SEALABILITY PROPERTIES OF FLUORINE-FREE FIRE-FIGTHING FOAMS

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ABSTRACT

This contribution compares the sealability performance of recently developed three synthetic foam formulations (that do not contain fluorosurfactants or fluoropolymers) with that of an aqueous film forming foam (AFFF). We apply the sealability methodology outlined in the Australian Defence Force Specification, DEF(AUST)5706. This methodology specifies a 0.28 m^2 small-scale indoor fire pan. The pan is first filled with 10 L of water and then 5 L of AVGAS (aviation gasoline, flash point of -50 ^{o}C) or heptane (flash point of -4 ^{o}C) is placed on top of the water. Foams were generated from a pressurised extinguisher with a foam nozzle as described in the standard's specification, set to create foams with expansion of 4:1. The foam spread across the fuel until the entire fuel surface was covered with foam. At 5-min intervals, a lit taper was introduced into the space above the pan area by passing it twice around the surface of the foam in a circular motion at a height of approximately 15 mm from the surface of the foam. The results demonstrate differences in the sealability performance between AFFF and fluorine-free foams (FfreeF). Under laboratory conditions, with a foam blanket 1-2 cm deep, best-performing FfreeF formulation (RF6) provides about 30% of the durability of an AFFF for protection against evaporation of low-flashpoint flammable liquids. We also note in the results the significant differences among FfreeF with almost no sealability of AVGAS vapours offered by the two other formulations.

KEYWORDS class B foams, fluorine-free foams, AFFF, RF6

INTRODUCTION

Modern high performance fire fighting foams used against fires of flammable (Class B) liquids have traditionally been based on low concentrations of fluorosurfactant additives. Fluorosurfactants gave these foams the ability to form thin, spreading films on surfaces of burning liquids, with the films providing significant resistance to diffusion of flammable vapours (i.e., sealability). These two properties, spreading and sealability, afforded fluorosurfactant-based foams fast extinguishment and long burn back characteristics. The fluorosurfactants has typically included perfluorooctyl sulphonate (PFOS) derivatives, perfluorooctanoic acid (PFOA) derivatives and telomer compounds. The perfluorinated entity of the molecule equipped fluorosurfactants with the stability to survive in a harsh fire environment. These same characteristics gave these molecules unexpected long-term stability in the receiving environment. As a consequence, there is growing interest in synthetic foams that do not contain fluorosurfactants and are readily biodegradable.

Fire fighting foams are employed to secure vapours from spills of volatile organic compounds. The use of a flux chamber to predict the vapour suppressing capability of a fire fighting foam is an evaluative procedure that has been widely applied by the fire safety industry. As found in the literature [1], rules of thumb and predictive charts have evolved, allowing fire fighters to use specific types of foams effectively. For example, Pignato recommends a 15-cm blanket of 6% AFFF to suppress a n-heptane spill for 60 min [1]. However, the research of Cousins and Briggs [2], which was replicated by Stubley and Mulligan [3], suggested that the synthetic based AFFF fire fighting foams may sometime be prone to enhancing the flammability of hydrocarbon fuels. Even though the predicted vapour suppression efficiency of fluorosurfactant and non-fluorosurfactant based foams appeared to have similar experimental response in tests from a flux chamber apparatus [4], it is unclear whether these foams provide adequate protection following the introduction of a naked flame source over the foam blanket, and if so, for what duration. The methodology presented in this article goes beyond the limited environment of a flux chamber and introduces an ignition source to explore ability of foams to maintain a safe working environment for the protection of emergency service personnel.

Consequently, in this contribution we examine a second experimental method, in addition to flux-chamber apparatus, to determine the efficiency of a fire fighting foam to suppress vapourisation and determine the ignition time. We also compare the present results, collected in an in-door atmosphere, with measurements collected for an artificial environment of a flux chamber, to compare the relative ranking of the foams obtained from the two approaches.

EXPERIMENTAL

Australian Defence Force Specification, DEF(AUST)5706, Annex A [5], provides a methodology to assess the performance of fire-fighting foams used for suppression of vapours of liquid fuels. The methodology involves exposing a foam covering a liquid fuel to a naked flame. This methodology is less rigorous but less practical that that of a flux chamber apparatus [4], and is adopted for the present study.

Annex A of DEF(AUST)5706 methodology specifies a 0.28 m^2 small-scale indoor fire pan. The pan needs be first filled with 10 L of water and then 5 L of AVGAS (aviation gasoline) at 20 ± 2 ºC placed on top of the water base, by pouring the AVGAS from an earthed safety can, as not to create a static discharge. In addition to AVGAS, we also performed experiments with heptane, a higher flush point fuel than AVGAS. Table 1 presents a comparison of the physical and flammability characteristics of the two fuels.

