EDGEWOOD CHEMICAL BIOLOGICAL CENTER
U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND
Aberdeen Proving Ground, MD 21010-5424

ECBC-TR-1384

REACTIVITY OF DUAL-USE DECONTAMINANTS WITH CHEMICAL WARFARE AGENTS

Matthew P. Willis
Lawrence Procell
John Davies
Brent A. Mantooth

RESEARCH AND TECHNOLOGY DIRECTORATE

July 2016

REPORT DOCUMENTATION PAGE

Form Approved

OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
XX-07-2016

2. REPORT TYPE
Final

3. DATES COVERED *(From - To)*
Mar 2010 – Dec 2013

4. TITLE AND SUBTITLE
Reactivity of Dual-Use Decontaminants with Chemical Warfare Agents

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Willis, Matthew P.; Procell, Lawrence; Davies, John; and Mantooth, Brent A.

5d. PROJECT NUMBER
BA09PHM303

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Director, ECBC, ATTN: RDCB-DRP-D APG, MD 21010-5424

8. PERFORMING ORGANIZATION REPORT NUMBER
ECBC-TR-1384

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Defense Threat Reduction Agency Joint Science and Technology Office,
8725 John J. Kingman Road, MSC 6201; Fort Belvoir, VA 22060-6201

10. SPONSOR/MONITOR'S ACRONYM(S)
DTRA JSTO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT:

Liquid-phase reactor experiments were performed with commercial products and decontaminants to identify viable dual-use products for the decontamination of the chemical warfare agents HD, GD, and VX. The chemical reactivity of the agents in the absence of mass transport limitations (e.g., dissolution of neat agent) was evaluated using a dilute liquid-phase reactor method. When coupled with material testing, the reactor results were used to determine the decontamination modes of action occurring within materials. Evaluation of the data indicated several agent-specific and several broad-spectrum (multiple agent) reactive decontaminants. The reactor analysis was used to identify several commercial products that may provide reactivity with multiple chemical warfare agents in the solution phase. The results indicated that HD was susceptible to oxidation under acidic and alkaline conditions, GD was reactive under alkaline conditions for several decontaminant chemistries, and VX was reactive under acidic and alkaline oxidation chemistries with buffer components. The results suggest that a highly reactive decontaminant for all agents could be achieved with a buffered, alkaline oxidative chemistry that maintains pH levels above 10. This study provides the foundation to enable the interpretation of the mode of decontamination (i.e., reaction or extraction) of chemical warfare agents from materials.

15. SUBJECT TERMS

GD	HD	Decontamination	Hazard mitigation
VX	Chemical warfare agent	Liquid-phase reactivity	

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Renu B. Rastogi
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER** *(include area code)*
U	U	U	UU	26	(410) 436-7545

Standard Form 298 (Rev. 8-98)

Prescribed by ANSI Std. Z39.18

Blank

PREFACE

The work described in this report was authorized under Defense Threat Reduction Agency Joint Science and Technology Office (DTRA JSTO) project no. BA09PHM303. The work was started in March 2010 and completed in December 2013.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release.

Acknowledgment

The authors acknowledge Dr. Charles Bass (Defense Threat Reduction Agency) for funding this work.

Blank

CONTENTS

FIGURES

TABLES

REACTIVITY OF DUAL-USE DECONTAMINANTS
WITH CHEMICAL WARFARE AGENTS

1. INTRODUCTION

Chemical warfare agent decontamination is the process of reducing or eliminating the hazards associated with chemical contamination. Often, the evaluation of a decontaminant's ability to eliminate hazards has focused on liquid-phase reactivity to detoxify the agent.[1–4] The liquid phase provides the ideal medium for reaction where solution chemistry may be optimized (e.g., pH, cosolvents, etc.) for the desired chemical reaction. However, chemical warfare agents must be removed from materials so that the contaminated materiel, such as vehicles or fixed-site facilities, can be returned to regular use without the need for protective equipment. To remove agent from a contaminated material, the reactive moieties of a decontaminant must penetrate the material to react in the material matrix, or the agent must be extracted out of the material into the decontaminant solution phase. The coupled transport and reaction dynamics indicate that highly reactive decontaminants may detoxify agents in the liquid phase, but if the decontaminant does not penetrate the material or extract the agent from the material, the decontaminant will not provide hazard mitigation of contaminated materials.

The approach developed in this study was to decouple the influences of the transport and reaction processes so that the mechanistic contributions of each process may be characterized. Experiments were performed for multiple agent–decontaminant combinations to characterize reactivity in the absence of mass transport limitations. The current evaluation summarizes the development and results of a dilute reactor technique that focuses on agent–decontaminant reactivity. The resulting data may represent the reactivity that occurs within a material, where the decontaminant and agent concentrations are dilute.

