DEACTIVATION OF BLISTERING AGENTS: LITERATURE REVIEW

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ABSTRACT.

Recently, the relevance of research into the design of effective systems for the decomposition of chemical weapons components has been dictated by the current large-scale Russian-Ukrainian war with a high probability of the enemy using chemical weapons to exterminate both the military and civilian population. The group of chemical warfare agents (CWA) of blistering action includes mainly stable liquid substances, a characteristic feature of which is inflammation of the dermal integument of varying degrees. A typical representative of this group is mustard gas, which, depending on the concentration, causes both local skin lesions and general organism poisoning. A review of studies and publications on the use of mostly chemical and some physical methods of mustard gas decontamination was conducted. A series of works focuses on the issues of maintaining high efficiency and controllability of decontamination processes, creating optimal conditions for the dissolution of hydrophobic toxic substrates with maximum contact between the degasser and the toxic substance. The analysis of data on the use of various formulations for the breakdown of chemical warfare agents has shown that the use of "green" systems based on hydrogen peroxide for the destruction of toxic substrates on an industrial scale and for individual decontamination is preferable to other methods. The sources of scientific information cited in this review indicate that there is currently a lack of universal decontamination systems for CWA decontamination that would guarantee rapid and effective degradation of these compounds. This problem requires additional search for optimization of decontamination systems.

Keywords:

Chemical warfare agents, sulfur mustard, degassing system, individual decontamination, hydrogen peroxide

INTRODUCTION

In accordance with the "Convention on the Prohibition of the Development, Production, Stockpiling, and Use of Chemical Weapons and on their Destruction" [1], the priority during the elimination of chemical weapons and chemical warfare agents (CWA) is to ensure the safety of individuals and protect the environment. Safety measures, both during routine destruction operations of chemical weapons and in emergency situations,

necessitate the establishment of a scientifically substantiated CWA decontamination system. This system should aim to exclude or minimize the impact of CWA hazardous factors on humans and the surrounding environment. Achieving this goal requires comprehensive exploration of both domestic and international achievements related to the deactivation processes. The problem of ecologically acceptable environmental decontamination, in cases of chemical weapon battlefield use or accidents, is one of the key directions of sustainable development. Utilizing the methodologies proposed in scientific literature for decontamination, using principles of "green chemistry," holds promise and potential for commercialization.

In addition to the challenges of large-scale industrial disposal of chemical weapon components, the problem of effective decontamination of toxic substances arising from terrorist acts as well as accidents in chemical and pharmaceutical production facilities arises. In this regard, special attention should be given not only to the decontamination of surfaces, walls, and other interior elements of premises for further use but also to the deactivation of chemical agents present on human and animal skin.

According to their physiological effects, there are six groups of chemical warfare agents: nerve-paralytic, vesicant (blister), systemic, asphyxiating, and irritant agents. In the context of the Russian-Ukrainian war, first two classes of chemical warfare agents: nerve-paralytic agents (organophosphorus compounds) and vesicant agents (mustard gas and its analogs) are considered to be the most dangerous ones [2].

The deactivation of chemical warfare agents in case of environmental contamination has become of particular interest recently due to the increasing concerns about internal security, terrorist attacks, and the threats of chemical weapon use [2, 3]. The urgency of efficient reactive systems developing for the decomposition of chemical warfare agents is also driven by the ongoing war in Ukraine, with a high probability of chemical weapons use. Incidents involving the use of nerve-paralytic and other chemical warfare agents have been documented during Russian military operations in Syria (2017), the Salisbury incident (2018), the poisoning of Navalny (2020), and the potential chemical attack in besieged Mariupol (2022). According to international experts' data [3], Russian Federation has accumulated significant quantities of poisoning agents like mustard gas, soman, lewisite, sarin, V-gas, etc., which have been used extensively (around 300 times) during the Syrian conflict. Therefore, there is a real threat of contamination of Ukrainian territories with vesicant agents (HD-type).

Chemical decomposition of ecotoxicants urges the search for technical solutions that partially align with the principles of "green chemistry." These solutions should meet several conditions, including commercial availability of reactants/equipment, high reactivity, and complete neutralization of chemical warfare agents (CWA) as a result. The decontamination system should also demonstrate universality in its ability to neutralize various classes of toxic compounds without special conditions for diverse applications and operation modes. Moreover, the system must ensure a high degree of ecological safety in both its chemical composition and the decomposition products of ecotoxicants. It should exhibit low corrosion activity and facilitate the removal of toxic substances from the skin surface of affected individuals. Additionally, the decontamination system should remain chemically stable during storage and transportation [4].

Meeting these conditions highlights the significance of maintaining of the high efficiency and controllability of decontamination processes. Additionally, it underscores the need to create conditions for the dissolution of hydrophobic toxic substrates with maximum contact between the decontaminant and the toxin [5].

