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Per- and Polyfluoroalkyl Substances

# Environmental Assessment of Various End-of-Life Pathways for Treating Per- and Polyfluoroalkyl Substances in Spent Fire-Extinguishing Waters

Daniel Maga, Venkat Aryan,* and Stefano Bruzzano

Fraunhofer Institute for Environmental, Safety, and Energy Technology (UMSICHT), Oberhausen, Germany

**Abstract:** Per- and polyfluoroalkyl substances (PFAS) are now thought to be far more prevalent in water bodies across the globe than previously reported. In particular, military bases, airports, and industrial sites are prone to contamination caused by runoff discharges from fire-extinguishing waters that contain PFAS such as aqueous film-forming foams (AFFF). These substances and their metabolites show a high degree of mobility as well as a low biotic and abiotic degradability; as a result, they are bioaccumulative and often migrate among the environmental compartments in addition to being toxic. As of now, there is no suitable end-of-life treatment process that is both technologically efficient and cost-effective for the handling of PFAS. Currently, the incineration of the collected extinguishing water at temperatures above 1100 °C is the recommended method for the disposal of PFAS to degrade material compounds. However, this method consumes extensive energy because it requires incineration of large quantities of water to treat a diluted fraction of PFAS. Aside from incineration, adsorption of PFAS on granulated activated carbon is one of the most widely used technologies, albeit with poor adsorption and often requiring very large downstream filtration systems. Finally, the application of functional precipitation agents using commercially available cationic surfactants is a novel approach (PerfluorAd® [Cornelsen] process) that enables the effective precipitation of PFAS from the spent fire-extinguishing waters. Hence, the goal of the present study was to investigate the environmental impacts emanating from the proper treatment of spent fire-extinguishing water with the aforementioned 3 end-of-life treatment scenarios. A life cycle assessment was conducted for this purpose. The results show that the PerfluorAd process outperforms the other 2 treatment technologies across all environmental impact categories except for ozone depletion. *Environ Toxicol Chem* 2020;00:1–11. © 2020 The Authors. *Environmental Toxicology and Chemistry* published by Wiley Periodicals LLC on behalf of SETAC.

**Keywords:** Perfluorinated carbons; Aqueous film-forming foam (AFFF); Catcher surfactants; Firefighting foams; Per- and polyfluoroalkyl substances (PFAS); Life cycle assessment (LCA)

## INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a complex family of more than 3000 anthropogenic chemicals (Wang et al. 2017). Per- and polyfluoroalkyl substances are either fully (perfluorinated) or partially (polyfluorinated) fluorinated compounds that are comprised of varying carbon chain lengths and always contain a perfluoroalkyl group. Per- and polyfluoroalkyl substances are surface-active substances in which all hydrogen atoms of the carbon skeleton are replaced by fluorine atoms (see Figure 1). Per- and polyfluoroalkyl substances can exist in various ionic states, namely, anions, cations, and acids (Hatton et al. 2018).

As a result of electronegativity and bond strength of the carbon-fluorine atoms, PFAS have high thermal and chemical stability (Wang et al. 2017). Moreover, PFAS also exhibit amphiphilic properties similar to other hydrocarbon surfactants. These properties are derived from their hydrophilic polar heads (sulfonate or carboxylate functional groups) and their hydrophobic nonpolar tails, which are fully saturated with fluorine atoms. In addition, the nonpolar tails are also oleophobic (Concawe 2016). These unique physiochemical properties make PFAS distinct from alternative hydrocarbon surfactants, and thus make them ideal for use in firefighting applications, particularly in suppressing class-B fires caused by flammable

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* Address correspondence to venkat.aryan@umsicht.fraunhofer.de
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**FIGURE 1:** One of the common per- and polyfluoralkyl substances–perfluorooctane sulfonic acid (US Environmental Protection Agency 2019).

liquids (Kissa 1994). Other applications for PFAS include use in textiles, construction, automotive, aviation, cookware, and so on (Concawe 2016).

In firefighting applications, certain PFAS substance groups, in particular fluorosurfactants, are added to aqueous film-forming foams (AFFF). Such formulations create a gas-impermeable layer of water on the surface of flammable liquids such as gasoline, diesel fuel, and other hydrocarbons and suppress the mixture of fuel in the foam. In this manner, the extinguishing effect of the foam can be increased and a re-ignition of the flammable liquid can be prevented (Concawe 2016). Aqueous film-forming foams are widely used in military as well as civilian applications (airports, industrial sites, and refineries) worldwide, with a concentration of up to 6%. The AFFF concentrates are, in themselves, mostly made up of water, with other components such as glycol ethers and ethylene or propylene glycol added to extend the lifetime of the foam (Sheinson et al. 2002). The market for extinguishing waters is growing globally, and is predicted to reach 3370 million dollars by 2021 (Frost & Sullivan 2015). This figure indicates an annual growth of 6%. In addition, it must be stated that fire protection in many cases (e.g., large tank farms, complex industrial plants, accidents on roads, railways, and waterways) cannot be ensured without AFFF extinguishing agents.

Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are the most commonly researched fluorosurfactants. These fall under the so-called P3 substances (polar, persistent, and pollutant) and are among the most persistent environmental pollutants. These substances as well as their metabolites show a high degree of mobility as well as a low biotic and abiotic degradability; as a result, they are bioaccumulative and often migrate among the environmental compartments in nature. In addition, they can also be toxic (Koskela et al. 2017). Due to their high risk potential, the European Commission has put these substances under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulations and developed a strategy for the management of persistent, bioaccumulative, and toxic and very persistent and very bioaccumulative substances (European Chemicals Bureau 2003). At present, PFAS can already be detected in drinking waters in concentrations that exceed recommended levels (Swedish Chemicals Agency 2015), leading to annual health-related costs estimated at 52 to 84 billion Euros in Europe alone (Goldenman et al. 2019). Moreover, PFAS also cause problems at wastewater treatment plants caused by foaming. Apart from spent firefighting foams, a prevalent problem is the spillage of fluorosurfactant containing AFFF mostly around airfields.