Table 1. Comparison of the physical properties of n-heptane and AVGAS.

Physical Property	n-Heptane [6]	AVGAS 100LL [7]
Colour	Clear	Blue
Vapour Pressure (kPa) @25 °C	6.1	38.0 min; 48.5 max
Density (g/cm^3) @ 20 °C	0.6839	0.69 [MSDS]
Flash Point (PMCC)* (°C)	-4	-50 [MSDS]

***** Pensky Martens Closed Cup

The foam was generated from a pressurised extinguisher with a foam nozzle as described in the specification of DEF STAN 42-40/2, Annex A, set to create a foam of expansion factor 4:1 [8]. The foam was gathered from the nozzle, by means of a foam collection backboard as described in NFPA 412 [9] to determine the foam expansion factor. Additional foam was collected from the backboard with a 4 L beaker for application in the experiment [9].

Two levels of foam application were examined in this experiment, with either 1.5 or 3.0 L of generated foam applied to the surface of the AVGAS fuel, corresponding to 1 and 2-cm foam layers on the fuel's surface. A foam layer of this depth typically has a potential of 10 min of suppression in a field scenario, with re-application required to maintain the VOC concentration below flammability limits [1]. Under laboratory conditions, 1-2 cm blankets of AFFF can provide protection for more than 6 h. The selection of 1-2 cm foam layers for this study allowed us to complete the experiments within a reasonable timeframe.

The foam was allowed to spread across the fuel until the entire fuel surface was covered by foam. When foam coverage was complete, a sealability experiment commenced. At 5-min intervals, a lit taper was introduced into the space above the pan area by passing it twice around the surface of the foam in a circular motion at a height of approximately 15 mm from the surface of the foam, as illustrated in Figure 1. The response was observed and noted as either: no ignition; a flash fire; or a permanent, full pan ignition.

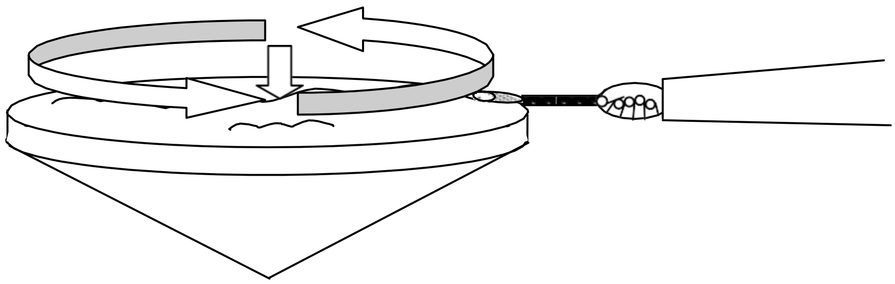

Figure 1. Schematic diagram of the lit taper pattern, 15 mm above the foam surface.

Furthermore, a series of experiments was carried out with foam solutions prepared from potable and synthetic sea water; the latter prepared by dissolving around 4.16 parts of inorganic salts in 95.84 parts of water. The synthetic sea water contained magnesium chloride ($MgCl_2 \times 6H_2O$) at 1.10% by weight, calcium chloride ($CaCl_2 \times 2H_2O$) at 0.16%, anhydrous sodium sulphate (Na_2SO_4), at 0.40%, and sodium chloride (NaCl) at a level of 2.50% by weight [5].

The fire fighting foams investigated included one AFFF formulation (FC-206CF manufactured by 3M Company, prior to the exit of 3M from manufacturing of fire-fighting foams), and three synthetic formulations, RF6 (manufactured until 2006 by 3M Australia), and Formulations A and B. RF6 foam passed ICAO Level B protocol. An improved version of RF6 is presently manufactured by Solberg in Norway as Arctic Rehealing Foam. Rehealing Foam meets ICAO level B. Formulations A and B were purchased in 2004 in Australia, where at the time they were marketed as Class B foams, albeit with no approval and listings to justify this application. RF6 contained a xanthan gum resin, while Formulations A and B did not have any resin. The concentration used for each product mix was prepared according to instructions on the manufacturer's label or literature and is summarised in Table 2.

Table 2. Fire fighting foams used in the present experiments and concentrations of use.

Foam Concentrate Use Level	FC-206CF	RF6	Formulation A	Formulation B
Recommended	6%	6%	0.4%	1-3%
Actual	6%	6%	0.4%	2%

FC-206CF constitutes a film-forming formulation. This means that this formulation possesses a positive *static* film spreading coefficient on *cyclohexane* under ambient conditions (taken as 20 or 25 ^{o}C)

$$S = \gamma_{C6H12-air} - (\gamma_{sol-air} + \gamma_{C6H12-sol}) \quad (1)$$

where the symbols on the right-hand side of Equation 1 denote the surface tensions of cyclohexane and foam solution, as well as the interfacial tension between cyclohexane and foam solution, respectively. Table 3 illustrates that, as expected, only the solution of FC-206CF would spread on cyclohexane. Note in particular, the very low interfacial tensions for Formulations A and B. Complete miscibility occurs when the interfacial tension approaches zero. Because of this consideration, one would expect a significant fuel pickup during forceful application of Formulations A and B, and, related to this phenomenon, poor or no backburn performance.

