Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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Analysis of the 2H-Evaporator Scale Samples (HTF-17-56, -57)

M. S. Hay
C. J. Coleman
D. P Diprete

September 2017

SRNL-STI-2017-00537, Rev. 0

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Prepared for
U.S. Department of Energy

SRNL-STI-2017-00537
Revision 0

Keywords: *2H Evaporator System, Radionuclides, Criticality*

Retention: *Permanent*

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REVIEWS AND APPROVALS

AUTHORS:

M. S. Hay, Advanced Characterization & Processing Date

C. J. Coleman, Analytical R&D Programs and Material Characterization Date

D. P. Diprete, Nuclear Measurements Date

TECHNICAL REVIEW:

L. Magwood, Advanced Characterization & Processing Date

APPROVAL:

B. J. Wiedenman, Manager Date
Advanced Characterization & Processing

D. E. Dooley, Director Date
Chemical Processing Technologies

P. W. Norris, Evaporator and ETP Manager Date
SRR, Tank Farm Facility Engineering

EXECUTIVE SUMMARY

Savannah River National Laboratory analyzed scale samples from both the wall and cone sections of the 242-16H Evaporator prior to chemical cleaning. The samples were analyzed for uranium and plutonium isotopes required for a Nuclear Criticality Safety Assessment of the scale removal process.

The analysis of the scale samples found the material to contain crystalline nitrated cancrinite and clarkeite. Samples from both the wall and cone contain depleted uranium. Uranium concentrations of 16.8 wt% 4.76 wt% were measured in the wall and cone samples, respectively. The ratio of plutonium isotopes in both samples is ~85% Pu-239 and ~15% Pu-238 by mass and shows approximately the same 3.5 times higher concentration in the wall sample versus the cone sample as observed in the uranium concentrations. The mercury concentrations measured in the scale samples were higher than previously reported values. The wall sample contains 19.4 wt% mercury and the cone scale sample 11.4 wt% mercury. The results from the current scales samples show reasonable agreement with previous 242-16H Evaporator scale sample analysis; however, the uranium concentration in the current wall sample is substantially higher than previous measurements.

TABLE OF CONTENTS

LIST OF TABLES vii
LIST OF FIGURES vii
LIST OF ABBREVIATIONS viii
1.0 Introduction 1
2.0 Experimental Procedure 1
3.0 Results and Discussion 3
4.0 Conclusions 5
5.0 Acknowledgements 5
6.0 References 6

LIST OF TABLES

Table 2-1. Sample Mass of the 2H-Evaporator Cone and Wall Samples 2

Table 3-1. Analytical Data for 2H-Evaporator Cone and Wall Samples. (Averages and %RSD values are of triplicate measurements) 4

LIST OF FIGURES

Figure 2-1. Samples from the 2H-Evaporator and sample retrieval tools 2

Figure 3-1. XRD of 2-H Evaporator Cone Sample HTF-17-56 4

Figure 3-2. XRD of 2-H Evaporator Wall Sample HTF-17-57 5

LIST OF ABBREVIATIONS

AD	Analytical Development
DWPF	Defense Waste Processing Facility
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
NCSA	Nuclear Criticality Safety Assessment
%RSD	Percent Relative Standard Deviation
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
XRD	X-Ray Diffraction

1.0 Introduction

The 242-16H Evaporator (2H-Evaporator) system concentrates liquid high level waste including the recycle stream from the Defense Waste Processing Facility (DWPF) to reduce waste volume in the tank farm. In the evaporator, silicon, primarily from the recycle stream, reacts with aluminum in the tank waste to form sodium aluminosilicate scale deposits in the evaporator pot and gravity drain line. The scale deposits are primarily nitrated cancrinite $Na_8(Al_6Si_6O_{24})(NO_3)_2 \bullet 4H_2O$, with smaller amounts of clarkeite, $Na((UO_2)O(OH))$.[1] The feed to the evaporator is typically depleted in U-235 and therefore the scale is also depleted in U-235. When the cancrinite/clarkeite scale builds up, the 2H-Evaporator pot is chemically cleaned using heated 1.5 M nitric acid. Sampling and analysis of the scale material is performed to provide data needed for a Nuclear Criticality Safety Assessment (NCSA) of the scale removal process.

Scale samples from two locations (wall and cone section samples) were obtained by Savannah River Remediation (SRR) prior to chemical cleaning. The samples were sent to Savannah River National Laboratory (SRNL) for analysis of uranium and plutonium isotopes needed for the NCSA assessment. The samples were also analyzed for mercury by cold vapor atomic adsorption spectroscopy and by X-Ray Diffraction (XRD) to identify the predominant crystalline phases present in the scale.

