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THE DESIGN OF PERSONNEL PROTECTIVE CLOTHING FOR PROTECTION AGAINST CBRN AGENTS: A REVIEW

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Chemical, Biological, Radiological and Nuclear (CBRN) agents are harmful to living organisms and their surroundings. Many incidents involving CBRN agents have been witnessed in the past. Moreover, CBRN agents are nowadays also being used as modern warfare agents. Protection against CBRN agents is essential from both industrial and national security points of view. There is a need to design personnel protective suits with CBRN protection.

In this review, recent advances in protection against CBRN agents using textile media are discussed in detail regarding their application in personnel protective suits. Different types of CBRN agents are presented along with recommended protection corresponding to the toxicity and concentration levels of these agents. Furthermore, various materials and methods used for the modification of textiles and barrier technologies to render protection against exposure to different CBRN agents are also discussed.

INTRODUCTION

Chemical, Biological, Radiological and Nuclear (CBRN) agents are dangerous for living beings and their surroundings. Many incidents involving CBRN agents have been witnessed in the past that include both intentional and accidental[1]. For example, the release of mustard gas in Iraq war, rockets fired at Damascus with chemical agents such as sarin nerve gas, anthrax laced letters mailed to federal officials in Washington DC were intentionally motivated incidents. However, non-intention incidents are also reported such as the Fukushima Daiichi nuclear plant where damaged reactors discharged radioactive materials[2].

Intentional incidents are driven by wars or terror motives whereas accidental incidents are predominantly attributed to human error or to technological failures. Hence, proper protection from CBRN agents is required to escape the intentional or accidental release of CBRN agents. Modern personnel protection equipment (PPE), including clothing, should have protection against CBRN agents for carrying out operations in CBRN incident places.

CBRN defence consists of CBRN passive protection, contamination avoidance and CBRN mitigation. For a rescue operation following a terrorist attack where there is chance of releasing unknown CBRN agents, a special suit must be worn to afford the highest protection level of protection. Similarly, in a battlefield situation, there is a need for CBRN protection in military clothing. For cases where the type of agents is already known, like in the industrial release of gas, it is easy to go for CBRN mitigation[3], but most often its take time to detect the type of agents used in an attack. Various types of CBRN are present in various forms and with varying concentration, and the level of protection offered by clothing must be designed accordingly. The ISO, EN, NFPA and OSHA standards are available for PPE and refer to the protective clothing, helmets, goggles, or other garments or equipment that are designed to protect the wearer's body from injury or infection[4].

Protection and comfort are contradictory properties but can be optimized based upon CBRN zones and accordingly the selection of appropriate chemical technology and barrier technology with proper garment design. Different available barriers technologies are impermeable, semi-permeable and permeable with the recent introduction of selectively permeable barriers. Fibrous barriers can readily capture CBRN agents that are present in particulate form.

For toxic gaseous protection various studies are going on for the identification of sorbent and adsorbent and the implementation within clothing. Similarly, there are various methods for the application of antimicrobial agents to textiles for protection against biological agents. Materials applications at the nanoscale, through the implementation of nanotechnology materials, further enhance CBRN protection. For testing penetration and permeation are important for clothing and when considering the whole garment, the additional Man-In-Simulant-Test (MIST) is there to make test methods more realistic.

In this paper the principles for protection against the CBRN agents, with a scope of using various materials through textile media, are discussed. The CBRN incidences are grouped in to four levels of protection based on different standards, for designing personnel protective garments according to the level of hazards. Subsequently, the clothing technology required for each level of protection is discussed, starting with the scope of different barrier technology for a specific level of protection and the role of different fibres and chemicals. The different types of potential adsorbent, sorbent, catalyst and bioactive agents against CBRN agents and its application to textile material are discussed. The principles involved in CBRN protection for different forms of agent are also discussed, that is:

- Agents which are present in solid particulate form like bacteria, radioactive particles etc. that can readily be removed by trapping in fibre networks
- Chemical agents which are mostly used in the form of poisonous gas and can be removed by using the application of adsorbent, sorbent and/or catalyst
- Biological agents that not only have to be filtered but also have to be killed in the media by using biocide fibre and finishes
- Protection against radiation and its effect on fibre and the need for decontamination is also considered.

TYPES OF CBRN AGENTS

The term CB in general refers to chemical and biological for industrial clothing, firefighter suits etc. whilst the terms CBR and CBRN are used when dealing with holistic protection like in war fields and for hazardous materials (HAZMAT) protection. The detection and assessment[3] of specific types of CBR agent at the place of an incident is very important. Detection can be via the symptoms of victims, sample tests[5,6] and more appropriately by CBR detectors where one such example is the robot-based Raman detector[7].

Chemical Agents

There are many harmful chemicals agents available that can be used as weapons, or that are present in industries and surroundings. The level of hazard of each agent varies from less hazardous to deadly. In a report by the Central Intelligence Agency (CIA), the potential CBRN agents that can be used in Terrorists attack have been given[8]. The potential chemical agents are of different types, blood agents that penetrate the skin, blistering agents that can damage the skin and nerve agents that affect the nervous system when inhaled.

Toxic cyanide compounds which can be mixed with chemicals to enhance skin penetration can be used as a blistering agent and Mustard which is the blistering agent in one of the potential chemical agents. Nerve agents such as sarin (GB), tabun (GA), and venomous agent X (VX) are highly toxic military agents. They can be used as chemical warfare agents and are Immediately Dangerous to Life and Health (IDLH) even if present in small quantities, i.e. 0.03 ppm, 0.03 ppm and 0.002 ppm, respectively[9]. GA, GB and VX are organophosphorus esters that form a major portion of the total agent[10].

There is a wide range of available industrial chemicals that are not toxic like nerve agents but are harmful if present in large quantities. Chlorine and phosgene are chocking agents that have a similar effect to mustard agents. In the category of pesticides, organophosphate variants such as parathion are in the same chemical class as nerve agents. Chemical agents can be used by poisoning food or spreading in the atmosphere using broader dissemination techniques.

Biological Agents

Thousands of potential biological agents have been described and studied to date that can potentially be used as warfare agents[11]. Biological agents are mainly pathogenic microorganisms from the categories of bacterium, virus, protozoan, parasite, or fungus, and toxins. Toxins in bio agents are referred to as poisons and produced biologically by bacteria, plants, or fungi[12]. Some examples of highly toxic biological agents are anthrax, botulinum and ricin. Bacillus anthracis, the bacterium that causes anthrax, can cause mass casualties whilst ricin is a toxin that is 30 times more potent than the nerve agent VX[8].

Radioactive and Nuclear Agents

Radiological agents are radioactive substances that emit high energy particles or gamma rays while undergoing radioactive decay. Nuclear materials are the key ingredients in nuclear weapons and include fissile, fussionable, and source material. The radiological materials used most often in nuclear weapons are concentrated forms of uranium-235 (the isotope of uranium with an atomic mass of 235) and plutonium-239[13]. Nuclear agents are radioactive material generated from nuclear fission or fusion, such as those produced by detonation of a nuclear weapon or releases from damaged nuclear power plants. Radiological agents are radioactive material generated as by-products and waste from the mineral processing industries, produced for use in industrial applications and medical therapy, or occurring naturally in the environment.

The explosion of a nuclear weapon is associated with the emission of a mixture of ionizing radiation, consisting of neutrons, high energy photons, and alpha and beta particles[14]. Gamma rays can penetrate tissue farther compared to beta or alpha particles but are less damaging locally. Beta particles are less penetrating and can be shielded by a thin sheet of metal. Whilst alpha particles carry more energy, they are easily shielded by a sheet of paper or clothing and present no external hazard. However, alpha particles are quite damaging if internalized because they deposit all of their energy in a very small volume of tissue.

Tiny, discrete radioactive fragments (less than 1 mm in size) associated with nuclear weapon detonations are also hot particles. This can cause extremely high exposures to localized areas in a short amount of time and may get embedded in the body[15] if proper protection is not there. Explosion of a nuclear weapon is the rarest of rare phenomenon, but radioactive materials can be dispersed by Radiological Dispersal Devices (RDD) rather than through explosion to cause destruction, contamination, and injury. The cellular effects of radiation, whether due to direct or indirect damage, are basically the same for the different kinds and dosages of radiation. The simplest effect is cell death. Flash burns are likely to occur on a large scale as a result of the air or surface burst of a nuclear weapon.

