SRS Tank 38H and 43H Supernate Foaming Studies and Tank 38H Reel Tape Solids Characterization

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1.0 EXECUTIVE SUMMARY

Radioactive waste samples retrieved from Savannah River Site (SRS) Tanks 38H and 43H (concentrate receipt and feed tanks, respectively, for the 2H Evaporator system) were evaluated with regard to their tendency to form foams during air sparging. This work was conducted due to recent processing issues and outages in the evaporator that were believed to have resulted from sample foaming. The samples evaluated for foam formation included supernate collected in April of 2014 (near the time of the evaporator outage) as well as historical samples available within the SRNL shielded cells facility. The April samples included one Tank 43H surface sample (HTF-43-14-42), one Tank 43H sub-surface sample (HTF-43-14-43), and one Tank 38H (HTF-38-14-41) surface sample. In addition, two Tank 43H samples (HTF-43-14-8 and HTF-43-14-9) and one Tank 38H sample (HTF-38-14-6) were also evaluated along with a blended sample of various historical Tank 38H and 43H samples. Characterization results for the April samples are also provided. The composition of the samples was similar to historical evaporator system samples received at SRNL.

A foam testing apparatus (Figure 1-1) and a general methodology to evaluate foam formation in waste supernate solutions were developed using air flow rates of 50-150 mL/min in a 1-inch ID column with sample sizes of approximately 35 and 50 mL. All supernate samples were observed to form foams when exposed to air bubbling through a fritted glass gas dispersion tube in the cylindrical glass vessels. Hysteresis effects and slow stabilization of foam columns were observed in some cases. Care must be taken during testing to determine whether a stable and representative foam column has formed. Fast air flow rates 500-1000 mL/min can result in nearly complete conversion of the liquid to foam and the formation of very high foam columns in these vessels and with these samples. Low air flow rates ($\leq$50 mL/min) may not result in the formation of a continuous foam layer across the upper liquid surface.

A summary of the foam volume data collected for all samples evaluated at ambient temperature with an air flow rate of 125 mL/min is provided in Table 1-1. The April 2014 Tank 38H sample (HTF-38-14-41) formed the most foam of any sample evaluated. Foam volume data versus the air flow rate through the solution is provided for this sample in Figure 1-2. Two supernate sample volumes and various air flow rates were evaluated. Constant air flow through this sample resulted in the formation of a stable (relatively constant volume) foam column within 5 minutes and higher flow rates resulted in increased foam volume (as expected). Results were similar for the two supernate volumes (35 and 50 mL) tested. However, at elevated temperature (40-65 ºC) no foam formation was observed for this sample, indicating that foam formation would not occur for the Tank 38H sample during evaporator operations at elevated temperature. Significant foam formation was also observed for the April 2014 Tank 43H supernate sample, although the timescale to form a stable (constant height) foam column was longer than was observed for the Tank 38H sample. A larger foam volume was observed for the 50 mL Tank 43H sample than was observed for the 35 mL sample, indicating that sample size effects impacted the results for this supernate sample. In addition, foam was observed to form at elevated temperature for the Tank 43H sample. For all samples, the foam columns rapidly dissipated as soon as air flow was stopped. Xiameter AFE-1010 antifoam is effective at stopping foam formation for the April Tank 38H and the surface Tank 43H (Figure 1-3) samples.

A Tank 38H reel tape probe was also received from the tank farm for inspection and characterization due to problems encountered during tank level measurements (Figure 1-4). Approximately 1.5 g of solids (as-received mass, no washing or drying conducted) were recovered from the probe surface. XRD analysis of the solids and ICP-ES analysis of the dissolved solids (aqua regia digestion) were conducted. XRD analysis indicated that cancrinite ($(Na_8(Al_6Si_6O_{24})(NO_3)_2 \cdot 4H_2O)$) was the primary crystalline phase and clarkeite ($Na[(UO_2)O(OH)] \cdot H_2O$) was a minor crystalline phase. The primary metal species present in the solids were Na, Al, Si, U, and Fe. A hot water (110 ºC) wash was conducted to evaluate the solubility of the reel tape solids. Analysis results indicated that the solids were not highly soluble in water with low to moderate concentrations of Na, Al, and Si being observed. Contact with 0.5 M HNO_3 at 50 °C for two hours resulted in significant (≥50 % assuming speciation assigned by XRD for major metals) dissolution of the solids. In contrast, contact of the reel tape solids with as-received Tank 38H supernate resulted in the precipitation of additional Al species from the solution, indicating that the supernate was supersaturated in this species. Modification of the supernate by water dilution or caustic addition effectively eliminated the Al precipitation.

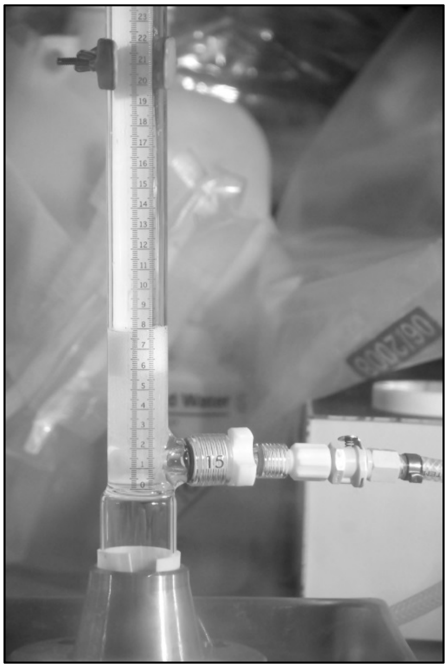

Figure 1-1. Foam Test Apparatus Containing Tank 43H Supernate Solution with Foam Column Above Liquid.

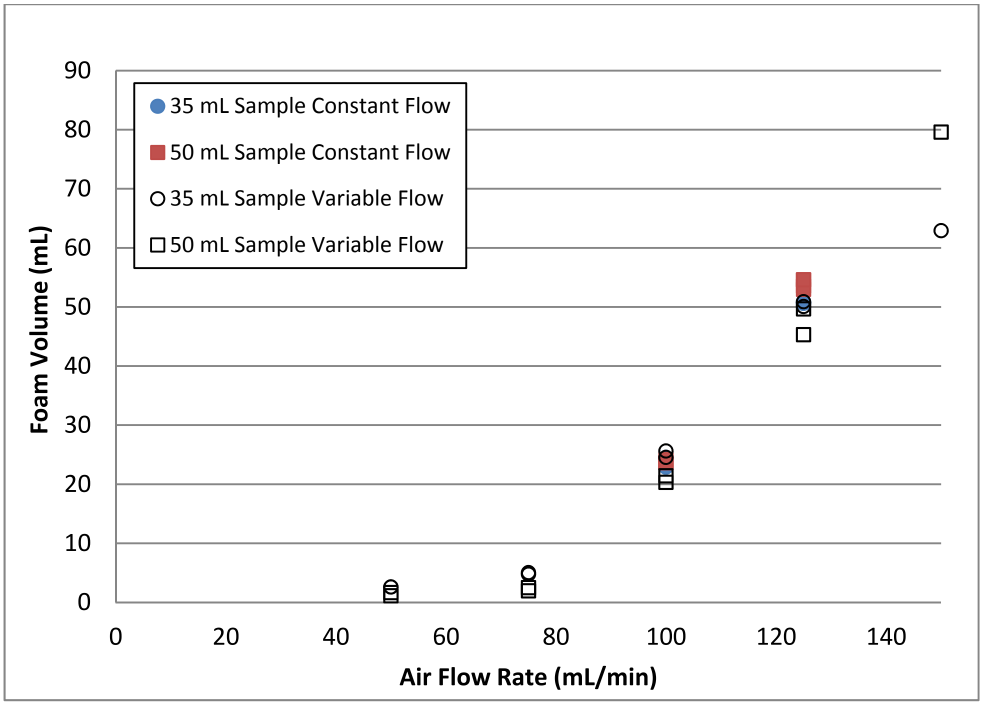

Figure 1-2. Tank 38H Supernate Foam Volume Data vs Air Flow Rate.

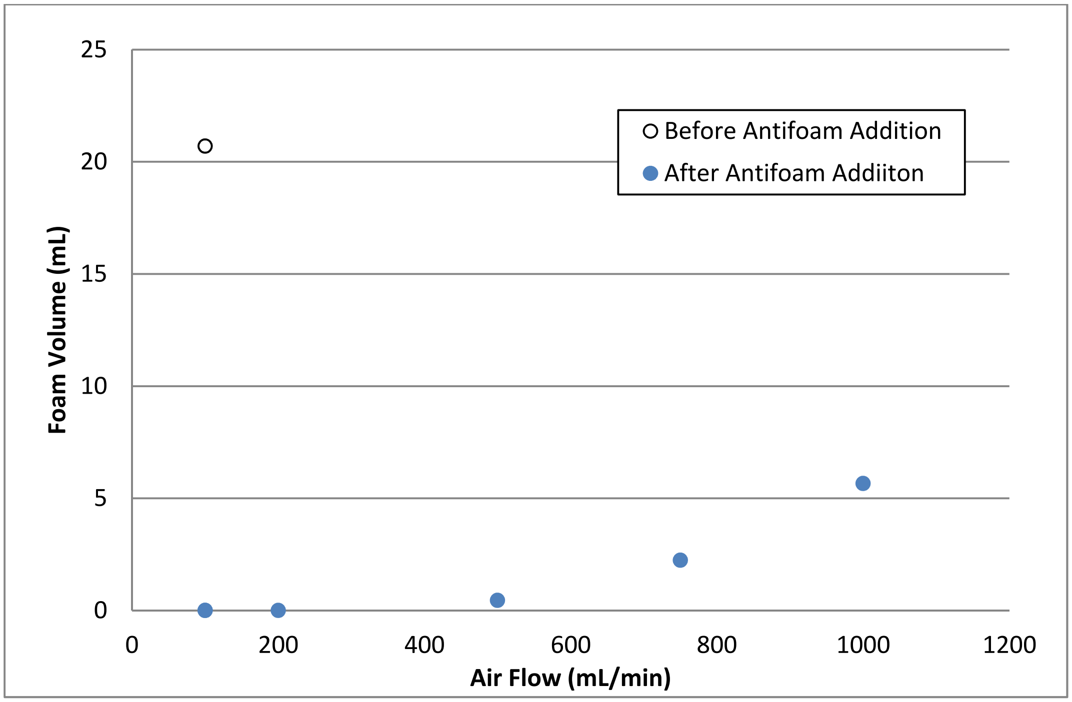

Figure 1-3. Tank 43H Surface Sample Foam Volume Data vs Air Flow Rate Before/After Xiameter AFE 1010 Anti-foam Addition (35 mL supernate sample + 1 mL antifoam).

