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WASTE TREATMENT PLANT LAW EVAPORATION: ANTIFOAM PERFORMANCE (U)

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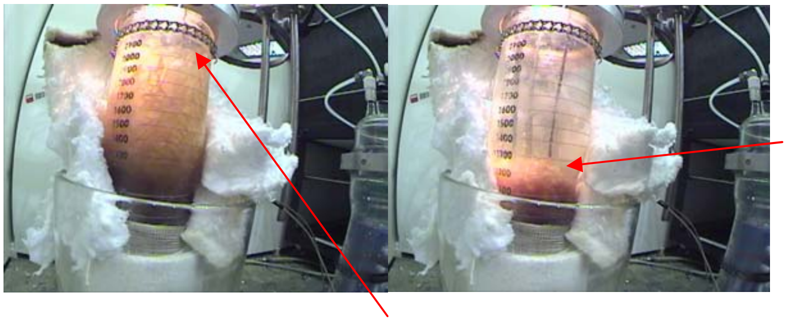

Liquid Height with Antifoam

Height of Foam without Antifoam

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DE-AC09-96SR18500

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LIST OF ACRONYMS

ADS	Analytical Development Section
amu	atomic mass units
DOE	Department of Energy
ESI MS	ElectroSpray Ionization Mass Spectrometry
GPC	GEL Permeation Chromatography
HS GC-MS	HeadSpace Gas Chromatography Mass Spectrometry
ICP-ES	Inductively Coupled Plasma-Emission Spectroscopy
LAW	Low Activity Waste
Mn	Number average Molecular Weight
Mp	Peak Molecular Weight. (The center of the molecular weight peak.)
Mw	Weight average Molecular Weight
NAS	Sodium Aluminosilicate
pAN102	Pretreated AN-102
pAN107	Pretreated AN-107
PS/DVB	Poly-styrene/ Di-Vinyl Benzene
RPP-WTP	River Protection Project-Waste Treatment Plant
SBS	Submerged Bed Scrubber
SRTC	Savannah River Technology Center
Sr/TRU	Strontium/Transuranic
TGA	Thermal Gravametric Analysis
WSRC	Westinghouse Savannah River Center
XRD	X-Ray Diffraction

1.0 SUMMARY OF TESTING

Evaporation is employed in several places in the Waste Treatment Plant (WTP) pretreatment process to minimize the volume of waste that must be treated in down-stream vitrification processes. Evaporation is the first unit process in pretreatment (Waste Feed Evaporators) applied before LAW vitrification (Treated Feed Evaporator), and concentrates ion exchange eluate (Cs Eluate Evaporator) prior to HLW vitrification. Secondary-waste recycle streams from the off-gas scrubbing system have been the major contributors to the total overall flow of both the Treated Feed Evaporator, and the Treated LAW Feed Evaporator. Prior testing of evaporation systems for process feed was completed to support compliance with regulatory permits and to prepare a model of the evaporation system. Previous tests also indicated a marked tendency for foaming in the WTP evaporators.[3]

To date, evaporation testing on a small scale could not attain the design basis evaporator flux. This has been the first work performed that investigates foaming during evaporation at design basis flux. The degree of foaming is known to increase with evaporator flux rate. Evaporation experiments to simulate both the Treated LAW Evaporator and the Waste Feed Evaporator were performed.

This report describes the work performed to determine the performance and fate of several commercial antifoams during evaporation of various simulants of Envelope A, B, and C mixed with simulated River Protection Project Waste Treatment Plant (RPP-WTP) recycle streams. Chemical and radiation stability of selected antifoams was also investigated. Contributors to this effort include: Illinois Institute of Technology (IIT), DOW Corning Analytical, and Savannah River Technology Center (SRTC).

1.1 OBJECTIVES

The overall objectives of the LAW Evaporation: Antifoam program are:

- **Evaluate the foaming tendencies of LAW Feed and LAW Melter Feed [7] in the WTP plant conditions.** In these tests, SRTC/IIT has determined the foaming tendencies in the LAW evaporator systems.
- **Identify through testing and analysis a suitable anti-foam reagent for use in plant evaporators.** In these tests, SRTC/IIT has made an initial antifoam recommendation for the LAW evaporators.
- Determine if tributyl phosphate (TBP) and normal paraffin hydrocarbons (NPH) create problems in evaporator operation and if so, at what concentration do these problems occur. In these tests, SRTC/IIT has determined the concentration of TBP and NPH that effect foaming in the evaporator.

To achieve these objectives, the RPP-WTP R&T organization via SRTC conducted bench-scale testing with simulants. Experimentation with the most appropriate mixtures from test matrices produced the following data:

1.2 CONDUCT OF TESTING

The four investigative phases are described in this report. They are:

1. Illinois Institute of Technology was contracted by SRTC to investigate several commercial antifoams. Based upon their initial investigations, several commercial antifoams were recommended for further testing.

2. DOW was contracted to perform antifoam stability experimentation and analysis. Antifoams to be tested were those recommended for further study by IIT.

3. SRTC Immobilization Technology Section (ITS) investigated the performance of three of these antifoams in high flux evaporation studies. A fourth antifoam was tested (Pulpaid®) by both DOW and IIT investigators. This antifoam required dilution with a solvent other than water. This was deemed undesirable by the customer, and eliminated from contention. DOW also demonstrated that Pulpaid® was not highly stable in caustic media like the other antifoams under consideration. This study resulted in the recommendation of DOW Q2-3183A as the antifoam of choice.

4. SRTC ITS performed irradiation studies of simulants containing the best performing antifoam. The simulants were subsequently analyzed by DOW analytical.

1.2.1 Antifoams Tested

Three DOW antifoams were tested. DOW analytical tested a fourth antifoam (DOW Pulpaid® Concentrate 3472), but this antifoam was eliminated as a possible candidate for ease of processing criteria.

1. DOW Q2-3183A
2. DOW 2-3930
3. DOW 1520 US
4. DOW Pulpaid® Concentrate 3472

These antifoams were chosen based upon discussions with DOW Corning experts and IIT researchers. IIT researchers are internationally recognized for their expertise in antifoam development and have developed and deployed antifoams for the SRS Defense Waste Processing Facility.

1.3 RESULTS AND PERFORMANCE AGAINST OBJECTIVES

The results contained in this document met the objectives contained in the RPP Task Specification: 24590-PTF-TSP-RT-01-005, Revision 0 as related to antifoam testing.

Key findings of these investigations are:

1. Studies conducted under this task have shown that the peak foaminess of Hanford waste will occur well after salt crystals precipitate from the solution thus indicating a particle stabilized foam mechanism. However, Hanford radioactive waste has been shown to foam severely when boiling is first initiated and no insoluble particles are present in the waste[3]. This indicates the presence of a surface-active agent that may be causing foaming at the onset of boiling. Analysis of the data from the evaporation of actual Hanford radioactive tank waste (241-AN102) indicates that foaming occurred at approximately 5 M Na. Additionally, foaming of Hanford waste in the 242-A Evaporator has been excessive, causing plant shutdown especially after the waste becomes saturated and solids begin to precipitate[4]. Thus, the foam stabilization mechanism in actual Hanford radioactive waste is two fold: (1) Surfactant stabilized foams at the low sodium concentrations and (2) Solids stabilized foams at high sodium concentrations. The solids stabilized foams may be aggravated by the presence of organic complexants.

2. Q2-3183A and 1520-US antifoams have good chemical stability in caustic media.

3. DOW 2-3930 and Pulpaid® 3472 antifoam has limited chemical stability in caustic media.

4. DOW Q2-3183A proved to be the best antifoam in Treated LAW evaporation studies.

5. DOW Q2-3183A has demonstrated very good chemical and radiation stability while being most effective as an antifoam agent for both solids stabilized foaming and surfactant based foaming.

6. A concentration of 1400 ppm has demonstrated comparable antifoam character to 2800 ppm, thus making higher concentrations unnecessary.

7. Waste feeds studied have less of a tendency to foam in a small-scale test and therefore antifoam performance was indeterminate. Evaluation of the Q2-3183A antifoam agent in the WTP pilot evaporator will be conducted. The simulants used for the Treated Feed Evaporation studies are foamier than the simulants used in the Waste Feed Evaporation experiments. Therefore Q2-3183A is recommended for use in the Waste Feed Evaporator pending results of WTP pilot evaporation experiments.

8. A de minimis level of 300 ppm for TBP/NPH was demonstrated by this task for the Treated Feed Evaporation system.

9. Concentration levels of up to 10,000 ppm of TBP/NPH have been tested with simulated waste feed recycles with no significant increase in foaminess. Concentrations higher than this are not expected in WTP. DOW Q2-3183A was able to reduce the foaminess of this feed even in the presence of 1% TBP/NPH. However, studies conducted using simulated treated LAW feed indicate that a lower de minimis value (<300 ppm) should be placed on the Waste Feed Evaporator system if the concentrations of complexants in the ultrafiltration recycle increase. Concentration levels of 10,000 ppm were tested, but concentration levels greater than 300 ppm are not expected in the incoming feed to WTP.

10. The presence of TBP/NPH in the Treated LAW Evaporator is considered unlikely[5] and was not studied further by SRTC. Previous ultrafiltration studies conducted by SRTC have shown that the filters will only allow soluble TBP/NPH through the filter. The solubility limit is < 1ppm TBP/NPH. Thus, the 300 ppm limit imposed by this study is well in excess of any actual concentration of TBP/NPH likely to be processed by the Treated Feed Evaporator.

11. Use of any of these antifoams leads to the potential for the formation of dimethyl mercury[6] in the evaporator if the temperature is increased above 50ºC.

1.4 QUALITY REQUIREMENTS

This work was conducted in accordance with the RPP-WTP QA requirements specified for work conducted by SRTC as identified in DOE IWO MOSRLE60. SRTC has provided matrices to WTP demonstrating compliance of the SRTC QA program with the requirements specified by WTP. Specific information regarding the compliance of the SRTC QA program with RW-0333P, Revision 10, NQA-1 1989, Part 1, Basic and Supplementary Requirements and NQA-2a 1990, Subpart 2.7 is contained in these matrices.

Researchers have followed the WSRC Quality Assurance Program, which was approved by WTP, and the WSRC Quality Assurance Management Plan (WSRC-RP-92-225). This program applied the appropriate quality assurance requirements for this task from NQA-1-1989, and NQA-2a-1990, Part 2.7, as indicated by the QA Plan Checklist in Section VIII of the Task Technical and Quality Assurance Plan for LAW Evaporation: Antifoam/Defoamer Testing for Low Activity Waste Solution, WSRC-RP-2001-00791, SRT-RPP-2001-00142, Rev. 0.

The SRTC Quality Assurance Department reviewed and evaluated DOW Corning Quality Assurance Program prior to the placement of the purchase order to DOW Corning. The evaluation performed was to ensure that the WTP QA requirements were imposed to DOW Corning, and that DOW Corning was compliant to the stated WTP QA requirements. DOW Corning maintains an ISO Quality Management System which is certified by an accredited ANSI-RAB certifying agent. The scope of work performed by DOW for this task (Testing and Analytical Services) in accordance with their ISO certified QA Program, meets the intent of NQA-1-1989 Quality Assurance Program applicable criteria.

A non-applicability justification for identifying Quality Assurance Program requirements to work performed at the Illinois Institute of Technology by Dr. Darsh T. Wasan was conducted by SRTC and agreed upon by RPP-WTP QA prior to initiating this work. Work conducted at the IIT under the direction of Dr. Darsh T. Wasan, Vice President and Motorola Professor of Chemical Engineering was considered for applicability to NQA-1, 1989. All the NQA-1, 1989, requirements were determined to be non-applicable to IIT and were documented in the task technical and quality assurance plan for this task[7].

1.5 ISSUES

No issues were raised concerning foaming in either the Treated LAW Evaporation process or the Waste Feed Evaporation process in the WTP. Several recommendations for future work have been made based upon information that has come to light in this investigation. These are:

- Fate of antifoam in the ultrafiltration process
- The impact of antifoam on slurry rheology. Antifoams contain surfactants that can affect (increase or decrease) slurry yield stress and consistency.

1.6 RECOMMENDATIONS

1. DOW Q2-3183A antifoam is recommended for use in all subsequent WTP testing and for use in the WTP Waste Feed and Treated Feed evaporators. However, given that antifoam technology will advance by the time the WTP will be started up, it is recommended that WTP evaluate the current antifoam technology and determine if a more suitable antifoam is available just prior to startup of the WTP.
2. DOW recommends that Q2-3183A be diluted with water 3-10 parts water to 1 part Q2 antifoam. DOW also recommends that the diluted antifoam be used immediately after mixing with water.
3. Dilution reduces the viscosity significantly and allows fine silicon solids to settle out of the suspension. The particles are readily suspended when agitated. However, if left standing in dead legs of transfer piping, the fine silicon solids (mean particle size of 15 microns.) may accumulate over time. Therefore, SRTC recommends that diluted antifoam transfer piping should be designed to minimize low points that may allow solids to accumulate over time.
4. Addition of the antifoam to the process without dilution should be considered; but, demonstration of this procedure has not been completed at this time.

2.0 DISCUSSION

2.1 IIT EXPERIMENTAL METHOD

As was recommended by SRTC, the evaporation flux rate was improved from 0.09 ml/min sq.cm (0.9 kg/min sq.m.) to 0.20 ml/min sq.cm (2 kg/min sq.m.) at 1 atmospheric pressure. To achieve the requested evaporation flux rate, modifications to the experimental set-up were made. The change to the existing set up was the addition of a metallic jacket, which acted as a heat accumulator. A heating coil that improved the heating area for the simulant inside the Fleaker™ was used in between the metallic jacket and the Fleaker™. A powerful hot plate was installed to give a better heating surface area. All these changes helped in significantly improving the evaporation flux rate. A schematic of the experimental setup in Figure 2-1 shows the new features.
Simulant was added batchwise. Liquid level and foam height were recorded as the solution was concentrated. All solutions were concentrated under vacuum (≅110 mm Hg (torr)).

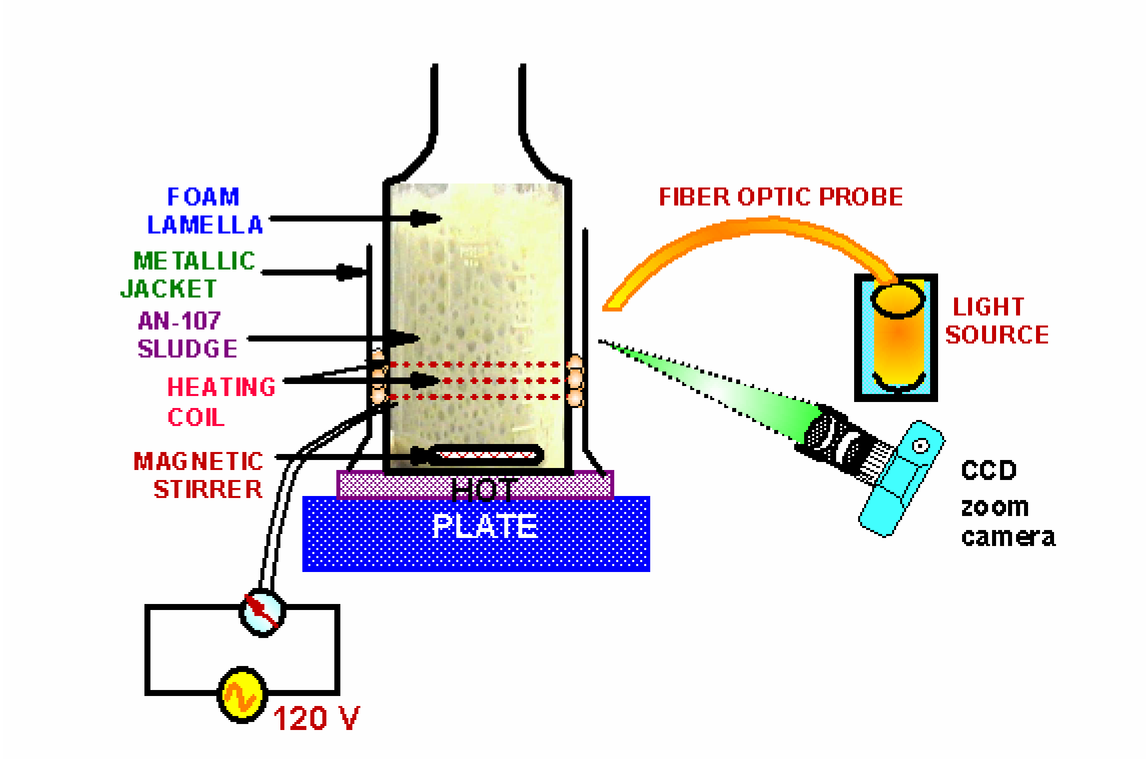

Figure 2-1IIT Experimental Setup

2.2 DOW ANALYTICAL EXPERIMENTAL METHOD

2.2.1 Method Applied for Chemical Stability Determination

Samples of all three antifoams were prepared in aqueous 3.0 M NaOH and were aged at 60 °C for the specified lengths of time ranging from 0 to 24 hours. The sample concentrations were adjusted from the requested 1000 ppm in order to obtain an acceptable response for the GEL Permeation Chromatography (GPC) analyses. The 1520 samples were prepared at 2000 ppm, the Q2-3183 samples were prepared at 1500 ppm and the 2-3930 samples were prepared at 3000 ppm. After heating, toluene was used to extract the polymer from the aqueous solution. The toluene phase was then filtered and analyzed by GPC.

An attempt was also made to determine the percent recovery of the polymer from the aqueous solutions. It proved to be difficult to extract the polymer from the antifoam directly with toluene in order to determine an initial polymer level. Consequently, the zero hour sample (sample shaken with toluene and 3 M NaOH without heating) was used as the basis for determining percent recovery for the remaining samples. Based on the extraction conditions, it is estimated that the error involved in the recovery could be as high as ±10%, meaning that there was only a small difference in the amount of polymer extracted as a function of aging time.

GC analyses were conducted on pentane extracts of aged solutions of the samples. The gas chromatograph was equipped with a flame ionization detector and a capillary column with a polydimethylsiloxane stationary phase.

GPC analyses were conducted on toluene extracts of the aged antifoam solutions using toluene as the eluent, PS/DVB size exclusion columns, a differential refractive index detector, and a relative polystyrene calibration curve for calculation of molecular weight averages.

2.2.2 Method Applied for Radiation Stability Determination

Samples were analyzed by headspace gas chromatography mass spectrometry (HS GC-MS) for the detection of low molecular weight cyclic siloxanes. Head space analysis was used to look for small fragments of antifoam generated by irradiation. This method was chosen since low molecular weight cyclic siloxanes tend to be volatile. A standard of decamethylcyclopentasiloxane was analyzed to obtain an estimated detection limit of 10 ppm for this and similar low molecular weight, volatile siloxanes. It is a reasonable assumption to assume that this HS GC-MS method will detect similar siloxane molecules with less than a molecular weight of approximately 600 amu (atomic mass units). Samples were also analyzed by positive ion electrospray ionization mass spectrometry (ESI MS) for the detection of ethylene glycol and propylene glycol. A standard containing ethylene glycol and propylene glycol was analyzed to obtain an estimated detection limit of 10 ppm for these two compounds. None of the target compounds was detected above the estimated reporting limit of 10 ppm.

Photograph 2-1 Cobalt Irradiation System

2.3 HIGH FLUX EVAPORATION EXPERIMENTAL EQUIPMENT

Initial experiments quickly demonstrated that the degree of foaming increases with boiling rate. In order to predict the degree of foaming that will be experienced in the WTP at the Hanford site, a high flux evaporation system was built. This lab scale system can produce boil-up flux rates comparable to those expected in the full scale process of 0.031 lbm/s-ft2.

A diagram of the bench-scale evaporator assembly used in treated feed evaporation studies is shown in Figure 2-1. The major components of the evaporator assembly were composed of borosilicate glass, quartz, Teflon®, and stainless steel. The evaporator vessel, constructed by SRTC glass shop personnel, was made of quartz glass with an inner diameter of 3.5 inches and a total volume of 2200 ml. A boil-up rate of 56.4 gm/min (0.12 lbm/min) matches the design basis flux in the WTP (0.031 lbm/s-ft2) (see Table A-14). A stainless steel heating coil was purchased and was placed inside the evaporator vessel to facilitate additional heat input, A Fisher 1000-watt IR 4100 infrared hotplate was used to supply adequate heat and stir the mixtures by magnetic coupling of a 1.5 inch, Teflon®-coated magnetic stirrer bar. A digital Fisher Brand pressure/vacuum gauge was used to monitor the internal pressure of the evaporator system while a thermometer monitored the temperature of the mixtures. Vacuum was pulled on the evaporator system by a Vacuubrand MZ 2C diaphragm pump.

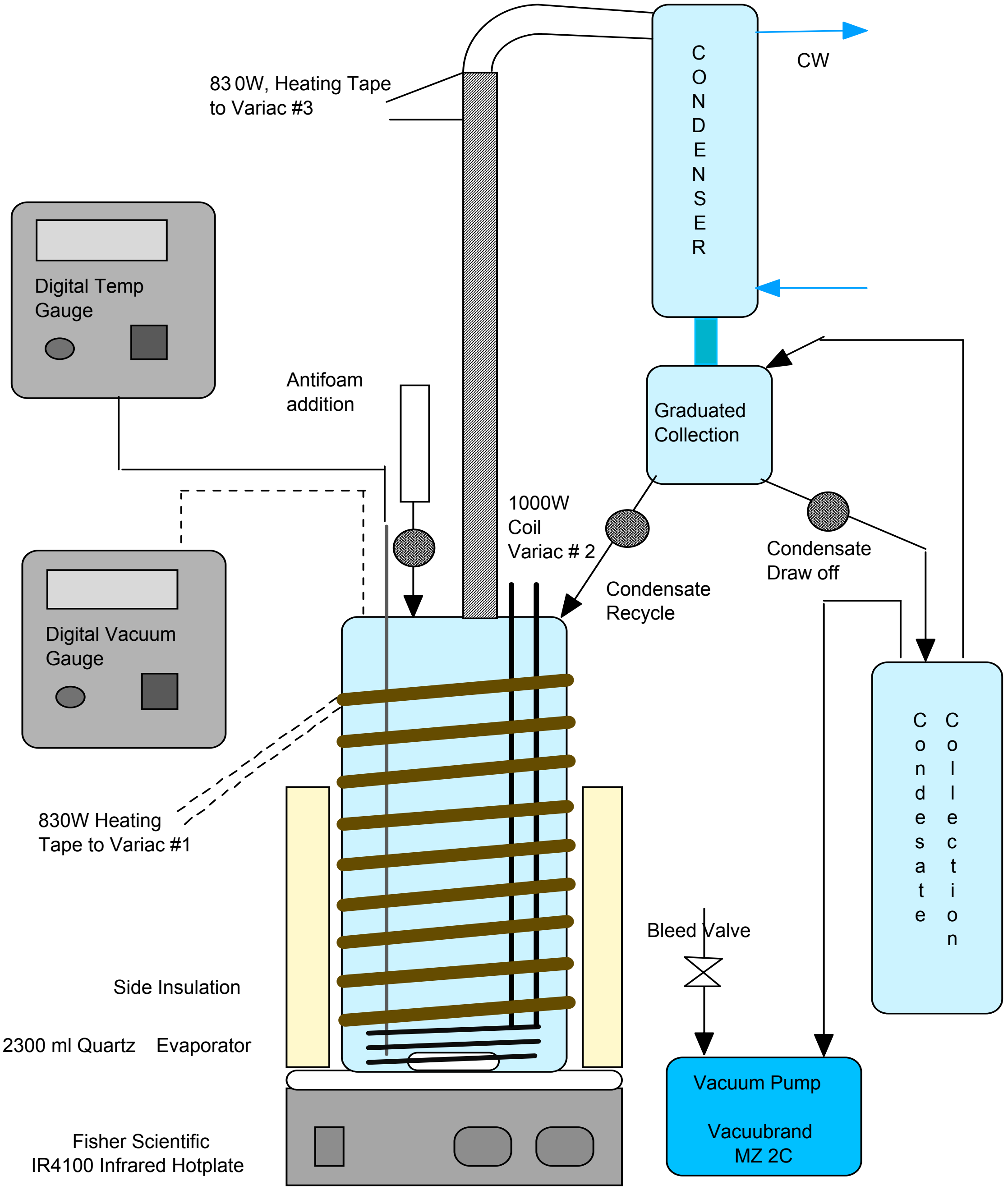

Figure 2-2 High Flux Evaporation Diagram

Photograph 2-2 High Flux Evaporation Equipment

2.3.1 Methods of Testing

Each experimental run was performed by the following procedure:

1. Initial charge of 1500 ml of a 50/50 mixture of feed and recycle
2. Evaporator vacuum initiated and maintained at 27 in Hg.
3. Heat applied to the off gas line (40% of Max), to prevent condensation
4. Full power applied to the hot plate while condensate is recycled to the evaporator
5. When steady boiling is achieved, condensate is routed to collection.
6. Time to collect 100 ml of condensate is measured with a stop watch.
7. Evaporator level (foam) is visually determined as condensate is being collected.
8. Power to the internal coil is stepped up from 0, 30, 60, and 100 percent.
9. Evaporator level (foam) and time to collect 100 ml increments of condensate is recorded at each power setting.
10. Power and evaporator vacuum are stopped after 500 ml of condensate is collected.
11. A 500 ml charge of 50/50 mixture of feed and recycle is added.
12. Steps above are repeated a total of 7 times.
13. A total of 5 liters of material is evaporated down to 1 liter of evaporator concentrate.
14. Condensate is then placed in recycle mode at 100 % plate power.
15. Diluted antifoam is added to the evaporator at boiling under vacuum conditions.
16. Time to collect 20 ml of condensate is measured with a stop watch and the condensate returned to the evaporator.
17. Internal coil power settings are repeated and boil-up rates are measured along with evaporator level.
18. The bottom heating tape is used to achieve maximum boil-up rates.

Figure 2-3 presents the calculated sodium molarity profile for the treated feed evaporation experiments as feed is added and condensate is removed. A sodium profile for the waste feed evaporator experiments would have half the sodium concentration due to the reduced starting sodium concentration (1 molar).

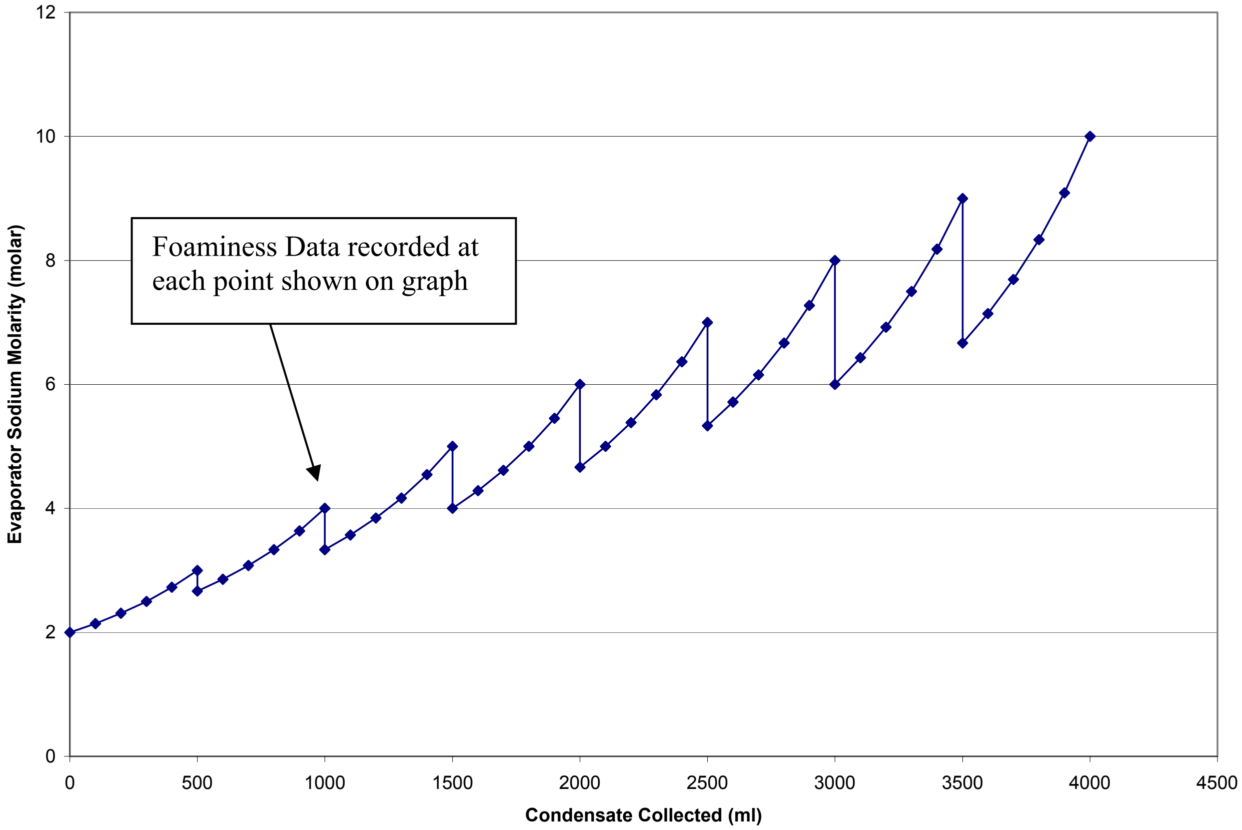

Figure 2-3 Typical Treated LAW Evaporator Experiment Sodium Molarity Profile All Points Are Calculated Na Concentrations

2.3.2 Method of Analysis

Data collected above was used to determine the boil-up rate and the percent foaminess during boiling. Percent foaminess was calculated using a material balance for the evaporator system. The volume of material feed to the evaporator was known along with the volume of condensate collected. This allows the volume of liquid in the evaporator to be determined. The total volume (including foam) of the evaporator was read from the graduations on the evaporator vessel. Percent foaminess is then calculated by subtracting the volume of liquid in the evaporator from the total and dividing by the liquid volume. Multiplication by 100 gives the percent. A plot of the percent foaminess versus boil-up rate was made for each set of conditions. The data was curve fitted to a linear profile forced through the origin. Results are presented in the results sections.

The greatest error is introduced by the determination of total evaporator volume, which fluctuated widely from moment to moment. A single technician was used to perform all of these observations to maintain consistency between runs. With this subjective error on a key reading, only differences in slope of greater than 15% were considered significant.

2.3.3 Treated LAW Evaporation Feed Simulants

The tanks within Envelope C are 241-AN-102 and 241-AN-107. Envelope C waste simulants are characterized from Hanford B plant waste that is produced during the Cs/Sr separation and encapsulation processes. Their high organic carbon contents, a result of organic complexing agents and their decomposition products, distinguish Envelope C wastes. Due to the complexing agent's concentration, an Envelope C waste requires the removal of increased ^{90}Sr and transuranic (TRU) component concentrations via Sr/TRU precipitation and filtration. The Sr/TRU precipitation procedure was used to pretreat the AN102 simulant. Pretreated AN102 was prepared by using 19 M NaOH, 2 M $Sr(NO_3)_2$, and 1 M $NaMnO_4$ to precipitate strontium and transuranic metals from the solution (Sr/TRU precipitation).

SRTC had previously pretreated AN102 via Sr/TRU precipitation. The Hanford Tank AN-102 simulant used for this work is a product of the lab-scale filtration study. For Sr/TRU removal, the Hanford waste was diluted to 6 M Na before increasing free hydroxide concentration by 0.8 M with 19 M NaOH, strontium concentration by 0.075 M using 1 M $Sr(NO_3)_2$, and manganese concentration by 0.05 M with 1 M $NaMnO_4$. This precipitated AN-102 Envelope C simulant was then cross-flow filtered, producing a filtrate with a measured density of 1.276 g/ml. Dark solids produced by post-filtration precipitation were observed when the filtrate was transferred. The filtered supernate of waste simulant Pretreated AN102 was used for Envelope C mixtures. Analytical results for pretreated AN102 simulants are reported in Appendix A Table A- 2.

Envelope C waste simulant, (AN-102) permeate from cross-flow filtration experiments was used in all treated LAW evaporation experiments. This feed was produced as a byproduct from strontium TRU precipitation and filtration experimentation. No ion exchange treatment was performed upon this feed, but any effect upon foaming is considered insignificant. The strontium TRU precipitation conditions which were employed to produce this permeate were:

- DI water addition to reduce sodium molarity from 6.5 to 6 molar,
- 50 wt% NaOH added to bring total hydroxide to 1 molar,
- Strontium nitrate addition (17 minute addition) to 0.075 molar,
- Sodium permanganate addition (17 minute addition) to 0.05 molar,
- Chemical addition at 50^{o} C followed by 4-hour hold at temperature.

Further dilution of this simulant with DI water was performed to reduce the specific gravity of the permeate to 1.22 gm/ml. This requirement is implemented in ion exchange process operations and was duplicated here.

Small-scale evaporation process simulations were performed using non-radioactive simulants. Treated LAW evaporation runs were performed using simulants that had been generated previously in cross-flow filtration experiments. Those experiments generated a cross-flow filtration permeate which was evaporated in this study. No ion exchange of this material was performed. No TBP/NPH was added to these feeds, because previous work has shown that these organics do not pass the filtration process at levels above solubility, and they have an affinity for solid surfaces, making transport out of ion exchange unlikely.

2.3.4 Treated LAW Evaporation Recycle Simulants

Two LAW melter off gas recycle simulants were used in this study; Duratek LAW Submerged Bed Scrubber (SBS), RM-01-025 (C2) and Duratek LAW SBS, B1 R9/04/02. Analytical analysis of these materials is presented in Appendix A.

Off-gas condensates collected from pilot-scale melter runs at Duratek were obtained for analytical testing at SRTC. Condensates were shipped from Duratek in either 55-gallon stainless steel drums or 55-gallon polyurethane drums. Before pulling samples, drum contents were thoroughly mixed with a circulating tube mixer. The LAW recycles used are designated as B1, and C2 according to melter feed formulations processed by the Duratek LAW melter. The B1, and C2 designations refer to the glass formulation for Subenvelopes B1, and C2 as categorized. Table 2-1 presents measured physical and chemical property data, respectively, for each recycle utilized. With very low total and insoluble solids contents, the Duratek Subenvelopes B1, and C2 LAW SBS recycles had densities that were virtually identical to that of water. Duratek C2 recycle had the highest sodium content. Lithium solids found in XRD analyses are due to lithium from all three recycles, with the highest concentration of lithium from C2 recycle.

Table 2-1 Physical Properties of Duratek LAW SBS Recycles

Physical Properties	**B1**	**C2**
pH Before Mixing	7.6	6.9
Density (g/ml)	1.00	1.03
Wt. % Insoluble Solids	0.11%	0.15%
Wt. % Total Solids	0.46%	1.61%

2.3.5 Waste Feed Evaporator Simulants

The foaming tendencies of UF Recycles with Envelope A, B, and C mixtures blended with HLW SBS recycle were investigated in the rig described in section 3.3. When this testing was initiated the best available information from WTP assumed that recycles were blended in various ratios as received into the plant wash vessel. Multiple solutions were tested as part of the Waste Feed Evaporation program.[11]

The ultrafiltration recycle consists of five different solutions: 1st wash, leach, 2nd wash, acid cleaning, and caustic rinse solutions. For the purposes of this testing, the recycles are blended together prior to transfer to the evaporator feed tank and subsequent blending with the melter off gas condensate. Simulants were generated for each individual stream in the recycle and blended together based upon the volume calculations conducted by WTP[8]. Formation of gels in the blended streams led to the addition of a caustic adjustment step to pH=13 in the recycle process. The basis and composition for each stream and the volume ratios of the blended recycle were documented in an interoffice memo, SRP-GDP-2002-00095 and are shown in Appendix A – Table A-4 through Table A-8.

HLW SBS Recycle Simulants

The condensate and scrub solutions generated during vitrification of the HLW are recycled back to the waste feed evaporator. Vitreous State Laboratory (VSL) pilot plant studies of the vitrification process had generated large amounts of this condensate. A sample of this condensate, with an as received pH of 3.6, was obtained from VSL and utilized during this study. Sample analysis of this condensate is shown in Table 2-2. XRD analysis indicated that the solids present in the sample were primarily quartz. This sample was utilized for all envelopes.

Table 2-2 HLW Melter Off-Gas Submerged Bed Scrubber Composition after Neutralization

Element / Anion	Molarity
Aluminum	2.77E-03
Boron	4.75E-02
Cadmium	6.60E-05
Calcium	2.47E-04
Chloride	1.49E-02
Fluoride	4.53E-03
Iron	1.60E-03
Lithium	2.99E-04
Manganese	2.20E-04
Nickel	8.70E-05
Nitrate	5.00E-03
Oxalate	3.10E-04
Phosphate	3.27E-03
Potassium	2.00E-04
Silicon	2.87E-03
Sodium	1.00E-02
Strontium	4.12E-04
Sulfate	3.96E-03
Zinc	5.18E-03
Zirconium	8.80E-05

Envelope A UF Recycles Simulants

The first wash for Envelope A was based upon dilution of the Envelope A matrix midpoint according to the dilution calculation provided by WTP.[7] The amount of oxalate was set to the same level as the waste feed on the assumption that the oxalate would be soluble to the same extent in the wash as it was in the waste feed. The leach solution and second wash were based on the assumption that the solids in the Envelope A waste were Envelope D solids. The compositions of leach and 2nd wash solutions from a PNNL study[9] on actual waste were used to generate the leach and 2nd wash simulants.

The acid cleaning solution was based on a WTP estimate[7] of the solids holdup in the filter system and the amount of acid cleaning solution to be utilized in cleaning the filter. The concentration of solids in the acid cleaning solution was determined and that amount of Envelope D simulated solids was dissolved in 2M nitric acid to produce the simulant. The caustic wash was simulated with 0.1M sodium hydroxide since all the solids held up in the filter were added to the acid cleaning solution. Compositions of the streams and blended recycle for Envelope A are shown in Appendix A - Table A- 5 and Table A- 6.