PROTECTION LEVELS FOR CBRN DEFENSE

Based on the level of hazards and concentration of CBR agents it is convenient to classify an incident according to Immediately Dangerous to Life or Health (IDLH). IDLH is defined by NIOSH[16] as "exposure to airborne contaminants that are likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment." Further, whether the incident is above or below IDLH at the place of incident or at a war field, the incident area can be classified in to hot zone, warm zone and cold zone as shown in Figure 1.

According to these zones the personnel protection ensemble, including clothing, has to be selected. In the hot zone CBR agents are at the level of or above IDLH and require use of the highest protection. For the warm zone, where the level is below or up to IDLH, a significant threat is still posed and requires higher protection levels. The cold zone is not dangerous to health[17].

In the design of PPE, comfort through heat relaxation air, heat and moisture transfer is also required. Therefore, the fabric protection level is chosen according to the zone and optimized for comfort. PPE includes

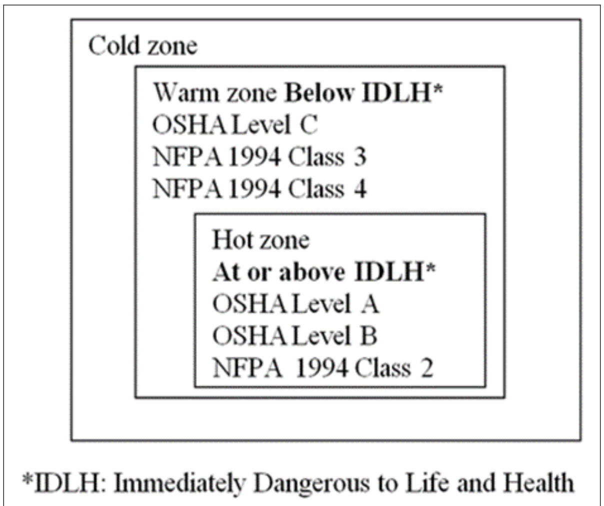

Figure 1: Different CBRN zones.

different types of clothing, each one of which is designed as per the protection level[18] from inner wear to coverall. The respiratory system is also selected based upon the required protection level from self-contained breathing apparatus (SCBA) for higher level of protection to a simple face mask. Other than these, gloves and boot variants must be considered.

Depending upon the level of hazard, PPE is classified into different types as per different standards such as Occupational Safety and Health Administration (OSHA)[19], National Fire Protection Association (NFPA) [20,21], European Standard (EN)[22] and International Organization for Standardization (ISO) standards[23]. Classifications are broadly similar and can be grouped in different levels as shown in Table 1.

PPE can also be classified and designed based on the forms and purpose of CBRN agents and specific to protection against gas, liquid spray, liquid splash, aerosol and particulate form as in the case of ISO standards and European standers (see Table 2). The highest protection for agents in the form of gases as in Type 1 requires a complete leak tight garment. The lower level of protection required for agents in the form of particulate utilises permeable barriers. Accordingly, the comfort level and operation time is decreased with leak tightness and higher efficacy.

In the following section details of first level to fourth level protection are discussed in more detail.

First Level of Protection

The highest level of protection is required against the highly toxic and harmful CBR agents above IDLH, that is within the hot zone. For example, in the presence of the nerve agent sarin (GB), at a concentration of more than 0.03 ppm, full body protection is required. This can be achieved by using an encapsulated and gas tight suit with a respiratory system inside.

Sometimes a disposable protective suit can also be worn over the encapsulating suit for extra protection and ease of decontamination. It covers protection from almost all types of agent whether in the form of gases, vapours, spray or liquids. Also, a suit that is designed for a specific form of agent comes under the first level of protection, like protection from highly toxic gases and vapour (as in Type 1 and Type 2 of ISO standards), protection from toxic liquid (as in Type 3 of ISO standard) as well as from spray (as in Type 4 of ISO standard). The clothing used should be completely impermeable as even a very small quantity of some agents, even in the ppm range, is very harmful to health.

Second Level of Protection

The higher level of protection is required against toxic and harmful CBR agents, airborne agents which are present above IDLH and liquid concentration below IDLH where full body protection is required. Break-

Level of protection	Respiratory requirement	Equivalent standards	Barrier technology	Commercially available suits
First Level Highest level of protection for both respiratory and skin. Airborne and liquid concentration above IDLH.	With SCAB inside	OSHA Level A, Type 1: (prEN 943 part 1)	Impermeable, optional Mylar layer, Re-flectants layers	Tychem® TK, Tychem® BR and Tychem® LV
Second Level Unknown CBRN, Highest level of protection for both respiratory and skin. Airborne concentration above IDLH and liquid con-centration below IDLH.	With SCAB outside	OSHA Level B, NFPA 1994 Class 2, Type 2: (prEN 943 part 1)	Impermeable	Tychem® TK, LV & BR with Tychem® to PP, Kap-pler Zytron with Zytron barrier, ONESUITE® Pro with Coretech Barrier™
Third Level Known CBRN, Lesser level of protection for both respira-tory and skin. Airborne and liquid concentration below IDLH.	With APR or Powered Air Purifying Respirator (PAPR)	OSHA Level C, NFPA 1994 Class 3, Type 4: (prEN 1512)	Semi-permeable and selectively permeable	LION Extended Response Suit. NFPA 1994 Class 3 En-semble. GORE® CHEMPAK® se-lectively permeable.
Fourth Level Biological and radiological particulate, Nuisance, Non-chemical, powder contamination.	Dust filter for radioactive contamina-tion	OSHA Level D, NFPA 1994 Class 4, Type 5: (prEN 1513)	Semi-permeable and permeable barrier, Cover-alls	Firefighters' protective clothing

Table 1: Designing PPE based on the different level of CBRN.

ISO 16602	Equivalent EN Standards
Type 1 Gas tight Protection against chemicals, vapours and toxic particles	EN 943-1, EN 943-2 Gas tight
Type 2 Non-gas tight Positive pressure suits	EN 943-1
Type 3 Non-gas tight Protection against high pressure liquid exposure or splash	EN 14605 Liquid tight suit
Type 4 Non-gas tight Protection against liquid chemical splash	EN 14605 Spray tight suit
Type 5 Non-gas tight Protection against air born dry particulate chemicals	EN ISO 13982-1 against solid particles
Type 6 Non-gas tight Limited protection against liquid aerosol	EN 13034 minor splash of irritant chemicals

Table 2: ISO and equivalent European standards for personnel protective suits.

through time is > 720 mins. for a highly toxic agent like mustard, soman, sarin etc. and > 480 mins. for a less toxic agent like acetone, ammonia, chlorine[17], which can be achieved by using encapsulated and but not necessarily gas tight suit equipped with an outside respiratory system. The highest level of respiratory protection is necessary, but a lesser level of skin protection is needed. Protection strategies are like that of first level of protection but against fewer chemicals and with little less resistance time.

Third Level of Protection

The lesser level of protection is required against CBR agents present below IDLH, for example ammonia at 40 ppm, mustard at 10 g/m^2 etc. The concentration(s) and type(s) of airborne substance(s) are known and criteria for using air purifying respirators are met. Where full body protection is required that can be achieved by using encapsulated and but not necessarily gas tight suit equipped with air purifying respirators (APR). Here, protection is required against the

CBRN agents of less toxic nature and there is more scope to increase comfort by using a semi-permeable and high efficient selectively permeable membrane.

Fourth Level of Protection
Least level of protection is required against the nuisance, non-chemical and powder contamination. Here mainly protection against the particulate form of CBRN agents is required which can be achieved by simply fibrous network. For this level of protection sometime use of coverall is sufficient for giving protection. More scope is there to increase the comfort by using permeable membrane and garment with ventilation.

CLOTHING TECHNOLOGY FOR CBRN PROTECTION

Different barrier technologies that can be used for personnel protection against CBRN agents are available and dependent on the level of protection, types of protection and comfort. These barrier technologies are impermeable, semi-permeable, selectively permeable and permeable.

Role of Structure and Principle of Protection
The compactness of fabric, and ultimately the air and moisture permeability of a clothing system, have to be considered based on protection level and comfort. Various barriers technologies from impermeable for maximum protection to permeable barrier for less protection and semi-permeable barrier with adequate protection must be selected based on the protection requirement while designing the personnel protective suit. For instance, in one study it was found that for protection performance against hot liquid splash, the air permeability is a dominant factor[24].

