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REVIEW PAPER

Respiratory Protection Against Chemical and Biological Warfare Agents

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ABSTRACT

Chemical and biological warfare (CBW) agents pose unavoidable threat, both to soldiers and civilians. Exposure to such deadly agents amidst the CBW agents contaminated environment can be avoided by taking proper protective measures. Respiratory protection is indispensable when the soldiers or civilians are surrounded by such deadly environment as contamination-free air is needed for respiration purposes. In this context, an attempt has been made to review the literature for the past five decades on development of various protective devices for respiratory protection against aerosols, gases, and vapours of CBW agents. This review covers structural, textural, and adsorption properties of materials used in gas filters and mechanical filters for the removal of CBW agents.

Keywords: Chamical warfare agents, biological warfare agents, respiratory protection, gas filters, mechanical filters, aerosols, CBW

1. INTRODUCTION

Air is a unique source of oxygen needed by a human being for respiration. It should be free from toxins and in breathable form to support life. Contamination of the same can occur either intentionally or accidentally, and depending upon its intensity and makes the life difficult. Chemical and biological contaminants with toxic properties have been abused as debilitating agents ever since these were employed in the WWI and were identified as chemical and biological warfare agents[1].

The use of chemical weapons was intended to cause maximum possible terror in the minds of the enemy with minimum mortality so that their morale was affected[1-2]. The chemical weapons, when deployed, rapidly fall on to the ground and exist in the environment as aerosols, vapours, and gases. By the time enemy detects these, they inhale the chemicals which would most effectively incapacitate them, helping in disarming and capturing the enemy[3].

The chemical warfare agents can be classified as non-persistent and persistent. Blood agents, choking agents, etc, fall into the category of non-persistent chemical warfare agents due to their low boiling point and high volatility, and nerve agents, blister agents, arsenicals, etc, come under the category of persistent chemical warfare agents owing to their high boiling point and low volatility. Only way to overcome the adverse effects due to chemical and biological warfare (CBW) agents is to take proper protective measures. Obviously, one has to understand the subject and practice it without which one is bound to make mistakes, thereby putting his/her health in deleterious conditions.

At a glance, the subject of protection is vast and to acquire better understanding, it is classified as technical and tactical protection. Technical protection discusses the technical aspects of methods, materials, and equipment to be used for the protection against CBW agents. It can further be classified as individual and collective protection systems depending on the number of personnel or groups to whom protection is to be provided. Individual protection involves the methods and equipment that an individual can use for protecting himself against toxic chemicals. Equipment such as gas mask, canister, protective clothing are discussed in detail. Chemical, biological, proof shelters, filtration systems, protection of food, water, and other supplies for more than one personnel are dealt in collective protection. Tactical protection, however, deals with movement and military action and measures to be taken for the deputation of staff to assist the troops to carry out missions without casualties and shifting of casualties and their treatment.

In the individual protection system, gas mask along with canister, protective clothing, gloves and boots are necessary and every individual must know the use of the equipment and its protection time. The equipments provide the protection for whole human body. Further, individual protection can be classified into respiratory protection and body protection. The protection provided to lungs and other parts of respiratory system in a contaminated zone and supply of breathable air amidst the contaminated zone is called respiratory protection. Body protection includes the measures to be taken for the protection of skin and other parts of the body such as hands, legs, skin, etc against blistering agents and other skin-penetrating toxic chemicals.

However, the protective measures are mainly dependent on the properties of the warfare agents and the extent of their exposure. Respiratory protection is of great importance

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as breathable air is the primary requisite for any individual and it can be provided by the gas mask and canister. This equipment provides protection for eyes, lungs, and other respiratory organs, thereby providing breathable air.

Gas mask is usually made of rubber materials which have the facility to integrate respiratory cartridge, eye lens to visualise, tube to drink water, and a valve for exhaling the air and facility to talk. The respiratory cartridge or canister attached to gas mask contains gas filter and aerosol filter. Activated charcoal impregnated with suitable metal salts, catalysts work as a gas filter and mechanical filters like felt or HEPA (high-efficiency particulate aerosol filter) work as aerosol filter[4]. The performance of the canister mainly depends on the mechanical filter and gas filter. The efficiency or service life of the gas filter and mechanical filter is influenced by the adsorption capacity of the gas filter. Adsorption capacity further depends on breakthrough behaviour of chemicals on gas filter, reactivity of the gas filter, physicochemical properties of mechanical filter and also mechanism of particulate capture, etc[5]. Keeping the above aspects in mind, various principles which describe the phenomena occurring in the protective equipment, their life time, methods of use, recent developments, etc, have been discussed.

2. PRINCIPLES OF RESPIRATORY PROTECTION

2.1 Creation of a Barrier

Protection to an individual or a group of individuals amidst the contaminated environment can be provided by creating a barrier between the individuals and the contaminated environment. In a clear sense, the individual should be separated from the contaminated zone by means of a barrier to avoid all possible chances of exposure to the chemical and biological warfare agents. Reliability of protection is critically influenced by the performance of the barrier when used against the agents, where, performance of the barrier is decided by its protective potential. Barrier with better protective potential can provide endurable protection to individuals against the CBW agents. The protective potential of the barrier depends mainly on its thickness, concentration of the agent which surrounds the barrier, type of the agent, its reactivity towards the barrier, temperature, materials by which the barrier is made, etc.

Apparently, larger the thickness of the barrier, better the protection provided to the individuals and it should be neutral towards the known chemical and biological warfare agents. Certain agents such as sulphur mustard have a tendency to penetrate the barriers, thereby deteriorating the protection levels[6-9]; hence, barriers should be efficient enough to avoid penetration of blister agents and corrosive agents like phosgene. Acid gases like phosgene and hydrocyanic acid corrode the stainless steel or metal barriers; hence, alternatives need to be identified.

