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

ECBC-TR-1383

TRANSPORT AND REACTIVITY OF DECONTAMINANTS TO PROVIDE HAZARD MITIGATION OF CHEMICAL WARFARE AGENTS FROM MATERIALS

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

RESEARCH AND TECHNOLOGY DIRECTORATE

June 2016

U.S. ARMY RDECOM

Disclaimer

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* XX-06-2016	**2. REPORT TYPE** Final	**3. DATES COVERED** *(From - To)* Mar 2010 – Dec 2013

4. TITLE AND SUBTITLE Transport and Reactivity of Decontaminants to Provide Hazard Mitigation of Chemical Warfare Agents from Materials	**5a. CONTRACT NUMBER**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Mantooth, Brent A.; Willis, Matthew P.; Procell, Lawrence; and Davies, John	**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-1383
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:

Decontamination of materials involves the physical and chemical interactions among several components including the agent, material, and decontaminant. The two-way interactions of each component (agent–material, agent–decontaminant, and decontaminant–material) contribute to the decontaminant performance and the resulting post-decontamination hazards associated with the material. Decontamination involves coupled transport and reaction mechanisms. Mass transfer processes limit the accessibility of the agent to the decontaminant and significantly influence performance. Three modes of action contribute to the decontamination of a material: chemical reactivity, agent extraction, and decontaminant penetration. Each mode contributes to the rate and extent of agent removal. A novel approach was developed to integrate liquid-phase reactor data and material testing to identify the modes of action that may occur for specific agent–material–decontaminant combinations. This approach illustrates that chemical reactivity does not necessarily correlate with agent removal from materials and indicates potential directions for future decontamination formulation approaches.

15. SUBJECT TERMS

GD	HD	Decontamination	Hazard mitigation
VX	Chemical warfare agent	Transport and reactivity	Material

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	34	(410) 436-7545

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.

Acknowledgments

The authors acknowledge Dr. Charles Bass (DTRA; Fort Belvoir, VA) for funding this work.

Blank

CONTENTS

FIGURES

TABLES

TRANSPORT AND REACTIVITY OF DECONTAMINANTS TO PROVIDE HAZARD MITIGATION OF CHEMICAL WARFARE AGENTS FROM MATERIALS

1. INTRODUCTION

Decontamination of materials is the process of reducing or eliminating the hazards associated with unprotected personnel using or interacting with high-value assets or materiel that have been contaminated with chemical warfare agent. Assets can range from military hardware such as radios, weapons, vehicles, or aircraft to domestic fixed-site facilities such as buildings or other public facilities. Post-decontamination hazards are related to the agent present in or on the material that was not removed by the decontamination process. This remaining agent (RA) could result in vapor emission that, in turn, generates inhalation exposures, or the agent may be contact-transferred from the material and result in a percutaneous (i.e., through the skin) exposure.[1]

In general, the evaluation of decontaminant performance and hazard mitigation has focused on liquid-phase reactivity to detoxify the agent.[2–5] However, the rate of removal of an agent from a material may not be entirely characterized by the rate of reaction in a liquid phase. When a material is contaminated with agent, various mass transfer processes, such as absorption via molecular diffusion or porous transport, redistribute the agent in and on the material (Figure 1).[6–11] For a decontaminant to remove the agent from the material, the decontaminant must access the agent. Therefore, the decontamination of a material involves coupled transport and reaction mechanisms that occur within the material and may be specific to each agent–material–decontaminant combination.[12]

The liquid phase provides the ideal medium for reaction where solution chemistry may be optimized (e.g., pH, cosolvents, etc.). Previous studies were conducted to evaluate the dilute liquid-phase reactor results and identify highly reactive chemistries.[13] However, to remove agent from a material, the reactive moieties must penetrate into the material to react in the material matrix, or the agent must be extracted into the decontaminant solution phase. Considering the coupled relationship between transport and reaction, it is possible that highly reactive decontaminants may detoxify agents in the liquid phase; however, if the decontaminant does not penetrate into the material or extract the agent from the material, the decontaminant may not provide hazard mitigation of the contaminated materials. A novel complementary analysis of liquid reactor and material data was used to identify the modes of action that provide decontaminant performance.

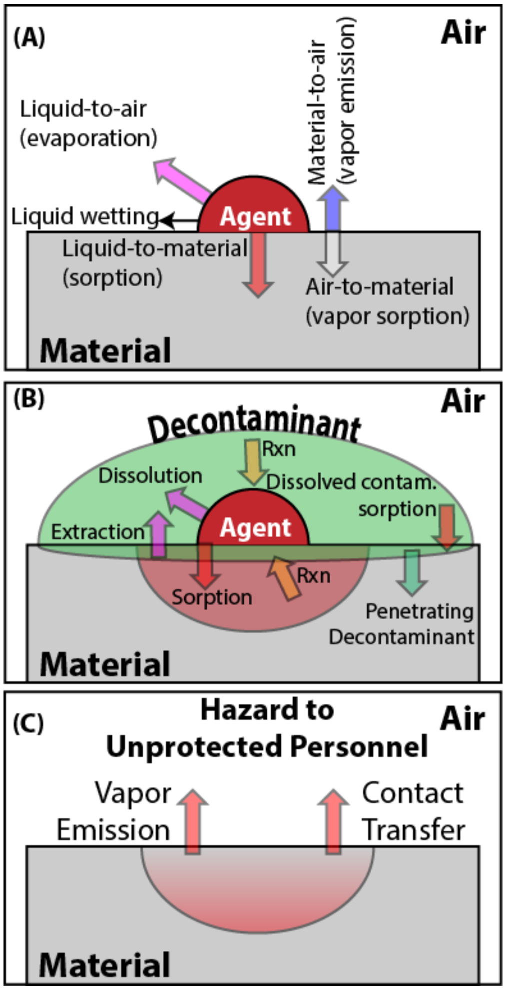

Figure 1. Illustration of the system components during the different experimental phases including (A) contamination, (B) decontamination (Rxn is reaction), and (C) post-decontamination.

2. BACKGROUND

Decontamination involves physical and chemical interactions among the agent, material, and decontaminant. The two-way interactions between each component (agent–material, agent–decontaminant, and decontaminant–material) contribute to the efficacy of the decontaminant and, as a result, to the post-decontamination hazards. Agent–material interactions result in a distribution of the agent in and on the material. The distribution is generated as a function of multiple mass transfer processes that may include liquid absorption into the material, liquid evaporation and subsequent vapor sorption, and adsorption onto the material surface.[7] The quantity of agent that strongly interacts with a material is dependent on the physical and chemical properties of both the agent and the material. Typical materials of interest include polymers or paint systems in which mass transport occurs via molecular diffusion.[7,14–17] Each of these agent–material interactions may result in significantly different distributions of agent in a material. Previous work demonstrated the effects of the chemistry and properties of liquid absorption in various polymers.[18–24] For example, some materials may present chemical (i.e., agent) resistivity by not allowing agents to absorb into the material, whereas other materials may be highly absorptive (e.g., tire rubber). Absorptive materials are often more challenging to decontaminate because of the reduced accessibility of the decontaminant to the agent located deep within the material, and therefore, are most likely to result in post-decontamination exposure if the decontaminant does not remove all of the agent.

