Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Stability of Dow Corning Q2-3183A Antifoam Agent in Irradiated Hydroxide Solution

T. L. White[a]; C. L. Crawford[a]; P. R. Burket[a]; T. B. Calloway[a]
[a] Savannah River National Laboratory, Aiken, SC, USA

To cite this Article White, T. L. , Crawford, C. L. , Burket, P. R. and Calloway, T. B.(2010) 'Stability of Dow Corning Q2-3183A Antifoam Agent in Irradiated Hydroxide Solution', Separation Science and Technology, 45: 12, 1849 — 1857
To link to this Article: DOI: 10.1080/01496395.2010.493813
URL: http://dx.doi.org/10.1080/01496395.2010.493813

Separation Science and Technology, 45: 1849–1857, 2010
Copyright © Savannah River Nuclear Solutions LLC (SRNS)
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.493813

Stability of Dow Corning Q2-3183A Antifoam Agent in Irradiated Hydroxide Solution

T. L. White, C. L. Crawford, P. R. Burket, and T. B. Calloway
Savannah River National Laboratory, Aiken, SC, USA

Researchers at the Savannah River National Laboratory (SRNL) examined the stability of Dow Corning Q2-3183A antifoam agent to radiation and aqueous hydroxide solutions. Initial foam control studies with the Hanford tank waste showed that the antifoam agent reduced foaming. The antifoam agent was further tested using simulated Hanford tank waste spiked with an antifoam agent that was heated and irradiated (2.1×10^4 rad/h) at conditions (90°C, 3 M NaOH, 8 h) expected in the processing of radioactive waste through the Waste Treatment and Immobilization Plant (WTP) at Hanford. After irradiation, the concentration of the major polymer components polydimethylsiloxane (PDMS) and polypropylene glycol (PPG) in the antifoam agent was determined by GPC. No significant loss of the major polymer components was observed after 24 h and only 15 wt% loss of PDMS was reported after 48 h. The presence of degradation products were not observed by gas chromatography (GC), gas chromatography mass spectrometry (GCMS), or high performance liquid chromatography mass spectrometry (HPLC-MS). G values were calculated from the GPC analysis and tabulated. These analyses indicate that any loss of effectiveness of the antifoam agent within 24 h of addition to the waste solution is not primarily due to chemical degradation but results from the separation and/or redistribution of the antifoam components from each other by physical means.

Keywords antifoam; caustic; degradation study

INTRODUCTION

The Department of Energy (DOE) Office of River Protection (ORP) is directed by Congress to manage the high-level waste clean up at Hanford under the River Protection Project (RPP) with the goals of waste remediation, closure of the tank farms, and protecting the Columbia River. Bechtel National, Inc. has been contracted to support the effort by building WTP to convert radioactive liquid wastes stored in tanks to stable glass. Various storage and reaction vessels are involved in the pretreatment of the waste prior to vitrification and will use pulse jet mixers (PJM) with the assistance of air spargers for mixing the tank contents. Foaming of the waste during the process needs to be minimized to avoid processing and hydrogen removal problems.

Hanford tank waste solutions have been shown to foam during plant evaporator foaming studies (1–3) and an antifoam agent (Dow Corning Q2-3183A) was determined to mitigate the foam in the evaporators (4). Foaming was also observed during filtering of a small radioactive Hanford tank sample (8). SRNL was directed by plant personnel to evaluate the antifoaming potential of Q2-3183A in simulated pretreatment filtration solutions subjected to pulse jet mixing. Bench-scale tests of Hanford simulants and radioactive waste using a foam column determined the antifoam agent reduced foaming (5) at ambient temperature and the antifoam agent was recommended for use in air sparge vessels. One of the main polymers, PDMS, in Q2-3183A has been determined to be stable by GPC in 3 M NaOH at 60°C for 24 h (4). This paper addresses the chemical and radiological stability of Dow Corning Q2-3183A antifoam agent under one set of conditions found in the plant process that is likely to facilitate degradation, mainly aluminum leaching conditions (90°C, 3 M NaOH, 8 h) found in the Ultrafiltration Process (UFP) (6).

Prior work (5) using foam column testing with Hanford radioactive and simulated waste containing Q2-3183A antifoam agent has shown that the antifoam agent becomes less effective over time and foaming gradually returns to the media. The report suggested the antifoam agent deactivation may be due to chemical breakdown of the antifoam components. Literature references suggest the loss in antifoam agent activity could also result from a change over time in the concentration of the original components (11) and how well the antifoam agent remains spread across the surfactant solution surface (12). A Co-60 gamma source and heating was used for this work to help determine if the chemical breakdown of the antifoam agent is occurring rapidly at aluminum leaching conditions and if evidence of physical separation of the antifoam components is observed during the UFP of the WPT.

Received 23 October 2009; accepted 17 March 2010.

Address correspondence to T. L. White, Savannah River National Laboratory, Aiken, SC 29808, USA. E-mail: thomas02.white@srnl.doe.gov

EXPERIMENTAL

A series of degradation studies were performed by adjusting simulated Hanford waste spiked with 2000 ppm Q2-3183-A (Table 1) to 3 M NaOH, irradiating with heating, and analyzing for polymer loss. The two temperature profiles, dose rate and time used for these tests were based on the WTP aluminum caustic leaching process (6). One set of conditions applied to a series of samples was irradiation at 2.4×10^4 rad/hr (gamma instrument source setting = 2.1×10^4 rad/hr) and heating at 60°C for two weeks (336 h). These represent a case where caustic leaching is not performed on the waste. Duplicate sealed samples were pulled at 48 h, 168 h, and 336 h and the loss of the two major polymer components in Q2-3183A (PDMS and PPG) was measured by GPC.

