Analysis of per- and polyfluoroalkyl substances (PFAS) extraction from contaminated firefighting materials: Effects of cleaning agent, temperature, and chain-length dependencies

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ABSTRACT

This investigation delves into the extraction dynamics of 22 per- and polyfluoroalkyl substances from PFAS contaminated firefighting materials. Two distinct test sets were executed: one contrasting a commercial product with water following an elaborate decontamination procedure, and the other assessing seven washing agents on materials from firefighting installations, with one agent examined at 22 °C and 50 °C. A general tendency for improved desorption at the higher temperature was observed. Furthermore, a discernible influence of the cleaning agent’s pH on the extraction of specific PFAS species was observed, elucidating the role of chemical environment in the extraction process. PFAS rebound was studied for a period of up to 157 days, this unveiled a gradual escalation in PFAS22 levels, indicative of a protracted desorption mechanism. Intriguingly, PFAS with abbreviated carbon chains (C4-C6) exhibit superior desorption efficiency compared to their elongated congeners, suggesting a chain-length-dependent decontamination potential. A comparative scrutiny between a commercially available cleaning product, featuring multiple washing and flushing steps, and a water-only treatment regimen underscores the potential efficacy of the former. This exhaustive investigation furnishes nuanced insights into PFAS extraction complexities, offering a foundation for informed decontamination strategies.

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1. Introduction

Aqueous film-forming foams (AFFFs) and fluoroprotein foams have historically been employed for pool fire mitigation, with per- and polyfluoroalkyl substances (PFAS)-based firefighting foams initially introduced in the 1960s, exhibiting enhanced fire suppression capabilities compared to PFAS-free counterparts [1,2]. Due to escalating environmental and health apprehensions associated with PFAS, coupled with stringent regulatory measures, there is a growing shift towards the adoption of fluorne-free foams. For instance, perfluorooctane sulfonate (PFOS), a prevalent PFAS component in historically used firefighting foams, is categorized as a reproductive toxicant and a suspected carcinogen [3]. Numerous PFAS compounds have demonstrated adverse effects, including reproductive and developmental issues, hepatic and renal impairment, immunological effects, and tumorigenesis in animal studies [4]. Transitioning from PFAS containing to fluorne-free foams poses challenges, notably the potential rebound of PFAS from contaminated equipment. Studies indicate the adsorption of PFAS onto equipment surfaces, with subsequent diffusion into macro and micro pores [5,6]. The slow diffusion from these pores during cleanout complicates the decontamination process, and the persistence of contamination over extended periods exacerbates the challenge, considering the desired decontamination timeframe of hours to days. Furthermore, PFAS exhibits the capability to form bilayers or bilayer aggregates, such as micelles, intensifying the complexity of decontamination efforts [7,8].

A report by the European Chemicals Agency (ECHA) [9] outlines the experience of two stakeholders who drained their old PFAS foams and replaced them with new fluorne-free alternatives,
resulting in PFAS contamination of the replacement products [9]. Consequently, it is evident that a mere drain and replace strategy is insufficient to prevent PFAS dispersion into the environment. The recommended decontamination approach, as stipulated by various institutions including the Bavarian State Ministry for the Environment and Consumer Protection, the Australian Department of Defense, Fire Rescue Victoria, the German Industrial Plants Fire Brigades Association, and firefighting foam producer Bioex, involves draining the old firefighting foam followed by one or multiple rinses with water [9,10]. However, the adequacy of water rinsing is debatable, contingent upon the system owner’s site’s specific requirements [11]. Following a dual flush with water, sampling one year after a firefighting foam transition revealed a PFAS-concentration (post-TOP) of up to 1.6 g/l in the replacement fluorine-free firefighting foam [12,13]. In another study, 34 µg/l of PFAS22 was identified four months after a thorough cleanout [14]. These findings underscore the necessity for a critical reevaluation of the efficacy of water rinsing as a sole decontamination measure in the context of PFAS-containing firefighting foam replacement. A survey of commercially available PFAS decontamination agents indicates a limited array of products. PerfluorAd, a cationic floculant [6,7], incorporates a plant-derived fatty acid and asserts biodegradability [6]. Its efficacy in eliminating anionic PFAS is documented [6], while its effectiveness against cationic or neutral PFAS is presumed to be suboptimal [7]. Arcadis presents “FluoroFighter,” exhibiting superior PFAS removal compared to water and methanol, as assessed by the total oxidizable precursor (TOP) assay [5]. LifeClean offers a decontamination product, comprising an aqueous solution of hydrochloric acid and chlorine dioxide with a pH of 2–3, as per the safety data sheet (SDS). The acidic nature, highlighted by Ross [7], may pose a corrosion risk to certain equipment.

