



## A decontamination system for chemical weapons agents using a liquid solution on a solid sorbent

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### ABSTRACT

A decontamination system for chemical warfare agents was developed and tested that combines a liquid decontamination reagent solution with solid sorbent particles. The components have fewer safety and environmental concerns than traditional chlorine bleach-based products or highly caustic solutions. The liquid solution, based on Decon Green™, has hydrogen peroxide and a carbonate buffer as active ingredients. The best solid sorbents were found to be a copolymer of ethylene glycol dimethacrylate and *n*-lauryl methacrylate (Polytrap 6603 Adsorber); or an allyl methacrylate cross-linked polymer (Poly-Pore E200 Adsorber). These solids are human and environmentally friendly and are commonly used in cosmetics. The decontaminant system was tested for reactivity with pinacolyl methylphosphonofluoridate (Soman, GD), bis(2-chloroethyl)sulfide (Mustard, HD), and S-(2-diisopropylaminoethyl) O-ethyl methylphosphonothioate (VX) by using NMR Spectroscopy. Molybdate ion ( $\text{MoO}_4^{2-}$ ) was added to the decontaminant to catalyze the oxidation of HD. The molybdate ion provided a color change from pink to white when the oxidizing capacity of the system was exhausted. The decontaminant was effective for ratios of agent to decontaminant of up to 1:50 for VX ( $t_{1/2} \leq 4$  min), 1:10 for HD ( $t_{1/2} < 2$  min with molybdate), and 1:10 for GD ( $t_{1/2} < 2$  min). The vapor concentrations of GD above the dry sorbent and the sorbent with decontamination solution were measured to show that the sorbent decreased the vapor concentration of GD. The E200 sorbent had the additional advantage of absorbing aqueous decontamination solution without the addition of an organic co-solvent such as isopropanol, but the rate depended strongly on mixing for HD.

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### 1. Introduction

The use of Chemical Warfare Agents (CWA) is a possible threat by terrorists or military organizations against military targets and civilian populations. In the event of such an attack, it will be necessary to clean up and eliminate the hazard in the affected area by using a system that will decontaminate, i.e. contain, react with, and detoxify, the chemical agent. The classical standard chemicals used by the U.S. Army to decontaminate chemical weapons are STB (super tropical bleach) slurry and DS2 (Decontamination Solution 2) [1]. Both decontaminants are very effective, but they are extremely corrosive and degrade most of the surfaces they interact with. Also, these decontaminants are harmful to the environment, and they are in the process of being replaced [2].

Extensive efforts have been made to formulate new decontamination systems. A review of some current systems has been published [2]. One approach to overcome the problems of using the previously mentioned decontaminants is to use sorbents to isolate the CWA. Usually, the absorption process is fast, and the sorbents reduce the agent hazard by decreasing its vapor pressure. The main disadvantage of the use of these solid sorbents is the fact that after the application, there are contaminated particles that have to be collected and decontaminated. Because of their limited reactive decontamination action, the potential for off-gassing is likely, especially since the materials used for the absorption have large surface areas and are very porous. The solid particles may become airborne, so the hazard may actually spread instead of being confined.

A system composed of sorbents that have the ability to decontaminate the absorbed agent seems to be the ideal solution. This goal may be achieved either by synthesizing particles that have active surfaces or by formulating blends of sorbents with active solid or liquid ingredients. The first approach is elaborate and potentially expensive, but research has been done in the area, for

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example with substituted dendrimers [3,4]. For the solids with active surfaces, nanoparticles were prepared as the oxides CaO and MgO [5]. Their ability to decontaminate CWA was extensively investigated [6–8]. The commercially available decontaminant FAST-ACT is based on nano-powders of titanium and magnesium oxides [2,9]. Tucker and Comstock describe a method for absorption of one or more components of decontamination solution onto water-soluble sorbitol or mannitol particles, so that the system can be transported as a solid and then dissolved in water before use [10]. Hoffman and McGuire developed a gel composition containing oxidizing agents and thickening or gelling agents to detoxify chemical and biological agents by application directly to a contaminated area. The gelling agent is a colloidal material, such as silica, alumina, or alumino-silicate clays, which forms a viscous gel that does not flow when applied to tilted or contoured surfaces [11]. Hoffman and Chiu developed solutions of detoxifying reagent for chemical and biological agents by coating small quantities of hydrophobic nanoparticles, such as hydrophobic fumed silica particles, to form a porous coating of insoluble fine particles around the solution, so the porous coating breaks down and the detoxifying reagent is delivered directly to the chemical or biological agent [12].

The second approach has been moderately successful. A solid sorbent Ambergard XE-555 resin (Rohm and Haas Company, Philadelphia, PA) was formulated as a blend of synthetic resins, including a high surface area carbonized resin, a strong acid ion exchange resin, and a strong base ion exchange resin [13].

For cleaning up a large contaminated area, a decontamination system should have the advantages: (1) it should be inexpensive and readily available in bulk; and (2) it should be environmentally benign and nontoxic, so that exhaustive cleanup of the decontamination materials is not essential, particularly in areas that were not measurably contaminated by CW agents. Commercially available sorbents were chosen that were chemically compatible with a liquid solution capable of decontaminating the CW agents. The solution must be absorbed by the sorbent particles while keeping its decontamination activity toward the CW agents. The sorbent must also absorb the CW agents, which requires that the sorbent be miscible with nonpolar (HD) and polar (VX) liquids. Once it is formulated, this combination should be very effective in decreasing the CWA hazard by providing physical separation of the CW agent from the atmosphere as well as chemical reactivity to neutralize the toxic properties of the CW agent.

