

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).

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

- 1) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
- 2) representation that such use or results of such use would not infringe privately owned rights; or
- 3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Development of Novel Foaming Solutions for High Level Waste (HLW) Processing

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. However, alternatives are being evaluated to potentially improve operations in support of the Salt Waste Processing Facility (SWPF) startup. The efficiency of alternative antifoams and the effectiveness of non-chemical methods for foam control were examined to improve HLW treatment at DWPF and to eliminate the flammability hazards associated with Antifoam 747 currently in use. Initial results indicate that Y-17112, a superspreader developed by Momentive Performance Materials, may be more suitable for use at DWPF. Non-chemical foam control strategies were also evaluated; however, they were found less effective than chemical methods and would be impractical to implement. Alternative chemical antifoams and process changes, e.g. sequencing, to mitigate foam generation during HLW treatment at DWPF will be further investigated in the future.

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature

Date

Development of Novel Foaming Solutions for High Level Waste (HLW) Processing

Project Team: D.P. Lambert, A.M. Howe, W.H Woodham, D.J. Newell, D. J. Adamson, M.E. Kinard, T.L. Earls, V. B. Timmerman, G. R. Golcar, A. A. Ramsey

Thrust Area: Environmental Stewardship

Project Start Date: October 1, 2017

Project End Date: September 30, 2018

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. However, alternatives are being evaluated to potentially improve operations in support of the Salt Waste Processing Facility (SWPF) startup. The efficiency of alternative antifoams and the effectiveness of non-chemical methods for foam control were examined to improve HLW treatment at DWPF and to eliminate the flammability hazards associated with the Antifoam 747 currently in use. Initial results indicate that Y-17112, a superspreader developed by Momentive Performance Materials, may be more suitable for use at DWPF. Non-chemical foam control strategies

were also evaluated; however, they were found less effective than chemical methods and would be impractical to implement. Alternative chemical antifoams and process changes, e.g. sequencing, to mitigate foam generation during HLW treatment at DWPF will be further investigated in the future.

FY2018 Objectives

- Identify alternative antifoam agents and non-chemical solutions for foam control
- Determine efficiency of alternative antifoam agents
- Determine effectiveness of non-chemical methods

Introduction

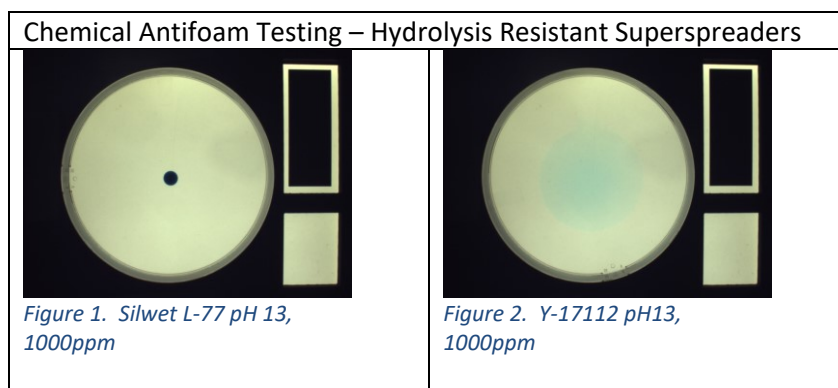
Foaming occurs during treatment of high level waste (HLW) at Savannah River Site's Defense Waste Processing Facility (DWPF) in the Chemical Process Cell (CPC) due to high gas generation from process steam and chemical off gas products¹. The presence of amphiphilic particles in the waste slurry stabilizes the foam. Efficient processing of HLW requires foam control, as foamovers lead to lower productivity and potential radioactive contamination of condensate streams. DWPF currently employs Antifoam 747, a surfactant produced by Momentive Performance Materials, as an antifoaming agent during waste treatment². While it controls foam, processing issues have arisen from its use. During DWPF chemical processing, antifoam must be effective up to 103°C and between a pH range of 3-13. Antifoam 747 is efficient at pH 6-8 but degrades outside this optimal pH range³. Savannah River National Laboratory (SRNL) has identified multiple flammable antifoam degradation products during laboratory scale experiments.

The efficiency of alternative antifoam agents and the effectiveness of non-chemical methods for foam control were evaluated as part of an effort to improve HLW treatment operations at DWPF and to eliminate, or reduce, the flammability hazards associated with Antifoam 747 currently in use.

Approach

Chemical Antifoam Testing

Through collaboration with antifoam experts at the Illinois Institute of Technology (ITT) the following hydrolysis resistant superspreaders, produced by Momentive Performance Materials, were identified and selected for further testing: Y-17112, Y-17309, Y-17581. The efficiency of these superspreaders along with Silwet L-77 (the main component of Antifoam 747) were tested across a wide pH range (1 – 13) at varying concentrations (100 ppm – 5000 ppm). A 50 μ L drop of antifoam solution was placed on a backlit Petri dish. Utilizing a specialized camera and software, the coverage area was measured over a 60 second time interval as each solution spread as shown in Figure 1 and Figure 2.