An application similar to decontamination of firefighting equipment is the regeneration of adsorbents used to treat PFAS contaminated water. Commonly employed adsorbents encompass granular activated carbon (GAC), powdered activated carbon (PAC), and various ion exchange resins. Factors influencing the regeneration process, as delineated by Lei et al., encompass porosity, functional groups, hydrophobicity, and PFAS type [15]. Enhancements in PFAS desorption during regeneration procedures have been reported with the use of organic solvents such as acetone, ethanol, methanol, and glycols, along with elevated temperatures, as compared to water [7,15–19]. The augmented solubility of PFAS in organic solvents is explained by the like-dissolves-like principle, as proposed by Lei et al. [15]. Furthermore, pH is identified as a crucial determinant affecting PFAS adsorption/desorption dynamics [20]. A higher pH induces deprotonation of PFAS molecules [3,15,21,22], resulting in a decrease in the zeta potential of the adsorbent [16,23]. This leads to a mutual increase in the negative charges of both PFAS molecules and the adsorbent surface, fostering repulsion between them. PFAS are compounds with hydrophobic and hydrophilic properties. While the head can interact electrostatically with substrates, the C–F chain can interact through hydrophobic bonds [15,24,25].

This study has put its focus on evaluation of different desorption medias (cleaning agents), the impact of pH and temperature in decontamination, and evaluation of the environment impact from some selected decontamination products. Further, decontamination of PFAS from different materials from real firefighting installations was evaluated. Focus of the current investigation has been on 22 PFAS substances. Since there is currently no legislation in place for decontamination of PFAS contaminated firefighting equipment, regulation governing the quality of water intended for human consumption (EU directive 2020/2184 and LIVFSS 2022:12) was used as input for the selection of the investigated substances.

2. Materials and methods

Laboratory-scale experiments were undertaken to assess various PFAS contaminated materials, cleaning agents, temperatures, and cleaning procedures. Two distinct evaluations were performed: firstly, a comparative analysis between a commercially available solution and water; secondly, an examination of diverse cleaning agents and temperatures via single batch treatment tests.

2.1. PFAS contaminated materials

Six different materials were evaluated in the current study. The materials were supplied by equipment owners and had all been in use in firefighting foam applications. To allow for small-scale tests in the lab, upon arrival, the materials were partitioned into smaller pieces.

The current investigation involved the assessment of six distinct materials sourced from firefighting foam applications. These materials, provided by equipment owners, underwent subdivision upon receipt to facilitate small-scale laboratory assessments. Three of the materials were derived from a singular fixed fire protection system within a military facility. Among these, a galvanized steel pipe (designated as P1-Steel) exhibited comprehensive coverage of rust and scale depositions on its interior surface. P1-Steel was cut into sub-pieces using a band saw. Additional materials from the same system included flange packings composed of EPDM (denoted as FP-EPDM) and seals extracted from ball valves (designated as S-PTFE). These materials were cut into sub-pieces using different pairs of scissors (sheet metal scissors and paper scissors). The seals, fabricated from PTFE, encompassed a combination of ball valve seat and gland seals. The fourth material consisted of steel pipes procured from an AFFF firefighting foam concentrate tank (designated as P2-Steel). To divide P2-Steel into sub-pieces, a pipe cutter was used. These pipes (P2-Steel), fully immersed in the concentrate for an extended duration, presented an apparently clean exterior devoid of visible deposits and rust. The dismantling of these pipes occurred during the transition from AFFF to fluorine-free firefighting foam (FFF). Accompanying the pipes was a sample of the old firefighting foam. The final two materials comprised a fire hose (designated as FH-EPDM, cut into sub-pieces using heavy-duty paper scissors) and a handheld fire extinguisher (abbreviated as HEX). HEX was sub-divided using the same band saw as P1-Steel. A new blade, different from the one used with P1-Steel, was used to avoid cross-contamination. The fire hose, manufactured by STS, featured an EPDM inner core and a polyester jacket, possessing a temperature rating of up to 450 °C with a diameter of 38 mm. The
handheld fire extinguisher, as indicated by its labelling, had contained film-forming foam and had an inner lining suspected, albeit unconfirmed, to be composed of polyethylene.

