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Revision 0

Results of Routine Strip Effluent Hold Tank, Decontaminated Salt Solution Hold Tank, and Caustic Wash Tank Samples from Modular Caustic-Side Solvent Extraction Unit during Macrobatch 4 Operations

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S. D. Fink

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REVIEWS AND APPROVALS

AUTHORS:

T. B. Peters, Author, SRNL/SASP Date

TECHNICAL REVIEW:

C. A. Nash, Technical Reviewer, SRNL/ACP Date

APPROVAL:

S. D. Fink, Manager, SRNL/SASP Date

S. L. Marra, Manager, SRNL/E&CPT Research Programs Date

D. J. Martin, Manager, H Tank Farm Engineering Date

EXECUTIVE SUMMARY

Strip Effluent Hold Tank (SEHT), Decontaminated Salt Solution Hold Tank (DSSHT), and Caustic Wash Tank (CWT) samples from several of the "microbatches" of Integrated Salt Disposition Project (ISDP) Salt Batch ("Macrobatch") 4 have been analyzed for ^{238}Pu, ^{90}Sr, ^{137}Cs, and by inductively-coupled plasma emission spectroscopy (ICPES). Furthermore, samples from the CWT have been analyzed by a variety of methods to investigate a decline in the decontamination factor (DF) of the cesium observed at MCU.

The results indicate good decontamination performance within process design expectations. While the data set is sparse, the results of this set and the previous set of results for Macrobatch 3 samples indicate generally consistent operations.

There is no indication of a disruption in plutonium and strontium removal. The average cesium DF and concentration factor (CF) for samples obtained from Macrobatch 4 are slightly lower than for Macrobatch 3, but still well within operating parameters.

The DSSHT samples show continued presence of titanium, likely from leaching of the monosodium titanate in Actinide Removal Process (ARP).

LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
CWT	Caustic Wash Tank
CF	concentration factor
DF	decontamination factor
DSS	Decontaminated Salt Solution
DSSHT	Decontaminated Salt Solution Hold Tank
IC	Ion Chromatography
ICPES	inductively-coupled plasma emission spectroscopy
ISDP	Integrated Salt Disposition Project
MCU	Modular Caustic-Side Solvent Extraction Unit
MST	monosodium titanate
RSD	relative standard deviation
SE	Strip Effluent
SEHT	Strip Effluent Hold Tank
SRNL	Savannah River National Laboratory

1.0 Introduction

During operation of the ISDP, salt waste is processed through ARP and the Modular Caustic Side Solvent Extraction Unit (MCU) in batches of ~3800 gallons. Monosodium titanate (MST) is used in ARP to adsorb actinides and strontium from the salt waste and the waste slurry is then filtered prior to sending the clarified salt solution to MCU. MCU uses solvent extraction technology to extract cesium from the clarified salt solution and concentrate cesium in an acidic aqueous stream (Strip Effluent – SE), leaving a decontaminated caustic salt aqueous stream (Decontaminated Salt Solution – DSS). Sampling occurs in the DSSHT and SEHT in the MCU process. The MCU sample plan[1] requires that batches be sampled and analyzed for plutonium and strontium content by Savannah River National Lab (SRNL) to determine MST effectiveness. The cesium measurement is used to monitor cesium removal effectiveness and the ICPES data are used to monitor inorganic carryover.

A previous report provided the results of several sets of microbatch results from Macrobatch 3 operations.[2]

Since that report, SRNL received subsequent SEHT and DSSHT samples from Macrobatch 4. Not all microbatch samples were delivered to SRNL for analysis. For each sampling period, one sample each from the DSSHT and SEHT were delivered to SRNL for analysis.

In addition to routine sample analysis for the DSSHT and SEHT, SRNL was tasked with investigating a decline in cesium DF observed in the facility. As part of this, several CWT samples were delivered for analysis.

In September 2011, during Macrobatch 4 operations, the flow to MCU was stopped, and additional Tank 21H material was added to Tank 49H. Therefore, Macrobatch 4 is broken into 2 operation periods, 4-a and 4-b.

Another change happened at MCU during the period of September 5-15. During that time period, the facility increased the flow rate of the CWT aqueous stream to 0.55 gallons per minute to reduce the hydroxide depletion.

2.0 Experimental Procedure

The samples were contained in 10-mL P-nut vials. SEHT samples were delivered in doorstops for shielding purposes, while the DSSHT and CWT samples were delivered in thief holders. Samples were removed from the holders and sent to Analytical Development for analysis. The DSSHT and CWT samples were not diluted or filtered. Some of the SEHT samples were diluted where necessary to reduce personnel exposure. SRNL measured the pH of all the SEHT samples using pH strips.

3.0 Results and Discussion

3.1 Plutonium Results. The ^{238}Pu and $^{239/40}$Pu results from the DSSHT and SEHT analyses are listed in Table 1. Entries in the "Source Material" columns (representing the feed from Tank 49H) are from a report[3] that calculated the values from known concentrations and blend volumes.

