



DECONTAMINATION: AN ENABLING CAPABILITY FOR CHEMICAL WARFARE AGENTS RISK MITIGATION

Chemical Warfare Agents, CWAs, include a wide group of highly toxic compounds that pose a serious threat to humans and environment. In the framework of the 30th anniversary of the Chemical Weapons Convention, CWC, the main treaty in the struggle against the use of these substances, we have focused on the different aspects of decontamination as a tool for risk mitigation.

Among the weapons of mass destruction, chemical weapons are probably one of the most brutal created by mankind and criminal events involving Chemical Warfare Agents (CWAs) represent one of the main threats in the modern international scenario. These highly toxic compounds have been used not only in war scenarios (such as the recent civil war in Syria), but also in terrorist and illicit actions

(e.g. the use of aggressive nerve agents in Salisbury, 2018) or for sabotage purposes. Chemical weapons are often inexpensive and relatively easy to produce even by small terrorist groups. In addition, unintentional events, such as the accidental release of substances from stockpile sites or buried obsolete munitions represent an important source of concern. The use of these substances, along with represent-

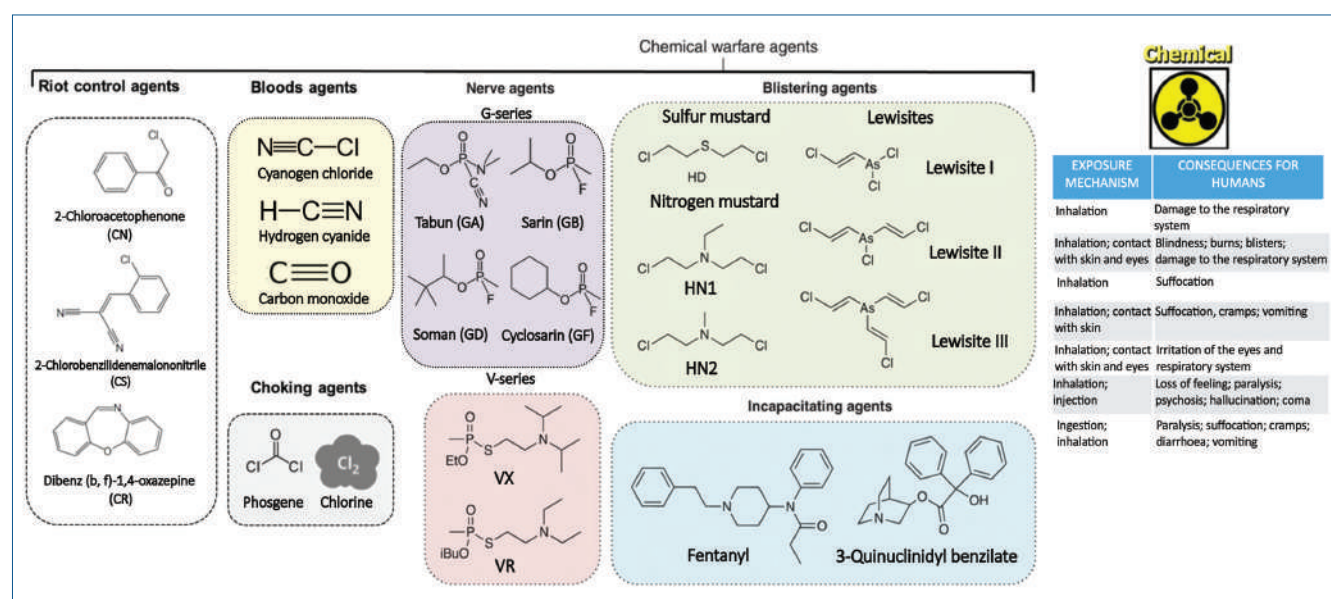


Fig. 1 - Categories of CWAs based on their toxicological effects on human beings



ing a real danger to humans, constitutes a threat to national defence, economy and especially the environment, because of the strong toxicity and persistence of these compounds in ecosystems.