2.2. Washing agents

Methanol (MeOH) and isopropyl alcohol (IPA) obtained from Merck were procured through VWR International, designated as ‘Methanol for analysis EMPARTA®’ and ‘2-propanol Emplura®’, respectively. The methanol exhibited a minimum purity of ≥99.8%, while the purity of 2-propanol was 99.9%. Milli-Q water was used consequently in all tests and is throughout the paper referred to as ‘water’. Caustic was prepared by dissolving sodium hydroxide in water (25 wt-%). The composition of the washing agents and their respective pH values are summarized in Table 1. Liquid A (Liq. A) was a special treatment agent, supplied by an external partner who asked for secrecy. Therefore, no further details than pH can be shared.

2.3. Batch tests with different washing agents and temperatures

The washing agents presented in Table 1 were used to treat the six different material samples, a summary of the tests is given in Table 2. All tests, except for tests with washing agent 3 (IPA, water, NaOH) were conducted at 22 °C. Tests with washing agent 3 were made at 22 °C and 50 °C. The lower temperature (22 °C) aligned with the controlled room temperature, while the higher temperature (50 °C) was chosen to induce a significant temperature change while mitigating the risk of burn injuries.

A schematic illustration of the test procedure is shown in Fig. 1. To account for inhomogeneous distribution of PFAS on the materials’ surfaces, several pieces of material were treated in each test. Further, tests were made in duplicates (A and B tests) to account for variations in the manual work (due to material availability a singleton test was made with S-PTFE). The number of pieces treated in each test were selected to achieve similar ratios of washing agent to contaminated surface area. The result presented in the result section is a calculated average of the results from the duplicate tests.

The sample coupons from each material were put in 1 L LDPE wide neck bottles with screw caps (supplied by VWR International, free of PFAS). Sufficient quantities of washing agents were applied to ensure complete coverage of the specimen coupons. The amounts of materials and volumes of washing agents were adjusted to obtain a ratio of agent to contaminated surface area of 3.2 ml/cm². The ratio was maintained for all sample coupons except HEX, for which the ratio was 4.8 ml/cm². The caps were tightened and the bottles were placed on a laboratory shaking table at 50 rpm. After 24 h, the material samples were removed from the bottles and flushed with water for approximately 20 s. Samples of the washing agents were collected, and the material samples were left to dry overnight. Half of the sample coupons from the A test and half of the coupons from the B test were sampled and used to evaluate PFAS rebound (cf. Fig. 1 and the section on PFAS rebound).

2.4. Evaluation of the commercial decontamination product

A proprietary PFAS decontamination product was provided by an undisclosed commercial entity under conditions of confidentiality. Therefore, no details about their identity or their solution can be shared. The supplied product was accompanied by a comprehensive procedural protocol, tailored for laboratory testing, to facilitate PFAS decontamination processes.

The experimental protocol encompassed a series of sequential processes, including preliminary rinses, treatments with dedicated agents, and intermittent water flushes interspersed between and following each treatment step. In total, eight distinct stages of washing and flushing were executed. While the washing steps were made by immersing the sample in the treatment agent, the flushing steps (between the washing steps) were made using a wash bottle. The water from the flushes were allowed to drain and the sample coupons were placed on clean absorbent paper for approximately 5 min. To establish a baseline, parallel experiments using water alone were conducted under identical conditions. The test specimens utilized for assessment comprised P1-Steel, P2-Steel, HEX and FH-EPDM. The quantities of treatment agent and flushing water employed varied proportionally with the dimensions of the treated material, ensuring complete immersion of the samples. All experiments were conducted in duplicate, and the volumes presented in Table 3 represent the average outcomes derived from these trials. Due to the many treatment steps, evaluation of the decontamination efficiency was made by comparing the extractable amount of PFAS from material sample coupons before and after the treatment. A schematic overview of the experimental workflow is depicted in Fig. 2. As in the 24 h batch tests, half of the sample coupons from the A test and half of the coupons from the B test were sampled and used to evaluate PFAS rebound.

