Analysis of 2H-Evaporator Scale Wall [HTF-13-82] and Pot Bottom [HTF-13-77] Samples

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June 2013

SRNL-STI-2013-00352

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Prepared for
U.S. Department of Energy

Keywords: Tank Farm, Sodium Aluminosilicate, Evaporator

Retention: ***Permanent***

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Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

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ACKNOWLEDGEMENTS

The author extends thanks to the multiple members of the SRNL Shielded Cells and AD organization members who processed the samples and provided analytical results, specifically, C. Coleman, R. Sullivan and D. Missimer.

EXECUTIVE SUMMARY

Savannah River Remediation (SRR) is planning to remove a buildup of sodium aluminosilicate scale from the 2H-evaporator pot by loading and soaking the pot with heated 1.5 M nitric acid solution. Sampling and analysis of the scale material has been performed so that uranium and plutonium isotopic analysis can be input into a Nuclear Criticality Safety Assessment (NCSA) for scale removal by chemical cleaning. Historically, since the operation of the Defense Waste Processing Facility (DWPF), silicon in the DWPF recycle stream combines with aluminum in the typical tank farm supernate to form sodium aluminosilicate scale mineral deposits in the 2H-evaporator pot and gravity drain line.

The 2H-evaporator scale samples analyzed by Savannah River National Laboratory (SRNL) came from the bottom cone sections of the 2H-evaporator pot [Sample HTF-13-77] and the wall 2H-evaporator [sample HTF-13-82].

X-ray diffraction analysis (XRD) confirmed that both the 2H-evaporator pot scale and the wall samples consist of nitrated cancrinite (a crystalline sodium aluminosilicate solid) and clarkeite (a uranium oxy-hydroxide mineral).

On "as received" basis, the bottom pot section scale sample contained an average of 2.59E+00 ± *1.40E-01* wt % total uranium with a U-235 enrichment of 6.12E-01 ± *1.48E-02 %*, while the wall sample contained an average of 4.03E+00 ± *9.79E-01* wt % total uranium with a U-235 enrichment of 6.03E-01% ± *1.66E-02* wt %.

The bottom pot section scale sample analyses results for Pu-238, Pu-239, and Pu-241 are 3.16E-05 ± *5.40E-06* wt %, 3.28E-04 ± *1.45E-05 wt* %, and <8.80E-07 wt %, respectively. The evaporator wall scale samples analysis values for Pu-238, Pu-239, and Pu-241 averages 3.74E-05 ± *6.01E-06* wt %, 4.38E-04 ± *5.08E-05 wt* %, and <1.38E-06 wt %, respectively. The Pu-241 analyses results, as presented, are upper limit values.

These results are provided so that SRR can calculate the equivalent uranium-235 concentrations for the NCSA.

Results confirm that the uranium contained in the scale remains depleted with respect to natural uranium. SRNL did not calculate an equivalent U-235 enrichment, which takes into account other fissionable isotopes U-233, Pu-239 and Pu-241. The applicable method for calculation of equivalent U-235 will be determined in the NCSA.

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LIST OF ABBREVIATIONS

DWPF	Defense Waste Processing Facility
HLW	High-Level Waste
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
LSC	Liquid Scintillation Counting
NCSA	Nuclear Criticality Safety Assessment
PHA	Pulse Height Analysis
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TTA	Thenoyltrifluoroacetone
XRD	X-Ray Diffraction
TTR	Technical Task Request

1.0 Introduction

Savannah River Remediation (SRR) is planning to remove a buildup of sodium aluminosilicate scale from the 2H-evaporator pot by the addition of dilute nitric acid solution.[1] Sampling and analysis of the scale material provides the data needed for SRR to perform a Nuclear Criticality Safety Assessment (NCSA) of scale removal by chemical cleaning. Evaporator scale samples [HTF-13-77] from the evaporator pot bottom and evaporator wall scale sample [HTF-13-82] were pulled by SRR and delivered to Savannah River National Laboratory (SRNL) in May 2013 for analysis for primary fissile isotopes and non-fissile isotopes of uranium.

