1. INTRODUCTION

Chemical warfare has been widely condemned since it was first used on a massive scale during the First World War. Chemical weapons are cheap, can cause mass casualties, and are relatively easy to produce, even by developing nations. They have been used in many conflicts during the 20th century, most recently by Iraq during the Iran-Iraq war as well as in terrorist attacks. The psychological impact of chemical weapons on society makes them ideal for terrorism, as shown by the release of nerve gas in the Tokyo subway system by members of the Aum Shinrikyo in 1995.

Chemical Weapons Convention (CWC) aims at the complete elimination of CWs. Organisation for the Prohibition of Chemical Weapons (OPCW), is an overseeing agency situated in The Hague, The Netherlands. It sends its inspectors around the world to monitor destruction of declared CWs (about 76,000 Metric tons of CWs stored in 8.6 million containers and munitions) under strict verification regime.

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Chemical Warfare agents are easy to prepare and use. In the current scenario, there is a wide spread belief that the likelihood of terrorist use of chemical and biological warfare agents is increasing. World has witnessed such evidences of terrorist interest and capabilities when Nerve Agent Sarin was released in 1995 by the Japanese terrorist Organization “Aum Shinrikyo” on the Tokyo Subway, instantly killing 12 people and injuring about 6000 people. Since terrorist attacks are deliberately designed to surprise, no trend analysis will ever perfectly predict them. They can leave a powerful psychological impact on a nation.

Many countries maintain chemical weapons in their arsenals to deter the use of this type of weapon against them, and to provide a retaliatory capability if deterrence failed. Some rogue countries can also accumulate military stockpile of Chemical Warfare Agents and use them at slightest provocation. Therefore, it is in the best interest of world to destroy the military stockpile of CWs. “Organization for the Prohibition of Chemical Weapons” (OPCW) situated in The Hague, The Netherlands, sends its inspectors around the world to monitor destruction process of the declared Chemical Weapons (CWs) and the precursors that are needed for industrial applications. The OPCW also tracks materials which terrorists can use to make chemical weapons, and ensures that such materials are not diverted from legitimate to prohibited purposes like production of weapons of mass destruction (WMDs).

World has a total of 76,000 Metric tons of Chemical Warfare Agents stored in 8.6 million containers and munitions. Out of six possessor countries; Russia has about 40,000 metric tons while USA has about 30,000 metric tons of both Blister and Nerve agents.

2. CHEMICAL WARFARE AGENTS

Chemical warfare agents are classified into three main categories:

- Blister or Vesicant agents: Sulfur Mustard, Nitrogen mustards and Lewisite
- Nerve Agents: Sarin, Tabun, Soman and VX
- Choking Agents: Chlorine, Phosgene, Diphosgene, etc.,

2.1 Blister or Vesicant Agents

Blister or vesicant agents cause wounds resembling burns and blisters. They also cause severe damage to the eyes, respiratory system and internal organs. The effect
of blister agents is delayed and the first symptoms do not occur until 2-24 hours. The structure of blister agents is given in Fig. 1

$$\text{Cl} - \text{S} - \text{Cl}$$

Sulfur Mustard

$$\left[ \text{Cl} - \text{S} - \text{Cl} \right]_n$$

Nitrogen Mustard

$$\text{Cl} - \text{S} - \text{AsCl}$$

Lewisite

(When n=1, 2 and 3 then, NH2, NH and N)

Figure 1. Structure of blister agents.

2.1.1 Sulfur Mustard – The King of Chemical Warfare Agents

Sulfur Mustard (Chemical Abstract Series [CAS] No. 505-60-2) is known as the king of chemical warfare agents. Military designation for Sulfur Mustard is H. However, HT and HD are used for technical grade and distilled agent respectively. It is a high boiling [b.p. 215°C (dec)] oily liquid, colourless when pure and pale yellow when impurities are present. Its odour is that of garlic, or mustard (hence its name). It is a potent chemical warfare agent capable of producing edema, ulceration and necrosis of the epithelial tissues of the eyes, skin and respiratory tract apart from causing extremely painful blisters when it comes in contact with the skin4 (Fig. 6). Severe exposures can result in sufficient systemic uptake to cause gastrointestinal, hematological effects and immunosuppression. Exposure to sulfur mustard has also been known to result in chronic bronchitis, recurrent keratitis and cancers of the respiratory tract and skin.

