SRNL-STI-2011-00515
Revision 0

Keywords: *DWPF, SRAT, antifoam*

Retention: *Permanent*

Improved Antifoam Agent Study
End of Year Report, EM Project 3.2.3

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September 30, 2011

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Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

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Prepared for
U.S. Department of Energy

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EXECUTIVE SUMMARY

Antifoam 747 is added to minimize foam produced by process gases and water vapor during chemical processing of sludge in the Defense Waste Processing Facility (DWPF). This allows DWPF to maximize acid addition and evaporation rates to minimize the cycle time in the Chemical Processing Cell (CPC). Improvements in DWPF melt rate due to the addition of bubblers in the melter have resulted in the need for further reductions in cycle time in the CPC. This can only be accomplished with an effective antifoam agent.

DWPF production was suspended on March 22, 2011 as the result of a Flammable Gas New Information/ (NI) Potential Inadequacy in the Safety Analysis (PISA). The issue was that the DWPF melter offgas flammability strategy did not take into account the H and C in the antifoam, potentially flammable components, in the melter feed. It was also determined the DWPF was using much more antifoam than anticipated due to a combination of longer processing in the CPC due to high Hg, longer processing due to Actinide Removal Process (ARP)/ Modular Caustic Side Solvent Extraction Unit (MCU) additions, and adding more antifoam than recommended. The resolution to the PISA involved and assessment of the impact of the antifoam on melter flammability and the implementation of a strategy to control additions within acceptable levels. This led to the need to minimize the use of Antifoam 747 in processing beginning in May 2011.

DWPF has had limited success in using Antifoam 747 in caustic processing. Since starting up the ARP facility, the ARP product (similar chemically to caustic sludge) is added to the Sludge Receipt and Adjustment Tank (SRAT) at boiling and evaporated to maintain a constant SRAT volume. Although there is very little offgas generated during caustic boiling, there is a large volume of water vapor produced which can lead to foaming. High additions and more frequent use of antifoam are used to mitigate the foaming during caustic boiling.

The result of these three issues above is that DWPF had three antifoam needs in FY2011:

1. Determine the cause of the poor Antifoam 747 performance during caustic boiling
2. Determine the decomposition products of Antifoam 747 during CPC processing
3. Improve the effectiveness of Antifoam 747, in order to minimize the amount used

Testing was completed by Illinois Institute of Technology (IIT) and Savannah River National Laboratory (SRNL) researchers to address these questions. The testing results reported were funded by both DWPF and DOE/EM 31. Both sets of results are reported in this document for completeness. The results of this research are summarized below

1. The cause for the poor Antifoam 747 performance during caustic boiling was the high hydrolysis rate, cleaving the antifoam molecule in two, leading to poor antifoam performance. In testing with pH solutions from 1 to 13, the antifoam degraded quickly at a pH <4 and pH >10. As the antifoam decomposed it lost its spreading ability (wetting agent performance), which is crucial to its antifoaming performance. During testing of a caustic sludge simulants, there was more foam in tests with added Antifoam 747 than in tests without added antifoam.
2. Analyses were completed to determine the composition of the two antifoam components and Antifoam 747. In addition, the decomposition products of Antifoam 747 were determined during CPC processing of sludge simulants. The main decomposition products were identified primarily as Long Chain Siloxanes, boiling point >400° C. Total

antifoam recovery was 33% by mass. In a subsequent study, various compounds potentially related to antifoam were found using semi-volatile organic analysis and volatile organic analysis on the hexane extractions and hexane rinses. These included siloxanes, trimethyl silanol, methoxy trimethyl silane, hexamethyl disiloxane, aliphatic hydrocarbons, dioctyl phthalate, and emulsifiers. Cumulatively, these species amounted to less than 3% of the antifoam mass. The majority of the antifoam was identified using carbon analysis of the SRAT product (40-80% by mass) and silicon analysis (23-83% by mass) of the condensate. Both studies recommended a better solvent for antifoam and more specific tests for antifoam degradation products than the Si and C analyses used.

3. The DWPF Antifoam 747 Purchase Specification was revised in Month, 2011 with a goal of increasing the quality of Antifoam 747. The purchase specification was changed to specify the manufacturer and product for both components that are blended by Siovation to produce Antifoam 747 for DWPF. Testing of Antifoam produced using both the old and new antifoam specifications perform very similarly in testing. Since the change in purchase specification has not improved antifoam performance, an improved antifoam agent is required.

Several other findings of testing are reported below, as requested by DWPF:

4. The storage of a 1:20 Mixture of Antifoam 747 and water, over a period of five weeks, had a negligible impact on spreading. It appears to be stable over a period of up to five weeks.
5. Blending of the Antifoam 747 purchased by the old specification and new antifoam produced with the new Antifoam 747 specification leads to poorer spreading performance than either antifoam by itself.

No work was completed to elucidate the role of the pH on Y -17580. More research needs to be conducted to reveal the role of alkali pHs on Y-17580's (also a component of Antifoam 747) decomposition on sludge foaming/ antifoaming.

Recommendations

The testing completed by IIT and SRNL researchers identified a number of issues, including:

1. The development of an improved antifoam agent is needed to maximize the attainment in the DWPF CPC without impact the melter offgas flammability or downstream processing facilities. An improved antifoam agent would decrease the amount and frequency of antifoam used in DWPF while minimizing CPC batch processing time. The antifoam needs to be more chemically resistant to hydrolysis, especially during caustic boiling phase of SRAT processing.
2. Improved understanding of the antifoam degradation products that result from the hydrolysis of the antifoam molecule. Current melter flammability strategy assumes that 80% of the antifoam is present in the melter feed to participate in redox and decomposition reactions. Testing by Newell and Koopman identified much lower amounts of antifoam present in their SRAT products. A better understanding of the degradation products is possible due to the improved analytical techniques used in this study and utilization of a better solvent for closing the antifoam mass balance during testing.
3. Continue working with IIT and Momentive to improve the stability of the antifoam in the presence of sludge with a pH from 2 to 14. Dr. Darsh Wasan and Dr. Alex Nikolov have a fundamental understanding of both the needs of DWPF in maximizing throughput and the chemistry of the antifoam and SRS sludge that will allow them to improve antifoam

chemical stability. Momentive is needed to both demonstrate the effectiveness of new antifoam components and to commercially produce the product for DWPF.

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AD	Analytical Development
ARP	Actinide Removal Process
CPC	Chemical Process Cell
DOE	Department of Energy
EM	Environmental Management Division of DOE
FAVC	Formic Acid Vent Condenser
FTIR	Fourier Transformed InfraRed Spectroscopy
GC-MS	Gas Chromatography-Mass Spectrometry
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
MCU	Modular Caustic Side Solvent Extraction Unit
MWWT	Mercury Water Wash Tank
NI	New Information
NMR	Nuclear Magnetic Resonance Spectroscopy
PISA	Potential Inadequacy in the Safety Analysis
PSAL	Process Science Analytical Laboratory
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SVOA	Semi-Volatile Organic Analysis
TOC	Total Organic Carbon Analysis
TT&QAP	Task Technical and Quality Assurance Plan
VOA	Volatile Organic Analysis

1.0 Introduction

Antifoam 747 is used during CPC processing to minimize foam. Antifoam 747 was developed for DWPF by Dr. Alex Nikolov and Dr. Darsh Wasan of the Illinois Institute of Technology (IIT).[1] However, Antifoam 747 hasn't been as effective during sludge batches SB5 and SB6, especially during the caustic boiling phase when the ARP product is added to the sludge in the first stage of processing in the SRAT. At the time the antifoam was developed, there was no plan to concentrate sludge while caustic. A variety of testing and analysis was completed by both SRNL and IIT to try to understand why Antifoam 747 isn't as effective as expected since it is limiting throughput in DWPF.

Foaming occurs primarily during boiling and acid addition operations. During these operations, there is a high flux of gases (steam during boiling, CO_2, NO_x during acid addition) that can form foam bubbles. To control foam during processing, the steam flow or acid addition rate can be limited or an antifoam agent added to minimize foam. The foam formed in DWPF process is very unstable, it will disperse if the steam flow is shut off or acid addition is stopped. Since foaming is a surface area phenomenon, it is hard to test at a small scale. For example a 10 foot tall, 1" in diameter column might seem feasible but the heat losses and wall effects make this testing unfeasible. Lab-scale testing is generally done at a much lower gas flux than the DWPF gas flux. Throughout this report, any testing with a gas flux will report the flux rate for comparison.

In order to maximize the effectiveness of Antifoam 747, the Savannah River Remediation (SRR) Anti foam 747 purchase specification[2] was modified to specify the manufacturer and product of both components and to ship both components to SRNL for testing along with the blended Antifoam 747. The majority of the testing reported here used the "new" Antifoam 747. However it should be noted that the new Antifoam 747 has not been used in DWPF as of the date of this report, although it has been used in a number of SB7 and SB7b tests with simulant and actual waste.

Antifoam 747 is composed of two components. Component 1, Silwet L77, is manufactured by Momentive. Silwet L77 is readily available commercially. Component 2, Y-17580, is also manufactured by Momentive. Y-17580 is produced exclusively for DWPF, and will be produced annually to minimize production costs. These two ingredients are combined together by Siovation and shipped to DWPF as needed.

SRR plans to double the sludge throughput. This requires the tank farm to produce sludge batches more quickly and the DWPF CPC to increase the production rate of melter feed. The addition of bubblers has effectively doubled the melting rate in the DWPF melter. DWPF currently limits the acid addition rate and the boilup rate during SRAT and SME processing. Both of these rates will need to be maximized to reach the melter feed production goals necessary to keep up with current melting rate.

1.1 Work Authorization

This work was requested by Task WP-3.2.3 as identified in the work authorization/task change request (TCR) for Waste Processing Area 3 (WP-3). This work was performed under the guidance of a Task Technical and Quality Assurance Plan (TT&QAP).[3]

1.2 Historical Foaming Summary in DWPF

Foaming was a noted technical issue in the DWPF CPC during development of the initial flowsheet. Dow Corning 544 was recommended as the DWPF antifoam in 1989.[4] There were several foamovers in DWPF pilot-scale testing in the Integrated DWPF Melter System (IDMS), most notably in the last four SRAT cycles using a Purex sludge simulant. There was also a foamover in DWPF during cold chemical runs in the first run with mercury added to the sludge. In addition, three additional foamovers[5] occurred in DWPF in early processing with Dow Corning 544 (DWPF Batches 50, 60, and 72).

Antifoam 747 was developed to replace Dow Corning 544. In testing by IIT and SRTC, Antifoam 747 was a much more effective antifoam agent, lasting about 8 times as long as Dow Corning 544. DWPF switched to Antifoam 747 in November 2011. No foamovers have occurred in DWPF since the implementation of Antifoam 747. However, the amount of antifoam needed to control foaming has increased dramatically since Antifoam 747 was first implemented. Of note there have been three foamovers in the last six shielded cells demonstrations.[6,7,8] The initial Antifoam 747 strategy recommended 100 ppm before SRAT cycle, 100 ppm before SRAT boiling, 100 ppm each 8 hours at boiling, 100 ppm before SME cycle, and 100 ppm each 8 hours for a total of about 1,000 ppm each batch. DWPF has used as much as 10,000 ppm each batch in recent processing (longer processing times and higher antifoam addition concentrations).

Antifoam 747 is approximately 50% C and 10% H by mass. If the C and H in Antifoam 747 are fed to the melter, there is the potential for the antifoam contributing to a flammable melter offgas. DWPF issued a PISA based upon "identification of an additional constituent (Antifoam 747) in the Melter feed (previously considered negligible) which represents a significant contribution to Melter Off-gas flammability". As a result of this finding, a study was completed to determine the potential for a flammable melter offgas. As the result of the ensuing study, DWPF has a new melter flammability strategy that includes the C and H contribution from Antifoam 747.

The result is that DWPF needs a more effective antifoam agent to maximize throughput and needs to use less antifoam to ensure that DWPF won't have a flammable melter offgas. It should be noted that the analysis subsequent to the PISA assumed that all the C and H in the antifoam was present in the melter feed. However, the Antifoam 747 has a fairly short processing life so is obviously decomposing. As a result, information is needed to understand the deactivation and decomposition of the antifoam and to determine how much antifoam/antifoam degradation product C and H is actually fed to the melter.

1.3 FY 11 Improved Antifoam Testing

The focus in FY11 was on (1) determination of the spreading rate of component 1, component 2 and Antifoam 747, (2) determination of the foam potential during boiling of various sludge simulants, and (3) determine the composition of Antifoam 747 and determine its primary decomposition products. Testing was completed by both IIT and SRNL to maximize the amount of testing completed.

1.3.1 *IIT Testing*

Nikolov and Wasan focused on the performance and deactivation of Silwet L77 (component 1), since this ingredient is a superspreader. In addition, IIT performed tests at boiling of a SB10B simulant (prepared by SRNL) to determine the foaminess both with and without Antifoam 747. IIT also collaborated with Momentive to perform Nuclear Magnetic Resonance (NMR) Spectroscopy of Antifoam 747 to determine its composition and the composition of the degradation products. IIT issued a monthly report summarizing their initial progress.[9]

1.3.2 *SRNL Testing*

Weinheimer and Lambert focused on the performance of component 1, component 2 and Antifoam 747 as received and at various pHs from 1-13. In addition, testing was completed using a new Teclis Foamscan instrument designed for foam testing to determine the foaminess of various sludge simulants. Other testing completed by SRNL but not funded by this task is also reported including the analysis of component 1, component 2 and Antifoam 747 as requested for the acceptance of the New Antifoam 747.

2.0 Experimental Procedure

Testing was completed by both researchers at IIT and SRNL during FY11. Siovation, the company that blends the two antifoam components, provided component 1, component 2 and Antifoam 747 to SRNL for acceptance testing. SRNL and IIT used the Siovation provided components for all testing. The testing completed is described below.

2.1 IIT Testing

IIT completed spreading testing of components 1, Silwet L-77 (Siovation Lot#11DSVX019) by adding it to DI water or a pH adjusted solution in a sample bottle. The solution was shaken (which had the tendency to produce foam) to mix. A 0.04 mL sample was removed from the sample bottle with a pipette and dropped onto a polystyrene petri dish. After 30 seconds, the spreading diameter was measured.

IIT completed boiling tests to determine the foaminess of the SB10B sludge simulant with and without Antifoam 747 (Siovation Lot#110684-0413). Testing was completed using a stirred beaker on a hot plate. Foaminess was measured as the slurry was concentrated to determine the peak foaminess of the slurry. The measured boiling flux during this testing was approximately 0.11 g/min/cm^2 SRNL Testing.

2.2 SRNL Testing

SRNL spreading testing for components 1 and 2 along with Antifoam 747 was completed by adding the component or antifoam to DI water or a pH adjusted solution in a 30 mL poly sample bottle. The solution was shaken (which had the tendency to produce foam). A 0.02 mL sample was removed from the sample bottle with a pipette and dropped onto a polystyrene petri dish. After 30 seconds, the spreading diameter was measured at two places (90° apart) and the average reported.

SRNL completed room temperature testing to determine the foaminess of various sludge simulants using the Teclis Foamscan instrument. 60 mL of slurry was added to a 3.55 cm diameter foam column. 400 sccm of nitrogen was bubbled through a fritted disk to form small bubbles (equivalent to a flux of 40.4 g/m/cm^2. After three minutes, the purge was stopped to determine the stability of the foam. Approximately 5 g of DI water was added to the column to rinse the sludge off the column wall, allowing the Foamscan camera to see the foam level. The foam volume and a number of additional parameters were calculated by the Foamscan software.

In addition, SRNL analyzed the antifoam components, Antifoam 747, and degradation products for compositional characterization. Analyses completed included wt% solids, density, surface tension, viscosity, NMR spectroscopy, carbon analysis, semivolatile organic analysis (SVOA), and Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES).

3.0 Results and Discussion

Testing was completed by both researchers at IIT and SRNL during FY11. The results and a discussion of the results are included in this section. Only the results that were documented by September 30, 2011 are included in this revision of the report.

3.1 IIT Results

IIT's FY11 Task was to determine the performance and deactivation (degradation) rates of the 747 antifoam's components (Silwet L77 and Y –IT580, delivered by Siovation) for caustic sludge SB10B vs. the boiling time (e.g., over 8-12 hours with an evaporation flux of 0.11g/min.cm2). Wasan/Nikolov tested the performance and deactivation of Antifoam 747, blended by Siovation for DWPF. Antifoam 747 is based on two Components: Momentive Silwet L77 and Momentive Y–IT580. Wasan/Nikolov also examined the deactivation (degradation) rate of Silwet L77 (from Siovation) in an aqueous solution with a pH of 11, and the foaminess of SB10B (provided by SRNL) during the boiling time. The foaminess that resulted from the degradation of the ingredients of Antifoam 747 was tested using SB10B.

3.1.1 *Deactivation Rate of Silwet L77*

It has been shown that in an aqueous solution, Silwet L77 had a maximum in spreading area at a specific concentration**[10]**. The maximum in the spreading area vs. concentration was a manifestation of the fact that super-spreading is driven by the Marangoni flow (a high surface tension at the spreading wedge and a low surface tension at the droplet apex). The data plotted in Figure 3-1 depict the final value of the spreading diameter of a 40 μl drop placed on the surface of a polystyrene petri dish vs. the concentration of a freshly prepared aqueous solution of Silwet L77 at a pH of 11. The final spreading diameter vs. Silwet L77 concentration had a maximum of 9.0 cm at 0.08 wt% (or 800 ppm).

The dynamics of Silwet L77 spreading on the polystyrene petri dish were monitored and videoed. It was observed that, as a result of the Silwet L77 hydrolysis, a small oil droplet (likely polymethyl disiloxane---requires verification) was trapped inside the spreading film and led to the local rupture of the spreading film by busting and causing dendrites to form. The oil droplets due to Silwet L77 hydrolysis should also affect the boiling process by causing local overheating, leading to eruptions.

