

Evaporator Cleaning Studies

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Summary

Operation of the 242-16H High Level Waste Evaporator proves crucial to liquid waste management in the H-Area Tank Farm. Recent operational history of the Evaporator showed significant solid formation in secondary lines and in the evaporator pot. Abrasive cleaning measures succeeded at maintaining operation; however, solid formation in portions of the evaporator may require chemical cleaning. The SRTC completed initial studies to develop a chemical cleaning flowsheet. These studies show the following.

- Dilute nitric acid (ca. 1.0 M) effectively dissolved sodium aluminosilicate at elevated temperature (90 °C) at an instantaneous rate of 2400 mg/L/h. The solids tested came from the 242-16H Gravity Drain Line.
- Caustic dissolution (3 M and 8 M) proved only slightly effective in dissolving the sodium aluminosilicate with an average rate of 10 and 60 mg/L/h based on aluminum concentrations, respectively.
- Permanganate did not increase the cleaning ability of caustic solutions.
- Concentrated nitric acid formed silica gel during dissolution tests.
- Liquid sample removed from the 242-16H Evaporator pot did not contain solids. Analysis of filtrate showed the presence of silicon and aluminum. This finding confirms that water flushes of the evaporator pot removed portions of the sodium aluminosilicate formed during processing of DWPF Recycle.

Additional samples remain necessary to ensure material identity in the evaporator pot. Analysis of these future samples will provide actinide partitioning information and dissolution characteristics of the solid material from the pot to ensure safe chemical cleaning.

Introduction

The 242-16H High Level Waste Evaporator processes radioactive waste from the feed tank (Tank 43H), concentrates the waste and discharges to the concentrate receipt tank (Tank 38H). During this processing the waste concentrates by 30-40%. However, during processing of Defense Waste Processing Facility Recycle stream, the concentration approaches 90%. Difficulty in flow in the Gravity Drain Line occurred in July 1997. Video inspection indicated solid deposits present in the Gravity Drain Line.¹ Laboratory experiments showed that compounds of the general formula, $\text{Na}_3\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, form readily under the evaporator

conditions.²⁻³ Additionally, personnel observed evidence of the sodium aluminosilicate compound in the Effluent treatment Facility⁴ and in Tank 41H.⁵

Video inspection of the evaporator pot showed material that resembled the material found in the GDL. Concentration, Storage, and Transfer (CST) Engineering requested that Liquid Waste Processing (LWP) perform preliminary studies on dissolving insoluble solids found in the 242-16H Evaporator pot. This request⁶ came after High Level Waste Operations experienced difficulty in transferring the contents of the evaporator pot. High Level Waste Engineering requested scoping studies to examine the possible cleaning of the evaporator with nitric acid and caustic permanganate. This report discusses the results of those studies.

Experimental

Dissolution studies used glass, graduated centrifuge tubes. Personnel used an oven to heat the samples to 90 °C. Researchers removed samples from the graduated cylinders using a 2-mL pipette and submitted for metals analyses by ICP-ES. Each centrifuge tube contained approximately 0.5 g of solids from sample numbered HTF-027. (The Shielded Cells of SRTC archived sample HTF-027 since original characterization.²) Dissolution tests occurred in duplicate in some cases. Analytical Development Section personnel analyzed the samples using Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES).⁷

Table 1 shows the solvents used in these studies. Solvents preparation used reagent-grade materials. Laboratory notebook WSRC-NB-97-62 contains data obtained during these tests and the procedures used.⁸ Personnel used routine analytical protocol for the samples in this report.⁹

Table 1. Cleaning Solvents

Inhibited Water ³
3 and 8 M NaOH
2 M NaOH and 1.5 M KMnO ₄
4 wt % Oxalic Acid ³
0.5, 1.0, and 1.5 M HNO ₃
Concentrated HNO ₃

The CST Engineering and Operations personnel attempted to retrieve a sample of the solid material from the evaporator pot using a sampling tool developed by Equipment Engineering personnel from SRTC. Sample collection in September 1998 obtained a 5-mL sample (HTF-094) from the evaporator and sent this material to SRTC. Personnel placed the sample in the Shielded Cells, filtered, and submitted the filter including residue for X-ray diffraction analysis¹⁰ and the filtrate for metals analysis by ICP-ES.