2.1.2 Mechanism of Action of Sulfur Mustard

After absorption into the body, HD rapidly cyclizes (seconds to minutes) in extracellular water. This cyclic compound is extremely reactive and quickly binds to intra- and extra-cellular enzymes, proteins, and other substances. Sulfur mustard has many biological actions, but the exact mechanism by which it produces tissue injury is not known. According to one prominent hypothesis, biological damage from HD results from DNA alkylation and cross linking in rapidly dividing cells, such as basal keratinocytes, mucosal epithelium, and bone marrow precursor cells. This leads to cellular death and inflammatory reaction, and, in the skin, protease digestion of anchoring filaments at the epidermal-dermal junction and the formation of blisters. The mechanism is outlined5 in Fig. 2.

2.1.3 Persistence of Sulfur Mustard - Ocean Dumping

A group of US Army researchers has measured the half-life of HD in sea water at different temperatures.6 These values are given in the accompanying table along with the corresponding rate constants.

Table 1. Half life of sulfur mustard distilled agent in sea water

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Sea water $t_{1/2}$ (min)</th>
<th>$k_r$, calculated (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>175</td>
<td>0.0040</td>
</tr>
<tr>
<td>15</td>
<td>49</td>
<td>0.0141</td>
</tr>
<tr>
<td>25</td>
<td>15</td>
<td>0.046</td>
</tr>
</tbody>
</table>

Figure 2. Mechanism of action of Sulfur Mustard on DNA
Despite the relative rapidity of the hydrolysis reaction, sulfur mustard has been found to persist in soil or even under water for periods of decades. In such incidents of long-term persistence, the common thread is the presence of bulk liquid agent. While the hydrolysis of dissolved sulfur mustard is relatively fast, the dissolution of HD does not occur rapidly. A likely sequence for the fate of bulk HD introduced into quiescent water would be the following:

- HD that initially dissolves from the droplet is hydrolyzed to thiodiglycol via intermediate sulfonium ion 7 (Fig. 3).

\[
\text{Cl-S-Cl} + \text{H}_2\text{O} \rightleftharpoons \text{Cl-S-OH} + \text{Cl-H}_2\text{O}
\]

**Figure 3. Thiodiglycol (TDG)**

- At the interface, however, where little water is present, the intermediate Sulfonium ion forms and reacts with another molecule of HD (rather than with water) to form 1,2-bis[(2-chloroethyl)thio]ethane (Q) and 1, 2-dichloroethane 8 (Fig. 4).

\[
\text{Cl-S-OH} + \text{Cl-S-Cl} \rightarrow \text{Cl-S-S-Cl} + \text{H}_2\text{O}
\]

**Figure 4.**

- Due to lack of appreciable agitation at the bottom of the Sea, a concentrated TDG layer builds up at the HD droplet-water interface. The TDG at the interface also reacts with the intermediate sulfonium ion to form stable sulfonium salts of the type 9 (Fig. 5).

\[
\text{H}_2\text{O} + \text{Cl-S-S-Cl} \rightarrow \text{Cl-S-OH} + \text{Cl-S-OH}
\]

**Figure 5.**

- The non-reactive sulfonium salts such as above and higher homologues (e.g., from the analogous reactions of Q) build up at the interface between the HD droplet and the bulk aqueous phase creating a thicker boundary layer.

- Dissolution of HD slows, because the driving force for diffusion of HD into the bulk aqueous phase decreases. Similarly, diffusion of water into the HD droplet also slows down if adequate agitation is absent, which lowers the observed rate of hydrolysis. However, if the water is subject to disturbance, such as a heavy rain and rapid flowing, it is less likely that H droplets would persist for significant periods.

