# SOAR

STATE-OF-THE-ART REPORT (SOAR)
JANUARY 2024

HDIAC-BCO-2023-484

# UNENCUMBERING THE WARFIGHTER: FUNCTIONALIZED MATERIALS FOR CHEMICAL AND BIOLOGICAL PROTECTIVE CLOTHING

*By Joseph Cole and Joel Hewett*
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JOSEPH COLE AND JOEL HEWETT

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# ABSTRACT

Over the past 20 years, the landscape of threats posed to U.S. forces by chemical and biological (CB) weapons agents has grown in both complexity and scope. While the CB protective overgarments currently issued to Warfighters are routinely improved upon and updated, they remain bulky, are cumbersome to wear, impose a high level of thermal strain on the wearer, and are reflective of decades-old technology. This state-of-the-art report surveys recent innovations made by government, military, academic, and commercial entities in producing the next generation of CB protective clothing, namely using a class of "functionalized materials" known as metal-organic frameworks (MOFs). This report particularly outlines a line of innovation that has resulted in the testing of a CB protective ensemble that can be worn as a standard duty uniform, not a bulky overgarment, helping to unencumber the Warfighter from the added thermal strain and weight burden.

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# EXECUTIVE SUMMARY

Over the past 20 years, the landscape of threats posed to U.S. forces by chemical and biological (CB) agents has grown in both complexity and scope. Several adversarial nation-states, transnational criminal organizations, and terrorist groups either possess or are likely to obtain CB weapons and delivery systems that, if used, could significantly degrade joint force operations. In part because the U.S. military has not faced a high risk of CB attacks since Operations Desert Shield and Desert Storm, there is a sharp need for technical innovations to enable a new generation of chemical and biological personal protective equipment (CB PPE) garments or ensembles that can provide the Warfighter with an enhanced level of protection, while remaining minimally obstructive to force mobility and maneuver.

While the CB protective ensembles currently issued to Warfighters are constantly iterated and improved upon by entities in the U.S. Department of Defense (DoD), standard-issue suits like the uniform integrated protection ensemble (UIPE) family of systems remain bulky, difficult to put on and secure, and cumbersome to wear during even moderate physical activity and impose a high thermal strain and health risks upon wearers. Moreover, the UIPE is reflective of decades-old technology: a heavy, activated-carbon protective inner layer housed in a multiple-piece overgarment ensemble that is worn on top of the Warfighter's standard duty uniform. Much as the War Department did before Operation Overlord and the invasion of Normandy—by impregnating the troops' uniforms with a protective chloramide—the DoD today sees a future of CB protection in which the Warfighter is "unencumbered" from the need to carry and don additional clothing to defend against a CB agent.

Central to the research and development goals of the Joint Program Executive Office for Chemical, Biological, Radiological and Nuclear Defense is to provide CB PPE that is lightweight and comfortable and, critically, uses a standard duty uniform as its base layer, to be supplemented only by a gas mask and hood, gloves, and CB protective footwear.

This state-of-the-art report surveys recent innovations made by government, military, academic, and commercial entities in producing the next generation of CB protective clothing, namely by the use of a class of "functionalized materials" known as metal-organic frameworks (MOFs). This report outlines a particularly promising line of innovation that has resulted from a collaboration among several universities, commercial entities, and the U.S. Army Combat Capabilities Development Command's Chemical Biological Center and Soldier Center.

Dubbed the "the Numat suit," a lightweight CB protective uniform enabled by MOFs was presented at the fifth annual DoD Chemical Biological Operational Analysis field experiment in May 2023. Both MOFs and other functionalized materials hold great promise in truly unencumbering the Warfighter from the thermal strain and weight burden of impractical CB overgarments.

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# SECTION 01 INTRODUCTION

## 1.1 ANTHRAX IN AMERICA

Resident Agent in Charge (RAC) Joseph Cole (one of the authors of this of this state-of-the-art report [SOAR]) recalls his own experience on 11 September 2001. That day dawned as a picturesque and colorful morning in the foothills of East Tennessee. The crisp autumn sunlight gave the atmosphere a vibrant energy, one that he and his spouse could not help but mirror, as they packed up the car for their final medical appointment before the arrival of their new baby. RAC Cole was happy to have taken the full workday off from his role as a special agent for the U.S. Environmental Protection Agency (EPA) Criminal Investigation Division, and like the sunlight, he was beaming.

They entered the doctor's office to a new world—the lobby's television screen showed a passenger jet crashing into one of the Twin Towers, an image forever seared into their memory. Little did they know, however, that the morning's attacks were only the start of a season of upheaval for the United States. Less than a month later, a series of anthrax-laden letters were delivered to multiple locations across the nation, infecting 17 people and taking the lives of 5 more—the first instance of biological terrorism in the nation in the twenty-first century [1]. Among the primary targets was the Hart Senate Office Building, a prominent landmark in the heart of Washington, DC (see Figure 1-1).

Figure 1-1. A Member of EPA's Emergency Response to the 2001 Anthrax Attacks Inserts a Sample Into a Vial in the Hart Senate Office Building *(Source: U.S. General Accounting Office [2])*.

Later that month, RAC Cole mobilized to the capital as a National Criminal Enforcement Response Team (NCERT) member. He gathered his personal items and prepared the bags for the brief yet reflective journey to the airport. The flight was somber, with only a few law enforcement agents and responders on board, each wearing a shared expression of wonder and silence. The moment they touched down, NCERT promptly assembled and chose the response gear—personal protective equipment (PPE) designed to protect against the potentially deadly spores. The team would be tasked to meticulously sift through an overwhelming mail volume; open, identify, and safely extract samples; and then decontaminate any anthrax-laden letters destined for Washington, DC. RAC Cole arrived in the city to see National Guard and other law enforcement officers patrolling—many clad in various combinations of chemical-resistant suits, coveralls, masks, and an occasional respirator [3]. Because PPE for chemical and biological (CB) threat protection can quickly cause a person to overheat, it was lucky that the daily highs rarely reached 80° F that month [4].

News reports and a government investigation later revealed that an alarmingly high number of letters had been sent, each carrying a potentially lethal payload of anthrax powder. The NCERT team was astonished to learn that at least one letter had carried around 2 g of the substance—a minuscule amount, yet powerful enough to cause havoc among the populace. If inhaled, less than a gram of anthrax powder could claim a life within days [5]. Moreover, as the Congressional Office of Technology Assessment had estimated in 1993, the release of just 100 kg (about the weight of a professional basketball player) of anthrax powder (Bacillus anthracis) could cause between 130,000 and 3 million deaths if deployed over Washington, DC, from an aircraft—a destructive effect roughly equivalent in the loss of life to a nuclear weapon [6].

The gravity of the situation demanded that the NCERT team adhere unwaveringly to its strict safety protocols. The no-fail requirements of the PPE gear were a constant reminder that the white powder that the NCERT members held in their hands—which looked ordinary and unremarkable—was instead an insidious threat. The process of "suiting up" was awkward and cumbersome; the protective ensemble was heavy, physiologically confining, and restricting in movement (see Figure 1-2). The process was slow, too, and demanded great patience. RAC Cole distinctly recalls struggling with the myriad of fastenings on the ensemble's many-layered suit and its supplied-air face mask, as he attempted to secure each piece in its rightful place. Nitrile gloves on each hand were overlayered with a thicker, synthetic rubber glove made from butyl. Once fully donned, the ensembles required further taping and adjustment before members were cleared to proceed.

RAC Cole recalls that, as the team processed the contaminated letters, he could hear his breath echo within the respirator and his gloved hands remained isolated from the outside world. That is, they did until he accidentally experienced a moment of misfortune that sent his pulse racing. While cutting one of the letters open, the edge of his scissors sliced through the tip of his butyl glove, leaving only the thin nitrile layer protecting his index finger from the anthrax spores. The realization hit him like a jolt, and a split second of panic swept over him. He swiftly composed himself, though, and recalled the safety procedures—this breach would be the last.

The gear had served its purpose, safeguarding the NCERT team against the invisible enemy. Yet, the extreme limitations of the PPE ensemble from the biological threat were undeniable. Across the intergovernmental anthrax response, garments and respirators often proved too heavy and laborious for long-duration use. Respondents sometimes opted to work without the proper PPE ensemble, either due to questions regarding the adequacy of the respirators to protect them or from concerns that the PPE hindered their ability to effectively respond [7]. There was no question that, at a minimum, the PPE significantly decreased manual dexterity.

The chemical and biological personal protective equipment (CB PPE) ensembles had met the required safety standards, but they were only tested within the highly controlled environment of a processing facility in Washington, DC. How would they perform in austere and harsh environments, like the arid terrain of the Middle East or the humid climate of the Indo-Pacific? How would the exigencies of armed conflict alter their effectiveness? As the officer in charge of the U.S. Army Reserve Consequence Management Unit, RAC Cole held concerns about the potential impacts down the line. It was clear that the protective gear was rooted in the past and had not kept pace with the rapid technological and