The effect of compactness of Kevlar woven fabrics and needle punched nonwoven felts on radiant heat protective performance has been studied. It has been observed that at all heat fluxes the protection time is linearly related to the thread density of warp and weft yarns for woven fabric and punch density for needle punched nonwoven, respectively[25].

Impermeable Barrier Technology
This type of barrier is mostly used for protection where the separation of internal microclimate from the outer atmosphere, that is complete importability to air, is required as in a personnel protective suit of first and second level of protection which is generally fully encapsulated. As shown in Figure 2, aerosol and liquid even in the form of splash and spray must not be able to pass through this barrier, and neither must air and other gases of very small molecular size.

A coated fabric can be used to achieve impermeability, but the use of an impermeable barrier restricts the air flow and the user's natural evaporation which leads to a highly uncomfortable condition. So, it is challenging to achieve comfort level by adequately cooling and dehumidifying the internal climate. As such no method is currently available which can adequately cool and dehumidifying people in encapsulation suits[26].

As heat and moisture flow is restricted through the barrier, in order to increase the comfort level, and hence response time, other means of heat relaxation and moisture removal have to be implemented. The use of smart materials and garment design can be one option to increase comfort in the microclimate. One option is to use fibre or yarn with more moisture absorption properties for the inner garment. This can be achieved by incorporating phase change materials microcapsules within a viscose fibre as in case of Outlast® yarn[27] and by modifying the fibre morphology as in Coolmax®[28].

From the range of fabric structures, knitted fabric structures are preferred. A study has been carried out on to the influence of fabric structure on the thermal and moisture management properties of knitted fabrics made up of these yarns[29]. Another approach is to use bulky clothing, long underwear and a hardhat (under the suit) which increases comfort by increasing the air gap between the person and the suit. To reduce heat transfer through a clothing system with an impermeable layer, and especially where radiation is present, a coverall is made from materials with more reflectance and worn wear outside of the clothing system.

Semi-Permeable Barrier Technology
Semi-permeable barrier technology in a clothing system consists of an intermediate layer with air filtration capability that is also permeable to water vapour. As shown in Figure 3, this barrier is impermeable to liquid in the form of spray and splash and permeable to air to a limited extent. Particles which are present in the air in the form of particulate are trapped by the barrier and toxic gases get adsorbed. As the barrier is permeable to moisture vapours, the moisture present in the microclimate of the clothing system can pass through the barrier and thus provide more comfort. For the third

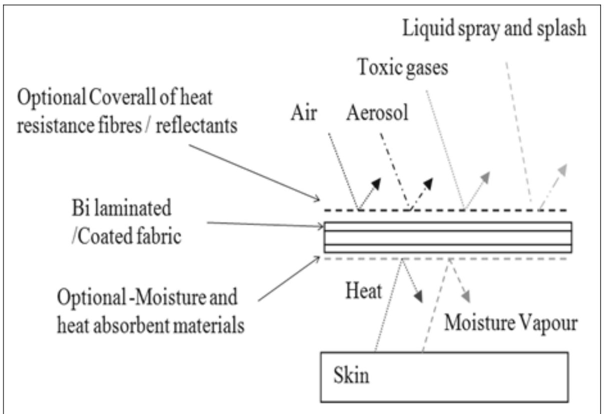

Figure 2: Impermeable barrier technology.

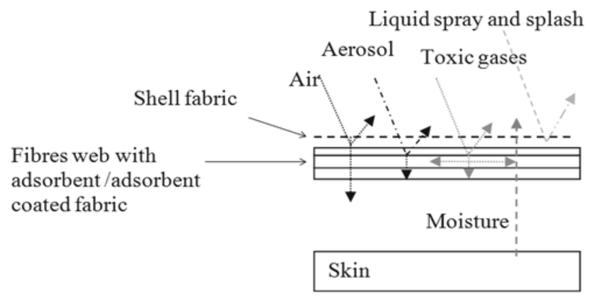

Figure 3: Semi-permeable barrier technology.

level of protection, semi-permeable barrier technology can be employed but is not suggested for first and second level protection, even though filter media are available for highly toxic gaseous. Semi-permeability can be achieved by using a fibrous web made from micro- and nano- fibres and by a microporous coating over the clothing. For gas adsorption, various adsorbent and sorbents materials are available which can be used in an intermediate layer to filter toxic gaseous. These can be applied in the form of a coating or by incorporating into fibre themselves.

It is important to consider the extent to which moisture is transmitted thorough a semi-permeable membrane. The moisture vapour diffusion of electrospun membranes has been compared with commercially available membranes, films and fabrics. It has been found that an electrospun estane membrane is much more transmissive than a film of the same material and exhibits comparable resistance to diffusion compared to an uncoated PTFE membrane. Estane film, PTFE membrane- laminate GORE-TEX shows a concentration dependent transportation behaviour[30].

Microporous films can be bi-laminate on a spunbonded polypropylene nonwoven for semi-permeability[31]. Various semi-permeable barrier technologies are available like the Zytron Chemical barrier, Coretech™ barrier and the GORE® CHEMPAK® ultra barrier fabric which use a thin, lightweight, high strength PTFE film for protection against the CB agent[32]. Similarly, Tychem® CPF 3 multi-layered barrier film is laminated to a durable 2.0 oz/yd^2 polypropylene substrate[33]. One CBRN protection suit has been made using a barrier filtering liner together with an oil repellent outer shell[34].

Selectively Permeable Barrier Technology

Selectively permeable membranes are designed to allow some molecules to permeate whilst blocking specific organic molecules. The selectively permeable barrier, as shown in Figure 4, generally uses a tri-laminate form with fabric as the outer and inner layers to provide strength and durability. It is the new evolving technology, where for personnel protective clothing system it is designed to permeate the water vapour molecules for sweat evaporation and to block the specific hazardous gas molecules for protection. Here, even though there is restriction to air permeation, moisture vapours can transport outside which is important from a comfort point of view. For designing an advanced protective fabric with less bulkiness and with the least number of layers this barrier technology would be a solution.

A selectively permeable membrane (SPM) can be used for protection against CBRN agents in concentrations below IDLH[35] with an approved respirator and for NFPA 1994 Class 3, that is for third level of protection.

Permeable Barrier Technology

Permeable barriers allow air and moisture to pass through and little protection can be added without affecting fabric permeability, as shown in Figure 5. The fibrous network with small pores can sometimes be used with an adsorbent to separate component from the passing air. Like in a work uniform affording minimal protection, from nuisance contamination only. The fabric consists of a permeable membrane and generally comes under fourth level of protection. For extra

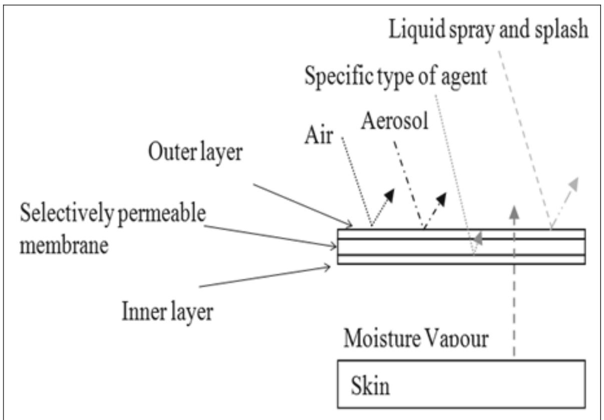

Figure 4: Selectively barrier technology.

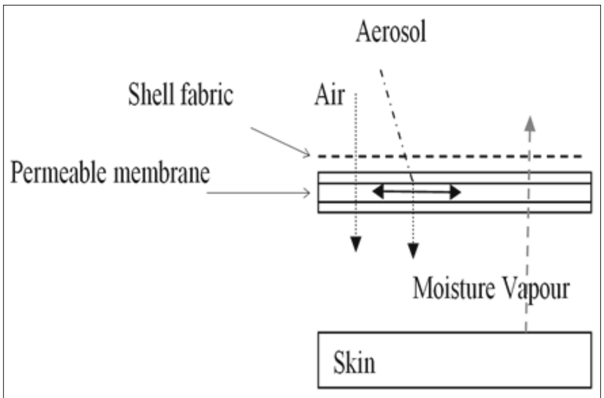

Figure 5: Permeable barrier technology.

protection there is provision to use an adsorbent layer on the fabric in powder form, a nonwoven fabric made from biocide, active fibres (as explained in the next section) and, if required, heat resistant fibres for high temperature applications.