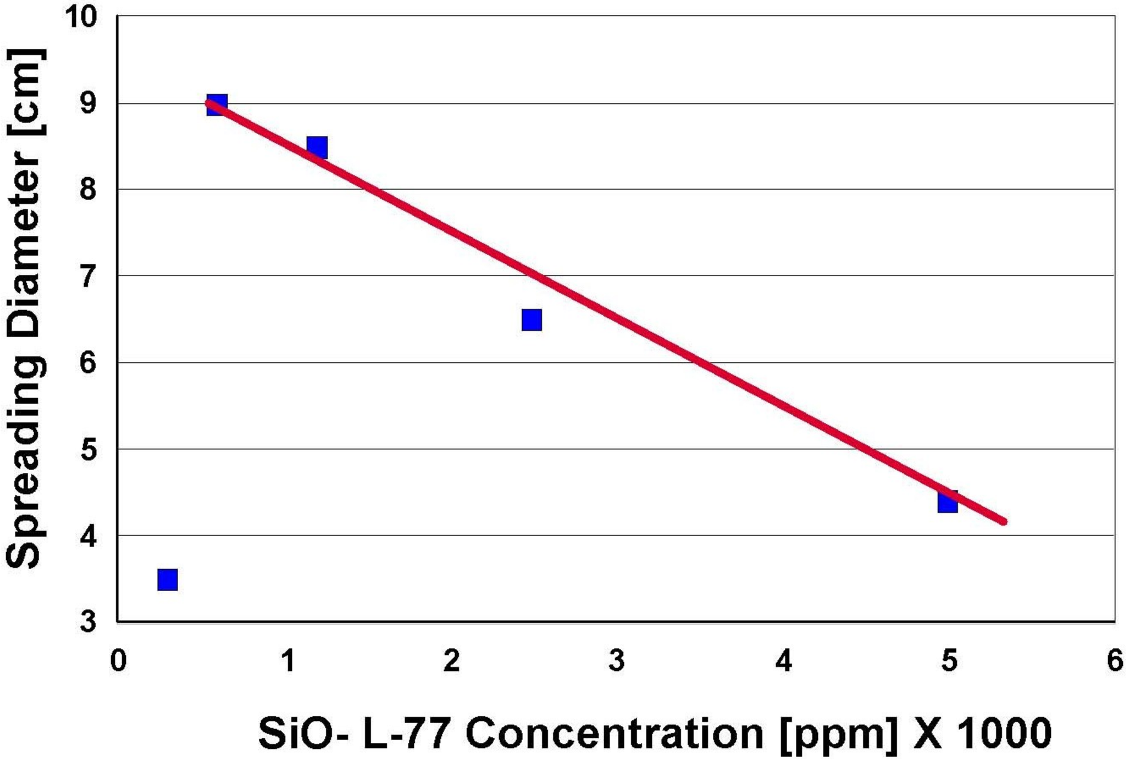

Figure 3-1: Equilibrium Spreading Diameter of 0.04 mL drop of Silwet L77 at pH 11

The data presented in Figure 3-1 were then used to evaluate the hydrolysis (degradation) rate of Silwet L77 at a pH of 11 and at a concentration of 5000 ppm (0.5 wt %) in an aqueous solution. In order to evaluate the effect of pH on the hydrolysis of Silwet L77, a 500 ml solution of at a concentration of 5000 ppm and a pH of 11 was prepared in a beaker and stirred at room temperature. A 40 µl volume of the sample was taken from the beaker and placed on the surface of a polystyrene petri dish; the final spreading diameter was then measured.

The data for the radius of spreading vs. time are presented in Figure 3-2. It was observed that the final spreading radius vs. time had a maximum at a time of 100-120 minutes and the value of spreading diameter was 9.5 cm. The cause of the maximum was assumed to be related to the hydrolysis of Silwet L77. With time, Silwet L77 hydrolyzed and its initial 5000 ppm concentration in the aqueous solution decreased. It was assumed that the products of hydrolysis were not surface active materials and would not affect the spreading. If so, as the initial 0.5 wt% concentration of Silwet L77 decreased with time, the diameter of the spreading would increase and follow the trend of the spreading curve presented in Figure 3-1.

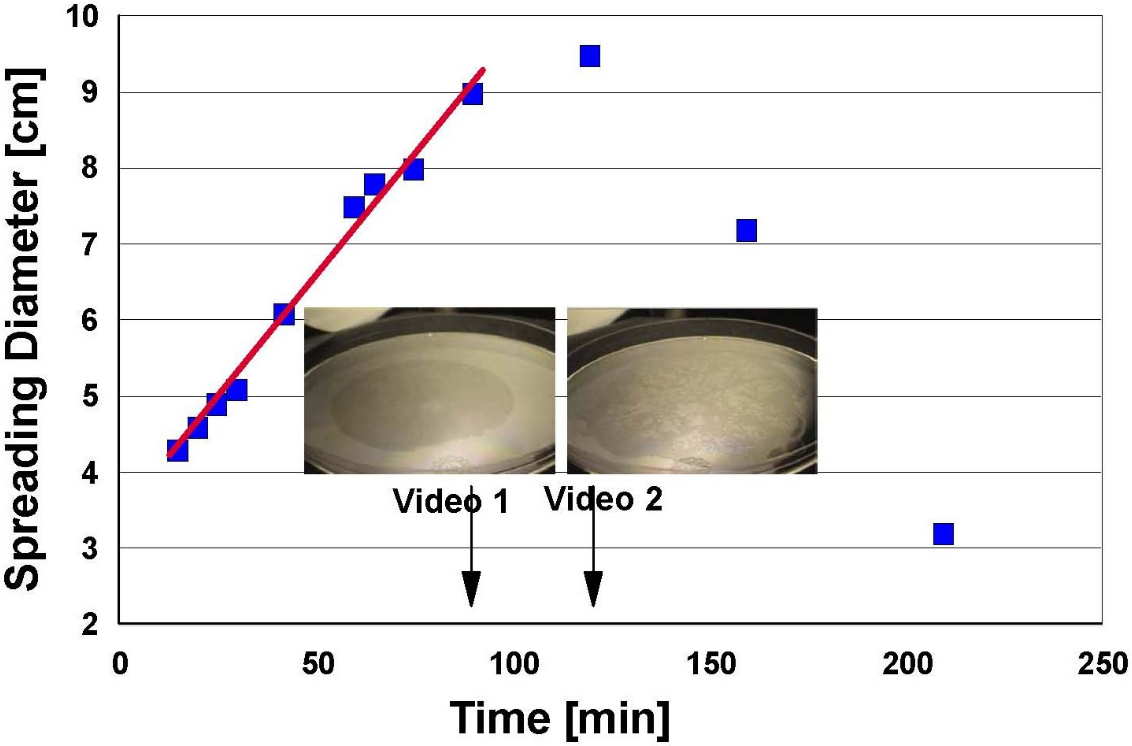

Figure 3-2: Spreading Diameter of 5000 ppm 0.04 mL drop of Silwet L77 at pH 11

The data presented in Figure 3-1 and Figure 3-2 reveals the linear dependence of the spreading radius vs. treatment time and concentration of Silwet L77. Based on the common values for the radius of spreading, one can combine the results presented in Figure 3-1 and Figure 3-2 and plot the Silwet L77 concentration vs. treatment time (see the data presented in Figure 3-3). The data for the Silwet L77 concentration vs. treatment time in Figure 3-3 follows the same linear dependence as the data presented in Figure 3-1 and Figure 3-2. The proposed approach can be used to estimate the hydrolysis rate of Silwet L77 at a pH of 11 vs. time. The estimated slope of the line presented in Figure 3-3 was 52 ppm/min, which is the rate of hydrolysis of Silwet L77 in an aqueous solution at a pH of 11 and room temperature.

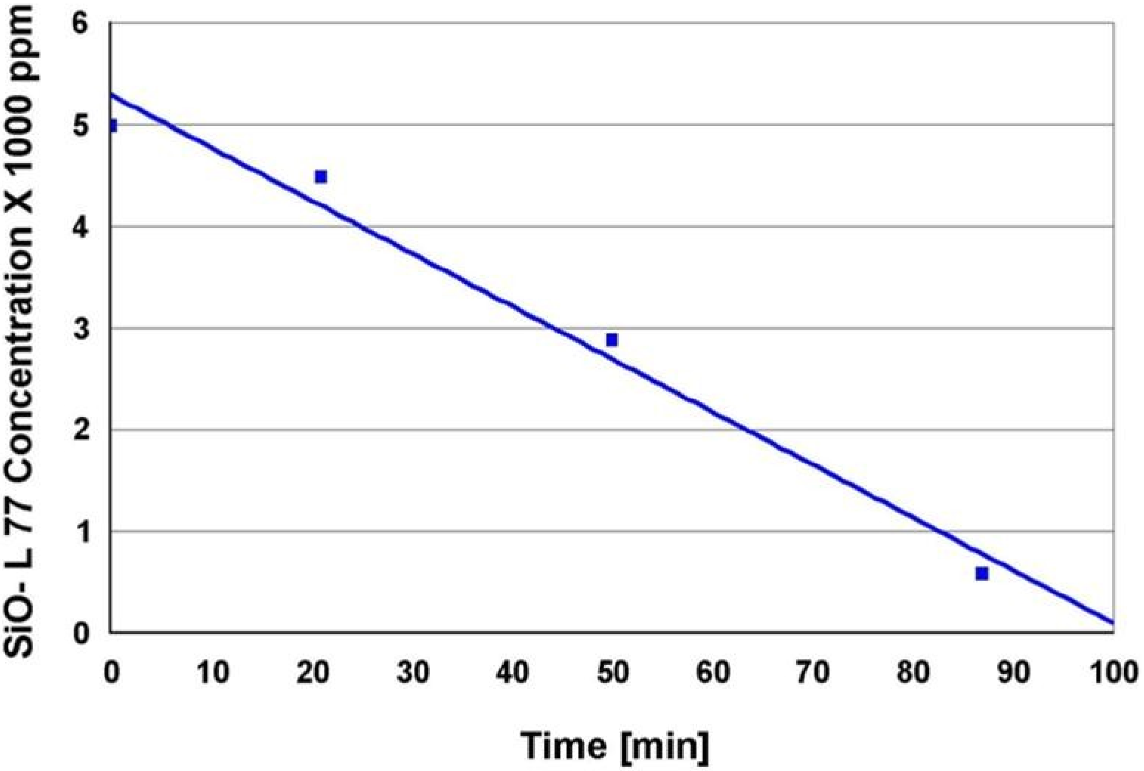

Figure 3-3: Decrease of Silwet L77 Concentration at pH 11

A study was conducted to examine the physical-chemical nature of the hydrolysis products of Silwet L77 at a pH of 11. A 500 ml Silwet L77 aqueous solution at a pH of 11 and a concentration of 5000 ppm was prepared in a beaker and stirred at room temperature for 3 hours. Then 13 ml was placed in a test tube and centrifuged at 2000G. The photos in Figure 3-4 depict the phases of separation. Red droplets are seen in the upper part of the tube, and a white, jelly-like matter appears at the bottom part of the tube. The red droplets are the oily phase. The red color is due to the presence of the red fat dye soluble only in the oily phase. The white jelly–like matter at the bottom is likely the hydrophilic longer silicone- polyether polymers with Na_2SiO_3.

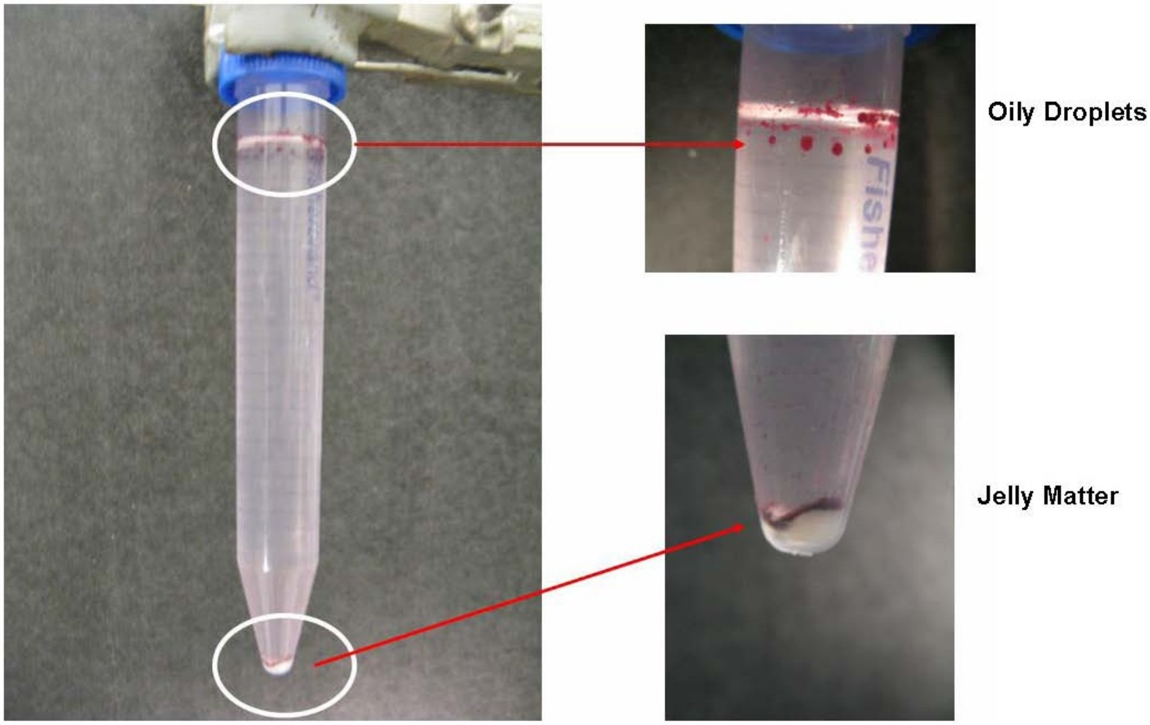

Figure 3-4: The Physical – Chemical Nature of Hydrolysis Products of Silwet L77

3.1.2 *Foaminess of SB10B Sludge Simulant*

SRNL provided IIT with SB10B sludge simulant for testing. The pH of the SB10B supernatant was 13.5-14.0, the total solids concentration was 17.5 wt%, and soluble solids were 5.5 wt%. The SB10B simulant had no added mercury or noble metals. The concentration of the total solids was calculated by measuring the difference in the weight of the SB10B suspension and solids left after the liquid phase evaporation at room temperature (25-27° C with a humidity of 40-50%). The concentration of the soluble solids in SB10B was calculated in the same manner as the total solids.

The foaminess of SB10B during boiling at an evaporation flux of 0.11g/min.cm2 was monitored. During boiling, water evaporated and the total solids concentration gradually increased. The foaminess vs. total solids was monitored and the data for the two runs are presented in Figure 3-5. The SB10B had a maximum in foaminess of 70 Volume% at 31-32 wt% total solids.

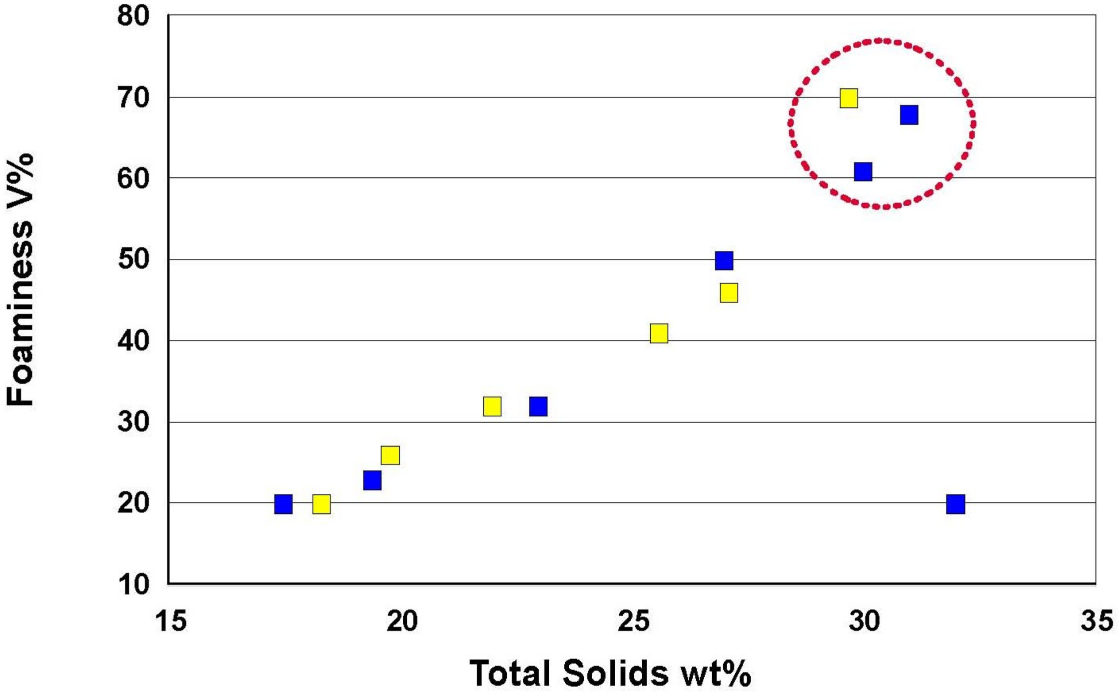

Figure 3-5: Foaminess of SB10B Sludge Simulant without Antifoam

5000 ppm Antifoam 747 was added to 500 ml SB10B, stirred for 15-20 minutes, boiled and then monitored for foaminess. The data for the foaminess vs. total solids concentration for the two runs are presented in Figure 3-6. The foaminess vs. total solids had a maximum of 300 Volume% at 25 wt% total solids. Figure 3-6 shows the data for SB10B foaminess without the presence of Antifoam 747 (for comparison). It is interesting to note that the presence of 5000 ppm Antifoam 747 led to a significant increase in the foaminess and the position of the maximum shifted from 30 wt% to 25 wt%. In order to examine the effects of aging that led to the antifoam's degradation, the experiment on foaminess was repeated after 24 hours. The data for foaminess vs. total solids for SB10B pretreated with 5000 ppm Antifoam 747 and stirred for 24 hours before boiling are also presented in Figure 3-6. No significant difference in the foaminess vs. total solids was observed between the SB10B added to Antifoam 747 on the same day and that added after the 24 hour pre-equilibration with Antifoam 747. Even after 48 hours, the foaminess vs. total solids followed the same foaminess curve illustrated in Figure 3-6.

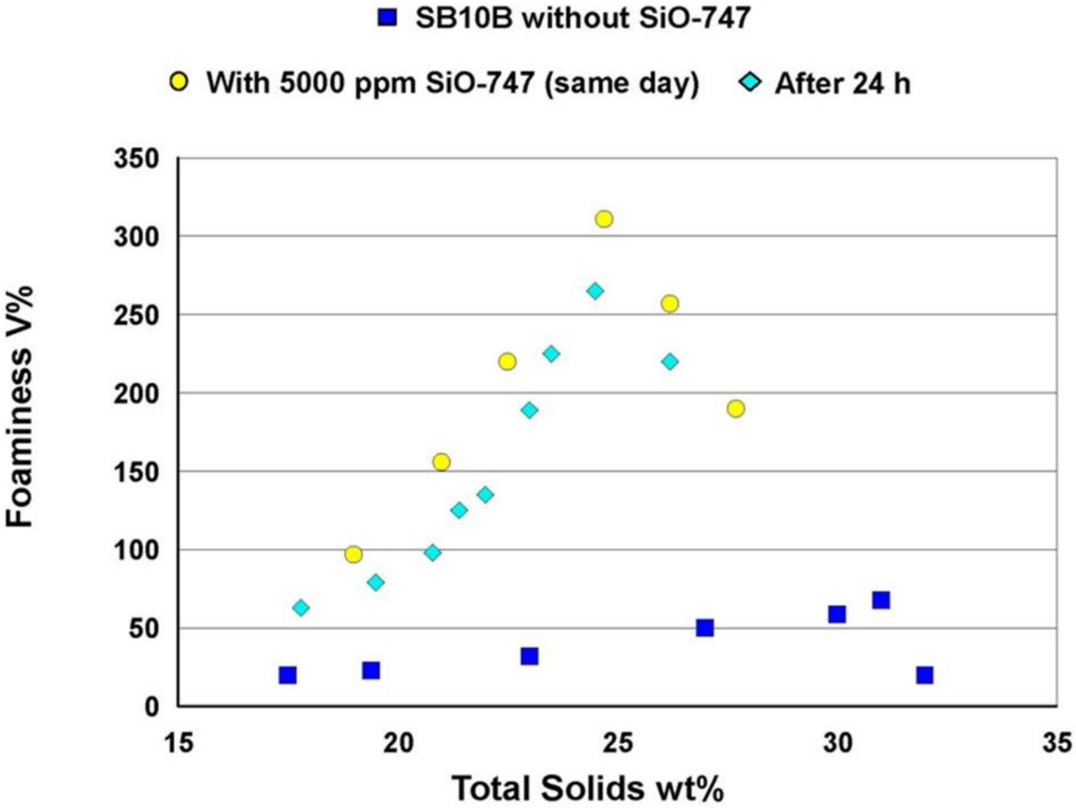

Figure 3-6: Foaminess of SB10B Sludge Simulant With 5000 ppm Antifoam 747

The effect of the concentration of Antifoam 747 on foaminess was also studied. The foaminess experiment was repeated by adding 2000 ppm Antifoam 747 to SB10B. The data are presented in Figure 3-7. The foaminess measurements conducted on the same day by adding Antifoam 747 to SB10B are marked with green triangles. The foaminess had a maximum of 320 Volume% at 29-30 wt% total solids. The foaminess for the 24 hour pre-equilibration of SB10B with Antifoam 747 is also presented in Figure 3-6 (the unfilled triangles). The foaminess vs. total solids followed the trend of the foaminess of SB10B that had Antifoam 747 added on the same day. The value of the maximum was the same (310 Volume %) and the maximum in foaminess shifts from 29-30 to 30-31 wt%. It is important to note that when 500 ppm Antifoam 747 was frequently added to the boiling SB10B pre-equilibrated with 2000 or 5000 ppm of Antifoam 747 (e.g., every 5 min.), the foaminess was quickly reduced to less than 20 Volume% and then rose up again after 5-6 minutes.

