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:

We put science to work.™

Savannah River National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

A U.S. DEPARTMENT OF ENERGY NATIONAL LABORATORY • SAVANNAH RIVER SITE • AIKEN, SC

Results for the Fourth Quarter 2014 Tank 50 WAC Slurry Sample

Chemical and Radionuclide Contaminants

Charles L. Crawford, Ph.D.

September 2015

SRNL-STI-2015-00060, Rev. 0

SRNL.DOE.GOV

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2015-00060
Revision 0

Keywords: *Tank 50, Waste Acceptance Criteria, Saltstone*

Retention: *Permanent*

Results for the Fourth Quarter 2014 Tank 50 WAC Slurry Sample: Chemical and Radionuclide Contaminants

C. L. Crawford

September 2015

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

Savannah River National Laboratory™
OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

REVIEWS AND APPROVALS

Signatures on File

AUTHOR:

C. L. Crawford, Process Technology Programs Date

TECHNICAL REVIEWS:

A. D. Cozzi, Engineering Process Development, Reviewed per E7, 2.60 Date

APPROVAL:

E. N. Hoffman, Manager Date
Engineering Process Development

A. P. Fellinger, Manager Date
Environmental & Chemical Process Technology Research Programs

E. J. Freed, Manager Date
DWPF & Saltstone Facility Engineering

R. E. Edwards, Jr., Manager Date
Nuclear Safety & Engineering Integration

C. B. Sherburne, Manager Date
Tank Farm Process Safety and Regulatory Engineering

EXECUTIVE SUMMARY

This report details the chemical and radionuclide contaminant results for the characterization of the Calendar Year (CY) 2014 Fourth 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 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 pertaining to the WAC provided in this report for the Fourth Quarter CY 2014 sample:

- SRR WAC targets or limits were met for all analyzed chemical and radioactive contaminants unless noted in this section.

- Of the forty-seven metal, anion, or organic contaminants listed in Attachment 8.1 and 8.2 of the WAC, three are above 10% of the WAC limit or target.[1] These contaminants and their percentage of the WAC limit or target are nitrate (32%), nitrite (10%), and mercury (24%).

- Of the fifty-six radionuclides contaminants listed in Attachment 8.3 and 8.4 of the WAC, four are above 10% of the WAC limit or target.[1] These radionuclide contaminants and their percentage of the WAC limit or target are ^{99}Tc (21%), ^{129}I (17%), ^{137}Cs (32%), and ^{137m}Ba (32%).

- Norpar 13 and Isopar L have higher detection limits[2] compared with the Saltstone WAC.[1] The data provided in this report is based upon the concentrations in the sub-sample, and due to the limited solubility of these materials in aqueous solution, may not represent the concentrations of the analytes in Tank 50.

Additional conclusions are:

- The low insoluble solids content increases the measurement uncertainty for species that are expected to be insoluble such as Isopar L and Norpar 13.

- Certain constituents requested in the Task Technical Request pertaining to Toxicity Characteristic Leaching Procedure (TCLP) and Underlying Hazardous Constituents (UHC) such as antimony, beryllium and thallium are not detectable. The total beta and total solids are 1.65E+06 pCi/mL and 28.09 wt%, respectively.

- The specific gravity and total gamma activity are reported as 1.2410 and 1.23E+06 pCi/mL, respectively.

- Minimum detection limits are reported for ^{59}Ni, ^{94}Nb, ^{247}Cm, ^{249}Cf, and ^{251}Cf as determined from the minimum detectable activity associated with the radiochemical methods used for these

radionuclides. The reported detection limits are above the requested SRR target minimum detection limit concentrations.[3] However, except for ^{94}Nb, they are below the estimated detection limits initially established by SRNL in 2009.[4] The reported detection limit for ^{94}Nb in this fourth quarter Tank 50 sample of <4.91E-01 pCi/mL is ~ 12% above the estimated ^{94}Nb detection limit of <4.38E-01 pCi/mL.[4]

TABLE OF CONTENTS

LIST OF TABLES

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
DSFE	DWPF & Saltstone Facility Engineering
E&CPT	Environmental & Chemical Process Technology
ETP	Effluent Treatment Project
GC/MS	Gas Chromatograph/Mass Spectrometer
HDPE	High Density Polyethylene
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
L	Liter
LLW	Low Level Waste
LSC	Liquid Scintillation Counting
MRL	Method Reporting Limit
mg	Milligram
mL	Milliliter
NA	Not Applicable
pCi/mL	Picocurie per Milliliter
PHA	Pulse Height Analysis
RSD	Relative Standard Deviation
SC	Shielded Cells (Facility)
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SVOA	Semi-Volatile Organic Analysis
TCLP/UHC	Toxicity Characterization Leaching Procedure/Underlying Hazardous Constituent
TIC/TOC	Total Inorganic Carbon/Total Organic Carbon
TTR	Technical Task Request
UHC	Underlying Hazardous Constituent

VDS	Variable Depth Sample
VOA	Volatile Organic Analysis
WAC	Waste Acceptance Criteria
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.