A second set of samples was subjected to the caustic leaching temperature profile of 90°C for 48 h and 60°C for 288 h. The dose rate was held at 2.4×10^4 rad/hr (gamma instrument source setting = 2.1×10^4 rad/hr) for 48 h and then increased to 7.4×10^4 rad/hr (gamma instrument source setting = 6.3×10^4 rad/hr) for 96 h. Duplicate sealed samples were pulled at 24 h, 48 h, and 336 h and the polymer loss was determined by GPC. Shorter sampling times were used for the 90°C experiment than the 60°C experiment because it was expected that decomposition of the polymers would occur more rapidly at the higher temperature. Gas chromatography mass spectrometry (GCMS) analysis of the 336 h samples was used to search for degradation products such as formaldehyde and cyclic dimethylsiloxanes. The increase in the dose rate after 48 h was done to limit the time in the gamma source to one week and affected 2 samples at 336 h. These samples received a similar overall dose as the 60°C samples and the increase in the dose rate was not considered high enough to greatly influence polymer decomposition rates.

Methodology for Antifoam Agent Degradation Studies

The antifoam agent degradation tests used a similar apparatus and methodology as described earlier (4,7). The samples of AY-102/C-106 waste simulant containing 16 wt% washed solids (8) were prepared with 2000 ppm Q2-3183A antifoam agent. The Q2-3183A antifoam agent (280 mg) was added from a 100,000 ppm stock solution to 14 g of simulated waste. The final antifoam agent concentration in the waste simulant of 2000 ppm was required to meet analytical instrument detection limits. One hundred and twelve milliliters of 19 M NaOH were added to 600 mL of simulant to replicate the aluminum leaching process (6). Samples for irradiation were contained in a ½ inch O.D. (0.035 inch wall) by 7.5 inch stainless steel tubes with welded plugs at the bottom and a ½ inch Swagelock connection at the top. These tubes were rigorously washed using ethanol, 1 M HNO_3, and water, and dried prior to use. The tubes were sealed with Swagelock fittings and placed in a manufactured aluminum heating block (Fig. 1). Heat tape and glass wool insulation were used to heat the block. Figure 1 shows the vessel and the heating block used.

Another set of samples was prepared following the same protocol as describe above with the exception that the simulant used was 12.9 wt% wash solids AY-102/C-106 simulated waste (8) (Table 2). After heating (90°C for 48 h followed by 60°C for 288 h) and exposing the samples to radiation, the samples were either sent for analysis or processed through steps designed to simulate the UFP (6) and then the resulting combined washes and solids samples were sent for analysis. A modified wash procedure (9) was performed using a centrifuge to filter the solids prior to each wash. Four 18-mL stainless steel sample tubes containing 15 mL of 12.9 wt% washed and caustic leached AY-102/C-106 simulated waste were emptied into Teflon centrifuge tubes. Inhibited water (1.35 mL of 0.1 M NaOH) was used to rinse the contents of the stainless steel tubes into Teflon centrifuge tubes. The Teflon tubes were placed into the centrifuge holders, the top latched, and the samples were centrifuged until the solids formed a button at the base of the Teflon tubes (15 min). The supernate (1.35 mL) was poured off into a glass vial with volume markings and labeled washings. Inhibited water (1.35 mL) was again added to the solids and the mixture was shaken until the solids dispersed. The centrifuge process was repeated until six washings of the solids had been performed and all six

TABLE 1
Main components of Q2-3183A

CAS #	Compound	wt%	State	Function	Comments
63148-62-9	Polydimethylsiloxane	40–70	Liquid	Antifoam	Carries treated silica
25322-69-4	Polypropylene glycol	40–70	Liquid	Antifoam	Lowers surface tension
none	Treated silica	5–10	Solid	Antifoam	Destabilizes foam
none	Treated Amorphous Silica	3–7	Solid	Antifoam	Destabilizes foam
9036-19-5	Octylphenoxy polyethoxy ethanol	5–10	Liquid	Emulsifying/ Dispersion	Promotes rapid dispersion
9082-00-2	Polyether polyol	3–7	Liquid	Wetting	Promotes rapid dispersion

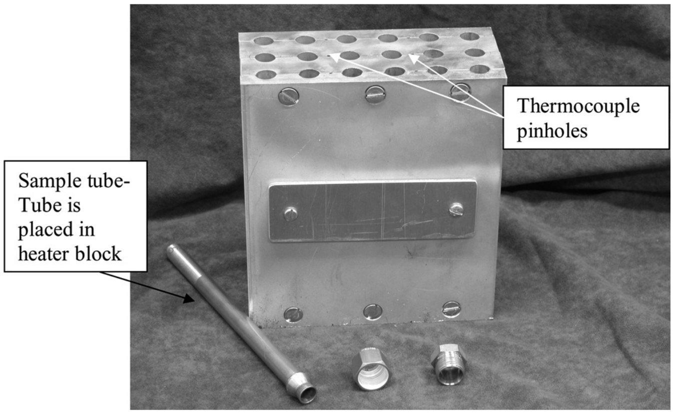


FIG. 1. Heating block for Q2-3183 degradation tests.

washings filled the glass vial to approximately 8.1 mL. The Teflon tube with the solids that remained in the centrifuge tube was capped and sent for analysis.

