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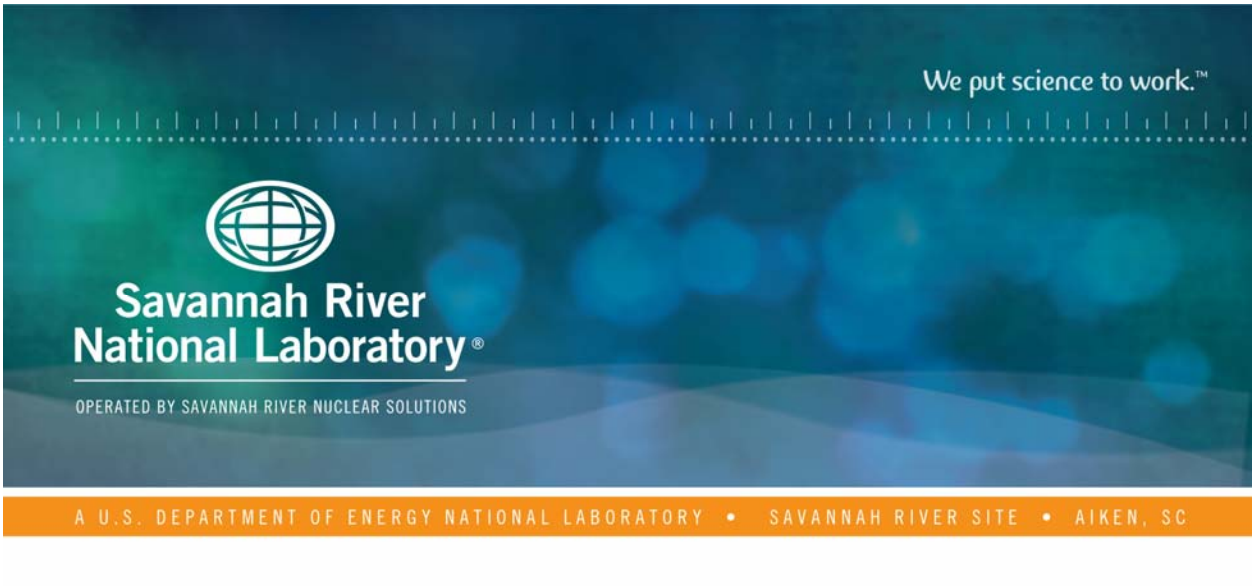

Analytical Results from Salt Batch 10 Routine DSSHT and SEHT Monthly Samples

T. B. Peters

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EXECUTIVE SUMMARY

Strip Effluent (SE) Hold Tank (SEHT) and Decontaminated Salt Solution (DSS) Hold Tank (DSSHT) samples from several "microbatches" of the Integrated Salt Disposition Project (ISDP) "macrobatch" Salt Batch 10 have been analyzed for ^{238}Pu, ^{90}Sr, ^{137}Cs, cations (via Inductively Coupled Plasma Emission Spectroscopy - ICPES), and in some cases anions (via Ion Chromatography Anions - IC-A). The analytical results from the current microbatch samples are similar to those from previous macrobatches. In the Modular Caustic-Side Solvent Extraction Unit (MCU), the Cs removal continues to exceed process requirements. The bulk chemistry of the DSSHT and SEHT samples do not show any signs of unusual behavior except for slightly elevated amounts of sodium in the SE samples. This summary represents the final Salt Batch processed through MCU prior to commencement of process and transfer line tie-ins to support the startup of the Salt Waste Processing Facility (SWPF).

