 94.6% of the activity of the  $^{137}\text{Cs}$  or  $1.14\text{E}+06$  pCi/mL.

The concentration of  $^{135}\text{Cs}$  is calculated by assigning all of the mass at 135 to cesium. It is assumed all the mass detected at mass 244 is  $^{244}\text{Pu}$ . The Pu alpha Pulse Height Analysis (PHA) method does not resolve the alpha activities of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ . 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 3rd Quarter 2013 Tank 50 Slurry Samples and WAC Targets for Radionuclide Contaminants Listed in Attachment 8.4 of the Saltstone WAC, Revision 12**

<b>Radionuclide</b>	<b>Method</b>	<b>Average Concentration (pCi/mL)</b>	<b>Std. Dev.</b>	<b>WAC TARGET (pCi/mL)</b>
Aluminum-26 ( $^{26}\text{Al}$ )	Gamma scan (Cs removed)	<1.66E-01	NA	2.88E+03
Cobalt-60 ( $^{60}\text{Co}$ )	Gamma scan (Cs removed)	2.56E-01	4.42E-02	9.747E+02
Potassium-40 ( $^{40}\text{K}$ )	Gamma scan (Cs removed)	<1.71E+00	NA	1.00E+02
Nickel-59 ( $^{59}\text{Ni}$ )	Ni-59/63	<7.16E+00	NA	1.13E+03
Selenium-79 ( $^{79}\text{Se}$ )	Se-79	3.28E+01	6.41E+00	1.90E+04
Yttrium-90 ( $^{90}\text{Y}$ )	Secular Equilibrium w/ Sr-90	1.93E+03	6.90E+01	3.15E+06
Zirconium-93 ( $^{93}\text{Zr}$ )	ICP-MS	<7.10E+01	NA	1.00E+05
Niobium-94 ( $^{94}\text{Nb}$ )	Gamma scan (Cs removed)	<3.57E-01	NA	1.53E+02
Rhodium-106 ( $^{106}\text{Rh}$ )	Secular Equilibrium w/ Ru-106	<2.57E+00	NA	1.13E+06
Ruthenium-106 ( $^{106}\text{Ru}$ )	Gamma scan (Cs removed)	<2.57E+00	NA	1.13E+06
Antimony-125 ( $^{125}\text{Sb}$ )	Gamma scan (Cs removed)	1.76E+01	6.15E-01	7.988E+03
Tellurium-125m ( $^{125m}\text{Te}$ )	Secular Equilibrium w/ Sb-125	1.76E+01	6.15E-01	1.828E+03
Tin-126 ( $^{126}\text{Sn}$ )	Gamma scan (Cs removed)	1.50E+02	1.17E+01	1.80E+04
Cesium-134 ( $^{134}\text{Cs}$ )	Gamma Scan	<1.14E+02	NA	1.82E+04
Cesium-135 ( $^{135}\text{Cs}$ )	ICP-MS	<2.17E+01	NA	1.50E+03
Barium-137m ( $^{137m}\text{Ba}$ )	Calculation (Secular Equilibrium w/ 94.6% of Cs-137)	1.14E+06	1.72E+04	3.75E+06
Cerium-144 ( $^{144}\text{Ce}$ )	Gamma scan (Cs removed)	<2.23E+00	NA	1.13E+05
Promethium-147 ( $^{147}\text{Pm}$ )	Pm-147/Sm-151 Liquid scintillation	<4.47E+01	NA	5.63E+06
Samarium-151 ( $^{151}\text{Sm}$ )	Pm-147/Sm-151 Liquid scintillation	<3.41E+01	NA	2.25E+04
Europium-154 ( $^{154}\text{Eu}$ )	Gamma scan (Cs removed)	7.70E-01 <sup>a</sup>	8.92E-02	1.615E+03
Europium-155 ( $^{155}\text{Eu}$ )	Gamma scan (Cs removed)	<1.08E+00	NA	1.13E+04
Radium-226 ( $^{226}\text{Ra}$ )	Ra-226	<2.10E+00	NA	1.00E+03
Radium-228 ( $^{228}\text{Ra}$ )	Gamma scan (Cs removed)	<1.38E+00	NA	1.00E+04
Actinium-227 ( $^{227}\text{Ac}$ )	Th-229/230	<1.01E-01	NA	1.00E+04
Thorium-229 ( $^{229}\text{Th}$ )	Th-229/230	9.89E-01 <sup>a</sup>	1.94E-01	1.63E+05