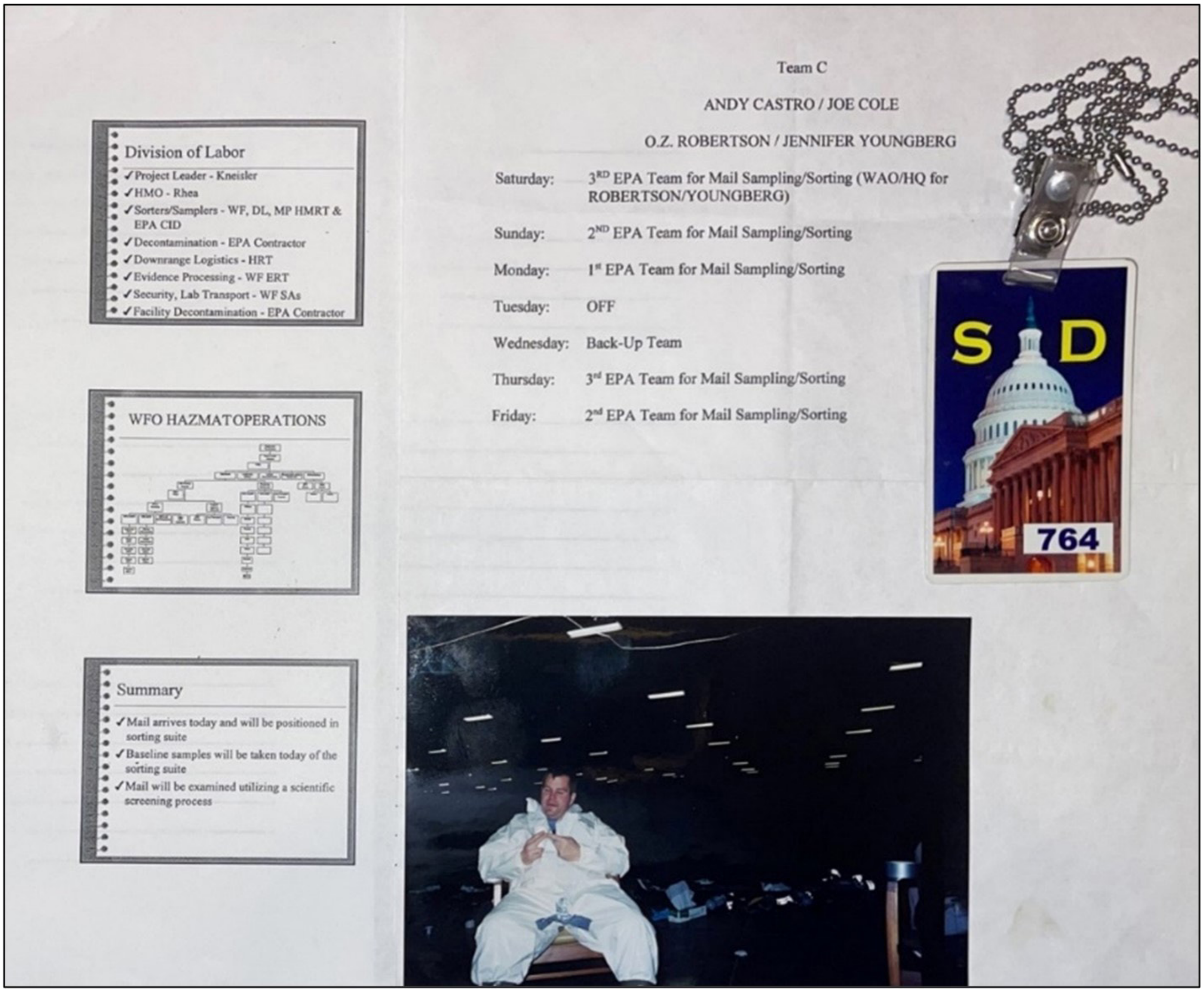


Figure 1-2. Snapshot of RAC Joseph Cole's Hot-Zone Entry, EPA NCERT Team Schedule, Organizational Chart, and Access Badge From the 2001 Amerithrax Response *(Source: J. Cole)*.

scientific advancements of the 1990s. As the year 2001 wore on—and as the nation began to contemplate a wider threat landscape—the need to apply scientific innovation and American industrial prowess to the creation of next-generation CB PPE ensembles became searingly clear.

## 1.2 BACKGROUND AND REPORT OVERVIEW

With the United States largely engaged in counterinsurgency operations in the Middle East since 2001, many strategic thinkers in the military realm deemed it unlikely that U.S. forces would face a chemical or biological weapon during combat operations. That strategic landscape has since changed.

### 1.2.1 The Modern CB Threat

Decreases in the cost of sophisticated laboratory equipment and the spread of accessible "how-to-build" information regarding CB warfare agents have aided their proliferation to nontraditional actors. In July 2022, Deborah G. Rosenblum, the Assistant Secretary of Defense for Nuclear, Chemical, and Biological Defense Programs, noted that these improvements have democratized the CB threat and made it "vastly more difficult" for militaries to counter the use of a CB weapon [8]. The high worldwide death toll of the SARS-CoV-2 pandemic has also revived interest among some terrorist and nonstate groups in acquiring biological weapons in particular [9].

However, the threat posed by adversarial nation-states remains the most acute CB threat to American forces. Adversaries like China, Russia, North Korea, and Iran have either demonstrated chemical or biological agents and weapons platforms or are known to be pursuing their development [8]. In the estimation of many military commanders as well as civilian scholars, the risk that conventional U.S. forces will face a CB weapon attack during armed conflict is the highest it has been in several decades (see Figure 1-3) [8, 9]. CB-based threats posed by China and Russia remain particularly acute for the United States and its allies [8, 9].

Figure 1-3. Example of Conventional Cold-War-Era Chemical Weapon: Projectile, 105-mm, Howitzer, M360 (T173) *(Source: Wright et al. [10])*.

In the European theater, a North Atlantic Treaty Organization (NATO) task force, in the wake of the Russian invasion of Ukraine in early 2022, completed a major overhaul of the organization's Chemical, Biological, Radiological and Nuclear (CBRN) Defence Policy [11]. The policy and strategy document naturally identifies Russia as its "most pressing" CBRN challenge, in part due to the country's continuance of legacy Soviet CB weapons programs. A 2018 chemical nerve-agent attack on former military intelligence officer Sergei Skripal and his daughter Yulia in Salisbury, England, is but one example of the Russian state's growing willingness to use offensive CB agents—and to do so with only limited efforts at obscuring their origin (see Figure 1-4) [12].


Figure 1-4. A Perfume Bottle Containing Novichok Nerve Agent, Used to Poison Sergei and Yulia Skripal in 2018 and Later Recovered *(Source: U.S. Department of State [13])*.

In the Indo-Pacific region, the NATO strategy also highlights China's "assertive behaviour pose" and pattern of relative disregard for international arms control entities as evidence of a potential interest in deploying CB weapons in the event of armed conflict [11]. While China is a signatory to the Biological Weapons Convention (which also covers toxin-based agents), assessments by both the U.S. Department of State and the U.S. Department of Defense (DoD) routinely conclude that China continues to drive internal research and development (R&D) in dual-use biological activities. Beijing has also never acknowledged the "existence or current disposition" of its Cold-War-era offensive biological weapons program, as one national defense scholar has noted [14].

With such a broad threat horizon, the impetus to improve CB personal protective equipment and garments for the individual Warfighter goes well beyond that of defending the armed forces during combat operations. As Section 1.1 makes clear, the threat of terrorism to the homeland remains and biological warfare agents are likely to only rise in the estimation of hostile adversaries. As Dr. Jiri "Art" Janata, professor emeritus at the Georgia Institute of Technology's School of Chemistry and Biochemistry has noted, biological warfare neatly fits the goals of terrorists, because such an attack can generate a high level of fear within a society—and wreak extensive economic damage upon it—for a relatively small financial spend by an adversary [15].

### 1.2.2 The Innovative Response

With the DoD pivoting since roughly 2018 toward preparation for potential large-scale combat operations with peer nations, the need for improved equipment to protect against CB threats has taken on a newfound importance. The joint staff and the service branches alike have updated their doctrine and procedures for CBRN operations, committed more funds to CBRN R&D and the acquisition of fieldable equipment and capabilities, and reorganized several of the DoD entities that oversee CB-related innovation activities across the department [8, 16, 17].

Most significantly, the DoD has reoriented its R&D efforts in CBRN defense in recent years toward a more "holistic" or generalized look at CB threats [18]. As Deputy Assistant Secretary of Defense for Chemical and Biological Defense Ian Watson explained in early 2023, "We can't develop a countermeasure for…every single toxin, every single biological potentiality, every single chemical potentiality" [17]. Instead of structuring its R&D efforts at producing protective measures to defend against a list of all known or expected hazards, military leaders are pursuing CBRN defense equipment that will protect Warfighters from any threat they may encounter [17].

While the array of CB protective measures and countermeasures is wide—from standoff sensors to presymptomatic diagnostics—the need for next-generation CB PPE garments and ensembles is widely acknowledged as one of the DoD's most critical. Within the department, the Joint Program Executive Office for Chemical, Biological, Radiological and Nuclear Defense (JPEO-CBRND) coordinates R&D projects for CB PPE protection and guides overall efforts to develop, field, and sustain broad CBRN defense capabilities for the Warfighter.

One of JPEO-CBRND's three modernization focus areas is the goal of "unencumbering the warfighter"—by fielding unobtrusive, next-generation individual protective ensembles that increase CB protection while also improving wearer comfort, mobility, and task performance (see Figure 1-5) [19]. The office routinely engages both government, academic, and commercial scientists and engineers in collaborative R&D to produce new CB protective garments for early-stage testing and feedback from troopers in every service branch [20].

R&D interest in next-generation CB garments is not limited to the DoD, however. At a whole-of-government level, the 2022 National Biodefense Strategy and Implementation Plan calls on federal entities to jointly strengthen domestic industrial


Figure 1-5. Unencumbering the Warfighter Is One of JPEO-CBRND's Modernization Focus Areas, as Well as an Enabling Technology for Other Operational Goals, Including Warfighter-Borne CB Sensors and Medical Interventions Integrated With Future Combat Uniform/Kit Ensembles *(Source: Colvin [19])*.

capacity for PPE production and to innovate "novel material[s]" for better protective clothing [21]. Reflecting the importance of JPEO-CBRND's goal of modernizing military CB protective garments, the national strategy echoes the JPEO's mission to make CB PPE more effective, affordable, reusable, and more comfortable [21].

As Dr. Jason Roos, the joint program executive officer for CBRND, described his office's vision in August 2019, "The idea of having to don a mask and don a suit and slug around…is really going to significantly impact the ability of our Warfighters to do their job, to maneuver and to fight." Instead, his office's ultimate goal is to fashion novel materials and fabrics that provide substantial CB PPE capabilities as a standard duty uniform itself. "How do we get to the point where," Roos asked, "[what] the Warfighter is wearing is actually their protective gear?" [20].

### 1.2.3 Study Methods and Scope

Mirroring the call to unencumber the Warfighter from overly restrictive and outdated CB PPE, this SOAR surveys recent R&D progress in designing, fabricating, and fielding next-generation CB protective garments. In doing so, this report finds a clear answer to the query of where the cutting edge of the field currently stands. Significant progress made since approximately 2018 in the application of novel "functionalized materials"—elsewhere termed "neutralizing, detoxifying, self-detoxifying, or self-decontaminating" substances—to the mission set of providing improved CB protective clothing, has delivered a new style of CB protective uniform that approaches Dr. Roos' vision of a wholly unencumbered Warfighter. During interviews with leading subject matter experts (SMEs) in this R&D space, the Homeland Defense & Security Information Analysis Center (HDIAC) found a general consensus that the fielding of combat-relevant next-generation CB PPE is very possible in the near term—perhaps only 3–5 years away.

The most promising class of functionalized materials investigated to date is known as metal-organic frameworks (MOFs). While other, non-MOF materials and chemistries remain of high interest to both DoD and outside researchers, the field at large shares a common set of engineering challenges and requirements. Whether using MOFs or another functionalized material, scientists and engineers within industry, academia, and the DoD laboratory system have found ways to effectively produce these molecules at a scale beyond the laboratory bench and then integrate them into/onto a fabric or substrate material.