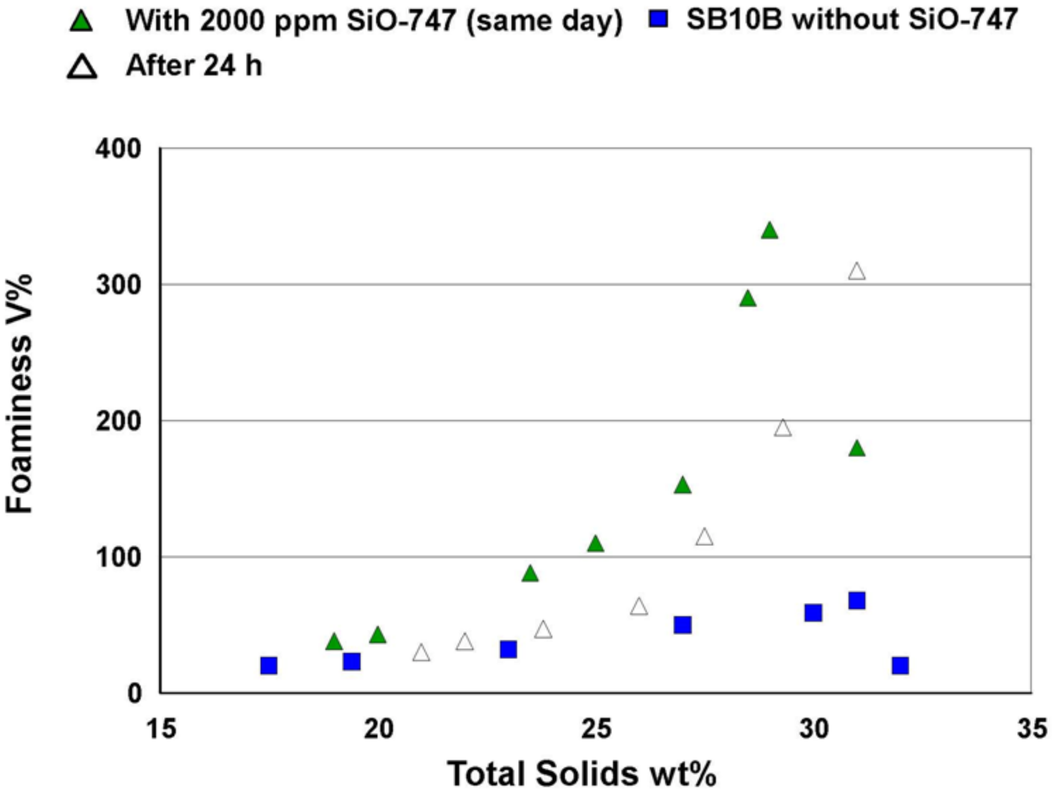

Figure 3-7: Foaminess of SB10B Sludge Simulant With 2000 ppm Antifoam 747

SB10B exhibited foaminess during the boiling of 70 Volume% at 31-32 wt% total solids. When SB10B (24 hours) was pre-equilibrated with either 2000 ppm or 5000 ppm Antifoam 747, it led to the foam enhancement by a factor 4.7 times compared to that of the sample without the added Antifoam 747. This foam enhancement is likely due to degradation of the Antifoam 747 components. At a pH of 13-14, the two components of Antifoam 747 were expected to hydrolyze. The Si-O-Si linkage is susceptible to hydrolysis in the high and low pHs, leading to the formation of polyalkyl siloxane oils which are less soluble in water, hydrophilic longer silicone-polyether polymers that are water soluble and less surface active, and Na_2SiO_3. More information about the decomposed products that result from Silwet L77 hydrolysis will be presented in the next report. Here, we present a study for estimating the rate of the hydrolysis of Silwet L77 in water at a pH of 11 at room temperate vs. time.

3.2 SRNL Results

SRNL performed analyses, including density, total solids, surface tension, total organic carbon concentration, SVOA, and NMR to characterize component 1, component 2, and Antifoam 747. In addition, spreading testing was completed to understand the spreading of component 1, component 2 and Antifoam 747 diluted with DI water and pH adjusted solutions to understand the stability of these materials. Testing was completed with the Teclis Foamscan instrument to measure the foaminess of various sludge simulants with and without added antifoam. Antifoam 747 was used in a variety of DWPF SRAT/SME simulations with both simulated sludge and real waste and the results will be summarized here. Of note are attempts to complete a mass balance to determine where Antifoam 747 and its degradation products partitioned. Lastly, antifoam acceptance testing was completed.

3.2.1 *Spreading Testing*

Since Silwet L77 is considered a "superspreader", testing was completed to determine the spreading diameter of diluted component 1, component 2, and Antifoam 747. This is similar to testing performed at IIT in section 3.1.1.

3.2.1.1 Stability of Diluted Antifoam Simulating DWPF Antifoam Preparation Tank

At the request of DWPF, testing was completed to determine the stability of Antifoam 747 in 1:20 diluted solution, simulating the preparation and storage of Antifoam 747 in DWPF. The solutions, containing 1 g Antifoam 747 and 19 g of DI water were tested periodically for approximately six weeks. No significant change in spreading was noted during this six week period. Results are summarized in Figure 3-8.

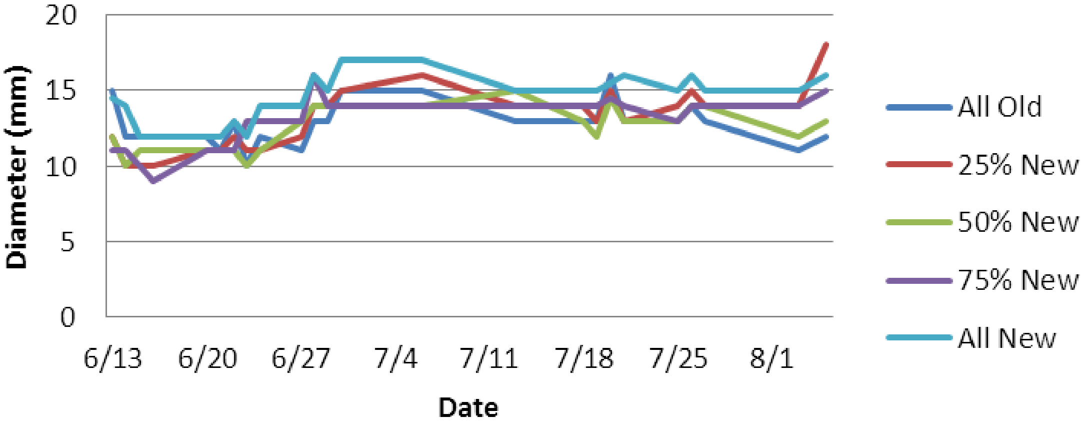

Figure 3-8: Stability of 1:20 mixture of Antifoam 747

At the request of DWPF, testing was also completed to determine whether the mixture of the new[1] Antifoam 747 (Siovation Lot# 110684-0413) and old Antifoam 747 (Siovation Lot# 101876-1111) would lead to problems in DWPF. Unless the antifoam storage tanks were emptied and cleaned as DWPF transitioned from the old to new Antifoam 747, there would be a mixture of both would be stored and used to control foam. The solutions, containing 1 g Antifoam 747 and 19 g of DI water were tested periodically for approximately six weeks. Testing demonstrated that the best performance occurred when pure old or new Antifoam 747 was used but there was no significant advantage to not mixing the solutions. Results are summarized in Figure 3-8.

3.2.1.2 Stability of Antifoam over pH 1 to 13

Testing was competed to determine the spreading of antifoam solutions over a pH range of 1 to 13. pH solutions were prepared by diluting 0.1 M HCl and NaOH solutions with DI water to the appropriate concentration. In

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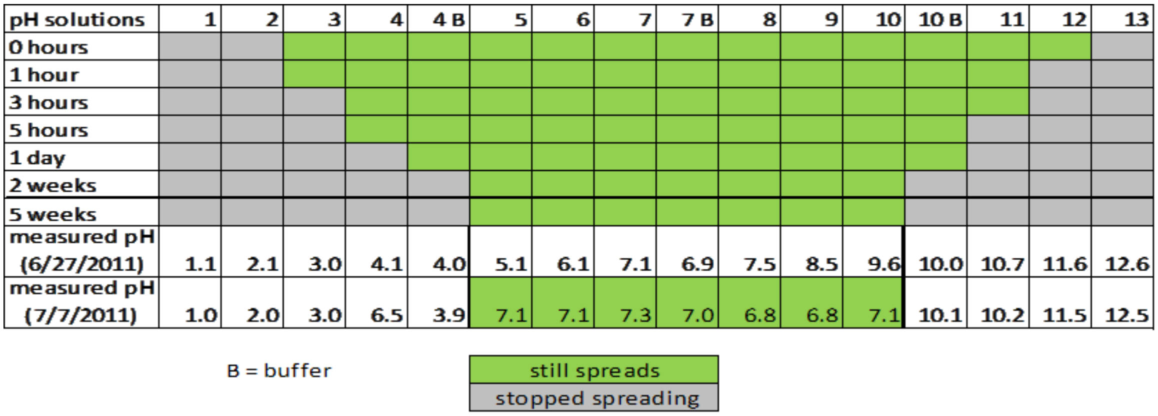
[1] DWPF revised their antifoam specification in 2010. The new antifoam specification required the blending of Momentive Silwet L-77 and Momentive Y-IT1780. The old antifoam specification was less specific and two different (but chemically similar) ingredients were used for components 1 and 2).

addition, pH 4, 7 and 10 buffers were used. 0.01 g of Antifoam 747 (Siovation Lot#110684-0413) was added to 10 g of each pH solution or buffer to produce a solution containing 1,000 ppm Antifoam 747. The solutions were stored at room temperature and were tested periodically over a five week period. The low pH (<4) and high pH (>10) solutions had virtually no spreading after just five hours. This demonstrates that in simple solutions at pH 5 to 9, the spreading was adequate, even after five weeks. Results are summarized in Table 3-1. The detailed testing data is summarized in Appendix A.



pH solutions	1	2	3	4	4 B	5	6	7	7 B	8	9	10	10 B	11	12	13
0 hours	▨	▨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	▨
1 hour	▨	▨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	▨	▨
3 hours	▨	▨	▨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	▨	▨
5 hours	▨	▨	▨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	▨	▨	▨
1 day	▨	▨	▨	▨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	▨	▨	▨
2 weeks	▨	▨	▨	▨	▨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	▨	▨	▨	▨
5 weeks	▨	▨	▨	▨	▨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	▨	▨	▨	▨
measured pH (6/27/2011)	1.1	2.1	3.0	4.1	4.0	5.1	6.1	7.1	6.9	7.5	8.5	9.6	10.0	10.7	11.6	12.6
measured pH (7/7/2011)	1.0	2.0	3.0	6.5	3.9	7.1	7.1	7.3	7.0	6.8	6.8	7.1	10.1	10.2	11.5	12.5

B = buffer

🟩 still spreads
▨ stopped spreading

Table 3-1: Stability of 1000 ppm Antifoam 747 at various pHs

3.2.2 *Teclis Foamscan Testing*

A Teclis Foamscan® Instrument was purchased to test the foaming tendency of various sludge simulants by sparging a gas through the slurry. It also determined the persistence of the generated foam by measuring variation in its volume, density, and drainage rate.

Liquid samples for Foamscan® are placed in a sample chamber. A glass column equipped with several pairs of conductivity electrodes is fixed onto this chamber. Foam develops in the sample chamber by sparging and rises into the glass column where it is viewed continuously by a video camera. Images from the video camera are captured by software along with conductivity measurements at each electrode. This data is used to calculate and plot foam volume and conductivity in real time. A photograph of the Foamscan® instrument is shown in Figure 3-1.

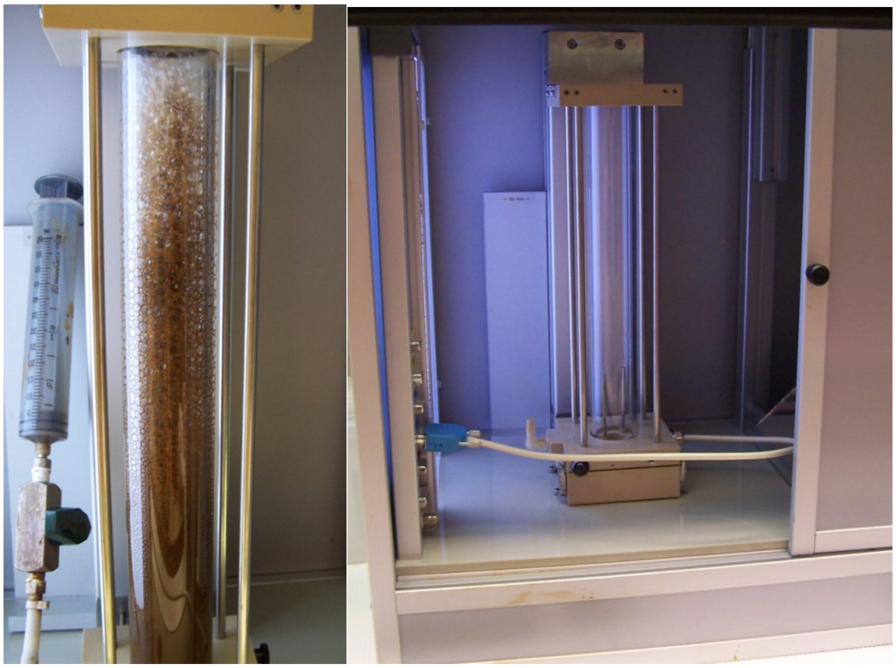


Figure 3-9: Photographs of Teclis Foamscan® Instrument

3.2.2.1 Foamscan® Testing of Sludge Simulants without antifoam

Testing of sludge simulants was a challenge in the Foamscan® due to the sticking of the slurry to the glass column. A video camera system is used to determine the height of the foam column but the camera was confused by the residue left after the gas sparging was stopped. As a result, 5 g of DI water was added after the sparging was stopped to clean off the glassware and allow the camera to accurately measure the foam height. In all of our testing, the foam was very unstable and collapsed within seconds of stopping the sparging.

Several sludge simulants were tested. As part of antifoam acceptance testing, an "acidified sludge" had been prepared where the sludge had been neutralized with nitric and formic acid to a pH of 7. pH 7 is close to the isoelectric point where the sludge is rheologically thickest and the sludge is most likely to foam extensively. In testing with the Acidified Sludge, the purge was automatically stopped by the program at 140 seconds since the foam was near the top of the glass column (220 mL). Thus 1,170 cm^3 of sparged gas produced 160 cm^3 of foam (14% of the nitrogen was trapped in the foam). The foaminess (foam volume/sludge volume) is >370% for the acidified sludge. Figure 3-10 shows graphs of the foam volume, sparge flowrate and the Bikerman Index[2]. The detailed testing data is summarized in Appendix A.

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[2] Bikerman Index is Defined as the Foam Volume, mL/Sparge Flow, sccm

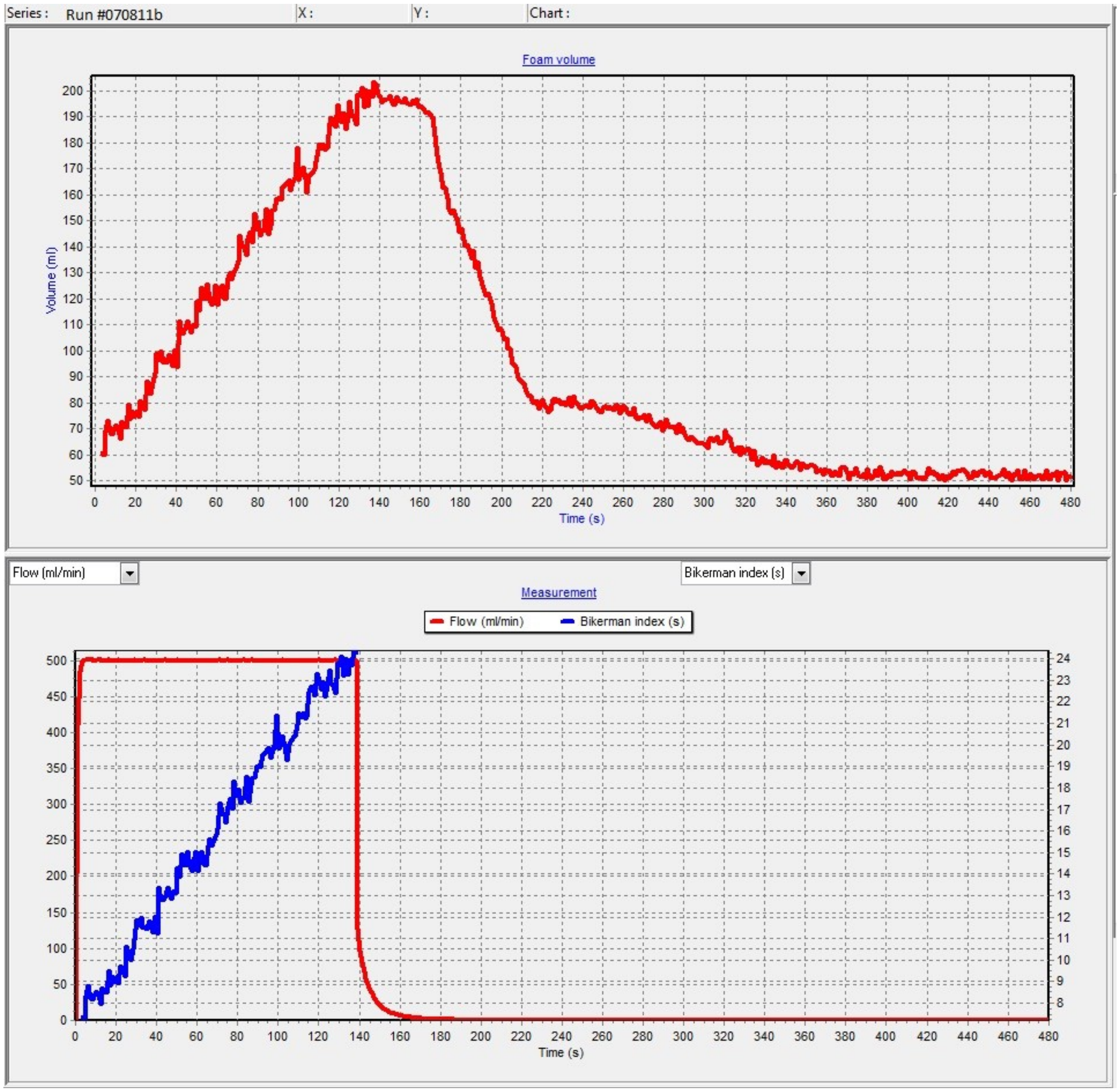


Figure 3-10: Foamscan® Testing of Acidified Sludge without antifoam

3.2.2.2 Foamscan® Testing of Sludge Simulants with added Antifoam Components and Antifoam 747

Testing of the acidified sludge with added component 1, component 2, and Antifoam 747 was completed without turning off the sparging (sparge rate 350 sccm). Additions were made at three minutes after the foam had stabilized. It was expected that the addition of these three solutions would decrease the foam. However, the addition of all three led to an increase in foam generation. Test AcidSludge080111a was completed with the addition of 10,000 ppm of Component 1 (Silwet L77) and the foam height roughly tripled. Test AcidSludge080111a was completed with the addition of 10,000 ppm of Component 2 (Y-17580) and the foam height more than tripled, required the manual stopping of sparging. Test AcidSludge080111e was completed with the addition of 10,000 ppm of Antifoam 747 (Siovation Lot#110684-0413) and the foam height roughly tripled. In this test the sparge rate was increased from 350 sccm to 400 sccm without the foam exiting the column.