Decontamination and detoxification of chemical warfare agents require the direct interaction between the agent and the decontaminant. Traditionally, reactor testing uses neat (pure) chemical agent dosed with an excess amount of liquid decontaminant, and reaction products are sampled from the reactor reagent volume. However, due to low solubility and/or slow rates of dissolution of the organic chemical agents (e.g., solubility of HD [distilled mustard agent, bis-(2-chloroethyl) sulfide] in water: 92 μg/mL),[5] the agent may not be distributed uniformly within the reactor and may present a heterogeneous solution of agent droplets within the decontamination solution. If the agent droplets do not readily or rapidly dissolve, the decontamination reaction occurs primarily on the surface of the liquid agent droplet, and the decontamination rate is mass transport limited because the dissolution rate is much slower than the decontamination reaction rates. Using neat reactor data alone does not facilitate characterization of the reactivity that may be occurring within a material.

A novel experimental method was developed to evaluate the reactivity of chemical warfare agents in the absence of these dissolution-based mass transport limitations. To circumvent dissolution rate limitations within the reactor, the liquid agent was first diluted in an aqueous-miscible organic solvent (2-propanol; Sigma-Aldrich Company; St. Louis, MO), which caused the agent to be rapidly dispersed upon introduction into the reactor and yielded a homogeneous solution to mediate dissolution-based transport limitations. As a result, the observed decrease in agent mass was directly attributable to the agent–decontaminant chemical reactivity and may be representative of material-phase reaction rates.

Several reaction chemistries were investigated including hypochlorites, perioxides, and hydroxides. In addition, solvents, such as 2-propanol or water and formulated products including several commercial off-the-shelf (COTS) cleaning solutions, were evaluated to identify the technologies that could provide detoxification of agents. The COTS cleaning solutions have the potential to be dual-use technologies that could be used for more than just chemical warfare agent decontamination. This characteristic would increase the use of the technology and decrease the logistical burden associated with transport and storage of decontaminants. The experiments in this study were focused on evaluating several chemistries under specific conditions and enabling the direct comparison of decontaminant performances to determine how chemical reactivity contributes to the decontamination of materials.

2. EXPERIMENTAL PROCEDURES

2.1 Methods

The chemicals used in this study were Chemical Agent Standard Analytical Reference Material grade HD, pinacolyl methyl phosphonofluoridate (soman or GD), and *O*-ethyl *S*-(2-diisopropylaminoethyl) methyl phosphonothioate (VX). Chemical agents were used only in properly certified surety facilities capable of handling such chemicals safely. The personnel handling the chemical agents for this study were fully trained and certified for such operations.

Before testing, decontaminant solutions were prepared according to the manufacturer's instructions, and 1.00 mL was added to each reactor vial (7 mL). The reactor vials were placed into a temperature-controlled shaker block (VWR International; Radnor, PA; part no. 12620-934) at 20 °C. The reactor vials were contaminated with 20 μL of dilute agent (target initial reactor concentration: 135.0 μg/mL of HD, 35.0 μg/mL of GD, and 25.0 μg/mL of VX) and vortexed for 5 s to homogenize the reactor. The initial concentrations were selected according to approximate relative toxicity levels and to provide an analytical dynamic range of at least 4 orders of magnitude.

Decontamination in the field is a highly labor-intensive effort with multiple limiting resources (e.g., decontaminant solution, time, and labor). Allowing decontaminants to remain on a surface for durations longer than 30 min often requires reapplying the decontaminant, consuming more solution, and requiring more labor. For these reasons, all reaction time periods used 30 min durations to identify technologies that provide performance in a relatively short time period. After the 30 min decontamination reaction residence time, the reactions were quenched by performing a liquid–liquid extraction of the reactor contents with 5 mL of 70/30% v/v hexane/dichloromethane (Sigma-Aldrich). Method development tests demonstrated a >99% extraction efficiency for HD, GD, and VX into the organic extraction solvent and sample stability for more than 24 h post-extraction.

The extraction samples were diluted and separation of analytes was performed using gas chromatography (GC) for HD and GD (Agilent 6890/7890 GC equipped with a 5975 mass selective detector [Agilent Technologies; Santa Clara, CA]) or using liquid chromatography (LC) with a mass spectrometer for VX (Agilent 1200/1290 series LC and Applied Biosystems [Carlsbad, CA] API5000/5500 triple-quadrupole mass spectrometer equipped with a TurboV ion source). Detailed analytical method specifications are provided in Shue et al.[6] All test conditions were evaluated using four replicates to calculate means and standard deviations.