Co-60 Source

The apparatus used for Co-60 irradiation of the samples was a JL Shepherd and Associate model 364 Co-60 gamma irradiation system. The temperature was controlled using a Cole Parmer Temperature Controller model #89810-02 and an I^2R Therm-o-watch Tow-VOVC over temperature controller. Calibrated Type K thermocouples (±2°C) were inserted through a pinhole in the center row of the block and into a face plate on the face of the heating block. The system was verified by monitoring the temperature of deionized water in open vessels during trial runs. The heating block was placed in the Co-60 gamma source for irradiation. The instrument nominal dose rate values were 2.1×10^4 rad/hr and 6.3×10^4 rad/hr. The nominal dose rate of 2.1×10^4 rad/hr was calculated using the specified WTP value of 10 Ci/L value and the radionuclide content of high level unwashed waste feed published in the WTP contract No. DE-AC27-01RV14136, Section C, Table TS-8.3 (available at http://www.hanford.gov/orp/). The radionuclide content used for this study represents the worst case scenario and considers both beta (primarily ^{90}Sr/^{90}Y)/gamma (primarily ^{137}Cs/^{137m}Ba) emitters of untreated high level waste. Thus absorbed dose conditions tested in this paper should bound those found in the plant based upon information available at the time of this study. The contract lists the high level waste feed unwashed solids maximum radionuclide composition on the basis of curies per 100 g of non-volatile waste oxides. Beta emitters ^{90}Sr/^{90}Y comprise 85.3% of the total curies and ^{137}Cs/^{137m}Ba comprise 12.8% of the total curies. The remaining 1.9% of the total curies derive from other trace radionuclides in the unwashed sludge slurry. These Ci/g values were converted to Ci/L units and the expected dose rate for a matrix with all of the listed radionuclides at their maximum values was calculated based on the known characteristics of the radionuclides, i.e., their "Q-values" or Watts/Curie values and their specific activities in Ci/g using published radionuclide characteristics tables, e.g., the "Integrated Data Base for 1991: U.S. Spent Fuel and Radioactive Waste Inventories, Projections, and Characteristics" (DOE/RW-0006, Rev. 7) published by Oak Ridge National Laboratory. Dose rates for the aluminum block (Fig. 1) were calibrated using Fricke dosimetry.

Simulated Hanford Waste

The simulant used for Q2-3183A antifoam agent foaming column tests and Q2-3183A antifoam agent degradation tests was based upon the composition of Hanford Tank AY-102/C-106 and was obtained from the waste simulant processed through the Semi-Integrated Pilot Plant (SIPP)

TABLE 2
Simulants and steps used for study

Steps	Set 1	Set 2
Simulant Used	16 wt% washed solids AY-102/C-106	12.9 wt% washed solids AY-102/C-106
Caustic leaching	Adjusted simulant with 19 M NaOH to 3 M NaOH (2)	Adjusted simulant with 19 M NaOH to 3 M NaOH (2)
Heating	Set #1 (maximum T profile for caustic leaching) – 90°C for 48 h then 60°C for 288 h (total of 336 h). Set #2 (maximum T without caustic leaching) – 60°C for 336 h.	The simulant was heated at 90°C for 48 h then 60°C for 288 h (total of 336 h). A subset of samples were then filtered and washed. Then all of the samples were sent to Dow Corning Analytical for GPC, GC, GCMS, and ESI-MS analyses.
Filtering/Washing	No filtering or washing. Sent to Dow Corning Analytical for GPC and GCMS analyses.	Used centrifuge to filter and washed with inhibited water (10).

(10). In particular, wash permeate solutions were combined with Hanford 241-AY-102/C-106 undissolved solids. These solids had undergone the washing step just prior to caustic leaching (6) and were ready for caustic leaching. A 16 wt% washed solids AY-102/C-106 or 12.9 wt% washed solids slurry was used for the stability tests (8).

Antifoam Agent Dow Corning Q2-3183

Table 1 summarizes the components of the Dow Corning Antifoam agent Q2-3183A and their function. The formulation acts as a defoamer to eliminate foam and as an antifoam agent to keep foaming reduced. The three antifoam components (PDMS, PPG, and treated silica) act in concert to address foaming while the ancillary agents help emulsify, disperse, and spread the antifoam agent across the foaming media. The antifoam agent Q2-31832A also contains a small quantity of xylenes and ethylbenzene (not shown in Table 1). SRNL has since analyzed the content of Q2-3183A and determined that the xylenes concentration is nominally less than 0.35 wt% and the ethylbenzene is less than 0.1 wt%. The xylenes have a lower flammability limit of 1.1 vol% and the ethylbenzene has a lower flammability limit of 1 vol%. The effects of xylene and ethylbenzene concentration on the WTP were not addressed by this effort.

GPC Analysis

All 18 mL sample tubes were received capped. The sample tubes were all emptied into individual 4 oz bottles and then rinsed with a number of solvent rinses. The sample tubes were rinsed with five 5 mL water rinses and three 10 mL toluene or tetrahydrofuran (THF) rinses. For each rinse, the sealed tube was shaken about one minute, allowed to set for 15–30 minutes, mixed with a vortex mixer for about one minute, and emptied into its corresponding collection vessel. The first organic solvent rinse was allowed to set overnight. 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 overnight, at which time the samples had all separated into a clear organic solvent layer over a faintly yellow aqueous layer with a layer of solids on the bottom. The upper organic layer was removed with an eyedropper and transferred to a one ounce vial and allowed to concentrate approximately 10 fold. The toluene extracts were concentrated at room temperature. The THF extracts were concentrated at room temperature until approximately 2 mL remained, dried to completeness in a 90°C oven (about 4 hours), and then taken back up in about 3 mL THF. The solvent concentrate was then filtered through a 0.45 µm filter and analyzed by GPC.

