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Perfluoroalkyl Substances in the Environment
Theory, Practice, and Innovation

Edited by
David M. Kempisty
Yun Xing
LeeAnn Racz
Dedicated to those who endeavor to ensure abundant, clean water for future generations.
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Foreword

Addressing the issues that poly- and perfluoralkyl substances (PFAS) raise will be an enduring challenge for our generation of environmental engineers and chemists. Other classes of trace organic chemicals, such as pharmaceuticals and personal care products, may raise concerns wherever and whenever wastewater impacts our aquatic environment; however, to quote Calvin Coolidge, “Nothing in this world can take the place of persistence.” In this manner, PFAS seem to have cornered the market.

It is not just the extreme persistence of their multiple carbon-fluorine bonds that have captured our attention. The unique surfactant behavior of many PFAS, particularly those associated with the use of aqueous film-forming foams (AFFFs), which are the focus of this book, is leading to many complications as we consider the environmental fate and transport of these otherwise relatively mobile substances. Moreover, as much as one might want to simplify the PFAS world into just perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), the chemistry, and everything that goes along with it, is much more complex than I think many of us imagined when we first started to study these chemicals. It is not just about the anions—there are neutrals and cations too! Indeed, developing multiple lines of analytical evidence to demonstrate that one has accurately accounted for the diverse chemistry of PFAS present at AFFF-impacted sites is a current focus of many research groups. Though I am a reluctant analytical chemist, I seem to be more often suggesting that we simply embrace the complexity of the PFAS chemistry (as best we can) in the environment if we want any hope of making sense of the complicated web of precursors and products.

Of course, it is not just the chemistry of the PFAS themselves and what happens to them in the environment that is so complex: the multitude of uses of PFAS has also led to considerable confusion, or at least complexity, related to sources of exposure. Folks can get confused pretty quickly when you explain that the chemicals that they have used to keep stains off of their carpets and clothing are kissing cousins of those that were used to put out fuel fires and are now contaminating their drinking water supply. Never mind the fact that we are really only starting to scratch the surface with respect to understanding their toxicity. Nevertheless, the exposures that are happening and have happened are real, and the public is left wanting at least an explanation, if not a solution, to this complicated problem.

This leads me to why this book and why now. On the whole, this collection of information is just what is needed at this point in time. In November 2016 the US Environmental Protection Agency issued its long-anticipated health advisories for PFOS and PFOA in US drinking water supplies. Since then, there has been an onslaught of media coverage of the issue, with local press outlets reporting on every new groundwater plume. As a result, many nonacademicians are having to quickly come up to speed on a variety of topics and issues specific to PFAS. For those who have not been directly engaged with the scientific discussions on PFAS for the past 15 years, this could seem a very daunting task. What this book provides is
information not just on the complicated chemistry and nomenclature, but also on the toxicology, regulatory approaches, analytical chemistry, and perhaps most importantly, the diverse ways in which environmental engineers are trying to remediate PFAS. Though it is downright impossible to capture every PFAS issue, particularly in this rapidly expanding research environment, Drs. Kempisty, Racz, and Xing have included a broad array of perspectives and cover an even broader array of PFAS topics. At the very minimum, this book will serve as an excellent gateway to the wild world of PFAS. Whether you are a federal, state, or local government official being thrust into the PFAS world, a student wanting to learn what all the fuss is about, or simply a member of the public trying to understand just why these chemicals are so difficult to treat, I would encourage you to engage with this book as much as you can. Take notes. Look up references. Follow your passion.

Good luck!

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Introduction

Per- and polyfluorinated alkyl substances (PFAS), often referred to as per- (and poly-) fluorinated compounds, have been used for years, providing desirable properties to many everyday products we use. From nonstick cookware to stain-resistant coatings on clothing and upholstery and even in our personal care products, perfluorinated compounds are common in our everyday environment. Particularly in the aviation and firefighting communities, perfluorinated chemicals have been incorporated into the agents used to fight hydrocarbon-based fires. A pivotal event highlighting the need for the best firefighting agent possible was a shipboard fire aboard the USS Forrestal in 1967. In the end, 134 sailors lost their lives, countless more were injured, and the loss of aircraft and ship damage was substantial. Lack of standardization, inadequate firefighting procedures, and a lack of capabilities for the firefighting operations were identified as major lessons learned from the incident. Improvements to the firefighting agents were made as a result of the tragic fire, and the use of aqueous film-forming foam (AFFF) containing perfluorinated compounds gained popularity over similar protein-based foams. AFFF use has continued, and although effective in extinguishing Class B hydrocarbon-based fires, perfluorinated compounds also have negative aspects associated with them; most notably, exposure has been linked to adverse health effects in humans. Other concerns include the long biological half-life in humans (on the order of years) and their persistence in the environment for periods of years and tens of years after application. Soluble in water, PFAS are now being identified in drinking water sources. Research continues to determine adverse health effect contributions due to various exposure routes, but nonetheless, a remedy for drinking water sources is needed.

This book discusses the various challenges of PFAS in our environment today. First, the diverse number of per- and polyfluorinated compounds is vast. In order to establish some kind of boundary condition for the scope of this book, discussion is primarily centered around PFAS contained in the firefighting and aviation community. Some discussion is involved outside of this scope, but it is limited. Section I, “Introduction and Analysis,” provides background of the issues we face today. Chapter 1 sheds light on the history, nomenclature, and chemistry associated with the compounds in the PFAS suite. Discussion on the different types of firefighting foams and the military specification requirements is also covered in this chapter.

There are analytical challenges with reaching statistically reproducible detection limits. In addition to the detection of the trace concentrations, the ubiquitous presence of potentially cross-contaminating Teflon and other fluorinated compounds in an analytical laboratory make the baseline analytical work center requirements more stringent than those for other more common environmental contaminants. Chapters 2 and 3 provide an overview of the various detection methods available to determine PFAS concentrations in various environmental media.

Regulatory perspectives, discussed in Section II, are another dynamic landscape, and navigating them presents another challenge. The US Environmental Protection
Agency released a health advisory in 2016 stating that water with a combined perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) concentration under 70 parts per trillion would result in no adverse health effects. The language went on to state that the advisory was not to be used for regulatory purposes, but with the lack of a maximum contaminant level for any perfluorinated substance, the health advisory has become a de facto regulatory limit. Further complicating things, individual states have established different allowable limits of PFAS to finished drinking water. Although not yet passed, New Jersey’s Drinking Water Quality Institutes has recommended setting a limit of 14 parts per trillion for PFOA and 13 parts per trillion for another perfluorinated substance, the nine-carbon perfluorononanoic acid. Different concentrations and different regulatory language (maximum contaminant limits, health advisories, and summed concentrations) complicate remedial goals, drinking water standards, and risk communication language for agencies working in multiple states, such as often occurs in the aviation and defense communities. Chapters 4 through 7 explore these regulatory perspectives and give practical recommendations for operating with these changing requirements.

Section III discusses toxicological profiles, which are still being developed and advanced. Chapter 8 is a comprehensive review of the human health risks associated with exposure to PFAS. Toxicity with early life exposures is discussed further in Chapter 9. Isomers are another suite of PFAS that deserve toxicological investigation; depending on the manufacturing process, up to 30% of the finished PFAS product can be in an isomer form. The toxicological profile for these isomers is different than that of their straight-chained counterparts and is discussed in Chapter 10.

Determining the true toxicity, reacting to the changing regulatory landscape, and being aware of analytical and sampling challenges all present challenges to the community responsible for developing a PFAS management strategy. Perhaps the most challenging aspect of dealing with legacy PFAS contamination is the remediation of impacted soil and water. Remedial treatment objectives influenced by changing regulatory standards and advisories can make identifying efficient and effective remediation methods difficult. A considerable portion of this book, Section IV, discusses methods employed with varying degrees of success. The remediation of soil media and short-chain PFAS compounds are covered in Chapters 17 and 21. Conventional approaches for treating PFAS-impacted water, such as activated carbon and its reactivation of spent media, are discussed in Chapters 11 and 13. More novel approaches employing redox processes are covered in Chapter 12. Additionally, combinations of the treatment technologies, such as an advanced oxidization process with activated carbon and ion exchange and activated carbon polishing, are covered in Chapters 14 and 16.

Although perfluorinated compounds are a daunting challenge across multiple fronts, there is a plethora of ongoing work to resolve these challenges. This book explores the challenges across the topical areas of regulation and management, toxicology, environmental remediation, and analytical sampling and analysis. The text also provides insight into the great amount of work progressing to address the challenges. We hope the readers find this text helpful in understanding the complexities
to a greater level. Our goal for this text is to have the analytical chemist and others practicing in the environmental engineering field appreciate PFAS regulatory issues and to increase understanding of PFAS toxicology. At the same time, an equal motivation for assembling this effort is to leave readers with an optimistic view of the meritorious efforts underway and the promising advances being seen across the PFAS spectrum.

