

Results for the Second Quarter Calendar Year 2019 Tank 50 Salt Solution Sample

C. L. Crawford

September 2019

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REVIEWS AND APPROVALS


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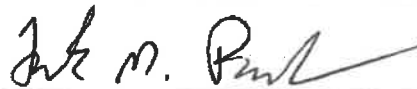

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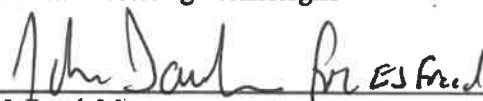

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EXECUTIVE SUMMARY

In this Technical Report, the chemical and radionuclide contaminant results from the Second Quarter Calendar Year 2019 (CY19) sample of Tank 50 salt solution are presented in tabulated form. The information from this characterization will be used by Savannah River Remediation (SRR) for the transfer of aqueous waste from Tank 50 to the Saltstone Production Facility (SPF), where the waste will be treated and disposed in the Saltstone Disposal Facility. This Technical Report compares results, where applicable, to SPF Waste Acceptance Criteria (WAC) Limits and Targets.¹ The chemical and radionuclide contaminant results from the characterization of the Second Quarter CY19 sampling of Tank 50 were requested by SRR personnel via a Task Technical Request (TTR)² and details of the testing are presented in the Savannah River National Laboratory (SRNL) Task Technical and Quality Assurance Plan (TTQAP).³ This Technical Report is part of Deliverable 2 relating to Task 1 from the SRR request.² Data pertaining to the regulatory limits for Resource Conservation and Recovery Act (RCRA) metals will be documented at a later time per the TTQAP for the Tank 50 Saltstone task.³

The following facts pertaining to the WAC are drawn from the analytical results provided in this report.

- WAC Targets or Limits were met for all analyzed chemical and radioactive contaminants for which the detection limits are below the WAC Targets or Limits.
- Isopar L^a has a higher detection limit⁴ compared with the current SPF WAC Limit value of 11 ppm¹ associated with flammability that has been in effect since revision 12 of the WAC dating back to July of 2013.⁵
- Nitrosamines were not detected in the Tank 50 salt solution sample above the instrument detection limits of <1 mg/L.
- The minimum detection limit (<2.43E-01 pCi/mL) is reported for ⁹⁴Nb as determined from the minimum detectable activity associated with the radiochemical method used for this radionuclide. The reported detection limit is above the requested SRR target minimum detection limit concentration.⁶ However, the minimum detection limit reported for the Second Quarter CY19 Tank 50 sample for ⁹⁴Nb is lower than the estimated detection limit of 4.38E-01 pCi/mL initially established by SRNL in 2009.⁷ Thus per guidance from SRR,⁶ SRNL continues to achieve as low as practical detection limits for this radionuclide.
- The average Sr-90 value for 2Q19 Tk 50 at 2.88E+05 pCi/mL ±3.45E+04 pCi/mL is ~7.6X higher than the average Sr-90 value (3.78E+04 pCi/mL ±7.99E+03 pCi/mL) derived from the previous three quarters prior to Tank Closure Cesium Removal (TCCR) processing and transfer of a significant volume with increased Sr-90 to Tank 50. The Sr-90 level in the TCCR product was measured at 9.32E+05 pCi/mL. Even though the Sr-90 increased significantly in this 2Q19 Tk 50 sample, it is still an order of magnitude below the WAC Limit of 2.62E+06 pCi/mL.

^a Isopar L is a trademark chemical (Isopar™ L) manufactured by ExxonMobil. It is a synthetic isoparaffinic hydrocarbon that is manufactured from a petroleum based raw material.

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LIST OF ABBREVIATIONS

AD	Analytical Development
CVAFS	Cold Vapor Atomic Fluorescence Spectroscopy
DMA	Direct Mercury Analyzer
DSA	Documented Safety Analysis
EDTA	ethylenediaminetetraacetate
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
LSC	Liquid Scintillation Counting
MRL	Minimum Reporting Limit
PHA	Pulse Height Analysis (alpha PHA)
RCRA	Resource Conservation and Recovery Act
SPF	Saltstone Production Facility
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SVOA	Semi-Volatile Organic Analysis
TCCR	Tank Closure Cesium Removal
TIC/TOC	Total Inorganic Carbon/Total Organic Carbon
TPB	tetraphenylborate
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
VDS	Variable Depth Sample
VOA	Volatile Organic Analysis
WAC	Waste Acceptance Criteria

1.0 Introduction

Tank 50 aqueous waste is analyzed on a quarterly basis and the results are compared to the Waste Acceptance Criteria (WAC) of the Z-Area Saltstone Production Facility (SPF).¹ The quarterly Regulatory Compliance samples pulled in Tank 50 should be characterized for both Limit and Target acceptance criteria in this WAC.¹ The information from this characterization will be used by Savannah River Remediation (SRR) for the transfer of aqueous waste from Tank 50 to SPF, where the waste will be treated and disposed in the Saltstone Disposal Facility. This Technical Report compares results, where applicable, to SPF WAC Limits and Targets.¹ A memorandum reporting the average Cs-137 value has been previously issued.⁸

