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Nitric Acid Cleaning of a Sodalite–Sodium Diuranate Scale in High Level-Waste Evaporators[#]

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ABSTRACT

The operation of a high-level radioactive waste evaporator was curtailed due to the presence of an aluminosilicate scale that contained sodium diuranate with a uranium-235 enrichment of approximately 3%. Utilizing pervious work, a plan to clean the evaporator system using a heated nitric acid and depleted uranium mixture was developed that addressed numerous safety issues. The sodium aluminosilicate scale was successfully removed during two cleaning cycles, but soluble silicon was not present in measurable quantities in the liquid samples taken during cleaning. Although this phenomenon was not observed in the laboratory tests, silicon was detected in a loose, solid phase discovered in the evaporator cone after the first cleaning cycle.

Key Words: Evaporator; Chemical cleaning; Aluminosilicate.

INTRODUCTION

The Savannah River Site (SRS) stores high-level nuclear waste in 49 underground storage tanks. The wastes are to be vitrified in the Defense Waste Processing Facility (DWPF) for permanent disposal. The available tank space must be managed to ensure viability of the separation canyons to support nuclear material stabilization and continued operation of DWPF. Under normal operations, the wastes are evaporated to reduce volume. The SRS has three operational atmospheric-pressure, high-level waste evaporators. Two evaporators are located in H-Area and one is in F-Area. The 242-16H (or 2H) evaporator was not operated from October 1999 to September 2001 due to the presence of a large amount of sodium aluminosilicate scale that contained sodium diuranate. The scale is very similar to that observed in the aluminum and pulp paper industries.[1–3] It was produced at SRS by reaction of the aluminate supplied by the plutonium separations facilities and the silicate from recycle water from the DWPF. The chemistry of high-level waste with elevated silicon levels thermodynamically favors the formation of aluminosilicates.[4]

The 2H evaporator was scaled to the point that the concentrated evaporator bottoms could not be removed through normal steam-lifting protocol. Previous work by Wilmarth and others[5,6] has shown that a dilute nitric acid cleaning solution is effective in dissolving the aluminosilicate scale and the sodium diuranate encrusted in the scale. A complete dissolution flowsheet was written for this operation by Boley et al.[7] The results of this cleaning operation and associated chemistry are presented in this paper.

The operational configuration is shown in Fig. 1. The evaporator pot is cylindrical with a conical bottom section and has a height of 16.5 ft and a diameter of 8 ft. Heat is normally supplied by a warming coil (25-lb steam) and a horizontal tube bundle (150-lb steam). The operating volume during caustic waste evaporation is approximately 1800 gal, and during acid cleaning, the volume was raised to 2800 gal. Figure 2 shows a schematic drawing of the evaporator internals. The flowsheet first required a water soak to remove soluble salts. Subsequently, dilute nitric acid (1.5-M free acid) containing 280 g/L depleted uranium, in the form of uranyl nitrate, was added and heated to around 90°C. The depleted uranium was added to ensure criticality safety in the neutralization tank prior to disposal in Tank 42H. An air lance in the evaporator pot provided agitation.

The Savannah River Technology Center (SRTC) analyzed liquid dip samples taken from the evaporator pot during the first acid strike and at the end of the second acid strike. Samples from H-canyon cleaning solution make-up tank and the acid unloading station were analyzed by SRTC and established the baseline characteristics of the acid cleaning solution. Samples of the cleaning solution in the H-canyon make-up tank were qualified for proper uranium and acid composition. Lastly, a sample of the loose solids that settled in the evaporator pot cone after the first acid cleaning was collected and analyzed.

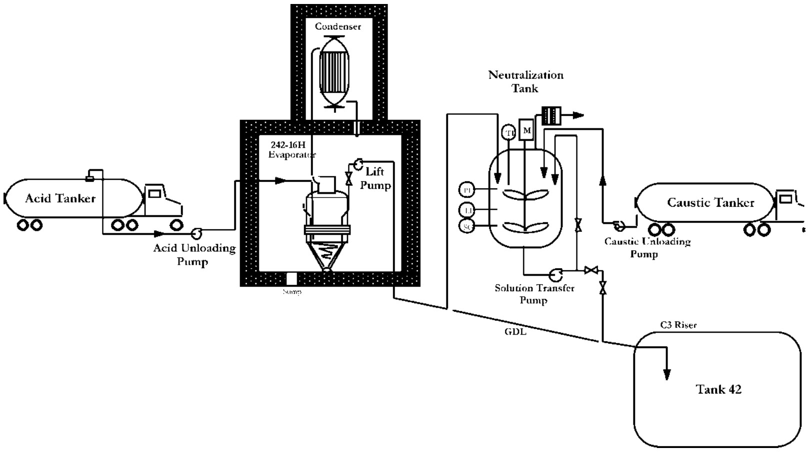

Figure 1. Field implementation of acid cleaning.

