SRNL-STI-2009-00585

**Key Words:**
**Tank 50**
**Waste Acceptance Criteria**
**Saltstone**

**Retention:**
**Permanent**

# RESULTS FOR THE THIRD QUARTER 2009 TANK 50 WAC SLURRY SAMPLE: CHEMICAL AND RADIONUCLIDE CONTAMINANT RESULTS

**Marissa M. Reigel**
**Cecilia C. DiPrete**
**Ned E. Bibler**

**NOVEMBER 2009**

Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808

**Prepared for the U.S. Department of Energy Under Contract Number DE-AC09-08SR22470**

SRNL™

## DISCLAIMER



**Printed in the United States of America**

**Prepared for**
**U.S. Department of Energy**

SRNL-STI-2009-00585

**Key Words:**
**Tank 50**
**Waste Acceptance Criteria**
**Saltstone**

**Retention:**
**Permanent**

# RESULTS FOR THE THIRD QUARTER 2009 TANK 50 WAC SLURRY SAMPLE: CHEMICAL AND RADIONUCLIDE CONTAMINANT RESULTS

**Marissa M. Reigel**
**Cecilia C. DiPrete**
**Ned E. Bibler**

**NOVEMBER 2009**

Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808

**Prepared for the U.S. Department of Energy Under Contract Number DE-AC09-08SR22470**

SRNL™

# REVIEWS AND APPROVALS

**AUTHORS:**

Marissa M. Reigel, Engineering Process Development Date

Cecilia C. DiPrete, Analytical Development Date

Ned E. Bibler, Process Technology Programs Date

**TECHNICAL REVIEWERS:**

Alex D. Cozzi, Engineering Process Development Date

**APPROVERS:**

John E. Occhipinti, Manager, Waste Solidification Engineering Date

Arthur W. (Skip) Wiggins, LWO Process Chemistry Date

Lori M. Chandler, Manager, Analytical Development Date

Sharon L. Marra, Manager, E & CPT Research Programs Date

Allan B. Barnes, Manager, Engineering Process Development Date

# TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| AD | Analytical Development |
| AA | Atomic Absorption (spectroscopy) |
| ARP/MCU | Actinide Removal Process/Modular CSSX Unit |
| CLFL | Composite Lower Flammability Limit |
| DDA | Deliquification, Dissolution, and Adjustment |
| 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 – (atomic) emission spectroscopy |
| ICP-MS | Inductively coupled plasma – mass spectroscopy |
| L | Liter |
| LLW | Low Level Waste |
| LSC | Liquid Scintillation Counting |
| LWO | Liquid Waste Operations |
| MDL | Method detection Limit |
| MRL | Method Reporting Limit |
| mg | Milligram |
| mL | Milliliter |
| 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 |
| SRS | Savannah River Site |
| SVOA | Semi-volatile organic analysis |
| TCLP/UHC | Toxic Characterization Leaching Procedure/Underlying Hazardous Constituent |
| 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 |
| WSE | Waste Solidification Engineering |
| WT % | Weight percent |

# EXECUTIVE SUMMARY

This report details the chemical and radionuclide contaminant results for the characterization of the 2009 Third Quarter sampling of Tank 50 for the Saltstone Waste Acceptance Criteria (WAC).[1] Information from this characterization will be used by Liquid Waste Operations (LWO) 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.

Recently, a review of the radionuclide inventory in Saltstone Vaults 1 and 4 identified several additional radionuclides, not currently in the WAC, which require quantification ($^{40}$K, $^{108m}$Ag, $^{133}$Ba, $^{207}$Bi, $^{227}$Ac, $^{228}$Ra, $^{228}$Th, $^{231}$Pa, $^{247}$Cm, $^{249}$Cf, $^{251}$Cf). In addition, several of the radionuclides previously reported with minimum detection limits below the requirements listed in the WAC required analysis with reduced detection limits to support future inventory reporting requirements ($^{22}$Na, $^{26}$Al, $^{59}$Ni, $^{94}$Nb, $^{106}$Ru, $^{144}$Ce, $^{152}$Eu, $^{155}$Eu, $^{226}$Ra). This added scope was formally requested in a revision to the standing Technical Task Request for CY2009 Saltstone support[2] and is further discussed in several supporting documents[3,4,5].

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

- The concentrations of the reported chemical and radioactive contaminants are less than their respective WAC targets or limits unless noted in this section.

- The reported detection limits for $^{59}$Ni, $^{94}$Nb, $^{247}$Cm, and $^{249}$Cf are above the limits requested by LWO;[4] however, they are below the achievable limits established by Analytical Development (AD).[5]

- The reported detection limit of isopropanol is lower than its WAC Limit for accident analysis in Appendix 8.1, but higher than its WAC concentration given in Table 4 for vault flammability. The higher detection limit is expected based on current analytical capabilities and is documented in the Task Technical and Quality Assurance Plan (TTQAP).[3]

- The reported detection limit for Isopar L is lower than its WAC limit for accident analysis in Appendix 8.1 but higher than its WAC concentration given in Table 3 in reference to vault flammability.