2.0 Experimental

2.1 Technical

The Second Quarter CY19 Tank 50 samples [a 200-mL sample obtained 6" below the surface (HTF-50-19-51) and a 1-L variable depth sample (VDS) obtained 66" from the tank bottom (HTF-50-19-52)] were obtained on May 7, 2019 and received at Savannah River National Laboratory (SRNL) on May 7, 2019.⁹

The contents of the 1-L slurry in the steel variable depth sampler were initially mixed by recycling some of the slurry using the transfer pump with both ends of the transfer line submerged in the sample. After initial mixing, a 30-mL aliquot and a 15-mL aliquot of the Tank 50 sample were pumped into a Teflon[®] and a glass container, respectively, with zero headspace. These two samples were used for Hg speciation testing.¹⁰ The remaining contents were then transferred by pumping into two different high-density polyethylene (HDPE) 1-L bottles. The original 1-L slurry was not composited into a single container prior to distribution into the individual 1-L bottles since the Tank 50 sample contains very little suspended solids and pumping occurred immediately after handling and positioning of the 1-L sample within the variable depth sampler inside the SRNL Shielded Cells Facility. The transferred slurry was left to settle in the bottles. Visual inspection of the inside of the steel sampler indicated there were no visible solids remaining in the sampler, so no clear supernate was returned to the sampler for rinsing. The entire sample was transferred out of the Shielded Cells and located in a radiochemical hood. The two small zero headspace vials for Hg speciation testing were put in shrouded containers and transferred to storage in a refrigerator. All transfers out of the Shielded Cells were made on the same day as sample collection. The 1-L bottles were agitated to thoroughly disperse the extremely limited suspended solids into the supernate. These suspended solids are typically only visible as trace solids at the bottom of the container upon prolonged storage of the material under static conditions. Aliquots of slurry samples were promptly collected with slurry pipettes to minimize settling effects and placed into HDPE bottles. Samples for volatile organic analysis (VOA) and semi-volatile organic analysis (SVOA) were removed from the 200-mL surface sample from within a radiochemical hood and were transferred using glass pipettes into clean glass sample vials with Teflon lined caps. Amber colored glass sample vials were used for the samples that were analyzed for nitrosamines to minimize exposure to light.

Unless otherwise stated, all concentrations presented in the tables (except upper limits) are averages based on analyses of triplicate aliquots of the Second Quarter CY19 Tank 50 sample. The standard deviation of each average is also presented. Several of the contaminants were either not detected in the slurry samples or detected at values below the method reporting limit (MRL). For contaminants not detected or detected below the MRL, 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. If only one value out of the triplicate analysis is above the detection limit, then that single value is reported and noted in the tables. Also, if only two values out of the triplicate analyses are above the detection limit, then the average of those two values is reported and noted in the tables. All VOA and SVOA were performed on the surface sample and all other analyses were performed on the variable depth sample. The VOA method is performed per SRNL

AD Procedure L16.1, ADS-2656.¹¹ This method is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) process that involves dilution of 1 mL of Tank 50 supernate with 4 mL of reagent water. The SVOA method is performed per SRNL AD Procedure L16.1, ADS-2657.¹² Both of these methods use discrete standards as detailed in the procedures.^{11,12} The SVOA method uses organic solvents to extract SVOA analytes that are analyzed by GC/MS. A 2 mL dichloromethane (or methylene chloride, CH₂Cl₂) volume is used to initially extract 10 mL of Tank 50 supernate for phenol. The Tank 50 supernate is then extracted with 2 additional 2-mL volumes of dichloromethane. The dichloromethane extracts are combined and concentrated before analysis. Tributyl phosphate is analyzed from a 2 mL hexane (C₆H₁₄) extract of 10 mL of Tank 50 supernate. Isopar L and Norpar 13 are analyzed from a 2 mL hexane extraction of 5 mL of Tank 50 supernate. Nitrosamines are analyzed by a separate SVOA method that uses 2 mL of dichloromethane as extractant and 10 mL of Tank 50 supernate with deuterated N-nitrosodimethylamine-d6 (NDMA-d6) as a standard along with a separate GC/MS analysis methodology. Data reported for inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are derived from the digested Tank 50 supernate (1 mL supernate diluted to 50 mL total volume) by the aqua regia method.¹³ The aqua regia method heats the Tank 50 supernate mixed with a 1:3 mixture of nitric acid/hydrochloric acid for 2 hours in sealed Teflon containers in an oven at 115 °C. Anion and the ammonium cation analyses are determined from Ion Chromatography (IC). Total Inorganic Carbon/Total Organic Carbon (TIC/TOC) analysis was used to measure the TIC (carbonate) and TOC components. The tetraphenylborate (TPB) anion and ethylenediaminetetraacetate (EDTA) were analyzed using High Performance Liquid Chromatography (HPLC). All the above analyses excluding VOA and SVOA used approximately 150 mL of the 1-L variable depth sample. 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. Total and soluble weight percent solids were determined on portions of the Tank 50 sample using the “Weight Percent Solids Determination Using a Furnace or Oven” procedure from the Environmental & Chemical Process Technology research programs section.¹⁴

Approximately 630 mL of the VDS were used to determine all the measured radionuclide concentrations in triplicate. Radionuclides reported using the ICP-MS method are converted from a reported mass per volume basis to activity per volume units using the specific activities (Ci/g) reported from the Department of Energy 1996 Integrated Data Base Report.¹⁵ The Cs-137 and C-134 radionuclides are determined from gamma spectroscopy. Total beta is measured from a radscreen method using Liquid Scintillation Counting (LSC). The total alpha is measured from the same method after removal of Cs-137 from the sample.