These dissolution studies occurred in borosilicate glass centrifuge tubes. Sodium hydroxide solutions etch such glass surfaces. Therefore, personnel measured the silicon concentrations of an inhibited water, 3M, and 8M sodium hydroxide solutions exposed to similar glassware at 90 °C to serve as blanks for the analysis of caustic dissolution data.

Experimental Results

Researchers performed dissolution tests on material removed from the 242-26H Gravity Drain Line in August, 1997 (Sample No. HTF-027). An earlier report documents the analysis of this sample.² Testing started with the understanding that this sample may exhibit slightly different physical and/or chemical characteristics than material from the evaporator pot. The plan called for collection of additional samples with confirmatory tests conducted prior to introduction of a cleaning agent in facility operations.

Caustic Cleaning Experiments

Wilmarth, et al.² previously examined the use of inhibited water, 3 M sodium hydroxide, and 4 wt % oxalic acid as chemical cleaning agents for the Gravity Drain Line. The dissolution rate of both silicon and aluminum in these tests conducted at 60 and 90 °C proved unfavorable for use in the Gravity Drain Line. However, the rate of increase of soluble silicon in the 3 M sodium hydroxide solution approached 200 mg/L/h at 90 °C. This dissolution rate might prove useful in a stagnant pot although not useful in a flowing pipe.

In addition to the 3 M NaOH tests, researchers tested a higher hydroxide concentration (8 M) and a mixture of 2 M sodium hydroxide and 2 wt % potassium permanganate. Engineering and Operations personnel reported that previous efforts used the permanganate mixture in evaporator operations. Table 2 contains the soluble aluminum concentrations measured by dissolving portions of the Gravity Drain Line material.

Table 2. Aluminum Concentrations* in Caustic Cleaning Tests

Time	2 M NaOH/2 wt % KMnO4	3 M NaOH	8 M NaOH
0			0.3
0.5	25.2		40.6
1	37.8	5.01	110
2	42.3	5.01	141
3			176
3.5	62.0		
5		54.5	

* Units of mg/L

Figure 1 shows the behavior of aluminum in these dissolution tests. Increasing the hydroxide ion concentration from 3 M to 8 M increased the rate of dissolution of aluminum from 10.9 mg/L/h to 58.7 mg/L/h. Addition of permanganate did not significantly affect the dissolution of aluminum into caustic solutions. The rate of dissolution for aluminum into 2 M NaOH / 2 wt % KMnO_4 averaged 17.7 mg/L/h.

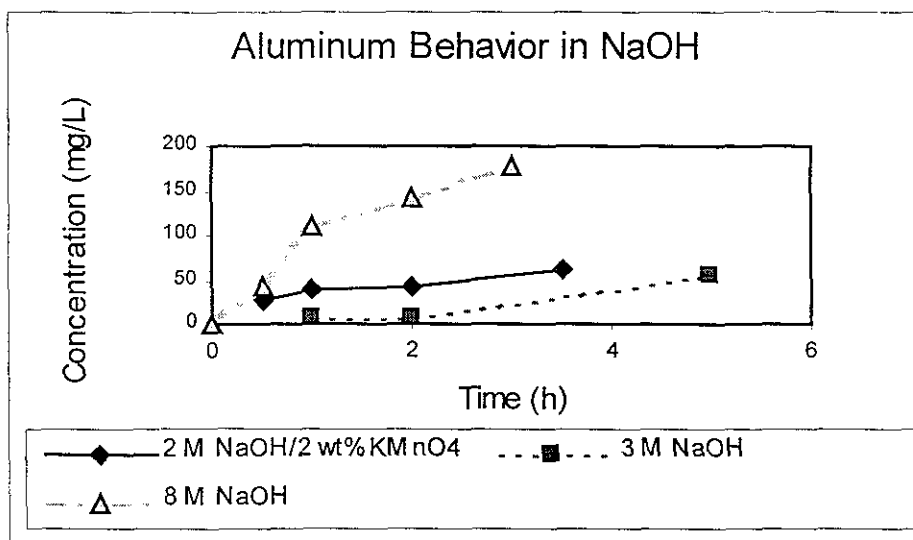


Figure 1. Aluminum Behavior in Caustic Dissolution Tests

Table 3 and Figure 2 display the resultant data for soluble silicon in these caustic dissolution tests. If the sodium aluminosilicate dissolves, the silicon and aluminum concentrations profiles should mirror one another. However, adverse reactions would alter the relative dissolution behavior. Personnel observed such altered behavior in comparing the silicon and aluminum data.

