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Tank 12H Acidic Chemical Cleaning Sample Analysis and Material Balance

C. J. Martino
S. H. Reboul
B. J. Wiersma
C. J. Coleman

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REVIEWS AND APPROVALS

AUTHORS:

C. J. Martino, Advanced Characterization and Processing Date

S. H. Reboul, Advanced Characterization and Processing Date

B. J. Wiersma, Materials Science and Engineering Date

C. J. Coleman, Analytical Development Date

TECHNICAL REVIEW:

M. S. Hay, Advanced Characterization and Processing, Review per E7 2.60 Date

APPROVAL:

F. M. Pennebaker, Manager Date
Advanced Characterization and Processing

S. L. Marra, Manager Date
Environmental & Chemical Process Technology Research Programs

J. R. Vitali, Manager Date
SRR Flowsheet Development & Facility Integration

EXECUTIVE SUMMARY

A process of Bulk Oxalic Acid (BOA) chemical cleaning was performed for Tank 12H during June and July of 2013 to remove all or a portion of the approximately 4400 gallon sludge heel. Three strikes of oxalic acid (nominally 4 wt % or 2 wt %) were used at 55 °C and tank volumes of 96- to 140-thousand gallons. This report details the sample analysis of a scrape sample taken prior to BOA cleaning and dip samples taken during BOA cleaning. It also documents a rudimentary material balance for the Tank 12H cleaning results.

The following are the key observations for Tank 12H Scrape Sample HTF-12-12-107 taken prior to BOA cleaning of the tank heel:

- Iron and manganese were the primary components, followed by aluminum, mercury, uranium, sodium, silicon, nickel and thorium.
- Compared with previous Tank 12H sludge samples, the scrape sample had a relatively low aluminum:iron ratio of approximately 1:3.
- In terms of activity on a wet basis, the primary radionuclides are strontium-90 at 8.7×10^3 $\mu\text{Ci/g}$ and cesium-137 at 1.7×10^2 $\mu\text{Ci/g}$.

The following are the key observations for the Tank 12H Supernate Samples taken during BOA cleaning. One sample was removed at the end of each BOA cleaning strike. Additionally, two intermediate samples were analyzed for the first BOA cleaning strike.

- The samples contained insoluble solids with a measured range of 0.00 wt % to 0.34 wt %. Chemical and radiological analyses were performed on solids-free filtrate.
- Fe^{2+} content was 2% or less of the total iron (ranging from 0.9% to 1.9%) for each strike.
- Based on the soluble ferric species concentrations at the end of each of the three BOA cleaning strikes, ferric ion reduction was the primary cathodic reaction during chemical cleaning and not hydrogen gas generation. Controlling the exposure time of the carbon steel to the oxalic acid appears to have been effective in mitigating evolution of the flammable gas.
- The major components in the supernate were iron, sodium, manganese, uranium, and aluminum.
- Pu-238 was present in the supernate at up to 0.6 $\mu\text{Ci/mL}$ (at the end of the first strike).
- I-129 and Am-241 were below the method detection limits.

The following are the key observations for the material balance constructed from the Tank 12H sample data:

- A material balance based only on an initial sample of tank heel solids from a single location and samples of solids-free supernatant liquid from the end of each strike requires multiple assumptions to be made that in-turn limit the applicability of the material balance for determining the amount and composition of the solids remaining in the tank.
- Components that had high, near-complete removal (>85%) include sodium, potassium, and phosphorus.
- Components that had moderate, significant partial removal (40% to 70%) include uranium, gross beta/gamma, chromium, iron, magnesium, calcium, zirconium, and silicon.
- Components that had low to borderline moderate, minor removal (15% to 35%) include plutonium, aluminum, manganese, copper, barium, and lithium.
- Components that had low, negligible removal (<6%) include mercury, thorium, and nickel.

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LIST OF ABBREVIATIONS

BOA	Bulk Oxalic Acid
C. I.	Confidence Interval
CVAA	Cold Vapor Atomic Absorption
EA	Environmental Assessment
HLW	High-Level Waste
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
LSC	Liquid Scintillation Counting
n	Number of replicate measurements
N/A	Not Applicable
OA	Oxalic Acid
PuTTA	Pu separation by Thenoyltrifluoroacetone
RSD	Relative Standard Deviation
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TIC/TOC	Total Inorganic Carbon/Total Organic Carbon
TT&QAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request

1.0 Introduction

In support of Savannah River Site (SRS) tank closure efforts, Savannah River Remediation (SRR), the tank farms operations contractor, implemented a bulk oxalic acid (BOA) cleaning process in High Level Waste (HLW) Tank 12H. After bulk waste removal efforts and subsequent aluminum dissolution, sludge washing, and mechanical heel removal, Tank 12H had an estimated 4400 gallons of sludge remaining.¹ Prior to initiating BOA cleaning, an initial scrape sample of the Tank 12H sludge heel was collected and then sent to the Savannah River National Laboratory (SRNL) for analysis of various chemical and radioactive components and physical properties. During BOA cleaning, dip samples were taken at the end of each strike and analyzed for iron oxidation state and other chemical and radioactive components. Additional dip samples were taken at intermediate points in the BOA process.

This work is outlined and authorized in a Technical Task Request² and a Task Technical and Quality Assurance Plan.³ Details of the BOA cleaning performed for Tank 12H during June and July of 2013 are compiled in a Completion Report.⁴

2.0 Initial Scrape Sample

2.1 Sample

On November 2, 2012, SRR sampled the accessible sludge at the bottom of Tank 12H. The sample (HTF-12-12-107) was delivered to SRNL on November 5 and placed into the Shielded Cells. Figure 2-1 contains photographs of the sample HTF-12-12-107 taken during sample receipt and opening. The sample consisted of brown solids that were not free-flowing and a small amount of free-flowing slurry. After removal of material from the sampler and separation of solids from the free-flowing portion of sample, HTF-12-12-107 was determined to contain 27.553 grams of wet solids and 0.868 grams of solids-free liquid. Analyses that are reported on a “wet solids” basis were performed on the 27.553 grams of wet solids after the removal of 0.868 grams of liquid.

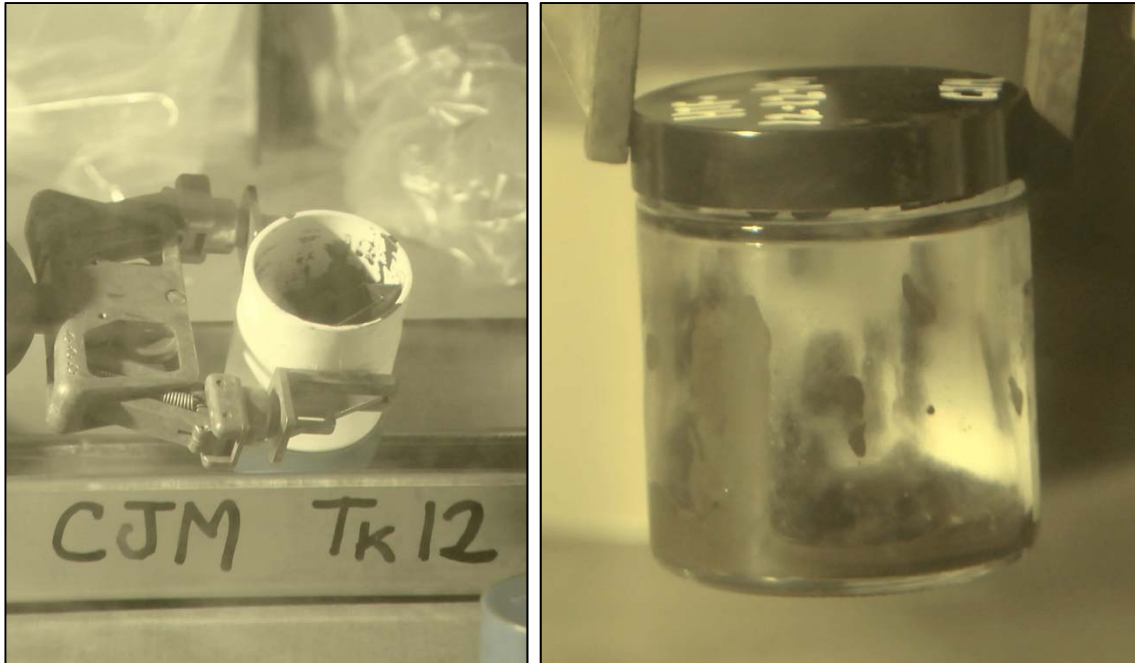


Figure 2-1. Tank 12H scrape sample HTF-12-12-107 received in a PVC container (left) and transferred into a 125 mL glass jar (right).

