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Fluorosurfactant retention in the foam blanket during gravitational drainage of an aqueous film-forming foam

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Abstract

A model aqueous film-forming foam (AFFF) comprising a fluorocarbon surfactant (6:2 FTSaB), hydrocarbon surfactant, solvent, and water was deployed on a heptane fire with the gravimetrically-drained foam solution collected at regular time intervals and analysed for surfactant concentration.

Foam drainage behaviour within the model foam system was non-linear for both control (no fire exposure) and fire-exposed tests, as would be expected. However, the concentration of fluorosurfactant within the drainage solution was initially lower, increasing with time. This suggests that the fluorosurfactants are retained within the foam blanket for longer than other constituents of the model foam. This is proposed to result from the unequal probability of rupture in bubbles comprising the foam blanket: as the rate of foam collapse decreases with time, bubbles with lower stability burst until those with a higher persistence and higher surfactant content remain.

Keywords

Firefighting foam; Surfactant drainage; Surfactants; Aqueous film-forming foam; Poly- and perfluoroalkyl substances; Free foam drainage; Coalescence; Coarsening; Gravitational drainage

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Introduction

Aqueous film-forming foams (AFFF) are deployed to rapidly suppress and extinguish liquid hydrocarbon-fuel (Class B) fires. Whilst specific AFFF formulations vary depending on intended use, common formulation constituents are surfactants, solvents, and water. AFFFs have been developed around the use of a mixture of hydrocarbon and fluorocarbon surfactants, the roles of which are poorly understood at a mechanistic level [1, 2].

Broadly, the fluorocarbon surfactants provide the foam with low surface tension, high stability, and resistance to destruction by fuel; all desirable qualities for an effective fire-fighting foam [1, 3]. The high carbon-fluorine bond strength contributes to the effective performance of foams [4], but also makes them highly resistant to degradation, thus, concern regarding the environmental persistence, bioaccumulation and toxicity of long-chain poly- and perfluoroalkylated substances (PFAS) has grown and is driving regulatory restriction of their use [3-6]. The carbon-fluorine bond strength increases with the degree of fluorination in the molecule [7]. Modern AFFFs utilise only short-chained (carbon chain $\leq$6) telomer-based fluorocarbons, which are not presently subject to the same restrictions as their long-chain homologues (carbon chain $\geq$6) [8-10].

AFFFs are supplied as concentrates, which, depending on the formulation, are proportioned at either 1%, 3% or 6% in water immediately before being passed through an aspirating nozzle to generate the foam. When deployed for firefighting, an AFFF suppresses and extinguishes a fire through multiple interdependent mechanisms (Figure 1). These are: 1) lowering the fuel temperature via the application of water; 2) separating the flames from the source of ignition; and 3) suppressing the release of flammable vapours through the formation of a foam blanket across the fuel surface and providing protection against re-ignition [11, 12].

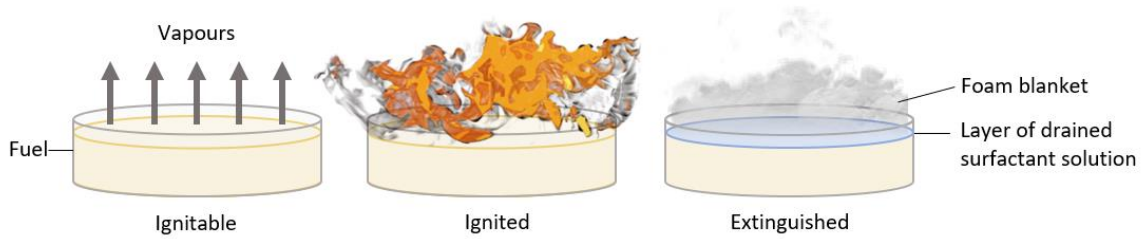

Figure 1. The fire extinguishment mechanisms of firefighting foam used on a liquid fuel (class B) fire.