<u>Radionuclide</u>	<u>Method</u>	<u>Average Concentration (pCi/mL)</u>	<u>Std. Dev.</u>	<u>WAC TARGET (pCi/mL)</u>
Thorium-230 ( <sup>230</sup> Th)	Th-229/230	3.90E-01 <sup>b</sup>	NA	6.26E+03
Thorium-232 ( <sup>232</sup> Th)	ICP-MS	<3.10E-03	NA	2.88E+03
Protactinium-231 ( <sup>231</sup> Pa)	Pa-231	<1.60E+01	NA	1.00E+03
Uranium-232 ( <sup>232</sup> U)	U-232	2.49E+00	1.23E+00	9.06E+03
Uranium-234 ( <sup>234</sup> U)	ICP-MS	<1.18E+02	NA	1.13E+04
Uranium-236 ( <sup>236</sup> U)	ICP-MS	<1.22E+00	NA	1.13E+04
Uranium-238 ( <sup>238</sup> U)	ICP-MS	3.93E+00	6.98E-02	1.13E+04
Neptunium-237 ( <sup>237</sup> Np)	ICP-MS	<6.63E+01	NA	1.00E+04
Plutonium-238 ( <sup>238</sup> Pu)	Pu238/241 Pu alpha PHA	7.66E+02	1.62E+01	2.13E+05
Plutonium-239 ( <sup>239</sup> Pu)	Pu238/241 Pu alpha PHA	7.33E+01	1.62E+01	2.13E+05
Plutonium-240 ( <sup>240</sup> Pu)	Pu238/241 Pu alpha PHA	7.33E+01	1.62E+01	2.13E+05
Plutonium-242 ( <sup>242</sup> Pu)	ICP-MS	<7.19E+01	NA	2.13E+05
Plutonium-244 ( <sup>244</sup> Pu)	ICP-MS	<3.34E-01	NA	7.02E+04
Americium-241 ( <sup>241</sup> Am)	Am/Cm	3.49E+00	3.48E-01	2.13E+05
Americium-242m ( <sup>242m</sup> Am)	Am/Cm	<5.00E-02	NA	4.50E+05
Americium-243 ( <sup>243</sup> Am)	Am/Cm	<9.50E-01	NA	2.13E+05
Curium-242 ( <sup>242</sup> Cm)	Am/Cm	<4.13E-02	NA	1.13E+04
Curium-244 ( <sup>244</sup> Cm)	Am/Cm	1.22E+01	7.71E+00	2.13E+05
Curium-245 ( <sup>245</sup> Cm)	Am/Cm	<2.26E+00	NA	2.25E+05

- a. Measurement calculated from duplicate samples rather than triplicate samples.  
b. Measurement calculated from a single value above the detection limit.

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).<sup>1</sup> A substituted alcohol, 4-methyl-3-hexanol, was detected in both replicates of the surface dip sample and measured at levels above the detection limit, 1.90E+00 mg/L, STDEV = 1.41E-01. At least one stereoisomer of this compound is an ant and almond bark beetle pheromone or pheromone synergist.<sup>8,9</sup> It is postulated that this material, like a previously reported isomer, 5-methyl-3-hexanol, are produced *in situ* and are not contamination products from any external source. It is known that ionizing radiation can result in the decomposition of water into hydrogen atoms and hydroxyl radicals (OH•).<sup>10</sup> The resulting hydroxyl radicals can react with organic materials to form substituted alcohols.<sup>11</sup> An analysis by SRR of the flammability and chemical impacts posed by 4-methyl-3-hexanol found no hazard was present and due to the extremely low concentration no formal review and authorization is required.<sup>12</sup>

