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Characterization of Tank 11H Samples from Tank Closure Cesium Removal (TCCR) Batch 3 - Intermediate and Final Samples

K. M. L. Taylor-Pashow

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November 2020

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LIST OF REVISIONS		
Revision Number	**Summary of Changes**	**Date**
0	Initial issue	11/2/2020
1	Includes additional analysis results for fourth interim surface and Post-Production surface and variable depth samples	11/13/2020

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EXECUTIVE SUMMARY

Savannah River Remediation (SRR) is currently operating the Tank Closure Cesium Removal (TCCR) process to remove ^{137}Cs from tank waste supernate using an ion exchange process. The TCCR unit processes dissolved salt from Tank 10H through a series of ion exchange columns containing crystalline silicotitanate (CST) and the effluent is then discharged to Tank 11H. Four interim samples pulled from Tank 11H during and just after the completion of processing of Batch 3 through the TCCR process have been analyzed for ^{137}Cs activity and density. The ^{137}Cs activity was found to decrease with each subsequent sample, which is consistent with the addition of decontaminated solution to Tank 11H. When compared to the expected composition from mixing the Tank 10H Batch 3 feed with the material already present in Tank 11H, the bulk chemical composition was as expected. A corrosion control sample collected from Tank 11H in June 2020 showed changes in the chemical composition and ^{137}Cs activity when compared to the composition measured at the end of Batch 2 processing. As there were no additions made to the tank during this period, these changes were attributed to leaching of the solids present in Tank 11H. Revision 1 of this report contains additional analyses of the fourth interim sample including inductively coupled plasma – mass spectrometry (ICP-MS) results and activities of other radionuclides. These results are consistent with the previously reported results, showing leaching from the Tank 11H heel. Notably, the ^{90}Sr activity was about 2.7x higher than calculated from a mixture of the original Tank 11H supernate and the Tank 10H supernate as treated by TCCR, suggesting additional leaching of Sr from the Tank 11H heel solids. In addition, Revision 1 includes analysis results for the Batch 3 Post-Production surface and variable depth samples collected in October of 2020. The Post-Production surface sample was similar in composition to the fourth interim surface sample, except for the increased Cs-137 and oxalate concentrations that were presumably associated with leaching of the Tank 11H heel solids.

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LIST OF ABBREVIATIONS

AD	Analytical Development
CST	crystalline silicotitanate
ELN	electronic laboratory notebook
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
M&TE	Measurement and Test Equipment
n/a	not applicable
PMP	polymethylpentene
RSD	relative standard deviation
SRNL	Savannah River National Laboratory
TCCR	Tank Closure Cesium Removal
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request

1.0 Introduction

Savannah River Remediation (SRR) is currently operating the Tank Closure Cesium Removal (TCCR) process to remove ^{137}Cs from tank waste supernate using an ion exchange process. The TCCR unit processes dissolved salt from Tank 10H through a series of ion exchange columns containing crystalline silicotitanate (CST) and the effluent is then discharged to Tank 11H. In support of the TCCR program, SRNL analyzed samples taken from Tank 11H during and at the completion of Tank 10H Batch 3 dissolved saltcake processing. Tank 11H serves as the receipt tank for the filtered and cesium removed product from the TCCR system. TCCR processing of Batch 3 commenced on July 30, 2020, and completed on August 28, 2020, after processing approximately 89,500 gallons. Three interim samples were collected from Tank 11H during processing, and a fourth interim sample was collected just after processing completed. A final set of Post-Production surface and variable depth samples were collected from Tank 11H prior to the transfer of material to Tank 50H. During the approximately 6-week period between the collection of the fourth interim sample and the Post-Production samples, the columns were flushed with caustic and water and the flushes were transferred to Tank 11H. From September 16 to 18, 2020, the CST columns were each flushed with 300 gallons of 2M NaOH for a total of 1,149 gallons. On September 21, 2020, a 100 gallon well water line flush was transferred to Tank 11H. On October 8, 2020, 400 gallons of well water were flushed through each column into Tank 11H for a total of 1,608 gallons. The Post-Production samples were collected on October 16, 2020.

During processing of Batch 3, different column configurations and flow rates were used. Table 1-1 provides a summary of the Batch 3 processing configurations as well as when the four interim Tank 11H samples were collected. The four columns in the TCCR unit are designated A, B, C, and D. Column D was first used during processing of Batch 3, while the first three columns had been used to varying extents during Batch 1A and Batch 2 processing. When a series of columns are listed in the configuration the flow proceeds in sequence through the columns in the order listed. All tank samples were delivered to SRNL for analysis.

Table 1-1. Summary of TCCR Tank 10H Batch 3 Dissolved Saltcake Feed Processing and Tank 11H Receipt Tank Sample Collection Events

Evolution	Column Configuration	Flow Rate (gpm)	Gallons Processed	Start Date	End Date
1	A	5	2,981	7/30/20	7/30/20
2	AB	5	22,222	8/1/20	8/4/20
3	AB	4	7,317	8/4/20	8/5/20
4	AB	8	5,691	8/5/20	8/5/20
5	Tank 11H 1st Interim Surface Sample HTF-11-20-70			8/6/20	8/6/20
6	ABC	8	8,130	8/6/20	8/7/20
7	ABC	5	9,485	8//7/20	8/9/20
8	Tank 11H 2nd Interim Surface Sample HTF-11-20-71			8/13/20	8/13/20
9	D	5	4,065	8/17/20	8/17/20
10	D	4	10,027	8/17/20	8/20/20
11	Tank 11H 3rd Interim Surface Sample HTF-11-20-74			8/21/20	8/21/20
12	ABCD	5	2,168	8/24/20	8/24/20
13	ABCD	4	17.344	8/24/20	8/28/20
14	Tank 11H 4th Interim Surface Sample HTF-11-20-77			9/1/20	9/1/20
15	Tank 11H Final Samples HTF-11-20-92 (Surface) and HTF-11-20-93 (Variable Depth)			10/16/20	10/16/20

At the start of Batch 3 processing Tank 11H contained the product (~58,000 gallons) of Batch 2 material that had been added to the tank from June 21 to 29, 2019 as well as a previous heel of about 19,700 gallons

present prior to the addition of the Batch 2 product. Tank 11H is also known to contain a layer of solids (level of ~4 inches) at the bottom of the tank.[1] Tank 11H does not possess any mixing equipment, and additions to the tank are made at the liquid surface.