In practical situations, the formation of thin films depends on the relationship of the *dynamic* surface and interfacial tensions with temperature (since fuel and foam solution are at an elevated temperature), and the type of fuel present [10]. For example, aliphatic hydrocarbons such as n-heptane have the surface tension in the order of 20 mN m^{-1}, whereas aromatics around 28 mN m^{-1}. For comparison, cycloxane displays the surface tension of 24 mN m^{-1}. In reference [10], we show that AFFF solutions would not spread on n-heptane, unless the level of fluorosurfactants in the foam solution exceeds the critical micelle concentration. In general, it is more challenging to form films on surfaces of aliphatic fuels, with fires of aliphatic fuels being more difficult to extinguish than those of aromatic fuels, ceteris paribus. As the spreading coefficient approaches zero, films tend to spread very slowly. For this reason, in our view, the spreading property of thin films of solution of fluorosurfacants is not as important for fire suppression as the improved sealibility of flammable vapours offered by the presence of fluorosurfactants.

Table 3. Surface and interfacial properties of foam solutions considered in this study.

	FC-206CF	RF6	Formulation A	Formulation B
Surface tension of foam solution, mN m^{-1}	16.4	26.4	24.0	27.0
Interfacial tension with cyclohexane, mN m^{-1}	4.3	2.4	0.6	0.8
Spreading coefficient for cyclohexane, mN m^{-1}	3.3	-4.8	-0.6	-3.8

Two replicates of the procedure using RF6 (1 cm foam thickness) were undertaken to confirm the reproducibility of the experiments, generating results of 25 and 30 min of vapour suppression for both trials, for an average of 27 min. The method was replicated for 2-cm thick layer of RF6 foam, resulting in over 60 min (65 and 70 min) of complete vapour suppression, having an average of 67 min of suppression. Figure 2 illustrates the results from the replicated experiments.

RESULTS AND DISCUSSION

Suppression of AVGAS vapours with foams made of potable water

Figures 2 and 3 indicated that the AFFF exhibited the best overall vapour suppression performance of AVGAS vapours with an observed protection of 70 min for with 1-cm layer of foam. Formulations A and B provided very little protection. It was noted that as the AFFF foam collapsed, during the last 20 to 25 min of the experiment, fire flashes were observed. This implied that the AFFF released significant amounts of hydrocarbon vapours to allow a flash fire. Thus, conservatively, the effective vapour suppression times of the AFFF correspond to 70 min for the 1-cm layer of AFFF foam, 30 minutes less than the flaming ignition time. The observed behaviour of 2-cm foam application resulted in 180 min of suppression before flashing and 195 min for full ignition. Consequently, the FC-206CF had two observed fire related responses that could signify completion of the experimental run; namely, a flash fire and full ignition. It is the first occurrence of a flash fire or full ignition (for foams displaying no flash fires) that was taken to denote a failure of a foam blanket to provide inadequate protection against reignition. The flash fire response was only observed with AFFF and Formulation B, although reproducible results were observed only for AFFF.

FC-206CF provided good vapour protection when the foam was present, and partial protection during about 20-25 min after the foam collapse. During the latter period, we observed flash fires but no sustained ignition. This observation appears related to the effect reported by Cousins and Briggs [2]. Cousins and Briggs found that kerosene filmed with a coating of a solution of AFFF was more readily ignited than un-filmed kerosene fuel. The foam solution was added to the kerosene surface using an eye dropper, carefully placing the foam solution on the fuel surface. However, the effect reported by Cousins and Briggs occurred during the initial application of an AFFF solution, whereas the effect observed in this research became evident during the final collapse of the AFFF foam and aqueous film. This implies that a limited amount of AFFF solution on a fuel surface creates the same conditions to allow a flash fire, as those reported by Cousins and Briggs.

Stubley and Mulligan [3] repeated the investigation of Cousins and Briggs [2] and found similar results for three hydrocarbon mixtures, namely kerosene, n-dodecane ($C_{12}H_{26}$), and tridecane ($C_{13}H_{28}$). In their investigation, Stubley and Mulligan offered two explanations for the behaviour of aqueous films on the studied hydrocarbon fuels. The first was based on the fractionation of light ends, in which the aqueous barrier promoted cold distillation of kerosene, allowing smaller more volatile fractions to separate and evaporate into the space above the fuel where it ignited when exposed to a naked flame. However, their experiments showed the same response for kerosene, n-dodecane, and tridecane, disproving the theory. The second proposal was the viscous film theory. This suggested that the water in the aqueous film evaporated, leaving the surfactants to emulsify the hydrocarbons into a potentially flammable mixture. The measurements with n-dodecane and tridecane demonstrated that the AFFF aqueous films tend to dehydrate, with the remaining surfactants on the fuel surface emulsifying hydrocarbon fuels and resulting in early ignition episodes, similarly to those observed in the present investigation.

