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Analysis of 2H-Evaporator Acid Cleaning Samples

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EXECUTIVE SUMMARY

The 2H-Evaporator acid cleaning solution samples were analyzed by SRNL to determine a composition for the scale present in the evaporator before recent acid cleaning. Composite samples were formed from the solution samples from the two acid cleaning cycles. The solution composition was converted to a weight percent scale solids basis under an assumed chemical composition. The scale composition produced from the acid cleaning solution samples indicates a concentration of 6.85 wt% uranium. An upper bound, one-sided 95% confidence interval on the weight percent uranium value may be given as $6.9 \text{ wt\%} + 1.645 \times 0.596 \text{ wt\%} = 7.9 \text{ wt\%}$.

The comparison of the composition from the current acid cleaning solutions with the composition of recent scale samples along with the thermodynamic modeling results provides reasonable assurance that the sample results provide a good representation of the overall scale composition in the evaporator prior to acid cleaning. The small amount of scale solids dissolved in the 1.5 M nitric acid during the evaporator cleaning process likely produced only a small amount of precipitation based on modeling results and the visual appearance of the samples.

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LIST OF ABBREVIATIONS

AD	Analytical Development
DWPF	Defense Waste Processing Facility
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
NAS	Sodium Aluminosilicate
NCSA	Nuclear Criticality Safety Assessment
%RSD	Percent Relative Standard Deviation
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation

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 $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, with smaller amounts of clarkeite, $\text{Na}((\text{UO}_2)\text{O}(\text{OH}))$.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. A recent report provided the composition of grab samples of the solids from the evaporator wall and cone section.² Like previous samples, the scale solids were found to be composed of primarily nitrated cancrinite and clarkeite. Although both scale samples contained depleted uranium, the wall scale sample was found to contain an unusually high concentration of uranium (16.8 wt%) compared with previous scale samples. The cone sample of scale solids contained a more typical uranium concentration (4.76 wt%).

As a result of the unusually high uranium concentration in the wall scale sample, samples of the acid cleaning solution were sent to SRNL for analysis based on the idea that the scale in the evaporator pot dissolved in the nitric acid cleaning solution would provide a more representative sample for determining the scale composition compared to using small grab samples of the solids.

The sample characterization was requested via a Technical Task Request³ and conducted based on a Task Technical and Quality Assurance Plan.⁴

2.0 Experimental

The 2H-Evaporator acid cleaning solution samples were received at SRNL on February 26, 2018. A total of four 100 mL dip bottles were received, two duplicate samples from the first acid strike (HTF-18-14 and HTF-18-15) and two duplicate samples from the second acid strike (HTF-18-25 and HTF-18-26). Each of the sample bottles was opened in the SRNL Shielded Cells and emptied into plastic bottles for storage. Table 2-1 provides the mass and a short description of each sample. The two samples from the first acid strike were white cloudy solutions containing a small amount (<1 wt%) of solids that settled rapidly to the bottom of the bottle. After standing overnight the cloudiness of the first strike samples did not appreciably diminish. The two samples from the second acid strike were clear colorless solutions containing no solids.

Composite samples were prepared for analysis by combining equal portions of a first acid strike sample with a portion of a second acid strike sample. To prepare Composite #1, sample HTF-18-14 was well mixed and ~40 g transferred to the composite #1 bottle. HTF-18-25 was then mixed and ~40 g transferred to the Composite #1 bottle. After mixing the contents of the Composite #1 bottle, the resulting solution was clear with a small amount of fine solids on the bottom of the bottle. Composite #2 was prepared in the same manner using samples HTF-18-15 and HTF-18-26. Each composite sample was filtered through a 0.45 μm nylon filter to remove any undissolved solids. The composite samples proved difficult to filter with each sample requiring 3-4 filters and several hours to filter all ~80 g of material.

Triplicate aliquots of each composite sample were submitted to Analytical Development (AD) undiluted for analysis by cold vapor-atomic adsorption spectroscopy to determine the mercury content of the samples, by inductively coupled plasma-mass spectrometry (ICP-MS) to determine the uranium isotopics, by separation/alpha spectroscopy to determine the plutonium isotopics, and by inductively coupled plasma-emission spectroscopy (ICP-ES) to determine Na, Al, Si, Fe, Mn, and other metals.

Density measurements were made on aliquots of the composite samples using calibrated volumetric tubes at ambient cell temperature (23 °C). The weight percent total solids in the composite samples were measured after drying weighed aliquots of the sample to constant weight in a conventional drying oven at 110 °C. All density and weight percent solids measurements were completed using three replicates of each sample. The pH was measured using pH indicating paper strips.