OBJECTIVES

The study was carried out to evaluate effective, safe and environmentally friendly methods of decontamination of chemical warfare agents (CWA) with blistering effects, in particular mustard gas, using the principles of green chemistry and modern reagents that can be used both in emergency situations and for personal protection.

METHODOLOGY

The methods of literature-systemic and critical analysis, the method of summarising results from various sources to create a comprehensive picture of the state of the scientific problem, and the method of comparative analysis of various approaches used in research on the topic of the review were used. The review presents the classification of CWA, physicochemical approaches to the decontamination of CWA with blistering effect, the study of reactions with mustard gas imitators; the use of oxidation systems based on H₂O₂ activated by hydrocarbonates, boric acid, molybdates; catalytic oxidation of mustard gas using nanodispersed metal oxides. The efficiency of the formulations is evaluated: measuring the efficiency of degassing with different substrates, temperature

conditions, pH environment, etc., and comparing them with existing NATO standards. This methodology makes it possible to study, compare and propose the most effective approaches to chemical mustard gas neutralisation with the possibility of practical use in both military and civilian protection.

RESULTS AND DISCUSSION

Toxic Action of Sulfur Mustard (Iprith)

Sulfur mustard (also known as bis(2-chloroethyl) sulfide or HD) belongs to the group of vesicant chemical warfare agents (CWA), which includes mostly stable liquids with high boiling points. One of the its characteristic features is the skin inflammation, ranging from redness to the formation of pus-filled blisters that may develop into ulcers [6, 7]. For the military applications of sulfur mustard, artillery chemical shells, explosive chemical aviation bombs, and chemical fuzes have been developed [8].

Sulfur mustard (HD) exhibits incapacitating effects through any mode of body entry. Even at low concentrations, sulfur mustard can cause irritation and damage to the mucous membranes of the eyes, nose, and upper respiratory tract. At higher concentrations, it can lead to systemic poisoning in addition to local effects [6-8]. During the first 2-5 minutes of exposure, HD penetrates the outer layers of the skin, and within 7-10 minutes, it dissolves in the subcutaneous fatty tissue. Within next 20-30 minutes, it is completely absorbed and enters the bloodstream. Following absorption, there is a latent period of toxic action lasting from two hours to a day, depending on the dose of CWA, temperature, humidity, skin structure, and moisture. HD demonstrates cumulative properties, meaning its effects can accumulate over time [6, 8–10].

Damage to cells in the basal layer of the epidermis leads to detachment of the epidermis from the dermis or, at high doses, direct necrosis and destruction of the epidermis. The content of the blister does not contain active sulfur mustard. The rate of HD absorption through the skin at a temperature of $21-23^{\circ}$ C is 1.4×10^{-3} mg/(min cm²), and at a higher temperature, it is 2.7×10^{-3} mg/(min cm²). The resorptive action of sulfur mustard can be explained by its high solubility in lipids [7–9].

Eyes are especially sensitive to sulfur mustard vapors. Painful chemical conjunctivitis, causing reflexive eyelid closure, occurs earlier than cutaneous symptoms but still after a delay of several hours. The cornea may become cloudy [6, 7, 11].

Respiratory manifestations of poisoning may include coughing, laryngospasm, hoarseness, and wheezing. In severe cases, a sensation of chest constriction and dyspnea may develop. Pneumonia can occur under strong exposure, and death may result from suffocation on the 3rd to 4th day [10-12].

The principal form of sulfur mustard application is aerosol. The minimum dose that causes blister formation on the skin is 0.1 mg/cm². The lethal dose through the skin exposure is 70 mg/kg, while the lethal dose for oral exposure to sulfur mustard is 2 mg/kg [6, 7]. The threshold toxic dose is 0.05 mg.min/L; through skin exposure, LD50 is 50-70 mg/kg; MACatm. - 2.10^{-6} mg/m³; MACwater - 2.10^{-4} mg/L [6, 8].

Cases of massive population exposure, which may occur due to sulfur mustard military application, should be prioritized for immediate decontamination. De-gassing the skin within 2 minutes is ideal, but decontamination measures performed within 15 or 20 minutes after exposure can reduce the size of existing blisters [8, 13].

2. Systems for the Chemical Neutralization of Sulfur Mustard and its Cognates

Bis(2-chloroethyl) sulfide is a polyfunctional compound composed of three main components: a central nucleophilic sulfur atom and two adjacent electrophilic carbon centers, each containing a chlorine atom.



Bis(2-chloroethyl) sulfide, commonly known as HD (sulfur mustard)

Due to partial positive charges on the carbon atoms directly bonded to chlorine, bis(2-chloroethyl) sulfide (HD) exhibits electrophilic properties, making it capable of reacting with nucleophilic reagents. The presence of two lone electron pairs on the sulfur atom imparts nucleophilic characteristics to HD, enabling it to interact with electrophilic reagents. Consequently, hydrolysis reactions are possible at one center, while oxidative processes can occur at the other [8, 14, 15].

