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SRNL-RPP-2005-00040, REVISION 0

Hydrogen Generation Rate Scoping Study of DOW Corning Antifoam Agent

September 2005

SAVANNAH RIVER NATIONAL LABORATORY

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Hydrogen Generation Rate Scoping Study of DOW Corning Antifoam Agent

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TABLE OF CONTENTS

LIST OF FIGURES iv
LIST OF TABLES v
LIST OF ACRONYMS vi
EXECUTIVE SUMMARY 1
1.0 TESTING SUMMARY 3
  1.1 OBJECTIVES 3
  1.2 TEST EXCEPTIONS 4
  1.3 RESULTS AND PERFORMANCE AGAINST SUCCESS CRITERIA 4
  1.4 QUALITY REQUIREMENTS 5
  1.5 R&T TEST CONDITIONS 5
  1.6 SIMULANT USE 6
  1.7 DISCREPANCIES AND FOLLOW-ON TESTS 7
2.0 EXPERIMENTAL 9
3.0 RESULTS AND DISCUSSION 13
  3.1 SIMULANT PREPARATION 13
  3.2 DOSIMETRY 19
  3.3 MEASUREMENT OF TOC CONTENT OF Q2-3183A ANTIFOAM 21
  3.4 HYDROGEN MEASUREMENTS VIA MASS SPECTROSCOPY 22
  3.5 INITIAL RADIOLYSIS/THERMOLYSIS TESTING 23
  3.6 REPEAT RADIOLYSIS/THERMOLYSIS TESTING 26
  3.7 SUMMARY OF DATA AND DISCUSSION 29
  3.8 SAVANNAH RIVER SITE EXPERIENCE WITH ANTIFOAM AGENTS 30
4.0 ANTIFOAM DEGRADATION ANALYSES AND RADIOLYTIC DECOMPOSITION SCHEMES 32
  4.1 ANTIFOAM DEGRADATION ANALYSES 32
  4.2 RADIOLYTIC DECOMPOSITION SCHEMES 33
5.0 CONCLUSIONS 44
6.0 REFERENCES 45
APPENDIX A. SAMPLE CALCULATION OF MEASURED HGR AND MINIMUM HGR 48
APPENDIX B. SIMULANT RECIPES 50
APPENDIX C. WTP HGR CORRELATION 58

LIST OF FIGURES

Figure 3-1. Base 0 wt% TOC simulant (right) and Native 4 wt% TOC simulant (left) 14
Figure 3-2. Filtration of the base simulant 15
Figure 3-3. Filtration of the native simulant 15
Figure 3-4. AN-107 Envelope C Simulant 18
Figure 3-5. Fricke Dosimetry Absorbance vs. Time Plot 20
Figure 3-6. Pressure vs. Time Plots for Radiolysis/Thermolysis Initial Testing 24
Figure 3-7. Pressure vs. Time Plots for Radiolysis/Thermolysis Repeat Testing 27
Figure 3-8. Pressure vs. Time Plots for Radiolysis/Thermolysis Repeat Testing Showing Best Linear Fits 27
Figure 4-1. Standard Curve for Molecular Weights vs. Retention Time for Polystyrene in Toluene 42
Figure 4-2. Standard Curve for Molecular Weights vs. Retention Time for Polystyrene in THF 42
Figure 4-3. PDMS Polymer Direct Radiolytic Decomposition Scheme 43
Figure 4-4. PPG Polymer Direct Radiolytic Decomposition Scheme 43

LIST OF TABLES

Table 1-1. Test Objectives 3
Table 1-2. Success Criteria 4
Table 1-3. Test Conditions 5
Table 2-1. Dow Corning Q2-3183A Constituents* 9
Table 3-1. Summary Recipes for Base and Native Simulants 14
Table 3-2. Base Simulant Filtrate Analysis 16
Table 3-3. Native Simulant Filtrate Analysis 17
Table 3-4. AN-107 Simulant Partial Analysis * 18
Table 3-5. Ferrous Sulphate ‘Fricke Dosimeter’ 20
Table 3-6. Measurement of TOC in Q2-3183A 21
Table 3-7. Mass Spectroscopy Gas Component Measurements in Blank and Standard 22
Table 3-8. Simulant Systems for Radiolysis/Thermolysis Initial Testing 24
Table 3-9. Hydrogen and HGRs for Radiolysis/Thermolysis Initial Testing 25
Table 3-10. Simulant Systems for Radiolysis/Thermolysis Repeat Testing 28
Table 3-11. Hydrogen and HRGs for Radiolysis/Thermolysis Repeat Testing 28
Table 3-12. Summary of Data 29
Table 4-1. Summary of Analyses Performed by Dow Corning for SRNL 35
Table 4-2. Gel Permeation Chromatography with Peak Height 36

Table B- 1. Base Simulant Recipe for 0 wt% TOC 50
Table B- 2. Batching Recipe for 1000-mL Base Simulant 0 wt% TOC 52
Table B- 3. Native Simulant Recipe for 4 wt% TOC 54
Table B- 4. Batching Recipe for 4 wt% TOC 56

LIST OF ACRONYMS

AFA	Antifoam Agent
ADS	Analytical Development Section
DWPF	Defense Waste Processing Facility
EDL	Engineering Development Laboratory
GPC	Gel Permeation Chromatography
HEDTA	n-(2-Hydroxyethyl)ethylenediaminetriacetic acid
HGR	Hydrogen Generation Rate
LAW	Low Activity Waste
MFT	Melter Feed Tank
MSDS	Material Safety Data Sheet
NDIR	Non-dispersive infrared detector
PDMS	Polydimethylsiloxane
PPG	Polypropyleneglycol
RPP-WTP	River Protection Program-Waste Treatment and Immobilization Plant
SME	Slurry Mix and Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
TOC	Total Organic Carbon

EXECUTIVE SUMMARY

The antifoam agent DOW Corning Q2-3183A will be added to waste streams in the Hanford River Protection Program-Waste Treatment and Immobilization Plant (RPP-WTP) to prevent foaming. It consists mostly of polydimethylsiloxane (PDMS) and polypropylene glycol (PPG). These and other minor constituents of the antifoam have organic constituents that may participate in radiolytic and chemical reactions that produce hydrogen in Hanford waste. It has been recommended by The WTP R&T Department recommended personnel to treat the organic compounds of the antifoam like the in a similar manner as other organic compounds that are native to the Hanford waste with respect to hydrogen production. This testing has investigated the radiolytic and thermal production of hydrogen from antifoam added to simulant waste solutions to determine if the organic components of the antifoam produce hydrogen in the same manner as the native organic species in Hanford waste. Antifoam additions for this testing were in the range of 4 to 10 wt% to ensure adequate hydrogen detection. Test conditions were selected to bound exposures to the antifoam agent in the WTP. These levels are higher than previously recommended values of 350 mg/L for actual applications in WTP tanks containing air spargers and pulse jet mixers. Limited degradation analyses for the organic components of the antifoam were investigated in this study. A more detailed study involving analyses of antifoam degradation and product formation is in progress at SRNL and results from that study will be reported at a later time.

The total organic carbon (TOC) content of the Q2-3183A antifoam was measured to be 39.7 ± 4.9 wt% TOC. This measurement was performed in triplicate with on three different dilutions of the pure antifoam liquid using a TOC combustion analyzer instrument with catalytic oxidation, followed by CO_2 quantification using an infrared detector.

Test results from this study indicate that the WTP HGR correlation conservatively bounds hydrogen generation rates (HGRs) from antifoam-containing simulants if the antifoam organic components are treated the same as other native organics. Tests that used the combination of radiolysis and thermolysis conducted on simulants containing antifoam produced measured hydrogen that was bounded by the WTP correlation. These tests used the bounding WTP temperature of 90ºC and a dose rate of 1.8×10^5 rad/hr. This dose rate is about ten times higher than the dose rate equivalent calculated for a bounding Hanford sludge slurry composition of 10 Ci/L, or 2×10^4 rad/hr. Hydrogen was measured using a quadrupole mass spectroscopy instrument. Based on the analyses from the 4wt% and 10wt% antifoam samples, it is expected that the HGR results are directly proportional to the antifoam concentration added. A native organic-containing simulant that did not contain any added antifoam also produced a measurable radiolytic/thermal hydrogen rates that was in bounded by the WTP correlation. A base simulant with no added organic produced a measurable radiolytic/thermal HGR that was ~ 2X higher than the predicted HGR.

Analysis of antifoam-containing simulants after prolonged irradiation of 52 Mrad and heating (23 days at 90ºC) indicates that essentially all of the PDMS and greater than 60% of the PPG components are degraded, likely to lower molecular weight species. The antifoam components were analyzed by extraction from the salt simulants, followed by gel permeation chromatography (GPC) by personnel at Dow Corning. A more detailed study of the antifoam degradation and product formation from radiolysis and thermolysis is currently in progress at SRNL. That study uses a dose rate of about 2×10^4 rad/hr and bounding temperatures of 90ºC. Results from that study will be reported in a future report.

1.0 TESTING SUMMARY

1.1 OBJECTIVES

The test objectives from the Implementation Letter (2005) and Letter of Instruction (2005) for this testing are given in Table 1-1. The initial measurements involved determination of the TOC content of the Q2-3183A antifoam. Bounding hydrogen generation rates (HGRs) were initially determined for simulants with and without antifoam by exposure to radiation and elevated temperature.

Table 1-1. Test Objectives

Test Objective	**Objective Met (Y/N)**	**Discussion**
1. Measure TOC for unit mass of Q2-3183A Antifoam agent.	Yes	The TOC content of the antifoam was measured to be 39% +/- 4.9% as discussed in Section 3.3 of this report.
2. Measure bounding HGR for irradiated Hanford waste solutions containing antifoam agent in place of native organic compounds.	Yes	Bounding HGRs measured less than predicted for the systems with antifoam. Predicted HGRs agreed better with the measurements by considering the antifoam to be immiscible in the simulants. See Sections 3.5 - 3.7 of this report.
3. Measure the HGR for the same waste solution without radiation.	No	Insufficient time to develop repeatable test method.

1.2 TEST EXCEPTIONS

No Test Exceptions have been issued in connection with this study.

1.3 RESULTS AND PERFORMANCE AGAINST SUCCESS CRITERIA

The Success Criteria from the Implementation Letter are given in Table 1-2. Tests were conducted at a maximum of 90 ºC, which is the bounding temperature limit of the WTP. Radiation dose was set at high enough so these tests could produce enough hydrogen gas to allow measurement/detection within about one week. Antifoam was added to the simulants at high (~ 10 wt%) and low (~ 4 wt%) levels much higher than recommended addition levels of 350 mg/L with 70 mg/L additions every 24 hrs. (Baich et al. 2003 and Hassan et al. 2004), to ensure enough TOC from the antifoam was available for measurable hydrogen generation.

Table 1-2. Success Criteria

List Success Criteria	Explain How the Tests Did or Did Not Meet the Success Criteria
1. HGR measurements for simulated Low Activity Waste (LAW) with DOW Corning Q2-3183A Antifoam agent addition exposed to bounding WTP conditions (radiation and temperature) is required.	Samples tested gave measurable quantities of hydrogen gas enabling successful comparison of measured and predicted HGRs.
2. Provide information on how well the antifoam agent is represented by the key variables in the WTP HGR Correlation: TOC concentration, TOC reactivity and temperature.	Comparison of the measured and the predicted HGRs indicate that better agreement is found when the antifoam is considered as immiscible because treating the antifoam TOC in the same manner as native soluble organic species in the WTP HGR correlation overpredicts the measured values.

1.4 QUALITY REQUIREMENTS

This work was conducted in accordance with the RPP-WTP QA requirements specified for work conducted by SRNL as identified in DOE IWO M0SRLE60. SRNL has provided matrices to WTP demonstrating compliance of the SRNL QA program with the requirements specified by WTP. The WTP/SRNL Implementation Letter and Task Technical and QA Plan (Burket 2005a) for this task includes the Quality Assurance Requirements matrix. Specific information regarding the compliance of the SRNL 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. No RW-0333P requirements were invoked for these investigations.

1.5 R&T TEST CONDITIONS

The Letter of Instruction (CCN 114192) and the Implementation Letter (CCN 116542) establish conditions to ensure that results are valid for project needs. Table 1-3 lists those conditions and indicates whether they were followed. It describes any circumstances and their consequences where deviations were required.

Table 1-3. Test Conditions

List R&T Test Conditions	Were Test Conditions Followed?
1. Recipes for three experimental LAW simulants are: A. Base Recipe (no organic materials) B. Native Recipe = Base recipe with native organic compounds added. C. Antifoam Recipe = same as B but with antifoam agent substituted for native organic compounds at two different concentrations of Low TOC and High TOC.	Yes. Simulant solutions were made with a base recipe with no organic added and with a native recipe containing native organic compounds. Two different levels of antifoam agent were added to the base recipe simulant. However, both the base recipe simulant and the native organic simulant initially made for this testing contained visible undissolved solids. Therefore, these original simulants were filtered and the filtrate was tested. Filtrate solutions were analyzed to determine concentrations used in the WTP HGR correlation (e.g., Al, Nitrate, Nitrite and TOC).

List R&T Test Conditions	Were Test Conditions Followed?
2. All simulants will be exposed to two temperatures of 90 ºC (bounding for WTP) and 60 ºC.	Yes/No. Original testing used the bounding temperature of 90 ºC. After initial data collected at 90 ºC was analyzed testing was decided to be repeated at 90 ºC instead of at 60 ºC. Therefore no testing at 60 ºC was performed for this task.
3. All simulants will be exposed to radiation dose high enough to generate detectable amounts of hydrogen from exposure lasting about two weeks or less.	Yes. A dose rate of 1.8E5 rad/hr was used for this study. All irradiated systems showed measured hydrogen levels of about 1 vol% in the headspace, about 100 times higher than the mass spectroscopy quantifiable limits.
4. Cover gas is air.	Yes. All testing was performed with air as the cover gas.
5. Detection limits expressed as HGR is better than 1E-7 g-mol/kg-day.	No. Detection limits for hydrogen using mass spectroscopy were determined to be about 100 ppm or 0.01 vol%. Substitution of this value into sample calculations to determine the measured HGRs for systems used in this testing (see Appendix A) indicates a quantifiable detection limit of ~ 2.9 E-7 g-mol/kg/day. Although this value is nearly equal to the specified detection limit of 1E-7 g-mol/kg/day, it is not ‘better than’. However, it is adequate to determine that the WTP HGR correlation bounds measurements obtained for bounding WTP conditions.

1.6 SIMULANT USE

This testing used simulants both of nominal high salt compositions and a simulant of waste from tank AN-107. Simulant recipes are described in Tables Table 3-1, Table 3-2, Table 3-3, and Table Table 3-4, and by Appendix B.

1.7 DISCREPANCIES AND FOLLOW-ON TESTS

Thermolysis test results were not repeatable with the methodology used. There was not enough time available to develop an alternative method.

A nominal hydrogen yield G-value for direct radiolysis of the antifoam agent of $G(H_2) = 5$ H_2 molecules/100 eV absorbed dose was used to support this work. This value is consistent with hydrogen yields reported for irradiation of various saturated hydrocarbons in the range of $G(H_2) = 3.8$ to 5.7 H_2 molecules/100 eV absorbed dose (Table 9.1 from Spinks and Woods 1990). An experimental measurement of this $G(H_2)$ value could verify/confirm that this is the correct value. The test systems used in this study could easily determine the $G(H_2)$ values by irradiation of pure antifoam material and subsequent quantitative analysis of the hydrogen gas by mass spectroscopy.

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2.0 EXPERIMENTAL

Simulant solutions were prepared using reagent-grade chemicals per the specified test conditions as a base recipe (no organic materials) and as a native recipe containing common organics native to the Hanford waste. A third AN-107 LAW simulant (Saito et al. 2001) was also used. The DOW Corning Q2-3183A Antifoam agent (AFA) consists of polydimethylsiloxane (PDMS) and polypropyleneglycol (PPG) and other constituents shown in Table 2-1 from the DOW Corning Material Safety Data Sheet (MSDS).

Table 2-1. Dow Corning Q2-3183A Constituents*

Chemical Name	Chemical Abstract System (CAS) #	Percentage Range
polydimethylsiloxane	63148-62-9	40 – 70 %
Ethylene oxide – propylene oxide copolymer glycerol ether	9082-0-2	3 – 7 %
Polyethylene glycol octylphenyl ether	9036-19-5	5 – 10 %
Polypropylene glycol	25322-69-4	40 – 70 %
Treated Amorphous Silica	-	3 – 7 %
Treated silica	-	1 – 10 %

*This material is a proprietary product from Dow Corning and thus the exact amounts of the various constituents are not specified and the nominal percentage ranges of these components are given in the MSDS.