DWPF Saltstone Facility Engineering (DSFE) requested that the Savannah River National Laboratory (SRNL) perform quarterly analysis on Tank 50 salt solution feed samples per a Task Technical Request (TTR).[5] The concentrations of chemical and radionuclide contaminants are measured to ensure the saltstone produced during each quarter complies with the current WAC.[1, 5, 6] This report documents the concentrations of chemical and radionuclide contaminants and discusses those results for the Fourth Quarter Calendar Year 2014 (4QCY14) samples collected from Tank 50 on October 2, 2014. In addition to the chemical and radionuclide contaminants associated with the WAC, other species in the 4QCY14 Tank 50 sample are reported as requested by DSFE.[5] These include constituents pertinent to the Toxicity Characteristic Leaching Procedure (TCLP) / Underlying Hazardous Constituents (UHC) and corrosion control and also radionuclides associated with inventory reporting requirements.

2.0 Experimental

2.1 Technical

On October 2, 2014, a single 1-L sampler (HTF-50-14-135) and a 200-mL sampler (HTF-50-14-134) were collected from Tank 50 for the 4QCY14 WAC analyses and delivered the same day to the SRNL Shielded Cells (SC).[7] The 200 mL sampler is a dip sample taken six inches below the surface and the 1-L variable depth sample (VDS) was pulled 35 inches from the bottom of the tank after running one agitator pump for at least 4.4 hours prior to pump shutdown and sampling. The VDS was left at depth for at least one hour for foil dissolution.

At SRNL, slurry samples (~10-12 mL each) from HTF-50-14-134 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 10-12-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 remaining slurry in the 200-mL sampler was agitated to disperse any solids and poured into a 125-mL Teflon® bottle and set aside. The 1-L VDS sample was transferred into a 2-L high-density polyethylene (HDPE) bottle. The transferred slurry was left to settle in the 2-L bottle. No solids were observed after being allowed to settle overnight, but traces of solids were visible after sitting for several days. Visual inspection of the inside of the sampler indicated there were no visible solids remaining in the sampler, thus no clear supernate was returned to the sampler for rinsing. The total weight of the transferred slurry was 1,418 g.

[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.

The 2-L HDPE bottle was agitated to disperse thoroughly the limited suspended 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 portion of a 290.51 g Toxicity Characteristic Leaching Procedure (TCLP) subsample 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 for the following analyses:

- 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.
- Three sets of 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.
- Twelve-mL aliquots were sent to the AD Dissolution Laboratory for digestion using an aqua regia method.[8] 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 – Emission Spectroscopy (ICP-ES), 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.
- Quadruplicate three-gram samples of both slurry and filtrate were used to determine the quantitative solids by remote handling/drying in the SRNL SC. A 15 WT% NaCl standard solution was performed in parallel. Data from the slurry and filtrate solids measurements were used to calculate the total insoluble solids. These measurements and resulting calculations were performed per Environmental and Chemical Process Technology (E&CPT) procedure L29, ITS-0078, Rev. 1, 'Weight Percent Solids Determination Using a Furnace or Oven'.[9]

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. Data collected during this study are recorded in SRNL Electronic Notebook, "4QCY14 Tank 50 WAC", B9180-000126-16.[10]

3.0 Results and Discussion

The following tables contain the results for the 4QCY14 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.[1] 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. Tank 50 4QCY14 Slurry Sample Chemical Results and WAC Limits[1]