2.5. PFAS rebound

To evaluate PFAS rebound in both batch-tested and commercially treated samples, specimens were enclosed within 1-L low-density polyethylene (LDPE) wide-neck bottles equipped with screw caps sourced from VWR International. The bottles were filled with Milli-Q water. Samples were collected after 14, 70 and 157 days, with subsequent analysis focusing on the quantification of PFAS species.

2.6. Sampling and analytical methods

For the batch tests and the commercial product, sampling was made as indicated in Figs. 1 and 2. Solid samples were stored in LDPE resealable bags at room conditions. Liquid samples were kept in 250 ml LDPE wide neck bottles at 4–6 °C.

To evaluate PFAS rebound, 15 ml liquid samples (15 ml) were

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<td>Summary of the batch tests with different agents and at different temperatures.</td>
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<td>Volume fractions and pH (at 22 °C) of the washing agents used in the tests.</td>
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collected from the 1 L LPDE wide neck bottles after 14, 70 and 157 days. The liquid samples were stored in 15 ml polypropylene falcon tubes at 4°C.

### 2.6.1. Target PFAS analysis

Sample preparation and analysis was made in accordance with ASTM D7979-19, Standard Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent, and wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) [26]. PFAS were analysed using liquid chromatography tandem mass spectrometry (LC/MS/MS) with a Waters Acquity i-class LC-system and a Waters triple quadrupole-XS mass spectrometer. A gradient from 95% of mobile phase A (10 mM NH4OAc in purified water) to 95% of mobile phase B (10 mM NH4OAc in 2:8 methanol:acetonitrile) was applied on a Waters C18 BEH, 2.1 mm × 100 mm, column at a flow rate of 0.45 ml min⁻¹. The mass spectrometer was equipped with an electrospray ionization source operating in negative mode.

### 2.6.2. Total oxidizable precursors (TOP) analysis

PFAS related compounds in the samples have been determined by oxidative transformation according to Houtz and Sedlak [27]. In short, the oxidation was performed under basic conditions by reaction with potassium persulfate and sodium hydroxide at 85°C for 6 h. Under these conditions, PFAS precursors are converted to primarily perfluoroalkyl carboxylic acids. To determine the level of PFAS formed, the samples were processed and analysed by target PFAS analysis with LC/MS/MS according to ASTM D7979-19.

### 2.6.3. Extraction of PFAS from solid materials

The solid materials were extracted with MeOH:H2O (1:1 by
of scale and rust deposits, an anticipated irregular distribution of PFAS on the sample coupons is acknowledged, thereby introducing an element of uncertainty to the obtained results. Although visual inspections revealed the absence of apparent depositions in all other samples, the potential for a heterogeneous distribution of PFAS cannot be definitively ruled out. To mitigate such variations, multiple sample coupons underwent treatment in each experiment, with tests being executed in duplicate for robustness and reliability.

3.1. Removal efficiency of the commercial solution

Due to the several steps involved in the cleaning procedure, these tests were evaluated by comparing extractable amounts of PFAS$_{22}$ before and after the cleaning procedure and by comparing the result from the PFAS rebound tests. The volumes used for flushing and washing are presented in Table 3. All tests were made as duplicates and the volumes presented are average values from the duplicate tests.