Accidents due to ocean dumping of chemical weapons have been reported in the Baltic Sea, the Adriatic, and in the Pacific Ocean and Japanese coastal waters. Most reports came from fishermen who had inadvertently snared plastic lumps of sulfur mustard in their nets. When
exposed to sea water, sulfur mustard forms a thick outer "crust" over a core of sulfur mustard which allows the lump to be brought to the surface where it can injure unsuspecting fishermen. These accidents began occurring shortly after the material was dumped and have continued throughout the intervening years (Fig.7) Note that in each location exposure continued through the date of the report (1980 in Japan, 1985 in Denmark) with the most recent reports coming from Italy in 1997.

Figure 6. Iranian soldier with sulfur mustard injury.

2.1.4 Antidotes for Sulfur Mustard Injuries

There are no antidotes available for sulfur mustard injury. Victims should be transferred from contaminated areas. Patient care should include supportive treatment protocols for skin injury and the blisters need to be treated like burn wounds in a special burn ward.

2.2 Nerve Agents

Nerve agents\(^2\)\(^3\) belong to a group of chemicals called "organophosphates". Nerve agents acquired their name because they affect the transmission of nerve impulses of in the nervous system. They are stable and easily dispersed, highly toxic and have rapid effects both when absorbed through the skin and via respiration. The first nerve agent (called "Tabun" or "GA") for military use was made in Germany in 1936. Another nerve agent, "Sarin" or "GB", was made in 1938 and "Soman" or "GD" was made in 1944. In the 1950's another nerve agent, "VX", was produced in England.

2.3 Structure and Physical Data of Nerve Agents

2.2.2 Mechanism of Action of Nerve Agents

All nerve agents act by inhibiting the enzyme Acetylcholinesterase (AChE), which breaks down the neurotransmitter acetylcholine. AChE is formed and released from the nerve cell to the receptor (muscles, glands etc.). It acts as a signaling system. AChE breaks down acetylcholine and recycles it for further usage.

Table 2. Structure and physical data of nerve agents is summarized

<table>
<thead>
<tr>
<th>Property</th>
<th>Tabun (GA)</th>
<th>Sarin (GB)</th>
<th>Soman (GD)</th>
<th>VX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Colourless to light brown</td>
<td>Colourless</td>
<td>Colourless</td>
<td>Amber coloured</td>
</tr>
<tr>
<td>Chemical Formula</td>
<td><img src="image" alt="Tabun GA" /></td>
<td><img src="image" alt="Sarin GB" /></td>
<td><img src="image" alt="Soman GD" /></td>
<td><img src="image" alt="VX" /></td>
</tr>
</tbody>
</table>
Thus AChE acts as a neurotransmitter controller. Nerve agents inhibit this vital enzyme. The result is the overstimulation of receptors. Thus paralysis occurs; the main cause of lethality is respiratory paralysis.

The inhibition occurs due to the phosphorylation of Serine OH present in the active site of the enzyme AChE.

2.2.3 Antidotes for Nerve Agent Poisoning

The effects of nerve agent exposure can be mitigated by the use of antidotes. The inhibited enzyme could be recovered. Many antidotes are available for nerve gas poisoning viz; Atropine and Oximes (such as Pralidoxime, Obidoxime dichloride and Diazepam). Pyridostigmine bromide is a prophylactic agent.

Further, two enzymes found in vivo; A-esterases actively hydrolyses the central phosphorous atom of some organophosphates. B-esterases acts as a decoy to protect acetylcholinesterase, preserving ability to breakdown acetylcholine.

3. PROTECTION AGAINST CWAS CONTRIBUTION OF DEBEL, BANGALORE

Chemical warfare agents are lethal by when they enter our body through respiratory system. The personnel who work in CW environment to carry out required R & D and
OPCW Related verification need respiratory protection mask. DEBEL, Bangalore has developed respiratory protective mask and suitable leak tester to ascertain the integrity of the mask (see Fig. 11 and 12).