David M. Kempisty
Yun Xing
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Section I

Introduction and Analysis
1 Fluorosurfactants in Firefighting Foams
Past and Present

Stephen H. Korzeniowski, Robert C. Buck,
David M. Kempisty, and Martial Pabon

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1.1 INTRODUCTION

Fluorosurfactants are a unique class of surfactants whose properties originate from
the substitution of hydrogen with fluorine along the carbon backbone that makes up
the hydrophobic part of a surfactant (Taylor 1999; Kissa 2001; Pabon and Corpart
2002; Buck et al. 2012). Fluorinated surfactants have been commercially available
since the 1950s. The most common commercial fluorosurfactants contain a perfluoroalkyl moity, $F(CF_2)_n-$, bound to a spacer group that is connected to a cationic,
anionic, amphoteric, or nonionic functional group (Figure 1.1).
The carbon-fluorine bond is very strong. The atomic volume and ionic radius of fluorine shield carbon from a chemical attack. Thus, the perfluoroalkyl moiety is very rigid compared with the analogous hydrocarbon equivalent. The rigidity, ionic character, and large molecular volume of the perfluoroalkyl moiety drive the unique adsorption and aggregation behavior of fluorosurfactants. Moreover, the perfluoroalkyl functional moiety has very low surface energy and is both hydrophobic and oleophobic. Therefore, in both aqueous and hydrocarbon solutions, fluorosurfactants have a driving force to move to the air–liquid interface. The high chemical and thermal stability, surface tension lowering, and efficacy at low concentration (e.g., 100 parts per million [ppm]) have led to the widespread use of fluorosurfactants where traditional hydrocarbon or silicone surfactants cannot achieve the required performance. In parallel to a high number of other uses, these and other properties have made fluorosurfactants useful and valuable in aqueous film-forming foam (AFFF), which is used to extinguish high hazard hydrocarbon and polar solvent fires.

1.2 FLUOROSURFACTANT CHEMISTRY

The two primary commercial production processes employed to synthesize the perfluoroalkyl moiety that is used to make fluorosurfactants are electrochemical fluorination (ECF) and the fluorotelomer process (Figure 1.2) (Taylor 1999; Kissa 2001; Pabon and Corpart 2002; Buck et al. 2011, 2012). Among the first commercially available fluorosurfactants were perfluoroalkyl sulfonates (PFSAs) (e.g., perfluorooctane sulfonate [PFOS], C8F17SO3–) and perfluoroalkyl carboxylic acids (PFCAs) (e.g., perfluorooctanoic acid [PFOA], C7F15COOH), manufactured using the ECF process (Taylor 1999; Kissa 2001; Pabon and Corpart 2002; Buck et al. 2012). Subsequently, fluorosurfactants derived from the fluorotelomer process were introduced some time later (10–15 years after ECF products). A wide array of fluorosurfactants containing typical surfactant terminal functionalities (e.g., anionic, cationic, amphoteric, and nonionic) have been made and used (Taylor 1999; Pabon and Corpart 2002; Buck et al. 2012).

1.2.1 ELECTROCHEMICAL FLUORINATION (ECF) PROCESS

A general synthetic scheme for synthesis of ECF-based products is shown in Figure 1.2(a). ECF accomplishes the substitution of hydrogen with fluorine by electrolysis of
alkane sulfonyl chlorides or fluorides of the type H(CH₂)ₙ₊₁SO₂X, where X is Cl or F in a hydrogen fluoride (HF) solution (Alsmeyer et al. 1994). ECF is a free radical process yielding perfluoroalkane sulfonyl fluoride molecules with both linear and branched perfluoroalkyl chains and chain length homologues. For example, an eight-carbon starting material (e.g., octane sulfonyl fluoride) would yield a perfluoroalkane...
Perfluoroalkyl Substances in the Environment

sulfonyl fluoride mixture composed of roughly 80% linear and 20% branched perfluoroalkyl chains and odd and even three- to eight-carbon-chain-length homologues. It is also worth noting that the electrolysis of alkane sulfonyl fluoride may also yield a homologous series of perfluorocarboxylic acids as impurities in percentage amounts. The perfluoroalkane sulfonyl fluoride is then reacted to create raw materials that can be used to make fluorosurfactants. Note that the “connector” in the ECF chemistry is a sulfonamidoalkyl group, –SO2N(R)CH2CH2–, as shown in Figure 1.2(a). The historic production using ECF manufactured long-chain perfluorohexanesulfonfyl (C6), perfluoroocotane sulfonfyl (C8), and perfluorodecanesulfonfyl (C10) products, with the majority being C8, of which PFOS is the most well-known product. When 3M, the major global ECF manufacturer, withdrew from PFOS, PFOA, and related chemistry in 2000–2002, it transitioned to short-chain, C4, perfluorobutane sulfonfyl chemistry. The reader is reminded that the short-chain (C4, perfluorobutane sulfonfyl) ECF-based fluorosurfactants are not used in AFFF because to date, no AFFF formulation containing them has met required firefighting specifications.

1.2.2 Fluorotelomer Process

The second route most widely practiced for the synthesis of a perfluoroalkyl moiety is the fluorotelomer process (Taylor 1999; Pabon and Corpart 2002; Buck 2011, 2012). In the fluorotelomer process, tetrafluoroethylene (TFE) is oligomerized with perfluoroethyl iodide (PFEI) (CF3CF2I), yielding a mixture of exclusively linear, even-carbon-number perfluoroalkyl iodides that are commonly called Telomer A. The fluorotelomer chain length could range up to n = 20, but was primarily n = 6, 8, 10, and 12, with 6 and 8 predominant in commercial products. Ethylene is then inserted into Telomer A to make Telomer B, perfluoroalkyl ethyl iodide raw material, which may then be reacted to make fluorotelomer alcohol raw material and/or acrylate/methacrylate monomers. These raw materials or other types are then used to manufacture fluorosurfactants, as shown in Figure 1.2(b). Historic fluorotelomer-based fluorosurfactants contained mainly n = 6 (C6) and n = 8 (C8) perfluoroalkyl moieties (CnF2n+1–), with the majority being C6. As the major global fluorotelomer manufacturers have fulfilled their commitment to no longer make long-chain C8 chemistry (USEPA 2010), the short-chain C6 fluorotelomer-based fluorosurfactants are presently made and used.

1.3 Long Chain and Short Chain: Terminology and Structures

The historic use of fluorosurfactants, including their use in firefighting foams, has partially contributed to the widespread presence of PFOS and PFOA, aka long-chain perfluoroalkyl substances, in the environment. The discovery of environmental contamination began with the work by Moody and Field (1999) and continues today (Anderson et al. 2016). In 2000, 3M announced that it would exit from C8 manufacture, including PFOS and PFOA and all commercial products related to them (3M 2000). In 2006, eight major fluorochemical global manufacturers committed to exiting the manufacture and use of PFOA, longer-chain homologues, and
related substances by the end of 2015 (USEPA 2010). Concurrent with these actions, the Stockholm Convention concluded that PFOS and PFOA meet the criteria to be classified as persistent, bioaccumulative, and toxic (PBT) substances (Stockholm Convention 2009; Matthies et al. 2016).

The PBT properties of the long-chain perfluoroalkyl substances, PFOS and PFOA, and the related long-chain raw materials and commercial products were the driving force behind manufacturers ceasing manufacture of these long-chain chemistries and transitioning to short-chain chemistry. To continue to deliver the unique and valuable properties of fluorosurfactants in uses where they are necessary for performance and to eliminate long-chain products, manufacturers have developed additional short-chain alternatives with fewer fluorinated carbons. The data on these alternatives are admittedly less than the data on their long-chain counterparts, but still exist in a considerable measure. Available data on short-chain fluorotelomer-based raw materials, products, and degradation products show that the short-chain alternatives have a more favorable environmental and human health profile (Environ 2014; Environ 2016; Buck 2015). Numerous short-chain products have been approved by regulators, and significant data are being required before the commercialization of new short-chain products. Therefore, today, short-chain ECF-based fluorosurfactants contain the perfluorobutane sulfonyl moiety, C₄F₉SO₂⁻, while fluorotelomer-based fluorosurfactants contain the perfluorohexylethyl moiety, C₆F₁₃CH₂CH₂⁻. Readers should note that there is a clear and distinct difference in what is considered long chain and short chain based on the origin chemistry and its connection to the corresponding perfluoroalkyl acid (PFAA) (Figure 1.3). Within the perfluoroalkane sulfonate (PFSA) family, all substances with a carbon chain length greater than or equal to six are considered long chain. In contrast, within the perfluorocarboxylic acid (PFCA) family, all substances with a carbon chain length greater than or equal to eight are considered long chain. This comes about because of the significant difference in bioaccumulation and toxicity properties between perfluorohexane sulfonate (PFHxS) and perfluorohexanoic acid (PFHxA), both called C₆s, but with dramatically different properties (Gannon et al. 2011).