In the 2 M NaOH / 2 wt % KMnO_4 system, the silicon concentrations increased to 196 mg/L; whereas, the aluminum concentration increased to only 62 mg/L. This 3X increase in rate of dissolution also occurred in the higher caustic (8 M NaOH) dissolution test. The final silicon concentration in the higher hydroxide test reached almost 650 mg/L with the aluminum reaching only 176 mg/L. In the 3 M hydroxide test, silicon levels increased to 963 mg/L as opposed to the 55 mg/L aluminum concentrations. These data indicate some factor influences the ratio of Al to Si in this matrix. However, in the three dissolution tests, the calculated solubility product constant of silicon and aluminum does not surpass the solubility product constant for the sodium aluminosilicate.³ The calculated K_{sp} in these tests ranged from 1.6×10^{-5} to 1.5×10^{-4} mol^2/L^2 versus a previously measured value of 1.50×10^{-4} mol^2/L^2 .

Table 3. Silicon Concentrations* in Caustic Cleaning Tests

Time	2 M NaOH/2 wt % KMnO ₄	3 M NaOH	8 M NaOH
0		0	0.1
0.5	26.6		52.6
1	54.3	43.5	165
2	99.6	315	352
3			650
3.5	196		
5		964	

* Units of mg/L.

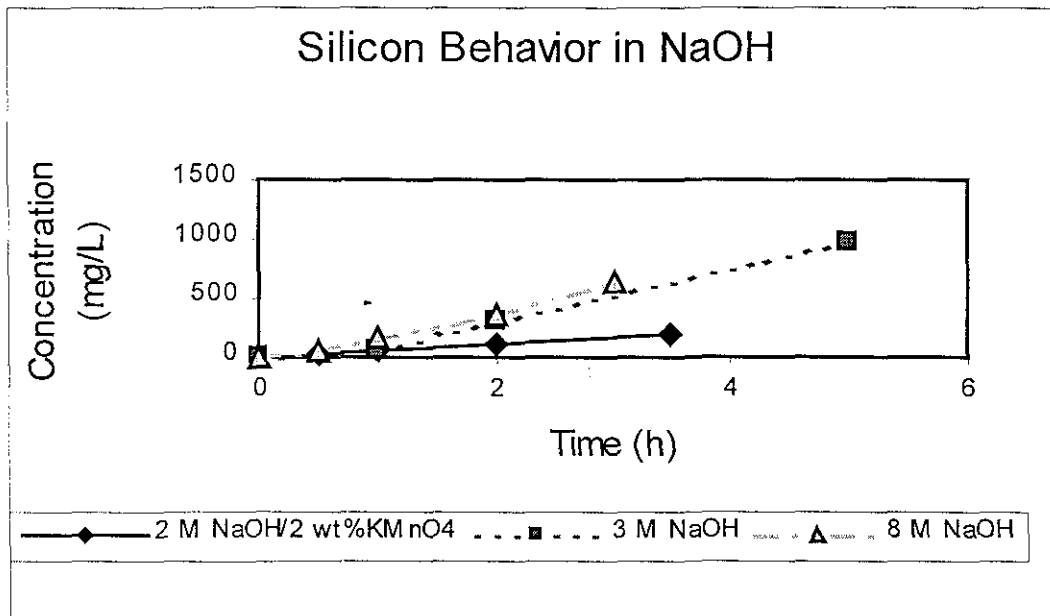


Figure 2. Silicon Behavior in Caustic Dissolution Tests

To ascertain the silicon contribution from the experimental apparatus, researchers placed the various solutions in the glass centrifuge tubes and heated to 90°C for a period of five hours. Table 4 provides the silicon concentrations measured in the 0.01M, 3 M and 8 M hydroxide solutions. As expected, an increased hydroxide level increases the rate of silicon dissolution at 90 °C. These dissolution rates contribute 110 to 250 mg/L of silicon to the systems. In the caustic permanganate experiments, the silicon contribution from the borosilicate glass accounts for the increased silicon levels. The silicon leaching from the glass test tube only accounts for 40% of the silicon excess (over the measured aluminum concentration) in the 8 M hydroxide test and only 20% in the 3 M tests.