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LIST OF ABBREVIATIONS

AD	Analytical Development
ARP	Actinide Removal Process
DF	Decontamination Factor
DSS	Decontaminated Salt Solution
DSSHT	Decontaminated Salt Solution Hold Tank
IC-A	Ion chromatography - anions
ICPES	Inductively-coupled plasma emission spectroscopy
ISDP	Interim Salt Disposition Project
MCU	Modular Caustic-Side Solvent Extraction Unit
MST	Monosodium titanate
NGS	Next Generation Solvent
SE	Strip Effluent
SEHT	Strip Effluent Hold Tank
SRNL	Savannah River National Laboratory
SSFT	Salt Solution Feed Tank
SWPF	Salt Waste Processing Facility
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request

1.0 Introduction

During operation of the ISDP, salt waste is processed through the Actinide Removal Process (ARP) and MCU in batches of ~3,800 gallons. MCU uses solvent extraction technology to remove cesium from salt waste and concentrate cesium in an acidic aqueous stream (the SE), leaving a decontaminated caustic salt aqueous stream (the DSS). Sampling occurs in the DSSHT and SEHT in the MCU process. The MCU sample plan requires that batches be sampled and analyzed on a monthly frequency for plutonium and strontium content by the Savannah River National Laboratory (SRNL) to determine Monosodium Titanate (MST) effectiveness.[i] (Even though MST is not currently used in the process, the analyses are still performed to provide other process monitoring data.) A Task Technical and Quality Assurance Plan (TTQAP) was prepared to cover routine analyses.[ii] The cesium measurement is used to monitor cesium removal effectiveness while the ICPES and IC-A is used to monitor inorganic carryover.

A previous report provided the results of several sets of sample results from earlier Macrobatch 10 operations.[iii] The sample results described in this report are from the remainder of Macrobatch 10 operations.

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 samples were delivered in "thief" holders. Samples of the same type were each composited into a single bottle. The SEHT samples were analyzed for ^{137}Cs, ^{238}Pu, and ^{90}Sr content, as well as for cation content (ICPES). The DSSHT samples were also analyzed for anion content (IC-A). The DSSHT and SSFT samples were sent for analysis without dilution or filtration. SEHT samples were sent for analysis with dilution (typically ~40 fold) using deionized water but without filtration.

2.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. For SRNL documents, the extent and type of review using the SRNL Technical Report Design Checklist is outlined in WSRC-IM-2002-00011, Rev. 2.[iv]

This work is classified as Production Support as per the controlling Technical Task Request (TTR).[v] The laboratory work, analysis, and the review meet the customer requested quality assurance needs. Records for this work are contained in an electronic notebook ELN-A4571-00084-36.

3.0 Results and Discussion

3.1 Results from DSSHT and SEHT Samples

The ^{137}Cs, ^{90}Sr, and ^{238}Pu results from the DSSHT and SEHT radiochemical analyses are listed in Table 1 for all SB10 samples.[iii] The source material (Tank 49H) entries were derived from customer blend calculations for Salt Batch 10 and are used for comparison.[vi]