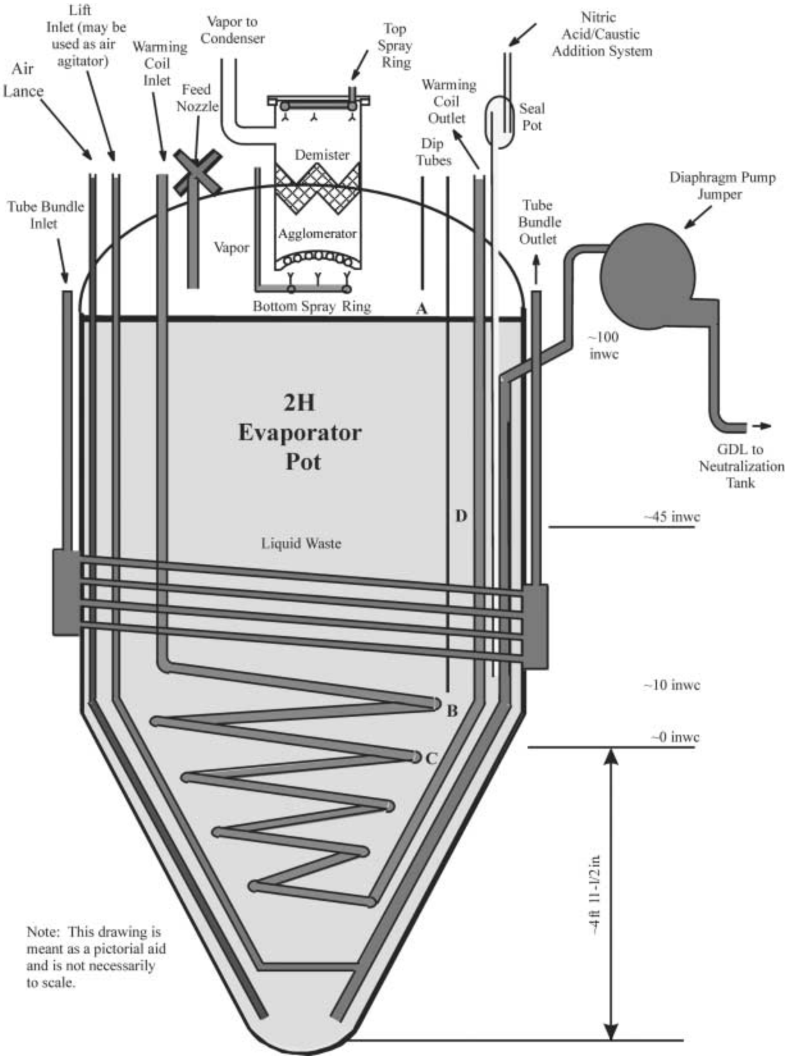

Figure 2. Evaporator pot schematic drawing.

ANALYTICAL METHODS

The pot dip samples were collected by dipping a metal bottle (~80 mL) approximately 12 in. under the liquid surface. The air lance had been suspended and the pot contents had been allowed to settle for approximately 30 min prior to the sampling. Thus, any solids or emulsions that are significantly more dense than the bulk cleaning solution had ample time to settle beneath the sampling zone.

Upon receipt at SRTC, the acid samples were either placed in the shielded cells or taken to a radiochemical laboratory, depending on the dose rate of the sample. The samples were opened, and if solids were observed, the entire sample was passed through a 0.45-μm filter. The solid phase was collected and analyzed. The x-ray diffraction (XRD) patterns were obtained with Cu K_α radiation on a Bruker Axs, Inc., instrument with a Siemens D500 goniometer. Scanning electron micrographs (SEM) and energy dispersive spectra (EDS) were obtained using the following instruments: Cambridge Stereoscan 250 scanning electron microscope, Tracor Northern Energy Dispersive x-ray analyzer and Mirocspec wavelength disperive analyzer. Portions of the solid samples were analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Samples were placed in an Instrument Specialist Incorporated 550E DSC. About 10 to 20 mg of material was placed in the calorimeter and was heated at 10°C/min from 25 to 600°C. The temperature rise or depression of the sample was monitored and converted to energy via calibration standards. Over a similar temperature range, the weight loss of samples was determined in DuPont V5.1A TGA equipment. About 20 to 40 mg of sample was placed in the TGA, and it was heated 10°C/min from 25 to 1000°C. About 2 mg of sample was mixed with 0.2 g of petroleum gel, a readily available and optically transparent mull media. The sample was mixed until a uniform color was achieved. The sample was squeezed between two potassium bromide plates until a film thickness of about 10 microns was achieved. The sample was in the sample compartment of a NICOLET 210 FT-IR spectrometer.

Elemental metals measurements were performed based on atomic emission from excited atoms and ions, using Applied Research Laboratories, Model Number: 3580 inductively coupled plasma atomic emission spectrometer (ICP-ES). Free hydroxide analysis was determined via an inflection point titration using a contained Radiometer TIM 900 automated titration system. Tributyl phosphate analysis was performed by gas chromatography/mass spectrometry using a Hewlett Packard model 5973 mass selective detector with a model 6890 gas chromatograph. The *n*-butanol analysis was performed by gas chromatography/mass spectrometry using a Hewlett Packard model 5971 mass selective detector with a model 5890 gas chromatograph. Carbon analysis was completed using a Tekmar-Dohrmann model DC-190 high temperature total carbon analyzer with an installed remote boat sampler for radiological samples.

An aliquot of the sample was analyzed by gamma spectroscopy analysis using a high-purity germanium detector. Strontium-90 separation and analysis, performed using an aliquot of the sample, was analyzed for Sr-90 using an Eichrom Sr-Spec based extraction procedure. An Sr-90 spiked blank, as well as an Sr-90 spiked sample, was analyzed with the sample batch to establish Sr-90/Y-90 counting efficiencies and Sr chemical recoveries. Once the extractions were complete, aliquots of the resultant Sr-90/Y-90 containing extracts mixed with liquid scintillation cocktail were counted on a Packard Instruments liquid scintillation counter.

The plutonium separation and analysis, performed using an aliquot of each sample, was subjected to a thenoyltriflouroacetone (TTA) separation. An aliquot of each sample was initially spiked with a Pu-239 tracer. A second aliquot of sample was analyzed along with the spiked sample. [H+] concentrations of the aliquots were adjusted to nominally 1 M with nitric acid. Subsequent reagent additions dilute the [H+] concentration further by less than 33%. All of the plutonium in the samples was reduced once using hydroxylamine. An anion complexing reagent (aluminum nitrate) was then added, and the solutions were oxidized with 4-M sodium nitrite. The plutonium was then extracted from the matrix using a TTA solution. The TTA layer was mounted on a counting dish; the mount was then analyzed by alpha spectroscopy.