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 Y7081-00081-24.

Table 2-1. Sample Masses and Descriptions of the 2H-Evaporator Acid Cleaning Samples

Sample ID	Sample Mass (g)	pH	Description
HTF-18-14	87.31	0-2	Cloudy white solution with a small amount of solids on bottom
HTF-18-15	87.01	0-2	Cloudy white solution with a small amount of solids on bottom
HTF-18-25	85.00	0-2	Clear colorless solution
HTF-18-26	85.04	0-2	Clear colorless solution

3.0 Results of the Sample Analysis

Table 3-1 contains the results from the analysis of the 2H-Evaporator Acid Cleaning composite samples. The table shows the average concentrations and the percent relative standard deviations (%RSD) for the triplicate sample preparations of each composite sample. The %RSD presented in the table only includes the uncertainty associated with sub-sampling/sample preparation in the Shielded Cells and analytical uncertainty of the measurement. The %RSD does not include sampling uncertainty associated with obtaining the sample from the evaporator pot. The estimated one sigma percent uncertainty provides an indication of the uncertainty associated with the analytical method as reported by AD. The table provides the average concentrations and %RSD of the Composite #1 sample in columns three and four respectively, of the Composite #2 sample in columns five and six, and of the combined results of the two composite samples in columns seven and eight. The combined results are the average of all six replicates, three from each composite sample.

All of the uranium results in Table 3-1 show good agreement between the replicates for each composite sample and between the two composite samples as indicated by the low %RSD. The results show the uranium to be depleted with a U-235 weight fraction of 0.61%. A total uranium concentration of 2.37E+03 mg/L was measured in the combined results.

The measured concentrations of plutonium and other metals (Hg, Al, Na, Si, Fe, and Mn) in the table also show good agreement between replicates and between the two composite samples. The one exception is the Fe concentration in the Composite #2 sample where a single replicate with a higher iron concentration is responsible for the large %RSD. The silicon concentration measured in both composite samples is significantly lower than the Hg, Al, Na, and U. Based on the composition of the evaporator scale samples previously analyzed,² the silicon concentration should be roughly in the same range as the aluminum concentration. The low silicon concentration in the composite samples likely indicates the precipitation of a major fraction of the silicon from the acid cleaning solution after the dissolution of the sodium aluminosilicate (NAS) portion of the scale. Presumably, much of the small amount of solids removed from the samples by filtration prior to analysis consisted of silicon dioxide. The iron and manganese concentrations are also significantly lower than the other metals in Table 3-1, however, these two metals are not major components of the evaporator scale. The weight percent solids and density measurements also show good agreement between replicates and composite samples.

The weight percent solids measured on the samples cannot be related to the scale solids in the evaporator in any straightforward way. The nitric acid used to dissolve the scale solids reacts with the three main components of the scale solids as shown in the chemical equations below. For example, each mole of the nitrated cancrinite, the major component of the scale solids, requires twenty-four moles of nitric acid to dissolve the solid into the acid solution. When the resulting solution is dried, eight moles of sodium nitrate and other nitrate salts are produced that were not part of the scale solids in the evaporator pot. The dried solids from the weight percent solids measurement contain a large amount of sodium nitrate and therefore, the value cannot be used to convert the solution concentrations to a weight percent dried scale solids basis.

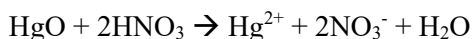
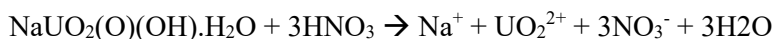


Table 3-1. Composition of Composite Samples of 2H-Evaporator Acid Cleaning Solutions