The 242-16H evaporator (2H evaporator) system concentrates high level waste consisting primarily of high-level waste (HLW) recycled to the SRS H-Area Tank Farm from the Defense Waste Processing Facility (DWPF). Historically, since the operation of DWPF, silicon in the recycle stream reacts with aluminum in the typical HLW to form sodium aluminosilicate mineral scale deposits in the evaporator pot and gravity drain line. The deposits are primarily nitrated sodium aluminosilicates with smaller amounts of clarkeite, Na((UO2)O(OH)). Nominally, the uranium in the scale is depleted in U-235 because the feed to the evaporator is depleted in U-235. In support of the criticality analysis, SRR obtained samples of evaporator scales from three different locations within the evaporator pot. SRR has requested that SRNL dissolve and analyze these samples for uranium and plutonium isotopic content and major radionuclide components. Crystallographic information for the samples was also requested.

The Technical Task Request (TTR) [1] and the Task Technical and Quality Assurance Plan [2] define the tasks and requirements for the performance of this characterization program by SRNL. In order to meet the SRR schedule needs, this report contains only the analytical results for uranium isotopes, plutonium isotopes, and crystallography for the 2H-evaporator pot scale samples. A revision to this report will contain the results for other radiochemical analyses that are being performed to gather information related to dose rate and hydrogen generation rate.

2.0 Samples

On May 15, 2013, SRR sampled scale materials from three locations in the 2H-evaporator pot and delivered the samples to SRNL. The sample holders included two evaporator wall samples [HTF-13-78 and HTF-13-82] and one evaporator pot bottom sample [HTF-13-77]. The sample holders were opened on May 16, 2013. The evaporator pot bottom sample contained 3.99 grams of material while the wall sample [HTF-13 82] contained 9.81 grams of scale samples, as shown in Figure 1. The evaporator Wall sample holder which was supposed to contain sample HTF-13-78 was empty.

2.1 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 contained in WSRC-IM-2002-00011, Rev. 2.

This work was performed in accordance with the requirements of the task technical request [1]. The experimental data are for these analyses are contained in Laboratory Notebook SRNL-NB-2013-00026 and various Analytical Development (AD) notebooks.

3.0 Experimental Procedure

Three "as-received" portions each of the evaporator pot bottom and wall scale samples (0.249 ± 0.035 g of the material in 100 mL dissolution volume giving an average digestion factor of 401.66 mL/g) were dissolved in the SRNL shielded cells using the sodium peroxide fusion digestion method. Uranium isotope analysis on the dissolved and diluted samples was obtained by using Inductively Coupled Plasma–Mass Spectrometry (ICP-MS). Plutonium isotopes Pu-238, Pu-239/240 and Pu-241 were measured on the dissolved and diluted samples by thenoyltrifluoroacetone (TTA) separation and alpha Pulse Height Analysis (PHA) and beta Liquid Scintillation Counting (LSC). Small portions (0.1 gram) of the original scale samples were analyzed by X-Ray Diffraction (XRD) to determine the crystalline phases present.

4.0 Results and Discussion

The XRD spectra for the two 2H evaporator scale samples are presented in Figures 2 and 3. XRD analysis confirmed that both the bottom cone section sample and wall sample from the 2H-evaporator consisted of clarkeite (a uranium oxy-hydroxide mineral) and nitrated Cancrinite (a crystalline sodium aluminosilicate solid) [3]. However, looking at the two XRD spectra (around 31^{o} (Two –Theta (degree))) there is an additional crystalline compound that was not positively identified with the XRD library. There appears to be more of this unidentified crystalline material in the wall sample.