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Once deployed, an AFFF is a disordered system, consisting of polyhedral gas bubbles separated by thin liquid films or lamella, which are applied to the surface of the burning fuel - forming a *foam blanket*. This system is out of equilibrium, with spatial and temporal liquid distribution governed by fluid dynamics in the foam [13]. A foam changes by drainage and by coarsening, also referred to as Ostwald ripening [14].

The overall stability of the foam blanket is an important measure of the performance of a firefighting foam. Drainage, the time-dependant flow of liquid from foam, is the most widely used parameter to quantify foam stability [15]. The liquid within a foam is confined into a network of channels (plateau borders) that are connected at nodes in fours, some liquid is also trapped between the thin and flat films formed between two bubble faces [16]. This network comprises the foam blanket, the stability of which influences foam drainage processes and is dictated by a complexity of interdependent mechanisms: 1) foam drainage by gravitational liquid flow; 2) shear stresses imparted by capillary pressure difference, inducing coarsening by diffusion of gas between bubbles; and 3) bubble coalescence caused by the rupture of liquid films between neighbouring bubbles [17-22].

Data relating to the behaviour of surfactants within AFFF mixtures are sparse, with the understanding of AFFF behaviour largely based on empirical observations or centred on foam degradation rate [22, 23], often at a scale ranging from single interface (microscopic) [24, 25] to several bubbles (macroscopic) [24, 26]. In addition, there are no recognised single or group of mechanisms capable of predicting the extinguishment times for different fire sizes [1], however, a selection of variables are used to evaluate the performance of firefighting foam [21, 27-29]. These include spreading coefficient, time required for 25% of the solution to drain from the foam, foam expansion ratio, refractive index of the drainage solution, and foam rheological properties [21, 27-29].

This work takes a novel approach to examine the behaviour of a simple model AFFF [8, 30] with particular focus on the gravimetric drainage rate and drainage solution concentrations using a time-series approach and four analysis methodologies. Modes of analysis were: 1) HPLC-HRqToF-MS

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analysis of fluorosurfactant concentration, 2) total oxidizable precursor assay for total detectable PFAS concentration, 3) analysis of dynamic surface tension, and 4) determination of refractive index. This multifaceted approach has allowed for the detailed evaluation of the drainage behaviour of the firefighting foam system and has enabled the identification of non-linear surfactant drainage behaviours from the foam blanket.

Experimental

Model foam preparation and characterisation

A simple model AFFF foam concentrate was formulated to pass an industry standard fire test (EN1568: Part 3, forceful informative test; Figure 2) on a heptane fuel. The foam contained a single commercially available fluorosurfactant, 6:2 fluorotelomer sulfonamido betaine (6:2 FTSaB; Capstone™ 1157, Chemours, US), extensively used in AFFF products. The commercially available, non-volatile content of Capstone 1157 has a purity of 95% with respect to 6:2 FTSaB with minor impurities belonging to other FTSaB homologues, perfluoroalkyl carboxylic acids (PFCAs), fluorotelomer sulfonates and other polyfluorinated alkylic compounds [10].

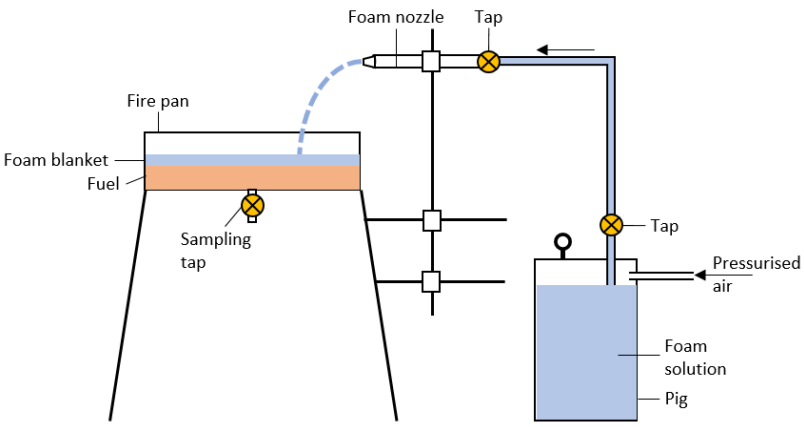

Figure 2. Schematic of the EN1568: Part 3 fire test.