Literature revealed that polymer or rubber coatings to stainless steel or metal barriers provide better protection against such gases[10-11]. However, metal panels, concrete bunkers, special rubber panels do not supply breathable air, water, etc, hence, need provisions. Porous provisions should be made in the barrier to allow breathable air, water, etc, and stop or hold contaminants like CBW agents. Filtration system can work as a porous barrier and provide breathable air and potable water by encapsulating the contaminants within itself. Encapsulation of the contaminants by the filtration systems usually takes place through physico-chemical phenomena such as physical adsorption or chemical adsorption, interception, impaction and diffusion, etc, and the occurrence of these phenomena is facilitated by the so-called gas filters and mechanical filters[4]. Adsorbents of high surface area have the capability to adsorb the contaminants, either physically or chemically, from the contaminated environment.

Mechanical filters, such as felt and high efficiency particulate aerosol filter, have the capability to remove the contaminant aerosols, dust particles, etc. Filtration system integrated with both mechanical filtration system and gas filter can effectively be used as a barrier for providing respiratory protection, either to individuals or group of individuals, against the chemical and biological warfare agents and nuclear dust.

2.2 Gas Masks–Historical Development

Protection against aerosols, vapours and gases containing the chemical and biological warfare agents and other toxic materials is of primary importance in the event of war, terrorist attack or accidental release. It can be achieved by wearing a gas mask to protect the face, eyes, nose, and lungs against poisonous gases, vapours, and bacteria. It is airtight, avoids leak from the peripherals except for connection with a neutraliser.

As per the literature, on US patent published in 1849, the gas mask was invented in 1847 by Lewis P. Haslett of Louisville, KY and the first design allowed breathing through nose or mouthpiece fitted with valves that permitted inhalation and exhalation of air[12]. Inhalation of breathable air was facilitated by a filter containing wool or porous material which was able to filter out the solid particulates but was found ineffective against aerosols, gases, vapours of poisonous gases, and bacteria. Followed by this, John Stenhouse[13-14] thoroughly investigated and realized the enhanced capability of activated charcoal relative to other adsorbents to hold toxic gases and to remove the contaminants from the polluted environment. He fabricated a design by incorporating charcoal-based filters in gas masks by keeping the powdered activated charcoal between the wire gauges.

In 1871, Tyndal[15] invented a gas mask that was incorporated with a respirator consisting of a valve chamber and a filter tube about four inches long, screwed on outside with access to it from the inside by a wooden mouthpiece. The respirator consisted of cotton wool saturated with glycerine, lime, and charcoal. Use of wool was intended for the removal of dust and smoke particles and the charcoal was intended for removing organic vapours. Following this, in 1874, Barton[16] designed a device consisting of rubber and metal face cover, head harness, glass eyepieces, rubber, and coated hood, exhalation and inhalation valves. The device was also furnished with a metal canister that consisted of alternating layers of filtering materials; charcoal, lime, cotton wool, etc. Subsequently, in 1877 Neally[17] designed a gas mask with a face cover that tightly fited the face and contained the eyepiecs made up of mica and glass. It also contained rubber tubes connected with gas filter. In 1902, Muntz[18] invented a basic gas mask that covered the whole head and contained a canister filled with carbon-based adsorbent in front. Later in 1903, Draeger company of Germany produced a gas mask containing face cover, rubber tube and canister filled with high-grade charcoal[19-22].

2.2.1 Development of Gas Marks for Military

Although it was invented in 18th century, its utility for military purposes was not realised until the first world war. Suitable military mask was not available for allied side soldiers when the Germans made first gas attack against them in 1915[20-25]. They used to protect themselves against the gas by means of cotton pads soaked with the suitable chemicals that decontaminated the warfare gases by covering their nose and mouth. Thereafter, research and development activities on the gas mask were accelerated.

At that time british army made a gas mask which contained a box filled with layers filled with charcoal and lime. It was connected with flexible tube to the face piece made up of rubberised cloth and covers the entire face while it was attached to the head by elastic tapes. Air from the respirator passed to the lungs of the wearer through flexible tube while the provision for exhaling the air was also incorporated.A pair of nose clips was provided for avoiding the leaking of air. The face piece protected eyes, lungs, and face and gave reliable protection. Although, it gave durable and reliable protection, military have started looking for alternatives due to the discomfort of nose clips and fogging of lenses. Later, this mask was modified to improve the comfort by removing the nose clips and by improving the face cover to provide long time protection against the blister agents like sulphur mustard[23].

Parallely, a gas mask named Tissot mask was developed by France for its Army[1]. It was comfortable to wear for longer intervals of time and contained a box filled with charcoal and lime that facilitated the filtration of air contaminated with CB warfare agents. Filtered air was made to pass through the tube from the box to the face piece and was bifurcated at the junction point of face piece and tube towards the eyepieces as the tube was divided into two parts, thereby preventing the fogging of lenses. The exhaled air was made to exit from rubber outlet or exhalation valve. The Tissot face mask was best in comfort, design and assured a good fitment on the face, and eliminating the danger of leaks. It provided lower breathing resistance and clearer vision, hence, it was adopted by allied Army until 1919. However, due to the difficulty in large-scale manufacturing of this mask, US Army started working on a simple mask that would contains all the advantages of the previous designs. The mask was fabricated from a rubber sheet and the eye lenses were made from unbreakable glass; however, these were kept clear by the Tissot principle of deflecting the cool air across these as it was breathed within. Deflection of incoming air current was facilitated by a rubber deflector[24].

A good progress has been made in fabricating the better mask for the present-day Armed Forces all over the globe. Improvements in comfort, reliability, low breathing resistance, large-scale production at reduced cost, clear vision without fogging, etc., and higher shelf life of the mask, have been achieved. It was very difficult at those times to converse by wearing the older versions of masks. Nevertheless, to over come this problem and to improve the speech transmission within wearers of gas masks, diaphragms were designed, incorporated, and successfully used. Later in 1925, gas masks were made from moulded face blanks with uniform quality and completely shaped mask provided improved comfort, convenience, and ease to manufacture. The eyepieces of the 1925 mask were shaped to give clear vision to sides and below. By the time of second world war, various types of masks for use by Army, for better speech transmission, with optical lenses, and for training were made available. These were cheap, lightweight and comfortable to wear with all provisions of better speech, better vision, and drinking water facility. The eyepieces were made up of tough transparent plastic and the canister was fitted with the face mask itself.

