

# Chemical Warfare Agent Degradation and Decontamination

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**Abstract:** The decontamination of chemical warfare agents (CWA) from structures, environmental media, and even personnel has become an area of particular interest in recent years due to increased homeland security concerns. In addition to terrorist attacks, scenarios such as accidental releases of CWA from U.S. stockpile sites or from historic, buried munitions are also subjects for response planning. To facilitate rapid identification of practical and effective decontamination approaches, this paper reviews pathways of CWA degradation by natural means as well as those resulting from deliberately applied solutions and technologies; these pathways and technologies are compared and contrasted. We then review various technologies, both traditional and recent, with some emphasis on decontamination materials used for surfaces that are difficult to clean. Discussion is limited to the major threat CWA, namely sulfur mustard (HD, bis[2-chloroethyl]sulfide), VX (*O*-ethyl *S*-[2-diisopropylaminoethyl] methylphosphonothioate), and the G-series nerve agents. The principal G-agents are GA (tabun, ethyl *N,N*-dimethylphosphoramidocyanidate), GB (sarin, isopropyl methylphosphonofluoridate), and GD (soman, pinacolyl methylphosphonofluoridate). The chemical decontamination pathways of each agent are outlined, with some discussion of intermediate and final degradation product toxicity. In all cases, and regardless of the CWA degradation pathway chosen for decontamination, it will be necessary to collect and analyze pertinent environmental samples during the treatment phase to confirm attainment of clearance levels.

## 1. INTRODUCTION

The 1994 release of nerve agent sarin in Matsumoto, Japan, and the 1995 release of the same agent in the Tokyo subway system by a domestic terrorist cult [1,2] shows that such attacks can be a reality. Cleanup requires a rapid and effective response. In addition, chemical warfare agents (CWA) continue to present real-time concerns while stored and demilitarized at eight existing military stockpile sites in the continental U.S. as well as at current and formerly used military sites where buried munitions have been identified. In these situations, there is possibility of CWA contamination of various media (e.g., soil, water, concrete, structures, and surfaces).

Site-specific factors must be considered in the selection of the most appropriate decontamination or clean-up approaches. These include:

- the amount and physical form (e.g., vapor plume vs liquid droplets) of CWA released,
- climate conditions (temperature, humidity, etc.),
- type of matrices to be decontaminated (e.g., non-porous surfaces; porous surfaces such as concrete, asphalt, or soil; metal surfaces; electronics; or human skin),
- size and complexity of the area or structures in question,
- future uses of the area or structures and anticipated human exposure,
- resource availability.

The rapid collection of this site-specific information, along with general knowledge about the chemical and physical properties of the CWA, their rate of environmental degradation, and specific CWA decontamination technology (advantages as well as disadvantages), can facilitate more rapid and effective response decisions. Such decision-making includes determining whether natural attenuation (passage of time and weathering) may be the most prudent approach.

Environmental fate studies of CWA have been compiled and reviewed by Small [3], Trapp [4], Clark [5], Sanches [6], Kingery and Allen [7], MacNaughton and Brewer [8], Rosenblatt *et al.* [9], and Munro *et al.* [10], among others. The principal degradation processes examined include hydrolysis, oxidation, photolysis, and microbial degradation. Volatilization is an important mechanism for the transfer of the more volatile CWA from soil or water to air.

In most instances, the chemical reactions utilized in commercial decontamination and detoxification processes are the same as those exhibited during natural attenuation, namely hydrolysis and oxidation. Decontamination solutions and procedures significantly increase the rate and efficacy of these naturally occurring degradation reactions. Further, when degradation occurs by several pathways, the degradation pathway(s) can be controlled. Dissolution of the agent in the decontamination solution is necessary for effective degradation. The chemistry of CWA decontamination has been reviewed by several, including Yang *et al.* ([11]; see also Yang [12,13]). This review incorporates available information concerning environmental degradation of CWAs for comparison with the rate of degradation when decontamination procedures are applied. Most of the reviewed technologies are applicable to surfaces (buildings, equipment, etc.), but mention is also made of methods

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**Table 1. Identity and Some Properties of Selected Chemical Warfare Agents<sup>a</sup>**

Chemical Warfare Agent	Mode of Action	Chemical Formula	CAS No.	Physical State	Water Solubility (g/L)	Vapor Pressure (mm Hg)	Hydrolysis Half-Life
HD; bis(2-chloroethyl)sulfide	Vesicant	C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub> S	505-60-2	Oily liquid	0.92	0.11	8.5 minutes <sup>b</sup>
VX; <i>O</i> -ethyl <i>S</i> -(2-diisopropylaminoethyl) methylphosphonothioate	Nerve agent	C <sub>11</sub> H <sub>26</sub> NO <sub>2</sub> PS	50782-69-9	Oily liquid	30	0.0007	41 days
GA; tabun; ethyl <i>N,N</i> -dimethylphosphoramidocyanidate	Nerve agent	C <sub>5</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> P	77-81-6	Oily liquid	98	0.037-0.07	8.5 hours
GB; sarin; isopropyl methylphosphonofluoridate	Nerve agent	C <sub>4</sub> H <sub>10</sub> FO <sub>2</sub> P	107-44-8	Liquid	Miscible	2.10	39-125 hours
GD; soman; pinacolyl methylphosphonofluoridate	Nerve agent	C <sub>7</sub> H <sub>16</sub> FO <sub>2</sub> P	96-64-0	Liquid	21	0.40	5.25 hours

<sup>a</sup>Properties at temperature of 20-25°C, pH of 6.6-8.6 [10,23].

<sup>b</sup>Hydrolysis limited by rate of solution.

applied by military personnel who may become contaminated in the field.

This review focuses on commonly used and commercially available decontamination methods and formulations [14,15,16]. For more experimental formulations, see Yang *et al.* [11]. Recently, available information considered suitable for decontamination of buildings following CWA release was compiled and evaluated for the U.S. EPA [14]. Liquid-based topical agents (including hypochlorite), foams, and gels were among the technologies evaluated.

From the standpoint of decontamination and detoxification following an accidental release, an incident of domestic terrorism, or destruction of stored agents, the primary CWA of concern are the vesicant or blister agent sulfur mustard [HD; *bis*(2-chloroethyl)sulfide] and four nerve agents [VX; *O*-ethyl *S*-{2-diisopropylaminoethyl} methylphosphonothioate, GA (tabun; ethyl *N,N*-dimethylphosphoramidocyanidate), GB (sarin; isopropyl methylphosphonofluoridate), and GD (soman; pinacolyl methylphosphonofluoridate)]. There are other G-series agents, but they are less common. Lewisite [dichloro(2-chlorovinyl)arsine], a vesicant agent, was manufactured in limited quantities and is only briefly mentioned in this review. The agents of primary interest are listed in Table 1 along with some properties that influence their environmental persistence.

## 2. CWA DEGRADATION

Most of the common (stockpile) CWA are subject to hydrolysis and will break down, in most cases, to generally less toxic chemicals in a matter of days to weeks [10]. Environmental degradation depends on the bulk amount of chemical present, the medium in which the chemical is present, and physical conditions of temperature, moisture, and pH.

It is noteworthy that additional studies are being conducted on the fate of chemical agents deposited on outdoor surfaces such as concrete, asphalt, sand, grass, and brackish water. The Chemical and Biological Warfare Agent Fate Research Program [17,18,19] is an international effort involving studies conducted in the U.S., U.K. (Porton Down), The Netherlands, and the Czech Republic. In addition to evaluating multiple surfaces, open air testing is designed to

simulate droplet deposition under multiple attack scenarios, and to incorporate various meteorological conditions such as temperature and moisture regimens. Some studies conducted in soils and on gasket materials under conditions of natural attenuation at Porton Down, UK, indicated that G-nerve agents and nerve agent VX were essentially non-detectable after three days [20].