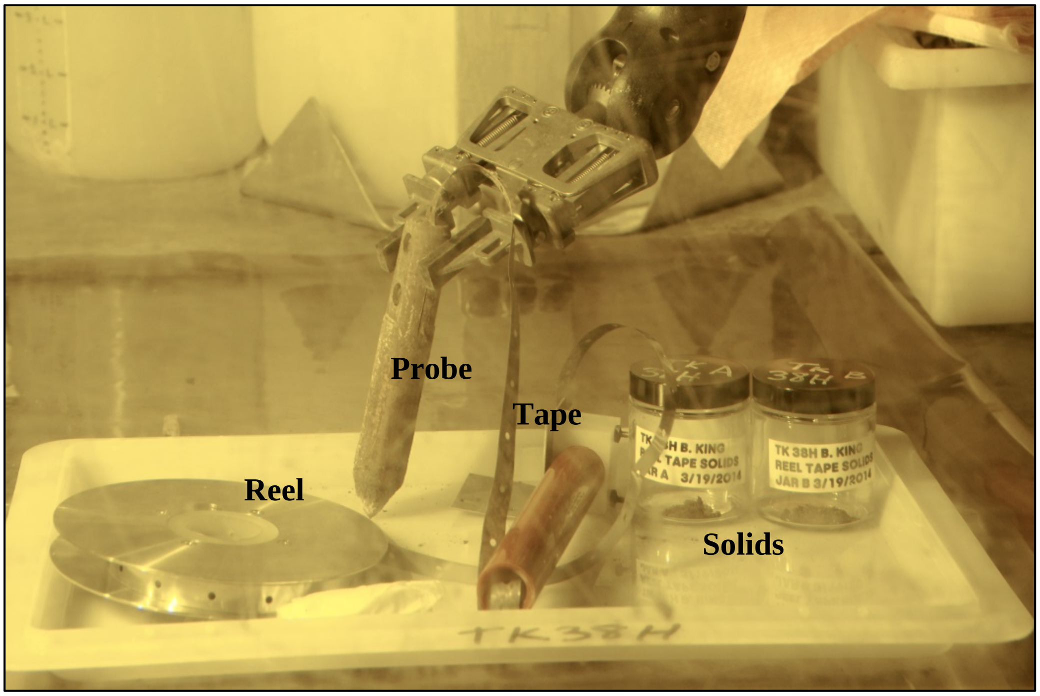

Figure 1-4. Tank 38H Reel Tape Probe and Solid.

Table 1-1. Ambient Temperature Foam Volume Data Summary for all 2H Evaporator System Samples Tested (125 mL/min air flow rate, unless otherwise indicated).

Sample	Tank	Liquid Volume (mL)	Foam Vol. (mL)
HTF-43-14-42 (April 2014 surface sample)	43	35	12.8
HTF-43-14-43 (April 2014 sub-surface sample)	43	35	6.2
HTF-38-14-41 (April 2014 surface sample)	38	35	50.7
HTF-43-14-8	43	35	5.9*
HTF-43-14-9	43	35	19.3
HTF-38-14-6	38	35	23.8
HTF-43-14-42 (April 2014 surface sample)	43	50	39.3
HTF-43-14-43 (April 2014 sub-surface sample)	43	50	8.3
HTF-38-14-41 (April 2014 surface sample)	38	50	53.9
HTF-43-14-8	43	50	8.5

* measured at 100 mL/min

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LIST OF ABBREVIATIONS

ADS	Analytical Development Section
ASTM	American Society for Testing Materials
HLW	High Level Waste
HTF	H Tank Farm
IC	Ion Chromatography
ID	Inside Diameter
ICP-ES	Inductively Couple Plasma Emission Spectroscopy
SCCM	Standard Cubic Centimeters per Minute
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
SVOA	Semi-volatile Organics Analysis
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TTQAP	Technical Task and Quality Assurance Plan
TTR	Technical Task Request
XRD	X-ray Diffraction

2.0 Introduction

Evaporator operations at the Savannah River Site are critical for removing excess water from radioactive waste supernates and minimizing the volume of High Level Waste (HLW) requiring storage. Tank 43H is the feed tank and Tank 38H is the concentrate receipt tank for the SRS 2H Evaporator System. Recent operational issues associated with radioactive material breakthrough into the off-gas treatment systems were believed to be associated with foaming of the waste during evaporation. As a result, Savannah River Remediation (SRR) requested that foaming studies be conducted at the Savannah River National Laboratory (SRNL) to confirm whether sample foaming could occur and evaluate the effectiveness of an antifoam reagent (Xiameter AFE 1010) at collapsing any foams observed. Supernate samples from Tank 38H and 43H were transferred to SRNL for characterization and foam testing. Historical Tank 38H and 43H samples were also evaluated for comparison.

Traditional methods for measuring the degree to which a liquid sample forms foam include the use of porous glass frits to introduce gas bubbles into a sample contained within a cylindrical column (ASTM D892-13; ASTM D1881-97; ASTM D7840−12; Bikerman, 1938; Tyrode, 2003). The degree of foaming varies with the sample temperature, volume, and concentration. The stability of foams varies depending upon the sample, with some samples quickly reaching a steady state foam height while other foam columns gradually build over time. Stable foam columns are observed when a dynamic equilibrium exists between the bubble formation rate at the bottom of the column and the rate of bubble collapse at the top of the column. Alternatively, other samples may have a tendency to form large bubbles which may bridge across the test cylinder and rise up the column prior to collapse resulting in erratic foam heights (referred to as collapsible foam). The height of the foam column can also vary depending upon the condition of the vessel surface in contact with the foam. Surface phenomena such as this can result in hysteresis effects and inconsistent results for a given sample. Another foam characteristic of interest is the “break time” or the time required for the foam to completely collapse under no flow conditions.

A goal of this testing was to develop a general apparatus and methodology for evaluating and comparing various Savannah River Site waste processing samples with regard to their tendency to foam. The development of methods for the evaluation of foam formation with actual waste samples is impacted by sample size limitations. The foam test methodology was developed targeting nominal samples in the range of 35-50 mL. Both ends of this volume range (35 mL and 50 mL) were evaluated when sufficient sample was available. Hysteresis effects were evaluated by sequential exposure of the sample to a series of increasing and then decreasing air flow rates. Since decreasing air flow rates result in lower foam heights, comparison of the second (descending) portion of this series to the first (ascending) portion allows for some evaluation of the impacts of wetting the vessel wall upon foam formation and hysteresis affects.

Foam testing was conducted in borosilicate glass vessels using an air sparge. Using air for sparging is representative of the process in the sense that the evaporators are operated under air. However, exposure to the volume of air required to produce the necessary flow rates for foam formation is not prototypical. In addition, it is likely that some carbon dioxide was absorbed during testing as a result of this exposure. The effect of sparging with air could be evaluated by conducting comparable tests using an inert gas (such as nitrogen), but no evaluations of this kind have been conducted thus far. In addition, borosilicate glass will etch in caustic solution potentially resulting in increased silicon and boron concentrations in the supernates. (Caustic solutions referred to as base baths are typically used to clean borosilicate glass vessels). Given typical test durations (2-3 hours) it is expected that only small increases in the boron and silicon concentrations occurred. The impact of glass dissolution during testing was not quantified. There were no visual signs of precipitation or other changes to the supernates during foam testing and the impact of glass etching is expected to be minimal.

Characterization of the Tank 38H reel tape solids was routine and included XRD analysis, acid digestion, and solubility evaluations in various liquids.

This testing was conducted following the requirements described in the associated Technical Task Request (TTR; Staub, 2014) and Technical Task and Quality Assurance Plan (TTQAP, King, 2014).

3.0 Experimental Procedure

3.1 Apparatus

Foam testing vessels (Figure 3-1) were prepared from approximately 1 and 1.5 inch inside diameter (ID; 26.4 and 37.0 mm, respectively) borosilicate glass tubing with one end closed to form a column for sample containment. Most of the tubing length was graduated with a millimeter scale with the zero point positioned at the bottom of the column to allow for measurement of the liquid and liquid + foam heights. A false bottom was added to the outer portion of the closed end of the cylinder to raise the vessel and facilitate easier reading of the fluid height. A stainless steel stand was constructed with a Teflon® sleeve to hold the cylinder in an upright position. A gas dispersion tube with a 1 cm outside diameter coarse glass frit was positioned in a horizontal orientation in the bottom of the column such that ~1 cm of liquid would be present below the frit when a test sample was transferred to the vessel. The gas dispersion tube was attached and sealed to the cylinder using threaded #7 and #15 Teflon® bushings with Viton® O-rings. The tube was removable and replaceable. The tubes were adjusted to center the frit in the middle of the vessel prior to each test. The fritted glass portion of the dispersion tube used with the 1 inch ID column (the primary column used for testing) was approximately 16 mm in length. A properly positioned 16 mm frit centered inside of the 26 mm ID column resulted in the production of a plume of bubbles rising vertically across the surface of the sample within the vessel.