The sample characterization was requested via a Technical Task Request[2] and conducted based on a Task Technical and Quality Assurance Plan.[3]

2.0 Experimental Procedure

The 2H-Evaporator scale samples were received at SRNL on June 23, 2017. Each of the samplers were opened in the SRNL Shielded Cells and emptied into glass jars for storage on June 28, 2017. Table 2-1 provides the mass of each sample. Figure 2-1 shows a photograph of the samples in the glass jars and photographs of the two emptied samplers.

A small amount of solids from each sample was sent to Analytical Development (AD) for analysis by XRD to determine the identity of any crystalline phases present in the sample. Other small portions of each of the two samples were dissolved in the Shielded Cells using the two different dissolution methods (aqua regia and sodium peroxide fusion). The aqua regia digestions were sent to AD for analysis by cold vapor-atomic adsorption spectroscopy to determine the mercury content of the samples. The solutions resulting from the peroxide fusion dissolution method were sent to AD for analysis by inductively coupled plasma-mass spectrometry (ICP-MS) to determine the uranium isotopics and for separation/alpha spectroscopy to determine the plutonium isotopics. All sample preparations were completed using three replicates of each sample and a reagent blank was submitted to AD along with the samples.

Quality Assurance
Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 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. Data are recorded in the electronic laboratory notebook system as notebook/experiment number Y7081-00081-19.

Table 2-1. Sample Mass of the 2H-Evaporator Cone and Wall Samples

Sample ID	Sample Type	Sample Mass (g)
HTF-17-56	Cone (Pot)	1.474
HTF-17-57	Wall	5.683

Figure 2-1. Samples from the 2H-Evaporator and sample retrieval tools

3.0 Results and Discussion

Table 3-1 contains the results from the analysis of the 2H-Evaporator scale samples. The tables show the average concentration and the percent relative standard deviations (%RSD) for the triplicate sample preparations. Results preceded by "<" indicate the analyte was below the limits of quantification. Results preceded by "≤" indicate that at least one of the replicates for the sample was above the limits of quantification while one or more of the replicates were below detection. The %RSD presented in the table only includes the uncertainty associated with sub-sampling and sample preparation in the Shielded Cells and uncertainty of the analytical method employed. The estimated one sigma percent uncertainty provides an indication of the uncertainty associated with the analytical method as reported by AD.

The uranium results in Table 3-1 appear consistent between the two scale samples with respect to the isotopic ratios. Both samples contain depleted uranium with a U-235/U-total percentage of 0.62% The wall sample shows a much higher uranium concentration (16.8 wt%) than the cone sample (4.76 wt%). That represents a difference of ~3.5X between the uranium concentrations in the two samples. Assuming all of the uranium is in the form of clarkeite, the cone sample contains ~6.5 wt% clarkeite and the wall sample ~23 wt% clarkeite.

The plutonium results in Table 3-1 also show a consistent isotopic ratio between the two scale samples. As observed with the uranium results, the wall scale sample shows a plutonium concentration ~3.4X higher than the cone scale sample. The plutonium in both samples is ~85% Pu-239 and ~15% Pu-238 by mass. The values in the table assume that all of the Pu-239/240 activity in the sample is due to Pu-239.

Mercury measured on the wall and cone samples contained 19.4 wt% and 11.4 wt% mercury, respectively. These mercury concentrations are higher than measured in previous analyses.

The XRD results (Figures 3-1 and 3-2) for both the cone and the wall sample show the presence of two crystalline phases; nitrated cancrinite $Na_8(Al_6Si_6O_{24})(NO_3)_2 \bullet 4H_2O$, and clarkeite, $Na((UO_2)O(OH))$. Both samples show the presence of an unidentified phase at ~31° two-theta that was observed to be present in previously reported XRD data.[4]

The results from the current scales samples show reasonable agreement with previous analytical results on the 2H-Evaporator scale samples from 2013[4,5] and 2010[6] with the exception of a substantially higher uranium concentration in the current wall sample when compared to previous measurements. A number of data quality checks were completed to confirm the substantially higher uranium concentration in the wall sample. The ICP-MS of the peroxide fusion digestions of the wall sample were re-analyzed yielding uranium concentrations consistent with the initial analysis. Additionally, the aqua regia digestions of the both the wall and cone samples were analyzed by ICP-MS and the uranium concentrations found were consistent with those measured in the peroxide fusion digestions.