Decontamination requires a direct interaction between the agent and the decontaminant. The removal of agent from a material could occur via several modes of action that can include a chemical reaction in which the decontaminant reacts with the agent inside the material or the solvent-mediated extraction of agent from the material. Penetration of the decontaminant species into the material will enhance the reactivity and/or extraction modes of the decontaminant action. The intermolecular decontaminant–material interactions may facilitate or inhibit the penetration of the decontaminant into the material.

Complementary liquid-phase reactor tests[13] and material tests are used to assess the chemical reactivity and the ability of a decontaminant to remove agent from materials. Ideally, a decontaminant will provide both reactivity and removal of the agent; however, due to mass transfer limitations associated with agent transport, high reactivity may not correlate with good removal of agent from materials. The objective of this study was to provide a screening tool to identify decontamination chemistries and formulations that will both detoxify and remove chemical agent from materials.

3. EXPERIMENTAL PROCEDURES

3.1 Methods

Chemical Agent Standard Analytical Reference Material grade bis-(2-chloroethyl) sulfide (also called distilled mustard or HD); pinacolyl methyl phosphonofluoridate (also called soman or GD); and *O*-ethyl *S*-(2-diisopropylaminoethyl) methyl phosphonothioate (VX) were used in this study. These agents were only used 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.

The panel test was used to determine the quantity of RA in a material after a decontamination process. The details of the panel test and calculation methods are documented by Lalain et al.;[25] a brief summary is provided here. Panels were 2 in. diameter disks of the materials being evaluated. Panels were preconditioned at 20 °C with 50% relative humidity for at least 1 h, contaminated with a 2 µL droplet of agent, and then aged for 60 min. During the aging period, agent mass was absorbed by a flux-based process.[7] The agent-contaminated area of the panel may affect the quantity of absorbed agent due to the different liquid–material interfacial areas. For this reason, photographs of every panel were acquired, and the contaminated area was quantified.

After the agent–material interaction period, the bulk liquid agent was removed from the panel surface with a water rinse process (60 mL of deionized [DI] water, applied as three 20 mL aliquots from a peristaltic pump [1.0 L/min] with a polyethylene tube [0.25 in. outer diameter]). After the water rinse, 4 mL of the decontaminant was applied to the material via pipette to fully wet the contaminated area. 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, which consumes more solution and requires more labor. For these reasons, all reaction time periods (liquid reactor and panel test) used 30 min durations to identify technologies that provide performance in a relatively short time period. After the decontaminant residence period, panels were rinsed with DI water, dried, and placed in extraction solvent (20 mL of chloroform for HD [Sigma-Aldrich; St. Louis, MO] or 2-propanol for GD and VX [Sigma-Aldrich]) for 60 min. Previous evaluations demonstrated the extraction efficiency from the materials (described in Section 3.3) of >99%.

Samples were diluted and the analytes were quantified 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).[26]

All test conditions were evaluated using four replicates to calculate means and standard deviations, with the exception of the water rinse reference condition, which was used as a daily control and was replicated 30–48 times for each agent–material condition.

3.2 Decontaminant Chemistries

The performance for existing decontaminants and commercial off-the-shelf cleaning products that are found on national stock number and aircraft cleaning lists were evaluated for effectiveness against HD, GD, and VX. The decontaminants (Table 1) were identical to those previously evaluated using a dilute liquid-phase reactor.[13]

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	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 Company; St. Paul, MN)	11.2
H	2-Propanol (Sigma-Aldrich)	-----
I	Oxone (E.I. du Pont de Nemours and Company; Wilmington, DE)	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

3.3 Panel Materials

The evaluated materials were previously identified as those able to retain HD, GD, and VX; therefore, these materials would require a significant level of hazard mitigation. The materials included a water-dispersible polyurethane (WDP) paint (MIL-DTL-53039) and an alkyd paint (MIL-PRF-24635). Two polymers were also selected, including polyethylene and a styrene butadiene rubber (SBR), which is a surrogate for tire rubber. Each of these materials presents significantly different chemistries that interact with the agents and decontaminants in different ways.

3.4 Data Analysis Methods

The ideal decontaminant should reduce the quantity of agent in the material by several orders of magnitude. The ability to remove agent from a panel is evaluated using a log difference (LD) relative performance metric.[13,25] The LD panel (LDP)

$$LDP = log_{10}\left(\frac{M_0}{M_{\text{Decon}}}\right) \tag{1}$$

quantifies the difference between the agent mass retained after a control condition (M_0) and the RA mass after decontamination (M_{Decon}). The 95% confidence interval (CI) for the difference is used to determine the statistical significance between the two conditions. If the CI included zero (i.e., if CI > LDP), the evaluated decontaminant did not remove agent from the material. If the LDP ± CI did not include zero, the decontaminant reduced the quantity of agent in the material by a statistically significant amount. The reduction can be described as LDP orders of magnitude (or by a factor of 10^{LDP} or percentage reduction by $[1 – 10^{–\text{LDP}}] \times 100\%$) compared with the control condition. Larger LDP values indicate better performance.

A water rinse process was used as the control condition for the analysis of panel data. The water rinse process removes the bulk of the liquid agent from the material, leaving behind any absorbed or surface-bound agent. The surface-bound agent may be adsorbed on the material surface or retained as a liquid in the macroscopic surface features of the material. The use of the water rinse process enables a characterization of the quantity of agent that strongly interacted with the material as a result of the contamination process and facilitates a quantitative assessment of the amount of agent removed from the material by the decontaminant. This isolation of the bulk liquid agent from the retained agent is a key factor in determining the ability of a decontaminant to remove agent from a material.

The quantity of agent retained by a material after the aging process depends on the agent–material interactions and can vary by up to 6 orders of magnitude across different agent–material combinations. The range of LDP values that may be observed depends on the mass of agent retained by the material and the analytical sensitivity, as defined by the analytical limit of detection (LOD). For example, a material that retains a small quantity of agent cannot have an LDP as large as that of a material that retains a larger quantity of agent. For the experimental conditions investigated in this study (i.e., 60 min age time at 20 °C), the agent retention is provided as the geometric mean for each agent–material combination (Table 2); all agent mass values are reported in nanograms. The LDP LOD (LDP_{LOD}) is the LD between the LOD mass and reference condition (M_0). As shown in Table 2, the HD–WDP paint combination was a system in which the agent significantly and variably wet the material, which resulted in a much larger contaminated area than did other agent–material combinations.

