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**Chemical Wide-Area Decontamination I:
Bulk Chemicals as Reactive
Decontaminants**

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PREFACE

The work described in this report was authorized under Defense Threat Reduction Agency Joint Science and Technology Office (DTRA JSTO; Fort Belvoir, VA) project number CB10662. The work was started in January 2019 and completed in February 2020.

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EXECUTIVE SUMMARY

This work was performed under Defense Threat Reduction Agency Joint Science and Technology Office (DTRA JSTO; Fort Belvoir, VA) project number CB10662. The work was focused on decontamination of prototypical exterior materials found at airports and seaports after a chemical warfare agent (CWA) attack. The preferable decontaminant technology should be inexpensive, easily prepared on a large scale, and effective on bis(2-chloroethyl) sulfide (HD) and 2-(diisopropylamino)ethyl]-O-ethyl methylphosphonothioate (VX). For this reason, simple one- or two-component formulations were considered for the use of the decontaminants. A variety of chemicals, including bases, organic peroxides, hypochlorites, and inorganic peroxides, were screened for efficacy against HD and VX on concrete and asphalt.

HD and VX could be removed from concrete using sodium diisochlorocyanurate (a swimming pool cleaner), persulfate (soil conditioner), and potassium hydroxide (a common base). Other bulk chemicals such as sodium percarbonate, Oxone, and high test hypochlorite (HTH) offered some reduction in retained CWA mass. The use of aircraft deicer as a cosolvent did not increase decontaminant performance on concrete. A cost-benefit analysis shows that there are many options for the decontamination of HD and VX on concrete using a simple, inexpensive one-component formulation.

The decontamination of asphalt was much more difficult. Oxone showed a moderate performance and reduced the contamination of HD and VX by 90%. Other decontaminants, such as Dahlgren Decon (First Line Technology, Fredericksburg, VA), persulfates, HTH, and Dichlor yielded only slight reductions in contamination. This is likely because the agent permeated into the coal tar (bitumen) contained within the asphalt, which is hydrophobic and resists decontamination. Increasing decontaminant application temperature, adding surfactants, using cosolvents, and adjusting the pH of the decontaminant led to only slight improvements in decontaminant performance. This result demonstrates that additional methods, such as the use of barrier polymers, must be considered for effective hazard mitigation of asphalt surfaces.

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CHEMICAL WIDE-AREA DECONTAMINATION I: BULK CHEMICALS AS REACTIVE DECONTAMINANTS

1. APPROACHES FOR CHEMICAL WIDE-AREA DECONTAMINATION

1.1 Background

An effective chemical wide-area decontaminant (CWAD) should enable a rapid response and recovery after a chemical warfare agent (CWA) attack at an aerial port or seaport of debarkation (APOD/SPOD). The CWAD technology should enable forces to sustain operations within a contaminated environment by restoration of essential capabilities with minimal operational interruptions. This means that following an attack, a warfighter can remove respiratory and ocular protection as quickly as possible, and vehicles can safely traverse through the contaminated area. The end goal is to support the development of a hazard mitigation approach that is affordable at a large scale, compatible with current decontaminant applicators, and effective on concrete and asphalt. Current decontaminant chemistries used for personnel and vehicle decontamination are not scalable to large-scale terrain decontamination scenarios because of prohibitively high cost, corrosivity, and poor efficacy at low concentrations. Moreover, previous studies on the environmental fate of chemical agents have shown that weathering by itself is insufficient to reduce post-attack vapor and contamination hazards within a reasonable timeframe.¹ Thus, there is a sizeable need for a CWAD technology that enables rapid response and recovery from a chemical weapons attack.

The chemical wide-area decontamination program varies from a traditional decontamination development program, which typically involves a specialized formulation designed with significant effort by a materiel developer. Development of a specialized formulation for large-scale use is impractical. Instead, this program is focused on evaluating existing bulk chemicals for use in a CWAD process. This work focuses on providing a one- or two-component aqueous mixture that can be prepared using widely available chemicals and a local water source. This approach side-steps the need for an expensive and tedious formulation effort. The primary outputs of this effort are twofold:

- identifying bulk chemicals that can be used for wide-area decontamination and
- providing guidance on preparation, application, and storage of the decontaminant.