Total organic carbon was measured in the neat Q2-3183A antifoam with an OI ANALYTICAL 1020 High Temperature Total Carbon Analyzer (ADS Procedure ADS-2255). The OI ANALYTICAL 1020 autosampler features a vertical quartz combustion tube packed with supported platinum catalyst, which receives a continuous flow of oxygen at 200 cc/minute. The furnace is normally maintained at 680°C. Samples are introduced into the combustion tube via a fixed volume sampling loop. Through catalytic oxidation the sample is completely oxidized to CO_2 and H_2O. The gas flow sweeps the CO_2-containing steam out of the combustion tube, through a condenser, and into a gas/liquid separator to trap most of the H_2O. Final H_2O removal is accomplished by a Nafion membrane dehumidifier with a countercurrent flow of dry oxygen. The dried CO_2-containing gas is then passed through a metallic copper halogen scrubber and to a CO_2-specific non-dispersive infrared detector (NDIR) for peak quantification. Calibration accuracy is verified before and after analysis at 100 ppm with a standard and recalibration is required if the response is outside of acceptance criteria (nominally 5%). Deionized water is also checked as a blank and the TOC content is verified to be less than 5 ppm. The OI ANALYTICAL system has dynamic range between 5 ppm and 50,000 ppm carbon with a precision of ± 15% or 5 ppm, whichever is greater.

The radiolysis and thermolysis test setup for this study used stainless steel vessels (nominally 7/16” ID x 7.5” length, or ~ 20 cc volume) contained in an aluminum block. Stainless steel vessels were constructed out of pipe stock cut and welded for the bottom seal. Swage connections were put on the vessels and the vessels were all initially pressure and leaked tested to 300 psig by the SRNL Engineering Development Laboratory (EDL). The aluminum block was direct-contact heated using thermal heat wrapping (Thermolyne model BWH01-020, 120V, 314 watt, 1 inch wide heavy insulated ‘Samox’ type). The heat-wrapped aluminum block containing the test vessels was wrapped with refractory insulating material. The power supply for the heat wrap used an I^2R ThermoWatch Model L14-1800 temperature controller. The temperature controller was redundantly controlled by a backup I^2R ThermoWatch Model TOW-VOVC overtemperature protection device. Both the temperature controller and the backup overtemperature unit used calibrated K-type thermocouples for temperature measurements.

The aluminum block containing the sample vessels was placed in a J. L. Shepherd Model 484 Cobalt-60 Gamma Irradiation device (chamber size is 10" width x 10" height x 40" length) and exposed to a dose rate of 1.8E05 rad/hr. The dose rate was measured by chemical Fricke dosimeter (Spinks and Woods 1990). The Fricke (ferrous sulphate) dosimeter involves the radiation-induced oxidation of ferrous ion (Fe^{2+}) to ferric ion (Fe^{3+}) at low pH in the presence of oxygen.

Sample vessels were connected to pressure transmitters via ~ 8 ft of steel capillary tubing (nominally 1/32" ID x 8' L, or ~ 5 cc volume). The pressure transmitters (Rosemount Model 1144) were calibrated by the EDL over the range of 0 to 25 psig prior to testing. These pressure transmitters have nominal specifications of 0.5% accuracy of calibrated span and 0.5% stability of upper range limit for 6 months. The Rosemount pressure transmitters are variable capacitance sensors that allow direct electronic sensing of gage pressure. The capacitance between the sensing diaphragm and the capacitor plate is electronically converted to a two-wire, 4-20 mA dc signal.

Filtrates from the simulants were initially weighed out into the steel vessels, followed by aqueous antifoam agent addition onto the top surface of the simulant. The vessels were connected to the capillary tubing via swage lock connectors. No attempts were made to mix the antifoam solution into the simulant solution (i.e., no stirring or agitation) before the systems were sealed. The vessel/capillary tubing connections were then leak-checked by pressurizing the vessel/capillary tubing system with ~ 50 psi compressed air. The system was sealed and the vessel/capillary connection interface was submerged under water. Any air bubbles observed were indication that the vessel/ capillary connection needed further tightening. All systems were checked until no visible air bubbles were observed from the submerged vessels. After this coarse leak-check of the vessel/capillary tubing interface was performed on each system, the vessel/capillary tubing was then connected to the pressure transmitter. As a final leak check of the total system, each system was then pressurized (to 15 – 20 psig) with air from a plastic syringe and sealed. These sealed and pressurized systems were monitored for several hours to monitor for any pressure losses. The sealed systems typically maintained less than 0.01 psig pressure loss during this final leak check.

After leak checks were completed, the systems were opened/equilibrated to atmosphere and resealed (valve closed) with ambient air as the cover gas. Total head-space system volumes were determined after testing by introducing small amounts (10 cc) of air into the systems with a syringe and measuring the resulting pressure increases. These measurements indicated that each head-space volume was ~ 17 cc when the systems were loaded with test solutions. This head-space volume consisted of the unfilled portion of the test vessel (20 cc total vessel volume minus about 15 cc of solution), the approximate 5 cc contained in the 8' capillary tubing, and other associated volume for swage connections and pressure transmitter connections.

Samples were heated to 90ºC in the irradiation device. Constant recording of the pressures and temperatures was performed using a computer and 'LabVIEW' software. When testing was complete, the radiation source was removed and the systems were allowed to cool to ambient temperature. Pre-evacuated (10 mTorr) steel 25-cc gas sampling bulbs fitted with gas-tight valves were then connected to the head-space of each system. The pressurized gases contained in the test system headspace were then expanded into the pre-evacuated gas sample bulb.

The gas sample bulbs were sealed and removed from the system, then transferred at sub-atmospheric pressure to the vacuum-evacuated manifold of a quadrupole mass spectrometry instrument for gas analysis. A Scotty Specialty Gas standard gas (Cat# 22561, Lot# 422208B, Mfg./Exp. date 11/19/04 – 11/19/06) containing 1 vol% each of carbon dioxide, carbon monoxide, hydrogen, methane and oxygen in 95 vol% Nitrogen was used to calibrate the mass spectrometer. Appendix A shows a sample calculation to determine the minimum quantifiable HGR for the system.

3.0 RESULTS AND DISCUSSION

3.1 SIMULANT PREPARATION

Simulant solutions used in this study were prepared for the test conditions as a base recipe without organic materials and as a native recipe containing common native organics in the Hanford waste (Implementation Letter 2005). Table 3-1 shows summary recipes for the simulants and Appendix B gives the as-batched composition of these two simulants. Simulant preparation resulted in a heterogeneous matrix for both recipes. The two simulants thus required filtration to separate an aqueous phase for testing. Figure 3-1 shows the two simulants as batched. The base simulant had significant settled white solids and the native simulant had a very cloudy appearance indicating suspended solids throughout the matrix. Figure 3-2 (base recipe) and Figure 3-3 (native organics recipe) show the filtrations for each simulant.

Table 3-2 shows the resulting base simulant filtrate composition that ADS determined. The last column of Table 3-2 showing average measurement values divided by the original batch target shows that the aluminum and nitrate/nitrite ions for the filtrate were less than targeted but the sodium was in good agreement with the batch target. Certain trace metal compounds were added to the simulant at nominally 5 mg/L. Only chromium was detectable in the filtrate. Table 3-3 shows filtrate analysis for the native simulant filtrate. The last column of Table 3-3 showing average measurement values divided by the original batch target shows that the aluminum was closer to target than the base simulant, but the nitrate/nitrite ions were less than targeted by about the same amount as the base simulant and the sodium was in good agreement again. Analysis of the native organic species (HEDTA and glycolate) showed less than 50% of target and the TOC analyses indicated overall TOC was only 31% of target. Several of the trace metal elements were detectable in the native simulant filtrate (Cr, Cu, Fe, Zn).

The AN-107 LAW Envelope C simulant is a complex mixture derived from cross-flow filtration testing at SRNL. Table 3-4 shows a partial composition of this simulant and Figure 3-4 shows a picture of it.

As described in the Experimental Section, all antifoam additions for this study were made by adding weighed amounts of aqueous antifoam solution onto the top surface of the simulants with no mixing or agitation. Visual observation of pre and post tested samples indicated that antifoam material was visible on the top surface of the simulants, i.e., the antifoam solution was not completely miscible in the caustic simulants. It has also been previously observed that the Q2-3183A antifoam forms immiscible droplets on the surface of caustic simulants (see for example Photograph 3-1 from Section 3 and Figures 14, 15 and 31 from Appendix B in (Baich 2003)).

Table 3-1. Summary Recipes for Base and Native Simulants

Constituent	Concentration	Contained in Base Simulant (yes/no)	Contained in Native Simulant (yes/no)
Al	1 M	Y	Y
Na	As required	Y	Y
NO_2^-	3 M	Y	Y
NO_3^-	3 M	Y	Y
OH^-	Ph ~ 13	Y	Y
Organic Compounds	-	-	-
Glycolic Acid (native)	3 wt% TOC	N	Y
HEDTA (native)	1 wt% TOC	N	Y
Antifoam	4 wt% TOC (high) or 1 wt% TOC (low)	Y/N*	N

* Base simulant tested with and without antifoam addition.

Figure 3-1. Base 0 wt% TOC simulant (right) and Native 4 wt% TOC simulant (left)

Figure 3-2. Filtration of the base simulant

Figure 3-3. Filtration of the native simulant

Table 3-2. Base Simulant Filtrate Analysis

0 wt% TOC	**Measured (mg/L)**	**Measured (mg/L)**	**Average (mg/L)**	**Avg./Batch***
Component	**# 217569 duplicate 1**	**# 217570 duplicate 2**		
Aluminum	12200	11200	11700	0.43
	(0.93 wt%)	(0.85 wt%)	(0.89 wt%)	
Cadmium	< 4.17	4.17		
Chloride	< 20	< 20		
Chromium	6.33	6.8	6.6	
Copper	< 2.83	< 2.83		
Iron	< 4.07	< 4.07		
Molybdenum	< 18.8	< 18.8		
HEDTA	< 50	< 50		
Nickel	< 3.8	< 3.8		
Nitrate	163000	165000	164000	0.88
	(2.629 M)	**(2.661 M)**	**(2.65 M)**	
Nitrite	118000	121000	119500	0.87
	(2.565 M)	**(2.630 M)**	**(2.60 M)**	
Sodium	167000	182000	174500	1.07
Sulfate	< 50	< 50		
Zinc	< 0.697	< 0.697		

* Note: If all additives in the original simulants had been completely soluble, then the Avg./Batch values would all be 1.0.

Table 3-3. Native Simulant Filtrate Analysis

4 wt% TOC	**Measured (mg/L)**	**Measured (mg/L)**	**Average (mg/L)**	**Avg./Batch***
Component	**# 217571 duplicate 1**	**# 217572 duplicate 2**		
Aluminum	21300	20800	21050	0.78
	(1.62 wt%)	(1.58 wt%)	(1.60 wt%)	
Cadmium	< 4.17	4.2		
Chloride	< 20	< 20		
Chromium	5.76	7	6.4	
Copper	4.5	3.78	4.1	
Glycolate	27000	25000	26000	0.20
Iron	4.19	< 4.07		
Molybdenum	< 18.8	< 18.8		
HEDTA	4590	4634	4612	0.14
Nickel	< 3.8	< 3.8		
Nitrate	166000	163000	164500	0.88
	(2.677 M)	**(2.629 M)**	**(2.65 M)**	
Nitrite	119000	115000	117000	0.85
	(2.587 M)	**(2.500 M)**	**(2.54 M)**	
Sodium	222000	215000	218500	1.03
Sulfate	< 50	< 50		
TOC	16800	18200	17500	0.31
	(1.18 wt%)	(1.28 wt%)	(1.23 wt%)	
Zinc	< 1.98	2.55		

* Note: If all additives in the original simulants had been completely soluble, then the Avg./Batch values would all be 1.0.

Table 3-4. AN-107 Simulant Partial Analysis *

AN107 Simulant			
Analyte	**(mg/L)**		
Al	236	0.018	wt%
Na	131,057	5.72	Molar
Nitrate	145,186	2.342	Molar
Nitrite	38,751	0.842	Molar
TOC (native)	11,070	0.868	wt%
TOC (AFA)**	-	0.200	wt%
TOC (total)	-	1.068	wt%
	Molar	-	-
Tot OH^-	1.39	-	-
Free OH^-	0.55	-	-
Density	1.276 g/mL	-	-

* Full analyses of this simulant presented in Tables 12 and 13 of Saito et al. (2001)

** Q2-3183A antifoam added to the AN-107 simulant at 0.5 wt% antifoam

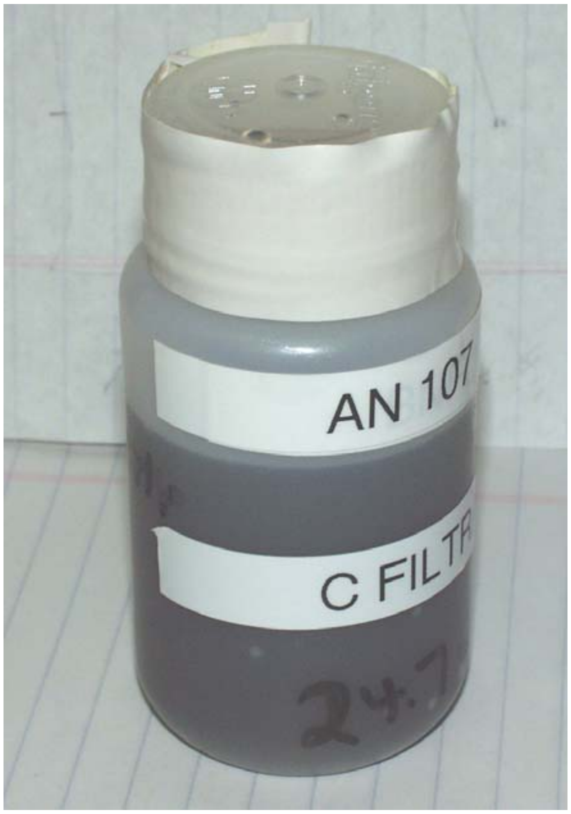


Figure 3-4. AN-107 Envelope C Simulant

3.2 DOSIMETRY

Aqueous ferrous sulphate Fricke dosimetry solutions were prepared per the composition given in Table 3-5. The dosimetry solutions were placed in identical steel vessels and the same aluminum block that was used for simulant irradiation in this study. The aluminum block containing the steel vessels with Fricke solutions was irradiated for one, two and three minutes in the identical position as was used for simulant irradiations. The absorbance of the irradiated solutions was then measured using a Tidus II Spectrometer instrument at 304 nm, which is the maximum absorbance wavelength for the oxidized ferric (Fe^{+3}) ion.

A plot of the absorbance vs. exposure time is shown in Figure 3-5. The slope of the absorbance (A) vs. exposure time gives a slope of 0.0018 absorbance units per sec. This slope can be used in the following equation (eq. # 3.38 from pg. 99 of Spinks and Woods 1990) to calculate the dose rate (D) in units of grays (Gy).

D (Gy) = (2.77 x ΔA)/ L,

With L equal to the optical pathlength of absorbance cell in meters.

Substituting in the measured change in absorbance per time and converting from grays to rads gives:

D (rad/hr) = ((2.77 x (0.0018/sec) x 3600sec/hr x (1rad/0.01 Gy))/ 1cm) * 100cm/m

D (rad/hr) = 1.8E+05 rad/hr

Error analysis of the best fit straight lines through the six data points indicates an error of ± 10% for the measured dose rate.

Table 3-5. Ferrous Sulphate 'Fricke Dosimeter'

Chemical	Amount	Vendor/Lot#
Concentrated H_2SO_4	5.7 mL	Fisher/#025810
$FeSO_4 \cdot 7H_2O$	0.070 g	Fisher/#984410
NaCl	0.015 g	Fisher/#995497
Deionized Water	Added to make 0.25L total volume	MilliQ filtration system

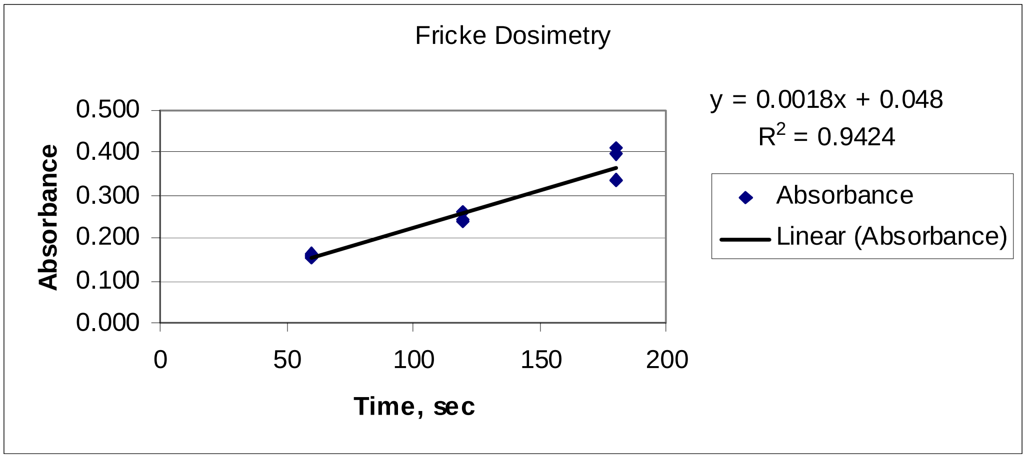


Figure 3-5. Fricke Dosimetry Absorbance vs. Time Plot

3.3 MEASUREMENT OF TOC CONTENT OF Q2-3183A ANTIFOAM

Table 3-6 shows the TOC analyses for the neat Q2-3183A antifoam by ADS. Three different dilutions were performed and a triplicate data set was measured for each dilution. The grand average result was 39.7 wt% TOC with a 12.3% relative standard deviation. Thus the reported value is 39.7 wt% TOC ± 4.9 wt%. The pre and post calibration 100 ppm TOC standards all measured in the acceptable range (100 ppm ± 10%) of 99 – 105 ppm. The 39.7 wt% TOC measured for Q2-3183A antifoam is reasonable considering the constituents listed in Table 2-1. The primary organic species are PDMS (with a calculated monomer $(CH_3)_2SiO$) TOC of 40 wt%) and PPG (with a calculated monomer (C_3H_6O) TOC of 62 wt%).