Mercury analyses performed at SRNL by Analytical Development (AD) included Total mercury using the Direct Mercury Analyzer (DMA) method and monomethyl mercury by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS). Other mercury (Hg) speciation data shown in Table 3-1, Table 3-2 and Table 3-5 are calculated from previous work as analyzed by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) by the Eurofins Frontier Global Sciences, Inc. laboratory in Seattle, WA.¹⁰ The parent sample for all mercury analyses performed at either SRNL or at Eurofins was obtained from the original Tank 50 sample within two days of sample receipt. As discussed above, the parent Tank 50 sample was obtained in near zero-headspace containers that were immediately refrigerated after removal from the Shielded Cells Facility on the same day of preparation. Monomethyl and ethyl mercury were determined from the Tank 50 parent sample obtained in the 30-mL Teflon bottle. All other species were determined from the 15-mL Tank 50 parent stored in the glass bottle. All samples sent to Eurofins Frontier Global Sciences, Inc. for analysis were diluted by ~ 2,500X by adding a 0.1 mL aliquot of Tank 50 sample to a total of 250 mL reagent water supplied by Eurofins. The samples for monomethyl and ethyl Hg also contained ~ 0.4% high purity HCl acid. The Hg species reported from Eurofins include elemental mercury (Hg (0)), ethyl mercury, and dimethyl mercury. Monomethyl, ethyl, and dimethyl mercury are organomercury species. The concentration values for the organomercury species ethyl mercury and dimethyl mercury are calculated from the Hg speciation data on a mg Hg/L basis.¹⁰ As a sample calculation for dimethyl mercury, information from Reference 10 shows that the reported average dimethyl mercury concentration on a mg

Hg/L basis is 0.0489 mg Hg/L. This value is then multiplied by the formula weight of dimethyl mercury from the WAC¹ (230.7 g dimethyl mercury/mole) divided by the molecular weight of Hg (200.6 g Hg/mole). Thus, the calculated concentration of the species dimethyl mercury is $0.0489 \text{ mg Hg/L} \times (230.7 \text{ g dimethyl mercury/mole} / 200.6 \text{ g Hg/mole}) = 0.0562 \text{ mg dimethyl mercury/L}$. Samples of Tank 50 submitted to SRNL AD for total Hg and methyl Hg analysis were submitted without dilution. These samples were diluted within the AD laboratories to meet the targeted calibration range of either the DMA instrument for total Hg or the CVAFS instrument for methyl Hg.

2.2 Quality Assurance

Quality Assurance requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60.¹⁶ SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.¹⁷ The customer requested that a Functional Classification of Safety Significant apply to this work.² Data collection and analysis methods used in this work comply with this requirement as detailed in the TTQAP.³

3.0 Results and Discussion

Analyzed nonradionuclide chemical concentrations, their standard deviations and their corresponding WAC Limits¹ are shown in Table 3-1 that correspond to the Attachment 8.1 Limits in the WAC.¹ Per the WAC, the Limits shown shall not be exceeded accounting for the analytical uncertainty in each measured concentration.¹ Analyzed nonradionuclide chemical concentrations, their standard deviations and their corresponding WAC Targets¹ are shown in Table 3-2 that correspond to the Attachment 8.2 Targets in the WAC.¹ Per the WAC, the Targets shown shall not be exceeded accounting for the analytical uncertainty in each measured concentration.¹ The Limits refer to a type of acceptance criteria that, if not satisfied, will have an adverse impact on repository requirements, whereas the Targets refer to a type of acceptance criteria that is set as a guideline to protect a Limit.¹ For the chemical contaminants and the radionuclides given in tables below, an analytical uncertainty of 2 sigma (2σ) shall be accounted for in sample analyses used to determine the analytical uncertainty vs. either the Limit or Target.¹ The standard deviations given in tables for this WAC report are taken as 1 sigma (1σ) values that are calculated from the normal 'standard deviation' function for either duplicate or triplicate values from within Excel[®] spreadsheets.