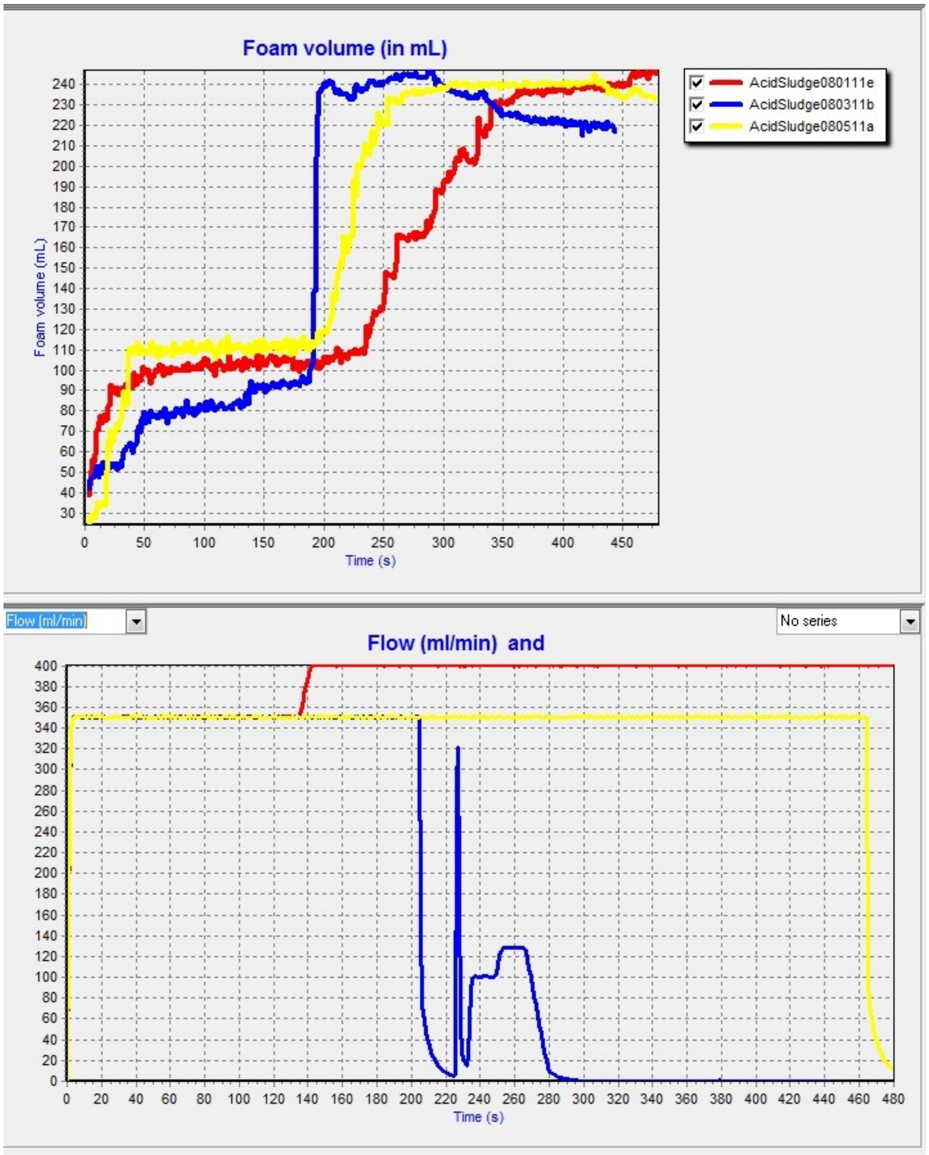


Figure 3-11: Foamscan® Testing of Acidified Sludge without antifoam

Foamscan® Testing of Sludges SB10B, HiFeHiMn, and LoFeHiMn did not produce sufficient foam to allow the calculation of any quantities for comparison. The detailed testing data is summarized in Appendix A.

3.2.2.3 Foamscan® Testing of Sludge Simulants with added mercury and noble metals

Foamscan® testing of acidified sludge with added noble metals and mercury was completed. The addition of mercury (added as HgO) had no impact on foaming. This is likely due to the high HgO density, causing the HgO to immediately drop to the base of the foam column and never become part of the slurry.

The addition of noble metals (0.0787 g of $AgNO_3$, 0.3274 g of $Pd(NO3)_2$ solution, 1.0142 g of $Rh(NO_3)_3$ solution, 0.1198 g of $RuCl_3$, and 6 g of water (AcidSludge072011cX) did produce more foam than a corresponding run without noble metals (AcidSludge072511a). The data is summarized in Figure 3-12. The detailed testing data is summarized in Appendix A.

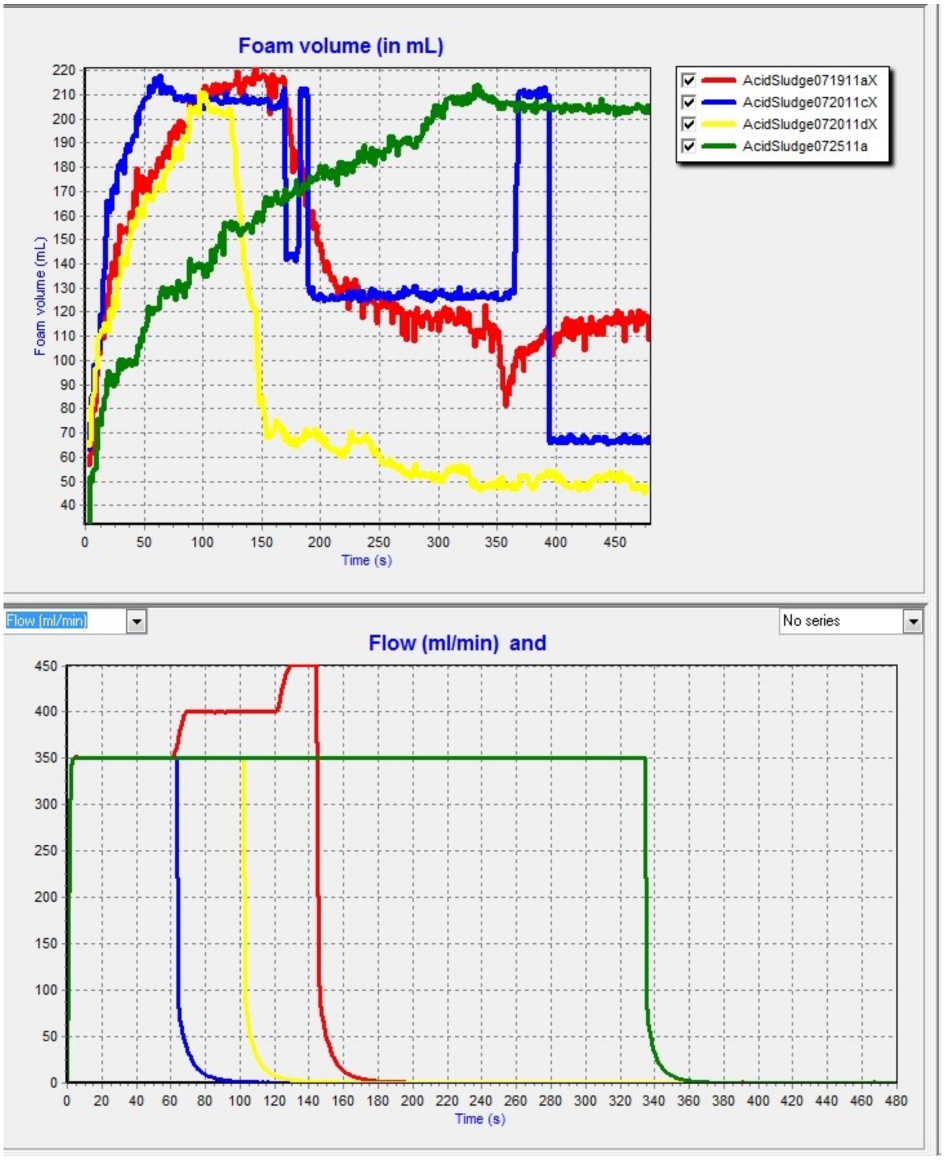


Figure 3-12: Foamscan® Testing of Acidified Sludge with and without added noble metals

3.2.3 *SRAT Cycle Testing*

Siovation Antifoam Lot #110684-0413 was tested on May 3, 2011 and Siovation Antifoam Lot #111128-0613 was tested on May 3, 2011 per antifoam acceptance procedure (Laboratory Scale Chemical Process Cell Simulations, ITS-0094, Rev. 4, 03-15-2010). Acidified sludge (SB6 Blend Acidified Sludge, ACSS-IIT1-6-2011, January 2011) was utilized during the testing. All acceptance criteria were met. The data from the test runs are shown in Table 3-2.

Table 3-2: Antifoam 747 Acceptance Testing Run Data

Parameter	Value	Value	Acceptance Criteria	Units
Lot #	110684-0413	111128-0613	NA	NA
Maximum foam height	<10%	21.6%	< 25%	Volume %
Average foam height	<5%	16.9%	< 25%	Volume %
Antifoam concentration	500	500	NA	ppm
Average boilup rate	5.5	> 1.0	> 0.83	g/min
Foam amount at conclusion of test	<5%	<4.2%	< 25%	Volume %
Foam dissipation time	<1	<5	< 30	Minutes

3.2.4 *Antifoam Analysis*

Two lots of Antifoam 747 (Siovation Lot# 110684-0413 and 111128-0613) were blended for DWPF in April and June 2011 under the revised antifoam purchase specification. Analysis and testing of both components and the blended antifoam was completed as part of the antifoam acceptance. Although this was not funded by this study, the data is concluded in this report for completeness. Because of issues with the antifoam impacting DWPF melter flammability, more extensive analysis of the antifoam was completed and will be reported in this section.

Siovation ships SRNL samples from each lot of component 1 and component 2 that are used to blend each batch of Antifoam 747. SRNL analyzes these samples as part of DWPF's Antifoam 747 Acceptance.

A sample from Siovation Antifoam 747 lot (110684-0413) was received by SRNL on 4/18/11 after being released by Siovation on 4/13/11. This antifoam lot was produced by combining two ingredients, lots 11DSVX019 and 11CSVX013 of Momentive Silwet L-77 and lot 11CSVC325 of Momentive Y-17580 US. Samples from each of the four lots were submitted to laboratories for analysis.

3.2.4.1 *Selected Physical Properties of Component 1, Component 2 and Antifoam 747*

Selected physical properties of the antifoam were measured for informational purposes.[11,12] These data are shown in Table 3-3 and Table 3-4 along with acceptance criteria or previous data for comparison.

Table 3-3: Selected Physical Properties of Components 1, 2 and Antifoam 747 in Siovation Lot# 110684-0413

Parameter	Silwet L-77 11DSVX019	Silwet L-77 11CSVX013	Y17580 US 11CSVC325	Antifoam 747 110684-0413	Antifoam Expected	Units
Density	1.00854	1.00714	1.04302	1.01075	1.01	g/mL
Solids Content	97.8	97.6	99.7	98.0	>95	Weight %
Viscosity	19.2	20.6	68.3	21.7	20-24	cP
Surface Tension of 1:10 dilution	24.4	24.7	20.4	23.0	20-24	Dynes/cm
% Carbon	44.9	45.2	41.4	45.3	49.1	Weight %
30 sec Spreading of 0.1 wt% in DI water	28.6	28.6	15.1	38.1		mm

Table 3-4: Selected Physical Properties of Components 1, 2 and Antifoam 747 in Siovation Lot# 110684-0613

Parameter	SilwetL-77 l1ESVX028	Y17580US l1ESVC329	Antifoam 747 111128-0613	Antifoam Expected	Units
Density	0.99755	0.99777	0.99756	1.01	g/mL
Solids Content	99.3	99.7	99.6	>95	Weight %
Viscosity	23.5	68.7	25.7	20-24	cP
Surface Tension of 1:10 dilution	20.3	24.6	20.0	20-24	Dynes/cm
30 sec Spreading of 0.1 wt% in DI water	27.0	43.5	50.0	NA	mm

3.2.4.2 Infrared Spectrum of Component 1, Component 2 and Antifoam 747

Fourier Transformed Infrared (FTIR) analysis of the four solutions was completed. The data is summarized in Figure 3-13 to Figure 3-16. FTIR analysis was also used to try to determine the antifoam components and antifoam degradation products. As these components are a blend of various molecular weight methyl siloxane molecules, it is difficult to use this analysis for anything but qualitative identification of possible degradation species.

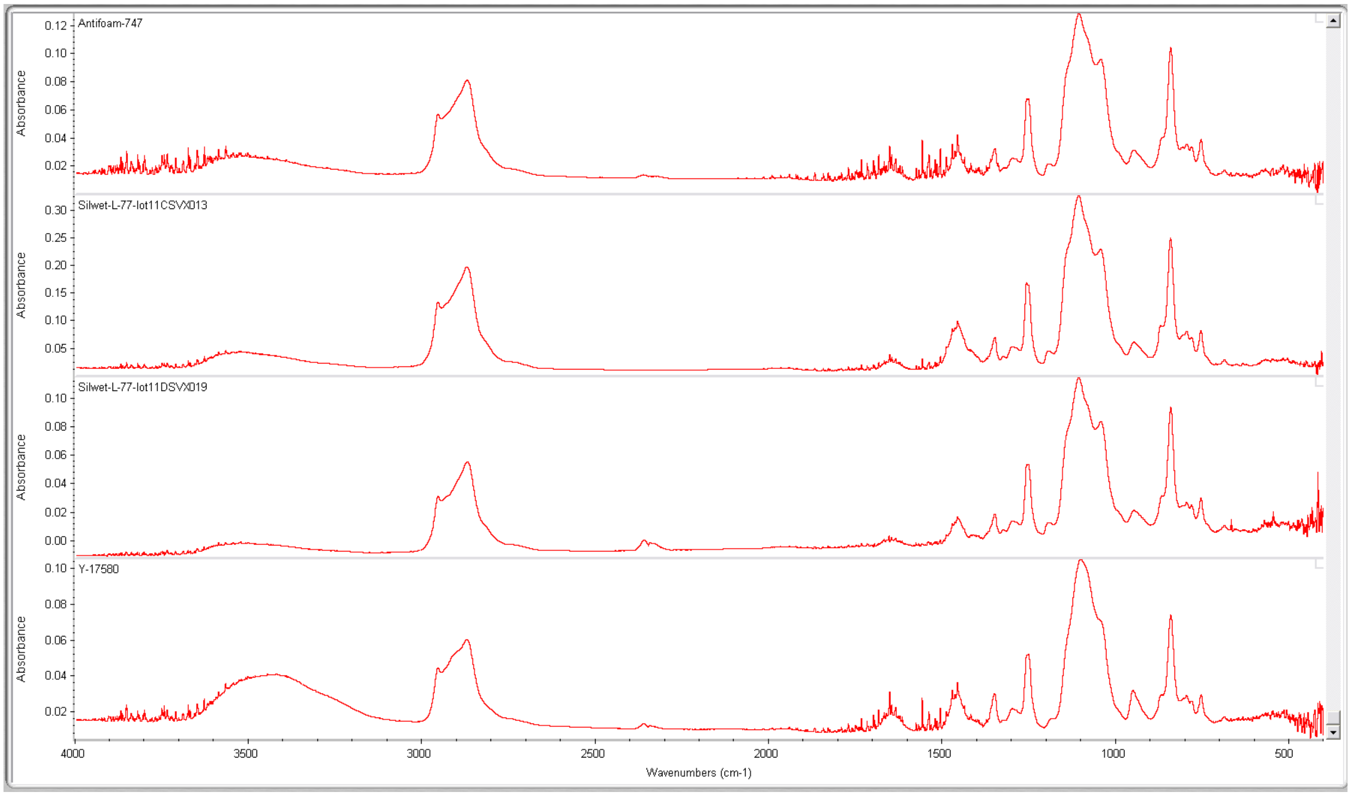


Figure 3-13: FTIR spectra for Antifoam 747, Silwet L-77 (Lot 11SCV813 and 11DSV819), and Y-17580 shown top to bottom