Table 1. Radiochemical Results for the DSSHT and SEHT Samples

Sample ID	Sample Date	^{238}Pu (dpm/mL)	^{90}Sr (dpm/mL)	^{137}Cs (dpm/mL)
DSSHT Samples				
MCU-18-171/172/173	5/31/2018	7.43E+04 (6.9%)	6.57E+05 (14%)	9.98E+04 (5.0%)
MCU-18-227/228/229	6/19/2018	6.60E+04 (26%)	5.78E+05 (27%)	2.92E+05 (5.0%)
MCU-18-307/308/309	7/16/2018	7.24E+04 (6.7%)	7.49E+05 (16%)	4.57E+04 (5.0%)
MCU-18-364/365/366	8/21/2018	4.73E+04 (5.7%)	4.69E+05 (17%)	5.41E+05 (5.0%)
MCU-19-80/81/82	2/17/2019	7.57E+04 (5.6%)	6.39E+05 (16%)	1.95E+04 (5.0%)
MCU-19-200/201/202	3/19/2019	7.63E+04 (6.7%)	6.66E+05 (16%)	6.66E+04 (5.0%)
MCU-19-354/355/356	4/12/2019	4.83E+04 (7.4%)	9.96E+05 (18%)	8.57E+03 (5.0%)
MCU-19-478/479/480	5/18/2019	4.87E+04 (6.6%)	9.81E+05 (16%)	9.24E+03 (5.0%)
SEHT Samples				
MCU-18-177/178/179	5/31/2018	<1.67E+02	<1.54E+04	1.20E+09 (5.0%)
MCU-18-224/225/226	6/19/2018	<3.38E+02	<1.91E+04	7.05E+09 (5.0%)
MCU-18-301/302/303	7/16/2018	<2.10E+02	<1.53E+04	6.31E+09 (5.0%)
MCU-18-361/362/363	8/23/2018	1.22E+02 (55%)	<1.98E+04	2.42E+09 (5.0%)
MCU-19-74/75/76	2/17/2019	<1.48E+02	<3.88E+03	5.86E+09 (5.0%)
MCU-19-206/207/208	3/19/2019	<1.17E+02	<1.35E+04	6.39E+09 (5.0%)
MCU-19-363/364/365	4/12/2019	<1.44E+02	<1.13E+04	3.82E+09 (5.0%)
MCU-19-487/488/489	5/19/2019	<1.11E+02	<1.78E+04	4.10E+09 (5.0%)
Source Material (Salt Batch 10) [vi]		6.77E+04 (5-10%)	8.17E+05 (15-20%)	3.95E+08 (5%)

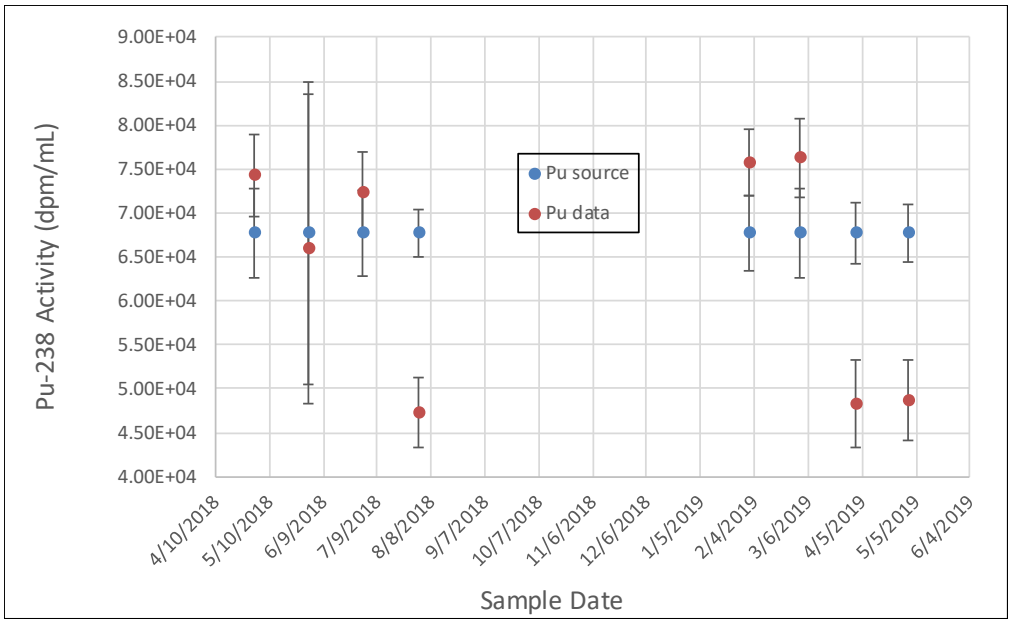
Values in parentheses are the 1 sigma analytical uncertainties as provided by Analytical Development (AD), except for the source material, which is the typical range of analytical uncertainties for which this customer calculation are derived.