Comparison of the average analyzed detectable values shown in Table 3-1 to the WAC Limits indicates that free hydroxide and nitrate anions and total mercury are the highest analytes relative to the WAC Limits at 21%, 17% and 20%, respectively. Comparison of the average analyzed values shown in Table 3-2 to the WAC Targets indicates that aluminum is the highest analyte relative to the WAC Target at 55%, with average TOC at a lower ratio to WAC Target of 26%. Good agreement for both total Hg and monomethyl mercury was obtained between the two analytical laboratories, i.e. the numbers are the same within analytical uncertainty. SRNL AD analysis indicates a total Hg average value of $63.5 \text{ mg/L} \pm 1.2 \text{ mg/L}$ compared to the Eurofins average value of $63.0 \text{ mg/L} \pm 0.88 \text{ mg/L}$.¹⁰ The uncertainty associated with the AD and Eurofins total Hg analysis is 20% (1-σ), so these reported average total Hg values are equivalent to within the method uncertainty. SRNL AD analysis of monomethyl mercury indicates a monomethyl mercury average value of $21.5 \text{ mg/L} \pm 0.12 \text{ mg/L}$ compared to the Eurofins average value of $20.7 \text{ mg monomethyl mercury/L} \pm 1.27 \text{ mg/L}$ that is calculated from the reported average monomethyl mercury of 19.3 mg Hg/L .¹⁰ The uncertainty associated with the AD and Eurofins monomethyl mercury analysis is 10% (1-σ) and 30% (1-σ), respectively, so these reported average total Hg values are within the method uncertainty. No VOA analytes (butanol, propanol, benzene and toluene) were detected above the indicated method detection limits from duplicate analyses as shown in Table 3-1 and Table 3-2. Analyzed radionuclide concentrations and the respective radiochemical analysis methods, their standard deviations and their corresponding WAC Limits and Targets are shown in Table 3-3 and Table 3-4, respectively. These tables correspond to Attachment 8.3 Limits and Attachment 8.4 Targets, respectively, from the WAC.¹ The minimum detection limit reported for Nb-94 of $<2.43\text{E-}01 \text{ pCi/mL}$ in Table 3-4 is above the

requested SRR target minimum detection limit of $2.0\text{E-}03$ pCi/mL⁶ but is lower than the estimated detection limit initially established by SRNL of $4.38\text{E-}01$ pCi/mL in 2009.⁷

Comparison of the average analyzed detectable values shown in Table 3-3 to the WAC Limits indicates that I-129 is the highest analyte relative to the WAC Limit at 37%. It should be noted that the average Sr-90 value for 2Q19 Tk 50 at $2.88\text{E+}05$ pCi/mL $\pm 3.45\text{E+}04$ pCi/mL is $\sim 7.6\text{X}$ higher than the average Sr-90 value ($3.78\text{E+}04$ pCi/mL $\pm 7.99\text{E+}03$ pCi/mL) derived from the previous three quarters prior to TCCR processing and transfer to Tank 50 (1Q19 Tk 50 Sr-90 value of $2.91\text{E+}04$ pCi/mL, 4Q18 Tk 50 Sr-90 value of $3.95\text{E+}04$ pCi/mL and 3Q18 Tk 50 Sr-90 value of $4.48\text{E+}04$ pCi/mL).^{18,19,20} Even though the Sr-90 increased significantly, it is still an order of magnitude below the WAC Limit of $2.62\text{E+}06$ pCi/mL. The increase in Sr-90 could be due to the $\sim 158,000$ gallon transfer of the post Tank 11H TCCR into Tank 50 prior to sampling in early May 2019.²¹ There was an initial transfer of 8,428 gallons from Tank 11 into Tank 50 on 3/8/19, then an additional $\sim 150,000$ gallons transferred from Tank 11 into Tank 50 during 4/25/19 through 4/26/19.²¹ Analytical results from the Tank 11H indicated that Sr-90 values were increased $\sim 6.5\text{X}$ ($9.32\text{E+}05$ pCi/mL) relative to the Tank 10H feed ($1.42\text{E+}05$ pCi/mL) that was attributed to leaching of the solids present in Tank 11H at start of processing.²² Comparison of the average analyzed detectable values shown in Table 3-4 to the WAC Targets indicates that Pu-238 is the highest analyte relative to the WAC Target at 26%. Similar trends were observed for the previous First Quarter 2019 Tank 50 sample for I-129 being the highest analyte relative to the WAC Limit at 44%, and for Pu-238 at 37%.¹⁸ Table 3-4 indicates that there were no detectable values in the triplicate samples analyzed for total alpha for the 2Q19 sample.

Table 3-1. Chemical Contaminants from Second Quarter CY19 Tank 50 Samples and SPF WAC, Revision 18, Attachment 8.1 Limits¹