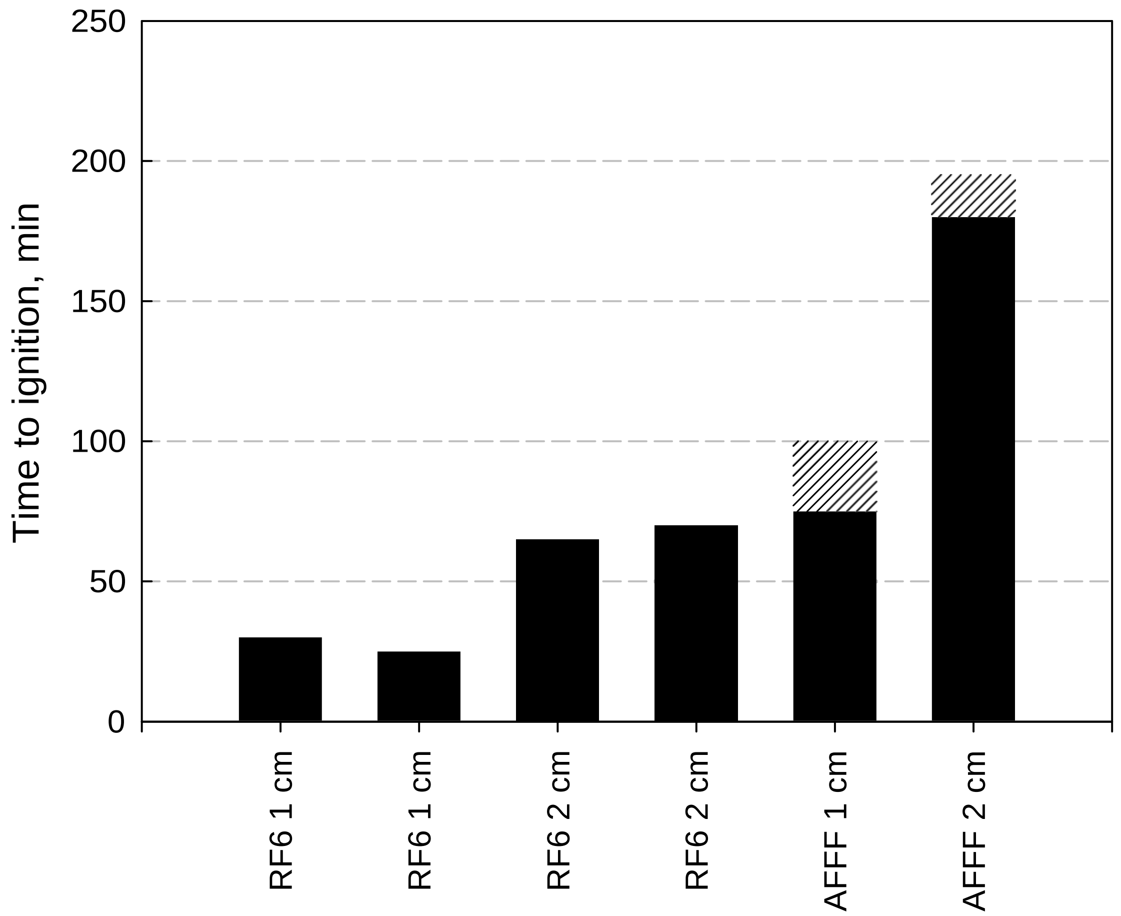

Figure 2. Reproducibility of suppression of flammable vapours by RF6 and AFFF; AVGAS fuel, potable-water foam. The shaded area in the results for AFFF indicates the time between

flash and sustained ignitions. Doubling of the thickness of a foam layer doubles the protection time, both for RF6 and AFFF formulations.

When the surfactant solution is not constantly supplied by a draining foam structure, the aqueous film slowly dissipates. Eventually films either evaporate or collapse through the hydrocarbon fuel to join the more dense water layer below. As a consequence of decreasing concentration of surfactants in the foam solution, or decreasing amount of foam solution on the surface of a hydrocarbon liquid, the AVGAS vapour builds to concentrations that support a flash fire. With time, the film weakens further until the concentration of the vapour becomes adequate to support ignition and continuous combustion. Flash fires pose dangerous conditions and should not be considered as an acceptable risk for emergency personnel. For this reason, a flash fire signifies a failure of a foam blanket to provide adequate protection.

