DEPARTMENT OF THE NAVY
NAVAL RESEARCH LABORATORY
4555 OVERLOOK AVE SW
WASHINGTON DC 20375-5320

IN REPLY REFER TO:
3900
Ser 6180/0015
11 Feb 2011

From: Commanding Officer, Naval Research Laboratory
To: Chief of Naval Research (Code 331 L. Couchman)

Subj: FIELD, LABORATORY, AND MODELING STUDIES OF AFFF AND FLUORINE-FREE FIREFIGHTING FOAMS

Encl: (1) One copy of subject report

1. Enclosure (1) is forwarded for your review and information.

2. This report presents results of field, laboratory, and modeling investigations of the mechanism of suppression of liquid fuel fires by low expansion foams during FY2010. The field studies compared suppression and burnback performance of two aqueous film-forming foams (AFFFs) qualified against the U.S. DoD Military Specification (MilSpec) and one non-fluorinated low expansion foam. The three foams were tested on four low flash point fuels. Laboratory studies of the rate of fuel vapor penetration of the foam layer show fuel differences which correlate with the burnback performance, indicating that the role of foam as a vapor barrier is a significant aspect of low expansion foam's suppression properties. As the initial portion of a computational modeling effort focused on foam behavior and interaction with fires, an unsteady state model for liquid drainage from low expansion foams was developed.

3. Significant findings include the fact that AFFF has significantly reduced performance on fuels whose surface tensions prevent film formation. Also, large differences in burnback resistance were observed between fuels with similar flash point.

4. The Naval Research Laboratory's points of contact are John P. Farley, Code 6186, (202) 4044-8459, e-mail: john.farley@nrl.navy.mil or James W. Fleming, Code 6185, (202) 767-2065, e-mail: james.fleming@nrl.navy.mil.

Richard J. Colton

RICHARD J. COLTON
By direction

Copy to:
COMNAVSEASYSCOM (Code 05P14 Berchtold)

Distribution Authorized to US Government Agencies and their Contractors Only;
All other requests shall be forwarded to: Commanding Officer Naval Research Laboratory, Wash. DC.
THIS INFORMATION HAS NOT BEEN APPROVED FOR PUBLIC RELEASE.

6180/0015A:BAW
February 11, 2011

Field, Laboratory, and Modeling Studies of AFFF and Fluorine-Free Firefighting Foams

Bradley A. Williams
Timothy Murray[1]
Christopher Butterworth[1]
Zachary Burger[1]
Ramagopal Ananth
Michael Conroy[2]
James W. Fleming

Combustion Dynamics, Code 6185
Navy Technology Center for Safety & Survivability
Chemistry Division, Naval Research Laboratory
Washington, DC

Clarence Whitehurst
John Farley

Shipboard and Field Operations, Code 6186
Navy Technology Center for Safety & Survivability
Chemistry Division, Naval Research Laboratory
Washington, DC

Ronald S. Sheinson[3]

Nova Research, Inc.
Alexandria, VA

[1] *NRL Student Temporary Employment Program*
[2] *National Research Council/NRL Postdoctoral Fellow*
[3] *current address: Sheinson Associates LLC, Silver Spring, MD*

Encl (1) to NRL Ltr
3900
Ser 6180/0015

Distribution Authorized to US Government Agencies and their Contractors Only;
All other requests shall be forwarded to: Commanding Officer Naval Research Laboratory, Wash. DC.
THIS INFORMATION HAS NOT BEEN APPROVED FOR PUBLIC RELEASE.

Executive Summary

This report presents preliminary results of field, laboratory, and modeling investigations of the mechanism of suppression of liquid fuel fires by low expansion foams. The field studies compared suppression and burnback performance of two aqueous film-forming foams (AFFFs) qualified against the U.S. DoD Military Specification MilSpec and one non-fluorinated low expansion foam. The three foams were tested on four low flash point fuels: gasoline, heptane, iso-octane, and methylcyclohexane. The first two fuels represent, respectively, the current and the possible future fuel for the MilSpec qualification test for AFFF. The final two fuels were chosen because they have similar flash points but different surface tensions, so that AFFFs will have difficulty forming film on iso-octane but can easily form film on methylcyclohexane. The AFFFs had significantly diminished fire extinguishment performance in cases where they could not form film. The extinguishment times increased from 20 sec to 35 sec with and without a film, respectively. The non-fluorinated foam performed as well or better than the AFFFs on iso-octane. Significant differences were found between fuels in burnback performance (the time for fire to spread across a foam-covered pool). Fuel differences in burnback were consistent for all three foams studied and did not correlate with fuel flash point or film formation. Laboratory studies of the rate of fuel vapor penetration of the foam layer show fuel differences which correlate with the burnback performance, indicating that the role of foam as a vapor barrier is a significant aspect of low expansion foam's suppression properties. Based on these measurements, both foam and film provide vapor barriers. The results for non-fluorinated foam show that foam alone can be very effective vapor barrier on certain fuels. As the initial portion of our computational modeling of foam behavior and interaction with fires, we have developed an unsteady state model for liquid drainage from low expansion foams.

US00000857

1.0 INTRODUCTION

Aqueous film-forming foam (AFFF) is widely used for fire protection against liquid fuel fires. AFFF is a type of low expansion foam, having an expansion ratio typically in the range of 5-10. It is applied to a burning liquid pool and covers the fuel surface, inhibiting vaporization of the fuel and acting as a physical barrier between fuel and air. AFFF was initially developed for Navy aircraft carriers, and is also used extensively in civilian airports.

The film-forming property of AFFF is made possible by the presence of fluorosurfactants, which lower the surface tension enough to allow a water layer to form on top of the fuel surface. It is thought that the water layer contributes to fire extinguishment by inhibiting evaporation of fuel and percolation of fuel through the foam. Fluorosurfactants lower the surface tension much more than do other types of surfactants; film formation in the absence of fluorosurfactants has not been demonstrated. On the other hand, the use of fluorosurfactants to achieve film formation is made problematic by fluorosurfactants having issues of environmental persistence and, in some cases, toxicity [1].

The extent to which film-forming ability is necessary for optimal fire suppression has major implications for future development of more environmentally friendly fire-fighting foams. If filming ability is critical in achieving good performance, then one of the choices is to search for fluorosurfactants which are more environmentally benign. If, on the other hand, film formation is not so critical, then other options are open.

Here, we report findings from the first year of a study which seeks to determine the key mechanisms of foam suppression of liquid pool fires. The objectives of this study include quantification of the key interactions among foam, film, fuel pool, and the fire. By using a combined experimental (laboratory and field) and computational modeling approach, the goal is to determine the relative importance of aqueous film and foam layers to pool fire suppression under different conditions of fuel volatility, application rate, and heat release rate.

The present report provides field test data from a test series comparing two U.S. DoD MilSpec-qualified AFFF formulations and a non-fluorinated non-film-forming foam, on fuels which have different surface tensions, so that the effect of film formation on fire extinguishment performance could be separated from other properties of AFFF. In addition to the field data, we report laboratory studies which investigate fuel penetration through foam, and preliminary results of computational modeling of foam drainage.

2.0 FIELD TEST PROCEDURES AND MATERIALS

Tests were performed at the Naval Research Laboratory's Chesapeake Bay Detachment test facility during July and August, 2010. The tests conducted for this ONR program were performed in conjunction with a series of tests for NAVSEA (the AFFF warrant holder), which compared AFFF performance on gasoline with commercial grade heptane, which is under consideration as a replacement fuel for gasoline in the AFFF MilSpec qualification tests. The

US00000858

conjunction of the two test series allowed additional comparisons to be made between fuels for the same AFFF formulations.

All fire tests described here were performed inside a large burn room, using a 28 ft^2 circular pan which is used in MIL-F-24385F [2] qualification tests. The tests used a ten second preburn time (the interval between lighting the fuel and commencement of foam application) and a 2.0 gallons/minute foam application rate. Both of these parameters are identical to the MIL-F-24385F testing protocol.

The only testing parameter that was changed from the MilSpec protocol, other than the fuels used, was the total time of foam application, prior to beginning the burnback test. The MIL-F-24385F protocol calls for a total foam application time of 90 seconds, including the time for fire extinguishment. For the fuels used in this test series, this length of foam application was found to produce an unreasonably long and highly variable burnback time. Therefore, the foam application time was reduced to 60 seconds.

In conjunction with the field tests, laboratory measurements of surface tension were conducted using a Du Nuoy Ring tensiometer.

2.1 Fuels Tested:

The following fuels were used in the field tests.

Gasoline (non-ethanol containing, unleaded)
This is the fuel currently used for MIL-F-24385 qualification tests. It typically has a flash point near -40°C. The measured surface tension of this fuel at an ambient temperature of 23°C was 23.7 dynes/cm.

Iso-octane (2,2,4-trimethylpentane, 99% minimum, Chevron-Phillips)
This fuel has a very low surface tension (measured value of the fuel as tested was 18.7 dynes/cm at 23°C) and it is difficult for even MilSpec AFFFs to film on it. The flash point of this compound is -7°C.