The TCCR effluent enters Tank 11H through Riser 2 on the top of the tank, and samples are collected from Riser 4. These two risers are approximately 90° apart relative to the central tank support column. The TCCR effluent enters the tank through a "down-comer" that ends three feet from the tank ceiling (at a height of 258 inches). The liquid level in Tank 11H during processing of Batch 3 increased from 31.7 inches at the start of processing to 63.7 inches at the completion of processing. Therefore, the distance between the end of the effluent "down-comer" and the surface of the liquid in Tank 11H ranged from 194.3 to 226.3 inches (or 16.2 to 18.9 feet).

2.0 Experimental Procedure

2.1 Tank 11H Interim Samples

A total of four interim samples were received from Tank 11H during and just after processing of Batch 3. Each sample was contained in a single 82-mL dip sample bottle. The samples were each placed into the Shielded Cells, opened, and then transferred into clear polymethylpentene (PMP) beakers for visual observation. The density of each sample was then measured, in duplicate, with a measurement and test equipment (M&TE) calibrated balance using 2-mL density tubes at ambient temperature. Samples used for density measurements were returned to the corresponding original sample bottle. Aliquots of each sample were then submitted to Analytical Development (AD) undiluted for gamma spectroscopy analysis as requested by the customer.[2] The fourth sample was also analyzed for the full suite of analytes described in the Task Technical and Quality Assurance Plan (TTQAP).[3]

2.2 Tank 11H Post-Production Samples

Two Tank 11H Post-Production surface and variable depth samples collected approximately 6 weeks (44 days) after completion of TCCR Tank 10H Batch 3 processing were received in single (~200 mL) dip bottles. The samples were each placed into the Shielded Cells, opened, and then transferred into clear PMP beakers for visual observation. Aliquots of each sample were submitted to AD undiluted for the suite of analyses requested by the customer. This suite included wet chemistry (Free OH^-, Total Inorganic and Organic Carbon, IC anion, and ICP-ES), gamma, and liquid scintillation counting analysis for the surface sample, but only gamma and liquid scintillation counting analysis for the variable depth sample. The density of each sample was then measured, in duplicate, with a M&TE calibrated balance using 2-mL density tubes at ambient temperature. Samples used for density measurements were returned to the corresponding original sample bottles.

2.3 Quality Assurance

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.[4] This work was performed following the applicable TTQAP.[3] The Task Technical Request (TTR) associated with this work[5] requested a functional classification of Safety Significant (see section 9.5 of the TTQAP entitled "Clarification of Safety Significant Functional Classification"). To meet the requested functional classification requirements, this report and calculations within received a technical review by design verification.[6] Data are recorded in the Electronic Laboratory Notebook (ELN) system.[7]

3.0 Results and Discussion

3.1 Tank 11H Interim Surface Samples

All the interim surface samples received from Tank 11H during TCCR processing were similar in appearance, clear and colorless with no evidence of solids. Photographs of the samples are provided in Figure 3-1.

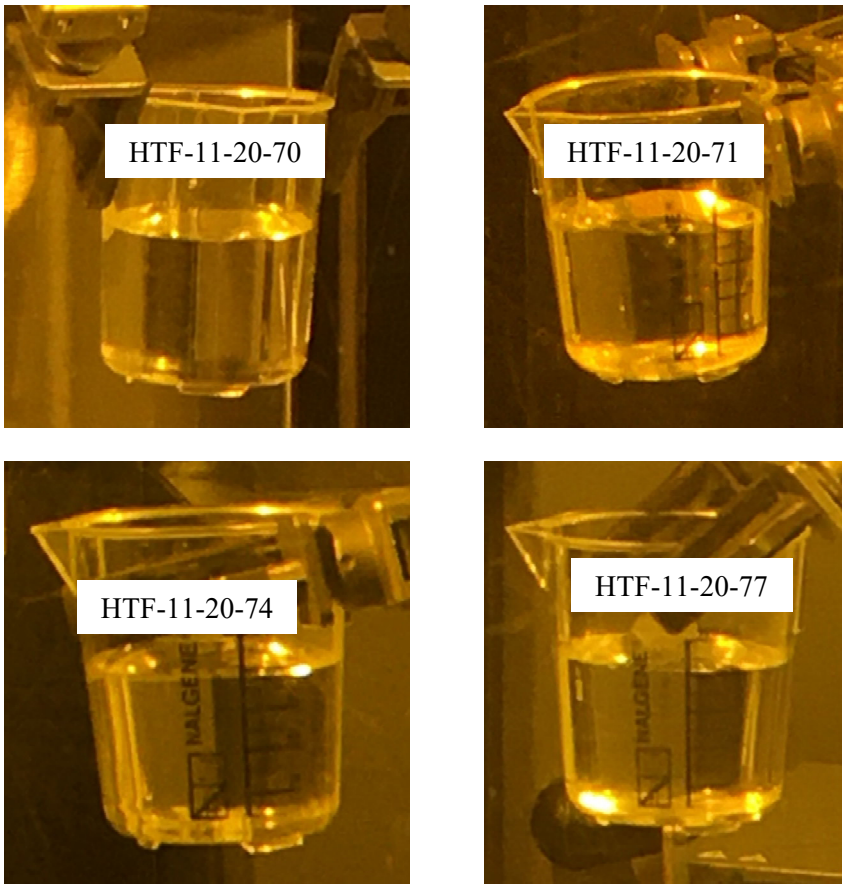

Figure 3-1. Photographs of the Four Tank 11H Interim Surface Samples.