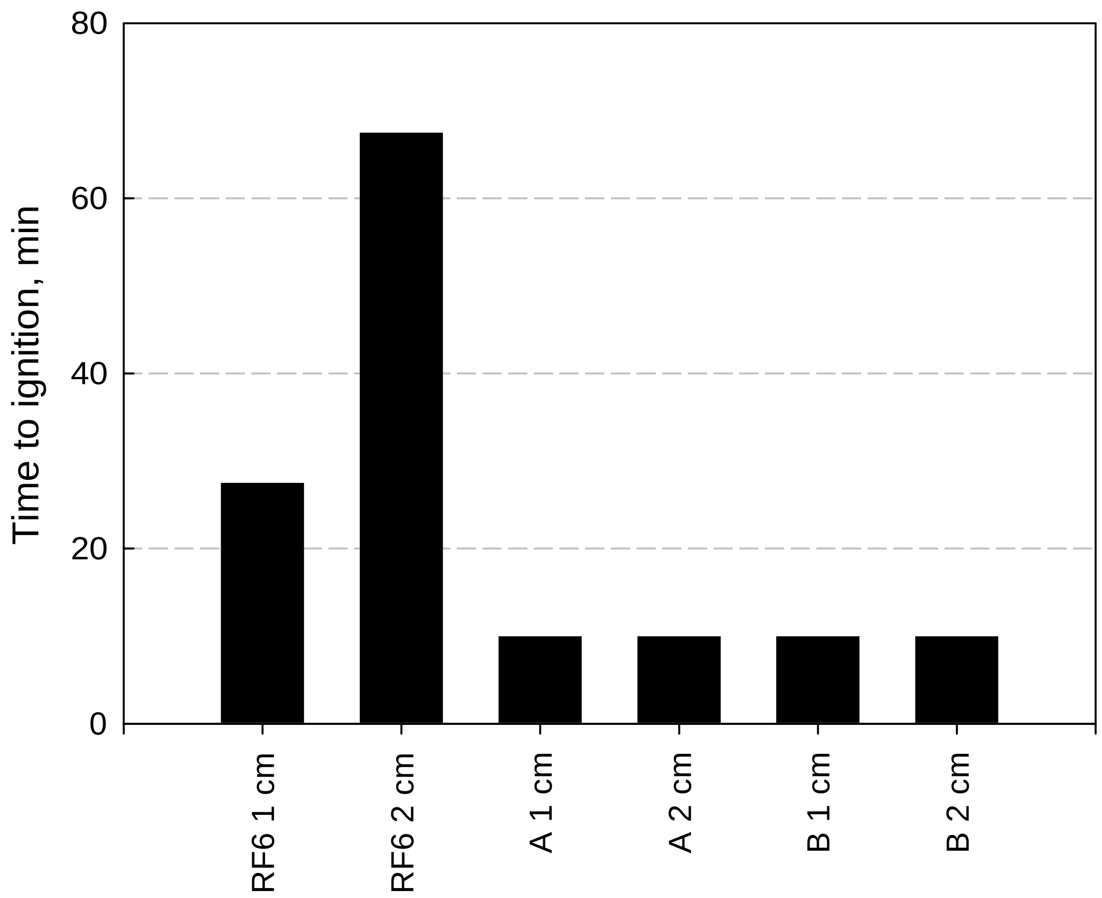

Figure 3. Comparison of performance of all formulation of FfreeF; AVGAS fuel, potable water foam.

Suppression of heptane vapours with foams made of potable water

Figure 4 compares the performance of FfreeF with that of a AFFF formulation, for 2-cm layers of foams. Clearly, these experiments demonstrate that n-heptane affords longer protection time, as a consequence of its lower vapour pressure of 6.1 kPa as compared to 38-48.5 kPa for AVGAS. The results for 2-cm layer of RF6 included in Figure 4 represent an average of two experiments that yielded 260 and 280 min of protection, respectively. This corresponds to a scatter of about 7%, with the overall error in the estimate of the protection time of 12.5%.