Methylcyclohexane (MCH, 99% minimum, Chevron-Phillips)
This fuel has a relatively high surface tension (measured value of the fuel as tested was 23.6 dynes/cm at 23°C), so AFFFs will easily film on it. The flash point of this compound is -4°C.

Heptane (commercial grade, isomeric mixture, Shell)
This fuel is used for AFFF qualification under the UL testing protocol, and is being considered for use in the MIL-F-24385 testing. The sample used in the field tests had a measured surface tension of 20.0 dynes/cm at 23°C. The flash point of the material used (manufacturer's data for the lot) is -9°C.

US00000859

2.2 Foams Tested:

The following foams were used in testing. For all tests, the foam concentrate was mixed at its nominal concentration (6% for Type 6, 3% for Type 3) in fresh (tap) water.

-*National Foam (now sold by Kidde Fire Fighting) Aer-O-Water 6-EM*: A Type 6 AFFF concentrate (intended to be mixed at 6% concentrate and 94% water) which has been qualified against the MilSpec MIL-F-24385F.

-*Buckeye Fire Equipment Company BFC-3MS AFFF*: A Type 3 AFFF concentrate (intended to be mixed at 3% concentrate and 97% water) which has been qualified against the MilSpec MIL-F-24385F.

-*Solberg (originally 3M) RF6 Foam*: A non-fluorinated, and hence non-film forming, foam which NRL has previously tested. On gasoline it takes a slightly longer time for flame extinguishment than AFFF (about 40 seconds, compared to 30 seconds MilSpec requirement) [3]. Comparing the performance of this foam to that of the AFFFs on isooctane, on which none of the foams form a film, allows us to assess whether the AFFFs have other properties, besides film formation, that contribute to suppression.

Properties of the foams produced by the concentrates when discharged through the "standard" nozzle used in MIL-F-24385F testing have been measured in previous testing in our laboratory. The measurement procedure to determine the expansion ratio (foam volume/volume of liquid contained in the foam) and drainage time (time for 25% of the liquid contained in the foam to drain) of foams is specified in MIL-F-24385F. For the three concentrates mixed at their nominal concentrations in fresh water, the expansion ratio, and 25% drainage times measured according to this procedure are given in Table I. The minimum values required for qualification are an expansion ratio of 5:1 and a drain time of 150 seconds. All three foams have similar expansion ratios near 10:1. The RF6 foam has a much slower drainage than the AFFFs, due to the presence of polysaccharides in the concentrate.

Table I: Expansion Ratios and 25% Drainage Times of Foams (Mixed at Nominal Strength in Fresh Water) and Tested According to MIL-F-24385F

Foam	Expansion Ratio	25% Drain Time (s)
National Foam 6-EM	9.0	262
Buckeye BFC-3MS	9.4	360
Solberg (3M) RF6	10.3	>720 (no drainage observed)

US00000860

3.0 FIELD TEST RESULTS

3.1 Film Formation and Sealability Test Results

The ability of AFFF to form an aqueous film on a hydrocarbon pool is governed by the spreading coefficient [4]:

$$\text{Spreading Coefficient} = \sigma_{fuel} - \sigma_{AFFF} - \gamma_{fuel\text{-}AFFF}$$

where σ_{fuel} and σ_{AFFF} are the surface tensions of the fuel and the AFFF solution, respectively, and $\gamma_{fuel\text{-}AFFF}$ is the interfacial tension between the two. The two surface tensions are on the order of 15-20 dynes/cm, while the interfacial tension is in the range of 2-4 dynes/cm. The MilSpec protocol requires determination of the numerical value of the spreading coefficient (must be at least 3 dynes/cm on cyclohexane fuel), as well as a "practical" test of film formation. In MIL-F-24385F [2], cyclohexane is the fuel used for both tests.

Film formation and sealing tests (from the MIL-F-24385F protocol, Section 4.7.6) were conducted on the fuel/foam combinations. The test procedure involves covering a fuel surface with foam, then displacing the foam by inserting a wire screen funnel and scooping out residual foam, so that the fuel surface can be covered by an aqueous film layer (if one is present), but no foam. After waiting 60 seconds, the operator attempts to ignite the fuel surface with a small butane flame that is placed approximately ½ inch above the surface. An inability to ignite the fuel surface indicates successful film formation (which inhibits fuel vaporization). If the fuel surface can be ignited, this means that a film has not formed.

For MIL-F-24385F qualification testing, cyclohexane is the fuel used. Cyclohexane has a high surface tension (24.5 dynes/cm, higher than any of the fuels tested here). Therefore, use of cyclohexane as the fuel is not a very stringent test of an AFFF's film forming ability. In the present study, heptane, methylcyclohexane, and iso-octane were used. Whether the foams are able to form film on the test fuel is important at interpreting the fire extinguishment data given below.

An additional test conducted, if film formation after 60 seconds were successful, was to disturb the fuel surface to disrupt the film layer, then attempt ignition after approximately five seconds. This indicated how rapidly a film layer could form--60 seconds is twice the allowable extinguishment time for full strength AFFF in the MIL-F-24385F protocol. The ability of AFFFs to form film after a longer length of time, but not after a short time interval is a consequence of dynamic surface tension. In a surfactant solution, the surface tension slowly approaches the equilibrium value (the static surface tension). An AFFF with a spreading coefficient which is only very slightly positive on a given fuel may not be able to form a film [5,6] if its dynamic surface tension is not able to approach the equilibrium value quickly enough.

The results of the film formation and sealability tests, as well as surface tension measurements for the fuels, are given in Table II. In these tests, ignition means that film did not form; no ignition means that film did form. As expected, the non-fluorinated RF6 foam was unable to form a film on any of the fuels tested. Both of the AFFF foams formed film on MCH, which has

US00000861

a high surface tension. On heptane, the Buckeye Type 3 formed a film; the National Type 6 was able to form a film after 60 seconds, but not after 5 seconds. Therefore, although it is technically film-forming on this fuel, a film might not be able to form on the time scale relevant to the extinguishment tests.

On iso-octane, the National Type 6 did not form film. The Buckeye Type 3 was able to prevent ignition in some, but not all trials. Therefore we consider the Buckeye AFFF as being marginal in terms of film formation for this fuel. Like the National Type 6 on heptane, film formation may not occur on the time scale relevant to fire suppression.

Table II: Film Formation and Sealability Test Results				
		Foam		
Fuel	**Fuel Surface Tension (dynes/cm)**	**National Type 6**	**Buckeye Type 3**	**RF-6 (Type 6)**
Iso-octane	18.7	No film	Marginal[1]	No film
Heptane	20.0	Marginal[2]	Film	No film
MCH	23.6	Film	Film	No film
Gasoline	23.7	Film Expected	Film Expected	No film Expected

[1] Fuel was ignited on some, but not all, attempts.
[2] No ignition occurred after waiting 60 seconds for film to form, but ignition occurred after a 5 second wait time.

3.2 Fire Suppression Test Results

The times required to extinguish the fire by foam application are shown in Table III. Two values on a particular entry in the Table indicates multiple tests were performed. The fire fighting protocol followed the MIL-F-24385F procedure. The foams were mixed at their nominal strength in fresh (municipal) water and the mixture was applied at a flow rate of 2.0 gallons/minute from the nozzle specified by MIL-F-24385F, following a 10 second preburn interval between ignition and the beginning of foam application.

MIL-F-24385F specifies a fire extinction time for a standard gasoline fire of no more than 30 seconds under these test conditions. Both of the MilSpec qualified AFFFs met this requirement easily, extinguishing the fire in slightly over 20 seconds. The RF6 foam did not meet the 30 second requirement, although it did achieve a reasonably close value of 35 seconds on one of the tests. In general, the non-fluorinated foam tended to show more test to test variability in fire out times than the AFFFs. This is consistent with the lack of film formation making the extinguishment of the last remnant of the fire more difficult (flames tends to flare up again if the firefighter's technique is not optimal). This greater sensitivity can be attributed to the lack of film, which suppresses fuel volatilization in areas not completely covered by foam.

US00000862

Based on the ability of the two AFFFs to qualify for the MilSpec and the measured surface tension of the gasoline sample, we expect the National and Buckeye AFFFs, but not the RF6 foam, to be able to form an aqueous film on gasoline.

All of the tests performed on fuel/foam combinations on which good sealing occurred showed fire out times of no more than 25 seconds. By contrast, with one exception (National Type 6 on heptane), all of the tests performed on fuel/foam combinations where no, or only marginal, sealing occurred, showed fire out times of at least 29 seconds. On iso-octane fuel, on which none of the foams were able to seal well, the AFFFs did not perform any better than the non-fluorinated RF6 foam. Thus it appears that film formation does indeed contribute to good AFFF fire extinguishment performance by 20%.