Table 1. ^{238}Pu and $^{239/40}$Pu Concentrations in the SEHT and DSSHT Samples

Sample ID	Date Pulled	^{238}Pu (dpm/mL)	$^{239/40}$Pu (dpm/mL)
DSSHT Samples			
MCU-11-501	May, 25 2011	1.13E+03 (4.65%)	2.08E+02 (6.44%)
MCU-11-727	June, 28 2011	2.56E+03 (4.55%)	4.68E+02 (5.41%)
MCU-11-760	August, 8 2011	1.26E+03 (8.87%)	7.83E+01 (57.2%)
MCU-11-1069	September, 29 2011	1.35E+03 (5.62%)	2.37E+02 (7.49%)
MCU-11-1239	October, 22 2011	7.24E+02 (5.04%)	1.49E+02 (6.88%)
MCU-11-1382	November, 27 2011	3.30E+03 (5.00%)	6.32E+02 (5.99%)
MCU-11-1650	December, 28 2011	1.22E+03 (5.12%)	2.22E+02 (7.36%)
MCU-12-79	January, 25 2012	8.74E+02 (5.84%)	1.40E+02 (9.50%)
MCU-12-240	February, 25 2012	3.43E+02 (6.59%)	6.15E+01 (12.6%)
SEHT Samples			
MCU-11-505	May 25, 2011	<2.89E+01	4.14E+01 (34.8%)
MCU-11-734	June 1, 2011	<7.80E+01	1.76E+01 (23.9%)
MCU-11-893	August 24, 2011	<3.09E+00	<9.08E+00
MCU-11-1073	September 29, 2011	2.06E+01 (57.5%)	<1.11E+01
MCU-11-1235	October 22, 2011	1.54E+01 (89.5%)	<7.89E+00
MCU-11-1383	November 27, 2011	2.28E+01 (83.8%)	<2.70E+01
MCU-11-1646	December 28, 2011	<3.95E+00	<7.99E+00
MCU-12-75	January, 23 2012	<1.61E+01	<3.97E+01
MCU-12-246	February 26, 2012	<4.96E+01	1.26E+02 (42.9%)
Source Material			
Batch 4-a	Start to August[ℜ]	2.93E+04	1.87E+03
Batch 4-b	September-February[Σ]	2.82E+04	5.48E+02

Values in parentheses are the analytical uncertainties.

From the DSSHT ^{238}Pu results, the Pu DF can be determined. There is a great deal of variation between samples, and this reflects the varying amount of MST that has

[ℜ] 2011
[Σ] 2011-2012

accumulated in the strike tanks. Given that, the most meaningful DF value is the overall average. The average is calculated to be 29.6 (73.7% relative standard deviation - RSD). See Table 2.

Table 2. Comparison of Average ^{238}Pu DF Values for Each Macrobatch

Macrobatch	^{238}Pu DF
1	1210 (94.8%)
2	194 (197%)
3	21.9 (118%)
4	29.6 (73.7%)

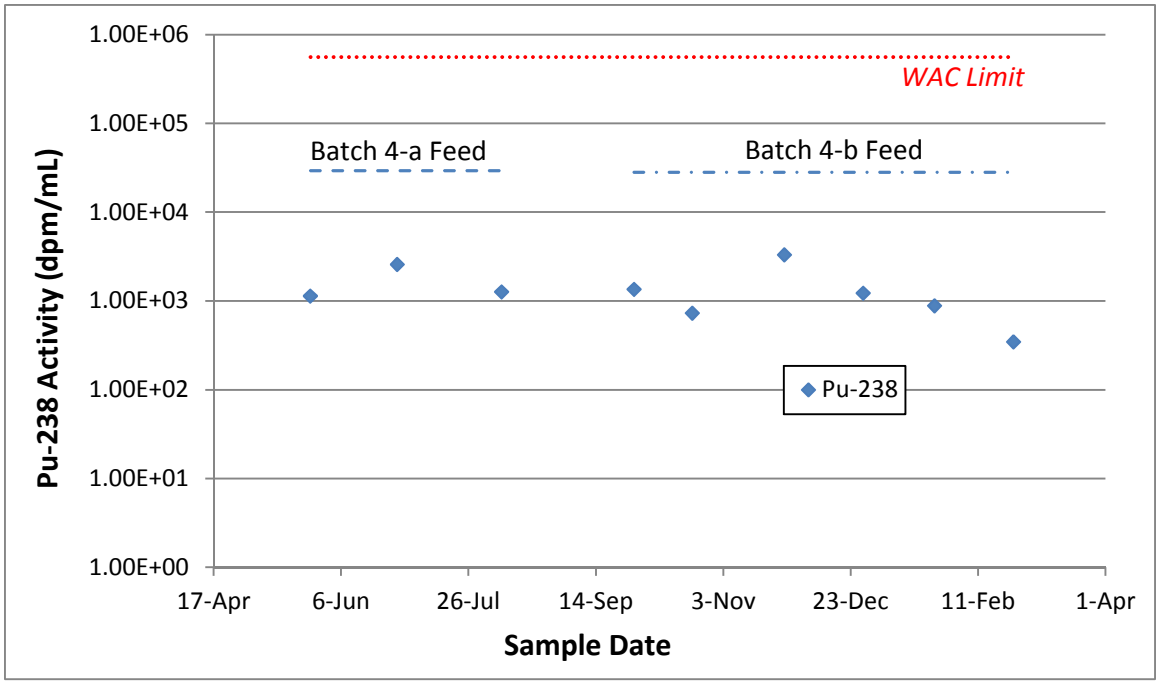
Values in parentheses are the relative standard deviation (RSD).

Comparisons to previous macrobatches [4,5,6,7,8,9,10,11,12,13,14,15,16] are also of limited value for several reasons. First, the ^{238}Pu activity varies from macrobatch to macrobatch. Second, plutonium removal is strongly related to the amount and time of MST accumulation at ARP. Third, the solution chemistry has a strong effect on plutonium removal.[17] Fourth, the overall averages of Macrobatch 1 and 2 contain data points during operations that were not typical, such as cold heel processing. See Table 2.

Macrobatch 3 and 4 share more similarities between them than they do with Macrobatch 1 and 2. Using previously documented solution chemistry models does not predict the large changes in DF values between macrobatches. Therefore, SRNL believes that the large DF differences are more due to variations in MST contact times at ARP. The previously mentioned differences in the operating parameters between macrobatches mean that the values in Table 2 do not indicate a noticeable decline in plutonium removal, or some process upset.

Figure 1 is the graph of the Macrobatch 4 ^{238}Pu DSSHT data over time.

Figure 1. Macrobatch 4 ^{238}Pu DSSHT Data



3.2 ^{90}Sr Results. The ^{90}Sr results from the DSSHT and SEHT analyses are listed in Table 3. Entries in the "Source Material" columns (representing the feed from Tank 49H) are from a report [3] that calculated the values from known concentrations and blend volumes.