Chemical Name (Formula)	Method	Average Concentration (mg/L)	Std. Dev.	WAC Limit (mg/L)
Aluminate (Al(OH) ₄ ⁻)	ICP-ES	1.37E+04 ^a	1.93E+02	4.08E+05
Ammonium (NH ₄ ⁺)	IC	<1.00E+02	NA	2.12E+02
Carbonate (CO ₃ ²⁻)	TIC	2.03E+04 ^b	1.15E+02	1.20E+05
Chloride (Cl ⁻)	IC	4.46E+02	1.78E+01	7.95E+03
Fluoride (F ⁻)	IC	<1.00E+02	NA	4.07E+03
Free Hydroxide (OH ⁻)	Total Base	3.28E+04 ^b	1.70E+02	1.58E+05
Nitrate (NO ₃ ⁻)	IC	7.45E+04	2.82E+03	4.37E+05
Nitrite (NO ₂ ⁻)	IC	1.88E+04	8.08E+02	2.14E+05
Oxalate (C ₂ O ₄ ²⁻)	IC	5.05E+02	2.62E+01	2.72E+04
Phosphate (PO ₄ ³⁻)	IC	1.20E+02	8.19E+00	3.14E+04
Sulfate (SO ₄ ²⁻)	IC	7.14E+03	3.12E+02	5.69E+04
Arsenic (As)	ICP-MS	<3.29E-01	NA	1.97E+02
Barium (Ba)	ICP-ES	1.65E+01 ^c	1.34E+00	6.19E+02
Cadmium (Cd)	ICP-ES	<3.95E+00	NA	3.10E+02
Chromium (Cr)	ICP-ES	4.14E+01	6.91E-01	1.50E+03
Lead (Pb)	ICP-MS	3.59E-01	1.14E-02	7.50E+02
Total Mercury (Hg)	DMA	6.35E+01	1.19E+00	3.25E+02
Elemental Mercury (Hg(0))	CVAFS	2.26E+00 ^d	5.18E-01	3.25E+02
Monomethyl Mercury (CH ₃ Hg)	CVAFS	2.15E+01	1.15E-01	3.50E+02
Ethyl Mercury (C ₂ H ₅ Hg)	CVAFS w/ Distillation	<1.01E+00 ^d	NA	3.73E+02
Selenium (Se)	ICP-MS	<3.29E-01	NA	3.75E+02
Silver (Ag)	ICP-ES	<8.53E-01	NA	6.19E+02
Aluminum (Al)	ICP-ES	3.88E+03	5.48E+01	1.16E+05
Potassium (K)	ICP-ES	3.27E+02	1.94E+01	3.03E+04
Butanol (C ₄ H ₉ OH)	VOA	<5.00E-01 ^e	NA	7.73E+00
Propanol (C ₃ H ₇ OH)	VOA	<2.50E-01 ^e	NA	1.88E+00
Phenol (C ₆ H ₅ OH)	SVOA	<1.00E+01 ^e	NA	7.50E+02
Tetraphenylborate [TPB] (B(C ₆ H ₅) ₄ ⁻)	HPLC	<5.00E+00	NA	5.00E+00
Total Organic Carbon (----)	TOC	1.92E+02 ^b	3.06E+00	4.50E+03
Isopar L (----)	SVOA	<3.30E+01 ^e	NA	8.75E+01 ^f

- Result is calculated from the measured Al concentration assuming all the Al is present as the OH compound.
- Measurement performed on filtered supernate samples.
- A similar value was also determined for the blank, so the average value reported is likely high biased.
- Mercury species calculated from data presented in Reference 10.
- Measurement performed on duplicate samples rather than triplicate samples.
- The WAC Limit shown in this table is based on bounding DSA concentrations for accident consequence analysis. A more restrictive limit for Isopar L is set to protect assumptions associated with flammability as shown in Table 3-5 below.¹

Table 3-2. Chemical Contaminants from Second Quarter CY19 Tank 50 Samples and SPF WAC, Revision 18, Attachment 8.2 Targets¹

<u>Chemical Name (Formula)</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC Target (mg/L)</u>
Aluminum (Al)	ICP-ES	3.88E+03	5.48E+01	7.00E+03^f
Boron (B)	ICP-ES	3.31E+01	2.53E-01	7.43E+02
Cobalt (Co)	ICP-MS ^a	<3.29E-02 ^a	NA	1.45E+02
Copper (Cu)	ICP-ES	<2.64E+00	NA	7.43E+02
Iron (Fe)	ICP-ES	1.37E+01 ^b	7.73E+00	4.95E+03
Lithium (Li)	ICP-ES	6.37E+00	9.66E-01	7.43E+02
Manganese (Mn)	ICP-ES	<6.26E-01	NA	7.43E+02
Molybdenum (Mo)	ICP-ES	1.67E+01	1.86E-01	7.43E+02
Nickel (Ni)	ICP-ES	<9.88E+00	NA	7.43E+02
Silicon (Si)	ICP-ES	<2.50E+01	NA	1.07E+04
Strontium (Sr)	ICP-ES	<6.81E-02	NA	7.43E+02
Zinc (Zn)	ICP-ES	6.02E+00	1.90E-01	8.03E+02
Dimethyl Mercury ((CH₃)₂Hg)	CVAFS	5.62E-02 ^c	8.38E-03	1.00E+00
Benzene (C₆H₆)	VOA	<1.50E-01 ^d	NA	3.10E+02
Methanol (CH₃OH)	VOA	e	NA	1.88E+00
Toluene (C₆H₅CH₃)	VOA	<1.50E-01 ^d	NA	3.10E+02
Dibutylphosphate [DBP] (C₈H₁₉O₄P)	IC	<2.50E+02	NA	3.47E+02
Tributylphosphate [TBP] ((C₄H₉O)₃PO)	SVOA	<7.50E-01 ^d	NA	7.50E+00
Total Organic Carbon (TOC)	TOC	1.92E+02	3.06E+00	7.50E+02^f
EDTA (C₁₀H₁₂N₂O₈⁴⁻)	HPLC	<1.00E+02	NA	3.10E+02
NORPAR 13 (C_nH_{2-n})	SVOA	<7.50E-01 ^d	NA	7.50E-01
Formate (CHOO⁻)	IC	1.21E+02 ^b	3.54E+00	6.38E+03

a. Cobalt based on the stable Co-59 isotope.

b. Only two detectable values from the analyzed triplicate set.

c. Mercury species calculated from data presented in Reference 10.

