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Results for the September Bimonthly Calendar Year 2022 Tank 50 Salt Solution Sample

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EXECUTIVE SUMMARY

In this Technical Report, the chemical and radionuclide contaminant results from the 2022 September bimonthly sample of Tank 50 salt solution are presented in tabulated form. The information from this characterization will be used by Savannah River Mission Completion (SRMC) 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 that were established at the time the Tank 50 sample was obtained.[1] The chemical and radionuclide contaminant results from the characterization of the 2022 September bimonthly sampling of Tank 50 were requested by SRMC personnel via a Task Technical Request (TTR).[2] 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 the TTR deliverable relating Salt Solution Analysis from the SRMC request.[2]

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

- WAC LIMITS and TARGETS were met for all analyzed chemical and radioactive contaminants for which the detection limits are below the WAC LIMITS and TARGETS.[1]

- Measured average concentrations of nitrate, nitrite and total mercury are approximately 24%, 9% and 12% of the WAC LIMITS, respectively.

- Measured average concentrations of Tc-99 and I-129 are approximately 19% and 20% of the WAC LIMITS, respectively.

- All other radionuclide average concentrations are at 4% or less of the WAC LIMITS and TARGETS.

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LIST OF ABBREVIATIONS

ACSM	Analytical Characterization and Sample Management
DMA	Direct Mercury Analyzer
HDPE	High-Density Polyethylene
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LSC	Liquid Scintillation Counting
MRL	Minimum Reporting Limit
Pu alpha PHA	Plutonium alpha Pulse Height Analysis
SDI	Salt Disposition Integration
SDU	Saltstone Disposal Unit
SPF	Saltstone Production Facility
SRNL	Savannah River National Laboratory
SRMC	Savannah River Mission Completion
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
VDS	Variable Depth Sample
WAC	Waste Acceptance Criteria

1.0 Introduction

Tank 50 aqueous waste is analyzed on a bimonthly basis, and the results are compared to the Waste Acceptance Criteria (WAC) of the Z-Area Saltstone Production Facility (SPF).[1,2] This bimonthly analysis is in addition to the full suite analyses conducted semiannually per X-TTR-Z-00025.[4] The information from this characterization will be used by Savannah River Mission Completion (SRMC) 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] Chemical and radionuclide analyses of salt solution are required to demonstrate that the composition of feed received into Z-Area is in compliance with the Saltstone Performance Assessment.[5]

2.0 Experimental

2.1 Technical

The September bimonthly CY22 Tank 50 sample [a 200-mL sample variable depth sample (VDS) obtained 66" from the bottom of the tank (HTF-50-22-99)] was obtained and received at Savannah River National Laboratory (SRNL) on September 27, 2022.[6]

The Tank 50 sample was received into the SRNL Shielded Cells Facility and then transferred into a radiochemical hood for handling. The contents of the 200-mL slurry in the steel sampler were initially mixed by swirling the container before opening. After initial mixing, an aliquot of the Tank 50 sample was poured into a 30-mL Teflon vial with near zero headspace. This sample was used for Hg analysis. The zero-headspace vial for Hg testing was transferred to storage in a refrigerator.[7] Aliquots of slurry samples were promptly collected with slurry pipettes to minimize settling effects and placed into High-Density Polyethylene (HDPE) bottles.

Unless otherwise stated, all concentrations presented in the tables (except upper limits) are averages based on analyses of triplicate aliquots of the September bimonthly CY22 Tank 50 sample. The 1-sigma 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.

Data reported for inductively coupled plasma mass spectrometry (ICP-MS) are derived from the digested Tank 50 slurry (1 mL supernate diluted to 50 mL total volume) by the aqua regia method.[8] 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 ºC. Anion analyses are determined from Ion Chromatography (IC) analysis of the as-submitted Tank 50 slurry. Approximately 150 mL of the sample was 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.[9] The Cs-137 radionuclide is determined from gamma spectroscopy. Plutonium isotopes (Pu-238, Pu-239 and Pu-240) are determined from a Plutonium alpha Pulse Height Analysis (Pu alpha PHA) method.