A summary of the measured densities for each of the four interim samples is provided in Table 3-1. For comparison the density of the post-Batch 2 Tank 11 sample was 1.152 g/mL (0.21% RSD, 26 °C)[8] and the density of the Tank 10H Batch 3 material being processed through TCCR and added to Tank 11H was 1.174 g/mL (0.18% RSD, 26 °C).[9] The density of a corrosion control sample collected on June 2, 2020, from Tank 11H was 1.190 g/mL (0.11% RSD).[10] The Tank 11H interim samples showed an increasing trend in density, with the exception of the fourth sample, which was slightly lower than the third sample, although the third sample had a slightly higher %RSD.

As discussed in the introduction, different column configurations were used during processing of Batch 3, including the use of one, two, three, or all four columns. The final column in Table 3-1 indicates which column configuration was run prior to collecting each Tank 11H sample.

Table 3-1. Summary of Tank 11H Interim Sample Densities

Sample ID	Date Collected	Density (g/mL) (%RSD)	Temp. During Density Measurement	Column Configuration Prior to Sampling
HTF-11-20-70	8/6/20	1.184 (0.12%)	24 °C	A and AB
HTF-11-20-71	8/13/20	1.219 (0.17%)	25 °C	ABC
HTF-11-20-74	8/21/20	1.237 (1.80%)	28 °C	D
HTF-11-20-77	9/1/20	1.214 (0.52%)	30 °C	ABCD

Undiluted Tank 11H interim samples were all submitted for gamma spectroscopy analysis to determine the ^{137}Cs activities. Duplicate samples were removed from each parent bottle and submitted for analysis along with a blank sample (deionized water) with each set. Analysis of the duplicate samples for the first and second interim samples (received and prepared on different days) showed about 20% RSD between the replicate samples. Samples from the first interim sample were re-prepared and reanalyzed by AD, resulting in nearly identical results. Based on this, new duplicate aliquots were prepared from both the first and second interim samples and were submitted for analysis, again without dilution. Results from analysis of the new duplicate samples showed high consistency between the duplicate samples as well as with the higher activity sample from the original set of duplicates. A summary of all ^{137}Cs activities for these two samples is provided in Table 3-2. The cause of the lower activity in the single sample in each set of original duplicates is unknown, but one possible explanation could be that contamination of the parent bottle with additional ^{137}Cs occurred between removing the first and second aliquots from each of the parent bottles. Therefore, the single sample result with lower ^{137}Cs may be a more accurate measure of activity of the Tank 11H sample, although this is not known for certain. A corrosion control sample (HTF-11-20-50) collected from Tank 11H on June 2, 2020 had a reported ^{137}Cs activity of 2.24E+06 dpm/mL.[10] The total supernate volume in Tank 11H at the start of Batch 3 processing was estimated to be approximately 77,732 gallons based on 12,791 gallons remaining after the transfer out of the soak water added prior to Batch 2[11], plus 6,947 gallons of 25 wt% NaOH added prior to Batch 2 processing, and the addition of 57,994 gallons from TCCR during Batch 2 processing. At the time HTF-11-20-70 was collected, approximately 38,211 gallons of Batch 3 had been processed and added to Tank 11H.

Table 3-2. Summary of ^{137}Cs Activities for the First Two Tank 11H Interim Surface Samples

	HTF-11-20-70		HTF-11-20-71	
Original Samples ^{137}Cs (dpm/mL)	1.47E+06	1.96E+06	1.63E+06	1.25E+06
Reprep. of Original in AD ^{137}Cs (dpm/mL)	1.49E+06	1.93E+06	n/a[a]	n/a
Resampling of Parent Bottle ^{137}Cs (dpm/mL)	1.94E+06	1.97E+06	1.62E+06	1.65E+06
Overall Average (%RSD)	1.79E+06 (13.6%)		1.54E+06 (12.5%)	

[a]n/a = not applicable

The duplicate analysis of the third and fourth samples gave consistent results and those are summarized in Table 3-3. The overall trend for the interim surface samples is one of decreasing ^{137}Cs activity over time, consistent with the addition of decontaminated solution to the tank from the TCCR columns. For comparison, the ^{137}Cs activity in the Batch 3 feed material in Tank 10H was 4.75E+07 dpm/mL (4.28% RSD).

Table 3-3. Summary of ^{137}Cs Activities for the Final Two Tank 11H Interim Surface Samples

Sample ID	Interim Sample #	^{137}Cs Activity (dpm/mL)	%RSD
HTF-11-20-74	3rd	1.49E+06	0.95%
HTF-11-20-77	4th	1.40E+06	0.00%[a]

[a]Duplicate samples gave identical results.

Comparison of the chemical composition in Tank 11H at the end of Batch 2 processing[8] (samples HTF-11-19-69/70) to the composition measured in a corrosion control sample (HTF-11-20-50) taken on June 2, 2020[10] showed an increase in aluminum and sodium concentrations indicating leaching of material during this ~11 month soak. The ^{137}Cs activity also increased significantly (170%) during this period. These results are provided in Table 3-4. The inductively coupled plasma – emission spectroscopy (ICP-ES) results for the fourth Tank 11H interim sample are shown in Table 3-5 below. As mentioned above, at the start of Batch 3 processing Tank 11H still contained the product from Batch 2 processing (~58,000 gallons) and the total supernate volume in the tank was estimated to be approximately 77,732 gallons. The expected composition in Tank 11H assuming mixing of the heel (using the composition measured for the 6/2/20 sample) with Batch 3 material added from TCCR is provided in Table 3-5 for comparison. (Mixing is provided in the tank chiefly by the plunging jet for transfers. That mixing is unanalyzed as to expected extent of mixing achievable.) Only the Al and Na were above the detection limit for the June 2020 Tank 11H corrosion control sample, and the concentrations of these elements measured in the fourth interim sample were consistent with what was expected based upon the mixing. While there were no chemical additions made to Tank 11H between processing of Batches 2 and 3, a TCCR column volume

Table 3-4. Composition of Tank 11H as Measured at the End of Batch 2 Processing Compared to a Recent Corrosion Control Sample

