Liquid Carbon Dioxide Cleaning as a Possible Game Changer for Removing Fireground Contamination

BY MICHAEL DUYCK, PRESIDENT, EMERGENCY TECHNICAL DECON (ETD), FIRE CHIEF (RET.); AND NELSON W. SORBO, PH.D., RESEARCH AND DEVELOPMENT, COOL CLEAN TECHNOLOGIES (CCT)

CO_2-based cleaning technology is an effective decontamination technology that is now available for advanced and specialized cleaning of firefighter gear, including coats, pants, hoods, gloves, leather boots, and other related clothing articles. CO_2 cleaning technology provides superior SVOC cleaning efficiencies compared with traditional water-wash cleaning methods and provides effective removal of NFPA-listed metals and biologicals, as will be presented below. Further, this technology has been shown to remove selected PFAS and lithium-ion battery (LIB) fire compounds. The background and value of CO_2 cleaning technology is presented in a series of FAQs to communicate how CO_2 technology is providing breakthroughs in firefighter gear decontamination.

What Is Liquid CO_2 Cleaning?

Liquid CO_2 (LCO_2) cleaning is an innovative cleaning technology that has recently been adopted to clean firefighter gear and accessories using pressurized LCO_2, which has cleaning chemistry similar to organic solvents. LCO_2 is very effective in removing many organic stains and residues typically found in dry-cleaning applications. This process can be enhanced using new additives to clean the widest ranges of stains on gear, including tar, oils, and paint, as shown below. LCO_2 cleaning is not new, as it was introduced as an alternative dry-cleaning technology almost 30 years ago.

How Do LCO_2 Cleaning Systems Work?

From the perspective of the user, LCO_2 cleaning systems (Figure E1) operate similarly to water-/extractor-based cleaners–both are loaded from the front, both use customized wash and rinse cycles, and both are controlled from a user-friendly touch screen. However, inside each machine the operations are quite different. Water-wash/extractor systems are very similar to traditional industrial garment front-loading "washing machines." The LCO_2 system has the following characteristics:

- Operates at a pressure that maintains CO_2 in a room temperature liquid state.
- Uses LCO_2 with selective additives to clean the gear without excessive agitation or high temperature.
- Penetrates the complex features of the gear much more effectively than traditional water-wash systems to remove far more hazardous compounds from the gear.
- Uses a closed loop cleaning process such that all the residues are collected inside the system—nothing is disposed of "down the drain." Further, 99+% of the CO_2 used in the process is recycled inside the machine.
- **Requires no supplemental drying.** Garments are removed from the vessel cool, dry, and ready for post processing.

Figure E1. LCO_2 Cleaning System in Emergency Technical Decon Facility, Eagan, MN, Processing Facility (left); Liners (center); and Outer Shells (right) Inside Cleaning Vessel

Source: Emergency Technical Decon.

LCO_2 systems require a source of liquid CO_2 (obtained from a gas company), compressed air, hot water or steam, cold water, and electricity. The typical cleaning cycle time is about one hour.

Are LCO_2 Machines Safe?

Yes. Each system must pass strict pressure vessel, plumbing, and electric safety code requirements. Hazardous operations assessments are conducted on each machine design to ensure the operational safety of its users. Further, each machine is equipped with sensors to monitor the concentration of CO_2 in the cleaning room. Frequently, these sensors are interlocked with other alarm and ventilation systems to ensure worker safety.

Are All LCO_2 systems the same?

No. While all these systems use LCO_2 as their base cleaning solvent, there are differences between various LCO_2 system manufacturers. These differences include the following:

- Additives used.
- Residue removal capability.
- Toxic compound (e.g., PAHs, SVOCs, VOCs, odors, metals, PFAS, particulate matter) removal capability.
- Processing times.

Does Using an LCO_2 Cleaning System Contribute Additional CO_2 Emissions to the Environment?

No. The LCO_2 used is all recycled CO_2 obtained from industrial gas companies that contract with large industrial CO_2 generators. Common sources of recycled CO_2 emissions are from ethanol and ammonia production facilities, iron steel furnaces, cement/lime kiln exhausts, and others. Other uses of recycled CO_2 include fertilizer/urea manufacturers, oil/coal bed methane recovery operations, food and beverage applications, weld gas, and others. Hence, the LCO_2 cleaning system does not add additional CO_2 to the environment.

What Happens to the Contaminants Removed from the Gear?