Hence, in recent years, the use of long-chained PFAS has been challenged or in some cases restricted (Tureková and Balog 2010), with both the United States and the European Union phasing out the use of long-chain PFAS (C-8s; Land et al. 2018). Consequently, manufacturers today offer formulations with material alternatives to PFOS and PFOA, that is, short-chain (C-4–C-6) perfluorinated compounds or partially fluorinated structures such as fluorotelomers. In particular, military-certified AFFF formulations frequently include anionic, cationic, and zwitterionic surfactants with perfluoroalkyl chain lengths ranging from C-4 to C-12 (Place and Field 2012). Consequently, AFFF containing fire-extinguishing agents with fluorosurfactants as an active component still remain the agent of choice. Although knowledge on any negative environmental impacts of these substances is still limited, several studies have already shown that even the shorter chain PFAS are equally potentially damaging to the environment (Lerner 2016). To reduce the potential harm to humans and nature caused by these substances, an efficient and environmentally friendly end-of-life treatment is needed.

In the present study, we investigate the end-of-life treatment of an AFFF containing Moussol®-based formulation that has a high concentration of fluorotelomer sulfonate (FTS), 6:2 FTS. Moussol-APS comprises a range of synthetic, alcohol-resistant, polymer and AFFF concentrate designed for safe, lasting fire-extinguishing results and high burn-back resistance on polar solvents, nonpolar foam-destroying hydrocarbons, and petroleum products. A detailed composition of Moussol-APS is presented in Supplemental Data, Table S3.

## The problem around the end-of-life handling of AFFF containing spent-extinguishing waters

Currently, there is no suitable end-of-life treatment process that is both technologically efficient and cost-effective for the handling of PFAS. There is also a significant lack of cost-effective fluorosurfactant-selective binding and adsorption agents in the market today. Hence, most employed processes to treat AFFF containing spent fire-extinguishing waters have yielded unsatisfactory efficiencies and at the same time have high operating costs. At present, the incineration of the collected extinguishing water at high temperatures—temperatures of above 1100 °C—is the recommended method for the disposal of PFAS to degrade material compounds (Monroe 1968; Taylor and Yamada 2003; Seow 2013). However, this method consumes extensive energy because it requires incineration of large quantities of water to treat a diluted fraction of AFFF.

Another widely used method for separating AFFF containing spent fire-extinguishing water is by adsorption using activated carbon (Xiao et al. 2017). Nevertheless, as a result of the poor adsorption of fluorosurfactants, very large filtration systems are required. Moreover, often in practical applications a low specific adsorption of fluorosurfactants on activated carbon in the range of approximately 0.01 to maximum

 

0.1% is achieved; this corresponds to 0.1 to 1.0 g of AFFF/kg activated carbon. Thus, the resulting accumulation of untreated residues from the water treatment process is rather high. For short-chained AFFF formulations as well as for some fluorocarboxylates, even lower specific adsorption values are achieved (Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen 2011). This poor adsorption capacity of both PFOS and PFAS on activated carbon could be attributed to their inherent amphiphilic properties.

The use of physical separation processes (e.g., capacitive deionization, membrane technology, or reverse osmosis) has thus far not led to technically successful or economically justifiable solutions. The removal of PFAS by capacitive deionization of the contaminated water is, in principle, possible; however, it is indeed expensive for the treatment of large quantities of fire-extinguishing water (Concawe 2016). The same applies for the separation process using membrane technology. In experiments with heavy contamination of PFAS, the complete remediation of groundwater required both the permeate and the concentrate to undergo further treatment after membrane filtration (Ahrens and Bundschuh 2014). The separation by reverse osmosis works but after the treatment, the thermal disposal of the resultant high concentrated aqueous waste is uneconomical (Reade et al. 2019). Oxidative methods are also considered to be uneconomical and are unlikely to be successful; this applies to both physical (with ultraviolet) and chemical (with ozone) processes or combined processes (with $H_2O_2$ and microwave radiation; Fath 2010). Moriwaki et al. (2005) published a method to decompose PFOS and PFOA in a solution using ultrasound. These results were confirmed by Vecitis et al. (2010). However, apart from being energy intensive, the ultrasound technique only degrades the alkyl chains, whereas the stable carbon-fluorine bonds remain intact.

## *The potential of functional precipitation agents for an efficient end-of-life treatment of AFFF containing spent-extinguishing waters*

It is well known—for example, from the analytical method of surfactant titration (Schmitt 2001)—that anionic and cationic surfactants form an ion-pair complex in aqueous media. This reaction commonly leads to precipitation depending on the molecular make-up (charge, molar mass, functional groups, etc.) of the 2 surfactants involved. Hence, typical PFAS components in AFFF media such the 1H,1H,2H,2H-PFOS anion may also interact more and less strongly with different cationic surfactants. Both electrostatic forces of the oppositely charged ions and hydrogen bonds as well as Van der Waals forces between (fluoro) alkyl chains contribute to the apparent binding interactions (see Figure 2). The interactions between the ionic bonds (red) and the Van der Waals interactions (blue) are symbolized by dashed lines. The sum of their bond energies and enthalpy changes can be quantified using isothermal titration calorimetry, and this analytical technique also offers the binding affinity and stoichiometry of the formed complex. The surfactants do not always combine in a ratio of 1:1, as explained in Supplemental Data, Section 1. Norvaišas et al. (2012) have found evidence for surfactants with pure hydrocarbon chains that the precipitation is primarily caused by interactions of the hydrophobic alkyl chains. In their isothermal titration calorimetry experiments, they were able to show the successive increase in bond energy and the completeness of the conversion with the increase in alkyl chain length. Furthermore, there is also an influence of temperature and salt concentration on complex formation and precipitation, respectively.

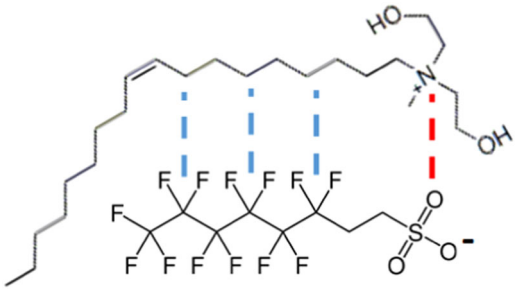


**FIGURE 2:** Schematic example representing the binding interactions of one 1H,1H,2H,2H perfluorooctanesulfonate ($H_4$PFOS) anion with the Bis(hydroxyethyl)methyloleylammonium cation in aqueous solution.