Nucleophilic Reactions

In general, the interaction of HD with nucleophilic reagents is described by the following reaction:



Under specific conditions, the simultaneous elimination of hydrogen chloride (HCl) may occur alongside the nucleophilic reactions of bis(2-chloroethyl) sulfide (HD), while the elimination of HCl becoming dominant in non-aqueous environments [14, 15].

The unique structure of bis(2-chloroethyl) sulfide is responsible for its high reactivity, as the central sulfur atom can undergo intramolecular nucleophilic substitution, displacing any chlorine atom to form an unstable episulfonium intermediate product (epi-HD) [16]. The highly strained epi-HD exhibits increased electrophilicity, forwarding its chemical degradation through hydrolysis and other nucleophilic substitution reactions.

Hydrolysis can be considered as a two-step process, with epi-HD intermediate products formed in the ratedetermining step, followed by a rapid reaction with water to yield the products depicted in Figure 1 [16].

Theoretically, HD can be decomposed through hydrolysis (Fig.1), but in reality, the process is complicated by the formation of toxic and stable aggregates of sulfonium ions, such as TG (thiodiglycol), H-TG, CH-TG, and H-2TG. Moreover, the slow dissolution rate of HD results in the ion products forming at the surface even before complete dissolution occurs [14, 16, 17].

The rate of hydrolysis is limited by the low solubility of bis(2-chloroethyl) sulfide in water, as well as the formation of intermediate hydrolysis products that protect the droplets of bis(2-chloroethyl) sulfide from hydrolysis and slow down the whole process. The formation of final products depends on the temperature, mechanical agitation rate (stirring), and the presence of other substances that influence the solubility and the rate of HD hydrolysis [16]. The hydrolysis mechanism depends on the amount of water and can proceed through two pathways, both of which lead to the formation of thiodiglycol and hydrochloric acid. In a dilute aqueous solution, bis(2-chloroethyl) sulfide rapidly transforms into the episulfonium ion, which further reacts with a water, producing the chlorohydrin of mustard and TG. If the amount of water is not enough to dissolve all of the bis(2-chloroethyl) sulfide, TG-type sulfonium aggregates are formed at the water-bis(2-chloroethyl) sulfide interface [16, 18].



Figure 1 Pathways of Hydrolysis of Sulfur Mustard HD [16]

The rate of HD hydrolysis in seawater is lower than in freshwater due to chloride ions shifting of the equilibrium between bis(2-chloroethyl) sulfide and the intermediate episulfonium ion towards the reactants [19]. It is believed that the formation of sulfonium aggregates is responsible for the high stability of bis(2-chloroethyl) sulfide in stagnant water, as they create a stable layer around the primary droplet, preventing further hydrolysis reactions of bis(2-chloroethyl) sulfide and promoting its prolonged life in the environment [16].

The HD decomposition rate increases with rising temperatures: at 0.6°C, half of the substance decomposes in 3 hours, at 10°C, it decomposes in 51 minutes, at 20°C, it decomposes in 10 minutes, and at 37°C, it decomposes in 3 minutes. Since the hydrolysis of HD is a reversible process, the introduction of acids slows it down. In an alkaline environment, the reaction rate increases because the alkali neutralizes the hydrogen chloride released and shifts the reaction equilibrium to the right [20].

Mustard gas (bis(2-chloroethyl) sulfide) readily reacts with salts of alkali metals of low weight carboxylic acids:



Since these reactions occur with quantitative yields of products, potassium acetate, for example, can be used both for decontamination purposes and for analytical purposes [8].

Electrophilic Reactions

All chemical transformations of HD involving the central sulfur atom, which possesses two lone electron pairs, belong to electrophilic reactions. Electrophilic reactions, especially oxidation and chlorination, are primarily used for the decontamination of mustard gas [8, 16, 17].

Under normal conditions, oxygen of the air does not react with HD, although HD can burn in the air at high temperatures. Any oxidizing agents (hydrogen peroxide, nitric acid, hypochlorites of alkali and alkaline earth metals) convert mustard gas into dichlorodiethyl sulfide oxide (HDO) and dichlorodiethyl sulfone (HDO₂) according to the following scheme [16]:



Figure 2 Oxidation of sulfur mustard HD [16]

Selective oxidation of sulfur mustard to the corresponding sulfoxide (HDO) (Fig. 2) represents an attractive deactivation strategy since the monooxidized product exhibits improved chemical stability, resulting in lower hydrolysis rates compared to HD. As a result, the sulfoxide HDO is relatively inert in biological systems and does not manifest skin-blistering effects. On the other hand, the sulfone HDO_2 is as toxic as the parent mustard HD. For this reason, effective decontamination is achieved only when sulfur mustard is selectively oxidized to the non-blistering sulfoxide. Therefore, careful monitoring of the oxidation process is essential during the deactivation of large batches to avoid harmful excessive oxidation to the sulfone.