Foam, fluorosurfactants, and firefighting have been inextricably linked for the past 50 years following the invention of AFFF in the 1960s. With the unique film-forming and surface tension properties provided by fluorosurfactants (Kissa 2001; Pabon and Corpart 2002), the category of AFFF was created approximately 50 years ago. This invention and subsequent application of fluorosurfactants for use in Class B foam concentrates forever changed the capability of firefighters worldwide to extinguish and rapidly control large-scale hydrocarbon liquid and polar solvent fires. This introductory chapter provides an overview of fluorosurfactant use in AFFF foams and concentrates. Subsequent chapters discuss challenges arising with the historic use of AFFF and the discovery of per- and poly-fluoroalkyl substances, PFAS, in the environment. Chapters explore issues associated with the remediation of impacted environmental media, particularly soil and water. The current regulatory landscape is also surveyed. The lack of published regulatory limits, and instead the presence of advisory limits, drives new decision logic regarding remedial options. Sampling and analysis considerations ensuring the integrity of analytical data at the low parts per trillion (ppt) range are discussed. Also, the ongoing development of the toxicological picture of PFAS is discussed in detail, as are efforts to understand the ecological impact of PFAS in the environment. The reader is also directed to a summary documenting the history and issues facing the use of AFFF prepared by the Fire Protection Association of Australia (FPAA 2017).

1.4 FIREFIGHTING FOAM BEFORE FLUOROSURFACTANTS

The need for and use of firefighting foams followed the introduction and wide-scale use of liquid hydrocarbons and later polar solvent fuels. Historically, water was used as the primary firefighting agent. However, water is more dense than liquid hydrocarbons and sinks, rendering it an ineffective bottom layer below a burning hydrocarbon surface. The ability to dilute or “lighten” water with air in concert with a foaming surfactant created a firefighting foam that floated on the burning liquid and prevented flammable vapor evolution. This higher-surface-area aqueous foam also provided a heat sink for the absorption of radiant heat and thus helped cool the burning surface and surrounding areas.

The early history of foam development was documented by Ratzer (1956). The earliest efforts to extinguish hydrocarbon liquid and/or petroleum fires were accomplished with aqueous mixtures of sodium bicarbonate, saponin (a glycoside with foaming characteristics), and acidic aluminum sulfate to extinguish a naphtha fire (Johnson 1877; Ratzer 1956). Concurrently, foam mechanically created from a solution of ammonium soap with dissolved borax (or ammonium sulfate) in a vessel that was connected to a gas cylinder containing either ammonia, nitrogen, or carbon dioxide under pressure was also developed (Gates 1903). The gas was used to force the liquid out of the vessel into another container. Additional cylinder gas was used to further enhance the foam generated in this mechanical process. By 1912, this equipment was broadly used in England (Ratzer 1956). Efforts ensued to find suitable materials to make mechanical foams more viable and effective. In 1937, water-soluble protein products were created by digestion of hoof or horn meal that were superior for mechanical foam generation (Weissenborn 1939). Consequently, other
Fluorosurfactants in Firefighting Foams

1.5 FLUOROSURFACTANTS IN AFFF

The invention of fluorosurfactants provided revolutionary new technology to advance firefighting foam. The initial discovery and innovation were catalyzed because the US Navy was simultaneously spraying a protein foam and a Class A powder (also called “dry chemical”) to fight Class B fires aboard ships. The Class A powder was helping to control the fire but was also partially breaking down the foam blanket, like any solid powder can do on classical aqueous foams. In 1963 (Gipe and Peterson 1972), it was shown that the addition of fluorosurfactants to a protein foam allowed that foam not to be significantly affected by a simultaneous projection of a Class A powder. After that first discovery, work continued on film-forming fluoroprotein (FFFP) and AFFF, where the foam was “lightened” further using fluorosurfactants. Incorporating fluorosurfactants dramatically lowered the foam’s aqueous surface tension, delivering unprecedented rapid wetting and spreading and establishing a new standard for effectively extinguishing hydrocarbon fuel fires. The full-scale implementation of that discovery was accelerated by the July 1967 USS Forrestal tragedy, during which more efficient firefighting foams could have limited the propagation of the jet fuel fire that took place on the flight deck. Additionally, specific fluorosurfactants were also used to generate foam (e.g., amphoteric fluorosurfactants having a positive and a negative charge on their hydrophilic part).

The first work on AFFF containing fluorosurfactants was carried out by the Naval Research Laboratory and 3M in the early 1960s and led to the development of 3M’s “Lightwater” AFFF products based on ECF chemistry (Gipe and Peterson 1972). As discussed above, there are two principal chemical processes for the synthesis of the perfluoroalkyl moiety to make fluorosurfactants used in AFFF: ECF and fluorotelomerization. Figure 1.4 provides structural examples of ECF-based and fluorotelomer-based fluorosurfactants that have been developed and used by the firefighting industry over four decades (Pabon and Corpart 2002; Buck et al. 2012; Place and Field 2012; Backe et al. 2013; Barzen-Hanson et al. 2017). Figure 1.4 shows structures of various fluorosurfactants, to include different functional types (e.g., betaine, sulfonate, carboxylate, and n-oxide), historic versus present-day products, and long-chain and short-chain fluorosurfactants.

1.5.1 ECF-BASED FLUOROSURFACTANTS USED IN AFFF

ECF-based fluorosurfactants used in AFFF are shown in Figure 1.4. As mentioned earlier, the ECF process was the first implemented to produce fluorosurfactants. The ECF process is also called the Simons process (Simons 1949). The two types of key fluorinated intermediates used to produce the ECF fluorosurfactants of Figure 1.4 are represented in Figure 1.5. They are obtained by the full fluorination of their corresponding hydrocarbon acid chloride and sulfochloride homologues. The full fluorination of alkyl acid chlorides also generates by-products that consist of fluorinated alkyl chains terminated by a fluorinated furan and pyran group (Banks et al. 1994).
FIGURE 1.4 (a–d) ECF-based and (e–k) fluorotelomer-based fluorosurfactants used in AFFF. (Adapted from Place, B.J., and Field, J.A., Environmental Science & Technology, 46, 7120–7127, 2012.)

Key intermediates

<table>
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<tr>
<th>Before electrofluorination:</th>
<th>C_{n}H_{2n+1}SO_{2}Cl</th>
<th>C_{n}H_{2n+1}COCl</th>
</tr>
</thead>
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<tr>
<td>After electrofluorination:</td>
<td>C_{n}F_{2n+1}SO_{2}F</td>
<td>C_{n}F_{2n+1}COF</td>
</tr>
</tbody>
</table>

Products

| n = 8 | PFOS |
| n = 7 | PFOA |
| n = 6 | PFHxS |

FIGURE 1.5 Key intermediates used for the production of the ECF fluorosurfactants presented in Figure 1.4.
These by-products were mainly used as fluids for the electronic industry. Increasing the number of carbon of the alkyl chain of the starting acid chloride (n value on Figure 1.4) increases the fraction of by-products that are produced.

Four major types of surfactants are used in ECF-based firefighting foams. Perfluoralkane sulfonates and perfluorocarboxylates are anionic surfactants, perfluoroalkane sulfamido amines are cationic surfactants, and perfluoroalkane sulfonamide amino carboxylates are amphoteric surfactants. Most firefighting foams are formulated with a mixture of anionic and amphoteric fluorosurfactants. Interestingly, typical amphoteric ECF fluorosurfactants, such as the one presented in Figure 1.4 (perfluoroalkane sulfonamido carboxylate), have their positive and negative charges on two distinct groups of the tertiary amine. For ECF-based fluorosurfactants, the amphoteric structure is designed in such a way that the isoelectric point of the surfactant is at the typical pH of the firefighting foam concentrate (in the range of pH 7–8.5). Cationic surfactants can be added as a minor fraction of the fluorosurfactant mixture for specific formulations.

The ECF process induces the formation of both linear and branched perfluoroalkyl moieties. Fluorotelomers are only linear for all processes starting with PFEI. In terms of performance in firefighting foams, branched fluorosurfactants are not as efficient as equivalent linear fluorosurfactants (Taylor 1999; Kissa 2001). This implies that, on average, to obtain a similar performance level, a firefighting foam based on an ECF-produced surfactant requires a higher fluorine content than a fluorotelomer-based firefighting foam. Historically, ECF-based fluorosurfactant firefighting foams used mainly long-chain perfluorooctane (C8) and perfluorohexane (C6) sulfonyl surfactants. In the early 2000s, attempts had been made to use short-chain ECF-based perfluorobutane sulfonyl fluorosurfactants. However, these did not meet the AFFF performance requirements stipulated in military specifications.

