SERDP

EXECUTIVE SUMMARY

Performance Improvements of ADA Fluorine-Free Foams Using New Additives

Sumaer Kamboj
Bill Gunter
ADA Technologies, Inc.

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SERDP Project WP22-3089

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Project: WP22-3089

TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

ACRONYMS AND ABBREVIATIONS

ADA	ADA Technologies, Inc.
AFFF	aqueous film forming foam
CAF	compressed air foam
DoD	Department of Defense
F3	fluorine-free foams
OSS	organosiloxane surfactant
SERDP	Strategic Environmental Research and Development Program

1.0 INTRODUCTION

Aqueous film-forming foams (AFFF) have been widely used for firefighting purposes, particularly for combating Class B (flammable liquid) fires. However, they have been found to contain toxic chemicals that pose significant environmental and health risks. As a result, the National Defense Authorization Act for FY 2020 mandated that all military sites phase out AFFFs by October 1, 2024. The Department of Defense (DoD) aimed to eliminate all fluorinated compounds from firefighting foam formulations and, in anticipation of this, the Strategic Environmental Research and Development Program (SERDP) funded research to develop alternative formulations for use against Class B fires. This study is part of the ongoing efforts to develop effective and environmentally friendly firefighting agents that can replace traditional fluorine-containing foams.

The introduction of fluorine-free foams (F3) presented an opportunity to mitigate the environmental and health risks associated with AFFFs while maintaining effective firefighting capabilities. Developing F3 formulations that met the updated MIL-SPEC standards for Class B firefighting foam was a critical step in this process. This study focused on the evaluation of various additives in F3 firefighting formulations, with the goal of identifying additives that could improve the performance of these formulations while adhering to the new environmental and safety standards.

2.0 OBJECTIVES

The primary objective of this study was to evaluate the effectiveness of various additives in F3 firefighting formulations in order to develop an F3 that met the updated MIL-SPEC standards for Class B firefighting foam. The study aimed to assess the impact of these additives on extinguishment time, burn-back time, and other relevant metrics while determining the potential benefits and limitations of using these additives in F3 firefighting formulations. Ultimately, the goal was to identify additives that could be used to meet current MIL-SPEC standards and contribute to the development of an effective, environmentally friendly F3 firefighting formulation.

To achieve this objective, the study focused on the following key areas:

- Investigate the performance of ADA Technologies, Inc.'s (ADA) F3 firefighting formulations containing various additives, including carbonates, polymers, and organosiloxane surfactants (OSS agents).
- Determine the compatibility of these additives with different delivery systems, such as compressed air foam (CAF) systems and non-aspirated systems with foam cannon nozzles.
- Evaluate the impact of these additives on extinguishment time, burn-back time, foam expansion rate, and other relevant metrics.
- Identify potential challenges and limitations associated with the use of these additives in F3 firefighting formulations, such as compatibility issues with specific delivery systems or reduced performance at higher ambient temperatures.

By addressing these key areas, the study aimed to contribute to the ongoing development of effective and environmentally friendly F3 firefighting formulations that could replace traditional fluorine containing AFFFs.

3.0 TECHNICAL APPROACH

The technical approach employed in this study involved a systematic evaluation of various additives in F3 firefighting formulations and their compatibility with different delivery systems. The study built upon the work conducted under the previous SERDP project WP20-5381, which focused on the development of two F3 formulations (42.8 and 50.8) containing a mixture of alkylglucose amide, OSS, and alkylpolyglucosides. These formulations were made using commercially available off-the-shelf products and mixed in batches ranging from 100 to 1000 mL. Before testing, the formulations were diluted to 3% in water.

To evaluate the effectiveness of different additives, this study focused on three main categories: carbonates, polymers, and OSS agents. Carbonate and polymer additives were milled into nanoparticles using a rotary mill to enhance their compatibility with the F3 formulations. The milling conditions were carefully controlled to ensure that the maximum temperature reached during the process was substantially below the decomposition temperature of each additive. The resulting nanoparticles were added to the F3 formulations at a concentration of 1%.

Two delivery systems were used to test the F3 formulations with different additives: a CAF system (Figure ES-1 and Figure ES-2) and a non-aspirated system with a foam tube nozzle. The CAF system was used for smaller 1-square-foot pan fire tests, while the non-aspirated system was used for larger 5- and 12.5-square-foot pan fire tests. The CAF system used a nitrogen line pressurized to 20 PSI to aerate the foam, which was injected inline by a 1000 mL syringe. Before exiting the nozzle, the aerated foam passed through a static inline mixer. In the non-aspirated system, the 3% diluted formulation was pressurized by nitrogen to 100 PSI in a stainless steel cylinder and controlled by a ball valve operated by the operator.