Chemical weapons, according to the Chemical Weapons Convention (CWC) [1], are defined as extremely toxic chemicals and their precursors, munitions, devices and any equipment specifically designed to be used directly in connection with such weapons, which, through their effects on life processes, can cause death or incapacity, temporary or permanent to humans and animals. From a historical perspective, the First World War is considered as the dawn of the “modern chemical warfare” in which more than 50 different chlorine-based CWAs (e.g. tear gases, chlorine, phosgene and diphosgene, mustard agents or yperite) were massively deployed on various battlefields, causing approximately 1.3 million of non-fatal casualties and 90,000-100,000 fatalities [2]. Then, starting from the 1930s, several organo-phosphate-based nerve agents were discovered and some of these were later developed for military purposes, although they were never “officially” used in warfare on a large scale [2].

Based on their effects on humans, CWAs are categorized in *blistering or vesicants* (which cause severe skin, eye and mucosal pain), *incapacitating agents* (e.g. fentanyl), *nerve agents* (acetylcholinesterase inhibitors which mortally affect the nervous system, e.g. sarin), *bloods agents* (inhibiting mitochondrial respiration in tissues, e.g. hydrogen cyanide), *choking agents* (causing severe pulmonary impairment, such as chlorine and phosgene) and *riot control agents* (causing temporary incapacitation, e.g. tear agents) (Fig. 1) [3, 4].

Although the CWC [1] prohibits development, production, acquisition, stockpiling, retention, transfer or use of chemical weapons by Member States, still nowadays CWAs represent a major safety and security threat to populations.

Countermeasures against CWAs

The development of suitable procedures for the safe identification, destruction and abatement of CWAs has been always an active area of research in the scientific community. Nowadays, countermeasures to deal with these dangerous substances are mainly based on “three pillars”:

- *detection*, that means revealing, identifying the agents and hazards, delineating the areas of contamination and monitoring the changes in concentration and dispersion of toxic agent;
- *protection*, using personal protective equipment (PPE) against hazardous agents;
- *decontamination*, that is the set of actions to remove hazardous materials from victims, personnel, areas, surfaces, objects, to reduce the potential contact with CWAs and to recover the initial situation of non-contaminated scenarios (Fig. 2).



Fig. 2 - Decontamination activities

In detail, the *NATO Triptych Decontamination* defines it as the removal and/or neutralization of chemical, biological, radiological and/or nuclear contamination. Decontamination plays an essential role in defending against aggressive and toxic substances by applying effective methods as quickly as possible, to avoid further victims and to resume normal activities. Decontamination implies the conversion and degradation of toxic chemicals into harmless products by destruction or detoxification.

Conventional decontamination methods

Conventional decontamination methodologies, well known since decades, are basically divided into physical, chemical and thermal ones [5].

Physical decontamination

It consists primarily in either removing or encapsulating contaminants. All materials used for the physical removal of chemical agents shall be treated as contaminated waste. However, since usually no actual destruction or detoxification is achieved, the contamination problems are merely relocated. Subsequent treatment of the relocated agent will always be required to achieve complete decontamination. For this reason, physical decontamination may be considered as a partial method, although the action of removing contaminants can still achieve the main aims of limiting the spread of contamination and reducing the associated risk through reduction of potential exposure. A combination of physical and chemical/thermal methods is generally necessary to active decontamination. Well known examples of physical decontamination are:

- washing/rinsing with water, organic solvents, mixtures and surfactants;
- accelerated evaporation by heating (optionally combined with vacuum techniques);
- adsorption and removal with solid adsorbents

- (e.g. clays, silica gel);
- removal of protective layers applied prior to contamination;
- burying or sealing contamination;
- scrubbing with brush or abrasive material;
- vacuum cleaning.