The novelty value of the PerfluorAd® process (Bluteau et al. 2019; Bruzzano and Cornelsen 2019, 2020) includes the application of commercially available cationic surfactants as a specific coagulant to provoke precipitation of (anionic) PFAS from AFFF containing spent-extinguishing waters. In addition, they can also precipitate other anionic co-surfactants in the AFFF formulation. Furthermore, the preferably applied structures are green chemicals (a mixture of different di- or triethanolamine quats based on vegetable fatty acids) to ensure nontoxic, biodegradable but also sustainable agent properties. There are several commercially available cationic structures used as functional surfactants within the care market (personal care, home care, and industrial applications) that are mostly sourced from the green chemicals product category (Anastas and Warner 2000) to provide nontoxic, biodegradable but also sustainable process agents. This is particularly true for their safe application within the PerfluorAd process.

The composition of the cationic surfactants in the PerfluorAd process may vary in: 1) chain length of the hydrophobic tail (e.g., C-6–C-18), 2) degree of esterification within the molecule, 3) number and nature of the alkyl or aryl groups at the central charge, 4) use of dimeric, oligomeric, or polymeric substructures, and 5) type and charge of the counterion.

Additional selection criteria may depend on the present (international) registration level, price, shelf life of the green chemical, as well as its storage and processing demands. The main goal of the present study is to understand the potential environmental impacts caused by different reliable options for the efficient end-of-life treatment of AFFF containing spent-extinguishing waters. Because only the treatment by incineration and by activated carbon are state-of-the-art, these 2 end-of-life treatment options are compared with

 

**TABLE 1:** List of end-of-life scenarios considered in the present study

| No. | End-of-life scenario | Description |
|---|---|---|
| 1 | Precipitation | Precipitation of PFAS in AFFF containing spent fire-extinguishing water by functional precipitation agents<br>Post-treatment with activated carbon<br>Post-treatment of activated carbon in hazardous waste incineration plant |
| 2 | Adsorption | Treatment of AFFF containing spent fire-extinguishing water with activated carbon<br>Post-treatment of activated carbon in hazardous waste incineration plant |
| 3 | Thermal treatment | Direct incineration of AFFF containing spent fire-extinguishing water |

PFAS = per- and polyfluoroalkyl substances; AFFF = aqueous film-forming foams.

the treatment by functional precipitation agents (PerfluorAd process).

## METHOD—LIFE CYCLE ASSESSMENT

The life cycle assessment (LCA) detailed in the present study includes a definition of the goal and scope (see *Goal and scope* section), a life cycle inventory analysis (see *Systems Under Study and Inventories* section), an impact assessment, and the interpretation of the results (see *Life Cycle Impact Assessment—Results and Discussion* section). The LCA was conducted considering the International Organisation for Standardisation 14040/44 standards (International Organisation for Standardisation 2006a, 2006b) using the commercial thinkstep GaBi Software System and Database for Life Cycle Engineering (compilation 9.2; DB Ver 8.7).

### Goal and scope

The overall goal of this LCA was to investigate the environmental impacts emanating from the proper treatment of spent fire-extinguishing water with 3 widely used end-of-life treatment scenarios as summarized in Table 1. Scenario 1 examines the impact of using functional precipitation agents to separate PFAS. Scenario 2 investigates the adsorption of PFAS by activated carbon as an end-of-life option. Finally, scenario 3 deals with the direct incineration of spent fire-extinguishing water as such without employing any downstream processing techniques.

Apart from these options, ion exchange is a potential technology but it performs well exclusively with smaller molecules. In the case of Moussol, it contains longer molecules (polar heads) that are traded under the name capstones. Hence, ion exchange was excluded from this analysis. Likewise, other remediation technologies such as redox manipulation, membrane filtration, reverse osmosis, or nanofiltration were also excluded because of the low stage of commercial readiness (Mueller and Yingling 2018).

***Functional unit and use concentrations of extinguishing water.*** To assess and analyze the potential environmental impacts caused by the end-of-life treatment of spent-extinguishing water, the functional unit—the proper treatment of 1 $m^3$ AFFF containing spent-extinguishing waters with a content PFAS of 0.0023 g/L—was chosen. In the present study, proper treatment was understood as the removal of more than 99% of the influent PFAS. The amount of 2.3 g PFAS/$m^3$ refers to a 1% Moussol solution that was assumed to be diluted during firefighting by a factor of 100.

Perfluorooctanesulfonic acid (6:2) FTS ($H_4$PFOS) and similar fluorosurfactants were observed to be quantitatively the most dominant substances in the $^{19}$F-nuclear magnetic resonance in combination with $^{13}$C-nuclear magnetic resonance spectroscopy experiments that were conducted. The molecular formula of the substance is $C_8H_5F_{13}O_3S$. Subsequently, we analyzed Moussol composition by means of high-performance liquid chromatography–mass spectrometry and observed N-[3-(dimethylamino)propyl]-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanesulphon-amide N-oxide and 1-Propanaminium, N-(carboxymethyl)-N,N-dimethyl-3-[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]-, inner salt, as well as small amounts of other PFAS such as 4:2 FTS and 8.2 FTS. However, we were not able to identify every PFAS substance (even after employing 30 analytical standards) against the measured total fluorine content.

Because the complete detection of all PFAS by high-performance liquid chromatography–mass spectrometry in the 1% Moussol solution was hardly possible as a result of limitations in analytics, the amount of PFAS was calculated based on the fluorine content and the molecular weight of the dominant substance—$H_4$PFOS. This had a molecular weight of 428 g/mol. The individual assumptions for calculating the mass of PFAS in one $m^3$ of extinguishing water are shown in Table 2.

***Geographical and technological scope.*** The geographical scope of the present study was in Europe. However, firefighting products similar to the Moussol solution analyzed in the present study are used worldwide. Key differences among regions may occur in the type of power mix. However, because

**TABLE 2:** Fluorine content in aqueous film-forming foam and mass of per- and polyfluoroalkyl substances per $m^3$ of spent-extinguishing water

| | Amount | Unit |
|---|---|---|
| Fluorine content in 1% Moussol® solution | 0.013 | % |
| Dilution factor of 1% Moussol solution in application | 100 | — |
| Fluorine content during application (dilution with extinguishing water) | 0.00013 | % |
| Estimated average molecular weight of PFAS | 428 | g/mol |
| Mass of PFAS per functional unit | 2.3 | g/$m^3$ |

PFAS = per- and polyfluoroalkyl substances.