Table 2. RA Mass and Determination of LDP LOD for all Agent–Material Combinations

Agent	**Material**	**M_0 (ng)**	**LOD (ng)**	**LDP_{LOD}**	**Contaminated Area Mean ± Standard Deviation (cm^2)**
HD	WDP paint	762,199	5054	2.18	2.36 ± 1.93
HD	Polyethylene	546,726	4812	2.06	0.08 ± 0.02
GD	Alkyd paint	934,652	407	3.36	0.33 ± 0.06
GD	Polyethylene	36,290	407	1.95	0.21 ± 0.04
VX	Alkyd paint	449,676	567	2.90	0.22 ± 0.02
VX	SBR	395,567	576	2.84	0.16 ± 0.04

The analysis discussed in Section 3.5 uses the LD results for dilute reactor and panel data, which are indicated as log difference reactor (LDR) and LDP, respectively. The LDR value indicates whether the decontaminant is chemically reactive with an agent. The LDP analysis indicates whether the decontaminant removes the agent from materials (i.e., the decontaminant can access and remove the agent that has been retained by the material). Both performance aspects of a decontaminant are important but are not necessarily correlated. However, integration of both performance components enables the identification of decontaminant processes that occur in the selected materials (e.g., extraction vs reaction).

3.5 Decontaminant Modes of Action

A quantitative approach was developed to describe the decontaminant mode of action for hazard mitigation performance. A conceptual example of the approach, based on the LDR and LDP relative performance metrics, is shown in Figure 2. Based on their performance in the dilute liquid-phase reactor and panel tests, decontaminants may be described by the properties identified for Categories I–IV. Category I, *REACT*, represents a decontamination technology that reduces the agent concentration in the reactor but leaves a high quantity of residual agent in the panel after the decontamination process. In other words, a Category I decontaminant is highly reactive with the agent, but it cannot extract the agent from materials or access the agent absorbed within a material. Category I decontaminants could be considered for bulk liquid or effluent decontamination applications, but these decontaminants do not remove the agent from materials.

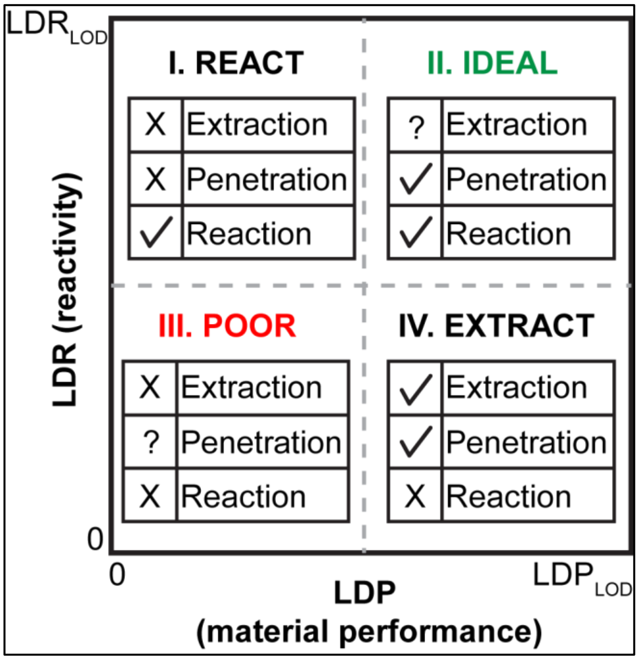

Figure 2. Decontaminant performance categories based on LD performance metric evaluation on panels (LDP) and in dilute liquid-phase reactors (LDR). Symbols: × does not occur, ✓ does occur, and ? may occur.

Category II, *IDEAL*, represents a decontamination technology that yields a low quantity of residual agent in both the dilute liquid-phase reactor and panel tests. This result indicates that the decontaminant has a high agent reactivity and an ability to remove the agent from the material (via solvent extraction or penetration and reaction).

Category III, *POOR*, represents a decontamination technology that did not reduce the quantity of agent in the material panel or in dilute liquid-phase reactor after the decontamination process. A Category III decontaminant can be characterized by poor material penetration, poor solubility with the agent, and/or low reactivity with the agent. Placed on the origin of the LD plot, this type of decontaminant was not reactive with the agent nor did it provide the solvency capacity to remove the agent from the material.

Category IV, *EXTRACT*, represents a decontamination technology that reduced the quantity of agent in the panel test but did not reduce the agent concentration in the dilute liquid-phase reactor. A Category IV decontaminant likely exhibits good solvency for the agent and penetrates into the material, but it is not reactive. During the decontamination process, the decontaminant extracts agent from the material, but it is unable to react with or detoxify the agent within the liquid phase. Decontaminants in Category IV could be considered as a preliminary option to remove gross contamination from a material, but they would require subsequent treatment by a reactive decontaminant (e.g., Categories I and II) for detoxification.

Decontaminant penetration into a material is a key factor in providing good performance. Without penetration, the rate of agent removal from a material is limited by the rate of contaminant mass transport to the material surface where it interacts with the decontaminant. Penetration facilitates the extraction, transport, or reactive moieties of the decontaminant with the contaminant in the material. Penetration of a decontaminant is primarily a decontaminant–material interaction. Although penetration into a material is likely to increase performance, a penetrating decontaminant may cause damage to the material, such as the swelling of polymers caused by solvents or any active ingredients in the decontaminant that can react with the material in addition to the agent. This study focused on the effects of decontaminant performance and did not evaluate material degradation.

4. RESULTS AND DISCUSSION

4.1 HD

Figure 3 shows a summary of the LDP results for HD on WDP paint and polyethylene. The dilute liquid-phase reactor results demonstrated that HD was susceptible to acidic hydrolysis and alkaline oxidation; the most-reactive decontaminants were B, C, E, F, and I.[13] The best-performing decontaminants for HD on polyethylene were A, C, E, F, H, I, and K, which yielded at least one LDP (90% reduction). Decontaminants C, E, F, and I were aqueous-based with highly reactive formulations. By comparison, decontaminants A, H, and K were solvent-based with negligible reactivity. The results demonstrated that comparable decontaminant–material performance can be achieved with both reactive and nonreactive decontaminants; optimal formulations may include an integration of solvent chemistries to extract the agent from the material and reactive chemistries to detoxify the agent.

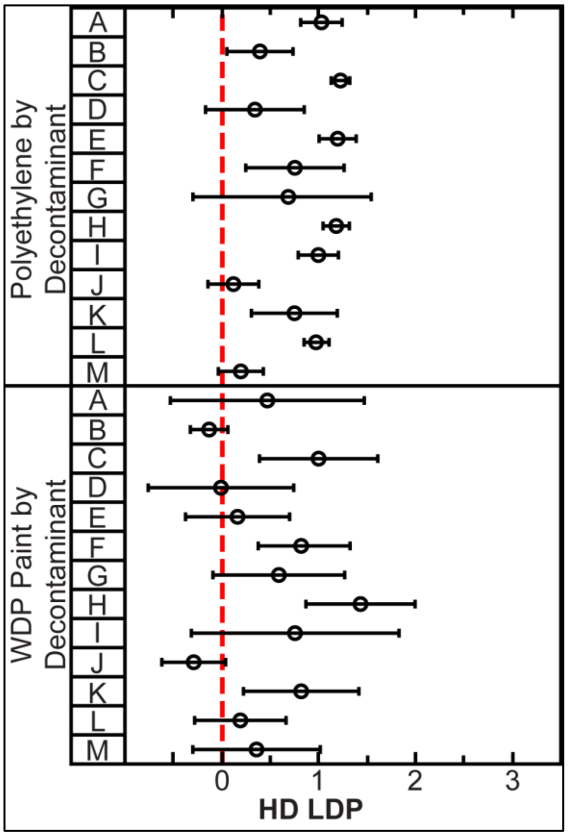

Figure 3. LDP with 95% CI for HD on polyethylene and WDP paint.