2.2 Experimental

Table 2-1 outlines the analyses requested for the wet solids portion of sample HTF-12-12-107. Table 2-1 also specifies the requested reporting units, the projected measurement method, and the requested minimum detection limits, where applicable.

There were no apparent large chunks that required crushing in the sample. For homogenization, the wet solids were mixed with a spatula prior to characterization.

Table 2-1. The requested analytes / units; and the projected measurement methods to reach the requested level of detection

analyte	units	measurement method	requested minimum detection
density	g/mL	solids bulk density	N/A
total solids	wt %	gravimetric drying	N/A
Sr-90	μCi/g and wt%	Sr-90	1.0E-03 μCi/g
Tc-99	μCi/g and wt%	Tc-99	5.0E-03 μCi/g
I-129	μCi/g and wt%	I-129	1.0E-04 μCi/g
Cs-137	μCi/g and wt%	gamma counting of Ba-137m	1.0E-03 μCi/g
Np-237, U-238	μCi/g and wt%	ICP-MS	1.0E-03 μCi/g
Pu-238, Pu-239/240	μCi/g and wt%	PuTTA	1.0E-03 μCi/g
Am-241	μCi/g and wt%	Cs-removed gamma	1.0E-03 μCi/g
metals	wt %	ICP-ES	N/A
Hg	wt %	CVAA	N/A
NO ₃ ⁻ , NO ₂ ⁻ , C ₂ O ₄ ²⁻	wt %	IC anions	N/A

There is not a routine method used to determine the bulk density of non-flowing wet solids. The Tank 12H scrape sample is too thick to use the method used for sludge slurries without diluting the material and too wet to use the method used for closure samples without first drying the material. The bulk density was measured by water displacement. An approximately 1 mL container of known volume was filled with a portion of wet solids and the remaining portion with water. For saturated wet solid cakes, the density from this displacement method will give values appropriate for conversion between the analytical results in this report (on a wet mass basis) and the in-tank sludge heel quantity (on a volume basis).

Total solids content was determined by drying nominally 0.35 gram portions of wet solids to a constant weight at 115 ± 5 °C. This measurement was performed in triplicate in conjunction with peroxide fusion sample digestion preparations.

Two main preparation methods were performed in triplicate on the Tank 12H scrape sample wet solids. Peroxide fusion digestion was used as the preparation for plutonium by the PuTTA method and metals by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES). Aqua regia dissolution was used as the preparation for the majority of the other analyses, including Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS), ICP-ES, Cold Vapor Atomic Absorption (CVAA), gamma counting (γ), Cs-removed gamma counting (Cs-r γ), and Sr-90 analysis. To achieve the requested detection limits for sample material with high overall beta/gamma activity, the radiochemical preparation methods for Tc-99 and I-129 had to be performed in the Shielded Cells.

From sample handling tasks, two types of sample liquids were available for analysis. The first liquid was the small amount of separable free liquid that was received with the sample. The second liquid resulted from leaching the wet solids with water for several days. Both liquids were filtered and diluted to provide the required volume for analysis. The analysis included Ion Chromatography (IC) for anions, acid titration for free hydroxide, Total Inorganic Carbon/Total Organic Carbon (TIC/TOC) analysis, and pH measurement.

2.3 Results and Discussion

The weight percentage of total solids was measured during sample drying required for the peroxide fusion digestion. Three total solids measurements were performed, averaging 49.7 wt % with a standard deviation of 2.6 wt %. Three determinations of the density were made by the method described in the previous section. The approximate bulk density of the saturated material averaged 1.65 g/mL with a standard deviation of 0.04 g/mL.

Table 2-2 and Table 2-3 contain the analysis results for the elemental and radionuclide components, respectively, for the wet solids from Tank 12H scrape sample HTF-12-12-107. These results contain the sludge interstitial liquid and are reported on a wet basis. Results are preceded by “<” when the analyte is less than the lower limits of quantification. The individual determinations of the preparations and measurements are reported, along with the “combined/best” result. In cases where the indicators suggested that one preparation method provided better analytical results or that lower limits or quantification were achieved, the combined/best result only includes results from the preferred preparation method. The combined/best results are reported as average values and the corresponding Relative Standard Deviation (RSD) values. RSD values are not reported when all measurements are less than the lower limits of quantification. The greyed out values in Table 2-2 and Table 2-3 are not used in the calculation of the combined/best values.

Table 2-2 results are exclusively by ICP-ES analysis, with the exception of mercury, which was measured by CVAA.

Table 2-2 shows that iron and manganese are the primary components of the solids, followed by aluminum, mercury, uranium, sodium, silicon, nickel and thorium. The sum of the components is low relative to previous Tank 12H sludge analyses because this analysis is reported on a wet basis and the material has significant water content. This material has an aluminum:iron ratio of approximately 1:3. The aluminum:iron ratio of HTF-12-12-107 is much lower than that of a composite of Tank 12H sludge samples taken during sludge retrieval and prior to the in-tank aluminum dissolution campaign. That previous Tank 12H sludge composite sample had an aluminum:iron ratio of approximately 5.8:1.⁵

Table 2-3 shows that the primary radionuclides in terms of activity in the wet solid sample are strontium-90 at 8.7×10^3 $\mu\text{Ci/g}$ and cesium-137 at 1.7×10^2 $\mu\text{Ci/g}$. All requested radionuclides were quantified in the Tank 12H scrape sample.

**Table 2-2: Elemental Analysis of Tank 12H Scrape Sample HTF-12-12-107
(wt %, wet basis)**

wt %	Aqua Regia Dissolution			Peroxide Fusion Digestion			Combined / Best		
	average	RSD	n	average	RSD	n	average	RSD	n
Ag	1.10E-02	3.5%	3	< 9.73E-02	--	--	1.10E-02	3.5%	3
Al	3.06E+00	3.1%	3	3.36E+00	8.9%	3	3.36E+00	8.9%	3
B	< 9.00E-03	8.7%	3	< 1.33E-01	--	--	< 9.00E-03	--	--
Ba	5.09E-02	4.2%	3	4.97E-02	2.3%	3	5.03E-02	3.3%	6
Be	< 3.16E-04	8.7%	3	< 3.94E-04	--	--	< 3.55E-04	--	--
Ca	2.95E-01	6.0%	3	4.39E-01	--	--	2.95E-01	6.0%	3
Cd	2.96E-03	10.3%	3	< 8.04E-03	--	--	2.96E-03	10.3%	3
Ce	5.82E-02	3.3%	3	< 4.60E-02	--	--	5.82E-02	3.3%	3
Co	6.72E-03	6.5%	3	< 1.04E-02	--	--	6.72E-03	6.5%	3
Cr	2.89E-02	6.5%	3	3.63E-02	9.5%	3	3.26E-02	14.5%	6
Cu	5.07E-02	5.1%	3	3.18E-02	1.3%	3	4.12E-02	25.5%	6
Fe	9.76E+00	2.8%	3	9.89E+00	3.6%	3	9.83E+00	3.0%	6
Gd	< 2.98E-02	--	--	< 7.76E-03	3.3%	3	< 7.76E-03	--	--
Hg	2.33E+00	0.9%	3	--	--	--	2.33E+00	0.9%	3
K	4.42E-02	3.6%	3	< 2.03E-01	--	--	4.42E-02	3.6%	3
La	3.15E-02	4.1%	3	2.65E-02	4.8%	3	2.90E-02	10.1%	6
Li	1.17E-01	23.9%	3	1.01E-01	29.5%	3	1.09E-01	25.0%	6
Mg	8.50E-02	4.0%	3	8.10E-02	6.2%	3	8.30E-02	5.3%	6
Mn	7.95E+00	7.5%	3	8.00E+00	10.6%	3	7.98E+00	8.3%	6
Mo	< 4.45E-03	--	--	< 5.53E-02	--	--	< 4.45E-03	--	--
Na	1.40E+00	4.7%	3	--	--	--	1.40E+00	4.7%	3
Ni	6.73E-01	7.8%	3	7.66E-01	10.2%	3	7.20E-01	10.9%	6
P	4.68E-02	23.1%	3	< 9.36E-02	--	--	4.68E-02	23.1%	3
Pb	1.20E-02	7.2%	3	< 4.60E-02	--	--	1.20E-02	7.2%	3
S	< 2.71E-01	--	--	< 3.37E+00	--	--	< 2.71E-01	--	--
Sb	< 1.56E-02	--	--	< 1.94E-01	--	--	< 1.56E-02	--	--
Si	--	--	--	8.15E-01	2.7%	3	8.15E-01	2.7%	3
Sn	< 5.34E-02	--	--	< 6.64E-02	--	--	< 5.34E-02	--	--
Sr	3.14E-02	4.9%	3	2.98E-02	2.9%	3	3.06E-02	4.7%	3
Th	5.93E-01	16.0%	3	6.14E-01	23.4%	3	6.03E-01	18.2%	6
Ti	7.32E-03	4.2%	3	9.41E-03	2.6%	3	9.41E-03	2.6%	3
U	1.88E+00	4.4%	3	1.95E+00	5.4%	3	1.91E+00	4.9%	6
V	< 2.85E-03	--	--	< 3.54E-03	--	--	< 2.85E-03	--	--
Zn	1.67E-02	5.0%	3	2.03E-02	3.4%	3	1.85E-02	11.2%	6
Zr	1.07E-01	20.6%	3	--	--	--	1.07E-01	20.6%	3