The % recovery values (area) are based on a five-point calibration curve created from the Q2-3183A control sample prepared directly in toluene and THF at concentrations of approximately 0.25% to 1.25% w/v. This would correspond to simulant samples containing approximately 500 ppm to 2500 ppm Q2-3183A when prepared according to the method used. The theoretical Q2-3183A amounts are based on an assumption of a complete transfer of the 14 g of sample (2000 ppm Q2-3183A) from the sample tubes to the extraction vessels, complete separation of the organic and aqueous phases used for the extraction, and a complete partitioning of the Q2-3183 to the organic phase. The height based % recovery values are based on a one-point calibration curve, using the Q2-3183A standard that was approximately 1%. GPC analyses were conducted on the samples using toluene or THF as the eluent, 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.

GCMS Analyses

Four samples were analyzed by headspace EI GC-MS. The instrument mass calibration was verified to be accurate on the same day the analyses were performed. A Hewlett Packard (HP) 6890 gas chromatograph (GC) equipped with a headspace sampler (HP 7694) and a mass spectrometer (HP 5973 MSD) was used. The GC column was a DB1 (30 m × 0.25 mm) with 0.5 um of film. The oven started at 50°C for 2 minutes and then rose to 250°C at a rate of 10°C per minute. The instrument was set at a constant flow of 1 mL per minute, a split injection of 50:1, and a headspace temperature of 180°C with an equilibrium time of 5 minutes. The mass spectrometer was set to use electron impact for ionization and scan range of 15 to 800 Da.

GCFID Analyses

Samples were poured out of the tubes without any dilution. The amount of material removed from each tube was approximately 6–7 grams. A known quantity of material from each tube was treated with a known quantity of dodecane as an internal standard. The sample and internal standard were then extracted with 2 g of pentane by shaking at room temperature for one hour. The extraction mixture was then centrifuged and the clear pentane layer was withdrawn and was analyzed on a GC equipped with a flame ionization detector (GC-FID).

The column was a RTX-1 30 m × 0.25 mm with a 0.1 micron film. The oven temperature started at 50°C for 2 minutes followed by an increase of 20°C/minute until 300°C where it was held for 5 minutes. The temperature was then increased at 30°C/min until 315°C was reached and held for 4 minutes. The inlet was heated to 280°C with a 50:1 split and an injection volume of 1 microliter. The detector temperature was set at 300°C and the range was set at 0. The carrier gas was hydrogen with a flow of 2.5 ml/min.

ESI-MS Analyses

The capped samples were opened, emptied into a glass vial, and rinsed 5 times with 4 mL of a 1:1 solution of methanol and chloroform containing 0.5 mM NH_4OAC for a total of 20 mL of solvent. Thirty milliliters of HPLC grade methanol was added and the mixture was shaken for two minutes. The sediment was allowed to settle followed by filtering the solvent layer or aqueous layer with a 0.45 um nylon disposable syringe filter. The filtered solutions were analyzed by direct infusion positive ion electrospray ionization mass spectrometry (ESI MS) using a triple quadrupole mass spectrometer. The instrument mass calibration was confirmed prior to analyzing these samples.

RESULTS AND DISCUSSION

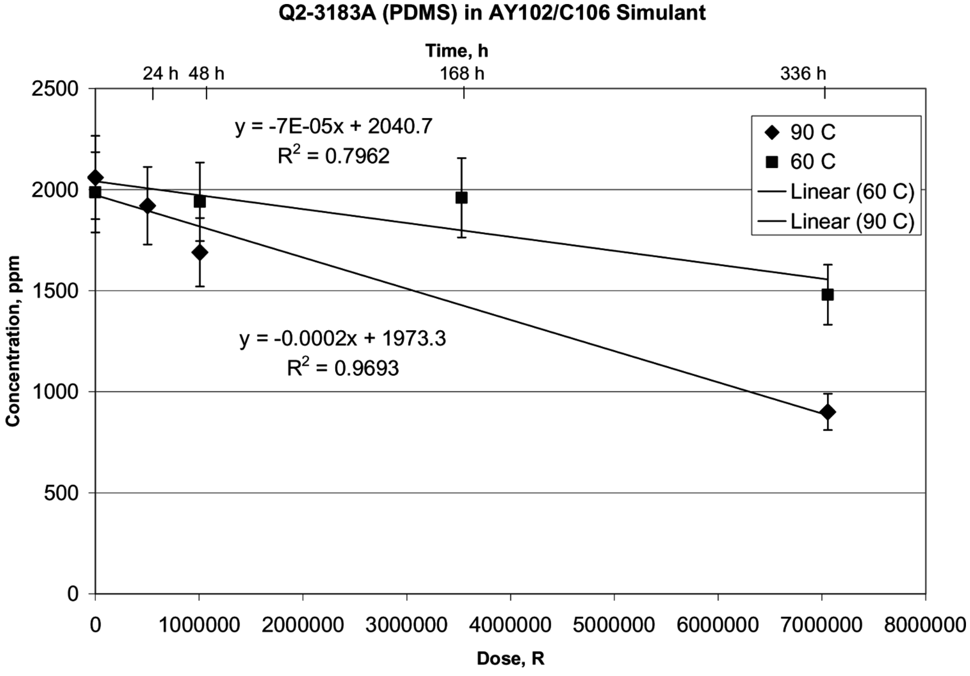
Heating and Irradiation of Hanford Simulated Waste with Caustic Leach