Role of Fibre and Chemical Used

Progress in the field of material science and exploration of materials for different performance with modern approaches is also applicable to CBRN protection. Various materials, including polymers and fibre, are available for protection against CBRN agents and can be used for enhanced protection levels in personnel protective suits. Many studies have been carried out to evaluate these materials against the specific types of CBRN agents and its application to textile. The network of fibre can be used to trap agents, especially in the form of particulate matter. Further, the efficiency of filtration can be extended to capture other form of CBRN agents by adding active agents or by coating with chemicals.

Protection from Chemical Agents

The potential chemical warfare agents used in an attack are generally in the form of toxic gases. For chemical agents above IDLH, an impermeable barrier which has resistance to chemical agents is required. For protective clothing with semi-permeable and permeable barriers, protection from these agents is mainly a gas phase application of adsorption, typically physical and chemical adsorption and by catalysis. The adsorbent and sorbent materials may be applied by lamination or by coating over a fabric or can be combined with nonwoven layers to form a composite structure. They can also be incorporated into the fibres themselves. Decontamination of liquid from the surface of personnel protective equipment involves the use of highly adsorbent fabric in the form of wipes. Table 3 provides a summary of some of the technologies described in this section.

There are varieties of adsorbent and sorbents available that can be applied to clothing for protection against chemical agents. The adsorbents and sorbents generally used are activated carbon[36], activated charcoal[37], silica gel, activated alumina, zeolites, porous clay minerals, and molecular sieves. Various methods of production of activated carbon from PAN-based precursors and specific application for air purification have been discussed by Bajaj and Dhawan[38].

Activated carbon can be used in the form of a composite structure by combining activated carbon with nonwoven layers and can be applied by coating a web with activated carbon particles as well as by impregnating wet laid web with carbon particles[39]. Permeable protective fabrics may contain an activated carbon layer, in the form of carbon loaded open cell foam or bonded carbon spheres to adsorb toxic vapours. In a comprehensive review, manufacturing, modification and application of activated carbon cloth in the adsorption of gases has been described[40].

The behaviour of activated carbon filters in respirators for personal protection against gases and vapours has been discussed by Brown[41]. Activated carbon has the shortcoming of weak physical interactions and therefore requires more chemical reactivity for efficient removal of gases. Thus, early gas masks were large, bulky, and burdensome to ensure proper protection for the user[42]. The chemical reactivity, that is the chemisorption properties, of activated carbon can be enhanced by treating with metal salts of copper, silver, zinc etc.[43,44] to produce materials such as whetlerite carbon.

Whetlerite carbon is in use for nuclear, biological and chemical filtration systems, to degrade highly volatile chemical warfare gases such as phosgene, cyanogen chloride, hydrogen cyanide, etc. also modified whetlerite can used as an adsorbent material for the in-situ degradation of sulphur mustard[45]. For additional protection against blood gases, triethylenediamine (TEDA) can be added. Higher vapour pressure chemicals, which are not removed efficiently by adsorption, are retained by chemical reaction with the carbon's impregnates[46]. Inorganic sorbents like silica gel and alumina are used to trap polar compounds. ASZM-TEDA carbon (activated carbon, impregnated with copper, silver, zinc, molybdenum, and triethlyenediamine) is the current military sorbent recommended for collecting classical chemical warfare agents[47].

Chemically Impregnated Fibres (CIF) are a recently developed technology, using smaller and more active sorbent particles of carbon, permanganate/alumina, or zeolite in impregnation solution. A rayon based activated carbon fibre (ACF) cloth impregnated with organometallic compound such as copper (II) nitrate has been shown to be a useful adsorbent for hydrogen cyanide gas[48]. INDA provides a list of the chemical impregnates required against various gases.

Nanoscience can provide new opportunities for high surface area of adsorbents for many toxic industrial chemicals and acid gases that are not well adsorbed by charcoal or activated carbon. The application of nanotechnology towards chemical protection can take the form of nanofibre that is made by electrospinning, but this only acts as a filter medium. In order to make use of them in removing chemical agents, specific catalytic materials should either be added to the polymers while spinning or coated with active particles after nanofibre fabrication.

A new adsorbent made from an activated carbon and carbon nanofibre (AC/CNF) composite has been prepared for use in a respiratory cartridge which can reduce weight compared to an activated carbon cartridge[49]. Due to their large surface area, electrospun mats possess the desired features for catalyst immobilization as a substrate for adsorbent media and can be encapsulated with ingredients[30]. Active ingredients such as polyoxometalates (POMs) adsorbed on microporous carbons exhibit the best activity for catalytic oxidation of mustard (HD) as reported by Walker *et al*.[50].

Functionalized polymer nanofibre membranes from PVC polymer were also fabricated with β-cyclodextrin (β-CD), o-iodosobenzoic acid (IBA), a blend of β-CD+IBA, and the synthesized catalyst was able to decontaminate paraoxon (a nerve agent stimulant) by hydrolysis[51]. In another study reactive polymer, polyacrylamidoxime (PAAO) and parent polyacrylonitrile (PAN) were blended and oxime-functionalized electrospun fibre mats were produced via electrospinning, which can hydrolytically decompose toxic organophosphate (OP) chemical nerve agents and pesticides[52].

Nanoparticle oxides can be tailored to have solid acid or solid base properties and hence adsorptive proper-

Tested chemical agent	Materials	Principles	Application techniques	Reference
Sarin and mustard gas analogues	MOF-5 Type MOFs	Selectively captures by sorbent	Effective binder is not available	61
Stimulant paraoxon and GD agent	UiO-66-NH2, a zirconium MOF, with polyvinylidene fluoride (PVDF)	Hydrolyse chemical/catalytic degradation	Electrospun fibre mats	63
Stimulant paraoxon agent	UiO-66-NH2, a zirconium MOF preconditioned onto nonwoven polypropylene (PP) fibrous mats	Catalytic degradation	Direct assembly on atomic layer deposition coated textiles	62
Volatile organic compounds (VOCs)	Impregnated activated carbon and carbon nanofibre (AC/CNF)	Adsorption	AC/CNF composite	49
Soman and soman stimulant	Polyoxometalates (POMs), incorporated into activated carbon and combined with metal oxide powders	Catalyst adsorption	Fibres and films form	50
Paraoxon, a nerve agent stimulant	β-CD, IBA, a blend of β-CD+IBA, and synthesized catalyst to PVC polymer	Catalysed destructive adsorption	Nanofibre membranes	51
Toxic organophosphate (OP) chemical nerve agents	Polyacrylamidoxime (PAAO) and parent polyacrylonitrile (PAN)	Hydrolytically decomposing	Electrospun fibre mats	52
Paraoxon nerve agent stimulant	Cellulose/polyethylene terephthalate (PET) blend nanofibres coated with zeolites as catalyst materials	Adsorption	Electrospun polymeric nanostructures	64
Toxic chemicals, nerve agents, phenols, polycyclic aromatic hydrocarbons, etc. non-volatile compounds	A nano-structured xerogel film comprising an immobilized bioactive enzyme, e.g. organo-phosphorous hydrolase	Adsorption and enzymatic degradation	Bioactive layer applied to textile substrate	65
Chemical or biological agents. Example H, G and V chemical warfare agents by XXCC3	Neutralising agent example XXCC3 [90% sym-bis(N chloro-2,4,6-trichlorophenyl) urea and 10% ZnO]	Neutralization	Microporous hollow fibres where the neutralising agents are in the fibre lumina	67
Chemical surrogate to nerve gas soman, example 0.1 % w/v pinacolyl methylphosphonate in butanol	Activated carbon felt (ACN-K) by phenolic precursor to activated carbon nonwoven fabric	Adsorption	Three layered needle punched composite	69

Table 3: Material technology for protection against chemical agents.

ties[46]. Nanocystalline metal oxide can be used for the removal of toxic compounds from the environment by catalysed destructive adsorption[53]. High surface reactivity of nano crystalline metal oxide coupled with high surface area and polar surfaces allows their use for the effective decontamination of chemical warfare agents and related toxic substances. These materials, made up of 4-7 nm MgO, CaO, Al_2O_3, ZnO, and others, exhibit unparalleled destructive adsorption properties even for chemical/biological warfare agents[54]. Metal oxide nanoparticles (MONPs) such as TiO_2 and MgO are currently used as potential catalysts for the decontamination of chemical biological warfare agents[55].