House air supply in the SRNL shielded cells facility was used for air sparging. Air was introduced through a manifold including a pressure regulator, a calibrated pressure safety valve set to release air at 15 PSIG, and a flow shut off and vent valve. Air flow to the system was controlled using a mass flow device. Air was introduced into the cells through a standard wall penetration containing a 1 PSIG check valve. Air flow rates ranging from 50 to 1000 mL/min (SCCM) were evaluated during method development with a more narrow range being used for the final sample evaluations (see Section 3.2).

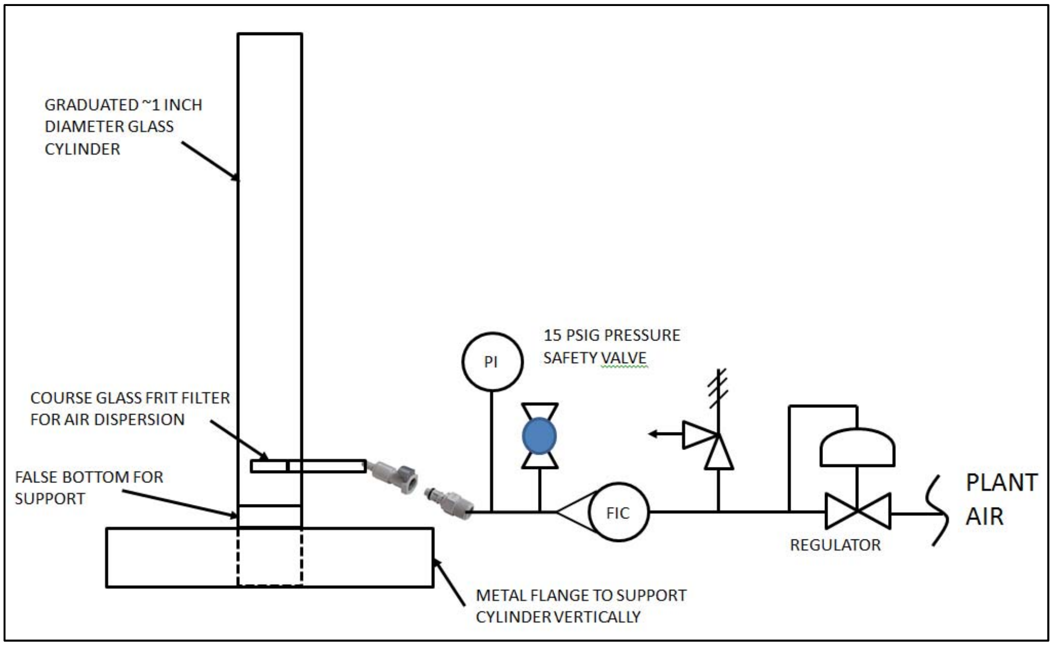

Figure 3-1. Foam Test Apparatus Design.

3.2 Test Methodology

The supernate volume was measured in a graduated cylinder prior to transfer to the foam test vessel. The foam volume at each air sparge rate was calculated from the height difference between the initial liquid and the liquid + foam height. Liquid and foam heights were measured by careful inspection (using a monocular) of the upper liquid:air interface within the column and selecting the average height observed during the 20-30 second measurement period. Depending upon the sample, the height of this interface could vary during measurement by as much as 10 mm or as little as 1 mm. The foam volume was then calculated using the foam height and the known cylinder cross sectional area. Direct utilization of the liquid height measured with no air sparging in these calculations does not account for the increased liquid height during sparging associated with fluid displacement by the air bubbles contained within the column of liquid. This displacement effectively raises the liquid level in the column. As a result, the liquid height in the vessel as a function of the air sparge rate was determined using 35 and 50 mL samples of (non-foaming) deionized water. This data was utilized to correct for air displacement effects. These corrections were small, but can be useful for determining whether sample foaming has occurred as opposed to volume expansion resulting from fluid displacement. This correction is most important for samples which do not form large foam volumes.

A composite blend of Tank 38H and 43H archived samples received in SRNL was used for foam testing method development using both the large and small diameter foam test vessels. Due to the fact that some archived evaporator samples planned for testing were small in volume (as small as 30-35 mL) the small diameter column was used for most testing. A standard test sequence was developed for testing using the 1 inch ID column which included constant and variable flow rate conditions. The standard test sequence selected is provided below.

1. Transfer 35 mL of supernate into the test vessel and record the liquid height in the vessel.

2. Turn on the air sparge at a constant flow rate of 100 mL/min for 20 minutes with foam data collection at 5 minute intervals.

3. Increase the air sparge to a constant flow rate of 125 mL/min and maintain this flow rate for 20 minutes with data collection at 5 minute intervals.

4. Turn off the flow and record the time required for the foam column to completely collapse.

5. Expose the sample to the following variable flow rate sequence and record the foam height after 5 minutes at each flow before adjusting the flow rate to the next target value: 50, 75, 100, 125, 150, 125, 100, 75, 50 mL/min.

6. If sufficient sample is available, transfer an additional 15 mL of supernate into the test vessel and record the liquid height in the vessel (giving a total sample volume of 50 mL).

7. Turn on the air sparge at a constant flow rate of 100 mL/min for 20 minutes with data collection at 5 minute intervals.

8. Increase the air sparge to a constant flow rate of 125 mL/min and maintain this flow rate for 20 minutes with data collection at 5 minute intervals.

9. Turn off the air flow and record the time required for the foam column to completely collapse.

10. Expose the sample to the following variable flow rate sequence and record the foam height after 5 minutes at each flow before adjusting the flow rate to the next target value: 50, 75, 100, 125, 150, 125, 100, 75, 50 mL/min.

This measurement sequence was intended: 1) to determine a steady state foam height over a 20 minute time scale at two intermediate flow rates (100 and 125 mL/min) known to produce measureable foam heights for most samples, and 2) to determine if there were significant hysteresis or sample volume effects using sequential variable air flow rates. Following foaming evaluations with a given sample, the vessel was rinsed 3-4 times with deionized water and the gas dispersion tube was soaked in deionized water for several hours. The vessel and the tube were then allowed to air dry prior to testing a new sample. Whenever the air flow was shut off to the supernate-filled test vessel for more than 1-2 minutes, the air supply line was disconnected from the gas dispersion tube using a quick-disconnect. This sealed the line leading to the dispersion tube and prevented back flow of supernate into the interior of the tube. This was done to help maintain the cleanliness of the dispersion tube and avoid clogging the frit.

Most testing was conducted at ambient temperature which ranged from 23-27 °C. Elevated temperature tests were not conducted under controlled conditions. Rather, the samples were heated on a stir plate to near 95 °C and then transferred to the foam test apparatus. Foam formation and height were then evaluated as the sample cooled. Transfer of the samples to the apparatus resulted in rapid cooling such that temperatures in excess of 65 °C could not be evaluated. Nonetheless, this method provided some insight as to the impact of elevated temperature on foam formation with these samples. Obviously, sample foaming in the evaporator pot would have to occur at elevated temperature since waste supernate evaporation generates the gas flux that produces foaming.

Xiameter AFE-1010 reagent produced by Dow Corning was provided by SRR for evaluation as an antifoam agent with the Tank 38H and 43H supernate solutions. Prior to use, 0.25 g of antifoam reagent was diluted with 4.75 g of deionized water to produce a diluted reagent solution containing 5% antifoam reagent by as-received mass (1:20 dilution), as is typically done prior to reagent use in the tank farm. The antifoam was added to selected samples either drop-wise or using a pipet to evaluate the reagent effectiveness at collapsing pre-formed foams at moderate to high air flow rates. Following the antifoam addition, the air flow rate was increased to evaluate whether foam formation was suppressed at higher flow rates. Antifoam evaluations were conducted after foam measurements were completed on all samples so that trace amounts of antifoam remaining in the vessel after cleaning would not effect the results.

3.3 Analysis

One recently received Tank 38H and two Tank 43H supernate samples were characterized as part of this testing program. SRS H Tank Farm sample HTF-38-14-41 was collected from the surface of Tank 38H in April of 2014. H Tank Farm samples HTF-43-14-42 and HTF-43-14-43 were collected from the surface and sub-surface, respectively, of Tank 43H in April of 2014. The as-received samples were generally clear with no visible solids, although the Tank 43H sub-surface sample was slightly darker in appearance. Upon standing for several hours a thin layer of solids was observed to form on the bottom of the bottle. All three supernate samples were filtered prior to analysis through 0.45 µm Nylon Nalgene syringe filters.

The density of each supernate was measured in duplicate in 2-mL glass density tubes. Sub-samples of each sample were also filtered through 0.45 µm Nalgene Nylon syringe filters. The filtrate was diluted directly into either deionized water or 1 M nitric acid. Dilution factors ranged from 8-12 for the supernate samples. The diluted samples were then submitted for analysis in the SRNL Analytical Development Section. Samples diluted in water were analyzed by IC (Ion Chromatography) anion, TIC/TOC (Total Inorganic and Total Organic Carbon), and Free Hydroxide methods. Samples diluted in acid were analyzed by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES).