Table III: Fire Out Time (s)				
		Foam		
Fuel	**Fuel Surface Tension (dynes/cm)**	**National Type 6**	**Buckeye Type 3**	**RF-6 (Type 6)**
Iso-octane	18.7	32,33 (no film)	32,33 (marginal film)	29,30 (no film)
Heptane	20.0	23,28 (marginal filming)	25 (film)	43 (no film)
MCH	23.6	22,23 (film)	19,20 (film)	33, 46, (no film)
Gasoline	23.7	22 (film expected)	21 (film expected)	35,41 (no film)

There does not appear to be a significant influence of flash point on foam suppression performance between the fuels tested. National and Buckeye AFFFs both had similar extinguishment times for MCH and gasoline, in spite of a large difference in flash point. It should be noted that all of these fuels have flash points significantly below ambient temperature, so this trend will not necessarily apply to fuels with flash points above room temperature.

3.3 Burnback (Re-ignition) Results:

Burnback tests were conducted according to the procedure described in MIL-F-24385F. After extinguishment is achieved in the tests described above, the foam application is continued, building up a foam layer that will be challenged for reignition. For the standard MIL-F-24385F tests on gasoline, the total time of foam application (including the time to extinguish the fire) is 90 seconds. After completion of the foam application, a 1 ft. diameter pan filled with burning fuel is placed in the middle of the 6 ft diameter burn pan. Fig. 1 shows the firefighter placing the starter pan at the beginning of the burnback test.

There is no direct contact between the starter pan fuel and the fuel or foam in the main burn pan. Heat release from the starter pan fire erodes the foam and in the case of low flash point fuels, ignites vapors which penetrate the foam layer. Eventually, the fire ignites outside the starter pan and spreads across the main burn pan. When the fire is judged to be self-sustaining outside the

US00000863

starter pan, the starter pan is removed. The burnback time is defined as the time interval from placement of the starter pan until the fire re-involves 25% of the main burn pan. The MIL-F-24385F requirement for burnback is a time of at least 360 seconds for full strength AFFF.

Figure 1: Firefighter placing the started pan in the foam-covered fuel at the beginning of the burnback test

In comparing test results for heptane done for the rebaselining of the MilSpec test procedure done concurrently with the tests reported here, it was discovered that heptane fires exhibit a much longer burnback time than gasoline. In order to give a reasonable and reproducible test result for the burnback time, it was decided that the foam application time for heptane fires should be reduced to 60 seconds from 90 seconds. The burnback times observed for heptane at 60 seconds foam application were longer than for gasoline at 90 seconds foam application. Comparison of two tests with National Foam AFFF with 90 second and 60 second application times show a burnback time approximately 80 seconds longer for the 90 second foam application.

Because iso-octane and methylcyclohexane have similar flash points to heptane, a 60 second foam application was used on these fuels as well (with the exception of one test of RF-6 foam in which a 45 second foam application was used). Results of the burnback tests are given in Table IV.

All three foams displayed longer burnback times on heptane than on gasoline even for a foam application time that was 30 seconds shorter. There were also substantial differences in burnback between fires of heptane, iso-octane, and methycyclohexane, even though these three fuels have very similar flash points. MCH fires exhibited the shortest burnback times for all three foams tested, and iso-octane the longest. This large difference in burnback times was unexpected, given the similarity in flash points. Also, the burnback times do not correlate with filming ability. Isooctane has the lowest surface tension among the fuels tested but exhibited longer burnback times than methylcyclohexane or gasoline, which have higher surface tension

US00000864

and filming ability. It suggests that the key factor governing burnback times for fuels with flash points below ambient temperature may not be either the flash point or the filming ability, but rather other differences between fuels which influence the rate of vapor penetration through the foam.

Table IV: 25% Burnback Times (s) for 60 Second Foam Application				
Fuel	**Surface Tension**	**FOAM**		
		National Type 6	**Buckeye Type 6**	**RF-6 (Type 6)**
Iso-octane	18.7	767	820	789[1]
Heptane	20.0	878[1], 758	674	563
MCH	23.6	522	499	503
Gasoline	23.7	652[2]	657[2]	512[2]

[1] 45 second foam application
[2] 90 second foam application

4.0 LABORATORY STUDIES OF VAPOR PENETRATION THROUGH FOAMS

One of the roles of foam in preventing reignition, particularly on fuels with flash points below ambient temperature, is to prevent / inhibit the vaporization of fuel to form a flammable mixture with air that can be reignited. That fuel passage through the foam contributes to reignition is apparent from field tests in which transient flames sweep across the foam during burnback, indicating a flammable vapor concentration, but not maintained in steady state. (Fig. 2).

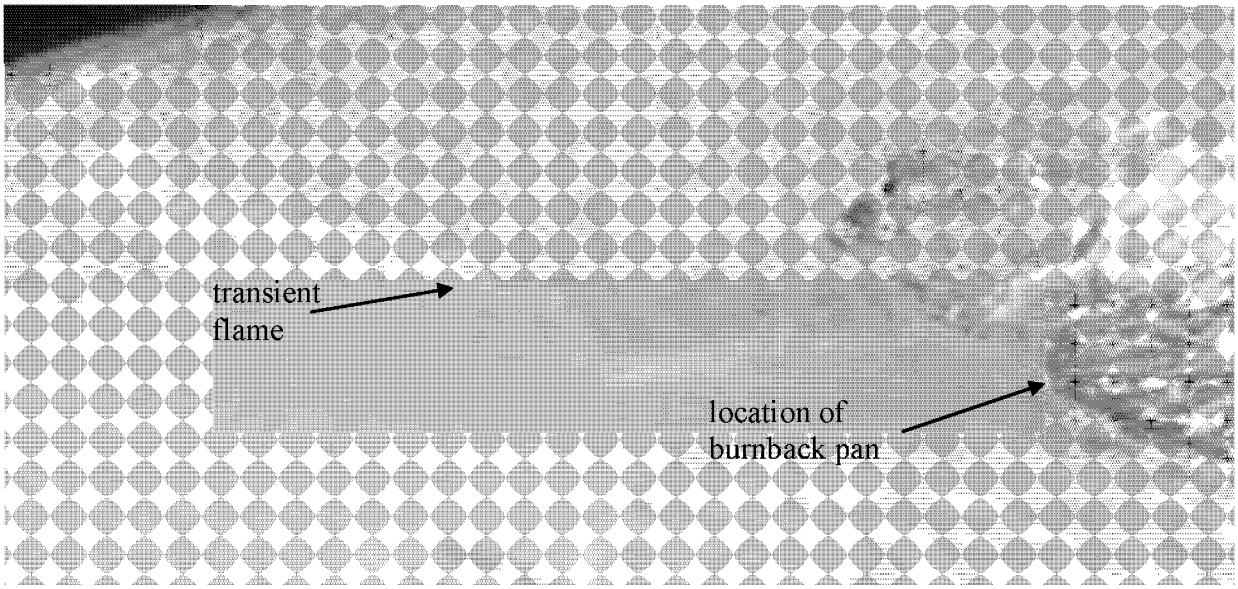

Fig 2: Transient flames observed during burnback test, demonstrating a flammable air/fuel mixture created by fuel vapor passage through the foam.

Previously, Moran et al. investigated fuel vaporization suppression by AFFF aqueous film in the absence of foam [6]. Schaefer et al. [7] compared the time for a flammable mixture to form

US00000865

through foams of RF6, other non-fluorinated formulations, and an AFFF formulation. Previous studies have not included a systematic comparison between fuels The significant differences observed in burnback times in the field tests discussed above indicates that fuel differences are significant in foam performance.

In the present series of tests, we investigate the rate of steady state fuel vapor transport through the three foams investigated in the field tests, on iso-octane, heptane, and methyl-cyclohexane.

4.1 Experimental Setup and Methodology

To quantify vapor passage through foam for different fuel/foam combination, we constructed a laboratory apparatus to study the passage of vapor through foams and aqueous films. The design, shown in Fig. 3, largely follows the design of Leonard and Burnett [4]. A nitrogen carrier gas passes through a porous frit in a stagnation flow geometry into a container containing fuel covered by film and/or foam. The nitrogen carrier gas picks up fuel vapor, and the mixture is analyzed in real-time by an FTIR spectrometer (Midac Corp.), which monitors the concentration of the fuel in the carrier gas.

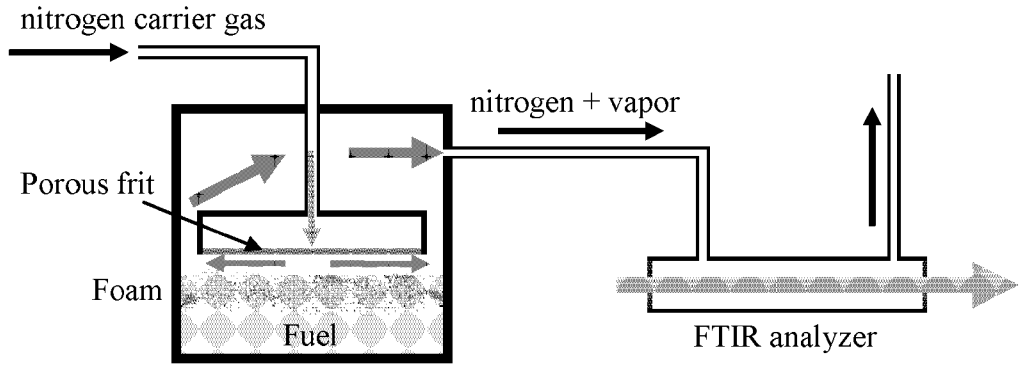

Fig. 3: Schematic of Vapor barrier test set-up.