Table 3. ^{90}Sr Concentrations in the SEHT and DSSHT Samples

Sample ID	Date Pulled	^{90}Sr (dpm/mL)
DSSHT Samples		
MCU-11-501	May, 25 2011	2.22E+03 (8.92%)
MCU-11-727	June, 28 2011	2.21E+03 (8.35%)
MCU-11-760	August, 8 2011	1.04E+04 (8.29%)
MCU-11-1069	September, 29 2011	3.21E+03 (10.7%)
MCU-11-1239	October, 22 2011	2.69E+03 (8.48%)
MCU-11-1382	November, 27 2011	3.21E+03 (9.27%)
MCU-11-1650	December, 28 2011	3.32E+03 (7.74%)
MCU-12-079	January, 25 2012	2.23E+03 (8.30%
MCU-12-240	February, 25 2012	3.81E+03 (8.74%)
SEHT Samples		
MCU-11-505	May 25, 2011	4.11E+02 (15.0%)
MCU-11-734	June 1, 2011	6.09E+02 (13.3%)
MCU-11-893	August 24, 2011	1.13E+03 (10.2%)
MCU-11-1073	September 29, 2011	1.45E+04 (7.70%)
MCU-11-1235	October 22, 2011	4.60E+03 (7.94%)
MCU-11-1383	November 27, 2011	5.35E+03 (8.18%)
MCU-11-1646	December 28, 2011	6.49E+02 (12.0%)
MCU-12-075	January, 23 2012	3.68E+03 (9.53%)
MCU-12-246	February 26, 2012	2.89E+03 (12.4%)
Source Material		
Batch 4-a	Start to August	3.69E+05
Batch 4-b	September-February	4.11E+05

Values in parentheses are the analytical uncertainties.

From the DSSHT ^{90}Sr results, the Sr DF can be determined. There is a great deal of variation between samples, and this reflects the varying amount of MST that has accumulated in the strike tanks. Therefore, the most meaningful DF value is the overall average. The average DF is calculated to be 133 (33.3% RSD). For the same reasons outlined in the ^{238}Pu data (section 3.1), comparisons to previous macrobatches are also of limited value. See Table 4.

Table 4. Comparison of Average ^{90}Sr DF Values for Each Macrobatch

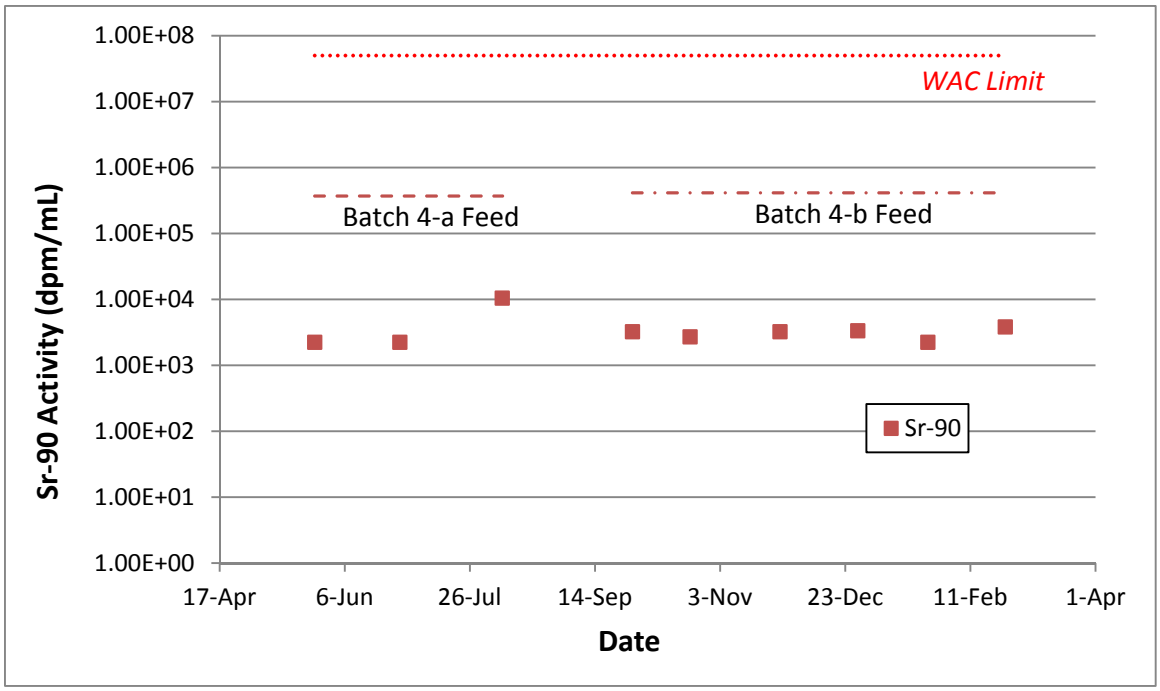
Macrobatch	^{90}Sr DF
1	489 (98.4%)
2	211 (48.8%)
3	116 (30.3%)
4	133 (33.3%)

Values in parentheses are the RSD.

Macrobatch 3 and 4 share more similarities between them than they do with Macrobatch 1 and 2. Using previously documented solution chemistry models does not predict the large changes in DF values between macrobatches. Therefore, SRNL believes that the large DF differences are more due to variations in MST contact times at ARP. The previously mentioned differences in the operating parameters between macrobatches mean that the values in Table 4 do not indicate a noticeable decline in strontium removal, or some process upset.

Figure 2 is the graph of the Macrobatch 4 ^{90}Sr DSSHT data over time.

Figure 2. Macrobatch 4 ^{90}Sr DSSHT Data



3.3 ^{137}Cs results The ^{137}Cs results from the DSSHT, SEHT, and CWT analyses are listed in Table 5. Entries in the "Source Material" columns (representing the feed from Tank 49H) are from a report[3] that calculated the values from known concentrations and blend volumes.