1.5.2 **Fluorotelomer-Based Fluorosurfactant Used in AFFF**

Fluorotelomer-based surfactants used in AFFF are shown in Figure 1.4 and are nominally derived from three structural families: (1) a thiol (–S–) in the spacer (e.g., \(-\text{CH}_2\text{CH}_2\text{S}–\text{CH}_2–\)), (2) a sulfonyl (–SO_2–) in the spacer (e.g., \(-\text{CH}_2\text{CH}_2\text{SO}_2–\text{N}–\)), or (3) an alkyl spacer (e.g., \(-\text{CH}_2\text{CH}_2\text{CH}_2–\) or \(-\text{CF}_2\text{H}_2\text{CH}_2–\)) between the perfluoroalkyl (C_nF_2n+1–) moiety and the surfactant functionality.

Figure 1.4 shows that the fluorotelomer-based surfactants used in firefighting foams are either amphoteric (fluorotelomer thioamido sulfonates or fluorotelomer sulfamido betaines, fluorotelomer betaines), cationic (fluorotelomer sulfamido amines), or anionic (fluorotelomer sulfonates).

Historically, as of the early 1970s, fluorotelomer-based surfactants used in firefighting foams contained perfluoroalkyl moieties, F(CF_2)_n–, with n = 6 or a mixture of different perfluoroalkyl chains with n = 6, 8, and 10 carbons, with a majority (>50%) comprised of n = 6. Today, all currently produced fluorotelomer-based surfactants (by Voluntary Stewardship Program signees; USEPA 2010) used in firefighting foams are based on C6 raw materials that contain a six-carbon perfluoroalkyl moiety, C_6F_13–. Historical accounts (Cortina and Korzeniowski 2008; Place and Field 2012; Backe et al. 2013; Kleiner 2016; Barzen-Hanson et al. 2017) note that the fluorotelomer chemistry employed in the AFFF products used either a perfluoroalkyl moiety with n = 6
or a mixture of n = 6 (C6) and n = 8 (C8). This clearly means (not implies) that the fluorotelomer-based fluorosurfactants used in the early Ansul/Ciba-Geigy and Eau et Feu (Atochem) consisted of either short-chain or both short- and long-chain fluorosurfactants, from the mid-1970s onward. Back in those days, as surprising as it can be for nonspecialists, some producers where able to pass the performance requirements of the most demanding standard in the world (MIL-F-24385 1969) by using fluorosurfactants made with a perfluoroalkyl moiety, $C_nF_{2n+1}^-$, where n = 6 only.

Fluorotelomer chemistry (Figure 1.4 lower part) was used to produce both the Ciba-Geigy Lodyne™ and Atochem Forafac™ branded surfactants. Atochem’s fluorosurfactant business was acquired by DuPont in 2002. This business was spun out into Chemours in 2015 and is now part of the Capstone™ line of products. Likewise, the Ciba-Geigy Lodyne firefighting fluorosurfactant and foam stabilizer business was acquired by the Chemguard Specialty Chemicals Division from Ciba Specialty Chemicals in 2003–2004. The Chemguard Chemicals Division became part of the Tyco group in 2011, and Tyco was acquired by Johnson Controls in 2016. Each of these chemistries used the basic fluorotelomer scheme. The Ciba-Geigy/Chemguard fluorotelomer-based surfactants were generally characterized by the $-CH_2CH_2-S-CH_3$ linkage. Likewise the Atochem/DuPont/Chemours fluorotelomer-based fluorosurfactants contained the $-CH_2CH_2-SO_2-N-$ linkage. The Qualified Products List (QPL) discussed below has all short-chain fluorotelomer products on the current 2017 QPL list for military specification MIL-F-24385F, the current acceptance specification used in the US Department of Defense (USDOD) (MIL-F-24385 1969).

1.6 FIREFIGHTING FOAMS: TYPES AND COMPOSITION

Fires are classified by the proper extinguishing agent. Class A fires consist of ordinary combustibles, such as wood, paper, fabric, and most kinds of trash. Water is usually used to extinguish Class A fires. For Class A, high-expansion and fluorine-free foams (F3, nonfluorinated hydrocarbon surfactants) are used. A Class B fire arises from flammable liquids or flammable gases, petroleum greases, tars, oils, oil-based paints, solvents, lacquers, or alcohols. Using water on a Class B fire (e.g., an oil-based liquid fire) is extremely dangerous. Petroleum-based fires burn significantly hotter ($\geq$350°F) than the boiling point of water (212°F). When water is placed on a petroleum-based fire, it instantly vaporizes to form steam, which expands rapidly, causing the liquid hydrocarbon liquid to splatter, cause burns, and spread the fire. Hence, AFFF is preferred for extinguishing high-hazard Class B fires.

In use, AFFF concentrate is mixed with either freshwater or seawater by a proportioning nozzle (Figure 1.6). The foam forms spontaneously upon ejection from the nozzle. A thin layer of AFFF foam rapidly spreads over the hydrocarbon fuel surface, acting as a thermal and evaporation barrier to inhibit and eventually extinguish combustion. The “film-forming” characteristic refers to the fact that both in application and even after the foam has dissipated, the aqueous layer formed from the AFFF concentrate mixture remains on the flammable liquid hydrocarbon surface, thereby preventing reignition. This occurs because the fluorosurfactant makes the surface tension of the water lower than the surface tension of the hydrocarbon, enabling it to float on the hydrocarbon surface at the air interface.
1.6.1 TYPES OF FIREFIGHTING FOAM

There are a number of ways to classify firefighting foams. One way is by chemical type, and another is by expansion ratio. In general, expansion ratios are classified as (1) low-expansion foams (with an expansion ratio of ≤20), (2) medium-expansion foams (having an expansion ratio from 20 to 200), and (3) high-expansion foams (with expansion ratios of >200). We will focus on the two chemical types of firefighting foams: (1) F3 that are fluorine-free and (2) AFFF containing fluorosurfactants, with a focus on AFFF. Historically, nonfluorinated mechanical protein-type foams are derived from either hydrolyzed protein-rich animal or vegetable materials using alkali/lime. Vegetable materials were developed later and used in a "synthetic" formulation whose origin is from hydrocarbon-derived materials. Beginning in the 1960s, various fluorosurfactants were developed and incorporated into both types of synthetic and protein-based firefighting foam agents (Briggs 1996). Further, it is also well known that water-miscible liquids, such as polar solvents (e.g., alcohols and ketones), tend to destroy conventional foams. To overcome this characteristic, formulations were created that contained polymeric/gel-type materials, which help prevent foam destruction. These types of foam agents are called alcohol resistant (AR). For current-generation fluorine-free foams, there is basic F3, as well as alcohol-resistant fluorine-free foam (AR-FFF). It should be noted that protein, high-expansion, Class A, and most training foams have historically been fluorine-free. The types of firefighting foam are shown in Figure 1.7.

---

**Fluorine-free foam (F3)**
- Basic fluorine-free foam (FFF)
- Protein
- Alcohol-resistant protein (AR-P)
- Synthetic

**Fluorinated foams**
- Fluoroprotein (FP)
- Film-forming fluoroprotein (FFFP)
- Alcohol-resistant film-forming fluoroprotein (AR-FFFP)
- Aqueous film-forming foam (AFFF)
- Alcohol-resistant aqueous film-forming foam (AR-AFFF)

**FIGURE 1.6** Schematic of AFFF concentrate and its use. It shows in pictorial form the ingredients used to concentrate foam to deploy to firewater.

**FIGURE 1.7** Types of firefighting foam.
1.6.2 AFFF Ingredients and Composition

The precise chemical composition of AFFF formulations is generally proprietary confidential business information as the ingredients are viewed by AFFF manufacturers and formulators as providing unique competitive benefit to their products. A firefighting foam is obtained by the dilution of a foam concentrate in water (generally a 3% or 6% foam concentrate, v/v). This water–foam concentrate mixture is called a foaming solution or premix (Figure 1.6).

The foaming base of a foam concentrate consists of either a mixture of hydrocarbon surfactants or a hydrolyzed protein. Synthetic foam concentrates can be distinguished from protein foam concentrates according to the foaming base. To simplify matters, our discussion on ingredients and composition only involves synthetic foam concentrates made from surfactants. The types of firefighting foams are listed in Figure 1.7.

In general, AFFF concentrates contain four main ingredients: (1) water, (2) surfactants (to provide the foam and film-forming properties), (3) solvents, and (4) various additives and modifiers. As previously stated, water-soluble polymers are added to obtain AR-AFFF. Typical ingredients are shown in Figure 1.8. Water is the major ingredient and generally is more than 60% of the composition.