2.2 Decontaminant Chemistries

This efficacy study was designed to characterize the performance level of existing decontaminants and COTS cleaning products that are found on National Stock Number (NSN) and aircraft-cleaning lists for HD, GD, and VX. This evaluation enabled the identification of technologies suitable for dual use as cleaning products and decontaminants. The evaluated decontaminants represent a range of active chemistries and reaction types including hydrolysis and acidic or alkaline-based oxidation. Table 1 provides a summary of the products that were evaluated for decontaminant performance. The pH values of the decontaminants were measured each test day within an hour of testing (Eutech Cyberscan pH 110 [Eutech Instruments; Landsmeer, The Netherlands]).

The solutions used as decontaminants in this evaluation included a wide variety of chemistries and potential applications. The range of products included formulations specifically designed for decontamination of chemical warfare agents to chemicals or COTS products that may be readily available in the event of contamination. Some selected chemistries are focused on solvent systems that may not react directly with chemical warfare agents but could provide extraction of agents from contaminated materials. The full list is provided in Table 2 and the instructions for the prepared decontaminants are in Table 3. Any product not listed in Table 3 was used as packaged.

Table 1. Summary of Evaluated Decontaminants with Code Letters Used in Figures

Code	Product Name (Company and Location)	pH
A	Aero Wash IV (Rochester Midland Corporation; Rochester, NY)	11.0
B	Chlor Floc (Deatrick and Associates, Inc.; Alexandria, VA)	4.0
C	Clorox bleach, 6% (The Clorox Company; Oakland, CA)	11.3
D	Deionized (DI) water	7.0
E	DF200 (Intelagard; Lafayette, CO)	10.0
F	Drano (S.C. Johnson; Racine, WI)	12.5
G	Floor-stripper concentrate (3M, St. Paul; MN)	11.2
H	2-Propanol (Sigma-Aldrich)	—
I	Oxone (E.I. du Pont de Nemours and Company; Wilmington, DC)	2.0
J	OxiClean (Church and Dwight Co., Inc.; Ewing, NJ)	10.5
K	PEAK antifreeze (Old World Industries; Northbrook, IL)	8.0
L	Simple Green concentrate (Sunshine Markers, Inc.; Huntington Beach, CA)	9.5
M	Windex (S.C. Johnson; Racine, WI)	10.8

—: not measured.

Table 2. Listing of Formulations Used in this Evaluation

Code	Decontaminant Name	Formulation Ingredients	Rationale
A	Aero Wash IV	Sodium nitrite, proprietary detergent blend	Surfactant designed for use on aircraft
B	Chlor Floc	Sodium dichloroisocyanurate, water	Previously used for chemical warfare agent decontamination
C	Clorox bleach 6%	Sodium hypochlorite, sodium hydroxide, water	Previously used for chemical warfare agent decontamination
D	DI water	Water	Negative control, potential for solvent action
E	DF200	Alkyl(C12-16)dimethylbenzylammonium chloride, *N*-tallow-*N*,*N*,*N′*,*N′*,*N′*-pentamethyl-1,3-propanediammonium dichloride, isopropanol, inert ingredients/water, hydrogen peroxide, diacetin	Decontaminant formulated for chemical warfare agents
F	Drano	Sodium hypochlorite, sodium hydroxide, (Na_2SiO_3) sodium silicate, water	Caustic solution, may be readily available
G	Floor-stripper concentrate	Benzyl alcohol, ethanolamine, polyethylene glycol trimethylnonyl ether, decyl(sulfophenoxy)benzene-sulfonic acid, disodium salt, water	Mixture of solvent chemistries
H	2-Propanol	Isopropanol	Solvent chemistry
I	Oxone	Potassium peroxymonosulfate (potassium hydrogenperoxomonosulfate), potassium bisulfate, potassium sulfate, dipotassium peroxodisulfate, magnesium carbonate	Acidic oxidative chemistry, used for VX laboratory waste decontamination
J	OxiClean stain remover	Sodium carbonate, sodium percarbonate, ethoxylated alcohol C12-16	Readily available peroxide generator, solid
K	PEAK antifreeze	Ethylene glycol, diethylene glycol, hydrogenated inorganic acid (proprietary)	Readily available solvent chemistries
L	Simple Green concentrate	2-Butoxyethanol, water	Readily available solvent chemistry
M	Windex (original)	Isopropanol, ethylene glycol monohexyl ether, ammonium hydroxide, Water	Readily available mixture of solvent chemistries in a basic pH

Table 3. Preparation of Decontaminant Formulations Used in This Study

Code	Decontaminant Name	Preparation
B	Chlor Floc	In accordance with manufacturer specifications, 15 min before use, mix one Chlor Floc tablet in 30 mL DI water until dissolved.
E	DF200	In accordance with manufacturer specifications, measure 24.6 mL of Solution 1, 24.6 mL of Solution 2, and 0.8 mL of Solution 3.
I	Oxone	In accordance with manufacturer specifications, 15 min before use, mix 7.5 g of Oxone with 30 mL of DI water until dissolved.
J	OxiClean Stain Remover	In accordance with manufacturer specifications, 15 min before use, mix 4.2 g of OxiClean with 30 mL of DI water until dissolved.