The potential for highly reactive nanoparticles to absorb destructively, i.e. to neutralize highly toxic substances such as the warfare nerve agents GA (tabun), GB (sarin), GD (soman), and VX, has been demonstrated in the laboratory[56]. Rajagopalanet *et al*.[57] show that nanocrystalline MgO reacts much faster and in higher capacity than typical activated carbon samples for organophosphorus compounds. A review[55] explains the various synthetic routes adopted for the preparation of metal oxide nanoparticles MONPs and highlights specific application to textile protection.

Synthetic polymeric sorbents are designed to collect specific chemical classes based upon their backbone structure and functional groups as shown in Figure 6 which shows the action of a metal-organic framework (MOF) in an electrospun mat. The sorbent forms a chemical bond with the contaminant or converts it into more benign chemical compounds. Sorbents[58] cover a wide range of highly porous materials, varying from simple clays and carbons to complexly engineered polymers. Commercially, SARATOGA®[59] is the family of adsorptive compounds dedicated for CBRN protection. MOFs with high surface areas and the ability to tailor chemical functionality in a controlled manner make ideal catalysts for air purification applications.

The removal of various toxic chemicals by MOFs as a sorbent[60] has been discussed, including suitability under water[42]. A study has also been carried out on suitability for the capture of harmful volatile organic compounds (including Sarin and mustard gas) by novel MOFs [$Zn_4(\mu_4\text{-}O)(\mu_4$-4-carboxy-3,5-dimethyl-4-carboxy-pyrazolato$)_3$] as a sorbent at ambient moisture conditions[61]. However, binding these materials to a substrate fabric and maintaining porosity is a challenge, and further work must be conducted to identify appropriate binders.

In a recent work, MOFs are bonded to textiles, like the highly tunable MOF material UiO-66-NH2 onto nonwoven polypropylene (PP) fibrous mats. Here, PP fibre is preconditioned using conformal metal oxide thin films and catalytic degradation of dimethyl 4-nitrophenyl phosphate (DMNP), a chemical weapon agent (CWA) stimulant, has been observed by Lee *et al*.[62]. Another simple method of making MOF-cloth by electrospinning of UiO-66-NH2a zirconium MOF, with polyvinylidene fluoride (PVDF) has been demonstrated by Lu *et al*.[63] who show capability in hydrolysing the chemical warfare stimulant DMNP and chemical warfare agent GD.

Nanofibre films of cellulose/polyethylene terephthalate (PET) have been coated with zeolites as a catalyst and detoxification studies of these functionalized membranes against nerve agent stimulant paraoxon were successful[64]. The concept of active protection against toxic agents, associated with that of self-decontamination, has recently been introduced by integrating biological catalysts (enzymes) also into textiles by enzyme immobilization and stabilization technologies. In one patent, a bioactive layer comprising a nano structured xerogel film with an immobilized bioactive enzyme has been applied to a textile substrate for protection against toxic chemicals such as pesticides, nerve agents, phenols, polycyclic aromatic hydrocarbons[65].

Cireli *et al*.[66] have coated plasma modified polypropylene fabric and cotton fabric with sol-gel derived carbon xerogel to prepare a specific fabric for separating and protecting breathing air from volatile organic compounds (VOCs). Barer and Besso[67] have patented a fabric made from microporous hollow fibres where the neutralising agents for detoxifying chemical or biological agents in the fibre lumina can be added. According to the required application and range of neutralizing agents can be added, but for this invention the neutralising agent XXCC3 [90% sym-bis (N chloro-2,4,6-trichlorophenyl) urea and 10% ZnO] is preferred for the protective fabric which can neutralize the H, G and V series of chemical warfare agents, as well.

For high level of protection from chemical agents,

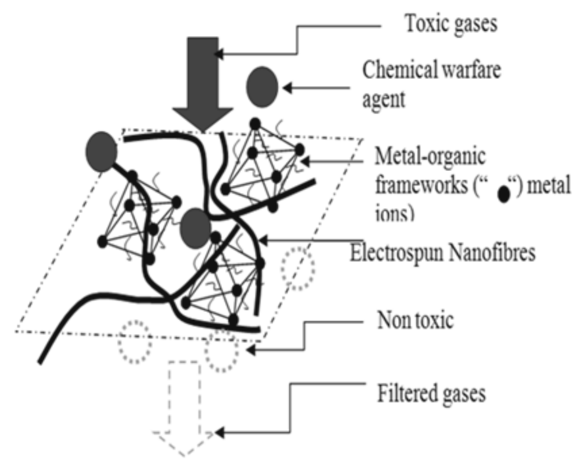

Figure 6: Purification action of metal-organic framework (MOF) in an electrospun mat.

where the chemical is present on the surface of clothing and for splash resistance fabric, the contaminant has to be removed using highly adsorbent materials. A decontamination pad for removal of CB agent has been patented which includes an adsorptive/absorptive knitted activated carbon layer exposed on a first surface, an activated carbon fabric attached to the other surface of the knitted layer and backed up on an impermeable layer[68]. A three-layered nonwoven cotton-based decontamination cotton wipe with activated carbon has been developed for cleaning up a chemical surrogate to the nerve gas soman, which can adsorb and neutralize gases and liquids that might be used in chemical warfare[69].

Protection from Biological Agents
Similar to chemical protection, fabric that is designed for biological protection and made from micro- and nano- fibre will provide the filtration but for enhanced applications a biologically active agent (biocide) and active agents should be added or be applied in the form of a coating. Biological agents of higher level pathogens like bacteria and viruses can be removed either by a fibrous assembly just by filtration or by special techniques such as the use of treated fibres, oil coating etc., and combinations thereof[70].

Not only is removal or trapping of biological agents required, but their growth must also be inhibited using antimicrobial agents. There are various types of antimicrobial agent that can be added just before extrusion, during fibre formation or applied over the surface of the textile substrate in the form of finishing agents, and these have been listed out in a comprehensive review by Gao and Cranston[71]. Table 4 provides a summary of some of the technologies described in this section.

Fibrous assembly made from cotton, fibreglass, polyester, polypropylene, or numerous other materials can be treated with antimicrobial agents for biological protection. Antimicrobial treatments include silver, silver salts, quaternary ammonium groups, and extensively conjugated dyes that act as oxygen photo activators[72]. Thermoplastic compounds that can be used for incorporating antimicrobial agents include materials such as polyamide (nylon 6 or 6,6), polyvinyl, polyolefins, polyurethanes, polyethylene terephthalate and styrene butadiene rubbers.

Like discussed earlier for the patent by Barer and Besso[67], neutralising agents for detoxifying biological agents can also be added in the fibre lumina. Foss Manufacturing Co. has patented a fibre technology for making synthetic antimicrobial fibre by incorporating inorganic antimicrobial additives. The polymer and additives in a monofilament or bi component form either a core sheath or a side by side configuration[73].

There is also the possibility of adding a bioactive agent during the meltblown process at different stages. A technology and appropriate manufacturing equipment have been developed to produce bioactive polypropylene fibres devoted to meltblown nonwovens. A nonwoven bioactive filter with antimicrobial agent (Sanitized® 99-19), containing quaternary ammonium salts has been produced by different production technologies (meltblowing, needle punching) and methods of biocide incorporation (bath, spraying). Higher biological activity was found in nonwovens subjected to a bath than in those which underwent spraying. Compared to meltblown nonwovens, the needled variety were more efficient[74].

A meltblown nonwoven fabric was modified[75] by introducing perlite as a biocidal agent into a polypropylene polymer stream with the help of a fibre-forming head and is recommended for constructing bioprotection in a respiratory system. Poly lactic acid (PLA) was used when validating model meltblown nonwovens for the construction of respiratory protection devices (RPD) against biological hazards. Conclusions were that the presence of biocide within the filter structure did not indicate a clear influence on bacteria survival while filter samples charged with the use of corona discharge can partly improve bioactivity of the filters[76].

Media should have more sites or surface for attachment of antimicrobial agents. The nanofibre mat made from electrospinning provides the high surface area for chemical attachment of biocides and other reactive compounds onto the inner liners of protective fabrics. In this manner bactericidal fibre mats were produced from the electrospinning of blends containing a biocide chlorhexidine (CHX) and other additives. The resultant fibre mats demonstrated bactericidal properties and killed representative bacteria of E. coli and S. epidermidis [52]. Bacteriocins were released from electrospun nanofibres and dissolved in N,N-dimethylformamide (DMF) which can be used to stop microbial growth[77].