Envelope B UF Recycles Simulants

The recycle compositions for Envelope B were identical to the Envelope A streams since Envelope D solids were utilized to generate the expected compositions for the Envelope A recycle, with the exception of the first wash. The 1st wash was determined in the same manner as the 1st wash for Envelope A with the substitution of the AZ-102 supernate composition in place of the Envelope A matrix midpoint. Compositions of the streams and blended recycle for Envelope B are shown in Appendix A – Table A- 8.

Envelope C UF Recycles

The recycle for Envelope C differs from Envelopes A and B in that a leach step is not conducted. The recycle consists only of a 1st wash, acid cleaning solution, and caustic rinse. The 1st wash solution for Envelope C was obtained from pilot plant studies at the Engineering Development Laboratory of SRTC conducted with AN-102 simulants. The acid cleaning conducted in the pilot plant testing was not prototypical and was not utilized. A simulant for the acid cleaning solution was developed in the same manner as the acid cleaning solutions for Envelopes A and B. Compositions of the streams and blended recycle for Envelope C are shown in Appendix A- Table A- 7.

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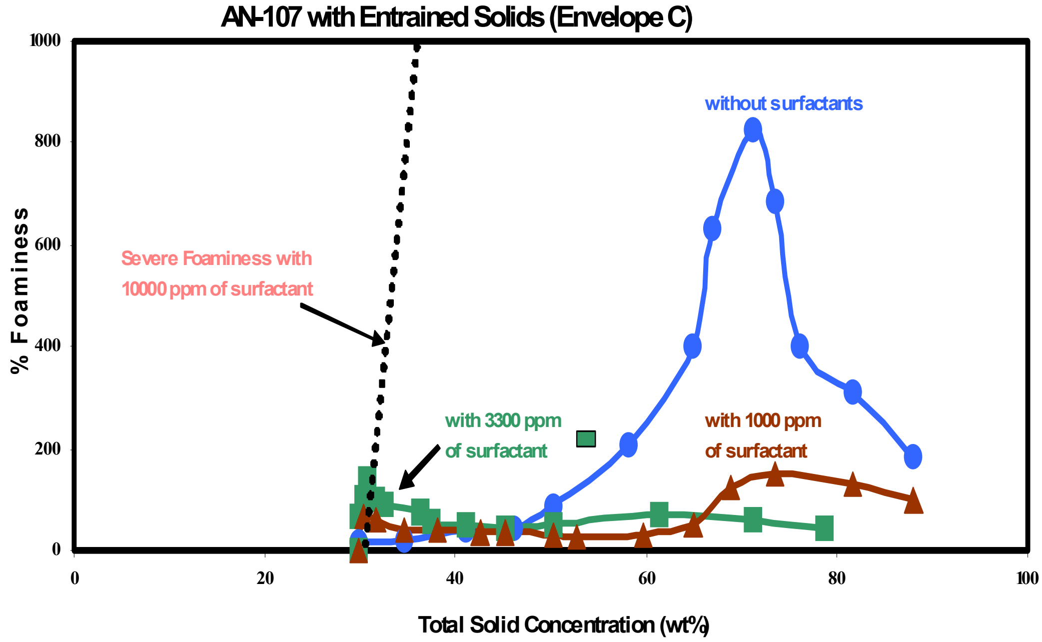
3.0 EXPERIMENTAL RESULTS

3.1 IIT INVESTIGATIONS

A copy of IIT's final report is presented in Appendix B. A review of the most important data is presented here.

IIT investigators stated that the mechanism of foam stabilization in three phase systems such as those in Hanford wastes involve insoluble waste particles in the foam lamella (interface between bubbles). These particles have both a hydrophillic and hydrophobic part that stabilizes foam.

IIT added commercially used surfactants *Hexadecyl tri-methyl ammonium bromide (cationic)* and *Dodecane sulphonic acid Na salt (anionic)* to AN-107 to study their effects on foaminess. These surfactants were found to be added as part of cleaning agents (Turco 4518) to Hanford Waste[10]. Addition of 3300 ppm of surfactant reduced foaminess by a factor 10 while 1000 ppm of surfactant reduced it by a factor of 5. Addition of 10,000 ppm of surfactant caused severe foaminess in AN107. This indicates that Hanford AN107 waste is likely to foam if the concentration of surfactant is between 3300 ppm and 10,000 ppm.

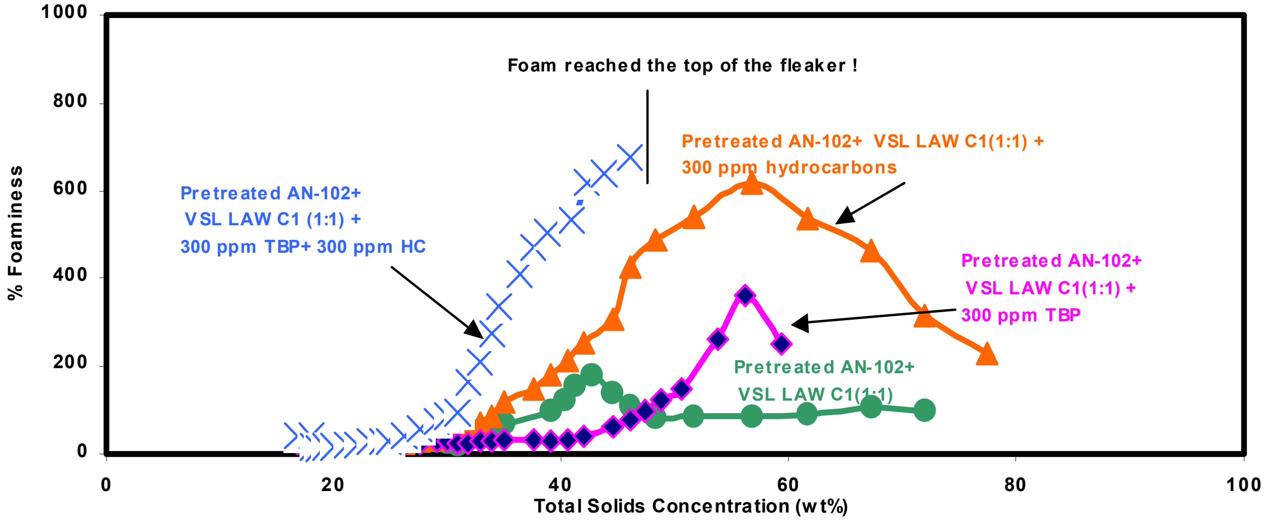


NOTE: Unless otherwise stated, total solids are all solids (dissolved and undissolved) after water is removed.

Figure 3-1 IIT Results with Added Surfactant

IIT tested 2800 ppm of the antifoam DOW CORNING 1520 US at a flux of 2 kg/min sq.m. (4.5% of design flux). It was found that the antifoam did not show any antifoaming efficiency and did not reduce foaminess. In a similar experiment, DOW CORNING Q2-3183A performed well at a concentration of 1400 ppm. IIT recommended that SRTC investigate the use of this antifoam. IIT also investigated DOW Corning 2-3930 and Pulpaid® 3472. Neither of these antifoams proved effective in IIT tests.

The graph below from IIT's Final Report shows the effect of added TBP/NPH. IIT studies indicate a de minimis level of 300 ppm TBP/NPH should be set for the WTP evaporators.



NOTE: Unless otherwise stated, total solids are all solids (dissolved and undissolved) after water is removed.

Figure 3-2 Effect of HC (300 ppm) and TBP (300 ppm) On Foaminess During Boiling of AN-102 VSL (Pressure 110 mm Hg, flux 2 kg/min sq.m)

3.2 DOW ANALYTICAL RESULTS

All of the DOW analytical reports are contained in Appendix C.

DOW's results indicated very good chemical stability of both Q2-3183A and 1520-US. DOW's 2-3930 antifoam showed a much higher degree of chemical degradation at the conditions tested. The GPC analysis also demonstrated that Q2-3183A is made up of not one, but two, families of chemical antifoam agents. The analysis also showed that 1520-US is made up of just one of these families of chemical species. This data alone would indicate that Q2-3183A would provide the best antifoam character. A blend of two antifoam agents would be more likely to be effective when different foam stabilization mechanisms are possible (surfactant or solids stabilized foam).

3.2.1 DOW 1520-US Antifoam Degradation Kinetics

The GPC chromatograms for the 1520 sample all consisted of a single polymer peak that is due to the polydimethylsiloxane portion of the antifoam that was extracted by the toluene. There was a small decrease seen in the molecular weight averages of the polymer over the course of the aging study, as shown in the molecular weight averages and chromatograms. Although the differences were very small, it is believed that they are real based on previous analyses of similar materials

3.2.2 DOW Q2-3183A Antifoam Degradation Kinetics

The GPC chromatograms for the Q2-3183 samples all consisted of two peaks, with the higher molecular weight peak being polydimethylsiloxane and the lower molecular weight peak being a mixture of Octylphenoxy polyethoxyy ethanol and polyether poloyol components extracted from the aqueous solution by the toluene. There was no significant difference seen in the molecular weight peaks over the course of the aging, as shown in the chromatograms. The small differences in the molecular weight averages of the polymer peak shown in the table are a result of the normal error of the method, plus the additional error attributed to the overlap of the two peaks. There were small differences noted in the apparent molecular weight of the lower molecular weight peak and also in the relative size of the lower molecular weight peak compared to the higher molecular weight peak. The lower molecular weight peak is more polar than the higher molecular weight peak and not as reproducible under the analysis conditions that were used, so these changes are not considered significant.

3.2.3 DOW 2-3930 Antifoam Degradation Kinetics

The GPC chromatograms for the 2-3930 samples showed a broad distribution of many partially resolved components. The complex nature of this sample type generally leads to poor reproducibility in this type of analysis, so it is difficult to say how significant the differences are in the 0 through 8 hour samples. There was definitely a significant difference seen in the 24 hour sample, which had much less material extracted by the toluene. The extracted material was also of a much lower molecular weight than in the other samples.

3.2.4 Waste Feed Sample Irradiation for DOW Analysis

Nine samples were prepared for irradiation studies with Q2-3183A antifoam. Seven samples were made-up using a concentrated blend of UF1B/VSL SBS that was spiked with antifoam prior to irradiation. Table 3-1 below presents a listing of the samples prepared for this study.

Table 3-1 Samples for Irradiation and Analysis by DOW

Sample	Sample description	Antifoam	Irradiation	Comment
1	DI with 1400 ppm DOW Q2-3183A antifoam	1400 ppm Q2-3183A	none	No rad no caustic blank
2	DI with 1400 ppm DOW Q2-3183A antifoam	1400 ppm Q2-3183A	7 day	No caustic blank
3	50/50 mix of UF1B/VSL SBS concentrated 5X	none	8 hour	No antifoam blank
4	50/50 mix of UF1B/VSL SBS concentrated 5X	1400 ppm Q2-3183A	none	No rad blank
5	50/50 mix of UF1B/VSL SBS concentrated 5X	1400 ppm Q2-3183A	8 hour	Nominal dose
6	50/50 mix of UF1B/VSL SBS concentrated 5X	1400 ppm Q2-3183A	8 hour	Nominal dose
7	50/50 mix of UF1B/VSL SBS concentrated 5X	1400 ppm Q2-3183A	7 day	Extended dose
8	50/50 mix of UF1B/VSL SBS concentrated 5X	1400 ppm Q2-3183A	7 day	Extended dose
9	50/50 mix of UF1B/VSL SBS concentrated 5X	1400 ppm Q2-3183A	2 day	Mid range dose

3.2.5 Visual Appearance of Irradiated Samples

Samples were observed to have what appears to be insoluble antifoam floating on the top of the container when the slurry was left to sit for several days. Irradiation was not the cause because un-irradiated samples (clear container) were observed having the same insoluble antifoam phase as the irradiated ones. Agitation was able to disperse this phase back into the bulk of the slurry. A photo of these samples follows.

Photograph 3-1 Insoluble Antifoam Phase Formation in Irradiated Waste Feed Samples

3.2.6 DOW Analytical Analysis of Irradiated Samples with Q2-3183A

The GPC chromatograms of the toluene extracts of the aqueous samples showed degradation of the siloxane portion of the sample as a result of the radiation treatment. The GPC chromatograms of the toluene extracts had two peaks in general, with the higher molecular weight peak being polydimethylsiloxane and the lower molecular weight peak being a second component extracted from the aqueous solution by the toluene. There was a definite change in the molecular weight of the siloxane portion of the sample, (see Table 3-2) as well as the amount of material that was recovered, as a function of time. The siloxane distribution appeared slightly higher in molecular weight in the 8 h and 2 day samples, but of lower molecular weight in the 7 day samples. There was also a general trend seen of less material extracted as the length of the radiation treatment increased. There was a large difference in the amount of material extracted from the no dose samples of antifoam in DI and UF1B (samples 1 and 4). It's possible that the presence of the UF1B has an effect on the efficiency of the extraction of PDMS with toluene. The following molecular weight averages are relative to polystyrene standards and are for the PDMS peak only (peak eluting between 10 and 15.5 minutes).

Sample 1 recovery was set at 100%. All other recoveries ratioed to Sample 1. Sample 2 indicates that a 7 day dose destroys the majority of the antifoam. Sample with UF1B and 200% recovery indicates that the toluene extraction method is incomplete in DI water reference.

Table 3-2 Molecular Weight Averages Relative to Polystyrene Standards

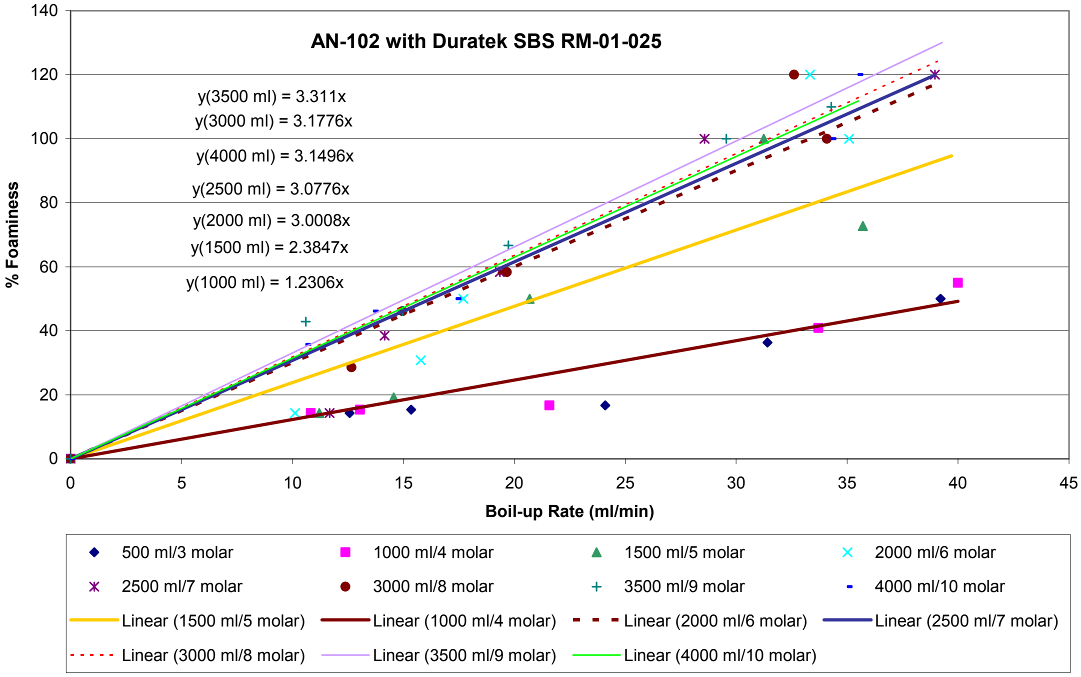
No.	Sample Description	Mp	Mn	Mw	Recovery (Relative to Sample 1)
1	D1/2-3183, no dose	31300	18700	35100	100%
2	D1/2-3183, 7 day dose	25700	11700	27600	7%
4	UFIB/2-3183, no dose	31800	19600	36300	200%
5	UFIB/2-3183, 8 h dose	31000	19900	39200	156%
6	UFIB/2-3183, 8 h dose	3100	19900	38600	179%
7	UFIB/2-3183, 7 day dose	14900	11500	19000	39%
8	UFIB/2-3183, 7 day dose	15600	12200	18900	37%
9	UFIB/2-3183, 2 day dose	307000	21000	50500	71%

Mp	Peak molecular weight
Mn	Number average molecular weight
Mw	Weight average molecular weight

3.3 SRTC HIGH FLUX RATE INVESTIGATIONS

3.3.1 Treated LAW Evaporator Foaming During Concentration

Initial evaporation runs demonstrated that the degree of foaminess increased with the degree of concentration. Figure 3-3 presents the degree of foaminess as each incremental charge of simulant was evaporated down. An initial evaporator charge of 1500 ml demonstrated only minimal foaming. Removing 500 ml of condensate and replacing it with another 500 ml charge of 50/50 mixture also demonstrated minimal foaming. A second addition began to increase the foaming character, while all additional concentration cycles demonstrated about the same degree of foaminess. Figure 3-3 presents the linearized percent foaminess for each addition and concentration cycle.



NOTE: A boil-up rate of 56.4 ml/min is equivalent to WTP Evaporator design basis flux of 0.031 lbm/s-ft2.

Figure 3-3 Foaminess During Concentration Cycle Using AN-102 with SBS RM-01-025

The sodium molarity of the diluted AN-102 permeate is approximately 4 molar. The sodium molarity of the SBS is approximately zero. A 50/50 mixture of the two would have a sodium molarity of about two. The sodium molarity in the evaporator starts at 3 molar after the first 500 ml of condensate is collected and then increases by one molar after each addition and boil off to a final concentration of 10 molar. The slope of the % foaminess versus boil-up rate increases with sodium molarity up to the limit at 10 molar, where it declines. The formation of solids may be the cause of the decline.

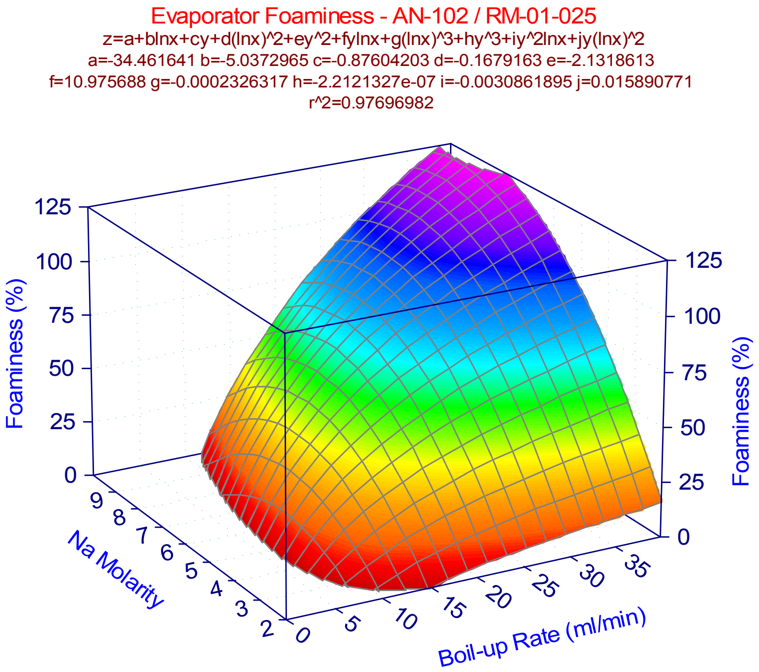
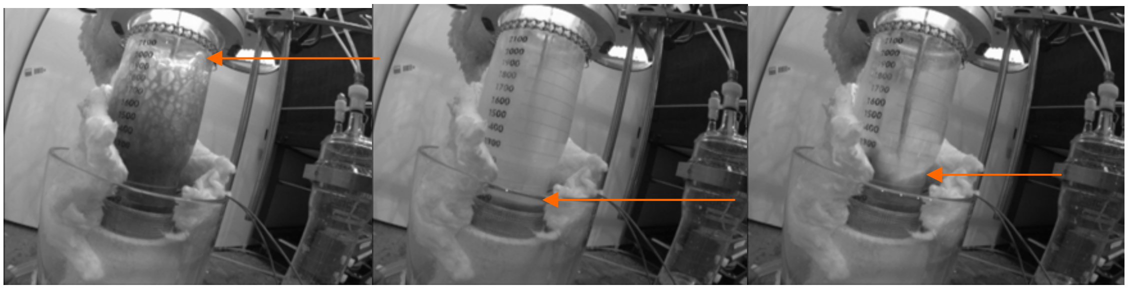


Figure 3-4 Plot of % Foaminess vs. Sodium Molarity and Boil Up Rate for AN102 with LAW Vitrification Recycle

The addition of antifoam is pictured below. Arrows indicate the foam level. When added, the system vacuum is lost and boiling stops until vacuum can be reestablished (5-10 seconds).


No Antifoam Vacuum Lost with Addition Boiling Restarted

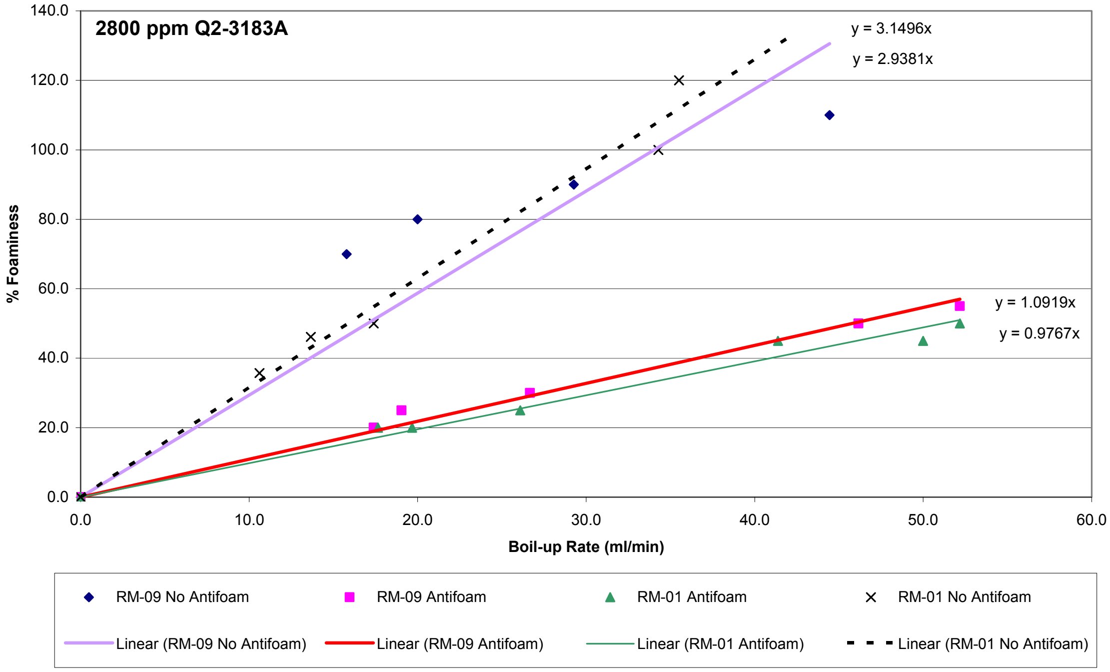
Photograph 3-2 2800 ppm Q2-3183A 50/50 AN-102/Duratek SBS RM-01-025

3.3.2 Comparison of Foaming Character of Two LAW SBS Feeds with AN-102 Simulant

The foaming character of two SBS feeds was tested in the treated feed evaporation system. AN-102 permeate with the following SBS simulants were used. These were given the names:

1. Duratek SBS RM1-01-025 (R1)
2. Duratek SBS RM9-04-02 (R9)

Chemical analysis of these feeds is presented in Appendix A. Figure 3-5 below presents the measured foaming character of the two different feeds during Treated LAW evaporation. The two upper lines demonstrate the reproducibility of % foaminess versus boil-up when each of SBS feeds is used. Increased boil-up rates up to the design flux of 57 ml/min could not be demonstrated without antifoam due to boiling over of the system. Boil-up rates up to about 90% of design utilized all the power input of the experimental equipment. Comparison of the two shows no significant difference in their tendency to foam and the addition of 2800 ppm of Q2-3183A antifoam performed equally well for each SBS feed.



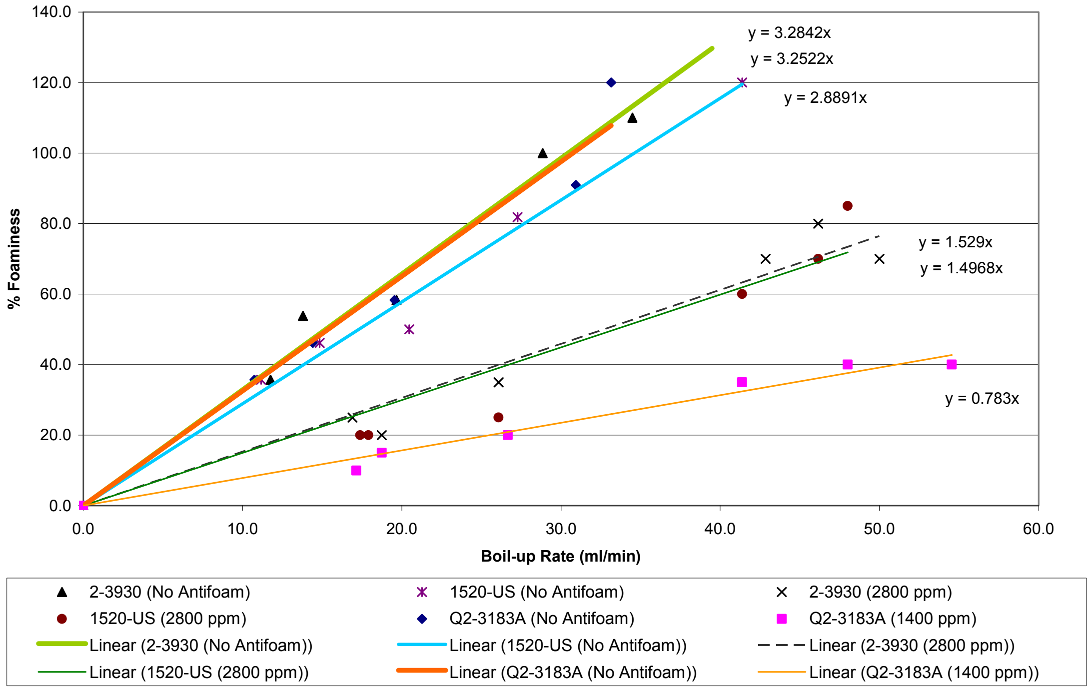
NOTE: A boil-up rate of 56.4 ml/min is equivalent to WTP Evaporator design basis flux of 0.031 lbm/s-ft2.

Figure 3-5 Comparison of Two SBS Recycles Using AN-102

From the figure above, it is obvious that no significant difference exists between the two SBS streams.

3.3.3 Performance of Three DOW Antifoams in LAW Evaporator

Three DOW antifoams were tested during a treated feed LAW evaporation process using AN-102 permeate and RM-01-025 SBS. An added antifoam concentration of 2800 ppm was used for the DOW 1520 US and DOW 2-3930 experiments and a concentration of 1400 ppm was used for the Q2-3183A antifoam run. The higher concentration of the 1520 US and 2-3930 was used because the quoted water content of these stock antifoams is as high as 60%. (i.e.,) putting the active ingredient on similar levels. Figure 3-6 below demonstrates that each of the antifoam agents were effective in reducing the foaminess in the Treated LAW evaporator, but Q2-3183A was significantly better than either the 2-3939, or the 1520-US.



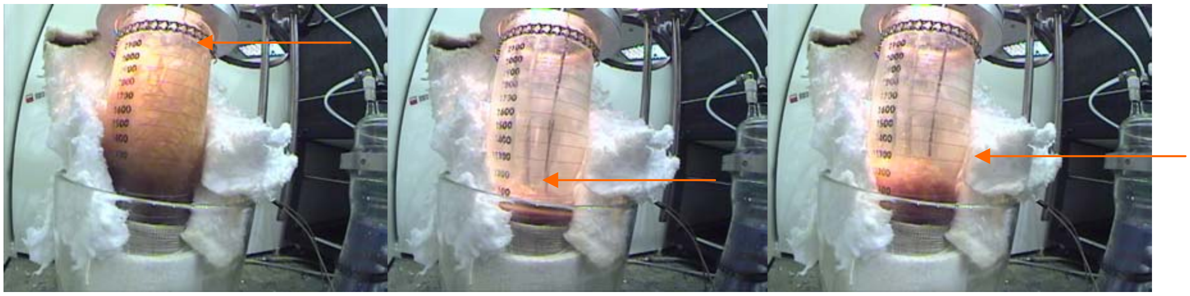
NOTE: A boil-up rate of 56.4 ml/min is equivalent to WTP Evaporator design basis flux of 0.031 lbm/s-ft2.

Figure 3-6 Comparison of 3 Antifoams Using AN-102 and RM-01-025 SBS

3.3.4 Q2-3183A Optimum Concentration Level in LAW Evaporator

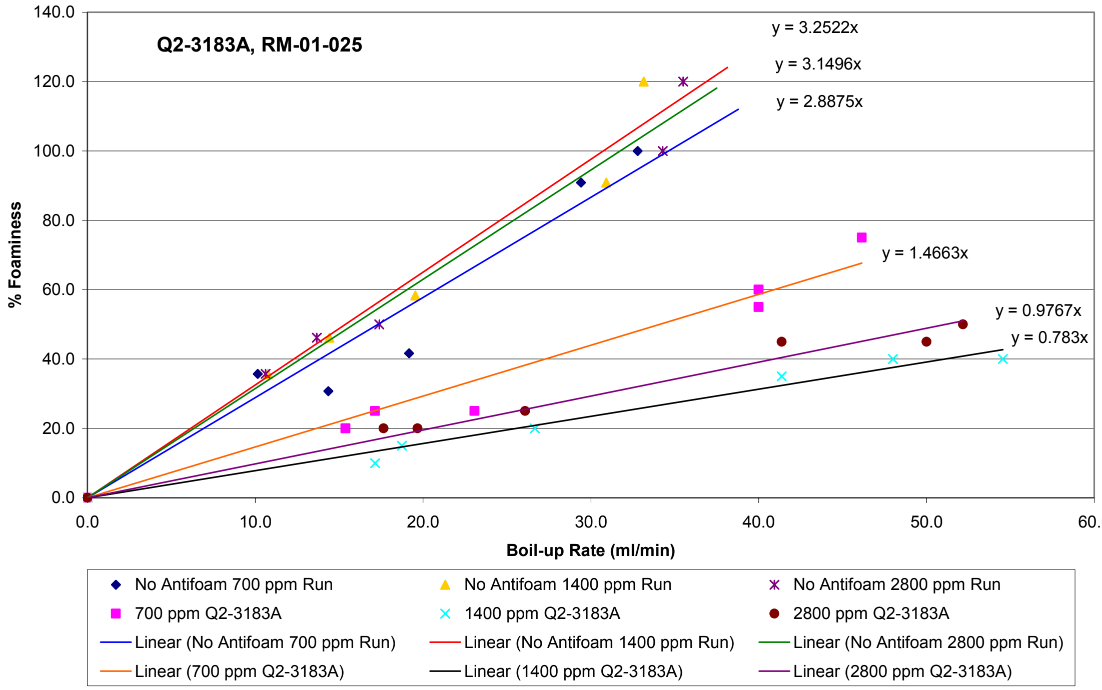
Once it was established that DOW Q2-3183A antifoam performs better than either of the other two tested antifoams, an attempt was made to determine an optimum concentration level. Figure 3-7 below presents the results of a series of identical treated feed LAW evaporation experiments in which the concentration of Q2-3183A antifoam was varied from 700 to 2800 ppm. The three upper lines demonstrate the reproducibility of the measured % foaminess for each of the runs. From this figure it can be seen that antifoam concentrations of 2800 and 1400 ppm both perform about the same. However, at the 700 ppm level, the Q2-3183A antifoam did not provide the same degree of antifoam performance. Therefore, the optimum Q2 concentration for this system is between 700 and 1400 ppm. The higher level was considered conservative and thus 1400 ppm was used in all subsequent runs.

The addition of antifoam is pictured below. Arrows indicate the foam level.



No Antifoam Vacuum Lost with Addition Boiling Restarted

Photograph 3-3 1400 ppm Q23183A 50/50 AN-102/Duratek SBS RM-01-025

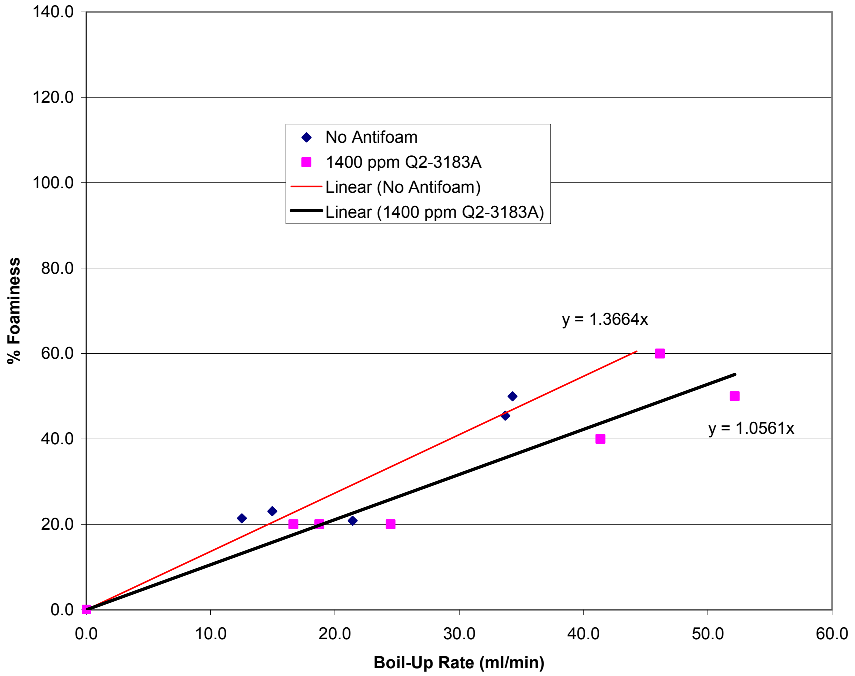


NOTE: A boil-up rate of 56.4 ml/min is equivalent to WTP Evaporator design basis flux of 0.031 lbm/s-ft2.

Figure 3-7 Q2-3183A Optimum Concentration Level

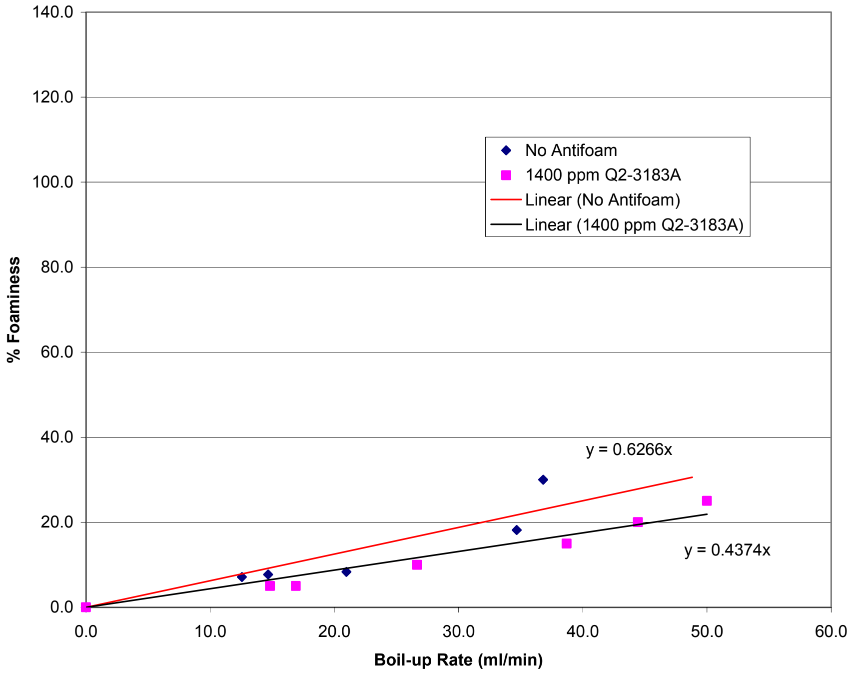
3.3.5 Waste Feed Evaporation Using Envelope A Feed

Two Envelope A evaporations were performed. UF1A (leach option) was produced as part of cross-flow filtration experimentation. An analysis of this feed is presented in Appendix A, Table A-9. The UF3A (no leach option) feed was made-up as described in Appendix A, Table A-10. Each of these feed materials demonstrated almost no foaming character. To further demonstrate this, the scale on the figures below was set equal to that used for the Treated LAW feed plots above. Antifoam was added (1400 ppm Q2-3183A) to these evaporation runs, but none was actually needed.



NOTE: A boil-up rate of 56.4 ml/min is equivalent to WTP Evaporator design basis flux of 0.031 lbm/s-ft2.

Figure 3-8 UF3A/VSL Evaporation with 1400 ppm Q2-3183A



NOTE: A boil-up rate of 56.4 ml/min is equivalent to WTP Evaporator design basis flux of 0.031 lbm/s-ft2.