RESULTS AND DISCUSSION

Cleaning Chronology

An in-depth description of the significant events and operational difficulties associated with the cleaning process is contained in a summary report.[8] Figures 3 and 4 track the evaporator pot temperature, the volume of cleaning solution in the evaporator pot, and the volume of overhead collection tank produced for the first and second acid strikes. As the pot contents reach the desired cleaning temperature, the pot volume decreases due to the evaporation of water and nitric acid from the pot and the collection of condensed vapor in the overhead collection tank system. There is good agreement between the volume decrease in the pot and the volume collected in the overhead collection tank. Table 1 provides a summary of the evaporator pot samples and values useful for the volume normalization of the components

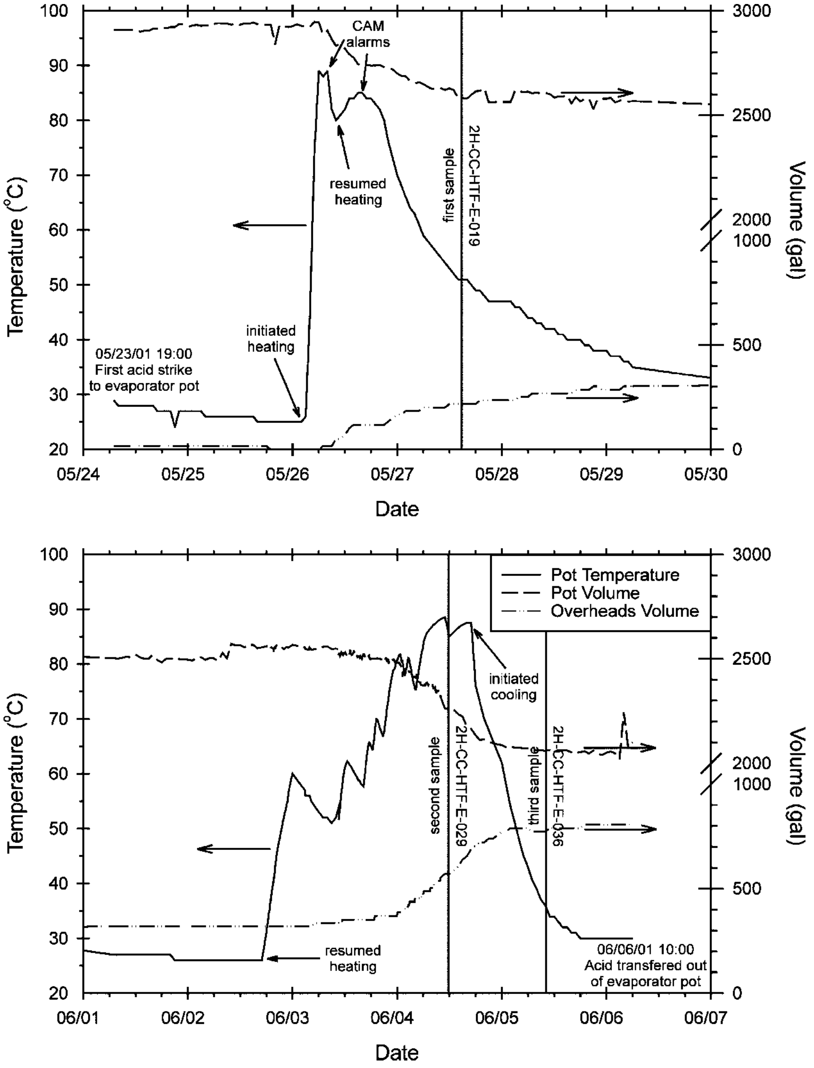

Figure 3. Temperature profile, pot evaporation, and overheads production for the first acid strike.

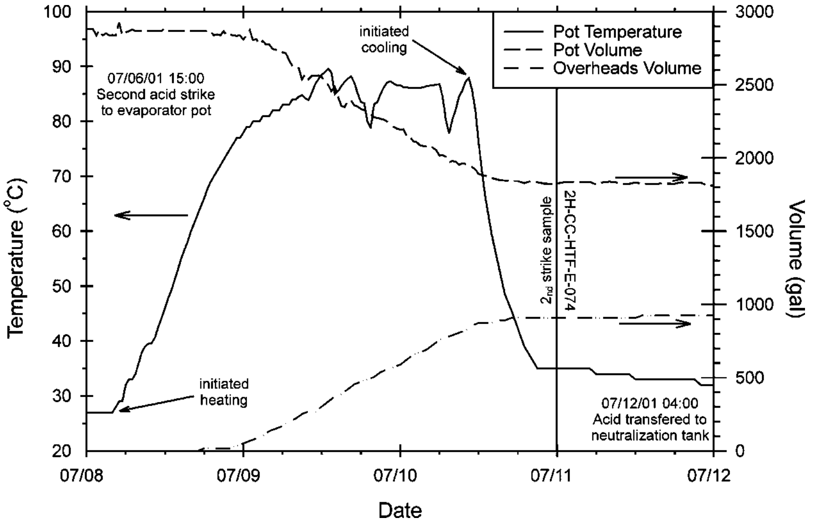

Figure 4. Temperature profile, pot evaporation, and overheads production for the second acid strike.

Table 1. Listing of evaporator pot liquid samples received during chemical cleaning and the corresponding sampling conditions.

Tank farm number	Date and time	Sample name	Temperature (°C)	Pot level (in.)	Pot volume (gal)
First acid strike				80	2810[a]
2H-CC-HTF-E-019	05-27-01 16:00	8-h pot	50	72	2560
2H-CC-HTF-E-029	06-04-01 11:30	16-h pot	87	62.5	2270
2H-CC-HTF-E-036	06-05-01 10:00	Post-cool down	36	55	2050
2H-CC-HTF-E-037					
Second acid strike				80	2810[b]
2H-CC-HTF-E-073	07-10-01 23:30	Post-cool down	35	47	1840
2H-CC-HTF-E-074					

[a] An estimated 2730 gallons of cleaning solution was charged to the pot.

[b] An estimated 1760 gallons of cleaning solution was charged to the pot, followed with 1050 gallons of water.

in these samples. Note that, in Table 1, the amount of cleaning solution charged to the pot was 2730 gal for the first strike and 1760 gal for the second strike. For upcoming analyses, the cleaning solution charged is taken to be at the composition of the baseline uranyl nitrate solution samples (Table 2).