Table 3-6. Measurement of TOC in Q2-3183A

		wt% C	**Measured Average ppm**	**%RSD**	**Dilution Factor**		**Raw data, mg C / L**		
CCV (Cal verification)	100 ppm	-	-	-	1		104.3	101.2	-
Q2-3183A antifoam	-	45.2	452282	8.3	20800		23.414	21.987	19.832
Q2-3183A antifoam	-	35.6	355547	6.7	10400		37.256	33.986	33.762
Q2-3183A antifoam	-	38.4	383564	2.0	5200		75.412	73.196	72.679
Post-CCV	100 ppm	-	-	-	1		99.80	104.70	-
	Avg.->	39.7		12.3	(% RSD of 10 measurements)				

3.4 HYDROGEN MEASUREMENTS VIA MASS SPECTROSCOPY

Hydrogen was measured in the gas collected in steel sample bulbs. The mass spectrometer was calibrated by a standard gas with 1 vol% hydrogen (10,000 ppm). A blank system was set up that contained no organic in the base simulant filtrate. This blank system was similar to all of the others exposed in the gamma irradiation device. Table 3-7 provides data measured from the standard and blank systems. All hydrogen measurements were within 4% of the target. Other components in the standard gas were measured at mass = 16 for methane and some residual atomic oxygen from the mass spectroscopy method, mass = 28 for nitrogen and carbon monoxide, mass = 32 for oxygen and mass = 44 for carbon dioxide. Trace amounts of hydrogen were measured in the blank system at 5 – 9 ppm. As expected the blanks consist primarily of air with the nominal oxygen (21 vol%) to nitrogen (78 vol%) ratio of ~ 0.27. The quantification limit for hydrogen was estimated from the mass spectroscopy spectra signal (peak and area under curve) for hydrogen at about 100X below the standard-gas level of 1 vol% (10,000 ppm), or about 0.01 vol% = 100 ppm.

Table 3-7. Mass Spectroscopy Gas Component Measurements in Blank and Standard

Date	**System**	**Target***	**Measured**	**Mass 16**	**Mass 28**	**Mass 32**	**Mass 44**
		Vol% H_2	**Vol% H_2**	**CH_4/O**	**N_2/CO**	**O_2**	**CO_2**
4/20/05	Std.	1.0	1.0282	0.96958	95.9810	1.0346%	0.98659
4/20/05	Blank	0	0.00095	1.58	78.0393	20.3139	0.065
5/05/05	Blank	0	0.00054	1.55	77.3388	20.9585	0.1497
5/05/05	Std.	1.0	1.0448	1.0116	95.9523	1.0054	0.98589
5/05/05	Std.	1.0	0.9964.5	1.0296	95.5209	1.3264%	1.1266

* Standard gas contained 1 vol% each of H_2, CH_4, CO, O_2 and CO_2 in 95% N_2

3.5 INITIAL RADIOLYSIS/THERMOLYSIS TESTING

Initial radiolysis/thermolysis testing used the base simulant, the base simulant with low and high antifoam addition, and the 4 wt% TOC simulant. Table 3-8 shows their compositions. The base simulant and the 4 wt% TOC native simulant were prepared as single samples and the low-antifoam/base simulant and high antifoam/base simulant were prepared in duplicate. These systems were irradiated and heated for 12 days and pressures and temperatures were monitored and recorded. Figure 3-6 shows some of the pressure vs. time data for these systems. The total pressurization increases in the order of low antifoam, high antifoam, base simulant and native simulant. Linear least squares fits through the data indicate excellent linearity since the R^2 coefficients are at least 0.999.

After 12 days of exposure the systems were allowed to cool to ambient temperature and the radiation source was removed. Gases collected at the end of testing at ambient temperature were analyzed by mass spectroscopy and the results are shown in Table 3-9. The hydrogen components were input into the ideal gas equation along with the system pressure, volume and temperature to calculate the moles of hydrogen produced during testing. The moles of hydrogen were used along with the total mass tested and the total time of testing to calculate the hydrogen generation rates (HGR) for each system. These values are also shown in Table 3-9. A sample calculation for the HGRs is given in Appendix A. All of the simulant parameters and the dose rate and temperature were input into the WTP HGR correlation (Appendix C) to predict HGRs for these systems. This calculation treats the TOC from the antifoam in the same manner as any native TOC in the simulant.

Table 3-9 shows these predicted HGRs for comparison to the measured values. The nominal variability in the WTP HGR correlation is approximately ± 3X. (Sherwood and Stock 2004). Lower HGRs are calculated by assuming complete immiscible antifoam agent. The only hydrogen contribution from immiscible antifoam is a minor radiolytic term due to direct radiolytic interaction/decomposition of the immiscible antifoam. Visual observation of the pre and post tested samples indicated immiscible antifoam on the top surface of the simulants. No attempts were made for this study to investigate the degree of miscibility for the antifoam solution with the various caustic simulants.

There is good agreement between the measured and predicted HGRs for the base simulant with no TOC added. The measured HGR of 3.2E-4 g-mol/kg/day compared to the predicted value of 1.7E-4 g-mol/kg/day gives a ratio of predicted/measured of 0.5. The hydrogen produced in this system should be exclusively from the radiolysis of water as there is no other hydrocarbon source for hydrogen production from other pathways. Table 3-9 shows that the predicted HGR for the native organic simulant (4.6E-3 g-mol/kg/day) is about six times higher than the measured value of 8.2E-4 g-mol/kg/day. The hydrogen sources for this native organic-containing simulant are water radiolysis, organic radiolysis, and organic thermolysis.

Table 3-8. Simulant Systems for Radiolysis/Thermolysis Initial Testing

			V56	V57	V58	V59	V60	V61
0 wt% TOC simulant	amount added:	(grams)	19.5474	16.943	16.8433	18.2713	18.3272	-
4 wt% TOC simulant	amount added:	(grams)	-	-	-	-	-	21.0993
AFA	amount added:	(grams)	0	1.7921	1.7726	0.4917	0.4684	0
Total mass		(grams)	19.5474	18.7351	18.6159	18.763	18.7956	21.0993
Total volume*		(mL)	14.8277	14.6443	14.5491	14.3514	14.3705	14.8461
TOC(AFA)	(=0.397 * AFA)	(grams)		0.7115	0.7037	0.1952	0.1860	-
wt%AFA		-	-	9.6	9.5	2.6	2.5	-
wt% TOC		-	-	3.8	3.8	1.0	1.0	-

* 4 wt% simulant density = 1.4212 g/mL; 0 wt% simulant density = 1.3183 g/mL;
pure antifoam density = 1.0 g/mL

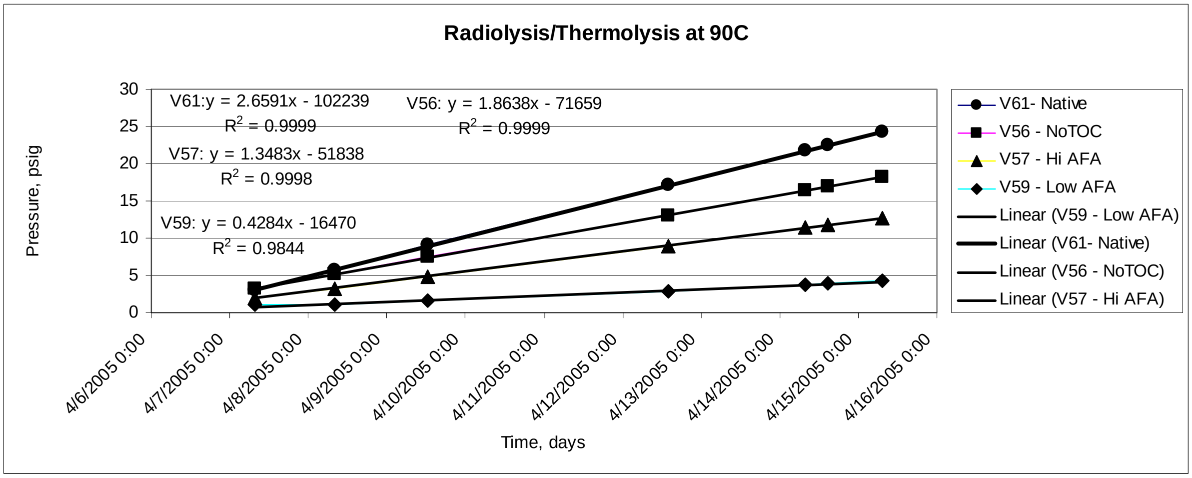


Figure 3-6. Pressure vs. Time Plots for Radiolysis/Thermolysis Initial Testing

Table 3-9. Hydrogen and HGRs for Radiolysis/Thermolysis Initial Testing

Radiolysis/Thermolysis InitialTesting	Units	No TOC	High AFA	High AFA (duplicate)	Low AFA	Low AFA* (duplicate)	Native, No AFA
Measured Hydrogen	vol %	**4.66**	**20.44**	**19.79**	**6.99**	**18.90**	**10.01**
Measured HGR Rad/Therm	g-mol/kg/day	**3.23E-04**	**1.24E-03**	**1.19E-03**	**2.67E-04**	**5.57E-04**	**8.21E-04**
Average Measured HGR Rad/Therm	g-mol/kg/day	**3.23E-04**	**1.22E-03**	**-**	**4.12E-04**	**-**	**8.21E-04**
Predicted HGR Rad/Therm (AFA miscible) [\$]	g-mol/kg/day	1.66E-04	1.28E-02	-	3.61E-03	-	4.56E-03
Predicted HGR Rad/Therm (AFA immiscible) [\$\$]	g-mol/kg/day	1.66E-04	1.05E-03	-	3.90E-04	-	4.56E-03
Ratio: Predicted (AFA miscible)/Avg.Measure	-	0.5	10.5	-	8.8	-	5.6
Ratio: Predicted (AFA immiscible)/Avg.Measure	-	0.5	0.9	-	0.9	-	5.6

* Note: this low AFA system developed a leak during testing.

[\$] From Appendix C, Predicted HGR Rad/Therm (AFA miscible) = $\text{HGR}_{\text{LAW0}} + \text{HGR\_imi}_{\text{AFA0}} + \text{HGR}_{\text{AFA0}}$

[\$\$] From Appendix C, Predicted HGR Rad/Therm (AFA immiscible) = $\text{HGR}_{\text{LAW0}} + \text{HGR\_imi}_{\text{AFA0}}$

3.6 REPEAT RADIOLYSIS/THERMOLYSIS TESTING

At the end of the initial testing period it was concluded by SRNL and WTP R&T personnel that further testing should be investigated using repeated systems (high and low antifoam) in addition to a new AN-107 simulant. The further radiolysis/thermolysis testing used similar duplicate simulant systems from the initial tests (duplicate low antifoam/base simulant and duplicate high antifoam/base simulant) along with a duplicate AN-107 simulant that contained relatively low 0.5 wt% amount of antifoam. Table 3-10 shows the details of these simulant compositions. These systems were prepared with fresh solutions and new sample vessels and were irradiated and heated for 5 days with pressure and temperature recording. Figure 3-7 shows some of the pressure vs. time data for these systems. The total pressurization is shown to increase in the order of low antifoam to high antifoam to AN-107 simulant. Note from Figure 3-8 that all three duplicate systems show good precision in the total pressure vs. time plots indicating no suspected leaks in the six systems during 5 days of testing.

Gases were collected from these radiolysis/thermolysis tests in the same manner as initial testing and the results are shown in Table 3-11. Measured and predicted HGRs are shown in Table 3-11. Three of the systems were sampled a second time for gas analysis to investigate residual gases contained in the headspace of the systems. The second analyses of the vessel headspace indicated that varying amounts of hydrogen were still present in the system headspaces after the initial gas sampling. Second analyses showed that between 30% and 90% of the original hydrogen remained in the system headspace after initial sampling and equilibration to atmospheric pressure.

Table 3-11 shows that the predicted HGR for the AN-107 native organic-containing simulant (3.8E-3 g-mol/kg/day) is about 5.8 times the measured value of 6.3E-4 g-mol/kg/day. The hydrogen sources for this native organic-containing and antifoam-containing AN-107 simulant are water radiolysis, organic radiolysis (from native organic and antifoam TOC) and organic thermolysis (from native organic and antifoam TOC). Since this AN-107 simulant contained relatively small amounts of antifoam (~ 0.5 wt%) vs. the other antifoam systems studied, there is very little difference in the predicted HGRs if one considers the antifoam as either entirely miscible (HGR = 3.8E-3 g-mol/kg/day) or entirely immiscible (HGR = 3.2E-3 g-mol/kg/day).

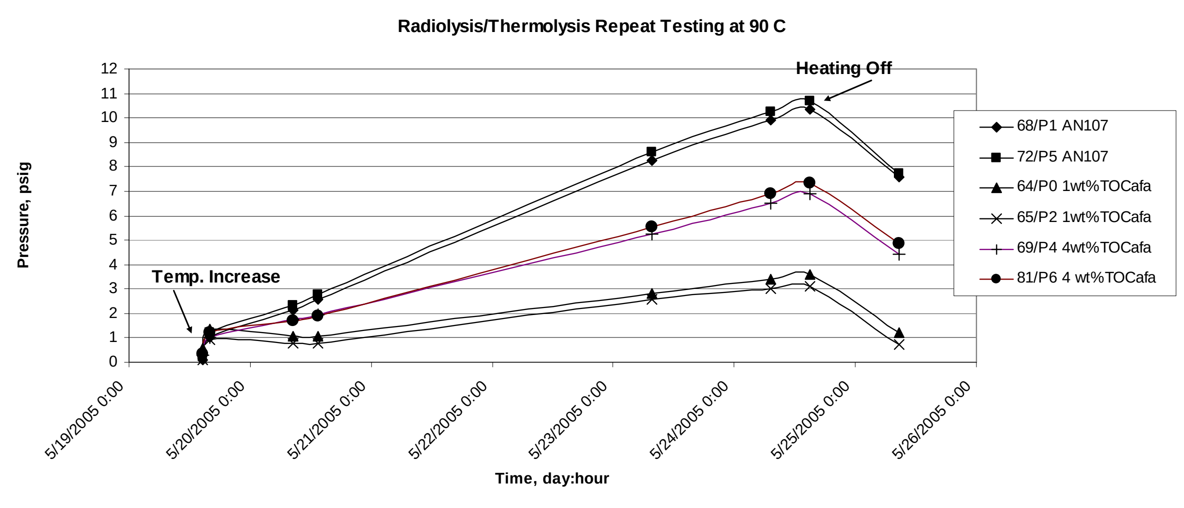


Figure 3-7. Pressure vs. Time Plots for Radiolysis/Thermolysis Repeat Testing

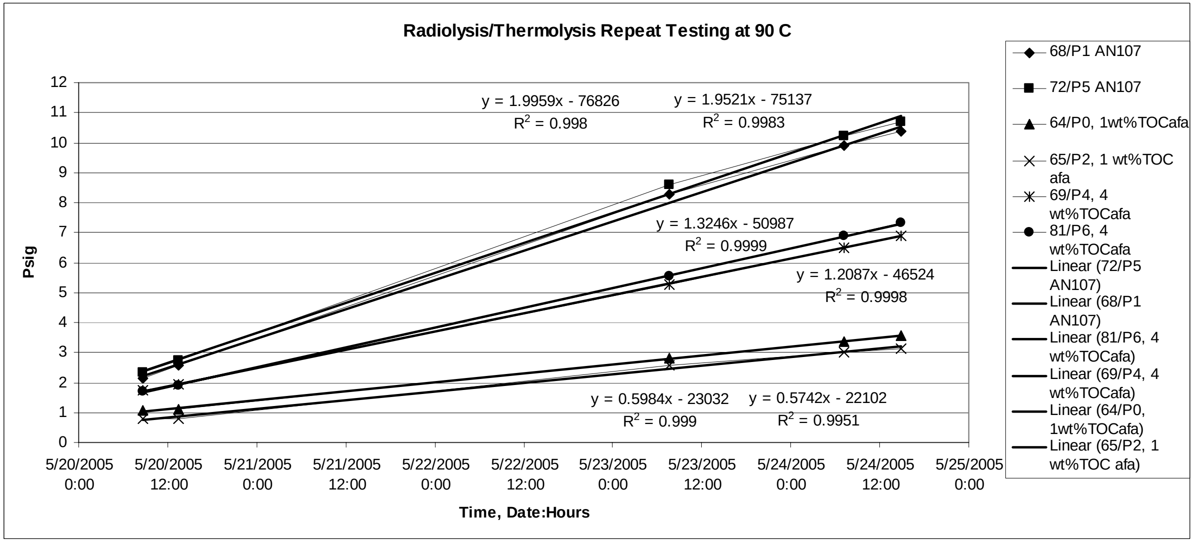


Figure 3-8. Pressure vs. Time Plots for Radiolysis/Thermolysis Repeat Testing Showing Best Linear Fits