Table 2-3: Radionuclide Analysis of Tank 12H Scrape Sample HTF-12-12-107 (wet basis)

analyte	method	avg. ($\mu\text{Ci/g}$)	avg. (wt%)	RSD	n
Co-60	Cs-r γ	8.05E-02	7.12E-09	6.0%	3
Sr-90	Sr-90	8.71E+03	6.38E-03	3.2%	3
Tc-99	Tc-99	2.88E-03	1.70E-05	6.6%	3
I-129	I-129	1.36E-03	7.72E-04	26.1%	3
Cs-137	γ	1.68E+02	1.93E-04	4.6%	3
Eu-152	Cs-r γ	1.38E-01	7.98E-08	9.9%	3
Eu-154	Cs-r γ	2.05E+00	7.60E-07	17.3%	3
Th-232	ICP-MS	6.01E-04	5.48E-01	16.5%	3
U-233	ICP-MS	2.55E-02	2.63E-04	10.4%	3
U-234	ICP-MS	2.56E-02	4.09E-04	7.9%	3
U-235	ICP-MS	3.00E-04	1.39E-02	3.9%	3
U-236	ICP-MS	2.88E-04	4.45E-04	8.0%	3
Np-237	ICP-MS	1.51E-02	2.14E-03	9.2%	3
U-238	ICP-MS	6.37E-03	1.90E+00	2.6%	3
Pu-238	PuTTA	3.19E+01	1.86E-04	13.8%	3
Pu-239/240	PuTTA	3.25E+00	--	5.6%	3
Pu-239	ICP-MS	2.49E+00	4.01E-03	2.1%	3
Pu-240	ICP-MS	5.48E-01	2.40E-04	10.2%	3
Am-241	Cs-r γ	2.16E+00	6.30E-05	13.7%	3

The analysis of the free liquid in the original sample and the liquid resulting from water leaching of the solids revealed that the liquid component of the sludge heel has a low salt content. The leached sample material appeared to be consistent with water dilution of the sludge interstitial liquid. Thus, the results for the free liquid and the sample leachate were combined. The liquid portion of the Tank 12H scrape sample was roughly pH = 10.0 to 10.5 with an approximate anion content of carbonate = 6500 mg/L, nitrite = 1600 mg/L, nitrate = 400 mg/L, and other anions <300 mg/L.

3.0 Chemical Cleaning Dip Samples

3.1 Samples

The Tank 12H BOA Cleaning campaign was executed in June and July of 2013. Details on tank conditions and process timing are contained in the completion report.⁴ Table 3-1 lists the samples received by SRNL, the approximate date and time the sample was taken, the day the sample was received by SRNL, a description of the processing stage when sampling occurred, the mass of material received, and the visual assessment of the sample appearance. As planned, SRR sampled near the surface of the liquid at the end of each strike and sent one sample each to SRNL and F/H Lab.⁶ Because unplanned additional samples were collected for F/H Lab analysis of pH at intermediate points during strike 1 and post-strike 3, sampling protocols included pulling additional samples for SRNL as well. Thus, five additional samples were received in addition to the three samples expected.

Table 3-1. BOA Cleaning Dip Samples

Sample Name	Date/Time	Receipt Date	Description	Sample Weight	Sample Appearance
HTF-12-13-93*	6/17/2013 17:00	6/24/2013	Strike 1	89.9 g	slightly hazy
HTF-12-13-96	6/18/2013 16:00	6/24/2013	Strike 1	71.4 g	slightly hazy
HTF-12-13-98	6/19/2013 6:30	6/24/2013	Strike 1	73.4 g	very hazy, light brown
HTF-12-13-100	6/19/2013 16:30	6/24/2013	Strike 1	73.9 g	hazy, light gray
HTF-12-13-102	6/20/2013 15:00	6/21/2013	Strike 1 End	134.2 g	very hazy, light gray
HTF-12-13-116	7/1/2013 16:00	7/3/2013	Strike 2 End	70.7 g	very hazy, light gray
HTF-12-13-127	7/16/2013 5:30	7/16/2013	Strike 3 End	61.9 g	hazy, light gray
HTF-12-13-133	7/26/2013 9:30	7/29/2013	Post Strike 3	83.6 g	slightly hazy

* sample vial was etched HTF-12-13-93, but accompanying paperwork indicated HTF-12-13-94

Analysis was performed on filtrate from three end of strike samples (HTF-12-13-102, 116, and 127) and two of the intermediate samples from the first strike (HTF-12-13-93, 100). Figure 3-1 contains photographs of the eight dip samples. Portions of the end of strike samples were utilized prior to the photograph being taken, so the volume does not represent the received volume in those cases. Based on the photographs, all samples exhibited some level of haziness, which indicates the presence of insoluble solids.