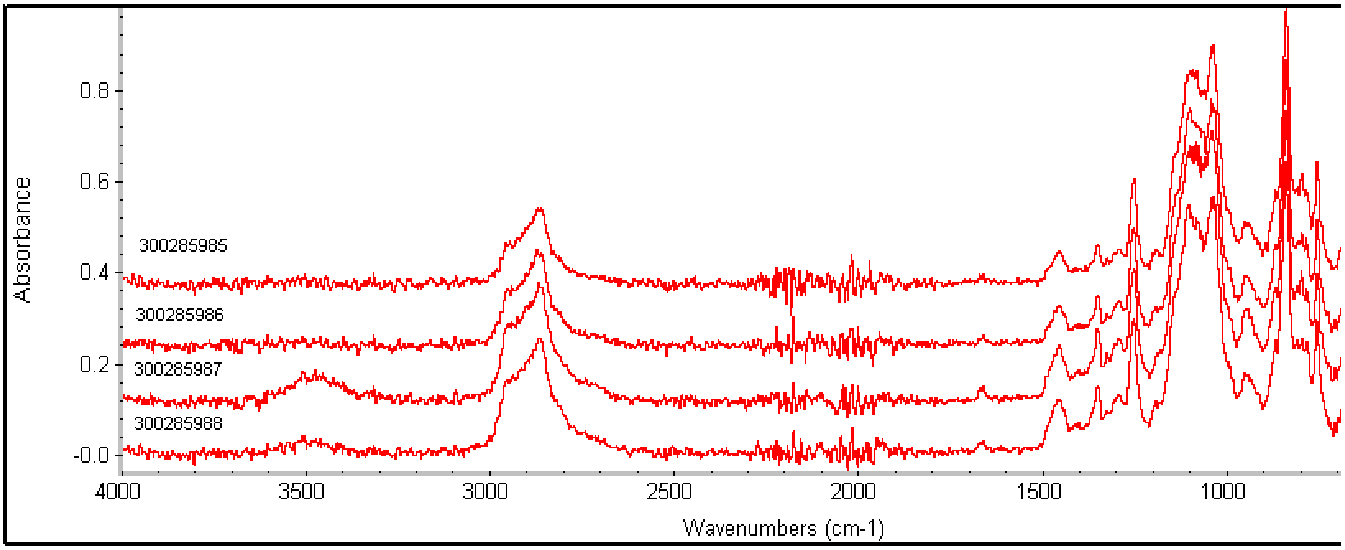
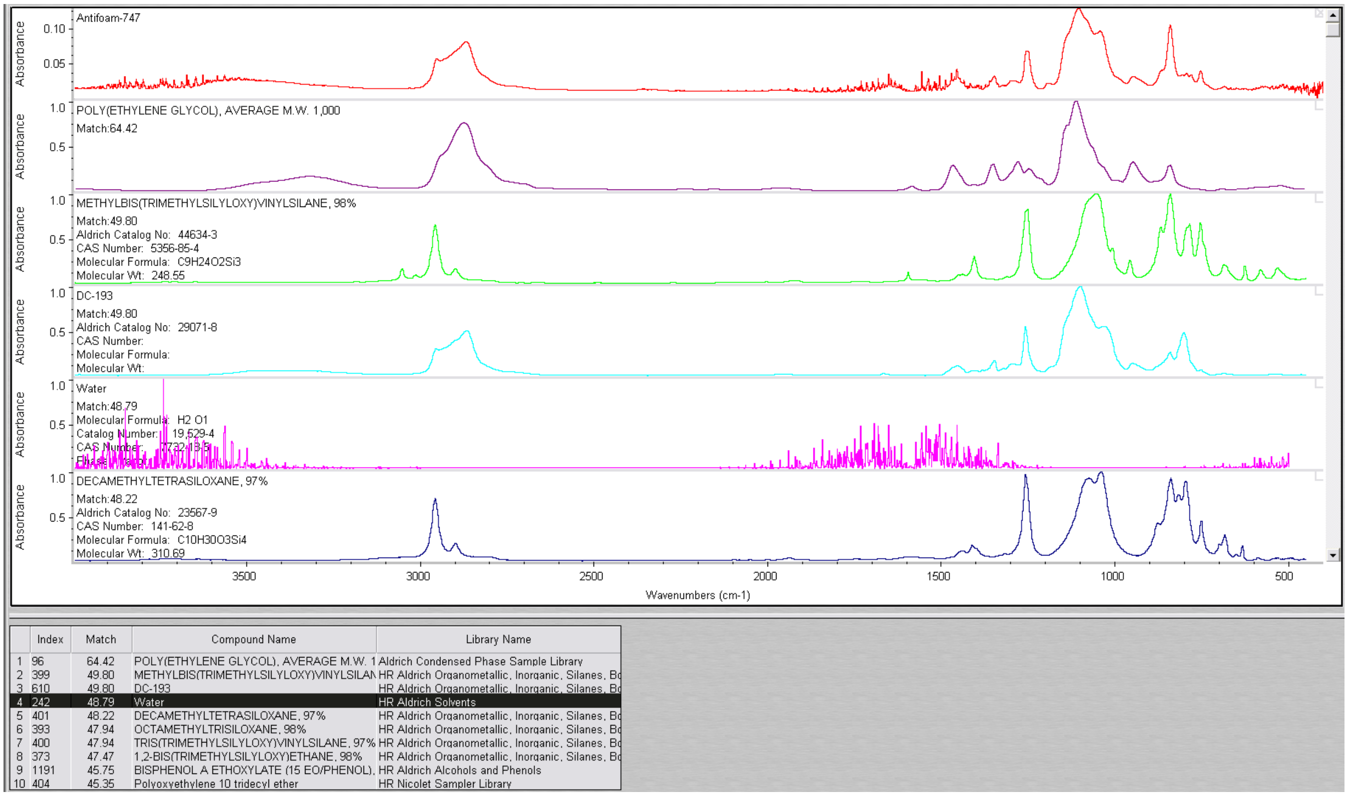


Figure 3-14: AD FTIR spectra for Antifoam 747, Silwet L-77 (Lot 11SCV813 and 11DSV819), and Y-17580 shown top to bottom

The FTIR spectra of the compounds in the FTIR database that are the closest matches to Antifoam 747 are summarized in Figure 3-15 and Figure 3-16



Antifoam-747

POLY(ETHYLENE GLYCOL), AVERAGE M.W. 1,000
Match:64.42

METHYLBIS(TRIMETHYLSILYLOXY)VINYLSILANE, 98%
Match:49.80
Aldrich Catalog No: 44634-3
CAS Number: 5356-85-4
Molecular Formula: C9H24O2Si3
Molecular Wt: 248.55

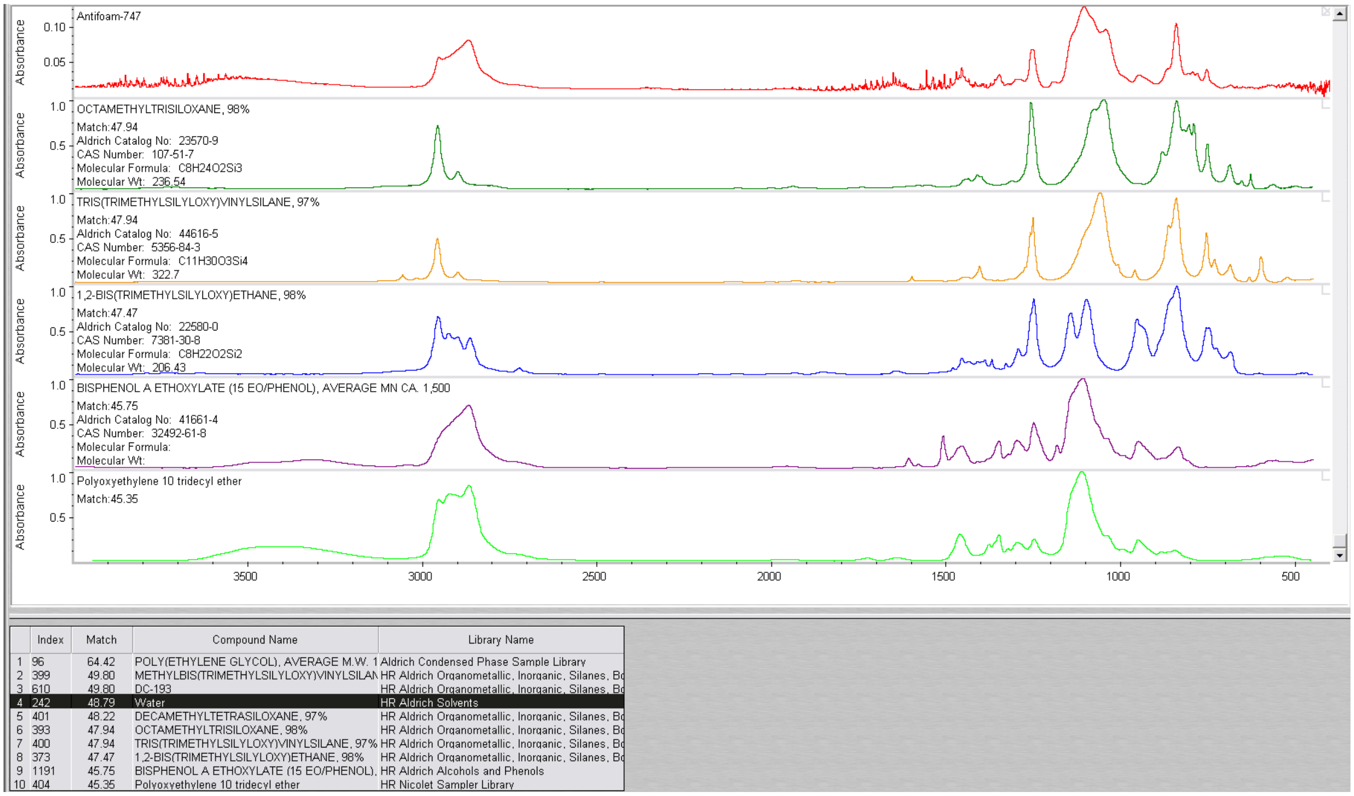
DC-193
Match:49.80
Aldrich Catalog No: 29071-8
CAS Number:
Molecular Formula:
Molecular Wt:

Water
Match:48.79
Molecular Formula: H2 O1
Catalog Number: 19,529-4
CAS Number: 7732-18-5

DECAMETHYLTETRASILOXANE, 97%
Match:48.22
Aldrich Catalog No: 23567-9
CAS Number: 141-62-8
Molecular Formula: C10H30O3Si4
Molecular Wt: 310.69

	Index	Match	Compound Name	Library Name
1	96	64.42	POLY(ETHYLENE GLYCOL), AVERAGE M.W. 1	Aldrich Condensed Phase Sample Library
2	399	49.80	METHYLBIS(TRIMETHYLSILYLOXY)VINYLSILAN	HR Aldrich Organometallic, Inorganic, Silanes, Bo
3	610	49.80	DC-193	HR Aldrich Organometallic, Inorganic, Silanes, Bo
4	242	48.79	Water	HR Aldrich Solvents
5	401	48.22	DECAMETHYLTETRASILOXANE, 97%	HR Aldrich Organometallic, Inorganic, Silanes, Bo
6	393	47.94	OCTAMETHYLTRISILOXANE, 98%	HR Aldrich Organometallic, Inorganic, Silanes, Bo
7	400	47.94	TRIS(TRIMETHYLSILYLOXY)VINYLSILANE, 97%	HR Aldrich Organometallic, Inorganic, Silanes, Bo
8	373	47.47	1,2-BIS(TRIMETHYLSILYLOXY)ETHANE, 98%	HR Aldrich Organometallic, Inorganic, Silanes, Bo
9	1191	45.75	BISPHENOL A ETHOXYLATE (15 EO/PHENOL),	HR Aldrich Alcohols and Phenols
10	404	45.35	Polyoxyethylene 10 tridecyl ether	HR Nicolet Sampler Library

Figure 3-15: FTIR spectra for closest matches to Antifoam 747



Antifoam-747

OCTAMETHYLTRISILOXANE, 98%
Match:47.94
Aldrich Catalog No: 23570-9
CAS Number: 107-51-7
Molecular Formula: C8H24O2Si3
Molecular Wt: 236.54

TRIS(TRIMETHYLSILYLOXY)VINYLSILANE, 97%
Match:47.94
Aldrich Catalog No: 44616-5
CAS Number: 5356-84-3
Molecular Formula: C11H30O3Si4
Molecular Wt: 322.7

1,2-BIS(TRIMETHYLSILYLOXY)ETHANE, 98%
Match:47.47
Aldrich Catalog No: 22580-0
CAS Number: 7381-30-8
Molecular Formula: C8H22O2Si2
Molecular Wt: 206.43

BISPHENOL A ETHOXYLATE (15 EO/PHENOL), AVERAGE MN CA. 1,500
Match:45.75
Aldrich Catalog No: 41661-4
CAS Number: 32492-61-8
Molecular Formula:
Molecular Wt:

Polyoxyethylene 10 tridecyl ether
Match:45.35

	Index	Match	Compound Name	Library Name
1	96	64.42	POLY(ETHYLENE GLYCOL), AVERAGE M.W. 1	Aldrich Condensed Phase Sample Library
2	399	49.80	METHYLBIS(TRIMETHYLSILYLOXY)VINYLSILAN	HR Aldrich Organometallic, Inorganic, Silanes, Bo
3	610	49.80	DC-193	HR Aldrich Organometallic, Inorganic, Silanes, Bo
4	242	48.79	Water	HR Aldrich Solvents
5	401	48.22	DECAMETHYLTETRASILOXANE, 97%	HR Aldrich Organometallic, Inorganic, Silanes, Bo
6	393	47.94	OCTAMETHYLTRISILOXANE, 98%	HR Aldrich Organometallic, Inorganic, Silanes, Bo
7	400	47.94	TRIS(TRIMETHYLSILYLOXY)VINYLSILANE, 97%	HR Aldrich Organometallic, Inorganic, Silanes, Bo
8	373	47.47	1,2-BIS(TRIMETHYLSILYLOXY)ETHANE, 98%	HR Aldrich Organometallic, Inorganic, Silanes, Bo
9	1191	45.75	BISPHENOL A ETHOXYLATE (15 EO/PHENOL),	HR Aldrich Alcohols and Phenols
10	404	45.35	Polyoxyethylene 10 tridecyl ether	HR Nicolet Sampler Library

Figure 3-16: FTIR spectra for closest matches to Antifoam 747 (continued)

3.2.4.3 Semivolatile Organic Analysis of Component 1, Component 2 and Antifoam 747

A Volatile Organic Analysis (VOA) and an SVOA was completed using a Gas Chromatograph/Mass Spectrometer (GC/MS). The method attempts to identify the materials in the sample. The species identified are summarized in the Table on the next two pages. Note that in cases where two species were identified as the same compound, the concentration of both species were added together and highlighted in yellow and in cases where three species were identified as the same compound, the concentration of all species were added together and highlighted in red. Note that for all four samples, the sum of all identified species was at best 50%. The results are summarized in Table 3-5 below.

Table 3-5: AD SVOA Results for Antifoam 747, Silwet L-77 (Lot 11SCV013 and 11DSV019), and Y-17580 shown top to bottom

Library/ID	Silwet L77 AD # 300285985 Lot# 11DSVX019	Silwet L77 AD # 300285986 Lot# 11CSVX013	Y-17580 AD # 300285987 Lot# 11CSVC325	Antifoam 747 AD # 300285988 Lot# 1106-0413
Sum	484,600	445,030	43,710	251,470
1-Aza-2-sila-5-boracyclopent-3-ene, 4,5-diethyl-1,2,2-trimethyl-3-(1-methylethenyl)-	209,000	158,500		
Trisiloxane, octamethyl-	110,000	31,200	520	2,090
tert-Butyl-[2-[2-[2-[2-[2-[2-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]dimethylsilane	52,000	124,000		38,500
2-[2-[2-[2-[2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy-trimethylsilane	23,000	2,200	11,000	20,000
Ethane, 1-ethoxy-1-methoxy-	22,000	34,000		
Hexaethylene glycol dimethyl ether	16,000	7,800		4,500
2-[2-[2-[2-[2-[2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethyl acetate	13,000			9,000
1-Propene, 3-[2-(2-methoxyethoxy)ethoxy]-	8,300	1,100		43,420
2-[2-[2-[2-[2-[2-[2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethanol	7,300	680	5,500	
tert-Butyl-[2-[2-[2-[2-[2-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]dimethylsilane	6,600	6,700		
2-[2-[2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy-trimethylsilane	5,400	3,600		
2-[2-[2-[2-[2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethanol	3,700		3,400	
3,6-Dioxa-2,4,5,7-tetrasilaoctane,2,2,4,4,5,5,7,7-octamethyl-	3,600			

Table 3-5: AD SVOA Results for Antifoam 747, Silwet L-77 (Lot 11SCV013 and 11DSV019), and Y-17580 shown top to bottom

Library/ID	Silwet L77 AD # 300285985 Lot# 11DSVX019	Silwet L77 AD # 300285986 Lot# 11CSVX013	Y-17580 AD # 300285987 Lot# 11CSVC325	Antifoam 747 AD # 300285988 Lot# 1106-0413
2-[2-[2-[2-[2-[2-[2-[2-[2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethanol	3,200		4,600	1,900
Oxazole, 2,5-diphenyl-	1,500			
.beta.-D-Mannofuranoside, 3,6,9-trioxadecyl-2,3:5,6-di-O-ethylboranediyl-		950		660
1,4,7,10,13,16-Hexaoxacyclooctadecane			1,100	
1-Benzazirene-1-carboxylic acid, 2,2,5a-trimethyl-1a-[3-oxo-1-butenyl] perhydro-, methyl ester		23,000		
1H-Indole, 1-ethyl-2-phenyl-				16,000
2-[2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy-trimethylsilane				1,300
2-[2-[2-[2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethanol		8,600		2,700
2-[2-[2-[2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethyl acetate				3,200
2-[2-[2-[2-[2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethyl acetate		11,000		8,000
2-[2-[2-[2-[2-[2-[2-[2-[2-[2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethanol			680	
2-[2-[2-[2-[2-[2-[2-[2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy-trimethylsilane		7,900		
2-[2-[2-[2-[2-[2-[2-[2-[2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy-trimethylsilane				12,000
3-(1,3-Dihydroxyisopropyl)-1,5,8,11-tetraoxacyclotridecane			11,000	4,100
Acetamide, 2-(5,7-dimethyl-[1,2,4]triazolo[1,5-a]pyrimidin-2-ylsulfanyl)-N,N-diphenyl-			1,600	
Benz[j]isoquinoline, 3,6,8-trimethyl-				2,400
Bis(2-methoxyethyl) phthalate		4,600		
Cyclotrisiloxane, hexamethyl-		3,000		

Table 3-5: AD SVOA Results for Antifoam 747, Silwet L-77 (Lot 11SCV013 and 11DSV019), and Y-17580 shown top to bottom

Library/ID	Silwet L77 AD # 300285985 Lot# 11DSVX019	Silwet L77 AD # 300285986 Lot# 11CSVX013	Y-17580 AD # 300285987 Lot# 11CSVC325	Antifoam 747 AD # 300285988 Lot# 1106-0413
Diphenyl-1,2,5-oxadiazole		8,900	2,600	
Dipropylene glycol monomethyl ether tert-Butyl-[2-[2-[2-[2-[2-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]dimethylsilane				48,000
Heptaethylene glycol			340	
Hexaethylene glycol monododecyl ether		1,200		
Hexagol			580	
Octaethylene glycol			450	
tert-Butyl-[2-[2-[2-[2-[2-[2-[2-methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]dimethylsilane				3,000
Tetraethylene glycol diethyl ether			340	
Tris(trimethylsilyl)borate		6,100		34,000

3.2.4.4 Nuclear Magnetic Resonance Spectroscopy of Component 1, Component 2 and Antifoam 747

Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy, is a research technique that exploits the magnetic properties of certain atomic nuclei to determine physical and chemical properties of atoms or the molecules in which they are contained. It relies on the phenomenon of nuclear magnetic resonance and can provide detailed information about the structure, dynamics, reaction state, and chemical environment of molecules. Most frequently, NMR spectroscopy is used by chemists and biochemists to investigate the properties of organic molecules.

NMR was used to determine the chemical structure of the antifoam components. C, H and Si NMR were performed by Dr. Fernando Fondeur of SRNL. The data are reported below in Appendix B.

3.2.4.5 Antifoam 747 Partitioning During SRAT Testing with Sludge Simulant

A series of five back-to-back SRAT cycles were performed [13] to determine the antifoam partitioning. As the antifoam is a minor component in DWPF processing, it is difficult to quantify the antifoam and its degradation products in the various product streams, offgas, and deposits generated during processing. For example, increases in concentration of Si in the condensate are likely degradation products. But what degradation products were produced that were condensed or scrubbed from the offgas to cause this increase in Si concentration?