Two approaches to wide-area decontamination are under consideration. The use of barrier lockdown technologies is one potential strategy for CWAD development. Many commercial products used in soil stabilization, environmental site remediation, and roadway protection form a polymeric membrane over a surface. These technologies may be used to provide a physical barrier on a contaminated surface, thereby locking in any vapor and reducing contact hazard posed by a chemical agent. These barrier decontaminants may provide a rapid short-term response and allow for a reduction in mission-oriented protective posture (MOPP) to

sustain operations. This novel decontamination approach has not been explored prior to this program.

Another strategy is the use of traditional reactive decontaminant formulations, which can directly remove the contaminant through chemical reaction. Leveraging a previous study (performed under Defense Threat Reduction Agency [Fort Belvoir, VA] project number CB3927), direct reduction in the amount of remaining agent correlates with a decrease in vapor and contact hazard across most materials. Directly eliminating the contaminant may prove more effective than barrier technologies as an initial response to a chemical weapon attack. Moreover, these technologies may be used after the initial response for eventual clearance-level recovery efforts.

The CWAD program aims to explore the use of barrier technologies and reactive decontaminants as part of a response and recovery effort, which initially focused on the short-term ability to reduce vapor and contact hazards. The overall contamination mitigation strategy may involve the use of barrier and reactive chemistries in coordination.

1.2 Literature Background

There is a substantial body of literature on the weathering of concrete, soil, and asphalt matrices although literature on the decontamination of these materials is sparse. However, there are some select examples of the use of oxidants as decontaminants. Review of these examples enables an informed selection of materials and decontaminants as well as logical development of test procedures to give reproducible and meaningful results.

The first laboratory study on the decontamination of mustard from soils, sands, asphalts, and concretes was performed in 1944 using bleaching powders.² Since then, work has been published on the reactions and interactions of these materials with chemical agents.

A great number of studies were performed as part of the Agent Fate program, which focused on the experimental measurements and computation modeling of the weathering of chemical agents on soil, asphalt, and concrete. The program was an international effort that included the United States, the Czech Republic, and Poland. The solid-state nuclear magnetic resonance (NMR) part of the program was completed at the U.S. Army Edgewood Chemical Biological Center (now known as the U.S. Army Combat Capabilities Development Command Chemical Biological Center; Aberdeen Proving Ground, MD), highlighting the reaction pathways of CWAs within concrete.³⁻⁷ Using carbon 13 (¹³C) or (phosphorus-31) ³¹P NMR, the degradation rates of bis(2-chloroethyl) sulfide (HD; CAS: 505-60-2) and 2-(diisopropylamino)ethyl]-O-ethyl methylphosphonothioate (VX; CAS: 50782-69-9) were measured. Degradation occurred over weeks to months, depending on the substrate, agent, and moisture content. Subsequent wind tunnel studies determined the evaporation rate of several CWAs on glass, soil, and concrete.^{1,8-11} Typically, weathering of non-persistent agents was slow, occurring over months to years. Thermogravimetric analysis (TGA) was also used in real time to measure vapor off-gassing.¹²

Other work has been performed by organizations within the United States and foreign countries on weathering and decontamination of concrete, soil, and asphalt. U.S. Environmental Protection Agency (Washington, DC) members have investigated the decontamination of building materials.¹³ Whereas much of this study focused on biological warfare agents, some work was performed on the decontamination of VX and mustard lewisite using bleach, hydrogen peroxide, and DF200. In addition, extensive work has been performed by the Agency for Defense Development (Yuseong District, Daejeon) in the Republic of Korea.¹⁴⁻¹⁸ These studies highlight the intrinsic reactivity and vapor emission rate of CWAs on soil, sand, and concrete and focus on unique characteristics such as water to cement (w/c) ratio and influences on evaporation and degradation rates. Work at the Israel Institute for Biological Research (Ness-Ziona, Israel) has investigated the degradation and evaporation of CWAs in asphalt, bitumen, bricks, tiles, and concrete.¹⁹⁻²¹ CWAs have typically been shown to persist longest in asphalt matrices, making them high priority decontamination targets. Finally, work conducted at the Institute of Chemical Defense (Beijing, China) has extensively studied sorption and diffusion in cement.²²⁻²⁴

The majority of these studies focused on environmental degradation or weathering, and only limited examples of decontamination processes were researched. However, these studies provide the groundwork for guiding substrate selection, developing extraction methodology, and developing analysis techniques.