Other possible reasons for the discrepancy between the aluminum and silicon concentrations include precipitation of aluminum as gibbsite or boehmite. However, x-ray diffraction of samples removed from dissolution studies only showed the sodium aluminosilicate compound. However, the aluminum could precipitate as an amorphous aluminohydroxy species which would not diffract an X-ray beam.

Table 4. Si Concentrations in Caustic Solutions (mg/L)

Time	0.01 M	3 M	8 M
0	0.158	5.61	5.61
0.5	1.38	5.61	5.63
1	0.161	5.98	8
3	4.73	130	154
5	14.58	291	365

Acid Cleaning Experiments

Caustic dissolution of the sodium aluminosilicate material formed in the 242-16H Evaporator Gravity Drain Line removed some of the material. The solubility of the silicate limits the effectiveness of this approach. Acid cleaning using concentrations compatible with the material of construction of the Evaporator might prove more effective. Personnel examined several concentrations of nitric acid yielding the aluminum concentrations shown Table 5.

Table 5. Aluminum Concentrations* in Nitric Acid Cleaning Tests

Time	1.5 M	1.5M	1.5 M	Conc. HNO3	1.0 M	0.5 M
0	4.1	4.1	0.3	2.8	10.3	1.1
0.5	2030	1700	1490	2090	1180	802
1	1990	1800	1560	2110	1350	863
2	2360	1920	1690		1560	934
3			1720		1760	990
3.5	2560					
4					1920	1130

* Units of mg/L.

Each of the tests shows a rapid increase in aluminum concentration to levels well above 1 g/L at 90 °C. The increase occurs almost at the 0.5 h sample in the 1.5 M nitric acid and concentrated nitric tests. In the 1.0 M and 0.5 M tests the concentrations increased slightly over the remainder of the 4 hour test as shown in Figure 3. Using the 0.5 h data, the rates of dissolution measured 1600 mg/L/h and 2350 mg/L/h at 90 °C for the 0.5 M and 1.0 M tests. For the 1.5 M nitric acid test, the rate averaged 3500 mg/L/h at 90 °C. These rates exceed those from the caustic testing by at least 2 orders of magnitude. Concentrated nitric acid increased the rate of dissolution only slightly above the rate measured in the 1.5 M nitric acid tests. The data shows that greater than 90% of the sample of sodium aluminosilicate dissolved in the 1.5 M tests with about 50% dissolved in the 0.5 M test.