A summary of the results of extractable PFAS from the sample coupons is shown in Fig. 3. The figure shows the sum of the 22 targeted PFAS species. Following water treatment and application of the commercial product to P1-Steel, the concentrations of extractable PFAS$_{22}$ experienced reductions by factors of four and two, respectively. After subjecting P2-Steel to water treatment, no discernible alteration in the sum of extractable PFAS$_{22}$ was evident. In contrast, the application of the commercial product resulted in a notable reduction of the sum of extractable PFAS$_{22}$ levels by a factor of 2.6. With HEX, water treatment results in a tenfold reduction in the sum of extractable PFAS$_{22}$, whereas the commercial product achieves a twentyfold decrease in the sum of PFAS$_{22}$. In the case of FH-EPDM, water exhibits superior efficacy compared to the commercial product, resulting in a 39-fold reduction in the sum of extractable PFAS$_{22}$. In contrast, the analogous metric for the commercial product is a 3.1-fold decrease. Considering the result from the PFAS rebound study, presented in Fig. 7, this supports the commercial solution to be more efficient for removal of the 22 studied PFAS species for P2-Steel, FH-EPDM and HEX. However, in the case of P1-Steel, the rebounding PFAS levels remain relatively consistent. This phenomenon is attributed to the anticipated material inhomogeneity inherent to P1-Steel. The disparate outcomes observed in FH-EPDM may be attributed to differences in pH between the water and the commercial product. Notably, distinct properties of EPDM, such as the electric potential at its surface (measured as zeta potential) [29], deviate from those of steel. Additionally, the reduced pH of the commercial product is implicated in the potential formation of micelles and bilayers [30], phenomena that may augment the complexity of desorption processes.

P1-Steel, HEX, and FH-EPDM exhibit predominant presence of PFOS, constituting 80% or more of extractable PFAS$_{22}$ substances. Conversely, in P2-Steel, the principal extractable PFAS is 6:2 FTS, accounting for more than 57%. This disparity is indicative of distinct firefighting foam generations, with 6:2 FTS (short-chain) characterizing the newer generation and PFOS (long-chain) representing the older generation [30]. Fig. 4 depicts the removal efficiency for the 22 studied substances. The removal efficiency was calculated as extractable PFAS (for the substance under investigation) from the treated material subtracted from extractable PFAS from the start material, the difference was then divided by extractable PFAS from the start material. The graph reveals a consistent trend of diminishing removal efficiency as PFAS chain length increases. This pattern aligns with prior observations in PFAS removal from water [31] and is attributed to the heightened mobility of shorter PFAS in aqueous environments and the diminished hydrophobicity of longer $C–F$ chains. Notably, FH-EPDM exhibits a less pronounced
decline in removal efficiency for longer chains compared to P1-Steel. Our proposition is that FH-EPDM engages in more robust hydrophobic interactions with PFAS, surpassing those of P1-Steel. A distinct drop in removal efficiency is observed for 6:2 FTS on P2-Steel, HEX and partially also on FH-EPDM. The reason for this has not been fully understood but we speculate on it being due to stronger interactions with the material, low solubility in water and the commercial product or slow desorption kinetics. In comparison to the 24-h batch tests (Fig. 5B), pH emerges as a significant determinant affecting overall removal efficiency, suggesting the involvement of robust electrostatic bonds.

3.2. Batch tests with different materials, agents and at different temperatures

3.2.1. Different materials and agents

A summary of the results with different materials and different agents is presented in Fig. 5. With P1-Steel and P2-Steel, the highest concentrations of PFAS$_{22}$ in the agent were observed using the agents with pH > 12. It is logical that the targeted PFAS are more efficiently removed at higher pH. This phenomenon aligns with the behavior of the commercial product. As pH rises, targeted PFAS molecules experience increased deprotonation, altering their electric potential and promoting repulsion of deprotonated species. Furthermore, the formation of micelles and bilayers is anticipated to be influenced by these pH-induced changes. The spread in the result for the A and B samples is relatively large for FH-EPDM (refer to the supplementary material). In addition, the difference between the result is for most of the agents relatively small. The average values reported in Fig. 5 should thus be treated with care. However, agent 7 clearly deviates from the other agents. With FH-EPDM, no clear effect of neutral or high pH can be observed. With agent 7 (pH < 2.0), the concentration of PFAS$_{22}$ is however lower (by a factor 2–5) compared to all other agents. While steel is hydrophilic, EPDM is hydrophobic [32] i.e., the interaction between steel and the targeted PFAS substances is assumed to be mostly electrostatic while the interaction between the targeted PFAS substances and EPDM to a larger extent could be assumed to be caused by hydrophobic interactions between the tail of the PFAS molecule and the EPDM (van der Waals interactions). In previous studies, it has been shown that pH has no significant impact on the adsorption governed by hydrophobic interactions only [33,34]. At neutral, or higher pH we believe that the desorption is governed by hydrophobic interactions but at low pH, electrostatic interactions play a more significant role. Further, diffusion of PFAS into EPDM is possible i.e., desorption may after a period become diffusion limited and less dependent on the type of agent.