The model foam also contained hydrocarbon surfactant, solvent and high purity water (18.2 MΩ.cm at 25 ºC) (Table 1). The model foam solution was prepared by diluting the model foam concentrate at 3% (by weight) in high purity water (18.2 MΩ.cm at 25 ºC) and characteristics determined (expansion

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ratio, surface tension, interfacial tension (foam solution/heptane) spreading coefficient (on heptane), and critical micelle concentration; Table 2).

Table 1. Composition of model foam concentrate. The concentrate was diluted at 3 % in high-purity water prior to fire exposure.

Role	Compound	Conc. (g L^{-1})
Fluorosurfactant	6:2 Fluorotelomer sulfonamido betaine (6:2 FTSaB) (in solution at 27%)	25.75
Hydrocarbon surfactant	Sodium-n-decyl sulphate (in solution at 28%)	53.10
Solvent	Diethylene glycol monobutyl ether	95.36
Water	High purity water (18. 2 MΩ.cm at 25ºC)	825.0

Table 2. Foam solution characterisation. Foam solution was prepared by the dilution of the model foam concentrate at 3 % in high purity water (18.2 MΩ.cm at 25 ºC). * The value for heptane fuel surface tension was provided by Sigma-Aldrich, UK. ¥ Spreading coefficient of the foam solution of heptane fuel was calculated ($S = \sigma_f - \sigma_d - \sigma_{df}$). CMC was determined for the model foam solution at low salinity.

Parameter		
Expansion ratio		7.52
Surface tension, foam solution, σ_f	*mN m* $^{-1}$ *at 20°C*	16.1
Surface tension, heptane, σ_d	*mN m* $^{-1}$ *at 20°C*	20.1 *
Interfacial tension (foam solution/heptane), σ_{df}	*mN m* $^{-1}$ *at 20°C*	3.53
Spreading coefficient (foam solution on heptane), S	*mN m* $^{-1}$ *at 20°C*	-7.53 ¥
Critical micelle concentration (CMC)	*mM at 20°C*	1.462
Foam solution applied	*L*	1.93 ± 0.06
Foam volume	*L*	14.5 ± 0.41

Fire exposure and sample collection

The foam solution was transferred to a stainless-steel pig, pressurised to 690 kPa, and forced through an aspirated nozzle to generate a foam at the point of use. Fire exposure was performed using an adapted EN1568: Part 3 fire test [31]. Heptane fuel (9 L) was added to a 0.25 m^2 stainless steel pan with a conical base and a sampling tap in the centre (Figure 2). To reduce contamination risks, all equipment was flushed prior to use using 20% acetone in high purity water. The heptane fuel was ignited and allowed to burn for 60 seconds prior to beginning foam application. Foam application rate was 700 ± 20 g min^{-1} for 2 min 45 s. The fire test was conducted in duplicate with a further non-fire test performed to provide control values. For the fire-exposed samples, the foam extinguished the fire

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at 1 min 44 s and 1 min 23 s, after extinction the foam application was continued for the full 2 min 45 s application window.

Following the application period, foam was allowed to drain gravimetrically, drainage solution was sampled from the tap at the base of the pan with all available drainage solution collected at 4-minute intervals for 20 minutes, after which, further samples were collected at 30 and 60 minutes. To ensure all foam drainage liquid was collected at each sampling time point, the tap at the base of the test pan was opened until the fuel began to drain. Any fuel collected within the sample was removed using a separating funnel prior to storage. In addition to the foam drainage, samples were collected from all points of potential contamination, including foam concentrate, dilution water, and directly from the aspirating nozzle. This was to ensure all potential sources of contamination were accounted for, and therefore, that any PFAS species found in the spent foam after exposure to fire can only have derived from the initial 6:2 FTSaB.

All sample vessels were cleaned using HPLC-grade methanol; foam generation and capture equipment (Figure 2) was cleaned using an acetone (20%) solution and rinsed using HPW.