Figures 2 and 3 summarize the duplicate GPC degradation analyses of PDMS and PPG. The error bars for both GPC analyses of the extracts are ±10% at the 95% confidence level. The PDMS shows the highest propensity to degrade which is illustrated in Fig. 2. After 48 h at 90°C, a loss of 15% of the polymer has occurred and at 336 h over half the polymer has degraded as well as a change in and shortening of polymer lengths. The PDMS peaks at 336 h are shifting to longer time which is lower molecular weight. Figure 2 illustrates the 90°C data showing degradation while the 60°C data shows very little degradation until exposure time reaches 336 h. This agrees with what has previously been observed at 60°C (4) under caustic conditions for a period of 24 h which is little or no PDMS degradation. Analyses of the sealed samples using GCMS revealed the presence of cyclic polydimethylsiloxanes consistent with PDMS polymer degradation and no formaldehyde greater than the instrument detection limit of 10 mg/L. Table 3 lists the name and boiling points of these compounds. Loss of the PDMS could eventually lead to the disruption of the silica solids and the PDMS leading to an increase in foaming.

The PPG polymer demonstrated excellent resistance to degradation under radiological, heating, and caustic conditions. Figure 3 shows no or little degradation except for the points at 336 h. In this case, about a 10% loss in polymer was observed which is still within the ±10% error of the method suggesting little or no polymer degradation is occurring. The GPC chromatogram showed no significant peak broadening indicating no change in the molecular weight distribution occurred. During washing steps in UFP (6), the PPG is expected to have some solubility in the wash water and thus could partition away from the other hydrophobic antifoaming components (PDMS and silica).

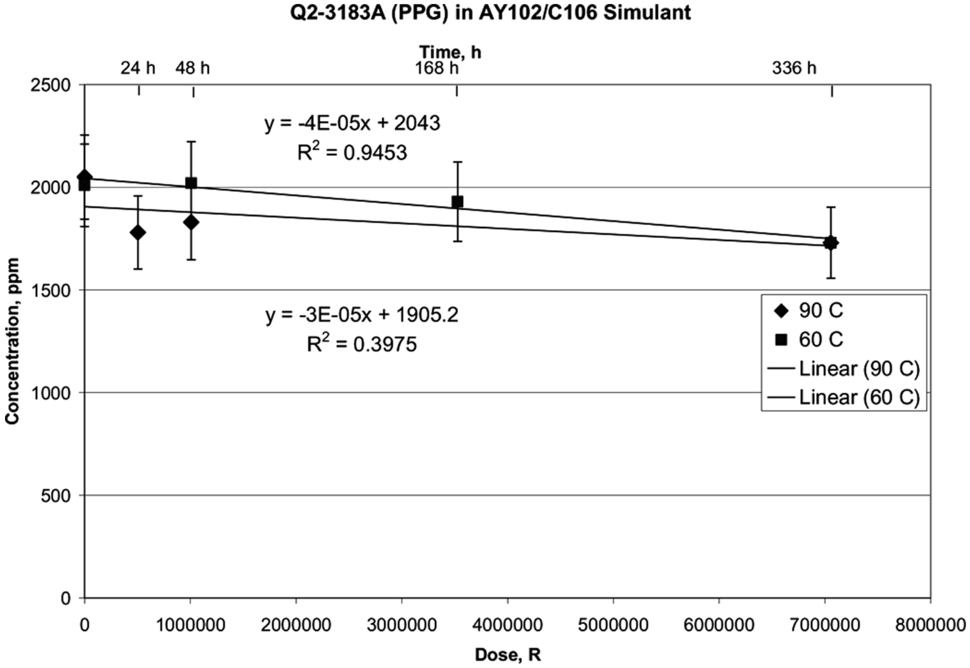
Caustic Leach and Filtering of Samples

To further understand the fate of Q2-3183A antifoam agent during the WTP process, 12.9 wt% washed solids



Each point is the average of duplicate samples.

FIG. 2. Loss of PDMS after an initial charge of 2000 ppm Q2-3183A in 16 wt% washed solids AY-102/C-106 simulant.



Each point is the average of duplicate samples.

FIG. 3. Loss of PPG after an initial charge of 2000 ppm Q2-3183A Antifoam in 16 wt% washed solids AY-102/C-106 simulant.

AY-102/C-106 simulated waste with 2000 ppm antifoam agent in sealed stainless steel tubes received a total dose of 8.1×10^6 rad while heated (90°C for 48 h followed by 60°C for 288 h) and then subjected to the aluminum leaching process. The samples were therefore adjusted with 19.0 M NaOH to 3 M NaOH prior to irradiating/heating to mimic the caustic leaching step of the aluminum leaching process. Some of the samples were exposed to heat only (90°C for 48 h followed by 60°C for 288 h) to determine if radiation plays a major role in the polymer breakdown at the leaching process temperature. Table 4 shows the results of heated samples and irradiated/ heated samples.

These values were normalized to 12.9 wt% washed solids AY-102/C-106 simulated waste 2000 ppm standards of Q2-3183A. A significant loss of the PDMS and the PPG polymers were only observed for the samples that were exposed to radiation and heat. The samples that were heated only saw a slight loss of PDMS. These polymer percent losses for the irradiated/heated samples are similar to what was seen previously under the same conditions (Figs. 2 and 3). Previously at the 90°C temperature, the average % polymer loss for PDMS was 56% for the 16 wt% washed solids while for the current set of samples with a slightly different simulant it was 27% for the 12.9 wt% washed solids. For PPG, the average % polymer loss previously was 16% while it was 14% for this set of samples. In all cases the PPG was less susceptible to degradation than the PDMS and the center of the PDMS peak (Mp) shifted to a lesser value indicating a shortening of the polymer length.