Table 5. ^{137}Cs Concentrations in the SEHT, DSSHT, and CWT Samples

Sample ID	Date Pulled	^{137}Cs (dpm/mL)
DSSHT Samples		
MCU-11-501	May 25, 2011	8.25E+05 (5.00%)
MCU-11-727	June 28, 2011	2.79E+06 (5.00%)
MCU-11-760	August 8, 2011	7.31E+06 (5.00%)
MCU-11-1069	September 29, 2011	7.82E+05 (5.00%)
MCU-11-1239	October 22, 2011	6.41E+05 (5.00%)
MCU-11-1382	November 27, 2011	6.57E+05 (5.00%)
MCU-11-1650	December 28, 2011	2.06E+06 (5.00%)
MCU-12-079	January 25, 2012	3.95E+05 (5.00%)
MCU-12-240	February 25, 2012	1.04E+06 (5.00%)
SEHT Samples		
MCU-11-505	May 25, 2011	1.86E+09 (5.00%)
MCU-11-734	June 1, 2011	1.94E+09 (5.00%)
MCU-11-893	August 24, 2011	1.92E+09 (5.00%)
MCU-11-1073	September 29, 2011	1.51E+09 (5.00%)
MCU-11-1235	October 22, 2011	1.77E+09 (5.00%)
MCU-11-1383	November 27, 2011	1.72E+09 (5.00%)
MCU-11-1646	December 28, 2011	1.76E+09 (5.00%)
MCU-12-075	January 23, 2012	1.48E+09 (5.00%)
MCU-12-246	February 26, 2012	1.37E+09 (5.00%)
CWT Samples		
MCU-11-863	8/22/11	3.57E+05 (5.00%)
MCU-11-866	8/22/11	9.11E+05 (5.00%)
MCU-11-889	8/24/11	5.74E+06 (5.00%)
MCU-11-903	8/25/11	6.13E+06 (5.00%)
MCU-11-1022	9/4/11	1.09E+06 (5.00%)
MCU-11-1028	9/5/11	2.16E+06 (5.00%)
MCU-11-1044	9/15/11	8.12E+03 (5.00%)
MCU-11-1045	9/15/11	6.49E+03 (5.00%)
MCU-11-1049	9/16/11	3.08E+03 (5.00%)
MCU-11-1050	9/16/11	2.92E+03 (5.00%)
Source Material		
Batch 4-a	Start to August	1.44E+08
Batch 4-b	September-February	1.21E+08

Values in parentheses are the analytical uncertainties.

From the DSSHT ^{137}Cs results, the Cs DF can be determined. There is a great deal of variation between samples, in which case the most meaningful DF value is the overall average, which is calculated to be 139 (63.6% RSD). See Table 6.

Table 6. Comparison of Average ^{137}Cs DF Values for Each Macrobatch

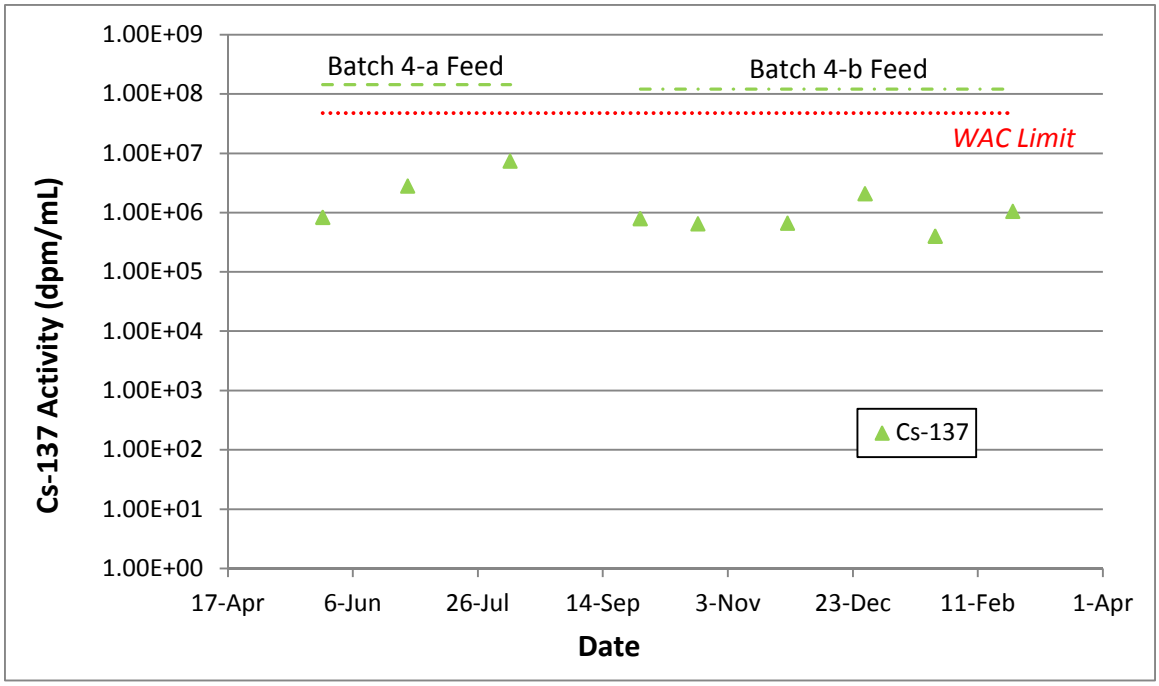
Macrobatch	^{137}Cs DF
1	168 (94.0%)
2	191 (44.8%)
3	164 (41.3%)
4	139 (63.6%)

Values in parentheses are the RSD.

As the ^{137}Cs behavior is much less sensitive to changes in the ARP operating parameters, there is less variation in the DF values between the different macrobatches, and direct comparisons are more valid.

Figure 3 is the graph of the Macrobatch 4 ^{137}Cs DSSHT data over time.

Figure 3. Macrobatch 4 ^{137}Cs DSSHT Data



From the SEHT ^{137}Cs results, the cesium CF can be determined.