Chemical and thermal decontamination

Chemical decontamination methods rely on chemical reactions, which transform toxic molecules into less or non-toxic substances. These reactions may be triggered by suitable chemical compounds, but also by UV/vis irradiation, by the use of plasma or by thermal treatment of contaminated substrates which may also lead to the chemical modification or destruction of the agent. Due to the specific nature of most chemical agents, hydrolysis and oxidation are the main reaction mechanisms that allow efficient decontamination. For instance, organosulfur blistering and phosphonothioate nerve CWAs have sulfur atoms that are susceptible to oxidation, whereas all nerve agents are sensitive to hydrolysis at the phosphorus atom. Chemical decontamination methods may belong to one or any combination of three processes:

- electrophilic (oxidation, chlorination);
 - nucleophilic (hydrolysis or other nucleophilic attack, e.g. with oximate);
 - complete destruction (full oxidation, thermal degradation, plasma-induced radical reactions).
- Over-stoichiometric oxidation reactions with active *chlorine-based oxidants* (e.g. bleach-based detergents, chlorinated lime, decontamination solutions with NaOCl and Ca(ClO)₂, sodium dichloroisocyanurate or chloramine-B) were among the first oxidants used in chemical decontamination processes and are still largely in use today. Dilute aqueous solution of hypochlorite is effective in degrading the nerve agent VX, or neutralization with aqueous NaOH destroys significant

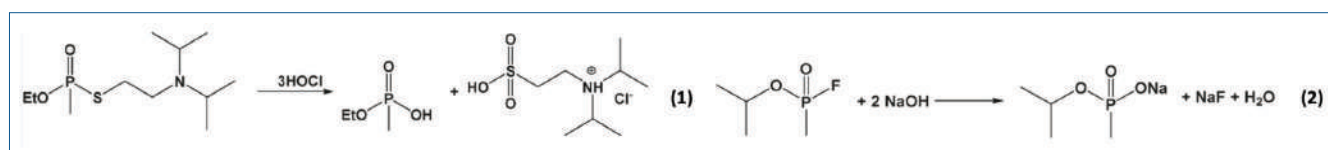


Fig. 3 - Reaction of VX with hypochlorite (1), hydrolysis of Sarin (GB) with aqueous NaOH (2)



amounts of sarin [6] (Fig. 3). Other oxidizing decontaminants rely on the action of chlorine dioxide, peroxyacids, peroxides, such as H_2O_2 and ozone. Many ready-to-use effective chemical formulations have been developed, since the 1960s. Historically the *DS-2 decontaminant solution*, in use by NATO armies until about the 1990s, containing NaOH (2%), diethylenetriamine (70%) and 2-methoxyethanol (28%), or the *M258 kit*, as well as the *M258A1* and *M280* skin decontamination kits, developed by the U.S. Army, and containing a towelette prewetted with a solution of phenol (10%), ethanol (72%), NaOH (5%), ammonia (0.2%), and water (12%), were used on vesicants or nerve agents to rapidly reduce their hazard. These conventional decontamination methods, even though mostly effective and safe for technical personnel, show some drawbacks. They need huge amounts of reactants and/or energy and this poses several non-negligible problems in terms of safety, sensitivity, selectivity, reliability, environmental and economical sustainability, costs and disposal of the detoxified by-products.

Innovative and modern decontamination methods

To overcome these drawbacks, in the last years the research has moved from over-stoichiometric decontamination to catalytic decontamination, through the development of more effective, cheap

and reliable heterogeneous and/or nanostructured solid materials. Various systems were explored in the literature: supported transition metals (V, Mo and Fe) polyoxometalates (POMs), porous oxides with catalytically-active metal sites (activated by light or with mild oxidizing agents), metal-containing silica and zeolite-based nanostructured solids, metal organic frameworks (MOFs) and modified activated carbons.

Recently, *layered inorganic materials*, such as phyllosilicate clays, in particular, Fe-containing natural montmorillonites [7] and synthetic smectite saponites, have been used effectively in the decontamination of hazardous CWAs, due to their advantages such as high robustness, high chemical versatility, enhanced adsorption capabilities and very low production costs.