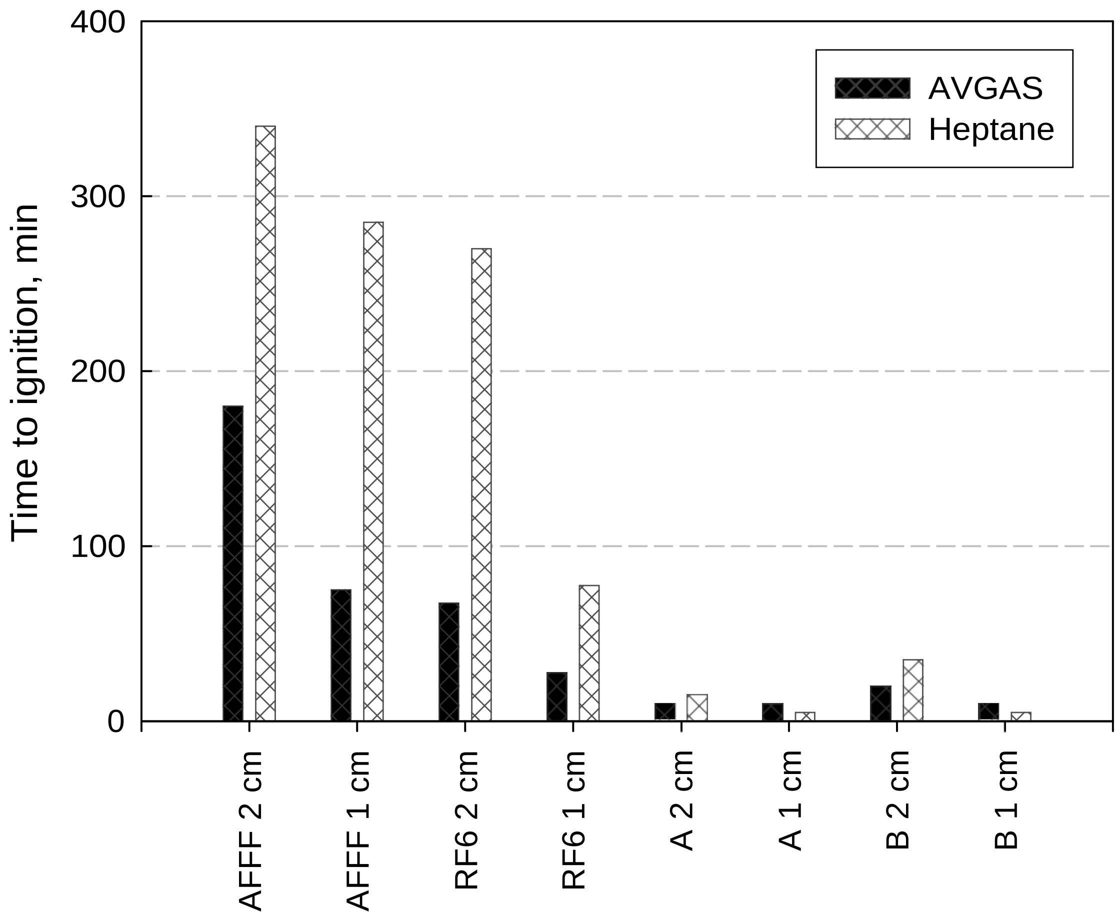

Figure 4. Comparison of the performance of all formulation of AFFF and FfreeF on AVGAS and heptane fuels. Potable water was used to prepare the foams. Note that for 2-cm blanket of Formulation A placed on the AVGAS fuel, flash fires were observed between 10 and 35 min. Consistently with the discussion in the text, we included the protection of 10 min in the figure.

For AVGAS, on average, doubling foam cover doubled the sealibility time. However, for n-heptane, doubling the foam cover increased the sealibility time 300% for RF6 and 120% for AFFF formulations. A strong effect of application density on vapour suppression was not the case for the other synthetic foams. Formulations A and B appear to perform erratically, for 2-cm foam layers there appears to be an improvement in the foam performance for lower-vapour pressure fuels, unlike for 1-cm foam layer. The switch to heptane does not alter the ranking of the foams. Formulations A and B ranked consistently with the results of the AVGAS experiments; i.e., they exhibited no effective vapour suppression capabilities.

Suppression of AVGAS vapours with foams made of sea water

A series of experiments was executed utilising foam mixtures with synthetic sea water applied to AVGAS fuel to observe the effect of the electrolytes. The same fire fighting foams were again applied following the previously described methodology. Electrolytes, like those found in synthetic sea water, have been shown to increase the rate of drainage of aqueous foaming mixtures of surfactant systems [11]. It was expected that all fire fighting foams considered in the present study would have a similar reaction to the electrolytes in sea water, causing the foams to collapse more quickly resulting in a reduction of vapour-sealability performance.

Figure 5 compares the results for sea-water experiments with those for the fresh-water measurements. The mix of synthetic sea water with foam concentrate decreased the effective vapour suppression time off AFFF and RF6. Both AFFF and RF6 appeared to collapse faster and had become less stable, resulting in ignition about 20-25 min earlier that for foams prepared from potable water. This corresponded to about 14-30% deterioration in the performance. In some instances the appearance of the foam changed, such that white sediment was observed to form in the foam structure as the foam progressed through its final phases of cellular collapse.

