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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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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. Additional analyses of the 4th interim sample are pending and will be documented in a revision to this report.

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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 a number of samples taken from Tank 11H during and at the completion of Batch 3 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 intermediate samples were collected from Tank 11H during processing, and a fourth was collected just after processing completed. A final set of samples will be collected from Tank 11H prior to the transfer of material to Tank 50H. All samples were delivered to SRNL for analysis.

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 intermediate 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.

Table 1-1. Summary of Batch 3 Processing

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 Interim 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 Interim 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 Interim 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 Interim Sample HTF-11-20-77			9/1/20	9/1/20

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. Tank 11H does not possess any mixing capabilities, so additions to the tank are added on to the liquid surface.

2.0 Experimental Procedure

2.1 Tank 11H Intermediate Samples

A total of four intermediate 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.[1] The fourth sample was also analyzed for the full suite of analytes described in the Task Technical and Quality Assurance Plan (TTQAP).[2]

2.2 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.[3] This work was performed following the applicable TTQAP.[2] The Task Technical Request (TTR) associated with this work[4] 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.[5] Data are recorded in the Electronic Laboratory Notebook (ELN) system.[6]

3.0 Results and Discussion

3.1 Tank 11H Intermediate Samples

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

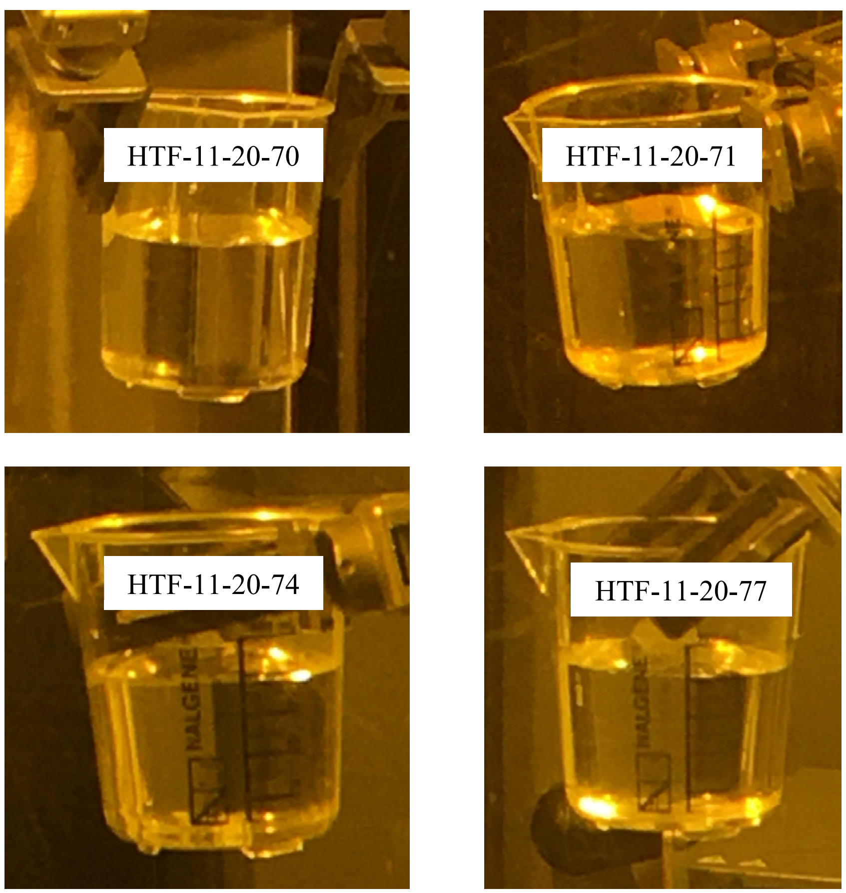

Figure 3-1. Photographs of the four Tank 11H Intermediate Samples.

A summary of the measured densities for each of the four intermediate 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)[7] 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).[8] The density of a corrosion control sample collected on June 2, 2020 from Tank 11H was 1.190 g/mL (0.11% RSD).[9] The Tank 11H intermediate 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, a number of 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 the Tank 11H sample.

Table 3-1. Summary of Tank 11H Intermediate 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 intermediate 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 intermediate 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 intermediate 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.[9] 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[10], 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 Intermediate 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 intermediate 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 Intermediate Samples

Sample ID	^{137}Cs Activity (dpm/mL)	%RSD
HTF-11-20-74	1.49E+06	0.95%
HTF-11-20-77	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[7] to the composition measured in a corrosion control sample taken on June 2, 2020[9] 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 4th Tank 11H intermediate 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 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 4th intermediate 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 column volume (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 was included in the calculated concentrations in the Tank 11H mix shown in Table 3-5.

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

Component	HTF-11-19-69/70	%RSD[a]	HTF-11-20-50	%RSD or 1-sigma uncertainty[b]	Percent Change
Sample Date	7/2/19	n/a[c]	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]The %RSD is based on the standard deviation of duplicate samples. [b]The %RSD reported for duplicate density measurements. The other values are the reported analytical method uncertainties. [c]n/a = not applicable.

Table 3-5. ICP-ES Result for the Tank 11H 4th Interim Sample (HTF-11-20-77)

Element	Tank 11H 4th 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%	1635	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%	88345	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[9] and 89,500 gallons of Tank 10H Batch 3 composition[8] 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. 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 4th Interim Sample (HTF-11-20-77)

Analyte	Tank 11H 4th 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[9] and 89,500 gallons of Tank 10H Batch 3 composition[8] 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.

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.

5.0 Future Work

Additional analyses of the 4th interim sample are pending and will be documented in a revision to this report.

6.0 References

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