HPLC-HRqToF-MS analysis

Prior to analysis, foam drainage solution samples were filtered using polyester syringe filters (PET-20/15 15 mm, 0.2 µm pore size ChromofilTM) and diluted by a factor of 333 using LC/MS grade methanol (Fisher scientific, UK). Analysis was performed using HPLC-HRqToF-MS (instrumental settings in Supplementary Table S1). The ESI was operated in both positive and negative instrument modes. Analysis was conducted in full scan MS mode. The PFAS concentration values for samples under the negative-mode run were determined by normalisation against the mass-labelled 6:2 FTS (6:2 fluorotelomer sulfonate, Wellington Laboratories, Canada) internal standard (50 ng mL^{-1}). All natives were calibrated against calibration solutions CS1-CS5 (2 – 1000 ng mL^{-1}) (Wellington Laboratories, Canada).

Due to the unavailability of appropriate positive-mode PFAS calibration solutions at the time of analysis, the PFAS concentration values were determined using a calibration series prepared from a

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purified Capstone™ 1157 derived 6:2 FTSaB (0.1 – 1000 ng mL^{-1}) (Capstone is a registered trademark of Chemours, US).

The exact chemical structure of Capstone 1157 has not been disclosed by the manufacturer, however, a number of sources agree on the structure (Figure 3) [10, 32].

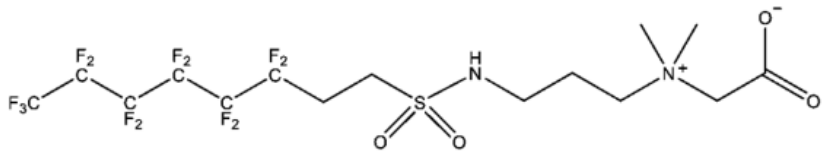

Figure 3. The proposed Capstone 1157 structure is 6:2 FTSaB (6:2 fluorotelomer sulfonamido betaine).

Dynamic surface tension

Analysis of dynamic surface tension was performed on an aliquot of each drainage sample using a bubble pressure tensiometer (Sita-Proline 115. Surface tension (mN m^{-1}) readings were taken for bubble lifetimes ranging from 160 to 20000 ms from which a surface tension evolution curve was generated.

Refractive index

Refractive index was analysed using a handheld refractometer to mimic field measurement capabilities and procedure.

Total oxidizable precursor assay

Total oxidizable precursor assay (TOPA) has been developed as a means of determining measurable PFAS concentrations through aggressive oxidation to abiotically-convert precursor compounds to more easily detectable compounds. All TOPA analyses for this study were conducted by an external contract research organisation (Envirolab services Pty Ltd., NSW, AU).

Total interfacial surface area estimation

A foam was formed from the model foam solution within the laboratory (DEF 41 branch-pipe) and observed using optical microscopy to estimate the mean bubble radius (r). This was used to calculate

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the total interfacial surface area required for complete adsorption of one litre of foam solution, which was 110 m^2 (calculations in Table S3 and Figure S1).

Results and Discussion

Foam drainage rate and volume

The volume of gravimetrically sampled foam drainage solution at each time point (0, 4, 8, 12, 16, 20, 30 and 60 min) was compared to the analysed 6:2 FTSaB concentration within the same. This enabled calculation of the proportion of the fluorosurfactant present within the solution over the drainage process (Figure 4).

