Removal of PFAS Compounds from Firefighter Gear using CO2+ Cleaning Technology: Preliminary Test Results

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Abstract

Carbon Dioxide (CO2) based cleaning technologies have been used for decades to solve innovative and complex cleaning and extraction challenges. Liquid CO2 (LCO2) cleaning systems were developed in the early 1990's as an alternative to traditional dry-cleaning systems. These early systems have evolved to be capable of effective cleaning and decontaminating firefighter gear. Cool Clean Technologies LLC (CCT) LCO2 based system "CO2-Plus" CO2+ has demonstrated superior SVOC/PAH removal of 99+% and shown effective removal of metals and biologicals based on numerous tests and designation by National Fire Protection Association (NFPA) as certified to clean and inspect firefighter gear. Expanding on these achievements, CCT performed initial tests to evaluate the effectiveness of removing selective per-and polyfluoroalkyl substances (PFAS) compounds from test swatches. These tests were performed mirroring the NFPA 1985 protocols. The results of these tests show that over 84% of the applied PFAS compounds were removed, with mass removal values exceeding those reported from others in the literature. Based on these favorable test results, CCT plans to refine PFAS cleaning protocols to achieve a PFAS removal efficiency > 99%.

Introduction - Background

The persistence and mobility of some PFAS, combined with decades of widespread use in industrial processes, certain types of firefighting foams, and consumer products, have resulted in PFAS being present in most environmental media at trace levels across the globe.[1] Elevated levels of PFAS in human blood have been associated with many human health concerns, including immune suppression and adverse developmental effects.[1,2] Additional potential consequences include the following: Increased risk of kidney and testicular cancer, elevated cholesterol, liver disease, decreased fertility, thyroid problems, and changes in hormone functioning.[3] Human exposure to PFAS is a public health concern that the Centers for Disease Control and Prevention (CDC) National Center for Environmental Health (NCEH) and the Agency for Toxic Substances and Disease Registry (ATSDR) are helping our local, territorial, tribal, state, and federal partner's address[3]. Over the last decade, interest in PFAS has been growing. ATSDR and state health partners are investigating exposure to, and possible health effects associated with PFAS in more than 30 communities across the United States.[4]

In addition to exposures experienced by the general populations, firefighters have an additional exposure route due to the use of aqueous film-forming foams (AFFFs) used to suppress fires and combustion byproducts from stain-resistant carpet and upholstery. Furthermore, PFAS are used in stain/water repellant fabrics as the layers of bunker gear. While much of this concern is the result of legacy AFFFs and gear, numerous accounts about PFAS have raised concerns about firefighter exposure to these chemicals as part of their duties: *"We're exposed to these chemicals every day," Captain Mitchell said. "And the more I looked into it, the more it felt like the only people who were saying these chemicals were safe were the people who make it."*[5]

In May 2019, the US Senate held a hearing on PFAS exposures. To address the issue of protecting firefighters and other affected people, legislation was introduced on 2/4/21 by Senator Gary Peters from Michigan, to develop training and best practices to limit exposure to PFAS in fire departments nationwide.[6] A bipartisan congressional task force was recently relaunched to address PFAS concerns through affected communities.[7] In a recent article [8], Dr. Birnbaum, the former head of National Toxicology Program, said that the problem of PFAS in turnout gear just recently appeared on her radar and there are many questions to entertain: *"Remember, all of these PFAS [used in turnout gear] are used as* *simple additives; they're just mixed in, so there's nothing that is chemically bonding them to the fabric or anything else," she said. "Over time they leach out, and people have shown the level of dust around where firefighting gear is stored as being very high."*

PFAS on Firefighter Gear

One source of PFAS exposure to firefighters is from the turnout gear itself. In a recent study, Peaslee et al. [9] have studies the impact of PFAS shed from protective clothing. Personal protective equipment (PPE) used by US firefighters, their "turnout gear", is manufactured from textiles that are made from fluoropolymers (one form of PFAS) or extensively treated by PFAS in the form of side-chain fluoropolymers.[10] These chemicals are used in firefighter textiles primarily to impart durable water and oil resistance.[11] This resistance prevents the turnout gear from becoming water soaked and adding significant weight to the PPE gear each firefighter must carry during a fire event. These PFAS include fluoropolymer materials such as polytetrafluoroethylene (PTFE) used as a moisture barrier in the inner layers of turnout gear. The results of this study showed that significant quantities of fluorochemicals are being shed from the textiles used in firefighters' PPE during the in-service lifetime of the garment. The sidechain fluoropolymers lead directly to perfluorooctanoic acid (PFOA) precursor materials in the environment, which provide another route of exposure to both users of the turnout gear and others in their immediate environment.