For this study, materials were studied with the goal to meet these criteria. The decontamination system is in the form of slurry, which has advantages over a liquid-only system in cases when runoff from decontamination operations is difficult to control. Also, slurry can be applied to a surface with less chance of being dispersed in the air, compared to a fine powder. After the liquid dries, the decontaminated powder can be easily swept off the surfaces.

The goal of this study is to develop and test a combined solid sorbent and liquid decontamination solution system that efficiently decontaminates the CWA, is environmentally benign, and has minimal risks to human health. The reactivity of the system was studied using Nuclear Magnetic Resonance (NMR) spectroscopy techniques to measure the kinetics of the reaction and show that the CWA in the matrix was destroyed to less toxic products.

The decontamination liquid is a modification of Decon Green™ solution, which is a hydrogen peroxide/carbonate solution that has been developed and tested for CWA decontamination [14–16]. Hydrogen peroxide suffers from restrictions on its stability in storage, handling, and transportation, yet the Decon Green™ solution has been successfully tested in the field.

Among the solids tested in this study were commercial natural products and polymeric sorbent powders that can absorb water as well as both polar and nonpolar organic compounds. For

one of the solids, Poly-Pore E200 Adsorber, organic solvents could be eliminated from the modified Decon Green™ formulation by providing the ability to absorb nonpolar compounds such as HD as well as the polar aqueous decontamination solution. Without this sorbent or an organic co-solvent, these two liquids formed two separate phases which do not efficiently decontaminate the agent.

## 2. Experimental

### 2.1. Materials

The following chemicals were purchased from Sigma–Aldrich and used as received: potassium carbonate ( $K_2CO_3$ , CAS No. 584-08-7), potassium molybdate ( $K_2MoO_4$ , CAS No. 13446-49-6), 50% hydrogen peroxide ( $H_2O_2$ , CAS No. 7722-84-1), Triton® X-100 (CAS No. 9002-93-1), sodium hydroxide (NaOH, CAS No. 1310-73-2), potassium bicarbonate ( $KHCO_3$ , CAS No. 298-14-6), potassium iodide (KI, CAS No. 7681-11-0), and isopropanol (CAS No. 67-63-0). Distilled deionized water from a Barnstead NanoPure system was used to prepare the solutions.

Samples of sorbents were received from the following companies: Grain Processing Corporation, IA: Water Lock A-220, A-221, B-204, G-500, G-504; AMCOL Health Beauty Solutions, LA: Poly-trap 6603 Adsorber and Poly-Pore E200 Adsorber; and Sorbent Product Company (SPC): DZ-100. Additional details about these solids are given in [Supplementary data](#). The solid sorbents that received detailed study were Polytrap 6603 Adsorber, a copolymer of ethylene glycol dimethacrylate and *n*-lauryl methacrylate; and Poly-Pore E200 Adsorber, an allyl methacrylate cross-linked polymer. These solids are human and environmentally friendly and are commonly used in cosmetics.

Standards of chemical weapons materiel were obtained from the CASARM program at Edgewood Chemical and Biological Center, Aberdeen Proving Ground, MD. The decontaminant system was tested for reactivity with pinacolyl methylphosphonofluoridate (Soman or GD, CAS No. 96-64-0), bis(2-chloroethyl)sulfide (Mustard or HD, CAS No. 505-60-2), and S-(2-diisopropylaminoethyl) O-ethyl methylphosphonothioate (VX, CAS No. 50782-69-9). Carbon-13 labeled HD (with one  $^{13}C$  label on each chloroethyl group, in random positions) was custom synthesized at ECBC and tested for purity by NMR [17].

*Note:* The neat agent standards are extremely toxic and must be handled in accordance with all applicable Federal laws and international treaties, using appropriate safety and security operating procedures.

### 2.2. Instrumental method

HD was studied by  $^{13}C$  NMR, using  $^{13}C$  labeled compound to improve the signal/noise ratio, and GD and VX were studied by  $^{31}P$  NMR. The initial studies of these reactions were performed with a High Resolution Magic Angle Spinning (HRMAS) NMR technique. Unfortunately, it was found that decomposition of the fresh peroxide solution generated sufficient pressure inside the rotor to push off the friction-fitted caps. This problem generated safety and contamination concerns for samples containing CW agents (see [Supplementary data](#) for details).

An alternative method was used. The reaction mixture of contaminated slurry was flame sealed in a liquid NMR tube, for operator safety. Tubes were run with a QNP probe for either  $^{31}P$  or  $^{13}C$ . The NMR peaks were broader than with either the liquid alone or on the HRMAS probe, but the resulting spectra were useable for kinetic determinations. The solid/liquid decontamination

mixture was packed as slurry into a 4 mm O.D. glass NMR tube. CW agent was spiked in the slurry, and the tube was flame sealed and inserted into a 5 mm O.D. glass tube, and flame sealed for double containment. Double containment was used for safety purposes for the experiments. The detection limit under these conditions was enough to measure at least 4 half lives of the reaction, to a concentration of less than 5–10% of agent relative to products. Due to the time needed to seal the tubes, the fastest time point that was typically collected was about 6 min after mixing. The low resolution of the spectra limited the ability to resolve a few closely spaced peaks, such as the VX peak and its N-oxide. The N-oxide was observed in liquid reaction runs to form from VX, and it reacted away somewhat slower than VX. It is assumed to be toxic, so the reported reactions include the rate of decrease of the sum of VX and the N-oxide.

One of the samples of slurry was allowed to react with VX, and then the NMR tube was broken so the solid could be extracted for analysis of residual agent by gas chromatography/mass spectrometry. Extraction for VX was performed using a mixture of pH 10 carbonate buffer solution and methylene chloride, with VX extracted into the organic solvent phase. Analysis was performed on an Agilent 6890 GC/5975 MSD system and compared to a VX standard solution.