Table 3-1. Analytical Data for 2H-Evaporator Cone and Wall Samples. (Averages and %RSD values are of triplicate measurements)

analyte	method	units	est. 1σ	Cone Sample HTF-17-56		Wall Sample HTF-17-57	
				average	RSD	average	RSD
U-233	ICP-MS	wt%	10%	4.48E-04	23%	1.58E-03	10%
U-234	ICP-MS	wt%	10%	8.98E-04	22%	3.14E-03	10%
U-235	ICP-MS	wt%	10%	2.97E-02	22%	1.04E-01	10%
U-236	ICP-MS	wt%	10%	1.84E-03	22%	6.53E-03	10%
U-238	ICP-MS	wt%	10%	4.73E+00	22%	1.67E+01	10%
Total U	calc.	wt%	--	4.76E+00	22%	1.68E+01	10%
U-235 / U	calc.	%	--	0.62%	0.6%	0.62%	0.2%
Pu-238	PuTTA	wt%	10%	3.89E-05	24%	1.20E-04	17%
*Pu-239	PuTTA	wt%	10%	1.98E-04	26%	6.94E-04	12%
Pu-241	Pu238/41	wt%	10%	<7.92E-07	--	≤2.51E-06	--
Hg	CV Hg	wt%	10%	1.14E+01	19%	1.94E+01	16%

calc. = calculation; est.1σ = estimated one sigma percent uncertainty as reported by AD.