A water soak of the evaporator pot contents was performed. A post-soak inspection revealed that a thick layer of scale remained on exposed portions of the evaporator below the operating level. Other than the removal of some white salt deposits noted, no significant changes were noted since the previous inspection. Due to the need for additional testing to lines, the evaporator pot was filled with water and emptied once more in the period leading up to the first acid strike.

Approximately 4500 gal of the 1.5-M nitric acid/depleted uranium cleaning solution was prepared by combining a depleted uranyl nitrate waste stream with water and additional nitric acid. Samples of the original depleted uranyl nitrate solution and prepared cleaning solution were sent to two laboratories for independent analysis: F-LAB to satisfy nuclear criticality safety requirements and SRTC to provide a baseline for comparison with subsequent pot samples. The cleaning solution was loaded into a tanker trailer and delivered to the 2H evaporator system.

For the first acid strike, 2730 gal of cleaning solution, as measured with a flow totalizer, were added to the evaporator pot, resulting in a pot-level reading to 2810 gal. The cleaning solution was sampled from the transfer line and labeled 2H-CC-HTF-E-018 for analysis. The transfer line was flushed with water, resulting in a pot volume increase to approximately 2930 gal.

Table 2. Comparison of analyses of initial cleaning solution by F-lab and SRTC.

Analyte	NCSE sample (F-Lab)	Courtesy cleaning-solution sample (SRTC)	Trailer acid sample 2H-CC-HTF-E-018 (SRTC)
Free acid	1.52 M	n.a.	1.4 M
Total acid	4.48 M	n.a.	n.a.
Density	1.43 g/mL	n.a.	1.39 g/mL
Total U	283.2 g/L	256 g/L	251 g/L
U-234	6 mg/L	b.d.l.	b.d.l.
U-235	691 mg/L	653 mg/L	696 mg/L
U-236	25 mg/L	b.d.l.	b.d.l.
U-238	282.5 g/L	298 g/L	244 g/L
Org./aq.	0.017%	n.a.	n.a.

n.a. = not analyzed, and b.d.l. = below detection limits.
Additional SRTC analyses are contained in Table 3.

Heating of the cleaning solution, using the evaporator warming coils and tube bundle, was initiated. The temperature of the heating solution reached 87°C, with little evidence of volume change due to thermal expansion. Heating was halted shortly thereafter as a response to alarms due to the release of radon from the scale as it. The first evaporator pot dip sample (2H-CC-HTF-E-019) was pulled and transported for analysis.

The cleaning solution remained in the pot while a scheme was developed to resume heating more slowly using only the warming coils, allowing for an additional 120 hr of soak time. When the pot temperature exceeded 80°C, the second pot dip sample (2H-CC-HTF-E-029) was taken and transported for analysis. Lastly, samples (2H-CC-HTF-E-036,37) were pulled after the pot temperature had been brought below 40°C.

A day later, the pot contents were transferred to the neutralization tank. The evaporator pot was inspected (Fig. 5), revealing that the majority of the deposits on the pot walls, warming coils, dip tubes, and supports had been removed during the first acid strike. Loose solids were evident in the bottom of the evaporator cone and were sampled (2H-CC-HTF-E-051) several days later, after significant drying had occurred. Although no more than 18 gal of this loose, solid material was left in the evaporator after the first acid strike, it is expected that a significant amount of this material was transferred from the pot to the neutralization tank before the post-cleaning inspection.

The spent cleaning solution was neutralized by the addition of 710 gal of 50 wt% (19-M) sodium hydroxide to the neutralization tank. Cleaning operations were suspended for about 2 weeks in response to a leak from the neutralization tank recirculation system into the containment dike. The neutralized tank contents and dike material was transferred to Tank 42H, and the dike area was brought to a save condition.

Limited by the size of the initial make-up tank, the amount of cleaning solution on hand was not adequate to fill the pot to the planned 80-in. level. Thus, only an estimated 1760 gal of cleaning solution was charged to the pot during the second acid strike. This was followed with 1080 gal of water to attain the desired cleaning solution volume corresponding to the 80-in. pot level. The impact was that the second acid strike was more dilute in acid concentration, approximately 0.9-M nitric acid, with an identical dilution of uranyl nitrate.

Heating was initiated and continued until the pot temperature had exceeded 80°C for about 24 hr, at which time cooling was initiated. Samples (2H-CC-HTF-E-073, 74) were pulled after the pot temperature had been brought below 40°C.

The pot contents were transferred to the neutralization tank, neutralized with 650 gal of 50 wt% sodium hydroxide and transferred to Tank 42H.