Section 3.2.1 outlines a particularly promising line of innovation that has resulted from a collaboration among several universities, commercial entities, and the U.S. Army Combat Capabilities Development Command's (DEVCOM's) Chemical Biological Center (CBC) and Soldier Center (SC). Dubbed "the Numat suit," a lightweight CB protective uniform enabled by MOFs was presented at the fifth annual DoD Chemical Biological Operational Analysis (CBOA) field experiment in May 2023. Both MOFs and other functionalized materials hold great promise to truly unencumber the Warfighter from the thermal strain and weight burden of impractical CB overgarments.

Because the production of CB-resistant gas masks, boots (including boot covers), helmets, ocular protection, and other peripheral body-worn materials presents R&D challenges very different from that of textiles or fabric-based garments, this report does not address the former. It also does not address gloves directly (in terms of garment design), but CB protective gloves may benefit from the innovations surveyed. Furthermore, as the name of the JPEO-CBRND office denotes, while the term "CBRN" includes radiological and nuclear threats, it is sometimes used to classify equipment that may not provide protection against some but not all four of its categories. To follow existing conventions, and for clarity, this report treats CB threats as a separate line of inquiry. Note also that PPE designed to defend against CB threats in a combat environment, as used in this report, is sometimes referred to by other sources as individual protective equipment (IPE).

To compile this SOAR on behalf of HDIAC, the authors reviewed peer-reviewed journal articles, government reports, webinars, and other published information on advances in CB PPE fabrics from approximately 2019 to the present. The majority of this report's relevant findings, however, were derived from 12 interviews conducted with leading SMEs in the field, conducted over telephone or video call. In addition to interviews, some SMEs provided source materials and written comments via email. In roughly equal percentages, these SMEs were drawn from industry, academia, and DoD scientific and technical research laboratories or entities.

Because of the specialized or "niche" nature of this R&D topic, HDIAC identified that the community of U.S.-based researchers actively working in this area is relatively limited. As a result, the insight gathered from the population of SMEs interviewed can be seen as representative of the field; indeed, almost all of the interviewees were familiar with (or worked closely alongside) the other SMEs interviewed and routinely named each other as having key information on the state of current R&D.

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# SECTION 02 THE EVOLUTION OF MILITARY CB PPE GARMENTS

The central task of CB protective garments is to provide a physical barrier between the skin or other body surface area and a CB warfare agent—whether in liquid, droplet, solid (powderized), aerosol, or vaporized form [22]. Often characterized as the Warfighter's "second skin," a protective clothing garment or ensemble can broadly be categorized as falling along a spectrum of permeability—from an unprotective, fully breathable fabric similar to a standard cotton t-shirt, to a fully encapsulated, impermeable suit worn in conjunction with a self-contained breathing apparatus (SCBA) or other air respirator [4, 22]. The latter is often informally called a "moon suit" or "bunny suit" in a civilian, medical research, or first-responder environment; it is an apt characterization, especially when equipped with positive air pressure (see Figure 2-1).

Figure 2-1. U.S. Air Force Airmen Carry a Dummy Toward a Decontamination Station During a Hazardous Material Training Exercise in 2019 *(Source: Belio [23])*.

## 2.1 CLASSES OF PROTECTION

Outside of the DoD, multiple domestic and international groups have established several performance classification schemes to structure the various levels of CB and CBRN protective ensembles and to detail each level's technical requirements. Others maintain more discrete standards that address equipment specifications and test procedures. These groups include the International Standards Organization (ISO), EPA, the U.S. Occupational Safety and Health Administration (OSHA), the National Institute for Occupational Safety and Health (NIOSH), and the nongovernmental National Fire Protection Association (NFPA) [24].

Protection levels set by OSHA and the EPA have been widely adopted in the hazardous materials and emergency response communities. (The OSHA-EPA protective measure sets are similar but not identical.) These range from Level A protection (as pictured in Figure 2-1) to Level D, which is usable only when there is no known atmospheric hazard to inhalation [24, 25]. The medical and biological-agent response communities use, at a minimum, protective ensembles that meet Level C requirements.

However, because the OSHA-EPA levels only describe performance levels and not technical particulars, many groups refer to a slew of standards maintained by the NFPA for supplemental guidance. (OSHA recommends as much in nonbinding guidance; note also that the consensus process by which NFPA sets standards is accredited by the American National Standards Institute [25].) NFPA standards address critical materials behavior like vapor permeation and are also used to certify the effectiveness of PPE equipment when tested as a full-suit ensemble [24, 25]. For example, *NFPA 1990: Standard for Protective Ensembles for Hazardous Materials and CBRN Operations*, which consolidates multiple NFPA standards effective January 2023, sets out ensemble classes similar to OSHA-EPA performance levels and includes design considerations tied to actual use (e.g., the effect of kneeling) [26, 27].

Within the DoD, CBRN protective levels are designated as mission-oriented protective postures (MOPPs), which range from MOPP 0 to MOPP 4 and differ for land-based or ship operations (see Figure 2-2) [28]. MOPP levels are intended to be an inherently flexible system, which allows commanders to tailor gear or PPE product usage requirements to the threat level [22, 28]. The significant differences between the tasks of emergency response and armed conflict, in both mission and capabilities, means that the four MOPP levels do not neatly align with OSHA-EPA levels of protection A through D. For example, MOPP Level 4 has been likened to OSHA's Level C, or as capable of reaching OSHA Level B when equipped with a respirator or SCBA [29].

This "nonalignment" of protection levels is a natural concession to the physiological and psychological difficulties of performing combat operations in the impermeable CBRN outergarments depicted in Figure 2-1 [22]. Warfighters can take approximately 50% more time to complete a task in MOPP 4 than when wearing standard battledress uniforms [22]. Even absent the stress of making enemy contact, the time to achieve MOPP 4 from baseline can top 8 minutes (see Figure 2-3) [4]. OSHA-EPA Level A impermeable suits are simply not feasible for battlefield use—the average wearer will reach an elevated core body temperature of around 99.9° F in roughly 15 minutes [27, 30]. When operating in a warm or hot climate, the rate of heating is even more accelerated—as it would be with any physical exertion [27].

| Ship MOPP | | Land MOPP | |
|---|---|---|---|
| Ship MOPP Level | Description | Land MOPP Level | Description |
| MOPP 0 | • IPE onboard and inventoried; all personnel sized and assigned IPE. | MOPP 0 | • Carry mask; IPE available (within arm's reach). |
| MOPP 1 | • IPE issued to all personnel and available (within arm's reach). | MOPP 1 | • Don protective suit. |
| MOPP 2 | • Carry mask, other IPE available.<br>• Activate detectors.<br>• Set condition MODIFIED ZEBRA. | MOPP 2 | • Don protective boots. |
| MOPP 3 | • Don protective suit.<br>• Don protective boots.<br>• Set condition ZEBRA (ship hatch closure/secure measures).<br>• Activate intermittent washdown. | MOPP 3 | • Don protective mask.<br>• Secure hood. |
| MOPP 4 | • Don protective mask.<br>• Secure hood.<br>• Don protective gloves.<br>• Set condition CIRCLE WILLIAM (ship hatch closure/secure measures) as required.<br>• Activate continuous washdown. | MOPP 4 | • Don protective gloves. |

Legend
IPE individual protective equipment
MOPP mission-oriented protective posture

Figure 2-2. Joint Ship/Land CBRN MOPP Comparison *(Source: Joint Chiefs of Staff [28])*.

## 2.2 A BRIEF HISTORY OF CB PROTECTIVE CLOTHING

The history of CB protective clothing, and its use in warfare, is more than just an interesting chronicle of past R&D efforts and the fielding of equipment in combat. Instead, its chronology provides key insights into how the CB protection mission has evolved over time and how those changes have guided the DoD's understanding of what capabilities are most needed in a next-generation CB PPE ensemble.

### 2.2.1 World Wars I and II

By any account, the history of protective equipment dates at least as far back as Homer's *Odyssey*, likely transcribed around 700 BCE. Its example was as mundane as it was effective: Laertes dons gloves

Figure 2-3. U.S. Marines Conduct CBRN Training and Familiarize Themselves With Level 4 MOPP Suits During Exercise Fuji Viper 20-2 on Camp Fuji, Japan, 20 November 2019 *(Source: Gosun [31])*.

to protect against thorns while working in the garden [32]. It was during World War I (WWI) that PPE for CB threats truly came of age, in response to the havoc that chemical agents like mustard gas and phosgene wrought along the trench lines in western Europe. Although German chemical agents took few Allied casualties relative to artillery and other arms, the "gas fright" engendered significant psychological damage to Allied forces, reducing combat effectiveness [33].

Military engineers and industry leaders in the Allied nations mobilized swiftly to address the challenge of chemical agent defense. The U.S. government assembled a blue-ribbon study program in early 1918, charging it to focus on the development of advanced gas-mask models first and other protective measures afterward [33, 34]. Although decent progress was achieved in improving gas-mask designs and fit, "personal protection [from gas] was always a problem," as the U.S. Army Combat Studies Institute later concluded. It was one that "neither side ever really solved in World War I" [35]. Soldiers mostly turned to wearing leather wherever possible, as well as stiff fabrics like waxed canvas or oilskin cotton duck. Some took to wearing capes simply to add another barrier to their uniforms.

The U.S. Army Chemical Warfare Service (CWS) did produce a notable milestone in CB PPE. In 1918, it issued limited numbers of a protective "anti-gas suit" to medical personnel and artillery gun crews [35]. Made from cotton sheeting impregnated with vegetable oils (typically linseed oil), the suit was a coverall that cinched tight at the ankles and wrists. Heavy cloth mittens and durable impermeable boots completed the ensemble (see Figure 2-4). Contemporaneous descriptions of the suit echo complaints from those who wear the CB PPE suits fielded today. The suit trapped heat and moisture, and few could wear it for longer than 30 minutes.

Figure 2-4. Pvt. John Sloan, 6th Infantry Medical Detachment, in an Anti-Gas Suit, Croix de Charemont, France, 20 August 1918 *(Source: Heller [35])*.

As one U.S. Army gas officer reported back to the CWS, he witnessed soldiers ripping off the suit "while working in an area reeking with mustard gas because they couldn't stand the discomfort any longer" [35].

Congress made the CWS a permanent part of the military establishment in 1920, and ongoing R&D into CB protective equipment spread to other areas of the War Department [36]. The interwar period saw the advent of both new chemical agents and weapons platforms for their delivery on the battlefield [4, 37]. By the outbreak of hostilities in World War II (WWII), the U.S. military still followed the tack of fusing a garment with a protective substance, but a chloramide designated "CC–2" now replaced linseed oil [38–40].