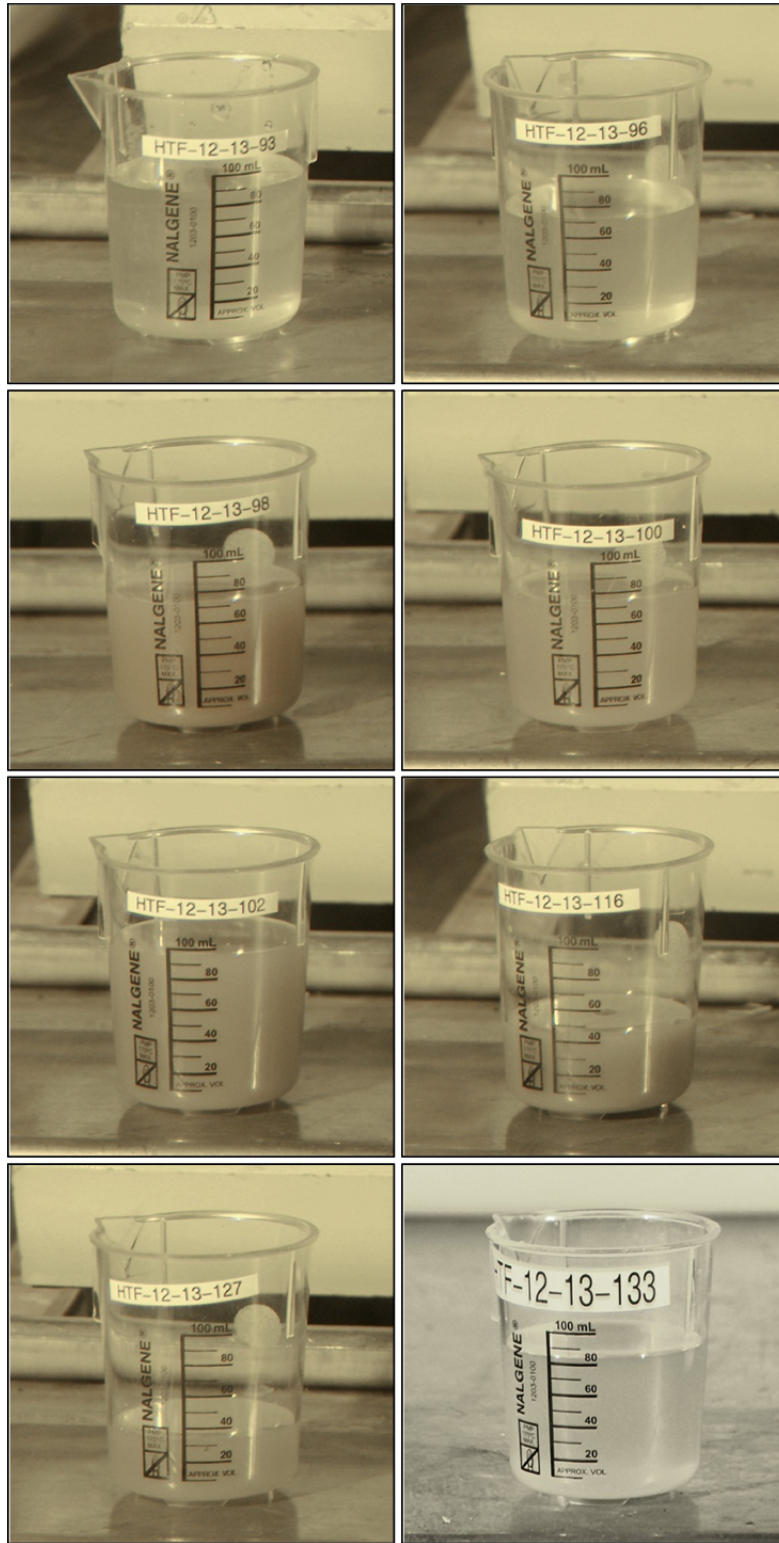


Figure 3-1. Tank 12H BOA Cleaning Dip Samples

3.2 Experimental

SRNL characterized the liquid portion of dip samples from Tank 12H in support of the BOA cleaning evolution. Additional soluble chemical and radiological components of the BOA cleaning process samples were obtained from a separate dip sample analyzed by F and H Area Laboratories (F/H Lab).⁴ SRNL analyzed the dip samples for the components outlined in Table 3-2.

The dip samples contained insoluble solids, but the solids were not used in the measurements other than quantifying the total and insoluble solids. For all other analyses, samples were passed through a 0.45 micron nylon filter and the filtrate was used for analysis.

Shortly after sample receipt, filtrate was analyzed in the shielded cells for Fe²⁺/Fe³⁺. Where samples could not be analyzed for Fe²⁺/Fe³⁺ in the same shift as they were received, the samples were removed from the stainless steel receipt bottles and a portion of the sample was filtered and the filtrate stored in a bottle that was covered to prevent exposure of the sample to light. The remainder of the analyses (for Tc-99, I-129, U isotopes, Np-237, Pu isotopes, and Am-241) were performed as a group on all BOA cleaning process end-of-strike samples after the sample from the last (third) strike was received.

Table 3-2. Requested BOA cleaning dip sample SRNL analyses

analyte	units	measurement method
Liquid density	g/mL	gravimetric
total solids, soluble solids, insoluble solids	wt %	gravimetric drying
Fe ²⁺ /Fe ³⁺ (soluble)	ratio	in-cells colorimetric
Tc-99 (soluble)	μCi/mL	Tc-99
I-129 (soluble)	μCi/mL	I-129
U-233, 234, 235, 236, and 238	μCi/mL	ICP-MS
Np-237 (soluble)	μCi/mL	ICP-MS
Pu-238, 239/240, and 241	μCi/mL	Pu-238/Pu-241
Pu-239 and 240	μCi/mL	ICP-MS
Am-241 (soluble)	μCi/mL	Cs-removed gamma

Portions of the as-received and filtered dip samples were dried to a constant weight at 110 ± 5 °C to determine total and soluble solids content, respectively. Insoluble solids content of the dip samples were calculated from the total and soluble solids results.

No target minimum detection limits were specified for the BOA cleaning process dip samples. For most analyses, undiluted samples were removed from the shielded cells and submitted to the various analytical methods.

The quality assurance protocol for the Fe²⁺/Fe³⁺ measurements involved performing additional measurements on Environmental Assessment (EA) glass.⁷ The EA Glass standard has a Fe²⁺/Fe³⁺ of 0.22 measured by Corning Labs and of 0.23 measured by SRNL. Historically, Fe²⁺/Fe³⁺ measurements of this material have been in a range of 0.17 to 0.24.

Additional analytes were measured and reported that are not included in the original request. Among these are additional analytes that were obtained by ICP-MS and Cs-removed gamma. Because it was needed to interpret the Fe²⁺/Fe³⁺ results, samples were analyzed by ICP-ES for iron, which in turn yielded information on many other elemental components.

3.3 Results and Discussion

Table 3-3 contains the results of the physical methods performed on the Tank 12H BOA cleaning samples. Result averages for density and weight percent total and dissolved solids are reported along with standard deviations. Calculated values for weight percent insoluble solids are reported along with a 95% confidence intervals (C.I.) determined from uncertainty propagation. The samples contained insoluble solids ranging from 0.00 wt % to 0.34 wt % (with 95% confidence intervals typically 0.1 wt % to 0.2 wt %). The slurry densities for the first and second strike samples were typically around 1.012 g/mL within experimental uncertainty. Both the density and the weight percent dissolved solids were lower for the third batch samples than for the first and second batch samples.

Table 3-3. Solids and Density Measurements for BOA Cleaning Dip Samples

Sample	Total Solids (wt% in slurry)			Dissolved Solids (wt% in filtrate)			Insoluble Solids (wt% in slurry)		Density (g/mL)	
	avg.	st.dev.	n	avg.	st.dev.	n	avg.	95% C.I.	avg.	st.dev.
HTF-12-13-93	1.35	0.03	3	1.35	0.08	3	0.00	0.22	1.012	0.002
HTF-12-13-100	1.44	0.03	3	1.36	0.06	3	0.09	0.16	1.010	0.004
HTF-12-13-102	1.63	0.08	4	1.51	0.09	4	0.13	0.15	1.014	0.002
HTF-12-13-116	1.76	0.06	3	1.43	0.07	4	0.34	0.13	1.011	0.002
HTF-12-13-127	0.82	0.08	4	0.76	0.06	4	0.06	0.13	1.007	0.002

Table 3-4. Iron Oxidation State Results for Soluble Portion of BOA Cleaning Samples

Sample Name	Sample Analysis		EA Glass
	Fe ²⁺ /Fe ³⁺	Fe ²⁺ /Total Fe	Fe ²⁺ /Fe ³⁺
HTF-12-13-102	0.013	0.012	0.22
Strike 1 End	0.020	0.019	0.22
HTF-12-13-116	0.015	0.015	0.20
Strike 2 End	0.010	0.010	0.20
HTF-12-13-127	0.009	0.009	0.21
Strike 3 End	0.017	0.016	0.21

Table 3-4 contains the iron oxidation state measurement results for the three end-of-strike samples. For comparison, the results for the quality assurance standard (EA Glass) are also included. For all three end-of-strike samples, Fe²⁺ content was 2% or less of the total iron (ranging from 0.9 % to 1.9%). The Fe²⁺/Fe³⁺ ratio for EA Glass matched the target value of and the historical range 0.17 to 0.24%

Corrosion of carbon steel in a reducing acid such as oxalic acid can result in the generation of hydrogen gas. However, electrochemical testing demonstrated that reduction of a ferric oxalate species, rather than hydrogen evolution, is the preferred cathodic reaction when dissolved sludge is present.^{8,9} In contrast, in pure oxalic acid,¹⁰ or after an extended period of stagnant exposure to carbon steel,^{11,8} hydrogen evolution may become the dominant cathodic reaction. The dominance of the hydrogen evolution reaction is presumed to be due to consumption of the ferric oxalate species, which results in an overall decrease in the concentration of ferric ion. Monitoring the total iron and the relative amount of ferric species present throughout the process assists in the assessment of whether there was a significant change in the ferric species.