The present-day gas mask (Fig. 1) has been made by eliminating all the discomforts and manufacturing difficulties observed in the previous designs. It was made using high-quality rubber materials that provide excellent protection against blister agents or vesicants. The sheet of bromobutyl rubber or butyl rubber is used to make face mask by injection moulds or compression moulds. The bromobutyl rubber or butyl rubber possesses better protective potential against highly penetrating agents like sulphur mustard. Eyepieces with non-shatterable plastic have been made up of cellulose acetate and have been used in the gas mask to provide wider vision to sides and below. Fogging problem is overcome by the application of Tissot princliple of deflection of air. Drinking water facility and diaphragm for better speech transmission, have also been incorporated in the present-day mask. Face seals are provided along with mask to tighten it over the head to have better fitment and to avoid

Figure 1. Personnel wearing the gas masks.

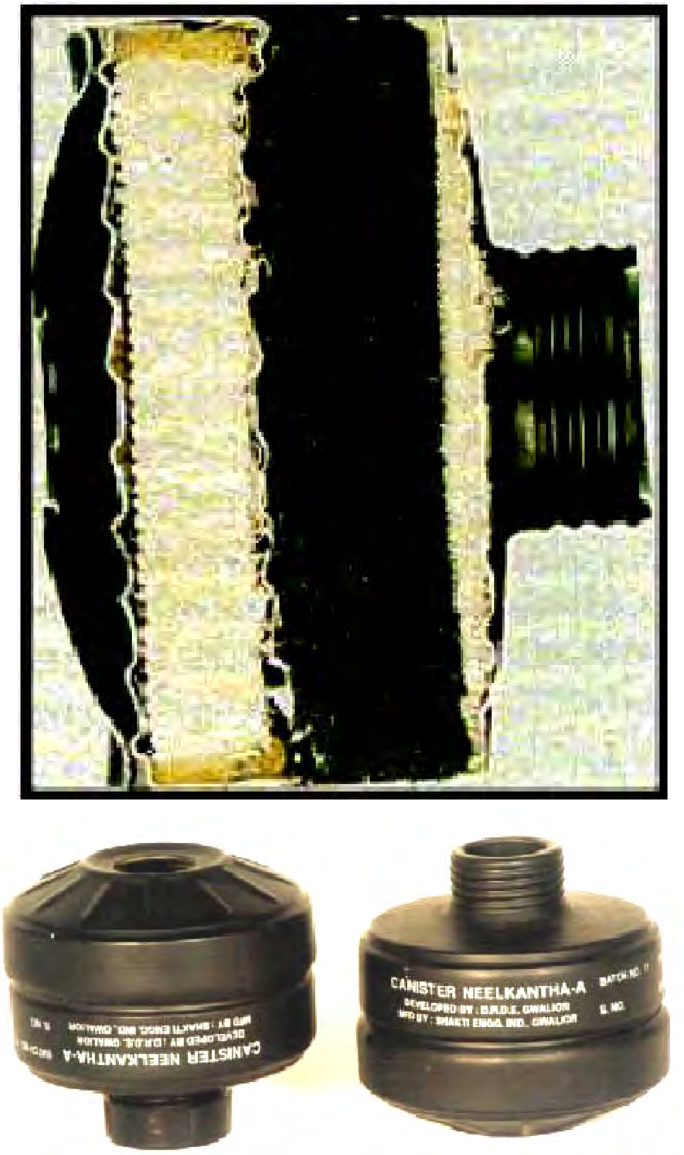


Figure 2. Canister and its cross section showing the gas filter (carbon) and mechanical filter (HEPA).

leaking of air[25-28]. Activated carbon modified with chemical ingredients like *Cu* (II), *Cr* (VI), *Ag* (I) and pyridine or *Cu* (II), *Ag* (I), *Zn* (II), *Mo* (VI), and TEDA impregnated (ASZMT) carbon have been incorporated in the canisters (Fig. 2) for the protection against blood agents, choking agents, etc[29]. Irritants, tear gases, dust, aerosols, bacterial spores were removed by the improvised mechanical filter, i.e., high efficiency particulate aerosol filter (HEPA)[30].

2.3 Gas Filters

Cotton pads and towels soaked with suitable chemicals were used as gas filters during the first world war[1,4]. Owing to their failure to provide long time protection against chemical warfare gases, attention was diverted to the alternative gas filters for use in respiratory boxes and cartridges. Charcoal was identified as the cheaper and reliable alternative for this purpose owing to its enhanced sorption properties and high surface area, and hence, was selected for use in gas masks. It was further modified by several chemical ingredients to tailor the chemical activity towards wide range of chemical warfare agents[31-33].

2.3.1 Structure of Activated Charcoal

Charcoal treated with steam or CO_2 or chemicals like zinc chloride, phosphoric acid, etc, at higher temperatures enhances the capacity to physisorb more amount of adsorbate relative to the untreated one. These enhanced sorption characteristics are the result of developed porous structure during the activation of carbonaceous material of mainly biological origin[4]. During the carbonisation process, most of the non-carbon elements are removed by the pyrolytic decomposition of the precursor and the resultant carbonised product contains more or less disordered elementary graphitic crystallites, with poorly developed porous structure. During the process of activation, the spaces between the elementary crystallites get cleared resulting in microcrystalline activated carbon of high surface area and wide pore size distribution. This activated carbon met with outstanding success in purification of contaminated atmospheres and most likely, it removes the toxic chemicals from the contaminated air and water streams, by physically or chemically adsorbing them[4, 34-36].

