Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Antifoam Development for High Level Waste (HLW) Processing - 21391

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Introduction

Foaming occurs during treatment of high level waste (HLW) at Savannah River Site's Defense Waste Processing Facility (DWPF) in the Chemical Process Cell (CPC) due to high gas generation from process steam and chemical offgas products [1]. The presence of amphiphilic particles in the waste slurry stabilizes the foam [2], [3]. Efficient processing of HLW requires foam control, as foamovers lead to lower productivity and potential radioactive contamination of condensate streams. DWPF currently employs Siovation Antifoam 747, a surfactant produced by Momentive Performance Materials, as an antifoaming agent during waste treatment. Despite its ability to control foam generation, processing issues have arisen from its use [4]. During DWPF chemical processing, a chemical antifoam agent must be effective at temperatures up to 103°C between pH 3-13. Antifoam 747 is effective at pH 7 but degrades as pH deviates [5]. Antifoam 747 is 90% by weight Momentive™ L77 and 10% by weight Momentive™ Y-17580. These ingredients are trisiloxane products, which are especially vulnerable to attack in acidic and caustic environments.

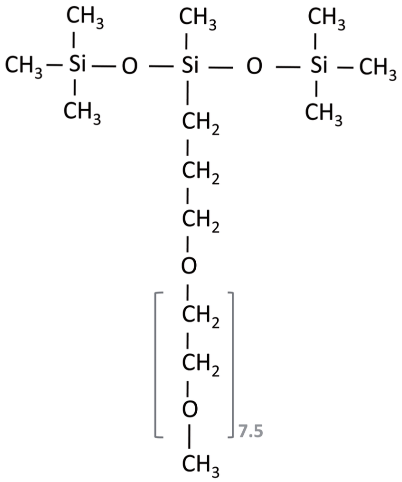

Figure 1. Structure of Momentive Silwet L77

Since Antifoam 747 readily degrades, periodic addition is required. Several processing concerns related to Antifoam 747 have affected DWPF operation. Its overuse warranted concern of potential flammable melter offgas under upset conditions due to the generation of carbon dioxide and hydrogen. As a result, a Potential Inadequacy in the Safety Analysis (PISA) was declared [6]. Antifoam contribution has been included in the melter offgas flammability strategy and the quantity of antifoam is monitored to ensure limits are not exceeded. Testing at Savannah River National Laboratory (SRNL) determined that propanal, trimethylsilanol, and hexamethyldisiloxane are generated as Antifoam 747 degrades, leading to a second PISA [7]. The formation of these byproducts poses additional flammability risks.

Table I. Decomposition Products of Antifoam 747

Compound	Formula	Molar Mass g/mol	Solubility	Lower Flammability Limit vol %
Propanal	C_3H_6O	58.08	200 g/L	2.6
Trimethylsilanol	$C_3H_{10}OSi$	90.20	0.995 g/L	0.5-0.6
Hexamethyldisiloxane	$C_6H_{18}OSi_2$	162.38	930.7 ppb	0.5-0.8

Furthermore, the methyl and ethyl groups of these compounds may be responsible for the formation of the methyl and ethyl mercury discovered in DWPF [8], [9]. The formation of organomercury has specifically been called out by DOE as a need for increased research[10].

Savannah River National Laboratory (SRNL) evaluated the effectiveness of thirty alternative antifoam agents from industry leading manufacturers as part of an effort to improve HLW treatment operations at DWPF and to reduce, or eliminate, the flammability hazards associated with Antifoam 747 currently in use. Two suitable alternative defoaming agents, Momentive™ Y-17112 and Evonik Surfynol® MD-20, demonstrated superior foam control during laboratory scale CPC experiments with non-radioactive sludge simulants. Both defoamers control foam over a pH range of 4-13 at boiling, with no flammable degradation products, and only minimal quantities (100 – 200 mg/kg) are required under glycolic acid conditions. To validate their effectiveness in a radioactive environment, sludge simulant containing fresh antifoam was irradiated utilizing a Co-60 gamma source. Both defoamers remained effective at foam control during vigorous boiling after prolonged irradiation (53,100 krad over 30 days) and flammable degradation products were not generated.

Simulant Development

A SB6A chemical sludge simulant was selected for testing, as it was the foamiest chemical simulant identified. Foaminess was further increased, by reducing particle size through high shear mixing.