In general, CWA will break down via oxidation or hydrolysis. While all agents (HD, VX, and G-agents) are subject to breakdown from both mechanisms, HD and VX contain sulfur atoms that are readily subject to oxidation. VX and the G-agents contain bonds to a central phosphorus atom which may be subject to hydrolysis, though VX hydrolysis can result in a toxic breakdown product. As a consequence, decontaminants for CWA are largely designed to oxidize or hydrolyze HD, oxidize VX, and hydrolyze the nerve agents (see Schemes in following discussions for chemical structure). Hydrolysis can be alkaline or acidic. An important category of decontaminant reactions is oxidative chlorination using hypochlorite in alkaline solution [11,21]. To detoxify small amounts of agent or agent-contaminated surfaces, solutions containing excess reactants are used to convert the agent to significantly less toxic products. A more detailed description of processes for each agent is described in the following sections.

### 2.1. Sulfur Mustard (HD; *bis*[2-chloroethyl]sulfide)

#### 2.1.1. Environmental Degradation

Modern formulations of sulfur mustard are often designated by the code letters HD (distilled sulfur mustard of 92% purity). Its first recorded use against combatants during wartime was in World War I (WWI) [3]. Chemically, HD is a strong alkylating agent that reacts with proteins and other macromolecules. Its toxic action is that of a vesicant that can damage the eye as well as produce painful and slow-healing lesions on the skin and in the lungs [22,23]. The onset of effects is often delayed. In addition to its acute effects, HD is a likely human carcinogen at high exposure concentrations. Sulfur mustard deployed in WWI, often referred to as yperite, was persistent in the environment and continued to cause injuries for days after release, especially in cold weather and in low-lying areas or structures such as trenches and basements.



**Table 2. Some Decontamination Methods and Technologies**

Technology	Applicable CWA <sup>a</sup> and Media	Comment (property)
Natural attenuation <sup>b</sup>	Applicable to all agents except destruction of bulk amounts  Multiple media	Site-specific; a preferred alternative when sufficient time is available to allow complete reaction; particularly suitable for terrain, croplands, some sensitive equipment; also possible for urban scenarios involving large complex areas receiving vapor or aerosol releases
Water (steam, sea water, etc.) <sup>b</sup>	All agents  Multiple media; including personnel (skin)  Steam for multiple media, including possible building ductwork	Immediate response in absence of more specific decontamination formulations; improved decontamination/neutralization with addition of soap (see below) and heat; salt-water may increase efficiency due to pH; heated water and steam augment hydrolysis
Soap and water wash <sup>b</sup>	All agents  Multiple media; including personnel (skin)	Immediate response in absence of more specific decontamination formulations; effective for physical removal of contamination from personnel, vehicles, aircraft, loading docks, building exteriors, etc.
Hypochlorite including hypochlorite formulations <sup>b</sup> Chlorine bleach (NaOCl solutions) High test hypochlorite [HTH; Ca(OCl)Cl + Ca(OCl) <sub>2</sub> ] Super tropical bleach [STB; Ca(OCl) <sub>2</sub> + CaO] Hydantoin (dichlorodimethylhydantoin) Activated solution of hypochlorite [ASH; buffered Ca(OCl) <sub>2</sub> ] Self-limiting activated solution of hypochlorite [SLASH; buffered Ca(OCl) <sub>2</sub> ]	All agents; less effective against VX at high pH; hydantoin used to detoxify HD  Select media – high potential for caustic damage; not recommended for personnel (skin) unless extremely dilute	Corrosive to materials; non-dilute solutions are extremely irritating to skin and respiratory system; 0.5% solution of NaOCl may be used to decontaminate human skin; potential for ignition if undilute HTH comes in contact with VX, HD or DS2; HTH not recommended for shipboard use; dry STB incompatible with HD
Fichlor <sup>c</sup> (sodium N,N-dichloroisocyanurate) and Fichlor-containing formulations including CASCAD <sup>®</sup>	VX Select media – potential caustic damage; not recommended for personnel	Stable, general disinfectant; corrosive; contact with combustible materials may cause fire
Chloramine-B (sodium N-chlorobenzenesulfonamide) including U.S. Army M-resin kits <sup>b</sup>	HD, VX Multiple media – potential caustic damage; not for direct skin/human decontamination	Less corrosive than bleach
Oxone (potassium peroxymonosulfate; KHSO <sub>5</sub> ) formulations including L-Gel <sup>c</sup>	HD, VX Multiple media Not designed for human decontamination	Stable; low toxicity but irritating to skin and respiratory system
meta-Chloroperoxybenzoic acid (m-CPBA; C <sub>7</sub> H <sub>5</sub> ClO <sub>3</sub> ) <sup>c</sup>	HD, VX  Multiple media Not designed for human decontamination	Unstable
Magnesium monoperoxyphthalate (MMPP; [HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CO <sub>3</sub> ] <sub>2</sub> Mg) <sup>c</sup>	HD, VX, GD Multiple media Not designed for human decontamination	Stable, mild oxidizer; low toxicity
Sodium hydroxide (NaOH) <sup>b</sup>	Nerve agents Select media – high potential for caustic damage; not recommended for personnel (skin) unless extremely dilute	Caustic

Table 2. contd....

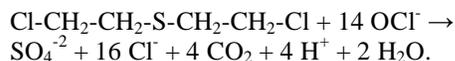
Technology	Applicable CWA <sup>a</sup> and Media	Comment (property)
Decontamination Solution 2 (DS2; 70% diethylenetriamine, 28% ethylene glycol monomethyl ether, 2% sodium hydroxide) <sup>b</sup>	All agents  Select media – high potential for caustic damage; not recommended for personnel (skin) unless extremely dilute	Military-unique decon solution; corrosive and destructive to many materials, metals, protective equipment and human tissues; flammable, incompatible with STB and HTH; undergoing replacement
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> ) with activators and co-solvents; Vaporized hydrogen peroxide <sup>c</sup>	HD, nerve agents  Multiple media; including possible buildings/ductwork; not designed for human decontamination	Unstable; forms non-toxic products that may nevertheless pose clean-up issues; current commercial use is as general disinfectant; toxic at high concentrations
Sandia Foam formulations (contains H <sub>2</sub> O <sub>2</sub> ) <sup>c</sup>	HD, nerve agents  Multiple media; not designed for human decontamination	Same action as H <sub>2</sub> O <sub>2</sub> ; provides visible means to identify applied decontaminant and to maximize adherence times. Greater cost than traditional methods; resulting non-toxic residues may present an additional clean-up issue
Decon Green (H <sub>2</sub> O <sub>2</sub> , potassium carbonate, potassium molybdate, propylene carbonate, surfactant) <sup>c</sup>	All agents  Multiple media – Not designed for human decontamination	Forms nontoxic products; designed as replacement for DS2; means to identify applied decontaminant and to maximize adherence times; some residue and cost disadvantages as above
TechXtract <sup>®</sup> (proprietary technology) <sup>c</sup>	Not tested on CWA  Especially for porous surfaces such as buildings – Not for human decontamination	Chemical extraction process
Reactive Skin Decontamination Lotion (RSDL) <sup>c</sup> (proprietary formulation)	Considered appropriate for multiple agents  For human (skin) decontamination	Minimally irritating to skin

<sup>a</sup>Agent(s) for which the technology is known to be effective or was found effective in laboratory tests.

<sup>b</sup>Traditional method or technology with a sustained history of use as final objective and site/release characteristics allow.

<sup>c</sup>Effective according to laboratory studies, but generally not as well characterized as those methods/technologies with a longer history of actual field use; several have the capacity to replace and improve on historical methods; others are “cross-over” technologies from commercial use as disinfectants against pathogens and are undergoing application development for CWA.