Previously, ARP stopped striking with MST while processing Macrobatch 8B as the source material was less than the Saltstone Waste Acceptance Criteria (WAC) limits. All sample results for Macrobatch 10 reflect the lack of MST use. The variances in the Pu and Sr DSSHT values are typical for the entirety of the Salt Batch 10 samples (for example, 4 of 8 ^{238}Pu results were above the source material value, while 4 were below, and 2 and 6 respectively for the ^{90}Sr). Variations in the ^{90}Sr and ^{238}Pu values compared to the source material are partly due to the individual

uncertainties associated with the ^{90}Sr and ^{238}Pu measurements, and not due to active attempts at Pu and Sr removal.

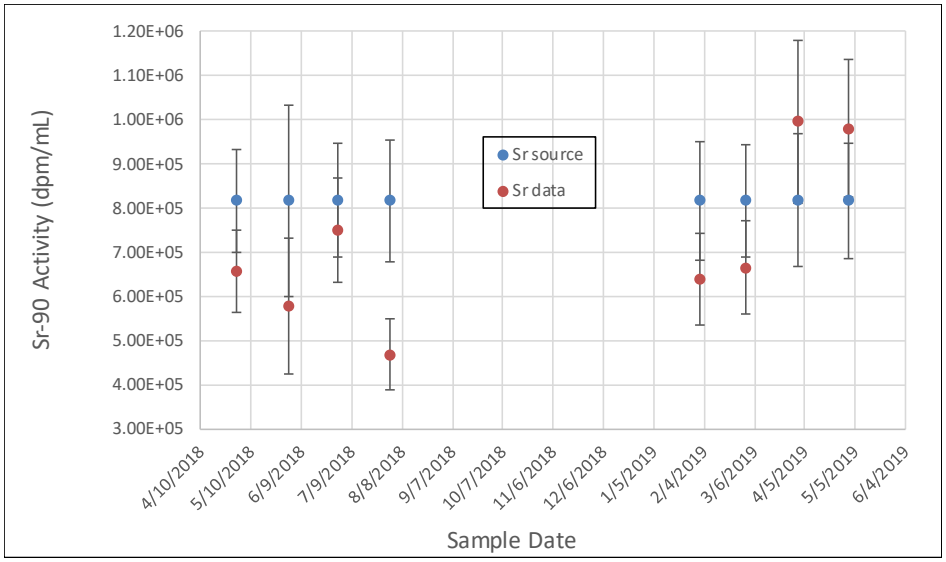
Another way to examine this is to graph the Salt Batch 10 ^{238}Pu and ^{90}Sr data compared to the source material. See Figure 1 for a graph of the ^{238}Pu data and Figure 2 for the ^{90}Sr data.

Figure 1. ^{238}Pu Data of the Source Material vs. all Salt Batch 10 Samples



For the comparison, we are assuming the 1-sigma analytical uncertainty associated with the source material values is of similar magnitude as for the Salt Batch 10 samples. Most of the data suggests any differences falls within the sum of the analytical method 1-sigma uncertainties. (Additionally, this assessment does not include the contribution from dilution that occurs within the MCU processing which further broadens the uncertainty bands.)

Figure 2. ^{90}Sr Data of the Source Material vs. all Salt Batch 10 Samples



The Decontamination Factors (DFs) for Pu, Sr and Cs are displayed in Figures 3 and 4. DF is defined as feed value divided by the sample result. The large variations are an indication that specific comparisons or conclusions are rendered difficult by the wide range of results which are a result of changes in operating conditions.