The HD–WDP paint LDP analysis yielded large CI values, which inhibited a statistical comparison of performance across decontaminants. Image analysis of panels after the agent–material interaction period (before the decontaminant was applied) demonstrated that the final contaminated area for HD on WDP paint varied from 0.1 to 6.0 cm^2 (Figure 4A). The red lines in Figure 4A outline the contaminated region of each panel. The observed range of contaminated areas influenced M_0 by 1 order of magnitude. The variance in spreading characteristics for paint systems was previously observed in this type of testing (data not shown) and was attributed to heterogeneity of the paint film. A nonlinear least-squares regression was used to identify whether the final contaminated area influenced the total retained agent mass for the water rinse control (Figure 4B). The analysis identified a power-law relationship between $\log_{10}(M_0)$ and the final contaminated area (A_i).

The regression was implemented to calculate an area-corrected LDP for each panel as follows: $LDP = 5.652A_i^{0.047} - \log_{10}(M_i)$, where *i* corresponds to the sample number. The area-corrected HD–WDP paint LDP values, based on the contaminated area, are given in Figure 4C.

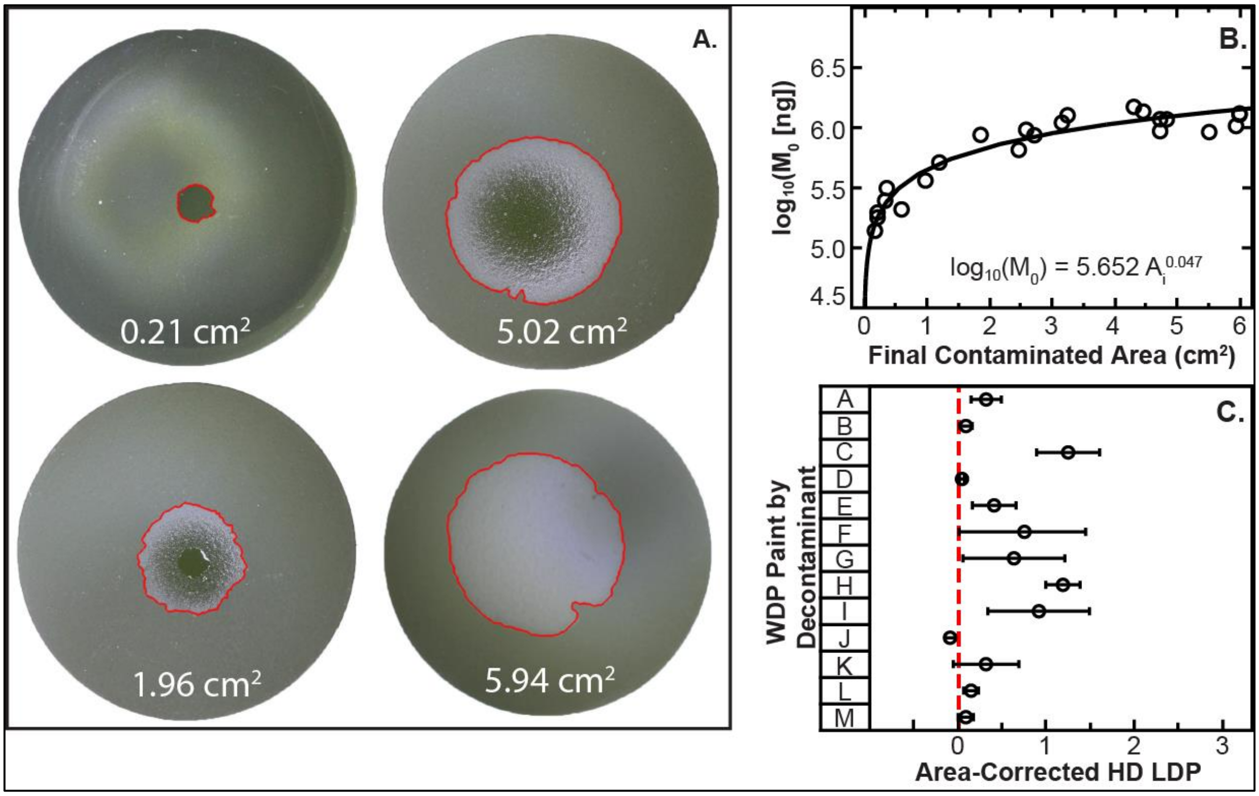

Figure 4. (A) Example photographs of HD on WDP paint after 60 min to quantify the final contaminated area. (B) Nonlinear correlation between $\log_{10}(M_0)$ and the final contaminated area for HD on WDP paint. (C) Corrected HD LDP on WDP paint based on nonlinear least-squares correlation for baseline retained agent mass.

The CI of the HD–WDP paint LDP values improved substantially, enabling a more-precise comparison of decontaminant performance. The large CIs were a result of the influence of agent retention due to the variable contaminated areas for each panel. The results demonstrated that the highest decontaminant performance was achieved with decontaminants C and H, which represent an aqueous reactive decontaminant C and an organic nonreactive solvent decontaminant H. By comparison, decontaminants B, D, J, L, and M yielded negligible performance for HD on WDP paint.

All agent–material combinations, with the exception of WDP paint, produced reproducible contaminated areas, with no significant effect on RA. Therefore, all other agent–material combinations used the direct comparison of extraction data rather than the area-corrected values.

4.2 GD

Figure 5 summarizes the LDP results for GD on polyethylene and alkyd paint at 20 °C. The dilute liquid-phase reactor results for GD demonstrated an elevated reactivity under alkaline conditions with a buffer to maintain a pH >10.5; the most-reactive decontaminants were

A, C, E, F, G, J, and M. The panel test results demonstrated that on polyethylene, all decontamination chemistries yielded comparable performances, with LDP values of 0.3 (reduction of 50%). The panel test results indicated that the decontaminants could not access the GD absorbed into the polyethylene material, which yielded low decontaminant performance. The results suggested that, despite a low quantity of total retained agent mass, a significant portion of the retained GD mass was within the polymeric material and was inaccessible to the decontaminants.

By comparison, the use of two decontaminants removed >98% of the retained GD from alkyd paint, with LDP values of 1.70 ± 0.25 and 2.88 ± 0.23 for decontaminants G and H, respectively. Decontaminants G and H were both solvent-based, but G was alkaline, which hydrolyzes the GD and enhances the decontaminant performances. By comparison, other alkaline technologies, such as A, C, E, F, J, and M, did not contain solvent components that would enable penetration into the coating. As a result, the LDP for these decontaminants was <0.54 (reduction by 71%). Decontaminants G and H did not provide high performance on the polyethylene compared with the alkyd paint. The differences in decontaminant performances were likely due to the solvent–material interactions, in which the decontaminant solvent was able to penetrate the alkyd paint but not the polyethylene material. The data provide strong indications of the significance of the decontaminant–material interactions in the removal of agent from a material and that agent removal from materials may be independent of chemical reactivity.