In the presence of an excess of oxidants, the process does not stop at the formation of the sulfoxide and sulfone. The sulfone is further transformed into β -chloroethane sulfonic acid, which undergoes complete destruction under harsh conditions [14, 15]:



From all the oxidation products, the most dangerous is dichlorodiethylsulfone, which toxicity is comparable to that of mustard gas. In other words, the decomposition of mustard gas through an oxidative mechanism is prioritized by stopping the oxidation at the stage of sulfoxide formation and preventing further formation of the toxic sulfone [14, 21].

It should be noted that currently, complete incineration of chemical warfare agents at high temperatures (> 1000 °C) is one of the common methods of neutralization. When sulfur mustard is burned, water and carbon dioxide are formed, as well as hydrogen chloride and sulfur dioxide, which are toxic upon inhalation [22]. Therefore, the development of environmentally friendly methods for the complete and selective transformation of sulfur mustard into non-toxic derivatives with the generation of limited waste and by-products still remains relevant.

The high oxidative activity of hypochlorous plays an important role during the decontamination of mustard gas, which, in alkaline environments, undergoes destruction, yielding a range of oxidation products and elimination (Reaction 4) [23, 24].



Hypochlorites are degassing substances of universal action and are used for detoxification of human skin, equipment and terrain [23, 24]. At the first stage of this rather complex process, sulfoxide is formed, which is further transformed into other products.

Despite the fact that hypochlorites are produced on a large scale and are relatively inexpensive, they, as degassing substances, have a number of significant disadvantages: low stability during storage; strong corrosive action on the surface during storage and use; relatively high toxicity, etc. Milder agents for CWA degassing are N-Cl derivatives of ammonia, amines, amides, ureas, hydantoins, urethanes, etc., so-called chloramines, which can be imagined as amide derivatives of hypochlorous acid (HClO and R(R') N- Cl). However, these compounds have its own disadvantages: lack of universality of action; weaker action at low temperatures; high consumption of solvents for water-insoluble reagents, etc. [23].

Thus, the mustard degradation methods discussed above have a number of limitations and disadvantages. Intensive studies of the reactivity of hydrogen peroxide and its activators (carbonates, molybdates, phthalates, etc.) have shown that the formulation of degassing compositions based on these compounds is one of the most promising directions for mustard gas decontamination [14, 17, 23]. In recent years, the activation of H₂O₂ under the action of silicates, vanadates, borates, bicarbonates, capable for in situ formation of the corresponding peroxoanions [16, 25-27], has become particularly relevant.

Reactions involving H₂O₂

Analysis of the significant variety of degassing systems shows , that the special attention is paid to systems based on hydrogen peroxide and its derivatives due to its dual universal nature: as an α -nucleophile in the form of an HOO⁻ anion and a mild oxidant in the form of H₂O₂ [10, 27, 28].

Hydrogen peroxide is a widely used oxidizer with a high content of active oxygen, has high solubility in aqueous solutions, and could be considered as an environmentally friendly (the only byproduct is water), but with weak oxidizing ability in the absence of activators [29, 30].

The most common mustard models in studies devoted to the oxidative destruction of HD by hydrogen peroxide and its derivatives are: diethyl sulfide (Et₂S), methylphenyl sulfide (MeSPh), ethylphenyl sulfide (EtSPh), hydroxyethylphenyl sulfide (PhSEtOH), chloroethylethyl sulfide (CEES) [16, 25, 31, 32].

The method of H_2O_2 activation by using bicarbonate ion was first described by Richardson D.E. and co-workers [31] in studies of sulfide oxidation reactions in water-alcohol mixtures. It was established that the catalytic effect of bicarbonate is associated with the formation of peroxomonocarbonate anion (HCO₄⁻) in the pre-equilibrium reaction between bicarbonate ion and H_2O_2 [27, 31, 32].

The study of the oxidation kinetics of diethyl sulfide and methylphenyl sulfide by hydrogen peroxide in aqueous and aqueous-alcohol environments revealed a significant increase in the reaction rate when ammonium bicarbonate (NH_4HCO_3) was introduced into the system [25, 32]. The formed peroxomonocarbonate anion oxidizes sulfides to sulfoxides [25, 27]:



In the range of pH 7–9, the catalytic effect of bicarbonate does not depend on the acidity of the medium, and at pH > 9 it sharply decreases [25, 31, 32].