- Isopar L and Norpar 13 have limited solubility in aqueous solutions making it difficult to obtain consistent and reliable sub-samples. The values reported in this memo are the concentrations in the sub-sample as detected by the GC/MS; however, the results may not accurately represent the concentrations of these analytes in the Tank 50 sample received by SRNL.

# 1.0 INTRODUCTION AND BACKGROUND

The Saltstone Facility is designed and permitted to immobilize and dispose of low-level radioactive and hazardous liquid waste (salt solution) remaining from the processing of radioactive material at the Savannah River Site.[1] Low-level waste (LLW) streams from the Effluent Treatment Project (ETP), H-Canyon, the DDA (Deliquification, Dissolution, and Adjustment) process, and the decontaminated salt solution product from the Actinide Removal Process/Modular 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 listed in the current Saltstone WAC. [1]

SRS Liquid Waste Operations (LWO) requested that Savannah River National Laboratory (SRNL) to perform quarterly analysis on saltstone samples.[2] The concentrations of chemical and radionuclide contaminants are measured to ensure the saltstone produced during each quarter is in compliance with the current WAC.[1,3,4] In addition to the current WAC, several radionuclides ($^{40}$K, $^{108m}$Ag, $^{133}$Ba, $^{207}$Bi, $^{227}$Ac, $^{228}$Ra, $^{228}$Th, $^{231}$Pa, $^{247}$Cm, $^{249}$Cf, $^{251}$Cf) were analyzed to support future inventory requirements.[2-6] In addition, several of the radionuclides previously reported with minimum detection limits below the requirements listed in the WAC required analysis with reduced detection limits to support future inventory reporting requirements ($^{22}$Na, $^{26}$Al, $^{59}$Ni, $^{94}$Nb, $^{106}$Ru, $^{144}$Ce, $^{152}$Eu, $^{155}$Eu, $^{226}$Ra). This report documents the concentrations of chemical and radionuclide contaminants for the 2009 third quarter samples collected from Tank 50 on July 1, 2009 and discusses those results in further detail than the previously issued results report.[7]

# 2.0 EXPERIMENTAL

On July 1, 2009, three 200-mL samplers (HTF-50-09-65, 69 and 70) were collected from Tank 50 for Third Quarter 2009 WAC analyses and delivered to the SRNL Shielded Cells (SC).

At SRNL slurry samples (~15 mL) from HTF-50-09-65 and 69 were transferred to glass vials with Teflon-lined caps. The vials were completely filled to minimize the void space and the volitization of organics. The aliquots were transferred to the Analytical Development (AD) Organic Analysis Laboratory for semi-volatile and volatile organic contaminant analysis (SVOA and VOA respectively).

After the samples for organic analysis were obtained, the slurries in the 200-mL samplers were combined into a 1-L high density polyethylene (HDPE) bottle according to the following procedure. Each steel sampler was agitated to disperse any solids in the slurry. After mixing the slurry in the steel sampler, the slurry was transferred to the 1-L HDPE bottle. The transferred slurry was left to settle. A portion of the clear supernate was returned to each steel sampler, mixed to mobilize any remaining solids, and again returned to the 1-L HDPE bottle. Visual inspection of the inside of each 200 mL sampler indicated that all the solids had been removed. The total weight of the transferred slurry was approximately 462 grams.

The 1-L HDPE bottle was agitated to thoroughly mix the solids into the supernate. Aliquots of slurry samples were promptly collected with slurry pipettes to minimize settling effects and placed in PE.

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

- Five-mL aliquots to the AD Ion Chromatography (IC) Laboratory for soluble anion analyses and soluble cation analyses.
- Three-mL aliquots to the AD Organic Analysis Laboratory for measurement of tetraphenlyborate and ethylenediaminetetraacetic acid 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.
- Approximately 70-mL aliquots were removed from the one-L HDPE bottle. After each seventy-mL aliquot was prepared, it was divided into one 50 mL and one 20 mL sample and sent to AD Radiochemistry Laboratory for radiochemical separations and analyses. Purpose of dividing each 70-mL sample was to allow the AD technicians to work with a lower amount of beta/gamma radiation by opening only one bottle while preparing and analyzing each aliquot.

- 12-mL aliquots of 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. 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-ES), inductively coupled plasma-mass spectroscopy (ICP-MS), and atomic absorption spectroscopy (AA) for Hg, As, K, Na, and Se.

A three-mL sample of the slurry was used to determine of the density of the slurry.