Mercury analyses performed at SRNL by Analytical Characterization and Sample Management (ACSM) included Total mercury using the Direct Mercury Analyzer (DMA) method.[10] As discussed above, the Tank 50 sample for mercury analysis was obtained in a near zero-headspace container that was immediately refrigerated after removal from the radiochemical hood on the same day of preparation.[7]

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.[11] SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.[12] 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 1-sigma standard deviations and their corresponding WAC LIMITS[1] 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 after accounting for the analytical uncertainty in each measured concentration.[1] Comparison of the average analyzed detectable values shown in Table 3-1 to the WAC LIMITS indicates that nitrate and nitrite anions and total mercury are present relative to the WAC LIMITS at 24%, 9% and 12%, respectively. The average nitrate and total mercury data for this bimonthly surface sample relative to the WAC LIMITS are similar to the previous reported data for the July 2022 Tank 50 WAC variable depth sample of 24% and 18%, respectively.[13]

Analyzed radionuclide concentrations and the respective radiochemical analysis methods, their standard deviations and their corresponding WAC[1] LIMITS are shown in Table 3-2. Similar data and WAC[1] TARGETS are shown in Table 3-3. Per the WAC, the TARGETS shown shall not be exceeded after 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 to the WAC LIMITS[1] (Table 3-2) indicates that Tc-99 and I-129 are the highest analytes relative to the WAC LIMITS at 19% and 20%, respectively. Comparison of the average analyzed detectable values to the WAC TARGETS (Table 3-3) indicates that none of the radionuclides are higher than 4% of the WAC TARGETS.[1]

Table 3-1. Chemical Contaminants from September Bimonthly CY22 Tank 50 Sample and SPF WAC, Attachment 8.1 LIMITS

Chemical Name (Formula)	Method	Average Concentration (mg/L)	Std. Dev.	WAC LIMIT (mg/L)
Nitrate (NO_3^-)	IC	1.04E+05	1.15E+03	**4.37E+05**
Nitrite (NO_2^-)	IC	1.82E+04	5.77E+01	**2.14E+05**
Total Mercury (Hg)	DMA	4.00E+01	1.96E+00	**3.25E+02**

Table 3-2. Radionuclide Contaminants from September Bimonthly CY22 Tank 50 Sample and SPF WAC, Attachment 8.3 LIMITS

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.	WAC LIMIT (pCi/mL)
Carbon-14 (^{14}C)	C-14 Liquid Scintillation	5.83E+02	3.20E+01	**1.13E+05**
Strontium-90 (^{90}Sr)	Sr-90 Liquid Scintillation	4.88E+03	5.57E+02	**2.62E+06**
Technetium-99 (^{99}Tc)	Tc-99 Liquid Scintillation	4.04E+04	1.74E+03	**2.11E+05**
Iodine-129 (^{129}I)	I-129 (w/ separation) Liquid Scintillation	2.04E+01	2.95E-01	**1.00E+02**
Cesium-137 (^{137}Cs)	Gamma Scan	7.73E+03	1.38E+02	**1.29E+06**
Plutonium-241 (^{241}Pu)	Pu238/241 Liquid Scintillation	9.46E+02	2.69E+02	**8.38E+05**

Table 3-3. Radionuclide Contaminants from September Bimonthly CY22 Tank 50 Sample and SPF WAC, Attachment 8.4 TARGETS

Radionuclide	Method	Average Concentration (pCi/mL)	Std. Dev.	WAC TARGET (pCi/mL)
Yttrium-90 (^{90}Y)	Secular Equilibrium w/ 100% of Sr-90	4.88E+03	5.57E+02	**2.62E+06**
Cesium-135 (^{135}Cs)	Cs-135	<1.61E+00	NA	**2.50E+02**
Barium-137m (^{137m}Ba)	Calculation (Secular Equilibrium w/ 94.6% of Cs-137)	7.32E+03	1.30E+02	**1.22E+06**
Thorium-230 (^{230}Th)	Th-229/230	< 2.55E+00	NA	**6.26E+03**
Uranium-234 (^{234}U)	ICP-MS	6.67E+01	8.20E-01	**3.12E+03**
Uranium-238 (^{238}U)	ICP-MS	1.05E+00	1.87E-02	**3.12E+03**
Plutonium-238 (^{238}Pu)	Pu238/241 Pu alpha PHA	2.06E+03	8.01E+02	**6.67E+04**
Plutonium-239 (^{239}Pu)	Pu238/241 Pu alpha PHA	6.64E+01	2.21E+01	**6.67E+04**
Plutonium-242 (^{242}Pu)	ICP-MS	< 3.91E+01	NA	**6.67E+04**
Americium-241 (^{241}Am)	Am/Cm	2.00E+00	6.02E-01	**6.67E+04**
Americium-242m (^{242m}Am)	Am/Cm	<1.98E-01	NA	**4.50E+05**
Americium-243 (^{243}Am)	Am/Cm	<3.07E-01	NA	**6.67E+04**