Table II. SB6A Chemical Sludge Simulant

Simulant	SB6A Chemical Sludge Simulant
pH	13.1
Total Solids, wt%	15.31
Insoluble Solids, wt%	10.18
Calcined Solids, wt%	10.97
Soluble Solids, wt%	5.13
Slurry Density, g/mL	1.1223
Supernate Density, g/mL	1.0414
Al, wt%	15.30
Ba, wt%	0.135
Ca, wt%	1.20
Cr, wt%	0.176
Fe, wt%	22.30
K, wt%	0.263
Mg, wt%	0.849
Mn, wt%	6.39
Na, wt%	15.5
Ni, wt%	2.92

S, wt%	0.328
Si, wt%	1.35
Zn, wt%	0.124
Zr, wt%	0.131
NO_2^-, mg/kg	9810
NO_3^-, mg/kg	9690
SO_4^{-2}, mg/kg	1430
$C_2O_4^{-2}$, mg/kg	850

The SB6A sludge was spiked with mercury and noble metals in later test phases, as they may catalyze the degradation of chemical defoamers.

Table III. SB6A Mercury and Noble Metal Concentration

Metal	**Concentration wt% total solids basis**
Hg	2.58
Rh	0.0165
Ru	0.0824
Ag	0.0103
Pd	0.0041

In addition, a Precipitate Reactor Feed Tank (PRFT) simulant containing monosodium titanate was prepared. Foaminess was induced by reducing particle size through high shear mixing.

Table IV. PRFT Simulant

Component	**Concentration, wt%**
H_2O	94.56
Monosodium Titanate	2.67
Na_2CO_3	0.43
$Na_2O\cdot Al_2O_3\cdot 3H_20$	0.41
$NaNO_2$	0.48
$NaNO_3$	0.52
K_2CO_3	0.03
NaOH	0.89
NaHCOO	0.01

Alternative Antifoam Agents

Antifoam experts at the Illinois Institute of Technology (ITT) identified the hydrolysis resistant superwetters Momentive™ Y-17112, Momentive™ Y-17309, and Momentive™ Y-17581 as alternative antifoam agents for HLW processing at DWPF. Seven additional superwetters and thirteen traditional antifoam agents were recommended by leading manufacturers and selected for further testing.

Table V. Superwetters Identified for Testing

Superwetter	**Type of Compound**
Momentive™ Y-17581	Superwetter

Momentive™ Y-17309	Superwetter
Momentive™ Y-17112	Superwetter
Chemours Capstone™ FS-3100	Fluorinated Superwetter
Chemours Capstone™ FS-50	Fluorinated Superwetter
Chemours Capstone™ FS-30	Fluorinated Superwetter
3M FC-4430	Fluorinated Superwetter
3M FC-4432	Fluorinated Superwetter
3M FC-4434	Fluorinated Superwetter
Evonik Dynol 607	Nonionic Superwetter

Table VI. Traditional Antifoams Identified for Testing

Antifoam	**Type of Compound**
BASF Foamaster® MO 2111 NC	Mineral Oil Defoamer
BASF Foamaster® MO 2140	Mineral Oil Defoamer
BASF Foamaster® MO 2172	Mineral Oil Defoamer
BASF Foamaster® MO 2185	Mineral Oil Defoamer
BASF FoamStar® ST 2412	Mineral Oil Defoamer
BASF FoamStar® ST 2420	Mineral Oil Defoamer
Dow XIAMETER® AFE-1010	Silicon Antifoam
Dow XIAMETER® ACP-1400	Silicon Antifoam
Dow XIAMETER® ACP-1430	Silicon Antifoam
Dow XIAMETER® AFE-1410	Silicon Antifoam
Dow XIAMETER® ACP-3183	Silicon Antifoam
Evonik Surfynol® AD01	Wetting surfactant
Evonik Surfynol® MD-20	Oxirane/Diol defoamer

Review of the individual safety data sheets and results from initial screening tests were utilized to down select and identify the best alternative chemical defoamers. A Teclis FoamScan foam analyzer was used to estimate the required concentration of each defoaming agent necessary to control foaming of a physical simulant. The foam column was filled with approximately 60 mL acidic (pH 4) or caustic (pH 13) physical simulant and continuously purged with air. Defoamer was added in concentrations ranging from 5 ppm to 500 ppm and the reduction in foam height was noted.