1.3 Developmental Approach

The experimental approach to developing an effective and fieldable wide-area decontaminant has been divided into four distinct stages (Figure 1). Each stage aims to advance the technology readiness level (TRL) as the program progresses. The level of analytical rigor is tailored to the needs of each development phase. The initial experiments will use rapid, semi-quantitative assessments to screen many different decontaminant chemistries (Stage 1). After a preliminary downselection, promising chemistries will be evaluated to determine if the decontaminant is safe, scalable, and logistically feasible (Stage 2). At this stage, 1–3 chemistries will be selected for optimization. Optimization will focus on turning the chemistry into a fieldable approach, determining the concentration of the decontaminant, prepare protocols, and the volume of the decontaminant application (Stage 3). These “stable configurations” will then be evaluated and compared with each other and current methods. The evaluation stage will focus on meeting key performance parameters (KPPs) for efficacy, material compatibility, and cost (Stage 4).

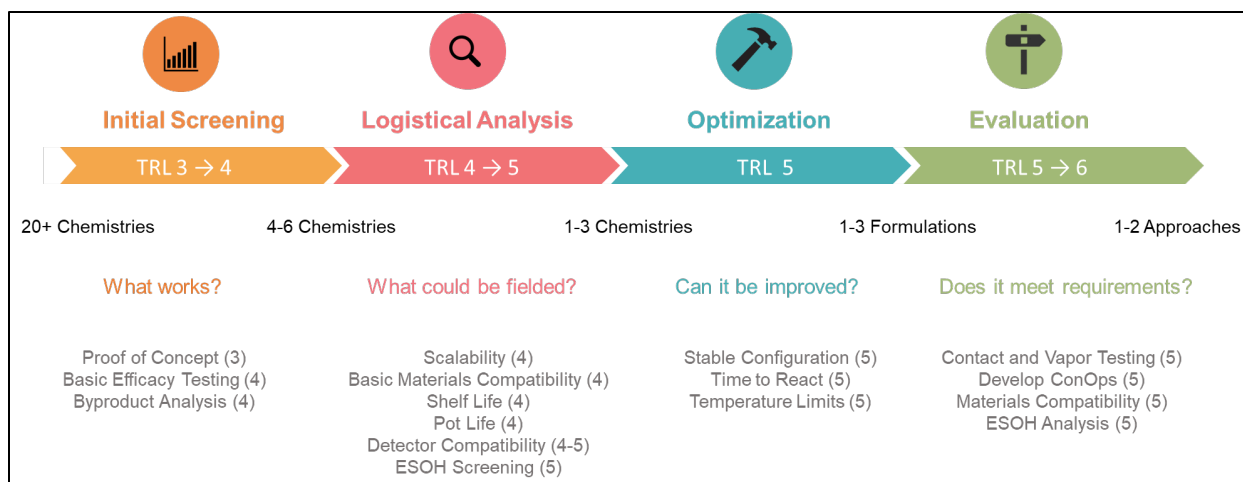


Figure 1. Approach for CWAD development.

For the entire development effort, two decontaminant approaches were considered (Figure 2). Reactive decontaminants, such as traditional oxidants, reduce vapor and contact hazards by directly reducing surface contamination. Barrier decontaminants are polymers that form a physical barrier between the contaminated surface and personnel. The focus of this report is on reactive decontaminants, which are cheaper and often simpler to prepare and apply. Information on screening, downselection, and efficacy of barrier polymers will be provided in subsequent reports.