[O=S(CH<sub>2</sub>CH<sub>2</sub>Cl)<sub>2</sub>] followed by sulfone formation [(O)<sub>2</sub>=S(CH<sub>2</sub>CH<sub>2</sub>Cl)<sub>2</sub>]. In the strongly basic solution, both the sulfoxide and sulfone undergo elimination reactions to produce the corresponding monovinyl and divinyl sulfoxides and sulfones. Small amounts of additional products are also formed. This oxidation process yields products of varying but lower, toxicity than that of the parent compound. For example, Lawson and Reid [27] reported mustard sulfoxide as non-irritating and the mustard sulfone as a vesicant. The vinyl sulfoxides and divinyl sulfone have mammalian oral LD<sub>50</sub> values of <100 mg/kg and are moderate skin irritants [10]. If, in the presence of excess reagent, the reaction goes to completion, nontoxic products are formed [21]:



Hydantoin, an organic halamine with a greater chlorinating power than STB or HTH produces the same above reaction products [14]. At ambient temperatures, the strongly basic Decontamination Solution 2 (DS2) reacts instantaneously with HD to form 2-chloroethyl vinyl sulfide which reacts further to form divinyl sulfide [3,11]. Magnesium monoperoxyphthalate (MMPP) can be used for the oxidation of HD.

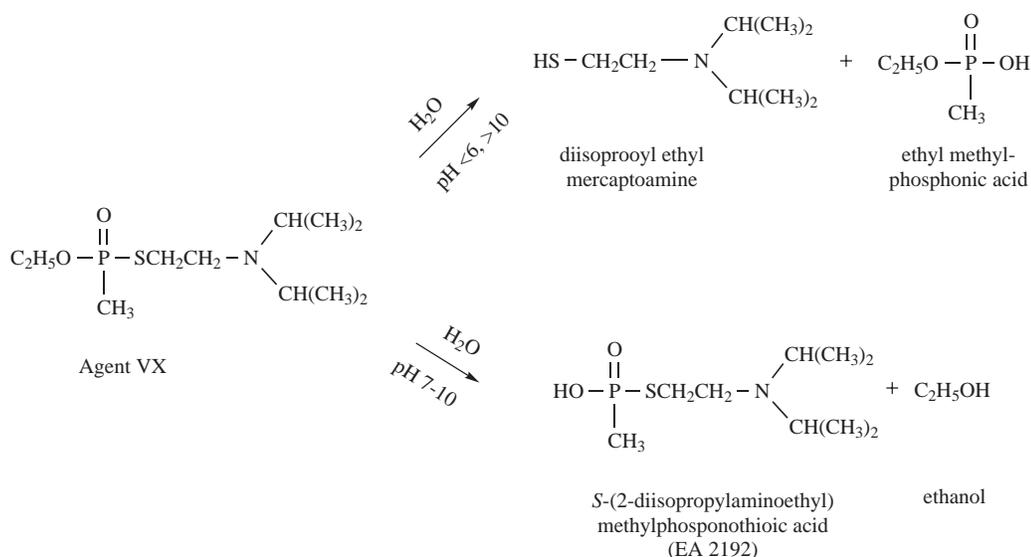
Chloramine-B and Packet II of the M258 and M280 systems (which contain Chloramine-B) can also be used to

decontaminate HD. This reaction is different than that with bleach. Chloramine-B dissolves in water to produce the Chloramine-B anion and OH<sup>-</sup>. The presence of ZnCl<sub>2</sub> maintains an acidic pH. The sulfur in HD reacts with the Chloramine-B anion to form a transient chlorosulfonium anion, which rapidly reacts to form mustard sulfimide, and with water to form mustard sulfoxide [11].

## 2.2. Nerve Agents

The nerve agents are alkylphosphonic acid esters in which the phosphorus is bonded to a hydrocarbon group. This C-P bond is resistant to hydrolysis. As indicated earlier, the nerve agents are generally divided into V agents, the primary one being VX and the G agents, the principal ones being GA, GB, and GD (see Table 1). V-agents such as VX contain a sulfur atom and are alkylphosphonothiolates. GA contains a cyanide group, while GB and GD contain a fluorine substituent group and are methylphosphonofluoridate esters. Although the C-P bond is resistant to hydrolysis, the CN-P and F-P bonds of the G-agents are readily hydrolyzed.

When relatively pure, the nerve agents are viscous, clear liquids. Agent VX is the least volatile (vapor pressure 0.0007 mm Hg at 20°C), while GB (vapor pressure 2.10 mm Hg at 20°C) is the most volatile of these standard threat nerve



**Scheme 2.** Primary hydrolysis pathways of VX in the environment.

agents [10]. The nerve agents are all anticholinesterases; they inactivate cholinesterases, the enzymes responsible for the breakdown of acetylcholine neurotransmitter. When cholinesterases are inactivated, the resulting prolonged neurotransmission can be manifest first as miosis and rhinorrhea and later as tremors, respiratory difficulties, or other symptoms and signs, depending on the affected portion of the nervous system.

The primary mode of nerve agent degradation in the environment is by rapid hydrolysis to the corresponding alkyl methylphosphonates. VX is hydrolyzed to ethyl methylphosphonic acid (EMPA), and more slowly to methyl phosphonic acid (MPA). GB degrades to isopropyl methylphosphonic acid, and GD is hydrolyzed to pinacolyl methylphosphonic acid. The degradation of GA is more complicated.

### 2.2.1. VX (*O*-Ethyl-*S*-[2-diisopropylaminoethyl] methylphosphonothioate)

#### 2.2.1.1. Environmental Degradation

Agent VX is a persistent, odorless, colorless-to-amber liquid. VX is far less volatile ( $10.5 \text{ mg/m}^3$  at  $25^\circ\text{C}$ ) than the G-agents and does not evaporate readily. It is estimated that 90% of VX applied to soil would be lost in 15 days [28]. A Henry's Law constant of  $3.5 \times 10^{-9} \text{ atm}\cdot\text{m}^3/\text{mole}$  [3] indicates that VX is essentially nonvolatile from water. VX is moderately persistent on bare ground where it may remain in significant concentrations for 2-6 days, depending on temperature, organic carbon content of the soil, and moisture [29]. Dissipation is the result of a combination of processes including evaporation, hydrolysis, and microbial degradation. In the laboratory, unstabilized VX of 95% purity decomposed at a rate of 5% per month at  $22^\circ\text{C}$  [30]. All four major degradation products (see Scheme 2) as well as MPA were detected within three days following deposition of VX on soil at low concentrations [31].

Under normal environmental conditions, VX is relatively resistant to hydrolysis [32]. VX hydrolysis in the environment is somewhat dependent on environmental pH, and the

hydrolysis rate increases as the pH increases [33]. With a limited source of moisture, reactions in the environment occur slowly, as dissolved VX forms an acid solution.