Antimicrobial nonwoven can be produced by grafting the biocidal agents with fibre forming polymers. Examples are quaternarized N-halamines[78,79] and quaternary ammonium/N-halamine[80] chemically grafted onto cellulose for antimicrobial property. Similarly, cationic polymer can be grafted to silver chloride modified cellulose fibres[81]. Polyester can also be covalently linked with heterocyclicmoieties (which could also be halogenated) to the surfaces of the polyester fibres then antimicrobial agents can be introduced into fibres by exposure to a source of oxidativechlorine[82]. Liu *et al*.[83] grafted polypropylene with N-halamine precursor, 2,4-diamino-6- diallylamino-1, 3,5-triazine (NDAM) followed by meltblown nonwoven fabric manufacturing and evaluated it for antimicrobial property as well as for respiratory resistance. Bacteria were killed by action of the active chlorine that were released by the PP -g–NDAM. PP can also be grafted at the fabric stage.

In one research paper, nonwoven fabric was grafted by using silane as the coupling agent with chitosan or $AgNO_3$ for antibacterial property[84].

It is also possible to imbibe functional properties through coating. N-halamine1-chloro-2,2,5,5-tetra-methyl-4-imidazolidinone can be coated onto polypropylene meltblown nonwoven fabrics, which exhibited great potential for use in protective face masks and air filters to combat airborne pathogens[85]. Lim *et al.*[86] have prepared multifunctional fibres by decorating with noble metal (Ag, Au and Pt metal) on the surface of polyester (PET)/PET-TiO_2 bicomponent filaments by means of photocatalytic deposition.

In a further study the authors made effective anti-bacterial PET filaments with enhanced antimicrobial property by selective photo-deposition of metal nano-particles on TiO_2 within tetragonal and cross-pillar shaped PET filaments. Ag and Pt metal photo-deposited fabrics of these fibres showed an excellent antimicrobial effect against two types of bacteria, staphylococcus aureus and klebsiella pneumonia, even in the dark condition and without the use of UV light[87].

It was found that precoating of filter fibres with TTO (Tea Tree Oil) could provide significant benefits in terms of rapidly inactivating captured microorganisms and look very promising for implementing this new technology in bioaerosol control[88]. Antibacterial treatment of nonwoven fabrics is easily achieved using nanosized silver colloidal solution. It was found that the bacteriostasis of water-based silver colloidal solution padded nonwovens is excellent against S. aureus

Tested biological agent	Materials	Application techniques	Reference
Escherichia coli bacteria	Microban® additive IB12 (active compound – silver), Viroksan (active compound – magnesium monoperoxyphtalate), to polypropylene	Meltblown	90
Moulds, yeast, and bacteria	Antimicrobial agent (Sanitized® 99-19) and containing quaternary ammonium salts to polyester and polypropylene	Meltblowing and needle punching	74
E. coli and S. aureus bacteria	Bioperlite additive to polypropylene	Meltblown	75
E. coli and S. epidermidis	Chlorhexidine (CHX)	Electrospinning	52
Enterococcus faecium HKLHS and listeria monocytogenes EGD-e	Plantaricin 423 bacteriocins	Electrospun for controlled delivery	77
Gram negative E. coli and gram positive S. aureus	Grafted cellulose fibre with quaternarized N-halamine	Coating of fibre with quaternarized N-halamine	78
Staphylococcus aureus and Escherichia coli	Grafted monochloro-s-triazine-based N-halamine precursor to cotton	Reactive dyes, dyeing method to bond HB onto cotton fabrics	79
Pathogenic microorganisms	N-chloramine functionalities to polyester	Chlorine bleach	82
Gram negative E. coli and gram positive S. aureus	Grafted polypropylene with N-halamine precursor, 2, 4-diamino-6- diallylamino-1, 3, 5-triazine (NDAM)	Meltblown	83
Bacteria	Grafted polypropylene by using silane coupling agent with chitosan or $AgNO_3$	Grafting at fabric stage	84
Bioaerosols of Staphylococcus aureus and Escherichia coli	N-Halamine1-chloro-2,2,5,5-tetramethyl-4-imidazolidinone	Coated onto polypropylene meltblown nonwoven fabrics	85
Staphylococcus aureus and Klebsiella pneumonia	Coating metal (Ag, Au and Pt metal) nanoparticles on the surface of polyester (PET)/PET-TiO_2 bicomponent filaments	Photocatalytic deposition	86
Staphylococcus aureus and Klebsiella pneumonia	Coating metal (A and Pt metal) nanoparticles on tetragonal and cross-pillar-shaped PET/TiO_2 filaments	Photocatalytic deposition	87
S. aureus and K. pneumonia	Nanosized silver colloidal solution	Padded nonwovens	89

Table 4: Material technology for protection against biological agents.

and K. pneumonia[89] where nanosilver damages the cell wall and the genetic composition of bacteria.

There are other techniques encompassing the use of cell lytic enzymes which represent an alternative to chemical decontamination or use of antibiotics to kill pathogenic bacteria, such as listeria. The surface incorporation of the listeria bacteriophage endolysin by covalent attachment to silica nanoparticles has been studied by Solanki *et al*.[91]. These enzymes, depending upon the target bacteria, can be selected and attached to silica nanoparticles or conjugates in a thin polymer film. A novel technique for killing microbes was introduced by Lakeland's MicroGard® treatment for use in the constituent part of glove fibres[92]. The technique attracts microbes using a miniscule electrical charge and instantaneously punctures their cell wall with a microscopic spike.

Protection from Radioactive Agents

Nuclear hazards require protection from radioactive particles and ionizing radiation. The radioactive particles can be removed using the principles of particulate filter and air cleaning, but rather than blocking particles or liquids, the garment must be designed to minimize the penetration of radioactive materials[93]. A simple example of removing radioactive particles from air by filtration is using glass fibre[94]. Glass fibres possess a high strength to weight ratio, have endurance to high thermal shock, outstanding dimensional stability, excellent moisture resistance, high surface area-to-weight ratio, and good chemical resistance[95]. Table 5 provides a summary of some of the technologies described in this section.

In one patent, a nonwoven fabric is designed for the removal of radioactive substance like organoiodines in small amounts from the gas phase by use of activated carbon fibre[96]. The activated charcoal can be impregnated with chemicals to enhance the removal efficiency for radio iodine. The impregnated chemicals are usually either iodine (I), potassium iodide (KI) or triethylenediamine (TEDA)[97]. Similarly, carbon fibre can be impregnated with potassium iodide, hydrogen sulphide, phosphine, mercury, arsine, TEDA, to remove the radioactive methyl iodide particles.

Obruchikov and Lebedev[98] studied the removal of radioactive methyl iodide from an air vapour mixture by adsorption on a Busofit carbon fabric modified with different additives. Out of the tested impregnates, the use of a barium iodide diazabicyclooctane complex compound as an impregnating reagent showed the most promising results. The adsorption properties of carbon fibre busofite type materials was studied and compared[99] with various sorbents.

It was found that compared to SKT-3 activated carbon, the efficiency of busofite activated carbon is higher for the removal of molecular iodine and methyl iodide from air. The authors also concluded that with thin layers of carbon fibre cloth it is possible to produce small filters/absorbers for catching iodine from the gaseous phase and furthermore carbon fibre cloth can be used together with Filtering Polymeric Fibrous Materials (FPP) material or glass fibre for filtering other agents from aerosols as well. As carbon fibre is heat resistant and hydrophobic it can be used in zones where high temperature and undesirable vapour phase agents are present.

Nanostructures also offer the possibility for selective adsorption of radioactive materials[46]. Using the electrospinning method, the novel nanofibre adsorbent polyvinyl alcohol/titanium oxide/zinc oxide (PVA/TiO_2/ZnO) functionalized with 3-mercaptopropyltrimethoxysilane (TMPTMS) was prepared[100] and its potential investigated for the adsorption of thorium from metal aqueous solutions.

Protection from Nuclear Agents

Nuclear weapons emit large amounts of thermal radiation as visible, infrared, and ultraviolet light known as 'Flash'[101] and radiation energy in the form of electromagnetic waves or charged particles. Electromagnetic waves of radiation include x-rays and gamma rays, and particulate radiation includes alpha, beta, and neutron radiation[13]. Therefore, the protection strategies from nuclear agents include protection from thermal flash and ionizing radiations.