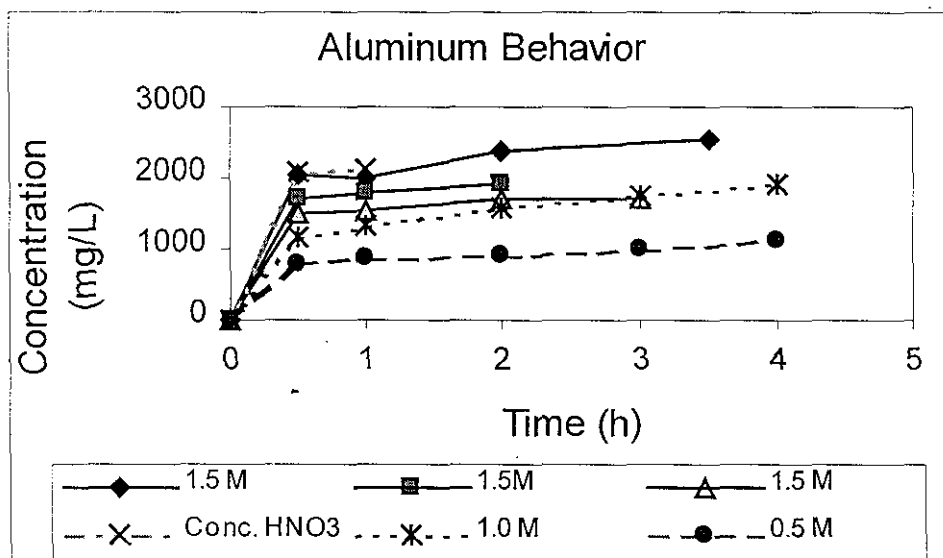


Figure 3. Aluminum Behavior in Acidic Dissolution Tests

The behavior of silicon in the acid dissolution tests differed significantly from that observed in the caustic dissolution tests. Table 6 contains the silicon concentrations from the tests conducted at 90 °C in the various nitric acid concentrations. In agreement with the aluminum behavior, an immediate, large increase in silicon concentration occurred in the first sample (0.5 h) taken from each of the 0.5 M, 1.0 M and 1.5 M nitric acid systems. Visual observations indicate no evidence of gas generation. The rate of dissolution from these tests at the 0.5 h sample agree well with the aluminum dissolution rates for the 0.5 M, 1.0 M and 1.5 M nitric acid systems.

Table 6. Silicon Concentrations* in Nitric Acid Tests

Time	1.5 M	1.5 M	1.5 M	Conc. HNO ₃	1.0 M	0.5 M
0	3.29	3.29	0.123	2.52	6.97	0.8
0.5	2007	1670	1450	213	1180	803
1	1930	1710	1470	120	1320	853
2	2150	1750	1530		1420	887
3			1480		1470	902
3.5	2230					
4					1480	940

* Units of mg/L.

The silicon concentrations in the concentrated nitric acid system differ greatly from those in other tests. The maximum concentration only reached 212.7 mg/L at the 0.5 h sample, whereas, the aluminum concentration reached 2086.6 mg/L. This low silicon concentration relative to the aluminum suggests quick dissolution followed by precipitation of the silicon. Visual observation of the sample at the 1 h sampling point revealed a three phase system. In the bottom of the centrifuge tube remained the un-dissolved sample. A second liquid phase existed with a third gelatinous phase floating on top. The gelatinous phase contained a silica gel. Literature details the formation of silica gels in nitric acid systems.¹¹

The data in this report indicates the use of a dilute nitric acid cleaning of the sodium aluminosilicate solids in the evaporator pot appears promising. Addition of dilute nitric acid to the pot would, however, require neutralization of the contents prior to discharge to Tank 38H, the concentrate receipt tank. To understand the chemistry of this neutralization, personnel treated the samples from the 1.5 M tests. As expected, solids formed during addition of 3 M NaOH. Figure 5 shows the X-ray diffraction pattern obtained from a sample of those solids. The pattern identifies the solids as sodium nitrate. The sodium aluminosilicate did not reform during the short period of the neutralization.

Evaporator Pot Sample (HTF-094)

Information learned from these experiments derived from a sample taken from the Gravity Drain Line. The higher temperatures of the evaporator pot might produce solids with different chemistries. Therefore, CST Engineering and High Level Waste Operations personnel worked with the Equipment Engineering Section of SRTC to develop and implement a sampling tool for the evaporator pot. A sample collected from the pot using this special tool arrived at SRTC. In the Shielded Cells, Researchers filtered the sample using a 0.45 micron, nitrocellulose filter but

failed to isolate measurable solids. They submitted the filter paper for X-ray diffraction and sent the filtrate for metals analysis by ICP-ES.