Figure ES-1. Compressed Air Foam (CAF) Delivery System

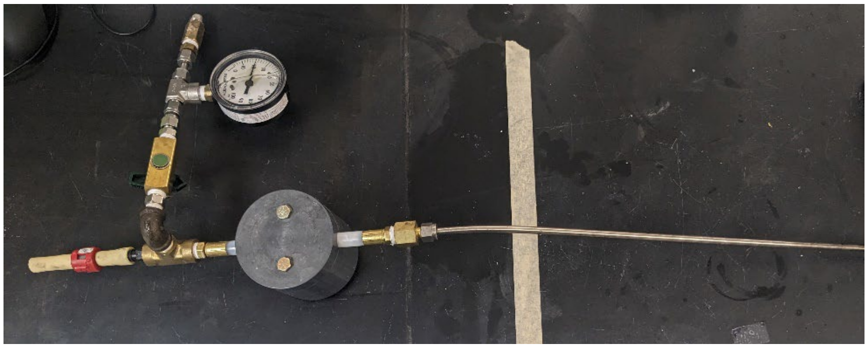

Figure ES-2. Close Up of CAF Delivery System Without Syringe and Nitrogen Line

Testing was conducted at ADA's facility in Littleton, Colorado, under ambient temperatures ranging from 50-90°F and an average humidityre of 30%. Steel pans were used for the tests, with fuel floating on a water layer to simulate the conditions specified in MIL-PRF-32725. The fuel amounts varied depending on the pan size: 300 mL for 1 ft^2, 1000 mL for 5 ft^2 (Figure ES-3), and 2500 mL for 12.5 ft^2 (Figure ES-4). The fires were allowed to pre-burn for 15 seconds before foam deployment.

Figure ES-3. 5 ft2 Class B Pool Fire (Heptane) Test with ADA Formulation

Figure ES-4. Setup of 12.5 ft^2 Fire Testing at ADA Facility

Extinguishment time, burn-back time, and formulation delivery rate were recorded for each test. Data was collected and plotted against delivery rate in gallons per minute per square foot (gpm/ft^2). The performance of each additive was compared to the base formulations (42.8 and 50.8) without additives, which were established as standards for comparison through repeat testing. Error bars were generated using the student t-test and given in a 90% confidence interval.

During testing of solid formulation additives such as carbonates and polymers, the solid powders underwent a milling process in the onsite planetary mill. Although size characterization of particles were not conducted, nanoparticles were created by using a planetary mill with 200g of steel ball media ranging in 1mm to 0.5mm to 0.3mm in a 2:1:1 ratio. Milling was conducted at 250 rpm for 2 hours with a 10 second on-time and 30 second off time. Temperature was monitored throughout the milling process to ensure temperature remained below the thermal degradation of each carbonate/polymer.

The technical approach adopted in this study aimed to provide a comprehensive understanding of how different additives impacted the performance of F3 firefighting formulations and their compatibility with various delivery systems. By analyzing the data collected from the tests, the study sought to identify additives that could improve the performance of F3 formulations while adhering to the updated MIL-SPEC standards for Class B firefighting foam.

4.0 RESULTS AND DISCUSSION

The results obtained from the experiments provided valuable insights into the performance of various additives in F3 firefighting formulations produced by ADA when used with different delivery systems. The findings of this study can be summarized and discussed as follows.

Carbonate 3 was found to enhance extinguishment and burn-back resistance (Figure ES-5 and Figures ES-6). However, when tested with the non-aspirated system, the carbonates exhibited little to no effect on extinguishment and, in some cases, reduced burn-back resistance. This suggests that the effectiveness of carbonate additives may be dependent on the delivery system used.