Solids recovered from the Tank 38H reel tape were characterized and evaluated for solubility in various solutions. A portion of the unwashed solids was submitted for X-Ray Diffraction (XRD) analysis. Another unwashed solid sub-sample was completely dissolved in aqua regia at elevated temperature (115 °C for 2 hours) in a Teflon® pressure vessel and analyzed by ICP-ES. A hot water wash of the unwashed reel tape solids was also conducted under these same conditions and the liquid was analyzed by ICP-ES, IC Anion, TIC/TOC, and SVOA. Additional solubility tests were conducted in water, dilute nitric acid, and modified and unmodified Tank 38H supernate. These samples were diluted in 1 M HNO_3 acid (dilution factor 3.5-4.5) prior to submission to ADS for analysis.

3.4 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

4.0 Results and Discussion

4.1 Sample Characterization

4.1.1 *Supernate Analysis*

The April 2014 Tank 38H and 43H supernate sample analysis results are provided in Table 4-1. Some solids were observed in the Tank 43H sub-surface samples which were filtered from the solution prior to analysis. In general, the analysis results are consistent with other historical 2H evaporator system samples. As expected, the Tank 38H sample is more concentrated (~7 M Na^+) than the Tank 43H samples (~3 M Na^+). Analysis results for the Tank 43H surface and sub-surface samples were very similar. The three supernate solutions primarily contain dissolved sodium salts of nitrate, nitrite, hydroxide and carbonate. The total inorganic carbon (TIC) concentrations correspond to 0.18 to 0.42 M carbon, which is presumably present as carbonate anion. No semi-volatile organic species were detected in any sample. Both formate (<0.05 M) and oxalate (<0.005 M) concentrations are low in all three supernate solutions and no semi-volatile organic species were detected. Based on the analysis results, there are no unusually high organic species present which would be expected to promote excessive foaming in these samples.

Measured densities for the April 2014 Tank 38H and 43H supernate are also provided in Table 4-2. The densities are typical for waste supernate solutions in the 3-8 M Na^+ range.

4.1.2 *Tank 38H Reel Tape Solids Analysis*

1.5 g of dark solids were scraped from the reel tape probe and recovered in glass jars. Small amounts of lighter colored solids which had more of the appearance of salt-cake were also recovered. No attempt was made to isolate and analyze the lighter-colored solids separately. XRD analysis of the unwashed solids (Figure 4-2) revealed that a feldspathoid cancrinite (Choi, 2005), aluminosilicate phase ($Na_8(Al_6Si_6O_{24})(NO_3)_2 \cdot 4H_2O$) and the uranium phase clarkeite ($Na[(UO_2)O(OH)] \cdot H_2O$) were the dominant crystalline phases. Analysis results for a portion of the solids following acid digestion are provided in Table 4-2 as the weight percentage of the original unwashed and undried solids. The sum of the weight percent values reported (27%) is well below 100% due to the fact that the anions associated with these metals are not included and the fact that the sample was not dried prior to analysis and the water content was unknown. Based on the acid digestion data, the solids composition was dominated by sodium (some of which was residual salt), aluminum, and iron. The silicon concentration was lower than expected based on the XRD results but low silicon concentrations are frequently observed by this digestion method. The presence of iron was surprising since iron is not a component of the phases identified by XRD. The uranium detection limit was high (1 wt. %) for this sample.

4.1.3 *Tank 38H Reel Tape Solids Solubility Evaluations*

A hot water wash of the reel tape solids was conducted following the same procedure used for acid digestion (Teflon® pressure vessel at 115 °C for 2 hours). Analysis results for the hot water wash solution reported on the same basis as the acid digestion result (wt. % of original solids mass) are also provided in Table 4-2. The results indicate that a significant fraction (10-30%) of the total sodium and aluminum present in the original sample dissolved in hot water (total wt. % dissolved metals of 6.5% versus 27% by acid digestion). In addition, a higher silicon concentration was observed for the hot water wash than observed by acid digestion. This inconsistency is additional indication that the silicon result reported by acid digestion is low. The only detectable anions observed by IC anion analysis of the hot water wash solution were nitrate, nitrite, and chloride. Low concentrations of inorganic and organic carbon and no detectable semi-volatile organics were observed in the hot water wash solution.

Reel tape probe solids solubility evaluations were also conducted in several additional solutions at 50 °C with agitation over a 2 hour period. Solutions tested included: water, 0.5 M HNO_3, Tank 38H supernate (HTF-38-14-41), HTF-38-14-41 diluted 50% by volume with deionized water, and HTF-38-14-41 spiked with NaOH to give a final target free OH near 6 M (~2 times the hydroxide concentration of the as-received sample). A water solubility test was also conducted at ambient temperature. Significant solids remained in all test bottles following contact with the liquids.

Analytical results for the filtered liquid portions of the samples exposed to water and nitric acid are provided in Table 4-3. Dilute nitric acid is effective at dissolving significant amounts of the reel tape solids. Primary soluble species in the nitric acid solution included Na, Al, Si, and U. Lower amounts of soluble Ca, Fe, Mg, Mn, and other trace metals were also observed. Based on the analytical results and assuming that the primary solid phases are cancrinite and clarkeite (based on the XRD results) greater than 50% of the reel tape probe solids dissolved in 0.5 M nitric acid at 50 °C. Significantly lower concentrations of Na, Al, and Si were observed for the heated and unheated water samples after contact with the reel tape solids relative to the sample contacted with nitric acid. Based on these results it appears that 0.5 M HNO_3 at 50 °C may be an effective cleaning reagent for reel tape probes coated with this type of solids.

Analytical results for the relevant species (Na, Al, Si, and U) are provided in Table 4-4 for the unmodified and modified Tank 38H supernate following contact with the reel tape solids. Calculated (based on the known dilution and modification and using assumed densities of 1.12 and 1.3 g/mL for water-diluted and caustic-adjusted supernate, respectively) concentrations are also provided in Table 4-4. The results indicate that contact with the as-received Tank 38H supernate with agitation at 50 ºC for two hours results in additional precipitation of Al as indicated by the fact that the aluminum concentration decreased by nearly 50% after contact with the reel tape probe solids. This indicates that the Tank 38H supernate is super-saturated in Al and that contact with the coated reel tape probe would result in further precipitation and coating of the probe. This is consistent with observations of additional probe coating in the tank farm. The April 2014 Tank 38H supernate was apparently unstable with regard to the precipitation of these phases. In contrast, dilution of the supernate with water or adjustment with caustic effectively eliminated Al precipitation.

Foam volume measurements were conducted for a total of seven evaporator system samples including the three April 2014 samples, three historical Tank 38H and 43H samples, and one blend of historical Tank 38H and 43H samples. The blended sample was used for method development. All remaining samples were evaluated using the standard method described in Section 3.2. If sufficient sample was available, 35 and 50 mL samples were evaluated.

Foam volume data (corrected for air sparge volume displacement) collected for the Tank 38H surface sample in the 1 inch ID column at ambient temperature is provided in Figure 4-3. The test sequence was as follows: 35 mL constant flow, 35 mL variable flow, 50 mL constant flow, and 50 mL variable flow. The Tank 38H supernate sample formed large foam volumes during air sparging. At moderate flow rates (100-125 mL air/min.) the foam volume was similar to the liquid volume. At the slowest flow rate (50 mL/min) a solid layer of foam did not form across the liquid surface (bubbles only observed on a portion of the surface). The foam formed and stabilized to a constant volume quickly. As a result, the constant and variable flow rate data were very similar and similar trends in the measured foam volumes were observed during the ascending and descending air flow rate portions of the test sequence. Similar results were also observed for the 35 and 50 mL samples. When air flow was stopped following the formation of the foam column at 125 mL/min collapse of the foam column was rapid and no foam remained after 15 seconds.

Foam volume data (corrected for volume displacement) collected for the Tank 43H surface sample in the 1 inch ID column at ambient temperature is provided in Figure 4-4. The same standard test sequence used for the Tank 38H sample was used for this sample. Significantly smaller foam volumes were formed with the Tank 43H surface sample than were observed with the Tank 38H sample. In addition, the foam volume stabilized more slowly and significantly greater foam volume formed with the 50 mL sample than was observed with the 35 mL sample. The upper foam surface was much more erratic than was observed for the Tank 38H sample. A second stagnant (as opposed to the dynamic primary foam) foam phase was observed to form above the primary foam column, presumably due to the presence of a localized impurity at the top of the foam column. It is believed that a stable foam volume was achieved for the 50 mL sample. When air flow was stopped following the formation of the foam column at 125 mL/min, the foam collapsed at a slower rate than was observed for the Tank 38H sample. Complete disappearance of all bubbles required 65 seconds.

Foam volume data (corrected for volume displacement) collected for the Tank 43H sub-surface sample in the 1 inch ID column at ambient temperature is provided in Figure 4-5. The standard test sequence described above was used for this sample except that higher flow rate data for the 50 mL sample was not collected due to operator error. Significantly smaller foam volumes were formed with the Tank 43H sub-surface sample than were observed with the Tank 43H surface sample. As observed for the Tank 43H surface sample, the foam volume stabilized slowly. In addition, significantly greater foam volume formed with the 50 mL sample than was observed with the 35 mL sample. The upper foam surface was erratic with occasional large bubbles being formed which rose up the glass column above the main foam band. A second stagnant (as opposed to the dynamic primary foam) foam phase was observed to form above the primary foam column, presumably due to the presence of a localized impurity at the top of the foam column. It is believed that a stable foam volume was achieved for the 50 mL sample. In this case, when air flow was stopped following the formation of the foam column at 125 mL/min, the foam collapsed quickly with completely disappearance of foam and bubbles within 15 seconds. The dramatic differences in the observed foam volumes for the Tank 43H surface and sub-surface samples was surprising since these samples were retrieved from the same tank at the same time and they were observed to have similar compositions. Perhaps the solids which were observed in the sub-surface sample destabilized the foam formed with this sample. Alternatively stratification within the tank with regard to a foam–producing organic species (with higher concentrations in the surface sample) could lead to different foam volumes for these samples.