Typically, a synthetic foam concentrate designed to be diluted at 3% into water contains from 5% to 10% by weight of hydrocarbon surfactants. High-performance foam concentrates also contain one or several fluorosurfactants. Fluorosurfactants, given their relatively high expense and effectiveness at low concentration, are a minor but critical ingredient in AFFF. The fluorosurfactant plays a role in the formation of the foam as well as the formation of a water film at the surface of the solvent. In active matter, they account for 0.6–1.5 wt% of the total weight of a foam concentrate. Fluorosurfactants also provide oil repellency to firefighting foams, and this property is key when foams are used in larger-scale and real conditions.

The formation of the water film at the surface of the hydrocarbon has the result that the emission of solvent vapors is stopped or highly reduced. As those vapors are

---

**FIGURE 1.8** Type of ingredients for a 3% foam concentrate.
Fluorosurfactants in Firefighting Foams

the fire source, it is very important to stop their emission. This water film formation occurs when the spreading coefficient (SC) of the foaming solution is positive. This coefficient is defined in Equation 1.1:

\[ \text{SC} = \lambda_s - (\lambda_{HC} + \gamma_L) \]  

(1.1)

where \( \gamma_s \) is the surface tension of the solvent, \( \gamma_{HC} \) is the interfacial tension between the solvent and the foaming solution, and \( \gamma_L \) is the surface tension of the aqueous foaming solution.

The use of hydrocarbon surfactants reduces the solvent–foaming solution interfacial tension (\( \gamma_{HC} \)), and fluorinated surfactants provide the foaming solution with a particularly low surface tension (\( \gamma_L \)). Without a suitable choice of these two types of components, the spreading coefficient of a foaming solution on a solvent would be negative and extinction impossible.

There are debates in the industry about the existence of an aqueous film with AFFF at elevated temperature conditions, but foams having the capacity to form an aqueous film at regular temperature demonstrate, in most cases, higher performances than F3 foams. A foam concentrate also contains polar solvents (up to 20 wt%) that contribute to the foam stability. 1,2-Propanediol and similar types of solvents are used to reduce the freezing point of foam concentrates stored in refineries, civil airports, or drilling platforms.

In addition to the classic foam concentrates, AR foam concentrates are polyvalent and can be used to extinguish polar solvent fires, such as ethers, ketones, or alcohols. Polar solvents are miscible in water and can solubilize most hydrocarbon and fluorinated surfactants. This results in the almost instantaneous disappearance of the firefighting foam when it is placed at the surface of the solvent. The most common solution to obtain a stable foam in contact with the polar solvent involves the addition of water-soluble polymers such as polysaccharide to the foam concentrate. In contact with the polar solvent, the polymer precipitates to form a protective layer at the interface that isolates the foam from the polar solvent and prevents its destruction. Modern AR-AFFF also contains water-soluble polymers modified with fluorotelomers. Additives providing anticorrosion, antimicrobial activity, and other properties are all part of typical AFFF formulations.

A generalized view of a typical AFFF Type 3 (3%) concentrate composition based on data taken from company websites, safety data sheet documents, company fact sheets, and various reverse engineering efforts and analytical testing is shown in Figure 1.9 (Cortina 2012). In Figure 1.9, a representative composition of the foam that is actually applied to a fire, a 3% AFFF concentrate diluted with 97 parts water, is shown. In this example, the combination of surfactants and solvents is approximately 1% of the final solution as employed in firefighting.

1.7 QUALIFIED PRODUCTS LIST (QPL)

AFFF is a highly efficient firefighting agent for extinguishing flammable liquid (Class B) fires. AFFF concentrates used by the US military must meet the requirements set forth in military specification MIL-F-24385 (1969). The specification is
under the control of the Naval Sea Systems Command, and the Naval Research Laboratory is the designated institution for certification evaluation for the USDOD’s AFFF QPL. AFFF is used globally by the US military, by the militaries of other countries, and in the majority of civilian applications worldwide as either a 3\% (Type 3) or a 6\% (Type 6) concentrate. The military specification AFFF concentrates are effective against a wide variety of Class B liquid hydrocarbon fire threats. Special formulations exist for use against alcohol and other water-miscible fuels.

The early use of fluorosurfactants in firefighting foams (AFFF) is well documented in a Naval Research Laboratory report (Gipe and Peterson 1972). The first fluorosurfactant work was a collaborative effort between the US Navy and 3M and began around 1961. This effort resulted in the 1964 introduction of the first AFFF product into Navy firefighting service inventory, the ECF-based 3M product FC-183. FC-194, which replaced FC-183 about 3 years later, was less viscous and could be used at a 6\% concentrate strength in freshwater with conventional foam-proportioning equipment. However, FC-194 had a significant drawback. FC-194 could not be used with seawater, essential for deployment on naval vessels. Subsequently, a seawater-compatible AFFF, FC-195, was developed, but it was never submitted for qualification under what became the well-known QPL and military specification MIL-F-24385, issued on November 21, 1969. The first AFFF on the QPL was FC-196 from 3M in 1969. Improvements and modifications to the AFFF agents continued. The next-generation AFFF, FC-200, had a pH of >7 and corrosion inhibitors added to limit any agent attack in seawater on the stainless steel storage vessels. FC-200 was QPL approved in January 1972. Of note, the FC-200 fluorine content (2.1\% w/v) was significantly reduced in this formulation compared with its FC-196 predecessor (3.2\% w/v).

For the first 4 years the QPL existed (1969–1973), 3M AFFFs containing ECF-based fluorosurfactants were the only products qualified under MIL-F-24385. 3M’s
development partnership with the Navy lasted nearly 10 years (~1963–1973) before the next product and company became listed. AFFF containing fluorotelomer-based fluorosurfactants from National Foam was qualified on the QPL in late 1973, followed by Ansul using a Ciba-Geigy fluorotelomer-based fluorosurfactant in 1974–1975. These products had between 0.7% and 0.83% w/v fluorine, or less than half of fluorine of the ECF product FC-200. In 1981, two more products were added to the QPL: 3M’s FC-206C and Ansul’s AFC-5, which contained 0.94% w/v and 0.61% w/v fluorine, respectively (Barzen-Hanson et al. 2017). In 1993, 3M’s Lightwater™ FC-203CF contained 1.8 wt% fluorine while National Foam’s Aer-O-Water 3EM contained 0.85 wt% fluorine; both were listed on the QPL (Kleiner and Jho 2009). Each of these products had passed the US military’s QPL specification MIL-F-24385. The data indicate that the AFFF containing fluorotelomer-based fluorosurfactants provided firefighting performance equal to that of the ECF-based AFFF products with substantially less fluorosurfactant content.

A chronology of the QPL is shown in Figure 1.10, with AFFF product descriptions given in Table 1.1. Even though ECF-based long-chain products (e.g., PFOS containing) are still in inventory at various sites globally (Darwin 2011), none are on the QPL today, in 2017. The reader is reminded that the short-chain (C4, perfluorobutane sulfonyl) ECF-based fluorosurfactants are not used in AFFF because, to date, no AFFF formulation containing them has been qualified. There has been significant changes in the QPL over the past 6 years (2011–2017) as the transition to AFFF containing short-chain C6 fluorotelomer-based surfactants has occurred.

With 3M’s exit (Type 6 withdrawn January 3, 2007, and Type 3 withdrawn August 8, 2010) from long-chain ECF-based fluorosurfactant manufacture for AFFF in the last decade, National Foam is the longest-standing company on the list, having come onto the QPL in 1973, followed close behind by Ansul (today Johnson Controls). Both Angus and Buckeye came off the QPL within the past 2 years, while at the same time ICL/Auxquimia (2015; now Perimeter Solutions), Amerex/Solberg (2016), and Dafo Fomtec AB are recent additions. Chemguard (since 1997) and Fire Service Plus (Type 6 added May 2011) are also on the May 2017 QPL (Figure 1.10). It is also noteworthy

![FIGURE 1.10](image-url)  
### TABLE 1.1
Qualified Products Database Comparison 2004–2017

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<th>Company</th>
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<th>Type 3</th>
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<tbody>
<tr>
<td>Tyco Fire Products/Ansul</td>
<td>FT</td>
<td>Type 3</td>
<td>Type 6</td>
<td>Type 3/6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>November 13, 2015</td>
<td>Ansluite AFC-3MS</td>
<td>Ansluite AFC-6MS</td>
</tr>
<tr>
<td>Amerex Corp./Solberg Corp.</td>
<td>FT</td>
<td>February 29, 2016</td>
<td>Arctic 3% MIL-SPEC AFFF</td>
<td>Arctic 6% MIL-SPEC AFFF</td>
</tr>
<tr>
<td>Dafo Tomtec AB</td>
<td>FT</td>
<td>November 3, 2015</td>
<td>Phos-Chek 3% AFFF</td>
<td>Chemguard C606-MS</td>
</tr>
<tr>
<td>Dafo Tomtec AB</td>
<td>FT</td>
<td>January 19, 2017</td>
<td>Fomtec AFFF 3%M</td>
<td></td>
</tr>
</tbody>
</table>

Note: FT = fluorotelomer; NR = tests were conducted but no date was noted; E = ECF.