The use of a novel and chemically engineered impregnite (a material used to coat or treat clothing to protect against chemical and/or biological agents in the form of vapors, aerosols, and small droplets [41]) was far from the most innovative aspect of this change, however. Looking to avoid the deficiencies of the anti-gas suit, the CWS aimed to integrate the CB protective properties of CC–2 into standard garments of all types—yielding resistant but still somewhat permeable CB PPE suits intended to be worn as a standard-issue uniform [39, 40].

Starting with the two-piece herringbone twill uniform commonly used by the Army after May 1941, military engineers dissolved micron-sized particles of CC–2 in acetylene tetrachloride (a strong solvent), added dissolved chlorinated paraffin as a binder, and saturated the uniform in a bath of the liquid. The solvent would then evaporate, leaving a finished garment [39]. (This process was later applied to garments made of wool, flannel, canvas, and cotton.) The finished CB protective uniform would then be paired with a hooded gas mask, long cotton gloves, and a jar of chloramide-laced ointment and chemically treated ankle-length long underwear and socks [40].

Despite some trial and error with other substances (a British "antivapor" impregnite was found in 1944 to greatly irritate the wearer's skin when used in tropical areas [38]), no substance was found that proved superior to CC–2's performance until a slight variant, CC–3, was produced near the end of the war [39]. CC–3 replaced its predecessor as the military's primary CB PPE impregnite due to its improved storage life [39, 40].

While chemical attack was the U.S. military's primary CB-threat battlefield concern, the CWS also addressed biological threats in creating its CB PPE. The Army considered the CC-impregnated uniforms to be "best available" PPE for biological warfare that "could be worn in comfort" [39]. (The only other option was impermeable suits used in the biological laboratories at what would become Fort Detrick, which had effects on the wearer similar to those of the WWI anti-gas suit.) As long as the sleeves and pants legs were cinched tight or stuffed inside of combat boots, the CWS estimated that the ensemble would achieve organism exclusion rates approaching 90% [39].

In all, the CWS produced or procured more than 18,000 tons of CC–2 and CC–3 between 1940 and 1945 for the war effort in both theaters [39]. Because the permeability of the protective uniform base allowed it to be easily laundered, the War Department also dispatched more than 30 expeditionary "theater of operations plants" across the Pacific and prior to D-Day, in the United Kingdom. For those uniforms that had lost an appreciable amount of their chloramide—whether due to decontamination, repeat washings, or regular wear and tear—these plants laundered and then re-impregnated duty uniforms with the CC solution (see Figure 2-5) [38, 39].

As it became clear to the Allied command that the frequency of chemical attacks witnessed during WWI was unlikely to be repeated, a fair amount of the CC-impregnated uniform stock was ultimately laid in reserve. However, given

Figure 2-5. Members of a Processing Company in Field Training Remove Clothing From Predryer Unit in the First Stage of the Impregnation Process, and Pipes at Lower Right Carry Gas-Resistant Solution to Impregnator Unit *(Source: Brophy and Fisher [38])*.

the all-encompassing criticality of the success of Operation Overlord in June 1944, "all assault forces" in the Normandy invasion—including sailors supporting the naval bombardment well off the French coastline—were issued uniforms impregnated with the anti-gas chloramide [42]. Those involved in the D-Day action were grateful for the extra protection but otherwise none too pleased—they routinely described the fatigues as clammy and stiff, giving off a sharp odor. The solution bath also left many garments with a chalky-white residue, found especially around the seams. As Ed Jeziorski, a machine gunner with the 507th Parachute Infantry Regiment, said about his jumpsuit shortly after Overlord:

> *"We received our jumpsuits and put those suckers on. I want to tell all they were the lousiest, the coldest, the clammiest, the stiffest, the stinkiest articles of clothing that were ever dreamed up to be worn by individuals. Surely the guy that was responsible for the idea…received a Distinguished Service Medal from the devil himself" [43].*

After WWII ended, research into CB protection continued and, like nearly every other facet of defense-relevant technical inquiry, was soon formalized into the state-supported enterprise that came to be known as "Big Science" [44]. Vannevar Bush's Office of Scientific Research and Development (OSRD) began to coordinate and fund the work of groups like the CWS, the U.S. Naval Research Laboratory, and others into how the next generation of CB PPE should evolve.

In a major survey report published in 1946 and declassified in 1960, the OSRD reviewed field-based and laboratory test data for the CC–2 uniforms on their durability, launderability, rate of impregnite loss, skin irritancy, and fabric breakthrough of mustard gas (H vapor) during chamber tests [45]. The OSRD also assessed a new class of impregnite: activated carbon. Whereas CC–2 reacts chemically with the mustard vapor to actively neutralize it, the carbon adsorbs it, passively rendering it inactive. As the OSRD report noted, "small amounts of adsorbed H are held so tenaciously [by a coating of activated carbon on fabric] that no injury is produced even by prolonged close contact of the skin with the contaminated fabric" [45]. Activated carbon would go on to become a major component of future CB PPE ensembles fielded by the DoD starting in the 1980s.

In fact, the R&D questions and challenges addressed in the 1946 OSRD review neatly mirror those that still face the CB PPE research community today. The OSRD scientists were well aware of the full scope of the protective challenge, as well as the tradeoffs involved in any design choice. In reviewing the qualities of an impregnite, they noted the need for it to be skin inirritant, to have "relative inactivity" against its substrate fabric, that it remain stable after impregnation, and that its chemical characteristics would allow it to retain its protection for long periods of time when exposed to an agent [45].

In reviewing candidate garments, they investigated the potential benefits of different fiber materials (including synthetics and carbon-containing rayon fibers) and tested the reactivity and user comfort of different weaves, knits, and layering structures (see Figure 2-6). They noted the importance of proper binder selection and how best to prepare fabrics and the impregnite itself to achieve an effective bond and debated among competing processes for applying and adhering the impregnite-binder mixture into or upon the uniforms.

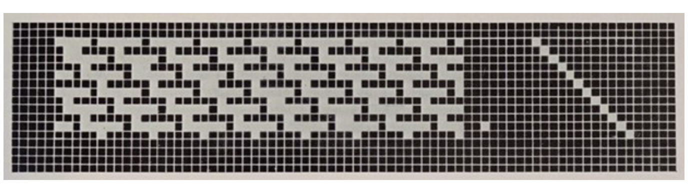


Figure 2-6. Diagram of Textile Construction of Carbon-Rayon Double-Twill Fabrics, 1946 *(Source: OSRD [45])*.

As early as 1946, the War Department had already conducted a month-long real-world trial of simulated combat to test whether the durability of carbon-coated herringbone twill uniforms would match the durability of their CC–2 and CC–3 counterparts experienced during the war. Notably, military scientists were already attuned to one great limiter of the efficacy of their ultimate product: the estimated cost per yard of a finished CB PPE fabric [45].

### 2.2.2 World War II–2010s

For a number of wide-ranging strategic, political, and technological reasons, the perceived need for battlefield-ready CB PPE for U.S. forces fell off dramatically in the postwar period and remained low through the 1980s. That both WWII and the Korean War had seen little risk of the widespread use of CB weapons diminished the threat significantly. Moreover, the massive expansion of global American military might and economic strength pushed the need for updated individual CB PPE down an ever-growing defense priority list—one that now included billion-dollar procurement programs for nuclear weapons and missile defense. Several classes of updated CB PPE and CBRN suits for the infantry were developed between 1946 and 1970, but widespread production was never authorized. This abstention was made in part to be in concert with the U.S. government's broader policy to discourage the use of CB warfare [4].

The sole adversary seen as possessing a significant CB PPE capability and the willingness to use it was the Soviets, but even this threat seemed limited well into the 1970s. The strategic imperative of American forces in Cold War Europe was to defend the Fulda Gap from a Soviet invasion, but updates to American warfighting doctrine gave primacy to the coordinated "maneuvering defense" of armor, mechanized vehicles, attack helicopters, and other air forces [46]. With infantry-led maneuver de-emphasized, the tactical use of CB PPE was slowly reframed as one of defense, rather than simply protection [4]. The military CB philosophy prioritized personal protection equipment that could provide stronger defensive "contamination avoidance" when needed, rather than the "always-on" but lesser protection of the CC–2-style CB uniforms [4].

As a result, military R&D in the 1970s shifted away from developing base CB protective uniforms and toward a defensive outergarment that would be donned only if a CB attack was deemed imminent or likely [4, 47]. This was done at least in part because of simplicity—as a U.S. Army technical bulletin noted in 1972, the "development trend is moving toward an elimination of the [multiple] inner layers of clothing" [47]. A CB PPE ensemble of overgarment(s) alone would be easier to put on and far easier to decontaminate and remove. Additionally, it could be designed to provide stronger protection to the wearer for a required period of time (e.g., 45 days' wear) [4, 47]. Critically, however, the military had learned the lessons of the impermeable WWI-era anti-gas suit. To be effective—and actually worn by the troops—a CB overgarment needed to retain a level of semipermeability (see Figure 2-7) [4, 22].

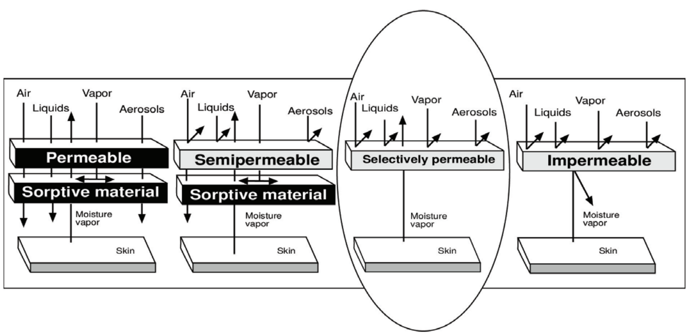



Figure 2-7. The Permeability Spectrum in CB PPE Textiles and Garments *(Source: Wartell et al. [4])*.

Selective or semipermeable CB PPE allows harmless molecules to transit a barrier while preventing toxicant and harmful molecules from entering [4, 30]. Most CB PPE overgarments developed to date for DoD use contain a form of activated (or "active") carbon to act as the sorptive material, embedded within an internal fabric layer. While impermeable PPE ensembles remain fielded by the DoD and have valuable capabilities for certain specialized uses, the overwhelming military preference for outergarments that allow limited air exchange remains [4, 22]. Boots, gloves, and other peripheral garments continue to be fabricated mostly from impermeable materials [4].

The risk that CB agents would be used in combat returned to the fore during the first Gulf War, with the threat of Iraqi chemical weapons attack deemed substantially high [22]. Among the coalition nations, the United States and the United Kingdom relied most heavily on CB PPE for their chemical defense posture, and the DoD planned to deliver over a million CB overgarments in theater [48]. A majority of the CB overgarments issued to U.S. forces were a version of the battle dress overgarment (BDO), a composite suit made from nylon and cotton in both a twist weave and tricot warp knit structure, with an inner layer of activated carbon [4]. The BDO was designed to provide a minimum of 24 hours of protection against 10 grams per square meter of chemical agent and to remain usable for up to 22 days if uncontaminated [4, 48].