TABLE 3
Cyclic polydimethylsiloxanes

CAS #	Compound	BP, °C
541-05-9	Hexamethylcyclotrisiloxane (D3)	128
556-67-2	Octamethylcyclotetrasiloxane (D4)	175
541-02-6	Decamethylcyclopentasiloxane (D5)	210
540-97-6	Dodecamethylcyclohexasiloxane (D6)	245

Analyses of the sealed 12.9 wt% washed solids AY-102/C-106 simulated waste samples after caustic leaching using GCMS, GC, and ESI-MS (HPLC-MS) revealed no concentrations of cyclic PDMS, short chain glycols, and formaldehyde greater than the instrument detection limit of 10 mg/L. These results indicate that after 2 weeks (336 h) of irradiation/heat the polymers have not completely degraded to generate high concentrations of these potential decomposition products.

After caustic leaching with irradiation/heat, some of the sealed 12.9 wt% washed solids AY-102/C-106 simulated waste samples were washed with inhibited water six times using a centrifuge to concentrate the solids after each wash step. This protocol was meant to determine if the antifoam components fractionate during the wash steps of the UFP process. The washes were combined and sent with the solids for GPC analyses. For PDMS in Fig. 4, the

TABLE 4
GPC analysis based on peak height of AY-102/C-106 simulant with 2000 ppm Q2-3183A–irradiated/heated caustic leached but unwashed samples

#	AY-102/C-106 sim. (wt%)	Dose, rad	Temperature, °C	% PDMS remaining	% PPG remaining
1	16% Washed Solids	8.1×10^6	90 for 48 h then 60 for 288 h	38	74
2	16% Washed Solids	8.1×10^6	90 for 48 h then 60 for 288 h	50	95
Average				44	84
4	12.9% Washed Solids	0	90 for 48 h then 60 for 288 h	87	104
5	12.9% Washed Solids	0	90 for 48 h then 60 for 288 h	97	103
Average				92	104
6	12.9% Washed Solids	8.1×10^6	90 for 48 h then 60 for 288 h	73	91
7	12.9% Washed Solids	8.1×10^6	90 for 48 h then 60 for 288 h	70	83
8	12.9% Washed Solids	8.1×10^6	90 for 48 h then 60 for 288 h	76	84
Average				73	86
9	16% Washed Solids	8.1×10^6	60 for 336 h	79	86
10	16% Washed Solids	8.1×10^6	60 for 336 h	71	83
Average				75	84

combined washes contained traces of the polymer while the bulk of the polymer was found to remain with the solids. The opposite was true for the more water soluble PPG which primarily remained with the combined washes as shown in Fig. 5.

Table 5 summarizes the results of the samples that underwent caustic leaching and washing. The average (n = 2) of the sum of the %PPG and %PDMS polymers in both the combined washes and the solids compares (Table 5) well with the initial feed shown in Table 4 (samples 6, 7, and 8). For PPG, the average % PPG was 86 for the feed and 67 for the combined washings and solids while for PDMS the values were 73 for the feed and 64 for the combined washings and the solids. A reason for the slightly lower % polymer values of the processed samples may be due to traces of polymer remaining in the stainless steel sample tubes since inhibited water was used as a rinse instead of solvent. Seal samples that underwent the caustic leaching only were sent for analysis and the tubes were rinsed out with the solvent that the polymers were soluble in.

The partitioning of PDMS and PPG during the washing of the solids was also observed by following the Q2-3183A antifoam agent containing 500 ppm of the fluorescent dye

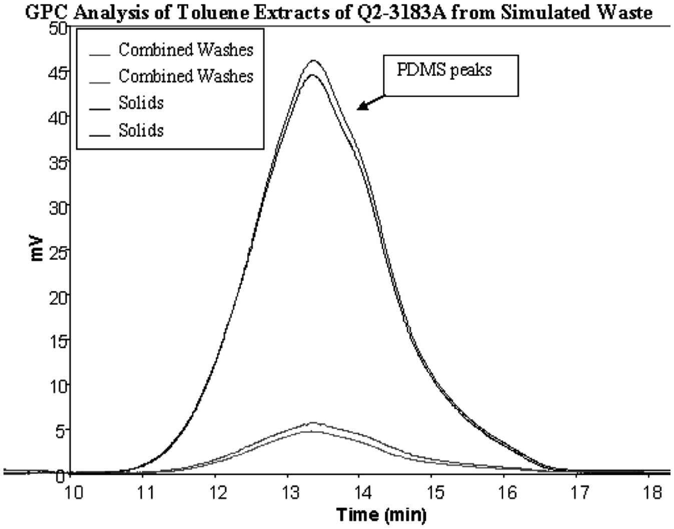


FIG. 4. GPC of Q2-3183A in 12.9 wt% Washed Solids AY-102/C-106 Simulant after 6 Washings – Chart indicates that PDMS primarily partitions to the solid phase during filtration. Peak height for the washes is significantly less than solids thus indicating very little PDMS is in the wash.