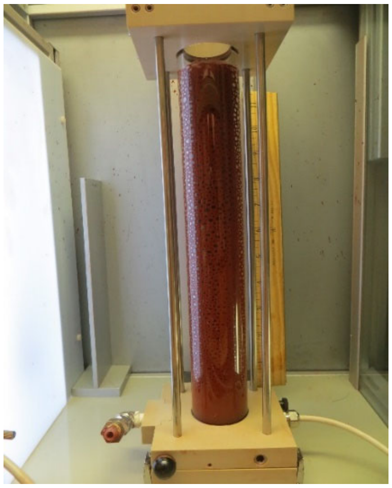

Figure 4. Caustic Physical Simulant; No Defoamer

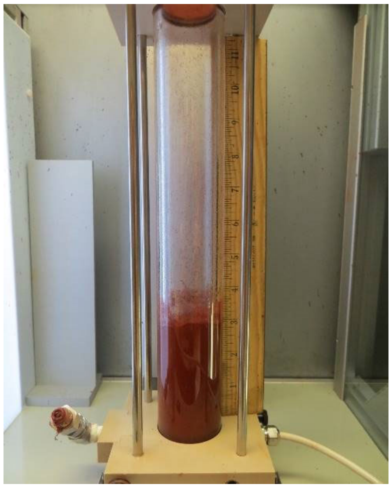

Figure 5. Caustic Physical Simulant; 25 ppm Evonik Surfynol® MD20

The superwetters and antifoams were also tested at a typical DWPF processing temperature of 102°C – 103°C in 150 mL acidic (pH 4) and caustic (pH 13) chemical simulants. Diluted antifoam was added in 5 mL aliquots and the time required for foam reformation was observed.

Table VII. Results of Initial Screening Tests

Effective	Moderately Effective	Ineffective	Not Tested
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Defoamer	Physical Simulant		Chemical Simulant	
	pH 4	**pH 13**	**pH 4**	**pH 13**
Siovation Antifoam 747	30 - 60 min	30 - 60 min	< 30 min	30 - 60 min
Evonik Surfynol® MD20	> 60 min	> 60 min	> 60 min	> 60 min
Momentive™ Y-17112	> 60 min	> 60 min	> 60 min	> 60 min
BASF FoamStar® ST 2412	> 60 min	> 60 min	> 60 min	> 60 min
3M FC-4430	> 60 min	> 60 min	> 60 min	> 60 min
Dow XIAMETER® AFE-1010	> 60 min	> 60 min	> 60 min	30 - 60 min
Momentive™ Y-17309	> 60 min	30 - 60 min	30 - 60 min	30 - 60 min
3M FC-4432	> 60 min	30 - 60 min	30 - 60 min	30 - 60 min
3M FC-4434	30 - 60 min	> 60 min	30 - 60 min	30 - 60 min
BASF Foamaster® MO 2111 NC	> 60 min	30 - 60 min	30 - 60 min	30 - 60 min
Dow XIAMETER® ACP-1430	30 - 60 min	30 - 60 min	▨	▨
BASF Foamaster® MO 2172	30 - 60 min	30 - 60 min	▨	▨
BASF Foamaster® MO 2185	30 - 60 min	30 - 60 min	▨	▨
BASF FoamStar® ST 2420	30 - 60 min	30 - 60 min	▨	▨
Evonik Dynol® 607	30 - 60 min	30 - 60 min	▨	▨
Dow XIAMETER® AEF-1410	< 30 min	> 60 min	▨	▨
Evonik Surfynol® AD01	30 - 60 min	< 30 min	▨	▨

Momentive™ Y-17581	< 30 min	< 30 min		
Chemours Capstone™ FS-3100	< 30 min	< 30 min		
Chemours Capstone™ FS-50	< 30 min	< 30 min		
Chemours Capstone™ FS-30	< 30 min	< 30 min		
BASF Foamaster® MO 2140	< 30 min	< 30 min		
Dow XIAMETER® ACP-3183	< 30 min	< 30 min		
Dow XIAMETER® ACP-1400	< 30 min	< 30 min		

Approximately 1000 ppm of Antifoam 747 was necessary to control foam generation for 15 minutes. However, only 25 ppm Momentive™ Y-17112 and Evonik Surfynol® MD-20 controlled foam reformation for over an hour. The test results of Antifoam 747 and the five best alternative antifoams are summarized in Table IX.