Component	HTF-11-19-69/70[a]	%RSD[b]	HTF-11-20-50[c]	%RSD or 1-sigma uncertainty[d]	Percent Change
Sample Date	7/2/19	n/a[e]	6/2/20	n/a	n/a
Density (g/mL)	1.152	0.21	1.190	0.107	3.3%
^{137}Cs (dpm/mL)	8.29E+05	2.13	2.24E+06	5.00	170%
Al (mg/L)	1010	1.40	2445	10	142%
B (mg/L)	0.352	3.02	< 26	n/a	n/a
Ca (mg/L)	1.90	2.61	< 5.2	n/a	n/a
Cr (mg/L)	4.92	4.02	< 14.8	n/a	n/a
Fe (mg/L)	1.33	2.67	< 7.0	n/a	n/a
K (mg/L)	172	3.71	< 289	n/a	n/a
Mo (mg/L)	1.81	1.96	< 59	n/a	n/a
Na (mg/L)	82300	0.26	96560	10	17%
P (mg/L)	14.8	2.87	< 319	n/a	n/a
Zr (mg/L)	0.757	2.99	< 5.7	n/a	n/a
Free OH^- (M)	1.18	2.40	1.03	10	-13%
NO_3^- (M)	1.03	1.22	1.11	10	8%
NO_2^- (M)	0.0622	0.99	0.0909	10	46%
SO_4^{2-} (M)	0.227	1.30	0.248	10	9%
Cl^- (M)	0.0119	0.00	0.0150	10	26%

[a]Samples collected at the conclusion of TCCR Tank 10H Batch 2 processing. [b]The %RSD is based on the standard deviation of duplicate samples. [c]Corrosion control sample collected on June 2, 2020. [d]The %RSD reported for duplicate density measurements. The other values are the reported analytical method uncertainties. [e]n/a = not applicable.

(130 gallons) of 3 M NaOH was added to Tank 11H when unused Column D was brought online between the second and third interim samples. This addition was included in the calculated concentrations in the Tank 11H mix shown in Table 3-5.

Table 3-5. ICP-ES Result for the Tank 11H Fourth Interim Surface Sample (HTF-11-20-77)

Element	Tank 11H Fourth Interim Sample Avg. Conc. (mg/L)	%RSD[a]	Expected Concentration Based on Mixing (mg/L)[b]	% Difference From Expected
Ag	< 1.19	n/a[c]	–[d]	–
Al	1735	0.41%	1.64E+03	6%
B	< 2.47	n/a	–[d]	–
Ba	< 0.87	n/a	–[d]	–
Be	< 0.05	n/a	–[d]	–
Ca	1.53	0.00%[e]	–[d]	–
Cd	< 1.44	n/a	–[d]	–
Ce	< 3.86	n/a	–[d]	–
Co	< 1.79	n/a	–[d]	–
Cr	8.67	1.30%	< 10.3	–
Cu	< 0.44	n/a	–[d]	–
Fe	< 1.38	n/a	–[d]	–
Gd	< 1.20	n/a	–[d]	–
K	84.1	4.04%	< 171	–
La	< 0.84	n/a	–[d]	–
Li	< 0.99	n/a	–[d]	–
Mg	< 0.08	n/a	–[d]	–
Mn	< 0.50	n/a	–[d]	–
Mo	< 5.71	n/a	–[d]	–
Na	98050	0.79%	8.83E+04	11%
Ni	< 8.81	n/a	–[d]	–
P	26.3	0.00%[e]	< 160	–
Pb	< 12.10	n/a	–[d]	–
S	10300	1.37%	–[f]	–
Sb	< 37.50	n/a	–[d]	–
Si	< 5.51	n/a	–[d]	–
Sn	< 10.60	n/a	–[d]	–
Sr	< 0.14	n/a	–[d]	–
Th	< 4.63	n/a	–[d]	–
Ti	< 0.37	n/a	–[d]	–
U	< 33.20	n/a	–[d]	–
V	< 0.96	n/a	–[d]	–
Zn	< 1.89	n/a	–[d]	–
Zr	< 0.56	n/a	–[d]	–

[a]The %RSD is based on the standard deviation of duplicate samples. The reported analytical method uncertainties (at two sigma) are 10% except for P and S which had reported uncertainties of 15% and 20%, respectively. [b]Based on mixing of 77,732 gallons of the Tank 11H composition as measured in the 6/2/20 corrosion control sample[10] and 89,500 gallons of Tank 10H Batch 3 composition[9] along with 130 gallons of 3 M NaOH from Column D. [c]n/a = not applicable. [d]Not calculated when both prior samples were below the detection limit. [e]Duplicate samples gave identical results. [f]Not measured in the 6/2/20 corrosion control sample.

Table 3-6 provides a similar comparison for the anion results. The measured anions, carbonate being the exception, were all within analytical uncertainty of the expected values. The carbonate was not measured in the recent corrosion control sample; however, using the carbonate concentration measured at the end of

Batch 2 processing, the concentration was about 31% higher than expected based solely on mixing of the liquids. An increase in carbonate concentration is consistent with the sorption of CO_2 from the air and reaction with hydroxide according to equation (1). This is likely to have occurred over the approximately 1 year that passed between processing of Batches 2 and 3.

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O \qquad (1)$$

Table 3-6. Anion and Carbon Results for the Tank 11H Fourth Interim Surface Sample (HTF-11-20-77)

Analyte	Tank 11H Fourth Interim Sample Avg. Conc.	%RSD[a]	Expected Concentration Based on Mixing (mg/L)[b]	% Difference from Expected
Free OH^- (M)	0.513	1.24	0.542	-5%
NO_3^- (M)	1.64	0.70	1.63	1%
SO_4^{2-} (M)	0.259	0.85	0.246	5%
NO_2^- (M)	0.327	0.47	0.331	-1%
Br^- (M)	< 6.26E-04	n/a[c]	–[d]	–
$C_2O_4^{2-}$ (M)	2.60E-03	0.31	–[d]	–
F^- (M)	< 5.26E-04	n/a	–[d]	–
Cl^- (M)	7.01E-03	0.85	0.0070 – 0.0074[e]	1%[f]
CHO_2^- (M)	< 2.22E-04	n/a	–[d]	–
PO_4^{3-} (M)	2.00E-04	1.87	–[d]	–
CO_3^{2-} [g] (M)	0.513	0.00	–[d]	–
TOC[h] (mg/L)	206	0.34	–[d]	–

[a]The %RSD is based on the standard deviation of duplicate samples. The reported analytical method 1-sigma uncertainties were 10%. [b]Based on mixing of 77,732 gallons of the Tank 11H post-Batch 2 composition as measured in the 6/2/20 corrosion control sample[10] and 89,500 gallons of Tank 10H Batch 3 composition[9] along with 130 gallons of 3 M NaOH from Column D. [c]n/a = not applicable. [d]Not calculated. [e]Range calculated when one value was below the detection limit. [f]From minimum value. [g]Calculated from total inorganic carbon (TIC) result. [h]Total organic carbon.