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

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

f. The WAC Targets for Al and TOC shown in this table are more restrictive than the corresponding WAC Limits shown in Table 3-1 to protect assumptions associated with thermolytic hydrogen generation.¹

Table 3-3. Radionuclide Contaminants from Second Quarter CY19 Tank 50 Samples and SPF WAC, Revision 18, Attachment 8.3 Limits¹

<u>Radionuclide</u>	<u>Method</u>	<u>Average Concentration</u> (pCi/mL)	<u>Std. Dev.</u>	<u>WAC Limit</u> (pCi/mL)
Tritium (³H)	Tritium Counting	7.23E+02	1.11E+01	5.63E+05
Carbon-14 (¹⁴C)	C-14 Liquid Scintillation	5.54E+02	1.62E+01	1.13E+05
Nickel-63 (⁶³Ni)	Ni-59/63	<2.08E+01	NA	1.13E+05
Strontium-90 (⁹⁰Sr)	Sr-90 Liquid Scintillation	2.88E+05	3.45E+04	2.62E+06
Technetium-99 (⁹⁹Tc)	Tc-99 Liquid Scintillation	3.45E+04	2.48E+02	2.11E+05
Iodine-129 (¹²⁹I)	I-129 (w/ separation) Liquid Scintillation	2.35E+01	3.88E+00	6.30E+01
Cesium-137 (¹³⁷Cs)	Gamma Scan	5.74E+05	5.20E+03	3.96E+06
Uranium-233 (²³³U)	ICP-MS	<3.19E+02	NA	1.13E+04
Uranium-235 (²³⁵U)	ICP-MS	2.32E-01	3.57E-03	1.13E+02
Plutonium-241 (²⁴¹Pu)	Pu238/241 Liquid Scintillation	5.24E+03	6.88E+01	8.38E+05
Total Alpha	Liquid Scintillation Counting (Cs removed)	<2.37E+04	NA	2.13E+05

Table 3-4. Radionuclide Contaminants from Second Quarter CY19 Tank 50 Samples and SPF WAC, Revision 18, Attachment 8.4 Targets¹

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.	WAC Target (pCi/mL)
Aluminum-26 (²⁶ Al)	Gamma Scan (Cs removed)	<2.22E-01	N/A	2.88E+03
Potassium-40 (⁴⁰ K)	Gamma Scan (Cs removed)	<3.09E+00	NA	1.00E+02
Cobalt-60 (⁶⁰ Co)	Gamma Scan (Cs removed)	<3.64E-01	NA	9.75E+02
Nickel-59 (⁵⁹ Ni)	Ni-59/63	<3.90E+01	NA	1.13E+03
Selenium-79 (⁷⁹ Se)	Se-79	6.49E+01	3.44E+01	1.90E+04
Yttrium-90 (⁹⁰ Y)	Secular Equilibrium w/ 100% of Sr-90	2.88E+05	3.45E+04	2.62E+06
Zirconium-93 (⁹³ Zr)	ICP-MS	<5.34E+02	NA	1.00E+05
Niobium-94 (⁹⁴ Nb)	Nb-94	<2.43E-01	NA	1.53E+02
Rhodium-106 (¹⁰⁶ Rh)	Secular Equilibrium w/ 100% of Ru-106	<6.26E+00	NA	3.12E+05
Ruthenium-106 (¹⁰⁶ Ru)	Gamma Scan (Cs removed)	<6.26E+00	NA	3.12E+05
Antimony-125 (¹²⁵ Sb)	Gamma Scan (Cs removed)	2.47E+01	2.03E-01	7.99E+03
Tellurium-125m (^{125m} Te)	Secular Equilibrium w/ 100% of Sb-125	2.47E+01	2.03E-01	1.83E+03
Tin-126 (¹²⁶ Sn)	Gamma Scan (Cs removed)	3.17E+02	9.11E+00	1.80E+04
Cesium-134 (¹³⁴ Cs)	Gamma Scan	<6.35E+01	NA	1.82E+04
Cesium-135 (¹³⁵ Cs)	Cs-135	2.35E+00	1.71E-01	2.50E+02
Barium-137m (^{137m} Ba)	Calculation (Secular Equilibrium w/ 94.6% of Cs-137)	5.43E+05	4.92E+03	3.75E+06
Cerium-144 (¹⁴⁴ Ce)	Gamma Scan (Cs removed)	<1.91E+01	NA	3.12E+04
Praseodymium-144 (¹⁴⁴ Pr)	Secular Equilibrium w/ 100% of Ce-144	<1.91E+01	NA	3.12E+04
Promethium-147 (¹⁴⁷ Pm)	Pm-147/Sm-151 Liquid Scintillation	<5.32E+01	NA	1.57E+06
Samarium-151 (¹⁵¹ Sm)	Pm-147/Sm-151 Liquid Scintillation	<4.32E+01	NA	2.25E+04
Europium-154 (¹⁵⁴ Eu)	Gamma Scan (Cs removed)	<1.50E+00	NA	1.62E+03
Radium-226 (²²⁶ Ra)	Ra-226	<5.14E+00	NA	1.00E+03
Radium-228 (²²⁸ Ra)	Gamma Scan (Cs removed)	<3.15E+00	NA	1.00E+04
Actinium-227 (²²⁷ Ac)	Th-229/230	<4.73E-01	NA	1.00E+04
Thorium-229 (²²⁹ Th)	Th-229/230	<4.91E-02	NA	1.63E+05
Thorium-230 (²³⁰ Th)	Th-229/230	<3.75E-01	NA	6.26E+03
Thorium-232 (²³² Th)	ICP-MS	<3.61E-03	NA	2.88E+03
Protactinium-231 (²³¹ Pa)	Pa-231	<1.09E+00	NA	1.00E+03
Uranium-232 (²³² U)	U-232	1.58E+00	2.02E-01	2.27E+03
Uranium-233 (²³³ U)	ICP-MS	<3.19E+02	NA	3.12E+03
Uranium-234 (²³⁴ U)	ICP-MS	<2.06E+02	NA	3.12E+03
Uranium-236 (²³⁶ U)	ICP-MS	<2.13E+00	NA	3.12E+03
Uranium-238 (²³⁸ U)	ICP-MS	2.30E+00	1.87E-02	3.12E+03