Chemical Name	Method	Average Concentration (mg/L)	Std. Dev.	WAC Limit[1] (mg/L)
Aluminate ($Al(OH)_4^-$)	ICP-ES	1.39E+04[a]	2.43E+02	4.08E+05
Ammonium (NH_4^+)	IC	<1.00E+01	NA	2.12E+02
Carbonate (CO_3^{2-})	TIC	1.32E+04[b]	2.88E+01	1.20E+05
Chloride (Cl^-)	IC	1.93E+02	6.66E+00	7.95E+03
Fluoride (F^-)	IC	<1.00E+02	NA	4.07E+03
Free Hydroxide (OH^-)	Total Base	2.87E+04[b]	1.70E+02	1.58E+05
Nitrate (NO_3^-)	IC	1.42E+05	1.16E+04	4.37E+05
Nitrite (NO_2^-)	IC	2.21E+04	1.87E+03	2.14E+05
Oxalate ($C_2O_4^{2-}$)	IC	4.18E+02	2.77E+01	2.72E+04
Phosphate (PO_4^{3-})	ICP-ES	4.42E+02[c]	1.22E+01	2.94E+04
Sulfate (SO_4^{2-})	IC	5.26E+03	9.81E+01	5.69E+04
Arsenic (As)	AA	<9.37E-02	NA	2.30E+01
Barium (Ba)	ICP-ES	< 9.00E-01	NA	6.19E+02
Cadmium (Cd)	ICP-ES	<1.73E+00	NA	3.10E+02
Chromium (Cr)	ICP-ES	3.38E+01	3.72E-01	1.24E+03
Lead (Pb)	ICP-MS	2.22E-01	7.50E-03	6.19E+02
Mercury (Hg)	CVAA	7.93E+01	1.12E+00	3.25E+02
Selenium (Se)	AA	<1.87E-01	NA	4.46E+02
Silver (Ag)	ICP-ES	<2.01E+00	NA	6.19E+02
Aluminum (Al)	ICP-ES	3.94E+03	6.90E+01	1.16E+05
Potassium (K)	AA	2.25E+02	1.12E+01	3.03E+04
Nickel Hydroxide	ICP-ES	< 1.06E+00[d]	NA	1.17E+03
n-Butanol	VOA	<5.00E-01[e]	NA	7.73E+00
i-Butanol	VOA	<5.00E-01[e]	NA	7.73E+00
i-Propanol	VOA	<2.50E-01[e]	NA	1.88E+00
Phenol	SVOA	<1.00E+01[e]	NA	7.50E+02
Isopar L	SVOA	<2.66E+01 ppm [e,f]	NA	1.10E+01 ppm
Total Organic Carbon	TOC	2.64E+02[e]	0.00E+00[g]	5.00E+03
Tetraphenylborate (TPB anion)	HPLC	<5.00E+00	NA	5.00E+00

(a) Result is calculated from the measured Al concentration assuming all of the Al is present as the hydroxide compound; (b) Measurement performed on filtered supernate samples; (c) Result is calculated from the measured P concentration assuming all of the P is present as the oxide compound; (d) Result is calculated from the measured Ni concentration assuming all of the Ni is present as the hydroxide compound; (e) Measurement performed on duplicate samples rather than triplicate samples; (f) Result is calculated from the reported concentration of < 33 mg/L and the density in Table 3-8; (g) All replicates showed identical TOC concentration.

Table 3-2. Tank 50 Slurry Sample Chemical Results and WAC Targets[1]

Chemical Name	Method	Average Concentration (mg/L)	Std. Dev.	WAC Target[1] (mg/L)
Boron (B)	ICP-ES	< 2.13E+00	NA	7.43E+02
Cobalt (Co)	ICP-MS	<1.70E-02	NA	1.75E+02
Copper (Cu)	ICP-ES	<1.09E+00	NA	7.43E+02
Iron (Fe)	ICP-ES	6.05E+00	1.15E+00	4.95E+03
Lithium (Li)	ICP-ES	1.07E+01	4.35E-02	7.43E+02
Manganese (Mn)	ICP-ES	<1.09E+00	NA	7.43E+02
Molybdenum (Mo)	ICP-ES	< 3.79E+00	NA	7.43E+02
Nickel (Ni)	ICP-ES	< 6.73E+00	NA	7.43E+02
Silicon (Si)	ICP-ES	3.12E+01	7.85E+00	1.07E+04
Strontium (Sr)	ICP-ES	<1.64E-01	NA	7.43E+02
Zinc (Zn)	ICP-ES	5.87E+00	1.14E-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	<2.50E+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 AD.

