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RESULTS FOR THE SECOND QUARTER 2009 TANK 50 WAC SLURRY SAMPLE: CHEMICAL CONTAMINANT RESULTS

Marissa M. Reigel
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OCTOBER 2009

Savannah River National Laboratory
Savannah River Nuclear Solutions
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Prepared for the U.S. Department of Energy Under Contract Number DE-AC09-08SR22470

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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
LWO	Liquid Waste Operations
MDL	Method detection Limit
MRL	Method Reporting Limit
mg	Milligram
mL	Milliliter
ND	Not determined
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
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
TIC/TOC	Total inorganic carbon/total organic carbon
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 contaminant results for the characterization of the 2009 Second 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 (SFT) in the Saltstone Production Facility (SPF) 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:

- The concentrations of all of the reported chemical contaminates were less than their respective WAC targets or limits based on an accident consequence analysis.

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

- 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 at 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-activity wastewater 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 it can be transferred to the Saltstone Facility for treatment and disposal. The low-level aqueous waste (LLW) must meet the specified waste acceptance criteria (WAC) before it is processed into saltstone.[1] The specific chemical contaminants and their respective limits are listed in the current Saltstone WAC.[1]

SRS Liquid Waste Operations (LWO) solicited 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] This report documents the concentrations of chemical contaminants for the 2009 second quarter samples collected from Tank 50 on May 20, 2009 and discusses those results in further detail than the previously issued results report.[5]

2.0 EXPERIMENTAL

On May 20, 2009, three 200-mL steel samplers, each labeled HTF-50-09-50, were collected from Tank 50 for second quarter 2009 WAC analyses and delivered to the SRNL Shielded Cells (SC).

One 200-mL sampler was allowed to settle and duplicate samples (~15 mL) of the supernate 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 analysis (SVOA and VOA respectively).

After the samples for organic analysis were obtained, the 200-mL samplers were combined into a 1-L high density polyethylene (HDPE) bottle according to the following procedure. Each steel sampler was mixed to disperse the solids in the slurry. After mixing the slurry in the steel sampler, the slurry was transferred to a 1-L HDPE bottle. The transferred slurry was left undisturbed to settle overnight. The following day, a portion of the clear supernate was returned to the steel samplers, 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 mass of the combined slurries was 598 grams.

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

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

- Six-mL aliquots to the AD Ion Chromatography (IC) Laboratory for soluble anion analyses and soluble cation analyses.
- Six-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.
- Twelve-mL aliquots to the AD Dissolution Laboratory for digestion using an aqua regia method at 110 ºC. No solids were reported in the final dissolution. Aliquots of dissolved slurries were then submitted to AD laboratories for 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.
- Six-mL aliquots to the AD Wet Chemistry Laboratory for TIC/TOC and Total Base analyses.

A 3-mL sample of the slurry was taken for determination of the density of the slurry in a radioactive hood in SRNL.

3.0 RESULTS AND DISCUSSION

The following tables contain the results for the 2009 Second Quarter WAC analyses for chemical contaminants. 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 and 3-2 are based directly on attachments 8.1 and 8.2, respectively, of the WAC.[1]

Table 3-1. Results for the 2nd 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	8.73E+03[a]	0.87	**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	2.06E+04[b]	1.26	**1.91E+05**
Nitrate (NO_3^-)	IC	1.09E+05	8.82	**5.29E+05**
Nitrite (NO_2^-)	IC	6.35E+03	2.02	**2.59E+05**
Oxalate ($C_2O_4^{-2}$)	IC	9.34E+02	1.95	**3.30E+04**
Phosphate (PO_4^{-3})	IC	5.34E+02	1.14	**3.56E+04**
Sulfate (SO_4^{-2})	IC	5.70E+03	1.96	**6.89E+04**
Arsenic (As)	AA	<2.34E-01	--	**7.50E+02**
Barium (Ba)	ICP-ES	4.65E-01	0.82	**7.50E+02**
Cadmium (Cd)	ICP-ES	<5.08E-01	--	**3.75E+02**
Chromium (Cr)	ICP-ES	4.18E+01	1.40	**1.50E+03**
Lead (Pb)	ICP-MS	4.73E-01	7.91	**7.50E+02**
Mercury (Hg)	AA	1.40E+01	16.5	**3.25E+02**
Selenium (Se)	AA	<4.70E-01	--	**4.50E+02**
Silver (Ag)	ICP-ES	<1.04E+00	--	**7.50E+02**
Aluminum (Al)	ICP-ES	3.77E+03	0.48	**1.41E+05**
Butanol & Isobutanol	VOA	<5.0E-01[c]	--	**2.25E+03**
Isopropanol	VOA	<5.0E-01[c]	--	**2.25E+03**
Phenol	SVOA	<1E-01[c]	--	**7.50E+02**
Isopar L	SVOA	<2.78E+01 ppm[c,d]	--	**1.50E+02 ppm**
Total organic carbon	TOC	4.40E+02[a]	6.82	**5.00E+03**
Tetraphenylborate (TPB anion)	HPLC	<5E+00	--	**7.50E+02**

a. Measurement performed on slurry samples.
b. Measurement performed on filtered supernate samples.
c. Measurement performed on duplicate samples rather than triplicate samples.
d. Result is calculated from the reported MRL of < 33 mg/L and the density of the slurry sample

.