# 3.0 RESULTS AND DISCUSSION

The following tables contain the results for the 2009 Third Quarter 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 %RSD 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 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 3rd Quarter 2009 Tank 50 Slurry Samples for Chemical Contaminants Listed in Attachment 8.1 of the Saltstone WAC.**

| Chemical Name | Method | Average Concentration (mg/L) | % RSD | WAC Limit (mg/L) |
|---|---|---|---|---|
| **Ammonium ($NH_4^+$)** | IC | <5.00E+01 | -- | **7.13E+03** |
| **Carbonate ($CO_3^{-2}$)** | TIC | 8.68E+03 | 0.66 | **1.45E+05** |
| **Chloride ($Cl^-$)** | IC | <2.50E+02 | -- | **9.68E+03** |
| **Fluoride ($F^-$)** | IC | <2.50E+02 | -- | **4.94E+03** |
| **Free Hydroxide ($OH^-$)** | Total base | 1.85E+04[a] | 0.92 | **1.91E+05** |
| **Nitrate ($NO_3^-$)** | IC | 1.19E+05 | 1.75 | **5.29E+05** |
| **Nitrite ($NO_2^-$)** | IC | 6.87E+03 | 4.00 | **2.59E+05** |
| **Oxalate ($C_2O_4^{-2}$)** | IC | 7.88E+02 | 2.35 | **3.30E+04** |
| **Phosphate ($PO_4^{-3}$)** | ICP-ES | 8.49E+02 | 1.62 | **3.56E+04** |
| **Sulfate ($SO_4^{-2}$)** | IC | 7.09E+03 | 2.22 | **6.89E+04** |
| **Arsenic (As)** | AA | <2.07E-01 | -- | **7.50E+02** |
| **Barium (Ba)** | ICP-ES | <5.10E-01 | -- | **7.50E+02** |
| **Cadmium (Cd)** | ICP-ES | <5.08E-01 | -- | **3.75E+02** |
| **Chromium (Cr)** | ICP-ES | 3.90E+01 | 0.87 | **1.50E+03** |
| **Lead (Pb)** | ICP-MS | 1.57E-01 | 24.9 | **7.50E+02** |
| **Mercury (Hg)** | AA | 1.17E+01 | 0.71 | **3.25E+02** |
| **Selenium (Se)** | AA | <4.15E-01 | -- | **4.50E+02** |
| **Silver (Ag)** | ICP-ES | <2.11E+00 | -- | **7.50E+02** |
| **Aluminum (Al)** | ICP-ES | 3.26E+03 | 0.36 | **1.41E+05** |
| **n-Butanol** | VOA | 6.5E-01[b] | 8.7 | **2.25E+03** |
| **Isobutanol** | VOA | <5E-01[b] | -- | **2.25E+03** |
| **Isopropanol** | VOA | <5E-01[b] | -- | **2.25E+03** |
| **Phenol** | SVOA | <1E-01[b] | -- | **7.50E+02** |
| **Isopar L** | SVOA | <2.79E+01ppm[b,c] | -- | **1.50E+02 ppm** |
| **Total organic carbon** | TOC | 3.07E+02 | 1.88 | **5.00E+03** |
| **Tetraphenylborate (TPB anion)** | HPLC | <5E+00 | -- | **7.50E+02** |

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

**Table 3-2. Results for the 3rd Quarter 2009 Tank 50 Slurry Samples for Chemical Contaminants Listed in Attachment 8.2 of the Saltstone WAC.**

| Chemical Name | Method | Average Concentration (mg/L) | % RSD | WAC TARGET (mg/L) |
|---|---|---|---|---|
| **Boron (B)** | ICP-ES | 1.87E+01 | 1.31 | **9.00E+02** |
| **Cobalt (Co)** | ICP-MS | 6.81E-02 | 5.01 | **9.00E+02** |
| **Copper (Cu)** | ICP-ES | <8.52E-01 | -- | **9.00E+02** |
| **Iron (Fe)** | ICP-ES | 1.44E+02 | 0.47 | **6.00E+03** |
| **Potassium (K)** | AA | 9.90E+01 | 1.67 | **3.67E+04** |
| **Lithium (Li)** | ICP-ES | <1.51E+01 | -- | **9.00E+02** |
| **Manganese (Mn)** | ICP-ES | 1.01E+02 | 0.27 | **9.00E+02** |
| **Molybdenum (Mo)** | ICP-ES | 4.17E+01 | 1.73 | **9.00E+02** |
| **Nickel (Ni)** | ICP-ES | <1.21E+01 | -- | **9.00E+02** |
| **Silicon (Si)** | ICP-ES | 7.15E+01 | 1.10 | **1.29E+04** |
| **Strontium (Sr)** | ICP-ES | <6.05E-01 | -- | **9.00E+02** |
| **Zinc (Zn)** | ICP-ES | 7.33E+00 | 0.83 | **9.75E+02** |
| **Benzene** | VOA | <2.5E-02[a] | -- | **3.75E+02** |
| **Methanol** | VOA | b | | **2.25E+02** |
| **Toluene** | VOA | <2.5E-02[a] | -- | **3.75E+02** |
| **TributylPhosphate (TBP)** | SVOA | <1E-01[a] | -- | **3.00E+02** |
| **EDTA** | HPLC | <1.00E+02 | -- | **3.75E+02** |
| **Norpar 13** | SVOA | <1E-01[a] | -- | **1.0E-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 and 3-2, all of the contaminants are within the WAC limits. However, Isopar L and Norpar 13 (Table 3-2) 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. It should be noted the WAC limit indicated for isopropanol is in reference to an accident consequence analysis and varies from the limit for isopropanol in the vault flammability study shown in Table 3-6.