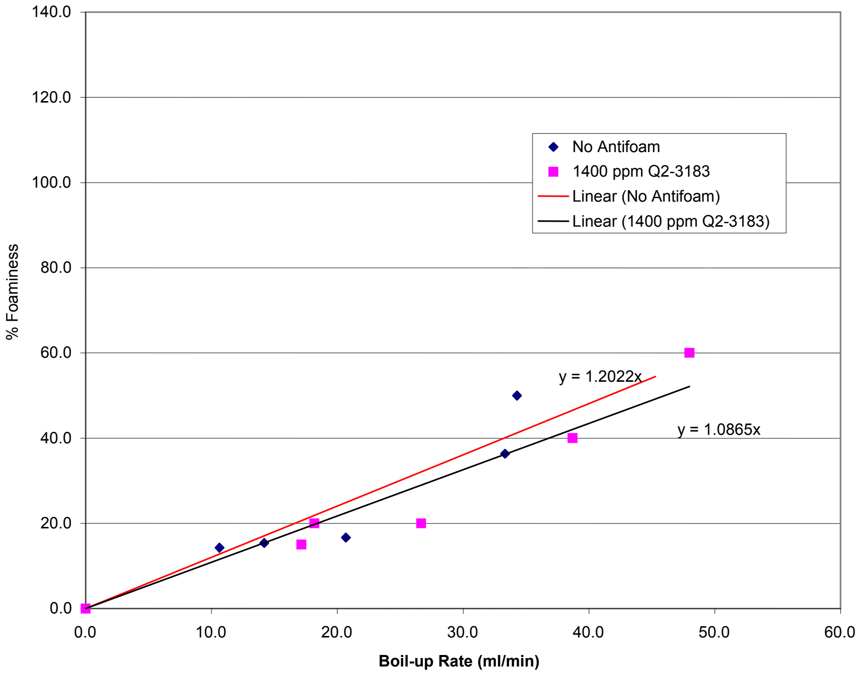
Figure 3-9 UF1A/VSL Evaporation with 1400 ppm Q2-3183A

3.3.6 Waste Feed Evaporation Using Envelope C Recycles

Envelope C recycle evaporations were performed with similar results to Envelope A recycle. Photograph 3-4 below demonstrates the minimal degree of foaming in these runs. Arrows indicate the foam level. Figure 3-10 presents the degree of foaming with increasing flux rate. Again foaming was not large and would not be expected to be a concern in the WTP at Hanford site.

No Antifoam Antifoam added Vacuum lost Boiling restarted

Photograph 3-4 UF3C/VSL with 1400 ppm Q2-3183A

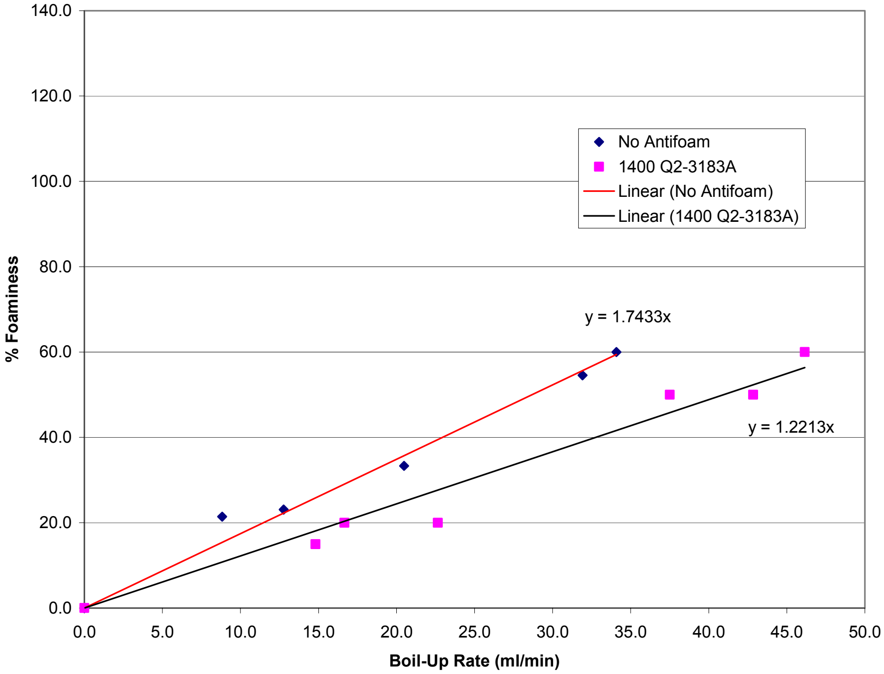


NOTE: A boil-up rate of 56.4 ml/min is equivalent to WTP Evaporator design basis flux of 0.031 lbm/s-ft2.

Figure 3-10 UF3C/VSL Evaporation with 1400 ppm Q2-3183A

3.3.7 Waste Feed Evaporation Using Envelope B Recycles

The addition of DOW Q2-3183A to an Envelope B recycle feed appeared to reduce the foaming slightly. However, foaming is still quite low for this envelope as well.

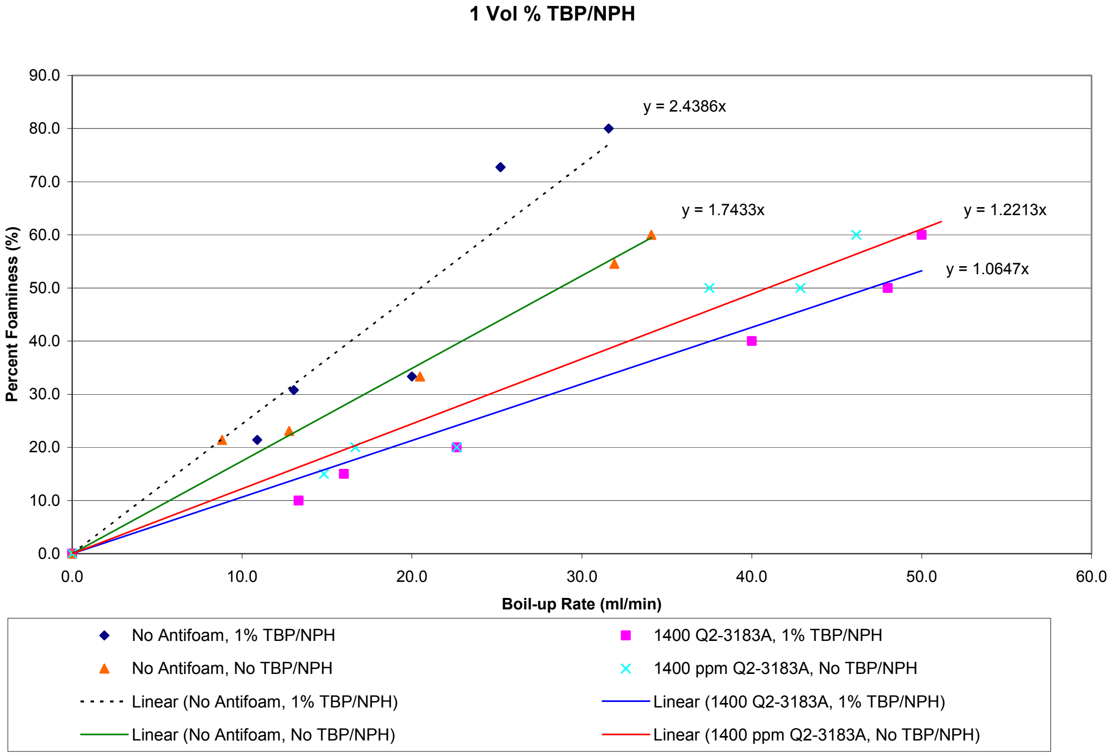


NOTE: A boil-up rate of 56.4 ml/min is equivalent to WTP Evaporator design basis flux of 0.031 lbm/s-ft2.

Figure 3-11 UF1B/VSL Evaporation with 1400 ppm Q2-3183A

3.3.8 Waste Feed Evaporation Using Envelope B Recycles with Separable Organic

In order to determine the de minimis level for separable organics in the waste feed evaporator, a feed containing up to one volume percent of a 50/50 mixture of TBP/NPH was concentrated 5 fold. Figure 3-12 presents the percent foaminess both with TBP/NPH and without. It can be seen that 1 vol % TBP/NPH increases the foaming tendency of this material, but only slightly. Higher concentrations of TBP/NPH were not deemed plausible and were not tested. This figure also presents the foaming character of the Envelope B simulant without the added TBP/NPH for comparison. In both cases, the addition of 1400 ppm Q2-3183A antifoam reduced the percent foaminess. The plot demonstrates that the antifoam negates the increase in foaminess caused by the TBP/NPH addition.



NOTE: A boil-up rate of 56.4 ml/min is equivalent to WTP Evaporator design basis flux of 0.031 lbm/s-ft2.

Figure 3-12 Effects of TBP/NPH in Waste Feed Evaporation

3.3.9 Antifoam Performance in Surfactant Based Foaming Systems

Up to this point, all of the systems that have been studied have been solids stabilized foam systems. Work done at IIT with surfactant based systems demonstrated that a small amount of surfactant can cause dramatic foaming. AN102 foamed with no solids at 5 M; hence, foaming was due to surfactants. An attempt to add a surfactant to the AN-102 simulant did not reproduce the foaming character observed with the radioactive sample.

In order to test the performance of DOW's Q2-3183A antifoam in a surfactant based system, a mixture of water and a commercial dish soap, (Sunny Lite) was used. Photograph 3-5 below demonstrates the effectiveness of 20 ppm of Q2-3183A in a system containing about 1 gram of surfactant. Stable foam was broken down by the addition and attempts to generate foam after the addition of antifoam were difficult.

No Antifoam 30 Seconds After Addition Mild Agitation

Photograph 3-5 Soapy Water with 20 ppm Q2-3183A

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4.0 FUTURE WORK

The work performed by DOW Chemical indicates that the antifoams are more stable in caustic solutions than previously expected. The fate of these antifoam agents and the effects upon the performance of the cross-flow filtration process should be studied. The silica containing solid[a], which are greater than 0.1 microns, added as part of the antifoam agent will not pass the 0.1 micron pore cross-flow filter (see Figure 4-2), but the soluble solvents also added with the antifoam will

Soluble components of the antifoam may have an impact on the LAW melter, while the silica solids may have a slight impact upon the HLW melter. Combustion of these chemical species in the prospective melter systems should be studied in the integrated pilot.

The formation of dimethyl mercury would not be expected at the mild operating temperature[6] of the evaporator. However, its formation in higher temperature evaporators has been demonstrated. The fate of dimethyl mercury and all of the organic compounds added with the antifoam will require additional study. No mercury compounds were used in this study. The Thermal Gravametric Analysis (TGA) scan for Q2-3183A below demonstrates the vaporization of solvent at ~400^o C, followed by antifoam decomposition between 450 ^{o}C and 700 ^{o}C. Residual weight represents the amorphous silica present in the antifoam. From this, it is expected that the antifoam solvent, compounds and degradation products could be present in the melter off-gas system. Further study is recommended in the integrated pilot.

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[a] Three different types of silica are included in the formulation of Q23183A (See Appendix A, Table A-1). The silica components are listed in the antifoam as trade secrets and the actual type, quantity and structure are not known. The role of silica in commercial antifoams has been widely discussed within the literature.[1, 2] Typically, commercial antifoams are mixtures of insoluble oils (e.g., Polydimethylsiloxane) with hydrophobic solids particles (e.g., silica). The oil acts as a carrier fluid which prevents the silica particle from completely immersing in the foam solution. The silica particle which resides at the oil-foam film interface acts to break the foam film.

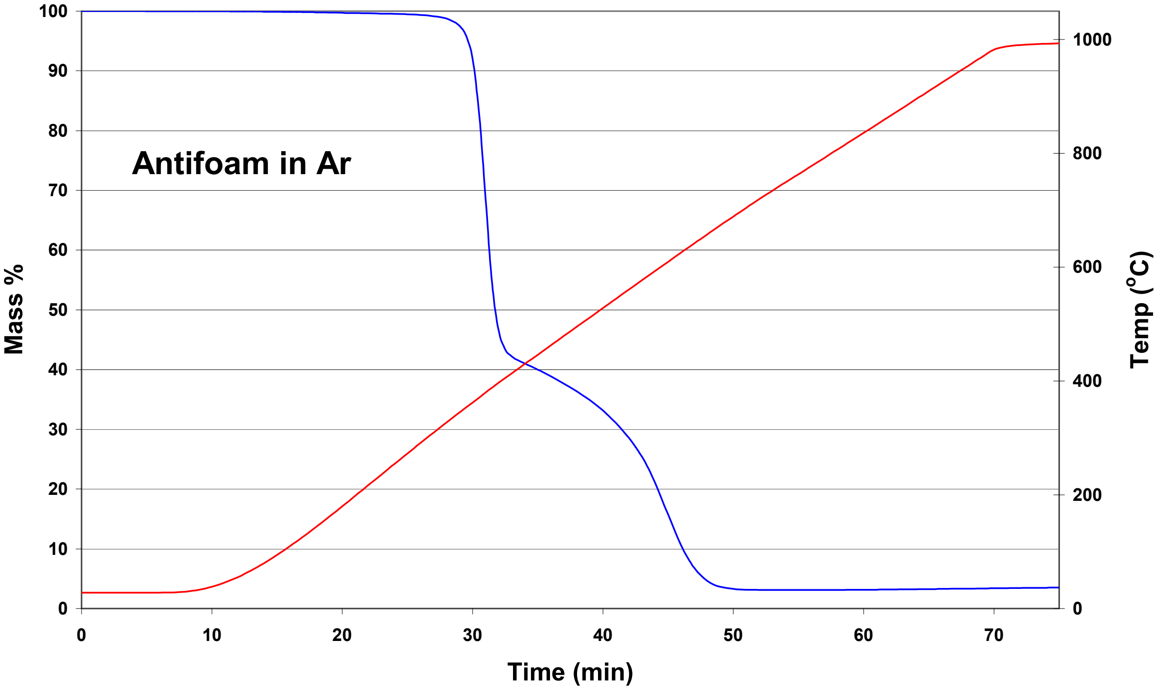

Figure 4-1 TGA Scan for DOW's Q2-3183A Antifoam

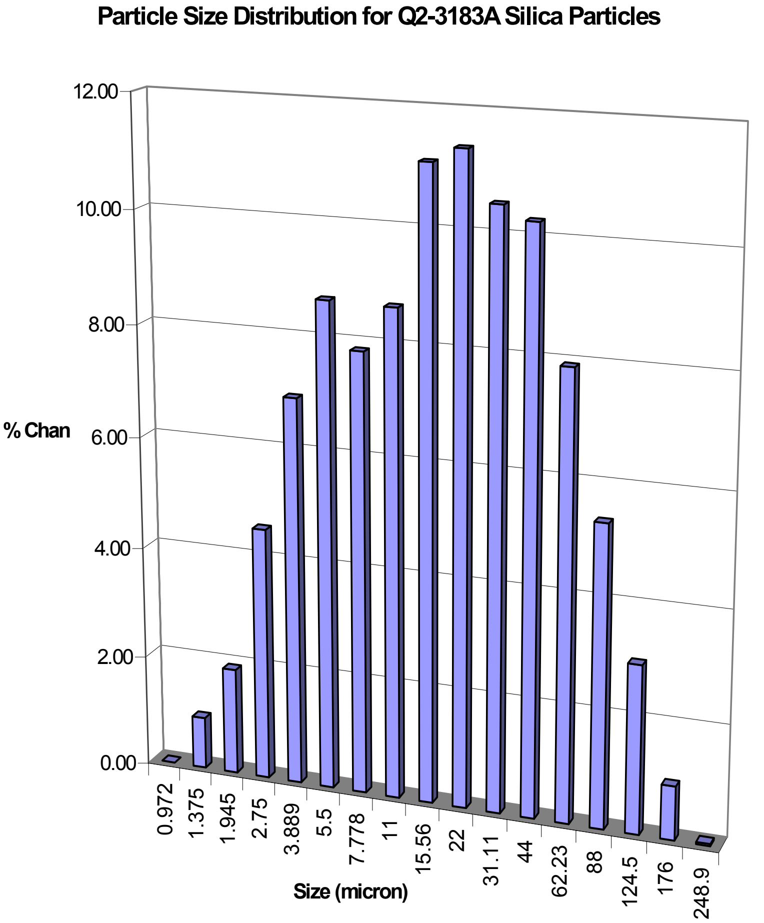

Figure 4-2 Particle Size Distribution for Q2-3183A Silica Particle

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5.0 RECOMMENDATIONS

1. DOW Q2-3183A antifoam is recommended for used in all subsequent WTP testing and for use in the WTP Waste Feed and Treated Feed evaporators. However, given that antifoam technology will advance by the time the WTP will be started up, it is recommended that WTP evaluate the current antifoam technology and determine if a more suitable antifoam is available just prior to startup of the WTP.
2. DOW recommends that Q2-3183A be diluted with water 3-10 parts water to 1 part Q2 antifoam. DOW also recommends that diluted antifoam be used immediately after mixing with water.
3. Dilution reduces the viscosity significantly, and allows fine silica solids to settle out of the suspension. A 10:1 dilution reduced the measured viscosity of the antifoam from 1000 Cps[b] at 25°C to 1.5 Cps. The particles are readily suspended when agitated. However, if left standing in dead legs of transfer piping, the fine silicon solids (mean particle size of 15 microns.) may accumulate over time. Therefore, SRTC recommends that diluted antifoam transfer piping should be designed to minimize low points that may allow solids to accumulate over time.
4. Antifoam addition to the process without dilution should be considered, but demonstration of this procedure has not been demonstrated at this time.

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[b] The MSDS quotes a viscosity range of 1800-3500 Cps.

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6.0 REFERENCES

1. Wasan, D. T. & Christiano, S.P., 1997, "Foams and Antifoams: A Think Film Approach," Handbook of Surface and Colloid Chemistry, ISBN: 0-8493-9459-7, CRC Press LLC, Boca Raton FL 33431, pg. 179-215.
2. Racz, G., Koczo, K & Wasan, D.T., "Mechanism of Antifoam Deactivation," J. or Colloid & Interface Sci. **181**, 124-135 (1996).
3. Crowder, M. L., Crawford, C. L., Saito, H. H., Calloway, T. B., Gibson, L. V., Burdette, M. A. & Crump, S. L., *Bench Scale Evaporation of a Large Hanford Envelope C sample (Tank 241-AN102*), WSRC-TR-2000-00469 Rev. 1, Westinghouse Savannah River Company, Aiken SC 29808, May 2001
4. Guthrie. M. D., *242-A Campaign 95-1 Post Run Document*, WHC-SD-WM-PE-055 Rev. 0, Westinghouse Hanford Company, Richland, WA 99352, February 1996,
5. J. R. Zamecnik and M. A. Baich, *Effects of TBP and NPH upon Crossflow Filter Performance (U)*, SRT-RPP-2002-00041, Rev. 0.
6. S. W. Rosencrance, *Evaluation of Potential for Chemical Formation of DimethylMercury at High pH in the Presence of Selected Organics in Collaboration with Frontier Geosciences-Final Report*, SRT-LWP-2003-00009.
7. J. E. Josephs and T. B. Calloway, *Task Technical and Quality Assurance Plan for-LAW Evaporation: Antifoam/Defoamer Testing for Low Activity Waste Solutions*, SRT-RPP-2001-00142, Rev. 0
8. M. E. Stone, *Waste Feed Evaporator Preliminary Test Matrix Revision 2,* SRT-GDP-2002-00095, Westinghouse Savannah River Company, Aiken, SC, October 8, 2002.
9. K. P. Brooks, et al. *Characterization, Washing, Leaching, and Filtration of AZ-102 Sludge,* BNFL-RPT-038, Rev 0. August 2000.
10. ERDA-1538-V2, Dec. 1975, *Waste Management Operations Volume 2 of 2*, Atlantic Richfield Corporation, Richland WA. Appendix II.1-F, Table II.1-F4.
11. M. E. Stone, T. B. Calloway, E. K. Hansen, & F. F. Fonduer, "Waste Feed Evaporation: Physical Properties and Solubility Determination", WSRC-TR-2003-00212, Westinghouse Savannah River Company, Aiken SC 29808, April 2003.

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APPENDIX A

Table A- 1 Antifoam Chemical Makeup

Quoted chemical composition from MSDS listings follow below:

DOW 1520 US (MSDS No. 04022046)

Wt%	Chemical Species
15.0 – 40.0	Polydimethylsiloxane
>60.0	Water

DOW 2-3930 (MSDS No. 03267067)

Wt%	Chemical Species
10.0 – 30.0	Dimethyl, methylhydroxypropyl, ethoxylated propoxylated siloxane
5.0 – 10.0	Polydimethylsiloxane
3.0 – 7.0	Dimethyl siloxane/silica reaction product
3.0 – 7.0	Dimethyl siloxane, hydroxyl-terminated
>60.0	Water

DOW Q2-3183A (MSDS No. 04022038)

Wt%	Chemical Species
40.0 – 70.0	Polypropylene glycol
40.0 – 70.0	Polydimethylsiloxane
5.0 – 10.0	Treated Silica (Trade Secret)
5.0 – 10.0	Octylphenoxy polyethoxy ethanol
3.0 – 7.0	Polyether polyol
3.0 – 7.0	Treated amorphous silica
1.0 – 5.0	Treated silica (Trade Secret)

Table A- 2 Composition of Un-Diluted AN-102 Permeate

WSRC-NB-2002-93 p. 35
File = Zamecnik Report 7-18-2002.xls
Concentration in Original Sample in mg/L (ppm)

USER ID	CCUF-AN102-PE-BAT1	CCUF-AN102-PE-10%	CCUF-AN102-PE-15%
Permeate	Batch 1	@13 wt%	@17 wt%
ADS 300-	178724	178725	178726
Al	7350	7540	7700
B	22.4	23.5	24.2
Ba	<0.024	<0.024	<0.024
Ca	91.7	95.8	102
Cd	34.5	35.6	38.1
Co	<0.088	<0.088	<0.088
Cr	149	153	137
Cu	3.49	3.67	4.15
Fe	0.53	0.46	0.63
Li	0.24	0.26	0.22
Mg	<0.168	<0.168	<0.168
Mn	0.17	0.34	0.50
Mo	28.4	28.5	29.0
Na	133000	138000	142000
Ni	195	200	201
P	573	577	553
Pb	36.2	39.9	42.1
Si	15.3	15.2	16.2
Sn	<0.7	<0.7	<0.7
Sr	28.0	26.1	26.4
Ti	<0.28	<0.28	<0.28
V	<0.26	<0.26	<0.26
Zn	3.03	2.24	2.35
Zr	0.47	0.44	0.55
La	<1.4	<1.4	<1.4
K	1770	2150	2380
S	2750	2830	2910
Nd	0.64	1.21	0.76

Table A- 3 Metals Analysis of Duratek Subenvelope A3, B1, and C2 LAW SBS Recycles

Duratek RM-01-025, -023 Inorganic Analytical Results

RM-01-025

Subenvelope **C1**, LAW formulation **LAWC22**

mg/L	**RM-01-025A**	**RM-01-025B**	**M-01-025 Average**
F	1500	1560	1530
HCO3	<100	<100	<100
Cl	1670	1390	1530
NO2	NA	NA	Not analyzed
NO3	1810	1820	1815
PO4	<100	<100	<100
SO4	2880	2850	2865
HC2O4	<100	<100	<100
mg/L	**RM-01-025A**	**RM-01-025B**	**RM-01-025 Average**
Ag	< 6.5	< 6.5	< 6.5
Al	41.4	42.8	42.1
As	< 7.5	< 7.5	< 7.5
B	2480	2480	2480
Ba	> 0.275	> 0.275	> 0.275
Ca	142	141	141.5
Cd	< 1.35	< 1.35	< 1.35
Co	< 0.25	< 0.25	< 0.25
Cr	23.8	23.8	23.8
Cu	< 0.2	< 0.2	< 0.2
Fe	73	70.1	71.55
K	155	156	155.5
La	< 0.3	< 0.3	< 0.3
Li	74.9	74.9	74.9
Mg	28.4	28.8	28.6
Mn	< 0.05	< 0.05	< 0.05
Mo	< 0.425	< 0.425	< 0.425
Na	1920	1930	1925
Ni	< 0.325	< 0.325	< 0.325
P	3.79	3.42	3.605
Pb	1.9	1.8	1.85
S	952	929	940.5
Sb	< 2.5	< 2.5	< 2.5
Se	< 2.2	< 2.2	< 2.2
Si	378	385	381.5
Sn	6.08	5.2	5.64
Sr	0.252	0.244	0.248
Ti	24.3	24.6	24.45
Tl	< 2.5	< 2.5	< 2.5
V	< 2.5	< 2.5	< 2.5
Zn	92.6	92.7	92.65
Zr	7.56	6.6	7.08
mg/L	**RM-01-025A**	**RM-01-025B**	**RM-01-025 Average**
pH	7.11	7	7.055
density	1.02	1.01	1.015
Wt%	**RM-01-025A**	**RM-01-025B**	**RM-01-025 Average**
Total Solids	1.47	1.52	1.495
Soluble Solids	1.45	1.46	1.455
Insoluble Solids	0.02	0.06	0.04

< Below detection limit.

Table A- 4 Acid Cleaning Solution Make-Up

The following steps will be utilized to makeup acid cleaning solutions for evaporation studies. All required information will be recorded in the RPP Evaporation Studies notebook.

Dried Solids Makeup (if required)

Obtain AZ-102 washed solids from sample storage.
Record label information from bottle.
Record weight of bottle.
Mix bottle as required to resuspend solids.
Transfer bottle into a tarred stainless steel pan.
Dry pan at 110° C until specified by researcher.
Record dried weight of solids and transfer to a polybottle.
Store polybottle with top open in a dessicator.

2M Nitric Acid Makeup (Perform in fume hood – Amounts are per liter)

Add 850 grams of water to a tarred polybottle.
Slowly add 179 grams of 70% nitric acid to flask. (Density = 1.4061 g/ml, M=15.7 molar)
Mix thoroughly.
Allow solution to cool.
Slowly add water until solution weight is 1064 grams. (Density = 1.0640 g/ml)
Mix thoroughly.
Allow solution to cool.

Cleaning Solution Makeup

In a fume hood, add 2M nitric acid to a tarred polybottle.
Place bottle on a stir plate and begin stirring.
Slowly add 7.22 grams of the AZ-102 dried solids to bottle per liter of acid.
Mix thoroughly to dissolve solids.
Label bottle:

Envelope A/B Acid Cleaning Solution
2M Nitric Acid
Date

Table A- 5 First Wash Simulant Recipe – Envelope A

1st Wash Simulant - Envelope A

Volume of Feed	1000 ml
In a Volumetric Flask of	1000 milliliter capacity

Record Tare Wt of Flask grams

Add	grams
Water	200

Next Add
Transition Metals and Complexing agents

Compounds	Formula	Mass Needed
Boric Acid	H3BO3	0.000
Cadmium Nitrate	Cd(NO3)2.4H2O	0.000
Calcium Nitrate	Ca(NO3)2.4H2O	0.000
Cesium Nitrate	CsNO3	0.000
Lead nitrate	Pb(NO3)2	0.000
Magnesium Nitrate	Mg(NO3)2.6H2O	0.000
Potassium Nitrate	KNO3	0.000
Zinc Nitrate	Zn(NO3)2.6H2O	0.000
Sodium Chloride	NaCl	3.508
Sodium Fluoride	NaF	2.843
Sodium Sulfate	Na2SO4	2.521
Potassium Molybdate	K2MoO4	0.000
Ammonium Acetate	CH3COONH4	0.000
Sodium Hydroxide	NaOH	19.97
Sodium Aluminate	Na2O.Al2O3.3H2O	29.51

Next Add		
Water	H2O	200

Mix vigorously.

Next Add		
Sodium meta-silicate	Na2SiO3.9H2O	1.064
Sodium Acetate	NaCH3COO.3H2O	0.000
Sodium Formate	HCOONa	0.000
Sodium Glycolate	HOCH2COONa	0.000
Sodium Oxalate	Na2C2O4	1.604
Sodium Phosphate	Na3PO4.12H2O	5.930

Add	grams
Water	200

Mix Thoroughly

Add	Formula	Mass Needed
Sodium Chromate	Na2CrO4	0.000
Sodium Carbonate	Na2CO3	22.166

Mix thoroughly.

Add	Formula	Mass Needed
Sodium Nitrate	NaNO3	72.46
Sodium Nitrite	NaNO2	46.21

Mix thoroughly.

Add	Formula	
Water	H2O	**To the Mark**

Record Final Weight grams

Label the Bottle as **First Wash Simulant - Envelope A**

Table A- 6 Second Wash Simulant Recipe

2nd Wash Simulant - Envelope A

Volume of Feed	1000 ml	
In a Volumetric Flask of	1000 milliliter capacity	
Record Tare Wt of Flask		grams
Add	grams	
Water	200	
Next Add		
Transition Metals and Complexing agents		
Compounds	Formula	Mass Needed
Boric Acid	H3BO3	0.000
Cadmium Nitrate	Cd(NO3)2.4H2O	0.000
Calcium Nitrate	Ca(NO3)2.4H2O	0.000
Cesium Nitrate	CsNO3	0.000
Lead Nitrate	Pb(NO3)2	0.000
Magnesium Nitrate	Mg(NO3)2.6H2O	0.000
Potassium Nitrate	KNO3	0.000
Zinc Nitrate	Zn(NO3)2.6H2O	0.000
Sodium Chloride	NaCl	0.609
Sodium Fluoride	NaF	0.000
Sodium Sulfate	Na2SO4	0.163
Potassium Molybdate	K2MoO4	0.000
Ammonium Acetate	CH3COONH4	0.000
Sodium Hydroxide	NaOH	25.24
Sodium Aluminate	Na2O.Al2O3.3H2O	19.82
Next Add		
Water	H2O	200
Mix vigorously.		
Next Add		
Sodium Meta-silicate	Na2SiO3.9H2O	0.576
Sodium Acetate	NaCH3COO.3H2O	0.000
Sodium Formate	HCOONa	0.000
Sodium Glycolate	HOCH2COONa	0.000
Sodium Oxalate	Na2C2O4	0.000
Sodium Phosphate	Na3PO4.12H2O	0.640
Add	grams	
Water	200	
Mix Thoroughly		
Add	Formula	Mass Needed
Sodium Chromate	Na2CrO4	0.000
Sodium Carbonate	Na2CO3	3.027
Mix thoroughly.		
Add	Formula	Mass Needed
Sodium Nitrate	NaNO3	0.14
Sodium Nitrite	NaNO2	0.271
Mix thoroughly.		
Add	Formula	
Water	H2O	**To the Mark**
Record Final Weight	grams	
Label the Bottle as	**Second Wash Simulant**	

Table A- 7 UF3C Blend Make-Up Recipe

Blending of UF Recycles: Envelope C

Densities	g/ml
1st wash	1.185
Acid Clean	1.06822
0.1M Caustic	1.002

Blending Calculation for 3000 ml

	UF-3 **Volume, ml**	**Required Weight, grams**
1st wash	1335	1582.00
Acid Clean	666	711.43
0.1M Caustic	999	1001.00
Totals	3000	3294.43
19M NaOH		1.34

Table A- 8 UF1B Blend Make-Up Recipe

Blending of UF Recycles: Envelope B

Densities	g/ml
1st wash	1.146
2nd wash	1.045
Leach	1.115
Acid Clean	1.066
0.1M Caustic	1.002

Blending Calculation for 3000 ml

	UF-3 **Volume, ml**	**Required Weight, grams**
1st wash	885	1014.21
2nd wash	885	924.98
Leach	123	137.15
Acid Clean	663	706.76
0.1M Caustic	444	444.89
Totals	3000	3227.9853
19M NaOH		195.11

Table A- 9 UF1A Analytical Report

			Recycle Only				Recycle Only
Analyte	**Method**	**Units**	**Filtrate**	**Analyte**	**Method**	**Units**	**Solids**
Na	AA	Molar	0.81	Ag	ICP-ES	µg/g	<301
Na	ICP-ES	Molar	0.79	Al	ICP-ES	µg/g	63590
OH-	Titration	Molar	0.293	B	ICP-ES	µg/g	502
total base	Titration	Molar	0.225	Ba	ICP-ES	µg/g	18
CO32	Titration	Molar	<1.0	Ca	ICP-ES	µg/g	2501
NO3	IC	Molar	0.337	Cd	ICP-ES	µg/g	13823
NO2	IC	Molar	0.111	Ce	ICP-ES	µg/g	27852
SO42	IC	Molar	0.00424	Cr	ICP-ES	µg/g	892
Cl-	IC	Molar	0.0101	Cu	ICP-ES	µg/g	<50
F-	IC	Molar	0.011	Fe	ICP-ES	µg/g	62648
HCO2	IC	Molar	0.011	La	ICP-ES	µg/g	<702
C2O42-	IC	Molar	0.00174	Li	ICP-ES	µg/g	6588
PO43	IC	mg/L	0.0043	Mg	ICP-ES	µg/g	1156
Ag	ICP-ES	mg/L	<4	Mn	ICP-ES	µg/g	2518
Al	ICP-ES	mg/L	1437	Mo	ICP-ES	µg/g	<100
B	ICP-ES	mg/L	63	Na	ICP-ES	µg/g	53185
Ba	ICP-ES	mg/L	<10	Ni	ICP-ES	µg/g	7119
Ca	ICP-ES	mg/L	<12	P	ICP-ES	µg/g	<682
Cd	ICP-ES	mg/L	<2	Pb	ICP-ES	µg/g	844
Ce	ICP-ES	mg/L	<14	Si	ICP-ES	µg/g	6408
Cr	ICP-ES	mg/L	4	Sn	ICP-ES	µg/g	464
Cu	ICP-ES	mg/L	7	Sr	ICP-ES	µg/g	6803
Fe	ICP-ES	mg/L	<2	Ti	ICP-ES	µg/g	<140
Hg	AA	mg/L	22	U	ICP-ES	µg/g	NA
K	AA	mg/L	89	V	ICP-ES	µg/g	2369
K	ICP-ES	mg/L	<481	Zn	ICP-ES	µg/g	5354
La	ICP-ES	mg/L	<4				
Li	ICP-ES	mg/L	<22				
Mg	ICP-ES	mg/L	<3				
Mn	ICP-ES	mg/L	<0.1				
Mo	ICP-ES	mg/L	<27				
Ni	ICP-ES	mg/L	<7				
P	ICP-ES	mg/L	67				
Pb	ICP-ES	mg/L	<16				
S	ICP-ES	mg/L	133				
Si	ICP-ES	mg/L	<9				
Sn	ICP-ES	mg/L	<23				
Sr	ICP-ES	mg/L	<4				
Ti	ICP-ES	mg/L	<4				
U	ICP-ES	mg/L	<116				
Zn	ICP-ES	mg/L	<2				
Zr	ICP-ES	mg/L	<12				

Table A- 10 UF3A Analytical Analysis

	UF3 No Leach Option Target	**UF3 Actual Comp**	**UF3 Actual Comp**
Density	1.081505	1.081505	1.081505
Component	**Molar**	**Mg/L**	**Molar**
Aluminum	0.1280	2670	0.1069
Boron	0.0000	LT Detectable	0.0000
Carbonate	0.0922	Not Analyzed	0.0000
Chloride	0.0265	754	0.0230
Chromium	0.0000	3	0.0001
Fluoride	0.0298	454	0.0258
Hyroxide	0.3840	Not Analyzed	0.0000
Nitrate	0.8164	45500	0.7937
Nitrite	0.2951	11900	0.2798
Oxalate	0.0053	400	0.0049
Phosphate	0.0071	583	0.0066
Potassium	0.000	LT Detectable	0.0000
Silicon	0.0023	336	0.0129
Sodium	1.4968	33900	1.5940
Sulfate	0.0078	650	0.0073
Cadmium	0.0007	54	0.0005
Iron	0.0092	428	0.0083
Lanthanum	0.0001	LT Detectable	0.0000
Magnesium	0.0002	5	0.0002
Manganese	0.0002	10	0.0002
Nickel	0.0007	30	0.0006
Zirconium	0.0008	59	0.0007

Table A- 11 VSL HLW Analytical Report

VSL HLW Supernate and Slurry Analytical Results
SUPERNATE 1/30/02 Shipped on 6/5/01
2 different samples (VSL-3A and VSL-3B) were submitted to SRTC Mobile Lab

mg/L	**VSL-3A**	**VSL-3B**	**VSL Supernate Average**
F	121	123	122
HCO3	<10	<10	<10
Cl	101	115	108
NO2	<10	<10	<10
NO3	150	150	150
PO4	<10	<10	<10
SO4	395	394	394.5
HC2O4	<10	<10	<10
Ag	<0.026	<0.026	<0.026
Al	62.7	63.5	63.1
As	0.825	0.821	0.823
Ba	0.018	0.036	0.027
Ca	12	12.1	12.05
Cd	6.83	6.86	6.845
Co	<0.01	<0.01	<0.01
Cr	0.119	0.119	0.119
Cu	0.362	0.265	0.3635
Fe	0.166	0.144	0.155
K	9.09	9.19	9.14
Li	33.4	33.8	33.6
Mg	1.84	1.84	1.84
Mn	9.95	10.1	10.025
Mo	0.015	0.015	0.015
Na	147	144	145.5
Ni	1.73	1.73	1.73
P	0.324	0.319	0.3215
Pb	<0.017	<0.017	<0.017
S	128	128	128
Si	22.7	22.9	22.8
Sn	0.162	0.165	0.1635
Sr	39.1	39	39.05
Ti	0.007	0.007	0.007
Zn	29.8	30	29.9
Zr	0.185	0.185	0.185

Weight Percent Solids

Wt%	**VSL-3A**	**VSL-3B**	**VSL Supernate Average**
Total Solids	0.218	0.222	0.22
Soluble Solids	0.19	0.182	0.186
Insoluble Solids	0.028	0.04	0.034

Table A- 12 High-Level Waste Feed Unwashed Solids Maximum Radionuclides Composition (Curies per 100 g Non-Volatile Waste Oxides

Isotope	Maximum (Ci/100 grams waste oxides)	Isotope	Maximum (Ci/100 grams waste oxides)	Isotope	Maximum (Ci/100 grams waste oxides)
^{3}H	6.5E-05	^{129}I	2.9E-07	^{237}Np	7.4E-05
^{14}C	6.5E-06	^{137}Cs	1.5E00	^{238}Pu	3.5E-04
^{60}Co	1E-02	^{152}Eu	4.8E-04	^{239}Pu	3.1E-03
^{90}Sr	1E+01	^{154}Eu	5.2#-02	^{241}Pu	2.2E-02
^{99}Tc	1.5E-02	-	-	^{241}Am	9.0E-02
^{125}Sb	3.2E-02	^{233}U	4.5E-06*	$^{243+244}$ Cm	3/0E-03
^{126}Sn	1.5E04	^{235}U	2.5#-07	-	-