For data collection, the foam is prepared and covers the fuel. The foam is generated by air sparging, rather than by the aspirated nozzle used in the field tests. Due to the small volume of foam required for the laboratory studies, the nozzle used in the field tests would not be practical. The expansion ratios of the foams generated by air sparging used for the vapor penetration studies were, however, similar to the values obtained with the field equipment given in Table I. Data from a typical run, using heptane fuel, foam produced from Buckeye Type 3 AFFF, and nitrogen carrier gas, are shown in Fig. 4. The IR spectrum, which contains absorption features due to heptane, water and carbon dioxide, is shown, along with a concentration vs. time plot of the analytes.

US00000866

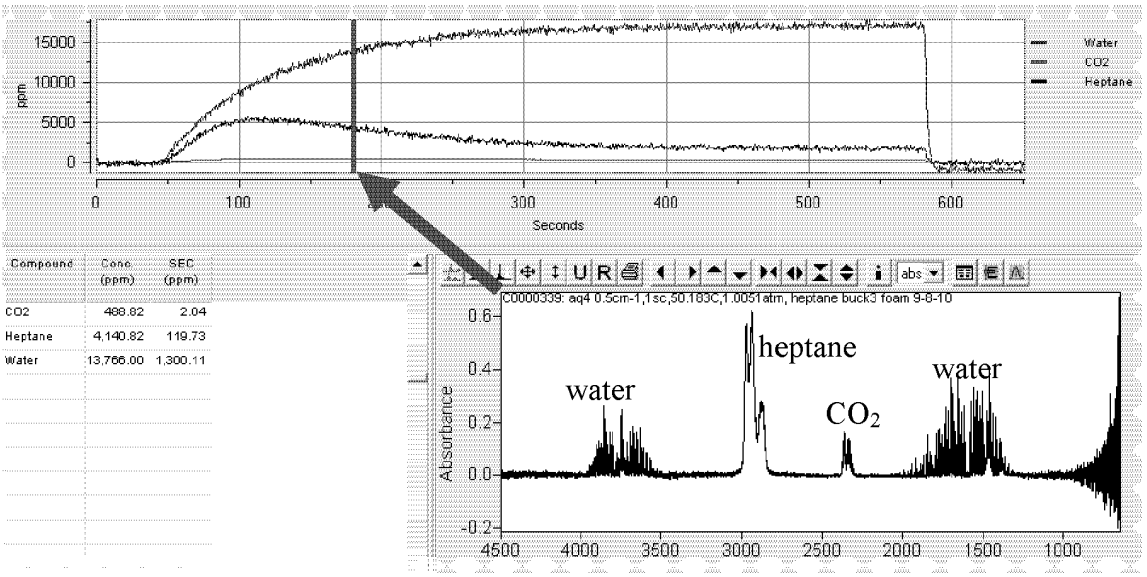

Fig. 4: IR spectrum and concentration vs. time plot of heptane vapor penetrating through AFFF. Line on concentration graph indicates time corresponding to spectrum

The data are analyzed by taking the steady state equilibrium concentration as a function of the carrier gas flow rate. At steady state, the amount of fuel vapor passing into the IR cell (vapor concentration x total gas flow rate) is equal to the fuel mass transfer rate from the pool to the gas. The data are plotted (Fig. 5) as the vaporization rate per unit area (gm/cm^2-s) vs. the ratio of the actual vapor concentration compared to the saturated vapor concentration. The measurements give a linear relationship, which reaches zero for saturated vapor, and can be extrapolated to the evaporation rate at a negligible vapor concentration.

Fig. 5 also compares the rate of fuel volatilization in the presence of Buckeye Type 3 AFFF foam to the rate in the absence of foam. Under this test condition, the fuel volatilization rate is reduced by approximately a factor of 50 by the presence of the foam.

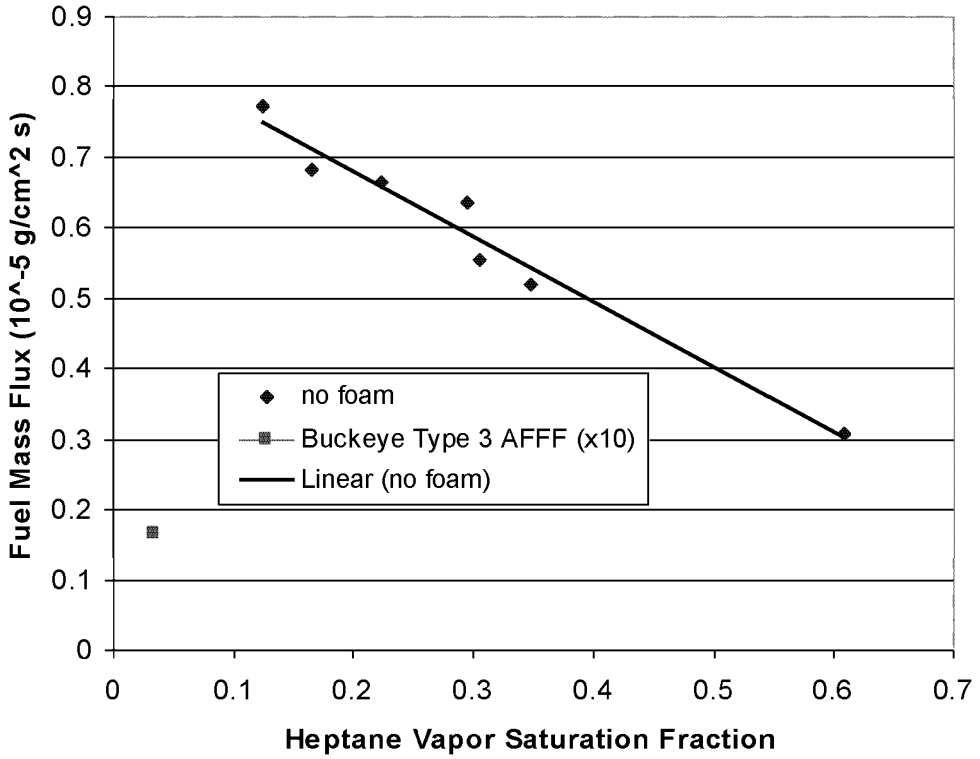

Fig. 5: Comparison of mass flux rates in the presence and absence of foam. The foam reduces the fuel volatilization by approximately a factor of 50.

4.2 Results for Different Fuel/Foam Combinations

We measured the reduction in fuel volatilization by foams for all the fuel/foam combinations investigated in the field tests described in Sections 2 and 3. These measurements clarify the role of fuel penetration through foams in explaining the differences in burn back times observed for fuels with similar volatilities.

Results for the steady state vaporization rate for the different foam/fuel combinations, and for each fuel without foam, are given in Table V. The porous plug standoff distance, and carrier gas flow rate, are held constant in this series of experiments. The effect of each foam inhibiting fuel volatilization is characterized by a Foam Blockage Factor (ratio of vaporization rate without foam to rate with foam). A blockage factor of one means the foam does not inhibit volatilization at all; a factor of infinity means that no vapor penetrates the foam.

US00000868

Table V: Steady State Vapor Concentrations and Foam Blockage Factors

	Fuel					
Foam	**Iso-octane**		**Heptane**		**Methylcyclohexane**	
	vapor conc.	**blockage factor**	**vapor conc.**	**blockage factor**	**vapor conc.**	**blockage factor**
none	**20900**		**28800**	**---**	**14600**	**---**
National	**950**	**22.0**	**2450**	**11.8**	**1400**	**10.5**
Buckeye	**1400**	**14.9**	**1750**	**16.5**	**2850**	**5.1**
RF6	**950**	**22.0**	**2700**	**10.7**	**1900**	**7.7**

The blocking factors range from roughly five to 20, with significant differences between fuels. Methylcyclohexane has the lowest blocking factor for all foams, and iso-octane the highest for two of the three. It is noteworthy that the ordering of the fuels by blocking factor is the same as the fuels' ordering by burnback times in the field tests.

Figure 6 plots the burnback times observed in the field tests (60 seconds foam application except in the case of the RF6/iso-octane combination, which had a 45 second foam application). The correlation coefficient between the two quantities is 0.82, indicating that the fuel vapor passage through the foam has a significant influence on burnback.