Usually, porous activated charcoal of coconut shell is unique and widely used for several applications including air filtration because of its high mechanical strength and adsorptive capacity. All the applications of active charcoal are critically controlled and affected by its pore size distribution. Most likely, the usual sorts of active charcoal contains pores of different sizes. Based on the size of the pores, these are termed as micropores (> 2 nm), mesopores (2–50 nm) and macropores (> 50 nm)[37-39]. Each type of pores has its specific function in the process of adsorption on active charcoal. In microporous carbon or charcoal, pores have been found to contribute significantly to adsorption by pore filling mechanism. Adsorption in these pores occurs due to the operation of dispersion component and it is caused by the overlap of force field of the walls of the capillary, leading to the van der Walls forces. Because of the micropores, active carbon adsorbs organic vapours of persistent nature at normal temperatures. Transition pores serve two purposes, one is capillary condensation of adsorbate and the other is the passage for the adsorbate to the micropores[40-42]. The macropores, however, enable the molecules of adsorbate to pass quickly towards the pores of smaller diameter situated deeper within the particles of activated carbon. When activated carbon is used as a catalyst support, the pores of larger sizes can become places for the deposition of the catalyst. The role of active carbon in carbon supported catalyst is not only limited to that of passive support but it also influences the activity, selectivity, and the ability to disperse the metals due to its high surface area and the added chemical nature of the surface.

2.3.2 Modification of Activated Charcoal

It was emphasised by many authors that, although activated carbon has the capacity to remove the toxic chemicals by the physisorption, it needs modification due to two reasons; one is for the destruction of chemicals of non-persistent nature, as the activated carbon was found to be ineffective when used against highly volatile non-persistent chemical warfare agents such as hydrogen cyanide, cyanogen chloride and phosgene and smokes[43-44] the other is its disposal after use; handling such contaminated carbon becomes difficult and raises concerns over safety. There is possibility of cross-contamination due to desorption upon its improper disposal after use.

To overcome these problems, a suitable carbon is needed with the capability to degrade physically adsorbed toxic chemicals *in situ*. Therefore, several modified impregnated carbons have been developed by treating activated carbon with suitable impregnant material. When toxic substances are adsorbed on modified impregnated carbons, the following processes may take place on the surface of carbon. These get adsorbed followed by chemical reactions such as neutralisation, hydrolysis, complex formation, catalytic reactions, and oxidation. Such a reactive carbon is expected to facilitate the destruction of the adsorbed substances. By modifying the surface with suitable impregnant materials, effective sorbent can be made to provide long-term, reliable protection against all known toxic chemicals. It is obvious that impregnation reduces the surface area and adsorption capacity, and thereby the life of the catalyst. Nevertheless, a satisfactory compromise between porosity of carbon and quantity of the impregnating material can be achieved and a better carbon with enough service can be made.

Another parameter that affects the life of the impregnated carbon is the method of impregnation. Improper impregnation leads to extraneous surface coating and inhomogeneous deposition of active species which block the pores of the carbon, thereby reducing the effective surface area responsible for physical adsorption. All these challenges can be met by the uniform impregnation using incipient wetness technique[45].

Whetzel[46], *et al.* in 1918 have prepared stable and hard impregnated carbon termed as whetlerite carbon. It consists of copper as active ingredient on charcoal. The whetlerite charcoal was able to give protection against chlorine, arsine, phosgene, hydrogen cyanide, etc. Similar kind of impregnated carbons based on copper, zinc, silver, cobalt, chromium, manganese, vanadium, molybdenum, etc., have been prepared till date by researchers for their use in NBC filtration systems against HCN, $CNCl$, AsH_3 and $COCl_2$[47]. Of these modified impregnated carbons, ASC whetlerite, which was composed of Cu (II), Ag (I) and Cr (VI) salts, was one of the most effective against non-persistent CW agents. This ASC whetlerite gives better protection against hydrogen cyanide, cyanogen chloride, phosgene, arsine, etc. However, carcinogen Cr (VI) was replaced by Mo (VI) and Zn (II) without affecting the efficiency. The resulting carbon was termed as ASZMT whetleirte.

However, certain active ingredients were found to get degraded on exposure to humidified air, aging, etc. hence necessitated the stabilisation. For this purpose, amines such as pyridine and tetra ethylene diamine were added to the above carbon which are nothing but the present-day NBC carbons[48-50]. ASC whetlerite and ASZMT whetlerite are still being used in NBC filtration systems for the protection against non-persistent and persistent chemical warfare agents. Altough, many other carbons such as ASVT carbon were also exploited for use in NBC filters, their use was limited due to limitations in physico-chemical properties.

3. REACTIONS OF CW AGENTS ON CARBON

3.1 Non-persistent CW Agents on Carbon

ASC whetlerite carbon is capable of providing protection against poisonous gases such as hydrogen cyanide, phosgene, arsine and cyanogens chloride. The impregnants present over the surface of the carbon react in stoichiometric ratio with impregnants and neutralise them to non-toxic products. Cu (II) which is present over the carbon plays a key role in removing hydrogen cyanide from the contaminated air. Copper (II) oxide present on the surface of carbon reacts with hydrogen cyanide in 1: 2 molar ratio. Typical reaction scheme is depicted below:

$$4HCN + 2\,CuO \rightarrow 2\,Cu\,(CN)_2 + 2\,H_2O$$

$$2\,Cu\,(CN)_2 \rightarrow 2CuCN + C_2N_2$$

$$C_2N_2 + H_2O \rightarrow (CONH_2)_2$$

Cromium (VI) plays a noticeable role in the reactive removal of cyanogen chloride. One mole of cyanogen chloride reacts with one mole of water in the presence of Cr (VI) to form cyanohydrin and hydrochloric acid. Cyanohydrine reacts with moisture present on the surface of carbon to form NH_3 and CO_2, where hydrochloric acid is removed by CuO as $CuCl_2$. The reaction mechanism is given below:

$$CNCl + H_2O \rightarrow HOCN + HCl$$

$$CuO + HCl \rightarrow CuCl_2 + H_2O$$

$$HOCN \rightarrow \text{Cyanuric acid}$$

$$HOCN + H_2O \rightarrow NH_3 + CO_2$$

On the other hand, one mole of phosgene reacts with one mole of water present on the surface of carbon to form one mole of Co_2 and 2 moles of HCl. Formed HCl reacts with CuO to form $CuCl_2$ and water.