GD vapor concentration was measured above the sorbent and sorbent/liquid systems using Solid Phase Microextraction, followed by Gas Chromatography/Mass Spectrometry (GC/MS). GD vapor above the sorbent was measured since it is the most volatile CW agent that was used in this study. A quantity of 0.25  $\mu\text{l}$  of neat GD was placed on the bottom of a headspace vial. A bed depth of 0.6 cm of powder was added. The vial was open for 30 min in a fume hood, then capped for subsequent headspace sampling at 2 h intervals. Sampling was done by inserting a Solid Phase Microextraction fiber through a septum into the vial for 30 min, then desorbing the fiber in an injection port of an Agilent 6890 GC with a 5975 MSD. Peak areas were calibrated relative to a GD standard calibration curve. The recovery of 1 ng GD corresponds to 0.007 mg/m<sup>3</sup> GD vapor concentration, determined from the calibration of the SPME measurements.

### 2.3. Decontamination system preparation

The following recipe was used for the liquid solution (in vol%): 44% isopropyl alcohol, 34% of 50% H<sub>2</sub>O<sub>2</sub>, 1.1% 5N NaOH, 5.9% Triton X-100, 15% of KHCO<sub>3</sub>/K<sub>2</sub>CO<sub>3</sub>/H<sub>2</sub>O (10 ml of this solution contains 0.80 g of KHCO<sub>3</sub> and 0.28 g of K<sub>2</sub>CO<sub>3</sub>), with solid K<sub>2</sub>CO<sub>3</sub> in an amount sufficient to adjust the pH of the decontamination solution to about 9 (approximately 0.2 g of K<sub>2</sub>CO<sub>3</sub> were dissolved in 10 ml of decontamination solution). A final concentration of 0.02 M K<sub>2</sub>MoO<sub>4</sub> was used in some of the decontamination solutions [16]. This mixture is a variation of the formulation of Decon Green<sup>TM</sup> with higher concentration of peroxide and bicarbonate/carbonate species, and a different amount and type of organic solvent.

All slurries are reported as weight ratios of solid to liquid. CW Agents were added by volume to measured weight of mixed slurry to produce the reported ratio, with the volumes corrected for literature agent densities.

The period of time between the preparation of the decontamination system (the slurry) and the spiking of the agent was 0.5–1 h. Within this period of time, the decontamination system was considered to be freshly prepared. Studies were also performed on stability of the decontamination liquid, before and after mixing with the solid, during storage either at room temperature or in a –20 °C freezer.

## 3. Results and discussion

### 3.1. Liquid decontamination solution

Decon Green<sup>TM</sup> was developed as an environmentally friendly decontamination solution [14–16,18–20]. One goal for this decontamination system is to formulate a system with a long period of activity after its application, with a target of overnight activity. The current liquid solution was modified from Decon Green<sup>TM</sup> to consist of 45 wt% isopropyl alcohol (IPA) as the co-solvent, and to increase the H<sub>2</sub>O<sub>2</sub> concentration from 10.5% to 17.5%. IPA was preferable to propylene carbonate, which is typically used in Decon Green<sup>TM</sup>. For use in the heterogeneous system, the amount of the surfactant was decreased to 6 wt% of Triton X-100.

Since the concentration of bicarbonate is a key aspect of the activity of the solution toward the various CWA, it is important to optimize its concentration. The amount of the solid carbonate was adjusted to set the pH of the decontamination solution to about 9. This value is a compromise of two conflicting requirements: the decontamination of HD is optimal at lower pH, as opposed to VX and GD, which is optimal at higher pH. The bicarbonate forms peroxocarbonate (HCO<sub>4</sub><sup>–</sup>) species that selectively oxidizes HD to its sulfoxide [19]. The concentration of HCO<sub>4</sub><sup>–</sup> is maximized near pH 7 and goes to zero near pH 11 [21]. However, the active species in the perhydrolysis of VX is the HOO<sup>–</sup> ion [18,22,23]. Since H<sub>2</sub>O<sub>2</sub> is a weak acid (pK<sub>a</sub> = 11.75 at 20 °C) [24,25], a higher pH is needed in order to increase the concentration of the HOO<sup>–</sup> species. Thus, the range of pH 8–9 is reasonable for a general purpose decontamination solution. At this pH range sufficient HCO<sub>4</sub><sup>–</sup> remains to oxidize the HD with a lifetime less than 2 min [26].

The stability of the modified decontamination solution without the molybdate salt was traced qualitatively with solid KI. At room temperature, its oxidation capability was kept for a month after preparation when stored in a capped plastic bottle wrapped with aluminum foil. The iodide oxidation activity of the decontamination solution including K<sub>2</sub>MoO<sub>4</sub> was retained only overnight. The loss of oxidation activity was indicated by the color change of the solution from deep red to colorless.

### 3.2. Solid sorbent

The solid sorbent was tested for its ability to absorb aqueous and organic solutions. The water absorbance specifications given by the various manufacturers were based on distilled water. For aqueous solutions, the absorbances were significantly lower, so measurement of the amount of decontamination solution that was absorbed by the various sorbents was performed. The absorbed amount of diethyl methylphosphonate (DEMP) was measured, since DEMP served as a stimulant for the G agents. The amount absorbed by the various sorbents as well as their compatibility with the decontamination solution and physical appearance are shown in Table 1.

### 3.3. Decontamination liquid containing IPA, combined with Polytrap 6603 sorbent

A good candidate based on Table 1 was the Polytrap 6603, due to its ability to absorb both decontamination liquid and DEMP. Preliminary experiments of a decontamination system with 6603 (1 part by weight Polytrap 6603: 8 parts by weight solution) showed no reaction of the sorbent and the decontamination solution.