<sup>a</sup> Test dates/Naval Research Laboratory report listed when available from QPL list. Listing on actual QPL followed at a later date.
that while three of the companies (National Foam, Ansul, and Chemguard) have been on the QPL for many years, there are an equal number of new entrants to qualify for arguably the world’s most difficult fire standard. These new QPL entrants are Fire Service Plus (FSP); Solberg Corporation; ICL, who purchased Auxquimia’s Class B foam business in 2014; Now Perimeter Solutions; and Dafo Fomtec AB. Current (2018) QPL AFFF products for Class B fires are shown in Table 1.2. The short-chain fluorosurfactants in all these products are C6 fluorotelomer-based products.

### TABLE 1.2
**QPL List (March 2018) MIL Spec MIL-F 24385**

<table>
<thead>
<tr>
<th>Type 3, 3% AFFF</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>AER-O-WATER 3E-C6 AFFF</td>
<td>National Foam, Inc.</td>
</tr>
<tr>
<td>ANSULITE AFC-3MS 3% AFFF</td>
<td>Tyco Fire Protection Products (JCI)</td>
</tr>
<tr>
<td>ARCTIC 3% MIL-SPEC AFFF</td>
<td>Amerex Corp., The Solberg Company</td>
</tr>
<tr>
<td>CHEMGUARD C306-MS 3% AFFF</td>
<td>Tyco Fire Protection Products (JCI)</td>
</tr>
<tr>
<td>PHOS-CHEK 3% AFFF MS</td>
<td>ICL Performance Products (now Perimeter Solutions)</td>
</tr>
<tr>
<td>TRIDOL-C6 M3 AFFF</td>
<td>National Foam, Inc.</td>
</tr>
<tr>
<td>FOMTEC AFFF 3% M: SWE &amp; USA</td>
<td>Dafo Foamtec AB</td>
</tr>
<tr>
<td>FIREADE MILSPEC 3</td>
<td>Fire Service Plus, Inc.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type 6, 6% AFFF</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>AER-O-WATER 6EM-C6 AFFF</td>
<td>National Foam, Inc.</td>
</tr>
<tr>
<td>ANSULITE AFC-6MS 6% AFFF</td>
<td>TYCO Fire Protection Products (JCI)</td>
</tr>
<tr>
<td>ARCTIC 6% MILSPEC AFFF</td>
<td>Amerex Corp., The Solberg Company</td>
</tr>
<tr>
<td>CHEMGUARD C606MS 6% AFFF</td>
<td>TYCO Fire Protection Products (JCI)</td>
</tr>
<tr>
<td>FIREADE MILSPEC 6 (Jan 2018)</td>
<td>Fire Service Plus, Inc.</td>
</tr>
<tr>
<td>TRIDOLC6 M6 AFFF</td>
<td>National Foam, Inc.</td>
</tr>
<tr>
<td>PHOS-CHEK 6% MILSPEC AFFF</td>
<td>ICL Performance Products (now Perimeter Solutions)</td>
</tr>
</tbody>
</table>


1.8 **FIREFIGHTING FOAM SELECTION AND USE**

The selection of a firefighting agent to extinguish a Class B fire is front and center today more so than it has been over the past 15 years due to the widespread environmental presence from historic use of AFFF (Willson 2016a). Numerous fire journal articles (and other media) have appeared debating the pros and cons of both general types of firefighting agents, F3 and AFFF containing fluorosurfactants. The selection decision requires a thoughtful consideration of multiple criteria, such as fire performance, life safety benefits, property protection, and environmental impact, including whether control of spent firewater is possible or practical. Balancing these criteria presents a set of difficult choices for regulators, firefighters, and those who routinely handle flammable liquids and require rapid fire extinguishment and control.
Fluorosurfactants in Firefighting Foams

to protect human life and property. A recent firefighting foam seminar in Singapore (SAA-IAFPA 2016) provided an open forum for discussion of these decision-making criteria, including numerous presentations highlighting critical insights into why AFFF is often chosen (Castro 2016; Jho 2016; Plant 2016; Willson 2016b). To illustrate the issues, performance, and fundamental property parameters, this section discusses foam properties (Table 1.3) and environmental properties (Table 1.4).

### TABLE 1.3
**Foam Properties: Comparison of AFFF and F3**

<table>
<thead>
<tr>
<th>Foam Property</th>
<th>Advantage</th>
<th>AFFF(^a)</th>
<th>F3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel repellency</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Film formation</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Foam spreading on fuel</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Fuel spreading on foam</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Fuel shedding</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Fuel pickup</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Fuel emulsification</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Flammability of contaminated foam</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Degradation of contaminated foam</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Heat resistance of foam</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>

\(^a\) Includes short-chain AFFF.

### TABLE 1.4
**Environmental Properties: Comparison of Short-Chain Formulations of AFFF and F3**

<table>
<thead>
<tr>
<th>Environmental Property</th>
<th>Advantage</th>
<th>AFFF(^a)</th>
<th>F3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquatic toxicity</td>
<td>Low</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Persistence</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Reduced foam, water resources used, and wastewater generation</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Reduced smoke and breakdown products generated</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Risk to life safety</td>
<td>Low</td>
<td>Low</td>
<td>Higher</td>
</tr>
<tr>
<td>Escalation potential</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Bioaccumulation</td>
<td>No</td>
<td>No(^b)</td>
<td>No</td>
</tr>
<tr>
<td>Disposal through PTOW or WWTP</td>
<td>Yes</td>
<td>Yes(^c)</td>
<td>Yes</td>
</tr>
</tbody>
</table>

*Note:* PTOW = publicly owned treatment works; WWTP = wastewater treatment plant.

\(^a\) Includes short-chain AFFF.

\(^b\) Short-chain AFFF.

\(^c\) With pretreatment.
Critical foam properties required to fight a Class B fire that are evaluated in selecting a firefighting agent are presented in Table 1.3, comparing AFFF (containing short-chain fluorosurfactants) and F3. For example, in hydrocarbon-type Class B fires, a firefighting agent that has fuel repellency, sheds the fuel, forms a film, is not contaminated by the fuel, and rapidly spreads across the burning fuel surface is highly advantaged versus an agent that does not have these critical properties. These properties are clear advantages of AFFF containing fluorosurfactants that fundamentally differentiate AFFF from F3. Both AFFF and F3, in general, appear to have a high resistance to heat, although one can argue that the mechanism for this heat resistance is different. For AFFF, the fluorosurfactants used in the formulation have better chemical and heat resistance than hydrocarbon surfactants. F3 is given a high rating as it believed that the current generation of fluorine-free foams have high loadings of polysaccharides (sugars and gums) to boost drain times and thus trap or keep water longer in the foam matrix. The presence of the trapped water should provide greater heat resistance.

The environmental properties of short-chain AFFF and F3 are shown in Table 1.4. Whereas the foam properties show many clear advantages for AFFF (Table 1.3), the environmental properties require discussion and explanation. Aquatic toxicity data for firefighting foam products have been discussed (FFFC 2006; Plant 2016). The available data show that AFFF products have significantly lower acute aquatic toxicity than the F3 used in comparative fire testing. The basis is also shown in Table 1.5 (FFFC 2006). Both indicate very clearly that each of the three AFFF products have significantly lower toxicity in both the rainbow trout and the fathead minnows. A lower LC$_{50}$ indicates the agent is more toxic.

Another important environmental property is persistence. The stability of the carbon–fluorine bonds in fluorosurfactants makes them and/or their terminal biodegradation products stable and therefore persistent in the environment (see Section 1.11 for a discussion). In contrast, F3s are made with hydrocarbon ingredients that are generally expected to biodegrade under normal foreseeable environmental conditions and thus are not considered persistent.