It is shown that regardless of the structure of mustard model compound, bicarbonate ions are effective activators of H_2O_2 in the oxidation process: the second-order rate constant for ~ is 100 times higher than for H_2O_2 , and, accordingly, the anion as an oxidant is more than two orders of magnitude more active compared to H_2O_2 [25, 31, 32].

At the same time, several reports noted the possible nucleophilic properties of HCO_4^- , CO_4^{2-} ions formed in the system: H_2O_2/HCO_3^- . In particular, it is stated that the HCO_4^- anion can act as a nucleophilic moiety during the decomposition of phosphoric acid esters [5, 25].

Boric acid B(OH)₃ can be regarded as another activator type for H_2O_2 in oxidation reactions. It forms peroxoborates which are strong oxidants upon interaction with in a wide pH range, [33-37]. It can be stated that the catalytic effect of boric acid is caused by the formation of different types of anions in the solution: monoperoxoborates (MPB), diperoxoborates (DPB) and peroxoboric acid (PBA) [35-37]. In works [36, 37] it was demonstrated that boric acid additives at $[B(OH)_3] >> [H_2O_2] >> [Et_2S]$ and pH > 8 strongly accelerate the oxidation of diethyl sulfide both in water and in a water-alcohol mixture (isopropanol/water 30:70 vol. %). The dependence of the observed Et2S oxidation rate constants in the H_2O_2 - B(OH)₃ system on pH in both aqueous and aqueous-alcohol environments (Fig. 3) has a maximum at pH ≈ 10 [36, 37].

It was shown that MPB and DPB exceed the oxidizing capacity of H_2O_2 both in water and in the iPrOH/water mixture ~ by 2 and 80-100 times, respectively. Therefore, boric acid serves as an effective catalyst for the oxidation of organic sulfides [37].

A group of perhydrate compounds, like urea hydrogen peroxide (carbamide peroxide, UHP), sodium peroxocarbonate (sodium percarbonate, SPC); sodium peroxoborate (sodium perborate, SPB) became widespread, due to the high content of H_2O_2 in solid, stable form [38, 39, 40].



Figure 3 Dependences of Et_2S oxidation rate constants vs pH in the mixture of isopropanol/water (\circ and \bullet) and water (\blacksquare), 25 °C: 1-[H₂O₂]₀ = 0.05 mol•t⁻¹; 2 and 3 - [H₂O₂]₀ = 0.02 mol•t⁻¹, [B(OH)₃]₀ = 0.2 mol•t⁻¹ [37]

It was found that UHP is an effective oxidizer of mustard model compounds, which provides a fairly high degree of substrate conversion, selectivity, and yield of reaction products (Table 1) [41]. Also tt should be taken into account the possibility of using UHP as an oxidation agent in anhydrous media [41]. The absence of toxic solvents, which are often used in large quantities, is a key feature of these ecologically benign degassing systems.

N⁰	Substrate	Product	Sulfoxide yield, %	Sulfone yield, %
1	s S	0=0	80	10
2	~~~s~~~		85	13
3			87	0,9
4			87	11

 Table 1 Solid-phase oxidation of sulfides with UHP at 85 °C [41]
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In the process of decontamination systems formulation, a certain amount of polymer is introduced into the composition to give formulations prolonging properties. The work [20] describes a degassing composition based on UHP for mustard gas decontamination of various surfaces. Modified water-soluble starch polymer was added into a composition as a film-forming agent to support the formation of a protective and insulating screen on the treated surface [20]. The work [42] demonstrated the effectiveness of an acrylic polymer thickener in maintaining the necessary viscosity level in the oxidation of mustard model compounds in microemulsion media.

Latel a certain part of attention was attracted to the use sodium percarbonate as an oxidizer for organic compounds of various classes, including sulfides [43, 44]. The authors of [45, 46] assume that SPC is involved in the in situ peroxomonocarbonate formation.

The effectiveness of SPC in micellar-catalyzed oxidation reactions has been described in papers [47, 48]. It is noteworthy that a large amount of research in organic synthesis is attributed to the selective oxidation of sulfides by SPC [44, 49]. In [50] a highly selective method for the synthesis of sulfoxides (99% product yield) in aprotic media was presented.

In a number of works devoted to the selective oxidation of sulfides, it is stated that sodium peroxoborate SPB provides high yields of target products, ecological friendly conditions, and stability in a wide temperature range (up to 55 °C) [45, 48, 51]. Thus, in the SPB /CH₃CO₂H system in the range of 50-55 °C, the oxidation of MeSPh proceeds with a yield of 70%, and dibutyl sulfide - 93% [52].