None of the radionuclide contaminants in Table 3-3 exceed the WAC limit.

**Table 3-3. Results for 3rd Quarter 2009 Tank 50 Slurry Samples and WAC Limits for Radionuclide Contaminants Listed in Attachment 8.3 of the Saltstone WAC.**

| Radionuclide | Method | Average Concentration (pCi/mL) | % RSD | WAC LIMIT (pCi/mL) |
|---|---|---|---|---|
| **Tritium ($^{3}$H)** | Tritium counting | 6.64E+02 | 12.2 | **5.63E+05** |
| **Carbon-14 ($^{14}$C)** | $^{14}$C Liquid scintillation | 3.58E+02[a] | 25.5 | **1.13E+05** |
| **Nickel-63 ($^{63}$Ni)** | Nickel-59/63 | 6.45E+01 | 48.5 | **1.13E+05** |
| **Strontium-90 ($^{90}$Sr)** | $^{90}$Sr Liquid scintillation | 9.53E+04 | 5.64 | **2.25E+07** |
| **Technetium-99 ($^{99}$Tc)** | $^{99}$Tc Liquid scintillation | 2.44E+04 | 1.53 | **4.22E+05** |
| **Iodine-129 ($^{129}$I)** | $^{129}$I (w/ separation) Liquid scintillation | 5.17E+00 | 2.52 | **1.13E+03** |
| **Cesium-137 ($^{137}$Cs)** | Gamma Scan | 1.26E+07 | 1.81 | **4.75E+07** |
| **Uranium-233 ($^{233}$U)** | ICP-MS | <1.46E+02 | -- | **1.13E+04** |
| **Uranium-235 ($^{235}$U)** | ICP-MS | 4.60E-01 | 3.47 | **1.13E+02** |
| **Plutonium-241 ($^{241}$Pu)** | Plutonium-238/241 Liquid scintillation | <8.15E+02 | -- | **8.38E+05** |
| **Total Alpha** | Liquid Scintillation Counting | <1.20E+05 | -- | **2.50E+05** |

a. Result is from a single sample, the other two samples provided upper limit results due to interference.

The total alpha is obtained from liquid scintillation counting (LSC) of the digested slurry. However this method detects both total alpha and total beta. Therefore, the alpha result is biased due to interference from the beta activity. In this sample, the $^{137}$Cs beta activity determined by gamma counting was 1.26E+07 pCi/mL and the total beta from LSC was 1.58E+07 pCi/mL (Table 3-8), which is higher than the $^{137}$Cs measured by gamma counting. The $^{137}$Cs activity is high enough to interfere with the alpha counting, resulting in a high bias result for the alpha counting. Therefore liquid scintillation counting (LSC) of digested samples should be performed after the cesium has been removed from the sample.

As shown in Table 3-4, none of the radionuclide contaminants exceed the targets listed in the latest revision of the WAC. However, in a revision to the standing 2009 TTR, the detection limits for several radionuclides were lowered in order to accommodate future inventory reporting requirements.[2,4] The reported limits of $^{59}$Ni and $^{94}$Nb are above the limits requested by LWO (6.59E+00 and 2.00E-03 pCi/mL respectively).[4] However, the reported detection limits are below the detection limits established by AD.[5]

**Table 3-4. Results for 3rd Quarter 2009 Tank 50 Slurry Samples and WAC Targets for Radionuclide Contaminants Listed in Attachment 8.4 of the Saltstone WAC.**