Although the panel tests demonstrated that GD was susceptible to liquid-phase reactive decontamination with several decontaminant technologies, few decontaminants yielded >70% removal from each material type. These results illustrated the need to consider material performance on sorptive materials during decontaminant development.

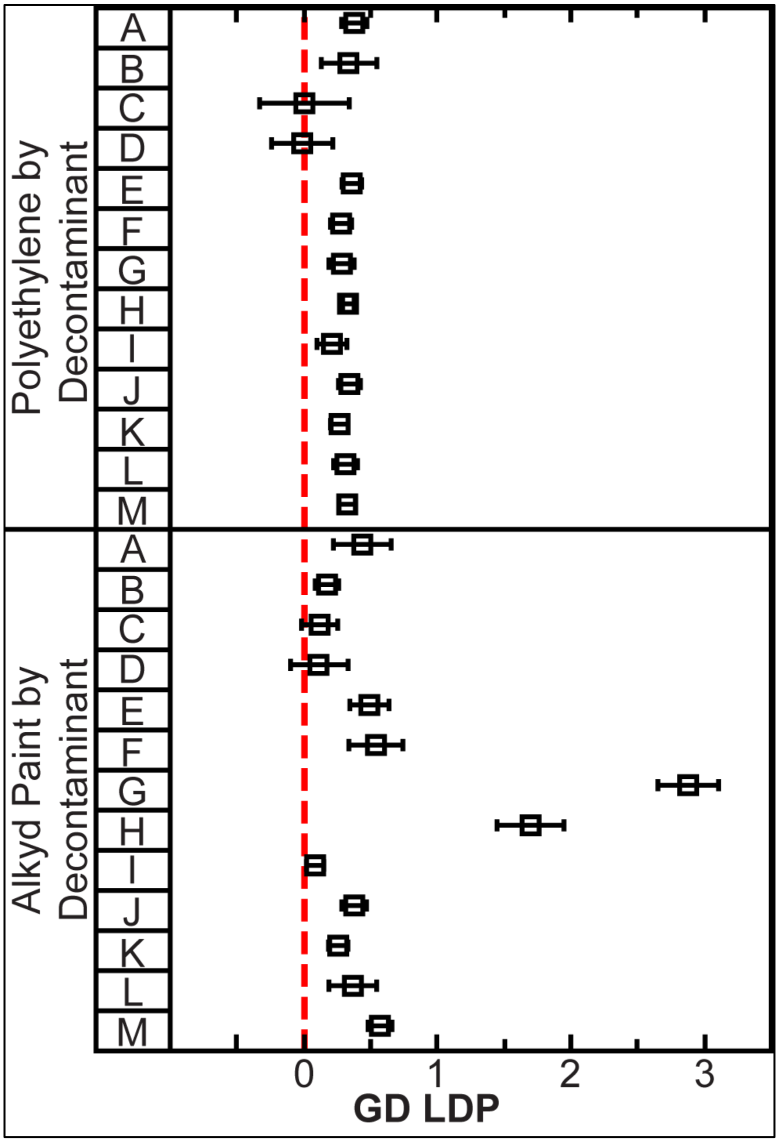

Figure 5. LDP with 95% CI for GD on polyethylene and alkyd paint.

4.3 VX

Figure 6 provides a summary of the LDP results for VX on alkyd paint and SBR at 20 °C. The dilute liquid-phase reactor results for VX demonstrated that decontamination was most effective with oxidative chemistries containing buffers that maintained the pH at <6 or >10; the most-reactive decontaminants were B, C, E, F, and I. The best-performing decontaminant on both materials was H (2-propanol), which was a solvent with no chemical reactivity. The panel test results reiterated that agent removal from materials can be achieved with pure solvent chemistries. Aqueous-based decontaminants yielded poor performance with VX on the hydrophobic materials SBR and alkyd paint.

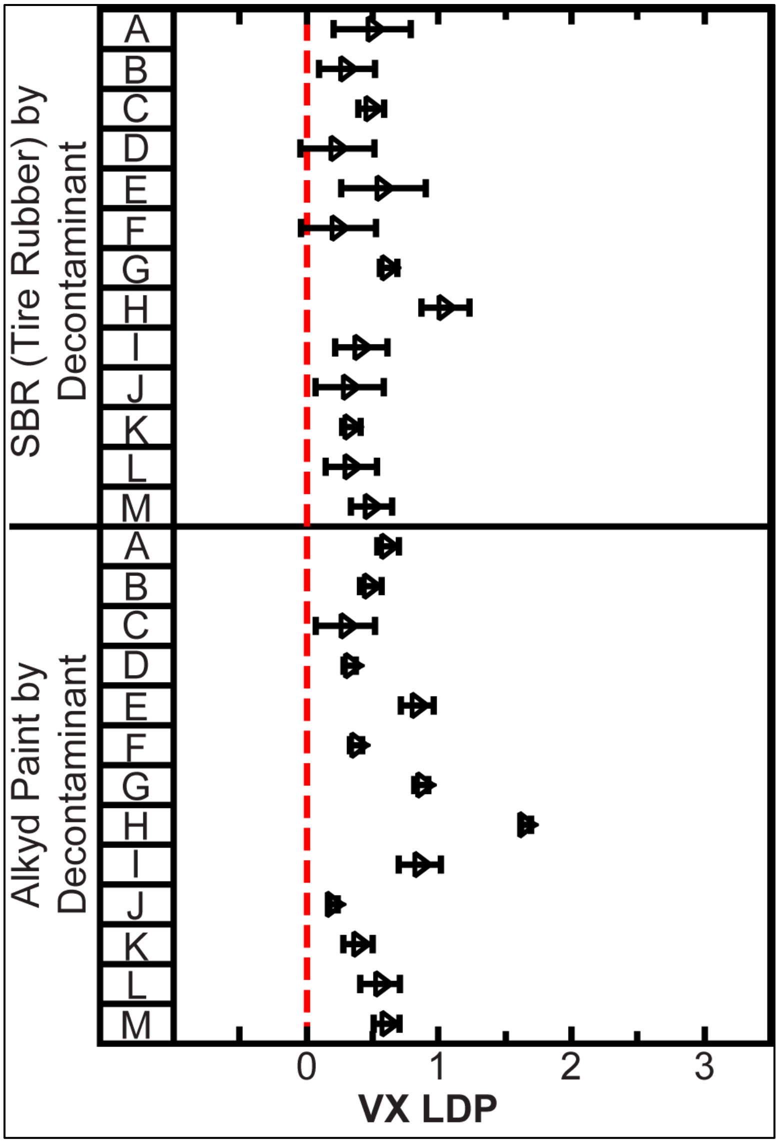

Figure 6. LDP with 95% CI for VX on SBR and alkyd paint.