The highest surface depositions, estimated from the extracted amount of PFAS$_{22}$ (pre-TOP) were 70 000 ng/cm$^2$, 830 ng/cm$^2$ and 4100 ng/cm$^2$ for P1-Steel, P2-Steel and FH-EPDM, respectively. Compared to what has previously been reported by Lang et al. (up to 10 000 ng/cm$^2$ of PFAS, post-TOP) [5] our results are in the case of P1-Steel and P2-Steel significantly higher. Given the potentially substantial dimensions of a fixed firefighting system, empirical analysis suggests that the decontamination process of such a system has the capacity to eliminate tens of grams of PFAS$_{22}$ from the surfaces within the system. Considering the dimensions of the fire hose in this study (FH-EPDM with length: 25 m and diameter: 38 mm), the estimated quantity of PFAS$_{22}$ potentially removed amounts to approximately 1.3 g. The result for FH-EPDM should be treated with care; diffusion of PFAS into the material could be expected because of the material's structure. Fig. 5D compares the result from the 24 h batch tests with agent 1 (water) and different materials. The black rectangle indicates materials from the same system. The contaminated surface areas of FP-EPDM and S-PTFE are associated with uncertainties; packings/seals are exposed to the ambient air on one side and to the liquid on the other side, the boundary is however not well defined. This makes it difficult to estimate the PFAS exposed area. Considering that the estimated contaminated area of FP-EPDM and S-PTFE may be conservative, the three materials from the same system show the highest surface deposition of PFAS$_{22}$.

To assess the desorption disparities among various PFAS species, we computed the relative proportion of (desorbed) C4–C6 by summing PFBA, PFPeA, PFBS, PFHxA, PFPeS, PFHpA, and PFHxS, then dividing by the total PFAS$_{22}$ concentration. The relative amount of PFAS$_{22}$ removed was calculated as the actual amount removed (for each agent) divided by the highest amount removed, for each material. While the individual proportions of PFAS species exhibited variability, their collective behaviour as a group (C4–C6), as depicted in Fig. 6, suggests a proclivity for easier desorption among shorter PFAS chains compared to longer counterparts. When more PFAS$_{22}$ was removed, the lower the share of C4–C6. This finding is similar to what is reported in Fig. 4 i.e., shorter chain
PFAS molecules tend to easier desorb from a contaminated surface. In practice this means that systems that have been exposed to short chain PFAS species only, may be easier to decontaminate than systems that also have been exposed to longer chain PFAS species.

### 3.2.2. Tests at different temperatures

Experiments involving Agent 3 were performed utilizing P1-Steel, P2-Steel, and FH-EPDM at both 22°C and 50°C. Analysis of individual PFAS concentrations, calculated as the mean of A and B samples, reveals a tendency toward increased desorption at elevated temperatures (see Table 4). Previous studies by Lang et al. [5] and Deng et al. [16] have documented an inclination towards elevated desorption rates at increased temperatures. Lang et al. focused on PFAS removal from steel pipes, while Deng et al. explored the regeneration of bamboo-derived granular activated carbon. Our current investigation substantiates Lang et al.’s observations and proposes that higher temperatures enhance PFAS removal from EPDM. We attribute this phenomenon to heightened solubility at elevated temperatures and propose it as an outcome of temperature-dependent desorption kinetics. With P2-Steel, a small decrease in the sum of PFAS22 is observed (cf. Fig. 5). This is attributed to the observed decrease in the concentration of 6:2 FTS at 50°C, which is the major constituent. The decrease is, however, small and could be due to heterogeneity deposition on the sample coupons. For PFAS comprising ten or more carbon atoms, elevated temperatures promote the desorption of carboxylic acids, whereas sulfonic acids exhibit a propensity to remain adsorbed to the materials. This observation, heretofore to our knowledge unreported and not fully comprehended, suggests that the distinctive molecular behaviour arises primarily from the variation in acid headgroups (sulfonic or carboxylic). Further elucidation of this phenomenon is warranted.