Analyte	Est. 1σ	Composite #1 Average mg/L	%RSD	Composite #2 Average mg/L	%RSD	Combined Average mg/L	%RSD
U-233	10%	2.12E-01	1.4%	2.06E-01	0.3%	2.09E-01	1.6%
U-234	10%	4.29E-01	1.9%	4.29E-01	1.2%	4.29E-01	1.4%
U-235	10%	1.45E+01	1.2%	1.44E+01	1.1%	1.44E+01	1.1%
U-236	10%	8.62E-01	0.2%	8.44E-01	1.2%	8.53E-01	1.4%
U-238	10%	2.37E+03	0.7%	2.35E+03	0.5%	2.36E+03	0.7%
U-Total	--	2.38E+03	0.7%	2.37E+03	0.5%	2.37E+03	0.6%
%U-235	--	0.61%	1.3%	0.61%	1.5%	0.61%	1.3%
Pu-238	15%	1.79E-02	8.3%	1.69E-02	7.8%	1.74E-02	7.9%
Pu-239*	15%	1.21E-01	9.2%	1.18E-01	8.2%	1.19E-01	7.9%
Pu-Total*	--	1.38E-01	9.1%	1.35E-01	8.2%	1.37E-01	7.9%
Hg	20%	3.51E+03	8.8%	3.74E+03	4.2%	3.63E+03	7.0%
Al	10%	4.05E+03	0.9%	4.04E+03	0.9%	4.05E+03	0.8%
Na	10%	5.13E+03	1.1%	5.11E+03	0.8%	5.12E+03	0.9%
Si	10%	5.67E+01	0.8%	6.01E+01	0.9%	5.84E+01	3.3%
Fe	10%	3.63E+01	0.7%	4.46E+01	36%	4.04E+01	27%
Mn	10%	2.01E+00	0.5%	2.13E+00	3.9%	2.07E+00	4.2%
Density (g/mL)	5%	1.07	0.1%	1.07	0.2%	1.07	0.2%
wt% Solids	5%	4.31%	7.3%	4.34%	3.5%	4.33%	5.1%
pH	--	0-2	--	0-2	--	0-2	--

* The Pu-239 mass was calculated assuming all the Pu-239/240 activity is from Pu-239. Pu-Total is the sum of the Pu-238 and Pu-239 masses.

4.0 Discussion

A discussion of the quality of the data presented in Tables 3-1 is in order since the previous analysis of a scale solids sample showing much higher than normal uranium concentration produced uncertainty about the average scale composition in the evaporator pot. Obtaining samples, solid or liquids, from the evaporator pot is difficult due to limited access points and the radioactive nature of the material. Therefore, the representativeness of the samples to the material in the evaporator as a whole (sampling uncertainty) is difficult to quantify. Dissolving the scale in the evaporator and then obtaining a solution sample should have a higher likelihood of being representative than collecting grab samples of solids from a couple of places in the evaporator. As long as all (or most) of the scale is dissolved and stays in the solution at the time of sampling, a well-mixed solution sample should provide a good representation of the overall scale composition.

The values presented in Table 3-1 show reasonably good sub-sampling/analytical uncertainty. The estimated uncertainties are on the order of 10-20% based on the estimated one sigma values for the analytical methods and the generally low %RSD. The low %RSD indicates no substantial problems with sub-sampling the samples. The good agreement between the two composite samples indicates consistency between separate sampling events of the acid cleaning solutions over two cleaning cycles. These results lend credibility to the representativeness of the samples with respect to the acid cleaning solutions in the evaporator.

The conversion of solution concentrations in Table 3-1 to a weight percent of the scale solids can be accomplished by assuming all of the scale solids are composed of the two phases identified in the recent analysis of the scale solids.² That analysis of the scale solids identified two crystalline phases in the x-ray diffraction analysis; clarkeite ($\text{NaUO}_2(\text{O})(\text{OH})\cdot\text{H}_2\text{O}$) and nitrated cancrinite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$). The other major component from the analysis of the scale solids was mercury although no crystalline forms of mercury were identified in the x-ray diffraction analysis. Assuming all of the uranium in the scale solids is present as clarkeite, all the aluminum as nitrated cancrinite, and all the mercury as mercury oxide in the scale solids allows the calculation of these elements as a weight percent of the scale solids.

For example, in Table 4-1 the solution concentrations of uranium, aluminum, and mercury (mg/L) from Table 3-1 are converted to a concentration of the associated crystalline phase (g/L) using the molecular weights of the elements and the molecular weights of the associated crystalline phase. The sum of these three phases then represents the grams per liter of all the scale solids dissolved into the acid cleaning solution. In Table 4-2, dividing the grams per liter of each phase by the sum yields a weight percent of each phase in the scale solids. From the weight percent of each phase the weight percent of each element can be calculated.