Table VIII. Test Results – Antifoam 747 and Best Alternatives

Defoamer	Concentration	Foam Control Duration
Siovation Antifoam 747	~ 1000 ppm	~ 15 min
Momentive™ Y-17112	~ 25 ppm	> 60 min
Evonik Surfynol® MD-20	~ 25 ppm	> 60 min
3M FC-4430	~ 75 ppm	> 60 min
BASF FoamStar® ST 2412	~ 300 ppm	> 60 min
Dow XIAMETER® AFE-1010	~ 250 ppm	~ 30 min

Antifoam 747 and the five down selected alternative defoamers were tested in laboratory scale experiments, simulating HLW processing in DWPF's Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mixed Evaporator (SME), utilizing a Mettler Toledo RC1mx Reaction Calorimeter. The instrument allowed for improved quality control: automated reagent additions, precise temperature control, repeatability, and data collection. Offgas instrumentation (gas chromatograph, mass spectrometer, and infrared spectrometer) was utilized to monitor for potential flammable offgas species and degradation products.

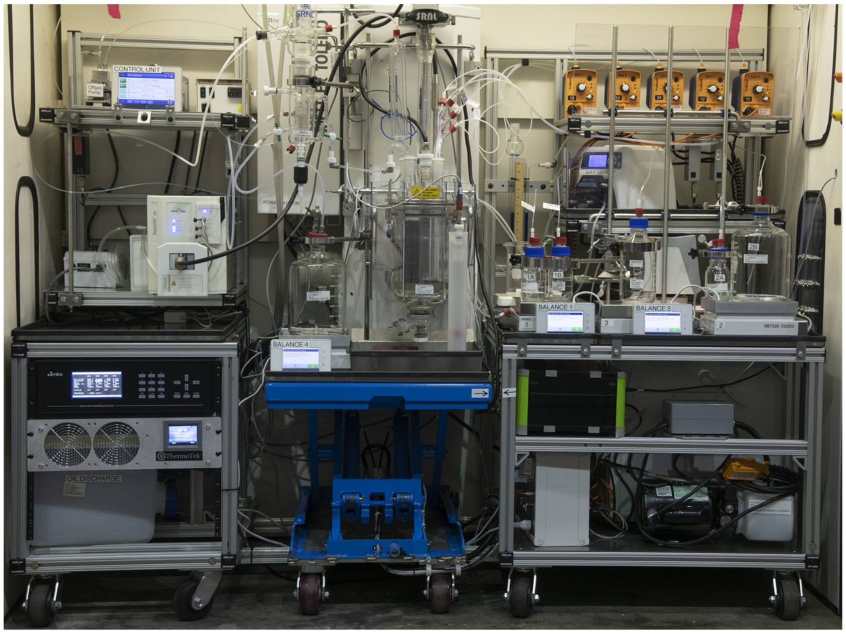

Figure 6. Mettler Toledo RC1mx Used for Laboratory Scale SRAT/SME Simulations

Conditions for testing included: SB6A sludge (foamiest identified), addition of mercury and noble metals (Ag, Pd, Rh, and Ru), addition of foamy PRFT simulant, the addition of nitric and glycolic acid (reducing acid to be implemented in DWPF in the future), and increased processing time due to large volume of strip effluent. SRAT and SME cycles consist of various phases including: caustic boiling, PRFT addition, acid addition, SRAT dewater, strip effluent addition, decontamination water addition, and process frit addition. Initially, the five best alternative defoamers were tested in shortened SRAT experiments consisting only of caustic boiling and PRFT addition. Momentive™ Y-17112, Evonik Surfynol® MD-20, and 3M FC-4430 controlled foam generation satisfactory. Concentrations of 50 mg/kg were sufficient to control foaming. While 3M FC-4430 was effective at controlling foam at a minimal concentration, it was rejected as an alternative defoamer for DWPF due the presence of highly reactive fluorine molecules. BASF FoamStar® ST 2412 and Dow XIAMETER® AFE-1010 were unsuccessful at controlling foam, resulting in large foamovers.