During the wash and rinse cycles, LCO_2 and its additives penetrate the gear's porous materials and components in addition to contacting nonporous surfaces, removing residues with the wash/rinse fluid mixture, which is then directed to a distillation vessel. In this vessel, the LCO_2/residue mixture is distilled, creating two fluid streams: gaseous CO_2 and still bottoms (i.e., the contaminants). The gaseous CO_2 is directed to a condensation chamber whereby gas is condensed into LCO_2, which is collected for reuse in the system storage tank. The residues and cleaning additives are collected in the bottom of the distillation vessel–these are periodically removed for safe disposal using a qualified method as determined by local, state, and federal regulations. The small quantity of gaseous CO_2 remaining in the cleaning vessel after gas recovery is vented from the system.

How Is LCO_2 Cleaning Different than Water-Based Cleaning?

There are four fundamental differences between LCO_2 cleaning systems and water-based cleaning systems: cleaning chemistry, penetration capability, agitation levels, and operating temperature.

Cleaning Chemistry. Water-based cleaning takes advantage of the highly polar nature of water to effectively remove water-based stains and uses selective additives (detergents, soaps) to solubilize nonpolar stains such as oils and greases. LCO_2 is a mildly polar cleaning solvent that effectively removes many simple oils but uses additives to effectively remove more polar soils. Hence, each solvent has its fundamental cleaning strengths and uses additives to expand the cleaning effectiveness to a wider range of residue removal chemistry. The additive types used for water-wash and LCO_2-based systems are quite different but when properly selected can provide effectiveness in cleaning.

Solvent Penetration Capability. For any cleaning system to be effective, the cleaning solution must contact the soil on or in the materials being cleaned. Because of the required complexity and design of firefighting gear (given its use of thick, tightly woven or nonwoven and often multilayer materials) and the mobility of these contaminants, studies[1] have shown that many of the most hazardous toxins have penetrated far into the gear material matrix. Hence, for effective cleaning of all parts of the gear, the penetration capability of each cleaning system plays a very important role. There is a wide difference between the penetration capabilities of water compared with LCO_2. The penetration capability can be characterized by two fundamental parameters–viscosity ("thickness" of a fluid) and surface tension (capability of wetting a surface). The viscosity and surface tension of LCO_2 are about 12 times less than that for water. Hence, LCO_2 can penetrate the dense complex parts of the gear far easier than water-based cleaning solutions. LCO_2 + additives can effectively solubilize the residues deep inside the garment matrix and transport it out of the garment to the bulk cleaning fluid. Therefore, with the correct cleaning additives to address a wide range of contaminants, LCO_2 systems can deep clean far more effectively than their water-wash counterparts. This increased level of contaminant removal rate has been demonstrated in research conducted both by the Fire Protection Research Foundation and North Carolina State University for separate LCO_2 cleaning systems.

Agitation Level. Agitation is important in both water-based and LCO_2-based cleaning systems. However, because of the wide difference in penetration capability between the two cleaning solutions, agitation is far more important and much more intense in a water-based cleaning system than in LCO_2 systems.

Operating Temperature. The temperature of the cleaning solution is also quite different. It is well understood that warm or hot water both enhances the cleaning capability of these systems and degrades the fabric more quickly than cold water systems. Hence, for water-based systems, the drive is to operate at the highest possible temperature without substantial damage to the garments. NFPA 1851, *Standard on Selection, Care, and Maintenance of Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting* (2020), specifies that the operating temperature should be no higher than 105°F. LCO_2 systems typically operate at temperatures no higher than room temperature (~75°F), and typically colder. As a result, there is far less temperature-generated wear on the garments than with water-wash systems.

When combining the effects of agitation and temperature on the durability of the gear after multiple washings, it is understandable that gear subjected to repeated water-wash cycles has substantially more wear than gear processed in LCO2 systems. These findings have similarly been demonstrated by LCO2 vendors that have independently evaluated the impact of their cleaning processes on key gear performance properties.

Which Type of System Cleans Better and Why?

The efficiency of cleaning is dependent on the contamination on the garment and the cleaning method used. As discussed previously, water-wash cleaning technologies are constrained by the water temperature and by the acceptable agitation level–both very important for effective cleaning. For LCO2 systems, this constraint is not important, as the CO2-cleaning chemistry is not impacted by temperature or agitation level. Figure E2 shows that, when evaluating oil, diesel, grease, tar, glue, paint, and other obvious signs of contamination, the LCO2 capability at Cool Clean Technologies (CCT) removes visual signs of contamination. Water-wash systems could not typically achieve this level of cleaning without exceeding the temperature and agitation constraints required for processing gear and would thus have to be subject to specialized cleaning using supplement cleaning agents to provide acceptable levels of stain removal.