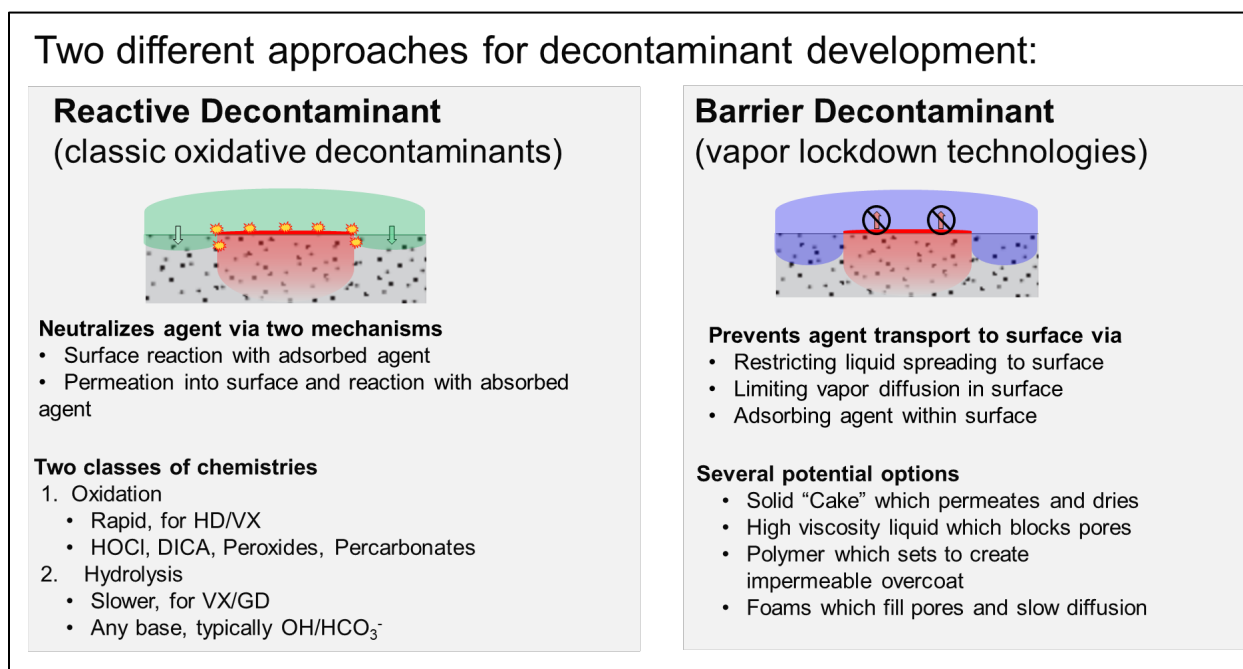


Figure 2. Reactive and barrier hazard mitigation approaches.

Stage 1 of this program is partially discussed in this report. This effort focused on identifying key reactive chemistries and screening them for efficacy. Over twenty initial decontaminant candidates were selected based on cost, availability, potential efficacy, and solubility (Section 3.2). These decontaminant candidates were screened for efficacy using a semi-quantitative method that focused on highlighting differences in decontaminant performance. The results from the screening provided a list of promising chemistries, which were downselected for further investigation. A similar screening will be performed for barrier polymer chemistries and will be outlined in a separate report.

For reactive decontaminants, five different viable chemistries were selected in the first stage. During the second stage, logistical analysis will determine which of these chemistries could be feasibly fielded as a decontaminant. The second phase focuses on the following key logistical questions:

- can the decontaminant be prepared safely on a large scale;
- does the chemistry degrade decontaminant applicators, protective equipment, and the concrete or asphalt substrates;
- what is the shelf and pot life of the decontaminant;
- does the chemistry used interfere with CWA detection methods; and
- will runoff from the decontamination pose a large risk to the environment?

These criteria will be used to downselect the initial list to 1–3 chemistries, which could be feasibly used as a decontaminant. The secondary goal of these studies is to provide evidence that this technology has been evaluated at the TRL4 level or higher. This downselected list of chemistries will then be used in the optimization phase (stage 3).

Stage 3 aims to take a feasible decontaminant chemistry and translate it into a decontaminant process. The goal is to provide a fundamental understanding of the controls of the decontaminant process. This understanding can be used to provide a stable formulation and decontamination procedure to be carried through for further testing. Process understanding will focus on addressing the following key questions:

- what concentration should the decontaminant be prepared at;
- how should the decontaminant be prepared;
- how long does the decontaminant take to react;
- how much decontaminant should be applied;
- at what temperatures is the decontaminant effective; and
- can the decontaminant be prepared using multiple water types?

A series of kinetic and optimization studies can provide the answers to these questions. This information can be used to develop tactics, techniques, and procedures (TTPs) for decontaminant application. Eventually, one or more decontaminant processes will be adopted and their relative strengths and weaknesses investigated.

The final phase (stage 4) focuses on evaluation of the optimized decontaminant processes. These include vapor and contact hazard analyses to determine if the efficacy of the decontaminant meets the KPPs outlined by the Technology Readiness Office (U.S. Government Accountability Office; Washington, DC) or other interested stakeholders. This also includes requirements for environmental health and safety, materials compatibility, and cost. At this stage, transition of the technology will be facilitated by coordination with the test and evaluation (T&E) community to enable demonstrations and larger scale testing.