* Pu-239 assumes entire Pu-239/240 activity is Pu-239

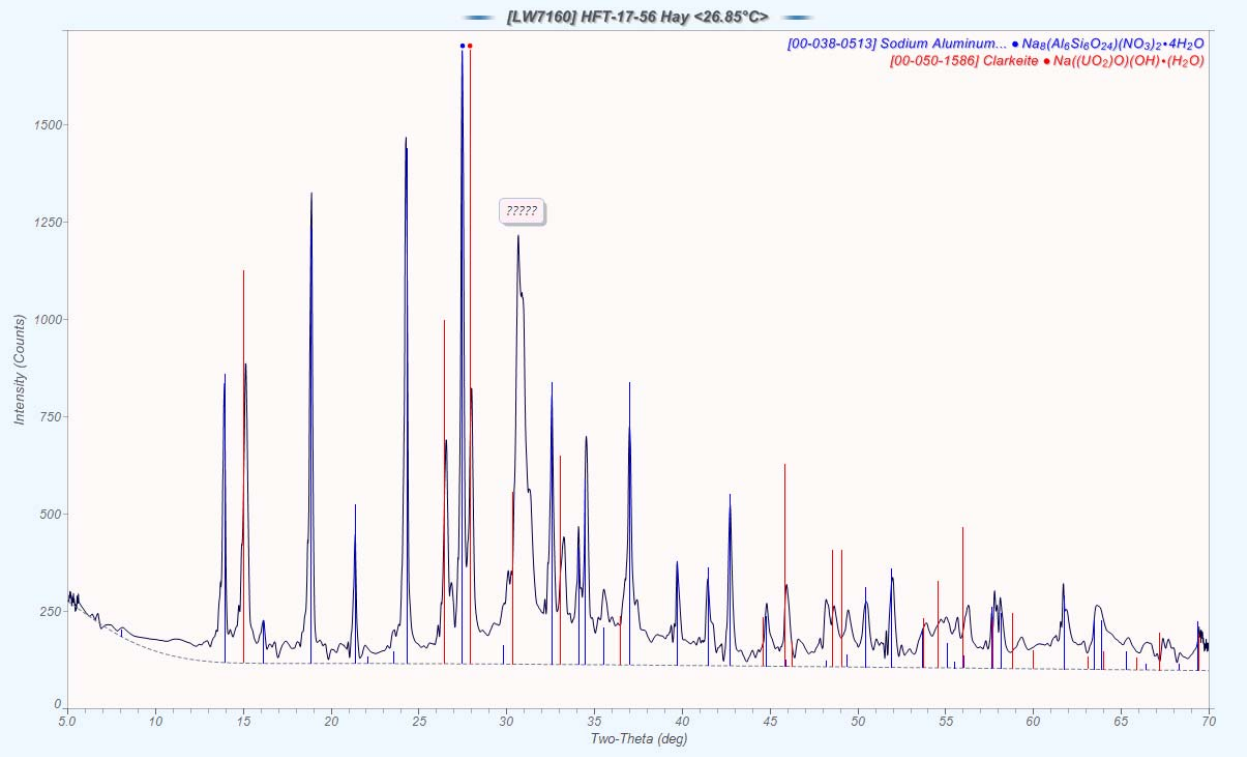

Figure 3-1. XRD of 2-H Evaporator Cone Sample HTF-17-56

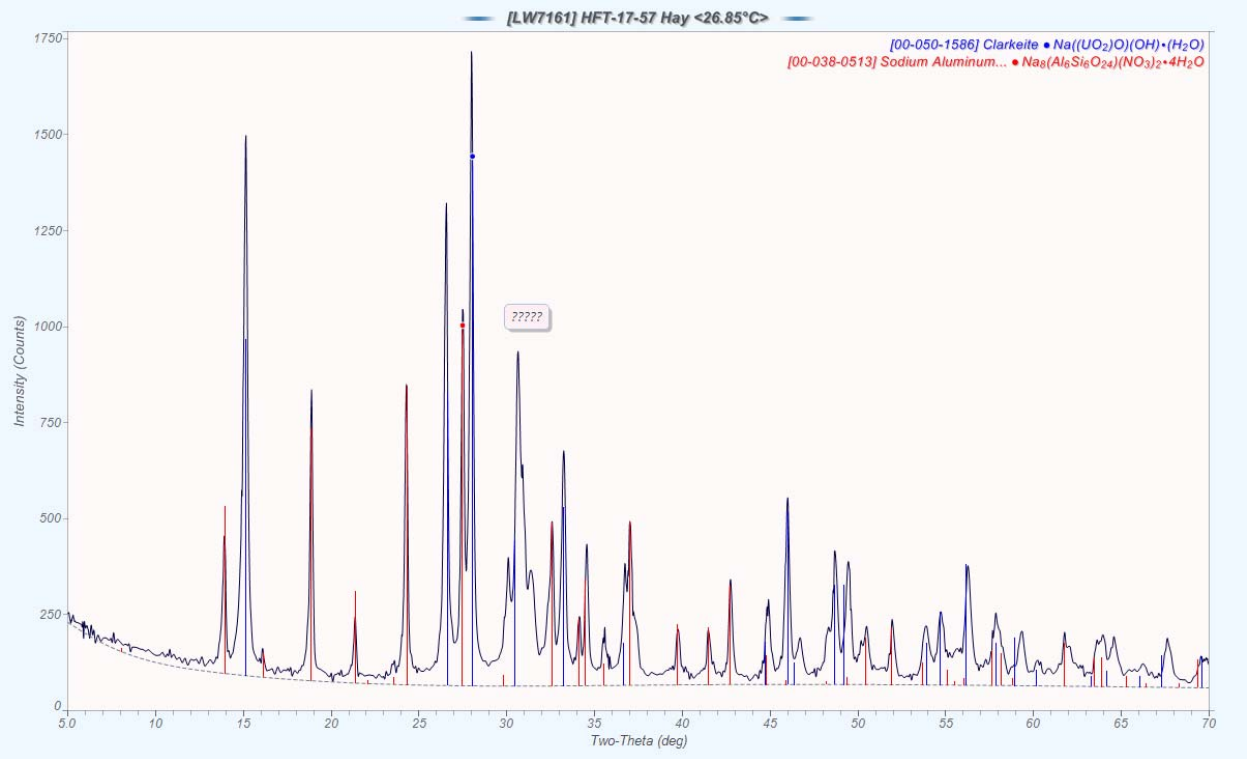

Figure 3-2. XRD of 2-H Evaporator Wall Sample HTF-17-57

4.0 Conclusions

The analysis of the 2H-Evaporator scale samples found the material to contain crystalline nitrated cancrinite and clarkeite. Both samples contain depleted uranium with the wall sample showing a uranium concentration of 16.8 wt% and the cone sample 4.76 wt%. The plutonium in both samples is ~85% Pu-239 and ~15% Pu-238 by mass and shows approximately the same 3.5 times higher concentration in the wall sample versus the cone sample as observed in the uranium concentrations. The wall sample contains 19.4 wt% mercury and the cone scale sample 11.4 wt% mercury. The mercury concentrations measured in the scale samples are higher than previous measurements. The results from the current scales samples show reasonable agreement with previous 2H-Evaporator scale sample analysis; however, the uranium concentration in the current wall sample is substantially higher than previous measurements.

5.0 Acknowledgements

The contributions of Phyllis Burkhalter and Denise Wheeler, in preparing the samples, and those of Mark Jones, Mira Malek, and Leigh Brown, for providing analytical services, are appreciated and acknowledged.

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