As indicated in Tables 3-1, 3-2 and 3-3, all of the contaminants are within the WAC limits or targets with the exception of Isopar L and Norpar 13.[1] Few contaminants are above 10% of the WAC limit or target. Nitrate, nitrite, and mercury are 32%, 10%, and 24%, respectively, of the WAC limit (Table 3-1). Only ^{99}Tc, ^{129}I and ^{137}Cs are 21%, 17% and 32%, respectively, of the WAC limit (Table 3-3). In October 2010, SRNL reviewed the MRLs for the organic constituents in Tank 50.[2] All of the MRLs are at or below the WAC targets for the organics with the exception of Norpar 13 and Isopar L. Norpar 13 has a MRL of 0.75 mg/L and is above the WAC target.[1] The MRL for Isopar L is < 26.7 ppm and above the WAC limit.[1] 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 are the concentrations as detected by the Gas Chromatography/Mass Spectrometry (GC/MS), but may not necessarily be an accurate representation of the concentrations of these analytes in Tank 50.

Table 3-3. Tank 50 4QCY14 Slurry Sample Radionuclides Results and WACT Limits[1]

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.	WAC Limit[1] (pCi/mL)
Tritium (^{3}H)	Tritium counting	4.50E+02	9.81E+00	5.63E+05
Carbon-14 (^{14}C)	C-14 Liquid scintillation	5.39E+02	4.04E+01	1.13E+05
Nickel-63 (^{63}Ni)	Ni-59/63	< 6.89E+00	NA	1.13E+05
Strontium-90 (^{90}Sr)	Sr-90 Liquid scintillation	1.20E+03	1.05E+02	3.15E+06
Technetium-99 (^{99}Tc)	Tc-99 Liquid scintillation	1.89E+04	8.20E+02	8.70E+04
Iodine-129 (^{129}I)	I-129 (w/ separation) Liquid scintillation	1.09E+01	1.86E+00	6.30E+01
Cesium-137 (^{137}Cs)	Gamma Scan	1.30E+06	3.34E+04	3.96E+06
Uranium-233 (^{233}U)	ICP-MS	< 1.65E+02	NA	1.13E+04
Uranium-235 (^{235}U)	ICP-MS	2.00E-01	2.05E-03	1.13E+02
Plutonium-241 (^{241}Pu)	Pu238/241 Liquid scintillation	2.30E+02	1.54E+01	8.38E+05
Total Alpha	Liquid Scintillation Counting	< 3.50E+02	NA	2.13E+05

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.[3] The reported detection limits of ^{59}Ni and ^{94}Nb are above the limits requested by SRR (6.59E+00 and 2.00E-03 pCi/mL, respectively).[3] The reported ^{59}Ni detection limit is below the quantification limit established by SRNL (2.00E+01).[4] The ^{94}Nb detection limit reported in Table 3-4 (<4.91E-01 pCi/mL), from a Cs-removal large aliquot method involving ammonium molybdophosphate (AMP), is ~ 12% higher than the detection limit estimated by SRNL (4.38E-01 pCi/mL).[4] A similar detection limit for ^{94}Nb (<3.53E-01 pCi/mL) was reported in the 3rd Quarter Tank 50 WAC analyses.[11]

The radionuclide ^{137m}Ba is the radioactive daughter of 94.6% of the beta decay of ^{137}Cs. 5.4% of the ^{137}Cs decays to stable ^{137}Ba. The half-life of the parent radionuclide (^{137}Cs) is six million 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 1.23E+06 pCi/mL.

The concentration of ^{135}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}Pu. The Pu alpha Pulse Height Analysis (PHA) method does not resolve the alpha activities of ^{239}Pu and ^{240}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.[1]

Table 3-4. Tank 50 4QCY14 Slurry Sample Radionuclide Results and WAC Targets[1]