Table 3-5 indicates that the dissolved iron concentration remained relatively constant for the three strikes ranging between 1100 to 1530 ppm. This concentration range is similar to what was observed during the laboratory work.⁸ Likewise the percentage of soluble iron that was ferric ion remained relatively constant, and very high at approximately 98-99%. At these levels of dissolved ferric ion concentrations, ferric oxalate reduction is expected to have been the dominant cathodic reaction throughout the process. Controlling the exposure time of the carbon steel to oxalic acid appears to have reduced the likelihood of ferric ion consumption.

Table 3-5, Table 3-6, Table 3-7 and Table 3-8 contain results for the analysis of the supernatant portion of the dip samples. In most cases, a single aliquot of undiluted sample was sent to the analyst for measurement, and thus no standard deviations are reported for these analytical results. Therefore, the analytical uncertainties should be considered as the nominal uncertainties for the analytical methods, which are 10 % for ICP-ES and 20 % for ICP-MS.

Table 3-5 contains the elemental analysis performed through ICP-ES. Although ICP-ES analysis was not in the original request for the dip sample analysis by SRNL, it was required in order to interpret the iron speciation results. The ICP-ES results reveal that BOA cleaning was effective in dissolving at least a portion of many elemental components of the Tank 12H heel sludge. The

dissolved components present at the highest levels in the dip samples are iron, sodium, manganese, uranium, and aluminum.

Table 3-6 and Table 3-7 contain the full fission product and actinide portions of the ICP-MS results. Table 3-8 contains the isotopic results that were measured by ICP-MS or radiochemical counting methods. I-129 and Am-241 were below the method detection limits in the supernatant portions of the dip samples throughout chemical cleaning. Pu-238 was present in the dip sample supernate at up to 0.6 $\mu\text{Ci/mL}$ (at the end of the first strike).

Measurement of strontium-90 and cesium-137 activities was not included in the analysis suite. However, beta/gamma was measured by Liquid Scintillation Counting (LSC) on samples prepared by dilution in nitric acid. This analysis was necessary to facilitate the removal of undiluted samples for the other analyses and the results are reported in Table 3-8. The beta/gamma measurement results can be used as an approximation of the combined activities of Sr-90 and its short-lived decay product Y-90, with a smaller contribution from Cs-137/Ba-137m.

Uranium exhibits a different trend from most of the other elemental and radiochemical analyses. The decrease in uranium concentration between the second and the third strikes is large relative to that for the other analytes. This low soluble uranium concentration in the third strike may indicate the lack of uranium available for dissolution. Thus, the removal of uranium from the Tank 12H heel may be nearly complete.

Table 3-5. ICP-ES Analysis of Soluble Portion of Tank 12H BOA Cleaning Dip Samples (mg/L)

element	Strike 1			Strike 2	Strike 3
	HTF-12-13-93	HTF-12-13-100	HTF-12-13-102	HTF-12-13-116	HTF-12-13-127
Ag	< 1.06E+00	< 1.06E+00	< 1.06E+00	< 1.06E+00	< 1.06E+00
Al	2.84E+02	3.13E+02	3.32E+02	4.24E+02	1.92E+02
B	< 1.95E+00	< 1.95E+00	< 1.95E+00	< 1.95E+00	< 1.95E+00
Ba	1.37E+00	1.13E+00	2.46E+00	3.04E+00	2.95E+00
Be	< 1.00E-01	< 1.00E-01	< 1.00E-01	< 1.00E-01	< 1.00E-01
Ca	3.95E+01	4.07E+01	4.85E+01	5.29E+01	2.24E+01
Cd	2.78E-01	2.91E-01	3.37E-01	2.99E-01	1.27E-01
Ce	< 1.00E+00	< 1.00E+00	< 1.00E+00	< 1.00E+00	< 1.00E+00
Co	< 2.11E-01	< 2.11E-01	< 2.11E-01	< 2.11E-01	< 2.11E-01
Cr	7.51E+00	7.31E+00	6.86E+00	8.06E+00	2.10E+00
Cu	2.51E+00	2.66E+00	3.61E+00	3.70E+00	2.75E+00
Fe	1.10E+03	1.32E+03	1.33E+03	1.53E+03	1.13E+03
Gd	< 2.35E+00	< 2.35E+00	< 2.35E+00	< 2.35E+00	< 2.35E+00
K	9.80E+00	9.23E+00	9.59E+00	9.83E+01	< 5.20E+00
La	< 1.42E+00	< 1.42E+00	< 1.42E+00	< 1.42E+00	< 1.42E+00
Li	8.31E+00	8.77E+00	8.66E+00	4.13E+00	3.74E-01
Mg	1.34E+01	1.45E+01	1.71E+01	1.30E+01	4.70E+00
Mn	7.09E+02	7.47E+02	8.36E+02	8.53E+02	2.73E+02
Mo	< 8.30E-01	< 8.30E-01	< 8.30E-01	< 8.30E-01	< 8.30E-01
Na	1.04E+03	1.07E+03	1.10E+03	6.02E+02	3.36E+02
Ni	1.23E+00	1.24E+00	5.42E+00	4.89E+00	3.90E+00
P	1.38E+01	1.55E+01	1.55E+01	1.31E+01	5.32E+00
Pb	< 9.80E-01	< 9.80E-01	< 9.80E-01	1.17E+00	9.98E-01
S	1.41E+02	1.39E+02	1.40E+02	1.01E+02	< 8.00E+01
Sb	< 2.90E+00	< 2.90E+00	< 2.90E+00	< 2.90E+00	< 2.90E+00
Si	1.19E+02	1.23E+02	1.34E+02	9.36E+01	3.02E+01
Sn	< 1.16E+00	< 1.16E+00	< 1.16E+00	< 1.16E+00	< 1.16E+00
Sr	3.75E+00	3.87E+00	3.99E+00	3.42E+00	1.43E+00
Th	6.04E+00	6.63E+00	1.15E+01	6.78E+00	7.31E+00
Ti	1.29E+00	1.41E+00	1.42E+00	1.07E+00	4.40E-01
U	4.99E+02	5.18E+02	5.42E+02	4.07E+02	5.84E+01
V	< 7.10E-01	< 7.10E-01	< 7.10E-01	< 7.10E-01	< 7.10E-01
Zn	< 1.98E-01	< 1.98E-01	5.46E-01	5.31E-01	4.48E-01
Zr	1.61E+01	1.75E+01	1.79E+01	1.40E+01	5.35E+00

