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Additional Analysis of the 2H-Evaporator Wall Scale Sample HTF-17-57

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EXECUTIVE SUMMARY

Savannah River National Laboratory previously analyzed scale samples from both the wall and cone sections of the 242-16H Evaporator prior to chemical cleaning. The samples were analyzed for uranium and plutonium isotopes required for a Nuclear Criticality Safety Assessment of the scale removal process. The analysis of the scale samples found the material to contain crystalline nitrated cancrinite and clarkeite and significant amounts of mercury. Savannah River Remediation subsequently requested additional analyses on the samples. Inspection of the sample bottles revealed that no sample remained of the cone scale (HTF-17-56) while approximately 4 g of the wall scale sample (HTF-17-57) remained. The wall sample was subsequently ground with a mortar and pestle, at which time it was discovered that the sample contained a significant amount of liquid, metallic mercury. The portion of the sample that was not mercury was approximately 3 g. This portion of the sample was analyzed to determine the concentrations of selected radionuclides. The following radionuclide concentrations were measured: <9.6E+02 dpm/g H-3, 2.9E+02 dpm/g C-14, 5.6E+03 dpm/g Tc-99, and 1.6E+02 dpm/g I-129. Blank samples were also analyzed to evaluate sample contamination from the Shielded Cells environment. All blank sample results were below detectable limits. Due to the limited sample size and the anticipated low levels of the target radionuclides, no replicate sample analysis was conducted.

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LIST OF ABBREVIATIONS

AD	Analytical Development
AMP	Ammonium Molybdophosphate
CST	Crystalline Silicotitanate
ELN	Electronic Laboratory Notebook
HPGe	High Purity Germanium
HTO	Hydrogen Tritium Oxide (tritiated water)
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
LSC	Liquid Scintillation Counting
MIK	Methyl Isobutyl Ketone
MST	Monosodium Titanate
NAA	Neutron Activation Analysis
NCSA	Nuclear Criticality Safety Assessment
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TTR	Technical Assistance Request
XRD	X-Ray Diffraction

1.0 Introduction

The Savannah River Site (SRS) 242-16H Evaporator (2H-Evaporator) system concentrates liquid high-level waste including the recycle stream from the Defense Waste Processing Facility (DWPF) to reduce waste volume in the SRS tank farm. In the evaporator, silicon, primarily from the recycle stream, reacts with aluminum in the tank waste to form sodium aluminosilicate scale deposits in the evaporator pot and gravity drain line. The scale deposits are primarily nitrated cancrinite $Na_8(Al_6Si_6O_{24})(NO_3)_2 \cdot 4H_2O$, with smaller amounts of clarkeite, $Na((UO_2)O(OH))$.[1] When the cancrinite/clarkeite scale builds up, the 2H-Evaporator pot is chemically cleaned using heated 1.5 M nitric acid. Sampling and analysis of the scale material is performed to provide data needed for a Nuclear Criticality Safety Assessment (NCSA) of the scale removal process. Scale samples from two evaporator locations (wall and cone areas) were obtained by Savannah River Remediation (SRR) prior to chemical cleaning. The samples were sent to the Savannah River National Laboratory (SRNL) for analysis of uranium and plutonium isotopes needed for the NCSA assessment. The samples were also analyzed for mercury by cold vapor atomic adsorption spectroscopy and by X-Ray Diffraction (XRD) to identify the predominant crystalline phases present in the scale. Additional radionuclide (H-3, C-14, Tc-99, and I-129) analyses were subsequently requested on the remaining samples through a Technical Assistance Request (TAR) revision.[2] Inspection of the sample bottles revealed that no sample remained of the cone scale (HTF-17-56), while approximately 4 g of the wall scale sample (HTF-17-57) remained. The wall sample was subsequently ground with a mortar and pestle, at which time it was discovered that the sample contained a significant amount of liquid, metallic mercury. The portion of the wall sample that was not mercury was approximately 3 g. This sample was used for the requested analyses.