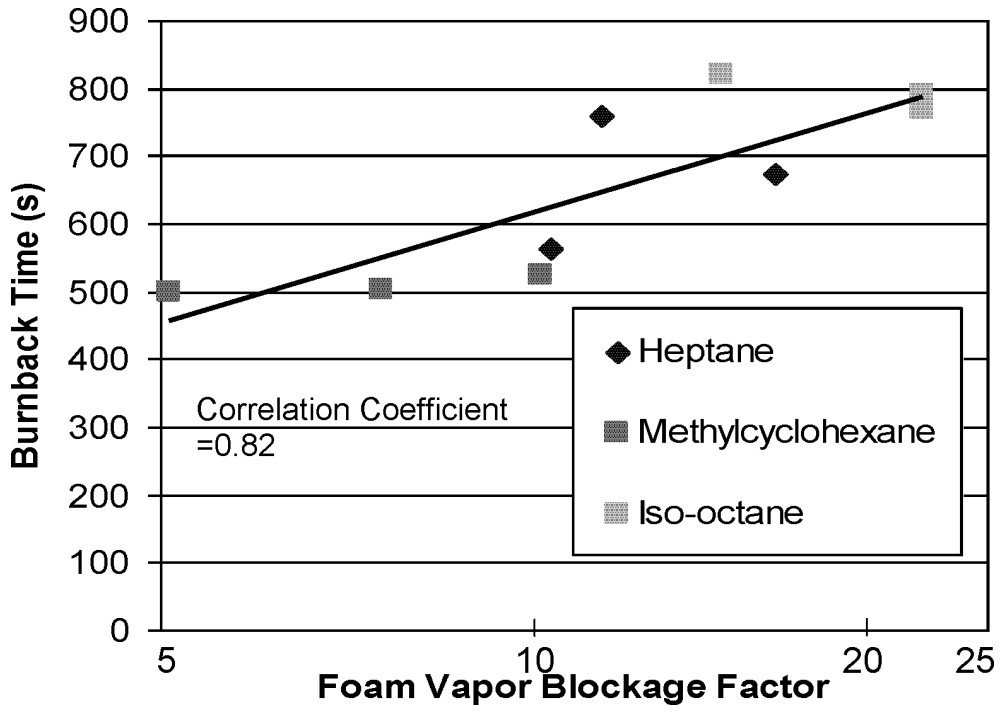

Fig. 6 Dependence of burnback time in field tests on the foam vapor blockage factor (ratio of steady state fuel vapor concentration without and with foam) measured in laboratory experiments.

5.0 MODELING

We have begun our modeling of the behavior of AFFF and its interactions with the fuel and fire, by developing a model for drainage of water from the foam. Water drainage from foam decreases the water content and its ability to resist heat from the fire, leading to foam erosion and increased fuel vapor permeation. On the other hand, the drained water plays two roles which promote suppression: (1) it cools the hot fuel by absorbing latent heat and sensible heat, and (2) forms a very thin film (of approximately 50 μm thickness) on the cooled fuel surface. The film acts as a seal for highly volatile fuels. Thus, the drained water reduces the fuel vapor pressure significantly and enables fire extinction and prevents re-ignition. Therefore, it is important to understand water drainage process in foams.

5.1 Free Drainage Model

We have modeled the drainage of liquid (mostly water) from a fixed volume of foam bed which is known as the free drainage. A low expansion foam is modeled as a network of mono-dispersed dodecahedral shaped bubbles [8]. Three bubbles form a liquid channel known as Plateau borders. The liquid flows through a network of channels inside the foam. Flow rate is dictated by gravity, capillarity, and viscous forces. These forces depend on the triangular cross-sectional area of a channel, which decreases with time as the liquid is drained from it. We solve time-dependent mass balance and momentum balance equations written across the foam bed volume. In this section we present preliminary results from the model applied to; (1) AFFF bench scale tests from literature, (2) 2.6 m^2 (28 ft^2) pan pool fires typically tested at Chesapeake Bay Detachment (CBD). We show how the drainage rate depends on expansion ratio, bubble size, slip, and solution viscosity.

The foam application rate for 2.0 gal/min application to a 28 ft^2 area is very small (0.05 cm/s) for low expansion (LoEx, e.g., AFFF) foams compared to that in a typical high expansion (HiEx) foam (8 cm/s). Therefore, a free drainage model is developed rather than using the advancing foam model [9], which was developed for high expansion foams (having expansion ratios on the order of 500-1000, compared to 5-10 for AFFF). In its present form, the free drainage model does not yet include three effects; (1) a time-dependent change in bubble size due to large drainage rates typical of the low expansion foams, (2) bubble coarsening by gas diffusing from small to large bubbles, and (3) slip at the channel walls. There are very few experimental measurements of bubble sizes and slip at the channel walls. These issues are being addressed both experimentally and computationally.

US00000870

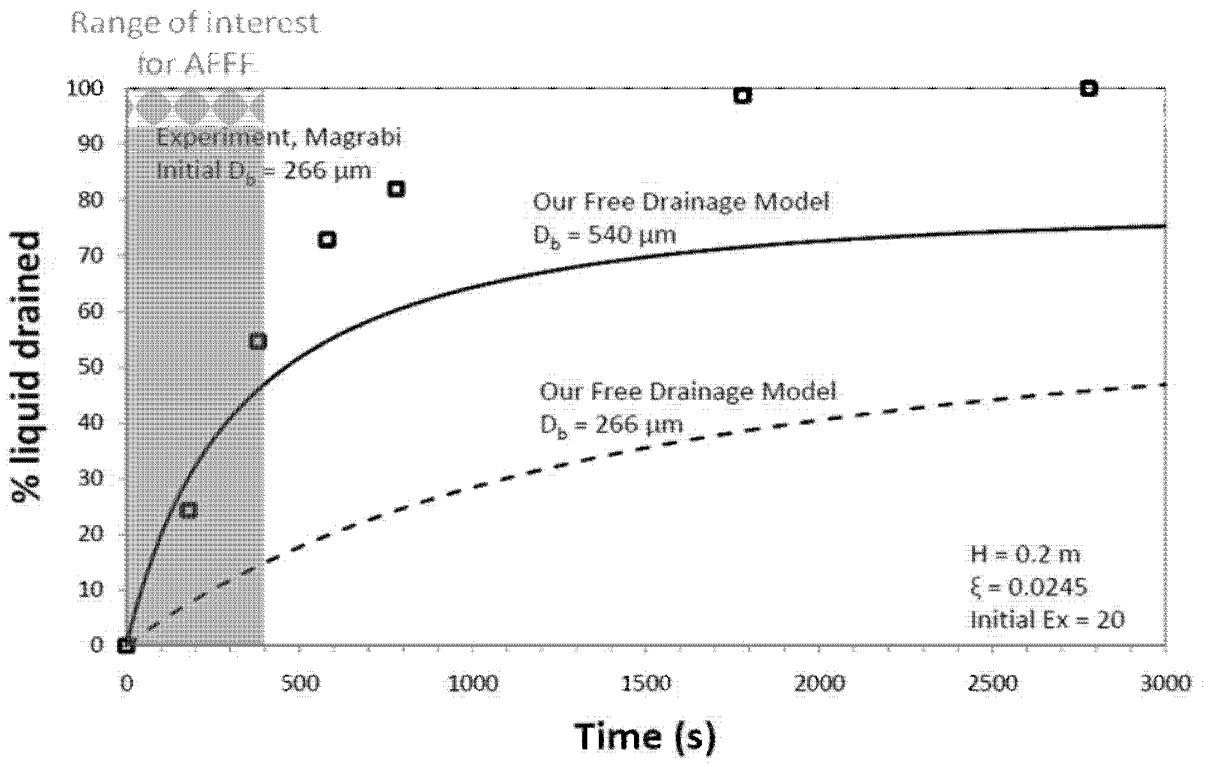

Fig. 7: Model prediction for effect of bubble diameter on liquid drainage, and comparison with AFFF experimental data (Ref. [10]).

Fig. 7 shows the model predictions for the drained liquid as a percent of the total liquid content present initially for foams with expansion ratio of 20 and bed height of 0.2 m. The drainage is shown for bubble diameters 266 and 540 μm. The initial drainage rate (slope of the curves near the origin) within the first 360 seconds (6 minutes) increases by 3.5 times as the bubble size doubles. As the bubble size increases, the channel (Plateau border) area increases at a fixed expansion ratio. The liquid drains faster in wider channels than in narrow channels. The shaded region represents the time scale relevant to U.S. Navy MilSpec testing. As part of the qualification protocol, foams are required to have a minimum of 360 sec burn back time. Clearly, bubble diameter has significant effect on free drainage from low expansion foams within the time scale of interest.