* (All tanks except AY-101/C-104)(2.0E-04 for AY101/C-104 only)

Table A- 13 Dose Calculations Table

2.20E-02	1.54E-04	Pu-241	0.0019	1.44E+01	4.81E-02	0.01	1.52E+04	1.48E+04	1.69E+00
		Pu-242		3.76E+05	1.84E-06	4.90			
9.00E-07	6.30E-09	U-233	0.0000	1.59E+05	4.35E-06	4.82	5.65E+02	5.65E+02	6.45E-02
		U-234		2.45E+05	2.82E-06	4.77			
2.50E-07	1.75E-09	U-235	0.0000	7.04E+08	9.85E-10	4.58	1.49E+02	1.49E+02	1.70E-02
		U-236		2.34E+07	2.96E-08	4.49			
		U-238		4.47E+09	1.55E-10	4.21			
		Cm-243							
3.00E-03	2.10E-05	Cm-244	0.0003	1.81E+01	3.83E-02	5.80	2.26E+06	2.22E+06	2.54E+02
		Cm-245		8.50E+03	8.15E-05	5.62			
		Cm-246		4.73E+03	1.47E-04	5.39			
1.00E-02	7.00E-05	Co-60	0.0009	5.27E+00	1.31E-01	2.60	3.39E+06	3.17E+06	3.62E+02
		Cs-134		2.06E+00	3.36E-01	1.72			
1.50E+00	1.05E-02	Cs-137	0.1276	3.02E+01	2.30E-02	0.83	1.62E+08	1.60E+08	1.83E+04
4.80E-04	3.36E-06	Eu-152	0.0000	1.33E+01	5.20E-02	1.29	8.06E+04	7.86E+04	8.97E+00
5.20E-02	3.64E-04	Eu-154	0.0044	8.80E+00	7.88E-02	1.53	1.04E+07	9.97E+06	1.14E+03
2.90E-02	2.03E-04	Eu-155	0.0025	4.96E+00	1.40E-01	0.13	4.83E+05	4.51E+05	5.15E+01
		Ra-226		1.60E+03	4.33E-04	4.78			
2.90E-07	2.03E-09	I-129	0.0000	1.57E+07	4.41E-08	0.08	3.04E+00	3.04E+00	3.47E-04
6.50E-06	4.55E-08	C-14	0.0000	5.73E+03	1.21E-04	0.05	4.19E+01	4.19E+01	4.78E-03
6.50E-05	4.55E-07	H-3	0.0000	1.23E+01	5.62E-02	0.01	4.81E+01	4.67E+01	5.34E-03
7.40E-05	5.18E-07	Np-237	0.0000	2.14E+06	3.24E-07	4.86	4.68E+04	4.68E+04	5.34E+00
		Np-239		6.45E-03	1.07E+02	0.43			
		Th-232		1.41E+10	4.93E-11	4.01			
		Ni-59		7.50E+04	9.24E-06	0.01			
		Ni-63		1.00E+02	6.92E-03	0.02			
1.50E-02	1.05E-04	Tc-99	0.0013	2.13E+05	3.25E-06	0.08	1.65E+05	1.65E+05	1.89E+01
1.00E+01	7.00E-02	Sr-90	0.8505	2.85E+01	2.43E-02	1.13	1.47E+09	1.45E+09	1.66E+05
		Ru-106		1.02E+00	6.79E-01	3.20			
3.20E-02	2.24E-04	Sb-125	0.0027	2.73E+00	2.54E-01	0.57	2.37E+06	2.09E+06	2.39E+02
1.50E-04	1.05E-06	Sn-126	0.0000	1.00E+05	6.93E-06	0.18	3.55E+03	3.55E+03	4.06E-01
9.00E-02	6.30E-04	Am-241	0.0077	4.33E+02	1.60E-03	5.54	6.49E+07	6.49E+07	7.40E+03
		Am-243		7.38E+03	9.39E-05	5.31			
1.18E+01	8.23E-02		1.00				1.72E+09	1.70E+09	1.94E+05

	RAD	HOUR	Minutes	
8 hr dose	1.55E+06	155.2	9310.4	@ 1e4 r/hr
24 hr dose	4.66E+06	465.5	27931.3	
8 hr dose	1.55E+06	2.0	121.1	@0.769e6 r/hr
2 day dose	9.31E+06	12.1	726.4	
7 day dose	3.26E+07	42.4	2542.5	

Table A- 14 Evaporator Scale Factors

Scaling Parameters for the Pilot-Scale Evaporator Test Facility

Linear Scale Factor	8.72	
Area Scale Factor	76	Based on 3 reboiler tubes (228 tubes in full scale reboiler
Volume Scale Factor	662.55	

Parameter	**Units**	**Full scale***	**Pilot scale**	**% of Full Scale**
recirculation vessel diameter	ft	13.00	1.49	11.47%
min liq height (cylindrical portion)	ft	7.33	10.65	145.32%
vessel height (conical portion)	ft	11.26	1.29	11.47%
liquid level range	ft	2.92	2.92	100.00%
min liquid vol. In Recir. Vessel	gal	11003.31	144.78	1.32%
max liquid vol. In Recir. Vessel	gal	13899.13	182.88	1.32%
Min residence time in recir vessel	min	1.5	1.5	100.00%
max recir flow rate	gpm	7335.54	96.52	1.32%
max res time	min	1.89	1.89	100.00%
evaporation rate in gpm	gpm	30.00	0.39	1.32%
evap rate in lbm/sec	lbm/s	4.17	0.05	1.32%
Enthalpy of evaporation	kW	4540.03	59.74	1.32%
recir vessel dia	ft	13.00	1.49	11.47%
x-sectional area	ft2	132.73	1.75	1.32%
recir vessel operating pressure	psi	1.00	1.00	100.00%
saturation temp. at oper. pressure	F	102.00	102.00	-
sp. Vol of water vapr at op press	ft3/lbm	323.00	323.00	100.00%
Vapor flux	lbm/s-ft2	0.031	0.031	100.00%
Vapor velocity at interface	Ft/s	10.15	10.15	100.00%
Condenser cooling water inlet temp	F	-	70.00	-
Condenser cooling water outlet temp	F	-	90.00	-
Cooling water flow rate	gpm	TBD	20.38	-
Reboiler tube OD	in	1.50	1.50	100.00%
Wall thickness	in	0.08	0.08	100.00%
Reboiler tube ID	in	1.33	1.33	100.00%
Flow area	in2	1.40	1.40	100.00%
Number of tubes	-	228	3	1.32%
Total flow area	ft2	2.21	0.03	1.32%
Tube height	ft	7.00	7.00	100.00%
Recirc flow rate	gpm	7335.54	96.52	1.32%
Recirc flow rate	ft3/s	16.34	0.22	1.32%
Sp gravity	-	1.33	1.33	100.00%
Recirc mass flow rate	lbm/s	1356.49	17.85	1.32%
Slurry velocity in tubes	ft/s	7.39	7.39	100.00%
Recirc piping ID	in	19.50	2.25	11.51%
Recirc piping x section area	ft^2	2.07	0.03	1.33%
Velocity in recirc piping	ft/s	7.88	7.82	99.27%
Liquid height at upper tube sheet	ft	10.42	10.42	100.00%
Pressure due to liquid height	psi	6.00	6.00	100.00%
Total pressure at upper tube sheet	psi	7.00	7.00	100.00%
Demister dia	ft	7.50	0.86	11.47%
Demister pads thickness	ft	1.00	1.00	100.00%
Vapor velocity through demister		TBD	TBD	100.00%

* Based upon the preliminary information presented at the November 2001 Design Review

APPENDIX B

FINAL REPORT ON SUBCONTRACT NO: AC 29929N

FOAMING IN HANFORD RPP-WTP LAW EVAPORATION PROCESSES

By

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February 27, 2003

EXECUTIVE SUMMARY

Experiments for foaminess of simulant mixtures Pretreated AN-102 + VSL LAW C1, Pretreated AN-107 + DURATEK during boiling were carried out at a pressure of 110 mm Hg and flux of 2 kg/min sq.m. Foaminess during boiling is also monitored for the simulant mixtures Pretreated AN-102 + VSL LAW C1, Pretreated AN-107 + DURATEK in the presence of hydrocarbons (HC) and tributyl phosphate (TBP). The antifoaming performance of two commercial antifoamers DOW 2-3930 and Q2-3183 A was studied. In addition, foaminess during boiling for the simulant AZ-101 is studied in the presence of HC, TBP and antifoamer DOW 2-3930.

The results are summarized as follows:

- For the simulant mixture Pretreated AN-102 + VSL LAW C1 (henceforth called as AN-102 VSL) foaminess decreases during boiling as compared to foaminess for Pretreated AN-102 alone. The maximum in foaminess shifts to a lower total solid concentration for An-102 VSL. Foaminess of the order of 200 vol % is observed at a total solid concentration of 40 wt %.

- For the simulant mixture Pretreated AN-107 + DURATEK (henceforth called as AN-107 D), foaminess increases during boiling and shifts towards higher total solid concentration. Foaminess of the order of 600 vol % is observed at a total solid concentration of 60 wt %.

- For the simulant AZ-101, a maximum in foaminess of the order of 60 vol % is observed during boiling at a total solid concentration of 45 wt %.

- A parametric study of the effect of HC, TBP on foaminess during boiling of simulants is carried out. For the simulant mixture and AN-107 D, hydrocarbon (300 ppm) increases foaminess and shifts the maximum in foaminess to a higher total solid concentration. For the simulant AZ-101 HC decreases foaminess at the maximum from 60 % to 50 vol %.

- For the simulant mixture, AN-107 D, and AZ-101, TBP (300 ppm) acts as an antifoamer at lower total solid concentration and decreases foaminess.

- Addition of HC (300 ppm) and TBP (300 ppm) to the simulant mixture causes excessive foaminess and experiments had to be stopped as the liquid foam reached the top of the Fleaker™. For the case of AN-107 D, addition of HC (300 ppm) and TBP (300 ppm) causes a decrease in foaminess. Similar results are observed for the simulant AZ-101 when HC and TBP are added.

- Antifoaming performance of two commercial antifoamers DOW 2-3930 and Q2-3183 A in simulant mixtures and AN-107 D were tested. Both the antifoamers were effective in reducing the maximum in foaminess by a factor of 15 (for e.g. For the

simulant AN-107 D + HC + TBP foaminess decreases from 600 vol % to 40 vol % in the presence of antifoamer). For the simulant mixture AN-102 VSL 1400 ppm of antifoamer DOW Q2-3183 A (foaminess is 10 vol%) had a better antifoaming performance than 1400 ppm of DOW 2-3930 (foaminess is 30 vol %).

- The simulant AZ-101 contains a large amount of insoluble solids (30 wt %) and foaminess is promoted by the bi-philic particles. The recommended classical antifoamer DOW 2-3930 was ineffective in reducing foaminess caused by bi-philic particles.

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FINAL REPORT

Savannah River Technology Center (SRTC) has reported severe foaminess in the bench scale evaporation of the Envelope C tank, which causes excessive carryover of radionuclides and non-radioactive waste to the condensate system. IIT researchers have been requested to understand the causes of foaminess and to provide methods to eliminate the foaminess in the evaporators. In this quarter we studied the foaminess during boiling of two simulant mixtures Pretreated AN-102 in combination with VSL LAW C1, Pretreated AN-107 in combination with DURATEK and simulant AZ-101 (3.5 wt %). The effect of hydrocarbons, tributyl phosphate alone and also the combined effects of hydrocarbons and tributyl phosphate on the foaminess during boiling of simulant mixtures and simulants were studied. The antifoaming efficiency of two commercial antifoamers DOW 2-3930 and DOW Q2-3183 A using the two simulant mixtures was studied. All experiments were conducted at a pressure of 110 mm Hg and a flux of 2 kg/min sq.m. The *first part* of the report concerns the study of foaminess during boiling of the simulant mixture AN-102 with VSL LAW C1, the *second part* concerns the other simulant mixture Pretreated AN-107 with DURATEK, and *third* part concerns the simulant AZ-101 (3.5 wt %).

PART I

Foaminess during boiling of simulant mixture Pretreated AN-102 + VSL LAW C1

Results of previous quarter for simulant Pretreated AN-102 showed a maximum in foaminess during boiling (evaporation of water) of the order of 550 vol % which occurred at a total solid concentration of 55 wt %. During the downstream evaporation of Pretreated AN-102 another sludge VSL LAW C1 is mixed with it. Foaminess during boiling of this simulant mixture is of interest for the pilot plant operation of the evaporator. In this quarter, we conducted experiments with simulants Pretreated AN-102 and VSL LAW C1 (henceforth called as AN-102 VSL) mixed in the ratio 1:1. The result for the foaminess during boiling versus the total solid concentration experiment is presented in **Figure 1**. A maximum in foaminess for AN-102 VSL is of the order of 200 vol % and occurs at a total solid concentration of 40 wt %. In the same graph foaminess of Pretreated AN-102 is shown as a reference curve. For the simulant Pretreated AN-102 foaminess is 550 vol % and occurs at 55 wt % total solid concentration. The maximum in foaminess for AN-102 VSL decreases from 550 vol % to 200 vol % and shifts from 55 wt % total solid concentration to 40 wt % total solid concentration. A plausible reason for decrease in foaminess is lower concentration of solids in VSL LAW C1. In the total solid concentration range of 30-50 wt % foaminess is about 200 vol %, which may be high enough to cause a sludge spill during evaporation. In the evaporation of AN-102 VSL hydrocarbons (N-paraffin) and tributyl phosphate (TBP) are present in an unspecified ratio. It is necessary to analyze the role of hydrocarbons (HC) and TBP on foaminess during boiling of AN-102 VSL. Here we present the results obtained for the effect of HC, TBP and the combined effect of HC and TBP on foaminess during boiling of AN-102 VSL.

Effect of hydrocarbons (300 ppm) on foaminess during boiling of AN-102 VSL

In our previous studies it was observed that addition of hydrocarbon facilitates foaminess. The effect of 300 ppm hydrocarbons on the foaminess of AN-102 VSL during boiling was studied. The hydrocarbon was emulsified in AN-102 VSL after 30 mins of stirring. The emulsified oil is dispersed as a droplet of millimeter size range and some of the droplets stay as oil lens on the top (**Figure 2**). The result of foaminess during boiling versus total solid concentration is presented in **Figure 3**. A maximum in foaminess of the order of 600 vol % occurs at a total solid concentration of 55 wt %. As a reference the curve indicating foaminess during boiling for AN-102 VSL without hydrocarbon is also shown. The presence of HC increased foaminess from 50 vol % to 300 vol % in the region of total solid concentration 35-55 wt %. As pointed in our previous studies, hydrocarbons added to Pretreated AN-102 enhance foaminess and shifts the maximum to a higher total solid concentration. The reproducibility of foaminess (for 2 runs) versus total solid concentration for two experimental runs performed is also presented in **Figure 3** and it was found that the error was less than 5%. Please note that as the concentration of hydrocarbon is increased foaminess is also expected to increase. The effect of TBP on foaminess of the boiling AN-102 VSL was also studied. From our previous observations, when trace amounts of TBP are added to AN-102 VSL, TBP behaves as an antifoamer and reduces foaminess.

Effect of tributyl phosphate (TBP) (300 ppm) on foaminess of AN-102 VSL

The simulant mixture AN-102 VSL with TBP was stirred for 30 mins and the oil phase was emulsified and dispersed as tiny droplets on the surface of simulant mixture (**Figure 4**). The foaminess during boiling versus total solid concentration for AN-102 VSL in the presence of TBP is presented in **Figure 5**. A maximum in foaminess of the order of 375 vol % is observed at a total solid concentration of about 55 wt %. In the same figure the curve for the foaminess during boiling of AN-102 VSL and hydrocarbons is also presented as a reference. Detailed analysis of the curve of foaminess in the presence of TBP reveals that upto a total solid concentration of 45 wt % foaminess is lesser than in the presence of AN-102 VSL and HC. The maximum in foaminess is at the same concentration as observed for the HC indicating a shift in the total solid concentration. We also monitored the effect of both TBP and hydrocarbons on the simulant mixture AN-102 VSL

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Effect of TBP (300 ppm) and hydrocarbons (300 ppm) on foaminess of AN-102 VSL

The simulant mixture AN-102 VSL with HC and TBP was stirred for 30 mins and the oil phase was emulsified and dispersed as millimeter sized droplets on the surface (**Figure 6**). Data for the foaminess during boiling of AN-102 VSL with TBP and HC is presented in **Figure 7**. In the same graph comparison of the combined effect of TBP and HC and the individual effect of TBP and HC on foaminess versus total solid concentration during boiling of AN-102 VSL is presented. Severe foaminess was observed at a total solid concentration of around 30 wt %. Foaminess steeply increases and at 45 wt % total solid concentration when foaminess was around 700 vol % experiments had to be shut down as the liquid foam reached the top of the Fleaker™. Experiments were repeated in order to confirm the reproducibility of the curves (**Figure 8**) and it was found that the error margin was about ± 5 %.

In this particular composition TBP did not act as an antifoamer. The performance of TBP depends on the composition of the simulant mixture. We have studied the effect of TBP, HC and the combined effect of TBP and HC on AN-102 VSL. Experiments were carried out to test the antifoaming efficiency of the two commercial antifoamers DOW 2-3930 and DOW Q2-3183 A as recommended by SRTC.

Antifoaming performance of DOW 2-3930 on the foaminess of AN-102 VSL and hydrocarbons

The antifoaming performance of DOW 2-3930 (1400 ppm) was tested in the presence of AN-102 VSL and HC (300 ppm). DOW 2-3930 was suggested to be a newly developed antifoamer. The antifoamer and hydrocarbons are dispersed as millimeter size droplets on the surface of the simulant after 20 mins of stirring (**Figure 9**). Data for the foaminess during boiling of AN-102 VSL with HC in the presence of antifoamer is presented in **Figure 10**. It is seen in this figure that the antifoamer reduces foaminess significantly by a factor of 9. In the same figure two reference curves are also presented. Foaminess is about 50-60 vol % in the operating concentration range of 30-40 wt % which indicates that the antifoamer is effective in reducing foaminess. However, foaminess of the order of 50 vol % at 30 wt % total solid concentration could be detrimental for the proper working of the evaporator. Experiments were carried out to test the antifoaming performance of DOW 2-3930 in the presence of AN-102 VSL, TBP and hydrocarbons.

Antifoaming performance of DOW 2-3930 on foaminess of AN-102 VSL, hydrocarbons and TBP

The goal of this study was to analyze the antifoaming performance of DOW 2-3930 in the presence of AN-102 VSL, TBP and HC. Two different levels of antifoam concentrations (1400 ppm and 700 ppm) were chosen for antifoaming performance. **Figures 11** and **12** depict the antifoamer degree of spreading of 1400 ppm and 700 ppm of antifoamer DOW 2-2930 on the surface of AN-102 VSL. The performance of 1400 ppm of the antifoamer was first tested with AN-102 VSL, hydrocarbons and TBP. The data for foaminess during boiling in the presence of antifoamer show that the foaminess is reduced by a factor of 15 (**Figure 13**). However, foaminess is only 30-40 vol % in the range of 25-35 wt % total solid concentration. Based on the results it was necessary to check if lower concentrations of antifoamer would be effective on AN-102 VSL, hydrocarbons and TBP. It is seen in **Figure 13** that foaminess is about 50 vol % in the region of 25-35 wt % total solid concentration. The antifoaming performance of two different concentrations of antifoamer was compared to test the efficiency. Foaminess in the presence of 1400 ppm of antifoamer is much less than in the presence of 700 ppm in the operating range of 25-50 wt % total solid concentration. To compare the antifoaming performance of commercial antifoamer Q2-3183 A experiments were carried out on AN-102 VSL, HC and TBP.

Antifoaming performance of DOW Q2-3183 A on AN-102 VSL, hydrocarbons and TBP

Two different levels of antifoam concentrations (1400 ppm and 700 ppm) were chosen for antifoaming performance of DOW Q2-3183 A. **Figures 14** and **15** depict the antifoamer degree of spreading of 1400 ppm and 700 ppm of antifoamer DOW Q2-3183 A on the surface of AN-102 VSL. It was decided to test the antifoaming performance of 1400 ppm of antifoamer in AN-102 VSL, hydrocarbons and TBP. From the **Figure 16**, it is seen that foaminess is reduced by a factor of 25 in the operating range of 30-50 wt % total solid concentration. In order to check the antifoaming performance at low concentrations testing was done at 700 ppm antifoamer concentration. With the addition of 700 ppm of antifoamer DOW Q2-3183 A foaminess was about 30 vol % in the range of 30-50 wt % total solid concentration (**Figure 16**). Comparison between the two levels of antifoamer concentrations is seen in the figure. It is evident that foaminess in the presence of 1400 ppm is lesser than in the presence of 700 ppm of antifoamer. The antifoaming performance of two antifoamers DOW Q2-3183 A and 2-3930 were also compared for AN-102 VSL, hydrocarbons and TBP.

Comparison of antifoaming performance of DOW 2-3930 and DOW Q2-3183 A on mixture, hydrocarbons and TBP

The two antifoamers DOW 2-3930 and DOW Q2-3183 A (1400 ppm) reduced foaminess when added to the mixture, hydrocarbons and TBP in traces. The antifoaming performance of two antifoamers is presented in **Figure 17**. In the range of 30-50 wt % total solid concentration foaminess in the presence of antifoamer DOW Q2-3183 A is less than in the presence of DOW 2-3930. Please note that the conditions at which the experiments were conducted in the laboratory are far away from the pilot plant operating conditions where the results may vary when experiments are carried out at higher fluxes.

PART-II

Foaminess during boiling of simulant mixture Pretreated AN-107 + DURATEK

Results of previous quarter for simulant Pretreated AN-107 showed that a maximum in foaminess occurred during boiling (evaporation of water). A maximum of the order of 350 vol % occurs at a total solid concentration of 60 wt %. During the downstream evaporation of Pretreated AN-107 another sludge DURATEK is mixed with it. Foaminess during boiling of this mixture is of interest for the pilot scale operation of the evaporator. We conducted experiments with simulants Pretreated AN-107 and DURATEK (henceforth called as AN-107 D) mixed in the ratio 1:1. The result for the foaminess during boiling of AN-107 D versus the total solid concentration experiment is presented in **Figure 18**. A maximum in foaminess for AN-107 D is of the order of 650 vol % and occurs at a total solid concentration of 60 wt %. In the same graph foaminess during boiling for Pretreated AN-107 is shown as a reference curve. For the simulant Pretreated AN-107 foaminess is 350 vol % and occurs at 60 wt % total solid concentration. The maximum in foaminess for AN-107 D increases from 300 vol % to 650 vol %. However, foaminess is about 300 vol % at a total solid concentration of 30-50 wt %. Foaminess is high enough to cause a sludge spill during evaporation. In the evaporation of AN-107 D hydrocarbons (N-paraffin) and tributyl phosphate (TBP) are present in an unspecified ratio. It is necessary to analyze the effect of hydrocarbons (HC) and TBP on foaminess during boiling of AN-107 D. Here we present the results obtained for the effect of HC, TBP and the combined effect of HC and TBP on foaminess of AN-107 D.

Effect of hydrocarbons (300 ppm) on foaminess of AN-107 D

In the first part of our report involving simulant mixture AN-102 VSL, it was observed that addition of hydrocarbon enhances foaminess and shifts the maximum to a higher total solid concentration. The effect of 300 ppm hydrocarbons on the foaminess of the AN-107 D during boiling was studied. The hydrocarbon was emulsified in simulant mixture AN-107 D after 30 mins of stirring. The emulsified oil is dispersed as a droplet of millimeter size range and some of the droplets stay as oil lens on the top (**Figure 19**). The result of foaminess during boiling versus total solid concentration is presented in **Figure 20**. A maximum in foaminess during boiling of AN-107 D and HC of the order of 725 vol % occurs at a total solid concentration of 60 wt %. As a reference the curve indicating foaminess during boiling for the simulant Pretreated AN-107 without hydrocarbon is also shown. The presence of HC increased foaminess from 75 vol % to 350 vol % in the region of total solid concentration 35-55 wt %. The reproducibility of foaminess (for 3 runs) versus total solid concentration for two experimental runs performed is presented in **Figure 21** and it was found that the error was less than 5%. Please note that as the concentration of hydrocarbon is increased foaminess is also expected to increase. The effect of TBP on foaminess of the boiling simulant mixture AN-107 D was also studied. From our previous observations as reported in first part when trace amounts of TBP are added to the AN-107 D, TBP behaves as an antifoamer and reduces foaminess.

Effect of tributyl phosphate (TBP) (300 ppm) on foaminess of AN-107 D

The simulant AN-107 D with TBP was stirred for 30 mins and the oil phase was emulsified and dispersed as tiny droplets on the top of AN-107 D (**Figure 22**). The foaminess during boiling versus total solid concentration for AN-107 D in the presence of TBP is presented in **Figure 23**. A maximum in foaminess of the order of 500 vol % is observed at a total solid concentration of about 65 wt %. In the same figure the curve for the foaminess during boiling of AN-107 D with hydrocarbons is also presented as a reference. Detailed analysis of the curve of foaminess in the presence of TBP shows that up to a total solid concentration of 45 wt % foaminess is much less than in the presence of AN-107 D and HC. The maximum in foaminess is at the same concentration as observed for the HC indicating a shift in the total solid concentration. We also monitored the effect of both TBP and hydrocarbons on foaminess during boiling of AN-107 D.

Effect of TBP (300 ppm) and hydrocarbons (300 ppm) on foaminess of AN-107 D

The simulant mixture AN-107 D with HC and TBP was stirred for 30 mins and the oil phase was emulsified and dispersed as millimeter sized droplets on the top of AN-107 D (**Figure 24**). Data for the foaminess during boiling of AN-107 D with TBP and HC is presented in **Figure 25**. A maximum in foaminess of the order of 650 vol % is observed at a total solid concentration of about 65 wt %. In the same graph comparison of the combined effect of TBP and HC and the individual effect of TBP and HC on foaminess versus total solid concentration during boiling of AN-107 D is presented. Foaminess steeply increases from 45 wt % total solid concentration and at a solid concentration of 65 wt % foaminess was around 650 vol %. We have studied the effect of TBP, HC and the combined effect of TBP and HC on foaminess during boiling of AN-107 D. Tests were also carried out for the antifoaming efficiency of two commercial antifoamers DOW 2-3930 and DOW Q2-3183 A as recommended by SRTC.

Antifoaming performance of DOW 2-3930 on the foaminess of AN-107 D

The antifoaming performance of DOW 2-3930 (1400 ppm) was tested in the presence of AN-107 D and HC (300 ppm). The antifoamer and hydrocarbons are dispersed as millimeter size droplets on the surface of the simulant after 20 mins of stirring (**Figure 26**). Data for the foaminess during boiling of AN-107 D with HC in the presence of antifoamer is presented in **Figure 27**. It is seen that the antifoamer reduces foaminess by a factor of 5. In the same figure two reference curves are also presented. It was also noticeable that in the operating concentration range of 30-50 wt % foaminess is about 50-60 vol %, which indicates that the antifoamer is effective in reducing foaminess. However, the antifoamer causes foaminess of the order of 50 vol % which could be detrimental for the proper working of the evaporator. In order to test the antifoaming performance in the presence of simulant mixture, TBP and hydrocarbons further tests were carried out.

Antifoaming performance of DOW 2-3930 on foaminess of AN-107 D, hydrocarbons and TBP

The antifoaming performance of DOW 2-3930 in the presence of AN-107 D, TBP (300 ppm) and HC (300 ppm) was tested. Two different levels of antifoam concentrations (1400 ppm and 700 ppm) were chosen for antifoaming performance. **Figures 28** and **29** depict the antifoamer degree of spreading of 1400 ppm and 700 ppm of antifoamer DOW 2-3930 on the surface of AN-107 D. The performance of 1400 ppm of the antifoamer was first tested with AN-107 D, hydrocarbons and TBP. It is seen in **Figure 30** that foaminess is reduced by a factor of 12 in the presence of the antifoamer. Foaminess is only 25-40 vol % in the region of 25-35 wt % total solid concentration. Based on these results it was necessary to check if lower concentrations of antifoamer would be effective. It is seen in **Figure 30** that foaminess is about 60-70 vol % in the concentration range of 25-35 wt % total solid concentration. If the antifoaming performance of two different concentrations of antifoamer were compared it is seen that foaminess in the presence of 1400 ppm of antifoamer is less than that in the presence of 700 ppm in the operating range of 25-50 wt % total solid concentration. We tested the other commercial antifoamer Q2-3183 A for its antifoaming performance using AN-107 D, hydrocarbons and TBP.

Antifoaming performance of DOW Q2-3183 A on AN-107 D, hydrocarbons and TBP

The antifoaming performance of DOW Q2-3183 A in the presence of AN-107 D, TBP (300 ppm) and HC (300 ppm) were tested. **Figures 31** depicts the antifoamer degree of spreading of 1400 ppm of antifoamer DOW Q2-3183 A on the surface of AN-107 D. From the **Figure 32**, it is seen that foaminess is reduced by a factor of 20 in the operating range of 30-50 wt % total solid concentration. Experiments were carried out to compare the antifoaming performance of the two antifoamers in the presence of AN-107 D, hydrocarbons and TBP.

Comparison of antifoaming performance of DOW 2-3930 and DOW Q2-3183 A on AN-107 D, hydrocarbons and TBP

The two antifoamers DOW 2-3930 and DOW Q2-3183 A (1400 ppm) reduced foaminess when added to simulant mixture AN-107 D, hydrocarbons and TBP. On comparing the two antifoamers (**Figure 33**) it is clear that in the range of 30-50 wt % total solid concentration foaminess in the presence of antifoamer DOW 2-3930 is slightly less than in the presence of DOW Q2-3183.

Foaminess in pilot plant (higher flux) may be different than the foaminess in the laboratory scale.

PART III

Foaminess during boiling of simulant AZ-101

Experiments were conducted to study foaminess during boiling of simulant AZ-101. The data for foaminess during boiling of AZ-101 versus total solid concentration is presented in **Figure 34**. A maximum in foaminess for AZ-101 is of the order of 65 vol % and occurs at a total solid concentration of 45 wt %. However, foaminess is about 50 vol % at a total solid concentration of 30-40 wt %. Foaminess is considerably high and therefore can cause a sludge spill during evaporation. In the downstream evaporation of AZ-101, hydrocarbons (N-paraffin) and tributyl phosphate (TBP) are present in an unspecified ratio. The effect of hydrocarbons (HC) and TBP on foaminess during boiling of AZ-101 is also studied. Here we present the results obtained for the effect of HC, TBP and the combined effect of HC and TBP on foaminess during boiling of AZ-101.

Effect of hydrocarbons (300 ppm) on foaminess during boiling of AZ-101

The effect of 300 ppm hydrocarbons on the foaminess of the AZ-101 during boiling was studied. The hydrocarbon was emulsified in the simulant mixture after 30 mins of stirring. The emulsified oil spreads as lenses of millimeter size range on the surface of the simulant AZ-101 (**Figure 35**). The result of foaminess during boiling of AZ-101 and HC versus total solid concentration is presented in **Figure 36**. A maximum in foaminess during boiling of AZ-101 and HC which is of the order of 60 vol % occurs at a total solid concentration of 50 wt %. As a reference, the curve indicating foaminess during boiling for the simulant Pretreated AZ-101 without hydrocarbon is also presented. The maximum in foaminess in the presence of HC has shifted towards a higher total solid concentration as observed for other simulants. The reduction in foaminess can be attributed to the specific interactions of HC with solid particles. Potentially, the particles become hydrophobic and behave as an antifoamer. The effect of HC on foaminess during boiling depends on the composition of the simulant. From our observations as mentioned in earlier parts of this report for simulants Pretreated AN-102 and Pretreated AN-107 when trace amounts of TBP are added to simulants, TBP behaves as an antifoamer and reduces foaminess. The effect of TBP on foaminess of the boiling AZ-101 was studied.

Effect of tributyl phosphate (TBP) (300 ppm) on foaminess of simulant mixture

The simulant AZ-101 with TBP was stirred for 30 mins and the oil phase was emulsified and dispersed as tiny droplets on the top of AZ-101 (**Figure 37**). The foaminess during boiling versus total solid concentration for AZ-101 in the presence of TBP is presented in **Figure 38**. A maximum in foaminess of the order of 60 vol % is observed at a total solid concentration of about 50 wt %. In the same figure the curve for the foaminess during boiling of AZ-101 is also presented as a reference. Analysis of the curve of foaminess in the presence of TBP shows that upto a total solid concentration of 45 wt % foaminess is much less than in the presence of AZ-101. Such a reduction in foaminess in the presence of TBP at lower total solids concentration is also observed for simulants Pretreated AN-102 and AN-107. The maximum in foaminess is at the same concentration as observed for the HC indicating a shift in the total solid concentration. We also monitored the effect of both TBP and hydrocarbons on foaminess during boiling of AZ-101.

Effect of TBP (300 ppm) and hydrocarbons (300 ppm) on foaminess of AZ-101

The simulant AZ-101 with HC and TBP was stirred for 30 mins and the oil phase was emulsified and dispersed as millimeter sized droplets on the top of AZ-101 (**Figure 39**). Data for the foaminess during boiling of AZ-101 with TBP and HC is presented in **Figure 40**. A maximum in foaminess of the order of 60 vol % is observed at a total solid concentration of about 50 wt %. In the same graph a comparison with foaminess during boiling of AZ-101 versus total solid concentration is also presented. Foaminess is less when the HC and TBP are added to the boiling simulant AZ-101. It is evident from the tests carried out that foaminess in the simulant AZ-101 is due to the presence of hydrophobic particles. TBP and hydrocarbon in the presence of hydrophobic particles in the simulant AZ-101 act as antifoamers. Tests were also carried out for the antifoaming efficiency of the commercial antifoamer DOW 2-3930 on AZ-101 as recommended by SRTC.

Antifoaming performance of DOW 2-3930 on foaminess of AZ-101, hydrocarbons and TBP

The antifoaming performance of DOW 2-3930 in the presence of AZ-101, TBP (300 ppm) and HC (300 ppm) was tested. The degree of spreading of 1400 ppm of antifoamer DOW 2-3930 on the surface of AZ-101 is depicted in **Figure 41**. The performance of 1400 ppm of the antifoamer was tested with AZ-101, hydrocarbons and TBP. The data for foaminess during boiling of AZ-101, TBP and HC in the presence of antifoamer DOW 2-2930 is presented in **Figure 42**. A maximum in foaminess of the order of 40 vol % is observed at a total solid concentration of 50 wt %. However, foaminess is 30-40 vol % in the region of 25-35 wt % total solid concentration which could be detrimental for the proper working of the evaporator. In conclusion, the antifoaming performance of DOW 2-3930 is not any better than the performance of HC and TBP. Foaminess in the case of simulant AZ-101 is due to the bi-philic particles and the classical antifoamer cannot reduce foaminess in this case.