Synthetic saponite clays [8] with relatively high surface acidity bearing in-framework Nb(V) sites were successfully employed in the selective oxidation of 2-(chloroethyl)ethyl sulfide (CEES), a simulant of the sulfur mustard, into non noxious products (*i.e.* sulfoxides) under mild conditions, in organic solvents with aqueous H_2O_2 (Fig. 4).

Biochemical decontamination [5] is based on agent-scavengers or enzymes capable to catalyse specific neutralization reactions. The main advantage is that enzymes are selective and also exhibit turnover (*i.e.* a single enzyme can perform the same decontamination reaction several times), whereas

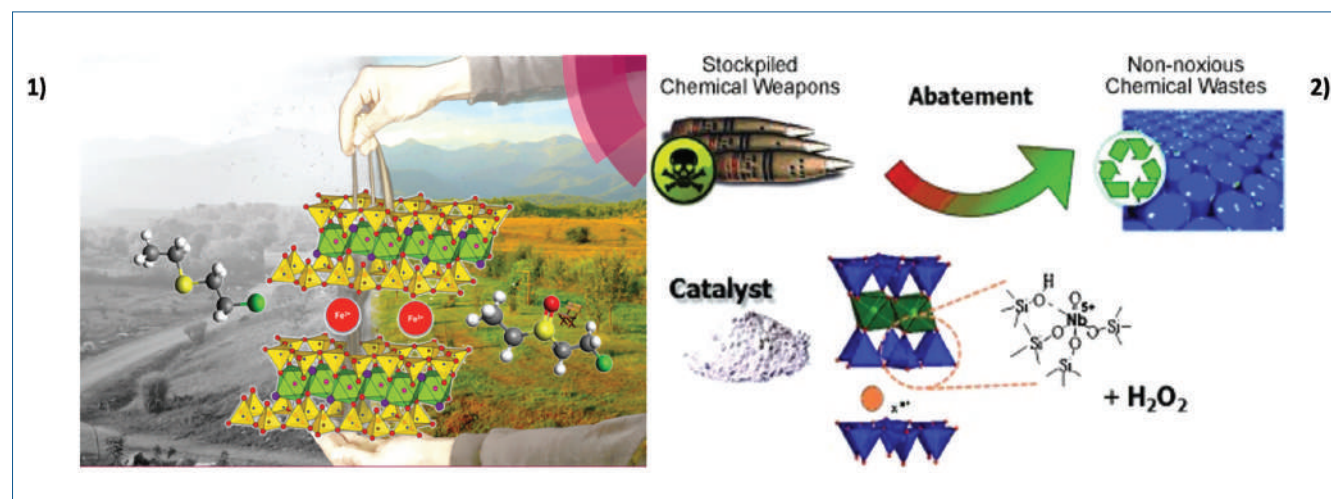


Fig. 4 - Iron-montmorillonite clays as active sorbents for the decontamination of hazardous CWAs [7] (1). A bifunctional NbV-containing saponite clay was prepared and found to be an optimal catalyst for the oxidative abatement of CEES [8] (2)

chemical reagents are normally consumed during each reaction. Hydrolytic enzymes can catalyse the hydrolysis of cholinergic agents, but the main limitation is related to the decrease of the pH of the reaction environment, due to the acidic nature of the hydrolysis products. Buffers are then used to maintain a neutral pH. Enzymes can act directly on agents, but also on the products from chemical neutralization reactions, increasing the overall reaction rate through continuous removal of these products.

An additional innovative technique is based on the application of nanostructured *photocatalysts* as decontaminants. They can be sprayed on contaminated surfaces to assist decontamination by adsorptive removal of CWAs. After adsorption, they participate in photocatalytic reactions and assist decontamination of CWAs in the presence of light radiation. For instance, photocatalytic decontamination of blister HD agent was studied using titania particles of different sizes and sunlight or UV-A light. HD was found to be completely decontaminated, to relatively nontoxic products, by TiO_2 within 6 h in the presence of sunlight [9] (Fig. 5).