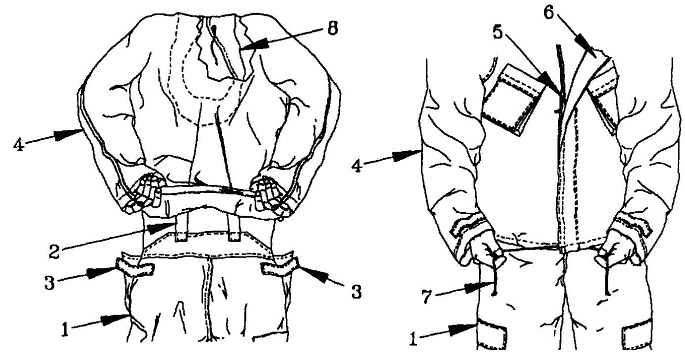
However, many of the BDOs held in prepositioned stocks were found to have been damaged by heat while in storage [49] and the reviews from Warfighters were poor. Although it was significantly more durable and protective than the 1970s-era polyurethane-lined chemical protective overgarment (CPOG), this improvement was "achieved at the expense of greater heat stress" [49]. Troops reported experiencing excessive sweating and a limited range of movement, and some came to envy the CB protective S3P "tropical suit" that the French forces wore in theater—a lightweight protective ensemble worn directly on the skin as a traditional uniform [49]. During Operation Desert Shield, many Warfighters turned to training in their impermeable rain gear and gas masks to acclimate themselves to the physical heat stress burden of operating in the BDO (see Figure 2-8).

In response to dissatisfaction with the BDO among the U.S. Marine Corps (USMC)—and their experience of it as "vapor-impervious"—a variant dubbed the "Saratoga" overgarment (OG84/BDO) was developed soon thereafter and fielded in

Figure 2-8. Four Soldiers From the 82nd Airborne Division Walk Around Their Camp Wearing Rain Suits, Gloves, and M-17A1 Protective Masks as They Try to Acclimate Their Bodies to the Heat of the Saudi Summer During Operation Desert Shield *(Source: DoD [50])*.

1993 [4, 51]. The Saratoga was a significant step forward in CB PPE design and chemistry. With similar performance requirements as the BDO, the Saratoga contained an innovative sorptive material, a layer of filtrating "spherical carbon absorbers" laminated between two thin layers of polyester liner [4, 52]. It functioned through a combination of "repelling an agent at the garment's surface" as well as "absorbing and encapsulating the agent in an activated charcoal barrier" [53]. Spherical adsorbers display much better performance than granular activated carbon, with only a slight increase in expense [52].

While most effective as an overgarment, initial USMC guidance allowed for the Saratoga to be worn directly over a layer of CB protective underwear when used in high-temperature climates [48]. Despite its durability, any interaction with water would swiftly and fully degrade its protection; it could be neither laundered nor reimpregnated [51]. Moreover, despite the "development trend" since 1972 toward producing single CB PPE overgarments for the sake of simplicity, donning the Saratoga remained a complicated task (see Figure 2-9).




**TM 10-8415-209-10**
**TH 8415-10/2**

(1) Don duty uniform (when specifically authorized, the Saratoga suit is the duty uniform). Tuck trouser cuff of duty uniform, if worn, into combat boots and lace for a comfortable fit.

(2) After selecting proper size, open vapor-barrier bag, remove Saratoga suit and perform PMCS IAW Table 2-1; if damaged, exchange item for a new one using designated supply system Retain containers and packing.

(3) Don overgarment trousers (1) over normal duty uniform (or underwear in hot climate).

(4) Fasten and adjust suspenders (2), then fasten waist band hook and pile tapes (3).

(5) Fold jacket hood (8) to inside of overgarmet jacket (4).

(6) Don overgarment jacket (4), close front slide fastener (5) and secure hook and pile fastener tape on front flap (6). The front slide fastener may be left partially open for comfort until unit MOPP directs it be closed.

Figure 2-9. Steps 1–6 for Donning the USMC CB Protective Overgarment Suit, Carbon Sphere (Saratoga) *(Source: Headquarters, Departments of the Army and Marine Corps [51])*.

Since the Saratoga came into use in the early 1990s, the DoD has progressed through two major cycles of CB PPE overgarment design and production, both of which drew a measure of inspiration from the Saratoga effort. Another point of contention during the first Gulf War was a lack of interoperability across the service branches in CB PPE equipment [54]. For instance, some services fielded hooded CB overgarments, while others did not, preventing cross-sharing of needed equipment. The National Defense Authorization Act for Fiscal Year 1994 moved responsibility for developing CB PPE from each branch and under leadership of the joint force, and by 1997, the new ensemble was ready. The DoD soon began procuring the new joint service lightweight integrated suit technology (JSLIST) garment in the hundreds of thousands [53].

The JSLIST remains in service today, and for good reason. When used during Operation Iraqi Freedom, the suit was "a big hit" among service members and the program deemed a success [55]. Designed as a two-piece garment (coat and trousers with adjustable suspenders), similar to the Saratoga, the JSLIST was noticeably lighter than the BDO ensemble and less bulky (see Figure 2-10) [53]. In its initial iteration, the JSLIST coat had an attached hood, so as to remove the logistical burden of an additional item, but later versions of the suit (Type II) returned to the integrated hood model [22, 54]. Functioning much like the Saratoga overgarment, the JSLIST is made from a nylon-cotton poplin ripstop material, enclosing a liner layer of a nonwoven fabric that is laminated to a layer of activated carbon spheres, and "bonded to a tricot knit back that absorbs chemical agents" [22]. Unlike the Saratoga, however, the JSLIST was designed to be launderable in the field up to six times, and, with proper use, could be worn for 45 days while providing a maximum of 24 hours of protection from CB threats [4, 22].

The JSLIST lived up to its name in some respects. Modern production processes for its carbon spheres increased their surface area and reduced the mass needed; as a result, each suit weighed only 6 lb [52, 56]. It also seemed likely to reduce the wearer's heat stress somewhat. In 1998, scientists at the U.S. Army Research Institute of Environmental Medicine tested the thermoregulatory responses of 12 test subjects performing 100 minutes of moderate exercise in an environmental chamber, as well as a field trial in Arizona. Five JSLIST prototypes were pitted against the BDO and the Saratoga suit. The BDO was found to impose the greatest heat stress, and the Saratoga the least—with the JSLIST ranging between the high and low measures of heat stress [57].

Figure 2-10. U.S. Army Sgt. Jordon Robbins, a Horizontal Construction Engineer Assigned to the 185th Engineer Support Company, Maine Army National Guard, Puts on His JSLIST During a Simulated Chemical Weapons Attack at Stones Ranch Military Reservation in May 2022 *(Source: Lucibello [58])*.

Feedback from other groups deployed in the Middle East concurred that the JSLIST heat stress was significant, and despite its selective permeability, it had difficulty "breathing" out heat and sweat vapor [56]. By the early 2010s, the DoD began to investigate starting a new design cycle; for all the JSLIST's capabilities, its "core design" and technologies were by then more than 20 years old [59].

By 2011, the DoD had built a clear vision of the way forward for its next generation of CB PPE. First, it would develop a new standard overgarment for the near term, named the uniform integrated protection ensemble (UIPE). Second, as the U.S. Army Chemical Warfare Service had done in 1940, the DoD had begun to envision its ultimate goal as integrating novel CB protection into the duty uniform itself to reduce the Warfighter's burden [60].

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# SECTION 03 GETTING BEYOND BARRIERS

Halfway through the movie *Jarhead*, a 2005 war drama that follows a group of Marines during their deployment in the first Gulf War, a staff sergeant walks into the tent structure where the leathernecks are bunking during Operation Desert Shield. SSgt. Sykes, played by Jamie Foxx, asks if the Marines have gotten settled in, then says, "Well, if you're not too busy…GAS! GAS! GAS!" To the tune of the 1971 pop hit "Get It On" by the band T. Rex, the Marines scramble to rip open their CB PPE overgarment storage pouches and get them on, while SSgt. Sykes times them with a stopwatch. With none of the Marines yet fully buttoned up, Sykes yells, "Stop it right now! Fifty-five seconds. You're all dead" [61].

The choice to use a 1970s-era song as the background music for the scene is an apt one. Despite the significant progress made since then in developing and fielding protective garments for CB threats, CB PPE ensembles like the Saratoga, the JSLIST, and even the UIPE could most accurately be described as incremental technological advancements over their predecessors [62, 63].

## 3.1 THE CURRENT R&D CHALLENGE

This is not at all to discount the substantial heat stress reductions that these suits have achieved, as well as the novel fabric materials, weaves, and combination structures that they have innovated. However, their reliance on activated carbon appears to limit their ultimate ability to achieve a new level of performance capabilities [4, 62]. The field effectiveness of activated carbon is limited by its "nonselective adsorption"—it can take in water from its external environment as well as the moisture emitted by the wearer's perspiration [64]. CB PPE enabled by activated carbon is heavy, provides limited protection against droplets, and is not suitable for use in a CB protective regular duty uniform [62].

The UIPE remains the most advanced CB PPE ensemble currently fielded, and its increments after 2011 have improved its thermal and protective qualities, as well as its overall fit and comfortability. However, it does not meet performance standards that are applicable to the future battlefield; it remains overly heavy and bulky for long-duration wear and does not present substantial longevity of wear to the Warfighter [30, 65]. A variant of the UIPE developed for special operations forces, the tactical advanced threat protective ensemble (TATPE), provided an upgrade in some characteristics, but its thermal burden did not improve as much as some DoD engineers had hoped [65].

Future CB PPE ensembles are unlikely to be developed as overgarments, and, indeed, some ongoing R&D led by the DoD is field-testing concepts for a single duty uniform [30]. Airmen have been testing the two-piece undergarment universal integrative ensemble chemical protective suit (called the 2PUG) well into 2022, to assess its comfort as a base uniform underneath a standard flight suit (see Figure 3-1) [66]. In December 2022,

Figure 3-1. Senior Airmen Noah Isom, 39th Airlift Squadron Loadmaster, Conducts Preflight Checks on a C-130J Super Hercules While Wearing the New Two-Piece Undergarment Universal Integrative Ensemble Chemical Protective Suit at Dyess Air Force Base, TX, 2 June 2021 *(Source: Hollowell [67])*.

troopers tested a CB PPE design from DEVCOM, named the chemical, biological duty uniform (CBDU), which seeks to replace the JSLIST with lighter and cooler garments. Similarly integrated into the duty uniform, and not an overgarment, the CBDU feels "like you're wearing a thicker set of pajamas," as cavalry scout SSgt. Zachary Keel remarked after several days of tests [68].