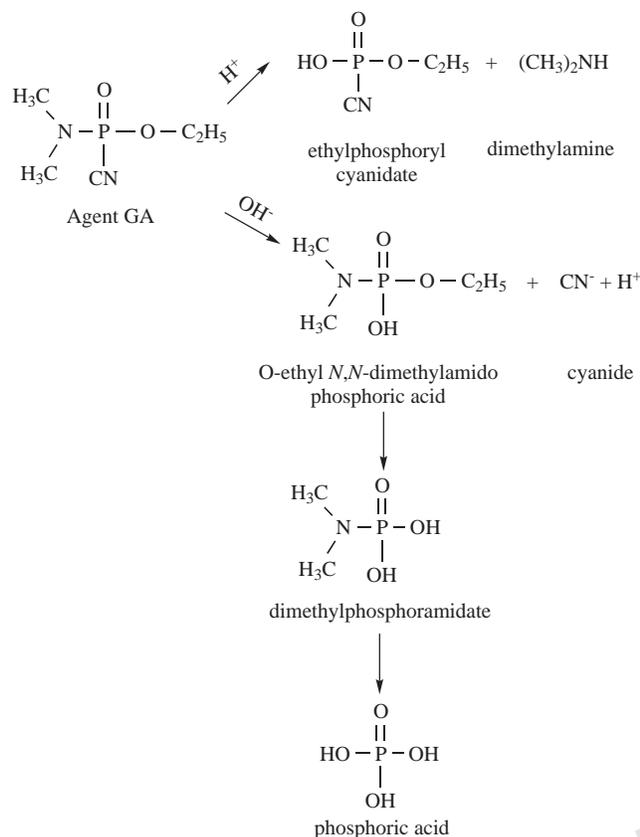
VX can be hydrolyzed by two pathways (See Scheme 2). In both acid and alkaline conditions, cleavage of the P-S bond predominates, resulting in formation of EMPA and diisopropylethyl mercaptoamine (DESH). The latter compound can be oxidized to *bis*(2-diisopropylaminoethyl) disulfide ([DES]<sub>2</sub>, also called EA 4196, or react with the diisopropyl ethyleneimmonium ion  $[\text{CH}_2)_2\text{N}^+(\text{C}_3\text{H}_7)_2]$  to form *bis*(2-diisopropylaminoethyl) sulfide. At neutral to alkaline pH (pH 7 to 10), the above pathway competes with dealkylation of the ethoxy group (cleavage of the O-P bond, followed by addition of a hydroxyl group), the latter pathway yielding the environmentally stable *S*-(2-diisopropylamino-ethyl) methylphosphonothioic acid (EA 2192) and ethanol. In a solution of 0.01 M VX and aqueous 0.1 M NaOH, VX was hydrolyzed to EMPA and EA 2192 ions in a ratio of 87% to 13%, respectively; under these conditions, the half-life of VX was 31 minutes [34,35].

Environmental degradation and alkaline hydrolysis results in formation of EA 2192 which is not only extremely stable in water but is toxic, with anticholinesterase properties [34,36]. Basic hydrolysis results in about 22% EA 2192 [11]. The mammalian oral LD<sub>50</sub> for EA 2192 is 0.6 mg/kg, whereas the oral LD<sub>50</sub> for VX is 0.1 mg/kg (see Munro *et al.* [10] for toxicity values). MPA is of low mammalian toxicity and, by structural analogy, EMPA is predicted also to be of low toxicity [10].

In an experimental study, trace amounts of VX on concrete surfaces (a neutral to alkaline surface) degraded with a half-life of 2-3 hours at room temperature. Degradation was by cleavage of the P-S and S-C bonds, with the major degradation product being DESH [37]. This result is consistent with alkaline hydrolysis within water films associated with the concrete surface.

#### 2.2.1.2. Decontamination

VX is one of the most difficult CWA to destroy [38]. Efficient VX hydrolysis requires acidic conditions; at a high



**Scheme 3.** Primary hydrolysis pathways of GA in the environment.

pH, the solubility of VX is significantly reduced [13]. Provided the pH is kept low, VX can be detoxified by copious amounts of aqueous bleach, i.e., solutions containing NaOCl or Ca(OCl)<sub>2</sub> with little formation of EA 2192 [11,13]. The products are DESH and EMPA. In reviewing the studies of Yang *et al.* [39] and others, Rosenblatt *et al.* [9] also suggest that, under strongly basic conditions with an alcoholic solvent, P-S cleavage is favored and VX could be degraded without the formation of EA 2192. If allowed to go to completion, the reaction of VX with NaOCl (sodium hypochlorite) yields carbon dioxide, water, and salts [40].

Perhydrolysis of VX (reaction with OOH<sup>-</sup>) is extremely rapid and also proceeds without the formation of EA 2192 [35,38]. However, the reaction with hydrogen peroxide is exothermic and dissipation of the heat so produced is critical. Caustic hydrolysis (hydrogen peroxide blended with sodium hydroxide) can also be used to neutralize VX without the formation of EA 2192. Caustic or alkaline hydrolysis is initiated by the nucleophilic attack of the hydroxide ion on the phosphorus atom in EA 2192. The proposed neutralization of bulk amounts of VX at the Newport, IN, Chemical Depot is based on the principles of caustic hydrolysis [41].

VX can be decontaminated by additional procedures. Chloramine-B (see Section 3 for chemical composition) can be used to decontaminate VX [11]. Fichlor effectively oxidizes/detoxifies VX, forming EMPA and a sulfonic acid [11]. EMPA is resistant to hydrolysis, but will slowly hydrolyze to MPA. MPA can be oxidized to phosphoric acid, carbon dioxide and water in the presence of hydrogen

peroxide, oxygen, and ultraviolet light [42]. No intermediates were formed in the case of MPA under this sequence. In aqueous or aqueous polar organic solvents, VX is rapidly oxidized by strong peroxyacids such as the peroxy-monopersulfate in Oxone<sup>®</sup>, magnesium monoperoxy-phthalate, peroxyacetic acid, and *m*-chloroperoxybenzoic acid [13, 43,44]. Nucleophilic substitution with P-S bond cleavage takes place with aqueous peroxycarbonate. These and additional neutralization reactions for VX were summarized by Yang [12,13]. VX reacts with DS2 to form the diester which further decomposes [45]. The resulting degradation products are of low toxicity.

## 2.2.2. GA (Tabun; Ethyl *N,N*-dimethylphosphoramidocyanidate)

### 2.2.2.1. Environmental Degradation

Agent GA present in the environment is subject to evaporation and hydrolysis. The vapor pressure is 0.07 mm Hg at 25°C, making Agent GA more volatile than VX. GA rapidly dissolves in water. Hydrolysis is more rapid under acidic and basic solutions than at neutral pH. Even under acidic and basic conditions, laboratory studies show that GA would persist with a half-life of hours [10]. Persistence in the environment may be even longer under certain weather conditions such as extreme cold.

Depending on pH, GA is hydrolyzed by two pathways [6,8] as shown in Scheme 3. At pH >7, GA is hydrolyzed by hydroxide anion, producing ethyl dimethylphosphoramidate and cyanide anion as initial products. The initial hydrolysis products can be further hydrolyzed to give dimethylphosphoramidate and finally phosphoric acid. The same products are formed under neutral conditions. At pH <5, GA is hydrolyzed to produce ethylphosphoryl cyanidate and dimethylamine.

### 2.2.2.2. Decontamination

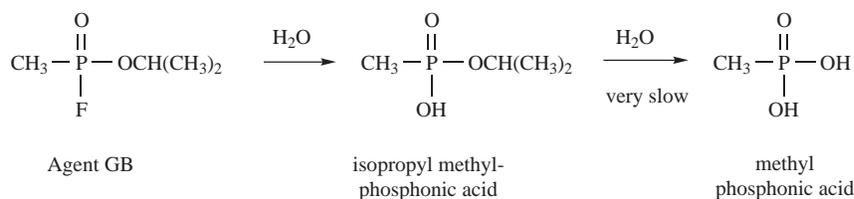
Aqueous solutions of hypochlorite successfully eliminate GA. The hypochlorite anion catalyzes the break of the P-CN bond, substituting a hydroxyl group on the P atom and releasing cyanide which is destroyed in the presence of an excess of hypochlorite [21,46]. The resulting phosphono compound (O-ethyl *N,N*-dimethylamido phosphoric acid) is less toxic than the parent compound [10]. Further hydrolysis results in phosphoric acid. G-agents are also easily decontaminated by dilute alkali and by hydrogen peroxide [47].