Typical SRAT processing with the Modular Caustic Side Solvent Extraction Unit (MCU) solution was performed during each SRAT cycle. In each SRAT cycle, at least 700 ppm of Antifoam 747 (Siovation Lot #101876-1111) was added (total of 10.9 g of antifoam was added for all five runs). Total antifoam recovery was 33% by mass (identified primarily as Long Chain Siloxanes, boiling point >400° C). The mass balance identified 0.7 g in the SRAT product, 1.9 g in the offgas condensate, and 0.2 g in various other samples. Hexane was used to extract the antifoam from the glassware and liquid products. Carbon tubes were used to trap any organic in the offgas. It was noted that hexane may not have been the best solvent for extracting antifoam and its degradation product from the solutions.

3.2.4.6 Antifoam 747 Partitioning During SRAT Testing with SB7b Sludge Simulant

A series of chemical cell simulations using SB7b simulant were completed to identify the antifoam degradation products and complete a mass balance on the added antifoam (SB7b-1, SB7b-2 and SB7b-3). [14] SRAT dewater condensate samples were analyzed for nitrite, nitrate, formate, mercury, and silicon. Silicon was assumed to be present as antifoam at 14 wt.% Si. The fraction of antifoam that could have been lost during dewatering was calculated from the dewater condensate mass, Si concentration, and mass of antifoam additions in the SRAT. An abbreviated summary is given in Table 3-8.

Table 3-6: SB7b Batch SRAT Dewater Condensate

	SB7b-1	SB7b-3	SB7b-2
Acid Stoichiometry	105%	115%	145%
Condensate mass, g	1,163	1,209	1,046
Nitrite, mg/L	<100	<100	<100
Nitrate, mg/L	6,100	3,400	2,900
Formate, mg/L	260	310	1,500
Potential antifoam loss	27%	66%	83%

Si mass in the dewater condensate increased with increasing acid stoichiometry. This increase implies more potential antifoam loss to the Mercury Water Wash Tank (MWWT) with increasing acid stoichiometry. Potentially a very high percentage of antifoam could have been lost during dewatering. The dewatered condensate mass was fairly large for a 4-L lab-scale SRAT run in all three cases (there were roughly 4,000 g in the SRAT at the start of dewatering and just under 3,000 g after dewatering). The large dewater mass may have inflated the potential antifoam loss. The maximum stripped antifoam mass, assuming all Si is associated with antifoam at 14% Si in antifoam, only amounts to 2.4 g of antifoam or less than a quarter percent of the collected condensate mass. The reader should be aware that these are bounding calculations. The Si in the condensate could as easily be disilicic acid from stripping some of the chemically dissolved SiO_2.

Nitrate and formate can be taken as nitric and formic acid respectively. Therefore, higher concentrations of these species imply that the condensate is more acidic. The amount of nitrate collected historically depends on how much nitrite is destroyed during dewatering versus during formic acid addition (nitrate and nitrite form from the NO_2 produced during nitrite destruction that gets absorbed into water droplets in the SRAT condenser, and nitrite subsequently converts to nitrate under fairly acidic conditions in the MWWT).

The concentration of condensate formate typically depends on the acid stoichiometry (higher stoichiometry, more formate in both SRAT and condensate). The formate concentration in the MWWT tends to decline over time as the SRAT pH slowly increases due to catalytic decomposition of formic acid/formate in the SRAT slurry. Dissolved mercury decreased with increasing acid stoichiometry. The anion data imply a rising pH of the condensate with increasing acid stoichiometry which should impact mercury solubility. The magnitude of the dissolved Hg drop from SB7b-3 to SB7b-2, however, seems to indicate that more than simply pH may be impacting Hg solubility.

Scoping samples were obtained in an attempt to learn more concerning the fate of antifoam during the CPC process. These samples included the SRAT dewater condensates analyzed for Si. In addition, hexane extractions were performed on SRAT and SME dewater condensates, the MWWT and Formic Acid Vent Condenser (FAVC) condensates removed following the SRAT and SME cycles (for SB7b-1 and 2 only), the SME product slurry, and the ammonia scrubber solution. Following the extractions, and draining of liquids and slurries from the lab equipment, the SRAT, SRAT lid, SRAT agitator, SRAT off-gas line, SRAT sample tube, SRAT pH probe, SRAT condenser, MWWT, SRAT condenser to FAVC line, and FAC were subjected to hexane rinses to recover any soluble organic material. A sample of SRAT product was also taken, diluted about 17 to 1 with de-ionized water, and centrifuged. The majority of the diluted supernate was discarded to remove formate (soluble total organic carbon, TOC). The remaining sample (primarily insoluble SRAT product solids) was analyzed for TOC.

Various compounds potentially related to antifoam were found using semi-volatile organic analysis and volatile organic analysis on the hexane extractions and hexane rinses. These included siloxanes, trimethyl silanol, methoxy trimethyl silane, hexamethyl disiloxane, aliphatic hydrocarbons, dioctyl phthalate, and emulsifiers. Cumulatively, these species amounted to less than 3% of the antifoam mass in all three runs when the measured concentrations were worked back through material balances. This small contribution in all three runs, however, came more than 50% from rinsing the MWWT with hexane.

The TOC results on the SRAT solids could explain as much as 40-80% of the antifoam mass assuming antifoam is 48% carbon. The hypothesis was that the antifoam, or at least the organic part of the antifoam, might be held on the surfaces of the insoluble solids. In that form, the organic material was potentially difficult to extract into solution with hexane.

The SRAT dewater condensate Si results presented in Table 3-7 could be derived from antifoam at 27-83% of the total antifoam. Combined with the TOC results on the SRAT product, the pair of results could nearly close an antifoam material balance.

Table 3-7. SB7b Batch Antifoam Balance

	SB7b-1	SB7b-3	SB7b-2
Acid Stoichiometry	105%	115%	145%
SRAT insoluble TOC as antifoam	80%	39%	48%
Dewater Si loss as antifoam loss	27%	66%	83%
Miscellaneous organics as antifoam	2%	<1%	2%
Sum	110%	106%	133%

There are several unproven assumptions in the antifoam balance, however, so these results should be taken as preliminary and scoping rather than definitive. A decomposed antifoam molecule could show up multiple places, such as a low molecular weight siloxane in the dewater condensate and as an adsorbed organic chain on the SRAT solids. The hexane rinses and extractions seemed to give rather uneven results, suggesting that lab technique is likely a factor. The TOC analysis required removal of TOC due to residual formate. The original plan was to dilute the formate such that its contribution to TOC would be less than 10% of any significant TOC due to antifoam, but the actual samples were potentially 50-75% TOC due to formate which had to be subtracted from the measured TOC to obtain the TOC potentially due to antifoam.

3.2.4.7 Antifoam 747 Demonstration During SRAT Testing with Actual Sludge

Antifoam 747 has been used in SRNL Shielded Cells SRAT/SME demonstrations with actual waste. Recent testing with Antifoam 747 is summarized in Table 3-8.

In testing with SB5 and SB6 waste, foaming was a significant problem in most of the demonstrations. In two of these demonstrations, antifoam was repeatedly added throughout the run. Note that the three foamovers occurred with 200-300 ppm antifoam added approximately two-thirds of the way through formic acid addition.

Table 3-8: Antifoam Observations in Shield Cells Demonstrations with Actual Waste

Run #	Sludge	Antifoam Used	Comments	SRAT Antifoam Added, mg/kg	SME Antifoam Added, mg/kg
SC-8	SB5 + Np	Old	Acid Addition Foamover	2,830	580
SC-9	SB6 Qual	Old	Acid Addition Foamover, No foam in SME	2,100[3]	200
SC-10	SB6 Blend?	Old	None	1,000	200
SC-11	SB7 Qual	Old	Acid Addition Foamover	1,000	200
SC-12	SB7b Qual	New	None	1,000	100
SC-13	SB5 Np	New	None	700	NA

3.3 Path forward

DWPF has decreased the quantity of antifoam they are using as a result of the response to the PISA. Approximately 950 gallons of Antifoam 747 were used in DWPF in between January 4 and September 30, 2011.

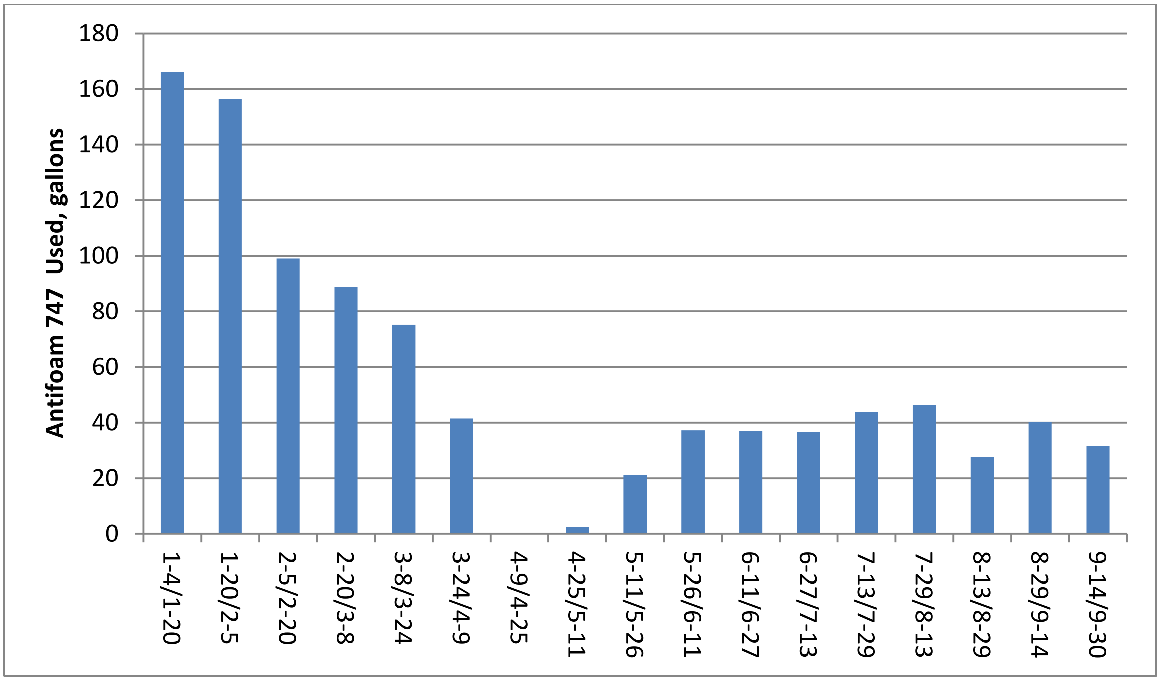


Figure 3-17 DWPF Antifoam Use from January 4-September 29, 2011

Testing in FY11 by researchers at IIT and SRNL, along with processing information gleaned from DWPF CPC processing, demonstrates the need for an improved antifoam agent for DWPF. Antifoam 747 was not designed for processing of highly caustic sludge. Antifoam 747 performed poorly in testing in solutions with a pH >10 and in testing with caustic sludges. The amount of

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[3] Caustic boiling (ARP Addition) in SRAT cycle. Foamover 2/3 way through formic acid addition.

material required to be processed under caustic conditions will increase once the Salt Waste Processing Facility is started up.

Instead of starting from scratch and developing an improved antifoam agent that is effective over a pH range of 3 to 14, it is recommended that the Silwet L77 structure should be changed to make it more resistant to hydrolysis attack. Other surfactants, such as those used in high pH bathroom cleaners, are stable for several years in storage. IIT researchers are confident that they can modify the molecular structure to make the Silwet L77 more resistant to hydrolysis. This would allow the use of less antifoam agent and maximize the time between antifoam additions.

One additional advantage of a more stable antifoam molecule is that less antifoam decomposition products would be produced. This would minimize the amount of decomposition products in the condensate, in the offgas piping and components, and in the recycle stream back to the tank farm. This would minimize the impact of the carbon and hydrogen in the antifoam which may impact the flammability strategies for other facilities.

4.0 Summary

DWPF adds Antifoam 747 to minimize foam produced by process gases and water vapor during chemical processing of sludge. This allows DWPF to maximize acid addition and evaporation rates to minimize the cycle time in the CPC. Improvements in DWPF melt rate due to the addition of bubblers in the melter have resulted in the need for further reductions in cycle time in the CPC. This can only be accomplished with an effective antifoam agent.

DWPF production was suspended on March 22, 2011 as the result of a Flammable Gas New Information/ (NI) Potential Inadequacy in the Safety Analysis (PISA). The issue was that the DWPF melter offgas flammability strategy did not take into account the H and C in the antifoam, potentially flammable components, in the melter feed. It was also determined the DWPF was using much more antifoam than anticipated due to a combination of longer processing in the CPC due to high Hg, longer processing due to Actinide Removal Process (ARP)/ Modular Caustic Side Solvent Extraction Unit (MCU) additions, and adding more antifoam than recommended. The resolution to the PISA involved and assessment of the impact of the antifoam on melter flammability and the implementation of a strategy to control additions within acceptable levels. This led to the need to minimize the use of Antifoam 747 in processing beginning in May 2011.

DWPF has had limited success in using Antifoam 747 in caustic processing. Since starting up the ARP facility, the ARP product (similar chemically to caustic sludge) is added to the SRAT at boiling and evaporated to maintain a constant SRAT volume. Although there is very little offgas generated during caustic boiling, there is a large volume of water vapor produced which can lead to foaming. High additions and more frequent use of antifoam are used to mitigate the foaming during caustic boiling.

The result of these three issues above is that DWPF had three antifoam needs in FY2011:

1. Determine the cause of the poor Antifoam 747 performance during caustic boiling
2. Determine the decomposition products of Antifoam 747 during CPC processing
3. Improve the effectiveness of Antifoam 747, in order to minimize the amount used

Testing was completed by IIT and SRNL researchers to address these questions. The results of this research are summarized below

4. The cause for the poor Antifoam 747 performance during caustic boiling was the high hydrolysis rate, cleaving the antifoam molecule in two, leading to poor antifoam performance. In testing with pH solutions from 1 to 13, the antifoam degraded quickly at a pH <4 and pH >10. As the antifoam decomposed it lost its spreading ability (wetting agent performance), which is crucial to its antifoaming performance. During testing of a caustic sludge simulants, there was more foam in tests with added Antifoam 747 than in tests without added antifoam.
5. Analyses were completed to determine the composition of the two antifoam components and Antifoam 747. In addition, the decomposition products of Antifoam 747 were determined during CPC processing of sludge simulants. The main decomposition products were identified primarily as Long Chain Siloxanes, boiling point >400° C. Total antifoam recovery was 33% by mass. In a subsequent study, various compounds potentially related to antifoam were found using semi-volatile organic analysis and volatile organic analysis on the hexane extractions and hexane rinses. These included siloxanes, trimethyl silanol, methoxy trimethyl silane, hexamethyl disiloxane, aliphatic

hydrocarbons, dioctyl phthalate, and emulsifiers. Cumulatively, these species amounted to less than 3% of the antifoam mass. The majority of the antifoam was identified using carbon analysis of the SRAT product (40-80% by mass) and silicon analysis (23-83% by mass) of the condensate. Both studies recommended a better solvent for antifoam and more specific tests for antifoam degradation products than the Si and C analyses used.

6. The DWPF Antifoam 747 Purchase Specification was revised in Month, 2011 with a goal of increasing the quality of Antifoam 747. The purchase specification was changed to specify the manufacturer and product for both components that are blended by Siovation to produce Antifoam 747 for DWPF. Testing of Antifoam produced using both the old and new antifoam specifications perform very similarly in testing. Since the change in purchase specification has not improved antifoam performance, an improved antifoam agent is required.

Several other findings of testing are reported below, as requested by DWPF:

7. The storage of a 1:20 Mixture of Antifoam 747 and water, over a period of five weeks, had a negligible impact on spreading. It appears to be stable over a period of up to five weeks.
8. Blending of the Antifoam 747 purchased by the old specification and new antifoam produced with the new Antifoam 747 specification leads to poorer spreading performance than either antifoam by itself.

No work was completed to elucidate the role of the pH on Y -17580. More research needs to be conducted to reveal the role of alkali pHs on Y-17580's (also a component of Antifoam 747) decomposition on sludge foaming/ antifoaming.

5.0 Recommendations

The testing completed by IIT and SRNL researchers identified a number of issues, including:

1. The development of an improved antifoam agent is needed to maximize the attainment in the DWPF CPC without impacting the melter offgas flammability or downstream processing facilities. An improved antifoam agent would decrease the amount and frequency of antifoam used in DWPF while minimizing CPC batch processing time. The antifoam needs to be more chemically resistant to hydrolysis, especially during caustic boiling phase of SRAT processing.
2. Improved understanding of the antifoam degradation products that result from the hydrolysis of the antifoam molecule. Current melter flammability strategy assumes that 80% of the antifoam is present in the melter feed to participate in redox and decomposition reactions. Testing by Newell and Koopman identified much lower amounts of antifoam present in their SRAT products. A better understanding of the degradation products is possible due to the improved analytical techniques used in this study and utilization of a better solvent for closing the antifoam mass balance during testing.
3. Continue working with IIT and Momentive to improve the stability of the antifoam in the presence of sludge with a pH from 2 to 14. Dr. Darsh Wasan and Dr. Alex Nikolov have a fundamental understanding of both the needs of DWPF in maximizing throughput and the chemistry of the antifoam and SRS sludge that will allow them to improve antifoam chemical stability. Momentive is needed to both demonstrate the effectiveness of new antifoam components and to commercially produce the product for DWPF.

6.0 Acknowledgements

The author would like to acknowledge the assistance of the Process Science Analytical Lab personnel and the Analytical Development group for their support with sample analysis. Each new antifoam lot is analyzed by D. R. Best and W. T. Riley. S. L. Crump's work with volatile and semi-volatile organic analysis is also acknowledged in the context of examining samples for antifoam and/or antifoam decomposition products. F.F. Fondeur completed the NMR analyses of component 1, component 2, and Antifoam 747.

The author also acknowledges the technical review assistance of M. E. Stone.

The author acknowledges the excellent support and collaboration that Dr. Darsh Wasan and Dr. Alex Nikolov have provided in first developing and then in their continued support of Antifoam 747. This collaboration has spanned over 15 years. Their technical knowledge in the fundamentals of foam during processing and the chemistry of the antifoam agent is unparalleled.

The studies were funded by a combination of direct support from the Defense Waste Processing Facility and the Department of Energy (DOE) Environmental Management (EM) funded Project 3.2.3.