2.3 Data Analysis Methods

The reactor extraction sample effluent contains a specific quantity of analyte, which must be greater than zero because negative mass is not physically realistic (i.e., the data has a left-censored domain). In addition, the chromatography systems used to quantify the analyte produce heteroscedastic data (i.e., the variance of the data is proportional to the magnitude of the signal). Left-censored and heteroscedastic data are commonly managed using a log transformation to maintain the left-censored characteristic and to remove the heteroscedastic variance.[7] The use of a log transformation is vital to this analysis as concentrations often span 4 orders of magnitude, wherein heteroscedastic variance would invalidate the assumptions used to calculate statistical confidence intervals (CIs).

The current evaluation implemented a relative decontamination performance metric with a log difference (LD) calculation. Relative performance metric calculations provide an indication of whether or not a hazard mitigation technology provided an improvement compared to a specified reference (e.g., positive control, reference technology, or alternate treatment condition). For example, the calculation can indicate if and by how much a hazard mitigation technology may produce lower potential exposure when compared with another technology.

The LD analysis for the liquid-phase reactor (LDR) determines, for a given agent–decontaminant combination, if the decontaminant reduced the agent concentration as compared with the positive control. The LDR analysis included the calculation of the LD and the 95% CI for the difference. The LDR is given by $LDR = \log\left(\frac{C_o}{C_t}\right)$, where C_o is the initial agent concentration in the reactor (i.e., the positive-control samples) and C_t is the agent concentration after the decontaminant residence time, *t*. The 95% CI for the difference is calculated under the assumption of unequal variance between the test conditions.[8] If the CI included zero (i.e., if CI > LDR), the evaluated decontaminant did not change the agent concentration during the reaction residence period.

Treatment of the decontaminant performance data with an LDR analysis enables the characterization of decontaminant performance based on the multiple orders of magnitude reduction required to provide hazard mitigation, compared with a linear percentage scale. Due to the highly toxic nature of chemical warfare agents, an LDR value of 3.00 (concentration reduction of 99.90%) or greater may still present enough agent mass to induce toxicological effects in humans. For example, the lethal dose of VX for a 70 kg person is 0.1 mg, and the no-observed-adverse-effect level (NOAEL) for a 70 kg person is approximately 10^{-3} mg. If the starting quantity of VX was a 5 µL droplet (5 mg), it would require an LDR value of 3.70 to reduce the agent concentration to a level below the NOAEL.

3. RESULTS AND DISCUSSION

3.1 HD

Decontaminant performances were characterized for liquid-phase reaction efficacy with HD at initial concentrations of 135,000 ng/mL or 0.85 mM of HD. Figure 1 provides a summary of the HD LDR results for each decontaminant. Decontaminants H and K (solvent chemistries) yielded LDR ± CI values that overlapped zero, which indicated negligible reactivity. Decontaminants A, G, and L yielded LDR values of less than 0.3, which corresponded to a reduction in the agent concentration of less than 50%. By comparison, decontaminants B, C, E, F, and I yielded LDR values >3, which represented a >99.90% reduction of the agent concentration within the 30 min reaction period. Four of the five most-reactive decontaminants (B, C, E, and I) were oxidants that rapidly oxidized the sulfur in HD. The most-reactive decontaminant with HD was B, with an LDR of 3.90 ± 0.33. Decontaminant B contained sodium dichloroisocyanurate, which dissociated in water to generate hypochlorous acid. Decontaminant F was another highly reactive decontaminant that provided effective hydrolysis of HD due to high concentrations of hydroxyl anion reacting via an S_N1 mechanism (substitution, nucleophilic, unimolecular reaction).[1]

The reactor results also demonstrated a significant level of neutral hydrolysis of HD in DI water (decontaminant D), with an LDR of 1.22 ± 0.06 or 94.0% reduction. The results demonstrated that (1) hydrolysis of neat HD is rate-limited by the rate of dissolution of HD into water,[5] and (2) the dilute reactor method can be used to isolate the reactive component of decontamination performance.

Decontaminants A, G, H, K, and L demonstrated lower reactivity and included solvents (H and K) and non-oxidative alkaline decontaminants (A, G, L). These product solutions contained organic solvents that reduced the polarity of the aqueous medium and greatly decreased the S_N1 hydrolysis rate. As the solution became less polar with the addition of organic solvents, the chloride ions produced from hydrolysis further inhibited the HD hydrolysis rate. The results suggested that the addition of cosolvents to mitigate mass transport limiting effects may decrease the decontamination reaction rate. Optimal decontaminants must leverage mass transport limitations with kinetic limitations. The experimental results suggested that HD was reactive in decontaminants that mediated acidic hydrolysis or alkaline oxidation, and the material-phase decontamination rates may enable hazard mitigation within 30 min.