4.4 Decontaminant Performance Evaluation

Identification and formulation of an optimal decontaminant requires leveraging dilute liquid-phase reactor results with material-specific panel test results. 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. The dilute liquid-phase reactor results suggest that a highly reactive decontaminant for each evaluated agent could be achieved with an alkaline oxidative chemistry, such as decontaminants C, E, or F.

Figure 7 illustrates the combined reactivity and material performance (LDR and LDP) results for HD. The decontamination categories for both LDR and LDP were defined as having a value of 1.0 LD, which was an acceptable level for screening decontaminants. However, higher LD values may be required to define decontamination categories that will provide sufficient hazard mitigation in the final decontaminant formulations.

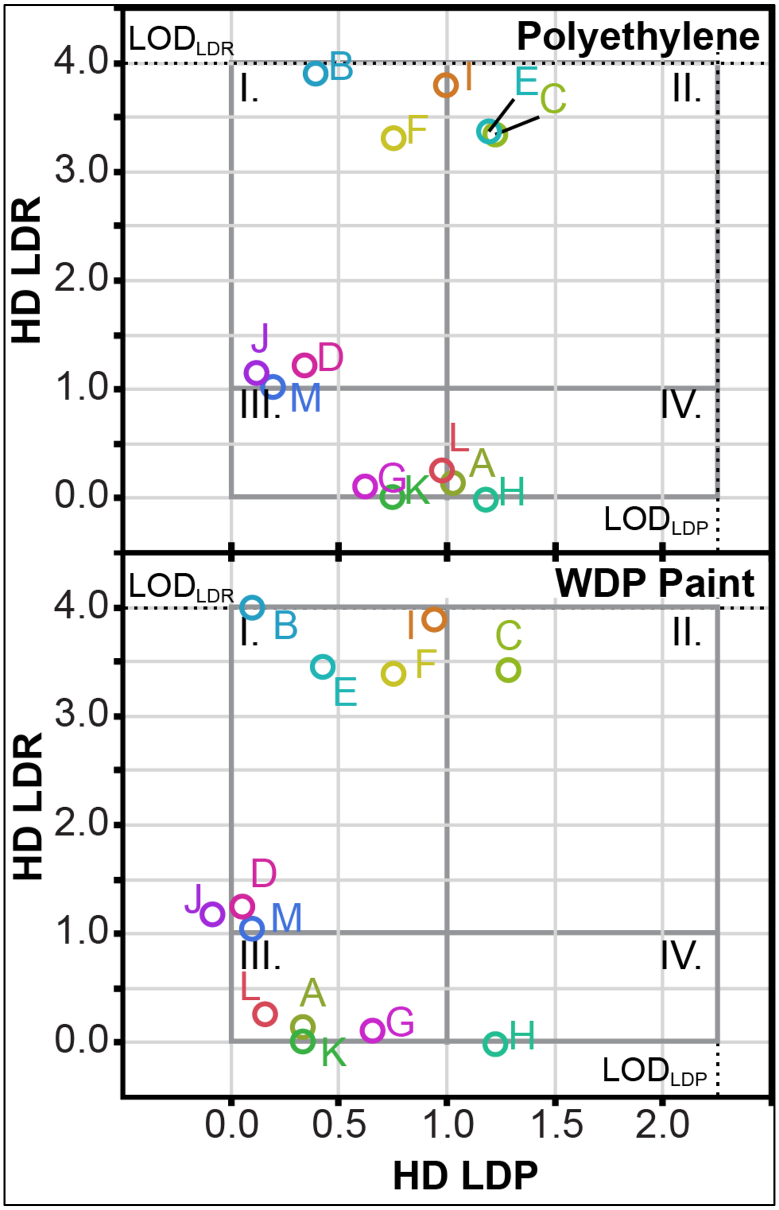

Figure 7. Reactivity and material performance analysis for HD on polyethylene and WDP paint.

The reactivity and material performance results for HD on polyethylene represent a range of decontaminant performance categories. Decontaminants B, D, F, J, and M were primarily reactive chemistries, and decontaminants A and H were primarily extraction chemistries. Several decontaminants, including C, E, and I, were within the ideal category, with a high level of detoxification and removal of HD from the polyethylene material by >1 LDP. By comparison, for HD on WDP paint, most of the decontaminants were within the reactive category. The results demonstrated that for HD on polyethylene and WDP paint, the best performance was achieved with decontaminant C, which was an aqueous-based alkaline oxidative chemistry.

Figure 8 illustrates the reactivity and material performance analysis for GD. The panel test results demonstrated comparable performances for all decontaminants on polyethylene. However, the integration of the dilute liquid-phase reactor results identified two performance categories. No decontaminants were in the ideal or extraction category, but decontaminants A, E, F, J, G, and M yielded elevated reactivity with approximately 50% removal of GD from the material. Furthermore, the liquid decontaminant effluent from Category I decontaminants (including E, J, G, and M) were detoxified as compared with the Category III decontaminants, which still contained >60% of the GD. The LDP results on alkyd paint demonstrated two high-performance decontaminants, G and H. The reactivity and material performance analysis demonstrated that the best-performing decontaminant for hazard mitigation of GD on alkyd paint was decontaminant G, which yielded approximately 99.9% removal of GD from the material and detoxified GD in the decontaminant effluent to the analytical LOD. Although decontaminant H removed >97.5% of the GD from the material, the decontaminant effluent retained 100% of the highly toxic agent.

Figure 9 illustrates the reactivity and material performance analysis for VX. The panel test results for VX on SBR demonstrated that decontaminant H yielded the greatest removal of VX from the material, with the aqueous decontaminants yielding <75% removal of VX. However, the analysis demonstrated that decontaminants C and E yielded the highest level of hazard mitigation of VX from SBR and detoxified VX in the decontaminant effluent. The best decontaminants for VX on alkyd paint were decontaminants E and I, which yielded 99.9% reduction of VX in the liquid-phase reactor and approximately 85% removal of VX from the alkyd paint coating. The results suggested that improved decontaminant performance could be achieved by integrating an organic solvent chemistry (e.g., H) with a reactive chemistry (e.g., E and I). Furthermore, comparison of the decontaminant performances across the agent–material pairs suggests that agent- and material-specific decontaminants may be required to achieve optimal agent removal and effluent detoxification.