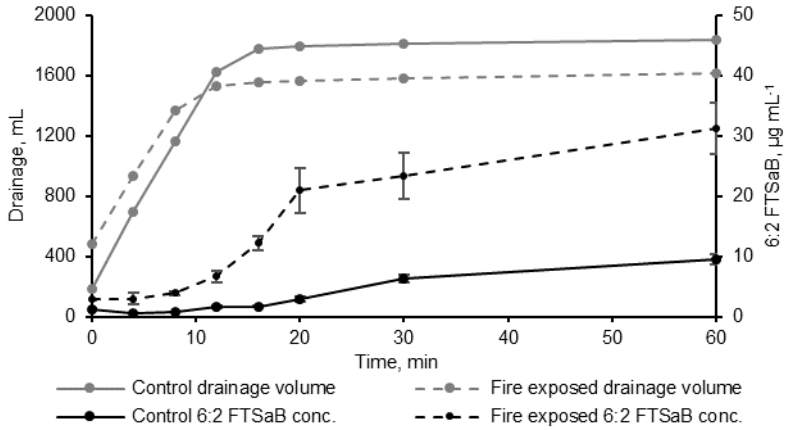

Figure 4. Left axis) Cumulative drainage volume for fire-exposed and control tests. **Right axis)** Concentration values of 6:2 FTSaB within time-series sampled foam drainage solution for fire-exposed and control tests. The 6:2 FTSaB analysis was performed using HPLC-HRqToF-MS analysis (n=4). Time (min) was measured from the point that foam application was stopped, thus +2 min 45 s following beginning of the foam application.

The initial rate of drainage was faster in the fire-exposed test; however, over the 60-minute drainage period the total volume of drainage solution collected was 1.61 L for the fire-exposed and 1.84 L for the control. This represents 83.7% recovery for the fire-exposed test and 95.6% for the control test. The higher temperature solution draining through the foam and the transfer of heat from the foam surface and within the fire-exposed foam are expected to have led to evaporation of the foam solution, resulting in the lower drainage solution volume [33]. Additionally, it is suggested that, although foams will emulsify fuel when they impact the fuel surface, fluorocarbons do not generally adsorb at the water/fuel interface as they are both hydrophobic and oleophobic, unlike hydrocarbon surfactants,

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which are only hydrophobic (2, 24). Further, there is potential for an antifoam effect from heptane fuel droplets captured within the foam. Broadly, antifoam agents break the films between bubbles [34]. Oils are widely employed to control foaminess and foam stability across various technologies. The extent of the antifoaming effect of the heptane fuel was not examined within this study. Whilst drainage of liquid films and foams, coarsening, and coalescence are recognised as the main processes which determine the longevity of a foam, due to the complexities of foam structure, their relative weighting and interactions are difficult to quantify [35].

A classic method for measuring drainage rate is the drainage half-life ($t_{½}$) - the time required for 50% of the original liquid present in the foam to drain [16]. This was estimated to be at 6.4 minutes for the control and 4.7 minutes for the fire-exposed samples. Whilst this is a useful indicator of drainage-rate, it does not provide any information relating to the composition of the foam profile in terms of composition or vertical density, both of which have implications for how well a foam can prevent fuel reignition.

The initial rate of gravimetric drainage following foam application was stable for 8 minutes in both the control and fire-exposed tests (Figure 4). Here the hydrostatic pressure at the base of the foam was greater than the capillary pressure, resulting in liquid flowing out of the foam system [19, 20]. Following the initial phase, we suggest there was an occurrence of capillary suction pressure within the narrowing plateau channels, which served as a counterbalance to the hydrostatic pressure driving the liquid drainage. Once the hydrostatic and capillary pressures become equilibrated and the equilibrated foam profile is observed, as here from 8 minutes after application and capillary pressures under gravity. Drainage of the liquid fraction over time lead to instability of the foam as a result of film rupturing, causing further foam drainage [24]. This observation was consistent with reported foam drainage behaviours, where the observed drainage rate for an AFFF was faster in the initial drainage stages before decreasing [1, 23, 30, 33]. Verbist, et al. (1996) described the drainage of liquid foam using a non-linear partial differential equation based on foam density as a function of time and vertical position, which suggested that film thinning is an important but often overlooked aspect of foam drainage.

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During this initial (first 8 minutes after end of application) phase, the rate of drainage was greater in the fire-exposed (171 mL min^{-1}) than in the control tests (146 mL min^{-1}). The impact of fire exposure is suggested to have increased the initial rate of foam degradation [1]. The increased temperature of the solution reduced the viscosity of the liquid, leading to an increased volume of solution around the plateau borders, and increasing the rate of thinning within the vertical lamellae [33, 36]. Bubble-size has been reported to correlate with drainage rate [1, 30] and although bubble-size was not monitored throughout the drainage period, the foam composition and foam generation method were consistent between tests. As the foam drains, bubbles coalesce and the surface area decreases to the point where the area is insufficient to adsorb all the 6:2 FTSaB resulting in its detection in drainage water. There are two processes that are likely to have contributed to the observed surfactant release: 1) the increase in average bubble size due to bubble-bubble coalescence, and 2) the disappearance of bubbles after coalescence with the atmosphere in the uppermost foam layer. The interface adsorption layer will contain both fluorocarbon and hydrocarbon surfactants, but the fluorocarbon is expected to dominate the surface layer as fluorinated surfactants have been shown to coarsen slower than hydrocarbon surfactants [37].