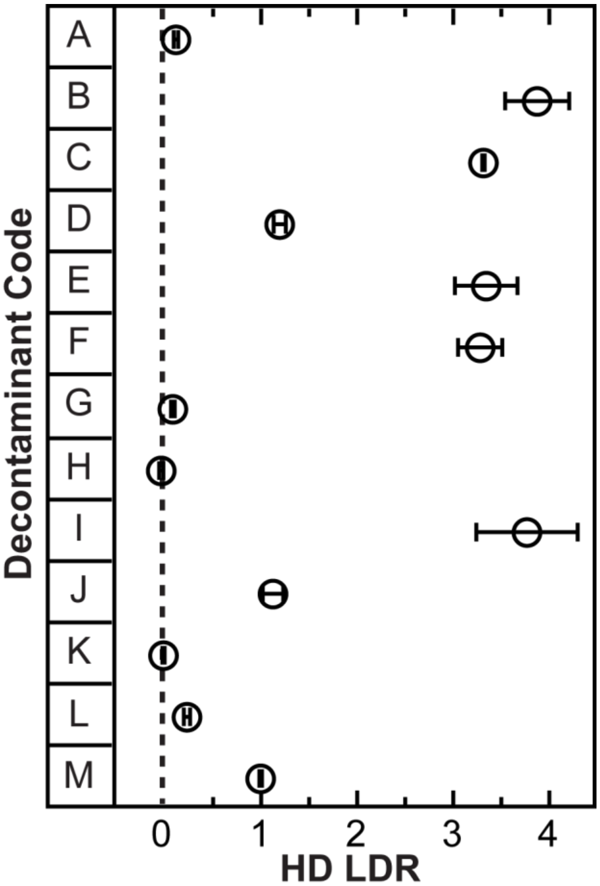

Figure 1. HD LDR for evaluated decontaminant technologies at 20 °C with a decontamination reaction time of 30 min. The error bars give the 95% CI levels on the LDR results.

3.2 GD

Decontaminant performances were evaluated for liquid-phase reaction efficacy with GD at initial concentrations of 35,000 ng/mL or 0.20 mM of GD. Figure 2 provides a summary of the GD LDR results for each decontaminant. The results demonstrated that several decontaminants yielded LDR values of 3 or greater, including A, C, E, F, G, J, and M. Analysis of the LDR results indicated a strong relationship between the pH of a decontaminant and its performance; the decontaminants with pH >10 yielded LDR values of 3 or greater, and those products with pH <10 yielded negligible decontaminant performance. The results aligned with the alkaline-mediated hydrolysis of GD.

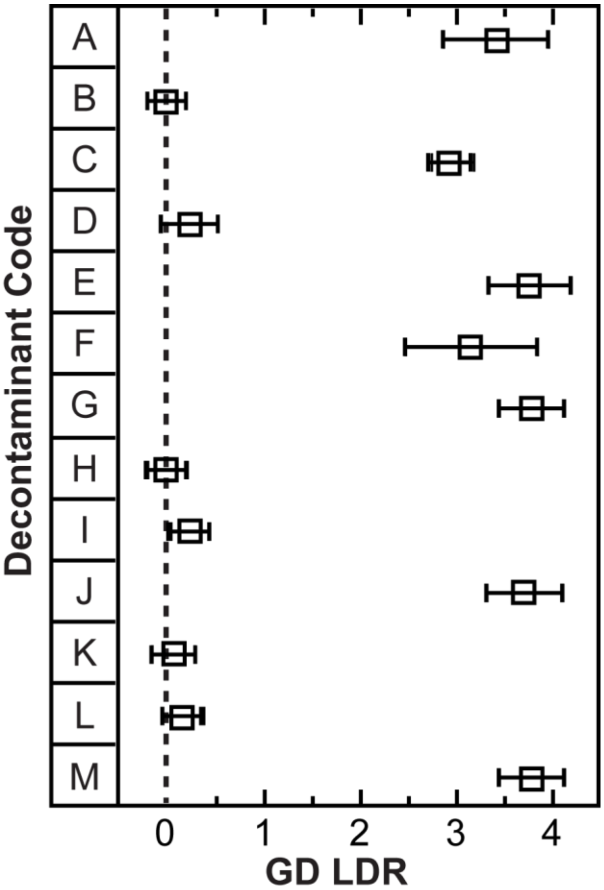

Figure 2. GD LDR for evaluated decontaminant technologies at 20 °C with a decontamination reaction time of 30 min. The error bars give the 95% CI levels on the LDR results.