$$COCl_2 + H_2O \rightarrow CO_2 + 2\,HCl$$

$$CuO + 2\,HCl \rightarrow CuCl_2 + H_2O$$

Arsine was found to get oxidised catalytically to As_2O_3 and As_2O_5 in the presence of CuO, Ag or Ag_2O, ZnO, and $Na_2ZnO_2^+$

$$2\,AsH_3 + 3\,O_2 \rightarrow As_2O_3 + 3\,H_2\,O$$

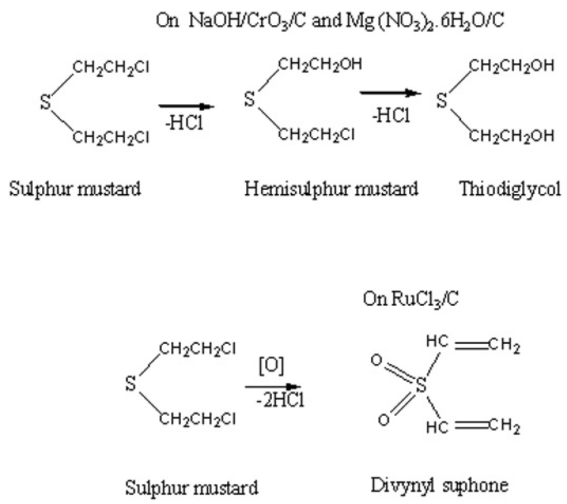
$$As_2O_3 + O_2 \rightarrow As_2O$$

3.2 Reactions of Persistent Chemical Warfare Agents on Carbon

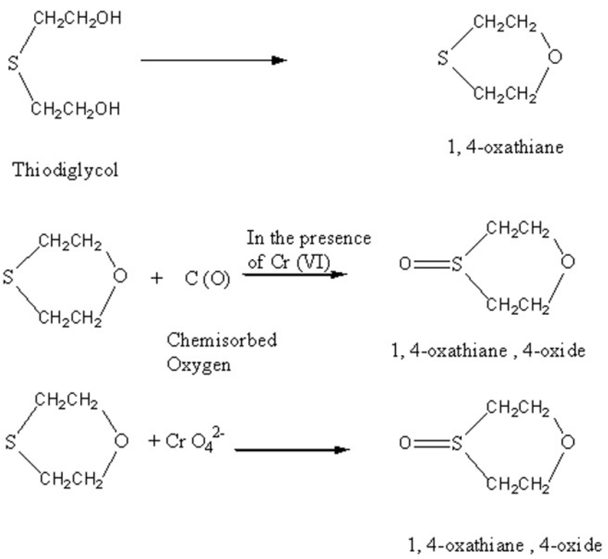
Persistent chemical warfare agents have a tendency to remain on the surface of carbon after these get physically adsorbed to the saturation capacity of carbon. By virtue of their chemical properties, they have negligible reactivity towards the carbon surface at room temperature. However, their reactivity is apparently affected due to the presence of water, impregnants, temperature, etc. The literature reveals that sulphur mustard decomposes at higher temperatures and gets hydrolysed at lower temperatures by producing thiodiglycol and chlorohydrin. Whereas, at elevated temperatures, it was found to get transformed to 1, 4-oxathiane, 1, 4-dithiane and 2 chloro ethanol[51]. These kind of reactions at room temperature on the surface of carbon play a prominent role in the *in situ* degradation or chemical adsorption of persistent CW agents within the filtration systems, thereby promoting protective capacity against persistent CW agents and safe disposal of filtration systems after their use. Fortunately, these kind of applications can be found in activated carbon impregnated with suitable chemicals. Although, activated carbon impregnated with *Cu*, *Cr*, and *Ag* has been used in NBC filtration systems, it has very low reactivity towards persistent CW agents like sulphur mustard. It undergoes hydrolysis reactions to a minimum extent on the surface of ASC whetlerite and it depends on the amount of water present on the surface of carbon.

Damico[52], *et al.* have developed similar kind of reactive carbon against thioether, a surrogate of sulphur mustard. This reactive carbon was based on active carbon impregnated with polyoxometallates which oxidized thioether which has promising future applications for *in situ* degradation of CW agents like sulphur mustard. Following this, Prasad[53-56] have developed various impregnated carbons based on $NaOH$, CrO_3, $Mg(NO_3)_2.6H_2O$, $RuCl_3.3H_2O$, etc, and have evaluated these for *in situ* degradation of sulphur mustard and its related compounds like thiodiglycol, diethyl sulphide, dibutyl sulphide. These agents underwent hydrolysis, elimination, and oxidation reactions by reacting with the active sites available on the surface of above carbons. Based on the experimental studies on $NaOH$, CrO_3 impregnated carbon thiodiglycol was found to get degraded to 1,4- oxathiane, 1, 4-oxathiane , 4-oxide as shown in Scheme I.

On $NaOH/CrO_3/C, Mg(NO_3)_2$; $6H_2O/C$ sulphur mustard was found to form hydrolysis products like thiodiglycol and hemisulphur mustard and the same was found to get oxidized on $RuCl_3/C$ by forming divynyl sulphone as shown in Scheme II.

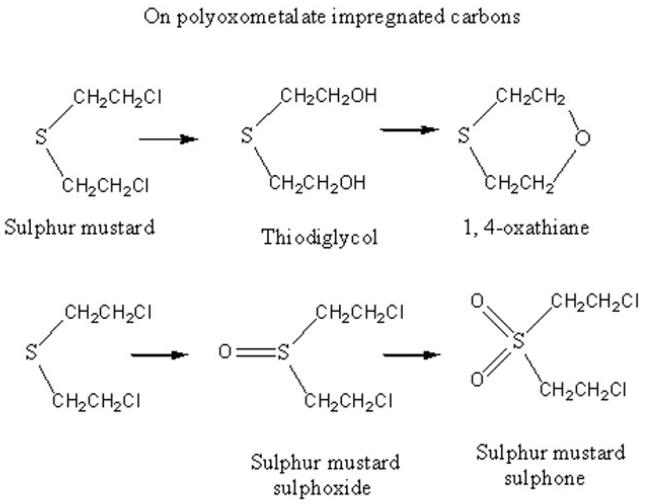


Scheme II



Scheme I

Soon after this, Beer Singh[57-58], *et al.* have developed several impregnated carbon based on polyoxometalates and modified whetlerite and examined the *in situ* degradation of blister agents like sulphur mustard. They have impregnated carbons with polyoxometalates like 11-molybdop-1 vanado phosphoric acid, phospho tungstic acid, silico tungstic acid, phosphomolybdic acid along with $RuCl_3$ and studied the degradation of sulphur mustard. Sulphur mustard reacted with the active ingredients on the surface of carbons, thereby forming non toxic products like 1,4-oxathiane, sulphur mustard sulphoxide and sulphur mustard sulphone. The reaction is shown in Scheme III.