## 2.2.3. GB (Sarin; Isopropyl methylphosphonofluoridate)

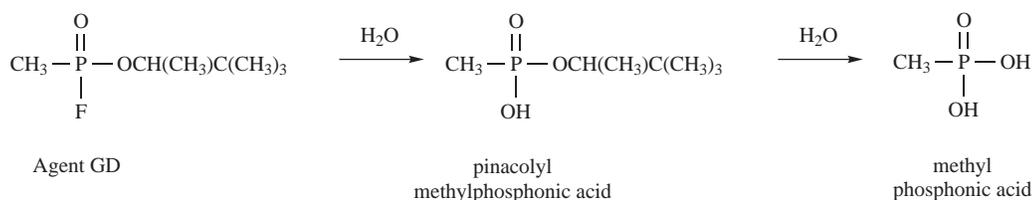
### 2.2.3.1. Environmental Degradation

GB is considered nonpersistent in the environment as it is volatile, soluble in water, and subject to acidic and basic hydrolysis. The evaporation rate of GB approximates that of water [9]. Hydrolysis rates are dependent on temperature, pH, and water quality, and estimated half-lives under ambient conditions are in the range of several days [10]. GB hydrolyzes under acidic and basic conditions, and metal ions catalyze the hydrolysis of G-agents such as GB [48].

The persistence of GB on surfaces has been studied. At 25°C and a loading of 3.33 mg/m<sup>2</sup>, GB persisted on concrete for only 2 hours [49]. It essentially disappeared from pulverized or intact concrete in ≤ 30 minutes [50].



**Scheme 4.** Primary hydrolysis pathway of GB in the environment.



**Scheme 5.** Primary hydrolysis pathway of GD in the environment.

The breakdown of GB results in only a few degradation products, which are relatively nontoxic [9,10]. GB hydrolyzes first through the loss of fluoride, to produce isopropyl methylphosphonic acid (IMPA) and hydrofluoric acid, and second, more slowly through the loss of the isopropanol to produce MPA [7,8,9]. The same products are produced under acidic conditions (Scheme 4). Orally, IMPA is of low acute and subchronic toxicity to mammals [10].

#### 2.2.3.2. Decontamination

GB is rapidly hydrolyzed in basic solutions; as a consequence, several decontamination systems are based on this chemistry. For example, the half-life of GB is 0.5 minutes at pH 11 and 25°C [48]. Aqueous sodium hydroxide has been used as a standard method for the decontamination of bulk GB from munitions [21]. The reaction products are sodium isopropyl methylphosphonate and sodium fluoride. The less corrosive sodium carbonate has also been used for bulk agent decontamination.

Decontamination systems include bleach solutions [NaOCl or Ca(OCl)<sub>2</sub>], and DS2 [11]. Since the 1950s, basic peroxide has been known to degrade GB [46]. The hydrolysis pathway in decontamination solutions is the same as that under environmental conditions. Hydrolysis in Oxone<sup>®</sup> solutions is relatively slow.

The U.S. Army M258 and M280 resin kits are active against GB. Towelette I detoxifies GB and GD by rapid nucleophilic substitution at the phosphorus. The fluoride ions of GB and GD are displaced by the phenoxide, ethoxide, and hydroxide anions to form the corresponding diesters and MPA [11].

#### 2.2.4. GD (Soman; Pinacolyl methylphosphonofluoridate)

##### 2.2.4.1. Environmental Degradation

GD is more persistent than GB. The vapor pressure of 0.40 mm Hg at 25°C [24] is lower than that of GB (but higher than that of GA), and volatilization is expected to take

several hours [3]. GD evaporates at about one-fourth the rate of water [9] (the water solubility is 21 g/L at 20°C [17]). Once dissolved, GD hydrolyzes under acidic and basic conditions to form fluoride (as HF) and pinacolyl methylphosphonate. Hydrolysis is slow under neutral conditions and may take up to 60 hours at pH 6 and a temperature of 25°C [11,51]. The primary hydrolysis product is pinacolyl methylphosphonic acid which slowly hydrolyzes (with the release of pinacolyl alcohol) to MPA (Scheme 5) [5,7,8].

Under field conditions, the measured decay of GD is rapid [31]. The Chemical and Biological Defense Establishment at Porton Down (UK), conducted outdoor experiments in which GD was deposited on 1-m<sup>2</sup> plots of soil at an areal concentration of 10 g/m<sup>2</sup>. Samples were collected immediately (Day 0) and during the following 3 days. The initial decomposition was from hydrolysis of the P-F bond as evidenced in the Day 0 samples. The phosphonate partial ester and MPA peaked in the Day 1 samples and declined subsequently. Pinacolyl alcohol was also detected.

Short-term field trials have been performed with GD droplets applied to silica sand at 5.21 g/m<sup>2</sup>, and laboratory experiments have been conducted with GD liquid applied to soil [18,19]. These studies have demonstrated potential for GD off-gassing due to volume displacement following actual and simulated rain events within hours after initial agent application. With repeated and simulated rain events, GD, *via* off-gassing from soil, declined to non-detectable concentrations at 73.3 hr post-application (following 5 simulated rain events).

##### 2.2.4.2. Decontamination

As noted above, hydrolysis of Agent GD is both acid- and base-catalyzed and is essentially complete in 5 minutes in a 5% sodium hydroxide solution [17]. Copper and imidazole accelerate GD hydrolysis [7]. Decontamination is based on rapid hydrolysis in basic solutions. Alkali salts such as Na<sub>2</sub>CO<sub>3</sub>, NaOH, or KOH rapidly detoxify GD by

converting it to MPA [52]. Chlorine bleach also catalyzes the decontamination reaction [46].

### 3. DECONTAMINANTS AND NEUTRALIZATION TECHNOLOGIES

When considering CWA decontamination of large-scale terrain, the practice of natural attenuation should be considered. As discussed above in Section 2, natural attenuation (i.e., degradation through the combined actions of sunlight, temperature, moisture, aeration, and microbial activity) will substantially reduce CWA concentrations in hours to weeks. Using standard decontamination techniques on large-scale terrain will quickly exhaust resources. If safe entry to a site is necessary, contaminated surfaces can be decontaminated, covered, or scraped and disposed of. Fire can also be used to clear limited areas in isolated areas where downwind transport is not a concern [15].

Many of the following, primarily liquid-based, mostly commercially available technologies were reviewed by Yang *et al.* [11] and U.S. EPA [14]. An earlier review by Yurow [21] describes decontamination technologies available at that time as well as experimental methods developed and tested by the U.S. Army. Elements of these reviews are included in the following discussion of decontaminants and neutralization systems. Additional references to specific technologies are cited during the discussion. Many of these decontaminants can, at least theoretically, be used against biological threat agents [e.g., anthrax (*Bacillus anthracis*)]. Unlike chemical decontaminants, which are not specifically regulated, biological decontaminants need to be approved by the U.S. EPA for specific pathogens under provisions of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (40 CFR 152, 156, 158). As of writing of this article, no products have been approved for threat biological agents such as anthrax, although EPA has given various site-specific crisis exemptions under FIFRA Section 18. For example, in 2002, EPA issued a crisis exemption for the use of bleach against anthrax in the decontamination of Washington, DC office buildings affected by the 2001 "anthrax letters" [14].

Key decontamination technologies and products are described in the following sections. Though some products are marketed as all-around decontaminants, most have certain limitations or are suited to specific agents and/or application scenarios and matrices. Table 2 lists the technologies discussed and summarizes operationally significant information.