The average CF for all Macrobatch 4 samples is 13.2 (8.58% RSD), versus an optimal process target of 15. See Table 7.

Table 7. Comparison of Average ^{137}Cs CF Values for Each Macrobatch

Macrobatch	^{137}Cs CF
1	10.3 (49.9%)
2	7.30 (51.0%)
3	11.1 (37.8%)
4	13.2 (8.58%)

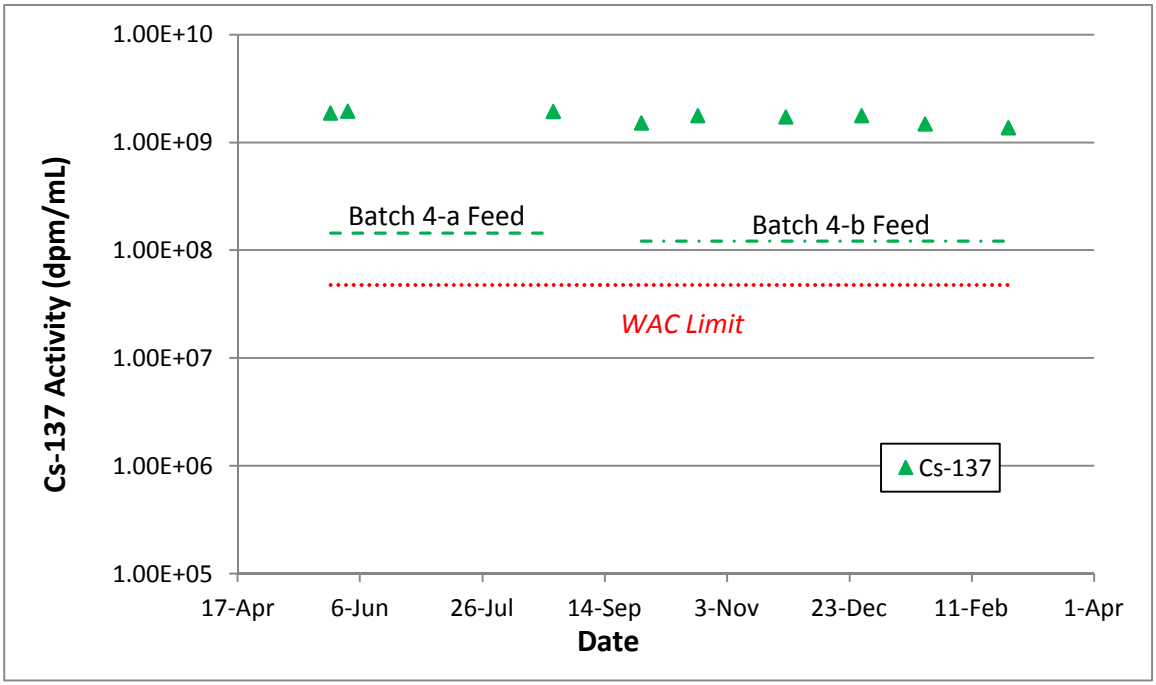
Values in parentheses are the RSD.

As with the DF data, there is less variation in the CF values between macrobatches. While the CF values are below the target values, process upsets and the addition of rainwater to the processing has lowered the overall CF values. However, there is an overall improving trend.

There is a curious coincidence in the DF and CF data. In order of best DF to worst, the order is Macrobatch 2>1>3>4. For the CF data, the trend is just the opposite, Macrobatch 4>3>1>2. At this time SRNL is unsure for the reason for these trends.

Figure 4 is the graph of the Macrobatch 4 ^{137}Cs SEHT data over time.

Figure 4. Macrobatch 4 ^{137}Cs SEHT Data



In the CWT samples, the variation in the ^{137}Cs results is striking. The range of results is over 3 orders of magnitude. This suggests that the caustic wash was inadequately cleansing the stripped solvent until some point between 5 September and 15 September 2011. The supposition is that poor washing fails to remove some trace organic compound that interferes with stripping performance causing reflux of cesium through caustic wash and into the extraction bank of contactors. The normal process expectation is that the stripped solvent will contain only trace amounts of cesium and that the caustic wash serves primarily to remove deleterious organic compounds, chiefly being those produced from the slow radiolytic decay of the solvent components. The data suggests poorer than expected mass transfer of the cesium to the strip acid. Attempts to identify organic impurities that may contribute to this adverse shift in process efficiency have provided only limited insight.[18]

3.4 ICPES Results. The ICPES results for the DSSHT samples are listed in Table 6, and the ICPES results for the SEHT samples are listed in Table 7.

In theory, the Macrobatch 4 material from Tank 49H undergoes a ~13 vol % dilution from ARP and MCU operations.[ץ] Therefore, comparisons between the source material and the DSSHT sample results should take this dilution into account.

A comparison of several of the more concentrated analytes (including B, Cr, Na, P, and S) shows that some of the individual samples show greater than expected dilution. For instance, the February 2012 (MCU-12-240) samples are an average of 65(±7.7)% of the Batch 4-a feed material sample results for those analytes. This would suggest additional dilution occurred at ARP or MCU for specific microbatches, possibly from rainwater addition from the sumps or other minor process upsets.

The August DSSHT sample (MCU-11-760 in Table 6) consistently gives results that are notably lower than that data points around it, even accounting for the previously noted decline. While SRNL cannot statistically invalidate the August sample results, these results are considered to be anomalously low. SRNL is unsure at this time for the reason for this variance.

The titanium results in the DSSHT samples are notable. In most cases, greater levels of titanium in solution have been observed than there is in the feed material. This implies that the MST from ARP is leaching small amounts of titanium or MST fines into solution. In prior work, SRNL has found evidence of Ti-containing solids in the DSSHT coalescer and pre-filters.[19] Testing at SRNL has shown that titanium leaching from MST increases at higher free hydroxide concentration in the waste solution; this is suspected as a leading contributor to the titanium component in the MCU samples.[20]

For the SEHT samples the opposite trend (Table 7) was noted. A comparison of several of the more concentrated analytes (including Al, Ba, Ca, Cr, Fe, Na, Mg, and Zn) shows that the February 2012 samples are an average of 225(±101)% of the May 2011 sample results for those analytes.[ק] This would seem to suggest increasing levels of carryover, across the duration of the macrobatch.