**Table 3-5. Results for the 3rd 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 12**

<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 <sup>a</sup>	NA	1.10E+01 ppm
Tetraphenylborate (TPB anion)	HPLC	<5.00E+00	NA	5.00E+00 mg/L
Ammonium (NH <sub>4</sub> <sup>+</sup> )	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 3rd Quarter 2013 Tank 50 Slurry Samples for Concentrations of “Other Organics” Impacting Vault Flammability, Listed in Table 4 of the Saltstone WAC, Revision 12**

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

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.<sup>4</sup> 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.<sup>4</sup> 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<sup>-</sup>). The low insoluble solids content makes subsampling difficult.

**Table 3-7. Results for the 3rd Quarter 2013 Tank 50 Slurry Samples for Saltstone Processing Criteria WAC Limits, Listed in Table 5 of the Saltstone WAC, Revision 12**

<u>Processing Criterion</u>	<u>Method</u>	<u>Value</u>	<u>Std. Dev.</u>
pH > 10	Calculated	>13	NA
2.5 M < [Na <sup>+</sup> ] < 7.0 M	ICP-ES/AA	5.19 M	0.0899
Total Insoluble Solids <15 wt%	Calculated	~0 wt%	NA



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 3rd Quarter 2013 Tank 50 Slurry Samples; Results Not Contained in Previous Tables**

<u>Constituent</u>	<u>Method</u>	<u>Average Value</u> <u>(mg/L, unless stated otherwise)</u>	<u>Std. Dev.</u>
Antimony (Sb)	ICP-ES	<2.73E+01	NA
Beryllium (Be)	ICP-ES	<9.41E-02	NA
Cyanide (CN)	a	NA	NA
Thallium (Tl)	ICP-MS	<1.03E-01 <sup>b</sup>	NA
Density (slurry)	Measured (23.4°C)	1.2353 g/mL	0.0021
Total Beta	LSC	1.16E+06 pCi/mL	6.82E+04
Total Solids	Measured	28.77 wt%	0.263

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.<sup>13</sup> The density of the slurry was measured at 23.4 °C. Natural Tl is composed of two isotopes, <sup>203</sup>Tl and <sup>205</sup>Tl 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 five values determined from two replicates for the mass 203 isotope and the three replicates for the mass 205 isotope.

As has been previously observed and reported for these Tl masses, as well as those for Pb (206 – 208), the blank gives a signal of the same magnitude.<sup>14</sup> In the past when this situation was observed, the samples were analyzed a second time, but the same result was found. The digestion acids were also examined.<sup>14</sup> 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. In light of the previous observations,<sup>14</sup> the values for both Pb (Table 3-1) and Tl are given as detection limits since there is likely little or no Pb or Tl in these samples.

The tank corrosion species listed in Table 3-9 were requested by DSFE.<sup>15</sup> Specific gravity was calculated by dividing the measured density of the slurry (given in Table 3-8 at 23.4 °C) by the density of water at the same temperature.<sup>16</sup>

**Table 3-9. Requests from the SFE for Corrosion Species from the 3rd 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	1.2385	0.0021
Total Gamma	b	1.14E+06 pCi/mL	9.94E+03

a. Calculated from the measured density of slurry and density of water at 23.4 °C<sup>16</sup>.

b. Calculated from the sum of measured gamma emitters.

The activities calculated for total gamma and  $^{137m}\text{Ba}$  are expected to be close for this sample because the total gamma activity is dominated by  $^{137m}\text{Ba}$ , the radioactive daughter of  $^{137}\text{Cs}$ . The total gamma activity was calculated by summing the measured gamma activity of the major gamma emitters:  $^{60}\text{Co}$ ,  $^{125}\text{Sb}$ ,  $^{126}\text{Sb}$ ,  $^{126}\text{Sn}$ ,  $^{137}\text{Cs}$  (via  $^{137m}\text{Ba}$ ),  $^{154}\text{Eu}$ , and  $^{241}\text{Am}$ .