It is important to note that while these technologies are identified as "effective" for certain agents, the term is generally used in reference to an evaluation in certain specific circumstances or in a controlled laboratory situation. The actual effectiveness of a technology or approach for a given site application must be verified through post-decontamination clearance sampling. The clearance sampling plan must identify an appropriate strategy including numbers and location of samples, sampling and analytical procedures and data quality objectives, as well as agent-specific target or "clearance" levels. While site-specific considerations must be factored into the selection of such clearance levels, many appropriate health-based criteria for air and soil have been established for such applications [23,53-56].

#### 3.1. Water

Water (H<sub>2</sub>O) can provide a simple and effective means of decontamination, particularly if copious amounts are available for rinsing and if there is not extensive liquid contamination. Under conditions of adequate water supply, rinsing can result in dilution and/or physical removal as well as hydrolysis sufficient to minimize risk. Potential for contaminated runoff could be a concern and would be dependent on the amount of CWA present; runoff water containment and testing would be prudent prior to release of rinse waters to public sewer systems or surface waters.

In certain domestic or military field operations, the availability of water is extremely limited, thus there exist current efforts to develop new and more portable technologies. However, water may have more realistic application in many civilian settings due to its more abundant supply. The use of sea-water or brackish water, which may be more efficient due to its pH and trace dissolved ions, should not be overlooked [8].

Water may be used alone in the decontamination of large open areas (streets, parking lots, etc.) as well as personnel. It is a recommended approach for large mass human decontamination in civilian settings [57]. Improved decontamination and neutralization may be obtained with the addition of soap and/or detergent, and heat (e.g., heated waters or steam).

**Water with addition of soap or detergent** is a combination approach incorporating physical removal and dilution of CW agents by the mechanical force of water applications and the surfactant properties of the solution, plus chemical hydrolysis by direct reaction with water enhanced by the presence of alkaline soaps or detergents. Commercial laundry soaps and detergents as well as aviation soaps are considered effective against agents [15,58]. For vehicles and surfaces, application can be simplified by the use of pressure or spray apparatus. Military recommendations for decontamination of metal machinery, vehicles, equipment, tires and hoses call for soap and water wash with water rinse, and containment of runoff with monitoring to assure that agent reactions have gone to completion and runoff solutions do not contain excess alkalinity or detergents at concentrations that would harm aquatic life [15]. Significant quantities of solution will be required, thus limiting use of this method in arid or otherwise dry climates.

Aircraft washdown is considered most effective when performed within a few hours after contamination, and the GAO reported [59] that the US Air Force considers hot soapy water to be the "most readily available decontaminant to remove chemical warfare agents on aircraft, airfields and equipment."

Soap (or shampoo) and water wash is a commonly cited personnel (including civilian) decontamination approach; warm water and soap are preferred over "plain" water if feasible (see also Section 3.9).

**Steam cleaning** is a potentially useful technology for CWA destruction, but available information was limited to its use as a disinfectant. Steam will augment the rate of hydrolysis of CWA. The method may be useful for decontamination of equipment, small confined areas, or building ductwork.

### 3.2. Strong Bases and Basic Solutions

Strong bases effectively neutralize the nerve agents as well as the vesicant Lewisite [17, 21]. Sodium hydroxide (NaOH) is extremely caustic and will damage skin, the lungs (if inhaled) and clothing, as well as equipment. Aqueous sodium hydroxide has been used as a standard method for decontamination of bulk GB in munitions. Because of its caustic nature, application is limited to some non-porous surfaces.

**Decontamination Solution 2 (DS2)** was developed after WWII because bleach solutions are unstable and not effective in cold weather. It has been a standard military decontaminant, but is no longer recommended for use because it is considered an environmental and human safety hazard due to its composition [59]. DS2 is a strongly basic, stable liquid composed of 70% diethylenetriamine, 28% ethylene glycol monomethyl ether (EGME), and 2% sodium hydroxide. The reactive conjugate component, the EGME base ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}^-$ ) reacts extremely rapidly with HD, VX, and the G-agents [11,21]. In early studies, the half-lives for HD, VX, and GB were all < 30 seconds at ambient temperature. DS2 reacts with HD to form the intermediate 2-chloroethyl vinyl sulfide ( $\text{CH}_2=\text{CH}_2\text{-S-CH}_2\text{CH}_2\text{Cl}$ ) plus hydrochloric acid, followed by the divinyl sulfide ( $\text{CH}_2=\text{CH}_2\text{-S-CH}_2=\text{CH}_2$ ) plus hydrochloric acid.

With the nerve agents, the DS2 conjugate base forms diesters (with release of diisopropyl ethyl mercaptoamine in the case of VX) which decompose more slowly to form products of low toxicity, i.e., EMPA in the case of VX. While highly effective as a decontaminant, DS2 is corrosive to skin, paint, and electronics, as well as seal and gasket materials. It should be noted that the EGME component of DS2 is a reproductive and development toxicant that is readily absorbed by the skin [60]. Thus, nearly all uses of EGME have been curtailed and replaced with other glycol ether congeners.

### 3.3. Hypochlorite Solutions

**Hypochlorite.** Chlorine-based bleaching or sterilizing solutions are highly effective at removing both chemical and biological contamination. Hypochlorite is considered a mature, commercially available technology, useful for treatment of contaminated surfaces of various sizes [14].

Common household bleach is available off the shelf as an aqueous solution of 2-6% sodium hypochlorite (NaOCl). Calcium hypochlorite ( $\text{Ca}(\text{OCl})_2$ ) is a powerful oxidizing agent and is a component of military decontaminants. Since WWII, chlorine bleach or chlorine-based solutions or solid/slurries have been used as general-purpose decontaminants on U.S. military personnel, equipment, clothing, building surfaces, and soil [21]. Undiluted household bleach is easy to obtain and inexpensive, but can be irritating to skin and is corrosive to many surfaces. A 0.5% hypochlorite solution with an alkaline pH can be used for decontamination of skin and is currently fielded by the U.S. military [58]. A 5.0% solution of sodium or calcium hypochlorite can be used for decontamination of equipment. A dilute solution of bleach decontaminates by both oxidation and hydrolysis. Procedures for use of hypochlorite solutions by first responders such as fire and rescue service personnel are outlined by the National Institute of Standards and Technology [61].

The effectiveness of bleach solutions has been improved by introducing stronger oxidants to the system. The inclusion of oxides assures a high pH which, with the exception of VX, promotes agent hydrolysis. Hypochlorite is not an ideal decontaminant for VX, particularly at high pH, but is effective when used in excess quantities and given sufficient reaction time. Some commercially-available hypochlorite decontaminants used on equipment and terrain by the U.S. military include the following.

**High test hypochlorite (HTH)** is composed of calcium hypochlorite [ $\text{Ca}(\text{OCl})\text{Cl} + \text{Ca}(\text{OCl})_2$ ] as a solid powder or a 7% aqueous slurry. The mixture contains approximately 70% available chlorine. HTH is a strong oxidizing agent and is an effective decontaminant of HD and G agents; the solution must be made acidic for decontamination of VX. HTH is very corrosive.

**Super tropical bleach (STB)** is a strong oxidizer, containing 95% calcium hypochlorite [ $\text{Ca}(\text{OCl})_2$ ] plus a strong base, calcium oxide (CaO). It contains at least 30% available chlorine. CaO produces  $\text{Ca}(\text{OH})_2$  in solution. STB is acquired as a solid powder or as 7, 13, 40, or 70% by weight as aqueous slurries. It is more stable than common bleach. Similar to HTH, it is an effective decontaminant for HD and G agents, but must be acidified to destroy VX. STB and HTH are standard U.S. Army field decontaminants [17]. However, STB is extremely irritating, corrosive to metals, and may ignite spontaneously when in contact with certain materials.

**Hydantoin** (dichlorodimethylhydantoin or DCDMH), an organic halamine developed in the 1990s by the U.S. Army, has greater chlorinating power than HTH or STB. It has been used to detoxify HD, nitrogen mustard, Lewisite, and phosgene (carbonyl chloride).