Table 4-1. Conversion of Element Concentrations to Associated Phase Concentration

Element	Combined Avg. Acid Cleaning Solution Conc. (mg/L)	Conc. As Associated Phase (g/L)	Associated Crystalline Phase
U-total	2.37E+03	3.43E+00	clarkeite ($\text{NaUO}_2(\text{O})(\text{OH})\cdot\text{H}_2\text{O}$) MW = 344.0
Al	4.05E+03	2.73E+01	nitrated cancrinite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$) MW = 1094.4
Hg	3.63E+03	3.91E+00	mercury (II) oxide (HgO) MW = 216.6
--	--	3.47E+01	Sum of the phases

Table 4-2. Conversion of the Associated Phase Concentrations to Elemental Weight Percent of Scale Solids

Associated Crystalline Phase	Conc. As Associated Phase (g/L)	Conc. As Associated Phase (wt%)	Conc. As Element (wt%)	Element
clarkeite	3.43E+00	9.89E+00	6.85E+00	U-total
nitrated cancrinite	2.73E+01	7.88E+01	1.17E+01	Al
mercury (II) oxide	3.91E+00	1.13E+01	1.04E+01	Hg
Sum of the phases	3.47E+01	1.00E+01	--	--

The 6.85 wt% uranium concentration in Table 4-2 should represent the highest concentration possible in the scale solids (+/- the uncertainty). This value falls within the range of the results from scale solids analysis (4.76 and 16.8 wt% uranium).² If other solids are present in the scale solids besides the three phases used in the calculations, the weight percent uranium would decrease.

Using uncertainty information provided by AD, the software package Gum Workbench Version 2.4.1.411⁵ was used to propagate the related input uncertainties into estimates of the uncertainty of the weight percent uranium determinations for the two acid cleaning solution composite samples and of the uncertainty for their average. The details of this uncertainty evaluation are included in the electronic laboratory notebook system in notebook/experiment number Y7081-00081-24. The estimated value of the weight percent uranium is 6.9 wt% with an estimated standard deviation of 0.596 wt%. In this case, only an upper bound on the uncertainty is needed for the weight percent uranium in the samples. Thus, an upper bound, one-sided 95% confidence interval on the weight percent uranium value may be given as $6.9 \text{ wt\%} + 1.645 \times 0.596 \text{ wt\%} = 7.9 \text{ wt\%}$.

The key assumptions in developing the weight percent uranium above are:

- The acid cleaning solution in the evaporator pot was well mixed when the samples were obtained so that the samples represent the bulk solution composition,
- That all of the scale solids dissolved into the acid in the first acid cleaning cycle remained in solution,
- The scale solids are predominantly composed of the three phases, nitrated cancrinite, clarkeite, and mercury oxide.

The first assumption, that the acid cleaning solution samples are representative of the bulk solution in the pot, is difficult to evaluate since the sampling after each cleaning cycle occurred from the same spot with a short time interval between sampling events. The duplicate samples show good agreement in composition but that would be expected from the sampling method as long as there are no fast settling solids.

The second assumption, that the scale solids that dissolved in the first acid cleaning cycle remained in solution, can be assessed to some degree using the data in Table 3-1 and thermodynamic modeling. In actuality, only the uranium, aluminum, and mercury are used in calculating the weight

percent uranium, so only those three elements need to remain dissolved in the acid cleaning solution. The analytical data for the acid cleaning solution samples in Table 3-1 indicates that most of the silicon precipitated from solution after dissolution of the scale solids into the acid in the evaporator. The thermodynamic modeling of the acid dissolution process in the evaporator is discussed in the following paragraphs.

The third assumption can be assessed to some degree by evaluating the analytical results of scale solids where uranium, aluminum, and mercury were all measured. There were three sample analyses on 2H-Evaporator scale solids completed in 2013 where the concentration of all three metals were measured.^{6,7} In those three samples shown in Table 4-3, after converting the weight percent uranium to weight percent clarkeite, the aluminum to nitrated cancrinite, and the mercury to mercury oxide, the three phases sum to between 79 – 100%. This indicates the assumption to use the three phases, nitrated cancrinite, clarkeite, and mercury oxide, is a reasonable approximation for the composition of the scale solids. The weight percent uranium could be increased slightly if most of the uranium in the scale solids is present as a compound with a lower molecular weight than clarkeite. Since uranium contributes most of the mass in clarkeite this increase can only amount to ~3% higher uranium concentration. Assuming all of the mercury is metallic mercury in the scale solids instead of mercury oxide would also increase the calculated uranium concentration but only by less than 1%. Finally, assuming a hydroxy cancrinite phase is present replacing half of the nitrated cancrinite could also raise the uranium concentration by ~5% in the calculations in Tables 4-1 and 4-2.