**Table 3-6. ICP-MS Analysis for Fission Products in Soluble Portion of Tank 12H BOA
Cleaning Dip Samples (mg/L)**

mass [m/z]	Strike 1			Strike 2	Strike 3	mass [m/z]	Strike 1			Strike 2	Strike 3
	HTF-12-13-93	HTF-12-13-100	HTF-12-13-102	HTF-12-13-116	HTF-12-13-127		HTF-12-13-93	HTF-12-13-100	HTF-12-13-102	HTF-12-13-116	HTF-12-13-127
59	< 3.50E-02	< 3.50E-02	7.53E-02	1.63E-01	1.03E-01	123	1.90E-02	2.45E-02	2.98E-02	1.63E-02	< 1.00E-02
82	< 1.36E+00	< 1.36E+00	< 1.36E+00	< 1.36E+00	< 1.36E+00	124	2.92E-02	2.47E-02	3.34E-02	2.83E-02	2.36E-02
84	< 1.75E-01	< 1.75E-01	< 1.75E-01	< 1.75E-01	< 1.75E-01	125	2.49E-02	2.50E-02	3.07E-02	2.06E-02	< 1.00E-02
85	2.93E-02	1.86E-02	< 1.50E-02	< 1.50E-02	< 1.50E-02	126	6.39E-02	6.47E-02	7.27E-02	5.57E-02	2.57E-02
86	< 9.00E-02	< 9.00E-02	< 9.00E-02	< 9.00E-02	< 9.00E-02	128	2.58E-01	2.55E-01	2.69E-01	< 1.85E-01	< 1.85E-01
87	6.86E-02	8.27E-02	7.58E-02	5.99E-02	2.03E-02	130	1.13E+00	1.35E+00	1.29E+00	9.95E-01	3.23E-01
88	2.45E+00	2.55E+00	2.64E+00	2.29E+00	1.00E+00	133	1.05E-01	1.23E-01	1.16E-01	7.88E-02	2.01E-02
89	< 1.00E-02	1.24E-02	9.40E-02	6.86E-01	4.76E-01	134	< 8.00E-02	< 8.00E-02	< 8.00E-02	< 8.00E-02	< 8.00E-02
90	3.11E+00	3.42E+00	3.49E+00	2.93E+00	1.22E+00	135	3.94E-02	2.02E-02	3.69E-02	4.10E-02	2.60E-02
91	2.69E+00	3.01E+00	3.09E+00	2.48E+00	9.07E-01	136	< 5.50E-02	< 5.50E-02	< 5.50E-02	< 5.50E-02	< 5.50E-02
92	3.03E+00	3.34E+00	3.33E+00	2.66E+00	9.93E-01	137	2.10E-01	1.96E-01	3.55E-01	3.81E-01	3.33E-01
93	4.06E+00	4.62E+00	4.55E+00	3.55E+00	1.38E+00	138	1.02E+00	8.82E-01	1.85E+00	2.39E+00	2.38E+00
94	3.19E+00	3.52E+00	3.47E+00	2.76E+00	1.05E+00	139	< 1.00E-02	< 1.00E-02	4.56E-02	6.37E-01	6.44E-01
95	1.16E-01	1.04E-01	9.78E-02	1.06E-01	5.80E-02	140	< 1.00E-02	< 1.00E-02	3.82E-02	5.45E-01	3.53E-01
96	3.24E+00	3.61E+00	3.62E+00	3.07E+00	1.16E+00	141	< 1.00E-02	< 1.00E-02	4.53E-02	5.32E-01	4.69E-01
97	4.25E-02	4.71E-02	5.40E-02	4.76E-02	1.91E-02	142	< 1.00E-02	< 1.00E-02	3.82E-02	5.05E-01	3.33E-01
98	5.34E-02	6.88E-02	7.18E-02	8.50E-02	3.63E-02	143	< 1.00E-02	< 1.00E-02	4.86E-02	5.19E-01	4.21E-01
99	2.16E-02	2.43E-02	1.91E-02	1.22E-02	< 1.00E-02	144	< 1.00E-02	< 1.00E-02	5.53E-02	5.61E-01	3.53E-01
100	1.01E-01	1.12E-01	1.31E-01	9.65E-02	3.61E-02	145	< 1.00E-02	< 1.00E-02	2.92E-02	3.45E-01	2.74E-01
101	2.46E+00	2.60E+00	2.60E+00	2.07E+00	1.07E+00	146	< 1.00E-02	< 1.00E-02	2.01E-02	2.63E-01	2.16E-01
102	2.28E+00	2.37E+00	2.38E+00	1.93E+00	9.90E-01	147	< 1.00E-02	< 1.00E-02	1.44E-02	1.98E-01	1.34E-01
103	1.05E+00	1.11E+00	1.14E+00	7.59E-01	2.40E-01	148	< 1.00E-02	< 1.00E-02	1.30E-02	1.60E-01	1.33E-01
104	1.08E+00	1.16E+00	1.15E+00	9.05E-01	4.39E-01	149	< 1.00E-02	< 1.00E-02	< 1.00E-02	2.54E-02	1.26E-02
105	< 1.50E-02	< 1.50E-02	< 1.50E-02	< 1.50E-02	< 1.50E-02	150	< 1.00E-02	< 1.00E-02	1.18E-02	1.53E-01	1.20E-01
106	< 2.50E-02	< 2.50E-02	< 2.50E-02	< 2.50E-02	< 2.50E-02	151	< 1.00E-02	< 1.00E-02	< 1.00E-02	2.87E-02	1.44E-02
107	2.17E-02	1.92E-02	7.12E-02	3.65E-02	2.05E-02	152	< 1.00E-02	< 1.00E-02	< 1.00E-02	4.38E-02	2.98E-02
108	1.63E-02	1.91E-02	1.08E-02	1.02E-02	< 1.00E-02	153	< 1.00E-02	< 1.00E-02	< 1.00E-02	2.41E-02	1.49E-02
109	< 5.50E-02	< 5.50E-02	< 5.50E-02	< 5.50E-02	< 5.50E-02	154	< 1.00E-02	< 1.00E-02	< 1.00E-02	1.12E-02	< 1.00E-02
110	3.04E-02	3.34E-02	4.24E-02	3.81E-02	1.65E-02	155	< 1.00E-02	< 1.00E-02	< 1.00E-02	1.02E-02	< 1.00E-02
111	3.00E-02	3.16E-02	3.79E-02	3.42E-02	1.28E-02	156	< 1.00E-02	< 1.00E-02	< 1.00E-02	1.08E-02	< 1.00E-02
112	8.04E-02	6.90E-02	8.83E-02	6.37E-02	1.70E-02	180	1.01E-02	< 1.00E-02	< 1.00E-02	< 1.00E-02	< 1.00E-02
113	< 4.10E-01	< 4.10E-01	< 4.10E-01	< 4.10E-01	< 4.10E-01	181	1.25E-01	1.32E-01	1.40E-01	1.05E-01	5.18E-02
114	6.21E-02	5.95E-02	6.78E-02	6.78E-02	< 2.00E-02	182	1.29E-01	3.02E-02	2.59E-02	2.46E-02	< 1.50E-02
116	7.33E-02	8.76E-02	1.40E-01	8.38E-02	8.72E-02	183	7.81E-02	1.77E-02	1.48E-02	1.20E-02	< 1.00E-02
117	1.46E-02	2.05E-02	1.87E-02	1.85E-02	1.66E-02	184	1.54E-01	4.30E-02	4.28E-02	3.55E-02	< 1.50E-02
118	6.65E-02	5.90E-02	5.72E-02	5.88E-02	3.47E-02	185	< 1.00E-02	< 1.00E-02	< 1.00E-02	< 1.00E-02	< 1.00E-02
119	2.30E+00	2.40E+00	2.48E+00	1.83E+00	3.09E-01	186	1.49E-01	3.27E-02	3.04E-02	2.93E-02	1.09E-02
120	5.83E-02	5.78E-02	6.14E-02	5.48E-02	4.44E-02	206	1.43E-01	1.50E-01	1.31E-01	2.52E-01	1.72E-01
121	1.78E-02	2.54E-02	2.35E-02	< 1.50E-02	< 1.50E-02	207	1.21E-01	1.23E-01	1.15E-01	1.98E-01	1.47E-01
122	2.05E-02	1.72E-02	1.80E-02	1.72E-02	1.14E-02	208	2.75E-01	2.76E-01	2.66E-01	5.04E-01	3.27E-01

Table 3-7. ICP-MS Analysis for Actinides in Soluble Portion of Tank 12H BOA Cleaning Dip Samples (mg/L)

mass [m/z]	Strike 1			Strike 2	Strike 3
	HTF-12-13-93	HTF-12-13-100	HTF-12-13-102	HTF-12-13-116	HTF-12-13-127
230	< 1.00E-02	< 1.00E-02	< 1.00E-02	< 1.00E-02	< 1.00E-02
232	3.88E+00	4.66E+00	9.57E+00	4.84E+00	7.03E+00
233	5.19E-02	7.50E-02	6.28E-02	5.43E-02	1.00E-02
234	8.34E-02	8.64E-02	8.07E-02	5.58E-02	< 1.00E-02
235	3.67E+00	4.16E+00	3.72E+00	2.67E+00	4.50E-01
236	1.01E-01	1.29E-01	1.30E-01	6.95E-02	< 1.00E-02
237	3.36E-01	3.33E-01	3.29E-01	2.54E-01	8.39E-02
238	4.69E+02	4.91E+02	4.93E+02	3.61E+02	5.91E+01
239	3.94E-01	4.96E-01	5.07E-01	3.83E-01	1.13E-01
240	2.86E-02	4.73E-02	3.85E-02	2.04E-02	< 1.00E-02
241	< 1.00E-02	< 1.00E-02	< 1.00E-02	< 1.00E-02	< 1.00E-02
242	< 1.00E-02	< 1.00E-02	< 1.00E-02	< 1.00E-02	< 1.00E-02
243	< 1.00E-02	< 1.00E-02	< 1.00E-02	< 1.00E-02	< 1.00E-02
244	< 1.00E-02	< 1.00E-02	< 1.00E-02	< 1.00E-02	< 1.00E-02