| Radionuclide | Method | Average Concentration (pCi/mL) | %RSD | WAC TARGET (pCi/mL) |
|---|---|---|---|---|
| **Sodium-22 ($^{22}$Na)** | Gamma scan (Cs removed) | 3.42E+00 | 16.4 | **1.25E+04** |
| **Aluminum-26 ($^{26}$Al)** | Gamma scan (Cs removed) | <7.52E-02 | -- | **2.88E+03** |
| **Cobalt-60 ($^{60}$Co)** | Gamma scan (Cs removed) | 4.38E+00 | 5.82 | **1.13E+06** |
| **Nickel-59 ($^{59}$Ni)** | Ni-59/63 | <7.03E+00 | -- | **1.13E+05** |
| **Selenium-79 ($^{79}$Se)** | Se79 | 2.02E+02 | 41.8 | **1.90E+04** |
| **Niobium-93m ($^{93m}$Nb)** | ICP-MS | 1.58E+02 | 16.4 | **2.85E+06** |
| **Niobium-94 ($^{94}$Nb)** | Gamma scan (Cs removed) | <3.05E-01 | -- | **1.53E+04** |
| **Molybdenum-93 ($^{93}$Mo)** | ICP-MS | 6.93E+04 | 16.4 | **1.18E+07** |
| **Ruthenium-106 ($^{106}$Ru)** | Gamma scan (Cs removed) | <3.49E+00 | -- | **1.13E+06** |
| **Antimony-125 ($^{125}$Sb)** | Gamma scan (Cs removed) | 3.28E+03 | 3.18 | **2.25E+06** |
| **Tin-126 ($^{126}$Sn)** | Gamma scan (Cs removed) | 8.63E+01 | 4.18 | **1.80E+04** |
| **Cesium-134 ($^{134}$Cs)** | Gamma Scan | <3.03E+03 | -- | **1.13E+06** |
| **Cesium-135 ($^{135}$Cs)** | ICP-MS | 8.20E+01 | 0.96 | **1.13E+06** |
| **Cerium-144 ($^{144}$Ce)** | Gamma scan (Cs removed) | <4.39E+00 | -- | **1.13E+05** |
| **Promethium-147 ($^{147}$Pm)** | Pm147/Sm151 Liquid scintillation | <7.84E+02 | -- | **5.63E+06** |
| **Samarium-151 ($^{151}$Sm)** | Pm147/Sm151 Liquid scintillation | <8.51E+02 | -- | **2.25E+04** |
| **Europium-152 ($^{152}$Eu)** | Gamma scan (Cs removed) | <6.80E-01 | -- | **7.28E+01** |
| **Europium-154 ($^{154}$Eu)** | Gamma scan (Cs removed) | 1.75E+02 | 6.70 | **2.25E+06** |
| **Europium-155 ($^{155}$Eu)** | Gamma scan (Cs removed) | <2.52E+00 | -- | **1.13E+04** |
| **Radium-226 ($^{226}$Ra)** | Gamma scan (Cs removed) | <1.79E+01 | -- | **7.97E+03** |
| **Thorium-229 ($^{229}$Th)** | ICP-MS | <9.62E+03 | -- | **1.63E+05** |
| **Thorium-230 ($^{230}$Th)** | ICP-MS | <9.54E+02 | -- | **6.26E+03** |
| **Thorium-232 ($^{232}$Th)** | ICP-MS | <4.96E-03 | -- | **2.88E+03** |
| **Uranium-232 ($^{232}$U)** | U232 | 8.05E+00 | 43.2 | **1.71E+05** |
| **Uranium-234 ($^{234}$U)** | ICP-MS | 1.87E+02 | 14.9 | **1.13E+04** |
| **Uranium-236 ($^{236}$U)** | ICP-MS | 1.63E+00 | 9.76 | **1.13E+04** |
| **Uranium-238 ($^{238}$U)** | ICP-MS | 1.79E+00 | 0.71 | **1.13E+04** |
| **Neptunium-237 ($^{237}$Np)** | ICP-MS | <1.07E+01 | -- | **2.50E+05** |

**Table 3-4 (continued). Results for 3rd Quarter 2009 Tank 50 Slurry Samples and WAC Targets for Radionuclide Contaminants Listed in Attachment 8.4 of the Saltstone WAC.**

| Radionuclide | Method | Average Concentration (pCi/mL) | %RSD | WAC TARGET (pCi/mL) |
|---|---|---|---|---|
| **Plutonium-238 ($^{238}$Pu)** | Pu238/241 Pu alpha PHA | 3.56E+03 | 14.6 | **2.50E+05** |
| **Plutonium-239 ($^{239}$Pu)** | Pu238/241 Pu alpha PHA | <2.20E+02 | -- | **2.50E+05** |
| **Plutonium-240 ($^{240}$Pu)** | Pu238/241 Pu alpha PHA | <2.20E+02 | -- | **2.50E+05** |
| **Plutonium-242 ($^{242}$Pu)** | ICP-MS | <5.77E+01 | -- | **2.50E+05** |
| **Plutonium-244 ($^{244}$Pu)** | ICP-MS | <2.68E-01 | -- | **7.02E+04** |
| **Americium-241 ($^{241}$Am)** | Gamma scan (Cs removed) | 5.05E+02 | 6.19 | **2.50E+05** |
| **Americium-242m ($^{242m}$Am)** | Am/Cm | 3.23E-01 | 41.2 | **3.68E-01** |
| **Americium-243 ($^{243}$Am)** | Am/Cm | 7.69E+00 | 40.5 | **2.50E+05** |
| **Curium-242 ($^{242}$Cm)** | Am/Cm | 2.67E-01 | 41.2 | **1.13E+04** |
| **Curium-244 ($^{244}$Cm)** | Am/Cm | 8.99E+02 | 31.6 | **2.50E+05** |
| **Curium-245 ($^{245}$Cm)** | Am/Cm | <3.00E+00 | -- | **2.25E+05** |

a. Result is from a single sample, the remaining 2 samples had MDA values.