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.	WAC Target[1] (pCi/mL)
Aluminum-26 (^{26}Al)	Gamma scan (Cs removed)	< 1.79E-01	NA	2.88E+03
Cobalt-60 (^{60}Co)	Gamma scan (Cs removed)	2.07E-01[a]	NA	9.747E+02
Potassium-40 (^{40}K)	Gamma scan (Cs removed)	< 1.29E+00	NA	1.00E+02
Nickel-59 (^{59}Ni)	Ni-59/63	< 7.79E+00	NA	1.13E+03
Selenium-79 (^{79}Se)	Se-79	1.48E+01[b]	3.19E-02	1.90E+04
Yttrium-90 (^{90}Y)	Secular Equilibrium w/ Sr-90	1.20E+03	1.05E+02	3.15E+06
Zirconium-93 (^{93}Zr)	ICP-MS	< 4.28E+01	NA	1.00E+05
Niobium-94 (^{94}Nb)	Gamma scan (Cs removed)	< 4.91E-01	NA	1.53E+02
Rhodium-106 (^{106}Rh)	Secular Equilibrium w/ Ru-106	< 4.73E+00	NA	1.13E+06
Ruthenium-106 (^{106}Ru)	Gamma scan (Cs removed)	< 4.73E+00	NA	1.13E+06
Antimony-125 (^{125}Sb)	Gamma scan (Cs removed)	6.40E+00	1.27E+00	7.988E+03
Tellurium-125m (^{125m}Te)	Secular Equilibrium w/ Sb-125	6.40E+00	1.27E+00	1.828E+03
Tin-126 (^{126}Sn)	Gamma scan (Cs removed)	1.24E+02	4.51E+00	1.80E+04
Cesium-134 (^{134}Cs)	Gamma Scan	< 1.69E+03	NA	1.82E+04
Cesium-135 (^{135}Cs)	ICP-MS	2.33E+01	5.47E-01	2.50E+02
Barium-137m (^{137m}Ba)	Calculation (Secular Equilibrium w/ 94.6% of Cs-137)	1.23E+06	3.16E+04	3.75E+06
Cerium-144 (^{144}Ce)	Gamma scan (Cs removed)	< 4.82E+00	NA	1.13E+05
Promethium-147 (^{147}Pm)	Pm-147/Sm-151 Liquid scintillation	<3.44E+01	NA	5.63E+06
Samarium-151 (^{151}Sm)	Pm-147/Sm-151 Liquid scintillation	<3.44E+01	NA	2.25E+04
Europium-154 (^{154}Eu)	Gamma scan (Cs removed)	< 8.69E-01	NA	1.615E+03
Europium-155 (^{155}Eu)	Gamma scan (Cs removed)	< 2.64E+00	NA	1.13E+04
Radium-226 (^{226}Ra)	Ra-226	< 3.10E+00	NA	1.00E+03
Radium-228 (^{228}Ra)	Gamma scan (Cs removed)	< 1.87E+00	NA	1.00E+04
Actinium-227 (^{227}Ac)	Th-229/230	<7.75E-03	NA	1.00E+04
Thorium-229 (^{229}Th)	Th-229/230	< 2.64E-02	NA	1.63E+05
Thorium-230 (^{230}Th)	Th-229/230	< 1.80E-02	NA	6.26E+03
Thorium-232 (^{232}Th)	ICP-MS	< 1.87E-03	NA	2.88E+03
Protactinium-231 (^{231}Pa)	Pa-231	< 1.07E+00	NA	1.00E+03
Uranium-232 (^{232}U)	U-232	2.46E+00	1.17E+00	9.06E+03
Uranium-234 (^{234}U)	ICP-MS	< 1.06E+02	NA	1.13E+04
Uranium-236 (^{236}U)	ICP-MS	< 1.10E+00	NA	1.13E+04
Uranium-238 (^{238}U)	ICP-MS	4.56E+00	7.17E-02	1.13E+04
Neptunium-237 (^{237}Np)	ICP-MS	<1.20E+01	NA	1.00E+04

Table 3-4. Tank 50 4QCY14 Slurry Sample Radionuclide Results and WAC Targets[1], cont.

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.	WAC Tareget[1] (pCi/mL)
Plutonium-238 (^{238}Pu)	Pu238/241 Pu alpha PHA	7.33E+02	4.82E+01	2.13E+05
Plutonium-239 (^{239}Pu)	Pu238/241 Pu alpha PHA	7.19E+01	4.82E+00	2.13E+05
Plutonium-240 (^{240}Pu)	Pu238/241 Pu alpha PHA	7.19E+01	4.82E+00	2.13E+05
Plutonium-242 (^{242}Pu)	ICP-MS	< 6.50E+01	NA	2.13E+05
Plutonium-244 (^{244}Pu)	ICP-MS	< 3.02E-01	NA	7.02E+04
Americium-241 (^{241}Am)	Am/Cm	< 2.07E+00	NA	2.13E+05
Americium-242m (^{242m}Am)	Am/Cm	<3.86E-02	NA	4.50E+05
Americium-243 (^{243}Am)	Am/Cm	<4.32E-01	NA	2.13E+05
Curium-242 (^{242}Cm)	Am/Cm	<3.19E-02	NA	1.13E+04
Curium-244 (^{244}Cm)	Am/Cm	1.71E+01	5.15E+00	2.13E+05
Curium-245 (^{245}Cm)	Am/Cm	<1.26E+00	NA	2.25E+05

a. Measurement represents data from single sample rather than triplicate samples.
b. Measurement represents data from duplicate samples rather than triplicate samples.