Figure 3. Pu and Sr DF Values for all SB10 Samples

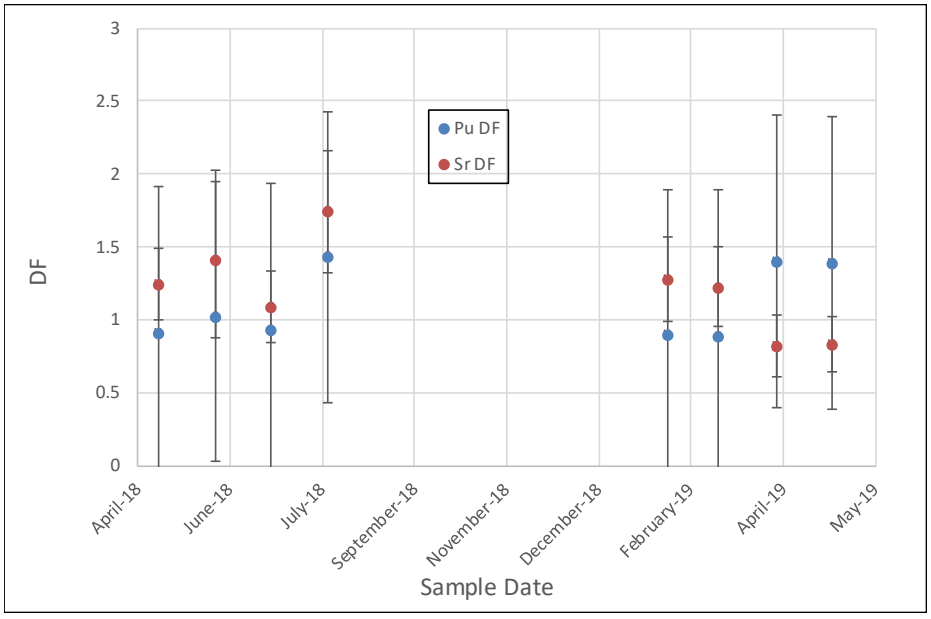
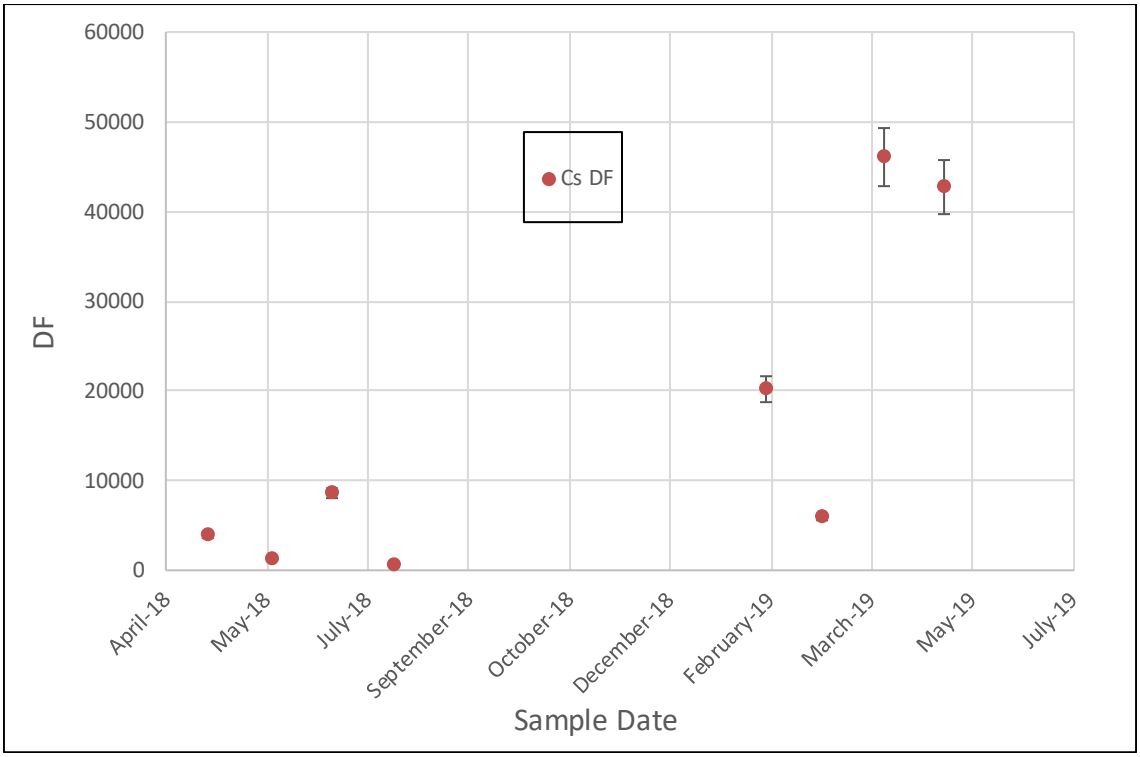