Table 3-7 provides the inductively coupled plasma – mass spectrometry (ICP-MS) results for the Tank 11H fourth interim sample. When compared to the Tank 10H Batch 3 results, there were several expected changes. Significant increases in concentration of the isotopes from 90 to 94 were observed, and these are attributed to the expected Zr and Nb leaching from the CST in the columns. Similarly, an increase was observed for the Hf isotopes from 176 to 180. Hf is a known contaminant in the Zr binder. An increase of ~780% was observed for m/z values of 196, 198, and 204 over the Tank 10H feed concentration. These isotopes are likely Hg. The major Hg isotopes between 199 and 203 are not reported by ICP-MS. When compared to the expected concentration calculated for the mix of liquid in Tank 11H, the values for these Hg isotopes are ~210% above the calculated value. The Cs isotope concentrations were measured to be 96-97% lower than measured in the Tank 10H feed. In contrast to what would be expected, the Rb (m/z 85 and 87) and Sr (m/z 88) concentrations were higher than in the Tank 10H Batch 3 feed, as well as higher than what was calculated for the Tank 11H mix. As these elements would be expected to be removed by the CST, the higher concentrations are indicative of leaching of these elements from the heel in Tank 11H. The minor uranium isotopes (234-236) all showed a decrease in concentration on the order of 80% from both the Tank 10H Batch 3 feed as well as the calculated concentration in the Tank 11H mix. In contrast however, ^{238}U showed an increase in concentration of 60% over the Tank 10H Batch 3 feed and was 15% higher than the calculated value for the Tank 11H mix. As discussed in a prior memo[8], this may be due to the difference in isotopic ratios between the Tank 10H liquid and the Tank 11H heel (including the leachable solids). . The ^{235}U enrichment in the Tank 10H feed was significantly higher (13.9%)[9] than the enrichment level in the Tank 11H pre-production sample (1.4%).[12] The ^{235}U enrichment level in the Tank 11H fourth

interim sample (2.1%) is consistent with leaching of lower enriched U from material remaining in Tank 11H at the start of TCCR processing.

The radionuclide activities in the Tank 11H fourth interim sample are shown in Table 3-8. For comparison the calculated activities based on mixing of the heel in Tank 11H (using activities measured in the Batch 2 post-production sample[8]) with the Batch 3 feed[9] are also shown. The ^{90}Sr activity was found to be ~2.7x the expected value indicative of additional leaching of ^{90}Sr from the Tank 11H heel. The Cs removed beta activity shows a similar increase. The technetium concentration also appears to be slightly increased (~30%) in the fourth interim sample relative to the expected concentration based on mixing. This difference is greater than the method uncertainty (4%RSD on replicate samples and 7.5% 1-sigma analytical uncertainty). The ^{238}Pu activity was 72% lower in the Tank 11H fourth interim sample when compared to the expected activity, while the $^{239/240}$Pu and ^{241}Pu were only ~40% lower. Removal of Pu by the CST columns is expected based on the teabag loading data;[13] however, the removal is not expected to be isotope dependent as all isotopes are in the same chemical form. Therefore, the variation seen in the isotope activities is most likely due to differing isotopic compositions in Tank 10H and Tank 11H discussed previously. As it appears there was some leaching of material present in Tank 11H, the results indicate the residual Tank 11H material is enriched in $^{239/240}$Pu and ^{241}Pu compared to ^{238}Pu. Similar results were observed in the Batch 2 post-production Tank 11H sample.[8]

Table 3-7. ICP-MS Results for Tank 11H Fourth Interim Surface Sample (HTF-11-20-77)