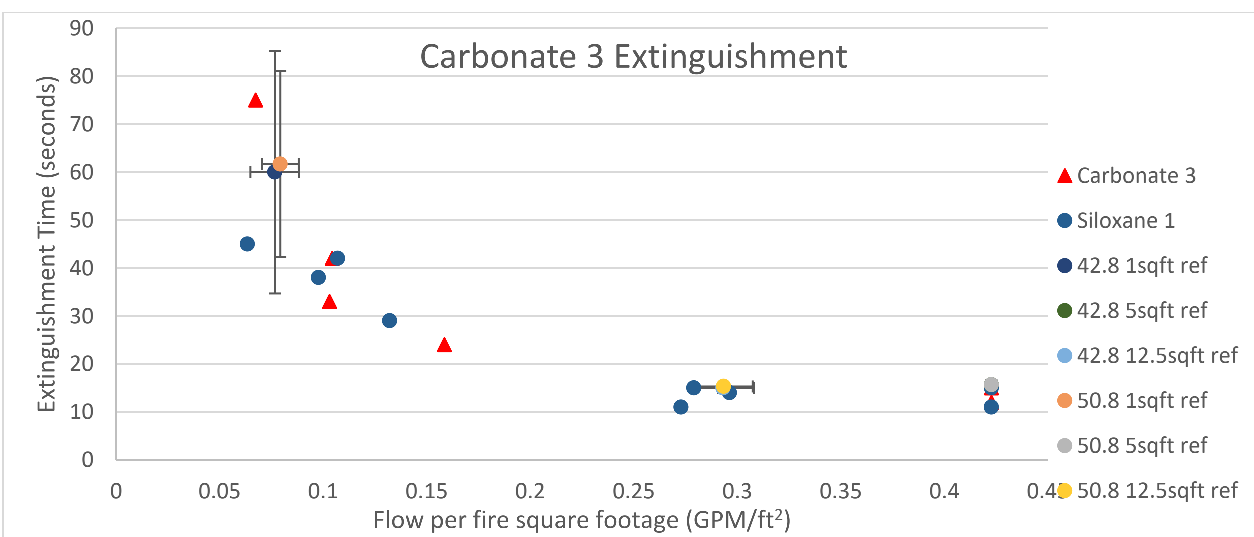

Figure ES-5. Carbonate 3 Extinguishment

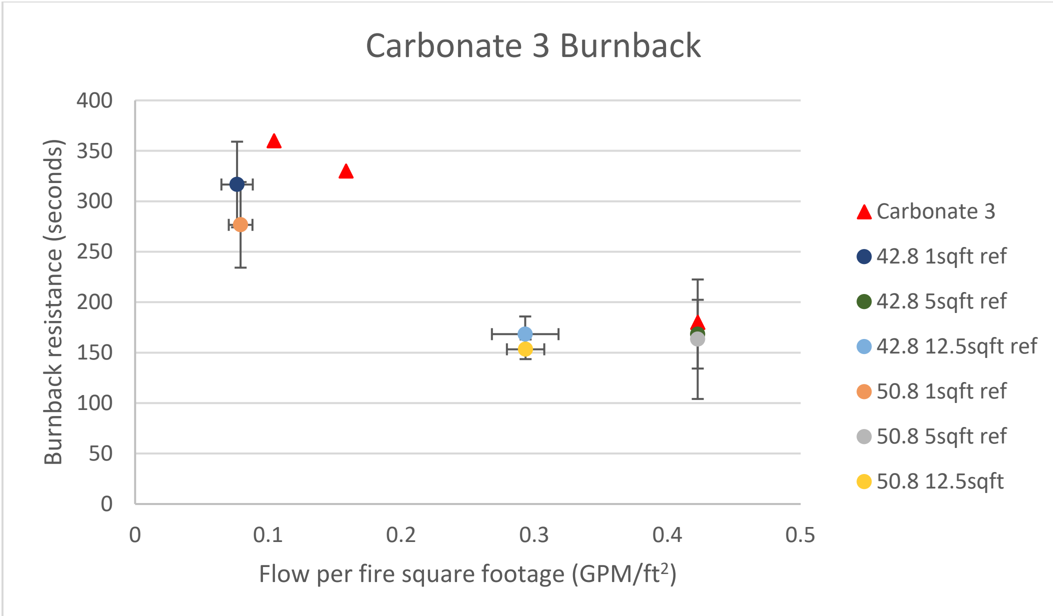

Figure ES-6. Carbonate 3 Burnback

Polymer additive 1 was observed to improve extinguishment time and burn-back resistance in the CAF and non-aspirated systems (Figures ES-7 and Figures ES-8). However, this polymer created non-Newtonian fluids that were not compatible with the non-aspirated nozzle used in the study. This highlighted the need for further investigation into the compatibility of polymer additives with different nozzle types and their impact on the overall performance of F3 firefighting formulations.