Scheme III

On the other hand, nerve agents and related compounds undergo hydrolysis reactions on the surface of carbon. Saxena[59], *et al*. have studied degradation of sairn, diethyl cyanophosphate, dimethyl methyl phosphonate, etc., on the surface of modified whetlerites and observed the formation of hydrolysis products, i.e., phosphonic acids of nerve agent and related compounds.

The above reactions facilitate the neutralisation of toxic compounds by forming non-toxic products. Based on the laboratory studies, these carbons have further promising future applications in universal NBC carbons/gas filters.

4. SURFACE CHARACTERISATION BY MICRO-ANALYTICAL TECHNIQUES

Use of porous carbons for various applications needs multi-faceted characterisation. Various modern analytical techniques provide information about physico-chemical properties of solids which are significantly influenced by pore structure of carbons[60]. Pore structure of carbon, in turn, plays an important role in the transport of adsorbed molecules inside the adsorbent particles. However, the adsorption-desorption isotherm is often used to calculate the specific surface area and pore size distribution[61], which are the fundamental quantities for characterising porous adsorbent. Specific surface area evaluation can be easily done using small part of the adsorption isotherm. Whereas, pore size distribution is reckoned either by multilayer adsorption isotherm or porosimetric measurements based on the penetration of liquid mercury into the mesopores; the distribution does not include micropores. However, information about micropores can be easily obtained by N_2 adsorption desorption experiments. Part of adsorption isotherm measured at low concentrations has also been used to predict the structural heterogeneity of porous solids[62].

Further, the impregnation tremendously affects the porosity and decreases the specific surface area. Hence, it needs attention as both the impregnants and surface area are very important for the removal of gases and vapours. Active carbon with suitable pore size distribution can be used for getting impregnated carbon with sufficient porosity and chemical reactivity. On the other hand, the specific surface area has been found to get affected by high moisture content and deteriorates the capacity[4]. Altough, moisture facilitates some degradation reactions, prolonged duration of exposure to humidity, temperature and storage reduce the effective life of impregnated carbon and deactivate the active ingredients. For example, in the case of whetlerite carbon *Cr* (VI) gets reduced to *Cr* (III) and *Cu* (II) gets reduced to *Cu* (I) and *Cu* (0). Obviously, the activity of catalyst was found to be reduced[43] and the same was examined by x-ray photoelectron spectroscopy and differential scanning calorimetry. In addition to the reduction of metal ions, these were found to form larger size crystallites within the pore structure, thereby blocking these and the same was studied by transmission electron microscopy and x-ray diffraction technique[63]. Brown[64], *el al* has shown that humid environment did not alter the oxidation state of *Cu* (II), however, it affected the reduction of *Cr* (VI) to *Cr* (III). He also clarified that *Cr* (VI) species are the active substances of impregnated charcoal against cyanogen chloride.

5. ADSORPTION BEHAVIOUR OF WAR GASES ON CARBONS

When a gas or vapours of toxic chemical come into the contact of active carbon, the toxic molecules get accumulated at the interface of the adsorbent due the operation of van der Waals forces as well as chemical forces. After getting accumulated, these penetrate or diffuse on to the surface of the solid, causing adsorption of vapours and this is how the gas filter or carbon facilitates the adsorptive removal of toxic chemicals from the contaminated environment.

The effectiveness of an adsorbent is critically controlled by the nature of adsorbent, nature of adsorbate, adsorption behaviour of the warfare agents on carbons, the distribution of the adsorbate or chemical in the adsorbent, and the contact time between the adsorbate and the adsorbent. These parameters in turn depend on the adsorption conditions, i.e., whether the adsorbate as well as the adsorbent are at rest, i.e., under static conditions and the adsorbent and adsorbate move wrt each other, i.e., under dynamic conditions. In static adsorption, the distribution of the adsorbate is uniquely decided by adsorption isotherm, whereas, in dynamic conditions, it is not only decided by isotherm but also by other factors such as the kinetics of adsorption, rate of transport of adsorbate to the surface of adsorbent, and the rate at which the molecules are being trapped by the surface.[4] Further, factors such as hydrophobicity of carbon surface[65] and surface chemicals sites also decide the distribution of adsorbate throughout the adsorbent.

In an attempt to understand the adsorption behaviour of sulphur mustard, a blister agent on carbons under static conditions, Prasad[66], *et al.* have studied the kinetics of adsorption of sulphur mustard and diethyl sulphide on various activated and impregnated carbons. They have used an equation based on linear driving-force model and observed that the rate of adsorption of the chemical is significantly influenced by the presence of impregnant material, which works as a barrier to the incoming adsorbate molecules within the carbon surface. Depending upon the reactivity the impregnant, it may also react with the adsorbate molecule and facilitate the formation of the product. Using this model, one could calculate the adsorption capacity of the carbons, equilibration time, i.e., time taken for reaching the equilibration capacity, and the equation is given below:

$$(M_t - M\ )/M_e = 1 - e^{Kt}$$

where $(M_t - M.)$ is the weight of the adsorbate at time t, M_e is the adsorption capacity, t is the time and K is the rate constant. It was also observed that the above parameters are greatly influenced by the surface area of the adsorbent.

On the other hand, the adsorption behaviour depends also on the diffusivity of the adsorbate molecules on the carbons, while it is a function of surface concentration of adsorbate and the porous structure. To understand the mode of diffusion of chemical warfare agents and the related compounds on the surface of carbons, Prasad[66], *et al.* have used the following empirical equation:

$$\log (M_t/M_e) = K.\ t^{\,n}$$

where M_t is the mass of the adsorbent at time t, M_e is the equilibration capacity of carbon, K is the adsorbate-adsorbent interaction constant, t is the time, and n is diffusional exponent. Depending on the value of the diffusional exponent and other kinetic parameters, they have described the kinetics of diffusion of sulphur mustard and diethyl sulphide, a related compound, found to follow Fickian-type diffusion as a primary mechanism along with chemical interaction as a secondary mechanism.