Hydrolysis of GD proceeds by phosphorus S_N2 nucleophilic attack, which yields the nontoxic product, pinacolyl methylphosphonic acid.[4] With a starting GD concentration of 0.2 mM, any decontaminant solution with a hydroxyl concentration ≥0.4 mM (or pH ≥ 10.6 with no buffer) would provide sufficient capacity to maintain alkaline conditions during the reaction period. The GD results indicated that the buffer in decontaminants E and J maintained an alkaline pH throughout the reaction residence period, despite a slightly lower initial pH. By comparison, decontaminant L did not have a significant buffer capacity, which decreased the reactor performance; the GD LDR was 0.17 ± 0.22 and was statistically similar to the positive control. Therefore, effective material-phase decontamination for GD requires the transport of alkaline-reactive moieties within the material.

3.3 VX

Decontaminant performance was evaluated for liquid-phase reaction efficacy with VX at an initial concentration of 25,000 ng/mL or 0.10 mM. Figure 3 provides a summary of the VX LDR results for each decontaminant. The results demonstrated that VX was reactive with several decontaminants, with LDR values ranging from 1.72 ± 0.05 to 3.08 ± 0.14 for decontaminants J and I, respectively. VX was highly reactive with oxidative chemistries under both alkaline (decontaminant J at pH 10.5) and acidic (decontaminant I at pH 2.0) conditions. Four of the five most-reactive decontaminants (B, C, E, and I) were oxidants that rapidly reacted with the VX via oxidative hydrolysis of the P–S bond,[4,9] which yielded VX LDR results that followed the same trend as those observed with HD.

VX reacts with hydroxide to result in cleavage of both P–S and P–O bonds. Decontaminant F provides hydrolysis of VX due to high concentrations of hydroxyl anion reacting via each pathway. At pH values of <6 and >10, cleavage of the P–S bond predominates, yielding nontoxic products. At pH values of 7–10, P–O cleavage yields *S*-[2-(diisopropylamino) ethyl] methyl phosphonothioic acid (EA-2192), which is almost as toxic as VX and is stable in caustic solutions.[3] Due to the production of EA-2192, VX cannot be effectively detoxified solely by base-catalyzed hydrolysis. The addition of hydrogen peroxide to alkaline solutions (decontaminant E) produces peroxy anion, HOO^-. Perhydrolysis of the P–S bond is very rapid, providing selective P–S bond cleavage and avoiding the formation of EA-2192.[10]

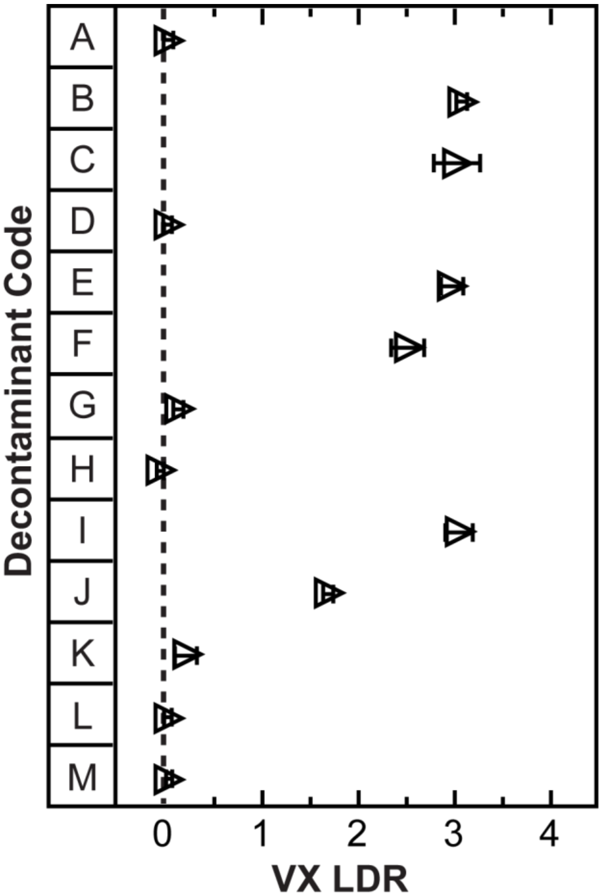

Figure 3. VX LDR for evaluated decontaminant technologies at 20 °C with a decontamination reaction time of 30 min. The error bars give the 95% CI levels on the LDR results.

A byproduct screening for toxic degradation products indicated that EA-2192 production was suppressed under highly acidic (decontaminant I) or highly alkaline (decontaminants E and F) conditions. By comparison, decontaminant J (pH 10.5) produced elevated levels of EA-2192. Reactor effluent analysis after the decontamination reaction showed a final pH of <10, which indicates that decontaminant J did not contain the buffer capacity for the production of acidic byproducts; therefore, it yielded an elevated production of EA-2192. The nonreactive decontaminants, including decontaminants A, D, G, H, K, L, and M, represented a range of pH conditions (decontaminant D at pH 7.0 to decontaminant G at pH 11.2), but they did not contain an oxidizing agent. The reactor results suggested that VX decontamination was the most effective with oxidative chemistries that contained buffers to maintain the pH at <6 or >10.