However, in the case of Formulation B, the use of synthetic sea water extended the durability of the foams and their performance by 10-15 min. Formulation B may contain surfactants that are not negatively impacted by inorganic salts. Since Formulation B was designed for fire extinguishment and on-site remediation of hydrocarbon fuels, Formulation B may contain bacteria as part of its composition. It is most likely that this mixture contains also emulsifiers or fatty acids to assist the break down of the hydrocarbons. Emulsifiers and fatty acids are known to have salt tolerance and may aid in the stabilisation of foam structure.

Comparison of performance

Table 4 summarises the foam performance and ranks the concentrates. The ranking of 1 corresponds to the longest sealability time, and the best performance. It follows from Table 4 that the performance ranking remains essentially unchanged through the five sets of experiments. Clearly the FC-206CF AFFF has the best vapour sealability, followed by RF6 and, then by Formulations A and B. This ranking is unaffected by fuel type, initial amount of foam and the presence of electrolytes in the water.

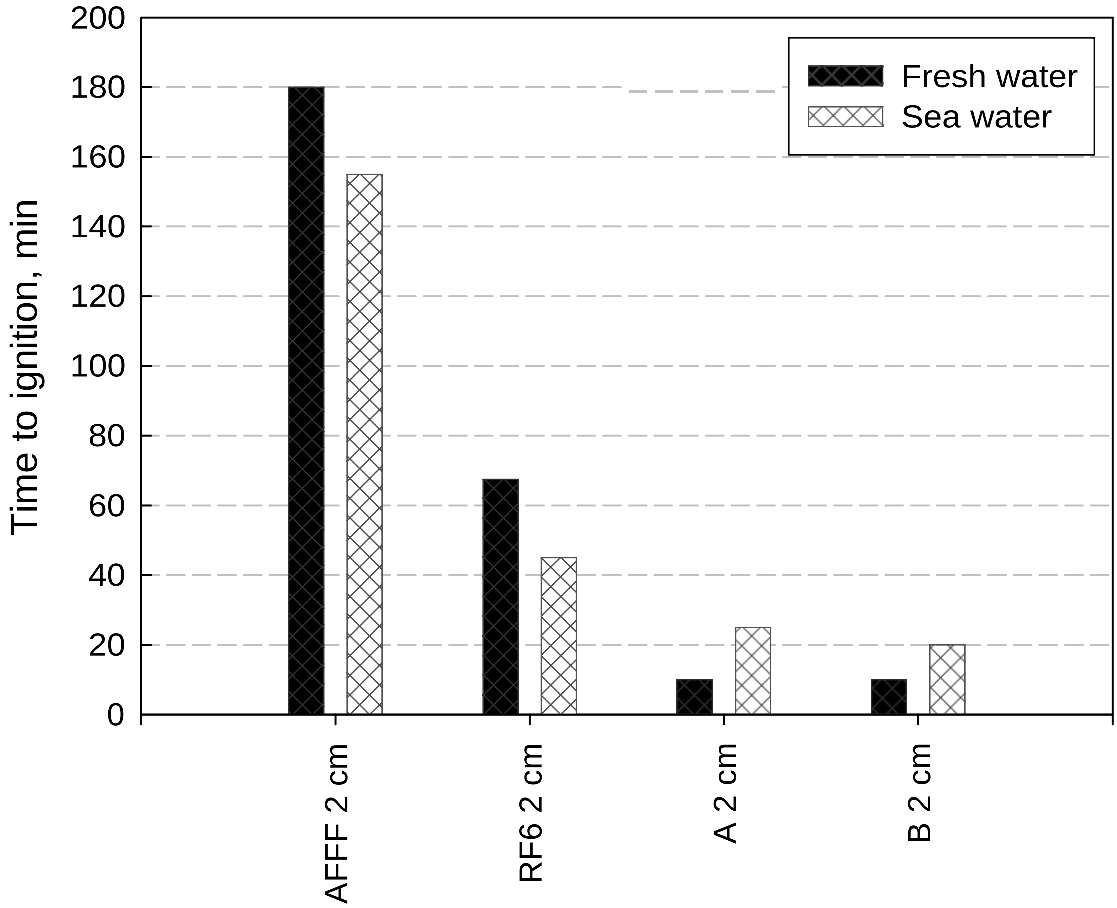

Figure 5. Comparison of the performance of all formulation of sea-water AFFF and FfreeF on AVGAS fuel.

We now compare the measurements of flux chamber experiments reported in reference 4 with the measurements of the present sealability experiments. Both sets of measurements show that as foam loses its ability to suppress flammable vapour, the vapour concentration rises to a level that is capable of supporting a flash fire or full ignition. As illustrated in Figures 3-6 of reference 4, once the vapour breakthrough occur and the fuel mass flux increases rapidly, the effectiveness of the foam decreases to such a level that the existing foam blanket quickly loses its functionality. Consequently, in a practical risk reduction situation, foam needs to be applied more frequently to prevent fuel ignition. Table 5 compares the observations from the sealability and flux chamber experiments.