Table 3-10 provides results for additional radionuclides not listed in the WAC but which now require quantification in order to support inventory-reporting requirements.

**Table 3-10. Additional Radionuclides Requested for Inventory Reporting Requirements or Based on Recommended Concentration for 2009 PA Implementation**

<u>Radionuclide</u>	<u>Method</u>	<u>Average Concentration (pCi/mL)</u>	<u>Std. Dev.</u>
Niobium-93m ( $^{93m}\text{Nb}$ )	ICP-MS	<6.92E+01	NA
Silver-108m ( $^{108m}\text{Ag}$ )	Gamma scan (Cs removed)	<4.55E-01	NA
Barium-133 ( $^{133}\text{Ba}$ )	Gamma scan (Cs removed)	<6.67E-01	NA
Bismuth-207 ( $^{207}\text{Bi}$ )	Gamma scan (Cs removed)	<4.55E-01	NA
Thorium-228 ( $^{228}\text{Th}$ )	Gamma scan (Cs removed)	<8.42E+00	NA
Curium-247 ( $^{247}\text{Cm}$ )	Am/Cm	<3.05E+00	NA
Californium-249 ( $^{249}\text{Cf}$ )	Am/Cm	<3.43E+00	NA
Californium-251 ( $^{251}\text{Cf}$ )	Am/Cm	<2.58E+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.
- $^{59}\text{Ni}$ ,  $^{94}\text{Nb}$ ,  $^{247}\text{Cm}$ ,  $^{249}\text{Cf}$ , and  $^{251}\text{Cf}$  are above the requested SRR target concentrations.<sup>2</sup> However, they are below the detection limits established by SRNL.<sup>3</sup>
- Norpar 13 and Isopar L have higher detection limits<sup>4</sup> compared with the Saltstone WAC.<sup>1</sup> 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.
- 4-Methyl-3-hexanol was detected in both replicates of the surface dip sample and measured at levels above the detection limit [1.90E+00 mg/L, Stdev = 1.41E-01]. The material is likely formed in situ due to radiolytic hydroxyl radical formation and reaction with trace levels of alkanes..
- The low insoluble solids content increases the measurement uncertainty for insoluble species.

## 5.0 References

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### Distribution

<b>Name:</b>	<b>Location:</b>	<b>Name:</b>	<b>Location:</b>
C. J. Bannochie	773-42A	K. R. Liner	704-S
M. J. Barnes	773-A	M. J. Mahoney	766-H
M. N. Borders	704-S	S. L. Marra	773-A
J. M. Bricker	704-30S	D. J. Martin	241-246H
L. W. Brown	773-A	D. H. McGuire	999-W
T. B. Brown	773-A	D. H. Miller	999-W
N. F. Chapman	766-H	P. W. Norris	704-30S
C. K. Chiu	704-30S	F. M. Pennebaker	773-42A
D. R. Click	999-W	M. M. Potvin	704-27S
L. H. Connelly	773-A	J. W. Ray	704-S
J. S. Contardi	766-H	M. M. Reigel	999-W
A. D. Cozzi	999-W	L. B. Romanowski	766-H
C. C. DiPrete	773-A	A. R. Shafer	704-27S
K. D. Dixon	707-7E	C. B. Sherburne	707-7E
K. M. Fox	999-W	D. C. Sherburne	704-S
E. J. Freed	704-S	S. P. Simner	766-H
J. C. Griffin	773-A	F. M. Smith	705-1C
E. W. Harrison	704-60H	A. V. Staub	766-H
P. J. Hill	766-H	S. A. Utlak	704-27S
E. N. Hoffman	999-W	J. R. Vitali	704-71F
J. F. Iaukea	704-27S	T. L. White	773-A
P. R. Jackson	703-46A	A. W. Wiggins	214-168H
C. A. Langton	773-43A	R. H. Young	773-A