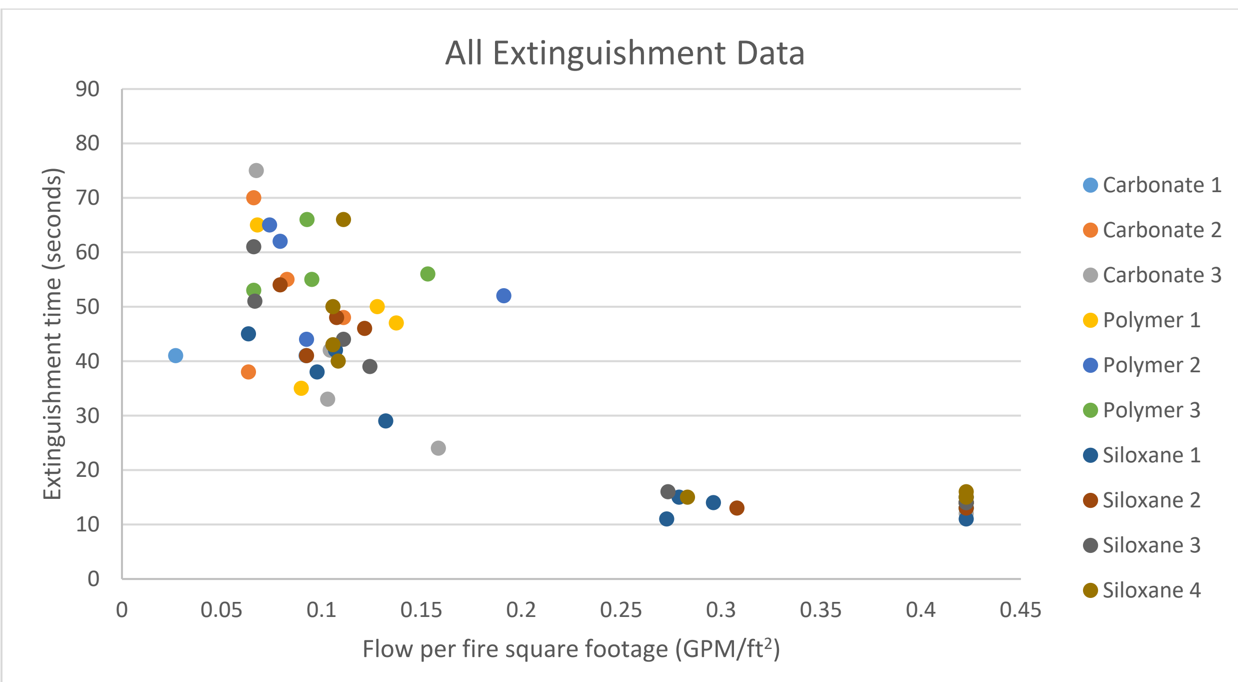

Figure ES-7. All Extinguishment Data

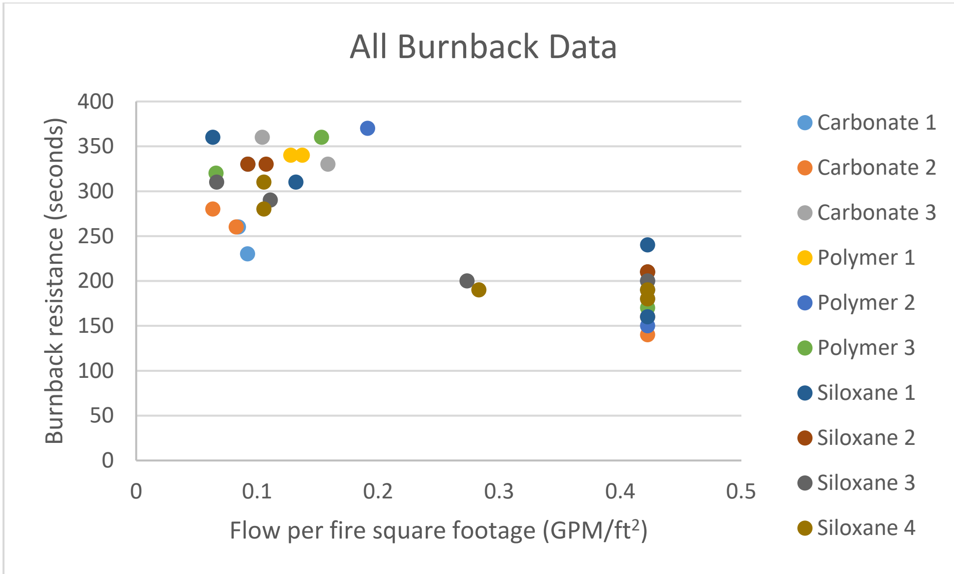

Figure ES-8. All Burnback Data

Siloxane surfactants demonstrated improvements in extinguishment and burn-back resistance in both delivery systems (Figure ES-9 and Figures ES-10). However, they also led to a decrease in foamability and were observed to have poorer performance at higher ambient temperatures. This indicated that while OSS additives may enhance certain aspects of the F3 formulations' performance, they may also introduce new challenges that need to be addressed.