2.0 Experimental Procedure

2.1 Preliminary Sample Preparation

Two mortar and pestle units were transferred into the SRNL Shielded Cells. The entire 4 g wall scale sample (HTF-17-57) was carefully and repeatedly ground to homogenize the sample. During this process it was discovered that a portion of the sample was composed of a ball of liquid mercury which was observed in the mortar bowl. The mercury was removed from the sample leaving approximately 3 g of wall sample for analysis.

2.2 Iodine Analysis Sample Preparation

A 0.7 g sub-sample of the ground wall scale sample was added to 0.5 ml of 2M KI solution in a 30 mL bottle. The non-radioactive iodine served as an internal standard. 8 ml of 8M nitric acid was added to the slurry and the bottle was immediately capped, mixed, and allowed to stand overnight. The following day, the dissolution was rendered caustic with the stepwise addition of 14 mL of concentrated NaOH solution to precipitate insoluble interfering radionuclides, to adjust the chemistry for subsequent resin decontamination treatments, and to reduce iodine to iodide to inhibit iodine losses from sublimation. 1g of monosodium titanate (MST) and 1g of crystalline silicotitanate (CST) were added to the bottle to complex a variety of radionuclides remaining in solution and the bottle was then capped and shaken for approximately 30 seconds. 10 ml of 2M NaOH solution was subsequently added to the bottle and the sample was filtered through a 0.45 µm Nylon Nalgene filter unit, removing the insoluble isotopes and the resins. The entire filtrate solution was removed from the SRNL Shielded Cells and submitted to Analytical Development's (AD) Nuclear Measurements Group for further radiochemical purification for I-129 analysis along with an identically prepared blank sample of oil dry. The samples were filtered again to remove insoluble solids that had continued to precipitate. The samples were then acidified with nitric acid and treated with ammonium molybdophosphate (AMP) to further reduce Cs-137 levels and with a diphosphonic acid based extractant to further reduce remaining levels of actinides which can co-precipitate with iodine in subsequent steps. Iodine in the samples was then reduced to iodide with sodium sulfite and complexed with silver to form insoluble AgI. The AgI was filtered off, and the filters were washed repeatedly with dilute nitric acid. The AgI precipitate from each sample was assayed for 50,000 seconds using low energy, high purity germanium (HPGe) gamma spectrometers for the low energy gamma and x-ray emissions characteristic of I-129 beta decay. Following the gamma analyses, the filters were loaded into heat-sealed polyethylene vessels (a.k.a. rabbits) and were submitted to the SRNL pneumatic neutron activation analysis (NAA) facility. The samples were then assayed for stable iodine recoveries using NAA.

2.3 Carbon-14 Analysis Sample Preparation

0.7 g of ground wall scale sample was transferred to a green shielded bottle along with 3 mL of deionized water (added for shielding purposes). This sample was submitted directly to AD for analysis. A sample of ground oil dry was identically prepared and submitted for C-14 analysis along with the wall scale sample to serve as a blank. In AD the samples were wet-ashed to oxidize carbon present in the samples to carbon dioxide using a combined silver-catalyzed persulfate and a sulfuric acid oxidation in a sealed system. The carbon dioxide was captured as carbonate in a sodium hydroxide capture agent. The samples were then subjected to a second purification. The carbonate was oxidized to carbon dioxide using nitric acid in a sealed system. The liberated carbon dioxide was then captured in an amine-based capture agent which was added to a liquid scintillation cocktail and then analyzed by liquid scintillation counting (LSC). The beta spectra from the LSC analysis were analyzed in both the C-14 and lower and higher energy beta regions to ensure no other beta species were present to bias the C-14 results high. A set of C-14 standards were also run through the same procedure for calibration purposes.

2.4 Tritium and Technetium Analysis Sample Preparations

The remaining ~0.7 g of ground wall scale sample was digested using the standard AD aqua regia dissolution and the entire sample was submitted for H-3 and Tc-99 analysis. A sample of ground oil dry was identically prepared and submitted along with the wall scale sample to serve as a blank.

The dissolution samples were steam distilled in the Nuclear Measurement Group's Radiochemistry Laboratories to separate the oxidized tritium from tritiated water (HTO) generated in the dissolution from interfering species. Aliquots of distillate were added to liquid scintillation cocktail and assayed by liquid scintillation counting. The LSC beta spectrum was analyzed in both the low energy tritium and high energy beta windows to ensure no higher energy beta species were biasing the tritium results high.