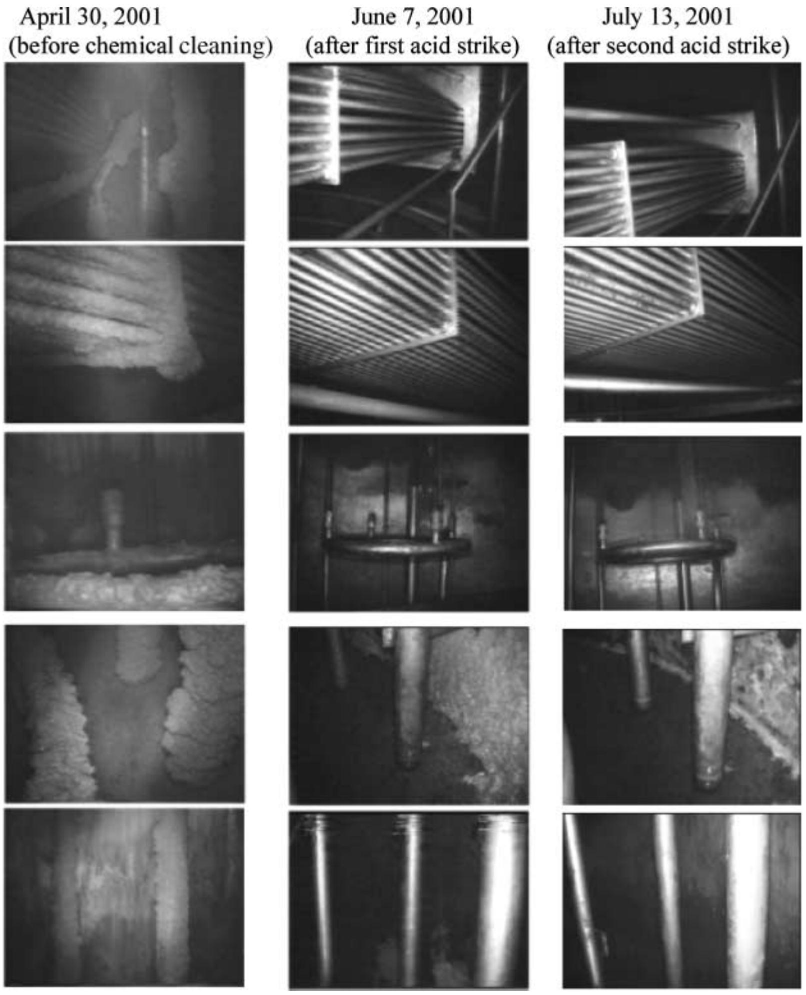

Figure 5. Comparison photographs of the 2H-evaporator pot interior taken before and after chemical cleaning.

The evaporator pot was inspected, revealing that the majority of the remaining deposits had been removed. The bulk of the material remaining in the evaporator pot could be classified as loose solids. Residual scale in the evaporator lift line and gravity drain line was removed by mechanical methods.

Sample Chemical Analyses

Analysis of Initial Acid Solution

F-Canyon personnel sampled the uranyl nitrate canyon stream. These samples were sent for organic analysis. At the time of cleaning solution preparation, two samples of the cleaning solution, as required by the criticality evaluation, were sent for acid and uranium isotopic analysis. A sample of the cleaning solution was also sent to establish the acid cleaning solution baseline. This sample, referred to as the "courtesy cleaning solution sample," was analyzed for organic constituents, as well as radionuclides and elemental composition.

Additionally, after the cleaning solution for the first acid strike was transferred from the tanker car into the evaporator pot, operations personnel sampled the liquid in the transfer line. This sample, referred to as the "trailer acid sample," was analyzed. The results for these sample analyses are presented in Table 2. The differences between the uranium isotope values are due to the different analytical methods used in the two different labs.

Chemical Analysis of Liquid Samples

Table 1 contains a listing of the liquid evaporator pot samples received during the first and second cleaning cycles. The samples, after filtering, were submitted for a number of analytes. The results are shown in Table 3. The main species that were targeted for monitoring scale dissolution were the bulk scale species (Na, Al, Si, and U) and other radionuclides trapped in the scale (Cs-137, Ce-144, Sr-90, and Sb-125), along with the free-acid concentration. For direct comparison, the tank volumes must be normalized as the liquid evaporated over the duration at elevated temperature (see Table 1).

For the major components, increased concentrations of sodium, aluminum, and uranium were observed in the 8-hr pot sample. However, silicon was not above the minimum detection level. The detection limit was high (338 mg/L) due to the spectral interference from the high uranium concentration. This behavior was not observed previously in laboratory dissolution of the scale, even in the presence of large amount of depleted uranium. Therefore, it is concluded that the elemental interference was not the source of the silicon discrepancies. Laboratory testing only examined the stability of the acid solutions for short periods of time (<8 hr). There are plausible explanations that include the formation

Table 3. Analytical results of liquid samples from pot cleaning.

Analyte	Units	Courtesy cleaning-solution sample	Trailer acid, 2H-CC-HTF-E-018	8-h pot 2H-CC-HTF-E019	16-h 2H-CC-HTF-E029	Post-cool down 24 h 2H-CC-HTF-E036	Second acid cleaning post-cool down 2H-CC-HTF-E073
Na	mg/L	194	186	6280	8090	8230	214.7
Al	mg/L	<237	<236	4250	4780	6150	<86
Si	mg/L	<303	<282	<338	<91	<118	<33
Cr	mg/L	<287	<282	<321	<743	<490	339
Cd	mg/L	23.7	24.2	29.0	29.4	34.3	23.5
Pb	mg/L	<287	<282	<322	<418	<490	276
Hg	mg/L		0.231	56.7	89.4	85.1	3.88
Free acid	M		1.4	0.918	1.00	1.18	1.5
Nitrate	mg/L		219,000	276,000	283,000	293,600	210,600
Sulfate	mg/L		1070	1220	896	890	826
DBP	mg/L	53	60	50	56	<100	69
TBP	mg/L	1.1	4.7	<1	<1	<1	<1
TOC	mg/L	110	130	126	110	119	120
F	mg/L		<20	<20	<224	<200	<20
Cl	mg/L		<20	<20	<224	<200	<20
nButanol	mg/L	2.2	<0.5	<0.5	<0.5	<0.5	<0.5
Uranium	mg/L	256,000	251,000	289,000	319,000	350,000	251,100
U-238	mg/L	298,000	244,000	283,300	353,494	422,000	216,700
U-235	mg/L	653	696	904	988.8	1350	585
Cs-137	dpm/mL		1.48E + 03	1.31E + 07	1.43E + 07	9.40E + 06	3.67E + 04

(*continued*)

Table 3. Continued.