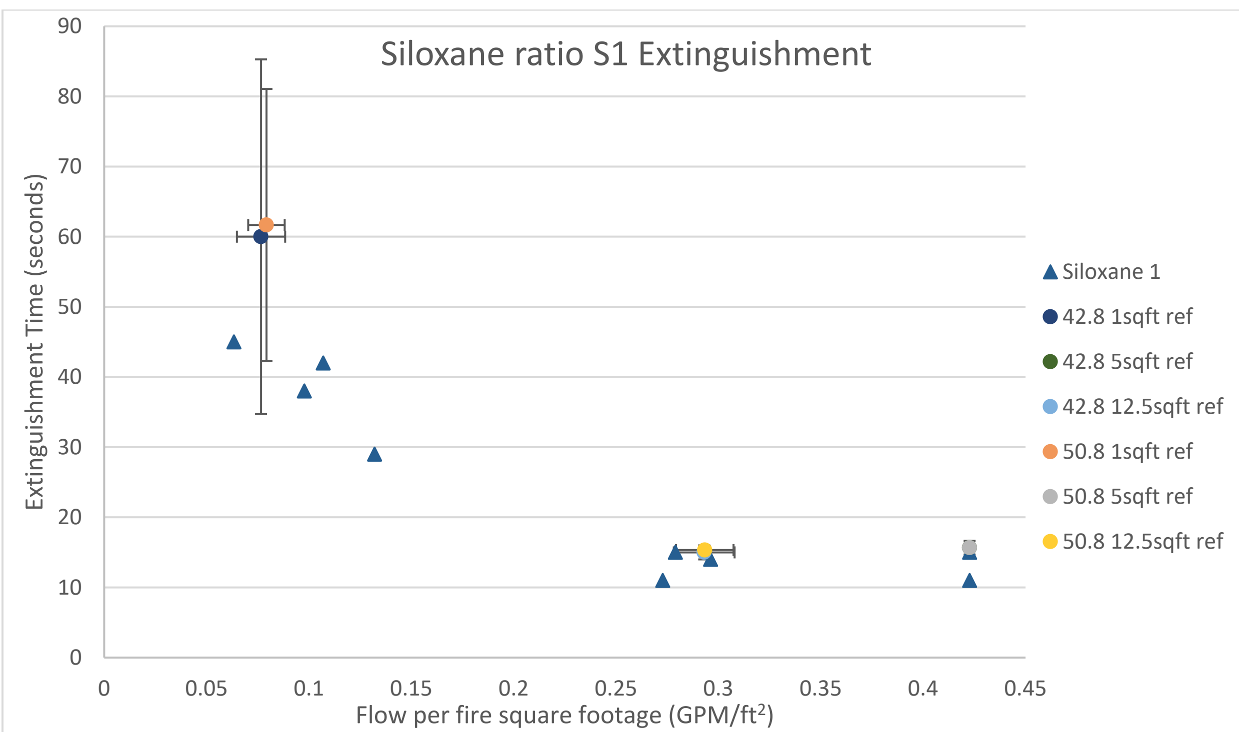

Figure ES-9. Siloxane ratio S1 Extinguishment

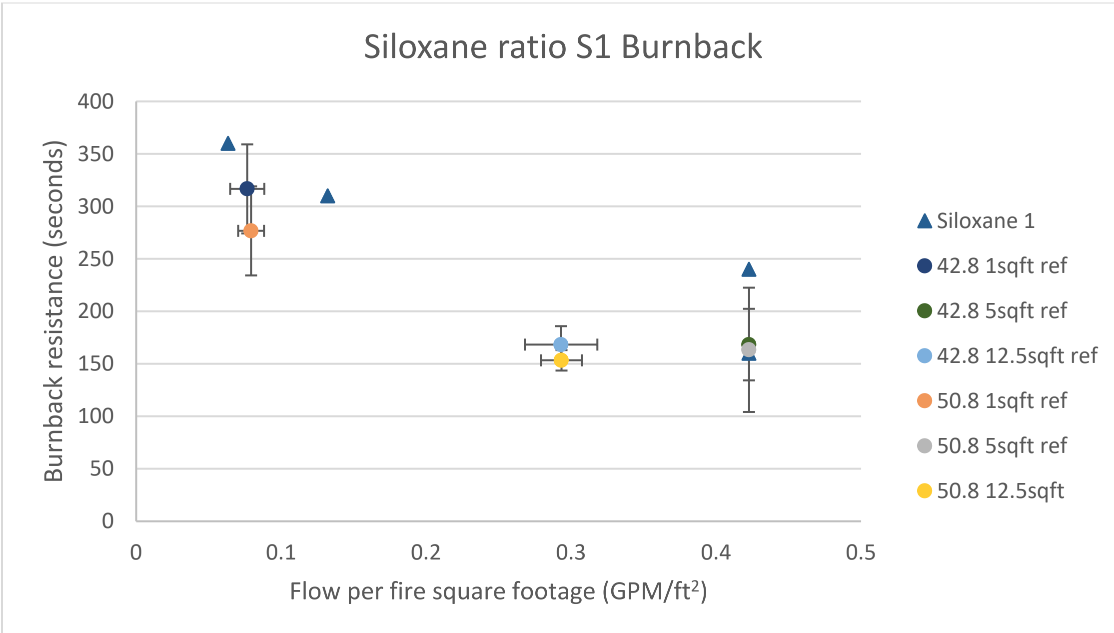

Figure ES-10. Siloxane Ratio S1 Burnback

When comparing the performance of various additives, it was found that certain formulations containing OSS agents displayed a qualitative observation of an aqueous film over gasoline, leading to improved extinguishment and burn-back (Figure ES-11). However, these formulations demonstrated reduced performance at temperatures above 70°F, and in some instances, they did not extinguish the 12.5 ft^2 fires. This underscored the importance of considering the impact of temperature on the performance of F3 firefighting formulations with different additives.

Figure ES-11. Film Formation Observed in Siloxane Ratio S1

This study faced several challenges and limitations in terms of methodology and testing conditions. Inconsistencies in the delivery rate of the CAF system, as well as differences in foam deployment methods by operators, contributed to variability in the results. Additionally, the study deviated from the MIL-SPEC protocol by not applying the formulation for a full 90 seconds, which could explain the discrepancies in burn-back times observed in the ADA facility and those recorded during MIL-SPEC testing.

Despite these limitations, the results of this study provided valuable insights into the performance of various additives in F3 firefighting formulations and their compatibility with different delivery systems. The findings can be used to guide further research and development efforts in creating alternative F3 firefighting formulations that meet the updated MIL-SPEC standards while eliminating the use of toxic AFFFs.

5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

In summary, carbonates had a potential to improve F3 performance when used with similar chemistry to ADA's formulation and deployed in CAF systems. Improved performance due to carbonates was likely due the energy of decomposition needed to break down these additives as well as the decomposition product of carbon dioxide which could aide in smothering fires. Polymer additives had the potential to improve burnback resistance by stabilizing the foam blanket and hence aid in vapor suppression. However, polymers had the potential to alter the rheology of a solution which could make it too viscous or give it shear thinning qualities making it difficult to proportion in current delivery devices used by DoD.

It should be noted that while polymers and carbonates did effect performance in certain conditions, the project team was unsuccessful in incorporating these additives in formulation concentrate without significant precipitation. For this reason, the performance improvements seen by the different siloxane ratios should be expanded on in future research. Siloxane surfactants demonstrated improvements in extinguishment and burn-back resistance in both delivery systems. The project team hypothesized that the spreadability and wetting qualities of OSS make it a potential target for further exploring vapor sealing film formation as seen in legacy AFFF. However, they also led to a decrease in foamability and were observed to have poorer performance at higher ambient temperatures. This indicated that while OSS additives may enhance certain aspects of the F3 formulations' performance, they may also introduce new challenges that need to be addressed.