Three additional historical 2H Evaporator System samples were evaluated in the foam test vessel using the standard test sequence described above. The foam volume data for all samples tested are summarized in Table 4-5. The largest foam volume was observed for the April 2014 Tank 38H surface sample. The second largest foam was observed for the 50 mL April 2014 Tank 43H surface sample. Interestingly, the lowest foam volume was observed for the April 2014 Tank 43H sub-surface sample, although no significant compositional difference was observed for the surface and sub-surface Tank 43H samples. The historical supernate samples generally produced less foam than was observed for the April 2014 samples and showed similar trends with regard to the foam characteristics (stable foams with more concentrated Tank 38H samples and more erratic and less stable foams with Tank 43H samples).

Foam tests were conducted at elevated temperature for the Tank 38H and 43H surface samples. The tests were conducted by heating the samples to 95 °C on a hot plate and then transferring the hot supernate to the foam test apparatus. Since the temperature was not controlled, the samples immediately began to cool. Foam volume data was collected at 5 minute intervals as the samples cooled at a constant air flow rate of 100 mL/min. Foam volume data for the Tank 38H and 43H samples are provided in Figures 4-6 and 4-7, respectively. Smaller foam volumes were observed for both samples than were observed at ambient temperature. The Tank 38H sample did not form any significant foam in the temperature range of 38-65 °C. The first foam was observed at 36 °C and the foam volume increased to the volume observed in previous tests as the sample cooled. The Tank 43H sample did form foam at the highest temperature tested, but the foam was smaller in volume relative to the foam volume observed at ambient temperature. In addition, the foam volume formed at ambient temperature with a separate sample was smaller than was observed with the variable temperature sample at slightly elevated temperatures (near 30 ºC). Results for this sample are complicated by the fact that the foam volume tends to increase with time as discussed in previous paragraphs. The lack of foam formation at elevated temperature with the Tank 38H sample indicates that foaming would not occur with this concentrated sample during normal evaporator operations.

The effectiveness of Xiameter AFE 1010 reagent at collapsing pre-formed foams was evaluated for 35 mL Tank 38H and 43H surface samples. Results for the two samples are provided in Figures 4-8 and 4-9, respectively. An 18 mL foam column was formed with the Tank 38H sample at an air flow rate of 125 mL/min before ~1 drop (25 mg) of antifoam reagent was added. The foam completely collapsed immediately upon addition of the antifoam to a volume of ~1 mL. The air flow rate was subsequently increased to 300 mL/min, resulting in the formation of 32 mL of foam. Addition of more antifoam reagent (400 mg cumulative total mass) resulted in immediate foam collapse to a volume near 2 mL. Increasing the air flow rate to 500 mL/min resulted in the formation of a small foam column (13 mL) which decreased in volume after the addition of more antifoam (1.24 g cumulative total mass). The air flow rate was then increased to 1 L/min and 26 mL of foam formed. Antifoam reagent was added (1.72 g cumulative total mass) to reduce the foam column to ~3 mL. Antifoam reagent was added to the Tank 43H sample following the elevated temperature tests at a flow rate of 100 mL/min. The addition of 1 mL of antifoam resulted in immediate and complete foam collapse. It was observed in this test that the first drop of antifoam which contacted the sample promoted foam collapse, so the additional antifoam is believed to have been unnecessary. The flow rate was subsequently increased to 1 L/min with minimal foam formation (~6 mL). For both supernate samples, the antifoam reagent was very effective at destroying pre-formed foams and minimizing the formation of new foam.

Figure 4-1. Solids Isolated from the Tank 38H Reel Tape Probe.

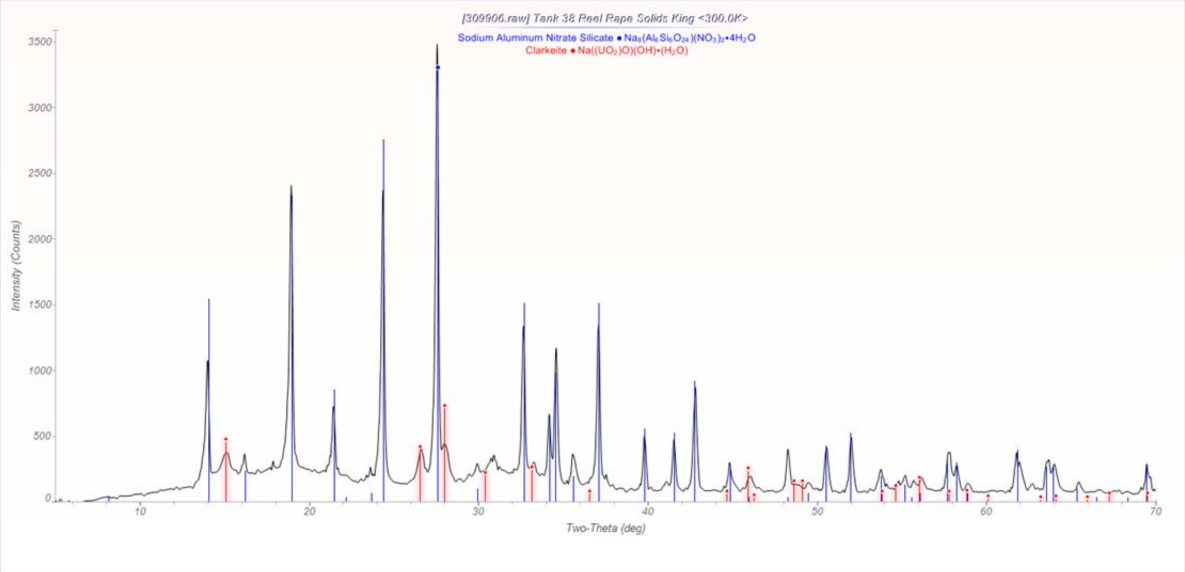

Figure 4-2. XRD Analysis Results for the Tank 38H Reel Tape Probe Solids.

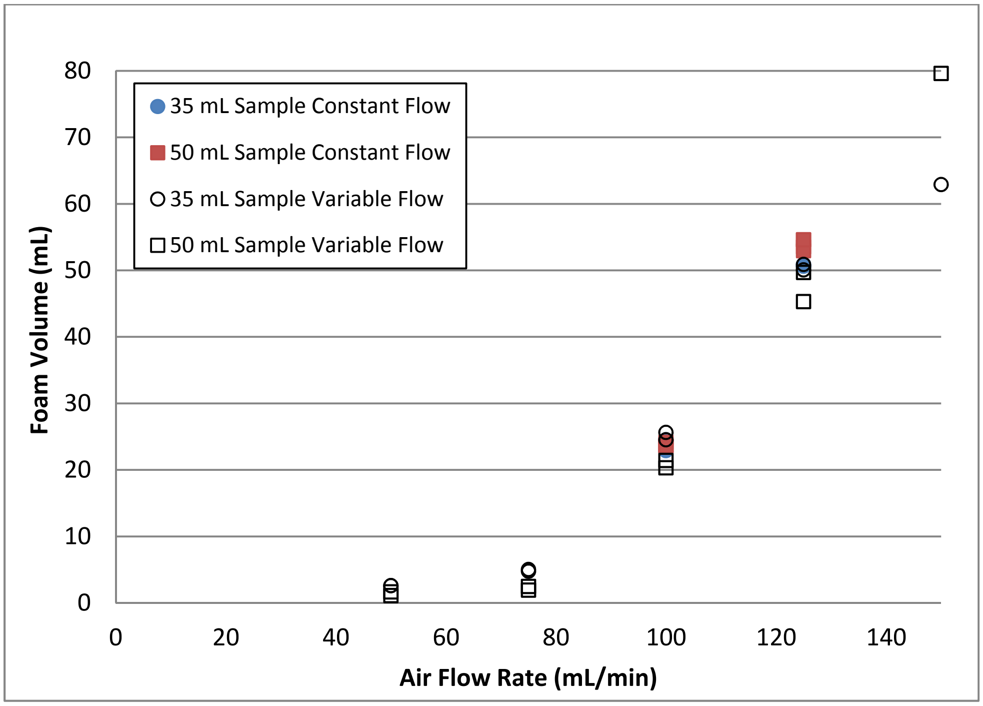

Figure 4-3. Foam Volume Data for the April 2014 Tank 38H Surface Sample (HTF-38-14-41; 1 in. ID Column, ambient).