Table 3-10. Simulant Systems for Radiolysis/Thermolysis Repeat Testing

			V68	**V72**	**V69**	**V81**	**V64**	**V65**
0 wt% TOC simulant	amount added:	(grams)	-	-	17.0923	17.0403	18.5072	18.3631
AN107 Sim	amount added:	(grams)	19.1442	19.1199	-	-	-	-
AFA	amount added:	(grams)	0.0988	0.1085	1.8271	1.8057	0.5364	0.5003
Total mass		(grams)	19.243	19.2284	18.9194	18.846	19.0436	18.8634
Total volume*		(mL)	15.1021	15.0927	14.7925	14.7317	14.5751	14.4297
TOC(AFA)	(=0.397*AFA)	(grams)	0.0392	0.0431	0.7254	0.7169	0.2130	0.1986
wt%AFA		-	0.51	0.56	9.66	9.58	2.82	2.65
wt% TOC(AFA)		-	0.20	0.22	3.83	3.80	1.12	1.05
wt% TOC(Total)		-	1.07	1.09				

* 0 wt% simulant density = 1.3183 g/mL; AN107 simulant density = 1.276 g/mL; pure antifoam density = 1.0 g/mL

Table 3-11. Hydrogen and HRGs for Radiolysis/Thermolysis Repeat Testing

Radiolysis/Thermolysis Repeat Testing	**Units**	**AN107, 0.5wt% AFA**	**AN107, 0.5wt% AFA**	**High AFA**	**High AFA (duplicate)**	**Low AFA**	**Low AFA (duplicate**
Measured Hydrogen	vol %	**5.79**	**6.09**	**9.42**	**13.32**	**2.43**	**2.23**
Measured HGR Rad/Therm	g-mol/kg/day	**6.31E-04**	**6.69E-04**	**8.96E-04**	**1.30E-03**	**1.91E-04**	**1.72E-04**
Average Measured HGR Rad/Therm	g-mol/kg/day	**6.50E-04**	**-**	**1.10E-03**	**-**	**1.81E-04**	**-**
Predicted HGR Rad/Therm (AFA miscible) [$]	g-mol/kg/day	3.79E-03	-	1.28E-02	-	3.61E-03	-
Predicted HGR Rad/Therm (AFA immiscible) [$$]	g-mol/kg/day	3.17E-03	-	1.05E-03	-	3.90E-04	-
Ratio: Predicted (AFA miscible)/Avg.Measure	-	5.8	-	11.7	-	19.9	-
Ratio: Predicted (AFA immiscible)/Avg.Measure	-	4.9	-	1.0	-	2.1	-

[$] From Appendix C, Predicted HGR Rad/Therm (AFA miscible) = $HGR_{LAW0} + HGR\_imi_{AFA0} + HGR_{AFA0}$

[$$] From Appendix C, Predicted HGR Rad/Therm (AFA immiscible) = $HGR_{LAW0} + HGR\_imi_{AFA0}$

3.7 SUMMARY OF DATA AND DISCUSSION

The data presented in Table 3-9 and Table 3-11 can be summarized into a single collection for comparison. Table 3-12 shows all of the data from the radiolysis and thermolysis combination testing. The HGRs shown in Table 3-12 are arranged in decreasing order for the various systems studied in this radiolysis/thermolysis testing. Systems that used replicate samples showed %RSD values in the range of 4 to 24%. The predicted HGR/measured HGR column shows that in all cases where antifoam is present, the predicted HGRs are bounding for the measured HGRs. The predicted and measured HGRs are in good agreement (predictied to measured ratios in range of 0.9 to 2.1) for both the high and low antifoam-containing base simulant when the antifoam is treated as immiscible. If one assumes the antifoam to be completely miscible in the HGR correlation, predicted HGRs are considerably higher than measured values, with predicted HGRs about 10 to 20 times the measured values.

Table 3-12. Summary of Data

Radiolysis and Thermolysis	**Avg. HGR**	**St. Dev.**	**% RSD**	**Predicted HGR/Measured HGR**	**Antifoam Predicted (Miscible or Immiscible)**
Simulant	(g-mol/kg/day)	(g-mol/kg/day)			
Base Simulant, High Antifoam *	1.2E-03	1.8E-04	16	11.1	**Miscible**
				0.9	Immiscible
Native Simulant, No Antifoam	8.2E-04			5.6	NA***
AN-107 Simulant, 0.5wt% Antifoam	6.5E-04	2.6E-05	4	5.8	**Miscible**
				4.9	Immiscible
Base Simulant, No Antifoam	3.2E-04			0.5	NA***
Base Simulant, Low Antifoam **	2.1E-04	5.0E-05	24	14.3	**Miscible**
				1.5	Immiscible

* High antifoam = 9.5wt% AFA, or 4 wt% TOC-AFA
** Low antifoam = 2.5wt% AFA, or 1 wt% TOC-AFA
*** No antifoam added to these simulants

The WTP HGR correlation is summarized in the Text Box shown in Appendix C. It predicts HGRs to within ±3 (Sherwood and Stock 2004). The correlation is applicable for HGRs from 1E-07 g-mol/kg/day up to 1E-2 g-mol/kg/day. In general the correlation terms can be summarized as follows.

Radiolytic Hydrogen:

Water radiolysis = f (nitrate, nitrite, dose)

TOC radiolysis = f (TOC, Temperature, reactivity coefficient)

Antifoam immiscible radiolysis = f (immiscible fraction AFA, dose)

Thermal Hydrogen Production:

TOC thermolysis = f (TOC, Temp., liquid fraction, reactivity coefficient, Al)

The TOC terms represent the liquid fraction of TOC deriving from either native organic species or from antifoam. Note that there is no thermal hydrogen production term for immiscible antifoam TOC.

An example WTP HGR correlation prediction for antifoam agent addition used in an engineering calculation is also given in Appendix C for the AN-107 simulant, the native simulant filtrate and the base simulant filtrate containing high and low additions of antifoam. The HGR predictions for the base simulant (with no added antifoam) can also be obtained from the base simulant containing antifoam by neglecting all of the AFA and TOC terms.

3.8 SAVANNAH RIVER SITE EXPERIENCE WITH ANTIFOAM AGENTS

Various antifoam agents are currently in use at the Savannah River Site (SRS). The main two areas of use are in the SRS Tank Farms with the Evaporators and at the SRS Defense Waste Processing Facility (DWPF). Three different antifoam agents developed by Dow Corning are identified with use in the SRS evaporators (Swingle 1999). The three antifoam agents are DC AF H-10 Emulsion and DC AF B Emulsion and DC 544 AF. The two emulsion antifoams contain about 10% PDMS. The DC 544 AF contains about 28% PDMS and 38% of a polydimethylsiloxane copolymer. Swingle and White indicate that none of the antifoam agents or their potential degradation products are expected to contribute to the composite lower flammability limit (CLFL) for the waste tanks and evaporators due to the limited quantities and the significant dilution in the tank farm equipment.

Antifoam agents used in the DWPF include the DC 544 from about 1996 to 2001 during initial operations. A newer antifoam agent was later developed because the DC 544 antifoam agent was not sufficiently effective. The newer antifoam agent is IIT747 developed by the Illinois Institute of Technology (Koopman 1999). Various technical reports from SRNL have investigated the use of these two antifoams in the DWPF processes (Daniel 1999, Lambert 2000, Koopman 2001, Fellinger 2002). Studies have focused on the effectiveness of the antifoam agent to reduce foaming in the DWPF process cells and any radiolytic or thermal decomposition of the antifoam agents to produce hydrogen during sludge processing has not been specifically studied. Hydrogen generation in the Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) is attributed mainly to radiolytic decomposition of water and transition metal catalyzed decomposition of formic acid used in the SRAT process (Fellinger 2002, Crawford 1995). A typical current IIT747 antifoam addition strategy for the main two DWPF processes are about 800 ppm addition before boiling in the SRAT with about 100 ppm added every 8 hours at boiling. Contents of the SRAT are passed on to the SME where 100 ppm antifoam agent is added before boiling, with 100 ppm added every 8 hours at boiling. Contents of the SME are fed to the Melter Feed Tank (MFT) and then to the DWPF melter.

One particular study involved testing unirradiated vs. irradiated IIT747 antifoam agent in the DWPF simulated sludge processing (Lambert 2000). Conclusions from that study suggest that unirradiated and irradiated antifoam are equally effective. The IIT747 antifoam was irradiated at a dose rate of $2\text{x}10^3$ rad/hr for a 14 day equivalent SRAT/SME cycle of $6.8\text{x}10^5$ rads. The study also analyzed for silicon-containing antifoam decomposition products in the condensates generated during processing. No differences were determined for silicon analyses from the nonirradiated and irradiated antifoam used during processing, suggesting that no significant steam stripping of any silicon-containing radiation degradation fragments were concentrated in the condensate.

4.0 ANTIFOAM DEGRADATION ANALYSES AND RADIOLYTIC DECOMPOSITION SCHEMES

4.1 ANTIFOAM DEGRADATION ANALYSES

Samples of the base simulant filtrate solution with added antifoam were analyzed by DOW Corning personnel. Table 4-1 shows the samples that were shipped to DOW. Each vessel sample # gives the details of each particular sample. The key to the sample labels is as follows:

TW-vessel number- wt% AFA, sample-type- analysis

Where
TW = Tom White (SRNL research personnel)
Vessel number = sample vessel number ID
Wt% AFA = 4 or 10 wt% (for labeling purposes only, see last column of Table 4-1 for actual wt% Antifoam values)
Sample type = 'S' for irradiated/heated sample, 'STD' for standard, 'B' for blank
Analysis = PDMS for polydimethylsiloxane and PPG for polypropyleneglycol

All four of the 'S' type samples were from radiolysis/thermolysis testing. These four samples had been exposed to 12 days dose at dose rate of 1.8E5 rad/hr, or a total of 5.2E7 rad (52 Mrad). The samples had also been exposed to 23 days of 90ºC (from combined radiolysis/thermolysis 12-day testing, followed by additional 11-day thermolysis-only testing). All of the 'STD' samples were prepared with antifoam added to base simulant filtrate shortly before shipment to DOW for analyses. The 'B' blank systems were base simulant filtrate containing no antifoam. Neat samples of the actual Q2-3183A antifoam 'controls' used in this study were also analyzed by DOW Corning. These control samples were prepared by Dow Corning personnel from the same batch of Q2-3183A antifoam used for the SRNL testing. The control samples used 10,000 ppm w/v of antifoam added to either tetrahydrofuran or toluene. These concentrations are shown as 1.12 and 1.15 wt% in Table 4-1.

The control samples were analyzed and the amounts of PDMS and PPG detected were set at 100% recovery. All simulant samples were extracted and analyzed for either PDMS or PPG by gel-permeation chromatography (GPC) by DOW Corning personnel. Results of the PDMS analyses in the toluene extracts and the PPG analyses in the THF extracts are given in the 'Analytical Solutions Report' from DOW Corning. All results in this report are given as '% recovery' or as 'percent of polymer remaining'. All data from extraction of the antifoam components in simulant are referenced to the control samples. Details of the extraction procedures are also given below in the Experimental Section of the 'Analytical Solutions Report' from DOW Corning. Standard curves were also generated for the two solvent systems by using polystyrene standards in either the toluene or THF solvents. These standard curves are shown as Figure 4-1 and Figure 4-2, respectively.

The key findings from the PDMS analyses (see Table labeled 'PDMS results (toluene)' from the Analytical Solutions Report from Dow Corning) were that the PDMS appeared to be completely absent in the 4S and 10S samples. Also there was excellent precision in PDMS analysis of the triplicate 4wt%AFA standards (vessels 71, 73 and 76 show 76% to 79% recovery). There appears to be a discrepancy in the recovery of the 4wt%AFA samples (actual ~ 2.5 wt% antifoam) and the 10 wt%AFA samples (actual ~ 9.5 wt% antifoam) vs. the control samples of ~ 1 wt% antifoam. Only ~ 80% recovery was realized for the simulants labeled 4 wt% antifoam vs. 120% recover from the simulants labeled 10 wt% antifoam. These recoveries were referenced to analysis of the control sample of pure antifoam at ~ 1wt%.

The PPG analyses indicate that the 4S and 10S samples show a broadening of the PPG peak relative to the control sample. The PPG peak is the main peak eluting from about 15.5 – 17 minutes in the 'THF/RI' plots in the Dow report. The Dow report 'PPG results (THF)' table on pg. 2 of 5 actually indicates > 100% recovery for the 4S and 10S samples using peak area analyses. However if these peaks are analyzed by reduction in peak height, the results show that at least 60% of the original antifoam PPG component has degraded for these samples. Both the PDMS and PPG tables showing analyses for reduction in peak height are shown below in Table 4-2. Peak height reduction analyses for PPG indicates that only 21% of the PPG remained for the 4S-PPG sample and only 39% of the PPG remained for the 10S-PPG sample. In other words 61-79% of the original PPG component is destroyed. Peak height information for PDMS in Table 4-2 shows that 0% of the PDMS remaind for both the 4S-PDMS and the 10S-PDMS samples.

These data for current testing show complete destruction of the PDMS and 61-79% destruction of PPG at 5.2E7 rad absorbed dose for these samples that had initial amounts of antifoam in the range of 2.5 to 9.5 wt%. These data are in agreement with earlier results reported for irradiation studies on ~ 1.4 wt% Q2-3182A antifoam in a concentrated blend of UF1B/VSL SBS simulant (Baich et al. 2003). Earlier work used three different doses of 8-hr (1.5E6 rad), 2-day (9.3E6 rad) and 7d (3.2E7 rad). Conclusions from that work indicated that the 7-day dose of 3.2E7 rads destroyed the majority of the 1.4 wt% original antifoam in the simulant.

4.2 RADIOLYTIC DECOMPOSITION SCHEMES

Initial steps of radiolytic degradation schemes of the main antifoam constituents PDMS and PPG are illustrated in Figure 4-3 and Figure 4-4. Figure 4-3 shows the PDMS polymer undergoing loss of $^{\cdot}H$ or $^{\cdot}CH_3$ radicals from the PDMS structure (Products 1 and $^{\cdot}H$ and Products 2 and $^{\cdot}CH_3$). These radicals are the precursors to the known radiolytic decomposition products of PDMS of hydrogen, methane and ethane (Spinks and Woods 1990; Chapiro 1962). Another pathway is direct bond breakage of the parent polymer to decompose the polymer into smaller chain molecules of Products 3 and 4. This mechanism is common in radiolytic polymer degradation and leads to a reduction in average molecular weight caused by the main-chain scission (Spinks and Woods 1990).

Similar radiolytic decomposition schemes for the other Q2-3183A antifoam polymer (PPG) are shown in Figure 4-4 . The initial radiolytic decay schemes shown in Figure 4-3 and Figure 4-4 are presented only to indicate possible pathways for hydrogen production. A more detailed report investigating the detailed degradation of these Q2-3183A antifoam polymer components is currently in progress at SRNL (Burket 2005b), and results will be reported at a later time.

Other degradative reactions of silicones involving thermal, hydrolytic, photostability and oxidative pathways have been discussed in detail by Brook (2000). For instance, silicones that are simultaneously exposed to irradiation and oxygen can breakdown via carbon oxidation and Si-C bond cleavage to give ultimate end-products of CO_2, H_2CO and SiO_2 (See Chapter 9 in Brook 2000). Certain volatile siloxane decomposition products (organosilicon compounds) such as hexamethylcyclotrisiloxane ($[(-CH_3)_2SiO-)_3]$ and oxtamethylcyclotetrasiloxane ($[(-CH_3)_2SiO-)_4]$ have also been reported.

The radiolytic reduction in PDMS average molecular weight can be seen in the Dow Corning report figures labeled 'Toluene/RI' for both the 4wt% and the 10wt% antifoam samples on page indicated as 'Page 4 of 5'. The irradiated 4 wt% antifoam sample (TW59-4S-PDMS) shown as the lower curve in the first Toluene/RI figure shows near complete loss at the higher molecular weight range of 10 - 17 minutes and lowering of peak area in the lower molecular weight range corresponding to the proposed PPG peak at 17-19 minutes. These data are interpreted to indicate a general reduction in the molecular weight of the PDMS and the PPG components of the antifoam. Similar conclusions can be drawn from the 10 wt% antifoam sample shown as the next-to lowest curve in the second 'Toluene/RI' figure.