Laitinen et al. presented a study in 2018 [12] which detailed the many aspects of toxic compound distribution and decontamination of firefighter gear due to exposure to combustion products. As part of that study, the location and distribution of four (4) PFAS on firefighter gear was evaluated. The goal of the study was to identify the chemicals that can be found on firefighting garments after exposure to smoke. Ten used firefighting garments were exposed to fire residues in the Netherlands and one new uncontaminated firefighting garment was analyzed for background concentrations. Based on these test findings, PFAS exposure data are distributed on all parts of the gear and found on all layers tested in the stomach area and back area. In addition, these data show that PFAS is not found on new garments except for PFHxA at sub-ng/sample levels. Another part of this study which looked at nine (9) additional garments exposed to one fire incident showed that the location of the most important detected PFAS chemicals were: inner neck area, upper and outer stomach area and upper and outer back area. These data are very important as they demonstrate the migration of PFAS compounds throughout the firefighter gear.

In a more recent study by Young et al. [13], samples of PFAS were taken from multiple sources among 15 fire stations in Massachusetts - collected from firehouses' living quarters, turnout gear locker rooms, and six wipes of station turnout gear. In the pilot testing of wipes of turnout gear taken, the five highest detected PFAS masses ranged from 5600 - 30,000 ng/wipe. Gear was reported to vary in age, washing frequency, and manufacturer, and there were wide ranges in masses of PFAS on gear wipes. While PFAS have not been previously reported in wipes of clothing, the levels of four (4) key PFAS and other perfluoroalkyl acids (PFAAs) in the gear wipes in this pilot study were typically orders of magnitude higher than the baseline levels.

As cited above, numerous sources have identified the problem of PFAS exposures to human health and the importance of limiting exposures to these chemicals. Firefighters carry an added burden as the gear they use to protect themselves during fire incidents also contains PFAS. Although there are efforts to limit exposures of PFAS by changing materials of manufacturing in both general products as well as in firefighter gear, these efforts will take significant time as turnout clothing can have a service life of up to 10 years. Until PFAS can be limited from use, we need to find the best way to decontaminate PFAS from firefighter gear, whether it comes from fire incidents, from the gear itself, or both. Finding the best PFAS cleaning technology for firefighter gear is an important advancement in the knowledge health and safety impacts to firefighters.

Effectiveness of Hazardous Compound Removal using Traditional Water Wash Technology vs CO2-Based Technology

CO_2 cleaning technology has been shown to be far superior to water-based cleaning technologies for removal of organics, removing 99+% of NFPA Polycyclic Aromatic Hydrocarbons (PAHs) based on internal testing [14] and independent 3rd party testing for National Fire Protection Association (NFPA) certification [15]. Published firefighter gear cleaning data using water-based cleaning technologies shows semi-volatile organic compounds (SVOC) removal efficiencies of washing 2 turnout sets of gear at 40% and washing 3 sets of gear at 15% [16]. In another study, the effectiveness of water-wash cleaning to remove PAHs from firefighter hoods found that the removal efficiency of this process for all PAHs was 75.5% [17]. Removal efficiencies for toxic metals is also favorable using the CO_2 cleaning technologies with removal efficiencies of 59% [15], equivalent to or better than water-wash test values. While garment damage is a common concern with traditional water-based cleaning systems, recent data have demonstrated that after fifty (50) CO_2 wash cycles there was insignificant impacts to the moisture barrier of the turnout tear, the most delicate and sensitive part of the turnout gear ensemble [18]. Further, this CO_2-based cleaning system captures and sequesters PFAS contaminants removed from the gear, which is subsequently disposed of in the hazardous waste facility. However, water-based gear treatment systems discharge PFAS and other toxic compounds directly to a waste discharged system to be processed downstream at a wastewater treatment facility. It is known that typical wastewater treatment systems do not remove PFAS, rather passes these compounds through the treatment facility as effluent which may be discharged to the environment and sludge which can used be as low-grade fertilizers [19]. The superior SVOC/PAH cleaning efficiency, the ability to clean without liner damage and sequestration of hazardous compounds removed the gear make the CO2+ cleaning system the preferred firefighter turnout cleaning technology. The missing decontamination piece is the effectiveness of PFAS removal from these garments.