Pu-239/240 analytical data was converted from activity units to wt% making the assumption that all activity measured as Pu-239/240 was from Pu-239. This assumption leads to somewhat higher masses of Pu-239 and total Pu. Since it is assumed that all measured Pu-239/240 activity is Pu-239, Pu-240 is not reported. Mass 238 from ICP-MS is acceptable for use as solely the U-238 mass because Pu-238 contributes an insignificant amount to that mass value. The total uranium values provided in the tables are sums of all uranium isotopes determined by ICP-MS.

Tables 1 and 2 contain the results for uranium and plutonium radionuclide analyses results. Analyses were performed in triplicate. A measure of uncertainty (±) as reported is the standard deviation of the multiple sample preparation analyses results. On "as-received" basis, the bottom pot section scale sample contained an average of 2.59E+00 ± *1.40E-01* wt % total uranium with a U-235 enrichment of 6.12E-01± *1.48E-02 %*, while the wall sample contained an average of 4.03E+00 ± *9.79E-01* wt % total uranium with a U-235 enrichment of 6.03E-01 ± *1.66E-02* %. The U-235 enrichment was calculated as the U-235 concentration divided by total uranium concentration.

Uranium-233 was the only uranium isotope in the pot scale sample which measured less than the instrument detection limit; averaging <1.88E-04 wt %. One of the triplicate U-233 runs in the wall sample measured less than the instrument detection limits (< 2.00E-

04 wt %) while the other two runs were above the instrument detection limits (2.41E-04 and 2.12E-04 wt %).

The bottom pot section scale sample analysis results for Pu-238, Pu-239, and Pu-241 averaged 3.16E-05 ± 5.40E-06 wt %, 3.28E-04 ± 1.45E-05 wt %, and <8.80E-07 wt %, respectively. The Pu-241 analyses results, as presented, are upper limit values.

The evaporator wall scale sample analysis results for Pu-238, Pu-239, and Pu-241 averaged 3.74E-05 ± 6.01E-06 wt %, 4.38E-04 ± 5.08E-05 wt %, and <1.38E-06 wt %, respectively. Again, Pu-241 analyses results, as presented, are upper limit values.

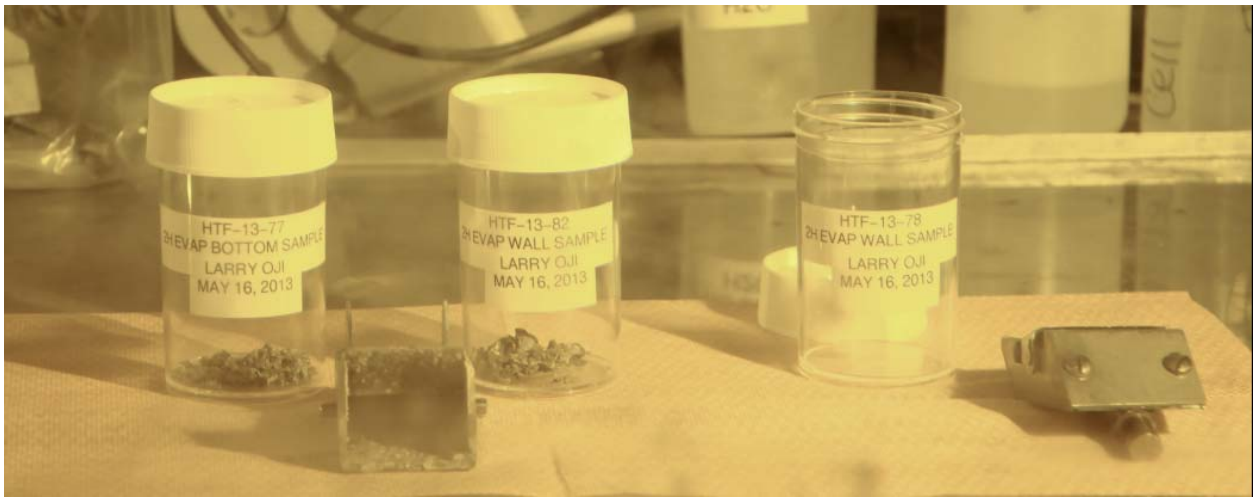

Figure 1 2H-Evaporator Samples; pot bottom sample HTF-13-77 and 2H-evaporator Wall scale samples HTF-13-82 and HTF-13-78. Wall sample HTF-13-78 contained no measurable sample.