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8.0 Appendix A – SRNL Spreading and Foamscan® Testing

A.1 SRNL Spreading Testing
A.2 Foamscan® **Testing**

A.1 SRNL Spreading Testing

Table A.1-1Spreading Diameter Results, mm for New & Old Antifoam 747 1:20 in DI water

Date	All Old	25% New	50% New	75% New	All New
6/13	15	12	12	11	15
6/14	12	10	10	11	14
6/15	12	10	11	10	12
6/16	12	10	11	9	12
6/20	12	11	11	11	12
6/21	11	11	11	11	12
6/22	13	12	11	11	13
6/23	10	11	10	13	12
6/24	12	11	11	13	14
6/27	11	12	13	13	14
6/28	13	14	14	16	16
6/29	13	14	14	14	15
6/30	15	15	14	14	17
7/6	15	16	14	14	17
7/13	13	14	15	14	15
7/18	13	14	13	14	15
7/19	13	13	12	14	15
7/20	16	15	15	15	16
7/21	13	13	13	14	16
7/25	13	14	13	13	15
7/26	14	15	14	14	16
7/27	13	14	14	14	15
8/3	11	14	12	14	15
8/5	12	18	13	15	16

Measured Diameter, mm of 10 uL drop after spreading for 30 seconds

Table A.1-2 Day 1 Spreading Diameter Results, mm for Antifoam 747: 1,000 in Various pHs

	Day 1: 6-27-11		8:30	9:30	10:30	11:30	1:30	2:30	3:30	4:20
pH	**measured pH**	**Solution/Antifoam mixture (mL)**	**0 hours**	**1 hour**	**2 hours**	**3 hours**	**5 hours**	**6 hours**	**7 hours**	**8 hours**
1	1.13	10.0346	6	6						
2	2.10	10.0040	6	7						
3	3.04	10.0377	56	45	37	10	6			
4	4.06	10.0231	52	57	65	49	54	55	50	54
4 buffer	4.00	10.0609	62	67	58	54	51	48	43	40
5	5.10	10.0663	45	60	56	57	48	50	47	50
6	6.06	10.0071	38	53	61	54	50	55	55	54
7	7.09	10.0350	50	50	63	56	54	54	58	61
7 buffer	6.92	10.1413	48	61	52	53	51	50	55	50
8	7.48	10.1116	50	58	58	57	54	51	43	59
9	8.51	10.0278	46	55	56	52	51	54	52	44
10	9.63	10.1228	52	56	65	52	57	52	53	53
10 buffer	9.96	10.0394	54	57	57	55	50	55	56	47
11	10.68	10.0791	54	52	43	40	13	9		
12	11.60	10.0047	13	8						
13	12.56	10.1153	6	6						

Measured Diameter, mm of 10 uL drop after spreading for 30 seconds

Table A.1-3 Day 2-35 Spreading Diameter Results, mm for Antifoam 747 1:1,000 in Various pHs

Date	6/29	6/30	7/7		7/12	7/13	7/18	7/19	7/20	7/21	7/25	7/26	7/27	8/3	8/5
pH	**Day 3**	**Day 4**	**measured pH**	**Day 11**	**Day 16**	**Day 17**	**Week 3**				**Week 4**				**Week 5**
1			**1.0**												
2			**2.0**												
3			**3.0**												
4			**6.5**												
4 buffer	**55**	**60**	**3.9**	**57**	**6 NS**										
5	**65**	**65**	**7.1**	**59**	**63**	**64**	**61**	**62**	**63**	**60**	**57**	**58**	**61**	**61**	**60**
6	**63**	**62**	**7.1**	**62**	**62**	**62**	**61**	**55**	**64**	**56**	**61**	**64**	**60**	**63**	**61**
7	**64**	**63**	**7.3**	**61**	**65**	**60**	**56**	**63**	**61**	**60**	**60**	**62**	**60**	**51**	**60**
7 buffer	**55**	**60**	**7.0**	**61**	**58**	**63**	**47**	**56**	**57**	**55**	**48**	**55**	**56**	**59**	**58**
8	**61**	**59**	**6.8**	**58**	**62**	**61**	**55**	**54**	**56**	**58**	**53**	**59**	**61**	**59**	**60**
9	**58**	**60**	**6.8**	**61**	**62**	**57**	**54**	**60**	**57**	**56**	**60**	**58**	**58**	**62**	**61**
10	**60**	**51**	**7.1**	**59**	**63**	**62**	**61**	**60**	**58**	**61**	**56**	**61**	**56**	**54**	**59**
10 buffer	**31**	**20**	**10.1**	**6 NS**											
11			**10.2**												
12			**11.5**												
13			**12.5**												

A.2 Foamscan® **Testing**

Table A.2-1 Batching for Foamscan® Runs

Acidified Sludge Testing			Density	wt % solids	A	B	C	D	E	F
Run Time, min					8	8	8	8	8	8
Sludge					Acidified	Acidified	Acidified	Acidified	Acidified	Acidified
Amount of Sludge, 60 mL			1.1214	17.8089%	67.284	67.284	67.284	67.284	67.284	67.284
Amount of antifoam			0.99756	99.5650%	0	0.00673	0	0.00673	0	0.00673
Element	**Concentration wt % (solids basis)**		**FW**	**MW**	Target	Target	Target	Target	Target	Target
Hg	3.263	HgO	216.5894	200.59			0.324	0.324		
Ag	0.014	AgNO3	169.8731	107.8682					0.0787	0.0787
Pd	0.079	15.27% in soln	696.9	106.42					0.3274	0.3274
Rh	0.038	4.93% in soln	2087.3	102.9055					1.0142	1.0142
Ru	0.217	41.74 % in RuCl3	242.1	101.07					0.1198	0.1198

Testing for:

- antifoam	
- mercury	**Basis of 0.3 g Hg**
- noble metals	**Basis of 0.05 g of each noble metal**
- varying sludges	**Basis of 100 ppm of antifoam, 0.0001 g antifoam/g sludge**

Table A.2-2 Results for Foamscan® Runs

Run #	Sludge Type	Repeated Run	Run Time (sec)	Weight of sludge (g)	Supernate added (mL)	Hg added (g)	Noble Metals added	Water added before (mL)	Water added after (mL)	Antifoam Added (g)	Effective Test	Reason	Starting Purge Rate (cm^3/min)	Total Gas Volume (mL)	Foam Up Time (s)	Bikerman index (s)	Foam Expansion	Foam Capacity	Foam Max Density	Foam Stability (s)	Liquid Stability (s)
070811a	SB10B		480		ALL 360	0	No	0	0	0	No - wrong purge, high bikerman		100	1132	N/A	15373			-0.024		
071111a	SB10B		480		ALL 360	0	No	0	0	0	No - insufficient foam		500	4003	N/A	15			0.014		
071311a	SB10B		480		0	0	No	0	0	0	No - insufficient foam		500	4003	N/A	18			0.002		
071311b	SB10B		480		60	0	No	0	0	0	No - insufficient foam		500	4003	N/A	17			0		
071311c	SB10B		480		120	0	No	0	0	0	No - insufficient foam		500	4003	N/A	13			-0.002		
071911a	SB10B - centrifuged		480		30	0	No	0	0	0	No - insufficient foam		300	1025	N/A	21			-0.0014		
071911b	SB10B - centrifuged		480		83	0	No	0	0	0	No - insufficient foam		350	3753	N/A	5			0.046		
071111a	SRAT		480		ALL 500+	0	No	0	0	0	No - insufficient foam		500	4003	N/A	15			-0.004		
071211a	SRAT		480		0	0	No	0	0	0	No - insufficient foam		500	1295	N/A	15			0		
071211b	SRAT		480		60	0	No	0	0	0	No - insuffici		400	1413	N/A	11			0		

Run #	Sludge Type	Repeated Run	Run Time (sec)	Weight of sludge (g)	Supernate added (mL)	Hg added (g)	Noble Metals added	Water added before (mL)	Water added after (mL)	Antifoam Added (g)	Effective Test	Reason	Starting Purge Rate (cm^3/min)	Total Gas Volume (mL)	Foam Up Time (s)	Bikerman index (s)	Foam Expansion	Foam Capacity	Foam Max Density	Foam Stability (s)	Liquid Stability (s)
											ent foam										
071211c	SRAT		480		180	0	No	0	0	0	No - insufficient foam		500	4003	N/A	16			0		
071211d	SRAT		480		300	0	No	0	0	0	No - insufficient foam		500	4003	N/A	14			0		
071211e	SRAT		480		360	0	No	0	0	0	No - insufficient foam		500	4003	N/A	17			0		
071211f	SRAT		480		420	0	No	0	0	0	No - insufficient foam		500	4003	N/A	13			0		
071211g	SRAT		480		480	0	No	0	0	0	No - insufficient foam		500	4003	N/A	14			-0.005		
070811a	Acidic		480			0	No	0	0	0	No - no water added after foaming		500	677	115	26	18	0.33	0.056	0	1
070811b	Acidic		480			0	No	0	5	0	YES at purge of 500		500	1143	138	24	17.3	0.18	0.058	65	2
071211	Acidic		480			0	No	0	0	0	No - insufficient foam		500	4003	N/A	22			0		
071911aX	Acidic		480			0	No	0	5	0	YES		350	924	144	29	11.1	0.24	0.09	125	12
072011bX	Acidic		480			0.3253	No	0	5	0	YES		350	865	149	37	33.3	0.25	0.03	0	43
072011cX	Acidic		480			0	YES	6	5	0	YES		350	362	63	37	24.9	0.6	0.04	332	1
072011dX	Acidic	YES	480			0	YES	6	5	0	YES		350	590	102	36	23.9	0.36	0.042	45	2
072111	Acidic		480	71.191		0.3247	No	0	5	0	No - no change when stir in Hg		350	894	154	34	25.2	0.22	0.04	0	7

Run #	Sludge Type	Repeated Run	Run Time (sec)	Weight of sludge (g)	Supernate added (mL)	Hg added (g)	Noble Metals added	Water added before (mL)	Water added after (mL)	Antifoam Added (g)	Effective Test	Reason	Starting Purge Rate (cm^3/min)	Total Gas Volume (mL)	Foam Up Time (s)	Bikerman index (s)	Foam Expansion	Foam Capacity	Foam Max Density	Foam Stability (s)	Liquid Stability (s)
072511a	Acidic		480	72.72		0	No	6	5	0	YES		350	1946	334	37	22.8	0.11	0.044	0	4
072511b	Acidic		480	80.1		0	No	0	5	0.806	No - Antifoam mixed in before run		350	64	11	41	10.1	3.73	0.099	0	21
072611a	Acidic		480	74.32		0	No	0	5	0.745	No - Antifoam mixed in before run		350	170	19	42	9.3	1.44	0.107	0	33
072711a	HiFeHiMn		480	74.16		0	No	0	0	0	No - insufficient foam		350	1118	N/A	22	3.6	0.16	0.274	0	0
072711b	LoFeHiMn		480			0	No	0	0	0	No - insufficient foam		350	1565	N/A	14	0	0	0	0	0
080111a	Acidic		180	70.12		0	No	0	0	0.711	YES - though purge turned off		350	719	124	17	9.5	0.14	0.105	1	1
080111b	Acidic	YES	400	repeat		0	No	0	3	repeat	after antifoam added to 1st run		350	526	90	39	8.7	0.43	0.114	0	24
080111c	Acidic	YES	480	repeat		0	No	3	4	repeat	showed performance of antifoam		350	199	480	8216	0	0	0.003	0	0
080111d	Acidic	YES	350	repeat		0	No	7	4	repeat	in multiple runs		350	149	420	38	12.9	1.47	0.077	155	13
080111e	Acidic		480	69.2		0	No	0	0	0.701	YES - Antifoam 747 Test		400	1027	N/A	37	0	0	0	0	0
080311b	Acidic		480	72.5		0	No	0	10	C2 0.736	YES - C2 Test		350	1081	443	95266	0	0	0.002	0	0
080511a	Acidic		480	74.45		0	No	0	6	C1 0.725	YES - C1 Test		350	1105	480	1291	0	0	0	0	0

9.0 Appendix B – Nuclear Magnetic Resonance Spectroscopy

B.1 Proton NMR
B.2 C-13 NMR
B.2 Si-29 NMR

B.1 Proton NMR

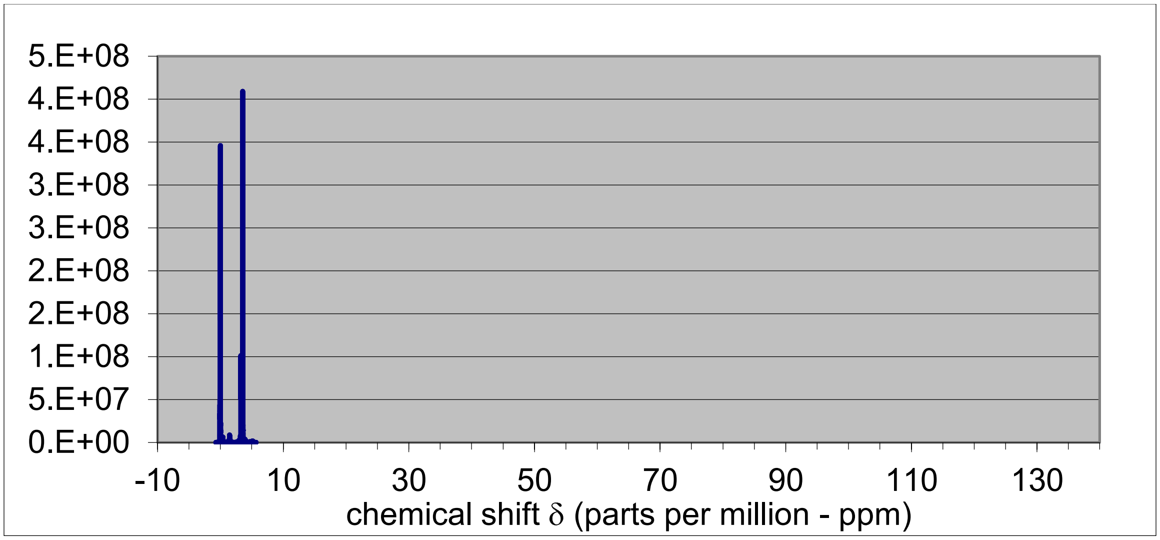

Figure B.1-1 H-1 NMR Spectrum of Silwet L-77 Lot#11DSVX019 (AD Sample ID 300285985)

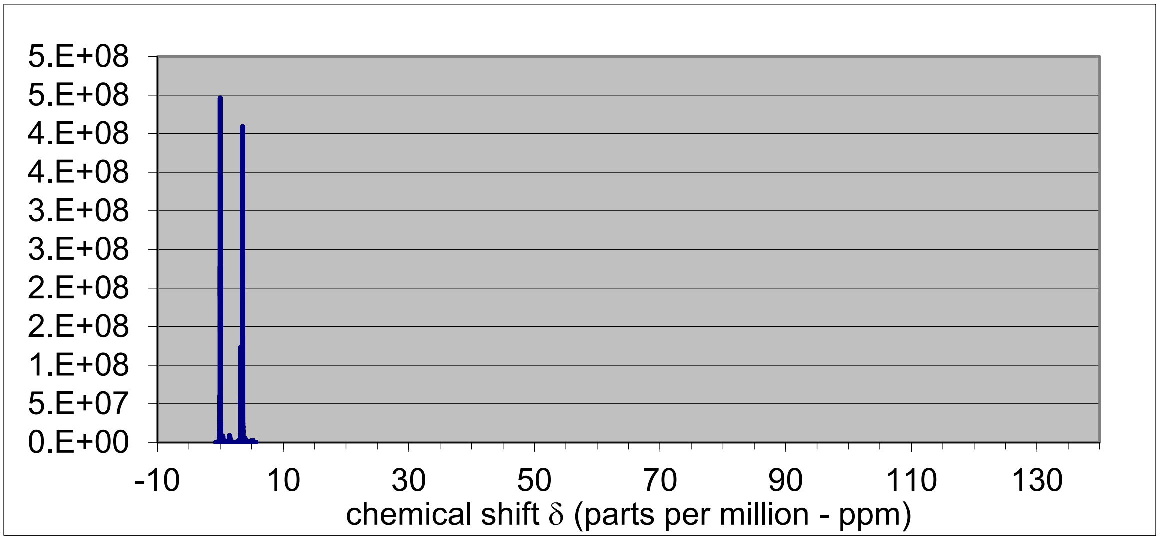

Figure B.1-2 H-1 NMR Spectrum of Silwet L-77 Lot#11CSVX013 (AD Sample ID 300285985)

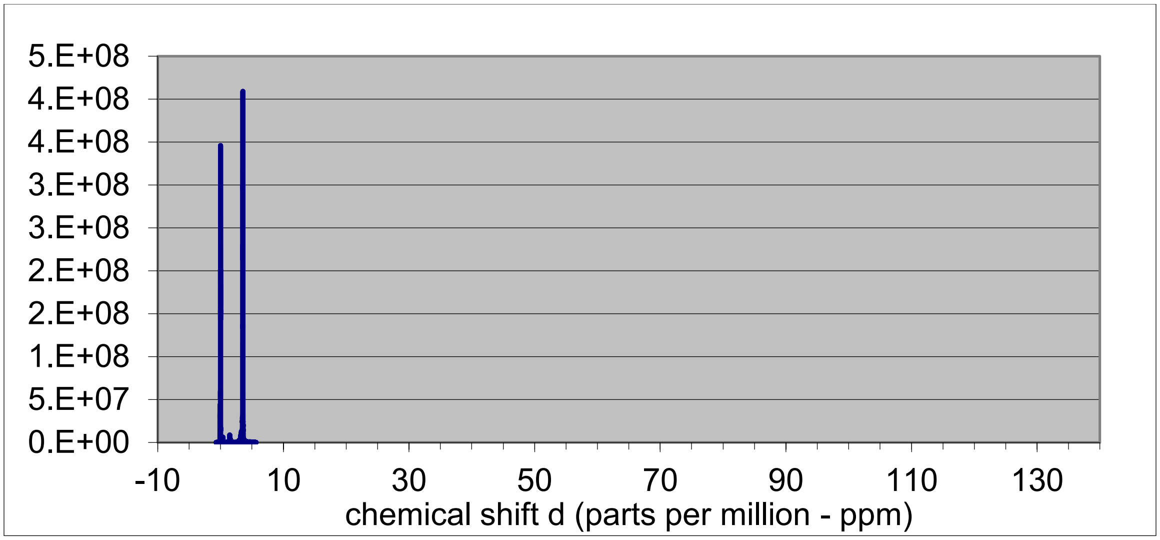

Figure B.1-3 H-1 NMR Spectrum of Y-17580 Lot#11VSVC325 (AD Sample ID 300285985)

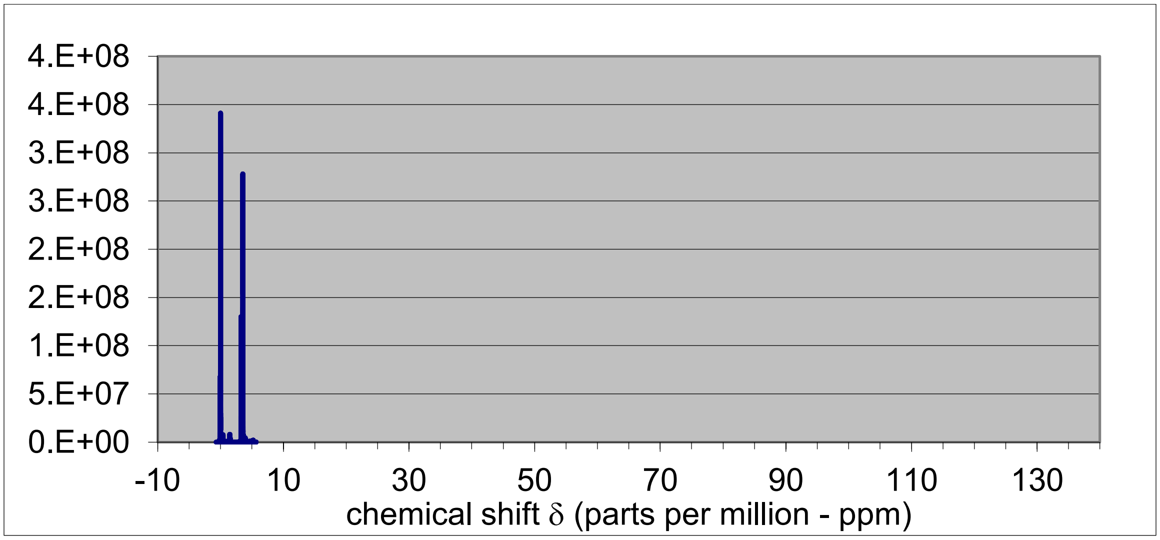

Figure B.1-4 H-1 NMR Spectrum of Silwet L-77 Siovation Lot#110684-0413 (AD #300285985)