According to [39], the rate of oxidation of individual substrates by peroxoborate anions is 7-10 times higher than the rate of oxidation by hydrogen peroxide, and, in addition, SPB has a fairly effective buffering effect. Corresponding processes of SPB oxidation of sulfides to sulfoxides have been described in literature [47-51, 53]. **Physical and catalytic methods of neutralization**

It should be noted that the use of ion exchange resins and sorbents based on fullerenes, or perfluorocarbons as polydegassing compounds considered as the one of the most promising areas of research on chemical degassers [14, 54].

Upon the formulation of effective decontamination systems, mesoporous metal oxides, zeolites, aerogels, metalorganic frameworks or functionalized activated carbon fibers are recently used as sorbents and/or catalysts [6, 30]. It was shown that functionalized activated carbon fibers are capable of adsorbing significant amounts of CEES mustard model compound (up to 340 mg/g) and serve as catalysts for the subsequent degradation of the poisonous substance [9]. But for the widespread usage as material for protective clothing certain problems are to be served like low flexibility, ineffective removal of moisture vapors, medium weight and comfort in use [9].

A promising approach is the use of metal oxides in nanodispersed form as degassing powders. Due to the high degree of dispersity, these compounds are capable at room temperature to initiate catalytic oxidation of various poisonous substances, including mustard gas, with the formation of low molecular weight inorganic molecules [55, 56]. Thus, it was shown that in the process of degassing with the use of nanosized aluminum oxide, the conversion of 80% was achieved in conversion of mustard gas into non-toxic products 80% [55].

The authors [57] studied the deactivation of chloroethylphenyl sulfide as a model compound for sulfur mustard bythe nanocrystals of mixed metal oxides Al₂O₃-Fe₂O₃, Al₂O₃-V₂O₅, and Al₂O₃-CuO in various media (isopropanol, acetone, n-hexane) at certain range if temperatures of 25, 35, 45, and 55°C. It was shown that the maximum deactivation level (100%) occurs in n-hexane at 55°C after 1 hour of reaction [57].

It should be emphasized that due to the hydrophobic nature of mustard gas, the optimal decontamination system should provide solubilization of substrate and at the same time promote high rates of decomposition of the poisonous substance. Therefore, organized nanoscale systems are used - micellar solutions and microemulsions, where reagents are concentrated at the interface between the micellar phase and water [17, 58].

In order to increase the reaction rate, metal containing catalysts are added in the composition of microemulsions. It was shown in [16] that aromatic sulfides were oxidized with a yield of 40-50% after 2-24 hours using the H_2O_2/Na_2MoO_4 system in a water-in-oil microemulsion. Oxidation of these substances is much more difficult process compared with typical mustard imitators. According to the authors, molybdate acts as an activator of hydrogen peroxide, generating singlet oxygen, which reacts with substrates dissolved in the "oil" medium.

Individual mustard decontamination

Solutions for individual decontamination of mustard gas are used in all units of the Armed Forces of Ukraine to prevent the effects of chemical weapons on both military and the civilian population, as well as for processing premises, military equipment, clothing, and the environment. The degassing of mustards requires the use of

effective (highly reactive, safe, ecological, mostly multi-degassing, cost effective) decontamination systems [59-61].

For human skin, uniforms, equipment, personal protective equipment, weapons, military equipment and terrain contaminated with mustard gas degassing, the following degassing recipes from individual antichemical packets (IAP) – IAP-8, IAP-9 are used IAP-11, DPP degassing package recipe; degassing recipes RD-2, RD-A; degassing solution No. 2-bsch; aqueous solutions of calcium hypochlorite (CH): DTS CH, aqueous solutions of SF-2U powder (Table 2) [59-63].

The role of the components in these systems could be described as follows: gasoline, kerosene, chlorobenzene accelerate the reactions of CWA with the degassing agent, contribute to rapid dissolution, complete removal of CWA from contaminated materials that absorb CWA; 2-ethoxyethanol and n-butanol help to dissolve the degassing agent in an aprotic environment; potassium isobutylate and sodium n-butylate interact with CWA to form non-toxic products; diethylenetriamine stabilizes the formulation against moisture, and also accelerates the reaction of CWA with the degassing agent [59-66].

The disadvantages of the above methods are the toxicity of the materials used, the multicomponent composition, in some cases the solutions are flammable; cause irritation when coming into contact with unprotected skin and short shelf life.