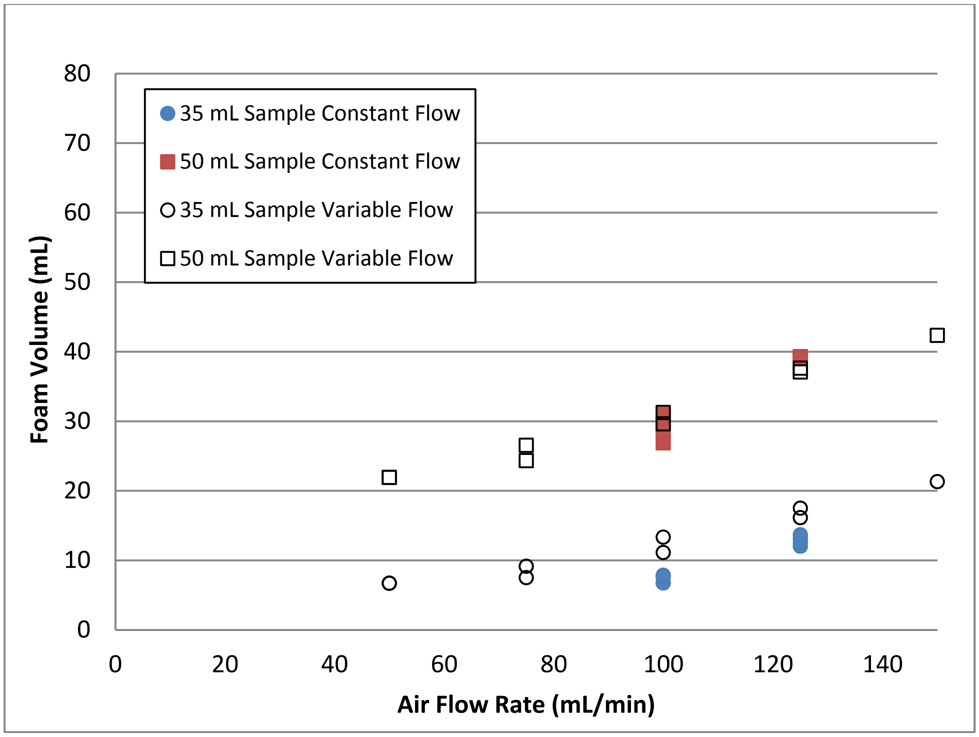

Figure 4-4. Foam Volume Data for the April 2014 Tank 43H Surface Sample (HTF-43-14-42; 1 in. ID Column, ambient).

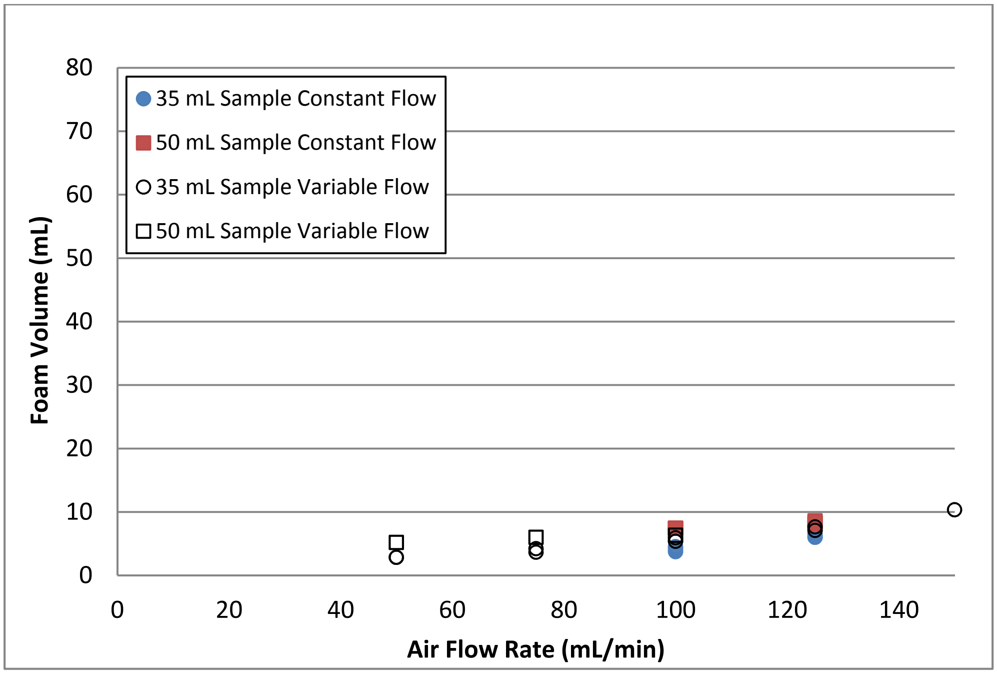

Figure 4-5. Foam Volume Data for the April 2014 Tank 43H Sub-surface Sample (HTF-43-14-43; 1 in. ID Column, ambient).

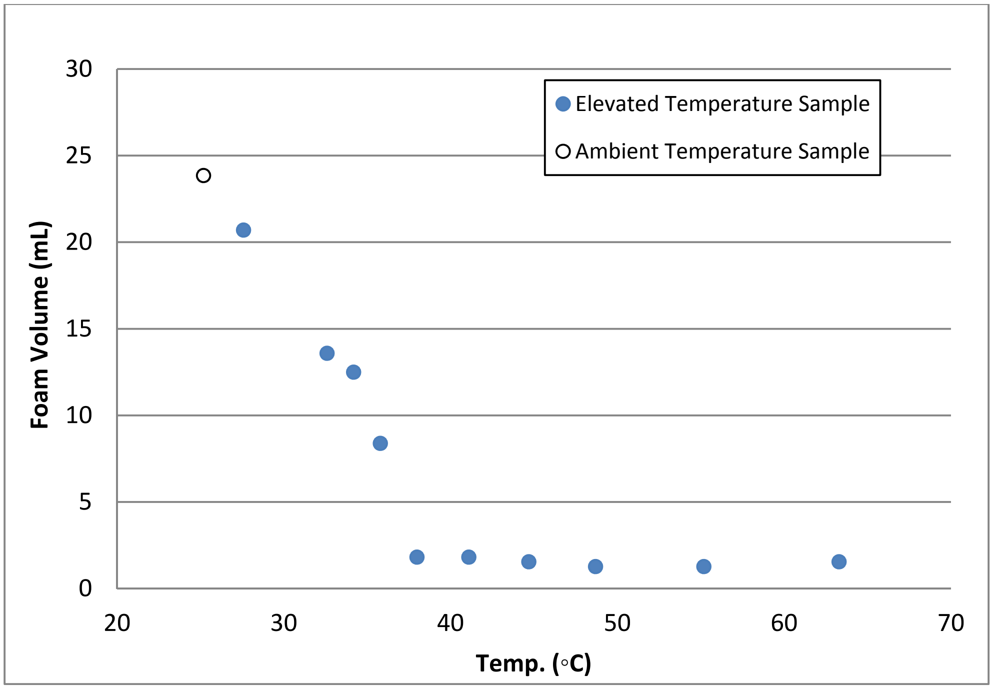

Figure 4-6. Elevated Temperature Foam Volume Data for the April 2014 Tank 38H Surface Sample (HTF-38-14-41; 1 in. ID Column, Note: Data collected at 5-minute intervals as the sample cooled going from the right to the left end of the x-axis.).

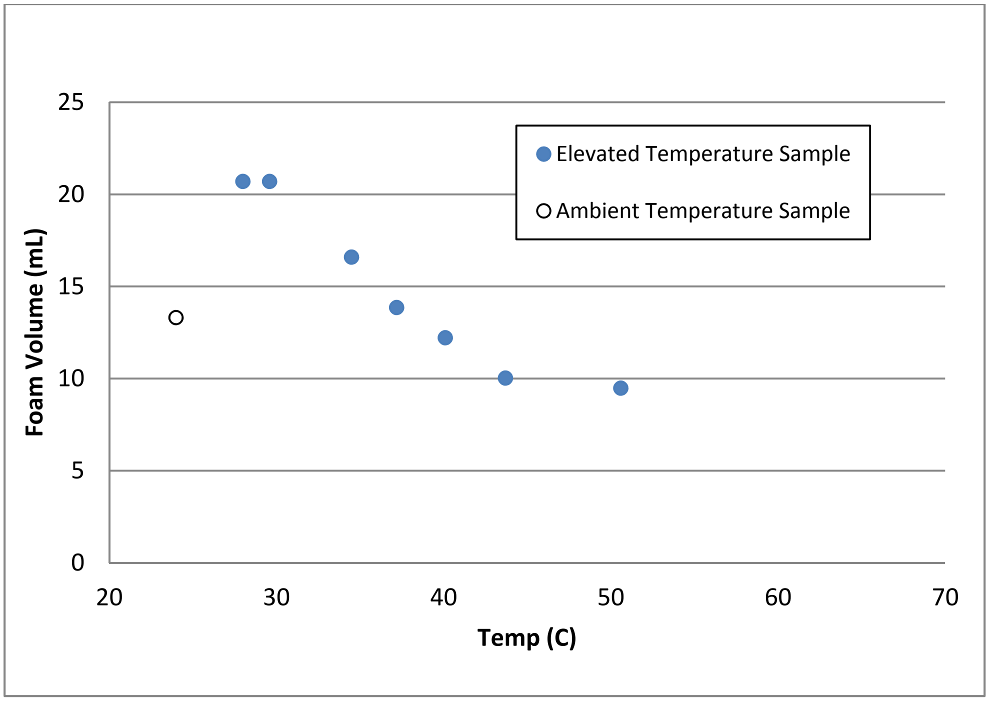

Figure 4-7. Elevated Temperature Foam Volume Data for the April 2014 Tank 43H Surface Sample (HTF-43-14-42; 1 in. ID Column. Note: Data collected at 5-minute intervals as the sample cooled going from the right to the left end of the x-axis.).