Using the 6603 sorbent in the decontamination mixture, the reaction of VX with the decontamination system showed rapid conversion to less hazardous materials, such as ethyl methylphosphonic acid (EMPA). The results show that a freshly prepared decontamination system neutralizes VX even in a ratio of 1:30

**Table 1**  
Interaction of sorbents with decontamination solution (IPA, no  $\text{MoO}_4^{-2}$ )<sup>a</sup> and diethyl methylphosphonate (DEMP)

Solid sorbent	A221	B204	A220	G500	G504	E200	6603	DZ100
Compatibility <sup>b</sup>	<18	<355	<66	<355	<210	<163	<91	<1555
Physical appearance	nd	Sticky	Very sticky	Jelly	Jelly	Slurry, paste	Slurry, paste	color change
Decon solution absorption <sup>c</sup>	6.4	4.0	3.3	4.4	3.4	13.4	12.1	5.1
DEMP absorption <sup>d</sup>	nd	nd	nd	nd	nd	>11.0 <sup>e</sup>	>11.0 <sup>e</sup>	nd
DEMP + decon solution absorption <sup>f</sup>	nd	nd	nd	nd	nd	>4.5 <sup>e</sup>	>3.6 <sup>e</sup>	nd

nd = Not determined.

<sup>a</sup> Decontamination solution with isopropyl alcohol (IPA) and without  $\text{K}_2\text{MoO}_4$ .

<sup>b</sup> In hours of activity toward KI. These numbers are based on measurements of a single sample using a semiquantitative method.

<sup>c</sup> Maximum weight in grams of decontamination solution absorbed by 1 g of solid.

<sup>d</sup> Maximum weight in grams of DEMP absorbed by 1 g of solid.

<sup>e</sup> Turned into a semi-sticky paste.

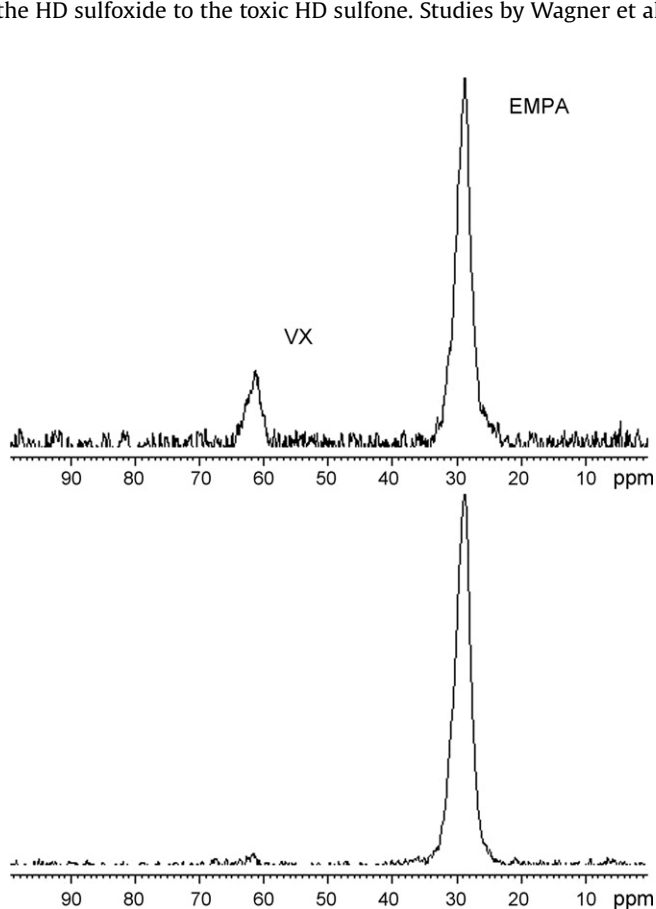
<sup>f</sup> Maximum weight in grams of DEMP absorbed by 1 g of solid after absorbance of about half the maximum amount of decontamination solution.

(agent to decontamination system) with a half life of 19 min, and considerably faster for a ratio of 1:50. The highly toxic breakdown product S-(2-diisopropylaminoethyl) methylphosphonothioic acid (EA-2192) was not detected. An example of the fate of VX in the decontamination system is shown in Fig. 1.

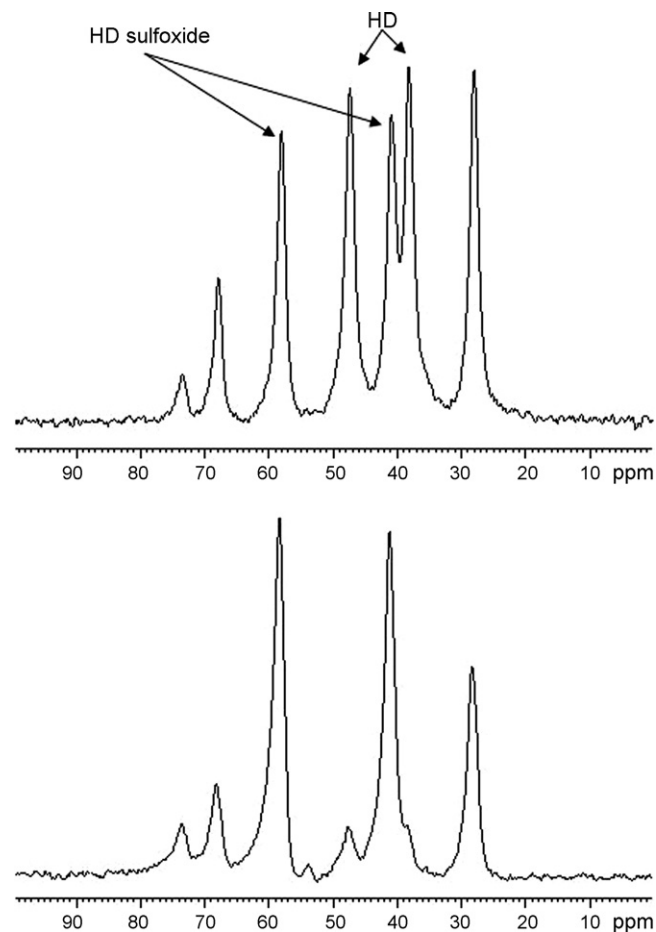
Reaction of HD with the decontamination system (1:50 ratio of HD to decontamination system) showed conversion to a much less hazardous compound, bis(2-chloroethyl) sulfoxide (HD sulfoxide). At a ratio of 1:50, the reaction had a half life of less than an hour. Typical results of the NMR measurements are shown in Fig. 2. These experiments are not capable of identifying secondary oxidation of the HD sulfoxide to the toxic HD sulfone. Studies by Wagner et al.