Fig.7 also shows experimental data of Magrabi et al [10] for a AFFF foam with an expansion ratio Ex=20 (liquid volume fraction α=0.05), bed height (H) of 20 cm, and initial average (fourth moment) bubble diameter of 266 μm. The model prediction for bubble diameter of 540 μm is in good agreement with the experimental data within the time scale of 360 s. As the time progresses, the water loss is so significant that coarsening of the bubbles may occur, which causes the average bubble size and drainage to increase in the experiments. The model predictions for 266 μm bubble diameter are lower by a factor of 3.5 compared to the experiments at 360 s. It is very difficult to measure bubble sizes accurately *in situ* in the experiments. An initially monodisperse foam can quickly become polydisperse (having a range of bubble sizes) at low expansion ratios. As one might expect, the model underpredicts the data significantly.

US00000871

Another factor is slip at the channel walls inside the foam can increase the drainage rate. Slip has been observed directly in experiments performed by Koehler et al. [11]. But, no such measurements are available for AFFF. It is possible that the permeability coefficient, ξ, that represents degree of slip may be higher than 0.0245 for AFFF (ξ=0.0051 represents no-slip [9]). The effects of increased slip at the walls in the model will be shown later.

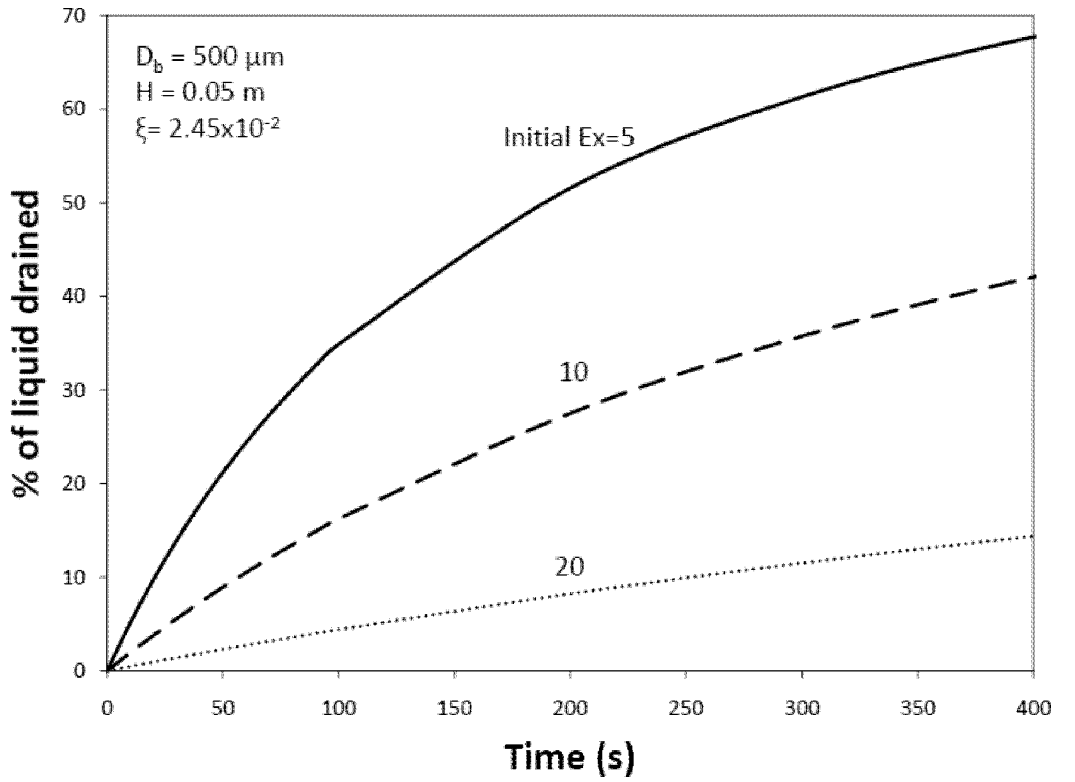

Fig.8. Model prediction for effect of initial expansion ratio on liquid drainage

Fig.8 shows the model predictions for liquid drained with time. The foam parameter values used are within the range applicable to the foams generated during MIL-F-24385F qualification testing:500 μm bubble diameter, bed height of 5 cm, and fuel pool area of 28 ft^2 (2.6 m^2). It shows that the initial drainage rates (slopes of the curves) decrease significantly with increased expansion ratios of 5 to 20. As the expansion ratio increases, the channel area decreases at a fixed bubble diameter. This increases the viscous and capillary effects which oppose the gravity effect. Clearly, foams with expansion ratios of 5 drains at very different rates than at 20.

Figs. 7 and 8 show that increase in expansion ratio and bubble size have opposing effects on the drainage rates. In the Figures, the expansion ratio (Ex) and bubble diameter are assumed to be independent. In practice, it is observed that the bubble diameter increases with expansion ratio. Quantitative data relating expansion ratio and bubble size are very specific to the foam generation technique and are not available at present.

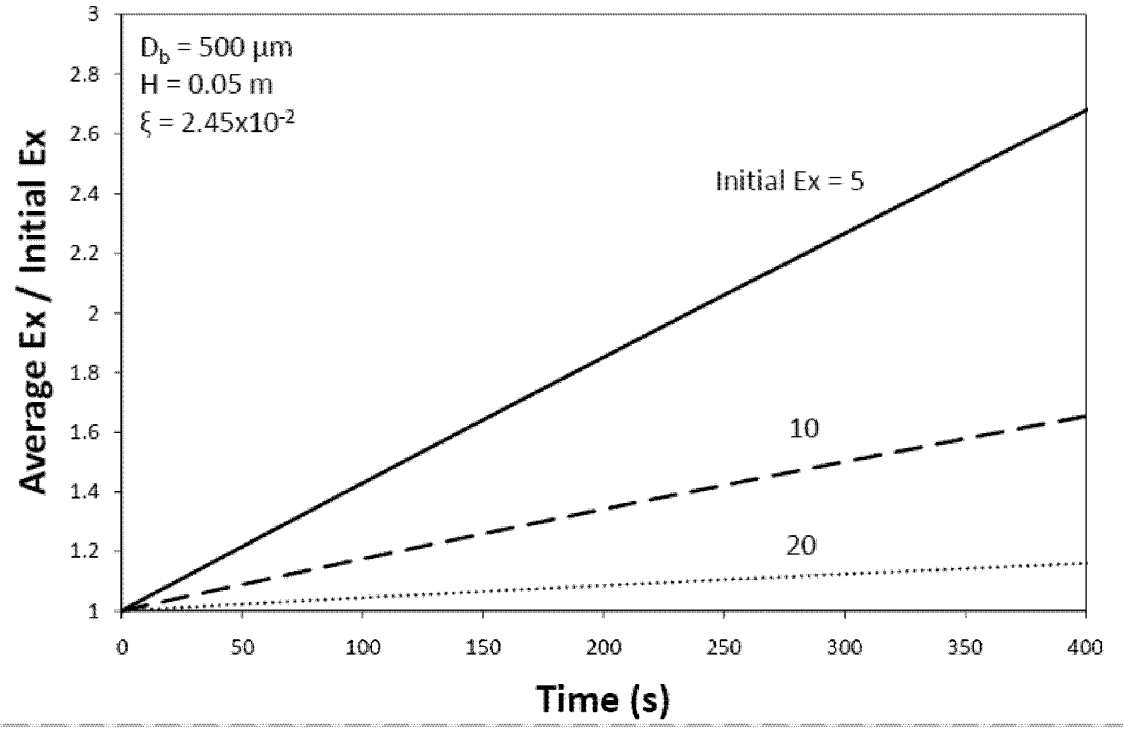

Fig. 9. Expansion ratio increases with time due to liquid drainage from the foam

As the liquid travels from the top of the foam bed to the bottom, the expansion ratio increases at the top and decreases in the bottom from its initial values. Thus there is a gradient in water content, expansion ratio, and local density of the foam across the bed height. However, the volume averaged water content of the foam decreases because of water loss from the foam. Fig. 9 shows the model predictions for volume average expansion ratio with time for different values of initial expansion ratio (5 to 20). It shows that expansion ratio increases with time as the liquid is lost from the foam due to drainage. The drainage rate (slope of the lines) decreases with increasing expansion ratio. The model predicts that the expansion ratios can increase by a factor of 1.6 in 400 s for Ex=10.