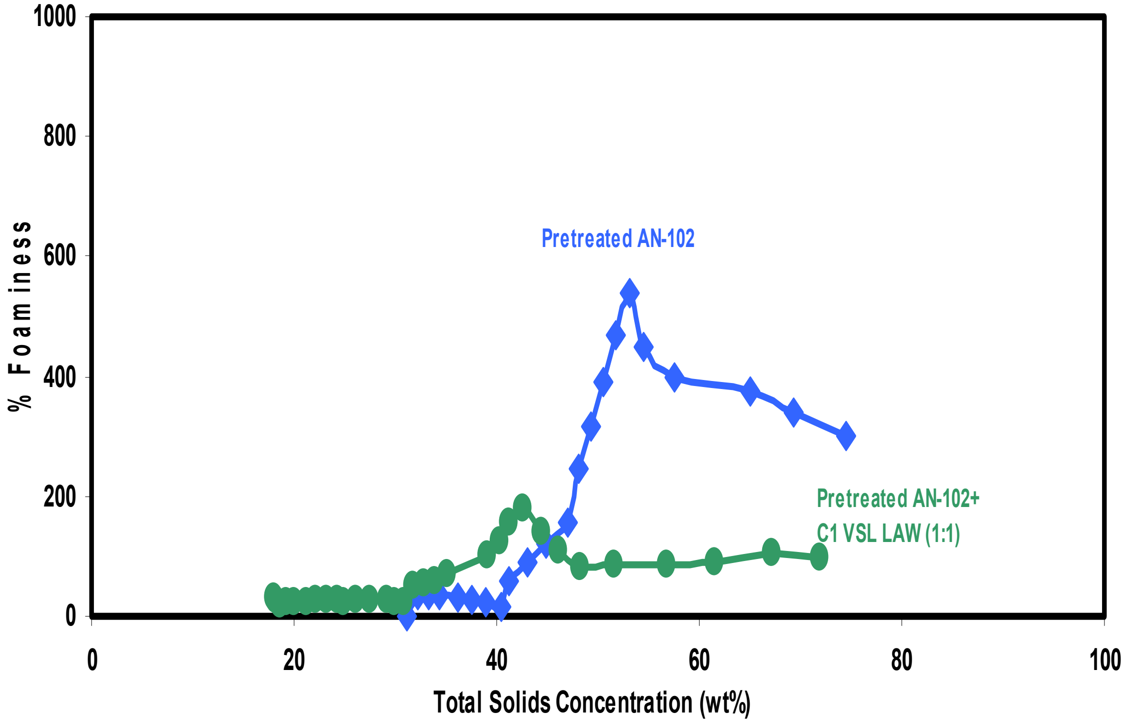


Figure 1: Foaminess during boiling of Pretreated AN-102 and VSL LAW Ca (1:1) (Pressure 110 mm hG, Flux 2 kg/min sq.m)

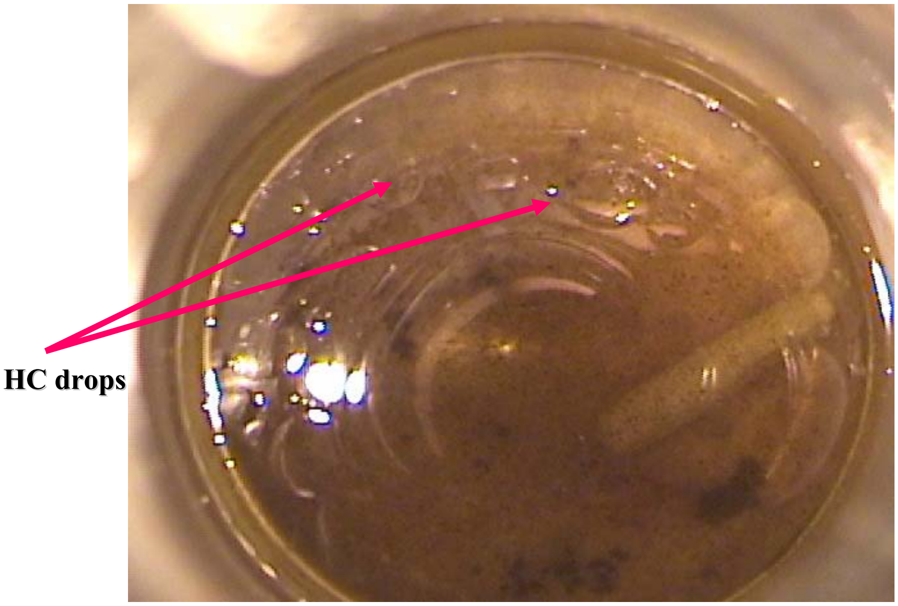


Figure 2: Photograph of emulsified hydrocarbon dispersed as droplet on the surface of AN-102 VSL

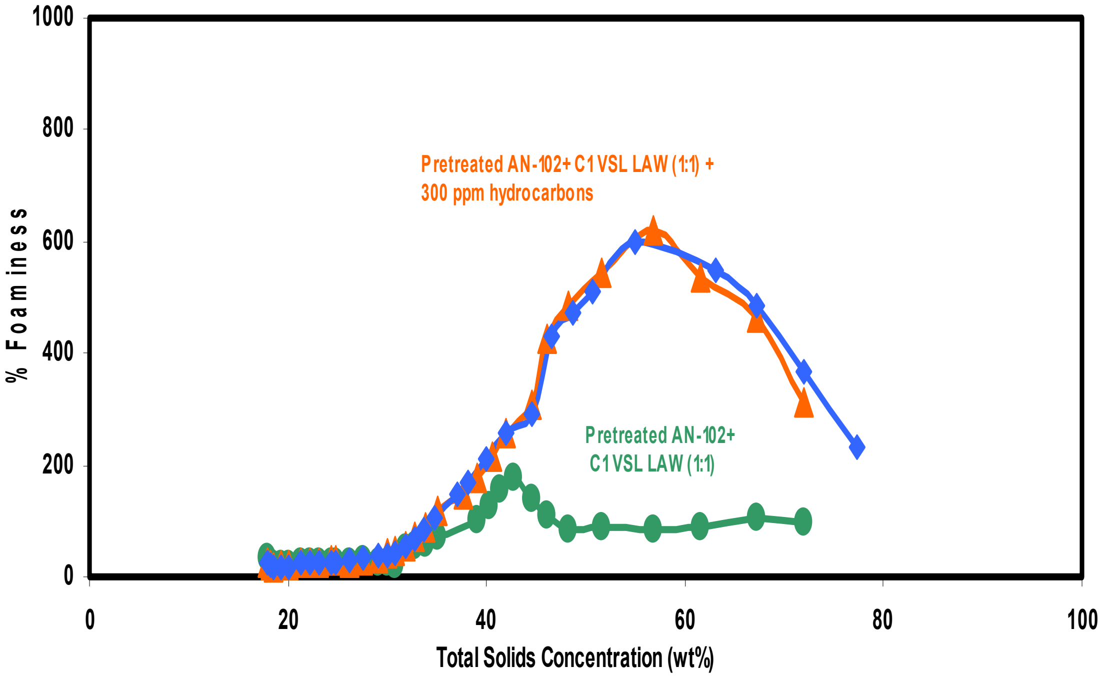


Figure 3: Effect of hydrocarbons (300 ppm) on foaminess during boiling of Pretreated AN-102 VSL (Pressure 110 mm Hg, Flux 2 kg/min sq.m)

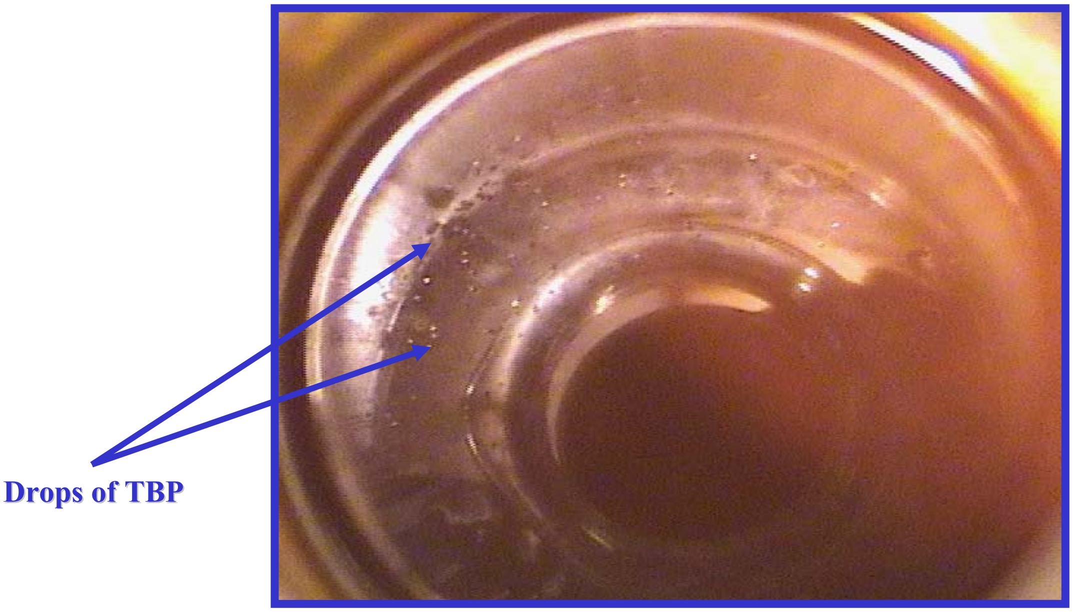


Figure 4: Photograph of emulsified TBP dispersed as millimeter size droplets on surface of AN-102 VSL

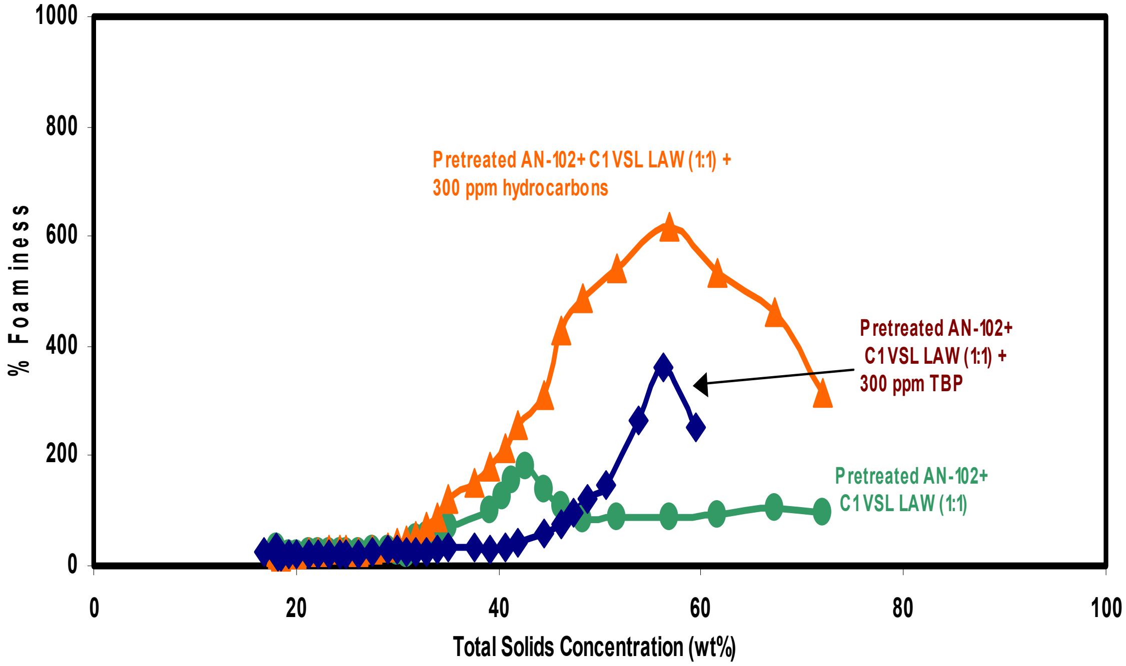


Figure 5: Effect of TBP (300 ppm) on foaminess during boiling of AN-102 VSL (Pressure 110 mm Hg, Flux 2 kg/min sq.m)

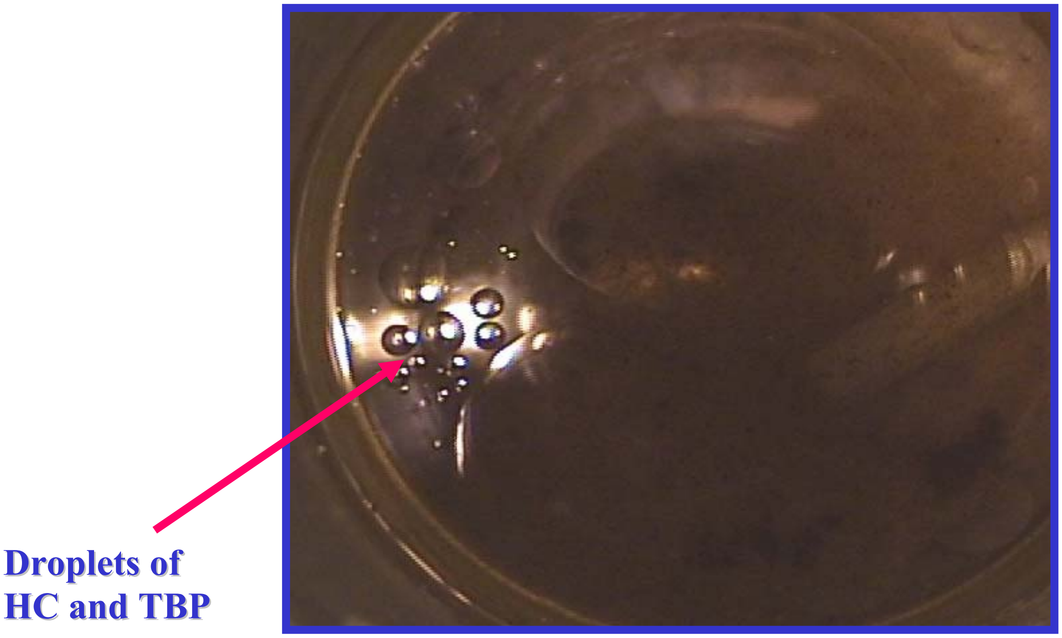


Figure 6: Photograph of emulsified HC and TBP droplets on the surface of AN-102 VSL

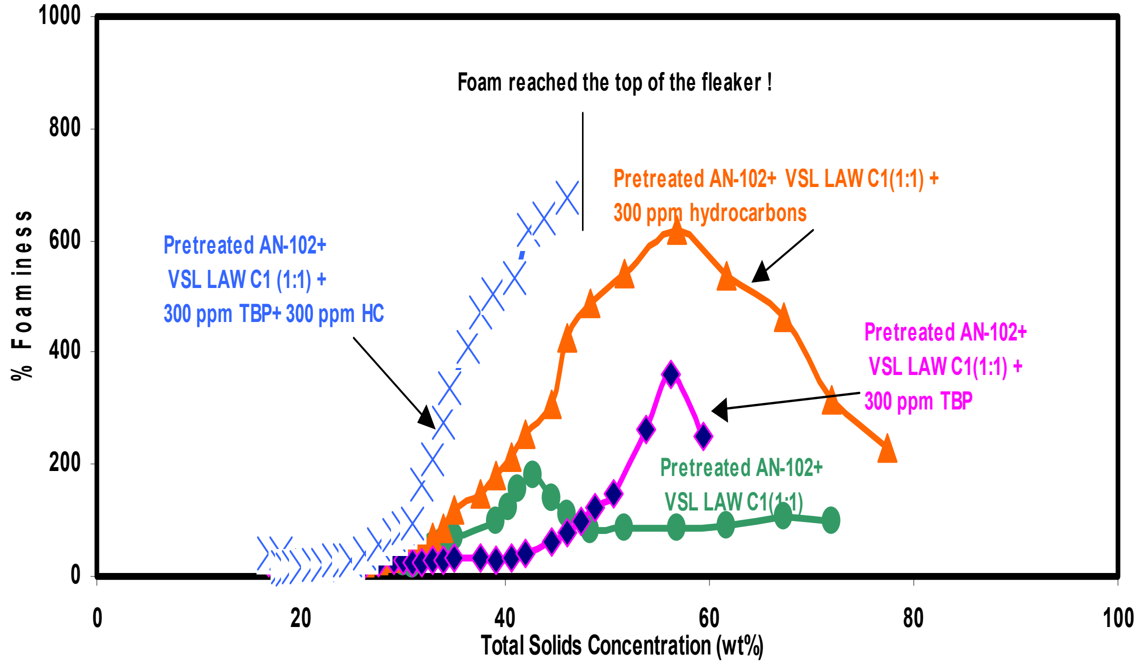


Figure 7: Effect of HC (300 ppm) and TBP (300 ppm) on foaminess during boiling of AN-102 VSL (Pressure 110 mm Hg, Flux 2 kg/min sq.m)

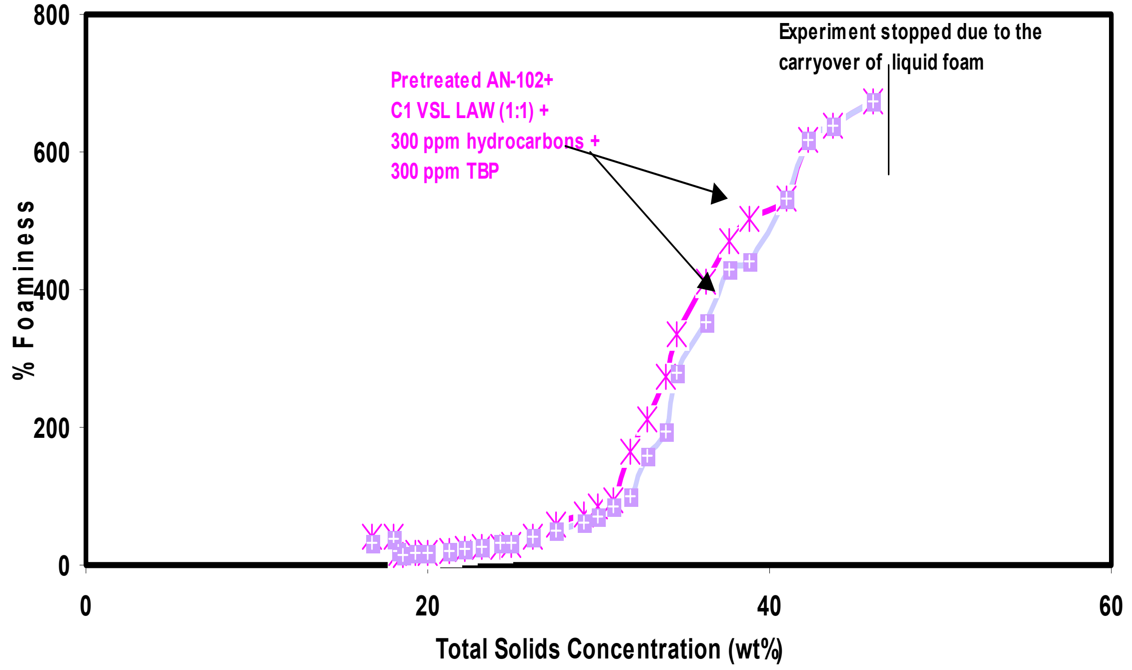
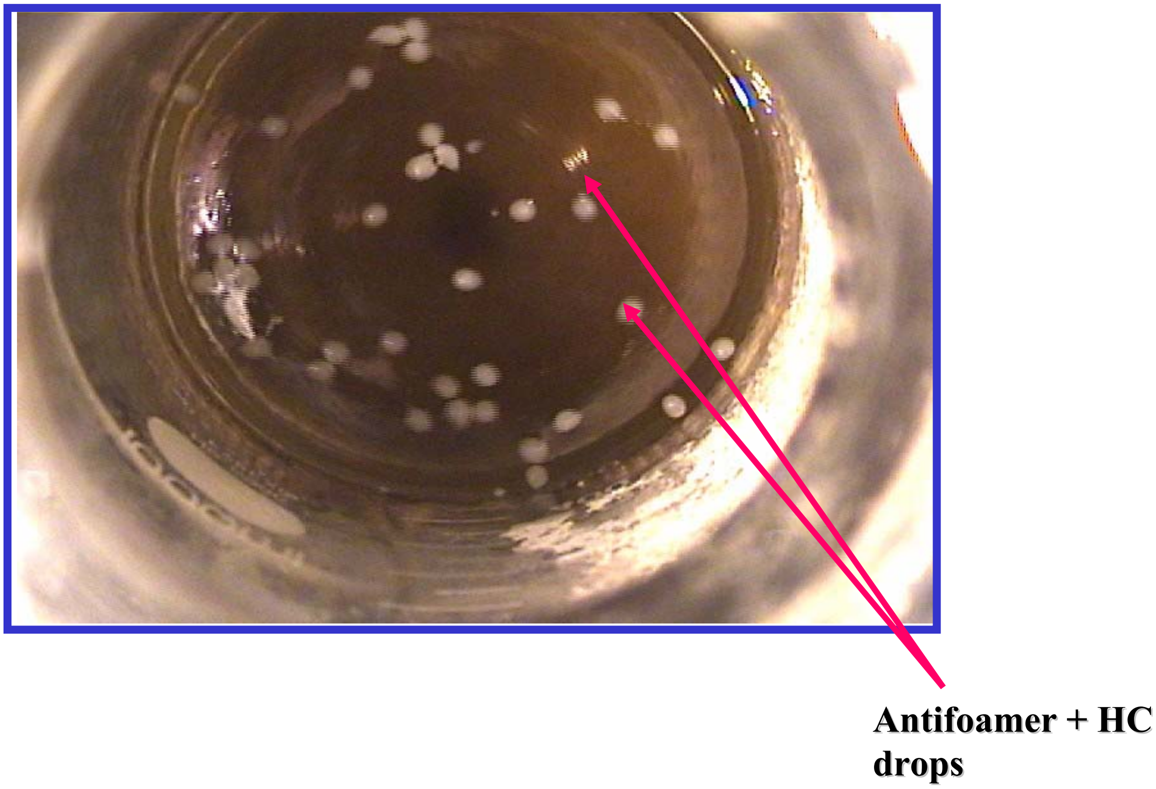


Figure 8: Reproducibility of curves showing effect of HC (300 ppm) and TBP (300ppm) on foaminess during boiling of AN-102 VSL (Pressure 110 mm Hg, Flux 2kg/min sq.m)



Antifoamer + HC drops

Figure 9: Photograph depicting HC (300 ppm) and antifoamer DOW 2-3930 on surface of AN-102 VSL

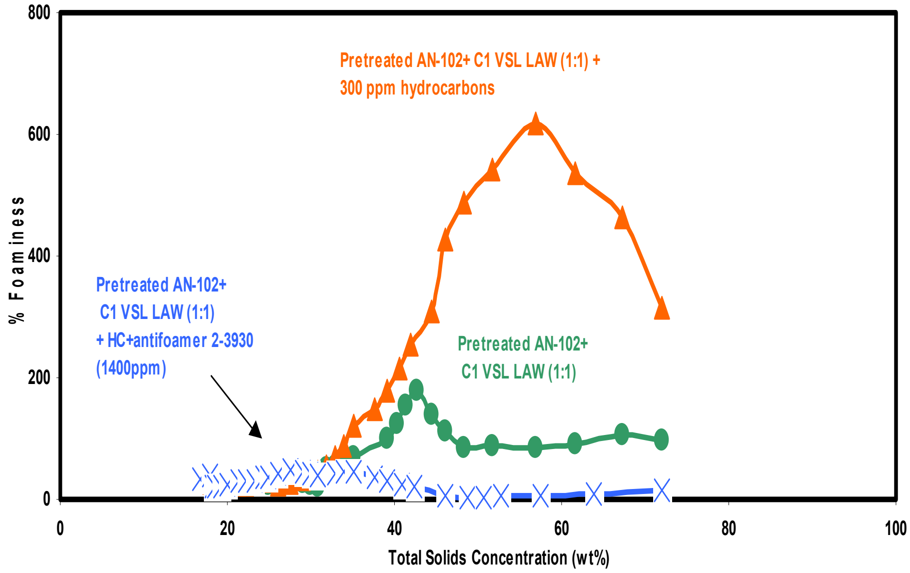


Figure 10: Antifoaming performance of DOW 2-3930 in the presence of HC (300 ppm)during boiling of AN-102 VSL (Pressure 110 mm Hg, Flux 2 kg/min sq.m)

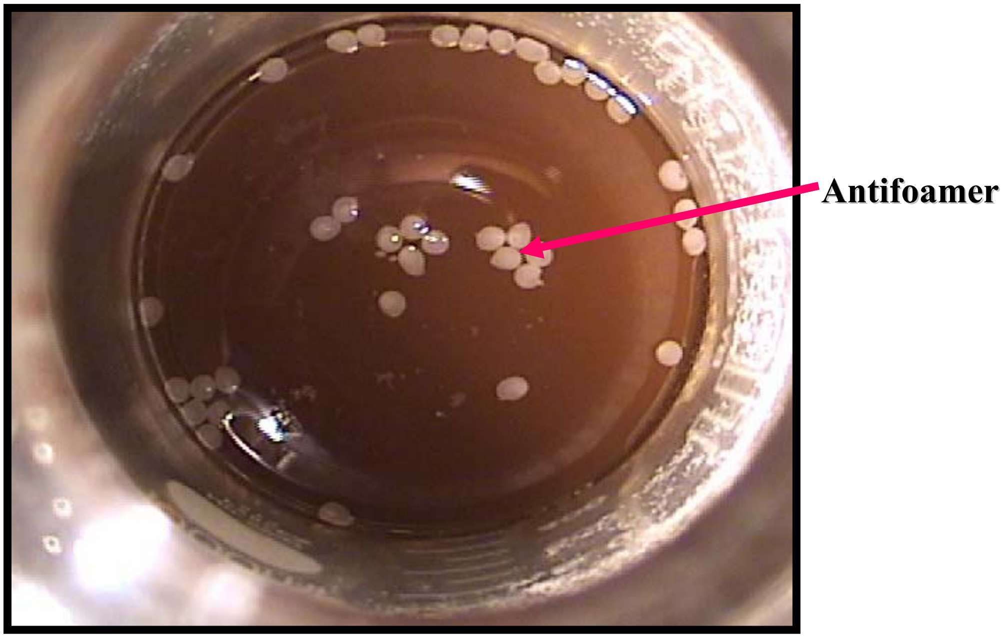


Figure 11: Photograph depicting the spreading of 1400 ppm of antifoamer DOW 2-3930 on surface of AN-102 VSL

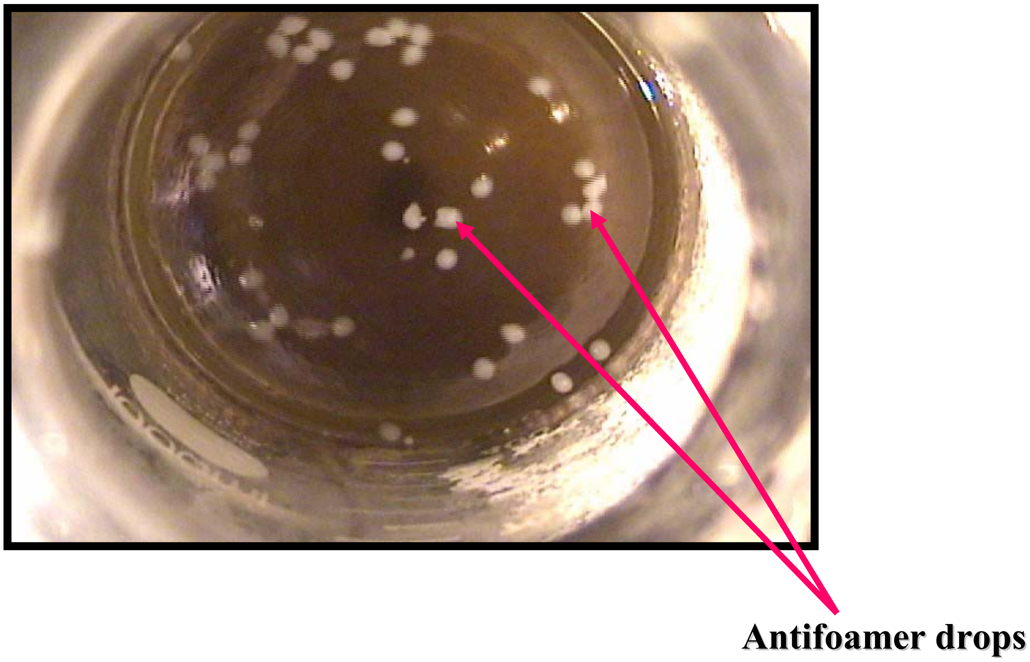


Figure 12: Photograph depicting the spreading of 700 ppm of antifoamer DOW 2-3930 on surface of AN-102 VSL

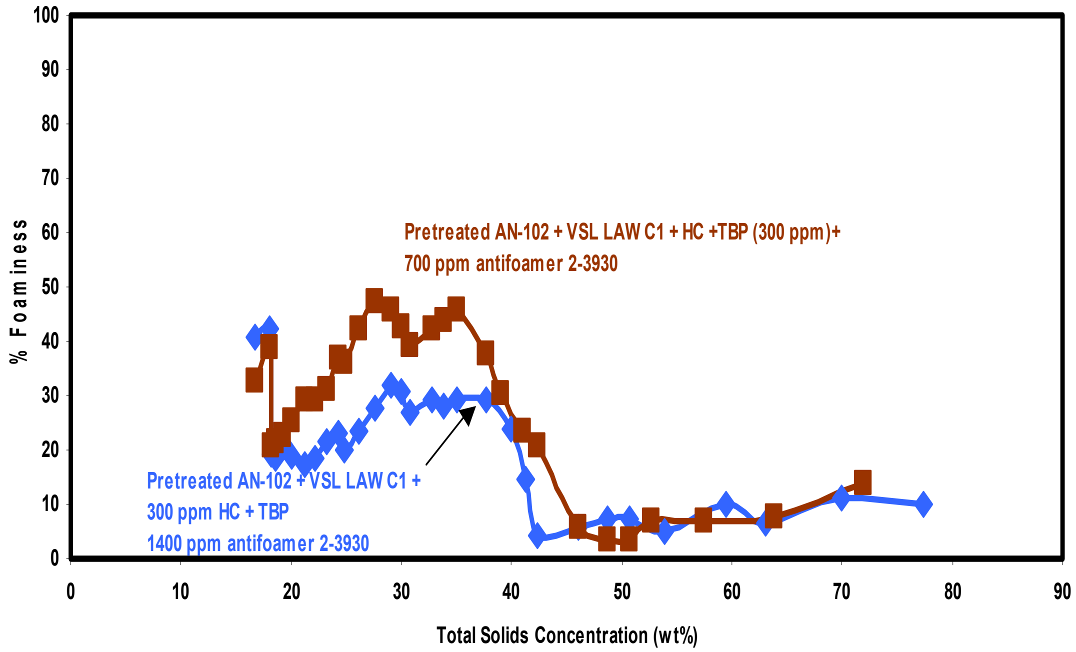


Figure 13: Antifoaming performance of two concentrations of DOW 2-3930 (1400 and 700 ppm) during boiling of AN-102 VSL + HC + TBP (300 ppm) (Pressure 110 mm Hg, Flux 2 kg/min sq.m)

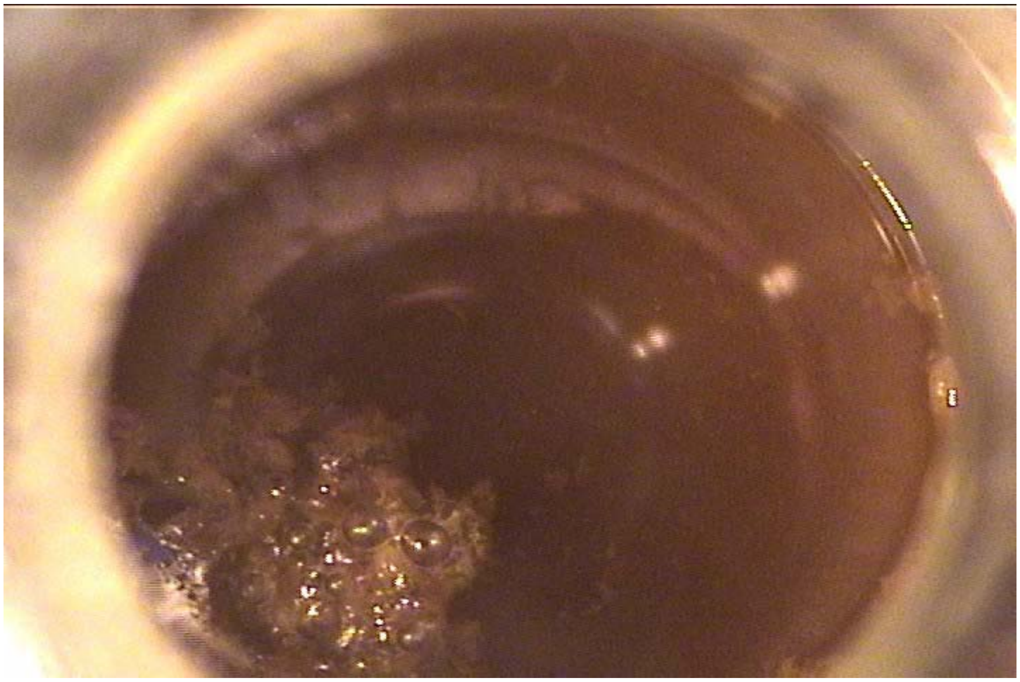


Figure 14: Photograph depicting the spreading of 1400 ppm of antifoamer DOW Q2-3183 A on surface of AN-102 VSL

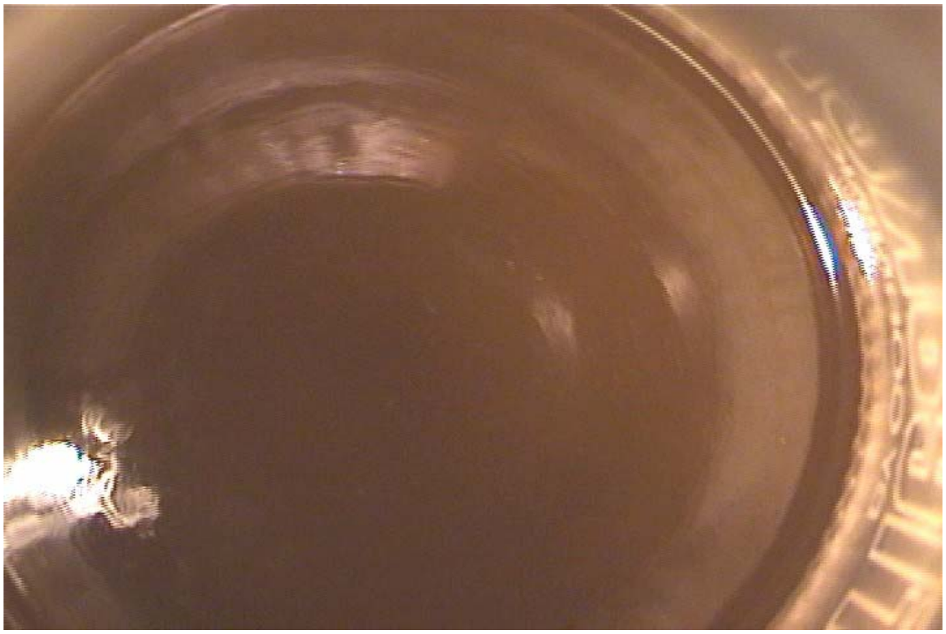


Figure 15: Photograph depicting the spreading of 700 ppm of antifoamer DOW Q2-3183 A on surface of AN-102 VSL

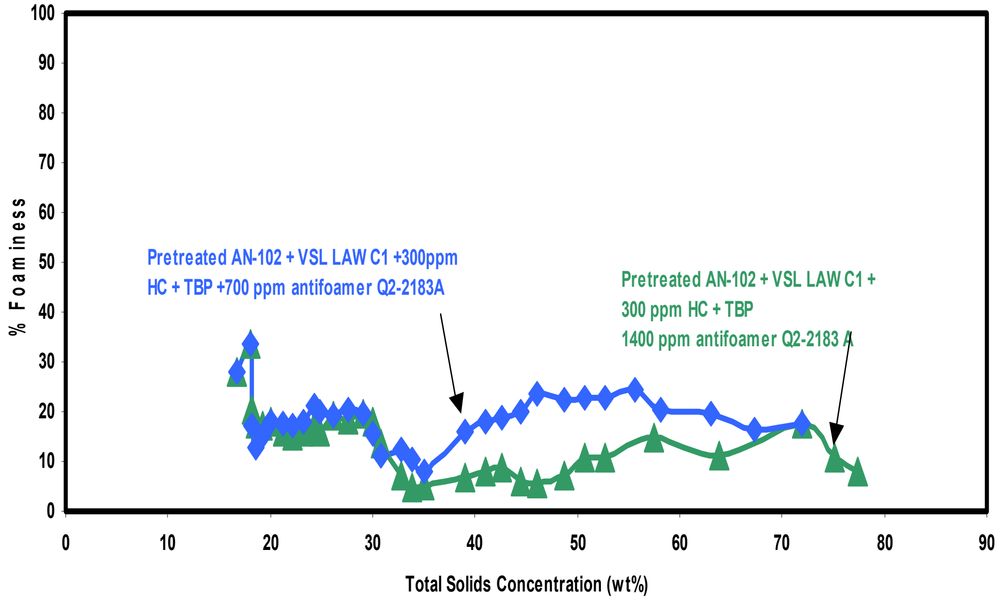


Figure 16: Antifoaming efficiency of two different concentrations of DOW Q2-3183 A (1400 and 700 ppm) during boiling of AN-102 VSL + HC +TBP (300 ppm) (Pressure 110 mm Hg, Flux 2 kg/min sq.m)

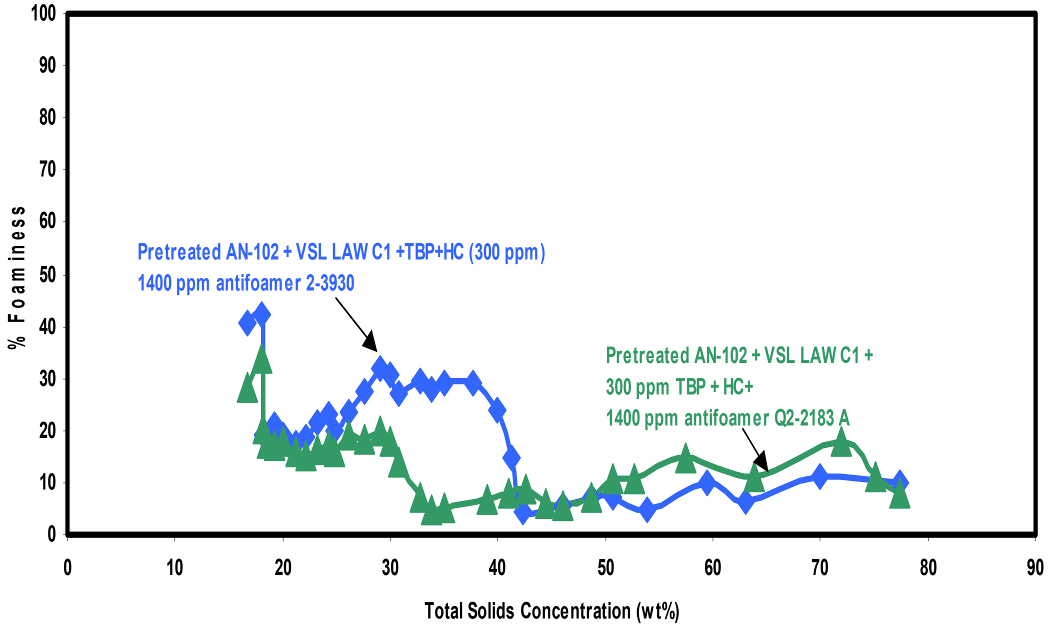


Figure 17: Comparison of antifoaming action of two different antifoamers DOW 2-3930 and DOW Q2-3183 A during boiling of AN-102 VSL + HC + TBP (300 ppm) (Pressure 110 mm Hg, Flux 2 kg/min sq.m)