Nuclear weapon flash burns are not only confined to the exposed areas but also affect through varying thickness of clothing. This in turn lowers the protection

Tested chemical agent	Materials	Application techniques	Reference
Sample aliquots of radioactive aerosols	Glass fibres	Fibrous matt	94
Radioactive methyl iodide from an air vapour mixture	Busofit carbon fabric modified with different additives like impregnates of barium iodide diazabicyclooctane complex compound	Busofit carbon treated fabric	98
Thorium from metal aqueous solutions	Novel nanofibre adsorbent PVA/TiO_2/ZnO functionalized with 3-mercaptopropyltrimethoxysilane (TMPTMS)	Electrospinning	100

Table 5: Material technology for protection against radiological agents.

level of clothing in terms of time span[102]. Therefore, the first requirement of heat flash protection is to have a flame-resistant outer which is able to reflect the maximum amount of radiation back[103] and to provide effective protection from radiant heat exposures. Emissivity, absorptivity and thermal resistance are the most important fabric properties[104]. The use of an impermeable membrane in the fabric system helps to minimize heat and mass transfer in double and multilayer fabrics[24]. So, the use of a reflective layer in the design of clothing will provide the first line of defence against thermal radiation when dealing with nuclear agents.

Example reflective layers include aluminized PET film (Mylar)and other RF shielding products. Apart for aluminium, two other metals, namely gold and silver, have more reflectance and can be used in the form of a film but are less cost effective[105]. Limited shielding may also be provided by using lead based materials[31]. Flexible aprons are available to shield the upper torso with a thickness up to as 0.33 mm of lead able to attenuate about 90% but only for low energy radiations[106].

The radiant and flame protective performance of aluminized fabrics have been studied by Jin *et al*.[107]. These were prepared using different aluminized films and different base fabrics. It was found that the radiant protective performance of aluminized fabrics is influenced by the base fabric, especially its surface roughness, and that the contribution of aluminized films to flame protective performance of aluminized fabrics is not as significant as to radiant protection. A similar study was carried out by Gahne and Sarlak[108] on radiant heat flux transfer through aluminised multi-layer fabric consisting of a layer of aluminium foil, glass fabric, and a layer of cotton fabric. Results showed that aluminised multi-layer clothing decreases the temperature of the skin sur-face significantly during exposure to a low radiant heat source.

Smart materials like microencapsulated phase change materials[109,110] for radiant heat protection have been developed for heat absorption and can be employed to avoid heat burn from radiation. Colourants are also available which can provide the protection against the radiations by increasing the reflectivity of the fabric after changing to colourless forms[111]. A study on the effects of moisture level on predicted second degree burn injury and heat transfer analysis for permeable turnout systems was carried out by Barker *et al*.[112]. They found that moisture negatively impacts on protective performance and suggested a similar future study for turnout with a vapour impermeable reflective layer.

In earlier research it has been found that Irradiation with nuclear radiation significantly reduced the strength of cotton yarns and the presence of water vapour and atmospheric oxygen during irradiation has little or no effect on the strength of the cotton yarn[113]. The relative order of stability toward nuclear radiation of some cellulosic fibres investigated was in the order acetate > rayon > cotton[114]. For wool fibre, the long-range elastic recovery was not lost, and considerable retention of strength was observed after expose to nuclear radiation[115]. In the case of Dacron polyester filament, the modulus of elasticity can be increased by exposure to high energy radiation due to crosslinking reactions at the early stages of irradiation[116]. In the case of gamma irradiation, serious weakening of cellulosic fibres and Nylon was observed but there was no visible effect on the strength of Type 81 Orion[117].

The fibre used in filter media should be synthetic rather than cellulosic. After capturing radioactive particles, it should be decontaminated as early as possible to limit the chance of a change in fibre properties and hence the performance.

Commercially, Tyvek® Classic Xpert, Tychem® C and Tychem® F garments are available for clothing that protects against radioactive contamination[93]. Another garment Tychem® ThermoPro provides triple hazard protection from chemicals, flash fire, and electric arc, and can be used to avoid burn injuries[118]. It is suggested to wear non-melting materials under Tychem® ThermoPro garments, these could include NOMEX® or other non-melting fabrics such as wool, cotton, silk and rayon[119]. Single skin construction Tychem® Reflector® garments are composed of heavy duty aluminized fabric made of a DuPont™ Nomex® / Kevlar® blend, laminated to a multi-layer barrier film[120]. The protective anti-nuclear garment is made of Demron, the only polymeric nano-metal fabric to offer true anti-nuclear radiation protection.

Techniques for Combined Protection

Sellik *et al*.[121] studied the capability of a single metallic oxide (magnesium oxide, MgO) to neutralize a chemical agent and to exhibit an antibacterial effect. This oxide acts through hydrolysis and oxidation reactions on the chemical agents and via hydrogen peroxide and oxygen containing intermediates and/or by direct action on the bacterial structures and leads to the formation of non-toxic degradation products because of their small size.

A project run by a US army chemical technology team for the development of protective clothing with self-detoxifying materials for CB protective clothing utilised an inner meltblown layer with carbon, an electrospun middle layer with catalyst and a treated outer shell of knitted fabric. The catalysts included were organophosphorus acid anhydrolase, polyoxymetalate and IBA-CD Iodosobenzoic acid-substituted β-cyclodextrin for the removal of G- agent, VX and mustard gas. The biolocidal treatments included treatment of fabric and films with N- halamines chemically grafted onto cellulose and Quarternary ammonium salts with alkyl chains chemically bond to fibres using dye molecules[122].

Another self-detoxifying suit is made by using an air impermeable concept with cover fabric, semi-permeable membrane and knit comfort liner placed within a chemical and biological garment that reacts with and decontaminates CWAs on contact[123]. The Demron suit made from nano-metal fabric offers chemical, biological, radiological, and heat stress (CBRN) protection.

Garment Construction

The construction of an encapsulation suit for first level of protection requires joining of all panels of the garment with accessories like zippers to ensure no leakage. For the construction of a suit for lower level of protection, like a firefighter suit, enough ventilation[124] and slits in the garment will aid heat loss.

The air gap between the fabric and skin also affects the skin burn further[125] and loose clothing can be selected to help avoid burns. The seam is sewn and then heat sealed to ensure complete impermeability for level 1 protection[92]. The seams used in protective garments are serged seams for disposable clothing where dry particles are a concern and bound seams with little improved liquid and particle repellency. However, for higher level of protection at levels A & B heat sealed seams are used in which seam is sealed by heat activated tape. For an additional and higher level of protection, stitched & double-taped seams can be used and especially for gas tight suits[126].

Material Development Based on Level of Protection

For the highest level of protection, that is first and second level, there is no compromise with protection, it is compulsory to use an impermeable barrier to ensure complete leak proofing even though semi-permeable barriers are available. This can simply be achieved using a coating and it includes the use of a reflective layer for nuclear radiation. For third level of protection there is a requirement to use a semi-permeable layer and a permeable barrier for fourth level of protection, to achieve comfort along with protection. As the use of semi-permeable and permeable barriers involve the passage of air through the clothing, there is a requirement to use adsorbent and sorbent, biocidal agents with clothing for added protection. As shown in the Figure 7, the selection of barrier and material technology is based on the level of protection.

Material Development Based for First Level and Second Level of Protection

Encapsulated suit with impermeable layers must be used for first and second level of protection made by coating technologies, the only difference is in the expected permeation resistance and the resistance to a number of chemicals.

Special coated material must be used to make a fully impermeable barrier for PPE. However, the protected internal environment of a totally encapsulating suit induces rapid fatigue and heat stress, limits vision, and impair communications. Many HAZMAT suits are made of barrier fabric laminates that are completely impermeable, like Tyvek reinforced polypropylene film laminates with a rugged outer shell fabric such as aluminized Kevlar and polybenzobisoxazole (PBO), worn with butyl rubber gloves[72].

One of the earliest film-based fabrics to be developed was SARANEX 23 (DOW) laminated to TYVEK (DU PONT). SARANEX barrier films are multilayer polymer (plastic) films consisting of a SARAN resin (polyvinylidene chloride, PVDC) core layer and different types of thermoplastic polymer resins for the outer layers[127]. Another patent[128] issued to Kappler, describes composite chemical barrier fabric that is heat sealable and exhibits greater than 8 hours permeation resistance to all ASTM F1001 chemicals.