Analyte	Units	Courtesy cleaning-solution sample	Trailer acid, 2H-CC-HTF-E-018	8-h pot 2H-CC-HTF-E019	16-h 2H-CC-HTF-E029	Post-cool down 24 h 2H-CC-HTF-E036	Second acid cleaning post-cool down 2H-CC-HTF-E073
Ce-144	dpm/mL	< detectable	< detectable	4.33E + 05	< det in diluted sample	< det in diluted sample	Not measured
Sr-90	dpm/ml		1.74E + 04	2.49E + 07	4.63E + 07	3.78E + 07	5.20E + 04
Sb-125	dpm/ml	< detectable	< detectable	3.74E + 05	6.45E + 05	< det w/dilution	1.54E + 02
Pu-239/240	dpm/mL		1.27E + 03	3.68E + 05	8.26E + 05	8.79E + 05	9.75E + 03
Pu-238	dpm/mL		1.42E + 03	5.48E + 07	5.74E + 07	3.62E + 07	1.14E + 06
Sp. gravity	g/mL		1.39	1.45	1.56	1.62	1.39

of high silicon to aluminum mineral phases such as mordenite. The results of the analysis of solids found in the evaporator pot and floating in the liquid samples are discussed as follows.

The normalized concentrations of free acid, aluminum, and sodium from the various samples taken during the initial acid strike are shown in Fig. 6. Volume normalization was performed by adjusting the data in Table 3 by the ratio of the pot volume at the time of sampling to the original volume of cleaning solution (volumes are contained in Table 1). The levels attained for sodium and aluminum plateau at the 8-hr sample through the post-cool down sample taken after approximately 24 hr. The normalized free acid concentration agrees well with the elemental data. The free acid is lowered to between 0.8 and 0.9 M in the three samples. As previously stated, CAM alarms ceased after several hours with the pot temperature near 85°C. The collection of the different data points indicates that the scale predominantly dissolved during the first 8 hr at pot temperatures near 85°C.

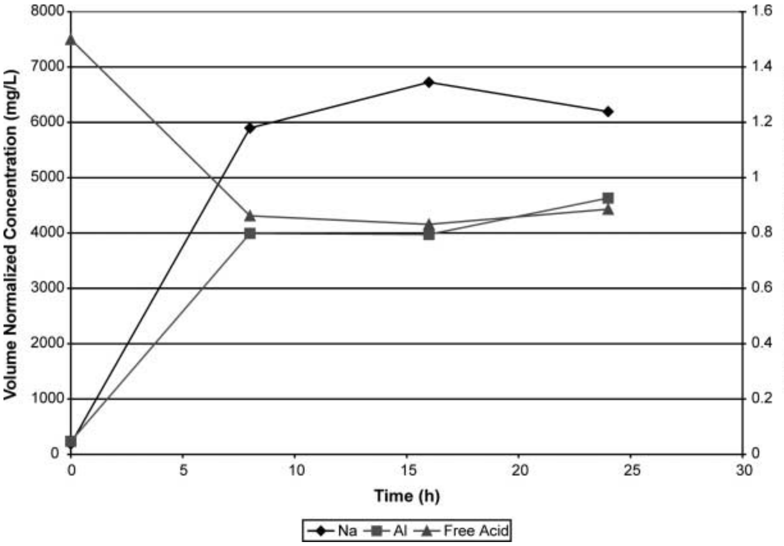

Figure 6. Plot of various normalized analyte concentrations for the first cleaning cycle.

Chemical Analysis of Solid Samples

As the dip samples from the evaporator pot were received, a small aliquot was originally poured into a glass vial to determine if solids were present. In each of the liquid samples from the evaporator pot during the first acid cleaning operation, solids were observed, and the entire liquid slurry was passed through a 0.45-μm filter. Figure 7 shows a photograph of the solids observed from the 8-hr liquid pot sample from the first acid strike. The material was yellow-reddish in color and floated on the surface of the uranium–nitric acid mixture. Portions of the solids were submitted for powder x-ray diffraction after drying at 100°C. The powder pattern exhibited peaks that corresponded to uranyl nitrate and did not contained peaks from other mineral phases.

Figure 8 shows a SEM image of the solids from the 8-hr pot sample and its associated EDS spectrum. The particle morphology appears to show small aggregates of uranyl nitrate particles. The EDS spectrum shows the presence of sodium, aluminum, and silicon. The relative ratios of the sodium,

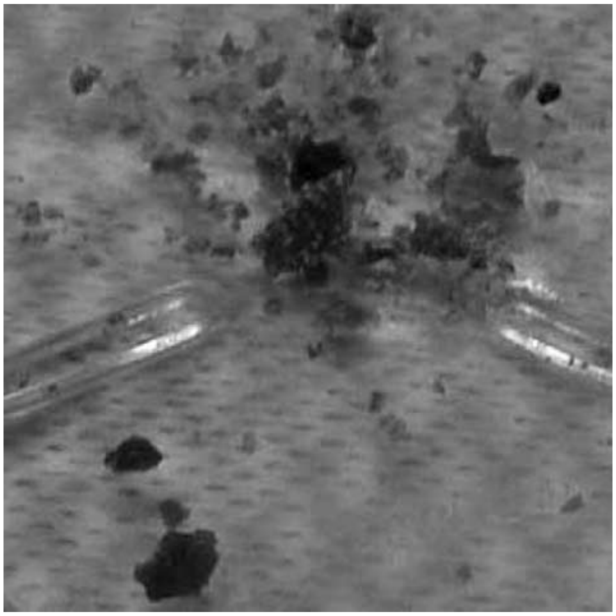

Figure 7. Photograph of solids from the evaporator pot liquid sample, first acid cleaning cycle.