Drainage solution surfactant concentration

The 6:2 FTSaB concentration was lower in the initial drainage solution for both control and fire-exposed samples. The concentration of 6:2 FTSaB within the drainage solution 4 minutes after application was 0.44 and 2.97 µg mL^{-1} for the control and fire-exposed samples, respectively, however, 20 minutes after application the concentration was 2.87 and 20.9 µg mL^{-1} for control and fire-exposed samples, respectively. The respective drainage volume for the control and fire-exposed samples represented 63.4 and 85.1% of the total applied volume of foam solution. However, after 8 minutes, the fluorosurfactant (6:2 FTSaB) concentrations, analysed by HPLC-HRqToF-MS, were 0.67 and 3.85 µg mL^{-1} for the control and fire-exposed samples, respectively, accounting for only 34.3% and 60.3%, respectively, of the total quantity of 6:2 FTSaB drained from the foam over the 60-minute drainage time. This suggests that, whilst the rate of drainage was relatively steady, the fluorosurfactant component (6:2 FTSaB) was retained within the foam blanket.

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To support the 6:2 FTSaB concentration values, the rate of dynamic surface tension evolution within the time-series samples of drainage solution was compared (Figure 5). The dynamic surface tension is an indicator of surfactant concentration within the drainage samples [38]. A strong inverse correlation was observed between the concentration of 6:2 FTSaB and the surface tension values at a set time point (20 s) for both the control (r = 0.90) and fire-exposed (r = 0.95) samples (Figure 5c). This provides further support to show that surfactant concentration within the drainage solution was lower in the early drainage stages compared to later drainage stages.