Because both suits remain in the testing phase, what material serves as their protective or active layer is unclear (although it is most likely a form of carbon); however, they both stand as waypoints pointing toward achieving what the JPEO-CBRND has laid as the DoD's goal of "unencumbering the warfighter." In fact, that vision has been in place through the JPEO-CBRND since at least 2011. At a briefing to an industry conference in September 2011, the office explained that its top-line goal for future CB PPE was "a mandate to reduce [the physiological] burden" by fielding a combat uniform that integrates "basic CBRN protective capabilities." The primary means of achieving this goal would be to combine or engineer new materials to provide "optimal protection" and the "lowest possible thermal burden" [60].

While the constituent materials and garment construction methods have changed significantly since WWII, the underlying engineering challenge remains remarkably the same. As a textile expert explained it in 1999 to the U.S. National Research Council, there are four "geometric" parameters and four "performance" parameters relevant to the requirements of CB PPE. Design tradeoffs among porosity, surface texture, voluminosity, and fabric thickness determine a fabric's relative geometry, while permeability, compressibility, extensibility, and toughness set how a fabric will perform [4]. These parameters constrain the extent to which CB PPE garments can meet the generalized requirements of the CB defense mission set for an individual. The technical requirements for CB protective fabrics or textiles are (listed generally from most to least important) [4]:

- Reduced Heat Stress
- Reduced Weight-to-Bulk Ratio
- Skin Compatibility
- Combat Uniform Configuration
- Longer Service Life
- Longer Shelf Life
- Fire Resistance
- Easier Laundering
- Capability of Being Decontaminated
- Reusability
- Durability
- Camouflage Capability
- Water Repellency
- Resistance to Perspiration
- Resistance to Petroleum Products
- Nontoxicity of Materials
- Compatibility With Other Items

The central thrust of the most cutting-edge R&D into next-generation CB PPE is to engineer, produce, and test novel material or chemical substances/molecules that can replace the layer(s) of activated carbon that currently provide CB protection within the liners of the JSLIST and UIPE [69, 70]. In turn, the most promising substances have been described as being reactive, agent reactive, neutralizing, detoxifying, self-detoxifying, self-decontaminating, and functionalized [62, 65, 69–74]. More colorfully, a few of the novel materials under investigation have been characterized as scavengers, set out to "destroy" CB warfare agents [71]. As Section 3.2 explores in more detail, the overarching concept that HDIAC has found to be representative of the state of the art in CB PPE is to "get beyond barriers, permeable or otherwise, and beyond adsorption" [75].

## 3.2 FUNCTIONALIZED MATERIALS

Found among the SMEs that HDIAC interviewed for this report was a general consensus that the fielding of combat-relevant next-generation CB PPE is very possible in the near term—perhaps only 3–5 years away. Within reach are garments that approach the JPEO-CBRND vision where what the warfighters are wearing "is actually their protective gear" [30, 65, 69, 70, 76]. While some SMEs differed in their estimation of what that timeline might be, those whose estimates were the longest generally shared a healthy skepticism that production costs for a liner or membrane layer of specialized functional materials would decrease enough to allow for production levels scalable enough to outfit the entire U.S. military force [30, 76].

For the near term, the most promising class of functionalized materials investigated to date is known as MOFs. Other materials of interest include small-diameter carbon nanotubes, peroxides, non-MOF zirconium hydroxide, and other specialized chemistries, many of them proprietary [30, 62, 72, 77]. Whether using MOFs or another functionalized material, scientists and engineers within industry, academia, and the DoD laboratory system have found ways to effectively produce these molecules at a scale beyond the laboratory bench and integrate them into/onto a fabric or substrate material.

By doing so, they have created functionalized, selectively permeable membranes that can effectively neutralize or detoxify a wide array of CB agents while letting needed gases pass through more freely [63, 65]. Due to both unique chemical properties and molecular geometries that allow for dramatically greater surface areas than traditional CB protective liner materials, they act to neutralize CB threat molecules that touch the fabric, rendering it safe to touch [65, 76]. As discussed in Section 3.2.1, one R&D group has produced more than a dozen full-body prototypes of an MOF-based, next-generation CB PPE uniform—five of which were extensively tested and worn at a DoD field experiment in May 2023 [69, 70].

### 3.2.1 MOFs

MOFs have been the subject of a growing amount of R&D interest over the past 20 years, as their chemistry and pore structure allows for their "tuning" or customization for a wide variety of applications [78]. MOFs are a crystalline hybrid material, made up of "metal clusters or centers" and a series of organic "linker molecules" that connect the clusters to form a three-dimensional structure or framework [79]. Of critical importance for the CB PPE mission, the flexibility in selecting constituent parts to build a framework means that the number of unique MOFs available for production rests in the several millions [76, 79]. Because MOFs present exceptionally high surface area and porosity, they are an ideal functionalized material to integrate into fibers or textiles to achieve a given application [79]. The addition of certain polymers as an MOF substrate can also enhance their reactivity with CB agents [72].

Researchers working on CB protective use cases for the DoD have been interested in MOFs for over a decade [30, 69, 70, 76]. One collaborative team of researchers from the DEVCOM CBC and

SC, the Defense Threat Reduction Agency (DTRA), Northwestern University, and North Carolina State University (NCSU) began conceptualizing their approach in 2010 to an MOF-enabled CB suit [69, 70]. It took several years to refine exactly how the MOFs of choice could best act as an absorbent. By 2016, they had electrospun MOF material into a textile-like form with enough surface area to test, finding that it could effectively capture and neutralize test agents (see Figure 3-2) [69, 70, 80].

Figure 3-2. A Scientist From DEVCOM CBC Separates MOF Material From an Aluminum Surface After Electrospinning It *(Source: DTRA [81])*.

Some public funding organizations lost interest in MOF-enabled textiles between approximately 2016–2018, as they perceived progress in producing real-world military fabric prototypes to have stalled somewhat [69, 70]. At that point, the primary R&D goal was to engineer workable MOF liners or membranes that could eventually be integrated into PPE garments—a difficult enough task [65, 69, 70]. Fortunately, during this period and directly after, the field at large made significant advances in the understanding of MOF-fiber composite behaviors, including the ability to produce high MOF loadings (i.e., integrating a substantial amount of MOF molecules with a fabric) and laying out several "universal methods to grow MOFs" directly on fibers [78]. Writing in 2019 with multiple other journal co-authors, Dr. Natalie Pomerantz and Dr. Gregory Peterson of DEVCOM and Dr. Gregory Parsons of NCSU explained that:

> *"Researchers are exploring classes of sorbent materials that can selectively accumulate and decompose target compounds for potential to enhance protective suits…Here…MOF deposition on substrates decreased both air and chemical permeation while increasing…chemical sorption. Future work should continue to explore how MOF deposition onto fiber and textile substrates impacts transport properties and chemical absorbance" [82].*

Also in 2019, a research group out of Northwestern University, in collaboration with DEVCOM and DTRA achieved the effective incorporation of an MOF-based (UiO-66-NH2) selectively permeable membrane into textile swatches, a major step forward in producing a workable and testable prototype [69, 70]. Numat built upon the research out of Northwestern to create garment prototypes in 2022, and by May of the following year, a true MOF-based CB PPE "product" was revealed for the DoD to review and assess [69, 70]. At the fifth annual CBOA field experiment, led by DTRA in its role as the lead technical office for the DoD Chemical and Biological Defense Program, what is currently known only as "the Numat suit" was first revealed (see Figure 3-3) [69, 70, 83].

Multiple SMEs identified Numat to HDIAC as a leader in the MOF space [62, 69, 70, 72, 84], and those who have partnered with its researchers to produce the suit have underscored the value of multi-organizational collaboration in achieving the milestone. Even a cursory review of the publicly released photos and videos of the suit shows how successful the effort has been. The suit is formfitting, if not exactly thin—one person involved in its development likened its thickness to a winter coat [69, 70]. While details of the suit's construction are understandably not for public

Figure 3-3. Screenshot From a DTRA Video From the May 2023 CBOA Field Experiment Depicting a Warfighter Wearing a Tan-Colored Numat Suit *(Source: DTRA [85])*.

consumption, it does contain a combination of both woven and nonwoven fabrics [69, 70].

The Numat suit's capabilities are enabled by the unique nature of MOFs. MOFs might be generally said to be both detoxifying as well as decontaminating—many CB-agent molecules react when encountering an MOF, typically undergoing hydrolysis [72]. Whether this action rises to the level of true detoxification is a continuing point of ongoing R&D, but the future fieldable MOF-enabled CB PPE that leading researchers envision is largely understood as allowing its wearer to continue operating in a CB-contaminated environment [65, 72]. The exceptionally high total surface area that can be engineered into MOF substances is also a key enabler of significantly reducing a CB uniform's thermal stress and weight. As Dr. Gregory Parsons described to HDIAC, the molecular surface area that MOFs present is so high that it is near the theoretical limit. "It's amazing," Dr. Parsons continued, that MOFs are even solid. Because MOF molecules are around 99% air, "you would think that they would just collapse…but they're mechanically stable. So, you have millions of metal atoms, and [in an MOF] every metal atom is exposed on the surface" [76]. As a result, when an MOF's metal atoms are set to a certain configuration, with particular organic linkers connecting them, "they can act to perform. They can act to speed up chemical reactions," Dr. Parsons explained (see Figure 3-4) [76].

Figure 3-4. A Conceptual Depiction of the Decontamination Action of a Single MOF Molecule *(Source: Benyo [86])*.

### 3.2.2 Textiles and Tradeoffs

It is critical to note that, despite the rapid and impressive advancement since approximately 2019 of MOF engineering in general and MOF-textile or MOF-polymer integration in particular, it is not at all settled that MOFs are destined to be the clearly superior functionalized material for CB PPE applications [30, 62, 64, 76]. As one SME told HDIAC, the functionality of an MOF substance can depend heavily on how it is fabricated, which can place a high-cost burden on production [62]. Just as OSRD noted in 1946, an utterly central characteristic of a successful CB protective substance is a relatively low cost. Indeed, one promising non-MOF garment type was also successfully demonstrated at CBOA in 2023. Guild Associates (Dublin, OH) produced more than 30 CB garment prototypes based on the reactive material, $Zr(OH)4$. Less expensive than an MOF-based suit, the prototypes are reactive, sorptive, and potentially reusable and have shown resistance to fuels [84].