CO2 cleaning and extraction systems produced by CCT have been used for decades to clean difficult and complex materials in aerospace, medical, industrial, and agricultural applications. Recently a study conducted by Centexbel [20] evaluated the use of CO2 cleaning technology to clean firefighter turnout gear in Europe. In this study, the researchers obtained a contaminated piece of turnout gear – a coat – cut it in half, cleaned one half in a standard water-wash cleaning system and the other half with a CO2-based cleaning system – similar to the CCT manufactured system. Samples of each layer of the turnout were evaluated before and after cleaning. The results from this study showed:

- The gear contains toxic products that are present in a significantly higher concentration in the clothing than legally permitted in Europe.
- 87% of these toxic products are in the outer layer and the moisture barrier.
- Industrial cleaning with water and detergents according to the ISO 6330 standard gives a cleaning efficiency (=chemical decontamination) of 27.4%.
- Industrial cleaning according to the CO2 cleaning technology gives a cleaning efficiency of 98.9%.

While the results of the Centexbel study are very important, this study did not follow the standard testing and evaluation protocols outlined in the NFPA standard.

CO2+: A CO_2-Based Firefighter Turnout Gear Cleaning System

Figure 1 – CO2+ FireFighter Gear Cleaning System – Emergency Technical Decon – Eagan, MN

CCT has developed numerous CO2-based cleaning systems to remove a wide range of contaminants from numerous articles: the CO2+ cleaning machine is shown in Figure 1 and the CO2+ process is depicted in Figure 2 below. The CO2+ cleaning system uses an environmentally friendly cleaning trade secrete solvent (CoolCare™) to clean the materials followed by a Liquid CO2

(LCO2) rinse cycle. The resulting process provides excellent cleaning performance without damage to the articles cleaned. At the conclusion of the CO2+ process, typically 40-70 minutes in duration, the contents are removed with no additional drying required. Furthermore, the residues removed from the gear are concentrated in the still bottoms and filter media, which are subsequently disposed as hazardous waste and not washed down the sewer where these wastes can cause problems again.

Figure 2 – CO2+ Cleaning Process

Test Objective and Approach

The objective of this test study is to identify if the CO2+ cleaning system which provides superior cleaning and decontamination results can also be effective from removal of PFAS compounds which are present on the firefighter gear and generated at firefighter incidents.

The approach to evaluate the effectiveness of CO_2 cleaning for PFAS removal is to rely on the existing cleaning protocols specified in the NFPA 1851 standard [21] combined with incorporation of PFAS analytical testing methodologies using CO_2-based cleaning process technology developed by the applicant. The NFPA is an international nonprofit organization devoted to eliminating death, injury, property, and economic loss due to fire, electrical and related hazards. The NFPA 1851 Standard [22] specifies test protocols for evaluation of decontamination efficiencies for specified metals and SVOCs and defines test load characteristics for the decontamination efficiency evaluations. This study used NFPA-1851 testing protocols to conduct the PFAS decontamination test evaluations. The use of this standard serves as a test baseline of which will be understood by persons in this field.

Typical turnout gear [22] is comprised of three distinct layers: the thermal liner, the moisture barrier and the outer shell. The thermal liner is the most critical component in turnout gear because it has the biggest impact on thermal protection and heat stress reduction. Together with the moisture barrier, the two layers account for up to 75 percent of the thermal protective performance of a turnout garment. The moisture barrier provides resistance to water, chemicals, and viral agents. The outer shell of a firefighter's turnout gear is the first line of defense, providing 25 to 30 percent of total thermal protection and shielding the inner components. Maintenance and repair of turnout gear is also governed by the NFPA 1851, which mandates that an advanced inspection of all personal turnout gear ensembles and ensemble elements be conducted at a minimum of every 12 months or whenever routine inspections indicate that a problem may exist. The importance of effective cleaning of firefighter turnout gear has been clearly and extensively detailed by Jeffrey Stull (a technical consultant for this project) in his 2018 article.[23] He identifies key contaminants commonly found on firefighter turnout gear and the importance of proper decontamination procedures to protect the health of the firefighter and details the steps necessary to validate cleaning effectiveness.