### 3.3. PFAS rebound

A summary of target PFAS analyses of the samples collected after 157 days is presented in Fig. 7. If the result in Fig. 7 is compared with the result in Fig. 5, a relationship between the sum of PFAS22...
PFAS22 in the agent after the 24 h batch test, the higher the concentration in the water after 157 days. Deviations from this relationship are expected to be caused by material inhomogeneity and uncertainties related to manual work and analyses. When PFAS rebound is evaluated from the sample coupons treated by the commercial solution (light grey coloured staples in Fig. 7), the same relationship is observed for P2-Steel and HEX. Material heterogeneity and the manual steeps with washing and flushing are believed to be the reason for the deviating results with P1-Steel and FH-EPDM. For almost all the materials and different agents, the concentration of PFAS22 increased over the period studied. This illustrates the process of decontamination of PFAS22 by water to be slow. The rate determining step has not been understood and was not within the scope of this study. However, we propose the formation and breaking of micellar structures or diffusion within the material to be accountable for the slow process of desorption.

3.4. In-depth analysis of PFAS removal from P2-Steel

3.4.1. Evaluation of PFAS removal from P2-Steel

Following the batch test procedure outlined in section 2.3, liquid
samples of the washing agent were collected after 24 h and analysed for 22 PFAS species (pre and post TOP). The concentrations of each PFAS species are summarized in Table 5 for various cleaning agents under evaluation. The table also includes the ratio of pre- and post-TOP analyses. Examination of the pre-TOP sum of PFAS suggests that cleaning agents with higher pH levels exhibit superior PFAS removal. However, the disparities diminish significantly when post-TOP results are compared. The PFAS concentration exhibits a 2–3-fold increase at pH > 12, whereas a substantial escalation of 74–84 times is observed at pH around 7, and a 13-fold increase at pH < 2.0. This underscores the profound influence of pH on the extraction of PFAS from the material. Additionally, it emphasizes that the conventional focus on specific PFAS species in analyses is inadequate for evaluating overall PFAS removal efficiency. The enhanced removal efficiency of targeted PFAS at elevated pH levels is attributed to increased deprotonation of the molecules, resulting in a heightened negative charge on the material surface. This negative charge facilitates repulsion between anionic PFAS species and the material surface, thereby improving PFAS removal. Additionally, pH levels influence micelle formation, contributing to the overall efficacy of PFAS removal processes.

The predominant PFAS identified in the targeted PFAS analysis is 6:2 FTS, constituting 80–99% of the pre-TOP 22 targeted PFAS. Oxidation in the TOP method is anticipated to transform 6:2 FTS predominantly into PFPrA (23% yield), PFBA (21% yield), PFPeA (24% yield), and PFHxA (17% yield) [35]. A discernible elevation in PFOA concentration is noted, possibly attributable to the oxidation of 8:2 FTS, as indicated by Martin et al., resulting in PFPeA (16% yield), PFHxA (19% yield), PFHpA (25% yield), and PFOA (20% yield) [35]. Post-TOP samples exhibit the expected increase in the aforementioned substances. However, the heightened levels of PFBA, PFPeA, and PFHxA in post-TOP samples treated with agents 1, 5, and 7 (samples with pH 7.7 or lower) cannot be solely attributed to the conversion of 6:2 FTS, 8:2 FTS, or other pre-TOP targeted
substances. Drawing from the findings of Martin et al. [35], we propose that the augmented levels of PFBA, PFPeA, and PFHxA may stem from 6:2 FTUCA or 6:2 FTAB, substances not targeted in the target PFAS analyses. In summary, the extraction of the targeted PFAS22 species demonstrates a preference for elevated pH conditions, as evidenced by the pre-TOP analyses. Conversely, distinct PFAS species, typically undetected in the target PFAS analysis, exhibit enhanced extraction by the pre-TOP analyses. Notably, despite being initially considered suboptimal cleaning agents based on pre-TOP assessments, e.g., agent 7 exhibit notable efficacy in post-treatment (post-TOP) analyses.