m/z	Avg. Conc. (µg/L)	% RSD[a]	m/z	Avg. Conc. (µg/L)	% RSD[a]	m/z	Avg. Conc. (µg/L)	% RSD[a]
59	< 1.00E+00	n/a	**133**	2.76E+01	1.14%	**179**	8.95E+00	0.67%
82	1.16E+02	0.86%	**134**	< 1.00E+00	n/a	**180**	2.36E+01	0.04%
84	< 1.00E+00	n/a	**135**	2.98E+00	4.33%	**181**	2.19E+00	4.21%
85	1.30E+02	2.71%	**136**	< 1.00E+00	n/a	**182**	1.12E+01	0.57%
86	1.66E+00	1.40%	**137**	6.84E+00	1.71%	**183**	6.28E+00	1.22%
87	2.77E+02	2.21%	**138**	6.22E+00	2.87%	**184**	1.32E+01	1.50%
88	5.82E+01	0.86%	**139**	< 1.00E+00	n/a	**185**	< 1.00E+00	n/a
89	< 1.00E+00	n/a	**140**	< 1.00E+00	n/a	**186**	1.23E+01	0.55%
90	7.93E+01	0.96%	**141**	< 1.00E+00	n/a	**187**	< 1.00E+00	n/a
91	1.66E+01	3.34%	**142**	< 1.00E+00	n/a	**191**	< 1.00E+00	n/a
92	4.19E+01	1.17%	**143**	< 1.00E+00	n/a	**193**	< 1.00E+00	n/a
93	1.53E+03	0.76%	**144**	< 1.00E+00	n/a	**194**	1.18E+00[b]	n/a
94	3.65E+01	0.76%	**145**	< 1.00E+00	n/a	**195**	1.09E+00[b]	n/a
95	7.75E+02	1.08%	**146**	< 1.00E+00	n/a	**196**	4.74E+01	0.88%
96	3.06E+01	2.59%	**147**	< 1.00E+00	n/a	**197**	6.45E+00	10.13%
97	7.37E+02	0.63%	**148**	< 1.00E+00	n/a	**198**	2.67E+03	0.73%
98	7.46E+02	0.61%	**149**	< 1.00E+00	n/a	**203**	< 1.00E+00	n/a
99	4.62E+02	0.73%	**150**	< 1.00E+00	n/a	**204**	1.56E+03	0.05%
100	7.78E+02	0.58%	**151**	< 1.00E+00	n/a	**205**	< 1.00E+00	n/a
101	1.64E+02	0.22%	**152**	< 1.00E+00	n/a	**206**	3.77E+01	0.65%
102	1.41E+02	1.71%	**153**	< 1.00E+00	n/a	**207**	3.33E+01	0.30%
103	1.08E+02	0.26%	**154**	< 1.00E+00	n/a	**208**	8.05E+01	0.45%
104	9.82E+01	0.10%	**155**	< 1.00E+00	n/a	**229**	< 1.00E+00	n/a
105	1.20E+02	0.13%	**156**	< 1.00E+00	n/a	**230**	< 1.00E+00	n/a
106	9.69E+01	0.23%	**157**	< 1.00E+00	n/a	**232**	< 1.00E+00	n/a
107	3.63E+01	0.31%	**158**	< 1.00E+00	n/a	**233**	< 1.00E+00	n/a
108	1.60E+01	3.66%	**159**	< 1.00E+00	n/a	**234**	1.61E+00	11.29%
109	2.82E+00	7.67%	**160**	< 1.00E+00	n/a	**235**	1.19E+01	0.65%
110	8.51E+00	0.93%	**161**	< 1.00E+00	n/a	**236**	2.28E+00	1.96%
111	1.15E+00	4.96%	**162**	< 1.00E+00	n/a	**237**	2.01E+00	1.81%
112	2.18E+00	0.09%	**163**	< 1.00E+00	n/a	**238**	5.63E+02	0.87%
113	< 4.00E+00	n/a	**164**	< 1.00E+00	n/a	**239**	1.69E+00	0.52%
114	2.47E+00	6.73%	**165**	< 1.00E+00	n/a	**240**	< 1.00E+00	n/a
116	1.12E+01	1.20%	**166**	< 1.00E+00	n/a	**241**	< 1.00E+00	n/a
117	7.86E+00	4.46%	**167**	< 1.00E+00	n/a	**242**	< 1.00E+00	n/a
118	2.13E+01	1.11%	**168**	< 1.00E+00	n/a	**243**	< 1.00E+00	n/a
119	1.46E+01	0.60%	**169**	< 1.00E+00	n/a	**244**	< 1.00E+00	n/a
120	2.90E+01	0.89%	**170**	< 1.00E+00	n/a	**245**	< 1.00E+00	n/a
121	< 1.00E+00	n/a	**171**	< 1.00E+00	n/a	**246**	< 1.00E+00	n/a
122	8.04E+00	4.38%	**172**	< 1.00E+00	n/a	**247**	< 1.00E+00	n/a
123	< 1.00E+00	n/a	**173**	< 1.00E+00	n/a	**248**	< 1.00E+00	n/a
124	1.29E+01	0.80%	**174**	< 1.00E+00	n/a	**249**	< 1.00E+00	n/a
125	< 1.00E+00	n/a	**175**	< 1.00E+00	n/a	**250**	< 1.00E+00	n/a
126	5.46E+01	0.63%	**176**	3.32E+00	3.74%	**251**	< 1.00E+00	n/a
128	< 1.00E+00	n/a	**177**	1.23E+01	0.20%	**252**	< 1.00E+00	n/a
130	< 1.00E+00	n/a	**178**	1.79E+01	1.23%			

[a]The %RSD is based on the standard deviation of duplicate samples. The reported analytical method 2-sigma uncertainty is 20%. [b]Results for a single sample, the duplicate sample was below the detection limit.

Table 3-8. Additional Radionuclide Activities in the Tank 11H Fourth Interim Surface Sample

Isotope	Tank 11H Fourth Interim Sample (HTF-11-20-77) (dpm/mL)	%RSD[a]	Avg. Analytical 1-Sigma Uncertainty	Expected Activity Based on Mixing (dpm/mL)[b]	% Difference from Expected
^{60}Co	< 2.23E+01	n/a	MDA	< 2.79E+01	n/a
^{90}Sr	4.35E+06	14.5%	14.8%	1.60E+06	171%
^{99}Tc	2.14E+04	3.97%	7.45%	1.64E+04	31%
^{106}Ru	< 2.25E+02	n/a	MDA	< 2.24E+02	n/a
^{125}Sb	< 1.66E+02	n/a	MDA	< 5.88E+01	n/a
^{126}Sb	1.47E+02	2.89%	5.07%	1.57E+02	-6.6%
^{126}Sn	1.47E+02	2.89%	5.07%	1.57E+02	-6.6%
^{144}Ce	< 8.11E+02	n/a	MDA	< 4.74E+02	n/a
^{154}Eu	< 6.58E+01	n/a	MDA	< 6.44E+03	n/a
^{241}Am	< 1.15E+03	n/a	MDA	< 6.39E+02	n/a
^{238}Pu	6.35E+03	1.89%	8.02%	2.29E+04	-72%
$^{239/240}$Pu	3.02E+02	3.52%	9.60%	4.90E+02	-38%
^{241}Pu	1.13E+03	5.01%	16.6%	1.84E+03	-39%
Alpha Count	< 1.44E+04	n/a	Upper Limit	< 1.38E+05	n/a
Beta Count	1.22E+07	2.32%	10.0%	3.42E+07	-64%
Cs Removed Alpha Count	< 2.90E+05	n/a	Upper Limit	< 8.34E+04	n/a
Cs Removed Beta Count	9.57E+06	0.22%	10.0%	3.10E+06	209%

[a]The %RSD is based on the standard deviation of duplicate samples. [b]Based on mixing of 77,732 gallons of the Tank 11H composition as measured in the Batch 2 post-production sample[8] and 89,500 of Tank 10H Batch 3 composition[9] along with 130 gallons of 3 M NaOH from Column D.