Table 3-5 and Table 3-6 list the chemical contaminants that affect vault flammability. These chemicals must be monitored to ensure flammable gases other than Isopar L, benzene, ammonia, and hydrogen do not contribute more than 10% of the Composite Lower Flammability Limit (CLFL).[1] To address the uncertainty of GC/MS results from earlier quarterly tank analyses, several modifications to SRNL sampling and analysis methodology have been implemented. First, either a second set of surface sample sub-samples are collected prior to combining the surface and dip samples, or alternatively, the entire surface sample is reserved for organic analyses. This additional sample material is held in reserve for later analysis pending the outcome of the first set of samples. For the 4QCY14 sample, a 200 mL surface sample was collected. Approximately 84 g of the surface sample was set aside and not combined with the dip sample. Secondly, the cell prepared blank is pH adjusted (made basic) and processed for analysis in the same manner as the actual tank samples to better detect contaminants introduced to the sample. Finally, the caustic used to adjust the blank pH is analyzed for contaminants.

Table 3-5. Tank 50 4QCY14 Slurry Sample Chemical Results Impacting Vault Flammability[1]

Chemical Name	Method	Average Concentration (mg/L)	Std. Dev.	WAC Limit[1]
Isopar L	SVOA	<2.66E+01 ppm [a,b]	NA	1.10E+01 ppm
Tetraphenylborate (TPB anion)	HPLC	<5.00E+00	NA	5.00E+00 mg/L
Ammonium (NH_4^+)	IC	<1.00E+01	NA	2.12E+02 mg/L

a. Measurement performed on duplicate samples rather than triplicate samples.
b. Result is calculated from the reported concentration of < 33 mg/L and the density in Table 3-8.

Table 3-6. Tank 50 4QCY14 Slurry Sample "Other Organics" Results Impacting Vault Flammability[1]

Chemical Name	Method	Average Concentration (mg/L)	Std. Dev.	WAC Concentrations[1] (mg/L)
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	0.05
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 Table 3-5or Table 3-6 with reported values above the WAC limit.[1] It should be noted that the detection limit for Isopar L was expected based on current SRNL capabilities.[2] 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.[2] 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.[1] The pH was calculated using the free base concentration (OH^-). The low insoluble solids content makes sub-sampling difficult.

Table 3-7. Tank 50 4QCY14 Slurry Sample Results for Saltstone Processing Criteria[1]

Processing Criterion [1]	Method	Value	Std. Dev.
pH > 10	Calculated	>13	NA
2.5 M < $[Na^+]$ < 7. 0 M	ICP-ES / AA	4.56 M	0.215
Total Insoluble Solids <15 wt%	Calculated	~0 wt%	NA

Table 3-8 provides constituents listed in the TTR[5] but not contained in the WAC. The results from Table 3-8 are used to support the Toxicity Characterization Leaching Procedure/Underlying Hazardous Constituents (TCLP/UHC) testing by a certified laboratory.[12] The density of the slurry was measured at 18.7 ºC. Natural Tl is composed of two isotopes, ^{203}Tl and ^{205}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 from the lowest detection limit determined from three replicates for the mass 203 isotope and 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 often gives a signal of the same magnitude.[13] 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.[13] The concentrated nature of these samples, which are diluted 1:4 during measurement, has often allowed these small values to be above the detection limit of the instrument. In light of the previous

observations,[13] the value for Tl has been given as a detection limit, since there was likely little or no Tl in those samples. This quarter the Tl signals are below the detection limit as shown in Table 3-8 and the Pb signals are sufficiently above the detection limit to produce an actual reported value as shown in Table 3-1.

Table 3-8. Tank 50 4QCY14 Slurry Sample Requests for Constituents for TCLP/UHC[12]

Constituent[12]	Method	Average Value (mg/L, unless stated otherwise)	Std. Dev.
Antimony (Sb)	ICP-MS	<2.98E-02 [b]	NA
Beryllium (Be)	ICP-ES	<1.91E-01	NA
Cyanide (CN)	a	NA	NA
Thallium (Tl)	ICP-MS	<2.42E-02[b]	NA
Density (slurry)	Measured (18.7ºC)	1.2391 g/mL	0.0123
Total Beta	LSC	1.65E+06 pCi/mL	4.30E+04
Total Solids	Measured	28.09 wt%	0.210

a. Currently, a routine method for detecting this species does not exist in SRNL.
b. Blank is of comparable magnitude, so there may be little or no Tl in the sample.