Aliquots of the dissolution samples were then analyzed for Tc-99. First a Tc-99m tracer was generated. Ammonium molybdate was bombarded with neutrons using one of two available SRNL neutron activation analysis facilities, activating Mo-98 to Mo-99. The activated ammonium molybdate was then dissolved in caustic, and the Tc-99m daughter of Mo-99 was extracted from the caustic solution using methyl isobutyl ketone (MIK). The MIK was then evaporated to dryness and the Tc-99m was reconstituted in a dilute nitric acid matrix. Large aliquots of sample were acidified with concentrated nitric acid, aliquots of Tc-99m tracer were added to each sample, and the pH of the solutions were then raised with the addition of NaOH. In addition to the samples, a blank and two calibration/validation Tc-99 blank spikes were also run through this process. Tc-99 was extracted initially with Eichrom TEVA resins under vacuum, the resin was washed repeatedly, then the Tc-99 was eluted. The Tc-99 was then re-extracted onto TEVA resin in the form of a filter disc, the disc was then added to a liquid scintillation cocktail. The liquid scintillation samples were then analyzed using NaI well gamma spectrometers to measure the Tc-99m tracer levels. The Tc-99m was allowed to decay away with a 6 hour half-life. The samples were then analyzed by liquid scintillation analyses for the Tc-99 beta. The beta spectra from the LSC analysis were analyzed in both the Tc-99 and lower and higher energy beta regions to ensure no other beta species were present to bias the Tc-99 results high. A set of Tc-99 standards were also run through the same procedure to calibrate the run. A laboratory blank was also run through this process.

2.5 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7, Procedure 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. This work was requested through a TAR revision.[2] This report received a technical review by design verification (Manual E7 2.60, Section 5.3). Data are recorded in the Electronic Laboratory Notebook (ELN) system as notebook/experiment number A2341-00117-14.

3.0 Results and Discussion

Analytical results for individual wall scale sub-samples (no replicates) and the oil dry blank samples are provided in Table 3-1 for the four requested radionuclides. Detectable levels of C-14, Tc-99, and I-129 were observed with Tc-99 contributing the greatest activity of these radioisotopes. The tritium (H-3) activity was below the method detection limit. Analysis results for the blank sample were below the limits of detection for all radioisotopes.

Table 3-1. Analytical Results for the 2H Evaporator Wall Scale Sample HTF-17-57 and Blank

Radionuclide	Wall Scale Sample (dpm/g)	Sample 1σ uncertainty	Wall Scale Sample (Wt. %)	Oil Dry Blank (dpm/g)	Blank 1σ uncertainty
H-3	<9.57E+02	MDA	<4.5E-12	<9.57E+02	MDA
C-14	2.87E+02	20%	9.7E-09	<5.60E+01	
Tc-99	5.60E+03	6.07%	2.5E-06	<5.83E+01	
I-129	1.59E+02	11.3%	2.4E-04	<1.02E+01	

4.0 Conclusions

The wall scale sample (HTF-17-57) contained the following radionuclide concentrations: <9.6E+02 dpm/g H-3, 2.9E+02 dpm/g C-14, 5.6E+03 dpm/g Tc-99, and 1.6E+02 dpm/g I-129. Including the mass of elemental mercury in the sample, the radionuclide concentrations are: <7.0E+02 dpm/g H-3, 2.1E+02 dpm/g C-14, 4.1E+03 dpm/g Tc-99, and 1.2E+02 dpm/g I-129. All blank sample results were below detectable limits.

5.0 Future Work

Since the remaining sample was consumed during this analysis, no additional characterization can be conducted.

6.0 References

1. M. S. Hay, C. J. Coleman, D. P DiPrete, "Analysis of the 2H-Evaporator Scale Samples (HTF-17-56, -57)", SRNL-STI-2017-00537, Rev. 0, September 2017.

2. J. R. Jacobs, "16H Evaporator Scale Additional Analyses", X-TAR-H-00040, Rev. 1, May 2020.

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