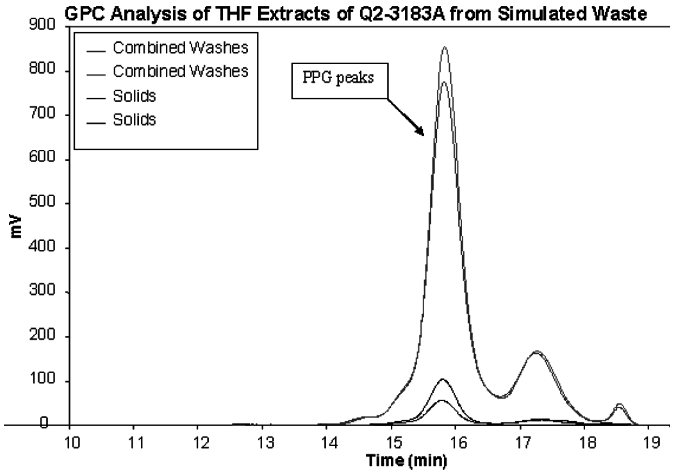


FIG. 5. GPC of Q2-3183A in 12.9 wt% Washed Solids AY-102/C-106 Simulant after 6 Washings – Chart indicates that PPG partitions to the wash solution. Peak height for the solids is significantly less than washes thus indicating very little PDMS is in the wash.

TABLE 5
GPC analysis based on peak height of AY-102/C-106 simulant with 2000 ppm Q2-3183A–irradiated/heated caustic leached and washed samples

#	AY-102/C-106 sim.	Dose, rad	Temperature, °C	Description	% PDMS	% PPG
1	12.9% Washed Solids	8.1×10^6	90 for 48 h then 60 for 288 h	Combined washes	7	58
2	12.9% Washed Solids	8.1×10^6	90 for 48 h then 60 for 288 h	Combined washes	6	63
3	12.9% Washed Solids	8.1×10^6	90 for 48 h then 60 for 288 h	Solids	56	8
4	12.9% Washed Solids	8.1×10^6	90 for 48 h then 60 for 288 h	Solids	58	4
Average of solids + combined washings (n = 2)					64	67

DFSB-K43 from Risk Reactor. The dye is soluble in ethylene glycol up to 0.7 g in 100 mL and was therefore expected to have an affinity for the similar compound PPG in the antifoam agent. Q2-3183A antifoam agent (2000 ppm) containing the dissolved dye was added to 12.9 wt% washed solids AY-102/C-106 simulated waste. The solution was centrifuged and washed 6 times and the washes were combined. Using a black light, the dye was observed predominately with the washes and a slight amount remained with the solids.

Analysis of Fig. 3 and the other chemical degradation data indicate the mechanism for loss of effectiveness of the antifoam agent especially within the first 24 h is likely due to the separation of the antifoam components from each other by physical means after addition to the waste solution. The example we have shown is the partitioning of PPG and PDMS during washing of the caustic leached samples. These two polymers did not significantly chemically degrade over a 24 h time period. Foam column studies on actual Hanford AN-104 post IX (6 wt% solids) at a flux rate of 2.2 ft^3/min/ft^2 with an initial charge of 555 mg/L of Q2-3183A showed some foaminess did return to the media after 24 h (5). Our studies using AY-102/C-106 simulated waste (with recycles) indicate this observation may not be due to chemical degradation but instead to a redistribution of the Q2-3183A components over time.

G Values Calculated

The G values for PPG and PDMS degradation were calculated for both the 90°C/60°C and the 60°C tests using the concentration vs. dose data shown in Figs. 2 and 3, respectively. The G value, in this case, is the measurement of the number of molecules of PDMS or PPG destroyed per 100 eV absorbed. In the Q2-3183A formulation, the PDMS and the PPG are listed in information from the manufacturer as varying from 40–70 wt%. The G values for each polymer were thus calculated over the range of 40 wt% to 70 wt% and the results are shown in Table 6. The G values were also calculated for two different cases where the polymers are either completely immiscible in the waste simulant, or completely miscible in the waste simulant. For PPG, the average molecular weight of 3500 was used and for PDMS the average molecular weight of 35,000 (ten-fold higher) was used. The ten-fold molecular

TABLE 6
G values for major polymer components of Q2-3183A

#	AY-102/C-106	Temp, °C	wt% polymer	G value immiscible # molecules/100 eV	G value miscible # molecules/100 eV
1	12.9% Washed Solids	90 then 60	at 40 PDMS	0.76	0.0015
2	12.9% Washed Solids	90 then 60	at 70 PDMS	1.3	0.0027
3	12.9% Washed Solids	90 then 60	at 40 PPG	2.2	0.0044
4	12.9% Washed Solids	90 then 60	at 70 PPG	3.8	0.0076
5	16% Washed Solids	90 then 60	at 40 PDMS	0.79	0.0016
6	16% Washed Solids	90 then 60	at 70 PDMS	1.4	0.00280
7	16% Washed Solids	90 then 60	at 40 PPG	2.2	0.00440
8	16% Washed Solids	90 then 60	at 70 PPG	3.8	0.0076
9	16% Washed Solids	60	at 40 PDMS	0.35	0.00070
10	16% Washed Solids	60	at 70 PDMS	0.61	0.0012
11	16% Washed Solids	60	at 40 PPG	1.9	0.0038
12	16% Washed Solids	60	at 70 PPG	3.4	0.0068

weight difference contributed to the higher calculated G values for PPG even though a large concentration of PDMS degraded during the two week tests. The results are summarized in Table 6. Calculated G values for PDMS and PPG degradation are higher for the immiscible case (next to last column in Table 6) vs. the miscible case in the last column of Table 6, because only the dose absorbed directly by the immiscible antifoam components is used in the immiscible case G value calculations. The fraction of the total dose absorbed by the immiscible antifoam components was calculated based on the weight fraction of the components in the total waste simulant. The immiscible case involves radiolytic decomposition of the PDMS and PPG components by direct absorption of the ionizing radiation. In contrast, the miscible case involves indirect decomposition of the PDMS and PPG components. In this case the reactive intermediates produced by ionizing radiation absorption in the waste simulant solvent could attack the dispersed, miscible antifoam components leading to degradation. It is likely that both mechanisms are active to varying degrees in these tests since the PDMS and PPG antifoam components have different levels of solubility in the aqueous waste simulants.