Experimental Methods

PFAS testing using the CO2+ cleaning system largely followed the protocols identified in NFPA-1851. Test swatches were prepared, surrogate garments were used, 40 pound ballast was used. As there are not 1851 standards detailing PFAS analysis and testing protocols and modified the doping and analytical procedures following protocols used in other EPA test methods:

- Perfluoroalkyl Substances were analyzed using LC/MS/MS following ASTM D7968 (M) [24];
- Legend Technical Services of St. Paul, MN was used as the analytical lab for these tests;
- Test swatches were cut to 3" x 6" following SVOC test protocols of 1851;
- Following NFPA protocols, swatches were doped with 200 ppm PFAS solution by applying 300 uL to the swatch, resulting in a doping mass of about 6000 ng/swatch PFAS to the swatch;
- Doping mases for four (4) PFAS analytes on the test swatches:
  - Perfluoro-n-octanoic Acid (PFOA) – 61,000 ng/g wet
  - Perfluoro-n-tetradecanoic Acid (PFTeDA) – 62,000 ng/g wet
  - Perfluoro-1-butanesulfonate (PFBS) – 52,000 ng/g wet
  - Perfluoro-1-octanesulfonate (PFOS) – 77,000 ng/g wet
- The list of PFAS analytes examined is presented in Table 1.

Table 1 – List of Analytes Examined

PFAS Analyte	RDL, ng/g wet
Perfluoro-n-butyric Acid (PFBA)	0.31
Perfluoro-n-pentanoic Acid (PFPeA)	0.63
Perfluoro-n-hexanoic Acid (PFHxA)	0.63
Perfluoro-n-heptanoic Acid (PFHpA)	0.31
Perfluoro-n-octanoic Acid (PFOA)	0.63
Perfluoro-n-nonanoic Acid (PFNA)	0.63
Perfluoro-n-decanoic Acid (PFDA)	0.63
Perfluoro-n-undecanoic Acid (PFUdA)	0.63
Perfluoro-n-dodecanoic Acid (PFDoA)	0.63
Perfluoro-n-tridecanoic Acid (PFTrDA)	0.63
Perfluoro-n-tetradecanoic Acid (PFTeDA)	0.63
Perfluoro-1-butanesulfonate (PFBS)	0.28
Perfluoro-1-hexanesulfonate (PFHxS)	0.29
Perfluoro-1-octanesulfonate (PFOS)	1.2
Perfluoro-1-decanesulfonate (PFDS)	1.2
6:2 Fluorotelomersulfonate	0.6
8:2 Fluorotelomersulfonate	1.2
N-Methylperfluorooctanesulfonamidoacetic acid	0.63
N-Ethylperfluorooctanesulfonamidoacetic acid	0.63
Perfluoro-1-octanesulfonamide (FOSA-I)	0.63
HFPO-DA (Gen X)	1.3

The CO2+ cleaning system located in the ETD facility in Eagan, MN was used for these tests, shown in Figure 1. The system was programmed for an 18-minute wash cycle using the 'Outer Shell' program, which has a cycle duration of about 70 minutes, which is characterized in Figure 2 above. The test swatches were inserted in the surrogate garments using procedures specified in NFPA 1851. At the completion of the cleaning cycle, the ballast and test garments were removed from the machine, the test swatches were collected and inserted into clean transfer tubes, which were subsequently returned to the Legends TS for analysis. Two tests were conducted, one on 29 January 2021 and a follow-up test on 26 February 2021.

Test Results and Discussion

The test results, shown in Table 2 and presented graphically in Figure 3, indicate effective PFAS removal for analytes reported. The average PFAS removal was about 84%.

Table 2 – PFAS Test Results

PFAS Analyte	PFAS Test 1 - 29Jan21	PFAS Test 2 - 26Feb21	Average
Perfluoro-n-octanoic Acid (PFOA)	88.2%	86.3%	87.3%
Perfluoro-n-tetradecanoic Acid (PFTeDA)	97.2%	98.5%	97.8%
Perfluoro-1-butanesulfonate (PFBS)	61.1%	59.6%	60.3%
Perfluoro-1-octanesulfonate (PFOS)	91.2%	91.3%	91.3%
Average	84.4%	83.9%	84.2%

Based on a review of the recent paper by Young et al [13], they report total PFAS mass loading from wipe tests ranging from 1.28 to 84.5 µg/swatch using at 3"x3" swatch and wipe solvent is IPA (equivalent to 0.02 – 1.45 ng/cm^2). Based on data provided by Laitnen et al. [12], they report sum of 4 PFAS totaling about 0.25 ng from a sample piece of turnout gear - 4 cm^2 (equivalent to 0.06 ng/ cm^2). For this study, we followed the NFPA outline of doping the swatch with 200 ppm PFAS solution by applying 300 uL to the swatch, yielding a loading of about 60,000 (range from 29,000 – 77,000) ng/swatch PFAS. The swatch dimensions were 3"x6" (116 cm^2). Hence the nominal loading on the test swatches was substantially greater than those identified in the literature: about 60,000 ng/swatch / (116 cm^2/swatch) = 517 ng/cm^2. The PFAS loading mass value is substantially more (about 500x) than observed in the literature cited above. Subsequent tests should be conducted using a concentration of about 1 ppm

PFAS, which will give us a nominal PFAS mass of 150-300 ng/swatch or about 2.6 ng/cm^2. Further, subsequent testing should employ the smaller NFPA 1"x2".