 

the investigated end-of-life scenarios have low power consumption, in general, the overall results might be similar also for other regions such as the United States. Furthermore, depending on the region, different regulatory limits for spent-extinguishing water discharges exist. In the United States, the federal long-term exposure health advisory level for drinking water is between 0.05 and 0.07 μg/L. In the European Union, some of the strictest guidelines are in the Scandinavian countries, with Denmark requiring concentrations less than 0.1 μg/L and Sweden less than 0.09 μg/L. In Germany, a varying set of limits from 0.1 to 10 μg/L exists, depending on the federal state. In the United Kingdom, the drinking water guidelines have a threshold of 1 μg/L for PFOS and 5 μg/L for PFAS (European Commission 2013; Ross and Hurst 2019).

***System boundaries.*** The LCA follows an attributional, end-of-life approach. It considers exclusively the environmental impacts of the proper treatment of AFFF containing spent-extinguishing waters. The collection of AFFF containing spent-extinguishing waters was excluded from the system boundaries because this step is necessary in all scenarios. Possible environmental hazards caused by improper treatment of extinguishing foams such as spillage or leakage into water bodies also were not investigated.

***Choice of impact categories.*** For calculating the environmental impacts, the life cycle impact assessment (LCIA) method Environmental Footprint EF 3.0 was used (Fazio et al. 2018). This method was developed and is recommended by the European Commission and the Joint Research Centre to measure the environmental performance of a product during its life cycle (European Commission 2012). The classification data and characterization factors used for the midpoint impact assessment in the present study were those defined by the International Reference Life Cycle Data System Handbook (levels of recommendation I and II), namely, acidification, climate change, eutrophication (freshwater, marine, and terrestrial), ionizing radiation, ozone depletion, particulate matter formation, photochemical ozone formation, fossil depletion, and resource use (mineral and metal).

## SYSTEMS UNDER STUDY AND INVENTORIES

In this section, the 3 appropriate end-of-life options to treat AFFF containing spent-extinguishing waters are described along with their life cycle inventory data: 1) precipitation of PFAS using functional precipitation agents, 2) adsorption of PFAS with activated carbon, and 3) thermal treatment via incineration. The investigated processes are visualised in Figure 3.

### *Scenario 1: Treatment of AFFF containing spent fire-extinguishing water using precipitation agents*

Apart from the core technology, where PFAS-specific coagulants are added to the AFFF stream (see *The potential of functional precipitation agents for an efficient end-of-life treatment of AFFF containing spent-extinguishing waters section*), the process also includes the maintenance of AFFF containers, vessels, sprinklers, and equipment cleaning. However, the environmental impacts from the equipment were neglected because of low relevance. Precipitation of the PFAS occurs within a maximum period of 30 min. The precipitate is filtrated, dewatered, and then routed to the thermal incineration process. Each case of PFAS contaminated spent fire-extinguishing water exhibits a unique pattern of contaminants along with other substances (e.g., AFFF components such as (co)surfactants, glycols, and fatty alcohols). As a result, it was necessary to adjust the composition of the PerfluorAd formulation, as well as to optimize post-treatment process steps such as the follow-up treatment by activated carbon adsorption in a stirred reactor (using powdered activated carbon) or in a fixed bed adsorber (safety filter).

Experiments show that in total approximately 0.017 g PerfluorAd were needed for the precipitation of PFAS in 1-L AFFF containing spent fire-extinguishing water (see Supplemental Data, Table S2). This means that approximately 20 g PerFluorAd are required per $m^3$ AFFF containing spent fire-extinguishing water. The demand for PerFluorAd can vary depending on the dilution of the AFFF (1–100%) as shown in Supplemental Data, Table S4. Furthermore, it can also be beneficial to use the PerfluorAd agent in combination with other primary coagulants (e.g., aluminium, iron, or polydiallyldimethylammonium salts) as well as flocculation aids (e.g., polyacrylates, polyacrylamides, or polyaluminium compounds) to minimize the amount of utilized process aids and thus the final amount of PFAS contaminated waste that needs to be disposed of. However, for the LCA, a process with no primary coagulants was assessed. A summary of the main material and energy demands as well as information on the source of background data is given in Supplemental Data, Table S4. The demand for granulated activated carbon strongly depends on the specific adsorption of PFAS on activated carbon. The range of the specific adsorption of PFAS was estimated to be between 0.01 and 0.1%. As a conservative assumption, 0.05% PFAS/granulated activated carbon was chosen as base case. This value fits to the finding that 0.4 mg of PFAS were removed per gram of granulated activated carbon (equal to 0.04%) before a breakthrough of PFAS was attained (Woodard et al. 2017). The ratio of 0.05% PFAS/granulated activated carbon is equal to a demand of 0.23 kg granulated activated carbon per $m^3$ of extinguishing water after precipitation with PerfluorAd. To understand the influence of the specific adsorption of PFAS on the LCIA results, a sensitivity analysis with varying loading factors between 0.01 and 0.1% was also conducted.

### *Scenario 2: Treatment of AFFF containing spent fire-extinguishing water using activated carbon*

Similar to scenario 1, the amount of activated carbon required depends on the specific adsorption of PFAS. To ensure consistency, the same maximum specific adsorption of 0.05%

 