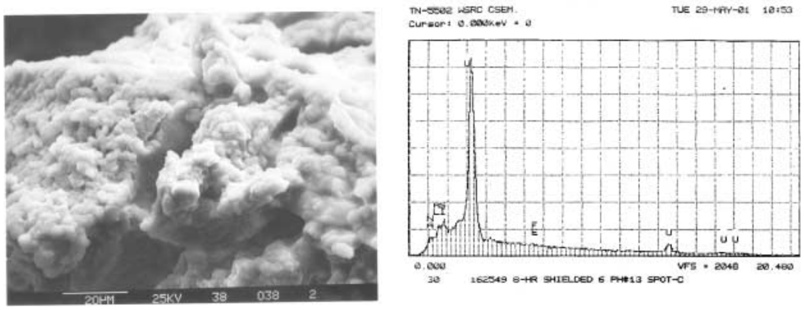

Figure 8. SEM micrograph and EDS spectrum of solids from the pot liquid sample.

aluminum, and silicon peaks differ from the original pot-scale samples from January 2000.[5] This material appears to be enriched in silicon compared to previous samples. The solid from the pot liquid sample was analyzed by IR spectroscopy and two thermal analyses (DSC and TGA). The IR spectrum of the solids recovered from the liquid dip sample is shown in Fig. 9. The spectrum shows no evidence of carbonate (peak position normally at $1570\,\mathrm{cm}^{-1}$ adsorption) or ammonia ligand (absence of $2800\,\mathrm{cm}^{-1}$ band). The IR spectrum does contain vibration bands from water, hydroxyls, nitrates, silicates, and predominantly the uranyl (UO_2) group. The lack of peak splitting

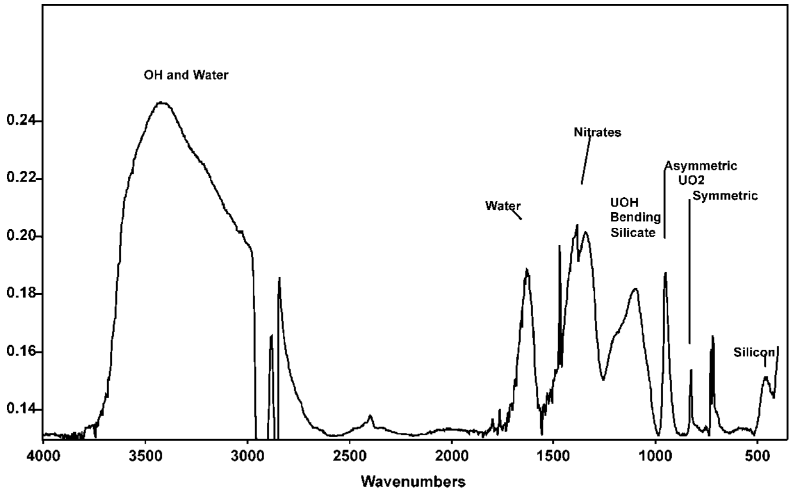

Figure 9. IR spectrum of solids from pot liquid sample.

at 950 cm^{-1} assigned to UO_2 is an indication of no coordination to the nitrate groups.[9] In addition, the broad adsorption of the hydroxyls and the nitrates indicates the amorphous character of the solid. The very narrow peak at 1470 cm^{-1} and the peak around 3000 to 2900 cm^{-1} are due to the lubricant (hydrocarbon) gel use to suspend the sample.

The thermograms from DSC and TGA measurements are shown in Fig. 10. The DSC measurement shows large endotherms associated with water loss between ambient temperature and 100°C and one centered near 200°C. Lastly, endotherms from nitrate salt melting are observed at 105 and 325°C. The TGA measurement agrees well with the DCS measurements. The temperatures at which endotherms were observed in the DSC correspond to weight losses in the TGA measurement. Total weight loss upon heating to 900°C was 57.8%.

Additionally, the solids from the liquid samples were analyzed after a fusion digestion was performed. The results of these analyses are shown in Table 4. The sample had a large amount of uranium, nearly 21 wt%. This, along with the water detected in the DSC/TGA experiments and the nitrate associated with uranyl nitrate, is the bulk of the sample composition. Silicon was detected at a concentration of 2.2 wt% but does not explain the fate of silicon in this dissolution process. Minor concentrations of other elements were detected and presented below.

After the first cleaning cycle was complete, personnel inspected the pot and found that the acid had substantially cleaned the evaporator pot. However, an accumulation of loose solids was observed in the evaporator cone. It is estimated that 9 to 18 gal of solids remained in the evaporator pot after the cleaning solution was removed. A large (30-g) sample of solids was collected (2H-CC-HTF-E-051) and sent for analysis.

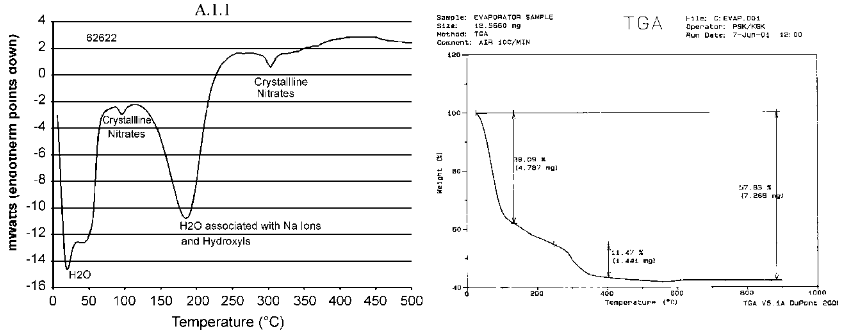

Figure 10. DSC and TGA of solids from the evaporator pot liquid sample.

Table 4. Analytical results from solids from the evaporator pot liquid sample (percentage).

Al	0.2864	Mo	0.0034
B	0.0110	Na	0.3774
Ba	0.0011	Ni	0.0234
Ca	0.0004	P	<0.0112
Cd	0.0028	Pb	<0.0233
Co	0.0107	Si	2.2247
Cr	<0.0232	Sn	0.0245
Cu	0.0207	Sr	0.0019
Fe	0.0737	Ti	0.0047
La	0.0160	U	20.8299
Li	0.0008	V	0.0239
Mg	0.0013	Zn	0.0017
Mn	0.0071	Zr	0.0345

An x-ray diffraction powder pattern was obtained from a portion of the sample and showed similar results to the solids recovered from the aqueous dip samples. The initial XRD analysis of the as-received sample indicated only uranyl nitrate. After washing with water or nitric acid, however, the XRD pattern indicated an amorphous material consistent with SiO_2 and a small amount of hematite (Fe_2O_3). Although the solution phase concentration of silicon was low, these loose solids were enriched in silicon and are likely the fate of silicon in the cleaning process.