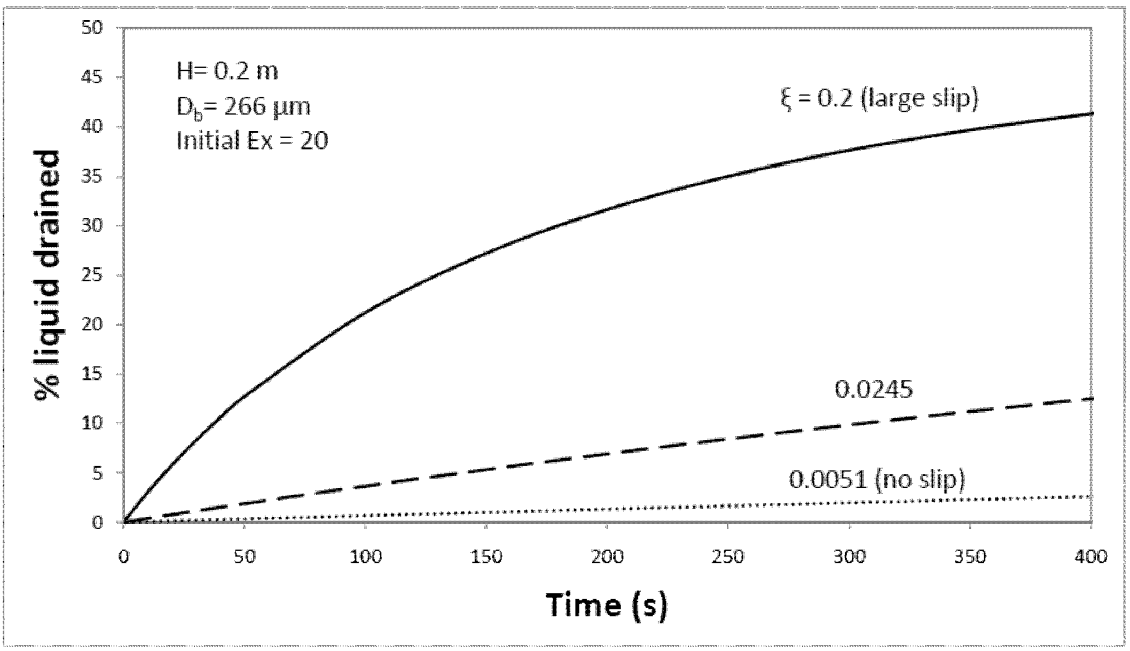

Fig. 10. Effect of slip on drainage rate.

The permeability coefficient, ξ, is a proportionality constant in the relationship between the drainage velocity and the driving force (gravity). It is a constant for a given surfactant solution in the model. It is directly proportional to the degree of slip between the liquid and air at channel walls, and indirectly proportional to liquid viscosity. A value of 0.0051 assigned to ξ represents no-slip condition. A value of ξ larger than 0.0051 can represent either a higher slip or a lower liquid viscosity. Fig. 10 shows that the drainage rate increases significantly with increasing slip. The permeability coefficient is very specific to the chemical composition of the surfactant solution, and a direct measurement is extremely difficult. Experiments are being conducted at NRL to determine the degree of slip for HiEx solutions using Fluorescent particle imaging velocimetry in micro channels. This work could be extended to low expansion foams.

Future work will focus on developing the models for low expansion foams by considering bubble size changes with time and slip effects. We will also perform bench-scale experiments for specific measurements of drainage rates at varying expansion ratios, bubble sizes, and chemical composition of the surfactant solution. Figs. 7-10 show how the drainage rate depends on expansion ratio, bubble size, slip, and solution viscosity. This may allow us to optimize the drainage rate of low expansion foam to increase the degree of cooling of hot liquid pool without significant loss of resistance to heat penetration.

5.2 Effects of liquid drainage on foam suppression of fires

The drained liquid from a foam; (1) cools the hot fuel by absorbing latent heat and sensible heat, and (2) in cases of AFFF foams, forms a very thin film (≈50 μm [4]) on the cooled fuel surface. The film acts as a seal for highly volatile fuels at ambient conditions. Thus, the drained liquid reduces the fuel partial pressure significantly and enables fire extinction and prevents re-ignition. In addition to drainage, the following phenomena are important

US00000874

1. Cooling of hot fuel by drainage
2. Spreading to seal the fuel surface
3. Resistance to fuel penetration
4. Resistance to heat penetration

Too much drainage can increase Ex significantly as shown in Fig.9 and reduce resistance to heat penetration, which can lower the burn back time. However, the burn back tests described in the previous sections show that the burn back time is well in excess of the minimum time of 360 s required by MIL-F-24385F. Therefore, there is room to increase drainage rate and still have acceptable burn back performance. An optimum value for the drainage rate will be determined using the model described in the previous section combined with drainage experiments, which will be performed.

5.3 Effects of density and yield stress on foam spread

Foam spreads on a surface by its own weight. It is commonly noticed that foam spreads slower than pure materials (such as water) mainly due to its low density. The density of foam, ρ_f, is directly related to its water content or the expansion ratio. It is given by $\rho_f = \rho_w/(Ex+1)$. Here ρ_w is the density of water (1000 Kg/m^3). For a typical low expansion foam, Ex=10 initially. This means it would take a roughly 11 times larger foam bed height (or hydraulic head) so that the foam bed has enough weight to spread at the same rate as water would. This has serious implications on foam's ability to spread on the fuel pool surface. This is especially crucial for foams that do not film (e.g., RF6). It is foam's light weight that allows it to float on water, but if it is too light it inhibits spreading at a fixed foam bed height.

Fig. 9 shows how Ex increases with time for a low expansion foam as predicted by our model for drainage. As the foam drains, expansion ratio and density decrease with time. This means tha a foam's ability to spread decreases with time at a fixed bed height due to decrease in the weight or hydraulic head. Therefore, foam drainage and spreading are coupled.

As the foam tries to spread under its own weight, it has to work against viscous and capillary forces, which hold the foam together. Foams are known to exhibit non-Newtonian flow behavior with a non-zero yield stress. This means a minimum foam bed height is needed to overcome the yield stress before the foam is able to spread. Therefore, in addition to the low density, viscosity and yield stress play important role in a foam's ability to spread on the liquid fuel surface.

The yield stress effect on spreading over a liquid pool was studied by Lattimer and Trelles [12]. The yield stress has been measured in the literature for a variety of systems including foams as reported by Gardiner et al. [13], and is shown below. The yield stress, τ_y, depends on the expansion ratio as

US00000875

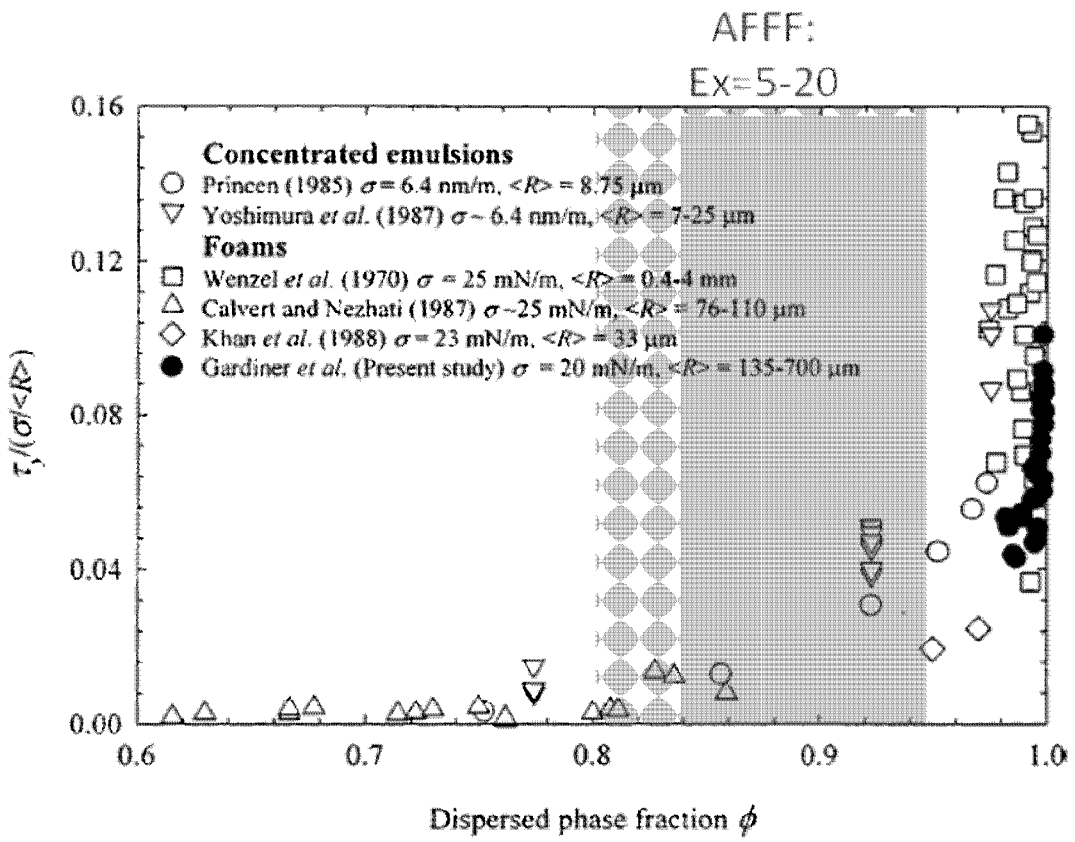

Fig. 11. Dimensionless Yield stress with liquid fraction for foams and dispersions (from Ref. [13]).

shown in Fig. 11. The gas volume fraction is ϕ=Ex/(Ex+1), σ is surface tension, <R> is the average bubble radius. Fig. 11 shows that the dimensionless stress increases from 0.008 to 0.0032 as the expansion ratio increases from 5 to 20 (ϕ increases from 0.83 to 0.95) applicable to AFFF foams. As the liquid drains, the yield stress increases due to the increase in Ex. Also, for AFFF foams with Ex =10, $\tau_y/(\sigma/(<R>)$ is about 0.02. Therefore, at a fixed Ex, the yield stress is inversely proportional to the bubble diameter. The yield stress of the foam can be reduced by increasing the bubble diameter and decreasing Ex. This may result in faster spreading of the foam on the fuel surface to improve extinguishment and to seal the fuel from re-ignition. Both modeling and experiments are needed to develop an understanding of the effects of bubble size and Ex on foam spread on liquid pools.