The August SEHT sample (MCU-11-893 in Table 7) consistently gives results that are notably lower than the data points around it, even accounting for the previously noted decline. While SRNL cannot statistically invalidate the August sample results, these results are considered to be anomalously low.

[ץ] Each 3600 gallon batch of material is mixed with 210 gallons of MST slurry, and is then combined with 1 volume of scrub acid for each 15 volumes of salt solution. This dilutes each 3600 gallons to 4050 gallons, or a ~13 vol % increase in volume. Macrobatch 4 did not add NaOH solution at ARP.

[ק] The increase does not take into account the changes in feed material. However, the calculated increase is probably conservative as the 4-b batch shows an overall decline in these analyte concentrations.

For the CWT samples (Table 8), no particular trend was noticed. The sample entry "-623-626" is for a composite of samples MCU-11-623, -624, -625, and -626. Likewise, "-666-669" is for a composite of samples MCU-11-666, -667, -668, and -669. Some analytes increase over the sample range, and some decrease. The expected concentration of Na is 10 mM or 230 mg/L (i.e., the caustic wash concentration feed setpoint). The data suggests a modest positive bias as much as 25% high on average. The data shows, only a modest decline in sodium (20%). This data suggests the feed-and-bleed strategy for washing is maintaining near the appropriate flow rates of reagents and the conservative positive bias from the set point should indicate an overall increase in scrubbing efficiency from the baseline.

Table 6. ICPES Results for the DSSHT Samples (mg/L)

Analyte	MCU-11-501	MCU-11-727	MCU-11-760	MCU-11-1069	MCU-11-1239	MCU-11-1382	MCU-11-1650	MCU-12-79	MCU-12-240
Ag	<1.46	<1.46	<1.46	<1.46	<1.46	<1.46	<1.46	<1.46	<14.4
Al	4080	4260	2480	2870	3320	3180	3180	2700	2840
B	77.4	67.7	47.4	53.1	65.2	58.1	57.6	50.6	52.2
Ba	5.84	2.06	5.21	0.65	2	<0.52	<0.52	<0.52	<0.63
Be	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08
Ca	2.26	1.77	2.34	1.53	0.97	<0.56	<0.56	0.62	<0.96
Cd	<0.7	<0.7	<0.7	<0.7	0.885	0.83	0.83	<0.7	<0.64
Ce	<6.03	<6.03	<6.03	<6.03	<6.03	<6.03	<6.03	<6.03	<6.03
Co	<0.97	<0.97	<0.97	<0.97	<0.97	<0.97	<0.97	<0.97	<0.97
Cr	60.5	61.3	37.1	39.7	44.3	42.1	42.1	37.5	37.9
Cu	0.81	1.07	0.7	0.82	0.96	0.79	0.79	0.75	0.76
Fe	1.33	1.17	1.43	1.41	0.97	1.02	1.02	0.84	0.51
Gd	<0.78	<0.78	<0.78	<0.78	<0.78	<0.78	<0.78	<0.78	<0.78
K	361	364	222	272	329	307	307	267	308
La	<0.54	<0.54	<0.54	<0.54	<0.54	<0.54	<0.54	<0.54	<0.54
Li	18.3	18	11.3	15.6	18.4	17.5	17.5	15	14.8
Mg	<0.15	<0.15	0.16	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15
Mn	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21
Mo	6.1	5.92	3.25	4.48	5.01	5.06	5.06	4.41	5.76
Na	128000	129000	93200	113000	126000	120000	120000	111000	109000
Ni	<1.6	<1.6	<1.6	<4.55	<1.6	<1.6	<1.6	<1.6	<1.6
P	229	228	142	147	166	150	150	129	139
Pb	<7.16	<7.16	<7.16	<7.16	<7.16	<7.16	<7.16	<7.16	<7.16
S	1970	2020	1160	1660	1900	1810	1810	1710	1410
Sb	<10.7	<10.7	<10.7	<10.7	<10.7	<10.7	<10.7	<10.7	<10.7
Si	331	193	226	88.1	167	53.6	53.6	85.1	88
Sn	<5.61	<5.61	<5.61	<5.61	<5.61	<5.61	<5.61	<5.61	<5.61
Sr	0.155	0.06	0.12	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Th	<2.68	<2.68	<2.68	<2.68	<2.68	<2.68	<2.68	<2.68	<5.35
Ti	0.44	2.56	0.7	2.77	1.08	10.6	<10.6	7.94	9.26
U	<32.7	<32.7	<32.7	<32.7	<32.7	<32.7	<32.7	<30	<32.7
V	<0.47	<0.47	<0.47	<0.47	<0.47	<0.47	0.47	<0.47	<0.47
Zn	13.4	7.04	11.1	5.51	7.43	5.78	5.78	7.84	5.27
Zr	<0.55	<0.55	<0.55	<0.55	<0.55	<0.55	<0.55	<0.55	<0.25

The analytical uncertainty for the ICPES samples is 10%.