in liquid phase have indicated that secondary oxidation to the sulfone does occur, but this reaction is slower by at least 2 orders of magnitude [27].

The results of the experiments with the 6603 sorbent system for VX, HD and GD are summarized in Table 2. Reaction of GD with the decontamination system showed rapid conversion (half life <3 min) to less hazardous compounds, primarily pinacolyl methylphosphonic acid. For VX, the molybdate ion makes no observable difference in the activity, although the times in each case are short, making distinction difficult. This is consistent with the previous results



**Fig. 1.** NMR spectra showing reactions of VX in Polytrap 6603 solid sorbent decontaminant slurry. Top panel: at 8 min after mixing showing VX and EMPA Peaks, using a 4 min run time (64 scans). Bottom panel: at 66 min after mixing showing predominant EMPA peak, using a 32 min run time (512 scans). The 6603 sorbent in the decontamination mixture was used with a freshly prepared decontamination system at a ratio of VX to decontaminant of 1:30.



**Fig. 2.**  $^{13}\text{C}$  NMR spectra of HD mixed in Polytrap 6603 solid sorbent decontaminant slurry. Top panel: at 15 min after mixing showing major HD peaks; bottom panel: at 66 min after mixing, showing predominant HD sulfoxide peaks. HD ( $^{13}\text{C}$  enriched) was reacted with the 6603 decontamination system at a 1:50 ratio without molybdate ion. The additional peaks are from the solvents.

**Table 2**  
Reaction of decontamination system (IPA, 6603 Sorbent)<sup>a</sup> with CW agents, with and without molybdate

Agent	MoO <sub>4</sub> <sup>-2</sup>	Wt. ratio of solid to decon liquid <sup>b</sup>	Ratio of agent to slurry <sup>c</sup>	Reaction half life (min)
VX	–	1:8.0	1:50	<5
VX	–	1:8.5	1:50	<5
VX	+	1:9.5	1:50	<4
VX	+	1:8.9	1:30	<4 for 82%; 19 for final 18%
HD	–	1:9.4	1:50	20
HD	–	1:9.7	1:50	49
HD	–	1:13.8	1:50	59
HD	+	1:10.2	1:50	<4
HD	+	1:9.95	1:10	<4 for first 80%; 19 for final 20%
GD	–	1:8.5	1:50	<3

<sup>a</sup> Decontamination solution with isopropyl alcohol (IPA).

<sup>b</sup> Ratio by weight of sorbent solid to decontamination liquid.

<sup>c</sup> Ratio of agent by weight (measured by volume and corrected to weight using literature density of CWA) to weight of slurry system.

[27], for which higher concentrations of molybdate were needed to accelerate the reaction for both VX and GD. For the reaction run with a 1:30 ratio of VX to mixture, it was observed that the reaction was bimodal. The half life was <4 min for 82% (which was consumed by the time the first data point was taken), and then slowed down dramatically to 19 min for final 18%. The fast segment is consistent with the other reaction rates. The slow segment may be a result of the consumption of the reagent, or to the lack of mixing in the slurry that causes locally high concentrations of VX relative to the reagent. The result may indicate the limit on the capacity of the system.

Reaction of HD in the presence of molybdate ion had a half life of <4 min for a ratio of 1:50 of agent to decontamination system. For a ratio of 1:10, the half life was <4 min for first 80%, but then it decreased dramatically to 19 min for final 20% of the HD. The fast segment is consistent with previous results. The slow segment is similar in rate to the mixtures without molybdate. For the runs without molybdate, the rates are significantly slower and also show more variation. Two runs that were nominally identical had rates that were different by more than a factor of two ( $t_{1/2} = 20$  and 49 min). Another run that had slightly more liquid in the mixture had a slower rate ( $t_{1/2} = 59$  min). Since the HD is very nonpolar, it is possible that it is not completely mixed with the polar solvent and peroxide in the NMR tube during the run. Wagner et al. [27] used a liquid microemulsion system to study the reaction, but the addition of the solid sorbent may affect the emulsion of the surfactant. Also, it is not clear how well the HD is being mixed with the slurry as it is added. Of course, it is also possible that a ratio of 1:10 simply exceeds the capacity of the reagent, and there is too much HD present (see also Section 3.4).