3.2 Tank 11H Post-Production Surface and Variable Depth Samples

A photograph of the Post-Production surface and variable depth samples is provided in Figure 3-2. The surface sample (HTF-11-20-92) was clear and colorless with no evidence of solids and was similar in appearance to the interim surface samples (Figure 3-1). The variable depth sample (HTF-11-20-93) was similar in appearance to the surface sample, but was slightly cloudy, indicating the presence of a small amount of solids.

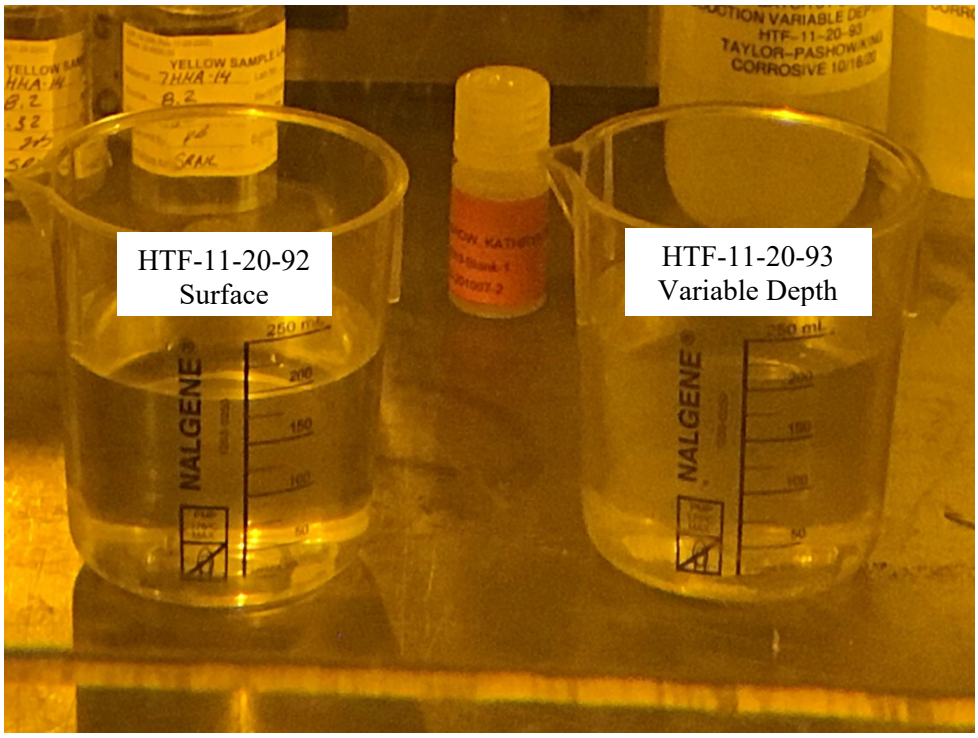

Figure 3-2. Photograph of the Tank 11H Post-Production Surface and Variable Depth Samples.

A summary of the measured densities for Post-Production surface and variable depth samples is provided in Table 3-9. These samples were collected after approximately 6 weeks of storage. The variable depth sample density is slightly higher (1.7%) than the density of the surface sample, which is less than the estimated uncertainty in density measurements of 3%. The final (fourth) interim surface sample density was 1.214 g/mL (Table 3-1), which was similar to the Post-Production surface sample. The Post-production variable depth sample density was higher than all the surface sample densities for Batch 3 processing except for the third interim sample (1.24 g/mL), which also had the highest %RSD (1.8%).

Table 3-9. Summary of Tank 11H Post-Production Sample Densities

Sample ID	Sample Type	Date Collected	Density (g/mL) (%RSD)	Temp. During Density Measurement
HTF-11-20-92	Surface	10/16/20	1.20 (0.79%)	23 ºC
HTF-11-20-93	Variable Depth		1.23 (0.32%)	

The ^{137}Cs gamma analysis results for the Post-Production surface and variable depth samples are provided in Table 3-10. The ^{137}Cs concentration in the variable depth sample was 2.6% higher than the surface sample, which is within the reported analytical 1 sigma uncertainty of 5%. Both results were slightly greater than the values reported for the third and fourth interim samples (Table 3-3) indicating that some additional ^{137}Cs leached into the solution from the Tank 11H heel during the 6-week storage period. The Post-Pretreatment surface sample Cs-137 concentration was 9% higher than the fourth interim surface sample, which is outside the reported analytical uncertainty.

Table 3-10. ^{137}Cs Activities for the Tank 11H Post-Production Surface and Variable Depth Samples

Sample ID	^{137}Cs Activity (dpm/mL)	%RSD
HTF-11-20-92	1.52E+06	3.3
HTF-11-20-93	1.56E+06	2.3

ICP-ES data for the Post-Production surface sample is provided in Table 3-11. These results are within 10% of the data reported for the fourth interim sample provided in Table 3-5, but metal and anion concentrations for the Post-Production surface sample are generally slightly lower than (as indicated by negative % difference values) the interim sample, which is consistent with the additional dilution of the Tank 11H material from the column and transfer line flush solutions. The concentrations for the major metal species are: 4.01 M Na^+, 0.29 M S, 0.06 M Al, and 0.002 M K^+. Replicate data was consistent except for the Ca data, where one result was below detection (<1.96 mg/L) and the other was 9.6 mg/L.

Anion and carbon results for the Post-Production surface sample are provided in Table 3-12. The concentrations of the primary anions in solution are: 1.6 M NO_3^-, 0.50 M OH^-, 0.47 M CO_3^{2-}, 0.33 M NO_2^-, and 0.25 M SO_4^{2-}. The anion concentrations agreed to within 10% with the results reported in Table 3-6 for the fourth interim surface sample, except for oxalate anion which appears to have increased in concentration during storage by a factor of 3.3 to give a final concentration of 8.5E-03 M. The increase in the oxalate concentration is presumably associated with leaching of oxalate salt from the Tank 11H heel solids.