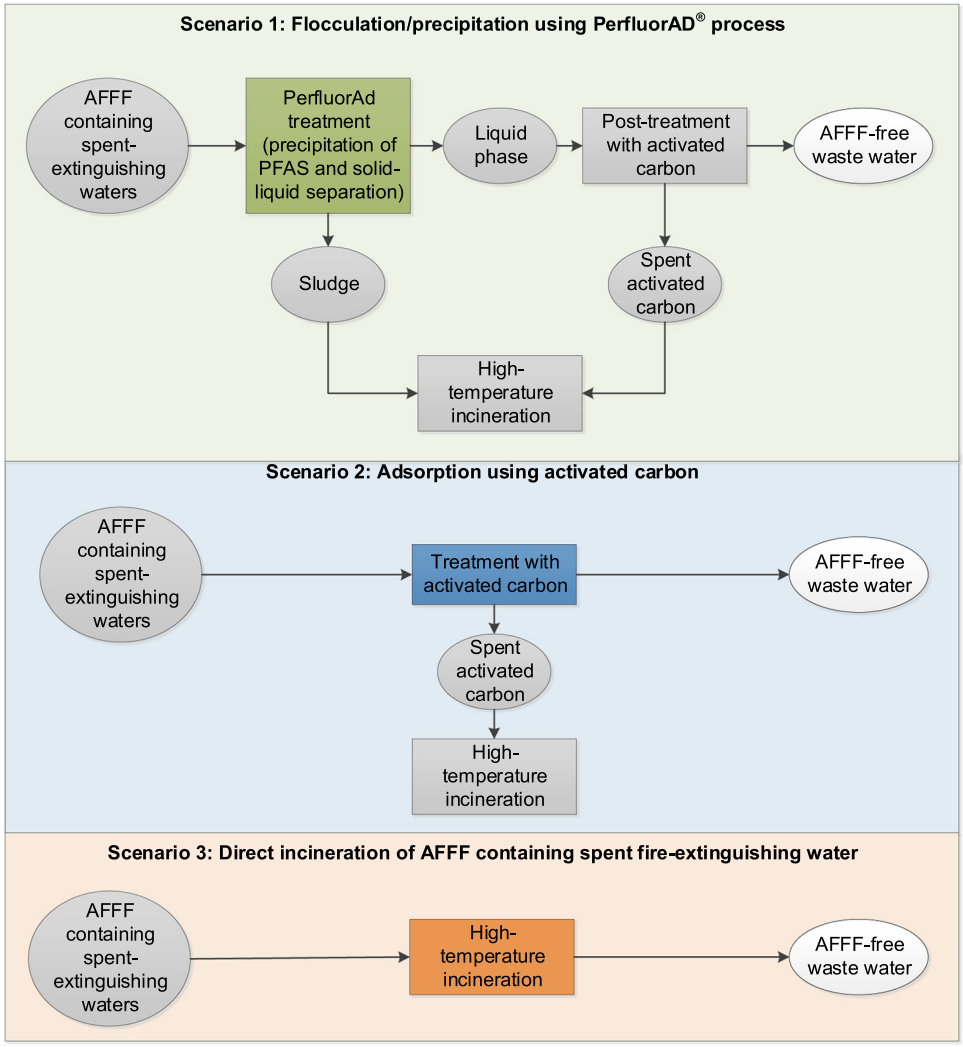


**FIGURE 3:** Scenarios for treating aqueous film-forming foams (AFFFs) containing spent fire-extinguishing waters using functional precipitation agents (scenario 1), activated coal (scenario 2), and direct incineration (scenario 3). PFAS = per- and polyfluoroalkyl substances.

was assumed as base case for scenario 2 as well. It should be noted that the need for activated carbon might be even higher because other substances, such as organic compounds, can affect the adsorption efficiency. The main material and energy requirements for the treatment of extinguishing water with activated carbon are summarized in Supplemental Data, Table S5.

### *Scenario 3: Thermal treatment of AFFF containing spent fire-extinguishing water*

Waste incineration plants are usually not specifically designed for the treatment of PFAS. To treat PFAS, a temperature of more than 1100 °C is required to eliminate the toxic constituents. However, technology exists to handle PFAS in hazardous waste incineration plants (HWIP). These HWIP usually combine a rotary kiln and secondary combustion chamber that is followed by a boiler and sophisticated flue gas cleaning system. Hazardous waste incineration plants are able to dispose of all kinds of hazardous waste: solid, liquid, gaseous, and pasteous (Vijgen and McDowall 2009). Although HWIP have energy recovery systems, in the case of AFFF containing spent fire-extinguishing water, no energy can be recovered. Hence, there is a net energy demand that equals the thermal energy demand of vaporization of water. In the case of incinerating water, usually natural gas-based boilers are used (Monroe 1968). Table S6 summarizes the inputs associated with the thermal treatment of 1 $m^3$ AFFF containing spent fire-extinguishing water.

## LIFE CYCLE IMPACT ASSESSMENT—RESULTS AND DISCUSSION

The impact assessment results (midpoint) calculated in the present LCA study are summarized in Table 3. Lower values appear in scenarios 1 and 3; the highest values in each impact category are shown in scenarios 2 and 3. As shown in Table 3, scenario 1 (the PerFluorAd process) outperforms the

 

**TABLE 3:** Results obtained for scenarios 1, 2, and 3[a]

| Impact categories | Unit/functional unit | Scenario 1 | Scenario 2 | Scenario 3 |
|---|---|---|---|---|
| Acidification terrestrial and freshwater | Mole of H+eq | 0.01 | 0.16 | 0.24 |
| Climate change | kg $CO_2$ eq | 1.8 | 28.3 | 320.4 |
| Eutrophication freshwater | kg P eq | 5E-06 | 4E-05 | 8E-06 |
| Eutrophication marine | kg N eq | 0.001 | 0.02 | 0.09 |
| Eutrophication terrestrial | Mole of N eq | 0.02 | 0.26 | 1.02 |
| Ionizing radiation—human health | kBq U235 eq | 0.07 | 0.56 | 0.09 |
| Ozone depletion | kg CFC-11 eq | 1.6E-10 | 3.1E-09 | 1.4E-14 |
| Respiratory inorganics | Disease incidences | 2.1E-07 | 3.3E-06 | 1.3E-06 |
| Photochemical ozone formation—human health | kg NMVOC eq | 0.004 | 0.07 | 0.27 |
| Resource use, energy carriers | MJ | 20.9 | 342.2 | 5072.0 |
| Resource use, mineral and metals | kg Sb eq | 1.9E-07 | 2.1E-06 | 1.6E-05 |

[a]The values provided are per functional unit—treatment of 1 $m^3$ aqueous film-forming foam containing spent fire-extinguishing water.

other 2 treatment technologies across all impact categories except for ozone depletion. Ozone depletion, however, is mainly driven by the background data used for activated carbon treatment in a furnace. Direct incineration (scenario 3) performs worst in 7 out of 11 LCIA categories. Finally, the treatment of AFFF containing spent fire-extinguishing water with activated carbon (scenario 2), also performs worst in 4 out of 11 LCIA categories.

To provide some context on the magnitude of the global warming impact, according to the German Federal Motor Transport Authority (2020), the average $CO_2$ emission for new cars in 2019 was 157 $g \times km^{-1}$. In comparison, the global warming impact from the treating 1 $m^3$ AFFF containing spent fire-extinguishing water equals 12 km (scenario 1), 180 km (scenario 2), and 2041 km (scenario 3). A graphical comparison of each impact category is shown in Figure 4.

Because in some environmental impact categories, such as global warming impact and marine eutrophication, the impacts from the thermal treatment of AFFF containing spent fire-extinguishing water (scenario 3) far exceed the impacts caused by the other 2 treatment alternatives, the ordinate contains a scale break.