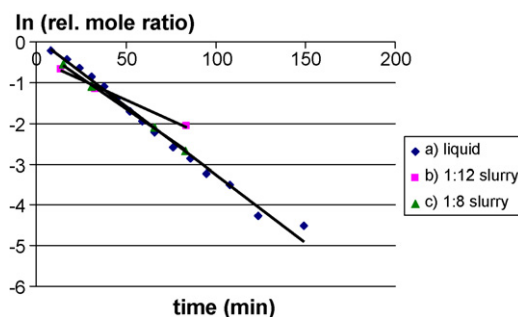
For the freshly prepared slurry, the period of time elapsed from preparation to its application was up to an hour. Yet the decontamination system with molybdate was active for several additional hours as indicated by its color. A color change from pink to white indicated when the active oxidizer ingredient was decomposed or consumed. The presence of K<sub>2</sub>MoO<sub>4</sub> in the slurry reduced the period of activity, but it was retained for at least 6–8 h.

Tests were carried out with stored decontaminant to determine how long activity was retained. The results are shown in Table 3. The absorption into the solid particles does not prevent H<sub>2</sub>O<sub>2</sub> from decomposition, since storage overnight at room temperature (for 22 h), with or without K<sub>2</sub>MoO<sub>4</sub>, causes the decontaminant to become ineffective for reaction with HD or VX. Keeping the decontamination system in a freezer at –20 °C for several days without molybdate leaves enough activity to decontaminate HD in a 1:50 ratio. Storage of the liquid with MoO<sub>4</sub><sup>-2</sup> in a freezer at –20 °C may decrease the effectiveness.

In order to compare the effect of the sorbent particles in the decontaminant, decontamination experiments were done using only the decontamination solution, without adding the sorbent particles. Fig. 3 shows a kinetic plot comparing the reaction of HD in a liquid decontamination solution with the decontamination slurry that has ratios of solid:liquid of 1:8 and 1:12, by weight, without molybdate ion. This data indicates that the presence of solid sorbent does not significantly affect the rate of reaction with the CW agent. When potassium molybdate was added to the liquid, the reaction was too fast to measure. The fact that a solid:liquid ratio of 1:8 is a little bit faster than 1:12 may suggest that the ratio of decontamination solution to sorbent does not seem to have a dominant influence on the decontamination activity as long as there is enough of the decontamination solution in the solid. This implies that no exact ratio has to be followed above a ratio of 1:8.

The results for reaction runs that are in the liquid, with no solid sorbent, are shown in Table 4. The half lives are in good agreement with literature values, although the solvent systems in the literature studies are slightly different. The results also show that the reaction rates for liquids are similar to the corresponding rates for the slurry system. The half lives for VX are all 5 min or less, with and without the molybdate, except for the slow segment in Table 2. The half life for HD is 20 min or more without molybdate, and 4 min or less with molybdate.

The vapor concentration of GD above the dry Polytrap 6603 sorbent was measured to determine how well the sorbent sequesters this volatile CWA. A comparison was made of the vapor pressure with GD deposited on top of the dry powder, under the dry powder, or on a glass slide with no powder present. Quantities of 0.25 μl of neat GD were placed in three vials: (a) above a 0.6-cm thick layer of Polytrap 6603, (b) below a 0.6-cm thick layer of dry Polytrap 6603,



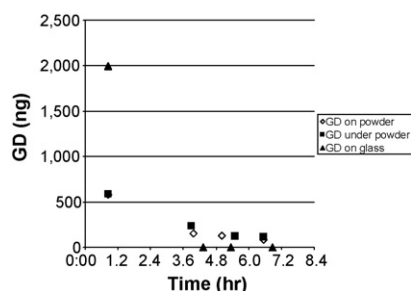
**Fig. 3.** Kinetic plot of the rate of reaction of HD, with a 1:50 weight ratio of HD to decontamination liquid with IPA, or to 6603 decontamination system (slurry). The decontamination solution consisted of (a) liquid solution only, (b) 1:12 solid sorbent to liquid, and (c) 1:8 sorbent to liquid.

**Table 3**  
Effect of the storage on the efficiency of the decontamination system (IPA, 6603 Sorbent) with CW Agents, with and without molybdate

Agent	Decon storage time and temperature <sup>a</sup>	MoO <sub>4</sub> <sup>-2</sup>	Wt. ratio of solid to decon liquid	Ratio of agent to slurry	Reaction half life (min)
VX	Immediate use	–	1:8.0	1:50	<5
VX	22 h (room temperature)	–	1:8.5	1:50	>1440
HD	Immediate use	–	1:13.8	1:50	59
HD	21 h (room temperature)	–	1:9.95	1:50	121
HD	4 days (–20 °C)	–	1:8.0	1:50	23
HD	4 days (–20 °C)	–	1:12.0	1:50	35
HD	6 days (–20 °C) <sup>b</sup>	+	1:10.2	1:50	<2
HD	6 days (–20 °C) <sup>b</sup> , 22 h (–20 °C) with MoO <sub>4</sub> <sup>-2</sup>	+	1:10.2	1:50	19
HD	11 days (–20 °C) <sup>b</sup> , 22 h (room temperature) with MoO <sub>4</sub> <sup>-2</sup>	+	1:9.95	1:50	>360

<sup>a</sup> Storage time and temperature of the decontamination liquid solution before the addition of sorbent and agent to measure reactivity.

<sup>b</sup> Solution without MoO<sub>4</sub><sup>-2</sup> stored in freezer (–20 °C).



**Fig. 4.** Recovery of GD above Polytrap 6603 sorbent powder, as determined by SPME. Measurements were done with GD on top of powder, GD under powder, and GD on an empty glass vial (no sorbent). The method was calibrated using a standard SPME method with agent standards.

or (c) without sorbent. The vial was open for 30 min, then capped for sampling at 2 h intervals, using Solid Phase Microextraction. The results are shown in Fig. 4. The vapor pressure from GD under, and on top of, the powder are both similar. However, the vapor pressure for GD on glass is much higher than it is above the sorbents, even though it decreases faster as the GD evaporates. This result indicates that the sorbent reduces the vapor pressure and hence the vapor hazard from the GD compared to the amount from GD that is not absorbed into sorbent. However, the sorbent alone does not eliminate the vapor.

