

FIREFIGHTING FOAM and the environment

Fluorosurfactant firefighting foams are environmentally persistent, with degradation products now existing in our air, water and even human breast milk. Roger Klein explains how the management of these foams is essential to minimising environmental risk.

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Foam is rightly considered to be an essential part of the armoury required operationally by the emergency services to fight fire. Different technical specifications are necessary depending on whether the fuel is Class A, carbonaceous (for example, wood, paper, structural fires, or car tyres, in which penetration and wetting are important) or Class B, liquid fire (with heavy hydrocarbons such as are found in the petrochemical industry and which

require thermally stable blanketing for excluding oxygen and efficient vapour suppression).

Modern firefighting foams for Class B risks, manufactured since the 1960s, have traditionally contained fluorosurfactant as their active principle because of its excellent chemical and thermal stability, as well as its firefighting efficiency. These fluorosurfactants, originally produced by the 3M Company using the Simons electrochemical fluorination process (ECF) and based on perfluorooctane sulphonate (PFOS) chemistry, have been increasingly replaced by fluorosurfactants manufactured by the telomer process, as a result of the withdrawal of PFOS-based products on environmental and toxicological grounds in May 2000.

Foams and additives for Class A risks, on the other hand, do not generally use fluorosurfactant but contain mixtures of hydrocarbon surfactants especially formulated to give good wetting and penetration for carbonaceous fuels. It is worth pointing out that the term surfactant is synonymous with detergent, a category that also includes household washing-up liquids, shampoos and shower gels. Detergents, or surfactants, have the property of being able to reduce the surface tension of water at the air-water interface, causing a water droplet to spread on a surface. They can also emulsify hydrocarbons, oils and greases forming micelles giving a milky colloidal suspension in water. All detergents or surfactants have both a hydrophobic (water-hating – usually hydrocarbon or fluorocarbon) part and a hydrophilic (water-loving – usually highly polar or charged) part to the molecule. Fluorosurfactants are distinguished from hydrocarbon surfactants in having a hydrophobic chain which is also oleophobic (oil-hating) enabling them to film-form at hydrocarbon-water interfaces, hence the acronym for foams derived from fluorosurfactants AFFF (aqueous film-forming foam). Fluorosurfactant foams have very high chemical, thermal and storage stability compared to hydrocarbon foams, thus offsetting the much greater expense of the fluorinated feedstock.

All surfactants affect the surface tension of water at the air-water interface by aligning the molecules so that the hydrophobic alkyl tail points towards the air and the hydrophilic polar head-group towards the water, as shown in Figure 1a. Surfactants can form



Figure 1a Surfactant effect on the surface tension of water

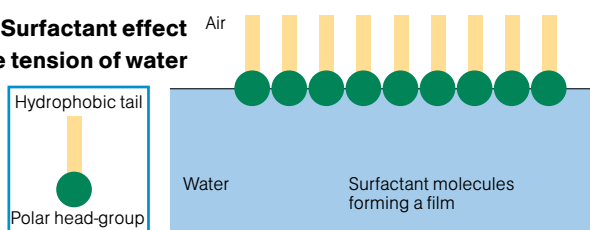
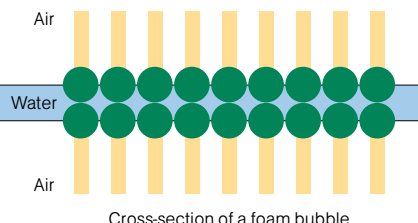


Figure 1b Surfactants form a double layer making up the surface of a bubble



micelles or double layered systems in the presence of water depending on concentration, giving rise to bubble formation in which there is air on both sides of a double layer of detergent molecules (Figure 1b).

All fluorosurfactants, whether manufactured by the PFOS-based Simons ECF method or the modern fluorotelomer process, break down chemically or biologically to produce highly stable, environmentally persistent fluorinated degradation products. These can be toxic and bio-accumulative to varying degrees. The combination of persistence, bio-accumulative potential and toxicity is known as the substance's PBT profile.

In the case of the legacy of PFOS-based products the end-product of breakdown is PFOS itself. PFOS has been found to be dispersed worldwide in a large variety of animal species including man, as well as in animals whose habitats are far removed from any obvious source of contamination such as the polar regions. PFOS is known to be toxic, affecting hormonal metabolism and reproduction in test species, and is bio-accumulative showing bio-magnification in the food chain. The lithium salt of PFOS is classified in the US as an insecticide for use against wasps and hornets. PFOS is so chemically stable that it will withstand hot nitric or sulphuric acid for 24 hours without decomposition!