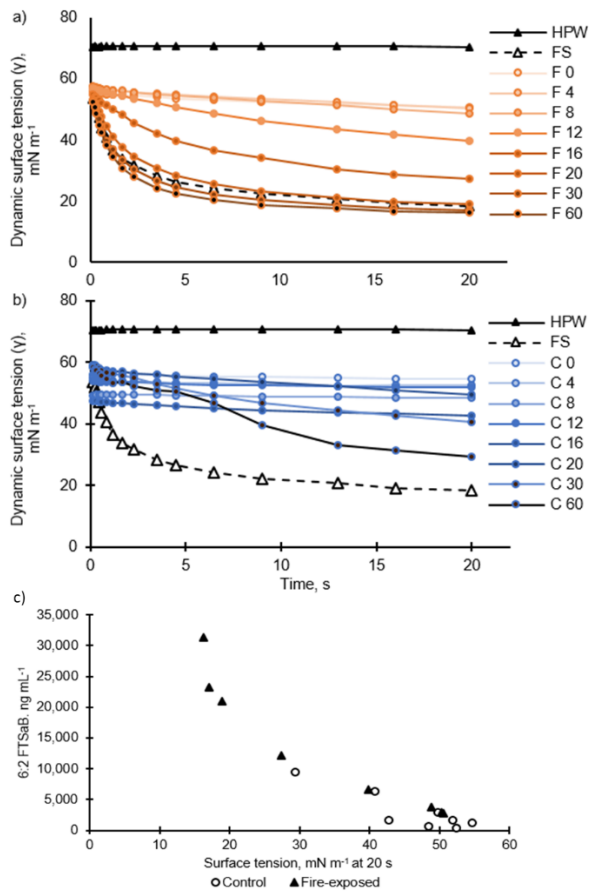

Figure 5. Comparison of the dynamic surface tension (γ) evolution for time-series sampled drainage solution taken for **a)** the fire-exposed foam (F= fire exposed; 0-60 = time sample taken following foam application) and **b)** the control (non-fire exposed) foam (C = control; 0-60 = time sample taken following foam application). Measurements were performed at 25 °C using a Sita – Proline 115 bubble pressure tensiometer. FS = foam solution; HPW = high purity water (18.2 MΩ cm^{-1}). Time (min) was measured from the point that foam application was stopped, thus +2 min 45 s following beginning of the foam application. **c)** Correlation between 6:2 FTSaB concentrations and dynamic surface tension values recorded at 20 s for each drainage sample for the control (r = -0.90) and fire-exposed (r = -0.95) samples.

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Additionally, TOPA results showed that total PFAS concentrations were within 25% and 11% of the 6:2 FTSaB concentrations as determined using HPLC-HRqToF-MS for the control and the fire exposed concentrations, respectively (results presented in Supplementary data Table S1).

The non-linear surfactant drainage dynamics exhibited within the presented data highlight a further complexity with regard to the behaviour of surfactant foams. Similar phenomena to this have been reported for emulsions [39, 40]; however, to the best of our knowledge it has not been reported in foams.

Whilst the scope of this study does not extend to the characterisation of the mechanisms involved, it is proposed that these results were caused by the unequal probability of rupture in bubbles comprising the foam blanket [21]. Coarsening processes cause larger bubbles to grow and smaller bubbles to vanish, leading to surfactant solution draining from the foam as it collapses [14]. The rate of foam collapse decreases with time, as bubbles with lower stability burst, until those with a higher persistence and higher surfactant content remain [19].

The concentration of 6:2 FTSaB within the drainage solution was consistently higher in the fire-exposed sample, ranging from 56 to 86% of the known 6:2 FTSaB concentration in the foam solution, in all drainage from the fire-exposed foam. It is proposed that the observed differences are a result of the increased temperature causing the bubbles closest to the heat source (at the pan edges and fuel surface) to expand and burst. Additionally, the rate of coarsening is enhanced at higher temperatures [15, 41]. Although the temperature of the fuel and apparatus was not monitored throughout the experiment, a higher rate of drainage was observed during the first 20 minutes of drainage solution sampling in the fire-exposed test (Figure 2), which we suggest was due to the higher temperatures, although further work would be required to provide confirmation.

Implications

Firefighting foam

The drainage dynamics are of particular significance within the context of aqueous film forming foam products. The assumption of consistency over time with regard to surfactant concentration in drainage

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water is built-into standardised methods for equipment commissioning and calibration. The US NFPA [27-29] standards for testing the correct performance of firefighting equipment, outlines two methods for checking the performance of proportioning equipment: refractive index and electrical conductivity. Electrical conductivity provides greater accuracy, but only in freshwater, thus refractometery is often the favoured method [42]. The refractive index of the foam drainage solution, tested once 25% drainage (by volume) is reached, is compared to a pre-prepared calibration curve to determine the surfactant concentration. The firefighting proportioning equipment is then adjusted accordingly [27].

Based on the results from this study, 25% drainage was achieved within 4 minutes of the foam application for both the control and fire-exposed foam. The refractive index for drainage solution samples for the model foam following 4 minutes of drainage time were analysed using a handheld refractometer (Bellingham + Stanley OPTi Duo), which is equivalent to that used during field-based equipment checks. Results show refractive indexes within these samples were lower than the freshly prepared foam solution (control = 1.3335 ± 0.0001, fire-exposed = 1.3334 ± 0.0001, fresh foam solution = 1.3337 ± 0.0001, HPW = 1.3330 ± 0.0001; n=3). Based on the NPFA method, for determination of surfactant concentration, there would be a 33.3% and 44.0% under-estimation for the control and fire exposed samples, respectively. It is likely, therefore, that existing methods for equipment commission and calibration will result in the incorrect set-up of firefighting equipment, leading to over proportioning of the foam concentrate, which, whilst having limited detrimental effect on product performance, may reduce the potential foam application time of a facility during an emergency response. Further, this may result in increased environmental impact as a result of chemical release at higher concentrations and additional economic implications of needing to purchase larger foam quantities.