The radiolytic decomposition schemes shown in Figure 4-3 and Figure 4-4 represent direct interaction of ionizing radiation with the polymers. These type reactions would be relevant for the immiscible AFA components in the simulant solutions. Other reaction schemes involving indirect radiolytic decomposition of miscible AFA organic components, which would be homogeneously mixed throughout the simulant solution, involve primary solvent (water) radiolysis, followed by attack of the miscible polymers by the reactive primary radicals formed from water radiolysis, i.e., $OH^{\cdot}$, hydrated electron (e_{aq}^-) and H. For instance, Table 8.2 'Generic Radiolysis Mechanism for Organic Solutes in Aqueous Solutions' from Spinks (1990) gives a summary of these types of reactions. Using RH_2 to represent the possible miscible AFA organic components (PDMS or PPG), the following reaction could account for hydrogen production from indirect radiolysis of the miscible antifoam components.

$$H^{\cdot} \text{ (from direct water radiolysis)} + RH_2 \rightarrow H_2 + RH^{\cdot}$$

Table 4-1. Summary of Analyses Performed by Dow Corning for SRNL

GPC Analyses							
Sample #	***Vessel #***	***Vol., mL***	***Description****	***Analysis***	**Simulant (g)**	**Antifoam (g)**	**Actual wt% Antifoam**
TW-57-10S-PDMS	57	15	10 wt% Q2-3183A Sample	GPC for PDMS	16.9430	1.7921	9.57
TW-58-10S-PPG	58	15	10 wt% Q2-3183A Sample	GPC for PPG	16.8433	1.7726	9.52
TW-59-4S-PDMS	59	15	4 wt% Q2-3183A Sample	GPC for PDMS	18.2713	0.4917	2.62
TW-60-4S-PPG	60	15	4 wt% Q2-3183A Sample	GPC for PPG	18.3272	0.4684	2.49
TW-62-4STD-PPG	62	15	4 wt% Q2-3183A Sample	GPC for PPG	18.4322	0.4876	2.58
TW-63-4STD-PPG	63	15	4 wt% Q2-3183A Sample	GPC for PPG	18.3617	0.4952	2.63
TW-66-B-PPG	66	15	Blank	GPC for PPG	19.6931	0	0.00
TW-67-4STD-PPG	67	15	4 wt% Q2-3183A Sample	GPC for PPG	18.3427	0.4733	2.52
TW-70-10STD-PPG	70	15	10 wt% Q2-3183A Sample	GPC for PPG	16.9532	1.7775	9.49
TW-71-4STD-PDMS	71	15	4 wt% Q2-3183A Sample	GPC for PDMS	18.3528	0.4660	2.48
TW-73-4STD-PDMS	73	15	4 wt% Q2-3183A Sample	GPC for PDMS	18.4280	0.4591	2.43
TW-74-B-PDMS	74	15	Blank	GPC for PDMS	19.7353	0	0.00
TW-76-4STD-PDMS	76	15	4 wt% Q2-3183A Sample	GPC for PDMS	18.3846	0.4733	2.51
TW-78-10STD-PDMS	78	15	10 wt% Q2-3183A Sample	GPC for PDMS	17.0815	1.7796	9.44
Q2-3183A Control-PPG	(THF)**		Neat Q2-3183A	GPC for PPG	880**	10	1.12
Q2-3183A Control-PDMS	(toluene)***		Neat Q2-3183A	GPC for PDMS	860***	10	1.15

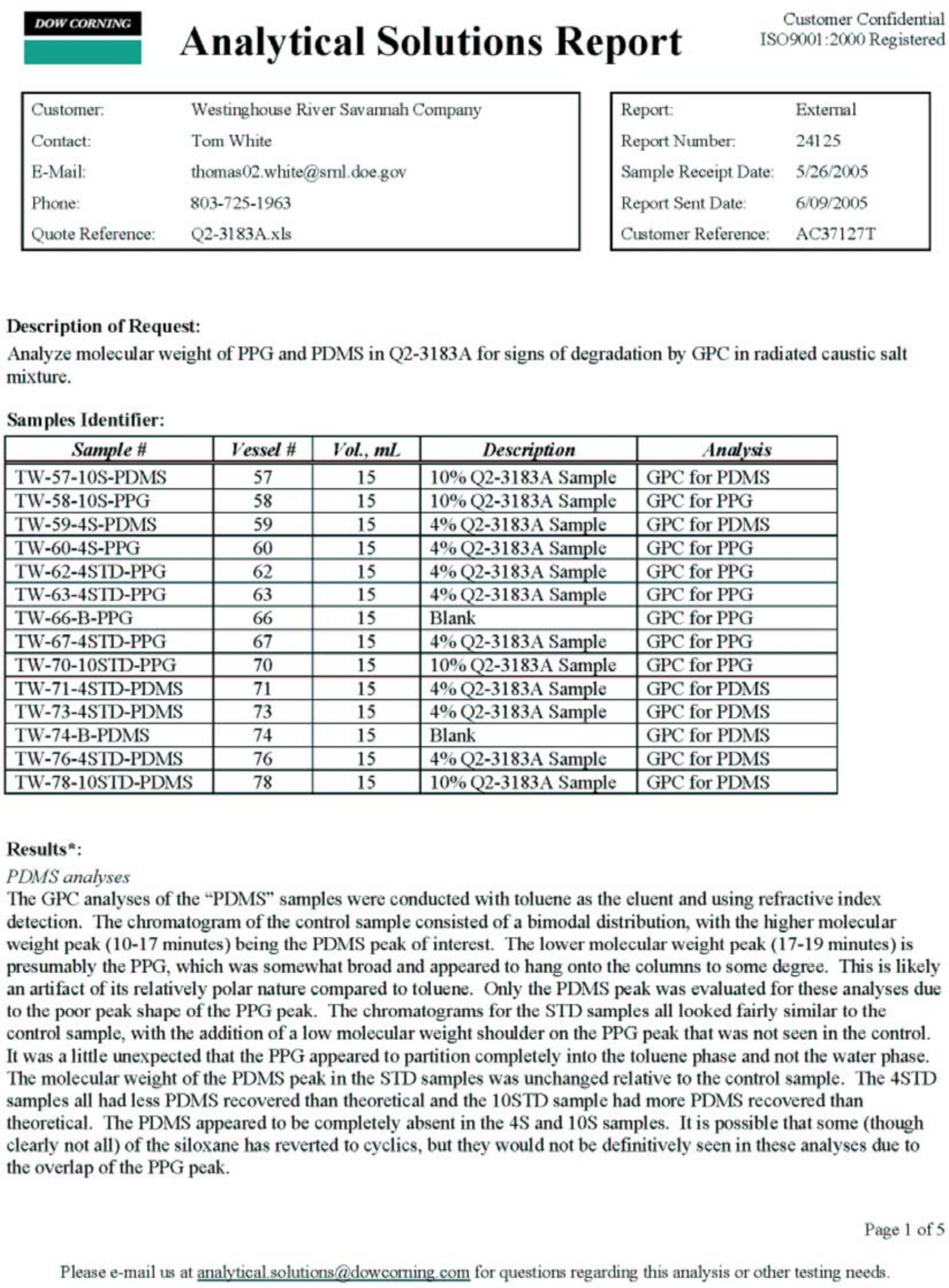
* Sample descriptions use 10 wt% Q2-3183A and 4 wt% Q2-3183A for labeling purposes. The actual wt% antifoam values are calculated and shown in this table in the far right column.

** antifoam directly in tetrahydrofuran (THF) at 10,000 ppm w/v; density THF = 0.88g/mL

*** antifoam directly in toluene at 10,000 ppm w/v; density toluene = 0.86g/mL

Table 4-2. Gel Permeation Chromatography with Peak Height

GPC Analyses by Peak Height					
Sample #	***Vessel #***	***Vol., mL***	***Description***	***Peak Height, mV***	***% Polymer Remaining***
PPG Analyses					
Q2-3183A Control-PPG			DC Control	90.5	100
TW-70-10STD-PPG	70	15	10% Q2-3183A Sample	100.6	111
TW-58-10S-PPG	58	15	10% Q2-3183A Irradiated Sample	35.1	39
TW-62-4STD-PPG	62	15	4% Q2-3183A Sample	70.2	78
TW-63-4STD-PPG	63	15	4% Q2-3183A Sample	72.6	80
TW-67-4STD-PPG	67	15	4% Q2-3183A Sample	69.9	77
TW-66-B-PPG	66	15	Blank	0	0
TW-60-4S-PPG	60	15	4% Q2-3183A Irradiated Sample	18.8	21
PDMS Analyses					
Q2-3183A Control-PDMS			DC Control	25.4	100
TW-78-10STD-PDMS	78	15	10% Q2-3183A Sample	30.6	120
TW-57-10S-PDMS	57	15	10% Q2-3183A Irradiated Sample	0	0
TW-71-4STD-PDMS	71	15	4% Q2-3183A Sample	20.5	81
TW-73-4STD-PDMS	73	15	4% Q2-3183A Sample	19.8	78
TW-76-4STD-PDMS	76	15	4% Q2-3183A Sample	20.3	80
TW-74-B-PDMS	74	15	Blank	0	0
TW-59-4S-PDMS	59	15	4% Q2-3183A Irradiated Sample	0	0



Analytical Solutions Report

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Customer:	Westinghouse River Savannah Company
Contact:	Tom White
E-Mail:	thomas02.white@srnl.doe.gov
Phone:	803-725-1963
Quote Reference:	Q2-3183A.xls

Report:	External
Report Number:	24125
Sample Receipt Date:	5/26/2005
Report Sent Date:	6/09/2005
Customer Reference:	AC37127T

Description of Request:

Analyze molecular weight of PPG and PDMS in Q2-3183A for signs of degradation by GPC in radiated caustic salt mixture.

Samples Identifier:

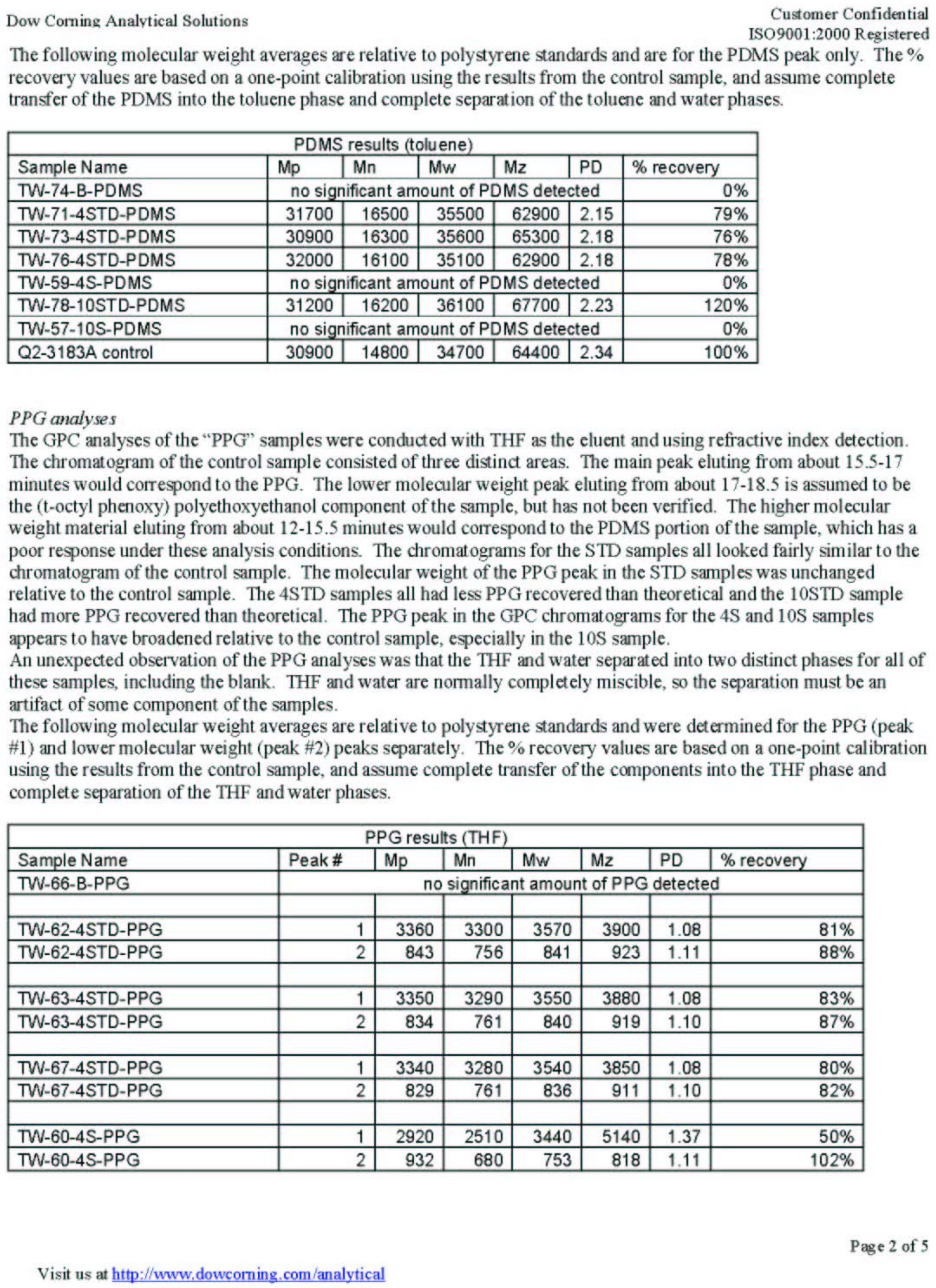
Sample #	*Vessel #*	*Vol., mL*	*Description*	*Analysis*
TW-57-10S-PDMS	57	15	10% Q2-3183A Sample	GPC for PDMS
TW-58-10S-PPG	58	15	10% Q2-3183A Sample	GPC for PPG
TW-59-4S-PDMS	59	15	4% Q2-3183A Sample	GPC for PDMS
TW-60-4S-PPG	60	15	4% Q2-3183A Sample	GPC for PPG
TW-62-4STD-PPG	62	15	4% Q2-3183A Sample	GPC for PPG
TW-63-4STD-PPG	63	15	4% Q2-3183A Sample	GPC for PPG
TW-66-B-PPG	66	15	Blank	GPC for PPG
TW-67-4STD-PPG	67	15	4% Q2-3183A Sample	GPC for PPG
TW-70-10STD-PPG	70	15	10% Q2-3183A Sample	GPC for PPG
TW-71-4STD-PDMS	71	15	4% Q2-3183A Sample	GPC for PDMS
TW-73-4STD-PDMS	73	15	4% Q2-3183A Sample	GPC for PDMS
TW-74-B-PDMS	74	15	Blank	GPC for PDMS
TW-76-4STD-PDMS	76	15	4% Q2-3183A Sample	GPC for PDMS
TW-78-10STD-PDMS	78	15	10% Q2-3183A Sample	GPC for PDMS

Results*:

PDMS analyses

The GPC analyses of the "PDMS" samples were conducted with toluene as the eluent and using refractive index detection. The chromatogram of the control sample consisted of a bimodal distribution, with the higher molecular weight peak (10-17 minutes) being the PDMS peak of interest. The lower molecular weight peak (17-19 minutes) is presumably the PPG, which was somewhat broad and appeared to hang onto the columns to some degree. This is likely an artifact of its relatively polar nature compared to toluene. Only the PDMS peak was evaluated for these analyses due to the poor peak shape of the PPG peak. The chromatograms for the STD samples all looked fairly similar to the control sample, with the addition of a low molecular weight shoulder on the PPG peak that was not seen in the control. It was a little unexpected that the PPG appeared to partition completely into the toluene phase and not the water phase. The molecular weight of the PDMS peak in the STD samples was unchanged relative to the control sample. The 4STD samples all had less PDMS recovered than theoretical and the 10STD sample had more PDMS recovered than theoretical. The PDMS appeared to be completely absent in the 4S and 10S samples. It is possible that some (though clearly not all) of the siloxane has reverted to cyclics, but they would not be definitively seen in these analyses due to the overlap of the PPG peak.

Please e-mail us at analytical.solutions@dowcorning.com for questions regarding this analysis or other testing needs.



The following molecular weight averages are relative to polystyrene standards and are for the PDMS peak only. The % recovery values are based on a one-point calibration using the results from the control sample, and assume complete transfer of the PDMS into the toluene phase and complete separation of the toluene and water phases.

PDMS results (toluene)						
Sample Name	Mp	Mn	Mw	Mz	PD	% recovery
TW-74-B-PDMS	no significant amount of PDMS detected					0%
TW-71-4STD-PDMS	31700	16500	35500	62900	2.15	79%
TW-73-4STD-PDMS	30900	16300	35600	65300	2.18	76%
TW-76-4STD-PDMS	32000	16100	35100	62900	2.18	78%
TW-59-4S-PDMS	no significant amount of PDMS detected					0%
TW-78-10STD-PDMS	31200	16200	36100	67700	2.23	120%
TW-57-10S-PDMS	no significant amount of PDMS detected					0%
Q2-3183A control	30900	14800	34700	64400	2.34	100%

PPG analyses

The GPC analyses of the "PPG" samples were conducted with THF as the eluent and using refractive index detection. The chromatogram of the control sample consisted of three distinct areas. The main peak eluting from about 15.5-17 minutes would correspond to the PPG. The lower molecular weight peak eluting from about 17-18.5 is assumed to be the (t-octyl phenoxy) polyethoxyethanol component of the sample, but has not been verified. The higher molecular weight material eluting from about 12-15.5 minutes would correspond to the PDMS portion of the sample, which has a poor response under these analysis conditions. The chromatograms for the STD samples all looked fairly similar to the chromatogram of the control sample. The molecular weight of the PPG peak in the STD samples was unchanged relative to the control sample. The 4STD samples all had less PPG recovered than theoretical and the 10STD sample had more PPG recovered than theoretical. The PPG peak in the GPC chromatograms for the 4S and 10S samples appears to have broadened relative to the control sample, especially in the 10S sample.

An unexpected observation of the PPG analyses was that the THF and water separated into two distinct phases for all of these samples, including the blank. THF and water are normally completely miscible, so the separation must be an artifact of some component of the samples.

The following molecular weight averages are relative to polystyrene standards and were determined for the PPG (peak #1) and lower molecular weight (peak #2) peaks separately. The % recovery values are based on a one-point calibration using the results from the control sample, and assume complete transfer of the components into the THF phase and complete separation of the THF and water phases.