Future work will focus on developing the models for low expansion foams by considering bubble size changes with time and slip effects. We will also perform bench-scale experiments for specific measurements of drainage rates at varying expansion ratios, bubble sizes, and chemical composition of the surfactant solution. Figures 7 to 10 show that the drainage rate depends on expansion ratio, bubble size, slip, and solution viscosity. This may allow us to optimize the drainage rate of low expansion foam to increase the degree of cooling of hot liquid pool without significant loss of resistance to heat penetration.

6.0 DISCUSSION

Extinguishment times for gasoline and methylcyclohexane fires by AFFF were about 20 seconds for AFFF solution at nominal strength, using fresh water. This compares to a requirement of 30 seconds under MIL-F-24385F. The similar extinguishment times for these two fuels indicate that the lower flash point of gasoline compared to MCH does not greatly affect extinguishment times.

On the other hand, fuel/foam combinations on which filming (measured in the absence of a fire) did not occur or was difficult (the non-fluorinated foam formulation for all fuels, and iso-octane with the two AFFF foams), showed extinguishment times ranging from approximately 30-40 seconds. On heptane, the AFFFs should have formed film, although in one case sealing might not occur within a few seconds. In terms of extinguishment, heptane was found to be an intermediate case, giving extinguishment times a few seconds longer than for gasoline fires, but shorter than the iso-octane fires, for both AFFFs tested.

Although not an objective of the test series, it was noted that extinguishment performance of AFFFs on heptane fires was adversely affected by elevated fuel and ambient temperatures that were encountered during testing. This was particularly apparent in the concurrent series of tests comparing gasoline and heptane as test fuels for the MIL-F-24385F protocol. Due to different temperature dependences of the surface and interfacial tensions of the AFFF/fuel system, the spreading coefficient tends to decrease slightly with temperature. Since film formation on heptane fuel is hampered by its low surface tension compared to gasoline (the spreading coefficient is close to zero [4]), even a slight further decrease with increasing temperature might hinder film formation.

For iso-octane, the non-fluorinated foam had shorter extinguishment times than the two AFFFs and was the only foam to achieve an extinguishment time under 30 seconds. Based on this observation, it is tempting to ascribe a major role in extinguishment to film formation. There appear to be other factors at work, however. The non-fluorinated foam (with polysacceride thickeners) had substantially better performance on iso-octane than on any of the other fuels. This is not explained by film formation, which did not occur for any of the fuels for this foam. Indeed, based on the results shown in Table V, it is likely that the foam formed an effective vapor barrier that contributed to a shorter fire extinguishment time despite the absence of a film.

It is not surprising that the AFFFs tested show decreased performance on fires of fuels on which they cannot easily form film. Since their intended mode of operation assumes film formation, one would expect decreased performance in cases where film formation does not occur. The non-fluorinated, non film-forming RF6 foam, however, is designed to have mechanical properties of foam which compensate for the lack of film formation. In particular, the rate of water drainage is greatly reduced and the foam has a lower yield stress. The shorter extinguishment times of iso-octane fires by the non-fluorinated foam compared to the AFFFs indicates that extinguishment performance in the absence of film formation can be improved by optimization of other properties of foam.

US00000877

An unexpected observation was the substantial difference in burnback times between the fuels. Since all of the model fuels (heptane, iso-octane, and methylcyclohexane) have very similar flash points, it was expected that they were likely to show similar burnback behavior to one another, but somewhat longer burnback times than for fires of gasoline, which has a lower flash point.

In fact, methylcyclohexane had similar burnback performance to gasoline, while the other two fuels had much longer burnback times, indicating better foam performance. This trend, while varying somewhat in magnitude, was consistent across all three foams tested. The ability for film formation does not appear to increase burnback time. Iso-octane, on which film formation is the most difficult, had the longest burnback times of any of the fuels tested.

Laboratory studies to measure the rate of fuel transport through the foams indicate that foam/fuel systems which better inhibit fuel passage through the foams are associated with longer burnback times. This finding intuitively makes sense, because the primary mechanism of burnback for low flashpoint fuels is vapor passing through the foam layer. However, the mechanisms of fuel transport through the foam, and the influence of fuel and foam composition, remain to be determined.

The initial phase of model development of foam drainage has captured some of the relevant phenomena and is consistent with the available experimental data. It is clear that low expansion foams such as AFFF are much more strongly influenced by drainage and variation of bubble size, leading to foam properties which are both height- and time-dependent. These properties must be adequately modeled to correctly describe the extinction process.

7.0 CONCLUSIONS

Comparing foam/fuel combinations for which AFFF can or cannot form film, we find that the presence of film decreases the extinction time by 40% for fuels with flash point well below the ambient temperature.

The burn back times for all foam/fuel combinations tested are 40 to 100 % longer than the minimum requirement of 360 sec. Nevertheless, there are significant differences between fuels, even ones with similar flash points. The trends observed for the different fuels are consistent for the different foams tested here.

The foam and film lower the vapor pressure of fuel significantly by possibly two mechanisms: (1) cooling of the hot fuel pool underneath, (2) when the fuel pool surface temperature is near ambient temperature, the film spreads faster than the foam to form a vapor seal. Therefore, increased drainage increases the cooling effect. The cooling, in turn, has effects due to (1) the lowering of the fuel vapor pressure, (2) the change in spreading coefficient fuel surface temperature, and (3) differences in fuel vapor permeation through the foam as a function of temperature. However, an excessively high drainage rate will shorten the foam lifetime and may decrease the burnback time significantly. The relative magnitudes of these mechanisms and optimum drainage rates will be determined by bench scale tests and modeling.

US00000878

This work was supported by the Office of Naval Research under Contract # N0001410AF00002

8.0 REFERENCES

1. C. A. Moody and J. A. Field, "Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams," Environ. Sci. Technol. 34 (2000) 3864-3870.

2. "Military Specification: Fire Extinguishment Agent. Aqueous Film-Forming Foam (AFFF) Liquid Concentrate", For Fresh and Sea Water" MIL-F-24385F, Naval Sea Systems Command, 7 January 1992.

3. R. S. Sheinson and S. Ayers, "Fire Fighting Performance of Fluorosurfactant-Free Alternatives to Aqueous Film Forming Foam (AFFF): Initial Evaluation of 3M RF6 And A Developmental Formulation," NRL Letter Report 6180/0303, 2004.

4. J. T. Leonard and J. C. Burnett, Suppression of Evaporation of Hydrocarbon Liquids and Fuels by Films Containing Aqueous Film Forming Foam (AFFF) Concentrate FC-196, NRL Report #7842, 31 December 1974.

5. E. K. Hyland and B. A. Williams "Characterization of the Dynamic Surface Tension of Aqueous Film-forming Foam", NRL/MR/6180-04-8749, 9 February 2004.

6. Moran, H.E., Burnett, J.C., and Leonard, J.T., "Suppression of Fuel Evaporation by Aqueous Films of Fluorochemical Surfactant Solutions", NRL Formal Report, FR-7247, 1 April 1971.

7. T. H. Schaefer,B. Z. Dlugogorski, and E. M. Kennedy, Sealability Properties of Fluorine-Free Fire-Fighting Foams (FfreeF), Fire Technol., 44 (2008) 297–309.

8. R.A. Leonard and R. Lemlich, "A Study of Interstitial Liquid Flow in Foams", AIChE Journal, 11 (1965) 18-24.

9. M. Conroy, R. Ananth, J. Fleming, J. Taylor, and J. Farley, "Liquid Loss from Advancing Foams with Very Low Water Content," NRL memorandum report, in press.

10. S. A. Magrabi, B. Z. Dlugogorski, and G. J. Jameson, "A comparative study of drainage characteristics in AFFF and FFFP compressed-air fire-fighting foams, " Fire Safety J., 37 (2002) 21.

11. S. A. Koehler, S. Hilgenfeldt, E. R. Weeks, and H. A. Stone, "Foam drainage on the microscale - II. Imaging flow through single Plateau borders, " J. Colloid Interface Sci. 276 (2004) 439-449.

12. B.Y. Lattimer and J. Trelles, "Foam spread over a liquid pool," Fire Safety J., 42 (2007) 249-264.

US00000879

13. B. S. Gardiner, B. Z. Dlugogorski, and G. J. Jameson, "Yield stress measurements of aqueous foams in the dry limit," J. Rheology, 42, (1998) 1437-1450.