4.0 Conclusions

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

- WAC LIMITS and TARGETS were met for all analyzed chemical and radioactive contaminants for which the detection limits are below the WAC LIMITS and TARGETS.[1]

- Measured average concentrations of nitrate, nitrite and total mercury are approximately 24%, 9% and 12% of the WAC LIMITS, respectively.

- Measured average concentrations of Tc-99 and I-129 are approximately 19% and 20% of the WAC LIMITS, respectively.

- All other radionuclide average concentrations are at 4% or less of the WAC LIMITS and TARGETS.

5.0 References

1 Harrington, S. J., "Waste Acceptance Criteria for Transfers to the Z-Area Saltstone Production Facility During Salt Disposition Integration (SDI) (U)", Savannah River Remediation, X-SD-Z-00004, Rev. 4, March 2021.

2 Brown, M., "Bimonthly Saltstone Support for Salt Solution PA Analyses", X-TTR-Z-00026, Rev. 0, August 2021.

3 Crawford, C. L., Hill, K. A., "Task Technical and Quality Assurance Plan for Bimonthly Saltstone Support for Salt Solution Performance Assessment Analyses", Savannah River National Laboratory, SRNL-RP-2021-04577, Rev. 0, September 2021.

4 Brown, M., "Routine Saltstone Support for Salt Solution and Grout Analyses", X-TTR-Z-00025, Rev. 0, August 2021.

5 "Performance Assessment for the Saltstone Disposal Facility at the Savannah River Site", SRR-CWDA-2019-00001, Revision 0, Savannah River Remediation, Aiken, SC, March 2020.

6 Crawford, C. L., "September Bimonthly Calendar Year 2022 Tk 50 Analysis", B9108-00327-27, SRNL E-Notebook (Production), Savannah River National Laboratory, September 2022.

7 McCabe, D. J., Crawford, C. L., Bannochie, C. J., Boggess, A. J. and Bishop, S. G., "Best Handling Practices for Elemental Mercury, Organo-Mercury Compounds, and Inorganic Mercury Compounds", SRNL-TR-2019-00243, Rev. 1, June 2020.

8 "Aqua Regia Dissolution of Sludge for Elemental Analysis"; Savannah River National Laboratory, Manual L16.1, Procedure ADS-2226, Rev. 10, July 2013.

9 "Integrated Data Base Report – 1996: U.S. Spent Nuclear Fuel and Radioactive Waste Inventories, Projections, and Characteristics", Oak Ridge National Laboratory, DOE/RW-0006, Rev. 13, December 1997. https://www.nrc.gov/docs/ML1028/ML102850100.pdf (accessed May 13, 2022).

10 White, T. L., Brown, L. W., Looney, B. B and Jones, M. A., "Total Mercury Analysis Comparison Deployment of Analytical Method for the Savannah River Site Liquid Waste System", Savannah River National Laboratory, SRNL-STI-2019-00056, Rev. 0, July 2019.

11 "Technical Reviews", Savannah River Site, Manual E7, Procedure 2.60, Latest Revision.

12 "Savannah River National Laboratory Technical Report Design Check Guidelines", Westinghouse Savannah River Company, WSRC-IM-2002-00011, Rev. 2, August 2004.

13 Crawford, C. L., "Results for the July 2022 Semiannual Tank 50 Salt Solution Sample", SRNL-STI-2022-00526, Revision 0, December 2022.

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