The next five properties in Table 1.4, from reduced foam and water resources used, deserve some discussion. AFFF has been selected as the product with the more

### TABLE 1.5

Aquatic Toxicity Comparison

<table>
<thead>
<tr>
<th>96 h LC$_{50}$ Test Fingerling Rainbow Trout</th>
<th>96 h LC$_{50}$ Flow-Through Test Fathead Minnow</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Agent</strong></td>
<td><strong>LC$_{50}$ (mg/L)</strong></td>
</tr>
<tr>
<td>Wetting agent</td>
<td>1.06</td>
</tr>
<tr>
<td>F3-A</td>
<td>63</td>
</tr>
<tr>
<td>F3-B</td>
<td>71</td>
</tr>
<tr>
<td>MIL-SPEC AFFF</td>
<td>2176</td>
</tr>
<tr>
<td>AR-AFFF</td>
<td>3536</td>
</tr>
<tr>
<td>UL AFFF</td>
<td>5657</td>
</tr>
</tbody>
</table>

*Note: UL = Underwriters Laboratories.*
desirable firefighting characteristics when compared with F3. The advantage originates from the demonstrated performance of AFFF versus F3 when considering time to control the fire to overall extinguishment time. It is generally accepted that AFFF will knock down, control, and extinguish Class B fires faster than F3. Some argue that there are some fire test data that show equal performance in putting out a fire. However, the majority of fire test data show AFFF perform superiorly to F3 (see Section 1.9). That AFFF extinguishes a fire faster leads to lower foam usage, reduced water usage, and reduced smoke and breakdown products due the shorter control and extinguishment times. With reduced foam and water resources used, it follows that firewater runoff and wastewater generation are also reduced. In light of faster control and extinguishment times, the edge for life safety risk is also given to AFFF. Life safety risk includes firefighters and any other personnel in the fire’s vicinity. In considering these properties as a whole, faster fire control in the view of many leads to a lower fire escalation potential, thus making AFFF the selection for use in a large-scale high-hazard Class B fire event.

The present-day short-chain C6 fluorotelomer-based products, raw material and degradation products, have been shown to have a more favorable toxicological and environmental profile than historic long-chain equivalents (FluoroCouncil 2017). Further, fluorotelomer-based C6 short-chain alternatives have been shown through various evaluations not to be bioaccumulative under current regulatory criteria (Conder et al. 2008). F3 is generally considered biodegradable and not bioaccumulative. The last environmental property, disposal, is very important. It is essential that all firefighting foams be properly disposed. Both the Fire Fighting Foam Coalition (FFFC) (2016a, 2016b) and FPAA (2017) have provided industry guidance for proper foam disposal. Foam, spent foam, and firewater must be disposed of according to local and state (and other government) authorities’ requirements.

In summary, selection of a firefighting foam for Class B fires involves consideration of multiple criteria, as shown in Tables 1.3 and 1.4. Over the years, many have invoked the phrase “fit for purpose” as guidance for selection. If the firefighter needs rapid knockdown and control, rapid extinguishment, extended burnback times, and the best life safety performance and asset protection, the choice in 2017 is clearly AFFF containing fluorosurfactants. F3 performance has improved dramatically over the past few years and has been selected by some users instead of AFFF where performance meets their requirements for life safety and ultimate property and asset protection. F3s have achieved many internationally recognized certifications, but to date not MIL-F-24385. A research initiative funded by the Strategic Environmental Research and Development Program (SERDP) titled “Fluorine-Free Aqueous Film Forming Foam,” dated October 29, 2015, seeks research proposals to identify a fluorine-free foam that meets or exceeds the performance criteria required in MIL-F-24385 (SERDP 2015).

1.9 AFFF AND F3: FIELD TEST PERFORMANCE AND EFFICACY

In addition to foam and environmental properties, actual efficacy comparisons in the field are essential to assess fire performance and select firefighting foam. The FFFC has published two studies comparing field test performance and the efficacy of
In 2011, the Naval Research Laboratory presented field test results of AFFF agents and F3 (Williams et al. 2011). AFFF extinguishment times on 28 ft² pool fires tested at full strength were on average 77% faster for gasoline, 88% faster for methylcyclohexane (MCH), and 70% faster for heptane than those of F3. For isooctane, the tested AFFF was unable to form a film and the F3 extinguished the fire 10% faster, highlighting the importance of film formation to foam performance. The AFFF tests extinguished the heptane and gasoline fires in 21–28 seconds. The time required to pass the MIL-F-24385 is 30 seconds. The F3 was unable to extinguish any gasoline or heptane fire in less than 30 seconds. To be on the QPL, AFFF products must meet these requirements to be used for military applications. The Federal Aviation Administration (FAA 2011) requires all US airports to carry AFFF agents that meet MIL-F-24385 and are listed on the QPL. In another field study reported at the 2013 Reebok Foam Conference, VS Focum (2013) summarized the company’s F3 development. The presentation contained side-by-side field test data done at the same facility under the same conditions comparing the fire performance of AFFF and F3. The results showed that AFFF performed significantly better than F3 in spray extinction tests (0.785 m²) using heptane, gasoline, and Kerosene Jet A-1, and in Spray Pan Fire Out tests in sizes 0.25, 0.785, and 7.06 m², while the values were similar in the 4.52 m² test. The Naval Research Laboratory has conducted field tests comparing AFFF and F3 (Hinnant et al. 2017a, 2017b). In pool fire tests, AFFF achieved extinguishment in 18 seconds, compared with 40 seconds for the F3. In foam degradation tests, F3 degraded after 1–2 minutes, while AFFF lasted 35 minutes before degrading (longer is better). Similar results from a series of foam degradation tests on AFFF and F3 were published earlier in International Fire Fighter in 2012 (Jho 2012). At a 2016 foam seminar (SAA-IAFPA 2016), field fire test results conducted on five commercially available short-chain fluorotelomer-based AFFFs and five commercially available F3 were presented (Castro 2016). The tests were run on four fuels: gasoline, heptane, Jet A-1, and diesel. The results showed that AFFF performed significantly better than F3 on all fuels except diesel, where they both put out the fire. None of the F3s were able to extinguish Jet A-1.

**Benefits to Firefighters**

- Reduced risk to life safety of the firefighters and those in the adjacent community
- Reduced release of toxic products of combustion
- Rapid fire extinguishment
- Reduced potential for the fire to spread
- Reduced use of foam and water leading to reduced firewater effluent, including both foam and products of combustion

**Key Firefighting Foam Properties**

- Suppression of flammable vapor release
- Cooling the fuel surface
- Protection from reignition and flashback
- Resist degradation due to radiant heat
- Resist mixing with the fuel
- Resist spreading over the fuel surface
- Resist breakdown by the fuel (e.g., polar solvents)

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Fluorosurfactants in Firefighting Foams

Jet A-1 is the fuel used in International Civil Aviation Organization fire tests, which determine the acceptability of foams for airport use in many countries.

Lastly, the reader is directed to a recently published information bulletin titled “Selection and Use of Firefighting Foams,” authored by the FPAA (2017). The FPAA has neatly articulated what a high level of firefighting performance provides firefighters, regardless of whether the foam contains fluorine (Figure 1.11). Additionally, the bulletin describes key foam properties that align with those presented in Table 1.3.

1.10 AFFF USE: BEST PRACTICES

It is imperative that the firefighting foam be fit for purpose. AFFFs should not be used for typical Class A fires (such as wood), forest fires and wildfires, residential fires, electrical fires (Class C), kitchens—commercial and residential, and computer, server, and any telecommunications equipment fires. In addition, AFFF products should not be used on a small car or truck fire where the potential for a large fuel spill is small and where water will suffice to extinguish the fire. AFFF is the foam of choice for fires where there is the potential for a significant flammable liquid hazard or where the rapid extinguishment of hydrocarbon fuel was necessary to avoid harm to people and/or property (e.g., armaments). This is why typical historic use of AFFFs has been in military operations, marine operations, and petroleum terminal, processing, and operations, as well as chemical and other industrial facilities. Considerations when determining the use of AFFF are many. The conversation appears to have shifted from performance to presence, and persistence is what really matters. Having perspective is critical in this discussion. Users of PFAS-containing products must consider the toxicological profile; the potential for exposure; the prevention of emissions; the protection of people, property, and the environment; and the use of risk-based analyses versus solely the precautionary principle (Figure 1.12) (Korzeniowski 2017).

AFFF safe handling, proper use, and disposal are essential. When it is appropriate to use AFFF and how a Class B fire is fought and extinguished are important. A universal consideration is minimizing human exposure and environmental release while protecting people and property. The potential environmental impact of Class B foam usage is critically important. There are three primary sources of potential environmental impact: (1) the fire’s combustion products, (2) the AFFF foam itself, and (3) resulting firewater. Foam and firewater must be disposed of in compliance with local, state, and/or country regulations. All foams have the potential to contaminate surrounding areas where foam has been used and the potential to be harmful to the environment if the fire is not fought properly with the right products and if the firewater effluent is not managed appropriately.