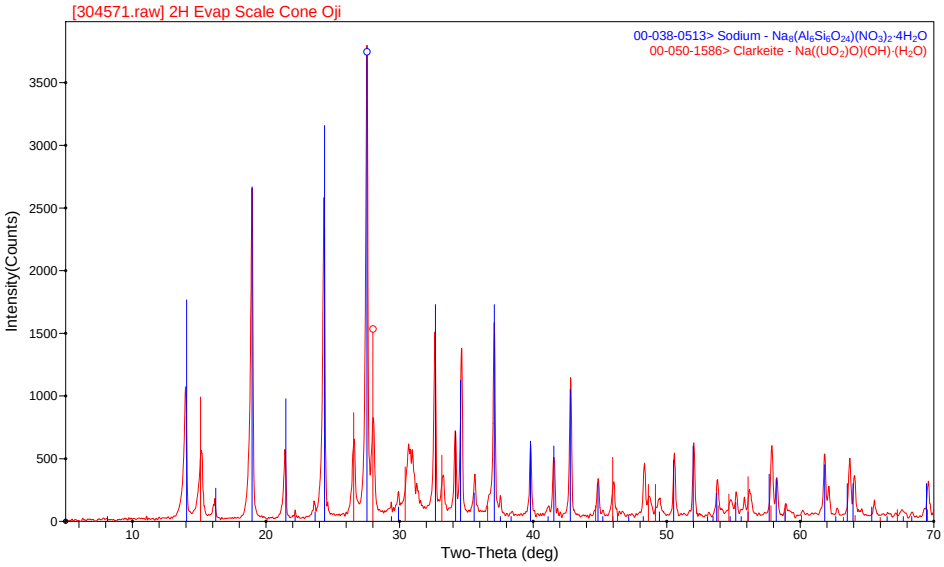

Figure 2 XRD analysis spectra result for 2H-evaporator pot bottom scale sample

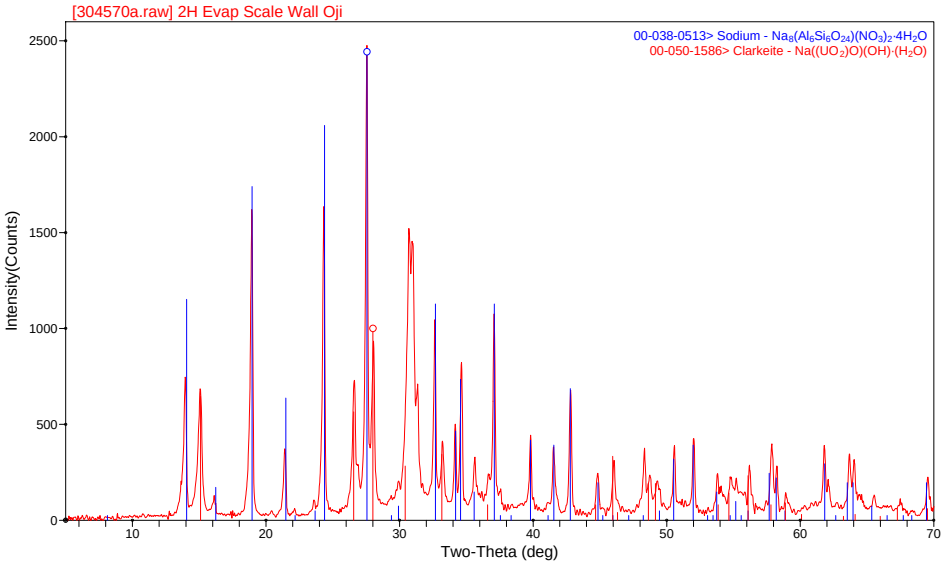

Figure 3 XRD analysis spectra result for 2H-evaporator wall scale sample

Table 1 Analysis of the 2H-Evaporator Pot Bottom Scale, HTF-13-77

Analyte	Preparation 1	Preparation 2	Preparation 3	Average	St.dev.	Units
U-233	<1.85E-04	<1.81E-04	<1.97E-04	**<1.88E-04**		wt %
U-234	4.84E-04	4.36E-04	4.45E-04	**4.55E-04**	*2.55E-05*	wt %
U-235	1.65E-02	1.55E-02	1.54E-02	**1.58E-02**	*6.19E-04*	wt %
U-236	6.81E-04	7.55E-04	7.43E-04	**7.26E-04**	*4.00E-05*	wt %
U-238	2.71E+00	2.56E+00	2.43E+00	**2.56E+00**	*1.41E-01*	wt %
U-Total	2.73E+00	2.58E+00	2.45E+00	**2.59E+00**	*1.40E-01*	wt %
U-235/Total U*100	6.05E-01	6.02E-01	6.29E-01	**6.12E-01**	*1.48E-02*	%
Pu-238	3.13E-05	3.71E-05	2.63E-05	**3.16E-05**	*5.40E-06*	wt %
Pu-239*	3.43E-04	3.14E-04	3.27E-04	**3.28E-04**	*1.45E-05*	wt %
Pu-241	<9.40E-07	<8.62E-07	<8.40E-07	**<8.80E-07**		wt %

***It is assumed that all measured Pu-239/240 activity is Pu-239. Thus, Pu-240 not reported.**

Table 2 Analysis of the 2H-Evaporator Wall Scale, HTF-13-82

Analyte	Preparation 1	Preparation 2	Preparation 3	Average	St.dev	Units
U-233	2.41E-04	<2.00E-04	2.12E-04	**≤2.18E-04**		wt %
U-234	6.41E-04	4.08E-04	6.75E-04	**5.75E-04**	*1.45E-04*	wt %