This roadmap has been developed and refined to meet the unique requirements of a wide-area decontaminant while aligning to the TRL benchmarks used in a traditional decontaminant development. The aim is to provide an effective and viable CWAD approach to be transitioned.

2. MATERIAL SELECTION AND RATIONALE

2.1 General Considerations

Concrete and asphalt were chosen as the substrates for study, as they are the principal construction materials found at APOD and SPOD sites.³⁷ Soil and sand were also considered during the early phases of the program. However, literature suggests that asphalt and concrete typically provide a larger off-gassing hazard and are more difficult to decontaminate than soil and sand.¹ Concrete and asphalt are highly variable materials, and their compositions depend on local construction guidelines and the availability of local materials.

Concrete and asphalt decontamination is further complicated by laboratory constraints of size, cost, and reproducibility. Test coupons are needed to be thin enough to fit testing apparatuses and be extracted easily. Materials are also needed to be prepared for a reasonable cost with a turnaround time of one month or less. Most importantly, the ability to generate reproducible data is key to being able to determine differences in performance between different decontaminants. Despite this, materials are needed to be representative of the fielded materials, which they are meant to replicate. Some variances are important to capture decontaminant evaluation, whereas others are not. In general, materials are selected to give a reproducible means of measuring the worst case scenario. The following decisions reflect these trade-offs:

- No use of large aggregates: droplets falling on a large aggregate do not permeate through the material and thus, are more easily decontaminated. The use of a large aggregate requires the use of thick coupons, which limits extraction efficiency and sample throughput.
- Coupons must be thinner than 0.25 in.: unless the contaminant breaks through the bottom of the coupon, coupon thickness likely has little impact on decontaminant performance. Thinner coupons can be used with current test methods and are more easily extracted.

- Coupons must be prepared in less than one month: this turnaround time is necessary to avoid delays in testing.

These guiding principles were used in the selection of concrete and asphalt coupons.

2.2 Concrete

Concrete is a common construction material used at APOD and SPOD sites. It consists of several aggregates bonded together with a binder, which cures to form a hard, durable surface. Many factors influence the strength and porosity of concrete, including binder and aggregate type, concrete age, and the w/c ratio. In modern applications, portland cement is a common, inexpensive binder made from kiln dried limestone, clay minerals, and gypsum. Another typical binder is calcium sulfoaluminate (CSA), which is a more expensive, but rapid curing alternative to portland cement. In addition to the binder, w/c ratio, and aggregate type play a significant role in determining cost, strength, and porosity of the concrete. Typical w/c ratios range from 0.5 for building construction to 0.3 for runways. Aggregates are largely chosen based on the availability of local stones and gravels. Factor variability makes the selection of a testing substrate difficult.

A large body of work has focused on the weathering of CWAs within various concretes. For persistent agents such as HD and VX, weathering by evaporation and reaction occurs over the course of months to years. Concrete can be reactive with CWAs through reaction with basic calcium hydroxide in the cement binder.³ Reactivity decreases as concrete ages due to calcium carbonate formation through reaction with atmospheric carbon dioxide.

The way the CWA permeates through the material also influences contact hazard and off-gassing rates. CWA, entrained within a material, evaporates more slowly than material that remains on the surface. Highly porous materials that experience rapid diffusion quickly soak up chemical agent, leading to decreased vapor off-gassing and contact hazard. Aggregate size and w/c ratio influence how the agent spreads, permeates, and evaporates from a material. Concretes, containing finer aggregate, experience slower CWA diffusion,^{22,23} which leads to slower permeation and greater contact and vapor hazard. Similarly, concretes with higher w/c ratios (such as those found on runways) tend to show slower spreading and readier evaporation of CWAs.

These factors were considered alongside practical considerations when a concrete was selected for the laboratory studies. Two main requirements were considered. First, the substrate must be <0.2 in. thick to fit current testing equipment and yield increased agent recovery from thinner substrates. Previous studies have shown that thick concrete coupons provide a difficult extraction challenge, and crushing the concrete is required to obtain reasonable extraction efficiencies.^{3,25} Second, the coupons must be prepared in bulk within a reasonable turnaround time.

Scoping studies initially considered the use of hardened cement paste (HCP) coupons. Previous reports have shown that thin HCP coupons can be used as an alternative to

thick concrete coupons in testing agent diffusion and vapor emission.²³ Initial efforts at creating thin coupons using HCP failed and resulted in brittle coupons with extremely long hydration times. These coupons could not be handled safely and took far too long to produce.