Figure 4. Cs DF Values for all SB10 Samples



The lack of MST use does not affect the ^{137}Cs removal and the values in the DSSHT are typical. The average concentration factor (= measured / source material) for the Cs measurements is 11.8, well within expected performance given the process outages.

The meaningful (present in non-trace quantities) ICPES and IC-A results for the DSSHT samples are listed in Table 3.

Table 2. ICPES and IC-A Results for the DSSHT Samples

Analyte	MCU-19-xxx Sample ID (mg/L)				
	Salt Batch 10[vi]	80/81/82	200/201/201	354/355/356	478/479/480
Al	6260	5990	6200	6590	5510
B	55.9	58.8	53.9	52.5	56.3
Cr	59.2	69.9	64.2	54.4	37.5
K	491	519	465	342	480
Na	141000	128000	131000	126000	123000
Si	21.2	89.1	108	105	105
Zn	3.19	6.46	4.88	8.32	4.81
F	98.8	<100	<100	<100	<100
Formate	222	<100	105	153	<100
Cl	674	590	579	611	657
Nitrite	33300	29600	28600	27800	30000
Nitrate	99800	97400	95400	80200	90600
Phosphate	389	348	330	198	256
Sulfate	4940	4980	4900	4080	4410
oxalate	410	405	460	446	497
% decline from feed concentration	NA	-0.22%	3.6%	13%	13%

The 1-sigma analytical uncertainty for the ICPES and IC-A analyses is 10%.
NA = not applicable.

The material from Tank 49H undergoes a ~13 vol % dilution in ARP and MCU while no MST is in use.[vii] Therefore, direct comparisons between the source material and the DSSHT sample results should take this into account. Of the reported analytes in Table 3, B, Cr, Na, nitrite, nitrate, and sulfate are the analytes that are only subject to dilution effects in the ARP/MCU system – they are not affected by the solvent extraction, and they typically have high solubility relative to the concentrations measured. These analytes are shaded in Table 2. In Table 3, the "% decline from feed concentration" row is the average of the six shaded analytes percentage decline compared to the value of their concentration in Salt Batch 10 feed. For example, for the MCU-19-478/479/480 sample, the six shaded analytes are an average of 87% of their respective concentrations in the Salt Batch 10 feed. This is reasonable of DSSHT samples from past history. The reasons for the lack of expected dilution are unknown in the first 2 samples. The effect is consistent across the range

of shaded analytes so this is unlikely to be an analytical effect. Stratification of soluble analytes in the feed tank seems unlikely, and evaporative losses in the feed are also unlikely.

The meaningful ICPES (B, K, Na) and IC-A (nitrate, nitrite) results for the SEHT samples are listed in Table 4.

Table 3. ICPES and IC-A Results for the SEHT Samples

Analyte	MCU-19-xxx Sample ID (mg/L)			
	74/75/76	206/207/208	363/364/365	487/488/489
B	90.1	95.1	82.6	92.1
K	66.7	<53.9	<61.2	73.9
Na	116	72.5	<264	134
Nitrite	<177	<453	<419	NM
Nitrate	<177	<453	<419	NM

The 1-sigma analytical uncertainty for each result is 10%.
NM indicates no measurement.

The boron values for all SB10 SEHT samples averages 92 mg/L, compared to the nominal value (108 mg/L), which is typical. The potassium results that exceed detection limits are slightly higher than typical (normally ~20-50 mg/L). The SEHT samples (except 363/364/365) show elevated Na (>~50 mg/L), which is atypical.