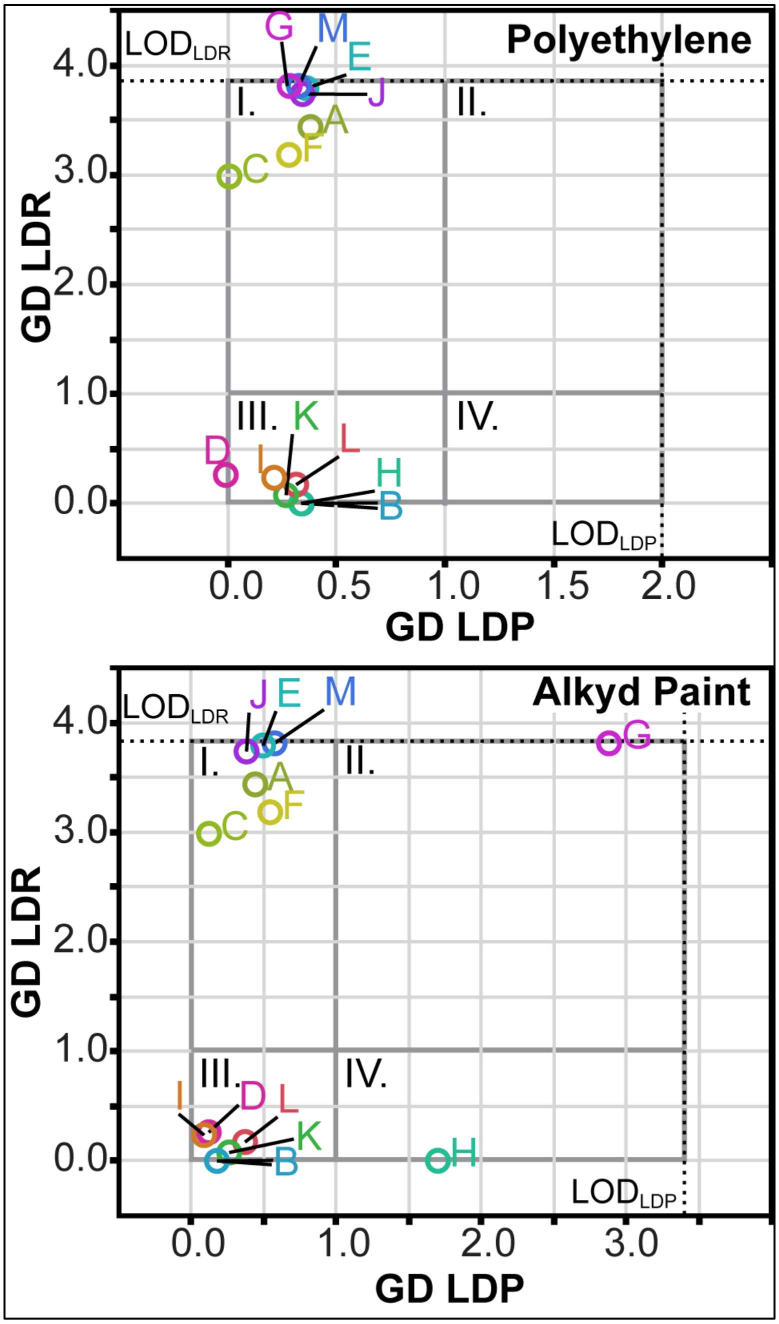

Figure 8. Reactivity and material performance analysis for GD on polyethylene and alkyd paint.

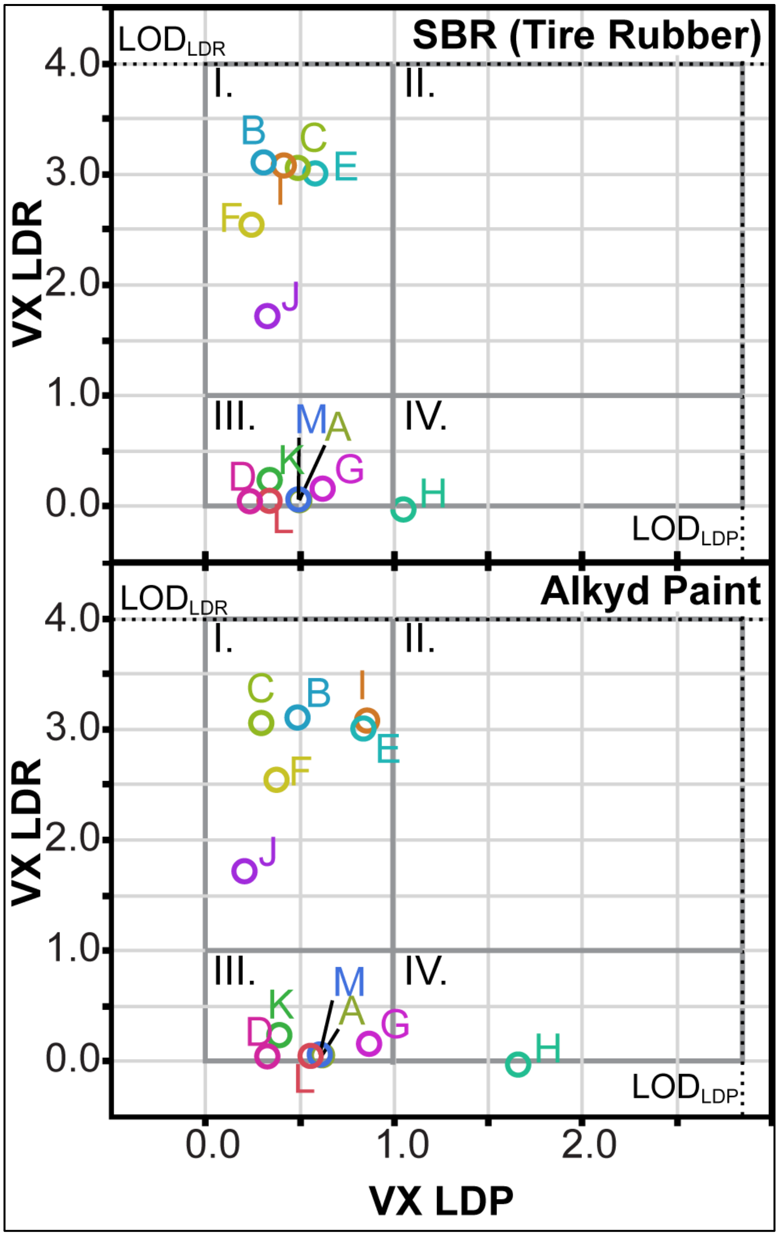

Figure 9. Reactivity and material performance analysis for VX on SBR and alkyd paint.

5. CONCLUSIONS

Reactive chemistries may detoxify agent in solution, but the ability to remove agent from a material is mediated by decontaminant–material mass transport mechanisms. Hazard mitigation to enable reuse of contaminated materials requires the removal of agent from the material. Therefore, the ability of a decontaminant to access the agent retained by a material can be as important as its chemical reactivity with the agent. A combined approach was developed that integrated two types of testing—dilute liquid-phase reactor results to determine chemical reactivity with panel testing to determine decontaminant performance on materials. This combined approach enabled a better understanding of the modes of action that contribute to decontaminant performance with materials.

Several decontaminant chemistries were evaluated for multiple agent–material combinations. The decontaminants illustrated each of the performance categories. However, any given decontaminant may exhibit a different category of performance on different agent–material combinations. For example, decontaminant G (a floor-stripper concentrate product) showed poor performance with HD and VX (Category III), was very reactive with GD, and removed GD from alkyd paint (Category II), but did not remove GD from polyethylene (Category I). The variable performance for a single decontaminant illustrates the unique interactions that can occur with each agent–material–decontaminant combination and the challenges encountered when identifying a universal decontaminant that works for all situations.