3.4 Performance Comparison

The ideal decontaminant would provide broad-spectrum performance across multiple agents. The LDR analysis enables an identification of agent-specific and broad-spectrum decontaminants, as illustrated in Figure 4. The agent-specific LDR analysis indicated that HD was susceptible to oxidation under acidic and alkaline conditions, GD was reactive under alkaline conditions regardless of the decontaminant formulation, and VX was reactive under acidic and alkaline oxidation chemistries. Analysis of the results suggests that broad-spectrum reactive decontamination could be achieved with an alkaline oxidative chemistry. Comparison of the LDR results for each agent–decontaminant condition demonstrates that the highest average performance was with decontaminant E, followed by decontaminants C and F; all of these are alkaline decontaminants with oxidative chemistries that include OH^- and OCl^-.

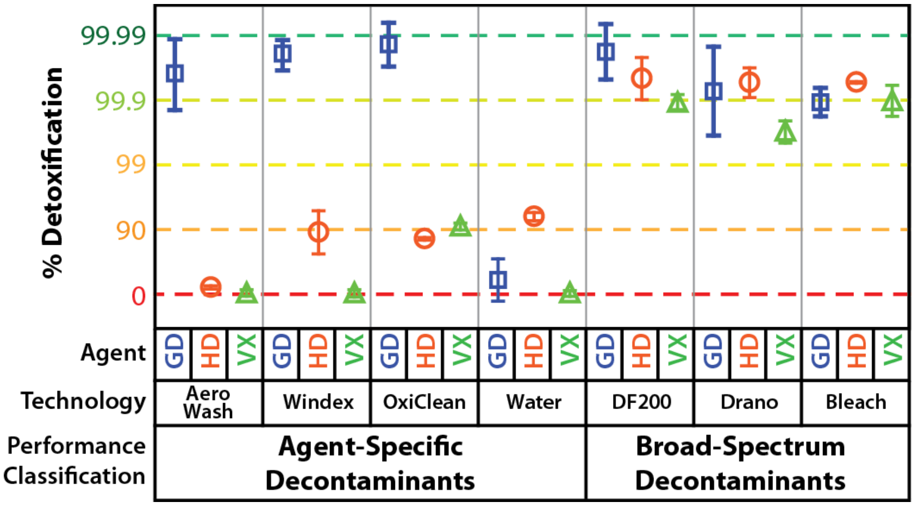

Figure 4. Comparison of performance (% detoxification) across agents to illustrate agent-specific vs broad spectrum performance.

Hydrolysis of GD in alkaline solutions produces the nontoxic pinacolyl methylphosphonic acid (PMPA) resulting from P–F bond cleavage. Alkaline solutions with a pH ≥10 (decontaminants A, C, E, F, G, J, and M) contain sufficient hydroxyl concentrations to resist acidification from the PMPA and from the hydrofluoric acid that is produced during the hydrolysis of GD to provide effective neutralization during the 30 min reaction period. Higher reaction rates with GD may be achieved in alkaline oxidative solutions (decontaminants C, E, and J) where the nucleophile may be more reactive than OH^- (i.e., OCl^- and HOO^-) and the percarbonate anion. The acidic oxidant (decontaminant I) reacted with the sulfur in HD and VX, but as GD does not have sulfur, decontaminant I was not an effective broad-spectrum decontaminant for GD.

VX and HD were detoxified in oxidative solutions (decontaminants B, C, E, I, and J). HD was typically more reactive as compared with VX, which led to slightly higher LDR values for HD. Hydrolysis of VX in alkaline solutions may yield the toxic EA-2192 product and cannot be effectively detoxified solely by base-catalyzed hydrolysis. However, the addition of hydrogen peroxide to alkaline solutions (decontaminant E) produces peroxy anion, HOO^-, which provides selective P–S bond cleavage and does not form EA-2192.

Therefore, decontaminant E provided a high level of performance with HD, GD, and VX and did not produce toxic byproducts. Decontaminant E could be implemented for bulk-liquid decontamination effluent if the specific agent is unknown when decontamination is performed. Furthermore, decontaminants C and F are commonly available NSN cleaning products that yielded reductions in HD, GD, and VX of >99.9 and 99.7%, respectively. Using the dilute liquid-phase reactor technique has led to the identification of several decontaminants that provide reaction efficacy for agent detoxification in the solution and material phases.