Table 7. ICPES Results for the SEHT Samples (mg/L)

Analyte	MCU-11-505	MCU-11-734	MCU-11-893	MCU-11-1073	MCU-11-1235	MCU-11-1383	MCU-11-1646	MCU-12-75	MCU-12-246
Ag	<0.432	<0.423	<0.403	<0.437	<0.384	<0.437	<0.0856	<0.787	<0.891
Al	2.72	2.75	2.70	2.74	2.48	3.29	3.07	8.14	9.82
B	<0.598	<0.586	<0.558	<0.604	<0.531	<0.604	0.205	<1.09	<1.23
Ba	0.435	0.342	0.268	0.440	0.192	0.188	0.202	0.402	0.464
Be	<0.024	<0.023	<0.022	<0.024	<0.021	<0.024	<0.00590	<0.043	<0.049
Ca	8.82	7.31	5.35	8.91	4.94	5.98	5.90	13.8	15.1
Cd	<0.207	<0.203	<0.193	<0.209	<0.184	<0.209	<0.0413	<0.377	<0.390
Ce	<1.78	<1.749	<1.66	<1.80	<1.59	<1.80	<0.357	<3.25	<3.68
Co	<0.287	<0.281	<0.268	<0.290	<0.255	<0.290	<0.056	<0.523	<0.592
Cr	0.305	0.302	0.276	0.308	0.229	0.311	0.339	0.722	0.897
Cu	2.15	2.03	1.91	2.17	1.73	2.14	2.07	4.82	5.44
Fe	11.6	11.75	10.5	11.7	9.73	11.9	11.3	25.4	30.5
Gd	<0.231	<0.226	<0.215	<0.233	<0.205	<0.233	<0.0472	<0.420	<0.476
K	<8.91	<8.73	<8.31	<9.00	<7.92	<9.00	6.05	<16.2	<18.4
La	<0.160	<0.157	<0.149	<0.161	<0.142	<0.161	<0.0325	<0.291	<0.329
Li	<0.432	<0.423	<0.403	<0.437	<0.384	<0.437	0.194	<0.787	<0.891
Mg	1.045	0.908	0.317	1.06	0.305	0.353	0.398	0.852	0.939
Mn	0.132	0.129	0.119	0.133	0.139	0.160	0.150	0.334	0.403
Mo	<0.793	<0.777	<0.740	<0.801	<0.705	<0.801	<0.159	<1.44	<1.63
Na	30.8	25.6	12.8	31.1	48.7	75.3	49.9	49.4	100.0
Ni	<1.35	<1.32	<1.26	<1.36	<0.421	<0.478	0.325	<0.862	1.60
P	<4.85	<4.76	<4.53	<4.90	<2.28	<2.59	1.00	<4.67	<5.28
Pb	<2.12	<2.08	<1.98	<2.14	<1.88	<2.14	<0.422	<3.86	<4.37
S	<22.2	<21.8	<20.7	<22.4	<19.7	<22.4	<4.43	<40.4	<45.8
Sb	<3.17	<3.10	<2.95	<3.20	<2.81	<3.20	<0.628	<5.77	<6.53
Si	2.68	1.78	2.02	2.71	1.29	2.11	2.45	<5.27	3.29
Sn	<1.66	<1.63	<1.55	<1.68	<1.48	<1.68	<0.330	<3.02	<3.42
Sr	<0.015	<0.015	<0.014	<0.015	<0.132	<0.150	0.0148	0.032	<0.031
Th	<0.793	<0.777	<0.740	<0.801	<0.705	<0.801	<0.159	<1.44	<3.26
Ti	<0.112	<0.110	<0.105	<0.114	<0.100	<0.114	0.0307	0.097	0.153
U	<9.68	<9.48	<9.03	<9.78	<8.60	<9.78	<1.93	<16.2	<19.9
V	<0.139	<0.136	<0.130	<0.141	<0.124	<0.141	<0.0266	<0.253	<0.287
Zn	17.6	13.4	15.6	17.8	11.7	13.8	13.3	29.3	33.9
Zr	<0.163	<0.160	<0.152	<0.164	<0.145	<0.164	<0.0325	<0.296	<0.153

The analytical uncertainty for the ICPES samples is 10%.

Table 8. ICPES Results for the CWT Samples (mg/L)

Analyte	MCU-11-558	MCU-623-626	MCU-666-669	MCU-11-1022	MCU-11-1023	MCU-11-1027	MCU-11-1028
Ag	<0.058	<0.146	<0.146	<0.058	<0.058	<0.058	<0.058
Al	48	<0.528	<0.528	0.432	0.478	0.51	0.473
B	0.22	<0.142	<0.142	0.237	0.104	0.205	0.265
Ba	0.0568	0.055	0.125	0.202	0.107	0.174	0.218
Be	<0.003	<0.008	<0.008	<0.003	<0.003	<0.003	<0.003
Ca	0.102	0.22	0.175	0.216	0.16	0.211	0.239
Cd	<0.026	<0.07	<0.07	<0.026	<0.026	<0.026	<0.026
Ce	<0.241	<0.603	<0.603	<0.283	<0.283	<0.283	<0.283
Co	<0.039	<0.097	<0.097	<0.038	<0.038	<0.038	<0.038
Cr	<0.041	<0.073	<0.073	<0.033	<0.033	<0.033	<0.033
Cu	<0.025	<0.063	<0.063	<0.025	<0.025	<0.025	<0.025
Fe	<6.3	<0.063	<0.063	<0.038	<0.038	<0.038	<0.038
Gd	<0.086	<0.078	<0.078	<0.031	<0.031	<0.031	<0.031
K	<1.03	<3.01	<3.01	<1.03	<1.03	<1.03	<1.03
La	<0.027	<0.054	<0.054	<0.027	<0.027	<0.027	<0.027
Li	0.047	<1.5	<1.5	<0.058	<0.058	<0.058	<0.058
Mg	0.0312	0.121	0.061	0.0636	0.0734	0.034	0.0692
Mn	<0.008	<0.021	<0.021	<0.021	<0.021	<0.021	<0.021
Mo	<0.247	<0.268	<0.268	<0.107	<0.107	<0.107	<0.107
Na	320	336	295	232	249	233	256
Ni	<0.182	<0.16	<0.16	<0.182	<0.182	<0.182	<0.182
P	10.8	10.4	<0.866	<0.656	<0.656	<0.656	<0.656
Pb	<0.286	<0.716	<0.716	<0.286	<0.286	<0.286	<0.286
S	7.04	<7.5	<7.5	<3	<3	<3	<3
Sb	<0.426	<1.07	<1.07	<0.426	<0.426	<0.426	<0.426
Si	1.26	1.78	2.82	4.33	3.2	3.82	4.75
Sn	<0.224	<0.561	<0.561	<0.224	<0.224	<0.224	<0.224
Sr	<0.002	<0.005	<0.005	0.0024	0.0028	0.0022	0.0028
Th	<0.107	<0.268	<0.268	<0.214	<0.214	<0.214	<0.214
Ti	<0.015	<0.038	<0.038	<0.015	<0.015	<0.015	<0.015
U	<1.31	<3.27	<3.27	<1.2	<1.2	<1.2	<1.2
V	<0.019	<0.047	<0.047	<0.019	<0.019	<0.019	<0.019
Zn	<0.026	<0.066	<0.066	<0.026	0.0456	<0.026	<0.026
Zr	<0.022	<0.025	<0.025	<0.022	<0.022	<0.022	<0.022