PPG results (THF)							
Sample Name	Peak #	Mp	Mn	Mw	Mz	PD	% recovery
TW-66-B-PPG	no significant amount of PPG detected						
TW-62-4STD-PPG	1	3360	3300	3570	3900	1.08	81%
TW-62-4STD-PPG	2	843	756	841	923	1.11	88%
TW-63-4STD-PPG	1	3350	3290	3550	3880	1.08	83%
TW-63-4STD-PPG	2	834	761	840	919	1.10	87%
TW-67-4STD-PPG	1	3340	3280	3540	3850	1.08	80%
TW-67-4STD-PPG	2	829	761	836	911	1.10	82%
TW-60-4S-PPG	1	2920	2510	3440	5140	1.37	50%
TW-60-4S-PPG	2	932	680	753	818	1.11	102%

Sample Name	Peak #	Mp	Mn	Mw	Mz	PD	% recovery
TW-70-10STD-PPG	1	3280	3230	3490	3810	1.08	116%
TW-70-10STD-PPG	2	829	757	829	900	1.10	115%
TW-58-10S-PPG	1	3100	3070	4960	8800	1.62	106%
TW-58-10S-PPG	2	1077	692	778	852	1.12	155%
Q2-3183A control	1	3310	3230	3450	3720	1.07	100%
Q2-3183A control	2	829	761	832	902	1.09	100%

The samples chromatograms are at the end of this report.

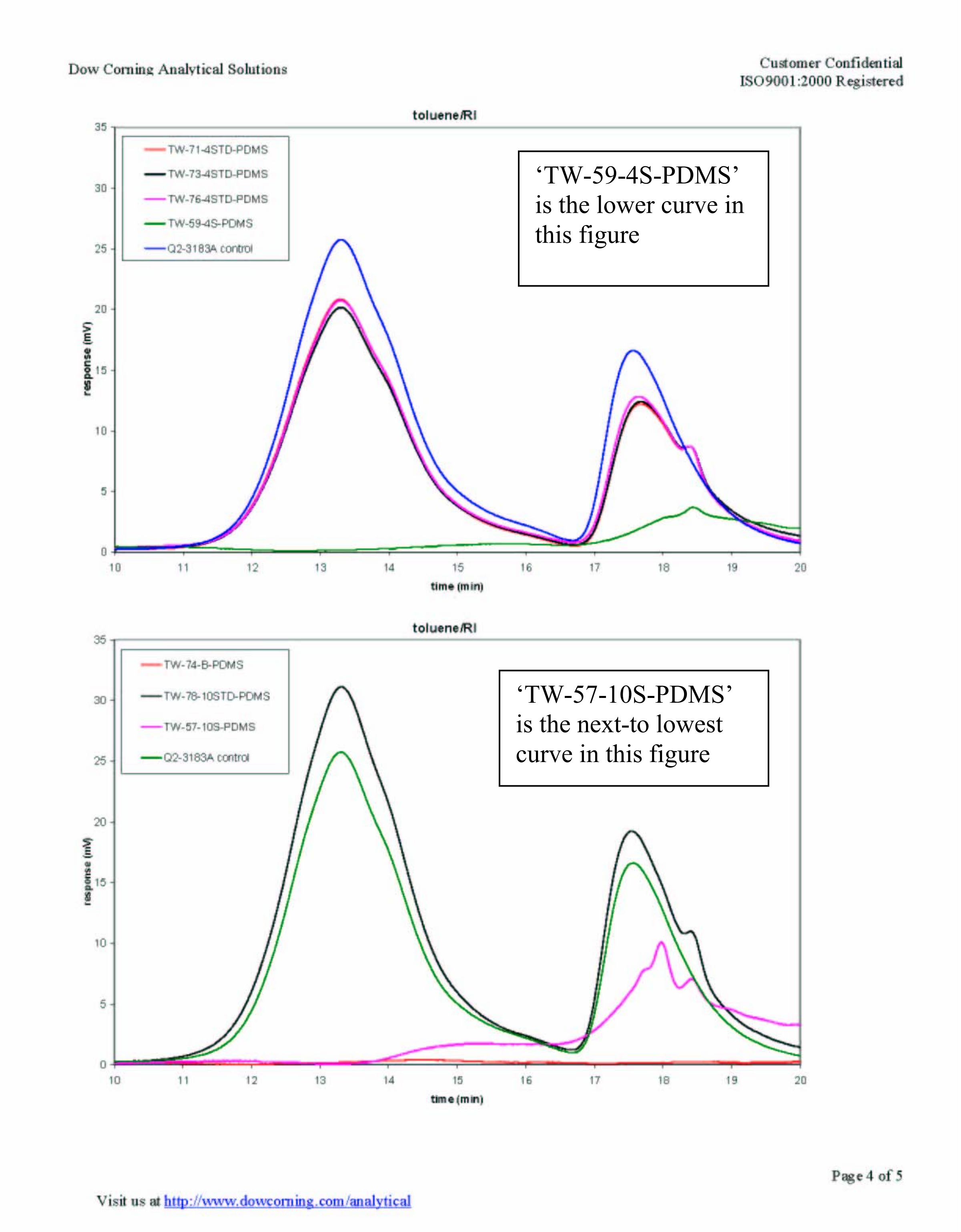
Experimental:

The sample tubes were all emptied into individual 4 oz bottles and then rinsed with a number of solvent rinses. The PDMS sample tubes were rinsed with two 10 mL water rinses and four 15 mL toluene rinses. The PPG sample tubes were rinsed with three 15 mL THF rinses. For each rinse, the sealed tube was shaken about one minute and allowed to set for 15-30 minutes before emptying into their corresponding collection vessel. The inside of the sample tubes were briefly scraped with a spatula before the first rinse in order to remove the majority of the solids from the inside of the tubes. After the rinses were complete, a small amount of solid on the inside wall of several vessels was observed, but it was assumed that the majority of the soluble polymer would have been removed in the rinsing. The collection vessels containing the initial samples and the solvent rinses were shaken on a wrist shaker for one hour and then allowed to settle for about two hours, at which time the samples had all separated into two layers.
GPC analyses were conducted on the samples using either tetrahydrofuran or toluene as eluents, PS/DVB size exclusion columns (2,000,000 MW maximum), 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 for this analysis have not been established. In general, the repeatability for other polymers analyzed in a similar manner by GPC is ±5-10% (relative).

* Note, results relate only to the items submitted for analysis.



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'TW-59-4S-PDMS' is the lower curve in this figure

'TW-57-10S-PDMS' is the next-to lowest curve in this figure

Page 4 of 5

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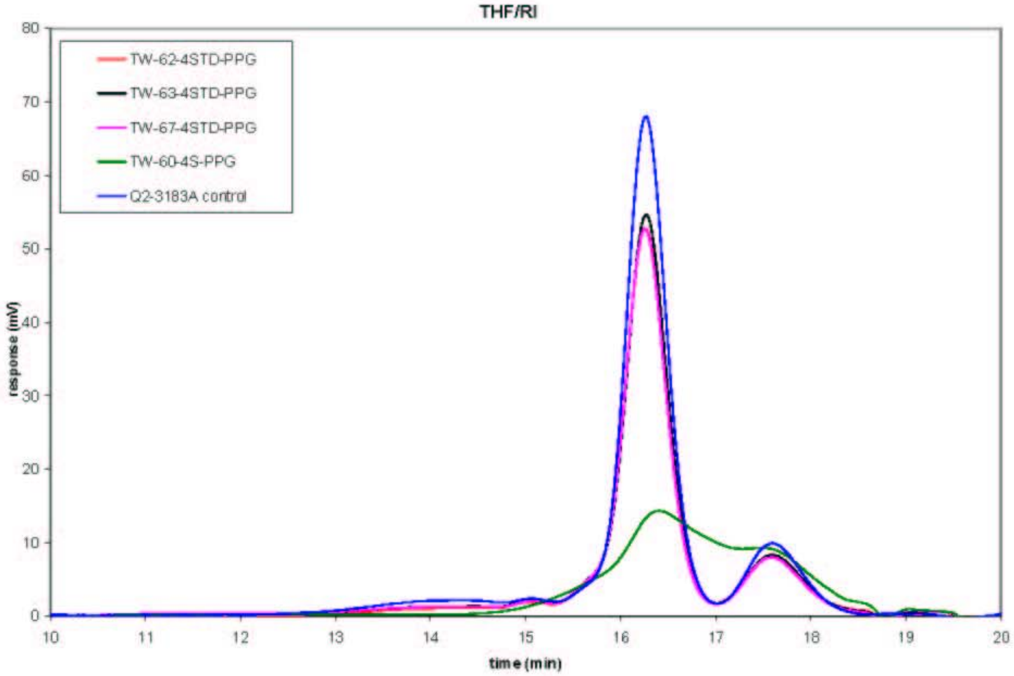
THF/RI
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TW-63-4STD-PPG
TW-67-4STD-PPG
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Q2-3183A control
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0
10
20
30
40
50
60
70
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time (min)
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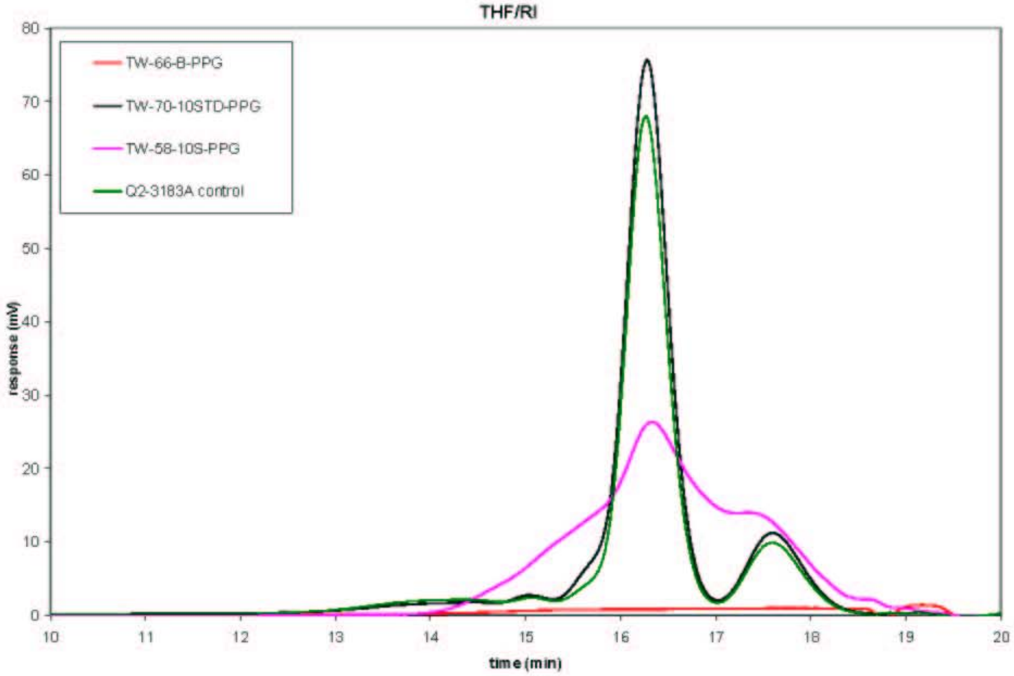
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Q2-3183A control
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10
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30
40
50
60
70
80
time (min)
10
11
12
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15
16
17
18
19
20

$\text{LogM} = 14.36 - 1.277\,X^{1} + 0.05699\,X^{2} - 0.00126\,X^{3}$ (toluene)

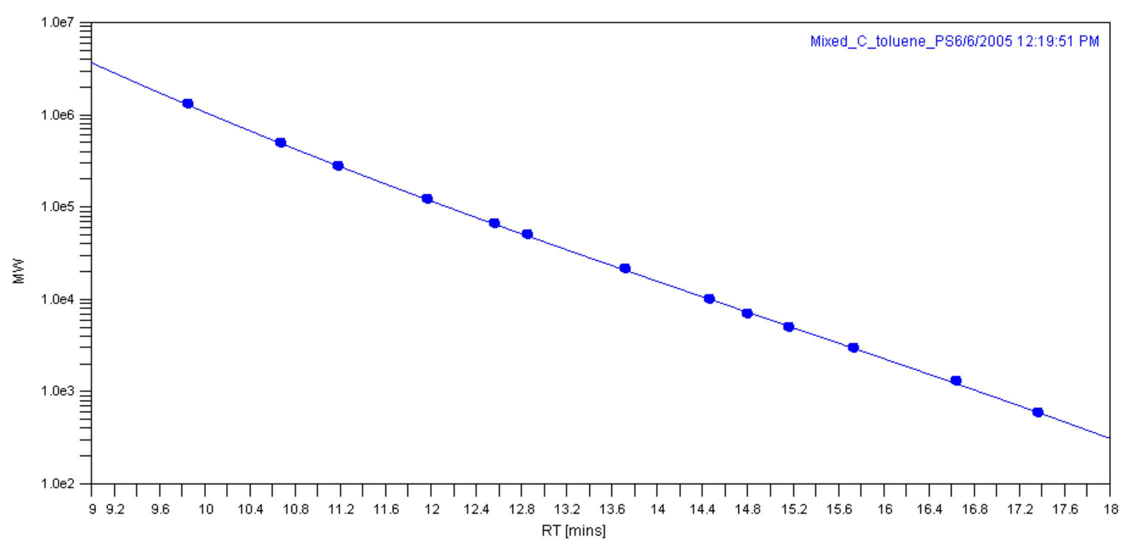

Figure 4-1. Standard Curve for Molecular Weights vs. Retention Time for Polystyrene in Toluene

$\text{LogM} = 12.5 - 0.8204\,X^{1} + 0.02637\,X^{2} - 0.0006083\,X^{3}$ (THF)

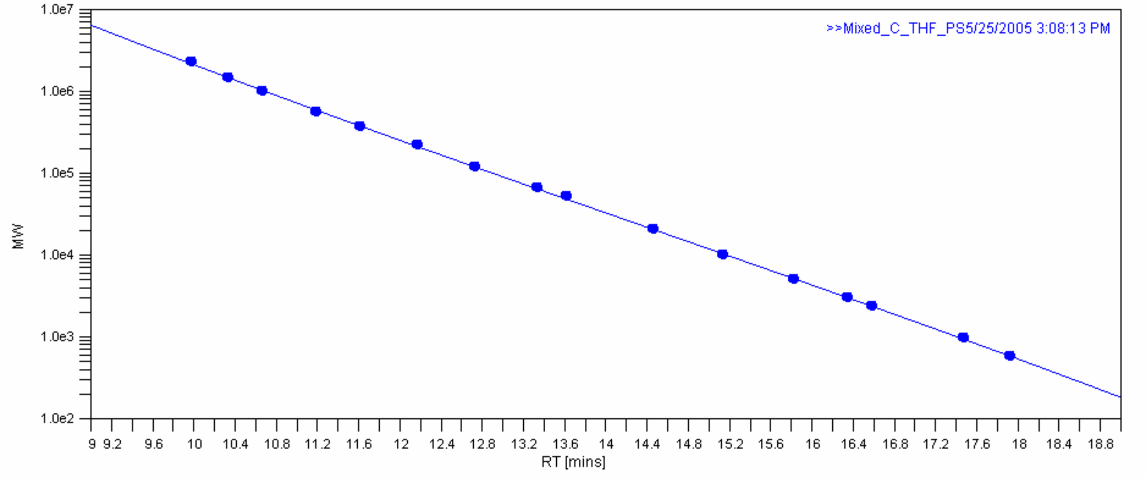

Figure 4-2. Standard Curve for Molecular Weights vs. Retention Time for Polystyrene in THF