3.4.2. AFFF composition and desorbed PFAS species

The firefighting foam concentrate provided together with P2-Steel was analysed with target PFAS analysis pre- and post-TOP. The target analysis of PFAS22 (pre-TOP) summarized to 45 mg/l with 6:2 FTS as the major constituent (95% by mass). Other species detected in noticeable concentrations were PFHxA (3%) and PFOA (1%). Post-TOP concentrations of PFAS22 summarized to 942 mg/l i.e., a factor of 21 higher than pre-TOP. The concentration of the sum of PFAS22 pre-TOP (0.9%) is similar to what has been previously reported for AFFF foam concentrates [36]. When the composition of PFAS22 in the AFFF firefighting foam is compared with the composition of PFAS found in the different agents, the compositions are similar for the agents with high PFAS removal (agent 2, 3 and 4); the concentration of 6:2 FTS ranges from 92% to 99% (compared to 95% in the concentrate).

In Section 3.2.1, it was deduced that the quantity of PFAS22 extractable from materials’ surfaces is in the gram range. To illustrate, 1 g of PFAS22 equates to a volume of 22 l of the firefighting foam concentrate under examination. We propose further studies to include life cycle analysis to evaluate the environmental benefits of decontamination.

3.4.3. SEM-EDX

Fig. 8 displays scanning electron microscopy (SEM) images of a singular P2-Steel specimen. The micrographs reveal a predominantly smooth surface marred by the presence of numerous pits. Notably, these pits serve as loci for substantial material deposition. Augmenting SEM analysis, energy-dispersive X-ray spectroscopy (EDX) substantiates the composition of the dark matter within the pits, revealing a significant fluorine content, reaching concentrations of up to 10% by weight. Furthermore, the SEM images corroborate a discernible reduction in the quantity of dark material subsequent to a 24-h treatment with agent 3.

4. Conclusions

The primary focus of the present investigation has been the extraction of 22 per- and polyfluoroalkyl substances (PFAS) species from PFAS contaminated firefighting materials. In the case of the material designated as P2-Steel, a comparative analysis of PFAS22 concentrations pre-treatment of the material (pre-TOP) and post-treatment of the material (post-TOP) yields two notable conclusions. Firstly, numerous PFAS compounds beyond the scope of the 22 targeted substances are evident. Secondly, the pH of the cleaning agent demonstrates a noteworthy influence on the extraction of specific PFAS species from the material. The impact of extraction temperature was explored using agent 3, revealing a propensity for enhanced desorption at 50 °C compared to 22 °C. PFAS rebound kinetics were investigated over a duration of 157 days, exhibiting a
gradual escalation in PFAS22 levels throughout the entire period, suggestive of a lengthy desorption process. Notably, PFAS with shorter carbon chains (C4–C6) exhibited greater desorption efficiency compared to their longer-chain counterparts. Consequently, a system exposed to shorter-chain PFAS may be more amenable to decontamination than a system exposed to longer-chain PFAS. A comparative analysis between a commercial product comprising cleaning agents and multiple washing and flushing steps and an identical process utilizing water only (without commercial agents) was conducted. The findings suggest a potential superiority of the commercial product over water-only treatment, although further investigation is warranted due to suspected material heterogeneity contributing to variability in the data.

Interests statement

The authors declare that they do not have any conflict of interest.

Declaration of AI-assisted technologies in the writing process

During the preparation of this work the author(s) used ChatGPT in order to improve language and readability. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

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CRediT authorship contribution statement

Sixten Dahlbom: Writing – review & editing, Writing – original draft. Methodology, Investigation, Formal analysis, Conceptualization. Fanny Bjarnemark: Writing – review & editing, Methodology, Investigation, Conceptualization. Björn Nguyen: Writing – review & editing, Methodology, Investigation. Sarunas Petronis: Methodology, Writing – review & editing. Tove Mallin: Writing – review & editing, Writing – original draft, Funding acquisition, Conceptualization.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.emcon.2024.100335.

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