The tank corrosion species listed in Table 3-9 were requested by DSFE.[10] The Specific gravity was calculated by dividing the measured density of the slurry (given in Table 3-8 at 18.7 °C) by the density of water at the same temperature.[14]

Table 3-9. Tank 50 4QCY14 Slurry Sample Requests from the DSFE for Corrosion Species[10]

Constituent	Method	Average Value	Std. Dev.
Specific Gravity	a	1.2410	0.0002
Total Gamma	b	1.23E+06 pCi/mL	1.83E+04[c]

a. Calculated from the measured density of slurry and density of water at 18.7 °C.[14]
b. Calculated from the sum of measured gamma emitters.
c. Value is the "standard error of the mean" rather than the standard deviation of the measurements since its calculation involves multiple radionuclides.

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, ^{137m}Ba, ^{154}Eu, and ^{241}Am.

Table 3-10 provides results for additional radionuclides required for quantification and support of inventory-reporting requirements as requested by DSFE.[10]

Table 3-10. Tank 50 4QCY14 Slurry Sample Radionuclides Results for Inventory Reporting Requirement[10]

Radionuclide[10]	Method	Average Concentration (pCi/mL)	Std. Dev.
Niobium-93m (^{93m}Nb)	ICP-MS	< 4.17E+01	NA
Silver-108m (^{108m}Ag)	Gamma scan (Cs removed)	< 7.30E-01	NA
Barium-133 (^{133}Ba)	Gamma scan (Cs removed)	< 1.42E+00	NA
Bismuth-207 (^{207}Bi)	Gamma scan (Cs removed)	< 4.64E-01	NA
Thorium-228 (^{228}Th)	Gamma scan (Cs removed)	< 1.80E+01	NA
Curium-247 (^{247}Cm)	Am/Cm	<1.68E+00	NA
Californium-249 (^{249}Cf)	Am/Cm	<1.68E+00	NA
Californium-251 (^{251}Cf)	Am/Cm	<1.42E+00	NA

4.0 Conclusions

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

- SRR WAC targets or limits were met for all analyzed chemical and radioactive contaminants unless noted in this section.

- Of the forty-seven metal, anion or organic contaminants listed in Attachment 8.1 and 8.2 of the WAC, three are above 10% of the WAC limit or target.[1] These contaminants and their percentage of the WAC limit or target are nitrate (32%), nitrite (10%), and mercury (24%).

- Of the fifty-six radionuclides contaminants listed in Attachment 8.3 and 8.4 of the WAC, four are above 10% of the WAC limit or target.[1] These radionuclide contaminants and their percentage of the WAC limit or target are ^{99}Tc (21%), ^{129}I(17%), ^{137}Cs (32%), and ^{137m}Ba (32%).

- Norpar 13 and Isopar L have higher detection limits[2] compared with the Saltstone WAC.[1]The data provided in this report is based upon the concentrations in the sub-sample, and due to the limited solubility of these materials in aqueous solution, may not represent the concentrations of the analytes in Tank 50.

Additional conclusions are:

- The low insoluble solids content increases the measurement uncertainty for species that are expected to be insoluble such as Isopar L and Norpar 13.

- Certain constituents requested in the Task Technical Request pertaining to Toxicity Characteristic Leaching Procedure (TCLP) and Underlying Hazardous Constituents (UHC) such as antimony, beryllium and thallium are not detectable. The total beta and total solids are 1.65E+06 pCi/mL and 28.09 wt%, respectively.

- The specific gravity and total gamma activity are reported as 1.2410 and 1.23E+06 pCi/mL, respectively.

- Minimum detection limits are reported for ^{59}Ni, ^{94}Nb, ^{247}Cm, ^{249}Cf, and ^{251}Cf as determined from the minimum detectable activity associated with the radiochemical methods used for these radionuclides. The reported detection limits are above the requested SRR target minimum detection limit concentrations.[3] However, except for ^{94}Nb, they are below the estimated detection limits initially established by SRNL in 2009.[4] The reported detection limit for ^{94}Nb in this fourth quarter Tank 50 sample of <4.91E-01 pCi/mL is ~ 12% above the estimated ^{94}Nb detection limit of < 4.38E-01 pCi/mL.[4]

5.0 References

1. Dixon, K. D., *Waste Acceptance Criteria for Aqueous Waste Sent to the Z-Area Saltstone Production Facility (U)*, X-SD-Z-00001, Rev. 13; Savannah River Site: Aiken, SC 29808; January 2014.