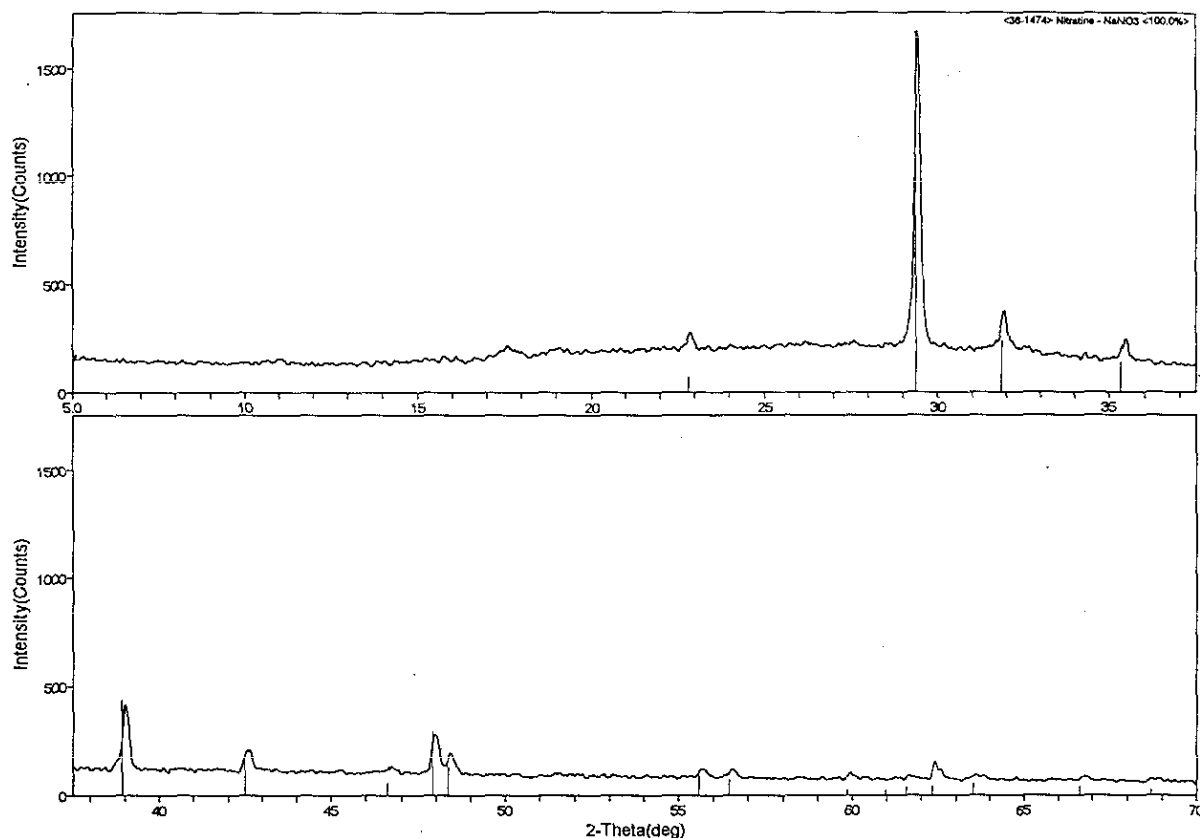


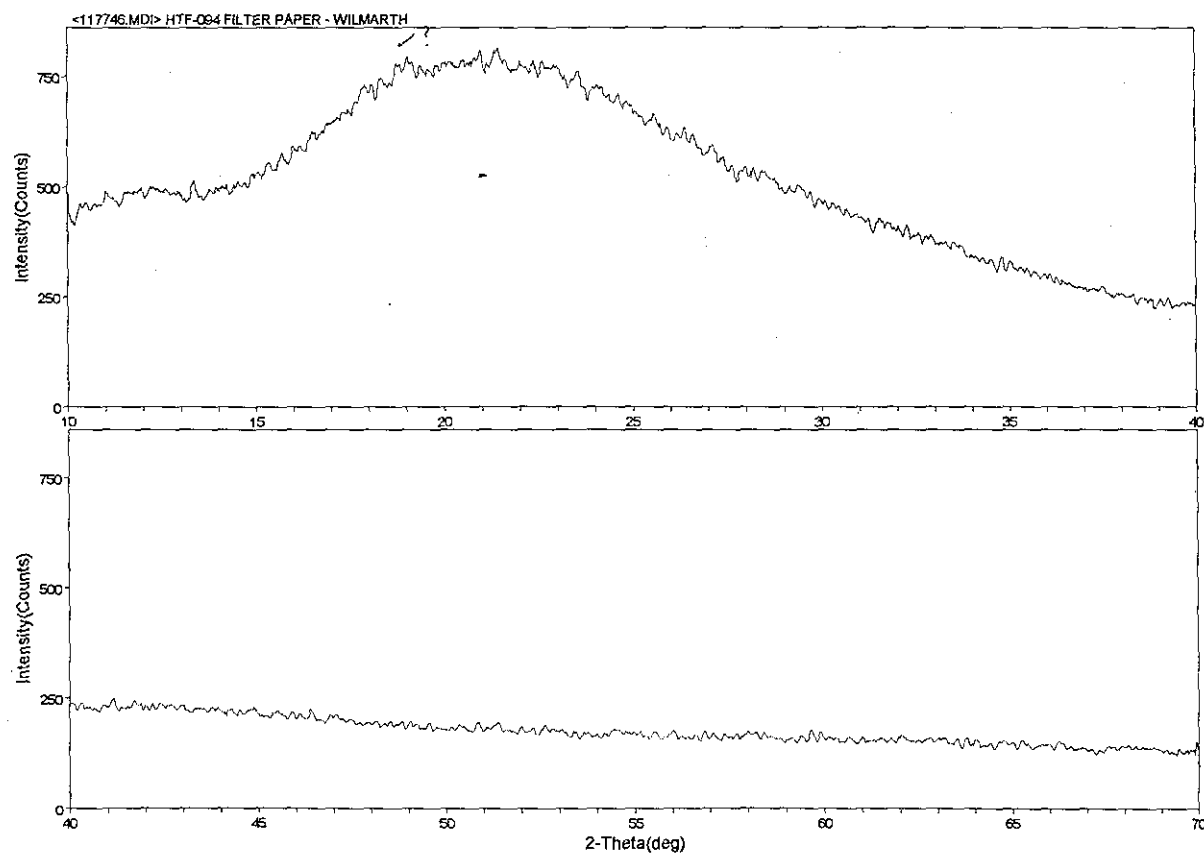
Figure 5. X-ray Diffraction Pattern from Neutralization Solids.