6. VAPOUR BREAKTHROUGH BEHAVIOUR OF CARBONS

It's well understood that the performance of the carbon bed, when used in an NBC filtration system, depends upon the capacity of the adsorbent and the rate of adsorptive or reactive removal of contaminants, as mentioned above, whereas, the adsorption capacity of the carbon bed depends further on the temperature at which the carbon bed is placed, amount of carbon in the bed, concentration of the agent, bed geometry, air flow rate, and particle size of the carbon. Jonas[67-68], *et al.* have conducted several gas breakthrough experiments using chemicals like carbon tetrachloride and nerve gas simulants like dimethyl methyl phosphonate, and explained the adsorption process occurring on the surface of carbon as a series of seven steps. These steps are physical adsorption, mass transfer, surface diffusion, intra-granular diffusion, intergranular diffusion, chemical reaction, and gas desorption and surface renewal[69-72]. He studied the breakthrough behaviour of carbons using modified Wheeler equation and observed that adsorption kinetics were greatly influenced by linear flow rate of gas mixture. The modified Wheeler equation is given as,

$$t_b = (W_e/C_0Q)\ [W - (\rho_b Q)/(k_v ln\ (C_0/C_x))]$$

where t_b is the gas breakthrough time, W_e is kinetic saturation capacity, C_0 is initial concentration, C_x is the exit concentration, Q is volumetric flow rate, W is weight of the carbon, r_b is the packing density of carbon bed and k_v is the rate constant.

The above equation is based on the linear relationship between gas breakthrough time and weight of carbon bed. The slope and intercept of the straight line resulting from such a plot yields values for the gas saturation capacity of the adsorbent and adsorption rate constant of the adsorbent. As per his observations, slowest adsorption kinetics exists at lower linear flow rates and becomes faster with increasing flow rate and the same was reflected in the observed values of rate constant while flow rate of gas mixture was varied. He also observed that pseudo first-order rate kinetics wrt gas molecules is operative when the concentration of active sites was much larger than the concentration of gas molecules and pseudo first-order rate kinetics wrt active sites was operative when the concentration of gas molecules was larger than the concentration of active sites. He also explained that the kinetic adsorption capacity of the carbon was unaffected by changes in linear flow rate, carbon granule size, and minute changes in concentrations, whereas, the rate constant and kinetic adsorption capacities were adversely affected by the increase of temperature. Following this, Prasad[73-75], *et al*. have conducted sulphur mustard vapour breakthrough experiments on various activated and impregnated carbons. They have recorded breakthrough data by changing bed length of carbon and observed that with increase of bed length of carbon, breakthrough time was increased non linearly until it reached an optimum length and then it increased linearly. They have used modified Wheeler equation for analysing the data and observed that with the increase of flow rate of gas mixture, rate constant was found to be increased while the kinetic saturation capacity remained unchanged. Smaller increase in concentration did not affect the rate constant and kinetic saturation capacity while the temperature adversely affected the above parameters.

These observations based on vapour breakthrough behaviour of sulphur mustard are consistent with observation made by Jonas[70], *et al.* with nerve gas simulant, i.e., dimethyl methyl phosphonate. In addition to this, Friday[76], *et al*. have studied breakthrough behaviour of cyanogen chloride and explained the kinetic processes occurring on the carbon bed in terms of mass transfer of war chemical from the gas phase to the surface of carbon granule. He explained that two kinds of mass transfer occurs, one is external mass transfer and the second is internal mass transfer. However, Nelson[77], *et al*. have observed that breakthrough time is inversely proportional to air-flow rate while logarithmic concentration is inversely proportional to service life of respiratory cartridge.

Based on the available breakthrough data of chemical warfare agents on carbons, it is apparent that bed length or weight of carbon, flow rate of agent-air mixture, concentration of agent, temperature, etc, are crucial parameters and are to be considered carefully. Service life of an NBC filter is critically influenced by the above-mentioned parameters, hence, they need to be optimized for getting better value.

7. PARTICULATE FILTERS OR MECHANICAL FILTERS

Although activated charcoal can provide sufficient protection against persistent and non-persistent chemical warfare agents, it was found to be ineffective against dust particles, aerosols and bacterial spores during the attack of irritants and tear gases by Germans at the time of first world war. Aerosols composed of solid particulates were not held by impregnated charcoal and these seemed to penetrate through the canister and deposited in the airways and other parts of respiratory system[1]. Of the inhaled or penetrated particles through nose or mouth, some of the particles may be exhaled subsequently. However, the size of the aerosol particles in the inhaled air usually ranges[78] from $< 0.1\ \mu$m to that $>185\ \mu$m.

Deposition of these aerosols and related particulates in the respiratory systems usually happens by five mechanisms. These include gravitational settling, inertial impaction, interception, electrostatic deposition, and diffusion caused by Brownian motion. In the smaller airways like alveoli, tranchea brochi, and other bifurcations, diffusion caused by Brownian motion is an important mechanism for the particles < ~ 0.1 μm. Inertial impaction is the most important mechanism for larger particles; these usually get deposited in larger airways and bifurcations. Gravitational settling becomes prominent only in smaller airways like bronchi and alveoli where airways are smaller and particle velocities are low. Moreover, deposition of the particles in the respiratory tract gets enhanced if the particles are electrostatically charged. Particles > ~30 μm rarely pass through the larynx since the larger particles deposit within mouth, nose and at the bifurcation of mouth and nose. Further, a very few particles > 10 μm enter the core of the lungs, however, > 90 Percent of particles of size ~ 1 μm reach the alveolar region. Although, > 90 per cent of the particles reach alveolar region, only ~ 20 per cent seem to be deposited there and only 14 per cent of 0.3 μm size, i.e., most penetrating particle size particles only deposit in the respiratory system[78].