U-235	2.70E-02	1.79E-02	2.77E-02	**2.42E-02**	*5.49E-03*	wt %
U-236	1.64E-03	9.35E-04	1.33E-03	**1.30E-03**	*3.52E-04*	wt %
U-238	4.40E+00	2.89E+00	4.71E+00	**4.00E+00**	*9.77E-01*	wt %
U-Total	4.43E+00	2.91E+00	4.74E+00	**4.03E+00**	*9.79E-01*	wt %
U-235/Total U*100	6.10E-01	6.15E-01	5.84E-01	**6.03E-01**	*1.66E-02*	%
Pu-238	4.05E-05	3.05E-05	4.13E-05	**3.74E-05**	*6.01E-06*	wt %
Pu-239*	4.49E-04	3.83E-04	4.83E-04	**4.38E-04**	*5.08E-05*	wt %
Pu-241	<1.71E-06	<9.84E-07	<1.46E-06	**<1.38E-06**		wt %

***It is assumed that all measured Pu-239/240 activity is Pu-239. Thus, Pu-240 not reported.**

5.0 Conclusions

The 2H Evaporator scale samples from the wall and bottom sections of the 2H-evaporator pot [bottom pot scale sample (HTF-13-77) and wall sample (HTF-13-82)] are composed of nitrated cancrinite (a crystalline sodium aluminosilicate solid) and clarkeite (a uranium oxy-hydroxide mineral).

On "as-received" basis, the bottom pot scale sample contained an average of 2.59E+00 ± *1.40E-01* wt % total uranium with a U-235 enrichment of 6.12E-01 % ± *1.48E-02*, while the wall sample contained an average of 4.03E+00 ± *9.79E-01* wt % total uranium with a U-235 enrichment of 6.03E-01% ± *1.66E-02* wt %. These results confirm that the uranium contained in the scale remains depleted with respect to natural uranium.

6.0 References

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