Other hypochlorite decontaminants include the following:

**Dutch powder** ( $\text{Ca}(\text{OCl})_2 + \text{MgO}$ ) has been used by some European countries.

**Activated solution of hypochlorite (ASH)** was developed by the Naval Biological Laboratory in the 1960s [62]. The general formula by weight percent is calcium hypochlorite (0.5%), sodium dihydrogen phosphate buffer (0.5%), Triton X-100 surfactant (0.05%), and water (98.95%).

**Self-Limiting Activated Solution of Hypochlorite (SLASH)** is 0.5% aqueous calcium hypochlorite buffered with sodium citrate/citric acid and detergent [11]. Aqueous solutions of hypochlorite successfully eliminated chemical agents HD, GA, GB, GD, and VX. Both ASH and SLASH are much less corrosive than STB.

### 3.4. Other Oxidizers

**Fichlor** (sodium *N,N*-dichloroisocyanurate) is a stable oxidizer and hydrolysis catalyst. Fichlor reagent reacts in water to produce hypochlorous acid. It has been used extensively in the food and beverage industry as an antimicrobial detergent [14]. This reagent effectively oxidizes/detoxifies VX, forming EMPA and a sulfonic acid [11].

**Chloramine-B** (sodium *N*-chlorobenzenesulfonamide) is a stable, water soluble, oxidizing compound effective with both HD and VX. It is less corrosive than the bleaches. Based on the contents of a Soviet decontamination kit

recovered in 1973, the U.S. Army developed a towelette impregnated with chloramine-B used in conjunction with a sealed glass ampule containing a solution of 5%  $\text{ZnCl}_2$ , 45% ethanol, and 50% water for decontamination of skin and personal equipment [11]. Chloramine-B dissolves in water to produce a caustic solution; however, the presence of the  $\text{ZnCl}_2$  maintains the pH of the solution between 5 and 6.

Related decontaminants are chloramine-T (sodium paratoluenesulfochloramine), dichloramine-B (benzenesulfo-dichloramide) and dichloramine-T (para-toluenesulfochloramine [21,63]. Only chloramine-B has been incorporated into military decontamination kits.

### 3.5. Hydrogen Peroxide

Much current U.S. Army research focuses on less caustic agents such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and enzyme decontamination. Hydrogen peroxide has long been used in the medical community as a biological sterilant. Solutions of  $\text{H}_2\text{O}_2$  with addition of peroxide activators such as carbonate, bicarbonate, and molybdate used with cosolvents such as butanol, ethanol, isopropanol, and surfactant produce rapid nucleophilic/oxidative decontamination of CWA [47]. These solutions decontaminate a broad spectrum of CWA, yielding nontoxic products.

Hydrogen peroxide is unstable and breaks down into nontoxic products — water and oxygen. Hydrogen peroxide is a strong, commercially available, oxidizing agent long used as a household disinfectant. The diluted form, 3-10%, is commercially available for home use. Decontamination occurs via generation of the nucleophile peroxy anion,  $\text{OOH}^-$ . Addition of peroxyacetic acid to  $\text{H}_2\text{O}_2$  increases the oxidizing power. Hydrogen peroxide is used as an ingredient for several formulations developed specifically for CWA decontamination (see below). Oxidizers such as hydrogen peroxide have been tested and shown to be effective for the detoxification of HD, G agents and VX [64]. Hydrogen peroxide combined with sodium hydroxide solution can be used to rapidly neutralize stockpile amounts of VX without formation of EA 2192 [38].

The U.S. Army Edgewood Chemical Biological Center evaluated aqueous hydrogen peroxide reagents on a test-tube scale [47]. The reagents were mixtures of hydrogen peroxide (11-30%), activators such as sodium bicarbonate, and cosolvents such as t-butanol. Co-solvents increase the contact between  $\text{H}_2\text{O}_2$  and the chemical agent, and activators increase the effectiveness of  $\text{H}_2\text{O}_2$ . The reaction speed increased as the concentration of activator increased. For example, GB in neutral peroxide (1.3 mL of 30%  $\text{H}_2\text{O}_2$  and 1.9 mL of t-butanol) exhibited an initial half-life of 67 hours (the reaction slowed prior to complete hydrolysis). When bicarbonate (0.037 M  $\text{NaHCO}_3$ ) was added to the solution, the reaction half-life was <1 minute. The reaction proceeds with the initial loss of fluoride.

For VX, the combination of peroxide, activator and cosolvent is an effective decontaminant, as the toxic EA 2192 product is not formed [47]. As noted above, hydrolysis of VX forms acidic products which slow the reaction; however, the reaction would go to completion in the presence of a large excess of decontamination solution. Addition of bicarbonate buffer also drives the VX reaction to

completion. Cassagne *et al.* [44] reported similar results for VX in  $\text{NaHCO}_3/\text{K}_2\text{CO}_3$ -buffered  $\text{H}_2\text{O}_2$  (pH 8).

HD is oxidized fairly slowly in a solution of 1.3 mL of 30%  $\text{H}_2\text{O}_2$  and 1.9 mL of t-butanol [47].  $\text{H}_2\text{O}_2$  solutions greater than 20%, with additions of t-butanol and bicarbonate (<1 M) decreased the reaction half-life to  $\leq 2$  minutes. Solid urea peroxide can be used instead of peroxide solutions. These reactions continued, albeit slower, at temperatures as low as  $-30^\circ\text{C}$ . Addition of molybdate in place of bicarbonate, acting through generation of either singlet oxygen or peroxomolybdate such as  $\text{MoO}(\text{OO})_3^{2-}$  or  $\text{Mo}(\text{OO})_4^{2-}$  oxidized the HD two orders of magnitude faster at the low temperature. Addition of molybdate to the peroxide did not interfere with the decontamination of VX.  $\text{H}_2\text{O}_2$  perhydrolysis, although slower than hypochlorite oxidation, selectively yields the non-vesicant sulfoxide.

**Vaporized hydrogen peroxide (VHP)** is a patented process of oxidizing fumigation. The vapor is generated from concentrated peroxide solutions (>30%  $\text{H}_2\text{O}_2$ ) [14]. At present this technology is commercially used in fumigation cabinets and to disinfect surfaces, but is under experimental investigation as a CWA decontamination technology. Modified vaporous hydrogen peroxide (mVHP) contains low levels of ammonia gas. This technology (both VHP and mVHP) has been tested in the laboratory for efficacy against CWA [65]. At a concentration of 250 ppm and with a contact time of 24 hours, mVHP reduced GD, deposited in a room-size chamber, to pinacolyl methylphosphonic acid. Although not corrosive, concentrated  $\text{H}_2\text{O}_2$  vapor is toxic and interacts with many surfaces, including concrete.

### 3.6. Peroxygen Oxidants (Peroxy Acids)

**Oxone<sup>®</sup>**, active ingredient potassium peroxymonosulfate ( $\text{KHSO}_5$ ), is a relatively stable, commercially available compound. Oxone<sup>®</sup> dissolved in water produces an acidic solution and can be used for the dissolution and detoxification of VX and HD. Oxone<sup>®</sup> was not found to be effective for the oxidation of GB or GD [11].

**meta-Chloroperoxybenzoic acid (m-CPBA;  $\text{C}_7\text{H}_5\text{ClO}_3$ )** is a strong oxidizing agent available as a powder. It is not particularly stable. m-CPBA can be used for the oxidation of HD and VX (oxidation occurs at the sulfur atom) [11].

**Magnesium monoperoxyphthalate (MMPP;  $[\text{HO}_2\text{C C}_6\text{H}_4\text{CO}_3]_2 \text{Mg}$ )** is a stable, water-soluble, solid peroxyacid that has been used as an antimicrobial. MMPP was active in oxidizing/detoxifying VX and GD. Reaction with VX formed the VX N-oxide prior to subsequent oxidation and hydrolysis into the nontoxic EMPA [44].