The values for $^{93m}$Nb and $^{93}$Mo in Table 3-4 are estimated from the ICP-MS result for mass 93. The entire signal at mass 93 is assigned to $^{93}$Zr, and since it is in secular equilibrium with $^{93m}$Nb, the maximum activity of the $^{93m}$Nb is equal to that of the $^{93}$Zr. The specific activity of $^{93}$Zr (2.51E-03 Ci/g) is used when calculating the activity concentration of $^{93m}$Nb. Similarly, $^{93}$Mo is estimated by assigning all of mass 93 to $^{93}$Mo and using the specific activity of $^{93}$Mo to calculate the concentration. The concentration of $^{135}$Cs is calculated by assigning all of the mass at 135 to cesium. $^{126}$Sn and $^{126}$Sb are in secular equilibrium for this sample; therefore their activities are equal. As a result, the measured activity of $^{126}$Sb was used for the $^{126}$Sn concentration since $^{126}$Sb was detected and $^{126}$Sn was below the MDL. Since no analyte was detected at mass 229 and because the $^{229}$Th and $^{230}$Th isotopes have identical electronic structures, the MDL measured for $^{230}$Th was used for the MDL for $^{229}$Th. The activity concentrations are then calculated from the specific activities for $^{229}$Th and $^{230}$Th. 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 limit for each radionuclide.

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 3rd Quarter 2009 Tank 50 Slurry Samples for Acceptance Criteria Limits for Chemical Contaminants Impacting Vault Flammability, Listed in Table 3 of the Saltstone WAC.**

| Chemical Name | Method | Average Concentration (mg/L) | % RSD | WAC Limit |
|---|---|---|---|---|
| **Isopar L** | SVOA | <2.79E+01 ppm | -- | **1.10E+01 ppm** |
| **Tetraphenylborate (TPB anion)** | HPLC | <5E+00 | -- | **5.00E+00 mg/L** |
| **Ammonium ($NH_4^+$)** | IC | <5.00E+01 | -- | **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 2009 Tank 50 Slurry Samples for Concentrations of "Other Organics" Impacting Vault Flammability, Listed in Table 4 of the Saltstone WAC.**

| Chemical Name | Method | Average Concentration (mg/L) | % RSD | WAC Concentrations |
|---|---|---|---|---|
| **n-Butanol** | VOA | 6.5E-01 | 8.7 | **0.75 mg/L** |
| **Tributylphosphate** | SVOA | <1E-01 | -- | **1.0 mg/L** |
| **Isopropanol** | VOA | <5E-01 | -- | **0.25 mg/L** |
| **Methanol** | a | a | | **0.25 mg/L** |
| **Norpar 13** | SVOA | <1E-01 | -- | **0.1 mg/L** |

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

None of the species considered in Tables 3-5 or 3-6 are above the WAC limit with the exception of Isopar L and isopropanol respectively. Although the reported detection limits for these analytes are greater than the WAC limit for vault flammability, they are below the WAC limits for accident analysis as shown in Table 3-1. The higher detection limits were expected based on current AD capabilities as documented in the TTQAP.[3] 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.

**Table 3-7. Results for the 3rd Quarter 2009 Tank 50 Slurry Samples for Saltstone Processing Criteria WAC Limits, Listed in Table 5 of the Saltstone WAC.**

| Processing Criterion | Method | Value | %RSD |
|---|---|---|---|
| **pH > 10** | Calculated | >13 | -- |
| **2.5 M < [$Na^+$] < 7. 0 M** | ICP-ES, AA | 3.72 M | 1.67 |
| **Total Insoluble Solids <15 wt%** | Calculated | 0.022 wt% | 255 |

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 value for the total insoluble solids was calculated by Engineering Process Development of SRNL from experimentally determined values for total solids and dissolved solids in the slurry supernate.[10]

Table 3-8 provides constituents listed in the Technical Task Request but are not contained in the WAC. The results are used in a series of calculations performed by the SRNL Engineering Process Development group to support TCLP/UHC testing by a certified laboratory.[9] The density of the slurry was measured at 24.0 ºC. An estimate of the maximum concentration of the natural nonradioactive element Tl in the sample could only be determined by measuring the detection limits for Tl using ICP-MS. Natural Tl is composed of two isotopes, $^{203}$Tl and $^{205}$Tl with fraction abundances of 0.295 and 0.705, respectively. The highest measured detection limit was for $^{205}$Tl. This highest detection limit for elemental Tl was then calculated by dividing the result for $^{205}$Tl by its fractional abundance.