Table 4. Summary of the results of sealability experiments with performance ranking.

Fuel	AVGAS	AVGAS	AVGAS	Heptane	Heptane
Thickness of a Foam Layer (cm)	1	2	2	1	2
Water Type	Fresh	Fresh	Sea	Fresh	Fresh
Foam Concentrate Ranking					
FC-206CF	1	1	1	1	1
RF6	2	2	2	2	2
Pyrocool FEF	3 - 4	3	3	3 - 4	4
Micro-Blaze Out	3 - 4	4	4	3 - 4	3

Table 5 illustrates that RF6 can effectively mitigate the vapours of flammable fuels, provided that the foam blanket of RF6 is replenished three times as often as it would have been for a good AFFF formulation. Formulations A and B provide little or no protection for vapour suppression. As far as we know, these formulations possessed no approvals and listings. From a practical perspective, current findings indicate the need to require approvals and listings of FfreeF during one's selection and purchasing processes, as done for AFFF formulations.

Predictive charts found in literature recommend thicker applications of AFFF foams when suppressing volatile hydrocarbons such as heptane, methyl ethyl ketone and toulene with frequent re-applications of AFFF. The predictive charts show the reapplication of 2.5 cm of AFFF every 10 min, about 20 cm of foam every 30 min, or 30 cm of AFFF every 60 min to achieve a vapour secure environment [1]. When the depth of foam in the study was increased with either RF6 or AFFF, the vapour suppression performance markedly increased. Therefore, when fire-brigade field application guidelines are followed, foam is typically reapplied every 20-30 min and foam depths are more significant than 1 cm. RF foam technology has been used with success to suppress vapours given off by large surface-area spills, for example by Idemitsu Kosan Co. Ltd., Japan.

Table 5. Sealability results for 1-cm thick foam blanket for AVGAS and n-heptane compared to the measurements of the flux chamber experiments (n-heptane only [4]).

	Sealability Method (AVGAS) Present study		Sealability Method (n-heptane) Present study	Flux Chamber (n-heptane)
	Time for Flash Ignition (min)	Time for Flaming Ignition (min)	Time for Flaming Ignition (min)	Vapour Break Through (min)
AFFF	180	195	285	159
RF6	None observed	50 – 65	75-85	48
Formulation A	None observed	10	5	0
Formulation B	None observed	10	5	0

CONCLUSIONS

In this contribution, we compared the performance of FfreeF formulations, available in Australia circa 2004, with a PFOS-based AFFF formulation for suppression of vapours of AVGAS (flash point of -50 ºC) and n-heptane (flash point of -4 ºC). In the comparison, we applied the methodology of the Australian Defence Force Specification DEF(AUST)5706.

We have argued that the occurrence of flash fires should constitute a failure criterion for foam blankets to suppress flammable vapours. Flash fires create a dangerous situation and should not be considered as an acceptable risk for emergency personnel. Therefore, this criterion was applied consistently to interpret the results of the present measurements. Flash fires appear to be a consequence of the fluorosurfactants present in AFFF formulations with the underlying phenomena engendering the behaviour being similar to those reported in the study of Stubley and Mulligan [3].

Our investigation has led to the following findings:

- Under laboratory conditions, with a foam blanket 1-2 cm deep, best-performing FfreeF formulation (RF6) provides about 30% of the durability of an AFFF for protection against evaporation of low-flashpoint flammable liquids. Increase in the foam thickness for either RF6 or AFFF indicates significant improvement in foam performance. The present measurements, including the ranking of concentrates, are very consistent with those of the flux-chamber apparatus of reference 4.

- On the basis of the present study and the success in applying RF foam technology to large surface spills (e.g., by Idemitsu Kosan Co. Ltd., Japan), we propose that RF6 and similar FfreeF formulations could provide satisfactory performance in practical situations. Large-scale experiments are required to verify this suggestion and to provide measurements of thicknesses of recommended foam layers and application frequencies, similar to those developed by Pignato [1] for AFFF. Future legislation may limit the use of fluorosurfactant-based foams in some countries, with RF6 or other RF6-like FfreeF providing an environmentally-acceptable alternative.

- The current measurements indicate that two other FfreeF formulations available in Australia in 2004 offer little or no performance for suppression of flammable vapours. The good performance of RF6 is a consequence of the presence of xanthan gum in its formulation. Marketing of two FfreeF (Formulations A and B) in Australia in 2004 was not supported by results of standardised suppression tests. The present results affirm a view that one must require approvals and listings of all foams considered during the selection and purchasing processes.

- Under laboratory conditions, inorganic salts present in the foam owing to the use of sea water tend to deteriorate the performance of AFFF and RF6 foams by between 14 and 30%.

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