Table IX. Test Results – Caustic Boiling and PRFT Addition

Defoamer	**Concentration Required to Control Foaming**	**Offgas Species**	**Comment**
Momentive™ Y-17112	50 mg/kg	*None above 50 ppb*	Silane – No Si-O
Evonik Surfynol® MD-20	50 mg/kg	*None above 50 ppb*	Gemini – No Si
3M FC-4430	50 mg/kg	*None above 50 ppb*	Fluorinated Superwetter

BASF FoamStar® ST 2412	NA	NA	Large Foamover; Stopped Experiment
Dow XIAMETER® AFE-1010	NA	NA	Large Foamover; Stopped Experiment

Siovation Antifoam 747, Momentive™ Y-17112, and Evonik Surfynol® MD-20 were tested in full SRAT/SME simulations with glycolic acid. 1625 mg/kg Siovation Antifoam 747 was necessary to control foaming during the first experiment. The purge was increased to prevent flammability, as trimethylsilanol and hexamethyldisiloxane were detected. Only 100 mg/kg Momentive™ Y-17112 and 200 mg/kg Evonik Surfynol® MD-20 were required to control foam in subsequent tests and degradation products were not detected in the offgas streams.

Table X. Test Results – Full SRAT/SME Simulations with Glycolic Acid

Defoamer	Siovation Antifoam 747	Momentive™ Y-17112	Evonik Surfynol® MD-20
Degradation Products in Offgas	Trimethylsilanol Hexamethyldisiloxane	*None above 50 ppb*	*None above 50 ppb*
Quantity of Defoamer Required (mg/kg)	*1625*	*100*	*200*
Solubility in Water	*Insoluble*	*Insoluble*	*Insoluble*
Commercial Ingredient	No	Yes	Yes
Volume per Batch	~19.5 gal	~1.2 gal	~2.4 gal

Since DWPF would benefit from implementing a new chemical defoamer prior to transitioning to the glycolic acid flow sheet, the SRAT/SME simulations were repeated with formic acid (the reducing acid currently in use). Under this condition, concentrations of 300 mg/kg Momentive™ Y-17112 and 1125 mg/kg Evonik Surfynol® MD-20 were necessary to control foaming. While both alternative defoamers outperformed Siovation Antifoam 747, Momentive™ Y-17112 was able to control foam at minimal concentrations under glycolic acid and formic acid conditions.

Irradiation Testing

To validate the effectiveness of Momentive™ Y-17112 and Evonik Surfynol® MD20 in a radioactive environment, SB6 Version 1 Recipe A sludge simulant containing fresh antifoam was irradiated utilizing a Co-60 gamma source. Subsequent boiling tests were performed. The goal of this testing was to determine whether the irradiation causes decomposition of the antifoam, which would make it less effective at foam control and produce new species in the offgas or slurry.

Two sets of irradiations were performed. The first set of irradiations simulated the dose received from being in the SRAT Receipt SB9 Alternate Reductant Blend Slurry for one week (typical dose of SB9 sludge-only processing). The second set of irradiations simulated the dose received from being in the Coupled Operations Curie Balance - Sludge and SWPF Feed for two weeks (worst case radiation dose to antifoam from high Cs-137 from high SWPF volume of SE, approximately 700 times the dose rate compared to the SB9 Alternative Reductant Blend Slurry irradiation).

Table XI. SRAT Receipt SB9 Alternate Reductant Blend Slurry

Isotope	Mass Concentration (wt. % solids)	Activity Concentration (Ci/gal slurry)	% RSD
Tc-99	1.58E-03	1.98E-04	2.6
U-233	6.65E-04	4.76E-05	2.3
U-234	7.71E-04	3.56E-05	0.4
U-235	3.18E-02	5.08E-07	0.8
U-236	1.84E-03	8.79E-07	1.5
U-238	3.29E+00	8.18E-06	1.0
Np-237	2.80E-03	1.46E-05	0.4
Pu-238	1.06E-03	1.36E-01	25
Pu-239	9.28E-03	4.27E-03	1.3
Pu-240	9.07E-04	1.53E-03	2.4
Pu-239/240	NA	6.81E-03	31
Pu-241	3.67E-05	2.82E-02	26
Am-241	5.58E-04	1.43E-02	22
Am-242	1.75E-07	1.27E-05	7.1
Am-243	8.04E-05	1.20E-04	19
Cm-242	4.26E-10	1.05E-05	7.2
Cm-244	8.23E-06	4.96E-03	11
Cm-245	< 1.1E-04	< 1.4E-04	NA