Table 5 contains the ICP-ES results for the digestions of the as-received sample, the dried sample, and the insoluble solids. During preparation of the dried as-received sample, the moisture content was determined to be 28%.

Table 5. ICP-ES analysis of as-received and washed cone solids samples.

Analyte	As-received sample (wt%)	Dried as-received sample (wt%)	Insoluble solids H_2O wash (wt%)	Insoluble solids 0.1-M HNO_3 wash (wt%)
Al	0.75	1.2	0.23	0.21
Fe	0.50	0.71	1.4	1.8
Na	n.a.	1.2	0.094	0.12
Si	7.0	12.1	41.9	41.5
U	17.2	30.2	0.75	0.42

n.a. = not analyzed.

Table 6. Equivalent nitrates and oxides in cone solids sample.

Compound	As-received sample (wt%)	Dried as-received sample (wt%)	Insoluble solids H_2O wash (wt%)	Insoluble solids 0.1-M HNO_3 wash (wt%)
$Al(NO_3)_3$	8.7[a]	9.5	1.78	1.63
Fe_2O_3	0.72	1.0	2.0	2.5
$NaNO_3$	2.8[b]	4.5	0.35	0.43
SiO_2	15.0	26.0	89.5	88.8
$UO_2(NO_3)_2$	36.3[a]	50.0	1.2	0.69
Free H_2O	28	0	0	0
Total	91.4	91.0	94.9	94.1

[a] The weight percentages in the wet as-received sample are calculated by including the water of hydration: $Al(NO_3)_3(H_2O)_9$ and $UO_2(NO_3)_2(H_2O)_6$.
[b] Calculated assuming sodium and aluminum present in a 1:1 ratio (as in the dried sample).

Table 6 demonstrates that mass balances of suspected (oxidized or nitrated) species in the as-received, dried, and insoluble solids samples account for 90 to 100 wt% of the material. Other compounds were noted to be present in some digestions at levels of less than 0.2 wt%. Table 7 summarizes the additional analyses performed on the as-received sample.

The solids washed with water and the solids washed with nitric acid left approximately the same insoluble material. The solids did not significantly change in volume or appearance during washing, and uranium, aluminum, and sodium were removed during washing.

Table 7. Additional analyses of the wet as-received cone solids sample.

Analyte	As-received sample
U-238	21.9 wt%
U-235	0.050 wt%
Hg	0.06 wt%
Sb-125	2.90×10^7 dpm/g
Cs-137	2.54×10^7 dpm/g
Sr-90	3.20×10^7 dpm/g
Pu-238	1.90×10^8 dpm/g
Pu-239/240	2.62×10^6 dpm/g

Table 7 contains additional analyses of the wet as-received sample, which likely contained more than 28% water. The dried as-received and the washed insoluble solids samples were dried at 115°C before cesium hydroxide dissolution. Drying at this temperature would drive off the free water, but metal-bound water would remain. The uranium analysis of the as-received sample indicates a U-235 enrichment of 0.23%, or approximately the same enrichment as the depleted uranyl nitrate cleaning solution.

Scale Mass Balance

As discussed previously, the first cleaning batch acid filled the pot to a volume of 2810 gal, but only 2730 gal of cleaning solution was used. The 80-gal discrepancy between the pot level and the acid volume corresponds to the volume of scale and other material originally present in the evaporator pot. This 80-gal estimate is substantially lower than the initial visual (conservatively large) estimate of 344 gal.

From a mass balance on sodium and aluminum in the volume-normalized, first acid strike, post-cool down sample coupled with the observation of nearly complete scale removal during the first strike, the amount of original aluminosilicate scale is estimated to be between 325 to 350 kg, vs the original estimate of about 3500 kg. Substantially less mass of scale was in the pot than the mass for which the cleaning plan was designed. Thus, two acid batches vs the five batches anticipated effectively removed the scale.

The cleaning data suggest that about 70 kg of total uranium was in the pot initially vs the flowsheet approximation of 300 kg. Based on the data, the weight percentage of uranium in the solids was about 18%, which is much higher than expected. The relatively large total uranium concentration in the initial cleaning solution, however, causes this approximation to be extremely unreliable.

It is not possible to precisely quantify the amount of loose solids that were present in the evaporator pot during the first acid strike. Assuming an initial 350 kg of scale, these solids likely contained about 54 kg of Si, but the solid mass estimate is much larger due to the mass of water and the co-precipitated uranyl nitrate from the cleaning solution. The total mass of siliceous solids present in the pot during the first acid strike is estimated to be 770 kg on a wet basis.

CONCLUSION

The operation of the 242-16H (2H) evaporator was curtailed in October 1999 due to the presence of an aluminosilicate scale that contained sodium diuranate with a uranium-235 enrichment of approximately 3%. The scale had built to the point where steam lifting of the evaporator concentrates was ineffective. Previous work had shown that dilute nitric acid was an effective chemical cleaning agent. An overall cleaning flowsheet was developed in calendar year 2000 that addressed numerous safety issues associated with cleaning the pot, neutralizing the uranium-bearing acid, and discharging the neutralized solutions to a waste tank. Beginning in May 2001, a depleted uranium and nitric acid mixture was added to the evaporator pot and heated to elevated temperatures. As a result of this action, the pot was cleaned and returned to service.

From the results of sample analyses, the amount of aluminosilicate scale was overestimated. Original estimates were about 3500 kg. Based on elemental analysis of the dip samples taken from the pot, the amount of scale is between 325 to 350 kg. Two acid batches versus the five batches anticipated effectively removed the scale. The original estimate of uranium was also high compared to cleaning data. Slightly less than 70 kg of total uranium was in the pot; whereas the flowsheet estimated approximately 300 kg. The dissolution of scale was more rapid than expected, with the removal of the majority of the aluminosilicate scale essentially complete by the time the first samples were pulled for analysis (8-hr sample). Silicon was not observed to be measurable in any of the liquid samples taken from the evaporator pot. Silicon was detected, however, in a solid phase discovered in the evaporator cone after the first cleaning cycle.

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