Table 3-2. Results for the 2nd 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	8.37E+00	11.5	**9.00E+02**
Cobalt (Co)	ICP-MS	1.31E-02	a	**9.00E+02**
Copper (Cu)	ICP-ES	<8.55E-01	--	**9.00E+02**
Iron (Fe)	ICP-ES	1.54E+02	4.72	**6.00E+03**
Potassium (K)	AA	1.20E+02	1.04	**3.67E+04**
Lithium (Li)	ICP-ES	<2.57E+00	--	**9.00E+02**
Manganese (Mn)	ICP-ES	1.03E+02	1.88	**9.00E+02**
Molybdenum (Mo)	ICP-ES	5.63E+01	1.08	**9.00E+02**
Nickel (Ni)	ICP-ES	1.44E+01	0.48	**9.00E+02**
Silicon (Si)	ICP-ES	1.00E+02	7.64	**1.29E+04**
Strontium (Sr)	ICP-ES	4.38E-01	3.66	**9.00E+02**
Zinc (Zn)	ICP-ES	9.40E+00	1.32	**9.75E+02**
Benzene	VOA	<2.5E-02[b]	--	**3.75E+02**
Methanol	VOA	c		**2.25E+02**
Toluene	VOA	<2.5E-02[b]	--	**3.75E+02**
TributylPhosphate (TBP)	SVOA	<1E-01[b]	--	**3.00E+02**
EDTA	HPLC	<1.00E+02	--	**3.75E+02**
Norpar 13	SVOA	<1E-01[b]	--	**1.0E-01**

a. Based on one measured value.
b. Measurement performed on duplicate rather than triplicate samples.
c. 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 have negligible solubility in aqueous solutions, which makes it difficult to obtain reliable sub-samples. The values reported in these tables are the MRL as detected by the GC/MS for each analyte but may not necessarily be an accurate representation of the concentrations of these two analytes in Tank 50.

Tables 3-3 and 3-4 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) in a Saltstone vault.[1]

Table 3-3. Results for the 2nd 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	% RSD	WAC Limit
Isopar L	SVOA	<2.78E+01 ppm[a,b]	--	**1.10E+01 ppm**
Tetraphenylborate (TPB anion)	HPLC	<5.00E+00 mg/L	--	**5.00E+00 mg/L**
Ammonium (NH_4^+)	IC	<5.00E+01 mg/L	--	**2.12E+02 mg/L**

a. Measurement performed on duplicate samples.
b. Result is calculated from the reported concentration of < 33 mg/L and the density of the slurry sample

Table 3-4. Results for the 2nd 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 (mg/L)
Butanol	VOA	<5.0E-01[a]	--	**0.75**
Tributylphosphate	SVOA	<1E-01[a]	--	**1.0**
Isopropanol	VOA	<5.0E-01[a]	--	**0.25**
Methanol	b	b		**0.25**
Norpar 13	SVOA	<1E-01	--	**0.1**

a. Measurement performed on duplicate rather than triplicate samples.
b. Currently, a routine method for detecting this species does not exist in AD.

None of the species considered in Tables 3-3 or 3-4 are above the WAC limit with the exception of Isopar L and isopropanol. As shown in Table 3-1, the concentrations of both analytes are below their respective WAC limit for the accident consequence analysis, but the detection limits are above the WAC limit for the vault flammability study shown in Tables 3-3 and 3-4 respectively.[1] The higher detection limits for both analytes were documented in the TT/QAP.[3]

Table 3-5 provides results for the processing criteria for transfers into the Saltstone Facility. This table is based on Table 5 of the WAC.[1]

Table 3-5. Results for the 2nd 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	3.85 M	4.42
Total Insoluble Solids <15 wt%	Calculated	≤ 0.30wt%	--

All of the results contained in Table 3-5 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.[7]

Table 3-6 provides constituents listed in the TTR 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.[6] The density of the slurry was measured at 22.7 ºC. Thallium was calculated by summing the ICP-MS results for masses of 203 and 205.

Specific gravity was calculated by dividing the measured density of the slurry (given in Table 3-6 at 22.7 °C) by the density of water at the same temperature (1.0020 g/mL).[8]

Table 3-6. 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 Concentration (mg/L)	%RSD
Antimony (Sb)	ICP-ES	<5.92E+00	--
Beryllium (Be)	ICP-ES	<3.98E-02	--
Cyanide (CN)	a.	a.	
Thallium (Tl)	ICP-MS	<7.24E-02	--
Density (slurry)	Measured (22.7 ºC)	1.189 g/mL	0.32
Total Solids	Measured	22.99%	0.39

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

Table 3-7. Requests from the WSE for Corrosion Species from Tank 50 Slurry Samples; Results Not Contained in Previous Tables.

Constituent	Method	Average Concentration	%RSD
Specific Gravity	a.	1.191	0.32

a. Calculated from the measured density of slurry and density of water at 22.7 °C

4.0 CONCLUSIONS

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

- The concentrations of the reported chemical contaminates were less than their respective WAC targets or limits based on an accident consequence analysis.

- 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 in reference to vault flammability. The higher detection limit was 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. The higher detection limit was expected based on current analytical capabilities as stated in the Task Technical and Quality Assurance Plan (TTQAP).[3]

- 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 at SRNL.

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