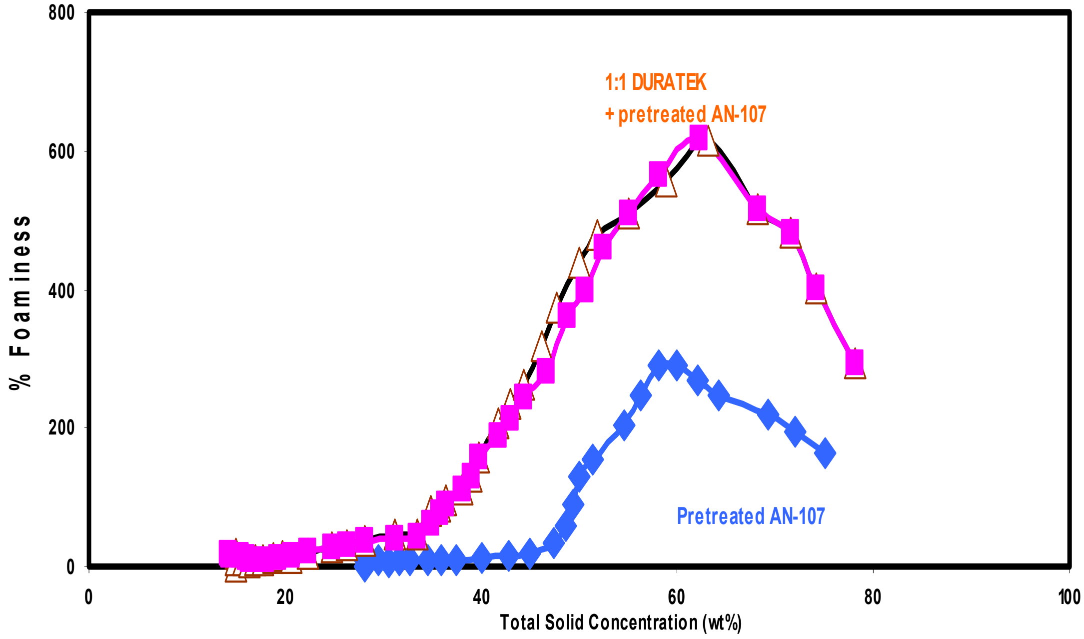


Figure 18: Foaminess during boiling of simulant mixture Pretreated AN-107 and DURATEK (Pressure 110 mm Hg, Flux 2 kg/min sq.m)

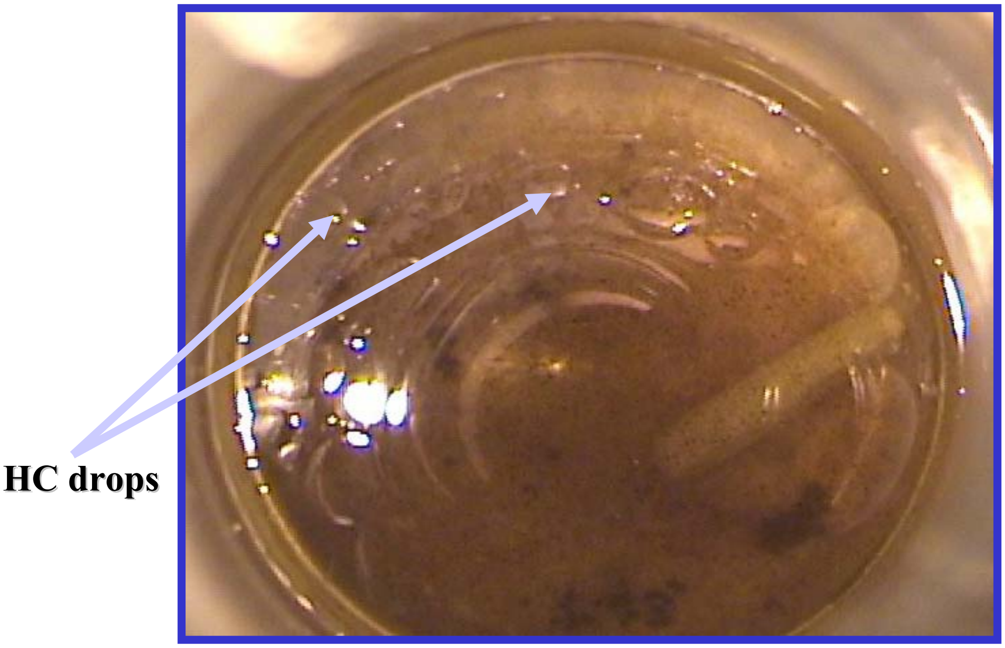


Figure 19: Photograph depicting millimeter size HC drops on the surface of AN-107 D

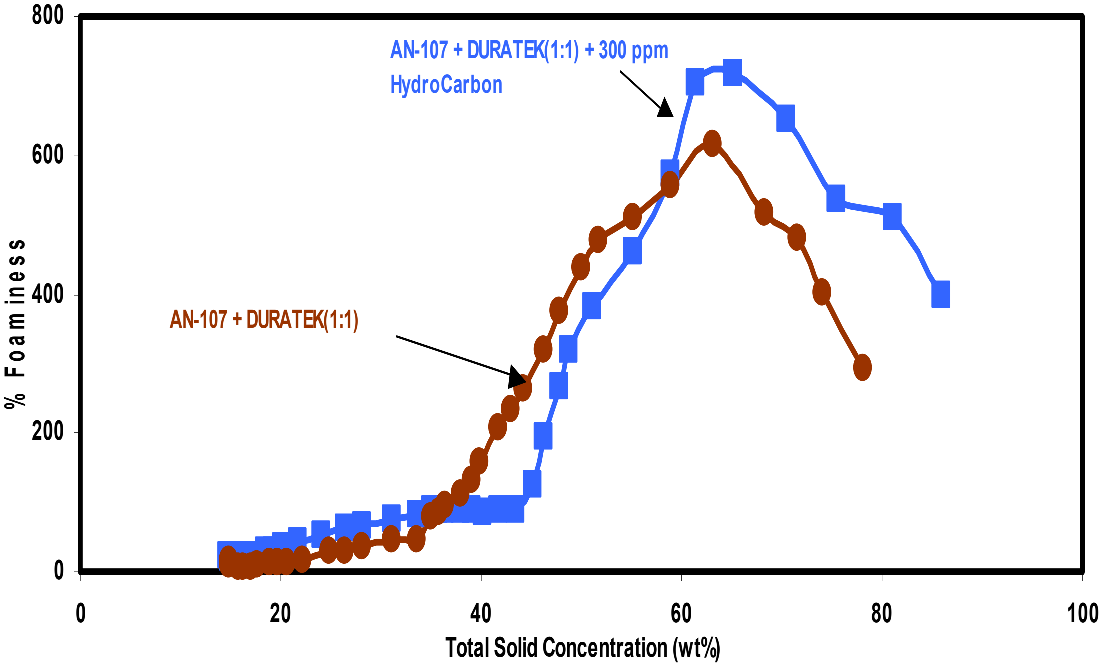


Figure 20: Effect of HC (300 ppm) on foaminess during boiling of AN-107 D (Pressure 110 mm Hg, Flux 2 kg/min sq.m)

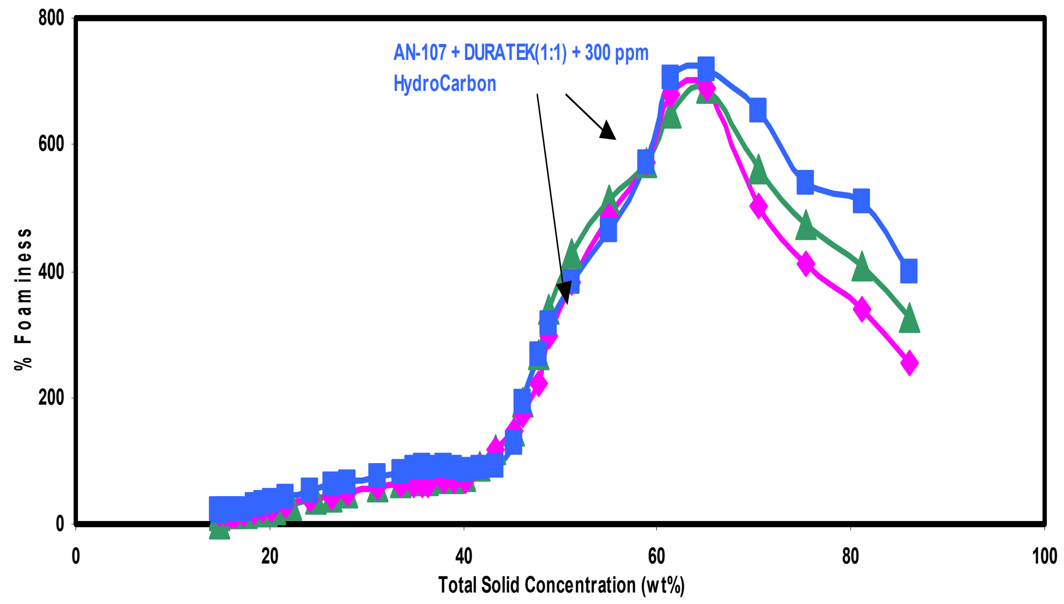


Figure 21: Reproducibility of curves showing effect of HC (300 ppm) on foaminess during boiling of AN-107 D (Pressure 110 mm Hg, Flux 2kg/min sq.m)

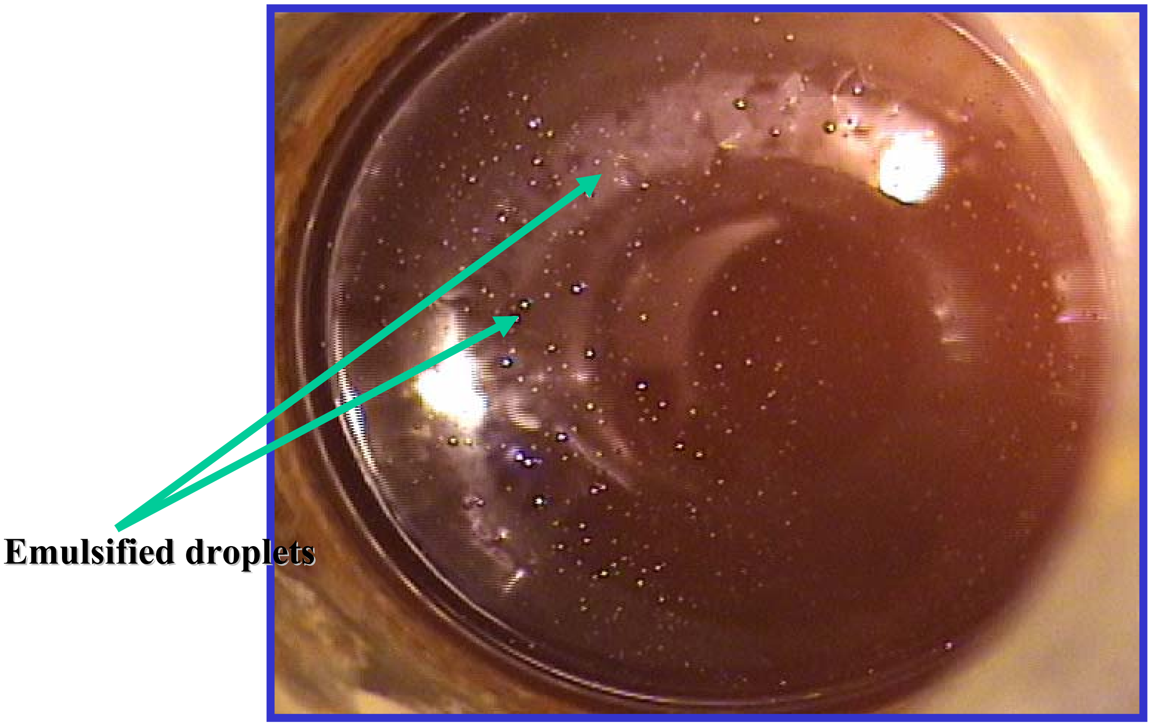


Figure 22: Photograph depicting emulsified droplets of TBP on surface of AN-107 D

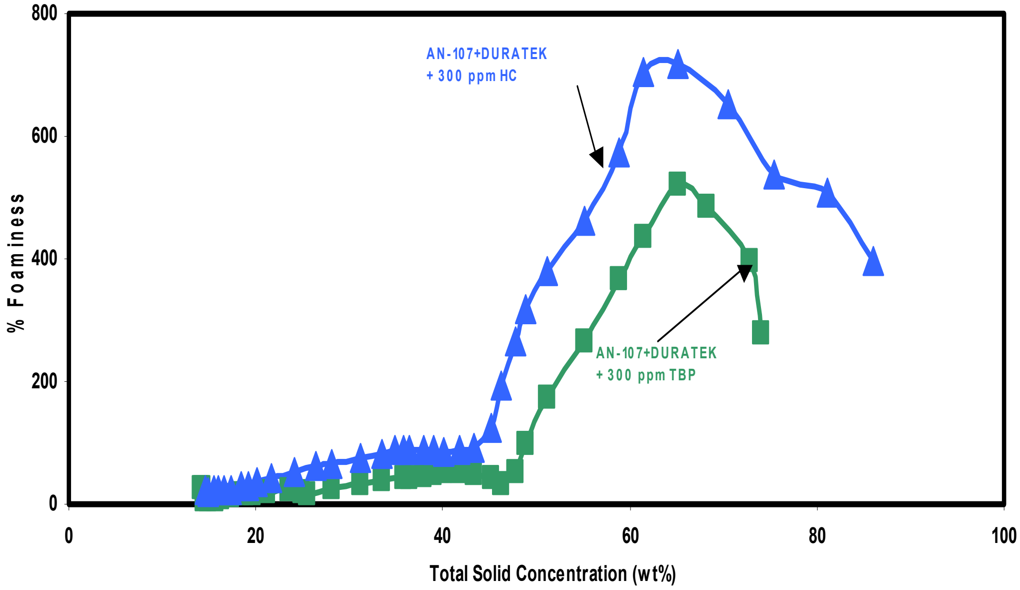


Figure 23: Effect of TBP (300 ppm) on foaminess during boiling of AN-107 D (Pressure 110 mm Hg, Flux 2kg/min sq.m)

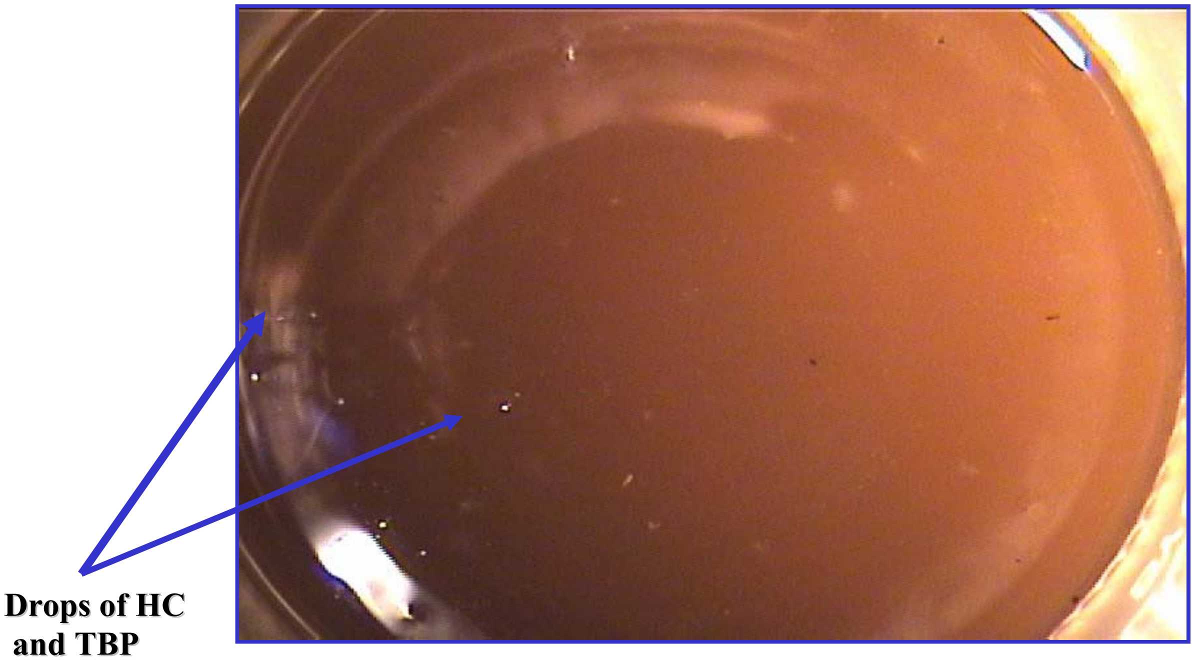


Figure 24: Photograph depicting emulsified droplets of TBP and HC on surface of AN-107 D

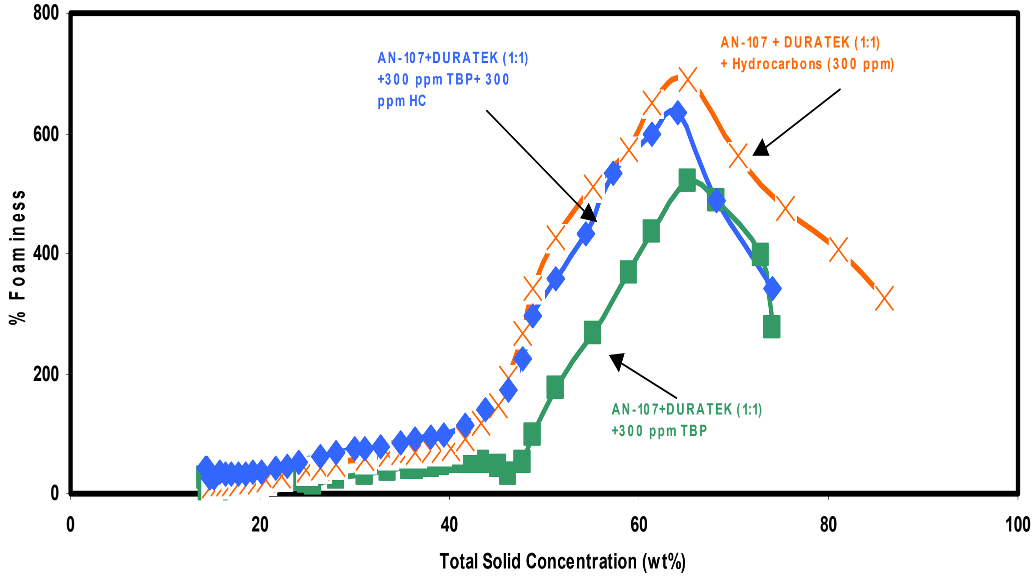


Figure 25: Effect of HC (300 ppm) and TBP (300 ppm) on foaminess during boiling of AN-107 D (Pressure 110 mm Hg, Flux 2 kg/min sq.m)

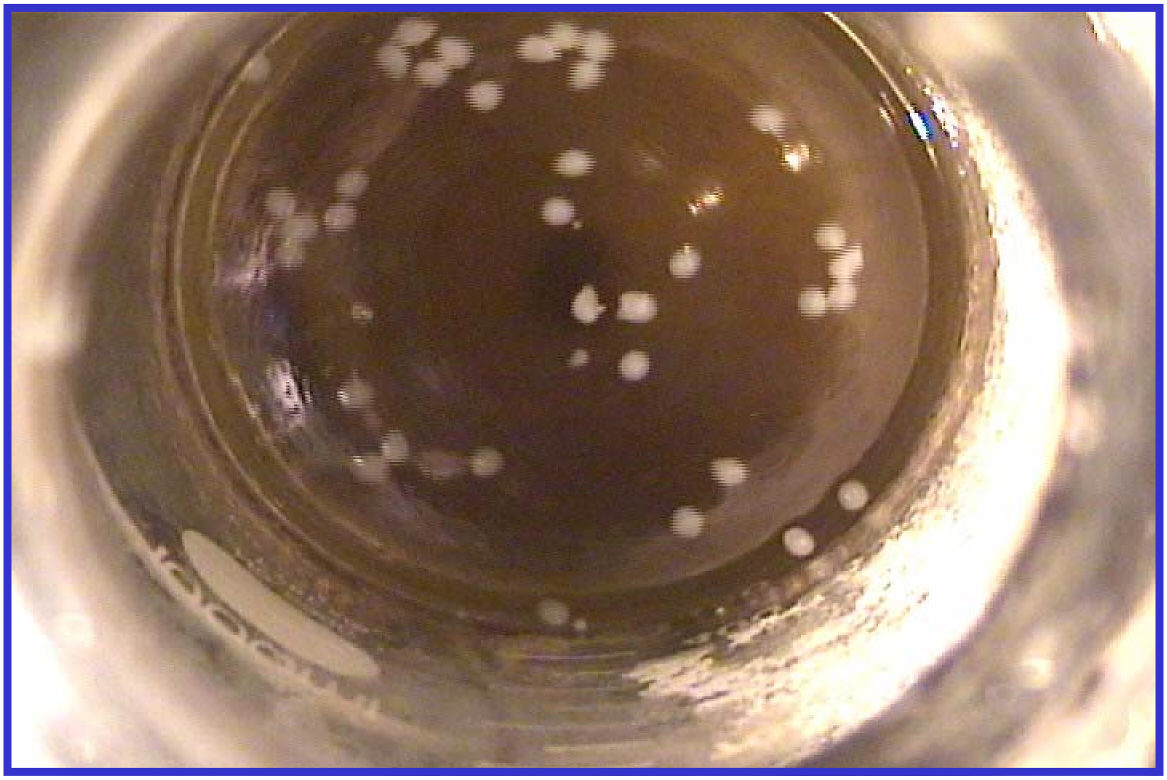


Figure 26: Photograph depicting emulsified droplets of HC and antifoamer DOW 2-3930 on surface of AN-107 D

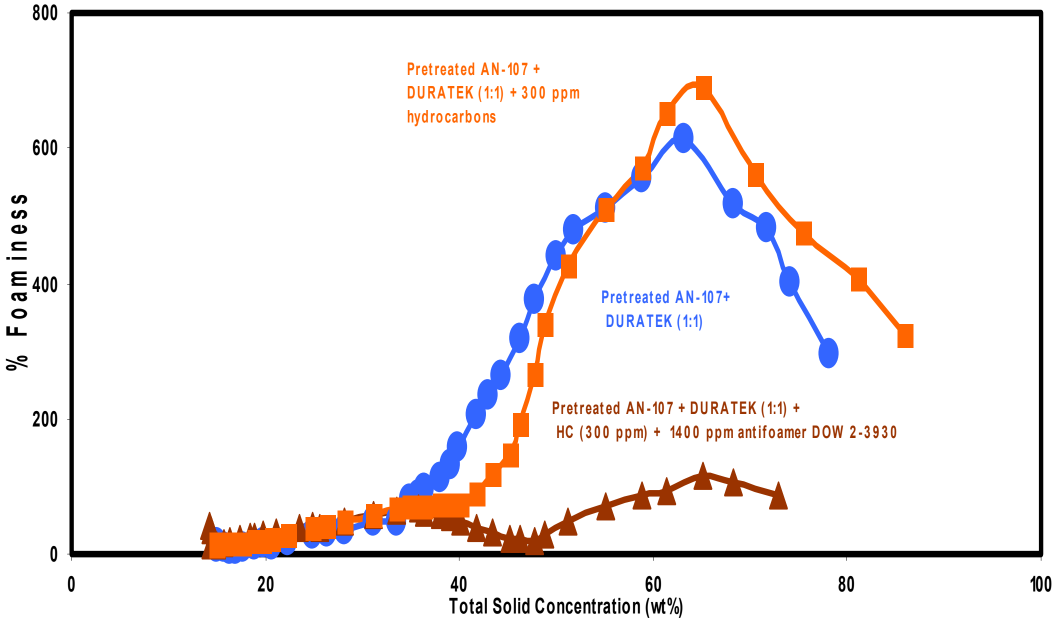
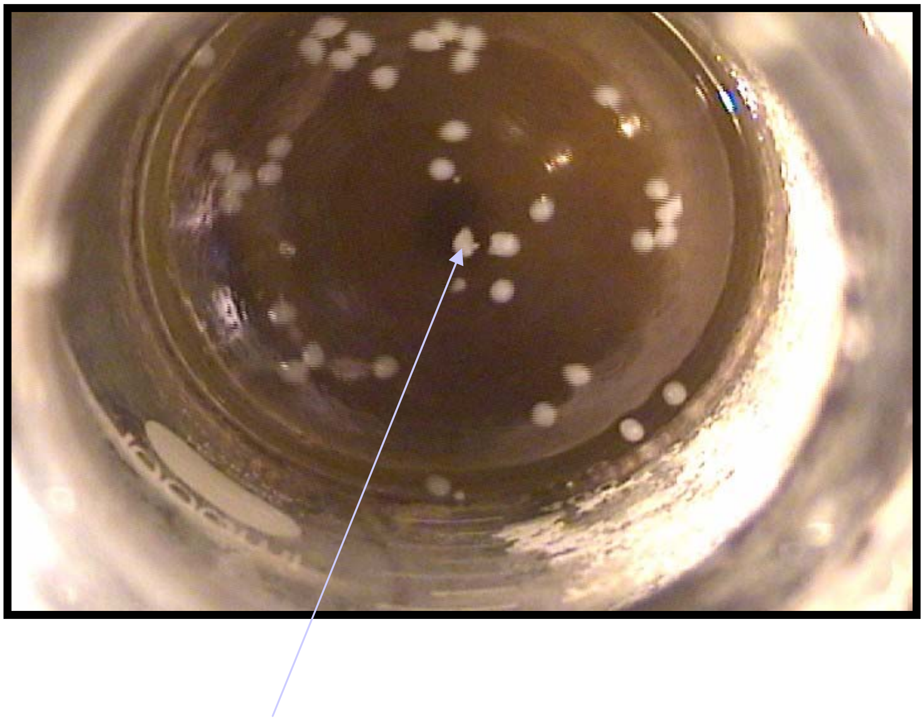
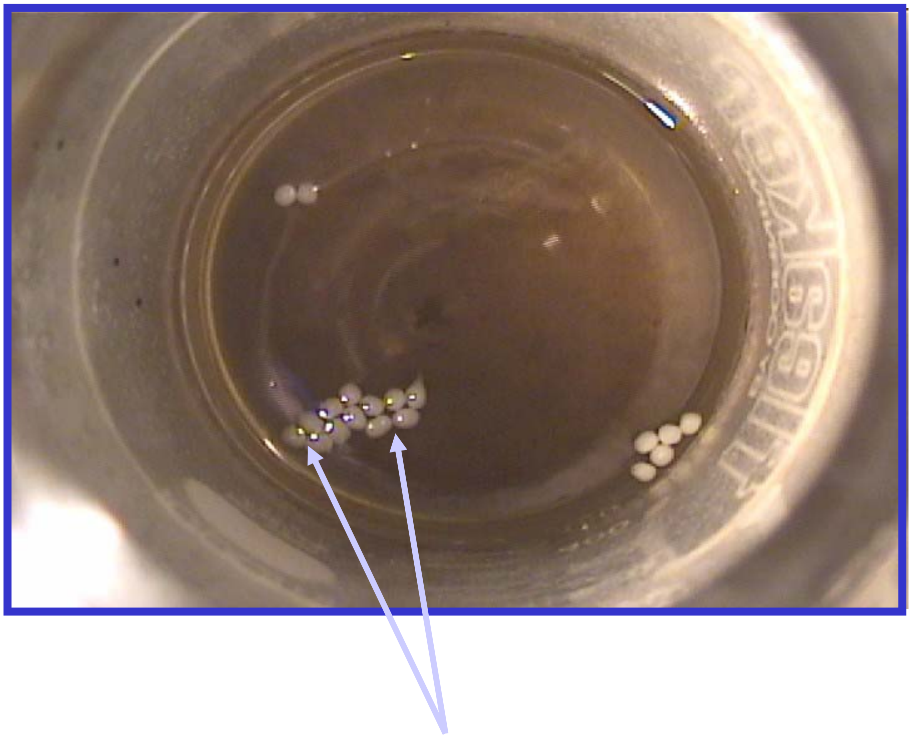


Figure 27: Antifoaming performance of DOW 2-3930 in the presence of HC (300 ppm) during boiling of AN-107 D (Pressure 110 mm Hg, Flux 2 kg/min sq.m)



Antifoamer, HC and TBP

Figure 28: Photograph depicting emulsified droplets of HC, TBP and 1400 ppm antifoamer DOW 2- 3930 on surface of AN-107 D



Drops of antifoamer, HC and TBP

Figure 29: Photograph depicting emulsified droplets of HC, TBP and 700 ppm antifoamer DOW 2- 3930 on surface of AN-107 D

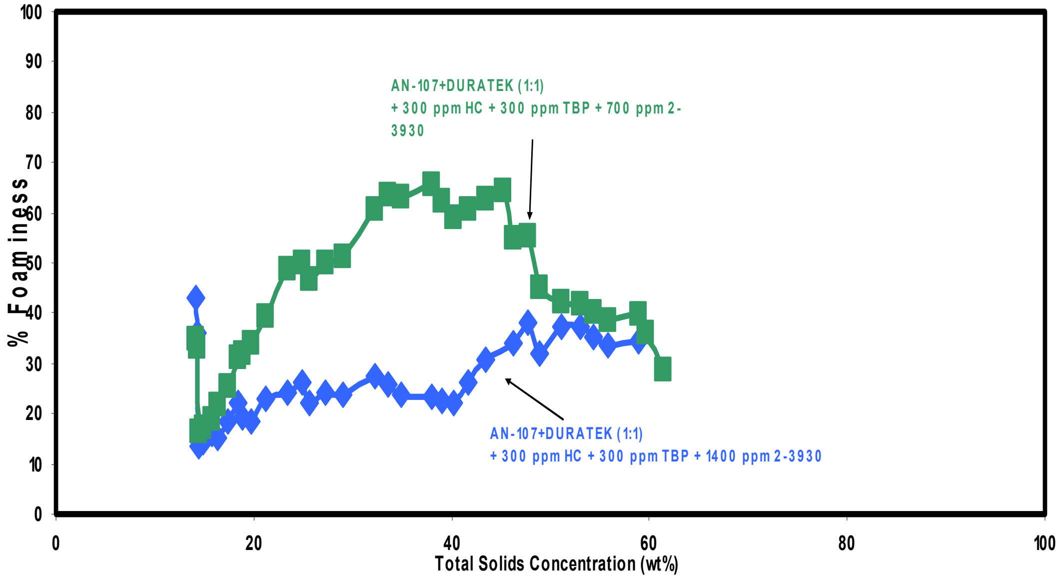


Figure 30: Comparison of antifoaming action of two different concentrations of DOW 2-3930 (1400 and 700 ppm) during boiling of AN-107 D + HC + TBP (300 ppm) (Pressure 110 mm Hg, Flux 2 kg/min sq.m)

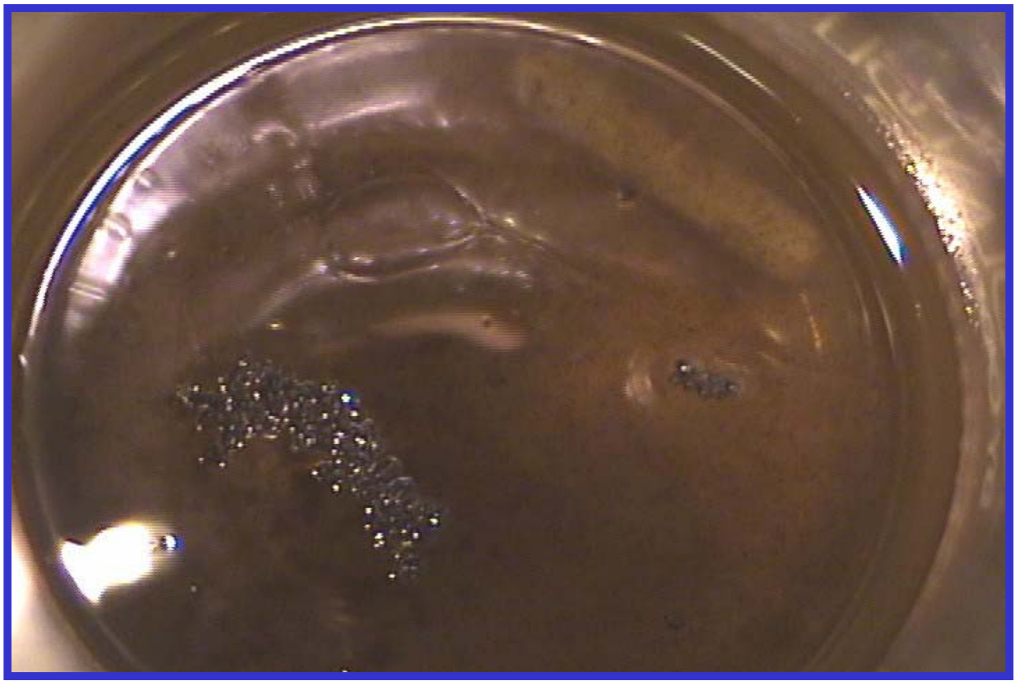


Figure 31: Photograph depicting the spreading of 1400 ppm of antifoamer DOW Q2-3183 A on surface of AN-107 D + HC + TBP

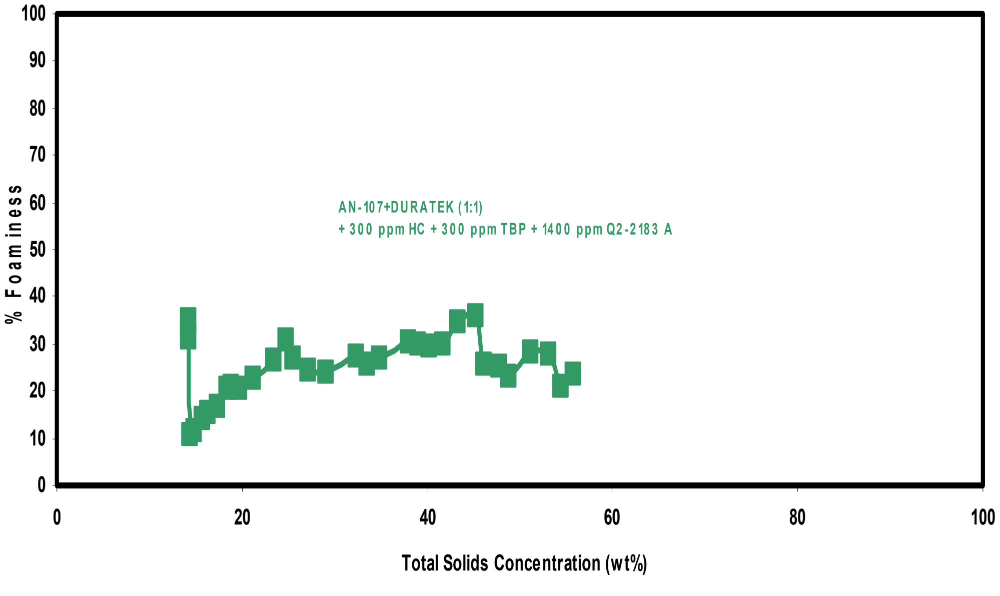


Figure 32: Antifoaming performance of DOW Q2-3183 A (1400 ppm) during boiling of AN-107 D + HC +TBP (300 ppm) (Pressure 110 mm Hg, Flux 2 kg/min sq.m)

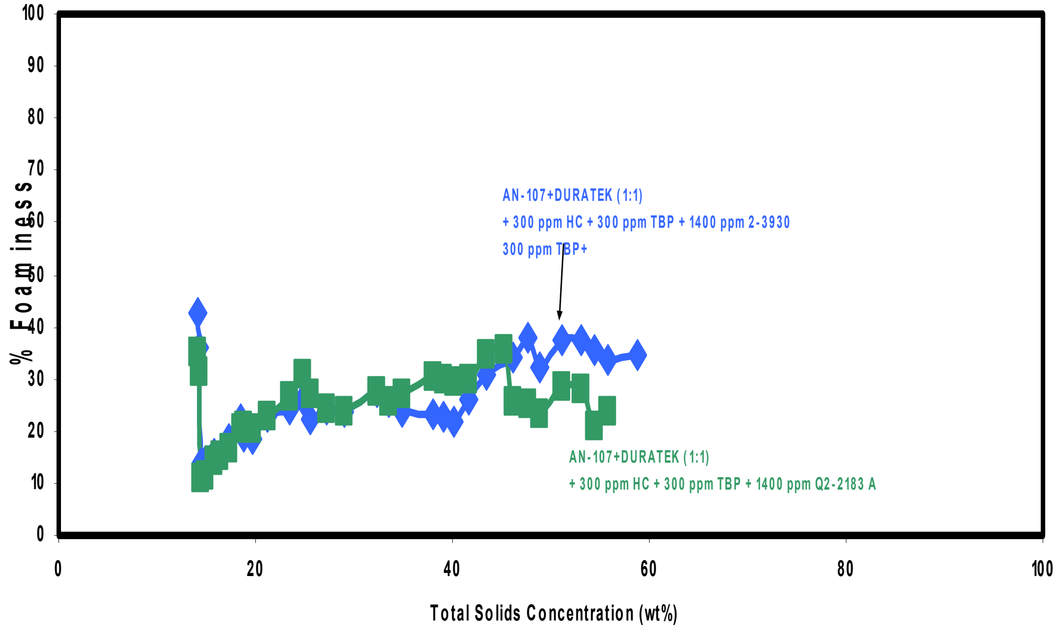


Figure 33: Antifoaming efficiency of two different antifoamers DOW Q2-3183 A and DOW 2-3930 (1400 ppm) during boiling of AN-107 D + HC +TBP (300 ppm)(Pressure 110 mm Hg, Flux 2 kg/min sq.m)

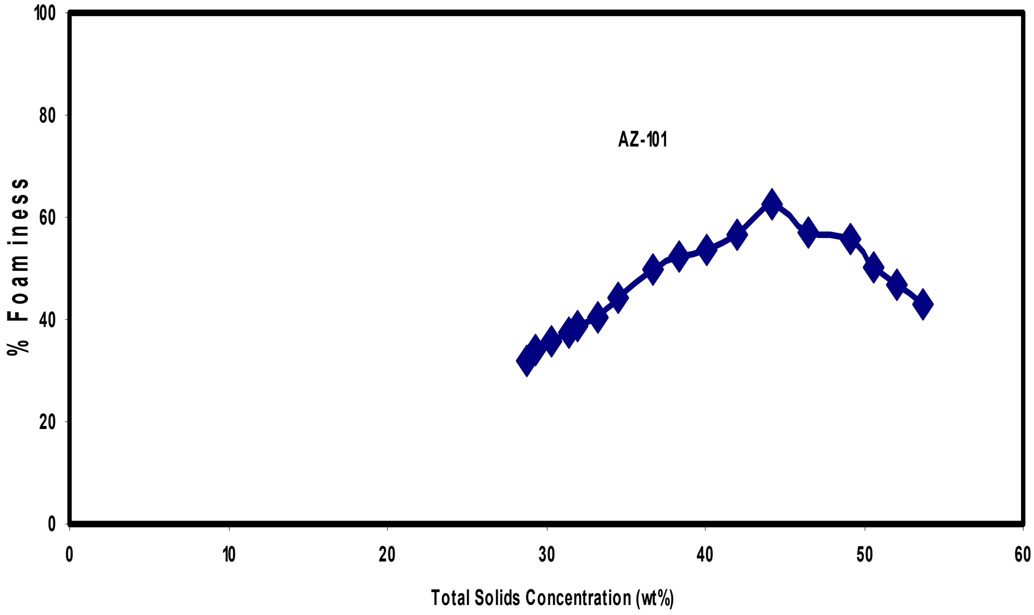


Figure 34: Foaminess during boiling of simulant AZ-101 (Pressure 110 mm Hg, Flux 2 kg/min sq.m)