Mechanical carryover of feed or DS into the SE samples cannot be the reason for this as the ratio of Na to K would mirror those solutions. Instead, it appears that the scrubbing or washing out of the Na and K has been less efficient in this salt batch.

3.2 Salt Solution Feed Tank Sample

A single sample of the Salt Solution Feed Tank (SSFT) was delivered to SRNL on April 18, 2019. This sample from the SSFT was to determine whether or not the material was showing variances from the contents of Tank 21H. The results are reported in Table 5.

Table 4. MCU-19-137 Sample Results (mg/L)

Analyte	Salt Batch 10[vi]	MCU-19-137
^{137}Cs	3.95E+08 (dpm/mL)	3.23E+08 (dpm/mL)
Al	6260	6579
B	55.9	61.0
Cr	59.2	57.9
K	491	546
Na	141000	149000
Si	21.2	<31.8
Zn	3.19	<25.4
F	98.8	<254
Formate	222	<254
Cl	674	711
Nitrite	33300	32300
Nitrate	99800	96000
Phosphate	389	<254
Sulfate	4940	4750
oxalate	410	404
% decline from feed concentration	NA	-0.31%

The analytical uncertainty for each result is 10%, except for the ^{137}Cs measurement, which is 5%.

The results show that other than a moderate decline in phosphate, the SSFT sample closely mirrors the contents of the salt batch feed tank (Tank 21H), as it should. Of the reported analytes in Table 5, B, Cr, Na, nitrite, nitrate, and sulfate are the analytes that are only subject to dilution effects in ARP (which is near zero) – they are largely immune from risk of change due to precipitation. These analytes are shaded in Table 5. In Table 5, the "% decline from feed concentration" row is the average of the six shaded analytes percentage decline compared to the value of their concentration in Salt Batch 10 feed.

4.0 Conclusions

During the range of the samples, MCU processed 328,000 gallons of feed. SEHT and DSSHT samples from several of the "microbatches" of ISDP macrobatch Salt Batch 10 have been analyzed for ^{238}Pu, ^{90}Sr, ^{137}Cs, cations (ICPES), and anions (IC-A). The analytical results from the current microbatch samples are similar to those from previous microbatches. In MCU the Cs removal

continues to exceed requirements. The bulk chemistry of the DSSHT and SEHT samples do not show any signs of unusual behavior. This summary represents the final Salt Batch processed through MCU prior to commencement of process and transfer line tie-ins to support the startup of SWPF.

5.0 References

[i] M. W. Geeting, "Interim Salt Disposition Project (ISDP) Sample Plan", U-ESR-H-00068, Rev. 5, April 28, 2009.

[ii] T. B. Peters, A. L. Washington II, F. F. Fondeur, "Task Technical and Quality Assurance Plan for Routine Samples in Support of ARP and MCU", SRNL-RP-2013-00536, Rev. 2, January 2019.

[iii] T. B. Peters, "Analytical Results from Salt Batch 10 Routine DSSHT and SEHT Monthly Samples", SRNL-STI-2018-00708, Rev.0, January 2019.

[iv] Savannah River National Laboratory, "Technical Report Design Check Guidelines", WSRC-IM-2002-00011, Rev. 2.

[v] Q. Nguyen, X-TTR-H-00026, July 22, 2013.

[vi] C. I. Aponte, "Blend Evaluation for Tank 49 Feed for ISDP Salt Batch 10", X-ESR-H-00893, Rev.0, July 24, 2017.

[vii] A. G. Garrison, "Evaluation of Interim Salt Disposition Project (ISDP) Macrobatch Dilution Bases Experienced at Actinide Removal Process and Modular Caustic Solvent Extraction Unit (ARP/MCU)", X-ESR-H-00724, Rev. 1, May 28, 2015.

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