Figure E2. Evidence of Effective Residue Removal Using CO_2 + Cleaning System from CCT: Top–as Received, Bottom–After Processing

Source: Emergency Technical Decon.

Which System Results in Better Cleaning Efficiency (Based on the NFPA 1851-2020 Requirements)?

NFPA 1851 (2020) states requirements for removal efficiency of three classes of toxins–SVOCs (semi-volatile organic compounds), metals, and bacteria. Cleaning system operators must conduct specific tests to document cleaning effectiveness by meeting a minimum contaminant removal level. The current minimum toxic compound removal level is as follows:

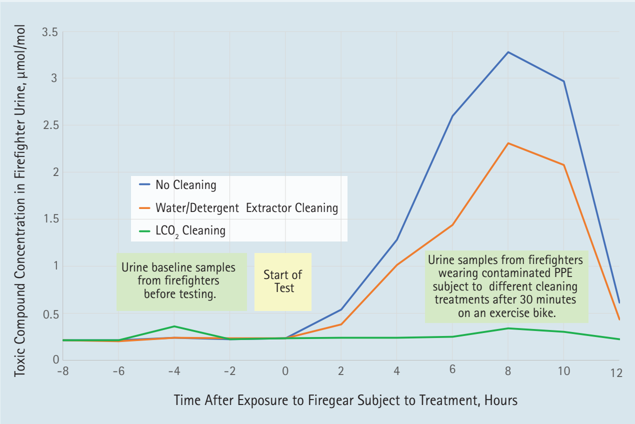
- For SVOCs and metals, removal of 50% of the applied materials.
- For biologicals, achieving greater than 3 Log reduction in klebsiella pneumoniae and staphylococcus aureus bacterial counts.

Water-based cleaning systems with the proper additives can meet these standards but typically need to resort to extensive prewash soaking procedures. However, in cleaning efficiency studies conducted in Europe, researchers found that, in the cases studied, the toxic material removal efficiency was poorer than expected.

A Finnish study evaluated the source of contamination from numerous firefighting events, the type and location of organic toxins on the gear, and the effectiveness of traditional water-based cleaning systems in removing these hazardous compounds. The study concluded water-washing did a poor job of removing PAHs and was responsible for transferring more contamination on the gear to less contaminated areas: Washing two garments yielded a washing efficiency of 40%; washing three garments yielded a washing efficiency of 15%.2 In another study, the effectiveness of water-wash cleaning to remove PAHs from firefighting hoods was evaluated. The study found that the removal efficiency of this process for all PAHs was 75.5%.3 In another study from Europe, CENTEXBEL reports that industrial cleaning with water and detergents according to the ISO 6330 standard gives a cleaning efficiency of 27.4%.4 In the Instituut Fysieke Veiligheid study cited earlier,1 it was found that contamination in water-wash garments "spreads over the different turnout garments in the washing machine, whereby the inner layer is also slightly contaminated was distributed through the garment whereby the contamination can accumulate." The reference continues1: "After cleaning the turnout garments it appears that residual contamination remains. After a cleaned turnout garment is used again, contamination can slowly but surely accumulate in the turnout clothing."

In a study conducted by the University of Leuven in Belgium, tests were performed with three groups of firefighters.[5] One group wore contaminated gear (not washed), the second group wore contaminated gear cleaned by industrial laundry (water-wash), and the last group wore contaminated PPE cleaned with LCO_2. Urine tests were performed to detect the presence of harmful substances. A profile of toxic compound concentration in subject firefighter urine is presented in Figure E3. These results showed that firefighters who wore the most contaminated gear (not washed) had the highest concentrations of toxic substances in their urine (about 8.5 times their preexposure baseline). The second highest obtained results were seen in the group of firefighters whose gear was washed in an industrial water laundry, with a toxic level average of about 5.7 times above the preexposure baseline.

Figure E3. Biomonitoring of Firefighter Toxic Compound Levels in Urine from Contaminated PPE Subject to Different Treatments



Source: Reference 5 on page 45.

In the group of firefighters whose gear was decontaminated with LCO_2, no significant increase in toxic substances in urine (about 8% above the preexposure baseline) was observed. This study clearly shows the impact of both effective and ineffective cleaning technologies on the exposure of these toxics to firefighters.