Other aqueous foam applications

Beyond firefighting foam, aqueous surfactant solutions are widely used for detergency purposes and have a wide variety of commercial and industrial uses including in cosmetics, cleaning products, food and beverage production, oil recovery, and gas recovery [43]. The importance of foam stability across

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these applications is varied, as are the modes of foam degradation observed (e.g. thermal, biological, chemical, time) [44]. However, the retention of surfactants within a foam for longer than other constituents, as reported herein, may have significance with regard to the stability and, thus, the performance of aqueous foams across other applications. For instance in food products such as mousse and ice cream, where foam stability is key to their long-term storage and quality [40] or in haircare products where surfactants stabilise the foams to increase their cleaning capabilities [45]. By increasing the understanding of the mechanisms behind surfactant behaviours in aqueous foams, it may be possible to utilise these mechanisms for the enhancement of formulations.

Limitations

The benefits of using particles to stabilise or destabilise foams is well acknowledged and increasingly used across the many aqueous foam applications [44, 46-48]. Hydrophilic particles collect in the plateau borders, where they serve to slow film drainage. Hydrophobic particles enter the water air/water surfaces of the foam where they cause destabilisation via the bridging-dewetting or bridging-stretching mechanism [44]. How the use of particles impacts on the rate of surfactant drainage is not explored within this study, however, understanding this may also help to further improve formulations.

This study did not monitor the temperature of the foam during degradation; therefore, the impact of system cooling on the drainage of the foam was not accounted for. However, the same mechanism was observed within the control and fire-exposed samples, for which it is logical to assume different temperatures were encountered. Further work is required to determine to what, if any, extent temperature may impact on the surfactant drainage behaviours observed herein.

Firefighting foams are complex mixtures and the understanding of interactions between formulation components is relatively unexplored. In addition, there are a large number of commercially available foam formulations, each designed to meet one or more of the various performance-testing standards, thus, there are a large number of potential interactions and mechanisms, which may be responsible for the observed performance.

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Conclusions

This study examined the gravimetric drainage rate of a simple single-surfactant model AFFF formulation, using a time-series approach and four analysis methodologies (HPLC-HRqToF-MS; TOPA; dynamic surface tension; and refractive index). Results from all modes of analysis used in this study demonstrated that the drainage behaviour within the model AFFF system was non-linear for both control (no fire exposure) and fire-exposed tests. The rate of foam drainage follows a typical trend for both the control and fire-exposed tests with drainage rate being greatest between 0 to 8 minutes and decreasing from 8 minutes. We suggest this to be the occurrence of capillary suction pressure within the narrowing plateau channels, with a counterbalance of hydrostatic pressure driving liquid drainage. Once the hydrostatic and capillary pressures become equilibrated the foam profile approaches equilibration around 8 minutes after application.

The concentration of 6:2 FTSaB in the drainage solution was not consistent throughout the drainage period. The concentration 4 minutes after application was 6.6 times lower in the control and 7.0 times lower in the fire exposed when compared to the concentration 20 minutes after application. This suggests that the fluorosurfactant (6:2 FTSaB) was retained within the foam blanket, although the full understanding of this mechanism requires further study. This phenomenon has not been previously reported in aqueous foams, however, similar has been observed in emulsion films where it is attributed to capillary phenomena.

The increasing pressure to develop environmentally friendly firefighting foams has led to rapid changes to firefighting products, such as the development of fluorine-free formulations. These contain only hydrocarbon surfactants, which have a higher surface tension and thus require additional components to compensate [37]. The effect of these formulation changes will alter the drainage dynamics, and other key parameters including stability mechanics and rheology within the foam, the understanding of which will be key to ensuring high performance of these alternative foam products.

Further, understanding of the observed retention of the fluorosurfactant within foams may lead to the enhancement of product formulations with greater command of the foam properties to suit the intended use. The next step in this work will be to further develop the understanding of the

mechanisms governing surfactant behaviour within the foam blanket with focus on the role of interactions between foam constituents.

Conflicts of interest

There are no conflicts of interest to declare.

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