## Contribution analysis of each scenario toward global warming impact

The contribution of each process to the global warming impact is shown in Figure 5. To improve readability, the ordinate is shortened for the range between 35 and 310 kg $CO_2$-eq. In the case of the PerfluorAd process (scenario 1), the highest contribution to global warming impact is caused by the post-treatment (67%) with activated carbon that covers both the production of activated carbon and the electrical demand of the adsorption process. The second highest contribution (13%) occurs in the treatment of the used activated carbon. The PerfluorAd treatment itself contributes to 12%. The thermal treatment of sludge, which contains the precipitated PFAS, contributes to 7% of the global warming impact.

In the treatment of AFFF containing spent fire-extinguishing water by activated carbon (scenario 2), 83% of the global warming impact refers to the treatment with activated carbon. The remaining 17% is caused by the disposal of the used activated carbon. In scenario 3, the thermal energy needed for incinerating the AFFF containing spent fire-extinguishing water causes the entire global warming impact. Similar results were also calculated for other impact categories. A complete overview of the contributions in each impact category is given in Supplemental Data, Table S7, and Supplemental Data, Table S8 shows the contribution analysis of each life cycle stage. For acidification and ozone depletion, the disposal of activated carbon highly influences the impacts.

## Sensitivities on loading capacity of activated carbon and dilution of AFFF

To understand the impact of the specific adsorption of activated carbon on the global warming impact, a sensitivity analysis was carried out. Therefore, the global warming impact was calculated for adsorption capacities between 0.01% (min) and 0.1% (max). Equal to 100 µg per gram granulated activated carbon, 0.01% was also observed by perfluorinated carbon isotherm measurements carried out by Calgon Carbon (Mimna 2017). The specific adsorption of activated carbon relates to the demand for activated carbon that is plotted against the *x* axis in Figure 6. The corresponding global warming impact per functional unit (FU) is plotted against the *y* axis.

In scenario 1, the lowest global warming impact is 1 kg $CO_2$-eq/FU (for an adsorption capacity of 0.1%) and the maximum global warming impact reaches 7.3 kg $CO_2$-eq/FU (for an adsorption capacity of 0.01%). For scenario 2, the lowest global warming impact is 14.1 kg $CO_2$-eq/FU (0.1% adsorption capacity) and the maximum global warming impact reaches 141.3 kg $CO_2$-eq/FU (0.01% adsorption capacity). Accordingly, the influence of the loading capacity is much higher in scenario 2 compared with scenario 1. However, scenario 1 always outperforms scenario 2.

Apart from the specific adsorption of activated carbon, the dilution of AFFF by additional fire-extinguishing also has an impact on the environmental impacts. In practice, fire-fighting foams such as AFFF are often diluted by a factor of 100 with fire-extinguishing water. However, in some cases the dilution

 

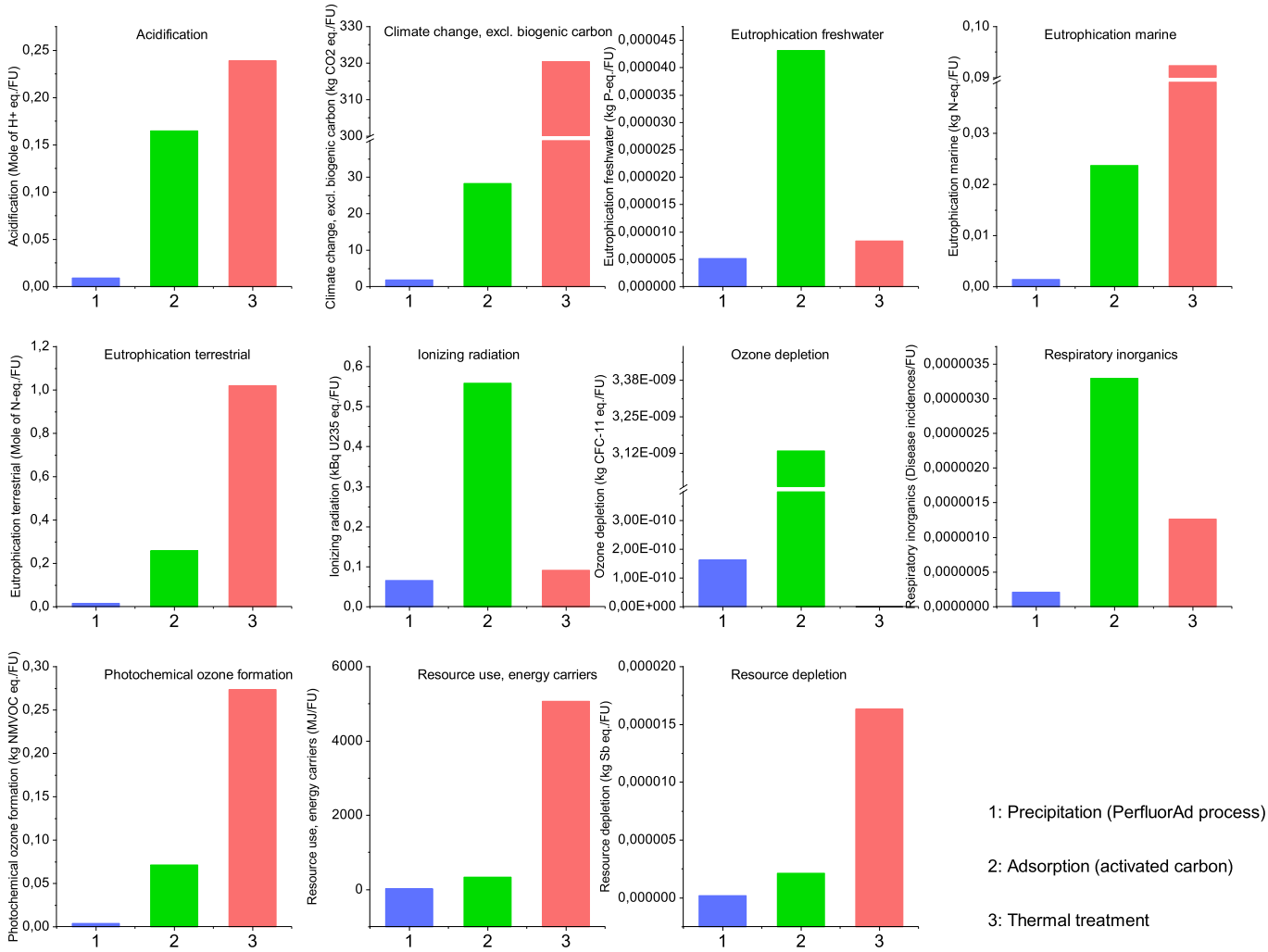


**FIGURE 4:** Environmental impacts caused by the treatment of 1 $m^3$ aqueous film-forming foam containing spent fire-extinguishing waters.