Table XII. Coupled Operations Curie Balance - Sludge and SWPF Feed

Isotope	SRAT Activity Concentration (Ci/gal)
Co-60	2.73E-01
Sr-90	7.38E+01
Y-90	7.58E+01
Ru-106	5.48E-02
Rh-106	5.48E-02
Sb-125	1.34E+00
Te-125m	3.27E-01
Cs-134	1.15E+00
Cs-137	2.50E+02

Ba-137m	2.37E+02
Pr-144m	1.89E-01
Pm-147	3.90E+01
Sm-151	3.93E-01
Eu-152	5.94E-03
Eu-154	9.98E-01
Eu-155	7.67E-01
Pu-238	2.37E+00
Pu-239	2.06E-02
Pu-240	1.38E-02
Pu-241	2.66E+00
Am-241	1.72E-02
Cm-244	1.71E-01

Approximations of radiation dose absorbed in the SB9 Alternate Reductant Blend Slurry and Coupled Operations Curie Balance - Sludge and SWPF Feed were determined based upon their nuclide distributions. The volumetric activity concentration and known radioactive decay energy per disintegration of each nuclide were used to calculate an energy deposition rate, or dose, to the sludge material. It is conservatively assumed that all radioactive decay energy from alphas, betas, and photons are deposited locally in the sludge and no energy escapes. This approximation is reasonable for very massive systems such as a waste tank. The resulting sludge dose rate estimates are given in Table XIII. And Table XIV.

Table XIII. SB9 Alternate Reductant Blend Slurry – Dose Rate Estimate

SRAT Receipt SB9 Alternate Reductant Blend Slurry					
Nuclide	SRAT [Ci/gal]	W/Ci	W/L	W/kg	Rad/hr
Tc99	1.98E-04	5.01E-04	2.62E-08	2.38E-08	8.58E-03
U233	4.76E-05	2.86E-02	3.59E-07	3.27E-07	1.18E-01
U234	3.56E-05	2.83E-02	2.66E-07	2.42E-07	8.71E-02
U235	5.08E-07	2.71E-02	3.64E-09	3.31E-09	1.19E-03
U236	8.79E-07	2.66E-02	6.18E-09	5.62E-09	2.02E-03
U238	8.18E-06	2.49E-02	5.39E-08	4.90E-08	1.76E-02
Np237	1.46E-05	2.88E-02	1.11E-07	1.01E-07	3.63E-02
Pu-238	1.36E-01	3.26E-02	1.17E-03	1.06E-03	3.83E+02
Pu-239	4.27E-03	3.02E-02	3.41E-05	3.10E-05	1.12E+01
Pu-240	1.53E-03	3.06E-02	1.24E-05	1.12E-05	4.04E+00
Pu-241	2.82E-02	3.20E-05	2.38E-07	2.17E-07	7.80E-02
Am-241	1.43E-02	3.28E-02	1.24E-04	1.13E-04	4.06E+01
Am242m	1.27E-05	4.05E-04	1.36E-09	1.24E-09	4.45E-04
Am243	1.20E-04	3.15E-02	9.98E-07	9.08E-07	3.27E-01
Cm242	1.05E-05	3.57E-02	9.90E-08	9.00E-08	3.24E-02
Cm-244	4.96E-03	3.44E-02	4.50E-05	4.09E-05	1.47E+01
				Total:	**4.54E+02**

Table XIV. Coupled Operations Curie Balance - Sludge and SWPF Feed - Dose Rate Estimate