Mechanical Methods for Foam Control

In addition, several non-chemical foam control strategies were proposed, discussed, and evaluated by a multi-disciplinary team, including DWPF process control engineers^{4,5}. The strategies that were ranked most likely to be effective for foam control were identified for further evaluation, including: the use of liquid spray/mist, agitators in the headspace, and ultrasonic energy. These alternative methods were tested in laboratory scale experiments using physical and chemical simulants. The simulant was heated to boiling ($\sim 100^{\circ}\text{C}$) and agitated, simulating DWPF processing. Foam generation was carefully monitored while the potential mechanical methods for foam control were tested. Process changes, particularly with respect to operations sequencing, (addition of acid while boiling, processing more dilute/concentrated slurries, delay boiling until chemical reactions are complete, etc.) were also identified as a feasible foam control strategy.

Mechanical Methods for Foam Control – Agitation

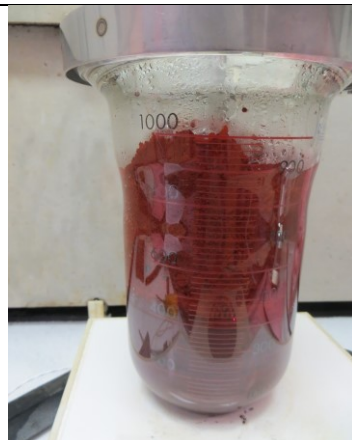


Figure 3. No Foam Control During Mixing/Boiling



Figure 4. Headspace Agitators During Mixing/Boiling

Results/Discussion

Chemical Antifoam Testing

Initial spread rate (cm^2/s) across a pH range of 1 to 13 and degradation time were utilized to determine the efficiency of each superspreader as an antifoam agent during DWPF chemical processing. Silwet L-77 and Y-17112 outperformed Y-17309 and Y-17581, achieving greater spread rates and sustaining chemical stability. Silwet L-77 attained the highest spread rates of $2.7 \text{ cm}^2/\text{s}$ and $2.0 \text{ cm}^2/\text{s}$ at pH 8.5 and 9 respectively. In extreme acidic and alkaline conditions, however, Silwet L-77 solutions failed to spread at all. Y-17112 achieved consistent spread rates between $1.0 \text{ cm}^2/\text{s}$ and $1.5 \text{ cm}^2/\text{s}$ across the entire pH range, even at lower concentrations. These initial results indicate that Y-17112 may be a more suitable antifoam agent for HLW waste treatment in DWPF. The efficiency of Y-17112 must first be confirmed in laboratory scale boil tests, which will replicate actual waste treatment.

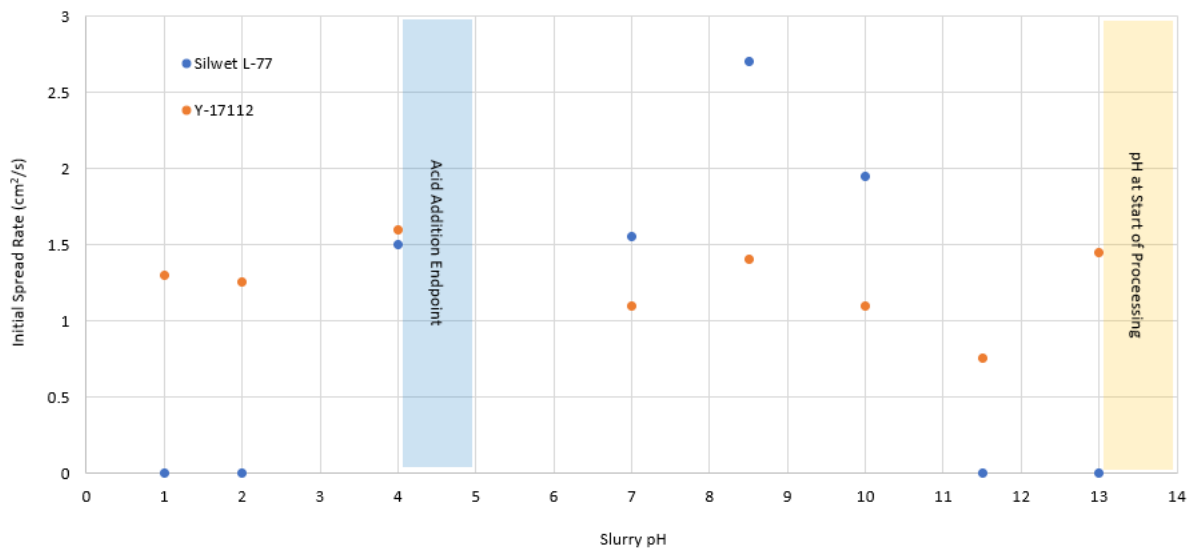


Figure 5. Initial Spread Rate (cm^2/s) of Silwet L-77 and Y-17112 Solutions (1000 ppm) Across pH Range

Mechanical Methods for Foam Control

During the initial test, where no method for foam control was implemented, the liquid level increased from 500 mL to 980 during boil up. The liquid level nearly doubled, resulting in foam generation of 96%. Ultra-sonication did not reduce foam production. Agitation through ultrasonic energy thickened the foam, stabilizing it further. Spraying the generating foam with fine water particles (at a rate of 380 mL/hr) reduced the foam level to 8%, but once the water mist was discontinued the foam level again increased to 96%. While spraying appeared promising, the quantity of water required to control foaming during HLW processing in DWPF would likely be inviable.