Table 4-3. Previous Scale Solids Samples Analytical Results for Aluminum, Uranium, and Mercury

Report Reference	Aluminum Concentration (wt%)	Uranium Concentration (wt%)	Mercury Concentration (wt%)	
SRNL-STI-2013-00267 ⁷	8.34	7.09	11.7	--
SRNL-STI-2013-00352 ⁸	13.3	2.59	5.67	--
SRNL-STI-2013-00352 ⁸	9.97	4.03	9.59	--
Elemental Concentrations Converted to the Associated Crystalline Phase				
	Nitrated Cancrinite Concentration (wt%)	Clarkeite Concentration (wt%)	Mercury Oxide Concentration (wt%)	Sum of the Three Phases (wt%)
SRNL-STI-2013-00267 ⁷	56.4	10.25	12.63	79.3
SRNL-STI-2013-00352 ⁸	89.9	3.74	6.12	99.8
SRNL-STI-2013-00352 ⁸	67.4	5.82	10.35	83.6

A thermodynamic model was developed using OLI Systems Inc., Flowsheet version 9.5.4. The model mixed a solids stream (evaporator scale solids) with a 1.5 M nitric acid stream using a simple mixing block. The solids stream contained cancrinite, clarkeite, and mercury oxide as inputs. The thermodynamic database in OLI software does not contain the nitrated form of cancrinite found in the scale solids, but the chemistry between the two forms of cancrinite should not vary significantly. The objectives of the thermodynamic modeling were to:

- Provide some assurance for the assumption that all of the scale solids dissolved in the first acid cleaning cycle remained in solution,
- Determine the volume of scales solids necessary to achieve the solution concentrations measured in the acid cleaning solution samples, based on the composition of the three phases shown in Table 4-2 along with the amount of acid used in the acid cleaning process,
- Provide insight into the propensity and composition of solids that might precipitate at higher scale solids loading during acid cleaning in the evaporator.

SRR supplied a value for the amount of scale dissolved (39 gallons) and volumes of 1.5 M nitric acid used (2200 gallons in cycle #1 and 2205 gallons in cycle #2) in the recent acid cleaning of the evaporator pot.⁸ Calculations were performed using a composition for the scale based on the values in Table 4-2 as amounts of cancrinite, clarkeite, and mercury oxide. The calculations predicted that after the scale was dissolved most of the silicon would precipitate as SiO_2 from the acid cleaning solution. No other solids formed in the modeling of the first acid cleaning cycle or in the combined first and second acid cleaning cycle composite. The software also predicted that to reach the uranium concentration found in the acid cleaning composite sample (Table 3-1), a volume of 45 gallons of scale solids at a predicted density of 3.41 g/mL would need to have dissolved during the two acid cleaning cycles. This value is reasonably close to the 39 gallons of scale solids provided by SRR based on visual inspection. As the amount of scale solids is increased in the model, while holding the volume of acid constant, the next solid to precipitate after SiO_2 is mercury oxide (HgO), followed by a uranyl hydroxide monohydrate ($\text{UO}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$), and then by the aluminum in the form of gibbsite ($\text{Al}(\text{OH})_3$). The uranium is predicted to start precipitating from the acid solution with the equivalent of 56 gallons of scale solids contacted in the first acid cleaning cycle. It should be noted that predicting the precipitation of solids from a solution, especially for aluminum, is difficult and complicated by the fact that under certain conditions species can reach supersaturated concentrations in solution.

The comparison with the composition of recent scale samples and the thermodynamic modeling results provides reasonable assurance that the sample results for the acid cleaning solutions provide a good representation of the overall scale composition in the evaporator prior to acid cleaning.

5.0 Conclusions

The 2H-Evaporator acid cleaning solution samples were analyzed by SRNL to determine a composition for the scale present in the evaporator before recent acid cleaning. Composite samples were formed from the solution samples from the two acid cleaning cycles. The solution composition was converted to a weight percent scale solids basis under an assumed chemical composition. The scale composition produced from the acid cleaning solution samples indicates a concentration of 6.85 wt% uranium. An upper bound, one-sided 95% confidence interval on the weight percent uranium value may be given as $6.9 \text{ wt\%} + 1.645 \times 0.596 \text{ wt\%} = 7.9 \text{ wt\%}$.

The comparison of the composition from the current acid cleaning solutions with the composition of recent scale samples along with the thermodynamic modeling results provides reasonable assurance that the sample results provide a good representation of the overall scale composition in the evaporator prior to acid cleaning. The small amount of scale solids dissolved in the 1.5 M nitric acid during the evaporator cleaning process likely produced only a small amount of precipitation based on modeling results and the visual appearance of the samples.

A recommendation for the future analysis of samples of scale solids is to measure other metal concentrations (Al, Si, and Na) besides uranium and mercury so a better mass balance of the scale solids can be obtained.

6.0 Acknowledgements

The contributions of Dee Wheeler, in preparing the samples, and those of Mark Jones and Leigh Brown for providing analytical services, are appreciated and acknowledged.

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