#### 3.4. Aqueous decontamination liquid (without IPA), combined with E200 sorbent

One of the constituents of the decontamination solution is isopropanol (IPA). Since IPA is a flammable solvent, it presents some potential hazards and restrictions for the shipping of the components of the decontamination solution. Also, it is an extra component of the liquid mixture that has to be combined for the decontamination system to be used. It would be advantageous to

eliminate the need for IPA or other organic co-solvents from the decontamination solution, in order to use only an aqueous solution. Unfortunately, the elimination of the IPA component results in poorer absorption of the aqueous decontamination solution into the 6603 particles.

Using the data of Table 1, E200 sorbent can be substituted for the 6603 solid sorbent, because E200 was capable of absorbing more of both aqueous and nonpolar (DEMP) compounds at the same time. This capability allowed the sorbent to absorb both the peroxide decontamination solution as well as nonpolar CW agent compounds. The sorbent may hold the liquids in close physical proximity for the decontamination reaction to take place, although we could not measure the amount of contact between the phases of liquid. Therefore, it is possible that the sorbent can replace the organic co-solvent in the decontamination system.

The liquid solution was formulated with the same reagent concentrations but using only water as a solvent. The results of the reactions of the decontamination system with no IPA and using E200 sorbent particles with the various CW are given in Table 5. The relatively short times of decontamination indicate that this system is a useful decontamination system.

The reaction half lives for GD are short, <2 min, in agreement with the previous results. GD is soluble in aqueous solution in low concentrations, so it is not expected that phase separation is an issue for this agent.

The results for VX are bimodal, which was only observed for VX in the 1:30 ratio for the 6603 sorbent (Table 2). For the low ratio of 1:50 VX to decontamination system, there is a fast decrease of the amount of VX before the first data point, indicating that the half life for the reaction of 66% of the VX is <6 min. The remaining 33% reacts with a half life of 17 min. Unexpectedly, for the 1:30 ratio, 82% of the VX reacts with a half life of <3 min, even though more VX is initially present. The actual kinetic data for these two runs is shown in Fig. 5, including dashed lines to represent the slow bound for the rate of the fast segment.

**Table 4**  
Reaction of decontamination solution (IPA) with CW agents, with and without molybdate

Agent	MoO <sub>4</sub> <sup>-2</sup>	Ratio of agent to total decon	Reaction half life (min)	Literature result (min)
VX	–	1:50	2.5	0.93 <sup>a</sup>
VX	+	1:30	5	3.2 <sup>b</sup>
HD	–	1:20	21	20 <sup>c</sup>
HD	+	1:50	<2	0.5 <sup>d</sup>
HD	+	1:10	<3	

<sup>a</sup> From Ref. [28]. Rate was measured for 0.01 M VX, using 0.33 M NaHCO<sub>3</sub>, 8.7 M H<sub>2</sub>O<sub>2</sub>, and *tert*-butyl alcohol as a solvent.

<sup>b</sup> From Ref. [27], using 0.1 M molybdate.

<sup>c</sup> From Ref. [19]. Rate was measured for 0.1 M HD, using 0.037 M NaHCO<sub>3</sub>, 4.0 M H<sub>2</sub>O<sub>2</sub>, and *tert*-butyl alcohol as a solvent.

<sup>d</sup> From Ref. [27], using 0.015 M molybdate.

**Table 5**  
Reaction of decontamination system with E200 sorbent (no IPA)<sup>a</sup> with CW agents, with molybdate used in all the solutions

Agent	Wt. ratio of solid to liquid decon	Ratio of agent to slurry	Reaction half life (min)
VX	1:9.9	1:50	<6 for 66%; 17 for 33%
VX	1:10.2	1:30	<3 for 82%; 18 for 18%
HD	1:9.7	1:50	8
HD	1:9.7	1:10	36
HD	1:10	1:10	<4
HD	1:10	1:10	<4
HD <sup>b</sup>	1:10.3	1:10	<4
HD <sup>b</sup>	1:10.3	1:10	229
GD	1:11.1	1:50	<2
GD	1:10.7	1:10	<2

<sup>a</sup> Decontamination solution without isopropyl alcohol (IPA) but with the same concentration of peroxide.

<sup>b</sup> Two HD runs were done on the same day with the same solutions. The first was well mixed, and the second was not mixed and has a much slower rate.

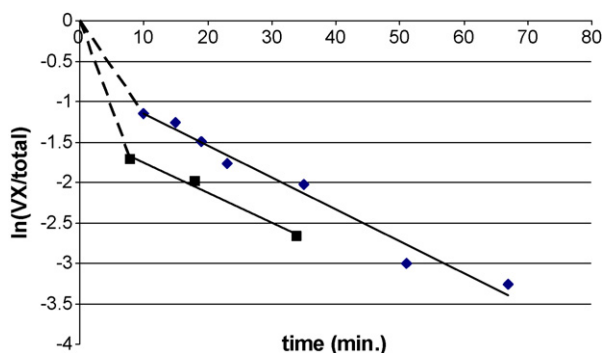
The fast initial reaction is consistent with the rates that were determined in liquid (Table 4) and in the 6603 sorbent system (Table 2). The reason that the reaction subsequently slows down is uncertain. However, it is known that the solution is slightly basic, and VX is not totally miscible in a basic solution. As a result, the kinetic data provides evidence that the VX is not totally mixing in the decontaminant, or that it is forming separated liquid phase droplets, which react slower or at the interface with the decontaminant. However, the VX still reacts reasonably fast. The reaction of VX with the liquid solution alone (with no IPA) was measured without solid sorbent, and the half life of the reaction was <5 min with mixing of the liquid.