Generally speaking, the base chemicals needed to fabricate MOFs are expensive; however, efforts are underway to probe the feasibility of producing predecessor materials on site within a future MOF-focused production facility to lower costs [76]. Even though MOFs can be more akin to "programmable smart sponges," as Dr. Omar Farha of Northwestern University has taken to describing them [69], at a certain cost threshold, their use may cease to be wise [69, 70, 84]. Activated carbon is so cheap by comparison, that it can be difficult to compete against. Regardless, to provide full CB protection, some MOFs may need to be combined with activated carbon or other chemistries to defend against some classes of chemical agents [84].

The dominant paradigm for MOF integration into a combat CB PPE uniform—including for the Numat suit—also requires that the MOF layer be affixed to an adhesive, which can degrade their effectiveness by blocking the pores of the frameworks [72]. Furthermore, as a rule of thumb, gluing or adhering one piece of fabric to another can increase the combined entity's stiffness by a power of eight (see Figure 3-5) [87]. One functionalized material that has been investigated for years alongside MOFs is zirconium hydroxide, which can be fabricated as an MOF but does not need to be to neutralize CB agents [62, 72]. At large, sorbent hydroxides, when modified, provide relatively strong protection relative to their production costs. Other candidate functions include conventional, biobased, and enzyme-based catalysts [74, 76]. Engineers have also recently looked into polyethyleneimine for CB applications, as it is an organocatalyst for the hydrolysis of nerve agents that remains inexpensive to procure [88].

There has also been a significant amount of R&D performed since 2020 in the use of inorganic nanoparticles and organic small-scale particles dispersed within polymeric substances to counteract biological weapons agents [64].

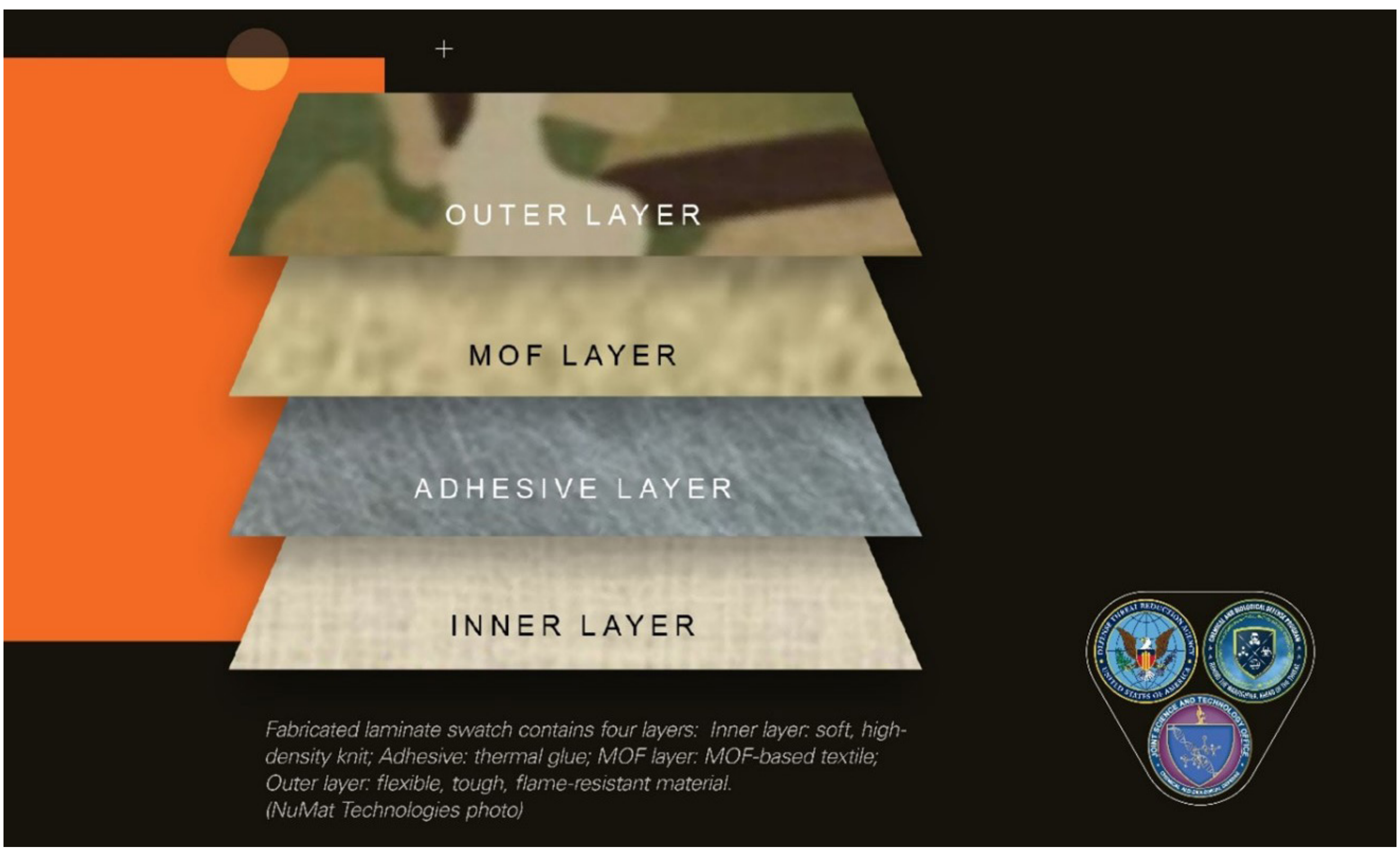


Figure 3-5. DoD Concept of a Fabricated Laminate Swatch for CB PPE That Contains Four Layers (Inner Layer: Soft, High-Density Knit; Adhesive Layer: Thermal Glue; MOF Layer: MOF-Based Textile; and Outer Layer: Flexible, Tough, Flame-Resistant Material) *(Source: DTRA [89])*.

While carbon nanotubes deposited in a polymer matrix received a fair amount of attention in the mid- to late-2010s as a potential CB membrane material, production prices to date have not permitted their study beyond a relatively small swatch, on the order of perhaps six inches per side [77, 84]. Their natural predecessor might be carbon nanodots or quantum dots, which are spherical particles measured in the nanometers, or even "graphene quantum dots" [64]. In at least one textile-focused research effort, carbon quantum dots retained a high level of "microbial inhibitions" even after 10 laundering or washing cycles [64].

Figure 3-6. A Conceptual Model of an MOF Type Likely to Be Used in a CB Protective Combat Garment *(Source: DEVCOM CBC [90])*.

Moreover, as a major May 2023 review of functionalized textiles in *Advanced Functional Materials* noted, as advanced as MOF technology has advanced in recent years, a lengthy path remains before the production of MOF-enabled CB PPE can yield "protective garments with high performance and low cost in the real world" [73]. In the absence of an extensive amount of data collected on the real-world use, longevity, durability, and repeat-wear efficacy of an MOF uniform suit—not to mention without hard-and-fast production or procurement performance requirements yet set—researchers cannot yet fully appraise MOF prototypes with much certainty (see Figure 3-6). As Dr. Gregory Parsons of NCSU told HDIAC, the world of using novel, next-generation functionalized materials for CB PPE is an entirely new field in which "everybody has a question, and no one knows the answer." Dr. Parsons continued, "there's all these questions that we really don't know yet if they're important" [76].

In other words, given that MOF-enabled PPE technology is so new—and as Section 3.2.1 detailed, it progressed in the 2010s with a rapidity seldom witnessed in any field of science and technology—there are too many active variables or parameters to yet discern how they might best interact. It will depend, Dr. Parsons said, on what problem is trying to be solved. Which parameters are expendable? If laundering a CB protective uniform causes a percentage of the MOF molecules to shed off, that is to be expected, but nobody yet knows what the optimal number of permitted washings should or will be [76]. If shedding is a concern, one option is to double the amount of MOF material embedded into the uniform's inner layer. That, however, could cause an even higher percentage of the MOFs in the interior of the layer to become air inaccessible and lose the ability to decontaminate a CB agent, or worse, the functionalized layer can become less bendable, even brittle [76]. Indeed, some MOF formulations are lacking in strength [62].

One of the most vexing (yet promising) R&D challenges is to determine whether a CB suit should contain a uniform type of MOFs or for multiple classes to inhabit it—a question delimited only by the millions of MOF materials that can be theoretically fashioned via computer-aided design [69, 70]. That is much of the work that is currently ongoing at DEVCOM: alighting upon specific candidate MOF structures and engineering them into an appropriate configuration before testing to determine what true capabilities they may demonstrate [66, 72]. Partnering with colleagues at NCSU, Northwestern University, DTRA, and beyond, researchers like Dr. Gregory Peterson can alter the size of MOF pores to optimize their chemistry for a certain type of CB threat agent or tweak the length of the organic linkers connecting the metal clusters. "You can imagine these things being like Tinker Toys, almost," Dr. Peterson told HDIAC, in that each component of an MOF can be tailored [72].

Finally, while this report mostly addresses the innovations in selectively permeable membranes enabled by functionalized MOF materials, the importance of innovation in fabric/textile design and their combination into garments cannot be minimized. Fabric functionalization processes are of immense importance to producing effective CB PPE, especially models that can be successfully commercialized and produced—likely in the millions—for use across the DoD [64]. Researchers are actively engaged in this work, examining the value of multiple methods, including in situ MOF growth on fibers, precursor seeding, surface functionalization, and the "MOF-first" integration of MOFs with polymers prior to the formation of fibers [78]. One significant benefit of MOFs is that they do not require the use of per- and poly-fluoroalkyl substances (PFAS) materials (see Section 4.2).

Moreover, while the functionalized material is critical, a CB PPE uniform fabric will be designed around it [30, 65]. A good multilayer garment concept can draw upon a multitude of fiber and fabric types, weaves, knits, densities, and lofts. As Dr. Kendra McCoy, Science and Technology Manager at DTRA, put it to HDIAC, the characteristics of neither the garment fabrics nor the functionalized material dictate overall performance of the system. Rather, it is the combination of their properties—undertaken with potential tradeoffs in mind—that helps DoD researchers fashion them into a viable and operationally relevant CB-defensive capability [65].

# SECTION 04 CONCLUSION

If one takes a look at some of the projections made by military groups and technology pundits of what the future of CB protection might look like, the impressive advances made over the last decade in functionalized materials for CB PPE can appear downright quaint. The field of "smart" or e-textiles promises to incorporate electronic- or computational-based sensors and functionalities into almost anything the Warfighter might wear [71, 75, 91]. These dynamic, biomimetic systems are ultimately intended to be integrated directly into the same CB PPE uniforms discussed in this report. As Dr. Sundaresan Jayaraman, professor in the School of Materials Science and Engineering at the Georgia Institute of Technology, noted to HDIAC, the DoD has long been interested in the concept of the "wearable motherboard," where standard fabric does not host but is the computer [92]. DEVCOM CBC has also expressed interest in this space and has worked to combine fabrics equipped with light-emitting diodes and photosensitive dyes, as well as MOFs to detect and then expedite the degradation of a CB agent that has come in contact with the exterior of a garment [93].