Another class of materials that has recently attracted attention are *metal organic frameworks (MOFs)*, highly porous crystalline materials formed by bonds between metal-based nodes and organic linkers with multiple coordination sites. Tailored crystalline MOFs with open Lewis acidic metal

sites can catalytically hydrolyse nerve agents both in aqueous solution and in solid state systems, unveiling unparalleled potential for MOF-based personal protection gears. One of the earliest examples of an effective MOF catalyst dates back to 2011: NENU-11, synthesized from the Keggin-type polyoxometalate anion $[\text{PW}_{12}\text{O}_{40}]^{3-}$, can efficiently absorb and degrade the G-type simulant DMMP [10]. Not long after NENU-11, HKUST-1 was also found to be efficient in the hydrolysis of sarin. One of most efficient divalent MOFs in catalysing the nerve agent hydrolysis is Zn-MFU-4l, which is a Zn-triazole MOF suitable for the hydrolysis of sarin and DMNP [10]. Recent advances in the development of water-stable mesoporous MOFs have enabled their use as enzyme carriers. In particular, MOF NU-1003 has the largest mesoporous apertures (4.6 nm) known to date for a Zr-MOF. This material was used to immobilize the hydrolysing enzyme, organophosphorus acid anhydrolase (OPAA) [11]. The catalytic efficiency in the degradation of nerve agent soman is significantly increased over immobilized OPAA in nanosized NU-1003 compared to the one on free OPAA in buffer. Another MOF composite structurally mimics phosphotriesterase's active site and its ligated histidine residues. By incorporating imidazole and its derivative into the pores of MOF-808, the obtained MOF composite achieved a rapid degradation of the nerve agent simulant DMNP in water and in a

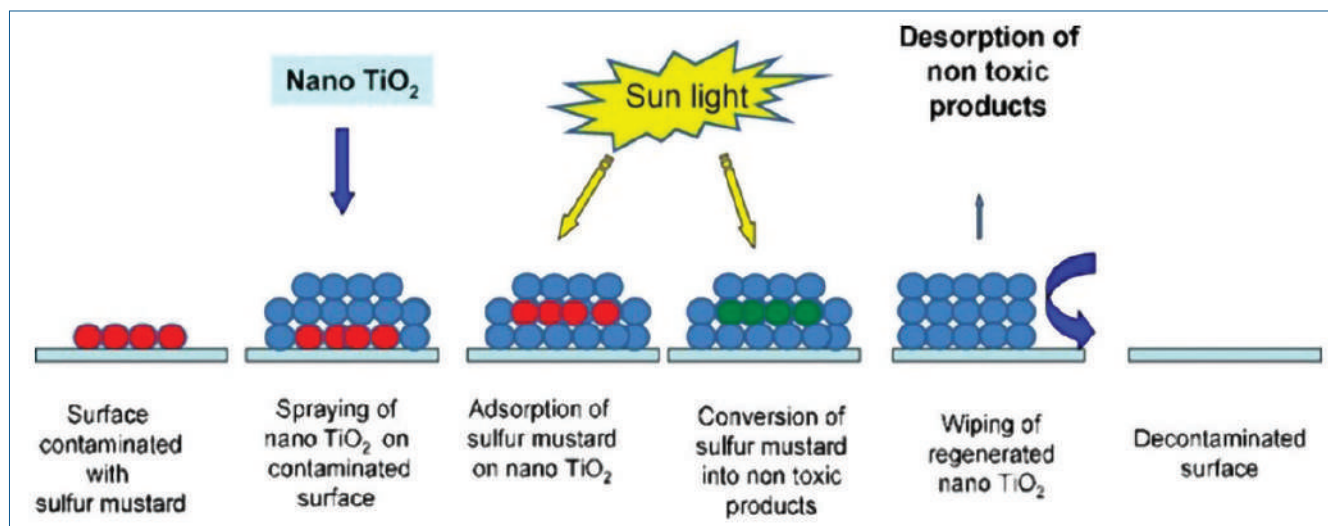


Fig. 5 - Photocatalytic decontamination of sulfur mustard (HD) with nano TiO_2 and sunlight [9]