Table 3-8. Radionuclides Analyzed in Tank 12H BOA Cleaning Dip Samples (μCi/mL)

analyte	method	Strike 1			Strike 2	Strike 3
		HTF-12-13-93	HTF-12-13-100	HTF-12-13-102	HTF-12-13-116	HTF-12-13-127
Co-60	Cs-r γ	--	--	--	--	8.56E-05
Tc-99	Tc-99	2.02E-04	2.23E-04	2.59E-04	1.25E-04	< 1.79E-05
Tc-99	ICP-MS	3.67E-04	4.11E-04	3.24E-04	2.07E-04	< 1.70E-04
I-129	I-129	< 1.09E-04	< 1.03E-04	< 4.91E-05	< 3.87E-05	< 2.64E-05
Eu-154	Cs-r γ	--	--	--	3.68E-03	2.72E-03
Th-232	ICP-MS	4.25E-07	5.12E-07	1.05E-06	5.31E-07	7.71E-07
U-233	ICP-MS	5.03E-04	7.26E-04	6.08E-04	5.26E-04	9.71E-05
U-234	ICP-MS	5.21E-04	5.40E-04	5.04E-04	3.49E-04	< 6.25E-05
U-235	ICP-MS	7.94E-06	8.99E-06	8.04E-06	5.77E-06	9.73E-07
U-236	ICP-MS	6.54E-06	8.37E-06	8.38E-06	4.50E-06	< 6.47E-07
U-238	ICP-MS	1.58E-04	1.65E-04	1.66E-04	1.21E-04	1.99E-05
Np-237	ICP-MS	2.37E-04	2.35E-04	2.32E-04	1.79E-04	5.92E-05
Pu-238	PuTTA	4.03E-01	5.14E-01	5.95E-01	3.27E-01	7.48E-02
Pu-239/240	PuTTA	2.87E-02	3.36E-02	4.31E-02	3.17E-02	6.94E-03
Pu-239	ICP-MS	2.45E-02	3.08E-02	3.15E-02	2.38E-02	7.01E-03
Pu-240	ICP-MS	6.52E-03	1.08E-02	8.77E-03	4.65E-03	< 2.28E-03
Pu-241	Pu238/41	9.59E-02	1.22E-01	1.42E-01	8.24E-02	1.94E-02
Am-241	Cs-r γ	< 1.84E-02	< 1.00E-02	< 3.77E-02	< 3.44E-02	< 3.44E-03
Beta/Gamma	LSC	2.58E+02	2.91E+02	2.94E+02	2.39E+02	1.01E+02

3.4 F/H Lab Samples

For every sample received by SRNL (see Table 3-1) an analogous sample was received by F/H Lab for analysis. Due to turn-around-time considerations, some analyses were performed at F/H Lab rather than at SRNL. Results for the F/H Lab samples are contained elsewhere.⁴

4.0 Material Balance

4.1 Process Timeline

In order to perform a material balance, information about actual processing volumes was used and additional information was provided by email.^{4,12,13}

Prior to initiating Strike 1, there was approximately 4406 gallons of sludge heel and the tank liquid level 1.5 inches (4070 gallons).

For Strike 1, 64,551 gallons of 8 wt% OA were added, followed by approximately 73,400 gallons of well water, bringing the Tank 12H liquid level to 54.2 inches (147,000 gallons). At the conclusion of Strike 1, 115,000 gallons were transferred from Tank 12H to Tank 51H bringing the Tank 12H liquid level to 11.71 inches (31,700 gallons) and leaving an estimated 1263 gallons of sludge heel.

For Strike 2, 18,271 gallons of 8 wt% OA were added, followed by 46,000 gallons of well water, bringing the Tank 12H liquid level to 35.43 inches (96,000 gallons). At the conclusion of Strike 2, 70,100 gallons were transferred from Tank 12 to Tank 51 bringing the Tank 12H liquid level to 9.56 inches (25,900 gallons). For neutralization, 250 gallons of 50 wt % NaOH were added, followed by 71,100 gallons of well water, bringing the Tank 12H liquid level to 35.8 inches (97,000 gallons). At the conclusion of neutralization, 73,004 gallons were transferred Tank 51H and 867 gallons were transferred Tank 11H, bringing the Tank 12H liquid level to 9.44 inches (25,600 gallons) and leaving an estimated 1225 gallons of sludge heel.

For Strike 3, 23,889 gallons of 8 wt% OA were added, followed by 46,200 gallons of well water, bringing the Tank 12H liquid level to 35.29 inches (95,600 gallons). At the conclusion of Strike 3, 71,300 gallons were transferred from Tank 12H to Tank 51H bringing the Tank 12H liquid level to 8.97 inches (24,300 gallons). For neutralization, 250 gallons of 50 wt % NaOH were added, followed by 69,078 gallons of well water, bringing the Tank 12H liquid level to 35.2 inches. At the conclusion of neutralization, 52,384 gallons were transferred Tank 51H and 41,544 gallons were transferred Tank 11H, bringing the Tank 12H liquid level to 2.0 inches and leaving an estimated 1,000 gallons of sludge heel.¹⁴

4.2 Material Balance and Discussion

In order to perform a material balance, the following assumptions were made. Each assumption limits the applicability of the material balance calculation.

- First, the results for the soluble portions of the dip samples are assumed to be the material removed from the tank. Thus, any suspended insoluble solids that may have been transferred are not included. From the sample analysis information, it is not possible to estimate the removal of insoluble components during BOA cleaning.
- Second, the initial scale sample analysis is assumed to be representative of the entire tank heel. Because the scrape sample was collected from only one area of the tank, we do not have any information on heel material from other areas of the tank. Variations in the tank

solids heel that are not reflected in the initial scrape sample analysis have not been considered.

Additional uncertainties are introduced by tank volume measurements and the analytical measurement uncertainties. Volatile elements, such as Hg, do not include losses through the tank ventilation system. Sodium is not expected to give a good mass balance for the third strike. The calculation does not include the contribution from sodium contained in the sodium hydroxide added for neutralization after strikes two and three.

A material balance based only on an initial sample of tank heel solids from a single location and samples of solids-free supernatant liquid from the end of each strike requires multiple assumptions to be made that in-turn limit the applicability of the material balance for determining the amount and composition of the solids remaining in the tank. Different assumptions can be made regarding initial composition of heel solids that can influence the material balance. For example, some material balances assume that the solids under the Tank 12H valve house have a composition more similar to the Tank 12H bulk sludge removal slurries than that of the initial scrape sample used in this analysis.

Results of the material balance are given in Table 4-1, Table 4-2, and Table 4-3. Masses of soluble constituents removed during each of the three strikes are given in the "Removed" columns and are based on results of the dip sample analyses of Section 3.3 and the process timeline of Section 4.1. In contrast, the total "Original" masses of the constituent are given in the first "Solids" column and are based solely on results of the scrape solids analyses. Estimated percentages of constituents removed through all three strikes are given in the far-right column and are calculated using a combination of the dip sample results and the scrape sample results of Section 2.3. As previously discussed, the removal percentage values should be viewed as order of magnitude estimates, since they are prone to high uncertainties due to expected sample heterogeneities, particularly those of the scrape solids sample. Nevertheless, the removal percentage figures are assumed to provide a reasonable indication of whether large or small portions of each constituent effectively dissolved during the course of the three cleaning strikes.

Based on the results, there appear to be four general categories of constituent removals: 1) those that are high, suggesting near-complete removal; 2) those that are moderate, suggesting significant partial removal; 3) those that are low to borderline moderate, suggesting minor removal; and 4) those that are trivial, suggesting negligible removal. Sodium, potassium, technetium, and phosphorus fall into the first category, with estimated removal values of 90% and above. Uranium, gross beta/gamma, chromium, iron, magnesium, calcium, zirconium, and silicon fall into the second category, with estimated removal values ranging from 40 to 70%. Plutonium, aluminum, manganese, copper, barium, and lithium fall into the third category, with estimated removal values ranging from 16 to 35%. Mercury, thorium, and nickel fall into the fourth category, with estimated removal values of 6% or less.

Final characterization of the tank heel during tank closure can be used to support and further understand the material balance for BOA cleaning. The material balance should be reevaluated when additional sample information becomes available.