The leak tester can test the face masks in few seconds whether the mask is free from any functional degradation that might have occurred due to faulty storage, transportation, ageing, etc. The leak tester is lightweight, microprocessor controlled and battery operated. These products have been thoroughly tested in CW environments. They have been accepted by the Armed Forces and the R & D laboratories working in CW projects.

4. DEMILITARIZATION; DESTRUCTION OF MILITARY STOCKPILE OF CWAs.

The CWC aims to eliminate an entire category of weapons of mass destruction by prohibiting the development, production, acquisition, stockpiling, retention, transfer or use of chemical weapons by signatory countries called States Parties (SP). CWC entered into force on 29th April 1997. About 184 countries so far have been signatories to OPCW, which is an international watchdog for the implementation of CWC. According to the declaration provided to OPCW, six possessor countries have about total of 76,000 tons of CWs contained in 8.67 million containers (storage vessels, munitions). Russia and USA have biggest arsenal; about 40,000 and 30,000 tons of military stockpiles of both Blister and Nerve agents respectively.

4.1 OPCW Verification of CW destruction

According to the provisions of the Chemical Weapons Convention (CWC), a State Party may select and apply the
appropriate destruction methods for its chemical weapons (CW). However, it should be noted that in the process of destroying chemical weapons the following methods are not permitted under the provisions of the CWC: dumping in any body of water, land burial or open pit burning. The destruction has to irreversible and environmental friendly.

4.2 Destruction Timelines

Each possessor country has to destroy the CW stockpile within ten years of entry into force. All possessor countries that have ratified to OPCW had to destroy the total stockpile before 28th April 2008. However, due to some unforeseen problems; political or technical, an extension up to 2012 has been granted some countries.

By the end of 2008, about 30 tons of CW and 3.1 million specialized CW containers (and munitions) have been reported to be destroyed under strict OPCW verification regime by the possessor countries.

4.3 DESTRUCTION TECHNOLOGIES

4.3.1 Destruction by High Temperature Incineration

Incineration of organic chemicals containing carbon, hydrogen, and oxygen leads to the formation of carbon dioxide and water. As chemical warfare agents also can contain fluorine, chlorine, nitrogen, phosphorus, and sulfur, incineration will produce hydrogen fluoride (GB), hydrogen chloride (H, HD, HT), nitrogen dioxide (GA, VR and VX), phosphorus pentoxide (GA, GB, and VX), and sulfur dioxide (H, HD, HT). All of these can be removed by scrubbing. In principle, incineration is an environmentally safe method of toxic waste disposal provided that the temperature used is sufficient to decompose the organic chemical into simple inorganic chemicals.

The incineration (at >800°C) followed by off gas treatment technology has been chosen for destruction of CW by most countries. The process is thermodynamically irreversible. Incineration has been adopted by all six possessors.

However, because some facilities improperly operated in the past, incineration suffers from a poor public image. Nonetheless, most CW has been destroyed by incineration alone than by all other technologies put together.

a. For Sulfur Mustard (HD):

\[(\text{CICH}_2\text{CH}_2)_2\text{S} + 6.5\text{O}_2 \rightarrow 4\text{CO}_2 + 3\text{H}_2\text{O} + 2\text{HCl} + \text{SO}_2\]

b. For Sarin (GB):

\[2(\text{CH}_3)_2\text{CHO(CH}_3\text{)POF} + 13\text{O}_2 \rightarrow \text{P}_2\text{O}_5 + 8\text{CO}_2 + 9\text{H}_2\text{O} + 2\text{HF}\]

c. For VX:

\[2\text{C}_{11}\text{H}_6\text{NO}_2\text{PS} + 38.5\text{O}_2 \rightarrow 22\text{CO}_2 + 26\text{H}_2\text{O} + \text{P}_2\text{O}_5 + 2\text{SO}_2 + 2\text{NO}\]

The by-products of the reaction are scrubbed in NaOH scrubbers and the liquid effluents are concentrated. The solids obtained are then disposed off by land filling or by other approved methods by the individual countries.