Separation appears to be the most significant problem for HD, which is the most nonpolar compound. Several repetitions of reactions with HD were conducted under essentially the same conditions, with 1 part agent to 10 parts decontaminant system. The results are shown in Table 5, lines 4–8. The results for the reactions indicate that the bulk decontamination system has the capacity to react with 1:10 weight ratio of HD to decontaminant. However, there is large variation in the amount of time that is needed to react with the HD, with half lives ranging from <4 min to 229 min. After addition of the agent, thorough mixing of the slurry is required to avoid localized high concentrations of HD, which overwhelm local concentrations of the H<sub>2</sub>O<sub>2</sub> oxidizer. In order to confirm this conclusion, the last two runs were done on the same day with the same mixture, shown in Table 5, lines 7 and 8. For one run, the HD in the slurry was well mixed by stirring, and the half life was <4 min. For another run, the HD was intentionally deposited as a droplet in one spot, and the half life was 229 min. Since the HD is a nonpolar liquid, it does not mix well by diffusion from dissolving in the aque-

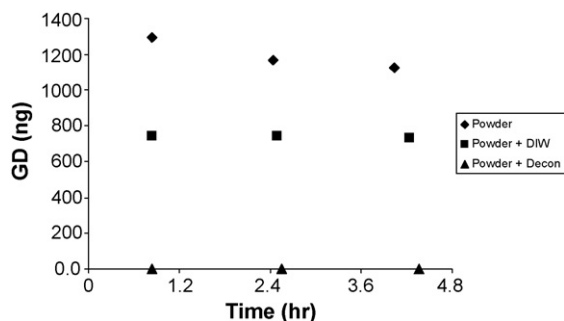
ous decontamination solution unless it is physically mixed, but it still reacts with the oxidizer eventually. The reaction rate with HD with the liquid alone could not be measured, since the HD did not dissolve to form a homogeneous solution.

In order to determine the residual VX to a lower concentration, the residue of a sample was analyzed by GC/MS. The reaction of VX with the E200 aqueous slurry with molybdate was followed by NMR, and the results are given in Table 5, line 2. After the reaction proceeded for 24 h, the sealed NMR tube was broken, and the solid was extracted with a mixture of pH 10 aqueous buffer and methylene chloride. VX partitioned into the methylene chloride phase of the extract. The signal for VX was compared to a standard of 10 µg/ml VX. Calculating back to the original VX spike on the solid sorbent, accounting for dilutions, and assuming 100% recovery [29], it was found that 99.96% of the VX had been destroyed. This type of study was not done for the GD or HD reactions. A systematic study of the residual agent in the decontamination system will be required in order to certify that the decontamination system meets regulatory requirements and to determine the requirements for disposal of the solid waste.

The recovery of GD above the sorbent system with decontamination solution was tested and compared to the recovery for sorbent alone, and for sorbent with distilled water. The results are shown in Fig. 6. They show that the sorbent and decontamination solution greatly decreases the GD vapor down to 1–2 ng. The measured partition coefficient between sorbent and vapor is a ratio of 149 under these test conditions. The vapor of 1 ng GD corresponds to 0.007 mg/m<sup>3</sup> GD, determined from the calibration of the SPME measurements. This value can be compared to the IDLH (Immediately Dangerous to Life and Health) vapor concentration of 0.05 mg/m<sup>3</sup>. This measurement confirms that the GD is decontaminated and the vapor hazard is greatly reduced by the aqueous E200 system.



**Fig. 5.** Kinetic plot of the rate of reaction of VX in a 1:50 ratio (◆) and 1:30 ratio (■) of agent to E200 decontamination system slurry. The weight ratio of solid to decontamination solution in the decontamination system was 1:10 for both. Dashed lines indicate the slowest limit of the fast reaction segment following the VX spike.



**Fig. 6.** Recovery of GD above E200 sorbent powder samples, as determined by SPME. Measurements were done with GD under powder, GD under powder with Distilled water (DIW), and GD under powder with decontamination solution.

#### 4. Conclusion and future work

A new decontamination system was formulated, and its efficiency to decontaminate the CW agents GD, VX, and HD was proved. It is composed of a liquid decontaminant with a solid sorbent. It uses components that have fewer safety and environmental concerns than traditional decontamination means. Its chemical effectiveness of decontamination is almost as efficient as the liquid Decon Green™, yet it has advantages over the liquid solution. The sorbent produces slurry when mixed with the liquid to provide physical support for the decontaminant, reducing the dispersal and runoff. The E200 sorbent allows the use of IPA as a co-solvent to be eliminated, which allows the decontamination solution to be formulated without using an organic solvent, reducing number of the components that need to be mixed.

Further research is necessary before this system can be fielded. It may be advantageous to find a sorbent that is better for absorbing nonpolar compounds like HD, so that mixing to achieve fast decontamination is not needed and the rate is not as variable. This effect may make a significant difference when CW agent is deposited on a surface, so that the sorbent will be required to absorb the agent off the surface and into proximity to the solution.

Since all the present experiments were done in sealed NMR tubes, testing should be done in open air to make sure that the peroxide concentration does not decrease faster in the open than it does in a sealed tube. Also, testing should be done on a variety of substrates to determine whether they have an effect on the decontaminating capacity of the system. Testing should be done on porous or nonporous substrates, such as concrete, asphalt, or painted surfaces, to determine whether the substrates have an effect on the decontaminating capacity of the system.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2008.04.083.

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