Table 7 lists the results of the ICP-ES analysis for metals. The results indicate a dilute caustic solution containing 0.5 M sodium ion concentration. Trace levels of boron, chromium, iron, magnesium, molybdenum, phosphorous, tin and zirconium occur. Measurements show elevated levels of aluminum (83.3 mg/L) and silicon (10.8 mg/L). The aluminum concentration equals about 2.5 times the concentration measured after 5 hours in inhibited water in previous dissolution tests (90 °C).² The ratio (~20) of sodium to aluminum agrees well with previously published data from this evaporator system.³ The level of sodium indicates an effective dilution factor of 80 from the historical Tank 43H sodium ion concentration.¹² Silicon concentrations relative to the aluminum concentrations indicate that prior to flushing the evaporator pot that silicon reached the solubility limit.

Personnel filtered the solution from sample HTF-094 and dried the filter paper to a constant weight with no resulting weighable accumulation of solids.. Figure 6 shows the X-ray diffraction pattern for the filter paper obtained with the objective of identifying any trace, crystalline solids present. The spectrum exhibits no diffraction pattern from solids on the paper. The background matches that for the amorphous spectrum of the filter paper.

Table 7. Analytical Results from HTF-094

Analyte	Concentration (mg/L)
Al	83.3
B	2.19
Ca	0.32
Cr	0.81
Fe	2.08
Mg	0.04
Mo	0.25
Na	2000
P	8.82
Si	10.8
Sn	0.34
Zn	0.11

**Figure 6. X-ray Diffraction Pattern from HTF-094 Filter Paper.**

Conclusions

Researchers completed initial studies to determine the feasibility of chemically cleaning the 242-16H High Level Waste Evaporator pot. The studies tested several suggested cleaning solvents including sodium hydroxide, caustic permanganate and nitric acid solutions. Tests examined the ability of these solvents to dissolve sodium aluminosilicate solids previously removed from the 242-16H Gravity Drain Line.

In general, caustic dissolution of the aluminosilicate material still proves of limited value. Testing examined three different concentrations of sodium hydroxide. The 3 M sodium hydroxide solution exhibited the best performance for the caustic solvents but dissolution rates remained orders of magnitude below those for other solvent systems. The addition of permanganate ion to the caustic system did not significantly increase the rate of dissolution of the sodium aluminosilicate.

Dilute nitric acid systems (ca. 1 M) appear to give the best performance. Dissolution of the sodium aluminosilicate occurred rapidly at 90 °C reaching at least 75% dissolution in 0.5 h. The tests showed no visual gas generation at these conditions. Concentrated nitric acid performed poorly as a solvent due to the formation of silica gel. Neutralization of the dilute nitric acid solvents with 3 M sodium hydroxide produced sodium nitrate solids which pose no significant concern for operations.

Personnel received and analyzed a sample from the 242-16H Evaporator pot. Sample collection followed several flushes of the pot using inhibited water. The sample contained no measurable solids as isolated by filtration. The X-ray diffraction analysis of the filter paper did not reveal any crystalline species. Metals analysis of the filtrate showed aluminum and silicon concentrations at the solubility limit prior to flushing the evaporator pot.

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