A seminal paper in 1999 from Jennifer Field's group at Oregon State University (*Environmental Science & Technology* 1999, 33, 2800; with a review 2000, 34, 200) demonstrated that high levels of PFOS persisted in groundwater at former US military firefighting foam-training sites a decade or more after the sites were last used. In some instances the groundwater was still found to be foaming! This sort of data suggests that perfluorinated materials like PFOS are extremely persistent in the environment with half-lives of the order of at least decades. The half-life is the time taken for 50 percent to disappear, so that seven half-lives are required to reduce a concentration to less than 1 percent of the starting value. Many perfluorinated materials are *exceedingly* persistent in the environment: for example, fluoromethane CF_4 is estimated as having an atmospheric half-life of between 10,000 and 20,000 years; trifluoroacetic acid CF_3COOH , the simplest perfluorocarboxylic acid extensively used as a catalyst by industry, has *no known degradation pathway* in the aqueous environment.

In a later study published in 2004 Jennifer Field (*Environmental Science & Technology* 2004, 38, 1828) demonstrated that the degradation product from fluorotelomer foams, the fluorotelomer sulphonate 6:2 FtS or H-PFOS, also accumulated at very high concentrations in groundwater, persisting for at least decades. Moreover, 6:2 FtS concentrations were generally higher than PFOS at those sites that had seen both ECF (PFOS-based) and fluorotelomer foams used. One site showed only PFOS as a contaminant and no 6:2 FtS indicating that no fluorotelomer foams had been used. Another site

exhibited incredibly high levels of 6:2 FtS, up to 14,600g per litre (14.6 mg/l), a decade or more after the site was last used. Interestingly the fluorotelomer sulphonate (6:2 FtS) is very persistent and clearly chemically highly stable in groundwater.

There is currently little information in the peer-reviewed scientific literature regarding the toxicity or bio-accumulative potential of the 6:2 fluorotelomer sulphonate. Reports have suggested that toxicity and bio-accumulation in limited test species are somewhat less than for PFOS, as might be expected based on the chemical structure. The chemical debris produced when fluorosurfactants break down may also include toxic materials such as perfluorooctanoic acid (PFOA), classified as a 'likely carcinogen' by the US Environmental Protection Agency, used in their manufacture. There is now a voluntary EPA industry Stewardship Program aimed at a complete phasing out of PFOA by 2015. Atmospheric breakdown of volatile fluorotelomer precursors has been implicated as the source of perfluorocarboxylic acids found dispersed worldwide.

The bottom line is that all fluorosurfactants, whether PFOS-based or fluorotelomer-based, produce very persistent long-lived fluorinated degradation products which are widely dispersed throughout the environment. Recent studies have identified such products throughout continental Europe, for example, in air samples, in rivers, lakes, soil and groundwater, in potatoes and in human breast milk, raising the toxicological spectre of maternal-foetal transmission. Prior to WWII and the manufacture of perfluorinated materials, which do not occur naturally, stored human serum samples were always negative for organic fluorine compounds. This is no longer true even for the general population not occupationally exposed to these chemicals.

Unfortunately, because these fluorinated materials are so environmentally persistent, continued release into groundwater, whether direct or indirect, will result in increasing concentrations as time passes resulting ultimately in the 'no observable effect' level being exceeded. This will occur whether or not the fluorinated material is toxic or relatively non-toxic; it will just take a longer or shorter time even for the relatively non-toxic compounds depending on the mass flow into groundwater. It is only a matter of time!

What can the fire service do to protect the environment from the effects of using foam operationally?

There are certain incidents in which foam must be used to protect human life or health even if this potentially puts the environment at risk. A decision has to be taken based on a comparative assessment of risk combined with a cost-benefit analysis given all the circumstances. This decision, which at the time has to be an operational one, must be grounded on well-established strategic guidelines which have established politically and socially acceptable



Perfluorinated substances are extremely persistent in the environment. In some foam-training sites, groundwater is still found to be foaming a decade or more after the site was last used.



limitations and constraints to human risk and environmental impact. In European member states local implementations of the EU Groundwater Directive forbid the discharge of organohalogens (this includes fluorosurfactants and their degradation products) to groundwater.