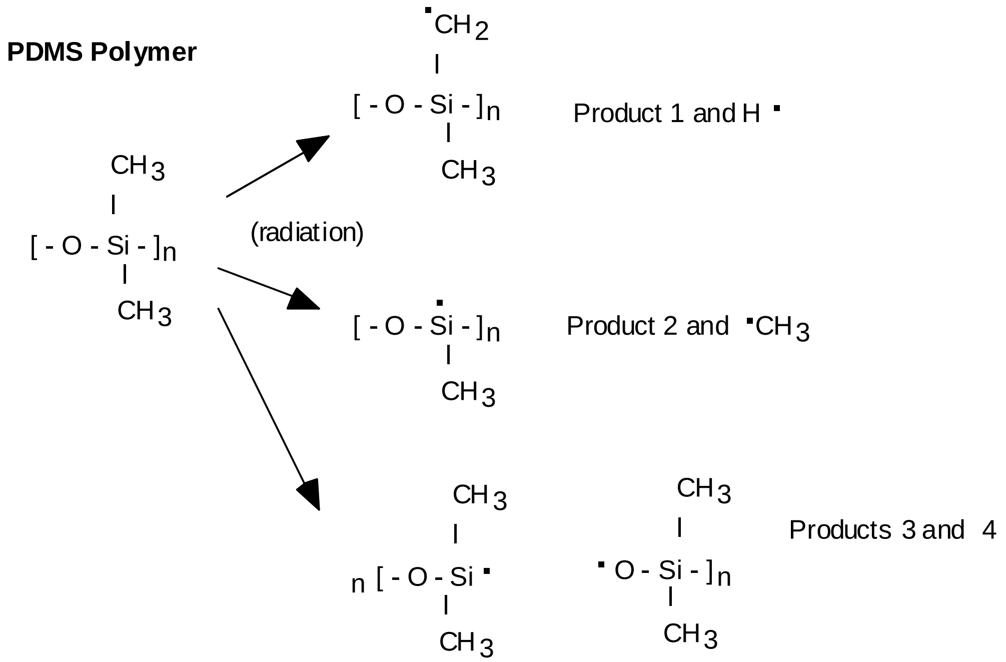

Figure 4-3. PDMS Polymer Direct Radiolytic Decomposition Scheme

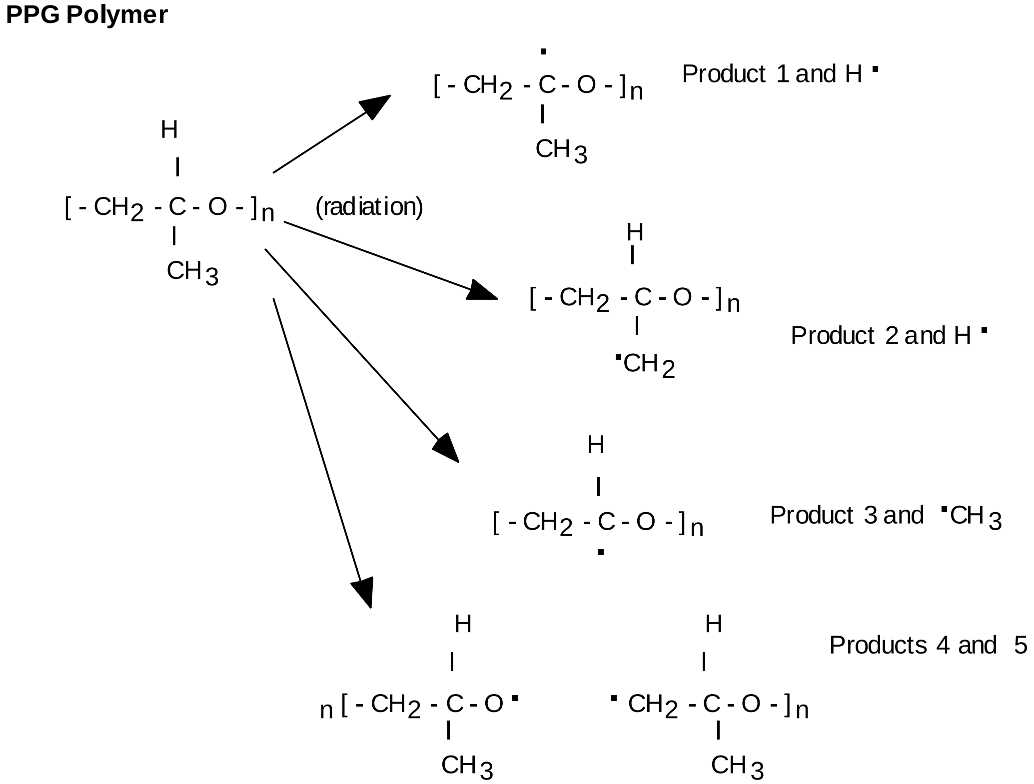

Figure 4-4. PPG Polymer Direct Radiolytic Decomposition Scheme

5.0 CONCLUSIONS

Results from this study indicate that the WTP HGR correlation bounds hydrogen generation rates (HGRs) from the combination of radiolysis/thermolysis of antifoam-containing simulants if the antifoam organic components are treated the same as native organics. Tests were conducted at the maximum process temperature of 90ºC. Tests conducted with thermal-only exposures following irradiations were inconclusive and need to be repeated with different methodology if this data is necessary.

Analysis of antifoam-containing simulants after prolonged irradiation of 52 Mrad and heating (23 days at 90ºC) indicates that essentially all of the PDMS and greater than 60% of the PPG components are degraded presumably to lower molecular weight species. The antifoam components were analyzed by extraction from the salt simulants, followed by gel permeation chromatography (GPC) by personnel at Dow Corning. Dose rates used in the current testing were higher than anticipated dose rates in the WTP in order to ensure enough hydrogen gas was produced for measurement. Parallel testing using a more representative dose rate of 10 Ci/L, or about $2E10^4$ rad/hr, will investigate the radiolytic and thermal degradation of the Q2-3183A antifoam (and degradation products) in more detail (Burket 2005b).

6.0 REFERENCES

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APPENDIX A.
SAMPLE CALCULATION OF MEASURED HGR AND MINIMUM HGR

Measured HGRs

The measured amount of hydrogen contained in the sample bulbs was used in the following calculation for all measured HGRs.

The equation used is:

HGR = g-moles H_2 / mass sample / exposure time (Equation #1)

The moles H_2 were calculated using the measured vol% H_2 in the collected gas sample and the ideal gas law via,

g-moles H_2 = ($p(H_2)$* V) / (R * T) (Equation #2)

With $p(H_2)$ =(final system absolute pressure at 25 ºC) * vol % measured H_2
V = measured head-space volume of each system
R = gas constant
T = 25 ºC = 298 ºK

For the base simulant filtrate with no added antifoam,
$p(H_2)$ = 34.2 psia = 2.33 atm * (4.66/100)
V = 0.017 L
R = 0.0820575 dm^3atm/K-mol
T= 25ºC = 298 ºK
Mass sample = 19.5474 g = 0.0195474 kg
Exposure time = 11.95 days

Substituting the above values into Equation #2 gives,

g-moles H_2 = (2.33*(4.66/100) * 0.017) / (0.0820575 * 298) = 7.54E-05 mol H_2

Substituting the calculated g-moles H2 and the sample mass and exposure time into Equation #1 gives,

HGR = 7.548E-05 moles H_2 / 0.0195474 kg / 11.95 days

HGR = 3.23E-04 g-mol/kg/day

Minimum HGRs

The minimum quantification limit determined for the mass spectroscopy hydrogen analysis was ~ 100 ppm, or 0.01 vol% H_2. Assuming no measurable change in system pressure, i.e., pressure = 1 atm, and all other parameters are the same as above (mass, temperature, head-space volume, irradiation time), substitution of these values into Equations #1 and #2 above gives a minimum HGR as:

g-moles H_2 = (1*(0.01/100) * 0.017) / (0.0820575 * 298) = 6.9E-8 mol H_2

HGR = 6.9E-08 moles H_2 / 0.0195474 kg / 11.95 days

HGR = 2.9E-07 g-mol/kg/day

APPENDIX B. SIMULANT RECIPES

Table B- 1. Base Simulant Recipe for 0 wt% TOC

Component	Molecular weight	Concentration	Units	Undiluted Concentration	Units	% Carbon	TOC mg/Liter
Acetate	59.04462	0	mg/Liter	0.00E+00	M	40.68	0
Aluminum	26.98154	26982	mg/Liter	1.00E+00	M		
Ammonium	18.03846	0	mg/Liter	0.00E+00	M		
Barium	137.33	0	mg/Liter	0.00E+00	M		
Boron	10.81	0	mg/Liter	0.00E+00	M		
Bromide	79.904	0	mg/Liter	0.00E+00	M		
Cadmium	112.41	5	mg/Liter	4.45E-05	M		
Calcium	40.08	0	mg/Liter	0.00E+00	M		
Carbonate	60.0092	0	mg/Liter	0.00E+00	M		
Cerium	140.12	0	mg/Liter	0.00E+00	M		
Cesium	132.9054	0	mg/Liter	0.00E+00	M		
Chloride	35.453	5	mg/Liter	1.41E-04	M		
Chromium	51.996	5	mg/Liter	9.62E-05	M		
Cobalt	58.9332	0	mg/Liter	0.00E+00	M		
Copper	63.546	5	mg/Liter	7.87E-05	M		
EDTA	288.20824	0	mg/Liter	0.00E+00	M	41.67	0
Fluoride	18.9984	0	mg/Liter	0.00E+00	M		
Formate	45.01774	0	mg/Liter	0.00E+00	M	26.68	0
Glycolate	75.04206	0	mg/Liter	0.00E+00	M	32.01	0
Hydroxide	17.00734	1701	mg/Liter	1.00E-01	M		
Iron	55.847	5	mg/Liter	8.95E-05	M		
Lanthanum	138.9055	0	mg/Liter	0.00E+00	M		
Lead	207.2	0	mg/Liter	0.00E+00	M		
Magnesium	24.305	0	mg/Liter	0.00E+00	M		
Manganese	54.938	0	mg/Liter	0.00E+00	M		
Molybdenum	95.94	5	mg/Liter	5.21E-05	M		
Neodymium	144.24	0	mg/Liter	0.00E+00	M		
HEDTA	275.23618	0	mg/Liter	0.00E+00	M	43.64	0
Nickel	58.69	5	mg/Liter	8.52E-05	M		
Nitrate	62.0049	186015	mg/Liter	3.00E+00	M		
Nitrite	46.0055	138017	mg/Liter	3.00E+00	M		
Oxalate	88.0196	0	mg/Liter	0.00E+00	M	27.29	0
Phosphate	94.97136	5	mg/Liter	5.26E-05	M		
Potassium	39.0983	0	mg/Liter	0.00E+00	M		
Rubidium	85.4678	0	mg/Liter	0.00E+00	M		
Selenium	78.96	0	mg/Liter	0.00E+00	M		
Silicon	28.0855	0	mg/Liter	0.00E+00	M		
Silver	107.8682	0	mg/Liter	0.00E+00	M		
Sodium	22.9898	163263	mg/Liter	7.102E+00	M		
Strontium	87.62	0	mg/Liter	0.000E+00	M		

Component	**Molecular weight**	**Concentration**	**Units**	**Undiluted Concentration**	**Units**	**% Carbon**	**TOC mg/Liter**
Sulfate	96.0576	5	mg/Liter	5.21E-05	M		
TIC	12.011	0	mg/Liter	0.00E+00	M		
TOC	12.011	0	mg/Liter	0.00	g/L		
Tungsten	183.85	0	mg/Liter	0.00E+00	M		
Uranium		0	mg/Liter	0.00E+00	ug/mL		
Zinc	65.38	5	mg/Liter	7.65E-05	M		
Zirconium	91.22	0	mg/Liter	0.00E+00	M		
Additional Organic Compounds						**% Carbon**	
Nitrilotriacetic Acid	188.12	0	mg/Liter	0.00E+00	M	38.31	0
Citric Acid	189.10	0	mg/Liter	0.00E+00	M	38.11	0
Iminodiacetic Acid	131.08	0	mg/Liter	0.00E+00	M	36.65	0
Succinic Acid	116.07	0	mg/Liter	0.00E+00	M	41.39	0
Glutaric Acid	130.09	0	mg/Liter	0.00E+00	M	46.16	0
Adipic Acid	144.12	0	mg/Liter	0.00E+00	M	50.00	0
Azelaic Acid	186.20	0	mg/Liter	0.00E+00	M	58.05	0
Suberic Acid	172.17	0	mg/Liter	0.00E+00	M	55.81	0
Sodium Gluconate	218.14	0	mg/Liter	0.00E+00	M	33.04	0
						Total :	0
Density (average)		1.4					
Planned wt % TOC		0					

Table B- 2. Batching Recipe for 1000-mL Base Simulant 0 wt% TOC

Volumetric Flask Tare Weight		grams
To the Volumetric Flask add:		
	grams	Actual Wt, grams
Water	100	
Transition Metals and Complexing agents		
Compounds	**Formula**	**Mass Needed**
Cadmium Nitrate	Cd(NO3)2.4H2O	0.01
Calcium Nitrate	Ca(NO3)2.4H2O	0.00
Cerium Nitrate	Ce(NO3)3.6H2O	0.00
Cesium Nitrate	CsNO3	0.00
Cobalt Nitrate	Co(NO3)2.6H2O	0.00
Copper Nitrate	Cu(NO3)2.2.5H2O	0.02
Ferric Nitrate	Fe(NO3)3.9H2O	0.04
Lanthanum Nitrate	La(NO3)3.6H2O	0.00
Lead nitrate	Pb(NO3)2	0.00
Magnesium Nitrate	Mg(NO3)2.6H2O	0.00
Manganous Chloride	MnCl2.4H2O	0.00
Neodymium Nitrate	Nd(NO3)3.6H2O	0.00
Nickel Nitrate	Ni(NO3)2.6H2O	0.02
Potassium Nitrate	KNO3	0.00
Rubidium Nitrate	RbNO3	0.00
Strontium Nitrate	Sr(NO3)2	0.00
Zinc Nitrate	Zn(NO3)2.6H2O	0.02
Zirconyl Nitrate	ZrO(NO3)2.H2O	0.00
Disodium Ethylenediaminetetraacetate	Na2C10H14N2O8.2H2O	0.00
n-(2-Hydroxyethyl)ethylenediaminetriacetic acid	C10H18N2O7	0.00
Sodium Gluconate	HOCH2(CHOH)4COONa	0.00
Citric Acid	C6H8O7.H2O	0.00
Nitrilotriacetic Acid	C6H9NO6	0.00
Iminodiacetic Acid	C4H7NO4	0.00
Succinic Acid	C4H6O4	0.00
Glutaric Acid	C5H8O4	0.00
Adipic Acid	C6H10O4	0.00
Azelaic Acid	C9H16O4	0.00
Suberic Acid	C8H14O4	0.00
Boric acid	H3BO3	0.00
Ammonium Acetate	NH4CH3COO	0.00
Sodium Chloride	NaCl	0.01
Sodium Fluoride	NaF	0.00
Sodium Sulfate	Na2SO4	0.01
Sodium Molybdate	Na2MoO4.2H2O	0.01

In separate container mix the following		
Add	**Formula**	**Mass Needed**
Sodium Hydroxide	NaOH	164.06
Aluminum Nitrate	Al(NO3)3.9H2O	375.13
Sodium Phosphate	Na3PO4.12H2O	0.02
Sodium Tungstate	Na2WO4.2H2O	0.00
Sodium Metasilicate	Na2SiO3.9H2O	0.00
Sodium Glycolate	HOCH2COONa	0.00
Sodium formate	NaHCOO	0.00
Sodium Acetate	NaCH3COO.3H2O	0.00
Sodium Oxalate	Na2C2O4	0.00
Add	grams	Actual Wt, grams
Water	200	
Mix thoroughly. Then add this solution to the volumetric flask.		
Add	Formula	Mass Needed
Sodium Chromate	Na2CrO4	0.02
Sodium Carbonate	Na2CO3	0.00
Mix thoroughly.		
Mix	Formula	Mass Needed
Sodium Nitrate	NaNO3	0.00
Sodium Nitrite	NaNO2	207.00
Water		100
Add and Mix thoroughly.		
Mix thoroughly and dilute to the mark.		
Record Final Gross Weight		grams
Measure the Density		g/mL
For INFO ONLY		
The final addition of water would be		175.18
a density of	1.322	g/mL.
Solution Labeling	Generic recipe at 0 wt % TOC	

Table B- 3. Native Simulant Recipe for 4 wt% TOC

Component	Molecular weight	Concentration	Units	Undiluted Concentration	Units	% Carbon	TOC mg/Liter
Acetate	59.04462	0	mg/Liter	0.00E+00	M	40.68	0
Aluminum	26.98154	26982	mg/Liter	1.00E+00	M		
Ammonium	18.03846	0	mg/Liter	0.00E+00	M		
Barium	137.33	0	mg/Liter	0.00E+00	M		
Boron	10.81	0	mg/Liter	0.00E+00	M		
Bromide	79.904	0	mg/Liter	0.00E+00	M		
Cadmium	112.41	5	mg/Liter	4.45E-05	M		
Calcium	40.08	0	mg/Liter	0.00E+00	M		
Carbonate	60.0092	0	mg/Liter	0.00E+00	M		
Cerium	140.12	0	mg/Liter	0.00E+00	M		
Cesium	132.9054	0	mg/Liter	0.00E+00	M		
Chloride	35.453	5	mg/Liter	1.41E-04	M		
Chromium	51.996	5	mg/Liter	9.62E-05	M		
Cobalt	58.9332	0	mg/Liter	0.00E+00	M		
Copper	63.546	5	mg/Liter	7.87E-05	M		
EDTA	288.20824	0	mg/Liter	0.00E+00	M	41.67	0
Fluoride	18.9984	0	mg/Liter	0.00E+00	M		
Formate	45.01774	0	mg/Liter	0.00E+00	M	26.68	0
Glycolate	75.04206	132911	mg/Liter	1.77E+00	M	32.01	42547
Hydroxide	17.00734	1701	mg/Liter	1.00E-01	M		
Iron	55.847	5	mg/Liter	8.95E-05	M		
Lanthanum	138.9055	0	mg/Liter	0.00E+00	M		
Lead	207.2	0	mg/Liter	0.00E+00	M		
Magnesium	24.305	0	mg/Liter	0.00E+00	M		
Manganese	54.938	0	mg/Liter	0.00E+00	M		
Molybdenum	95.94	5	mg/Liter	5.21E-05	M		
Neodymium	144.24	0	mg/Liter	0.00E+00	M		
HEDTA	275.23618	32407	mg/Liter	1.18E-01	M	43.64	14142
Nickel	58.69	5	mg/Liter	8.52E-05	M		
Nitrate	62.0049	186015	mg/Liter	3.00E+00	M		
Nitrite	46.0055	138017	mg/Liter	3.00E+00	M		
Oxalate	88.0196	0	mg/Liter	0.00E+00	M	27.29	0
Phosphate	94.97136	5	mg/Liter	5.26E-05	M		
Potassium	39.0983	0	mg/Liter	0.00E+00	M		
Rubidium	85.4678	0	mg/Liter	0.00E+00	M		
Selenium	78.96	0	mg/Liter	0.00E+00	M		
Silicon	28.0855	0	mg/Liter	0.00E+00	M		
Silver	107.8682	0	mg/Liter	0.00E+00	M		
Sodium	22.9898	212102	mg/Liter	9.226E+00	M		
Strontium	87.62	0	mg/Liter	0.000E+00	M		
Sulfate	96.0576	5	mg/Liter	5.21E-05	M		
TIC	12.011	0	mg/Liter	0.00E+00	M		
TOC	12.011	56000	mg/Liter	56.00	g/L		