Table 3-4. Radionuclide Contaminants from Second Quarter CY19 Tank 50 Samples and SPF WAC, Revision 18, Attachment 8.4 Targets¹, continued

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.	WAC Target (pCi/mL)
Neptunium-237 (²³⁷ Np)	ICP-MS	<2.32E+01	NA	1.00E+04
Plutonium-238 (²³⁸ Pu)	Pu238/241 Pu alpha PHA	1.75E+04	3.41E+02	6.67E+04
Plutonium-239 (²³⁹ Pu)	Pu238/241 Pu alpha PHA	5.36E+02	2.51E+01	6.67E+04
Plutonium-240 (²⁴⁰ Pu)	Pu238/241 Pu alpha PHA	5.36E+02	2.51E+01	6.67E+04
Plutonium-242 (²⁴² Pu)	ICP-MS	<1.26E+02	NA	6.67E+04
Plutonium-244 (²⁴⁴ Pu)	ICP-MS	<5.84E-01	NA	7.02E+04
Americium-241 (²⁴¹ Am)	Am/Cm	7.96E+00	1.85E+00	6.67E+04
Americium-242m (^{242m} Am)	Am/Cm	<1.21E-01	NA	4.50E+05
Americium-243 (²⁴³ Am)	Am/Cm	<1.10E+00	NA	6.67E+04
Curium-242 (²⁴² Cm)	Am/Cm	<1.00E-01	NA	1.13E+04
Curium-244 (²⁴⁴ Cm)	Am/Cm	4.40E+00	2.29E+00	6.67E+04
Curium-245 (²⁴⁵ Cm)	Am/Cm	<2.67E+00	NA	2.25E+05
Total Alpha	Liquid Scintillation Counting (Cs removed)	<2.37E+04	NA	6.67E+04

The following tables show various chemical contaminants (Table 3-5), organic species (Table 3-6) and processing constituents (Table 3-7) related to the Saltstone Disposal Unit (SDU) that are referred to in the WAC per Tables 2, 3 and 4, respectively.¹ Isopar L has a higher detection limit⁴ compared with the current SPF WAC Limit value of 11 ppm¹ shown in Table 3-5 associated with flammability that has been in effect since revision 12 of the WAC dating back to July of 2013.⁵

Table 3-5. Chemical Contaminants Impacting Saltstone Disposal Unit (SDU) Flammability from Second Quarter CY19 Tank 50 Samples and SPF WAC, Revision 18, Table 2 Limits and Targets¹

Chemical Name (Formula)	Method	Average Concentration (mg/L)	Std. Dev.	WAC Limit/Target
Isopar L (----)	SVOA	<2.71E+01 ppm ^{a,b}	NA	1.10E+01 ppm (Limit)
Tetraphenylborate [TPB] (B(C ₆ H ₅) ₄)	HPLC	<5.00E+00	NA	5.00E+00 mg/L (Limit)
Ammonium (NH ₄ ⁺)	IC	<1.00E+02	NA	2.12E+02 mg/L (Limit)
Total Mercury (Hg)	DMA	6.35E+01	1.19E+00	3.25E+02 mg/L (Limit)
Monomethyl Mercury (CH ₃ Hg)	CVAFS	2.15E+01	1.15E-01	3.50E+02 mg/L (Limit)
Dimethyl Mercury ((CH ₃) ₂ Hg)	CVAFS	5.62E-02 ^c	8.38E-03	1.00E+00 mg/L (Target)

- Measurement performed on duplicate samples rather than triplicate samples.
- Result is calculated from the reported concentration of <33 mg/L and the density of the slurry sample listed in Table 3-8.
- Mercury species calculated from data presented in Reference 10.