Several decontaminants, such as decontaminants C (bleach) and E (DF200), demonstrated significant chemical reactivity with HD, GD, and VX; however, very few decontaminants demonstrated consistent material performance (i.e., LDP) across all agent–material combinations. One of the most-consistent, high-performance material decontaminants was H (2-propanol), which did not demonstrate reactivity with agent but did provide agent extraction from the material. When considering a decontaminant for hazard mitigation, the results demonstrated the need to balance both agent–decontaminant chemical reactivity and the ability of the decontaminant to access the agent in the material. Future formulations need to integrate multiple modes of action to remove agent from materials and provide detoxification. The combined approach of dilute liquid-phase reactor data with panel test data provides the characterization of the potential modes of action for decontaminants and enables the identification of ideal chemistries for integration into decontamination technologies.

LITERATURE CITED

1. *Potential Military Chemical/Biological Agents and Compounds*; Field Manual 3-11.9; U.S. Department of Defense: Washington, DC, 10 January 2005.

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

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

4. 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. *Environ. Health Perspect.* **1999,** *107* (12), 933–974.

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

6. Willis, M.P.; Mantooth, B.A.; Lalain, T. Novel Methodology for the Estimation of Chemical Warfare Agent Mass Transport Dynamics, Part I: Evaporation. *J. Phys. Chem. C* **2011,** *116* (1), 538–545.

7. Willis, M.P.; Mantooth, B.A.; Lalain, T. Novel Methodology for the Estimation of Chemical Warfare Agent Mass Transport Dynamics, Part II: Absorption. *J. Phys. Chem. C* **2011,** *116* (1), 546–554.

8. D’Onofrio, T.G.; Navaz, H.K.; Markicevic, B.; Mantooth, B.A.; Sumpter, K.B. Experimental and Numerical Study of Spread and Sorption of VX Sessile Droplets into Medium Grain-Size Sand. *Langmuir* **2009,** *26* (5), 3317–3322.

9. Markicevic, B.; Li, H.; Sikorski, Y.; Zand, A.; Sanders, M.; Navaz, H. Infiltration Time and Imprint Shape of a Sessile Droplet Imbibing Porous Medium *J. Colloid Interface Sci.* **2009,** *336* (2), 698–706.

10. Markicevic, B.; Navaz, H.K. The Influence of Capillary Flow on the Fate of Evaporating Wetted Imprint of the Sessile Droplet in Porous Medium. *Phys. of Fluids* **2010,** *22* (12).

11. Markicevic, B.; Navaz, H.K. Primary and Secondary Infiltration of Wetting Liquid Sessile Droplet into Porous Medium. *Transp. Porous Media* **2010,** *85* (3), 953–974.

12. Love, A.H.; Bailey, C.G.; Hanna, M.L.; Hok, S.; Vu, A.K.; Reutter, D.J.; Raber, E. Efficacy of Liquid and Foam Decontamination Technologies for Chemical Warfare Agents on Indoor Surfaces. *J. Hazard. Mater.* **2011,** *196*, 115–122.

13. Willis, M.P.; Procell, L.; Mantooth, B.A.; Davies, J.; Lalain, T. Liquid Phase Reactivity of Decontaminants to Provide Hazard Mitigation of Chemical Warfare Agents. *J. Hazard. Mater.* Submitted for publication, 2013.

14. Hansen, C.M. *Hansen Solubility Parameters: A User's Handbook.* 2nd ed.; CRC Press: Boca Raton, FL, 2007; p 519.

15. Schwope, A.D.; Goydan, R.; Little, A.D.; Reid, R.C. *Methodology for Estimating the Migration of Additives and Impurities from Polymeric Materials*; EPA 560/5-85-015; U.S. Environmental Protection Agency, Office of Pesticides and Toxic Substances: Washington, DC, 1990.

16. Schwope, A.D.; Klein, J.M.; Sidman, K.R.; Reid, R.C. Sorption-Desorption Phenomena of Chemicals from Polymer (Paint) Films. *J. Hazard. Mater.* **1986,** *13*, 353–367.

17. Frisch, H.L.; Stern, S.A. Diffusion of Small Molecules in Polymers. *CRC Critical Reviews in Solid State and Materials Sciences* **1983,** *11* (2), 123–187.

18. Dubey, V.; Gupta, A.K.; Maiti, S.N. Mechanism of the Diffusion of Sulfur Mustard, a Chemical Warfare Agent, in Butyl and Nitrile Rubbers. *J. Polym. Sci. B Polym. Phys.* **2002,** *40* (17), 1821–1827.

19. Dubey, V.; Gupta, A.K.; Maiti, S.N.; Rao, N. Diffusion and Sorption of Sulfur Mustard and bis(2-chloroethyl)ether in Elastomers: A Comparative Study. *J. Appl. Polym. Sci.* **2000,** *77* (11), 2472–2479.

20. Dubey, V.; Parmar, T.; Saxena, A.; Agarwal, D.D. Thiocompounds as Simulants of Sulphur Mustard for Testing of Protective Barriers. *J. Appl. Polym. Sci.* **2009,** *111* (2), 928–933.

21. Harogoppad, S.B.; Aithal, U.S.; Aminabhavi, T.M. Diffusion of Organic-Solvents into Polyurethane Network from Swelling Measurements. *J. Appl. Polym. Sci.* **1991,** *42* (12), 3267–3270.

22. Harogoppad, S.B.; Aminabhavi, T.M. Diffusion and Sorption of Organic Liquids through Polymer Membranes .5. Neoprene, Styrene Butadiene Rubber, Ethylene Propylene Diene Terpolymer, and Natural-Rubber Versus Hydrocarbons (C8-C16). *Macromolecules* **1991**, *24* (9), 2598–2605.

23. Harogoppad, S.B.; Aminabhavi, T.M. Diffusion and Sorption of Organic Liquids through Polymer Membranes .2. Neoprene, SBR, EPDM, NBR, and Natural-Rubber Versus Normal-Alkanes. *J. Appl. Polym. Sci.* **1991**, *42* (8), 2329–2336.

24. Harogoppad, S.B.; Aminabhavi, T.M. Diffusion and Sorption of Organic Liquids through Polymer Membranes .8. Elastomers Versus Monocyclic Aromatic Liquids. *J. Appl. Polym. Sci.* **1992,** *46* (4), 725–732.

25. 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 (ADA566601).

26. 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 (ADA546021).

Blank

ACRONYMS AND ABBREVIATIONS

CI	confidence interval
DI	deionized
GC	gas chromatography
GD	pinacolyl methyl phosphonofluoridate
HD	bis-(2-chloroethyl) sulfide
LC	liquid chromatography
LD	log difference
LDP	log difference panel
LDR	log difference reactor
LOD	limit of detection
RA	remaining agent
Rxn	reaction
SBR	styrene butadiene rubber
VX	*O*-ethyl *S*-(2-diisopropylaminoethyl) methyl phosphonothioate
WDP	water-dispersible polyurethane

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)
Decontamination Sciences Branch
RDCB-DRP-D
ATTN: Mantooth, B.
Willis, M.
Procell, L.
Davies, J.
Shue, M.

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

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