Another especially fruitful field of R&D, long in development but recently highlighted by DTRA, is best described as a materially responsive or adaptive membrane. The interpenetrating polymer network (IPN) is made of an electroactive and conductive polymer, carbon fibers, plastic strands, and other tethers [94]. When voltage is applied, the system can switch at will between an open configuration—a high level of permeability similar to normal clothing—and a closed structure, which closes a garment's permeable gaps and provides a high level of CB protection (see Figure 4-1).

An even more adaptive CB protection technology—albeit one much further into the future—is being actively explored at DEVCOM CBC by coprincipal investigators Dr. Jennifer Lee and Dr. Marilyn Lee. By incorporating synthetic biology approaches with cell-free protein synthesis (CFPS) technologies, the project team aims to cast fibers that contain DNA programs that are enacted by cell-free transcription, translation, and/or metabolism [95]. CFPS-enabled fibers could endow a fabric with CB threat sensing, decontamination, and programmable functions, while remaining completely biosafe to the wearer and, notably, not requiring the sustainment of any living cells [95].

Two other aspects of the state of the art in CB protective PPE are deserving of a brief discussion. Section 4.1 touches upon the importance of collaboration and cross-discipline interactions in delivering successful innovations to the Warfighter, while Section 4.2 addresses ongoing efforts within the DoD to find novel alternatives to PFAS, which are currently relied upon in some CB PPE garments used by the Warfighter.

## 4.1 ORGANIZATIONAL COLLABORATION

Like all research-intensive areas of R&D, groups innovating in the CB PPE space—including academic, commercial, and government—are never fully equipped with the funding

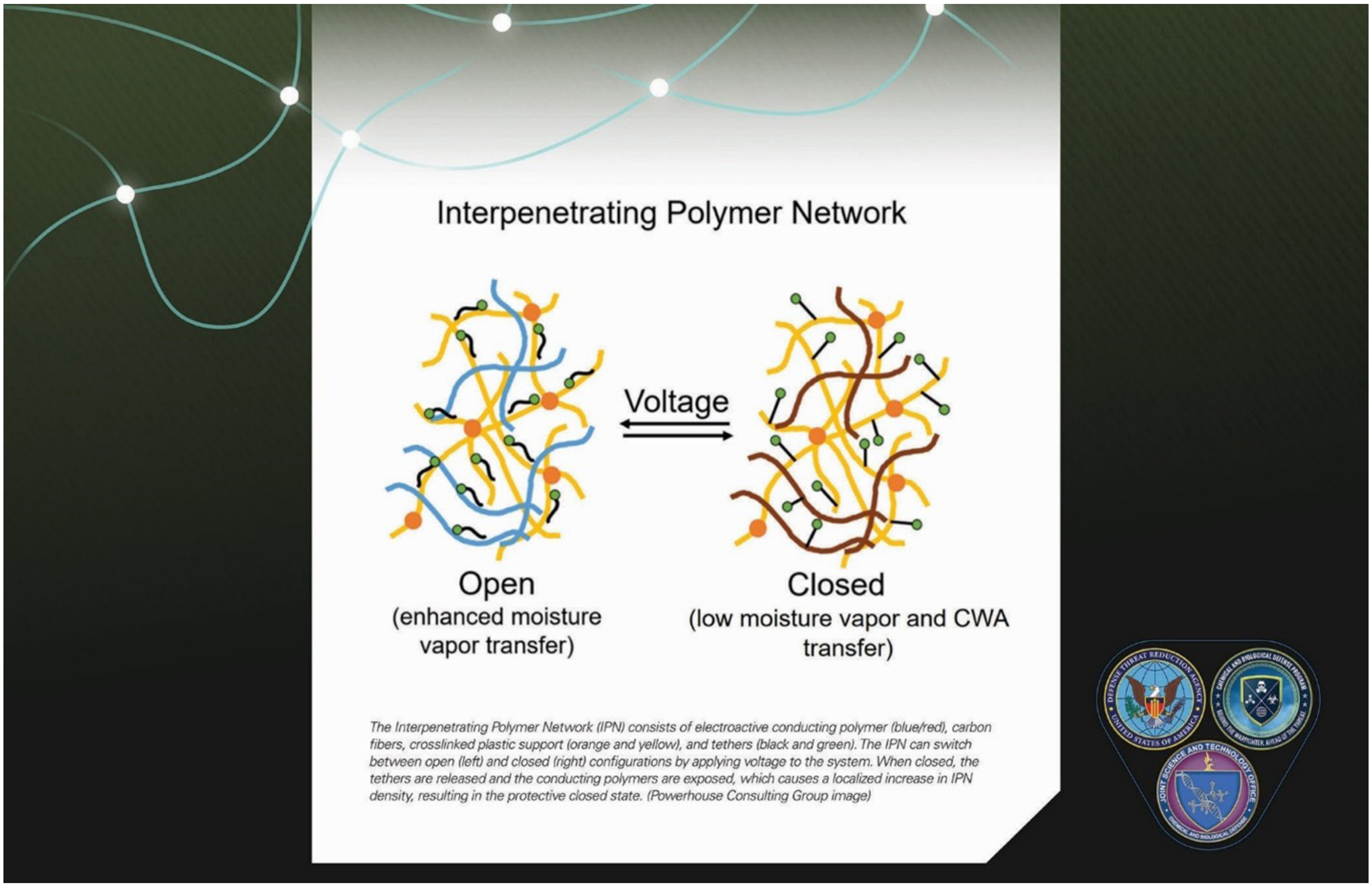


Figure 4-1. The IPN Consists of Electroactive-Conducting Polymer (Blue/Red), Carbon Fibers, Crosslinked Plastic Support (Orange/Yellow), and Tethers (Black/Green) *(Source: DTRA [94])*.

necessary to bring their advancements to production quickly or easily. However, tapping key partnerships and collaborative efforts is a critical means to overcoming this hurdle. Cooperation between JPEO-CBRND, research institutions, and industry partners has facilitated shared resources, expertise, and innovation in protective ensembles. In the recent history of DoD-funded CB PPE development, these collaborations have proved nothing less than critical in achieving more efficient development processes, cost savings, and advancements in protective ensemble technologies.

As Dr. Omar Farha of Northwestern University stressed to HDIAC, without his broader group's collaborative partnership with Numat (see Section 3.2.1), the cutting-edge Numat MOF-enabled CB uniform that debuted in May 2023 would have been significantly delayed—if it were able to be produced at all [69]. "Depositing things on fabrics is easy," said Dr. Farha, "if you do it the wrong way." It was having the input from a technology-transfer-minded partner that kept practical issues of scaling and cost forefront in the minds of the R&D team [69].

A similar value drawn from collaboration can be seen at the NCSU Nonwovens Institute (NWI) in Raleigh, NC, which stands as a landmark site in American textile- and fabric-related R&D and commercialization efforts. The NWI was first funded in 1991 by the National Science Foundation (NSF) as the first of five NSF Industry/University Cooperative Research Centers (I/UCRC) established across the nation [87]. Prior to the NWI's creation, there was a dearth of collaboration in the nonwovens space, but the institute has more than reversed that trend by developing "know how" for its members, as Dr. Behnam Pourdeyhimi, NCSU professor and NWI Director, explained to HDIAC. With a membership of more than 60 companies and around 50 NCSU Ph.D. students engaged in textile research, the NWI makes good use of its 100,000-ft$^2$ facilities and manufacturing space. Given the shortcomings of the DoD's CB PPE during the early 1990s (discussed in Section 2.2.2), it is an interesting quirk of history that it was U.S. Army general and commander of coalition forces in the first Gulf War Norman Schwarzkopf's older brother Alexander who was pivotal in founding the NSF I/UCRC program and, ultimately, the NWI [74].

In addition to the national partnerships between government, academia, and industry previously discussed, international cooperation is equally crucial. Sharing best practices, research findings, and technological advancements with allied nations can promote global preparedness and ensure that protective ensembles meet the highest standards of effectiveness and reliability.

## 4.2 ALTERNATIVES TO PFAS

PFAS is a group of synthetic chemicals widely used in various industries and products due to unique properties in resistance to heat, water, and oil and the ability to repel stains and provide nonstick surfaces. Products such as firefighting foams, nonstick cookware, waterproof clothing, food packaging, and many other consumer and industrial applications also use PFAS [96].

Now widely known derisively as "forever chemicals" due to their persistent nature, bioaccumulation ability, and potentially harmful effects on human health and the environment, PFAS has recently come under regulatory scrutiny. The EPA has acknowledged the issue through initiatives such as the PFAS Action Plan and EPA Council on PFAS; however, the current regulatory framework lacks federal rules and standards [97].

Studies have linked PFAS exposure to adverse health outcomes, including developmental issues, liver damage, immune system disruption, and an increased risk of certain cancers. The strong carbon-fluorine covalent bonds in many PFAS congeners contribute to their long-lasting presence in the environment. Prominent PFAS compounds include perfluorooctanesulfonic acid, perfluorooctanoic acid, and GenX. Multiple human cohorts, both occupational and nonoccupational, offer valuable insights into the environmental implications of PFAS and associated health effects. Firefighters, for instance, face significant exposure due to using PFAS-containing aqueous film-forming foams along with the subsequent risk of PFAS contamination of their PPE.

The DoD is actively researching alternatives to PFAS-based PPE garments and equipment, not only for firefighting applications but also for protection against CB agents. Veronica St. Claire, chief technology officer and science and technology lead at the JPEO-CBRND office, explained to HDIAC that PFAS materials are currently used in UIPE garments, both for water-phobic coatings and in the semipermeable membrane that houses an activated-carbon protective layer. She noted that, as a result, finding PFAS-free alternatives was a "huge technology gap" that the DoD is actively engaging with for the next generation of CB protective garments [98].

JPEO-CBRND has issued several public request for information solicitations to engage industry and academia in identifying and encouraging R&D in advanced solutions to replace PFAS and secure the continued safety of Warfighter uniforms and CB PPE [98]. At a higher level, a DoD PFAS task force is coordinating efforts across the department to address PFAS mitigation activities and aid in the transition to PFAS alternatives wherever possible [99].

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# UNENCUMBERING THE WARFIGHTER: FUNCTIONALIZED MATERIALS FOR CHEMICAL AND BIOLOGICAL PROTECTIVE CLOTHING

*By Joseph Cole and Joel Hewett*

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