Table 3-6. Other Organics Impacting SDU Flammability from Second Quarter CY19 Tank 50 Samples and SPF WAC, Revision 18, Table 3 Concentrations¹

<u>Chemical Name (Formula)</u>	<u>Method</u>	<u>Average Concentration (mg/L)</u>	<u>Std. Dev.</u>	<u>WAC Concentrations (mg/L)</u>
Butanol (C ₄ H ₉ OH) ^a	VOA	<5.00E-01	NA	0.75
Tributylphosphate[TBP] ((C ₄ H ₉ O) ₃ PO) ^a	SVOA	<7.50E-01	NA	1.0
Propanol (C ₃ H ₇ OH) ^a	VOA	<2.50E-01	NA	0.25
Methanol (CH ₃ OH)	b	NA	NA	0.05
NORPAR 13 (C _n H _{2n}) ^a	SVOA	<7.50E-01	NA	0.75

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

Table 3-7. Processing Constituents from Second Quarter CY19 Tank 50 Samples and SPF WAC, Revision 18, Table 4 Limits¹

<u>Processing Constituents</u>	<u>Method</u>	<u>Value</u>	<u>Std. Dev.</u>	<u>WAC Limit</u>
pH	Calculated	>13	NA	> 10
Sodium Concentration	ICP-ES	4.94 M	6.74E-02	2.5 M < [Na ⁺] < 7.0 M
Total Insoluble Solids	Calculated	~0 wt %	NA	< 15 wt %

Table 3-8 contains additional measured constituents per the TTQAP.³ There were no detectable nitrosamine species in the Tank 50 surface sample via the SVOA analyses shown in Table 3-8 as was the case in the previous First Quarter 2019 Tank 50 sample.¹⁸

Table 3-8. Additional Measured Constituents³

<u>Constituent</u>	<u>Method</u>	<u>Average Value</u>	<u>Std. Dev.</u>
Density (slurry)	Measured (21.9°C)	1.2157 g/mL	0.0015 g/mL
Specific Gravity	a	1.2180	0.0015
Total Solids	Measured	23.66 wt %	0.08 wt %
Total Beta	LSC	1.59E+06 pCi/mL	3.83E+04 pCi/mL
Total Gamma	b	5.43E+05 pCi/mL	3.03E+03 pCi/mL ^c
Beryllium (Be)	ICP-ES	<2.37E-01 mg/L	NA
N-Nitrosodimethylamine (C₂H₆N₂O)	SVOA	<1 mg/L	NA
N-Dioctylnitrosamine (C₁₆H₃₄N₂O)	SVOA	<1 mg/L	NA

a. Calculated from the measured density of slurry and density of water at 23.0 °C.²³

b. Calculated from the sum of gamma emitters (Sb-126, Sn-126, Sb-125, Eu-154, Am-241, Co-60 and Ba-137m).

c. Value is the “standard error of the mean” rather than the standard deviation of the measurements since its calculation involves multiple radionuclides.

4.0 Conclusions

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

- WAC Targets or Limits were met for all analyzed chemical and radioactive contaminants for which the detection limits are below the WAC Targets or Limits.
- Isopar L has a higher detection limit⁴ compared with the current SPF WAC Limit value of 11 ppm¹ associated with flammability that has been in effect since revision 12 of the WAC dating back to July of 2013.⁵
- Nitrosamines were not detected in the Tank 50 salt solution surface sample above the instrument detection limits of <1 mg/L.
- The minimum detection limit (<2.43E-01 pCi/mL) is reported for ⁹⁴Nb as determined from the minimum detectable activity associated with the radiochemical method used for this radionuclide. The reported detection limit is above the requested SRR target minimum detection limit concentration.⁶ However, the minimum detection limit reported for the Second Quarter CY19 Tank 50 sample for ⁹⁴Nb is lower than the estimated detection limit of 4.38E-01 pCi/mL initially established by SRNL in 2009.⁷ Thus per guidance from SRR,⁶ SRNL continues to achieve as low as practical detection limits for this radionuclide.
- The average Sr-90 value for 2Q19 Tk 50 at 2.88E+05 pCi/mL ±3.45E+04 pCi/mL is ~7.6X higher than the average Sr-90 value (3.78E+04 pCi/mL ±7.99E+03 pCi/mL) derived from the previous three quarters prior to Tank Closure Cesium Removal (TCCR) processing and transfer of a significant volume with increased Sr-90 to Tank 50. The Sr-90 level in the TCCR product was measured at 9.32E+05 pCi/mL. Even though the Sr-90 increased significantly in this 2Q19 Tk 50 sample, it is still an order of magnitude below the WAC Limit of 2.62E+06 pCi/mL.

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