Table 1. Results of Non-chemical Foam Control Tests

Non-chemical Method	Liquid Level Prior to Boiling (mL)	Liquid Level During Boiling (mL)	Foam Level (%)
No Foam Control	500	980	96
Water Spray/Mist (~380 mL/hr)	500	540	8 ¹
Headspace Agitators	450	750	67
Ultrasonic Energy (750 Watts; 20 kHz)	400	>1000	>100

¹During spraying/misting; Foam level increased to 96% once spray/mist was stopped

²Ultra-sonication led to a thicker more stable foam

The use of agitators in the headspace reduced the rate of foam generation and a maximum foam level of 67% was achieved. Space in DWPF processing tanks, however, is limited due to the presence of existing equipment and instrumentation, making the installation and use of additional agitators in the headspace impractical⁶. These results suggest that the implementation of effective non-chemical foam control strategies in DWPF are not feasible. Alternative chemical antifoams and process changes to mitigate foam generation during HLW treatment at DWPF will be further investigated in the future.

FY2018 Accomplishments

- Meeting with antifoam experts at Illinois Institute of Technology (IIT); Led to identification of hydrolysis resistant superspreaders.
- Tested the efficiency of superspreaders Y-17309, Y-17581, Y-17112 against Silwet L-77 across broad pH range; Y-17112 was identified as a possible replacement for Antifoam 747 currently used in DWPF.
- Collaborated with Savannah River Remediation (SRR) to identify possible non-chemical foam control strategies; Liquid spray/mist, headspace agitators, and ultrasonic energy, were selected and tested.

Future Directions

- Test superspreaders Y-17309, Y-17581, and Y-17112 in laboratory scale SRAT/SME cycles, simulating DWPF chemical processing.
- Perform SRAT/SME cycles with process changes: Addition of acid while boiling, processing more dilute/concentrated slurries, delay boiling until chemical reactions are complete, etc.

References

1. Calloway, J. T. B.; Martino, C. J.; Jantzen, C. M.; Wilmarth, W. R.; Stone, M. E.; Pierce, R. A.; Josephs, J. E.; Barnes, C. D.; Daniel, W. E.; Eibling, R. E.; Choi, A. S.; White, T. L.; Crowley, D. A.; Baich, M. A.; Johnson, J. D.; Vijayaraghavan, K.; Nikolov, A. P.; Wasan, D. T., *Radioactive Waste Evaporation: Current Methodologies Employed for the Development, Design and Operation of Waste Evaporators at the Savannah River Site and Hanford Waste Treatment Plant*. 2003, (37327), 157-170.
2. Koopman, D. C. *Comparison of Dow Corning 544 Antifoam to IIT747 Antifoam in the 1/240 SRAT*; WSRC-TR-99-00377; Savannah River Technology Center: Aiken, SC, 2000.
3. Lambert, D. P.; Koopman, D. C.; Newell, J. D.; Wasan, D. T.; Nikolov, A. P.; Weinheimer, E. K., *Improved Antifoam Agent Study End of Year Report, EM Project 3.2.3*. 2011.
4. Ramsey, A. A.; Golcar G., *Meeting Minutes from 12/05/2017 Brainstorming Session for Developing Non-chemical Foaming Solutions for Control of Foam in the DWPF Chemical Process Cell*; SRNL-L3100-2017-00066; Savannah River National Laboratory: Aiken, SC, 2018.
5. Ramsey, A. A., *Meeting Minutes from 02/08/2018 Follow-up Meeting Regarding Task 2A – Identification of Non-chemical Solutions for Foam Control*; SRNL-L3100-2018-00017; Savannah River National Laboratory: Aiken, SC, 2018.
6. Hansen, E. K., *Determination of the 1/6th Scale SERT Agitator Speeds*; SRNL-ITS-2005-00202, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2005.

Acronyms

CPC	Chemical Process Cell
DWPF	Defense Waste Processing Facility
HLW	High Level Waste
ITT	Illinois Institute of Technology
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SWPF	Salt Waste Processing Facility

Intellectual Property

Non-disclosure agreement between Savannah River National Laboratory (SRNL), Savannah River Remediation (SRR), and Momentive Performance Materials regarding the exact composition of Silwet L-77, Y-17581, Y-17309, and Y-17112.