Based on numerous tests conducted by CCT and others, CO_2-based cleaning systems routinely remove SVOC/PAH contamination at efficiencies greater than 99%. LCO_2 cleaning systems exceed the NFPA removal efficiency requirements for specified metals and biological removal targets with the correct additives and process configurations. CCT-based cleaning systems have documented evidence of biological removal rates of greater than 3.2-4 Log for bacteria tested (Escherichia Coli, Staphylococcus aureus, Pseudomonas aeruginosa, MRSA) when exposed to the cleaning solution ranging from 1 to 60 minutes.[6]

What About Removal of PFAS, Lithium-Ion Battery Fire Residues, Asbestos?

Currently, there is significant concern about newer types of hazardous products that firefighters are exposed to including per- and polyfluoroalkyl substances (PFAS) also known as "forever chemicals," residues from lithium-ion battery fires, and asbestos. While each product is different, effective firefighting gear cleaning technologies must be capable of removing these substances. It is noted that the next revision of NFPA 1851 (to be consolidated into the new NFPA 1850) standard is expected to address these types of contaminants and how the gear can be best cleaned. With respect to PFAS removal, CCT conducted a study that showed that there was an average 84% removal rate for the four selected PFAS compounds tested.[7] It is also noted that water-wash technologies can also remove PFAS, as evidenced by measurable concentrations of PFAS in our lakes and streams.

Lithium-ion battery fire emissions are a growing concern due to their rapidly expanding use in society. Emissions from these fires are known to produce a wide range of hazardous compounds including hydrofluoric acid, lithium compounds, cobalt compounds, and other hazardous materials. CCT recently conducted a study on removal of an expected lithium-ion battery fire emission compound (Li_2CO_3) and reported a removal efficiency of 80%, which closely matched data from earlier cobalt cleaning efficiency tests demonstrated in NFPA 1851 cleaning verification undertaken by UL.[8]

Regarding asbestos, this substance is typically considered a particulate type of contamination. LCO_2 cleaning systems have long been recognized as an effective particle removal technology often used to process clean room garments. Though no direct removal data is available, LCO_2 cleaning systems are expected to effectively remove asbestos fibers from gear.

Are There Any Garment Durability Issues with LCO_2-Based Cleaning Systems?

CCT conducted a study to evaluate the impact of the LCO_2-based cleaning process on the durability of outer shell and moisture barrier/thermal liner components of the gear.[9] Testing of moisture barrier and outer shell samples was conducted using recognized test methodologies from NFPA and others. Samples of moisture barriers and outer shell were subjected to up to 30 consecutive cleaning cycles. UL performed the sample testing at its laboratory with supplemental analyses by CTT. The results from outer shell tests showed the following:

- No change in the relative degree of water droplet spread on the sample after 10, 20, and 30 wash cycles compared with unwashed outer shell samples.
- Insignificant changes in spectrophotometric measurements between unwashed and successively cleaned outer shell samples.
- No diminishment of trim brightness was observed when a flashlight was directed toward the trim portion of the sample under dark conditions.
- Minimal change in the breaking strength, tear resistance, and shear strength of samples after 30 CO_2 process cycles.
- Insignificant changes in Thermal Protective Performance (TTP) and Total Heat Loss (THL) values from 30 wash cycles compared to their baseline values.

As summarized by UL, moisture barrier and thermal liner test results showed insignificant changes to key thermal barrier parameters of the turnout gear, which include related NFPA 1971 requirements for new gear. The breaking strength, tear resistance, and shear strength showed minimal changes to their baseline values after 30 LCO_2 process cycles. After-flame and char length in both the warp and fill directions were well below the action levels and there was no melting or dripping observed. Flammability tests on several liner products were conducted as part of this evaluation. Samples were exposed to 5, 10, 25, and 30 LCO_2 liner wash cycles. The flammability evaluations showed no measurable difference from the "as received" values. The end result was the tests show gear will last longer and perform better if cleaned with LCO_2.

Can LCO_2 Systems Clean Gloves, Helmets, Boots, and Other Gear?

Because of their unique cleaning chemistry, LCO_2-based cleaning systems can process articles typically not cleaned in water-based systems, including gloves, helmet suspensions, leather boots, harness systems, drag rescue devices (DRDs), and radio holders.

What Is the Availability of CO_2 Cleaning Systems?

There are at least two ISPs that have been verified for advanced cleaning and sanitization according to NFPA 1851 (2020). Both organizations provide these services to the fire service in North America, currently at one location. Emergency Technical Decon (ETD) is in the process of expanding the number of sites with these capabilities. ETD also rents CO_2-based cleaning systems to qualified fire departments. These systems are completely automated, requiring only that the operators select the correct cleaning recipe on the touchscreen, load/unload the gear, and ensure that the system maintains the correct facilities elements–electricity, chilled water, hot water/steam, compressed air, and cleaning agents/additives. Periodically, the operator can remove the residues from the still for appropriate disposal.