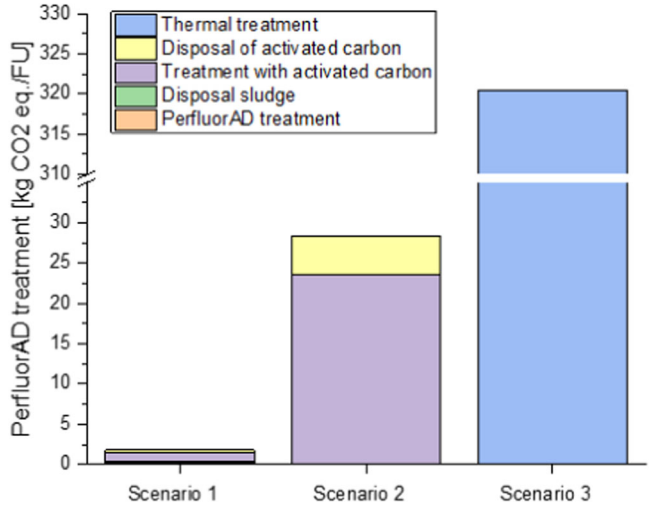


**FIGURE 5:** Contribution of processes to the global warming impact of treating of 1 $m^3$ aqueous film-forming foam containing spent fire-extinguishing waters.

might also be smaller, up to only 10 times. In the case of thermal treatment (scenario 3), the dilution factor has no notable influence on the environmental impacts because HWIP operate at high temperatures to thermally degrade hazardous substances, and the fluctuations in concentration of the input stream do not have an influence. However, in scenario 1, when diluting by 10 times instead of 100 times, more precipitant is required per FU (0.2 kg precipitant/FU instead of 0.02 kg/FU). In addition, more sludge needs to be disposed of (1.2 kg/FU instead of 0.12 kg/FU), assuming a 95% efficiency in the separation process through precipitation. This 95% is a rather conservative assumption because laboratory experiments showed efficiencies of between 97 and 98%, depending on the (ionic) background of AFFF containing wastewater. Consequently, post-treatment using activated carbon resulted in the overall separation efficiency of more than 99%. The amount of activated carbon required for the post-treatment is 2.25 kg/FU instead of 0.23 kg/FU. As shown in Figure 7, lower dilutions of AFFF lead to a higher global warming impact. The global warming impact for a 10-fold dilution for scenario 1 is 16.3 kg $CO_2$-eq/FU (which is roughly an 800% increase in comparison with the standard 100% dilution).

 

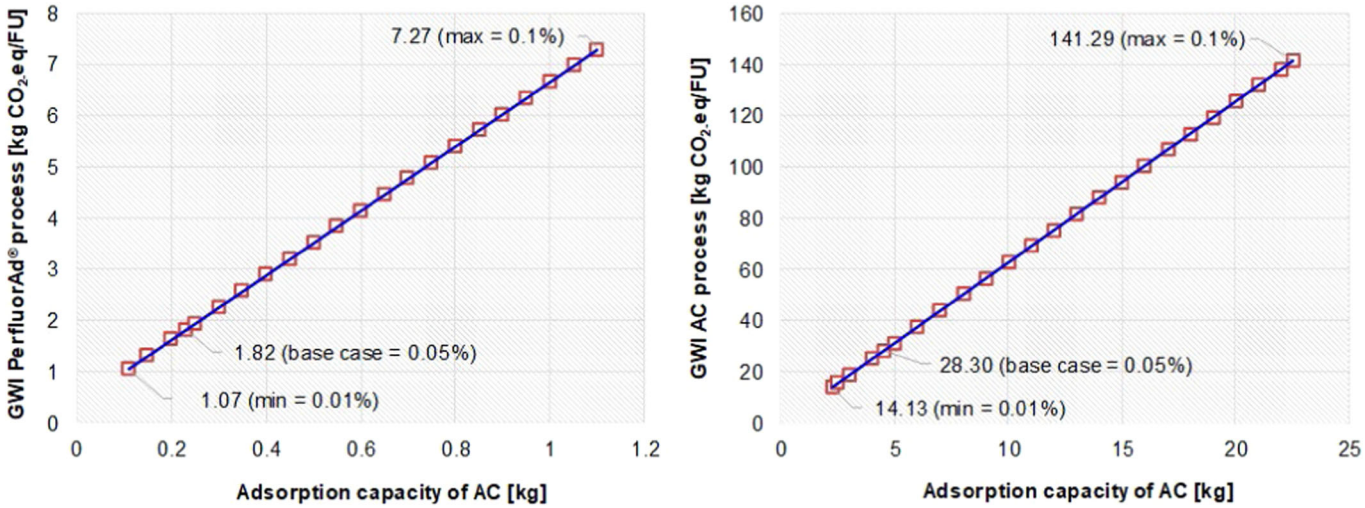


**FIGURE 6:** Sensitivity analysis of the impact of the loading capacity of activated carbon to the global warming impact. GWI = global warming impact; AC = activated carbon.

In particular, in scenario 2 higher amounts of activated carbon are needed for the proper treatment because the maximal specific adsorption of the activated carbon is reached much earlier. Assuming a dilution by a factor of 10, the global warming impact is 282 kg $CO_2$-eq/FU (which is roughly a 900% increase in comparison with the standard 100% dilution). This value is already close to the 320 kg $CO_2$-eq/FU that was calculated for thermal treatment (scenario 3). In conclusion, the specific demand of PerfluorAd is hardly affected by the dilution of AFFF (see Supplemental Data, Table S2). However, the dosage of the PerfluorAd (10.2 g/L) added to the AFFF media may affect the specific demand of PerfluorAd in practice.