4.3.2 Destruction of Lewisite & Nerve Agents by Russian Federation

Russian Federation has about 6771 tons of lewisite stored at the sites of Gorny (293 tons), Kambarka (6349 tons) and Kizner (129 tons)

**Lewisite**;

\[\text{CICH}=\text{CHAsCl}_2 + 6\text{NaOH} \rightarrow \ldots \rightarrow \text{As} + 2\text{CH}=\text{CH} + \text{Other products}\]

The approach reported in the late 1990s as having been selected as the preferred technology in Russia for the destruction of lewisite is that of alkaline hydrolysis by hot sodium hydroxide followed by subsequent electrolysis.

The finely dispersed metallic arsenic contains some inorganic impurity. In the technical product which has been dried up under a moderated temperature, up to 10% of moisture remains. After subsequent sublimation in a flow of an inert gas, technical grade arsenic is obtained that can be used as a starting raw material in electronic industry.

The destruction of Nerve agents has been through chemical neutralisation. The processes are irreversible and environmental friendly. The reactions for Nerve agents (Sarin & Soman) and for VX are given at Fig. 13.

**Nerve Agents Sarin and Soman**:

\[\text{RO}=\text{PO} + \text{HO} + \text{NH}_2 \rightarrow \text{RO} = \text{PO} + \text{OR} = \text{PO} + \text{NH}_2 + \text{HF}\]

**and for VX**;

\[\text{H}_3\text{C} + \text{CICH}_2\text{CH}_2\text{N(C}_2\text{H}_5)_2 \rightarrow \text{iC}_4\text{H}_9\text{OK} \rightarrow \text{iC}_4\text{H}_9\text{O}
\]

\[\text{iC}_4\text{H}_9\text{O} \rightarrow \text{KO} \rightarrow \text{CH}_3\]

**Figure 13.**

4.3.3 Destruction of S M by Chemical Neutralization or Chemical and Bio-degradation

Aberdeen Chemical Destruction Facility (ABCDF), Maryland, USA, has a different approach towards the destruction of Sulfur Mustard. It is a combination of chemical neutralization followed by bio degradation. ABCDF has declared about 1472.44 tons of HD stored in 0.9 kilo liter vessels. Sulfur mustard drained from the bulk container and is hydrolyzed using hot water and sodium hydroxide, wherein Thiodiglycol [(HO-CH2CH2)2 S] is formed. The later is then shipped to Du Pont Chamber works where it is irreversibly disposed of through a classified bio-treatment process.

5. CONCLUSION

Chemical warfare agents pose a serious and credible threat to the mankind. The world has witnessed the havocs created by the CWs during World War I and during recent Iran-Iraq conflicts. That, terrorists may use CWAs as a
weapon of mass destruction has been shown in 1995 sarin gas release incident in Tokyo subway. That, CWAs can also be used against innocent civilian population has been demonstrated when Iraq used Sulfur Mustard against its own Kurdish population in mountainous region of Iraq in 1998 14.

Although chemical warfare agents are stockpiled by several countries either as deterrents or for retaliatory measure, possibility of terrorist sabotage cannot be ruled out. Natural calamities may also lead to catastrophic release of CWs in to the environment of the possessor countries. Ease of preparation of CWs further necessitates the control on precursor chemicals that are produced by several industries worldwide for industrial purposes and it has to be strictly monitored that these precursor chemicals are not diverted for illegitimate purposes like preparation of Weapons of Mass Destruction (WMDs) by terrorists groups. The work carried out by OPCW to implement CWC to mitigate the presence of these dreadful chemical agents is highly appreciated. There are only six possessor countries in the world that maintain military stockpile. Nevertheless, 184 countries of the world support the CWC and are signatories to OPCW, with Iraq being the latest entrant.

REFERENCES
1. For details see; www.opcw.org.
10. (Theobald, N.; Ruhl, N.-P., Chemical warfare agent munitions in the Baltic Sea, Deutsche Hydrographische Z., 1994, 46, 121-131.).