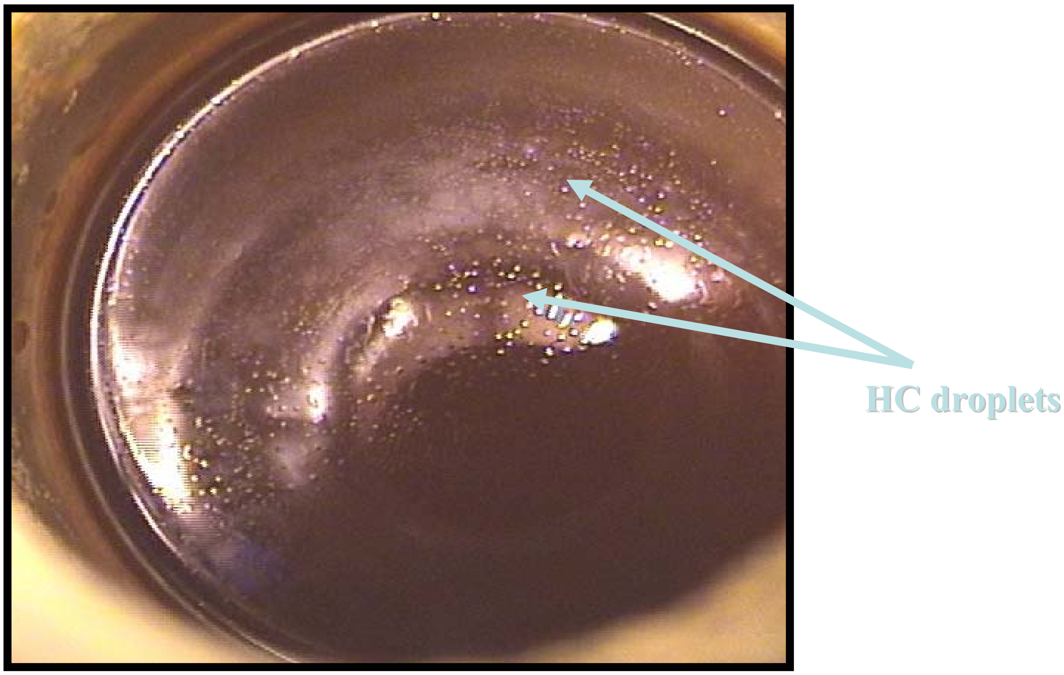


Figure 35: Photograph depicting the emulsified HC droplet on surface of AZ-101

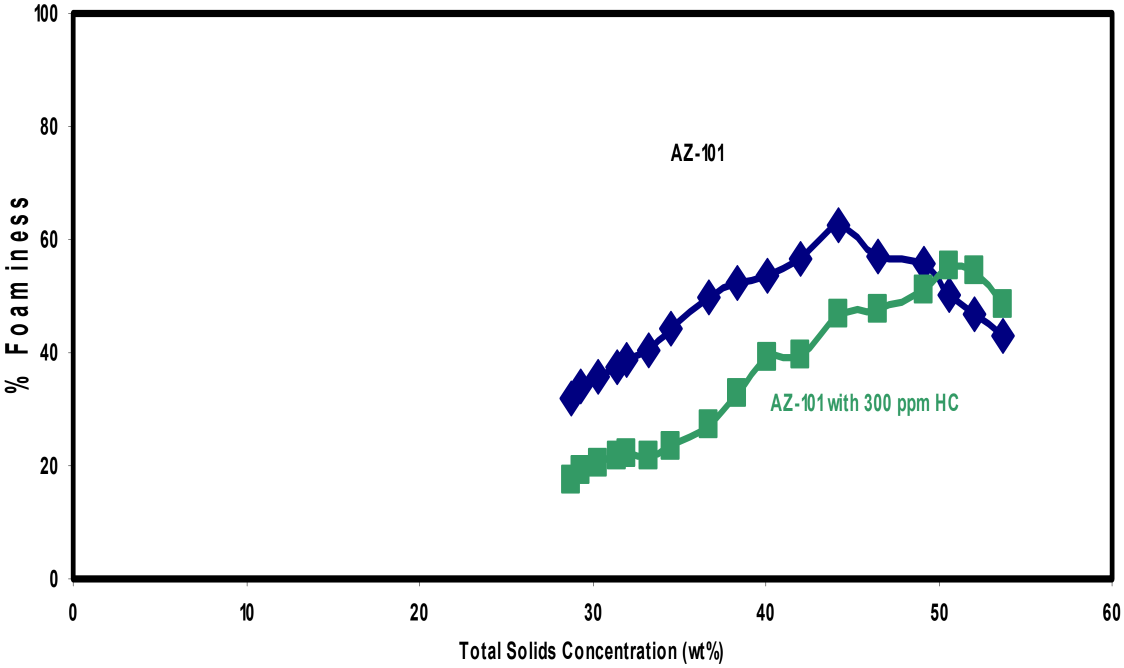
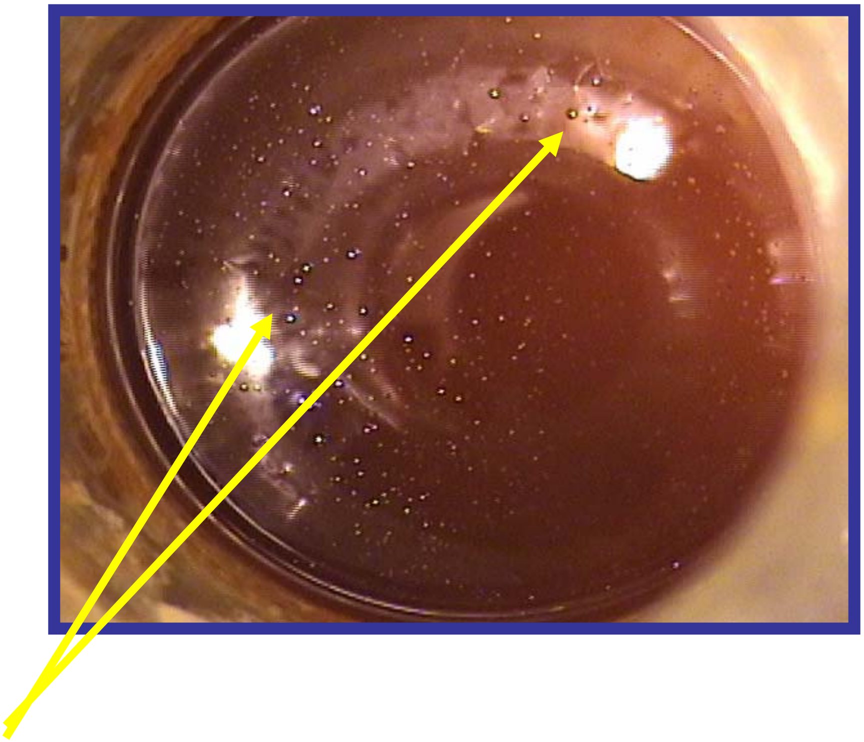


Figure 36: Effect of HC (300 ppm) on foaminess during boiling of AZ-101
(Pressure 110 mm Hg, Flux 2kg/min sq.m)



Millimeter size emulsified TBP droplet

Figure 37: Photograph depicting the emulsified TBP droplet on surface of AZ-101

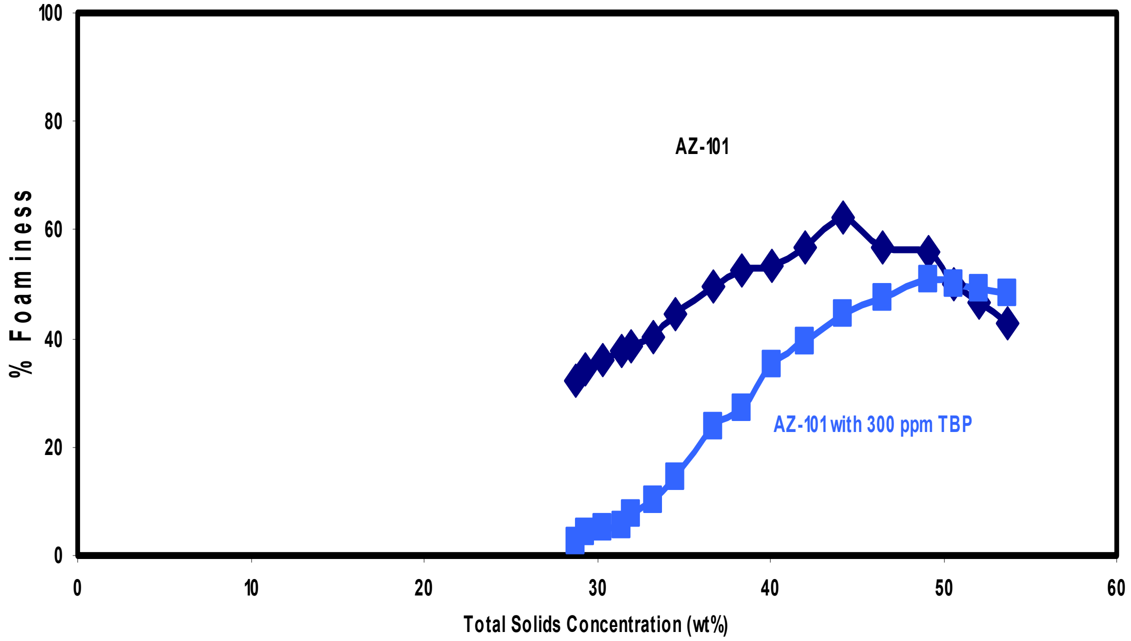


Figure 38: Effect of TBP (300 ppm) on foaminess during boiling of AZ-101 (Pressure 110 mm Hg, Flux 2kg/min sq.m)

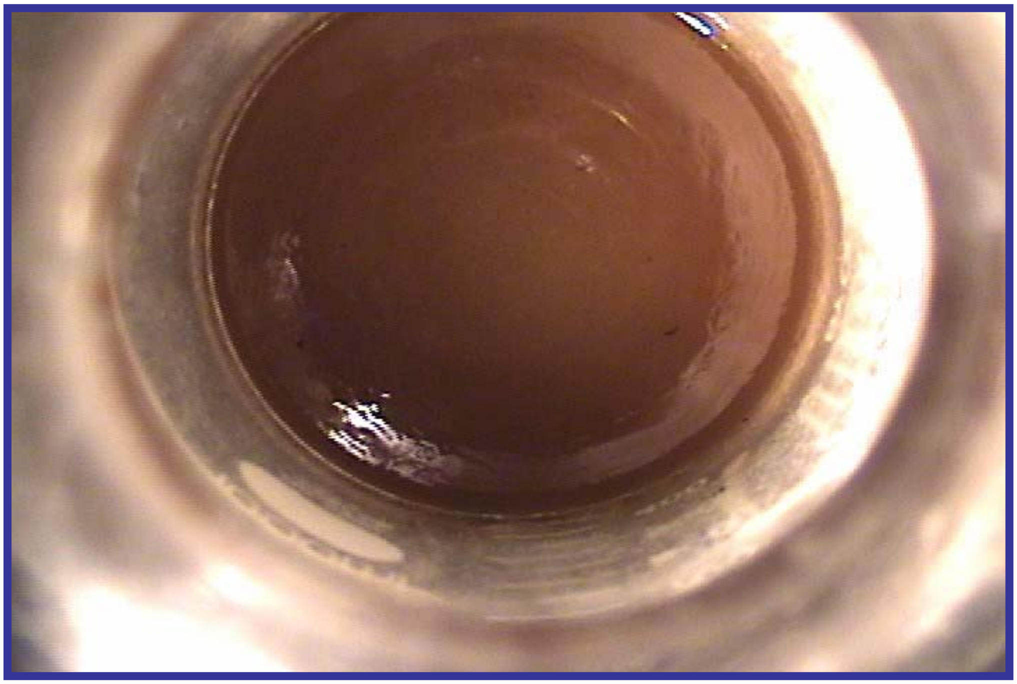


Figure 39: Photograph depicting the emulsified TBP and HC droplet on surface of AZ-101

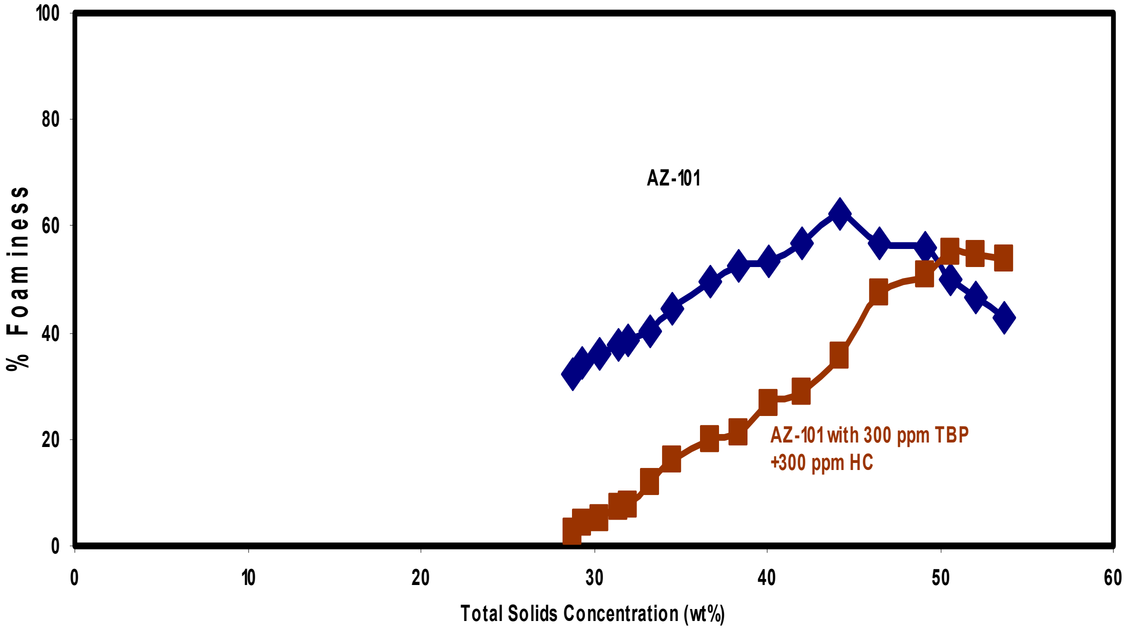


Figure 40: Effect of HC and TBP (300 ppm) on foaminess during boiling of AZ-101 (Pressure 110 mm Hg, Flux 2kg/min sq.m)

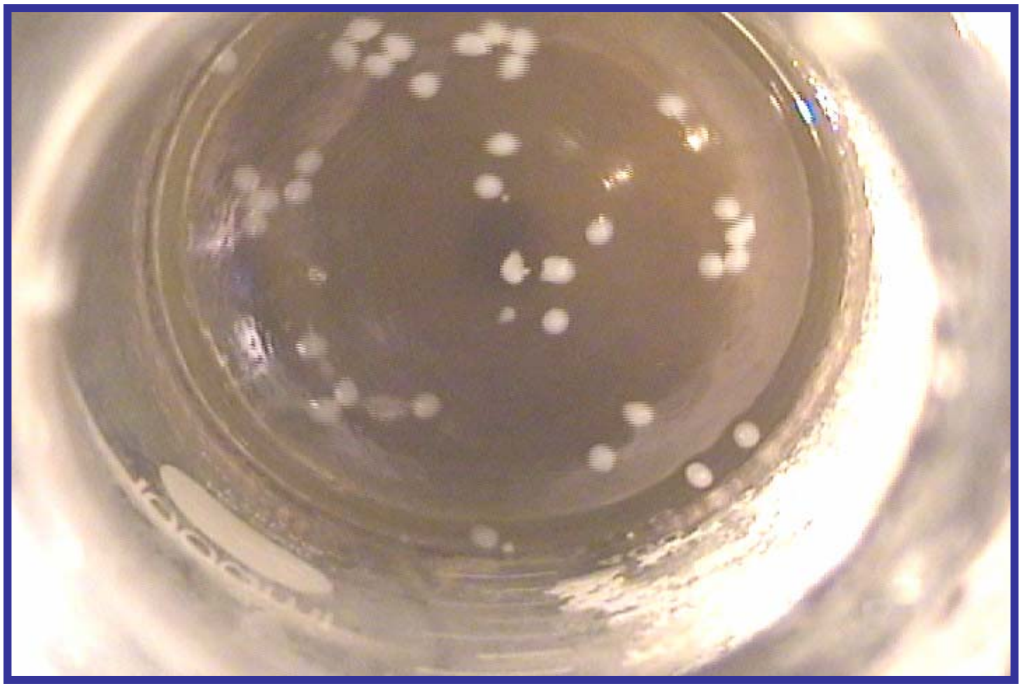


Figure 41: Photograph depicting the emulsified TBP and HC droplet with the antifoamer DOW 2-3930 on surface of AZ-101

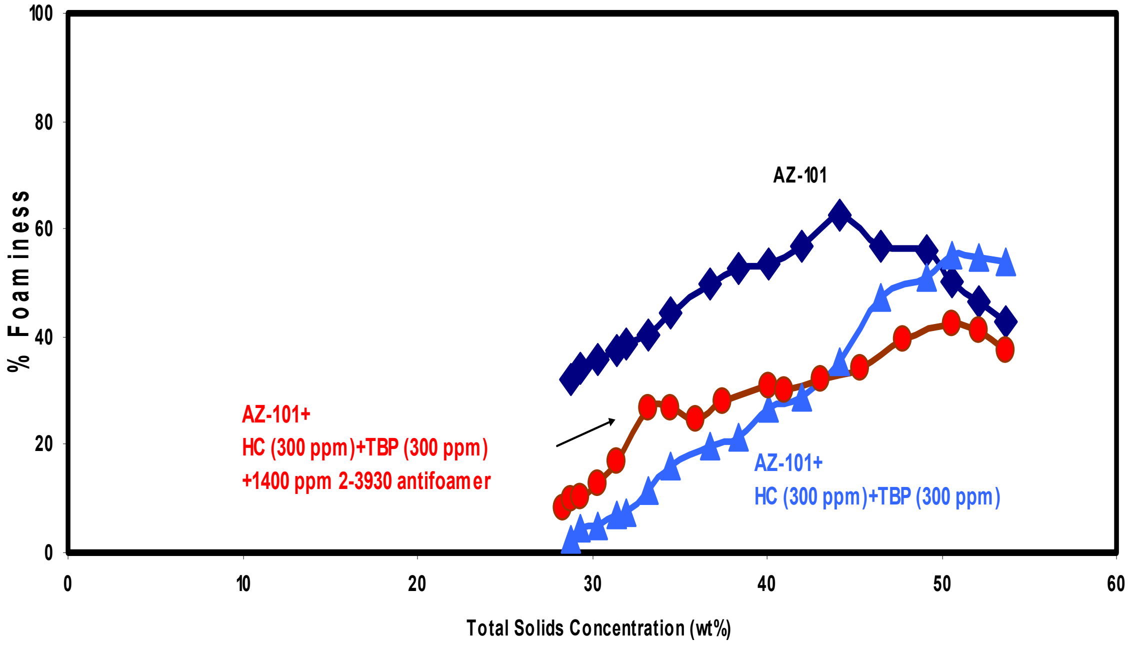


Figure 42: Antifoaming performance of DOW 2-3930 in the presence of HC and TBP (300 ppm) on foaminess during boiling of AZ-101 (Pressure 110 mm Hg, Flux 2kg/min sq.m)

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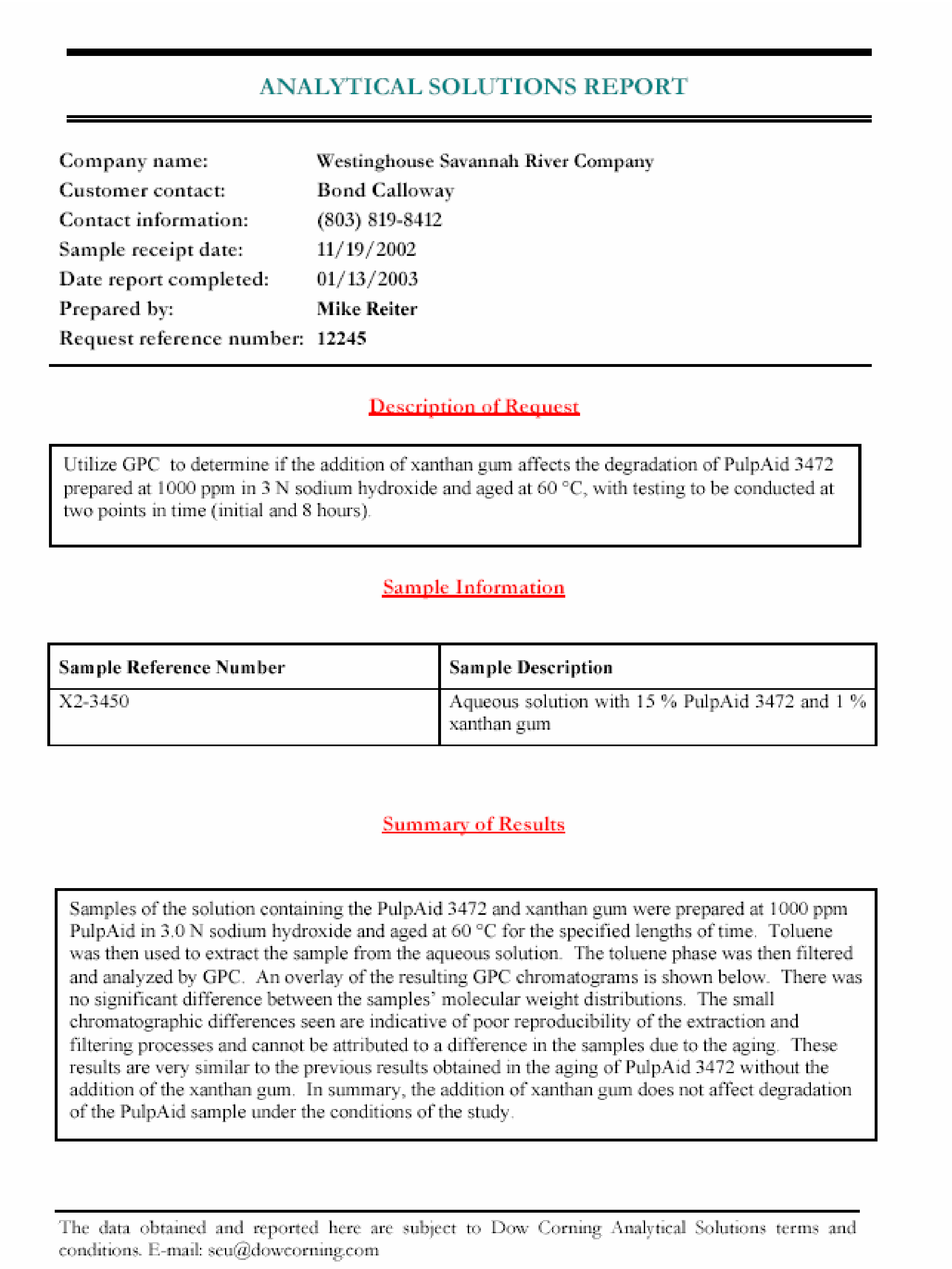
APPENDIX C

DOW ANALYTICAL REPORTS



ANALYTICAL SOLUTIONS REPORT

Company name:	Westinghouse Savannah River Company
Customer contact:	Bond Calloway
Contact information:	(803) 819-8412
Sample receipt date:	11/19/2002
Date report completed:	01/13/2003
Prepared by:	**Mike Reiter**
Request reference number:	**12245**

Description of Request

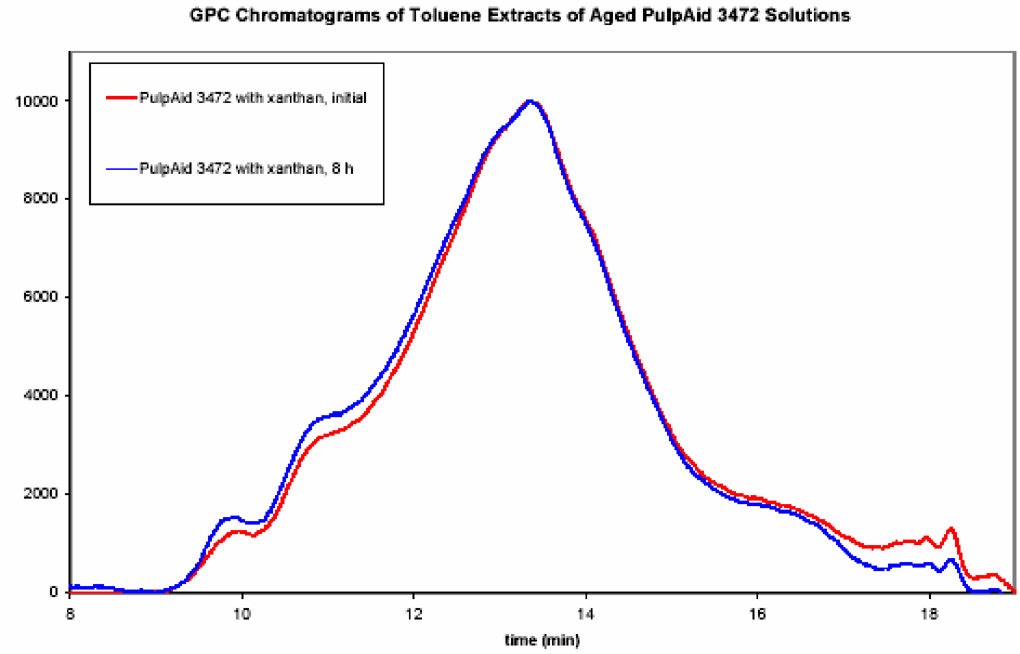
Utilize GPC to determine if the addition of xanthan gum affects the degradation of PulpAid 3472 prepared at 1000 ppm in 3 N sodium hydroxide and aged at 60 °C, with testing to be conducted at two points in time (initial and 8 hours).

Sample Information

Sample Reference Number	Sample Description
X2-3450	Aqueous solution with 15 % PulpAid 3472 and 1 % xanthan gum

Summary of Results

Samples of the solution containing the PulpAid 3472 and xanthan gum were prepared at 1000 ppm PulpAid in 3.0 N sodium hydroxide and aged at 60 °C for the specified lengths of time. Toluene was then used to extract the sample from the aqueous solution. The toluene phase was then filtered and analyzed by GPC. An overlay of the resulting GPC chromatograms is shown below. There was no significant difference between the samples' molecular weight distributions. The small chromatographic differences seen are indicative of poor reproducibility of the extraction and filtering processes and cannot be attributed to a difference in the samples due to the aging. These results are very similar to the previous results obtained in the aging of PulpAid 3472 without the addition of the xanthan gum. In summary, the addition of xanthan gum does not affect degradation of the PulpAid sample under the conditions of the study.



Experimental

Samples were prepared using the same concentration of PulpAid 3472 as in the previous result that did not use the xanthan gum. The PulpAid/xanthan mixture dispersed easily in the 3N sodium hydroxide to form a homogeneous cloudy mixture, but did not completely dissolve. GPC analyses were conducted on the toluene extracts of the aged PulpAid solutions using toluene as the eluent, PS/DVB size exclusion columns and a differential refractive index detector.

The data obtained and reported here are subject to Dow Corning Analytical Solutions terms and conditions. E-mail: seu@dowcorning.com

DOW CORNING

Customer Confidential

ANALYTICAL SOLUTIONS REPORT

Company name: Westinghouse Savannah River Company
Customer contact: Tom White and Bond Calloway
Contact information: (803) 819-8412
Sample receipt date: 01/07/03
Date report completed: 01/23/03
Prepared by: Mike Reiter and Herb Brothers
Request reference number: 12743 and 12787

Description of Request

Utilize GPC and GC techniques to determine the degradation of 1520 Antifoam, Q2-3183A Antifoam, and 2-3930 prepared at 1000 pm in 3 N sodium hydroxide and aged at 60 °C, with testing to be conducted at six points in time (initial, 1 hour, 2 hours, 4 hours, 8 hours and 24 hours).

Sample Information

Sample Reference Number(s)	Sample Description
0001336101	1520 antifoam
0001255340	Q2-3183A antifoam
1525719	2-3930

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Summary of Results

GC

Quantitation from GC experiments

Samples of all three products were prepared at a nominal concentration of 1000 ppm in aqueous 3.0 N NaOH and were aged at 60 °C for the specified lengths of time. After heating, the samples were extracted with pentane and dodecane was added as an internal standard to enable quantitation of identifiable components within the extracts. Components in the extracts were of low concentration and were numerous, making identification and quantification difficult. A series of dimethyl cyclic siloxanes were identified by retention time matching to reference compounds, but given the complexity of the chromatograms, all identifications are tentative. Identification and quantification of these identified components were used as indicators of sample degradation across the time points examined. In addition, a sum total of identified peaks is reported for each type of sample. Identified peaks include the dimethyl cyclic siloxanes (up to D20) referenced above and trimethyl-ended linear siloxane oligomers up to MD18M (D represents $Me_2SiO_{2/2}$ and M represents $Me_3SiO_{1/2}$ functionality); again, all identifications are highly tentative. Not all peaks present in the chromatograms were identified and the sum total of unidentified peaks is also reported for each type of sample. Results are presented in the table below as weight percents of the samples used in the preparations. Precision and accuracy parameters for this type of analysis on this type of sample have not been determined.

Appearances

Due to the low concentration levels of the prepared samples, observations related to appearances of the samples in 3 N NaOH were not always straightforward. Described below are general observations noted by the GC analyst.

It was noted that there were insoluble particles in all of the 1520 antifoam samples as evidenced by the presence of particles on the top of the solution and on the sides of the vessel.

All of the Q2-3183 samples appeared clearer than the 1520 samples. Overall they were mostly clear but were possibly very slightly hazy. It was noted that there were clear globules present on top of all of the solutions. The globules appear to be a liquid phase immiscible with the aqueous phase.

The 2-3930 solutions seemed to gradually clarify with the longer incubation periods with the 8 hour sample being very clear with no visible insoluble particulates. The sample that was heated for 24 hours appeared hazy, however.

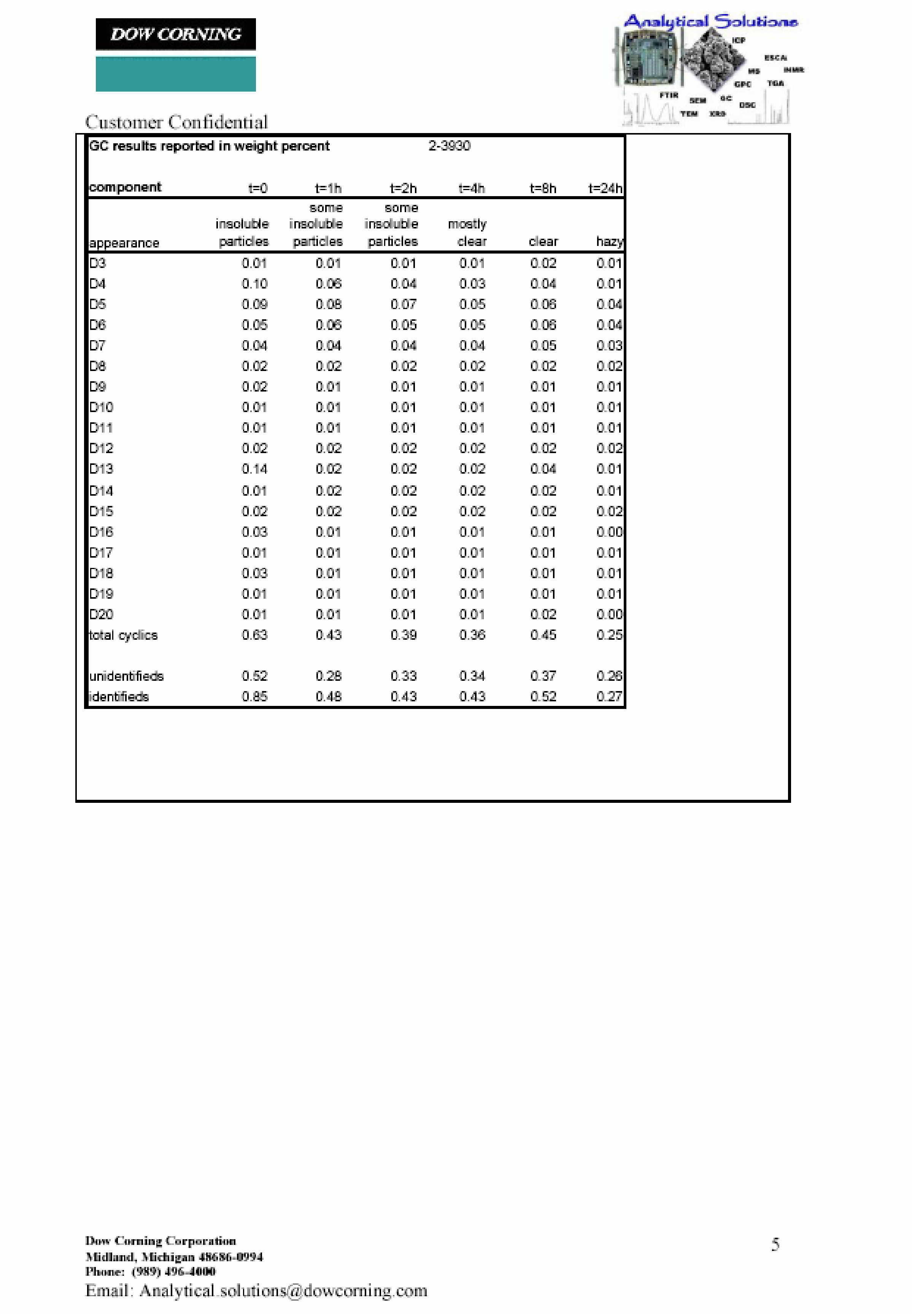
Conclusion from GC experiments

All of the samples appear to be undergoing a change as a function of being heated at 60 °C as evidenced by minor changes in the concentration of components observed in the pentane extracts. The changes observed by this test are subtle and may not reflect changes occurring in the portion of the sample that is not extracted into pentane.

GC results reported in weight percent			1520 antifoam			
component	t=0	t=1h	t=2h	t=4h	t=8h	t=24h
appearance	insoluble particles present	insoluble particles present	insoluble particles present	insoluble particles present	insoluble particles present	insoluble particles present
D3	0.02	0.01	0.01	0.01	0.01	0.01
D4	0.01	0.01	0.01	0.01	0.01	0.01
D5	0.01	0.02	0.01	0.02	0.01	0.01
D6	0.01	0.04	0.04	0.03	0.05	0.06
D7	0.01	0.04	0.05	0.04	0.05	0.06
D8	0.01	0.02	0.02	0.01	0.02	0.03
D9	0.01	0.01	0.01	0.01	0.02	0.02
D10	0.01	0.01	0.01	0.01	0.01	0.01
D11	0.01	0.01	0.01	0.01	0.02	0.01
D12	0.01	0.03	0.03	0.03	0.05	0.06
D13	0.02	0.04	0.04	0.04	0.06	0.09
D14	0.02	0.03	0.03	0.02	0.03	0.04
D15	0.02	0.04	0.04	0.03	0.04	0.06
D16		0.04	0.04	0.04	0.06	0.07
D17		0.03	0.03	0.03	0.08	0.05
D18		0.04	0.02	0.03	0.06	0.06
D19		0.02	0.03	0.03	0.06	0.07
D20		0.01	0.03	0.03	0.05	0.06
total cyclics	0.15	0.43	0.47	0.43	0.68	0.77
unidentifieds	0.63	0.53	0.49	0.50	0.67	0.84
identifieds	0.24	0.57	0.61	0.59	0.96	1.05
total	0.87	1.10	1.10	1.08	1.63	1.89

GC results reported in weight percent Q2-3183A

component	t=0	t=1h	t=2h	t=4h	t=8h	t=24h
appearance	globules present; v. slight haziness	globules present; v. slight haziness	globules present; v. slight haziness	globules present; v. slight haziness	globules present; v. slight haziness	globules present; v. slight haziness
D3	0.01	0.01	0.01	0.01	0.01	0.01
D4	0.04	0.04	0.03	0.02	0.01	0.00
D5	0.01	0.02	0.01	0.01	0.00	0.01
D6	0.01	0.02	0.03	0.02	0.03	0.04
D7	0.01	0.03	0.04	0.03	0.03	0.04
D8	0.02	0.02	0.02	0.02	0.02	0.03
D9	0.00	0.01	0.01	0.01	0.01	0.02
D10	0.00	0.01	0.01	0.01	0.01	0.01
D11	0.00	0.01	0.01	0.01	0.01	0.02
D12	0.01	0.02	0.03	0.03	0.04	0.06
D13	0.08	0.11	0.12	0.12	0.12	0.16
D14	0.01	0.02	0.03	0.03	0.03	0.04
D15	0.01	0.02	0.05	0.02	0.02	0.06
D16	0.20	0.25	0.26	0.27	0.26	0.28
D17	0.01	0.04	0.05	0.05	0.03	0.06
D18	0.23	0.32	0.33	0.35	0.33	0.35
D19	0.01	0.03	0.04	0.04	0.04	0.06
D20		0.07	0.04	0.10	0.04	0.06
total cyclics	0.66	1.03	1.12	1.12	1.02	1.28
unidentifieds	0.88	1.30	1.35	1.43	1.34	1.51
identifieds	0.84	1.34	1.46	1.44	1.29	1.67
total	1.71	2.65	2.81	2.87	2.63	3.18



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GC results reported in weight percent 2-3930

component	t=0	t=1h	t=2h	t=4h	t=8h	t=24h
appearance	insoluble particles	some insoluble particles	some insoluble particles	mostly clear	clear	hazy
D3	0.01	0.01	0.01	0.01	0.02	0.01
D4	0.10	0.06	0.04	0.03	0.04	0.01
D5	0.09	0.08	0.07	0.05	0.06	0.04
D6	0.05	0.06	0.05	0.05	0.06	0.04
D7	0.04	0.04	0.04	0.04	0.05	0.03
D8	0.02	0.02	0.02	0.02	0.02	0.02
D9	0.02	0.01	0.01	0.01	0.01	0.01
D10	0.01	0.01	0.01	0.01	0.01	0.01
D11	0.01	0.01	0.01	0.01	0.01	0.01
D12	0.02	0.02	0.02	0.02	0.02	0.02
D13	0.14	0.02	0.02	0.02	0.04	0.01
D14	0.01	0.02	0.02	0.02	0.02	0.01
D15	0.02	0.02	0.02	0.02	0.02	0.02
D16	0.03	0.01	0.01	0.01	0.01	0.00
D17	0.01	0.01	0.01	0.01	0.01	0.01
D18	0.03	0.01	0.01	0.01	0.01	0.01
D19	0.01	0.01	0.01	0.01	0.01	0.01
D20	0.01	0.01	0.01	0.01	0.02	0.00
total cyclics	0.63	0.43	0.39	0.36	0.45	0.25
unidentifieds	0.52	0.28	0.33	0.34	0.37	0.26
identifieds	0.85	0.48	0.43	0.43	0.52	0.27

GPC

Samples of all three antifoams were prepared in aqueous 3.0 N NaOH and were aged at 60 °C for the specified lengths of time. The sample concentrations were adjusted from the requested 1000 ppm in order to obtain an acceptable response for the GPC analyses. The 1520 samples were prepared at 2000 ppm, the Q2-3183 samples were prepared at 1500 ppm and the 2-3930 samples were prepared at 3000 ppm. After heating, toluene was used to extract the polymer from the aqueous solution. The toluene phase was then filtered and analyzed by GPC.