Fluorosurfactants are highly stable and do not mineralize by biodegradation (see Section 1.11). As a result, AFFF emissions to the environment from historic use in fire training and firefighting have left a measurable environmental footprint, even decades after use according to recently published research (Anderson et al. 2016). The importance of proper use, handling, and disposal of AFFF has thus become a subject of intense discussion (Seow 2013; DEHP 2016a, 2016b; USEPA 2016). In
response, guidance has been developed and promulgated by manufacturers and regulators to AFFF users to cease the use of AFFF for training and only use it in active firefighting to protect people and property. The Umwelt Bundesamt (UBA) (the German Environment Agency), in collaboration with firefighting foam manufacturers and firefighters, published guidance for the proper use, handling, and disposal of AFFF in 2013 (UBA 2013). The two industry groups, FFFC and FPAA, have done a significant amount of work to raise awareness for best practices and proper use and disposal of foam. The FFFC published both a best practice guidance document and a flyer detailing critical best practices in handling AFFF to fight Class B fires (FFFC 2016a, 2016b). As described earlier, the FPAA has also recently provided guidance on foam use (FPAA 2017). The FFFC, FPAA, and UBA documents should be consulted before use of Class B foam. In brief, everyone using AFFF should diligently work to eliminate foam discharge to the environment. A first way to ensure this is to be sure that all training foams are nonfluorinated. AFFF and firewater should be contained followed by treatment and approved disposal to ensure minimal or no releases to the environment. Advanced planning, preparation, and practice are ways to identify and prevent uncontrolled foam or firewater releases and thereby minimize the environmental impact from firefighting events. Lastly, active monitoring of foam generation and delivery systems for leaks and proper preventative maintenance of foam systems should be a requirement.

AFFF products containing fluorosurfactants provide the firefighter with the most effective agents on the market today. As set forth in the FFFC guidance document (FFFC 2016a, 2016b), not only is AFFF the product of choice for Class B fires, but also the use of the multipurpose AR-AFFF or AR-FFF foam concentrates allows the firefighter to stock one product that can be used to extinguish either a hydrocarbon or a polar solvent fire. Not using the correct foam agent would result in ineffective

firefighting and could result in increased environmental contamination and slower fire extinguishment with potential catastrophic results.

Finally, while the FFFC and FPAA industry associations have done a significant amount of work to raise awareness and promote AFFF best practices, there are those that are opposed to the use of any fluorine-containing foam (Vierke 2016). It is the opinion of this chapter’s authors that the reader—and the regulatory community, nongovernmental organizations, and firefighting community—should consider and carefully weigh the positives and negatives of fluorochemicals in protecting people and property when deciding if the use of AFFF is warranted.

1.11 SUMMARY AND CONCLUSIONS

This chapter has highlighted the historical aspects of fluorosurfactants used in the firefighting industry and their evolution until present day. From protein-based foams and long-chain fluorochemical-containing foams to today’s short-chain fluorosurfactant and fluorine-free foams, a wide range of firefighting products were covered. The nomenclature, performance, and attributes of each of the above were discussed. The principle of operation as it pertains to extinguishing fire, the chemistry of the fluorosurfactants, and the differences between the two main manufacturing processes were covered. The QPL and the required firefighting specifications of the USDOD were explained. Although a lot of material was covered in this opening chapter, numerous other factors remain that need consideration and merit further exploration in order to fully understand the complexities associated with PFAS decisions. This summary section provides a touch point on these issues, and subsequent chapters explore these challenges further.

The historic use of long-chain-containing AFFF has resulted in legacy contamination to soil, sediment, and waters, including groundwater, surface water, and drinking water. Being persistent, the environmental footprint of the fluorosurfactants in AFFF remains for extended periods of time, even decades after use (Place and Field 2012; Backe et al. 2013; Anderson et al. 2016; Barzen-Hanson et al. 2017). In addition, the fluorosurfactants in AFFF and their degradation products are often water soluble and migrate beyond the point of use, in some cases over substantial distances, and have impacted drinking water sources for adjacent communities (Hu et al. 2016). Much work continues in this area of fate and transport; numerous studies have been conducted and published that illuminate our understanding of what happens to these surfactants in the environment, to include biodegradation pathways (Liu and Mejia Avendaño 2013). Field monitoring studies continue to identify the fluorosurfactants and degradation products present at contaminated sites. These degradation products are of great interest to the AFFF community. The formation of stable end products, such as PFOS and PFOA, has been shown to occur with both ECF-based perfluoroalkane sulfonyle-based fluorosurfactants (Rhoads et al. 2008; Liu and Mejia Avendaño 2016; Mejia Avendaño et al. 2016; Zhang et al. 2017) and fluorotelomer-based fluorosurfactants (Moe et al. 2012; Liu and Mejia Avendaño 2013; Butt et al. 2014; Zhang et al. 2016; Buck 2017). Data on the physical-chemical properties (e.g., water solubility and adsorption) of the identified substances are being compiled and efforts to fill data gaps initiated. Environmental monitoring and scoping is ongoing and
expanding. The presence of legacy contamination at sites historically associated with fire training activities and accident sites is generally understood (Moody and Field 1999, 2000; Moody et al. 2002, 2003), but a complete picture of the contamination footprint considering accidental releases, equipment testing and calibration areas, and undocumented disposal activities has not yet been realized. Determining the scope of the contamination is essential to understanding the magnitude of cleanup required to protect environmental and human health.

Work completed thus far to delineate the extent of the environmental affected has revealed widespread contamination and spurred intense work to identify effective remediation technologies. A recent review summarized many of the approaches (Merino et al. 2016). Additionally, some research has identified means for capturing fluorosurfactants in foam and firewater at the site of use as a best practice that can allow continued use of AFFF with minimal environmental impact (Pabon and Corpart 2002; Baudequin et al. 2011, 2014; Scholz 2014). Many chapters follow describing some the methods being investigated to remedy PFAS contamination in various environmental matrices in timely and cost-effective manners.

Another challenging aspect of PFAS is associated with the analytical methodology. The analytical methods and sample preparation procedures required to isolate, identify (aka structure speciation), and quantify fluorosurfactants and their degradation products have been the subject of numerous reviews (Martin et al. 2004; Powley et al. 2005; Larsen and Kaiser 2007; Place and Field 2012; Backe et al. 2013; Barzen-Hanson and Field 2015; Barzen-Hanson et al. 2017; Dauchy et al. 2017; Munoz et al. 2017). The importance of sample preparation and the use of controls, method blanks, isotopic standards, and rigorous laboratory hygiene practices, in order to be able to achieve reliable and reproducible identification and quantification, cannot be overstated. Fluorosurfactants used in AFFF are present, along with numerous other substances, including the products of combustion. Fluorosurfactants themselves can be especially difficult to isolate, identify, and quantify because they are often bound to environmental matrices, such as soil or sediment. Challenges remain when samples are prepared in aqueous solutions as the fluorosurfactants often stick to surfaces and/or rapidly concentrate at air–liquid interfaces. An additional challenge is ensuring that sample preparation does not induce chemical changes to the fluorosurfactant analyte. For ionic species with terminal sulfonate and carboxylate groups, liquid chromatography followed by tandem mass spectrometry (LC-MS/MS) is preferred. For neutral, nonionic species, such as fluorotelomer alcohols, gas chromatography followed by MS is the preferred analytical instrumentation. An extensive discussion on the nuances of the analytical chemistry is presented in Chapter 2.

As discussed earlier, short-chain C6 fluorotelomer-based products have been shown to have a more favorable toxicology than historic long-chain equivalents (Environ 2014 and 2016; Buck 2015; Jacobs 2016). Further, fluorotelomer-based C6 short-chain alternatives have been shown through various evaluations not to be bio-accumulative under current regulatory criteria (Conder et al. 2008; Gannon et al. 2011; Environ 2014; Buck 2015; Hoke et al. 2015). Work in this area continues and is extensive. Readers are directed to later chapters in the book describing more of these efforts and their evolving findings.
Understanding the scope of the environmental contamination is one important front that is advancing, but another question remains: How clean is clean? The current lifetime health advisory issued by the Environmental Protection Agency (EPA) is set at 70 ppt for the sum total of PFOS and PFOA. However, this is only an advisory and, as explicitly stated in the EPA language, is not to be used as a regulatory standard. If and when a maximum contaminant level under the Safe Drinking Water Act is established, will it be the same value? The toxicological data gaps being filled and the advancing analytical techniques with improved limits of detection will influence the federal regulatory landscape. Additionally, states can (and have) set their own limits on allowable levels of PFAS. The dynamic regulatory framework further contributes to the complexities of managing perfluorinated chemical use associated with firefighting activities.

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Fluorosurfactants in Firefighting Foams


Per- and Polyfluoroalkyl Substance Analysis to Support Site Characterization, Exposure, and Risk Management


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Understanding Precursor Contributions


Managing Risk from Perfluorinated Compounds in Drinking Water


Emerging Contaminant Monitoring as a Host Nation Guest


Challenges of Managing Emerging Contaminants


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**Ion Exchange for PFAS Removal**


Occurrence of Select Perfluoroalkyl Substances at US Air Force Aqueous Film-Forming Foam Release Sites Other than Fire Training Areas


A Preliminary Treatment Train Study


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