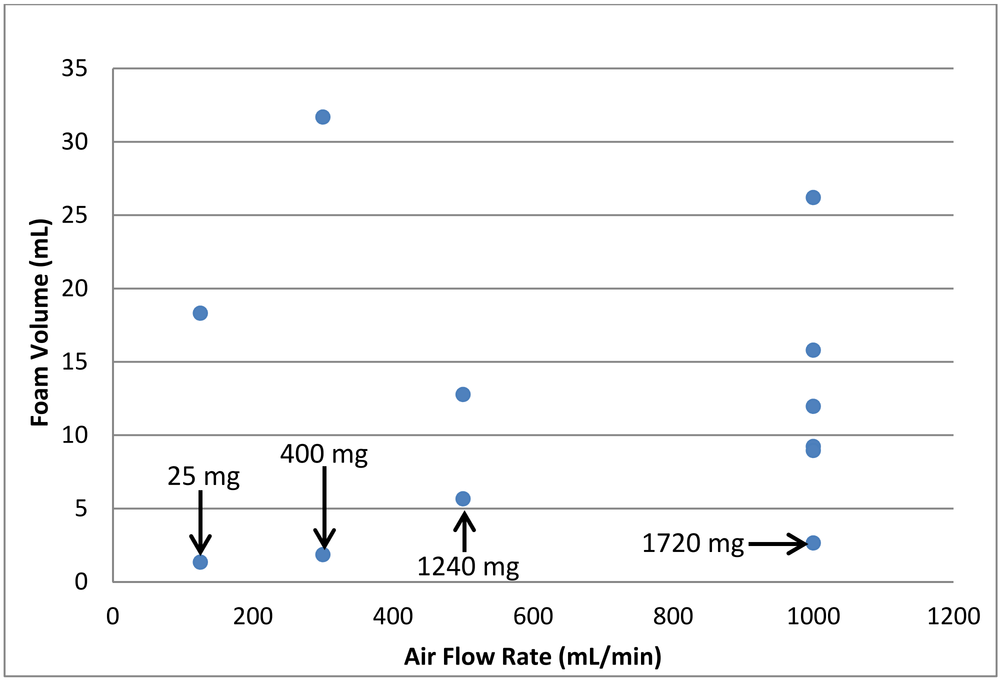

Figure 4-8. Foam Volume Data During Antifoam Reagent Addition (cumulative mass added at various times indicated) with the April Tank 38H Surface Sample (HTF-38-14-41; 1 in. ID Column, ambient; Note: The time of data collection and the total volume of antifoam additions increased from left to right. Higher foam volumes observed at a given flow rate correspond to readings prior to antifoam additions.).

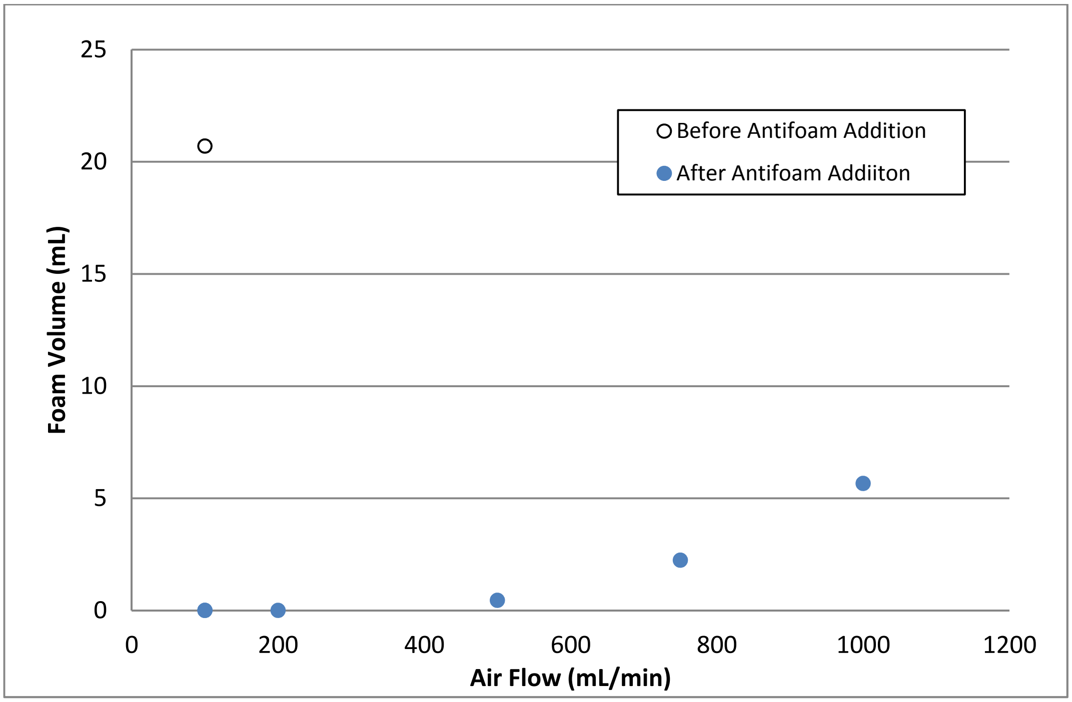

Figure 4-9. Foam Volume Data During Antifoam Reagent Addition for the April Tank 43H Surface Sample (HTF-43-14-42; 1 in. ID Column; Note: The time of data collection increased from left to right.).

Table 4-1. Tank 38H and 43H Filtered Supernate Analysis Results.

Component/Method	**HTF-38-14-41 (Tank 38H surface)**	**HTF-43-14-42 (Tank 43H surface)**	**HTF-43-14-43 (Tank 43H sub-surface)**
	Molarity		
Al	0.032	0.01	0.02
B	0.02	0.01	0.01
Ca	0.0001	0.00005	0.00005
Cr	0.0009	0.0004	0.0004
Fe	0.0001	0.0001	0.0001
K	0.01	0.004	0.01
Li	0.01	0.01	0.00
Na	**7.14**	**3.00**	**3.06**
P	0.004	0.002	0.002
Si	0.01	0.01	0.01
U	0.0005	0.0002	0.0002
Zn	0.0001	0.00004	0.00005
Formate	0.040	0.017	0.017
Chloride	0.004	<0.003	<0.003
Nitrite	**1.871**	**0.814**	**0.817**
Nitrate	**1.035**	**0.446**	**0.452**
Phosphate	0.003	<0.0009	0.001
Sulfate	0.022	0.009	0.009
Oxalate	0.003	<0.001	0.001
Free OH	**2.88**	**1.17**	**1.19**
Other Base	<0.19	<0.17	<0.22
	mg/L		
Total Carbon	5780	2486	2508
Total Inorganic Carbon	5078	2128	2168
Total Organic Carbon	699	335	337
SVOA	<1	<1	<1
	g/mL		
Density	1.274	1.122	1.128

Table 4-2. Tank 38H Reel Tape Probe Solids Acid Digestion and Hot Wash Solutions Analysis Results.

Component	**Acid Digestion**	**Hot Water Wash**
	Wt. %	
Na	**12.4**	**3.18**
Al	**10.8**	**1.44**
Si	**0.19**	**1.43**
Fe	**1.81**	<0.01
P	0.79	<0.19
Ca	0.44	<0.17
Mn	0.31	<0.002
Mg	0.19	<0.07
Cr	0.04	<0.004
Ba	0.01	<0.002
Cd	0.01	<0.003
Sr	0.01	<0.001
Th	0.03	<0.03
Zn	0.01	<0.005
	mg/L	
Formate	---	<5
Fluoride	---	<5
Chloride	---	6
Nitrite	---	8
Nitrate	---	40
Phosphate	---	<5
Sulfate	---	<5
Oxalate	---	<5
Total Carbon	---	62.9
Total Inorganic Carbon	---	13.7
Total Organic Carbon	---	49.2
SVOA	---	<1

Table 4-3. Tank 38H Reel Tape Probe Solids Solubility Data for Water and Acid Contact Solutions.

	Contact Liquid (Temp.)		
Component	**Water (ambient)**	**Water (50 °C)**	**0.5 M HNO_3 (50 °C)**
	mg/L		
Ag	<0.26	<0.22	<0.24
Al	**3.76**	**7.40**	**562.50**
B	<1.16	<1.00	<1.05
Ba	<0.15	<0.13	0.33
Be	<0.09	<0.07	<0.08
Ca	0.46	<0.32	**23.80**
Cd	<0.44	<0.37	0.43
Ce	<1.26	<1.08	<1.14
Co	<0.20	<0.17	<0.18
Cr	<0.36	<0.31	0.47
Cu	<0.44	<0.37	<0.39
Fe	**1.18**	**<0.42**	**18.25**
Gd	<0.42	<0.36	<0.38
K	<8.59	<7.36	<7.75
La	<0.31	<0.27	<0.28
Li	<0.21	<0.18	0.48
Mg	<0.09	<0.07	**8.93**
Mn	<0.20	<0.17	**11.84**
Mo	<1.81	<1.55	<1.63
Na	**113.81**	**115.15**	**696.24**
Ni	<2.61	<2.24	<2.35
P	<7.72	<6.62	<6.96
Pb	<2.14	<1.83	<1.93
S	<327.04	<280.39	<295.02
Sb	<2.76	<2.37	<2.49
Si	**2.73**	**6.13**	**472.03**
Sn	<2.53	<2.17	<2.29
Sr	<0.09	<0.07	0.25
Th	<2.03	<1.74	<1.83
Ti	<0.15	<0.13	<0.14
U	<21.24	<18.21	**96.37**
V	<0.31	<0.27	<0.28
Zn	<0.17	<0.15	0.48
Zr	<0.19	<0.16	<0.17

Table 4-4. Tank 38H Reel Tape Probe Solids Solubility Data for Tank 38H Supernate Contact Solutions.

	Tank 38H		Diluted Tank 38H		Caustic-Adjusted Tank 38H	
Component	After Contact	Before Contact	After Contact (calc.)	Before Contact	After Contact	Before Contact (calc.)
	mg/L					
Na	1.50E5	1.64E5	7.83E4	8.20E4	1.81E5	1.91E5
Al	**449**	**863**	412	431	735	776
Si	**345**	**274**	138	137	236	246
U	89	108	45	54	78	97

Table 4-5. Foam Volume Data Summary for all 2H Evaporator System Samples Tested (1 in. ID column, ambient, 125 mL/min, unless otherwise indicated).