CONCLUSION

The major aim of this paper was to investigate the impact that caustic leaching (90°C, nominal 2.1×10^4 rad/h) has on the Dow Corning Q2-3183A antifoam agent. Samples of AY-102/C-106 simulated waste containing the antifoam agent were heated and irradiated followed by analysis where the two main polymers in the antifoam agent, PDMS and PPG, were followed by GPC. Sealed samples were also submitted for GC/MS and GC analysis to determine volatile decomposition products and HPLC-MS (ESI-MS) analysis to determine polar decomposition products in the waste.

The main antifoam polymer PPG did not significantly degrade after 24 h of heating (90°C) and only showed minor degradation with heating and irradiating (2×10^4 rad/hr gamma) in the range of 14% to 16%. The PDMS polymer showed only minor 8% degradation with heating, but degraded in the range of 27% to 56% with both heating and irradiation. These analyses indicate that any loss of effectiveness of the antifoam agent especially within the first 24 h is likely due to the separation/redistribution of the antifoam components from each other by physical means (i.e., filtration) after addition to the waste solution. The treated silica will be separated during the filtration process and the polymer components likely separate after addition. PPG is more hydrophilic than PDMS/treated silica and has been shown to separate from PDMS during washing steps. Further, the distribution of treated silica in the PDMS is likely to change over time resulting in antifoam agent exhaustion (11). At this point, addition of more antifoam agent would be required. Future work should include analysis of the potential safety effects (e.g., flammability) of the xylene and ethylbenzene on the WTP process.

ACKNOWLEDGEMENTS

The authors would like to thank Dow Corning Analytical for significant contribution. The authors would especially like to thank Mike Johnson, formerly of British Nuclear Fuels Inc., who initiated the Hanford WTP work at SRNL. The authors would also like to thank Dr. Darsh T. Wasan and Dr. Alex D. Nikolov, Illinois Institute of Technology, for their continued consultation and guidance throughout this project.

REFERENCES

1. Crowder, M.L.; Crawford, C.L.; Saito, H.H.; Calloway, T.B.; Gibson, L.V.; Burdette, M.A.; Crump, S.L. (2001) Bench Scale Evaporation of a Large Hanford Envelope C Sample (Tank 241-AN102), WSRC-TR-2000-00469 Rev. 1, Westinghouse Savannah River Company, May 2001.
2. Eibling, R.E.; Nash, C.A. (2000) "Hanford Waste Simulants Created to Support the Research and Development on the River Protection Project – Hanford Waste Treatment Plant," WSRC-TR-2000-00338, Rev. 0, Westinghouse Savannah River Company, September 2000.
3. Calloway, T.B.; Zamecnik, J.R.; White, T.L.; Jones, T.M.; Hassan, N.M.; Eibling, R.E.; Duignan, M.R.; Crawford, C.L. (2005) Fate and Effect of Antifoam on the Hanford Waste Treatment Process: Part 1, submitted for presentation to the ICEM meeting, September 2005, Glasgow, Scotland.
4. Baich, M.A.; Stone, M.E.; White, T.L.; Calloway, T.B. (2003) Waste Treatment Plant Evaporation: Antifoam Performance (U), WSRC-TR-2003-00216, Rev. 0, Westinghouse Savannah River Company, August 2003.
5. Hassan, N.M.; Stone, M.E.; White, T.L.; Calloway, T.B. (2004) Evaluation of Foaming/Antifoaming in WTP Tanks Equipped with Pulse Jet Mixers and Air Spargers, WSRC-TR-2004-00387, Westinghouse Savannah River Company, September 2004.
6. Boh, M.D. (2001) System Description for Ultrafiltration Process System, 24590-PTF-3YD-UFP-00001, Bechtel, December 2001.
7. Walker, D.D.; Duffey, C.E. (2005) Radiolytic, Thermal, and Physical Degradation Testing of Spherical Resorcinol-Formaldehyde Resin, WSRC-TR-2004-00075, Westinghouse Savannah River Company, June 2005.
8. Burket, P.R.; Jones, T.M.; Calloway, B.T.; White, T.L. (2005) Evaluation of Foaming and Antifoam Effectiveness During the WTP Oxidative Leach Process, WSRC-TR-2005-00263, Westinghouse Savannah River Company, July 2005.
9. Poirier, M.R.; Burket, P.R.; Siler, J.L.; Zamecnik, J.R. (2003) Filtration, Washing, and Leaching of a AY-102/C-106 Sample, WSRC-TR-2003-00240, Westinghouse Savannah River Company, June 2003.
10. Duignan, M.R.; Adamson, D.J.; Calloway, T.B.; Fowley, M.D.; Qureshi, Z.H.; Steimke, J.L.; Williams, M.R.; Zamecnik, J.R. (2005) Final Report: RPP-WTP Semi-Integrated Pilot Plant, WSRC-TR-2005-00105, Westinghouse Savannah River Company, June 2005.
11. Denkov, N.D.; Marinova, K.G.; Christova, A.H.; Cooper, P. (2000) Mechanisms of action of mixed solid-liquid antifoams: 3. Exhaustion and reactivation. *Langmuir*, 16: 2515–2528.
12. Shah, D.O.; Jha, B.K.; Christiano, S.P. (2000) Silicone antifoam performance: Correlation with spreading and surfactant monolayer packing. *Langmuir*, 16: 9947–9954.