Total alpha, beta, and Cs-removed beta analysis results for the Tank 11H Post-Production surface and variable depth samples are provided in Table 3-13. Results for the surface sample are similar to the fourth interim surface sample (Table 3-8), except the Cs-removed alpha data could not be reported for the Post-Production sample due to unusually high levels of beta activity (presumably from ^{90}Sr) in the sample after Cs removal and concerns over false positives from beta spill-over into the alpha channel.

Table 3-11. ICP-ES Result for the Tank 11H Post-Production Surface

Element	HTF-11-20-92 (Surface) mg/L	%RSD[a]	% Difference from Fourth Interim Sample[b]
Ag	<1.19	n/a[c]	n/a
Al	1635	1.3%	-6%
B	<2.47	n/a	n/a
Ba	<0.865	n/a	n/a
Be	<0.053	n/a	n/a
Ca	≤5.80	n/a	n/a
Cd	<1.44	n/a	n/a
Ce	<7.17	n/a	n/a
Co	<1.79	n/a	n/a
Cr	8.645	1.6%	-0.3%
Cu	<0.517	n/a	n/a
Fe	<2.18	n/a	n/a
Gd	<1.20	n/a	n/a
K	76.35	11.4%	-9%
La	<0.836	n/a	n/a
Li	<1.86	n/a	n/a
Mg	<0.084	n/a	n/a
Mn	<0.155	n/a	n/a
Mo	<5.71	n/a	n/a
Na	91300	1.4%	-7%
Ni	<8.81	n/a	n/a
P	24.05	3.8%	-9%
Pb	<12.1	n/a	n/a
S	9280	1.5%	-10%
Sb	<23.1	n/a	n/a
Si	<5.41	n/a	n/a
Sn	<10.6	n/a	n/a
Sr	<0.140	n/a	n/a
Th	<4.63	n/a	n/a
Ti	<0.368	n/a	n/a
U	<33.2	n/a	n/a
V	<0.958	n/a	n/a
Zn	<0.652	n/a	n/a
Zr	<0.555	n/a	n/a

[a]The %RSD is based on the standard deviation of duplicate samples. The reported analytical method uncertainties (at two sigma) are 10% except for P and S which had reported uncertainties of 15% and 20%, respectively. [b]Table 3-5. [c]n/a = not applicable.

Table 3-12. Anion and Carbon Results for the Tank 11H Post-Production Surface Sample

Analyte	HTF-11-20-92 (Surface)	%RSD[a]	% Difference from Fourth Interim Sample[b]
Free OH^- (M)	0.499	0.00[c]	-3%
NO_3^- (M)	1.60	0.21	-2%
SO_4^{2-} (M)	0.251	0.59	-3%
NO_2^- (M)	0.326	0.00[c]	-0.3%
Br^- (M)	<1.25E-03	n/a[d]	n/a
$C_2O_4^{2-}$ (M)	8.51E-03	0.00[c]	227%
F^- (M)	<5.26E-03	n/a	n/a
Cl^- (M)	7.15E-03	0.28	2%
CHO_2^- (M)	< 2.22E-03	n/a	n/a
PO_4^{3-} (M)	<1.05E-03	n/a	n/a
CO_3^{2-} (M)[e]	0.472	0.06	-8%
TOC[f] (mg/L)	209	4.41	1%

[a]The %RSD is based on the standard deviation of duplicate samples. The reported analytical method 1-sigma uncertainties were 10%. [b]Table 3-6. [c]Duplicate samples gave identical results. [d]n/a = not applicable. [e]Calculated from total inorganic carbon (TIC) result. [f]Total organic carbon.

Table 3-13. Total Alpha, Beta, and Cs-Removed Beta in the Tank 11H Post-Production Surface and Variable Depth Samples

Method[a]	HTF-11-20-92 Surface Sample (dpm/mL)	%RSD[b]	HTF-11-20-93 Variable Depth Sample (dpm/mL)	%RSD[b]	% Difference of Post-Production Surface from Fourth Interim Surface Sample[c]
Gross Alpha	<4.02E+05	n/a	<2.71E+05	n/a	n/a
Total Beta	1.20E+07	2.96%	1.35E+07	0.53%	-2%
Gross Cs-Removed Beta	1.04E+07	0.68%	–[d]		+8%

[a]A cesium-removed alpha value could not be measured due to unusually high levels of beta activity in the sample after Cs removal and concerns over false positives from beta spill-over into the alpha channel. [b]The %RSD is based on the standard deviation of duplicate samples. The reported analytical method 1-sigma uncertainties were 10% for total beta and 15% for Cs-removed beta. [c]Table 3-8. [d]Not measured.

4.0 Conclusions

Four interim samples collected from Tank 11H during and just after the completion of processing of Batch 3 through TCCR have been analyzed for ^{137}Cs activity and density. The ^{137}Cs activity decreased with each subsequent sample, consistent with the addition of decontaminated solution to Tank 11H. When compared to the expected composition from mixing the Tank 10H Batch 3 feed with the material already present in Tank 11H, the bulk chemical composition was as expected. A corrosion control sample taken from Tank 11H in June 2020 showed changes in the chemical composition and ^{137}Cs activity when compared to the composition measured at the end of Batch 2 processing. The largest change in bulk chemical composition was the increase in Al concentration seen between the two samples. As there were no additions made to the tank during this period, these changes were attributed to leaching of the solids present in Tank 11H. The increase in carbonate concentration is likely due to the sorption of CO_2 from the air and reaction with hydroxide present in the tank. Additional results (ICP-MS) and other radionuclides were consistent with leaching of material from the Tank 11H heel. Notably, the ^{90}Sr activity was about 2.7x higher than was calculated based on mixing of Batch 3 feed with the Batch 2 product already present in Tank 11H. Analysis of the Post-Production surface and variable depth samples revealed that changes in the surface composition

were limited to a small (8%) increase in the Cs-137 concentration and a 3-fold increase in the oxalate concentration. The Post-Production variable depth sample had a slightly higher (1.8%) density and contained slightly higher (2.6%) ^{137}Cs and 13% higher total beta than the surface sample. The differences in the gamma and density results for the surface and variable depth samples are not greater than the measurement uncertainty.

5.0 Future Work

No additional analysis is planned for the TCCR product solution currently stored in Tank 11H.

6.0 References

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