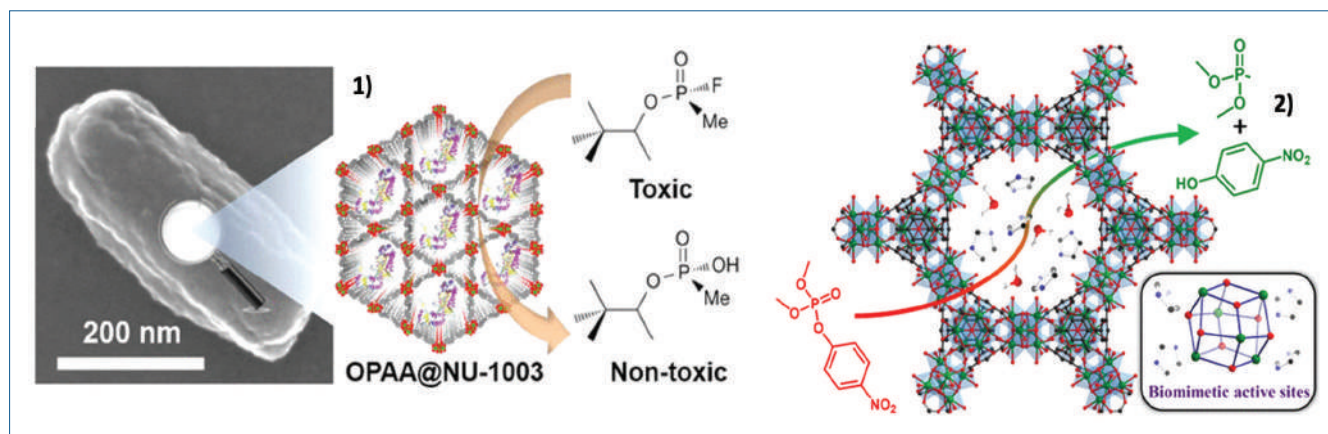


Fig. 6 - MOF (NU-1003)-enzyme carrier for the catalytic degradation of soman [11] (1). Biomimetic degradation of a NA simulant by incorporating imidazole bases into a MOF [12] (2)

wet environment without a liquid base [12] (Fig. 6). This new promising class of porous nanomaterials lends itself to many interesting applications, given their versatility in the catalytic hydrolysis of CWAs, although there are still some issues related to their stability, costs and scalability of synthesis.

Conclusion

The lists of highly toxic compounds that can be used as weapons and included among banned or strictly controlled substances is regularly updated, thanks to a periodic review of the CWC. This represents a constant challenge and a stimulus for the scientific community, in search for new technologies and innovative methods to be applied in the development of novel systems and materials with the aim of a safe, efficient and sustainable decontamination of CWAs, leading increasingly to a mitigation of the risk associated with these substances and consequently to a safer society free of chemical weapons.

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Decontaminazione: una capacità abilitante per la mitigazione del rischio di agenti per la guerra chimica

Il termine “armi chimiche” include un’ampia serie di composti altamente tossici che rappresentano una potenziale minaccia per gli esseri umani e per l’ambiente. A trent’anni dalla firma della Convenzione sulle Armi Chimiche, CWC, il trattato più importante che bandisce lo sviluppo e l’uso di queste sostanze, si vuole sottolineare qui l’importante ruolo delle tecniche di decontaminazione come mezzo per ridurre il rischio di uso criminale di aggressivi tossici.