Component	Molecular weight	Concentration	Units	Undiluted Concentration	Units	% Carbon	TOC mg/Liter
Tungsten	183.85	0	mg/Liter	0.00E+00	M		
Uranium		0	mg/Liter	0.00E+00	ug/mL		
Zinc	65.38	5	mg/Liter	7.65E-05	M		
Zirconium	91.22	0	mg/Liter	0.00E+00	M		
Additional Organic Compounds						**% Carbon**	
Nitrilotriacetic Acid	188.12	0	mg/Liter	0.00E+00	M	38.31	0
Citric Acid	189.10	0	mg/Liter	0.00E+00	M	38.11	0
Iminodiacetic Acid	131.08	0	mg/Liter	0.00E+00	M	36.65	0
Succinic Acid	116.07	0	mg/Liter	0.00E+00	M	41.39	0
Glutaric Acid	130.09	0	mg/Liter	0.00E+00	M	46.16	0
Adipic Acid	144.12	0	mg/Liter	0.00E+00	M	50.00	0
Azelaic Acid	186.20	0	mg/Liter	0.00E+00	M	58.05	0
Suberic Acid	172.17	0	mg/Liter	0.00E+00	M	55.81	0
Sodium Gluconate	218.14	0	mg/Liter	0.00E+00	M	33.04	0
						Total :	56689
Density (average)		1.4					
Planned wt % TOC		4					

Table B- 4. Batching Recipe for 4 wt% TOC

Volumetric Flask Tare Weight		grams
To the Volumetric Flask add:		
	grams	Actual Wt, grams
Water	100	
Transition Metals and Complexing agents		
Compounds	**Formula**	**Mass Needed**
Cadmium Nitrate	Cd(NO3)2.4H2O	0.01
Calcium Nitrate	Ca(NO3)2.4H2O	0.00
Cerium Nitrate	Ce(NO3)3.6H2O	0.00
Cesium Nitrate	CsNO3	0.000
Cobalt Nitrate	Co(NO3)2.6H2O	0.00
Copper Nitrate	Cu(NO3)2.2.5H2O	0.02
Ferric Nitrate	Fe(NO3)3.9H2O	0.04
Lanthanum Nitrate	La(NO3)3.6H2O	0.00
Lead nitrate	Pb(NO3)2	0.00
Magnesium Nitrate	Mg(NO3)2.6H2O	0.00
Manganous Chloride	MnCl2.4H2O	0.00
Neodymium Nitrate	Nd(NO3)3.6H2O	0.00
Nickel Nitrate	Ni(NO3)2.6H2O	0.02
Potassium Nitrate	KNO3	0.00
Rubidium Nitrate	RbNO3	0.00
Strontium Nitrate	Sr(NO3)2	0.000
Zinc Nitrate	Zn(NO3)2.6H2O	0.02
Zirconyl Nitrate	ZrO(NO3)2.H2O	0.00
Disodium Ethylenediaminetetraacetate	Na2C10H14N2O8.2H2O	0.00
n-(2-Hydroxyethyl)ethylenediaminetriacetic acid	C10H18N2O7	32.76
Sodium Gluconate	HOCH2(CHOH)4COONa	0.00
Citric Acid	C6H8O7.H2O	0.00
Nitrilotriacetic Acid	C6H9NO6	0.00
Iminodiacetic Acid	C4H7NO4	0.00
Succinic Acid	C4H6O4	0.00
Glutaric Acid	C5H8O4	0.00
Adipic Acid	C6H10O4	0.00
Azelaic Acid	C9H16O4	0.00
Suberic Acid	C8H14O4	0.00
Boric acid	H3BO3	0.00
Ammonium Acetate	NH4CH3COO	0.00
Sodium Chloride	NaCl	0.01
Sodium Fluoride	NaF	0.00
Sodium Sulfate	Na2SO4	0.01
Sodium Molybdate	Na2MoO4.2H2O	0.01

In separate container mix the following		
Add	**Formula**	**Mass Needed**
Sodium Hydroxide	NaOH	178.18
Aluminum Nitrate	Al(NO3)3.9H2O	375.13
Sodium Phosphate	Na3PO4.12H2O	0.02
Sodium Tungstate	Na2WO4.2H2O	0.00
Sodium Metasilicate	Na2SiO3.9H2O	0.00
Sodium Glycolate	HOCH2COONa	173.63
Sodium formate	NaHCOO	0.00
Sodium Acetate	NaCH3COO.3H2O	0.00
Sodium Oxalate	Na2C2O4	0.00
Add	grams	Actual Wt, grams
Water	200	
Mix thoroughly. Then add this solution to the volumetric flask.		
Add	Formula	Mass Needed
Sodium Chromate	Na2CrO4	0.02
Sodium Carbonate	Na2CO3	0.00
Mix thoroughly.		
Mix	Formula	Mass Needed
Sodium Nitrate	NaNO3	0.00
Sodium Nitrite	NaNO2	207.00
Water		100
Add and Mix thoroughly.		
Mix thoroughly and dilute to the mark.		
Record Final Gross Weight		grams
Measure the Density		g/mL
For INFO ONLY		
The final addition of water would be		36.82
a density of	1.404	g/mL.
Solution Labeling	Generic recipe at 4 wt % TOC	

APPENDIX C. WTP HGR CORRELATION

Text Box. WTP PROJECT HGR CORRELATION (Sherwood and Stock 2004)

This correlation needs G-value terms for the radiolysis of water from alpha and beta/gamma sources, $G_0(H_2)^{\alpha}$ and $G_0(H_2)^{\beta/\gamma}$, and from interactions of the primary radiolysis products with organic compounds, $G_{TOC}(H_2)^{\alpha}$ and $G_{TOC}(H_2)^{\beta/\gamma}$. Units for the G-values are number of H_2 molecules per 100 eV of respective radiation absorbed by the waste.

The terms for water radiolysis from alpha and beta/gamma sources are:

$$G_0(H_2)^{\alpha} = 1.05/\left(1 + 2.4[NO_3^-] + 0.62[NO_2^-]\right) + 0.35/\left(1 + 3900[NO_3^-] + 1400[NO_2^-]\right), \qquad (1)$$

and

$$G_0(H_2)^{\beta/\gamma} = 0.34/\left(1 + 2.4[NO_3^-] + 0.62[NO_2^-]\right) + 0.11/\left(1 + 120[NO_3^-] + 43[NO_2^-]\right). \qquad (2)$$

Here, the nitrate/nitrite concentrations are in moles/liter (M). G-values representing hydrogen formation from interactions of alpha and beta/gamma radiolysis products with dissolved organic compounds are:

$$G_{TOC}(H_2)^{\alpha} = 0.5a_0(\,f\,[TOC])\exp(-Q_{rad}/RT), \qquad (3)$$

and

$$G_{TOC}(H_2)^{\beta/\gamma} = a_0(\,f\,[TOC])\exp(-Q_{rad}/RT). \qquad (4)$$

Here: $a_0 = 2.49 \times 10^6$;
f = “reactivity coefficient” for organic species; $f = 0.7$ (0.4) for double-(single-)shell tank waste;
[TOC] = concentration in weight percent of total organic carbon in the liquid phase;
Q_{rad} = 44,300 J/mol, activation energy;
R = 8.314 J/K-mol, the gas constant; and
T denotes waste temperature in Kelvin.

The total G-values, $G(H_2)$, for alpha and beta/gamma sources are just the respective sums of these G-values for radiolysis of water and interactions of radiolysis products with organic compounds:

$$G(H_2)^{\alpha} = G_0(H_2)^{\alpha} + G_{TOC}(H_2)^{\alpha}, \qquad (5)$$

and

$$G(H_2)^{\beta/\gamma} = G_0(H_2)^{\beta/\gamma} + G_{TOC}(H_2)^{\beta/\gamma}. \qquad (6)$$

The hydrogen generation rate (HGR) results when the G-value terms are multiplied by appropriate factors:

$$\boldsymbol{HGR}_{\mathbf{rad}} = f_L\, C\, [H^{\alpha}\, G(H_2)^{\alpha} + H^{\beta/\gamma}\, G(H_2)^{\beta/\gamma}] \text{ gram-moles } H_2\text{/day per kg-waste}, \qquad (7)$$

where: H^{α} and $H^{\beta/\gamma}$ are the respective decay heat loads for the waste in watt/kg;
f_L is the fraction of liquid in the waste; and
C (= 0.00895) is a conversion factor from (molecules H_2/100 eV)(watt/kg) to gram-moles of H_2 per kg-day.

Thermolysis provides another source of hydrogen; the hydrogen generation rate is given directly as

$$\boldsymbol{HGR}_{\mathbf{therm}} = a_T(\,f\,[TOC])[Al]^{0.4}\, f_L \exp(-Q_T/RT\,) \text{ gram-moles } H_2\text{/day per kg-waste}. \qquad (8)$$

Here: $a_T = 2.76 \times 10^9$;
f = “reactivity coefficient” for organic species; $f = 0.7$ (0.4) for double-(single-)shell tank waste;
[TOC] = concentration in weight percent of total organic carbon in the liquid phase;
[Al] = total concentration of aluminum species in liquid phase, in weight percent;
f_L = liquid weight fraction of waste;
Q_T = 89,300 J/mol, activation energy;
R = 8.314 J/K-mol, the gas constant; and
T is the waste temperature in Kelvin.

The total hydrogen generation rate is then:

WTP HGR Correlation Predictions for Antifoam Agent Addition Correlation Used As In Engineering Calculation

David J. Sherwood

Waste Properties:

$i := 0..3$

Simulant$_i$:=	Liquid fraction, f_L: f_{L_i} :=	[NO_3^-] (M): $NO3_i$:=	[NO_2^-] (M): $NO2_i$:=	Native [TOC] (wt.%): TOC_i :=
AN107_AFA	1	2.34	0.84	0.87
B_native	1	2.64	2.55	1.24
C_LowAFA	0.97	2.64	2.61	0
C_HighAFA	0.89	2.64	2.61	0

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[Al] (wt.%): Al_i :=	Native TOC Reactivity: f_i :=
0.018	0.7
1.6	0.7
0.89	0
0.89	0

Exposure Conditions: Decay heat based on dose rate of 1.8 x 10^5 rad/hour; 1 rad = 0.01 W*s/kg; 3600 s/hr.

$D := 0.01 \cdot 1.8 \cdot 10^5 \cdot \frac{1}{3600}$ $\qquad D = 0.50$ W/kg

$H^{\beta/\gamma}$ (W/kg): H_i :=	T (°C): T_i :=
D	90
D	90
D	90
D	90

Correlation Terms:

$$G_{0_i} := \frac{0.34}{1 + 2.4 \cdot NO3_i + 0.62 \cdot NO2_i} + \frac{0.11}{1 + 120 \cdot NO3_i + 43 \cdot NO2_i}$$

$$G_{TOC_i} := 2.49 \cdot 10^6 \cdot \left(f_i \cdot TOC_i\right) \cdot \exp\left[\frac{-44300}{8.314\left(T_i + 273\right)}\right]$$

$$HGR_{rad_i} := 0.00895 f_{L_i} \cdot H_i \cdot \left(G_{0_i} + G_{TOC_i}\right)$$

$$HGR_{therm_i} := 2.76 \cdot 10^9 \cdot f_{L_i} \cdot \left(f_i \cdot TOC_i\right) \cdot \left(Al_i\right)^{0.4} \cdot \exp\left[\frac{-89300}{8.314\left(T_i + 273\right)}\right]$$

$$HGR_{LAW_i} := HGR_{rad_i} + HGR_{therm_i}$$

$G_{0_i} =$	$G_{TOC_i} =$	$HGR_{rad_i} =$	$HGR_{therm_i} =$	$HGR_{LAW_i} =$
0.048	0.64	$3.077 \cdot 10^{-3}$	$4.755 \cdot 10^{-5}$	$3.125 \cdot 10^{-3}$
0.038	0.912	$4.252 \cdot 10^{-3}$	$4.079 \cdot 10^{-4}$	$4.66 \cdot 10^{-3}$
0.038	0	$1.659 \cdot 10^{-4}$	0	$1.659 \cdot 10^{-4}$
0.038	0	$1.522 \cdot 10^{-4}$	0	$1.522 \cdot 10^{-4}$

Antifoam Agent Addition:

Concentration of antifoam agent TOC introduced by weight percent is: $AFA_i :=$

AFA_i
0.2
0
1
4

Immiscible Model: AFA Mixture is Second Phase

Assumed G-value for AFA mixture is $G_{imi.}(H_2) = 5$ H_2 molecules per 100 eV $G_{imi.} := 5$

The resulting G-value for the AFA addition is $G_{AFA_i} := G_{imi.} \cdot \frac{AFA_i}{100}$

$G_{AFA_i} =$
0.01
0
0.05
0.2

The associated HGR is $HGR\_imi_{AFA_i} := 0.00895 H_i \cdot G_{AFA_i}$

$HGR\_imi_{AFA_i} =$
$4.475 \cdot 10^{-5}$
0
$2.238 \cdot 10^{-4}$
$8.95 \cdot 10^{-4}$

NOTE: Set HGR_imi.AFA to zero for Miscible Model (next). $HGR\_imi_{AFA_i} := 0$

Summary of Results

Miscible Model: AFA Mixture Dissolves in LAW

Assume that the AFA addition is miscible, and that it produces TOC with reactivity $f_{AFA} = 0.7$. Then it creates additional hydrogen from these radiolysis and thermolysis terms:

Reactivity parameter for AFA TOC, f_{AFA}, is 0.7: $f_{AFA_i} :=$

$$\begin{bmatrix} 0.7 \\ 0 \\ 0.7 \\ 0.7 \end{bmatrix}$$

$$G\_TOC_{AFA_i} := 2.49\cdot10^{6}\cdot\left(f_{AFA_i}\cdot AFA_i\right)\cdot\exp\left[\frac{-44300}{8.314\left(T_i+273\right)}\right]$$

$$HGR\_rad_{AFA_i} := 0.00895\, f_{L_i}\cdot H_i\cdot G\_TOC_{AFA_i}$$

$$HGR\_therm_{AFA_i} := 2.76\cdot10^{9}\cdot f_{L_i}\cdot\left(f_{AFA_i}\cdot AFA_i\right)\cdot\left(Al_i\right)^{0.4}\cdot\exp\left[\frac{-89300}{8.314\left(T_i+273\right)}\right]$$

$$HGR_{AFA_i} := HGR\_rad_{AFA_i} + HGR\_therm_{AFA_i}$$

$G_{AFA_i} =$	$HGR\_imi_{AFA_i}$	$G\_TOC_{AFA_i}$	$HGR\_rad_{AFA_i} =$	$HGR\_therm_{AFA_i}$	$HGR_{AFA_i} =$
0.01	0	0.147	$6.58\cdot10^{-4}$	$1.093\cdot10^{-5}$	$6.69\cdot10^{-4}$
0	0	0	0	0	0
0.05	0	0.735	$3.191\cdot10^{-3}$	$2.524\cdot10^{-4}$	$3.444\cdot10^{-3}$
0.2	0	2.941	0.012	$9.263\cdot10^{-4}$	0.013

Total Hydrogen Generation Rates:

These are calculated for the Miscible Model:

$$HGR\_AN107_{AFA} := HGR_{LAW_0} + HGR\_imi_{AFA_0} + HGR_{AFA_0}$$

$$HGR\_B := HGR_{LAW_1} + HGR\_imi_{AFA_1} + HGR_{AFA_1}$$

$$HGR\_C_{Low} := HGR_{LAW_2} + HGR\_imi_{AFA_2} + HGR_{AFA_2}$$

$$HGR\_C_{High} := HGR_{LAW_3} + HGR\_imi_{AFA_3} + HGR_{AFA_3}$$

HGRs, with units of g-mole H_2 per day per kg waste:

<u>Predicted</u>:	<u>Measured</u>:	*<u>Predicted/Measured</u>*:
$HGR\_AN107_{AFA} = 3.794 \times 10^{-3}$	5.9×10^{-4}	$\frac{HGR\_AN107_{AFA}}{5.9 \times 10^{-4}} = 6.4$
$HGR\_B = 4.66 \times 10^{-3}$	7.2×10^{-4}	$\frac{HGR\_B}{7.2 \times 10^{-4}} = 6$
$HGR\_C_{Low} = 3.61 \times 10^{-3}$	2.5×10^{-4}	$\frac{HGR\_C_{Low}}{2.5 \times 10^{-4}} = 14$
$HGR\_C_{High} = 1.279 \times 10^{-2}$	1.1×10^{-3}	$\frac{HGR\_C_{High}}{1.1 \times 10^{-3}} = 12$

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