Coupled Operations Curie Balance – Sludge and SWPF Feed					
Nuclide	SRAT [Ci/gal]	W/Ci	W/L	W/kg	Rad/hr
Co-60	2.73E-01	1.54E-02	1.11E-03	1.01E-03	3.64E+02
Sr-90	7.38E+01	1.16E-03	2.26E-02	2.06E-02	7.40E+03
Y-90	7.58E+01	5.54E-03	1.11E-01	1.01E-01	3.63E+04
Ru-106	5.48E-02	5.95E-04	8.62E-06	7.83E-06	2.82E+00
Rh-106	5.48E-02	1.89E-02	2.74E-04	2.49E-04	8.97E+01
Sb-125	1.34E+00	3.37E-03	1.19E-03	1.08E-03	3.90E+02
Te-125m	3.27E-01	8.69E-04	7.51E-05	6.82E-05	2.46E+01
Cs-134	1.15E+00	1.02E-02	3.10E-03	2.81E-03	1.01E+03
Cs-137	2.50E+02	1.01E-03	6.67E-02	6.06E-02	2.18E+04
Ba-137	2.37E+02	3.94E-03	2.47E-01	2.24E-01	8.07E+04
Pr-144m	1.89E-01	3.43E-04	1.71E-05	1.56E-05	5.60E+00
Pm-147	3.90E+01	3.67E-04	3.78E-03	3.44E-03	1.24E+03
Sm-151	3.93E-01	7.41E-04	7.69E-05	6.99E-05	2.52E+01
Eu-152	5.94E-03	7.65E-03	1.20E-05	1.09E-05	3.93E+00
Eu-154	9.98E-01	9.08E-03	2.39E-03	2.18E-03	7.84E+02
Eu-155	7.67E-01	7.59E-04	1.54E-04	1.40E-04	5.03E+01
Pu-238	2.37E+00	3.26E-02	2.04E-02	1.86E-02	6.68E+03
Pu-239	2.06E-02	3.02E-02	1.65E-04	1.50E-04	5.39E+01
Pu240	1.38E-02	3.06E-02	1.11E-04	1.01E-04	3.65E+01
Pu-241	2.66E+00	3.20E-05	2.25E-05	2.04E-05	7.36E+00
Am-241	1.72E-02	3.28E-02	1.49E-04	1.36E-04	4.88E+01
Cm-244	1.71E-01	3.44E-02	1.55E-03	1.41E-03	5.08E+02
				Total:	**1.58E+05**

Gamma irradiation was performed using a J.L Shepherd Model 484 Co-60 gamma irradiator. This model features a 10” x 10” x 40” irradiation chamber with two Co-60 radionuclide sources at one end to deposit a desired dose rate as a function of the target’s distance to the source (Figure 7). Dosimetry at various points in the irradiator was performed by the vendor at the time of installation with NIST traceable calibration. Additional dose rate modeling was performed at SRNL using Monte Carlo N-Particle version 6.1 (MCNP 6.1), an industry standard and highly benchmarked radiation transport code. Dose rate modeling accounts for geometric and self-shielding attenuation of the target itself. The volumetric average dose rate to the sludge given the experimental setup and vessel placement within the irradiator was determined to be 74.2 krad/hr.

Figure 7. Photo of Irradiation Setup

Glass vessels were filled with approximately 150 mL SB6 Version 1 Recipe A sludge simulant. An antifoam concentration of 500 ppm was targeted. Two lots of Momentive™ Y-17112 were tested: Momentive™ Y-17112-14DSV and Momentive™ Y-17112-19FSV. Irradiation was also performed on a "Blank" that did not contain antifoam, acting as a control. The vessels were sealed and placed as close to the Co-60 source as possible. Two vessels were placed in the irradiator at a time. The vessels were continuously purged with gas (0.5% krypton and 20% oxygen in nitrogen) at a flow rate of 0.5 sccm (standard cubic centimeter per minute). Standard condition is defined as 0°C and 1 atm. The offgas was collected in Tedlar bags and later analyzed by VOA. The sludge was irradiated for the required timeframe as indicated in Table XV and Table XVI.

Table XV. SB9 sludge-only Dose – Irradiations

Antifoam	SB6 V1RA Simulant (g)	Antifoam Concentration (ppm)	Time Irradiated (min)	Simulated Dose Rate (rad/hr)	Simulated Dose One Week (krad)
Blank	168.3	0	62	454	76.3
MD-20	168.2	505	62	454	76.3
Y17112-14DSV	168.4	505	62	454	76.3
Y17112-19FSV	168.4	505	62	454	76.3

Table XVI. Maximum Coupled Dose - Irradiations

Antifoam	SB6 V1RA Simulant (g)	Antifoam Concentration (ppm)	Time Irradiated (days)	Simulated Dose Rate (rad/hr)	Simulated Dose Two Weeks (krad)
Blank	168.3	0	30	1.58E+05	53,100
MD-20	168.3	505	30	1.58E+05	53,100
Y17112-14DSV	168.3	505	30	1.58E+05	53,100
Y17112-19FSV	168.4	505	30	1.58E+05	53,100

Post irradiation boiling tests were performed to determine whether the defoamers remained effective at controlling foam. The sludge was heated and agitated on a hot plate until vigorous boiling was achieved. The liquid and foam height was closely monitored for approximately one hour. Post irradiation sludge samples were analyzed for VOA and SVOA compounds.