Name	Chemical composition
IAP-8, IAP-9	68,8% dimethylformamide, 23,7% 2-ethoxyethanol, 7,5% 2-sodium ethoxyethoxylate
IAP-11	5,6% lanthanum(III) nitrate hexahydrate, 65,5% triethylene glycol, 25% 2-(2- ethoxyethoxy)ethanol, 0,8% NaOH, 2,6% water
DPP	50% sodium salt of dichloroisocyanuric acid, 44% CaO, 6 % aerosil
RD-A	49% gasoline Б-70, 12,4 % diethylenetriamine, 11,4% 2-ethoxyethanol, 20,4% n- butanol, 6,8 % sodium n-butylate
RD-2	37,6 % kerosene KO-30, 48,3% chlorobenzene, 5,2 % 2-ethoxyethanol, 4,7 % isobutanole, 3,8 % potassium isobutylate, 0,4 %. Oxyphos-A
IDP	Degassing solution №1 (2% solution of dichloramine in dichloroethane), №2-asch (2% NaOH aqueous solution with 5% ethanolamine, 25% ammonia solution)
Degassing solution №2-bsch	10% NaOH, 25% ethanolamine, 65 % water
DTS CH	56% Ca(OCI) ₂ , 24% Ca(OH) ₂ , 8% CaCI ₂ , 10% CaCO ₃ , 2% water
SF-2U	25% alkylbenzene sulfonates, 50% sodium triphosphate, 18% sodium sulphate, 7% water
M291	0,5 % Sodium hypochlorite, 1 % soap solution in water
DS2	70 % diethylenetriamine, 28 % 2-methoxyethanol, 2 % NaOH

Table 2 Individual mustard decontamination systems [59-63]

The usage ofe systems based on hydrogen peroxide and peroxoanions [38, 67-70] gives an opportunity to eliminate the shortcomings of the above-described degassing methods and increase the rate of mustard gas decomposition. Thus, the authors of the patent [71] proposed a decontamination formulation for the decomposition of HD substances by action of peroxy compounds using environmentally safe hydrogen peroxide reagents and potassium molybdate activator.

Table 3 shows the formulation composition and its influence upon the half-life of HD. Table 3 demonstrates that the half-life of a toxic compound primarily depends on the concentration of the potassium molybdate activator. Despite the availability of various variations of IAP used from the 60s to the 90s, it is worth analyzing the

composition of individual degassing means of mustard, adopted for usage in NATO military formations. One of the first IAPs used in the USA for mustard decontamination was polydegassing bag No. 2 of the M 258 skin decontamination kit [72].

At the end of the 20th century this package was replaced by an individual anti-chemical package M 258A1, which is a plastic case containing two sets of napkins impregnated with degassing solutions No. 1 and No. 2, wrapped in foil plastic. In 1996, the M-295 kit (recipe similar to M-291, Table 2) was adopted for usage of the US Army. At this time, military units of NATO use RSDL (Canada), M291 and M295 (USA), as well as MK1 (Great Britain) individual degassing packages, showed sufficient performance against both nerve-paralytic and blistering agents [63].

N⁰	K ₂ MoO ₄ ,	50% H ₂ O ₂ , g	Cosolvent	Surfactant	t _{1/2} , s
	mg		i-PrOH, g	Triton X-100, g	
1	2,4	0,236	0,471	0,214	39
2	3,6	0,295	0,432	0,214	<30
3	2,4	0,295	0,432	0,214	32
4	2,4	0,295	0,432	0,214	345
	-				(-30°C)

Table 3 Formulation of composition and half-life periods of HD [71]

The M-291 and M-295 kits share the same formulation, developed on the basis of Ambergard XE-555 resin (a mixture of halogenated styrene/divinylbenzene resins). CWA is rapidly transferred to and retained within the resin particles. The presence of acidic and basic groups in the resin contributes to the destruction of the trapped chemical agent both by acid and alkaline hydrolysis. M291 consists of three main components - fiber gasket (6 pcs), activated carbon and ion exchange resin Ambergard XE-555. Activated carbon, in addition to its direct, sorption action, also performs the role of an indicator. The presence of a black color indicates that the CWA, even if sorbed, is still on it and must be removed [63].

After World War II, the DS2 mixture (Table 2) was used as a non-aqueous deactivator for HD. Treatment of HD with DS2 results to the sole formation of divinyl sulfide within 1 min. Although DS2 is corrosive to the skin, it is suggested for emergency use for field decontamination [16, 62].

RSDL is offered by a number of manufacturers and used by armed forces of various countries [4]. Careful tests of RSDL showed a high efficiency in the processes of sulfur mustard deactivation [73]. Pads made of special Opcell polystyrene material instead of a cotton are used for impregnation, due to the higher sorptive properties compared to the usual fibrous materials [4, 73].

The English Individual MK1 degassing package, which includes Fuller's earth, is also effective against mustard gas. Fuller's earth differs from ordinary clay of the montmorillonite group by a large percentage of water and lack of plasticity [4, 74].

Hydrogen peroxide is also actively used in decontamination packages produced on an industrial scale for NATO military and rescue teams as a part of Decon Green systems, DF-200, as effective polydegassing compositions [76–78]. Table 4 shows the decontamination efficiency of compositions used for treatment of various surfaces impregnated by mustard or model compounds.