4. CONCLUSIONS

Dilute liquid-phase reactor experiments were used to compare the decontamination performance of several COTS products against the chemical warfare agents HD, GD, and VX. Using the dilute reactor approach has resulted in the identification of the reactivity of several agent–decontamination chemistries in the absence of mass transfer limiting processes, which may align with material-phase reaction rates. The agent-specific results indicated that HD was susceptible to oxidation under acidic and alkaline conditions, GD was reactive under alkaline conditions for several decontaminant chemistries, and VX was reactive under acidic and alkaline oxidation chemistries with buffer components. These results suggest that a highly reactive decontaminant for all agents could be achieved with a buffered alkaline oxidative chemistry that maintains pH levels above 10. Common commercial products bleach and Drano (decontaminants C and F, respectively) yielded elevated broad-spectrum reactivity with all chemical agents.

Blank

LITERATURE CITED

1. Yang, Y.C.; Baker, J.A.; Ward, J.R. Decontamination of Chemical Warfare Agents. *Chemical Reviews* **1992,** *92*, 1729–1743.

2. Talmage, S.S.; Watson, A.P.; Hauschild, V.; Munro, N.B.; King, J. Chemical Warfare Agent Degradation and Decontamination. *Current Organic Chemistry* **2007,** *11* (3), 285–298.

3. Munro, N.B.; Talmage, S.S.; Griffin, G.D.; Waters, L.C.; Watson, A.P.; King, J.F.; Hauschild, V. The Sources, Fate, and Toxicity of Chemical Warfare Agent Degradation Products. *Environmental Health Perspectives* **1999,** *107* (12), 933–974.

4. Kim, K.; Tsay, O.G.; Atwood, D.A.; Churchill, D.G. Destruction and Detection of Chemical Warfare Agents. *Chemical Reviews* **2011,** *111* (9), 5345–5403.

5. Bizzigotti, G.O.; Castelly, H.; Hafez, A.M.; Smith, W.H.B.; Whitmire, M.T. Parameters for Evaluation of the Fate, Transport, and Environmental Impacts of Chemical Agents in Marine Environments. *Chemical Reviews* **2009,** *109* (1), 236–256.

6. Shue, M.; Lalain, T.; Mantooth, B.; Humphreys, P.; Hall, M.; Smith, P.; Sheahy, M. *Low-Level Analytical Methodology Updates to Support Decontaminant Performance Evaluations*; ECBC-TR-883; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2011; UNCLASSIFIED Report.

7. Box, G.E.; Hunter, S.J.; Hunter, W.G. *Statistics for Experimenters: Design, Innovation, and Discovery*. 2nd ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2009; p. 664.

8. Lalain, T.; Mantooth, B.; Shue, M.; Pusey, S.; Wylie, D. *The Chemical Contaminant and Decontaminant Test Methodology Source Document, Second Edition*; ECBC-TR-980; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2011; UNCLASSIFIED Report.

9. Industrial & Engineering Chemistry ResearchYang, Y.C. Chemical Detoxification of Nerve Agent VX. *Accounts of Chemical Research* **1999,** *32* (2), 109–115.

10. Yang, Y.C.; Berg, F.J.; Szafraniec, L.L.; Beaudry, W.T.; Bunton, C.A.; Kumar, A. Peroxy Hydrolysis of Nerve Agent VX and Model Compounds and Related Nucleophilic Reactions. *Journal of the Chemical Society-Perkin Transactions* **1997,** *2* (3), 607–613.

Blank

ACRONYMS AND ABBREVIATIONS

CI	confidence interval
C_o	initial agent concentration
COTS	commercial off-the-shelf
C_t	concentration time
DI	deionized
GD	pinacolyl methyl phosphonofluoridate
HD	distilled mustard agent, bis-(2-chloroethyl) sulfide
LC	liquid chromatography
LD	log difference
LDR	log difference for reactor
NOAEL	no-observed-adverse-effect level
NSN	National Stock Number
PMPA	pinacolyl methylphosphonic acid
S_N1 mechanism	substitution, nucleophilic, unimolecular reaction
t	decontaminant residence time
VX	*O*-ethyl *S*-(2-diisopropylaminoethyl) methyl phosphonothioate

DISTRIBUTION LIST

The following individuals and organizations were provided with one Adobe portable document format (pdf) electronic version of this report:

U.S. Army Edgewood Chemical
Biological Center (ECBC)
RDCB-DRP-D
ATTN: Procell, L.
Davies, J.
Mantooth, B.
Shue, M.

Defense Threat Reduction Agency
J9-CBS
ATTN: Moore, E.

Department of Homeland Security
DHS-ORD-CSAC
ATTN: Famini, G.

G-3 History Office
U.S. Army RDECOM
ATTN: Smart, J.

ECBC Technical Library
RDCB-DRB-BL
ATTN: Foppiano, S.
Stein, J.

Office of the Chief Counsel
AMSRD-CC
ATTN: Upchurch, V.

Defense Technical Information Center
ATTN: DTIC OA

ECBC Rock Island
RDCB-DES
ATTN: Lee, K.


EDGEWOOD CHEMICAL BIOLOGICAL CENTER
A U.S. Army RDECOM Laboratory