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

| Constituent | Method | Average Value (mg/L, unless stated otherwise) | %RSD |
|---|---|---|---|
| **Antimony (Sb)** | ICP-ES | <1.05E+01 | -- |
| **Beryllium (Be)** | ICP-ES | <3.51E-01 | -- |
| **Cyanide (CN)** | a. | a. | |
| **Thallium (Tl)** | ICP-MS | <9.72E-02 | -- |
| **Density (slurry)** | Measured (24.0 ºC) | 1.1815 g/mL | 0.44 |
| **Total Beta** | LSC | 1.58E+07 pCi/mL | 0.66 |
| **Total Solids** | Measured | 22.61% | 0.29 |

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

The tank corrosion species listed in Table 3-9 were requested by Waste Solidification Engineering (WSE).* Specific gravity was calculated by dividing the measured density of the slurry (given in Table 3-8 at 24.0 °C) by the density of water at the same temperature.[9]

**Table 3-9. Requests from the WSE for Corrosion Species from Tank 50 Slurry Samples; Results Not Contained in Previous Tables.**

| Constituent | Method | Average Value | %RSD |
|---|---|---|---|
| **Specific Gravity** | a | 1.1847 | 0.44 |
| **Barium-137m ($^{137m}$Ba)** | b | 1.19E+07 pCi/mL | 1.81 |
| **Total Gamma** | c | 1.19E+07 pCi/mL | 1.81 |

a. Calculated from the measured density of slurry and density of water at 24.0 °C
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 $^{137m}$Ba. The half-life the parent radionuclide, $^{137}$Cs, is 5x that of the daughter, $^{137m}$Ba, therefore the two radionuclides are in secular equilibrium. Radionuclides in secular equilibrium have the same activity associated with decay. Thus the activity of $^{137m}$Ba is 94.6% of the activity of the $^{137}$Cs or 1.19E+07 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, $^{126}$Sn, $^{137}$Cs (via $^{137m}$Ba), $^{154}$Eu, and $^{241}$Am.

* Requested in an electronic mail message from S. D. Hevel on December 20, 2007. (See page 30 of WSRC-NB-2007-00189.)

Table 3-10 details additional radionuclides not listed in the WAC and now require quantification in order to support inventory reporting requirements.

**Table 3-10. Additional Radionuclides Requested for Inventory Reporting Requirements.**

| Radionuclide | Method | Average Concentration (pCi/mL) | %RSD | REQUESTED TARGET (pCi/mL) |
|---|---|---|---|---|
| **Potassium-40 ($^{40}$K)** | Gamma scan (Cs removed) | <2.87E+00 | -- | 1.00E+04 |
| **Silver-108m ($^{108m}$Ag)** | Gamma scan (Cs removed) | <4.31E-01 | -- | 1.00E+04 |
| **Barium-133 ($^{133}$Ba)** | Gamma scan (Cs removed) | <8.96E-01 | -- | 1.00E+04 |
| **Bismuth-207 ($^{207}$Bi)** | Gamma scan (Cs removed) | <3.81E-01 | -- | 1.00E+04 |
| **Actinium-227 ($^{227}$Ac)** | Gamma scan (Cs removed) | <9.50E+00 | -- | 1.00E+04 |
| **Radium-228 ($^{228}$Ra)** | Gamma scan (Cs removed) | <1.04E+00 | -- | 1.00E+04 |
| **Thorium-228 ($^{228}$Th)** | Gamma scan (Cs removed) | <1.35E+01 | -- | 1.00E+04 |
| **Protactinium-231 ($^{231}$Pa)** | Gamma scan (Cs removed) | <2.16E+01 | -- | 1.00E+04 |
| **Curium-247 ($^{247}$Cm)** | Am/Cm | <4.59E+00 | -- | 1.43E-11 |
| **Californium-249 ($^{249}$Cf)** | Am/Cm | <4.82E+00 | -- | 1.33E-10 |
| **Californium-251 ($^{251}$Cf)** | Am/Cm | <3.00E+00 | -- | 1.00E+02 |

In a revision to the standing 2009 TTR, additional radionuclides were added to accommodate future inventory reporting requirements.[2,4] As shown in Table 3-10, $^{247}$Cm and $^{249}$Cf surpass their requested targets as requested by LWO.[4] However, the reported detection limits are below the detection limits established by AD. [3]

# 4.0 CONCLUSIONS

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

- The concentrations of the reported chemical and radioactive contaminants are less than their respective WAC targets or limits unless noted in this section.