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	Degassing composition, wt%	Surface type	E, (%)	Poison agent
1	76,8 UHP, 6,3 cetylpyridinium chloride, 13,5 activator (ammonium bicarbonate, boric acid and salts), 3,4 sodium hydroxide, (H_2O_2 - 0,98 M) [37]	interior elements of premises, human and animal skin	62	MeSPh
2	78,5 UHP, 16,8 ammonium bicarbonate, 4,6 CTAB, 0,1 sodium hydroxide, (H ₂ O ₂ - 0,97 M) [37]	interior elements of premises, human and animal skin	58	MeSPh
3	30 CTAC1, 30 isobutylamine, (H ₂ O ₂ -2,06 M), ret - water [79]	surfaces of buildings, equipment, soil,	20	MeSPh
4	25-30 benzyltrimethylammonium chloride, 5-10 benzyltriethylammo-nium chloride, 50-55 2 amino-2- methyl-1-propanol 2-10 sodium perborate tetrahydrate 10-15 water [80]	surfaces of buildings, equipment	61	HD
5	RSDL [73]	the surface of the protective suit; painted steel plate	99,9 99,9	CEES
6	RSDL Fuller's land [81]	human hair in vitro	73 85	CEES
7	hydrogen peroxide (3-30%) adsorbed on microporous activated carbon [30]	protective clothing, air filters	95	HD

 Table 4 Degassing efficiency (E, %) of decontamination compositions against mustard and its model compounds

Table 4 show that the effectiveness of formulations No. 1 and 2 exceeds one of composition No. 3. Compositions No. 1 and 2 also increase shelf life of the composition up to 1 year compared to composition No. 3 (2-3 months) without losing the speed of CWA decomposition processes. The composition manufacturing process is high-tech and waste-free, has simple technological design and does not require complex energy-consuming equipment (Table 4) [38].

According to [73], during the use of RSDL lotion for protective suit and a painted steel plate contaminated with mustard gas degassing, the efficiency of the process is higher compared with hair decontamination (Table 4, No. 5 and No. 6). The authors [81] draw attention to the fact that the release of residual amounts of pollutant from the hair can lead to health problems.

Hydrogen peroxide (3-30%) effectively decomposes mustard gas adsorbed on microporous activated carbon used in protective clothing and air filters (Table 4, No. 7). HD degassing efficiency at ambient temperature within 1-24 hours depending on H_2O_2 concentration achieves 95%, HD is oxidized to non-toxic sulfoxide. NMR spectroscopy data showed that the reaction took place in micropores: the microenvironment facilitates decomposition and adsorbs the reaction product [30].

Thus, the efficiency of degassing depends on the composition of the degassing system, type of contaminated surface, and impurities that can accelerate the mustard gas decomposition.

CONCLUSIONS

The war in Ukraine, conflicts in the Middle East have shown that today CWA can be used as a weapon of mass destruction. These facts prove the need of new methods of CWA disposal developing through converting toxic substances into less harmful or harmless compounds. Due to the fact, that some of these products may still have a toxicity, it is critical to develop selective methods under decontamination conditions. The use of many reagents to neutralize CWA generates large amounts of waste that become pollutants when released into the environment. Therefore, the CWA degradation process should preferably involve environmentally friendly reagents and form a minimal amount of non-toxic products.

The issues of maintaining sufficiently high efficiency and controllability of decontamination processes, search for proper conditions for dissolving hydrophobic toxic substrates with maximum contact between the degasser and the poisonous substance remain challenging for researchers.

It worth noting that during the development of systems for individual decontamination, in addition to the main function of CWA detoxification, it is important to fulfill the following conditions: long shelf-life of formulation and formation of a protective layer on the degassing surface after treatment. These conditions are met by introduction a certain amount of polymer or chemosorbent into the composition, creating the necessary viscosity of the solution. As a result, chemically active protective and degassing coatings or protective and preventive screens are formed on the treated surfaces.

The analysis of data on the use of various formulations for the splitting of CWA gives reason to draw an important conclusion: the use of "green" systems based on hydrogen peroxide both for the destruction of toxic substrates on an industrial scale and for individual decontamination is preferable compared to other methods.

It is possible to increase the environmental attractiveness and economic feasibility of oxidizing-nucleophilic systems based on hydrogen peroxide, the concentrated solutions of which are dangerous during storage, transportation, and working with them, by using alternative solid sources of H2O2, for example, peroxysolvates of urea and sodium carbonate, sodium perborates. They are non-toxic, storage-stable products of commercial availability, that can be used as effective degassing systems for long-term storage, in contrast to hydrogen peroxide solutions with activators, whose functionality is limited in time.

The sources of scientific information cited in this review indicate that, to date, there is a lack of universal degassing systems for CWA decontamination that would guarantee rapid and efficient degradation of these compounds. This problem requires additional optimization of decontamination systems.

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