Examining these data from the perspective of PFAS removal capability of the CO2+ cleaning system, these data demonstrate that approximately 84% of the nominal 6000 ng/swatch (52 ng/ cm^2) was removed, or about 44 ng/ cm^2, indicating that the CO2 + chemistry should have the carrying chemistry to capture most if not all the PFAS on these substrates assuming typical loading rates. However, this hypothesis will need to be verified by further testing.

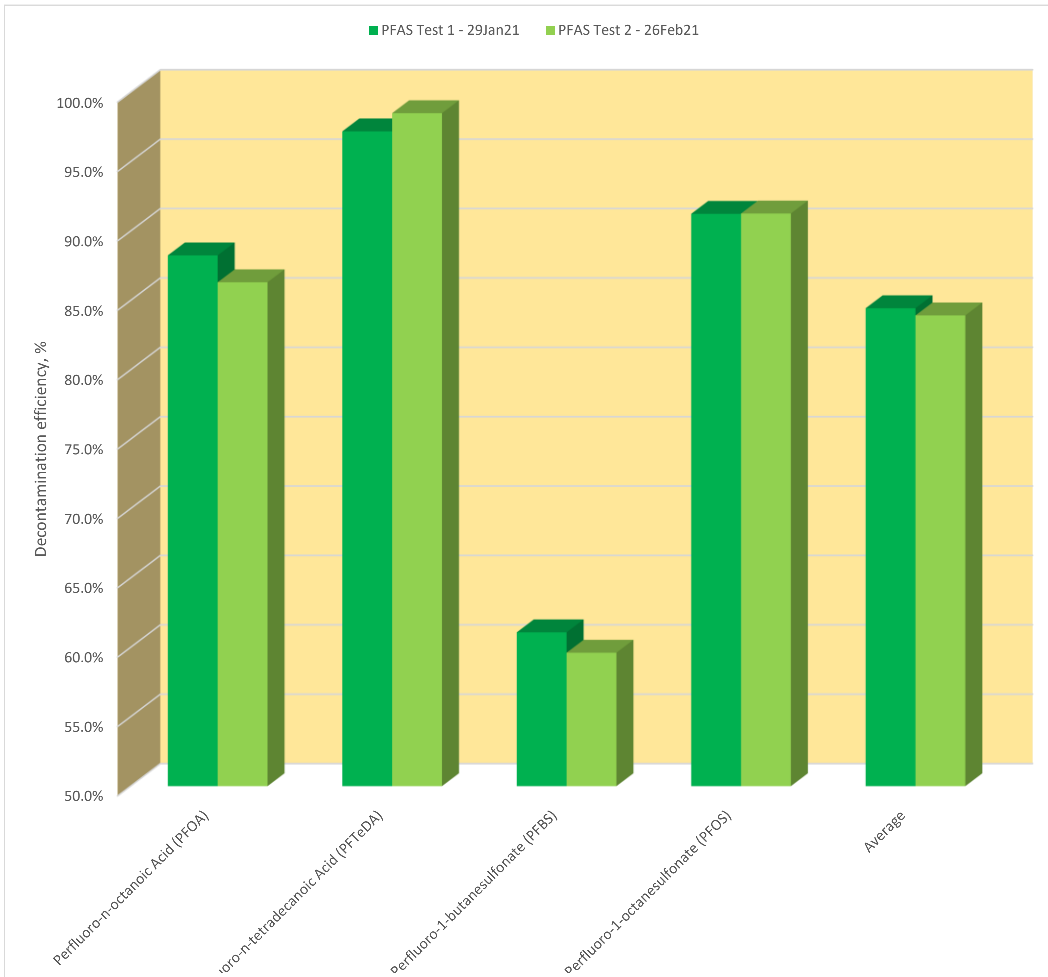

Figure 3 – PFAS Decontamination Test Results using test protocols similar to NFPA 1851.

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