The offgas collected in the Tedlar bags was evaluated by VOA by Analytical Development. 100 mL of gas was collected via an airtight syringe and injected into the GCMS for separation and mass spectrometer analysis. The sludge was also examined by VOA and SVOA post irradiation. If the antifoams were to degrade, one would expect to detect methane, methanol, ethane, ethylene, ethyleneoxide, and dimethylsiloxane. No volatile organic compounds or semi volatile organic compounds were identified above the method detection limits. The method detection limit for VOA was 0.2 mg/L or 0.25 mg/L. The method detection limit for SVOA was 1 mg/L. During post irradiation boiling tests, foam was only generated in the "Blank" (Figure 8). The SB6 Version 1 Recipe A sludge simulant containing Momentive™ Y-17112-14DSV, Momentive™ Y-17112-19FSV, and Evonik Surfynol® MD20 did not foam post irradiation. The results are reported in Table XVII for the SB9 sludge-only dose irradiations and in Table XVIII and XIX for the maximum coupled irradiations.

Table XVII. SB9 Sludge-only Dose – Slurry Results

Antifoam	VOA Offgas (mg/L)	VOA Post Irradiation Sludge (mg/L)	SVOA Post Irradiation Sludge (mg/L)	Foam Generation Post Irradiation Boiling
Blank	< 0.25*	< 0.25*	< 1*	Yes
MD-20	< 0.25*	< 0.25*	< 1*	No
Y-17112-14DSV	< 0.25*	< 0.25*	< 1*	No
Y-17112-19FSV	< 0.25*	< 0.25*	< 1*	No

*Below Method Detection

Table XVIII. Maximum Coupled Dose – Offgas Results

Antifoam	VOA Week 1 (mg/L)	VOA Week 2 (mg/L)	VOA Week 3 (mg/L)	VOA Week 4 (mg/L)
Blank	NA†	< 0.2*	< 0.2*	< 0.2*
MD-20	< 0.2*	< 0.2*	< 0.2*	< 0.2*
Y17112-14DSV	NA†	< 0.2*	< 0.2*	< 0.2*
Y17112-19FSV	< 0.2*	< 0.2*	< 0.2*	< 0.2*

† Offgas Quantity Collected Insufficient for Analysis
*Below Method Detection Limit

Table XIX. Maximum Coupled Dose – Slurry Results

Antifoam	VOA Post Irradiation Sludge (mg/L)	SVOA Post Irradiation Sludge (mg/L)	Foam Generation Post Irradiation Boiling
Blank	< 0.2*	< 1*	Yes
MD-20	< 0.2*	< 1*	No
Y17112-14DSV	< 0.2*	< 1*	No
Y17112-19FSV	< 0.2*	< 1*	No

*Below Method Detection Limit

Figure 8. Maximum Coupled Dose Post Irradiation Boiling Tests – Blank (left); Y-17112-14DSV (right)

These results indicate that Momentive™ Y-17112 and Evonik Surfynol® MD20 did not significantly degrade and remained effective at foam control after being exposed to a simulated dose equivalent to 53,100 krad in a caustic environment (bounding for antifoam degradation) for a prolonged period of time (30 days). Furthermore, exposing Momentive™ Y-17112 and Evonik Surfynol® MD20 to these conditions did not lead to the formation of flammable degradation products.

Conclusion

Foaming of high-level waste (HLW) slurries is an issue at the Defense Waste Processing Facility (DWPF) Chemical Process Cell (CPC) which is currently mitigated with a chemical antifoam agent. The effectiveness of non-chemical methods for foam control and the efficiency of alternative antifoams were examined to improve HLW treatment at DWPF and to eliminate the flammability hazards associated with Siovation Antifoam 747 currently in use. Two suitable alternative defoaming agents, Momentive™ Y-17112 and Evonik Surfynol® MD-20, were identified. Both defoamers control foam over a pH range of 4-13 at boiling, with no flammable degradation products, and only minimal quantities (100 – 200 mg/kg) are required under glycolic acid conditions. Furthermore, Momentive™ Y-17112 and Evonik Surfynol® MD20 did not significantly degrade and remained effective at foam control after being exposed to a simulated dose equivalent to 53,100 krad in a caustic environment (bounding for antifoam degradation) for a prolonged period of time (30 days).

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