B.2 C-13 NMR

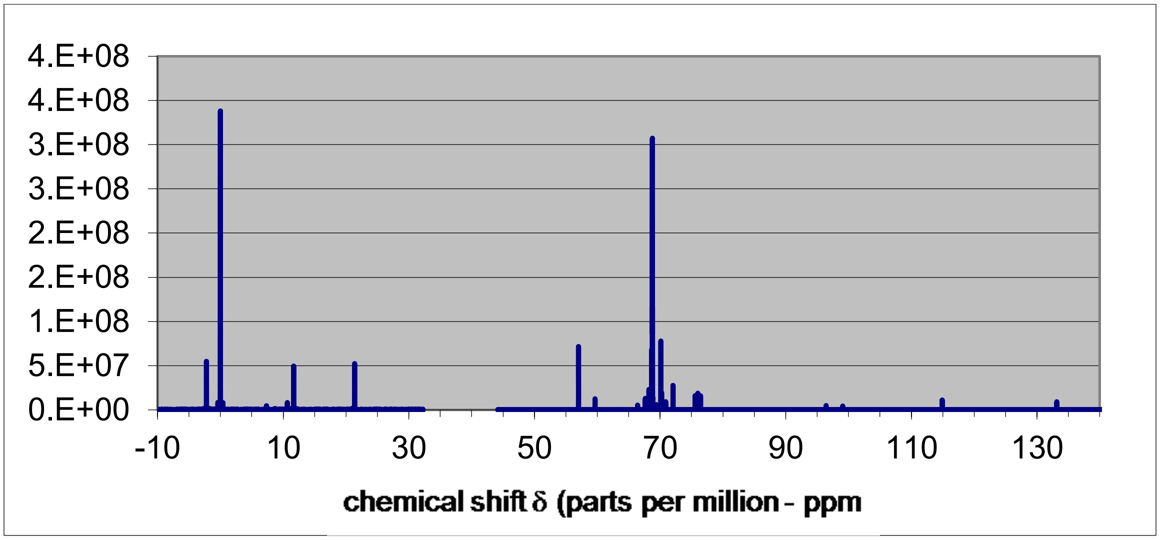

Figure B.2-1 C-13 NMR Spectrum of Silwet L-77 Lot#11DSVX019 (AD Sample ID 300285985)

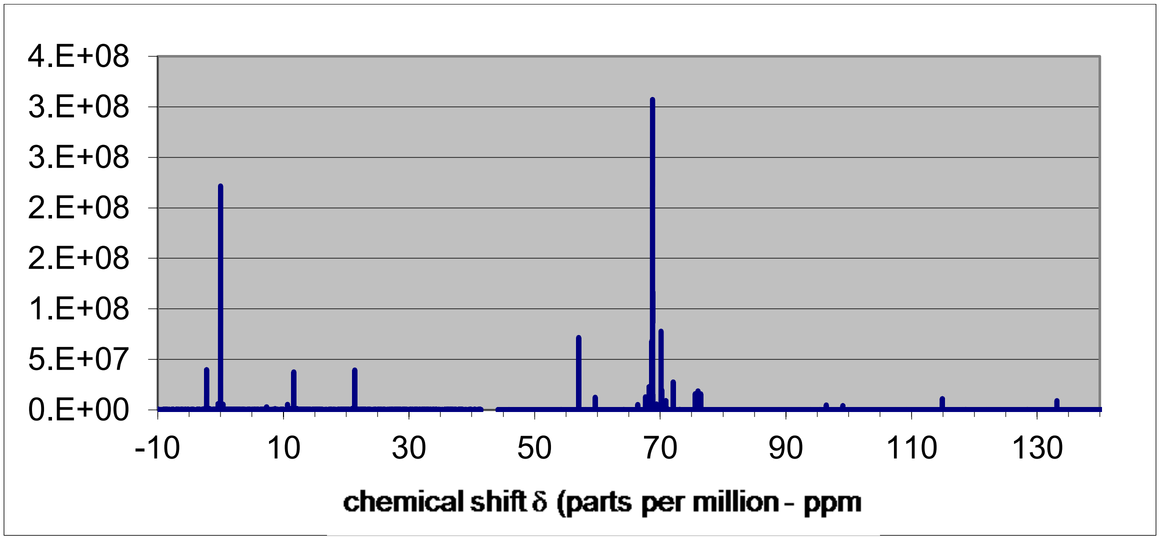

Figure B.2-2 C-13 NMR Spectrum of Silwet L-77 Lot#11CSVX013 (AD Sample ID 300285985)

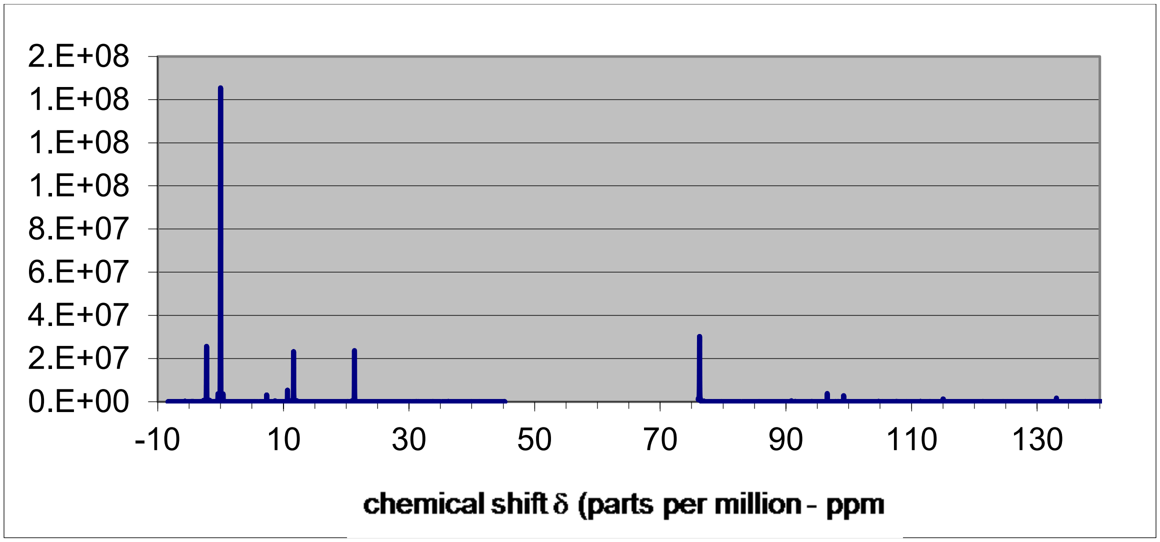

Figure B.2-3 C-13 NMR Spectrum of Y-17580 Lot#11VSVC325 (AD Sample ID 300285985)

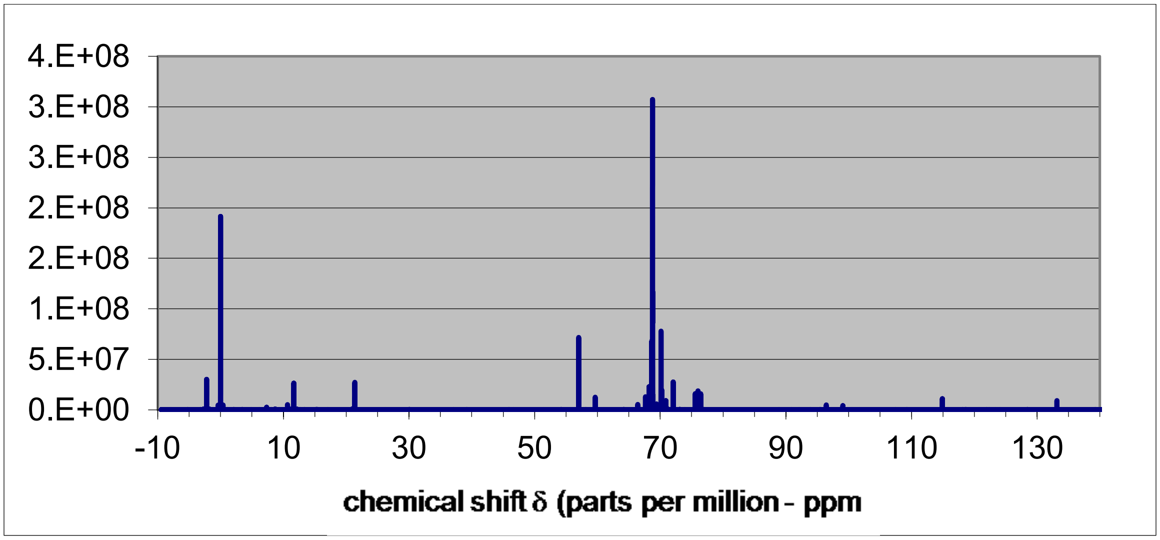

Figure B.2-4 C-13 NMR Spectrum of Silwet L-77 Siovation Lot#110684-0413 (AD #300285985)

B.3 Si-29 NMR

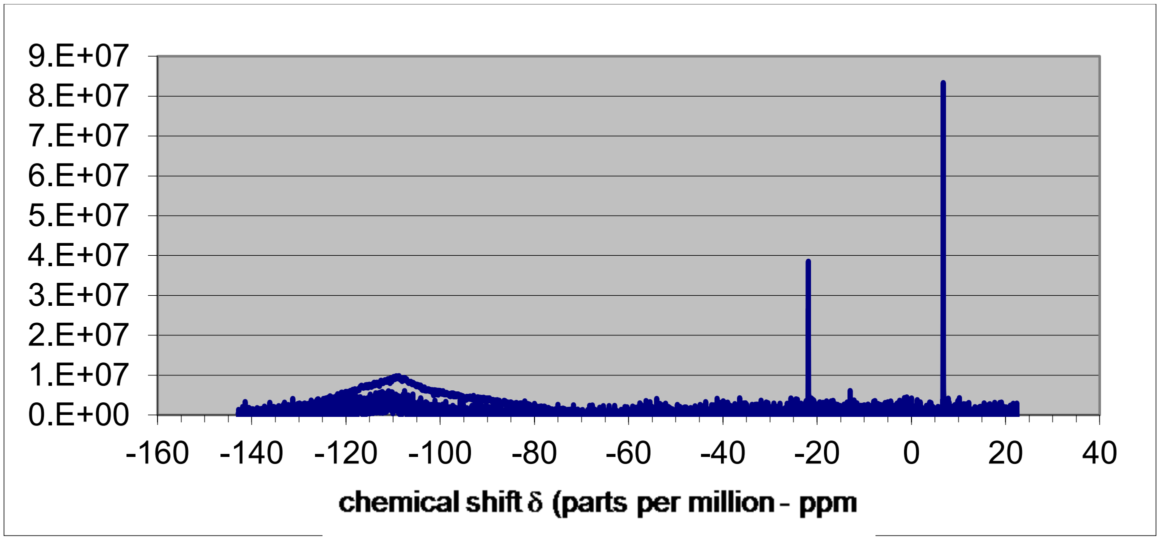

Figure B.3-1 Si-29 NMR Spectrum of Silwet L-77 Lot#11DSVX019 (AD Sample ID 300285985)

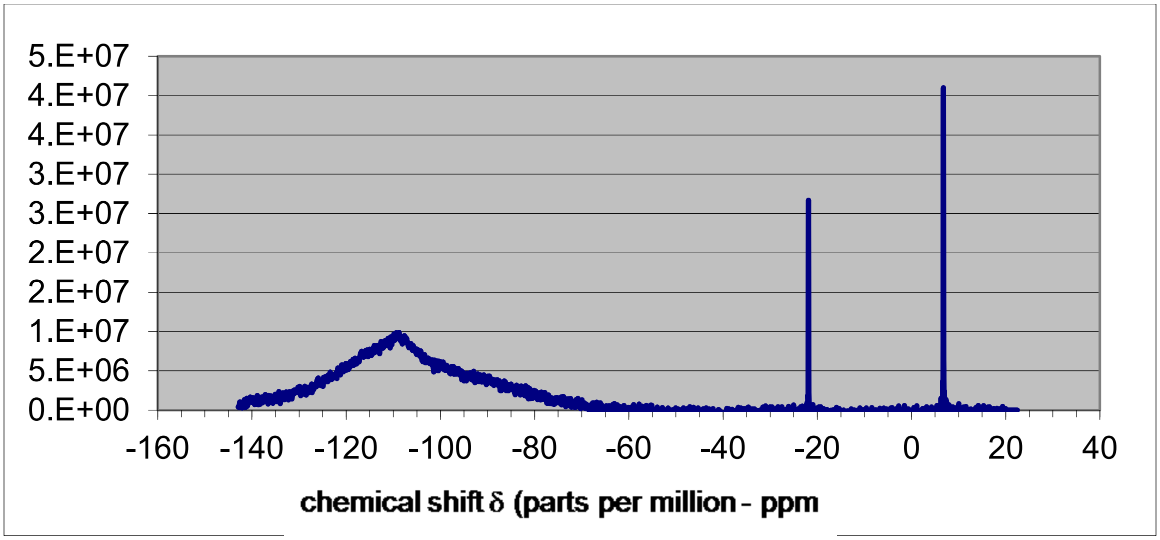

Figure B.3-2 Si-29 NMR Spectrum of Silwet L-77 Lot#11CSVX013 (AD Sample ID 300285985)

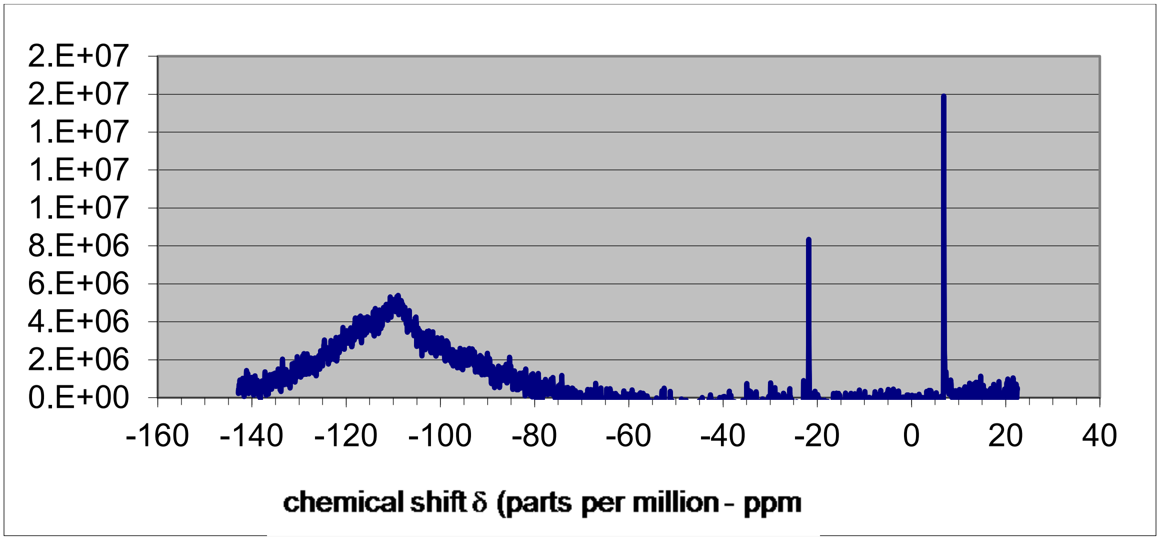

Figure B.3-3 Si-29 NMR Spectrum of Y-17580 Lot#11VSVC325 (AD Sample ID 300285985)

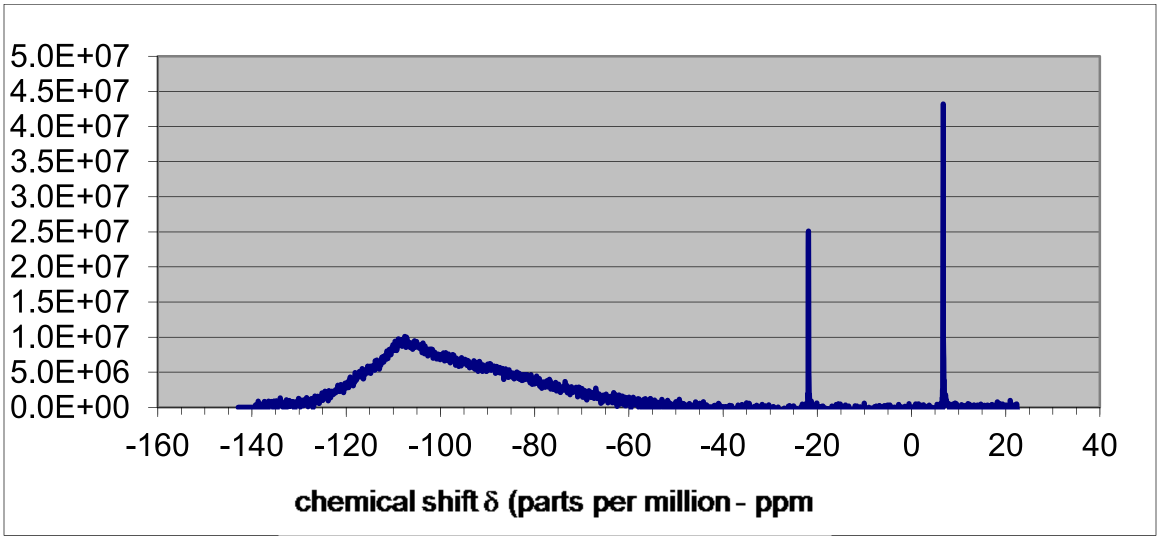

Figure B.3-4 Si-29 NMR Spectrum of Silwet L-77 Siovation Lot#110684-0413 (AD #300285985)

Distribution List

A. B. Barnes, 999-W
S. D. Fink, 773-A
B. J. Giddings, 786-5A
C. C. Herman, 999-W
S. L. Marra, 773-A
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
C. J. Bannochie, 773-42A
J. F. Iaukea, 704-30S
J. E. Occhipinti, 704-S
D. K. Peeler, 999-W
J. W. Ray, 704-S
D. C. Sherburne, 704-S
M. E. Stone, 999-W
J. R. Zamecnik, 999-W
J. M. Bricker, 704-27S
T. L. Fellinger, 704-26S
E. W. Holtzscheiter, 704-15S
A. V. Staub, 704-27S
M. T. Keefer, 766-H
D. P. Lambert, 999-W
D. C. Koopman, 999-W
J. D. Newell, 999-W
D. R. Best, 999-W
R. E. Eibling, 999-W
F. F. Fondeur, 773-A
W. T. Riley, 999-W
A. P. Fellinger, 773-41A