### 3.7. Foams and Gels

Foams and gels are formulated to be non-corrosive and are marketed as “environmentally friendly,” as they break down into nontoxic chemicals. For example, as noted above, the  $\text{H}_2\text{O}_2$  component breaks down into oxygen and water. Another reason for the development of these products was to provide a more effective means to visibly identify where decontaminant has been applied and to maximize adherence times. However, these products tend to cost more due to sole source suppliers. In addition, resulting residues, though nontoxic, may present an additional clean-up issue [14]. These

newer decontamination techniques have not been as well tested as the traditional methods. Foams and gels act by a combination of oxidation and hydrolysis.

**Sandia Foam** was developed by Sandia National Laboratory and is commercially available (see U.S. EPA [14]). Sandia Foam is a combination of surfactants and oxidizers, including H<sub>2</sub>O<sub>2</sub>, sold as several formulations. The foam is actually a liquid that can be applied as foam, liquid, or aerosol, depending on the application apparatus. It has been tested and is purported to be effective against chemical and biological agents. Its action against agents would be primarily that of H<sub>2</sub>O<sub>2</sub>.

A newer version of Sandia Foam, DG-200, has been laboratory tested against nerve and vesicant agents [14]. Decontamination of GD was 99.98% effective in one minute and 78.13% effective against HD in the same time period. A similar Sandia Decon formulation was tested at Edgewood Chemical Biological Center with the following results. In one hour, 100% of the agents HD, GD, and VX were decontaminated. This product was also effective against other toxic chemicals such as hydrogen cyanide, carbon disulfide, and phosgene.

**DECON GREEN™** was patented at Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, by Wagner and Yang in 2001 [64,66]. DECON GREEN™ is a solution of H<sub>2</sub>O<sub>2</sub>, potassium carbonate, potassium molybdate, propylene carbonate, and the surfactant Triton X-100. DECON GREEN™ may be used as a sporicidal and chemical detoxification agent. As of 2005, DECON GREEN™ had been tested only in the laboratory. DECON GREEN™ is targeted to replace DS2.

**Canadian Aqueous System for Chemical-Biological Agent Decontamination (CASCAD®)** is a proprietary mixture that contains Fichlor as an active ingredient and several surfactants [14]. The mixture contains both a powder and a liquid, packaged separately; when combined, foam is generated. The formulation was developed in Canada in the late 1980s by the Canadian Defense Research Establishment, Ottawa, Ontario, and is commercially available in Canada, as well as through the U.S. Department of Defense. Based on Canadian testing, the CASCAD® system was effective against vesicant and nerve agents.

**L-Gel** is a spray-on decontamination gel developed at Lawrence Livermore National Laboratory [14,67]. It is considered effective against both chemical and biological agents. The oxidant Oxone® which contains the peroxy-monosulfate anion as active ingredient is the moderate strength oxidizer; the oxidizer is formulated with a silica gelling agent. L-Gel has been tested in the field and laboratory [67]. Preliminary tests indicate that L-Gel is relatively non-toxic and non-corrosive. As noted above, Oxone® oxidizes VX to non-toxic products.

### 3.8. Other Liquid-Based Technologies

**TechXtract®** is a proprietary contaminant extraction technology that is commercially available [14]. The extraction process can be applied to porous building materials to emulsify and extract compounds. The solubilizing and mobilizing formulation contains emulsifiers; flotation,

wetting, and sequestering agents; buffered organic and inorganic acids; and hydrotropic chemicals. The resulting wet-vacuumed liquid contains the extracted contaminants.

### 3.9. Decontamination of Personnel

Most of the products and technologies described thus far are not intended for direct use on the skin. The following are products made specifically for the decontamination of unprotected skin of exposed persons. To be most effective, decontamination following exposure to any chemical or biological agent should be done within the first minute or two after exposure [58]. In the absence of specific decontamination solutions, timely physical removal is imperative. In emergency situations, common household products such as soap and warm water, absorbent talcum, flour, etc. can be effective in removing CWA from contaminated skin [68]. OSHA's Best Practices document notes that several agencies recommend the use of a good surfactant such as hand dishwashing detergent while showering for rapid physical removal of agent ([www.osha.gov](http://www.osha.gov)).

**M258 and M280** systems were developed by the U.S. Army. They are based on kits recovered from Soviet military vehicles in 1973 [11]. The kits consist of two sealed packets. Packet I contains a towelette pretreated with a decontamination solution of 72% ethanol, 10% phenol, 5% NaOH, 0.2% ammonia, and about 12% water. Packet II contains a towelette impregnated with Chloramine-B and a sealed glass ampule filled with a solution of 5% ZnCl<sub>2</sub>, 45% ethanol, and 50% water. The glass ampule is broken immediately prior to use and added to the towelette in Packet II. Towelette I is effective against the G-agents and Towelette II is designed to decontaminate both HD and VX [11].

**M291** resin kit is used by the U.S. military for chemical casualty decontamination. The M291 resin kit contains a dry, black resin that rapidly adsorbs the chemical agent. Carbonaceous material physically removes the agent from the skin. An ion-exchange resin then neutralizes or detoxifies the chemical agent [58].

**RSDL** (Reactive Skin Decontamination Lotion), a newer product developed by the Canadian Defense Research Establishment, is available commercially through a Canadian company and is being provided via the U.S. Department of Defense to first responders in the United States. RSDL is a yellow viscous liquid, impregnated in a sponge pad contained in a foil pouch. It is considered a broad spectrum decontaminant. It is minimally irritating, and can be removed with water. In 2003, following tests by Battelle's Medical Research and Evaluation Facility, Columbus, OH, the U.S. Food and Drug Administration gave approval for use of RSDL [69].

Finally, although not a decontamination procedure, it should be noted that as part of protection of military personnel, reactive coatings, i.e. surface coatings that would neutralize chemical and biological agents, are being developed [70]. These coatings are not commercially available at this time.

## CONCLUSIONS

Site-specific considerations such as the amount and physical form of CWA released, climate conditions, type of

matrices to be decontaminated, size and complexity of the area or structures in question, future uses of the area and associated human exposure, as well as resource availability, are critical in determining the most appropriate decontamination or clean-up approach(s). However, general knowledge about the chemical and physical properties of the CWA, their rate of environmental degradation, and specific advantages and disadvantages of available CWA decontamination technologies, can facilitate more rapid and effective response decisions. This includes the consideration of natural attenuation as a decontamination method.

Although natural attenuation is not always considered a 'decontamination technology,' the chemical reactions and detoxification pathways utilized in the specific decontamination technologies follow the same chemical reactions (i.e., hydrolysis and oxidation) as would take place during natural attenuation/environmental degradation. While decontamination solutions and procedures can significantly increase the rate and efficacy of these naturally occurring degradation reactions, a review of historically-used CWA decontamination solutions shows that many of them are irritating, corrosive, and often damaging to the environment or items to be decontaminated.

The application of natural attenuation (time and weathering) may be a practical if not preferred alternative if there is sufficient time to allow reactions to occur naturally. This may be especially true for large areas or where sensitive items cannot be effectively decontaminated without damage. When considering large areas, the time for natural attenuation, e.g., days to weeks, may be similar to the time it would take to identify and implement a decontamination plan. In either case, environmental clearance sampling would be required.

New decontamination materials and technologies that are effective as well as environmentally acceptable are now becoming more readily available; however, such products still have certain limitations, and generally result in more significant cost.

It is important to note that, although many different technologies and products have been developed, it is unlikely that a single technology will be applicable to all situations. Many scenarios will require consideration of more than one technology.

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