Table 4-1. Material Balance for Major Chemical Components

Analyte	Removed (kg)				Soldis (kg)		Removal*
	Strike 1	Strike 2	Strike 3	Total	Original	Remaining	
Al	145	113	52	309	925	616	33%
Ba	1	1	1	3	14	11	19%
Ca	21	14	6	41	81	40	51%
Cr	3	2	1	6	9	3	64%
Cu	2	1	1	3	11	8	29%
Fe	580	406	305	1291	2704	1413	48%
Hg***	<23	<14	<4	<41	641	>600	<6%
K	4	26	<1	32	12	-19	>100%
Li	4	1	0	5	30	25	17%
Mg	7	3	1	12	23	11	53%
Mn	364	226	74	664	2194	1530	30%
Na	479	160	91	730	386	-344	>100%
Ni	2	1	1	5	198	193	2%
P	7	3	1	12	13	1	91%
S	61	27	<22	88	--	--	--
Si	58	25	8	91	224	133	41%
Sr	2	1	0	3	8	5	36%
Th	5	2	2	9	166	157	5%
U	236	108	16	360	526	166	68%
Zr	8	4	1	13	29	16	44%
Th-232**	4	1	2	7	151	143	5%
Total U**	216	97	16	329	526	197	63%

* Removal percentages are reported with greater precision than overall uncertainty warrants

** Dip sample values by ICP-MS *** Dip sample values from F/H-Lab

Table 4-2. Material Balance for Radionuclides

Analyte	Removed (Ci)				Solids (Ci)		Removal*
	Strike 1	Strike 2	Strike 3	Total	Original	Remaining	
Tc-99	0.113	0.033	0.005	0.151	0.079	0	>100%
Eu-154	--	0.98	0.73	1.71	56.5	54.8	3%
Np-237	0.101	0.047	0.016	0.164	0.415	0.251	40%
Pu-238	259	87	20	366	877	511	42%
Pu-239/240	18.8	8.4	1.9	29.1	89.4	60.3	33%
Pu-241	62.0	21.9	5.2	89.1	--	--	--
$\beta+\gamma$	1.28E+05	6.34E+04	2.73E+04	2.19E+05	4.84E+05	2.65E+05	45%

* Removal percentages are reported with greater precision than overall uncertainty warrants

Table 4-3. Material Balanced based on F/H Lab Dip Sample Characterization

Analyte	Removed				Solids		Removal*
	Strike 1	Strike 2	Strike 3	Total	Original	Remaining	
Al (kg)	<29	96	56	151	925	774	16%
Fe (kg)	384	358	302	1045	2704	1658	39%
Mn (kg)	342	219	76	637	2194	1557	29%
$\beta+\gamma$ (Ci)	1.09E+05	7.88E+05	4.55E+03	9.02E+05	4.84E+05	-4.18E+05	>100%

* Removal percentages are reported with greater precision than overall uncertainty warrants

Table 4-4 contains a comparison of the Tank 12H BOA cleaning with previous acidic chemical cleaning results for Tanks 5F and 6F.^{15,16} Note that for Tanks 5F and 6F, the cleaning process flowsheet differed considerably from that used for Tank 12H. Also the material balances for Tank 5F and 6F chemical cleaning were established differently than the mass balance for Tank 12H. The material balances for Tanks 5F and 6F were calculated using a set of dip samples and an end-of-process solids sample, while the material balance for Tank 12H used analogous dip samples but a pre-cleaning solids sample. Relative to Tank 5F and 6F, the Tank 12H material balance likely lacks accuracy when solids are nearly completely removed and the method of calculation allows for removal percentages of >100%.

With a couple of exceptions, the estimated removal percentages for the Tank 12H samples are on the same order of magnitude as those seen in previous BOA cleaning campaigns. For example, during BOA cleaning of Tank 5F, a) uranium, aluminum, calcium, and sodium showed high removal; b) zirconium, lithium, manganese, and magnesium showed moderate removal; c) iron, silicon, chromium, and barium showed low removal; and d) nickel showed negligible removal. Although the removal values for Tank 5F are not identical to those of Tank 12H, they are reasonably consistent, with exception of those for aluminum. However, given the difference between the PUREX receipts at Tank 5F (low aluminum) and the HM receipts at Tank 12H (high

aluminum), a clear difference of aluminum chemistry is to be expected. Also, a low temperature aluminum removal campaign had been performed in Tank 12H prior to BOA cleaning, likely causing the aluminum remaining in the tank heel to be exclusively the more difficult to dissolve boehmite phase. Plutonium and technetium removal were considerably higher in Tank 12H than for either Tank 5F or 6F; and removal of strontium (as evident through gross beta/gamma removal) was lower in Tank 12H than in Tanks 5F and 6F. The lower calculated uranium percent removal in Tank 12H compared with the previous campaigns is likely due to initial heel heterogeneity. The lower levels of soluble uranium in the third strike cleaning solution is consistent with a high degree of uranium removal from Tank 12H.

Table 4-4. Comparison of Calculated Removal Percentages During the Current Tank 12H BOA Cleaning and Previous Tank 5F and 6F Chemical Cleaning

Analyte	Material Balance, % Removal		
	Tank 12H	Tank 5F	Tank 6F
Fe	48%	21%	69%
U	63% - 68%	89%	79%
Mn	30%	40%	47%
Ni	2%	1%	2%
Na	>100%	88%	75%
Al	33%	81%	85%
Pu-238	42%	5%	13%
Pu-239/240	33%	6%	14%
Tc-99	>100%	41%	2%
$\beta+\gamma$	45%	83%	87%
Np-237	40%	70%	73%
Hg	<6%	--	--
Ca	51%	92%	91%
Th	5%	--	--
Si	41%	26%	89%

5.0 Conclusions

The following are the key observations for Tank 12H Scrape Sample HTF-12-12-107 taken prior to BOA cleaning of the tank heel:

- Iron and manganese were the primary components, followed by aluminum, mercury, uranium, sodium, silicon, nickel and thorium.
- Compared with previous Tank 12H sludge samples, the scrape sample had a relatively low aluminum:iron ratio of approximately 1:3.
- In terms of activity on a wet basis, the primary radionuclides are strontium-90 at 8.7×10^3 $\mu\text{Ci/g}$ and cesium-137 at 1.7×10^2 $\mu\text{Ci/g}$.

The following are the key observations for the Tank 12H Supernate Samples taken during BOA cleaning. One sample was removed at the end of each BOA cleaning strike. Additionally, two intermediate samples were analyzed for the first BOA cleaning strike.

- The samples contained insoluble solids with a measured range of 0.00 wt % to 0.34 wt %. Chemical and radiological analyses were performed on solids-free filtrate.
- Fe²⁺ content was 2% or less of the total iron (ranging from 0.9% to 1.9%) for each strike.
- Based on the soluble ferric species concentrations at the end of each of the three BOA cleaning strikes, ferric ion reduction was the primary cathodic reaction during chemical cleaning and not hydrogen gas generation. Controlling the exposure time of the carbon steel to the oxalic acid appears to have been effective in mitigating evolution of the flammable gas.
- The major components in the supernate were iron, sodium, manganese, uranium, and aluminum.
- Pu-238 was present in the supernate at up to 0.6 µCi/mL (at the end of the first strike).
- I-129 and Am-241 were below the method detection limits.

The following are the key observations for the material balance constructed from the Tank 12H sample data:

- A material balance based only on an initial sample of tank heel solids from a single location and samples of solids-free supernatant liquid from the end of each strike requires multiple assumptions to be made that in-turn limit the applicability of the material balance for determining the amount and composition of the solids remaining in the tank.
- Components that had high, near-complete removal (>85%) include sodium, potassium, and phosphorus.
- Components that had moderate, significant partial removal (40% to 70%) include uranium, gross beta/gamma, chromium, iron, magnesium, calcium, zirconium, and silicon.
- Components that had low to borderline moderate, minor removal (15% to 35%) include plutonium, aluminum, manganese, copper, barium, and lithium.
- Components that had low, negligible removal (<6%) include mercury, thorium, and nickel.

6.0 Quality Assurance

Data are recorded in the electronic laboratory notebook system, notebook numbers A6583-00032.

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 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.

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