2. Crump, S. L., *Determination of Method Reporting Limits for Select Analytes by GC/MS*, SRNL-TR-2010-00206, Rev. 0; Savannah River National Laboratory, Aiken, SC 29808; October 2010.

3. Dixon, D. B., *Minimum Detection Limits for Saltstone Quarterly WAC Analyses*, SRR-WSE-2013-00005, Rev. 1; Savannah River Site, Aiken, SC 29808; January 2013.

4. Diprete, C. C., *Overview of Capability to Measure Radionuclides of Interest for Saltstone*, SRNL-L4000-2009-00028, Rev. 0; Savannah River National Laboratory, Aiken, SC 29808; June 2009.

5. Hodges, B. C., *Saltstone Support for Salt Solution Analyses - FY2015*; Savannah River Remediation, X-TTR-Z-00006, Revision 0, September 9, 2014.

6. Crawford, C. L., *Task Technical and Quality Assurance Plan for SRNL Support of Tank 50H Waste Acceptance Criteria (WAC) Analyses*; SRNL-RP-2013-00761, Rev. 1; Savannah River National Laboratory: Aiken, SC 29808; 2014.

7. CST Tank Request Form, CST-2014-00097, September 3, 2014.

8. Coleman, C. J., *Aqua Regia Dissolution of Sludge for Elemental Analysis*; *Manual L16.1, Procedure ADS-2226*, Rev. 9; Savannah River National Laboratory: Aiken, SC 29808; 2009.

9. Procedure L29, ITS-0078, *Weight Percent Solids Determination Using a Furnace or Oven*.

10. Crawford, C. L., *4QCY14 Tank 50 WAC Characterization*, B9180-00026-16, SRNL E-Notebook (Production), Savannah River National Laboratory, October 2014.

11. Crawford, C. L., *Results for the Third Quarter 2014 Tank 50 WAC Slurry Sample: Chemical and Radionuclide Contaminants*; SRNL-STI-2014-00492 Rev. 0, December, 2014.

12. Miller, D. H., *Task Technical and Quality Assurance Plan for SRNL Support of TCLP Preparation and Analysis for Saltstone – FY2015*; SRNL-RP-2014-01020, Rev. 0; Savannah River National Laboratory: Aiken, SC 29808; September, 2014.

13. Bannochie, C. J., *Results for the Second Quarter 2013 Tank 50 WAC Slurry Sample*; SRNL-STI-2013-00390, Rev. 0; Savannah River National Laboratory: Aiken, SC 29808; 2013.

14. *Handbook of Chemistry and Physics*, 94th ed.; Edited by Haynes, W. M., CRC Press: Boca Raton, FL, 2014.

Distribution

Name:	Location:	Name:	Location:
P. M. Almond	773-43A	C. A. Langton	773-43A
J. P. Arnold	707-3E	J. N. Leita	704-56H
C. J. Bannochie	773-42A	K. R. Liner	704-S
M. J. Barnes	773-A	M. J. Mahoney	705-1C
J. M. Bricker	704-S	S. L. Marra	773-A
L. W. Brown	773-A	D. J. Martin	766-H
T. B. Brown	773-A	D. H. McGuire	999-W
N. F. Chapman	766-H	F. M. Pennebaker	773-42A
C. K. Chiu	704-30S	M. M. Potvin	704-27S
L. H. Connelly	773-A	J. W. Ray	704-27S
J. S. Contardi	704-56H	S. H. Reboul	773-42A
A. D. Cozzi	999-W	M. M. Reigel	773-42A
C. L. Crawford	773-42A	M. A. Rios-Armstrong	766-H
C. C. DiPrete	773-A	L. B. Romanowski	705-1C
K. D. Dixon	705-1C	K. H. Rosenberger	705-1C
R. E. Edwards	766-H	A. R. Shafer	766-H
A. P. Fellinger	773-42A	C. B. Sherburne	707-7E
E. J. Freed	704-S	F. M. Smith	705-1C
J. C. Griffin	773-A	M. E. Smith	704-30S
E. W. Harrison	241-152H	B. A. Speight	707-7E
P. J. Hill	766-H	A. V. Staub	241-156H
E. N. Hoffman	999-W	S. A. Utlak	704-27S
J. F. Iaukea	704-27S	J. R. Vitali	704-30S
P. R. Jackson	703-46A	T. L. White	773-A
V. Jain	766-H	A. W. Wiggins	704-61H
V. M. Kmiec	704-30S	R. H. Young	773-A