- The reported detection limits for $^{59}$Ni, $^{94}$Nb, $^{247}$Cm, and $^{249}$Cf are above the limits requested by LWO;[4] however, they are below the achievable limits established by Analytical Development (AD).[5]

- The reported detection limit of isopropanol is lower than its WAC Limit for accident analysis in Appendix 8.1 but higher than its WAC concentration given in Table 4 for vault flammability. The higher detection limit is expected based on current analytical capabilities and is documented in the Task Technical and Quality Assurance Plan (TTQAP).[3]

- The reported detection limit for Isopar L is lower than its WAC limit for accident analysis in Appendix 8.1 but higher than its WAC concentration given in Table 3 in reference to vault flammability.

- Isopar L and Norpar 13 have limited solubility in aqueous solutions making it difficult to obtain consistent and reliable sub-samples. The values reported in this memo are the concentrations in the sub-sample as detected by the GC/MS; however, the results may not accurately represent the concentrations of these analytes in the Tank 50 sample received by SRNL

# 5.0 REFERENCES


1. Ray, J. W., "Waste Acceptance Criteria for Aqueous Waste Sent to the Z-Area Saltstone Production Facility (U)," X-SD-Z-00001, Revision 8, December 2008.

2. Staub, A.V., "Saltstone Formulation, Quarterly Analyses, TCLP Preparation-CY2009." HLW-SSF-TTR-2009-0002, Rev. 1, June 2009.

3. DiPrete, C. C. and Bibler, N. E., "Task Technical and Quality Assurance Plan for the Tank 50 Waste Acceptance Criteria (WAC) Analyses", SRNL-RP-2009-00600, Revision 1, June 2009.

4. Staub, A.V., "Minimum Detection Limits for Saltstone Quarterly WAC Analyses." LWO-WSE-2009-00163).

5. DiPrete, C. C., "Overview of Capability to Measure Radionuclides of Interest for Saltstone", SRNL-L4000-2009-00028, June 2009.

6. Zeigler, K. E., and Bibler, N. E., "Analytical Study Plan for All Tank 50 Waste Acceptance Criteria (WAC) Quarterly Samples," SRNL-ADD-2008-00026, Revision 0, February 2008.

7. Bibler, N. E, and DiPrete, C. C., "Tables Containing Results for the Third Quarter 2009 Tank 50 WAC Slurry Sample: Chemical and Radionuclide Contaminant Results," SRNL-TR-2009-00340, Revision 0, September 2009.

8. Cozzi, A. D., "SRNL Support of TCLP Analysis for Tank DDA Samples, Task Technical and Quality Assurance Plan," WSRC-TR-2007-00406, September 2007.

9. Fowler, R. C., "Tank 50 Compliance Plan for Transfers to Saltstone," X-WCP-H-00014, Rev. 7, January 2008.

10. Zeigler, K. E., Bibler, N. E., and DiPrete, D. P., "Characterization of Tank 50 Slurry for Saltstone Waste Acceptance Criteria," April 2007 Samples, WSRC-STI-2007-00554, November 2007.

11. Perry's Chemical Engineers' Handbook, 6th Edition, p 3-57, Editor D. W. Green, McGraw-Hill Book Co., NY, 1969.

# 6.0 ACKNOWLEDGEMENTS

The authors wish to thank the following people of AD in SRNL for their assistance and helpful discussions, and quick turnaround with the results for these samples: Surjeet Bhutani, Leigh Brown, Damon Click, Steve Crump, David DiPrete, Clint Gregory, Curtis Johnson, Mark Jones, Mira Malek, Jake Venzie, Susan Wells, Kathy White, Tom White, and Boyd Wiedenman.

**Distribution:**

J.L. Adams, 704-14Z
A.B. Barnes, 999-W
M.J. Barnes, 773-A
C.H. Beheler, 704-14Z
N.E. Bibler, 773-A
P.L. Bovan, 704-27S
L.M. Chandler, 773-A
N.F. Chapman 766-H
A.D. Cozzi, 999-W
D.A. Crowley, 773-43A
C.C. DiPrete, 773-A
A.D. England, 704-14Z
S.D. Fink, 773-A
E.J. Freed 704-56H
C.W. Gardner, 773-A
B.J. Giddings, 786-5A
J.C. Griffin, 773-A
J.R. Harbour, 999-W
S.D. Heath, 704-Z
C.C. Herman, 999-W
P.J. Hill, 766-H
C.A. Langton, 773-43A
K.R. Liner, 704-S
M.J. Mahoney, 766-H
S.L. Marra, 773-A
D.J. Martin, 241-246H
D.J. McCabe, 773-42A
P.W. Norris, 704-Z
J.E. Occhipinti, 704-S
E. Patten, 704-Z
F.M. Pennebaker, 773-42A
J.W. Ray, 704-S
M.M. Reigel, 999-W
A.L. Richardson, 210-S
L.B. Romanowski, 766-H
A.R. Shafer, 704-27S
D.C. Sherburne, 704-S
A.V. Staub, 704-Z
A.W. Wiggins, 704-61H
R.H. Young, 773-A