The observed appearance of the aqueous solutions was similar to what was seen in the GC analysis preparations, with one exception. The 2-3930 aqueous solutions prepared for GPC analysis all had a small amount of white globules floating on the surface that appeared to be a liquid that was immiscible with the aqueous phase. These samples were prepared at three times the concentration that was used in the GC analysis, which may explain the difference in appearance that was observed.

The precision and accuracy have not been experimentally determined for this type of GPC analysis on these specific sample types, but a statement regarding the significance of the results will be made based on experience with similar types of analyses.

1520 antifoam

The GPC chromatograms for the 1520 samples all consisted of a single polymer peak that is due to the polydimethylsiloxane portion of the antifoam that was extracted by the toluene. There was a small decrease seen in the molecular weight averages of the polymer over the course of the aging study, as shown in the molecular weight averages and chromatograms below. Although the differences were very small, it is believed that they are real based on previous analyses of similar materials. An attempt was also made to determine the percent recovery of the polymer from the aqueous solutions. It proved to be difficult to extract the polymer from the antifoam directly with toluene in order to determine an initial polymer level, and so the zero hour sample (sample shaken with toluene and 3 N NaOH without heating) was used as the basis for determining percent recovery for the remaining samples. Based on the extraction conditions, it is estimated that the error involved in the recovery could be as high as ±10%, meaning that there was only a small difference in the amount of polymer extracted as a function of aging time.

Sample Name	Mp	Mn	Mw	recovery
1520 antifoam, 0 h	26700	13300	27300	100%
1520 antifoam, 1 h	26000	12900	26800	109%
1520 antifoam, 2 h	26200	13100	26100	104%
1520 antifoam, 4 h	26000	12800	25700	93%
1520 antifoam, 8 h	25700	12670	25500	97%
1520 antifoam, 24 h	24600	12200	24800	87%

Q2-3183 antifoam

The GPC chromatograms for the Q2-3183 samples all consisted of two peaks, with the higher molecular weight peak being polydimethylsiloxane and the lower molecular weight peak being a second component extracted from the aqueous solution by the toluene. There was no significant difference seen in the molecular weight of the polydimethylsiloxane peak over the course of the aging, as shown in the chromatograms below. The small differences in the molecular weight averages of the polymer peak shown in the table below are a result of the normal error of the method, plus the additional error attributed to the overlap of the two peaks. There were small difference noted in the apparent molecular weight of the lower molecular weight peak and also in the relative size of the lower molecular weight peak compared to the higher molecular weight peak. The lower molecular weight peak is more polar than the higher molecular weight peak and not as reproducible under the analysis conditions that were used, so these changes are not considered significant. The polymer recovery percentages below are for the sum of both peaks and were calculated the same as above and showed a similar trend in results.

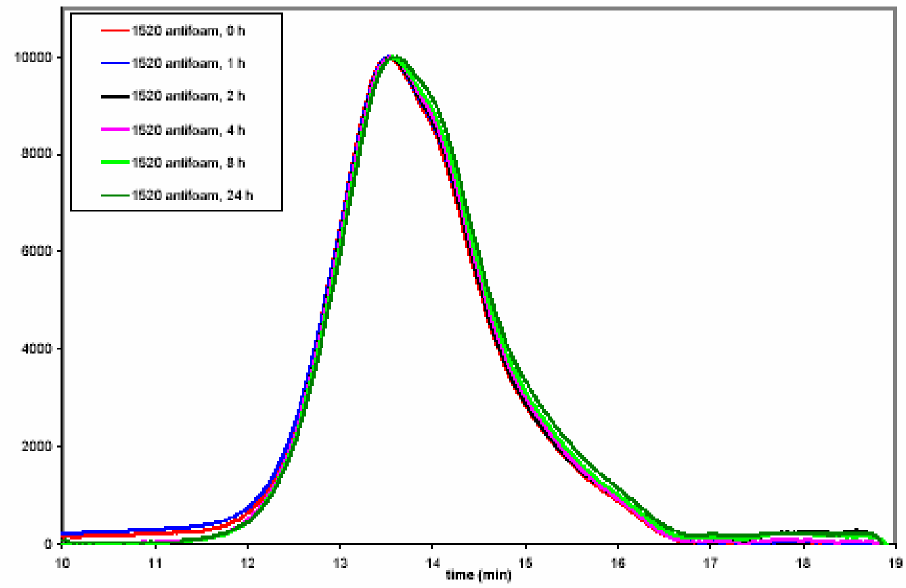
Sample Name	Mp	Mn	Mw	recovery
Q2-3183 antifoam, 0 h	31800	18900	35600	100%
Q2-3183 antifoam, 1 h	31800	19200	36900	109%
Q2-3183 antifoam, 2 h	32100	19800	36500	113%
Q2-3183 antifoam, 4 h	31800	19600	35600	101%
Q2-3183 antifoam, 8 h	32400	19200	37000	91%
Q2-3183 antifoam, 24 h	32100	19300	35500	89%

2-3930 antifoam

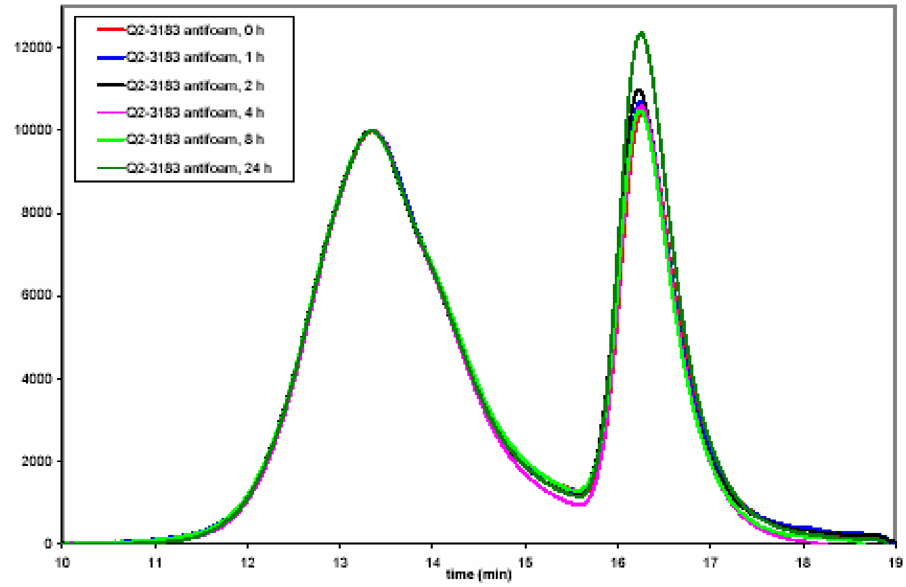
The GPC chromatograms for the 2-3930 samples showed a broad distribution of many partially resolved components. The results in the following table are for the entire distribution. The complex nature of this sample type generally leads to poor reproducibility in this type of analysis, so it is difficult to say how significant the differences are in the 0 through 8 hour samples. There was definitely a significant difference seen in the 24 hour sample, which had much less material extracted by the toluene. The extracted material was also much lower molecular weight than in the other samples.

Sample Name	Mp	Mn	Mw	recovery
2-3930 antifoam, 0 h	29900	2250	116000	100%
2-3930 antifoam, 1 h	31500	2790	102000	100%
2-3930 antifoam, 2 h	31300	2930	103000	152%
2-3930 antifoam, 4 h	33300	2980	98200	153%
2-3930 antifoam, 8 h	33900	2540	106000	110%
2-3930 antifoam, 24 h	2340	1340	24000	56%

GPC Chromatograms of Toluene Extracts of Aged 1520 Antifoam Solutions



GPC Chromatograms of Toluene Extracts of Aged Q2-3183 Antifoam Solutions



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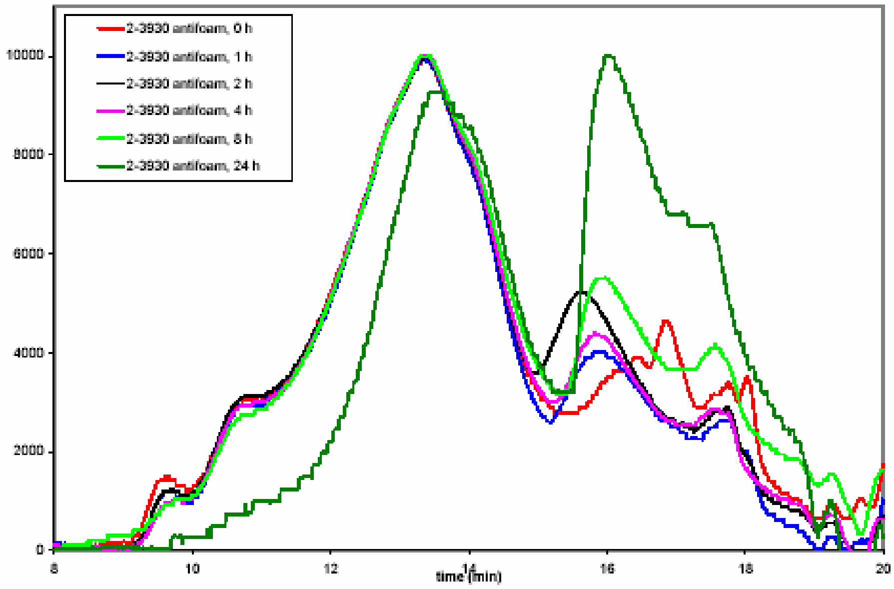
GPC Chromatograms of Toluene Extracts of Aged 2-3930 Antifoam Solutions



Experimental

GC analyses were conducted on pentane extracts of aged solutions of the samples. The gas chromatograph was equipped with a flame ionization detector and a capillary column with a polydimethylsiloxane stationary phase.
GPC analyses were conducted on toluene extracts of the aged antifoam solutions using toluene as the eluent, PS/DVB size exclusion columns, a differential refractive index detector, and a relative polystyrene calibration curve for calculation of molecular weight averages.

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ICP ESCA MS NMR GPC TGA FTIR SEM GC DSC TEM XRD

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Analytical Solutions Report

Customer: Westinghouse River Savannah Company
Customer Contact: Tom White
Phone and/or Email:
Sample Receipt Date: 5/22/2003
Report Date 6/2/2003
Prepared by: Mike Reiter and Jeff Kelly
Request Reference Number: 14219

Description of Request:

Analyze byproducts from degradation study of Dow Corning Q2-3183A Antifoam under caustic and radiated conditions. The change in average molecular weight of the silicone polymer over time can be determined, as well as the composition and concentration of lower molecular weight silicone species formed during degradation. Identification of polyethylene glycol byproducts can be tested using headspace or other appropriate MS method.

Sample details

Sample Identifier:	Comments:
#1	DI water/antifoam; No radiation
#2	DI water/antifoam; 7 day dose
#3	UFIB; 8 hr dose
#4	UFIB/Anifoam; no dose
#5	UFIB/Anifoam; 8 hr dose
#6	UFIB/Anifoam; 8 hr dose
#7	UFIB/Anifoam; 7 day dose
#8	UFIB/Anifoam; 7 day dose
#9	UFIB/Antifoam; 2 day dose

Techniques Requested

GPC, GC-MS

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Results Summary:

Mass Spectrometry

Samples were analyzed by headspace gas chromatography mass spectrometry (HS GC-MS) for the detection of low molecular weight cyclic siloxanes. A standard of decamethylcyclopentasiloxane was analyzed to obtain an estimated detection limit of 10 ppm for this and similar low molecular weight, volatile siloxanes. It is a reasonable assumption to assume that this HS GC-MS method will detect similar siloxane molecules less than a molecular weight of approximately 600 Da.

Samples were also analyzed by positive ion electrospray ionization mass spectrometry (ESI MS) for the detection of ethylene glycol and propylene glycol. A standard containing ethylene glycol and propylene glycol was analyzed to obtain an estimated detection limit of 10 ppm for these two compounds.

Mass Spectrometry Results Table

	ESI MS		HS GC-MS
	ethylene glycol	propylene glycol	low molecular weight siloxanes
Sample #1	ND	ND	ND
Sample #2	ND	ND	ND
Sample #3	ND	ND	ND
Sample #4	ND	ND	ND
Sample #5	ND	ND	ND
Sample #6	ND	ND	ND
Sample #7	ND	ND	ND
Sample #8	ND	ND	ND
Sample #9	ND	ND	ND

ND = none detected above the estimated reporting limit

The estimated reporting limit is 10 ppm (ug/ml) for all specified analytes

Mass Spectrometry Date/Time of Analysis

	27-May-03 ESI MS	27-May-03 to 28-May-03 HS GC-MS
Sample #1	3:46 PM	7:28 PM
Sample #2	3:55 PM	8:08 PM
Sample #3	4:01 PM	8:48 PM
Sample #4	4:07 PM	9:29 PM
Sample #5	4:11 PM	10:09 PM
Sample #6	4:16 PM	10:49 PM
Sample #7	4:20 PM	11:29 PM
Sample #8	4:25 PM	12:10 AM
Sample #9	4:29 PM	12:50 AM

Gel Permeation Chromatography

The GPC chromatograms of the toluene extracts of the aqueous samples showed degradation of the siloxane portion of the sample as a result of the radiation treatment. The GPC chromatograms of the toluene extracts had two peaks in general, with the higher molecular weight peak being polydimethylsiloxane and the lower molecular weight peak being a second component extracted from the aqueous solution by the toluene. There was a definite change in the molecular weight of the siloxane portion of the sample, as well as the amount of material that was recovered, as a function of time. The siloxane distribution appeared slightly higher molecular weight in the 8 h and 2 day samples, but lower molecular weight in the 7 day samples. There was also a general trend seen of less material extracted as the length of the radiation treatment increased. There was a large difference in the amount of material extracted from the no dose samples of antifoam in DI and UFIB (samples 1 and 4). Its possible that the presence of the UFIB has an effect on the efficiency of the extraction of PDMS with toluene. The following molecular weight averages are relative to polystyrene standards and are for the PDMS peak only (peak eluting between 10 and 15.5 minutes).

Sample Name	Mp	Mn	Mw	recovery (relative to sample 1)
#1 (DI/2-3183, no dose)	31300	18700	35100	100 %
#2 (DI/2-3183, 7 day dose)	25700	11700	27600	7%
#4 (UFIB/2-3183, no dose)	31800	19600	36300	200%
#5 (UFIB/2-3183, 8 h dose)	31000	19900	39200	156%
#6 (UFIB/2-3183, 8 h dose)	31000	19900	38600	179%
#7 (UFIB/2-3183, 7 day dose)	14900	11500	19000	39%
#8 (UFIB/2-3183, 7 day dose)	15600	12200	18900	37%
#9 (UFIB/2-3183, 2 day dose)	30700	21000	50500	71%

It should be noted that the toluene extraction was performed on only a portion of the sample as delivered. The sample bottle was shaken before removing the portion of the sample for extraction, but it is unknown how representative it was of the entire sample.

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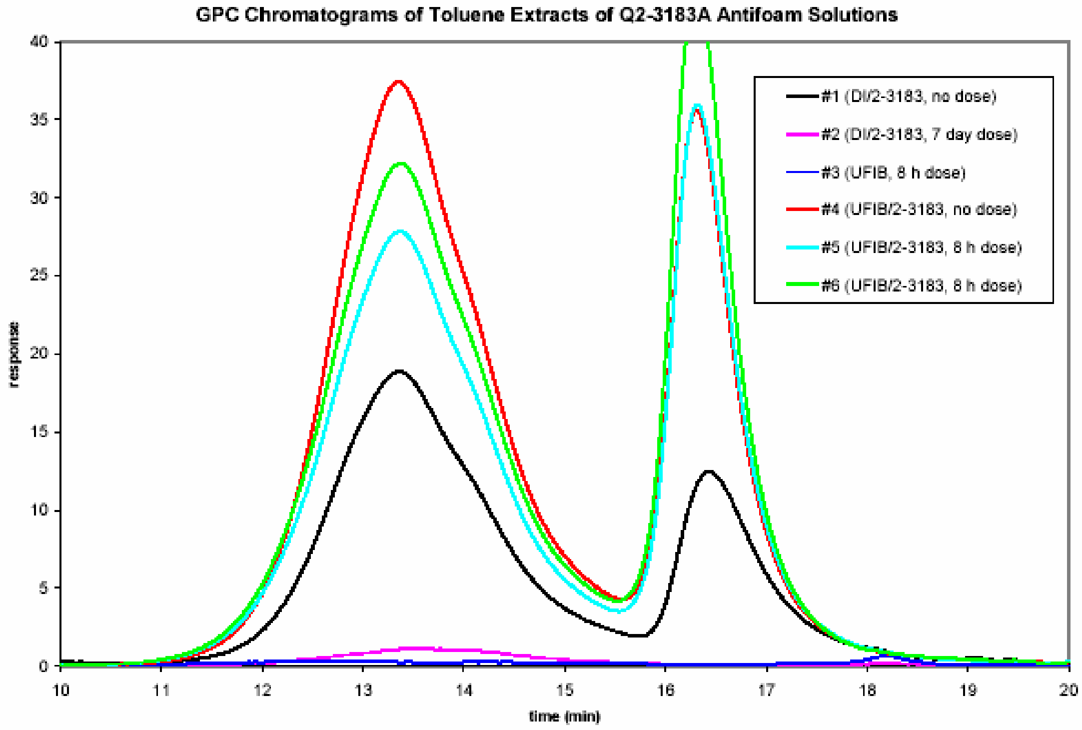
GPC Chromatograms of Toluene Extracts of Q2-3183A Antifoam Solutions

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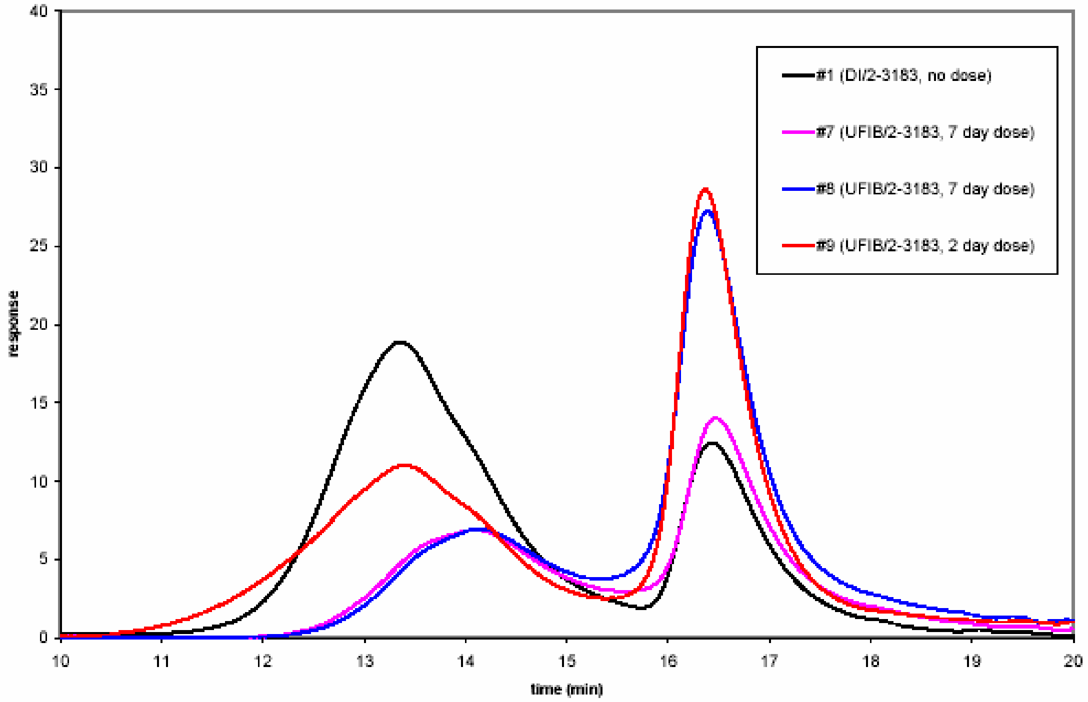

GPC Chromatograms of Toluene Extracts of Q2-3183A Antifoam Solutions

Experiment Details:

Mass Spectrometry

HS GC-MS results acquired using an Agilent 5973/6890 equipped with an Agilent 7694 headspace sampler. ESI MS data acquired using a PE Sciex API 350 triple quadrupole mass spectrometer using direct infusion positive ion electrospray ionization.

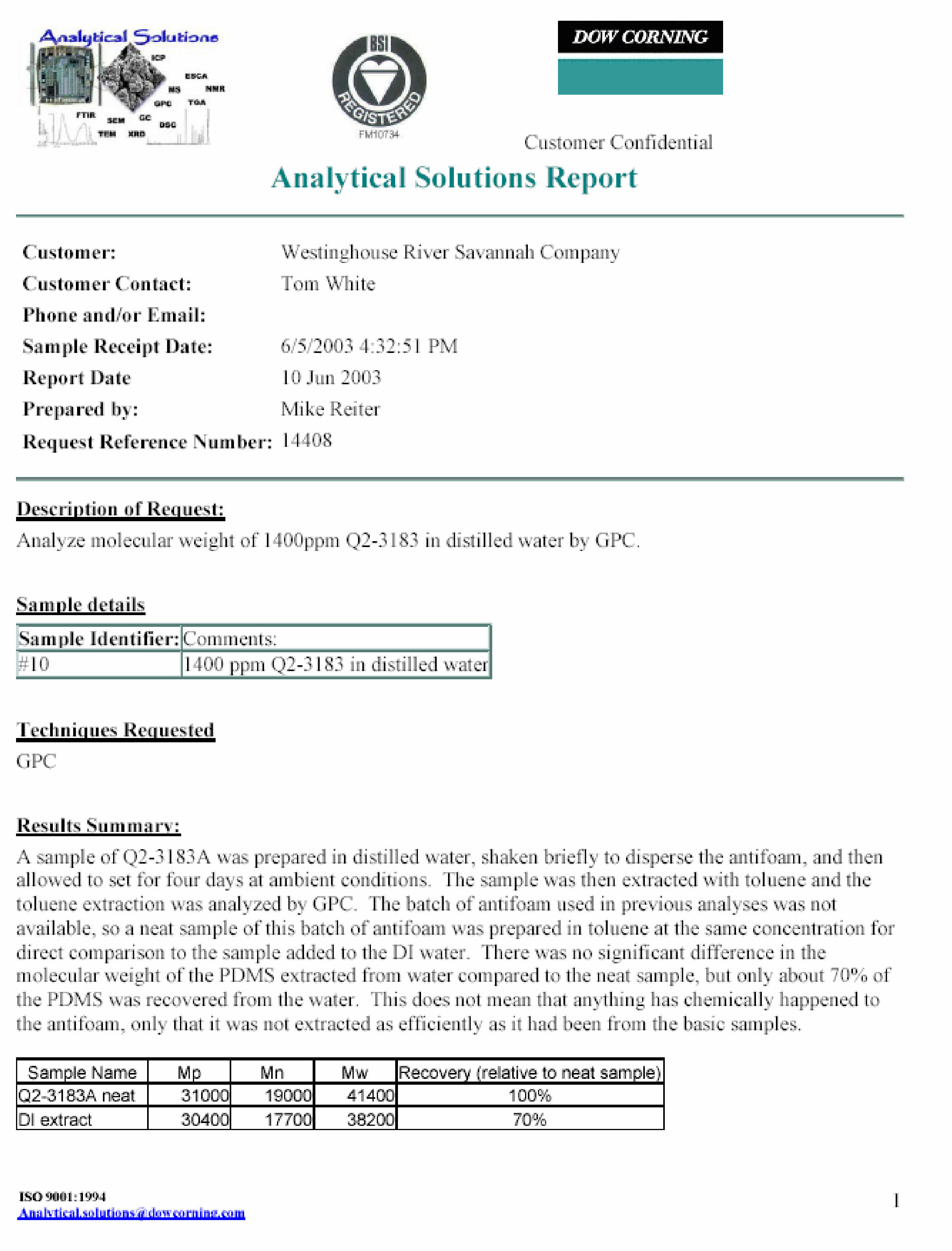
Gel Permeation Chromatography

GPC analyses were conducted on toluene extracts of the aqueous solutions using toluene as the eluent, PS/DVB size exclusion columns, a differential refractive index detector, and a relative polystyrene calibration curve for calculation of molecular weight averages. The toluene extracts were performed at 9:30 AM on May 27, 2003. The toluene extracts were analyzed by GPC starting at 10:30 AM on May 27, 2003. The samples were analyzed in order from sample 1 through sample 9, analyzing one sample every 30 minutes.

Statement of Accuracy and Precision:

Mass spectrometry results should be considered semi-quantitative only. No precision and accuracy studies have been done on this sample matrix using the specified target molecules. One-point standards were analyzed to establish approximate detection limits as specified in the results summary.

The precision and accuracy have not been experimentally determined for this type of GPC analysis on this specific sample type. Repeatability for similar samples analyzed by GPC is ±5%



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Analytical Solutions Report

Customer: Westinghouse River Savannah Company
Customer Contact: Tom White
Phone and/or Email:
Sample Receipt Date: 6/5/2003 4:32:51 PM
Report Date 10 Jun 2003
Prepared by: Mike Reiter
Request Reference Number: 14408

Description of Request:

Analyze molecular weight of 1400ppm Q2-3183 in distilled water by GPC.

Sample details

Sample Identifier:	Comments:
#10	1400 ppm Q2-3183 in distilled water

Techniques Requested

GPC

Results Summary:

A sample of Q2-3183A was prepared in distilled water, shaken briefly to disperse the antifoam, and then allowed to set for four days at ambient conditions. The sample was then extracted with toluene and the toluene extraction was analyzed by GPC. The batch of antifoam used in previous analyses was not available, so a neat sample of this batch of antifoam was prepared in toluene at the same concentration for direct comparison to the sample added to the DI water. There was no significant difference in the molecular weight of the PDMS extracted from water compared to the neat sample, but only about 70% of the PDMS was recovered from the water. This does not mean that anything has chemically happened to the antifoam, only that it was not extracted as efficiently as it had been from the basic samples.

Sample Name	Mp	Mn	Mw	Recovery (relative to neat sample)
Q2-3183A neat	31000	19000	41400	100%
DI extract	30400	17700	38200	70%

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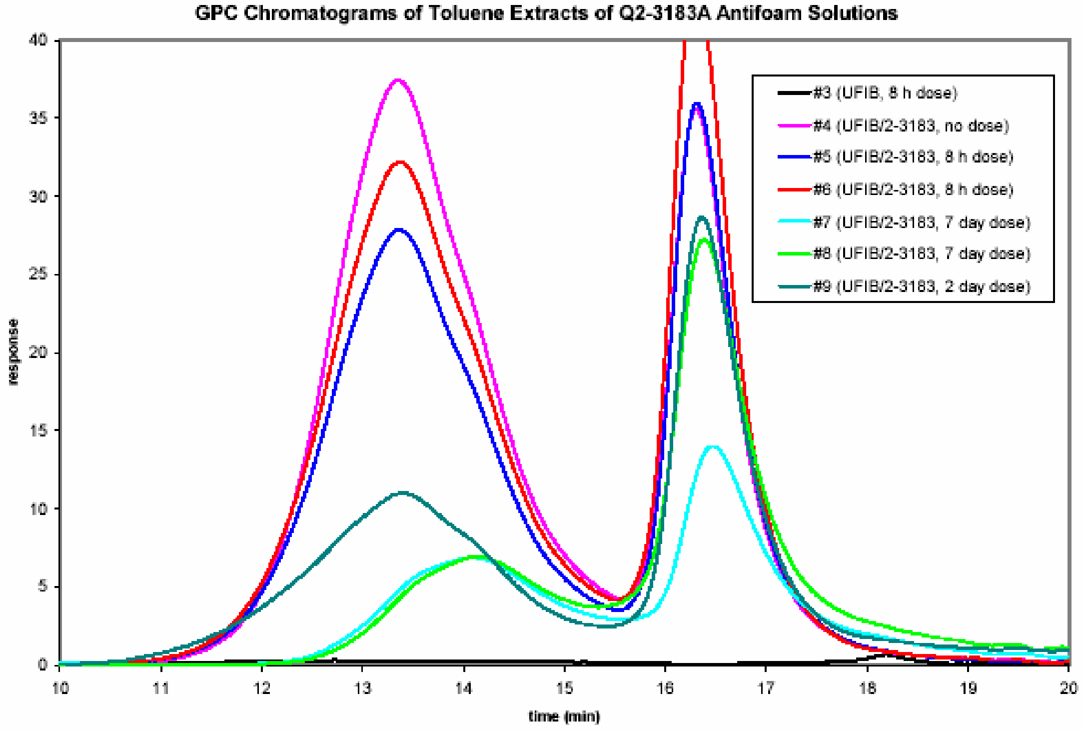
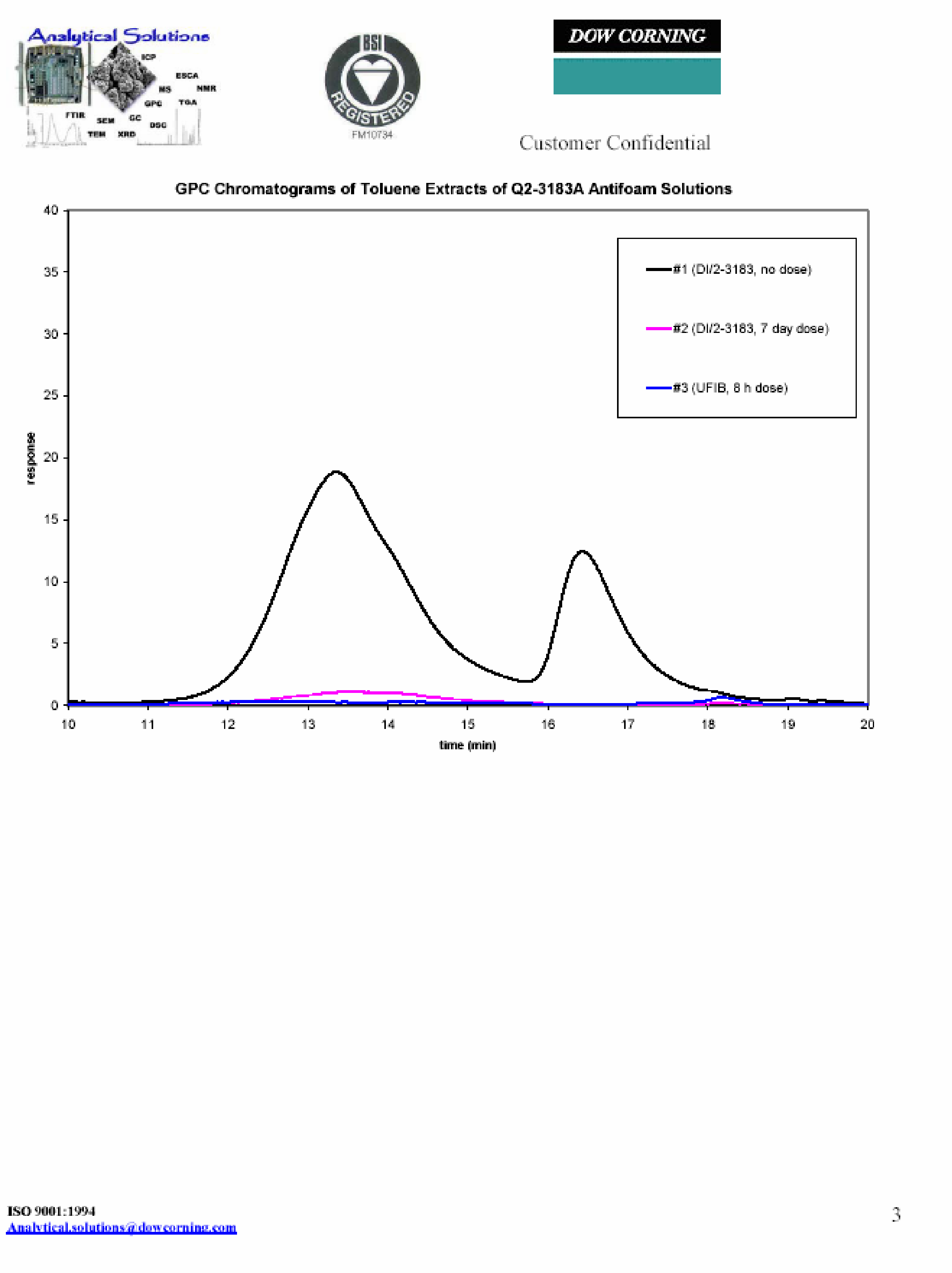


GPC Chromatograms of Toluene Extracts of Q2-3183A Antifoam Solutions



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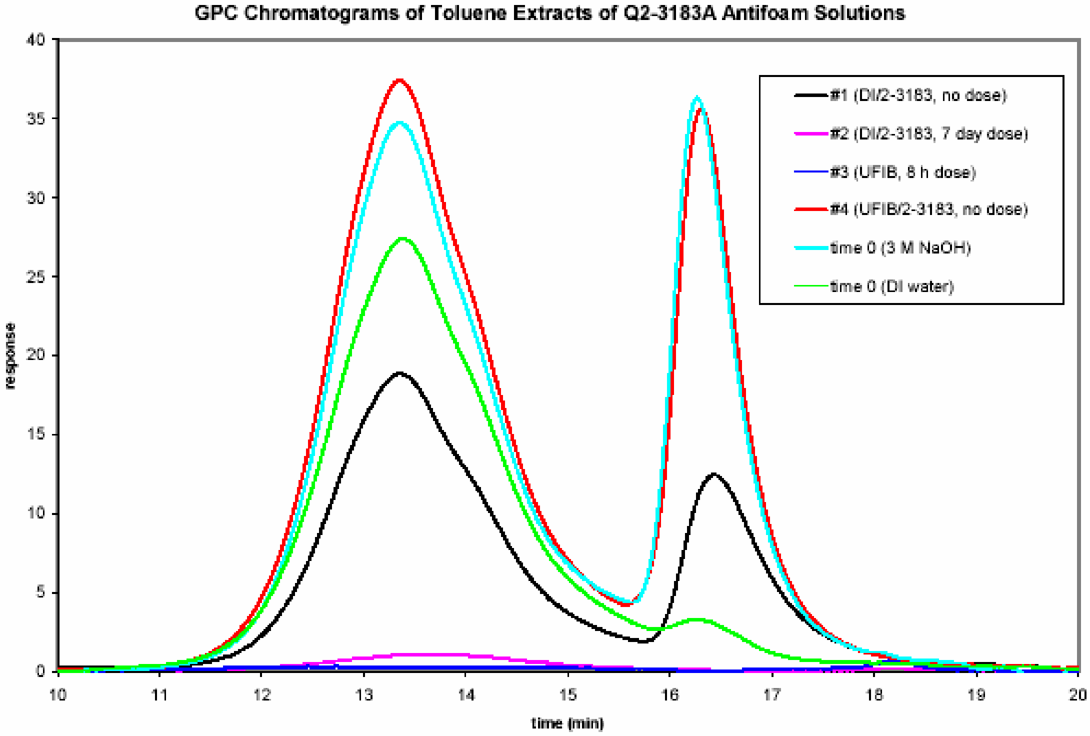
GPC Chromatograms of Toluene Extracts of Q2-3183A Antifoam Solutions



GPC Chromatograms of Toluene Extracts of Q2-3183A Antifoam Solutions

Experiment Details:

GPC analyses were conducted on toluene extracts of the aqueous solutions using toluene as the eluent, PS/DVB size exclusion columns, a differential refractive index detector, and a relative polystyrene calibration curve for calculation of molecular weight averages.

Statement of Accuracy and Precision:

The precision and accuracy have not been experimentally determined for this type of GPC analysis on this specific sample type. Repeatability for similar samples analyzed by GPC is ±5%.