Sample	Tank	Liquid Volume (mL)	Foam Vol (mL)
HTF-43-14-42 (April 2014 surface sample)	43	35	12.8
HTF-43-14-43 (April 2014 sub-surface sample)	43	35	6.2
HTF-38-14-41 (April 2014 surface sample)	38	35	50.7
HTF-43-14-8	43	35	5.9*
HTF-43-14-9	43	35	19.3
HTF-38-14-6	38	35	23.8
HTF-43-14-42 (April 2014 surface sample)	43	50	39.3
HTF-43-14-43 (April 2014 sub-surface sample)	43	50	8.3
HTF-38-14-41 (April 2014 surface sample)	38	50	53.9
HTF-43-14-8	43	50	8.5

* measured at 100 mL/min

5.0 Conclusions

All of the 2H evaporator system samples (Tank 38H and 43H samples) evaluated produced foam during air sparging. The largest foam volumes were observed for two of the three most recently received samples (April 2014 Tank 38H and 43H surface samples). An apparatus and method were developed to evaluate and compare foam formation in various samples, although hysteresis effects can complicate these comparisons. The Tank 38H surface sample (which formed the largest ambient temperature foam volume) would not be expected to foam during evaporator operations since no foam forms with this sample at temperatures greater than 38 °C. In contrast, some foam was observed to form with the Tank 43H surface sample at temperatures as high as 65 °C. Xiameter AFE-1010 antifoam was effective at collapsing preformed foams and minimizing foam formation in both the Tank 38H and the 43H surface samples at addition rates less than 10 g of as-received antifoam reagent (diluted before addition) per gallon of supernate. It is anticipated that significantly lower antifoam addition rates would effectively collapse pre-formed foams and prevent foam formation under the evaporator operating conditions.

6.0 Recommendations

Larger sample sizes are preferred for foam testing. Additional testing is recommended to confirm that sample size effects on the foam volume measurements are sufficiently minimized for a sample size of 50 mL. Additional studies might also be conducted to better understand the temperature dependence of the foam volume.

7.0 References

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Appendix A. Foam Data for Historical Evaporator System Samples

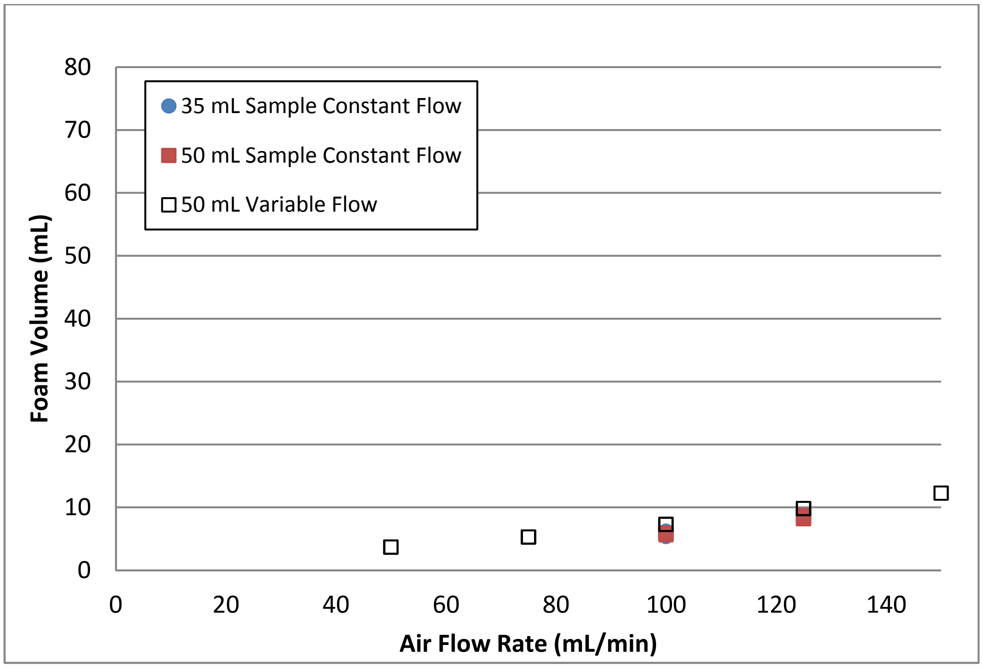

Figure A-1. Foam Volume Data for Historical Tank 43H Sample HTF-43-14-8 (1 in. ID Column, ambient).

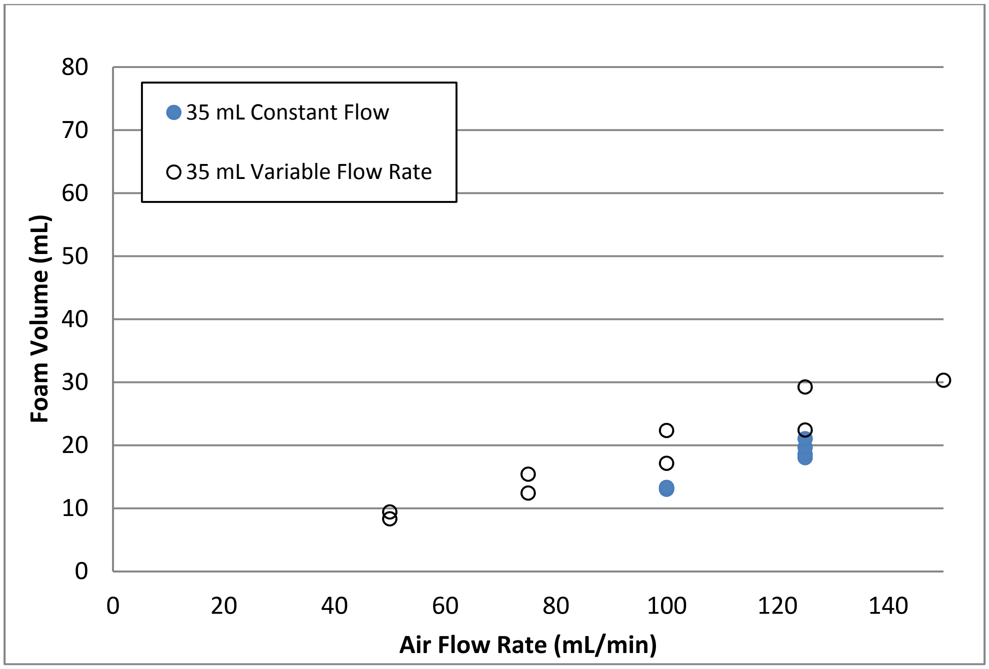

Figure A-2. Foam Volume Data for Historical Tank 43H Sample HTF-43-14-9 (1 in. ID Column, ambient).

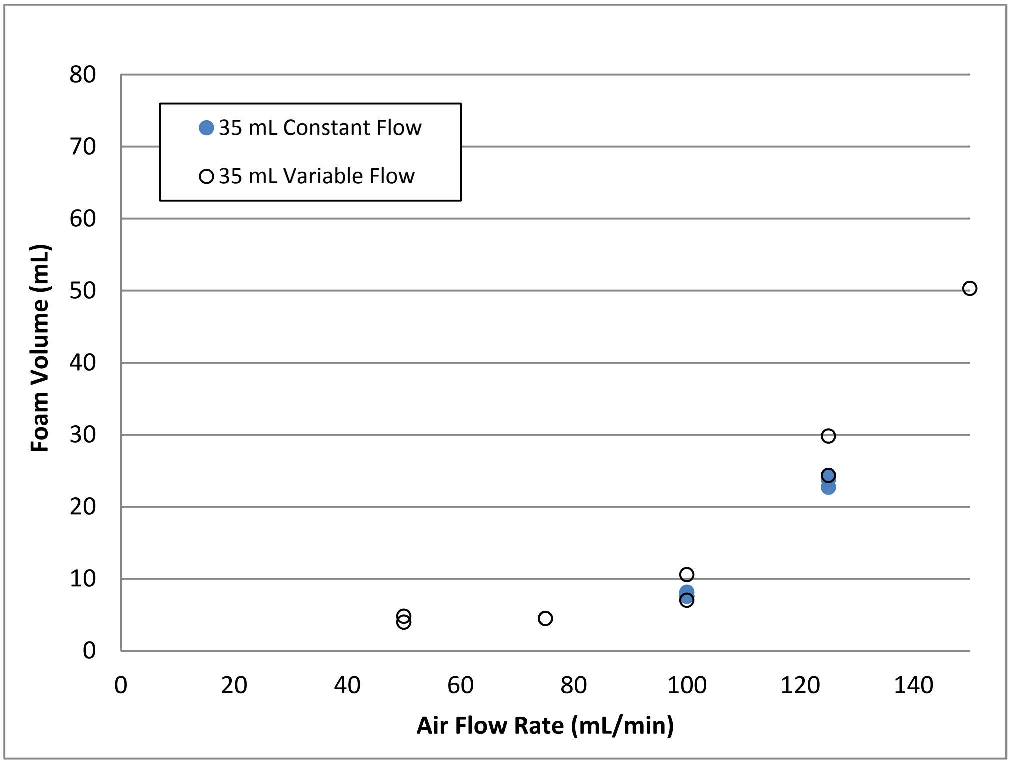

Figure A-3. Foam Volume Data for Historical Tank 38H Sample HTF-38-14-6 (1 in. ID Column, ambient).

Distribution:

S. L. Marra, 773-A
W. D. King, , 773-42A
D. P. Lambert, 999-W
C. J. Martino, 773-42A
M. L. Restivo, 773-42A
D. J. Adamson, 999-W
T. B. Brown, 773-A
D. H. McGuire, 999-W
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
Records Administration (EDWS)
P. R. Jackson, DOE-SR, 703-46A
J. A. Crenshaw, 703-46A
D. J. Martin, 241-152H
J. R Vitali, 766-H
A. W. Wiggins, 705-1C
G. P. Flach, 773-42A
D. I. Kaplan, 773-43A