REFERENCES

1. Heus, Ronald; Exposure to Smoke–An overview report of the studies to exposure routes, contamination and cleaning of turn-out gear and the skin barrier function; Instituut Fysieke Veiligheid; August 21, 2018.
2. *Contamination and decontamination of firefighting garments–Laboratory tests*, Finnish Institute of Occupational Health, Laitinen J, Tuomi T, Vainiotalo S, Laaja T, Rantio T,Parshintsev E, Kiviranta H, Koponen J, Pyrstöjärvi P,Kemmeren M, Heus R.; August 28, 2018.
3. *Firefighter hood contamination: Efficiency of laundering to remove PAHs and FRs*; Alexander C. Mayera, Kenneth W. Fent, Stephen Bertke, Gavin P. Horn, Denise L. Smith, Steve Kerber, and Mark J. La Guardia; *JOURNAL OF OCCUPATIONAL AND ENVIRONMENTAL HYGIENE*; 2019, VOL. 16, NO. 2, 129–140.
4. CENTEXBEL NFPA 1851 *Chemical Decontamination Efficacy Test*, 2019.
5. *Study Report on the Concentration of Harmful Substances in Urine Samples in Firefighters Wearing Contaminated PPE, PPE Cleaned by an Industrial Laundry and LCO_2 Cleaned PPE*; The University of Leuven: Leuven, Belgium, 2018; as reported in *Firefighters' Clothing Contamination in Fires of Electric Vehicle Batteries and Photovoltaic Modules—Literature Review and Pilot Tests Results*; Ewelina Szmytke, Dorota Brzezinska, Waldemar Machnowski, and Szymon Kokot; *Int. J. Environ. Res. Public Health 2022*, 19, 12442. doi.org/10.3390/ijerph191912442.
6. Testing conducted by Japan Food Research Laboratory, Microbiological Research Section, June 2009.
7. Removal of PFAS Compounds from Firefighter Gear Using CO_2 + Cleaning Technology: Preliminary Test Results, N.W. Sorbo, Cool Clean Technologies, March 2023.
8. Removal of Lithium from Firefighter Protective Clothing Using CO_2 + Cleaning: Preliminary Test Results; N.W. Sorbo, Cool Clean Technologies; April 2023.
9. A Report on the Impact of CO_2-Based Cleaning Technology on Firefighter Turnout Gear: Outer Shell Performance and Moisture Barrier/Thermal Liner Samples after 30+ Cleaning Cycles; N.W. Sorbo, Cool Clean Technologies; February 2023.

2. Should we be addressing additional contaminants? As previously indicated, a limited number of chemicals and biological challenges are used for measuring cleaning effectiveness. This is primarily for pragmatic purposes, and the current choices for surrogate contaminants are intended to represent a range of chemical classes and properties. To wit, there can be large differences in the ease of removing some chemicals compared to others. For example, some polycyclic aromatic hydrocarbons (PAHs) come out of clothing at significantly greater percentages than others.

The new edition of NFPA 1851 may contain procedures for evaluating removal of a much larger range of contaminants. So, instead of 5 PAHs, a battery of 20 PAHs would be evaluated. Standard test methods and associated criteria for the ability to remove other contaminants would also be offered. Consideration is being given to certain chemicals of concern, such as brominated fire retardants, dioxins and related substances, PFAS, and others. Consideration is also being given to evaluate the removal of asbestos, though this subject is fraught with concerns over liability issues. This is particularly true if firefighter exposure is documented and originally contaminated gear cannot be guaranteed to be fully cleaned.

Perhaps the most contemporary set of contaminants of concern are those associated with electric vehicle fires (or for the broader category of mobile or stationary energy storage systems). Fires involving these systems are known to create unique contamination problems and only a few studies have investigated the ability to successfully remove the decomposition products of these fires that impinge on and adsorb onto turnout gear materials. Consequently, an effort is underway to better understand and establish standardized procedures for this form of specialized cleaning that could address electric vehicle fires. Research by some organizations for characterizing these fires has already documented specific hazards in terms of their rapid heat release and decomposition products. Based on an initial examination for ensuing contaminants that can include a number of lithium, cobalt, phosphorous, and

Figure 13. EV Research Fire Conducted by Boston Fire Department, Fire Safety Research Institute, and Worcester Polytechnic Institute

Source: UL's Fire Safety Research Institute.