The analytical uncertainty for the ICPES samples is 10%.

3.5 IC-Anions Results. A number of CWT samples were also analyzed by the Ion Chromatography (IC)-Anions method. Table 9 lists the results.

Table 9. IC-Anions and pH Results for CWT Samples (mg/L)

Sample	Nitrate	pH	Sample Date
MCU-11-558	437	n.m.	6/1/2011
MCU-11-623-626	447	n.m.	6/8/2011
MCU-11-666-669	572	n.m.	6/15/2011
MCU-11-863	550	9-9.5	8/22/2011
MCU-11-864	570	9-9.5	8/22/2011
MCU-11-865	491	9.5-10	8/22/2011
MCU-11-866	541	9.5	8/22/2011
MCU-11-886	731	9.5	8/23/2011
MCU-11-887	592	9.5	8/23/2011
MCU-11-888	543	9.5	8/24/2011
MCU-11-889	504	9.5	8/24/2011
MCU-11-898	518	9.5	8/24/2011
MCU-11-899	515	9.5	8/24/2011
MCU-11-903	484	9.5	8/25/2011
MCU-11-904	521	9.5	8/25/2011
MCU-11-1022	523	9.5	9/4/2011
MCU-11-1023	507	9.5	9/4/2011
MCU-11-1027	473	9.5	9/5/2011
MCU-11-1028	505	9.5	9/5/2011
MCU-11-1044	<10	n.m.	9/15/2011
MCU-11-1045	<10	n.m.	9/15/2011
MCU-11-1049	<10	n.m.	9/16/2011
MCU-11-1050	36	n.m.	9/16/2011

n.m. = not measured

The analytical uncertainty for all IC-Anions is 10%. pH results typically have an uncertainty of ±0.5 pH units.

In all cases, all analytes except nitrate were below detection limit (10 mg/L). Excluding samples after September 5, 2011 (i.e., MCU-11-1044, MCU-11-1045, MCU-11-1049, and MCU-11-1050 samples), the averages of all samples is 528(±64) mg/L, or 0.00852 M. If the entire nitrate in the CWT samples is from the strip acid, then this concentration

of nitrate also brings in an equimolar amount of protons (0.00852 M). As the protons will react with the NaOH on a 1:1 basis, this would drive the free hydroxide down to 0.00148 M, which corresponds to a calculated pH of 11.2. As the measured pH values are ~9.5, the drop in pH does not match the nitrate concentration. This implies that the low measured pH values are due to factors beyond that of reaction with entrained strip acid. Uptake of atmospheric CO_2 might account for the added decline in the low measured pH.

The pH results suggest that the high ^{137}Cs activity and high nitrate results are correlated with having a pH far below desired levels. Recall that the pH of the fresh CWT material should be 12 (0.01 M NaOH).

The drop in nitrate in sample CWT-1044 and later occurs at the same time as the drop in ^{137}Cs activity. There is a relationship between the nitrate and the ^{137}Cs that is not as simple as $CsNO_3$ leaving the solvent into the CWT, as the concentration of nitrate and cesium do not match.

The changes in both the nitrate and ^{137}Cs concentrations correspond to the increase in the CWT flowrate to 0.55 gallons per minute (see Section 1.0). The increase in flow rates of the aqueous CWT stream that occurred between 5 September 2011 and 15 September 2011 appear to have been effective in preventing large scale migration of the ^{137}Cs into the CWT stream.

4.0 Conclusions

Macrobatch 4 was split into two operating periods and feeds, 4-a and 4-b, due to issues associated with transfer pumps in the Tank Farm and assembling the Macrobatch.

For the DSSHT samples, the overall average DF values for ^{238}Pu, ^{90}Sr, and ^{137}Cs are comparable to Macrobatch 3. There does not appear to be any negative trends in the performance for these elements.

For the SEHT samples, the very large variability in the ^{238}Pu and ^{90}Sr samples makes drawing a conclusion difficult. For the ^{137}Cs, the DF values are slightly lower than for Macrobatch 3. The CF is slightly higher than that for Macrobatch 3. The ICPES data does show a curious ~2 fold increase in several common analytes (including Al, Ba, Ca, Cr, Fe, Na, Mg, and Zn) over the period of all the samples. This would seem to suggest increasing levels of carryover, across the duration of the macrobatch.

For the CWT samples, a clear difference exists between the samples of 5 September 2011 and earlier and the samples 15 September 2011 and later. In the intervening time, the changes implemented in the CWT stream caused a sharp decline in ^{137}Cs and nitrate

concentration apparently giving the desired beneficial improvement in system performance.

5.0 Recommendations, Path Forward or Future Work

After restart of MCU, the periodic DSSHT and SEHT samples should be continued. SRNL recommends analyzing these monthly samples for the same battery of analyses as what is currently being performed. SRNL also recommends pulling routine CWT samples and analyzing for ^{137}Cs and anions. This is a new sample stream for SRNL, but the utility of monitoring the CWT for ^{137}Cs is useful.

5.0 References

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Distribution:

K. M. Fox, 999-W
S. D. Fink, 773-A
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