## *Limitations of the study*

The prime focus of the present study is to understand the environmental impacts accrued from the end-of-life handling of AFFF containing spent fire-extinguishing water. Although a broad range of possible environmental impacts is covered by the LCA, potential toxicological effects (human toxicity and ecotoxicity) caused by improper treatment of AFFF were not investigated. For all end-of-life options we assumed a proper treatment of AFFF, although in practice the process efficiency of treating AFFF with activated carbon can be negatively influenced (e.g., by too long use times of activated carbon). For the PerfluorAd process, too low amounts as well as too high amounts of the precipitant can negatively affect the efficiency of the precipitation (Cornelsen et al. 2018). Thus, the correct amount of PerfluorAd is crucial for the efficiency of the process. In addition, experiments were exclusively carried out with Moussol-APS. The precipitant showed a high selectivity, in particular with regard to PFAS, with long-chain molecules. There are other commercial AFFF formulations with different PFAS compositions

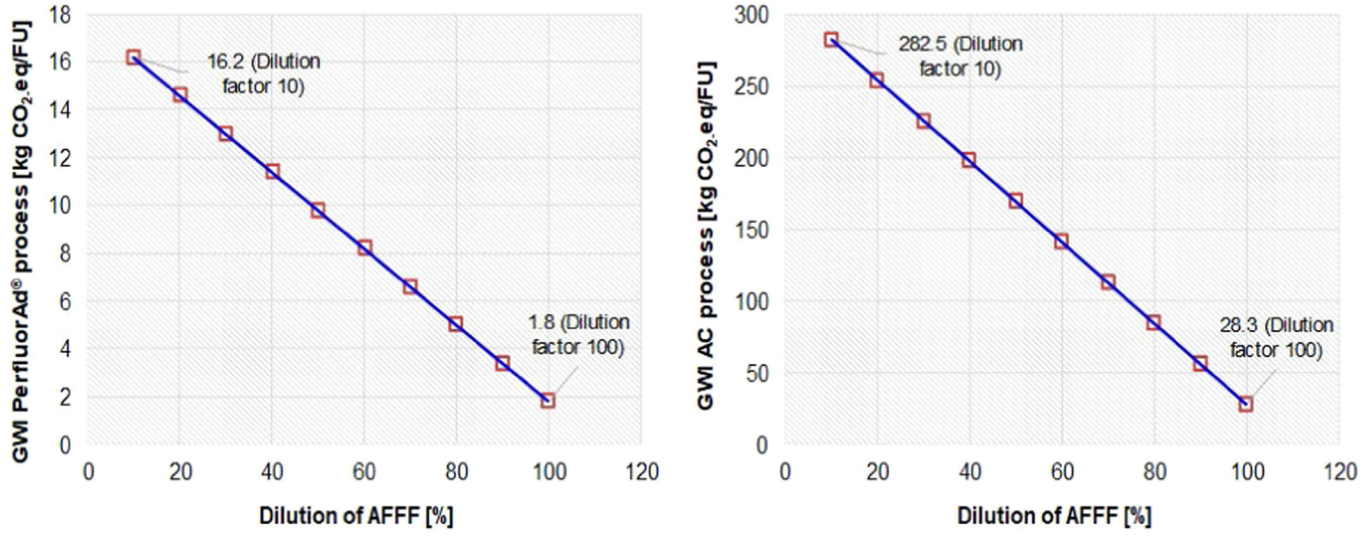


**FIGURE 7:** Sensitivity analysis of the impact of the dilution of aqueous film-forming foam (AFFF) to the global warming impact (GWI).

 

(e.g., those using PFAS with smaller chains). However, most commercial AFFFs today still largely contain long-chained molecules (Swedish Chemicals Agency 2015). A potential risk might occur from the precipitant when it is released into the environment. In the case of the selected precipitant, we do not expect any harmful impacts because it is already approved by the REACH regulations and has been used in the market for decades. For thermal treatment, we calculated the amount of energy that is needed for incinerating AFFF containing spent fire-extinguishing water. In practice, the energy demand might be even higher because of energy losses from the incineration process. Finally, the LCA study did not investigate the environmental impacts that are caused by transportation processes of raw materials such as absorbents or precipitation agents. In addition, we have neglected transport processes linked to the disposal of waste such as used activated carbon. However, in the case of the PerfluorAd process, the amount of activated carbon needed as well as the amount of precipitated sludge are much smaller compared with that in scenario 2.

## CONCLUSIONS

The present study applied a LCA to determine and comprehend the environmental impact of 3 different end-of-life options for AFFF containing spent fire-extinguishing waters. Scenario 1 examined the impact of using functional precipitation agents (PerfluorAd process) to separate PFAS from contaminated waters. Scenario 2 investigated the adsorption of PFAS by activated carbon as an end-of-life option. Finally, scenario 3 dealt with the direct incineration of spent fire-extinguishing waters as such without employing any downstream processing techniques. The LCA results clearly show that the PerfluorAd process performs best in nearly all investigated impact categories. This remains unchanged even when considering higher loading capacities of activated carbon as well as lower dilutions (high concentration) of AFFF with fire-extinguishing waters. In the case of treating AFFF containing spent fire-extinguishing waters with activated carbon (scenario 2), huge amounts of activated carbon are required because of the low specific adsorption capacity of PFAS. In addition, blockage of activated carbon beds might even reduce their lifetime. The highest environmental impacts were observed in scenario 3, the thermal treatment of AFFF containing spent fire-extinguishing waters. This is because a lot of energy is required for incinerating water at high temperatures of approximately 1100 °C to assure the complete thermal degradation of PFAS.

In conclusion, besides good environmental performance, the PerfluorAd process provides an effective way going forward in handling PFAS in spent fire-extinguishing waters using existing commercial, environmentally friendly cationic surfactants as coagulants. Such cationic structures used as functional surfactants can be sourced from the widely available green chemicals product category within the care market (personal care, home care, and industrial applications), to provide a nontoxic, biodegradable, and sustainable processing agent besides easily fulfilling the criteria for inter(national) registration. In addition, the functional precipitation agents used in the PerfluorAd process can also precipitate other anionic co-surfactants in the spent fire-extinguishing waters. Whereas at the same time, they can also be utilized in combination with other primary coagulants (e.g., aluminium, iron, or polydiallyldimethylammonium salts) as well as flocculation aids (e.g., polyacrylates, polyacrylamides, or polyaluminium compounds) to minimize the amount of PFAS in the final contaminated effluent waste.

*Supplemental Data*—The Supplemental Data are available on the Wiley Online Library at https://doi.org/10.1002/etc.4803.

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*Disclaimer*—The authors declare that there are no conflicts of interest regarding this publication.

*Data Availability Statement*—Data, associated metadata, and calculation tools are accessible from the corresponding author (venkat.aryan@umsicht.fraunhofer.de).

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