A foam concentrate with the correct specifications for the specific job must be used. The current trend towards using a fluorosurfactant foam originally formulated for Class B hydrocarbon fires at a lower induction rate as a 'one stop' solution for Class A carbonaceous fires, should be strongly discouraged. Class B fluorosurfactant foams do not penetrate carbonaceous fuels nearly as efficiently as properly formulated Class A products, so calling into question their 'fitness for purpose' with all its legal implications. Moreover, because most Class B foams contain fluorosurfactant and most Class A fires, for example wildland or bushfires, require the highly dispersive application of foam directly onto vegetation and soil with no possibility of containing run-off, there is a very serious risk of contaminating surface and groundwater with highly persistent fluorinated degradation products. This is environmentally highly irresponsible, given that normal Class A concentrates do not contain fluorochemicals. The arguments given for a 'one stop' philosophy range from procurement issues to a form of institutional laziness "... we can't expect firefighters to distinguish between different types

of foam concentrate on the incident ground ...". Why not? That is what training is for!

If a fluorosurfactant foam must be used, and there are situations especially at fixed installations in the petrochemical and chemical process industries where this is still considered essential, then containment and subsequent treatment of fire-water run-off can be used to limit the environmental impact. Good bunding of storage areas, with bund volumes calculated to take all the stored volume of fuel *plus* the foam used to control the fire, together with drainage systems that can be isolated, provide one solution. Allowing very large volumes of contaminated run-off to go to the local water treatment works may not be feasible. Old industrial chemical sites represent a huge environmental problem. They are generally inadequately bunded, near to watercourses and often surrounded by later office and residential development. At the Allied Colloids fire in the UK in 1992 the local water undertaking had to open the storm valves to protect its water treatment beds, needed for the sewage outflow from a very large urban region. This contaminated the Aire and Calder river systems and produced a 40-50 kilometre 'river kill'.

Where possible, run-off should be contained for subsequent treatment and disposal by bunding and sealing access to the drainage system. If petroleum spirit interceptors have been fitted, for example, on motorways, airport runways or training areas, it should be remembered that the detergent action of foam is very effective at thoroughly cleaning them by destroying their function and carrying through hydrocarbon deposits! For incidents requiring Class B foam at which containment is all but impossible, for example motorway incidents, aircraft crashes, petrol station fires, fires involving shipping or harbour facilities, one should consider alternative solutions. Currently there are commercially available Class B foam concentrates that are completely fluorosurfactant free, have the relevant approvals such as EN 1568 and ICAO and satisfy the industry standard LASTFIRE for both mains water and seawater. Other approaches include either greatly reducing the fluorosurfactant content of the foam concentrate or replacing it entirely with a high molecular weight, environmentally benign (according to the manufacturer) non-degradable fluoropolymer capable of stabilising the foam bubble structure.

An argument often put forward in the industry against fluorine-free Class B and Class A foam concentrates is that these are more acutely toxic to the aquatic environment than fluorosurfactant-containing

AFFF foams because they use hydrocarbon surfactants. All foams contain surfactants which are detergents that cause lowering of the surface tension of water from its normal value of 72 dynes/cm² to between 20 and 30 dynes/cm². This lowering of the surface tension of water is adverse to most organisms. Acute toxicity is, by definition, short-term and most ecosystems recover rapidly, except under arid or desert conditions. But what is important to remember is that the acute toxicity of different foams must be compared *at their final working concentration* as finished foam, not as the concentrate. When this is done there is often little to choose between the various formulations.

Alternative extinction technologies may be more appropriate than classical foam systems in specific instances. For example, water mist or fog, compressed air foam systems (CAFS), hydrophilic gels, or free-radical chain-breaking powders. Combined branches using both powder and foam may have a place also,

especially in the petrochemical industry.

Finally, do not forget that although acute toxicity is short-lived and systems generally recover, the same cannot be said for chronic effects. Especially if this involves discharging a highly persistent contaminant into groundwater, an increasingly rare and valuable resource in Australia and many parts of the world. Continuing discharge of highly stable contaminants such as the fluorocarbon sulphonates to groundwater will lead to increasing levels over time with unknown and unpredictable results given what little we know of their long-term toxicity and bio-accumulative potential. The precautionary principle dictates that we should avoid such 'opened ended' contamination scenarios if at all possible. Remember, protect your groundwater, protect your livelihood!

MORE INFORMATION

For more information, contact Roger Klein on rogeraklein@yahoo.co.uk.



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