On the other hand, as discussed above, the CW agents delivered through different means exist in the environment as aerosols, gases, and vapours. In addition, as per theory, all the particulates behave in a similar way. Either these are of chemical nature or of biological nature, i.e., bacteria and other related matter (most of the bacteria are 0.3 ìm or larger in dia). These particles have a tendency to strongly attach to the surface when these make contact by colliding due to the operation of van der Waals forces, electrostatic forces, and surface tension.

Filters are designed in such a way to enhance and provide the possibilities for the particles to colloid with filter materials and get captured by the operation of the above forces where the contamination-free air passes through the filter[5]. Generally filters are composed of randomly woven mat of very fine fibres arranged to be perpendicular to the air flow. The gas molecules passing through the filter media are compelled to change the direction and pass around all the individual filter fibres, and in doing so, these make contact with filter fibres depending on properties. Plastic, glass or paper fibers are commonly used in filtration systems and the particles are captured when these colloid with the individual filter fibres. Aerosol particle capture by mechanical filtration systems occurs usually by four mechanisms, these are inertial impaction, interception, diffusion caused by Brownian motion, and gravitational settling. Another mechanism based on electrostatic attraction also facilitates the particulate capture by filter fibres, which occurs usually in electrostatic filters not in mechanical filters[5].

Inertial impaction occurs when the particles cannot follow the abrupt changes in direction of the gas streamlines due to their inertia. The particle continues in a relatively straight path and makes the impact with filter fibre and gets captured. Mass and velocity are the most important variables that determine the degree of inertial impaction. Higher velocities and larger particle size or mass increase the particle capture by inertial impaction mechanism.

Interception occurs when a particle has low enough inertia that it tends to follow the gas streamlines but is captured because its diameter is large enough for it to make contact while passing the filter fibre. The most important variables contributing to interception are the true physical diameter, the diameter of filter fibres and the density of the filter fibres. Large and light particles experience higher degrees of interception. Interception is the only filtration mechanism that does not rely on the particle departing from the carrier gas streamline.

Brownian motion is the random chaotic motion of very small particles as these are bombarded by the surrounding gas molecules. Brownian motion causes the particle to deviate from the carrier gas streamline which increases the possibility of making the contact with filter fibres. Brownian motion is the most predominant mechanical method of particle capture for smaller particles of size < ~0.1 μm. The longer the particle is in close proximity to a filter fibre, the greater the chance that it will make an impact on the filter fibre and gets captured, therefore lower velocities improve the particle capture by Brownian motion.

Gravitational settling is the deviaton of the particle from its gas streamline due to the action of force of gravity and electrostatic deposition occurs when electrostatic attraction causes particles to deviate from gas streamlines.

Electrostatic filter fibres are positively charged on one side and negatively charged on the other side and the charged particles get attracted to the sections of the filter fibres and get captured. The stronger the individual charges, the lower the velocities, smaller the particles, the more efficient will be the electrostatic deposition.

The overall efficiency of a filter depends on the individual efficiencies of the five basic deposition mechanisms at a given particle size and velocity[5]. Fibrous filters generally exhibit high efficiencies when challenged with relatively larger particle sizes (> 1–5 μm) because of high degrees of inertial impaction and interception. Filters also have high efficiencies at much smaller particle sizes because of Brownian motion. There is an intermediate particle size, about 0.3μm, that is dominated by neither Brownian motion nor the impaction/interception mechanism. This 0.3 μm particle size is referred to as MPPS and particles larger or smaller than MPPS are trapped more efficiently by the filter, however, trapping of particles with MPPS is facilitated by high-efficiency particulate aerosol filters[79].

During the time of first world war, cotton pads, towels, paper, cellulose, asbestos, etc. were used in the gas masks to filter out these small particles of irritant smoke; however, their protective potential was limited due to the inability to filter out the smaller particles. These problems were over come to certain extent using felt. The canisters were fabricated at that time by confining the charcoal and soda lime within the felt to remove the fine particles of irritant smokes. Later, further improvisation during 1942 were carried out by replacing the felt. A new type of particulate mechanical filter was made using cheap cellulose fibre-based products and it was found to have lower breathing resistance. These were also found to be cheaper than felt and gave better protection against irritant smokes. These were found to be highly fibrous and could even remove fine smoke from burning electrical insulation such as bakelite and were also found to remove tobacco smoke and smokes of all other kinds[1].

Present-day canisters use highly efficient particulate mechanical filter called high-efficiency particulate aerosol filter (HEPA). HEPA filters are composed of thin films of randomly arranged packed glass fibres of small diameter. HEPA is fabricated by compressing the mixture containing micro-sized glass fibres along with binders, support in the form of papers or thin films[80]. The glass fibre orientation in the filter is managed to remain perpendicular to the gas flow. These provide high-breathing resistance and give higher particulate removal efficiencies. This air filter can remove at least 99.97 percent of airborne particulates of 0.3 mm diameter. Fibre density, diameter, and the thickness of the filter are the key points which play critical roles in the filtration of particulates. HEPA cannot remove the particulate < 0.3µm, hence, viruses having size < ~ 0.12µm cannot be removed by HEPA. For this purpose, another advanced filter media, called ultra-low penetration air filter (ULPA) can be used. An ULPA filter (theoretically) can remove from the air at least 99.999 per cent of dust, pollen, mold, bacteria, and all airborne particles with a size of 0.12 mm or bigger.

8. FUTURE PROSPECTS

For the coming years, researchers need to pay more attention to the development of gas masks which can be used for longer intervals of time amidst the battlefield conditions. Reusable, biodegradable, user-friendly masks with enhanced protective potential against blister agents need to be developed to avoid disposal problems. Rubber materials composed of nanomaterials and carbon fillers can be used for the fabrication of gas masks to improve the protective potential against sulphur mustard. Design improvisations shall be made to overcome problems related to fogging of lenses, leaking of air, breathing resistance, and ergonomics. Carbons with enhanced capacity to react with both persistent and non-persistent chemical warfare agents shall be made available for the use in NBC canisters. Advanced mechanical filters composed of nanofibrous filter medium incorporated with nanomaterials, with low breathing resistance and higher particulate removal efficiencies, 99.99 per cent for 0.1 µm or larger sizes, can be achieved and these filters can be incorporated in to the advanced canisters.

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