Tychem® TK exhibits an outstanding chemical barrier and comprises three layers, PVC, Teflon and PVC[129]. Its barrier has been tested against 260 challenge chemicals with no observed breakthrough after exposures of up to 8 hours. Tychem® Responder® CSM is a patented fabric specially developed for chemical weapon demilitarization and made of multiple barrier films laminated to both sides of a high strength polypropylene substrate[130]. Similarly, Tychem® BR Multilayer composite barrier is made by laminating to a strong, nonwoven substrate[31]. Ansel Barrier® HPPE 5 layer laminated barrier with permeation breakthrough

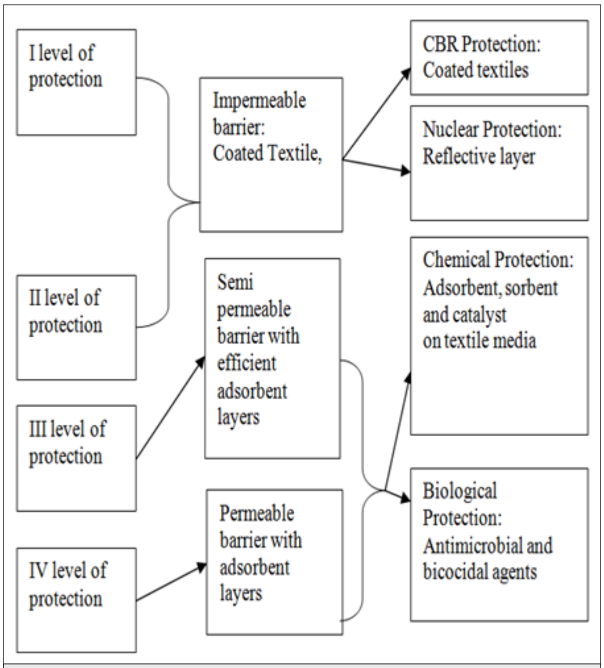

Figure 7: Designing of personnel protective clothing against CBRN agents.

times as per EN374[131], Interceptor®[132] and Zytron 500[133] garments are other garments that are designed for first level of protection.

For heavy liquid hazards, multilayer fabrics in the form of coverall to encapsulated configuration like ChemMax® 3 and ChemMax® 4 with six-layer protective barrier and Dupont Tychem® CPF 3 multilayer fabrics are commercially available products. For further protection from heavy liquid splash up to the level A multi-layer composite barrier laminated to a strong, nonwoven substrate like Tychem® BR Tychem® LV can be the choice. One such suit with first level of protection is the military's toxicological agents protective (TAP) suit. The HAZMAT suit also comes under this category.

Material Development for Third Level of Protection

Third level of protection includes protection against minor splashes and also protection from light splash. This is made possible using a semi-permeable layer and by using fabric made from a porous web such as SMS fabric, laminated by microporous film, or a web made from micro- and nano- fibre can be employed. As these barriers are permeable to air, a technology for capturing toxic gases has to be used along with this barrier as discussed previously.

For protection against light splash the suits available are ChemMax® 1 constructed with a unique polyethylene barrier film and a continuous filament polypropylene nonwoven and PROSHIELD® NexGen® with a microporous film laminated to a nonwoven fabric. Furthermore, protection from ChemMax® 2, Tychem QC polyethylene coated fabric and Tychem SL can be used for a little more protection.

Materials for selectively permeable membranes (SPMs) are made up of films of poly(vinyl alcohol), cellulose acetate, cellulosic cotton, and poly (allylamine). These SPMs have been tested and are effective barriers to CB agents[72]. A functionalized polymer such as organic acid-modified ionomer for selective permeability clothing system can be used in the form of composites films fastened over a fabric just by overlaying, or alternately can be adhered to clothing by means of heat sealing, high frequency welding or adhesive[134]. There is also scope to use a porous functional fibre made by the mixing of active particles during spinning[135].

One example of a commercially used SPM in fabric is the GORE® CHEMPAK® selectively permeable membrane which is made with a non-carbon based membrane that does not adsorb chemicals or degrade over time[136]. In a patent Langley *et al*. invented selectively permeable chemical protective films and composite fabrics that will provide chemical protection and moisture vapour transmission and allow evaporative cooling to occur[127].

The IAAFF Team investigated and evaluated selectively permeable materials that could be implemented in a garment system[137]. One such application is Joint Service Lightweight Integrated Suit Technology (JSLIST) which is designed for protection against CBR agents, and battlefield contaminant where the bulky charcoal layer is replaced with a selectively permeable membrane to reduce the weight and to obtained more comfort[138]. Similarly, another suit with selectively permeable barrier is the LION Extended Response Suit (NFPA 1994 Class 3 Ensemble suits) which comes with a trilaminate construction and consists of selectively permeable barrier film laminated between outer and inner knitted textiles[17].

Material Development for Fourth Level of Protection

Protection against dry particles is generally based on their particle size. For very fine particles greater than 1 micron a single barrier of SMS fabric is sufficient as in case of SafeGard® SMS fabric and Tempro®. For particles size less than 1 micron the fabric comprising of 3 barrier layers is sufficient as in the commercially available Micromax® NS, Micromax® 3P.

Another example is the firefighter suit, where for managing heat stresses ventilation strategies can be used. Challenges to ventilation such as garment placement, protection, wearability and durability has been discussed for protective firefighter suits[124]. The comfort level of firefighter suits with chemical and biological protection has concluded that there is less comfort compared with a standard ensemble[139].

One example where a permeable barrier can be used is Structural firefighters' protective clothing with self-contained breathing apparatus (SCBA) which may provide limited protection against some hazards. Barker *et al*.[140] developed a prototype protective firefighter suit with added chemical and biological (CB) protection.

TEST METHODS FOR CBRN CLOTHING

For CBRN protective fabric, other than general physical testing it is more important to test against penetration and permeation. The penetration test includes the measurement of penetration resistance or repellency of clothing against the specific CBRN agent present in liquid form. The related standard methods for liquid penetration testing are: ASTM F903 - 10 inter laboratory results suggests that it gives a relatively high confidence in the precision[141], ASTM F1359 / F1359M - 16a and EN463: 1994 - 'Jet Test', EN468: 1995 - 'Spray Test' are for the whole garment.

The permeation test includes the measurement of permeation in terms of breakthrough time of clothing against the specific CBRN agent present in gas form (ASTM F1001 Permeation Data for ASTM Recommended List of Chemicals), at specific time and concentration. The related standard methods for liquid permeation testing are ASTM F739 - 12e1, EN374-3 or EN ISO 6529 and TECMIPT Test Operations Procedures (TTOP) 8-2-501 (Swatch Testing)[142].

Conventional permeation test procedures were significantly modified by developing a model based on real data and the application of the new procedures to several chemical material systems showed more consistent measurements of chemical barrier performance in measuring cumulative permeation as compared with determining breakthrough times[143]. The test methods for evaluating performance against the CBRN agents present in the form of solid particulates are DIN EN ISO 13982-1, CSN EN 1073-1.

Developments are on-going to make tests more realistic. Ormond and Barker[144] investigated the variability of human subject testing compared to that of the manikin testing by developing the next generation manikin CB protection research. The Man In Simulant Test (MIST) is to evaluate the ensemble in actual condition to human subject by using nontoxic stimulant[145]. The ASTM F2588 and TOP 10-2-022 standards explain the Man-In-Simulant-Test (MIST) which is the primary method for the evaluation of full ensemble chemical protective clothing. There are various other test methods which are very specific to the given application and condition like ASTM F 2701-08 test method for evaluating heat transfer through protective clothing upon contact with a hot liquid splash.

CONCLUSIONS

With the increasing use of CBRN agents and their incidences, efficient personnel protective suits must be designed accordingly to include appropriate barrier and material technologies. The agents present in particulate form can easily be trapped by porous textile media but for toxic gases and biological agents there is a need to use active agents over a textile media.

Various adsorbent, sorbent, catalyst and biocidal agents are available that have been tested against harmful chemical and biological agents. These agents can be applied to textile media through various techniques, by impregnating fibres, coating over a fabric, multilayer composites, adding polymer melt into the fibre and sometimes by in-situ polymerization with fibre forming polymer. There is also scope to use novel materials with appropriate application techniques for the further enhancement of protection performance in protective suits.

Further work is required to develop barrier technologies with consideration of comfort. In general, greater protection often leads to multilayers and a bulky suit which affects comfort and impedes performance of the wearer. Therefore, the design and development of a protective suit is a great challenge. It is also felt necessary to use a single layer structure to reduce the bulk and weight of clothing. For this purpose, a selectively permeable barrier is preferred - even though commercially available they are not efficient enough for higher level of protection. However, developments are still going on here to achieve improved protection against CBRN by using thinner textile ensembles.

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