However, using a quickset CSA cement, coupons could be produced rapidly with a one-week turnaround time. These coupons (Figure 3) developed strength rapidly and could be produced in a thickness of approximately 1/8 in. Moreover, preliminary studies using methyl salicylate showed no breakthrough of the material within 48 h using a 20 μ L drop. Similarly, no breakthrough was seen after 4 h with HD and VX. In addition, fresh CSA concrete coupons have a pH typical of aged portland cement, making accelerated aging unnecessary. Whereas typical airfield construction uses the slower curing portland cement, some airfield applications use CSA cement depending on the region and building requirements.* Therefore, 1/8 in. thick CSA coupons were used throughout this study.



Figure 3. Thick concrete coupon (left) and 1/8 in. thick CSA quickset coupon (right).

2.3 Asphalt

Asphalt is a primary component in roadways, parking lots, and taxiways found at APOD and SPOD sites. Similarly to concrete, asphalt consists of an aggregate held together by binder. Asphalt uses coal tar (bitumen) as a binder, which is applied hot and then cooled to form a solid surface.

The interactions between CWAs and asphalt have been the subject of a few, limited studies. Asphalt is a highly variable material; therefore, agent retention and vapor emission depend on many factors. Asphalt with higher bitumen content tends to retain more chemical agent, as most agents can be solubilized by the bitumen. Bitumen is highly oleophilic and readily absorbs nonpolar CWAs such as HD. As with concrete, inclusion of larger aggregates leads to more channeling around aggregates and thus, increases agent permeability

* Personal communication between Neil A. Hawbaker (U.S. Army Combat Capabilities Development Command Chemical Biological Center; Aberdeen Proving Ground, MD) and Dr. Craig Rutland, Pavement SME (U.S. Air Force Civil Engineer Center; Tyndall FL.) on 19 February 2019.

and vapor emission. Asphalt ages by photo-oxidation and forms an oxide “skin”, which likely decreases agent permeability.²⁶ This skin is washed away by rain, so it is most often found on asphalt used in hot, dry environments. Asphalt restoration is also quite common, and polymer composite micro-overlays used in the restoration process greatly decrease permeability to chemicals.

Because asphalt is difficult to produce in a laboratory, most studies utilize asphalt samples taken from the real world. However, each coupon may have been exposed to different levels of rain, sunlight, and oil, and large aggregate sizes may pose coupon-to-coupon variability. Moreover, extraction of agent from thick asphalt coupons is difficult and often requires multiple extractions by different solvents.²⁷ Therefore, coated bitumen sheets (Figure 4) were used in lieu of asphalt in this study. Bitumen sheets, typically used in roofing and waterproofing, have been used as a reproducible surrogate for asphalt.²² The sorption of agent into bitumen is likely the limiting aspect of decontamination and is captured effectively using bitumen roofing sheets. Other factors, such as sun-aging and uses of large aggregate and protective overlays, which are not captured by using bitumen sheets, tend to limit agent sorption. Thus, results obtained by using bitumen sheets are likely the worst case scenarios for decontamination. Decontaminants that are effective on bitumen sheets are likely to be effective in the real world on asphalt samples. Bitumen sheets are also a more homogenous substrate and likely, will provide more reproducible results. By minimizing sample-to-sample variability, the performance difference between decontaminants will be more apparent. This will allow a downselection of decontaminants, and performance on real world materials can be verified using large aggregate-containing asphalt in subsequent studies.



Figure 4. Thick asphalt sample from local roadway (left) and asphalt shingle coupon (right).

3. DECONTAMINANT SELECTION AND SOLUBILITY STUDIES

3.1 Decontaminant Classes

Initially, many decontaminant chemistries were considered for CWAD applications. A large collection of literature on the decontamination of CWAs exists and can be used to inform CWAD development, which originally focused on the decontamination of HD and VX; both are persistent agents that are readily retained within materials. Both agents display uniquely different chemistries and provide unique formulation challenges.

Decontamination of HD is typically accomplished using oxidative chemistry and is largely hindered by mass transport and overoxidation to the vesicant sulfone, bis(2-chloroethyl) sulfone (CAS: 471-03-4). Primarily, HD has poor water solubility, so dissolution of HD may require a cosolvent or elevated temperatures, or both, to effectively bring the agent into contact with the decontaminant solution. In addition, the oxidation product, bis(2-chloroethyl) sulfone, retains vesicant properties. A decontaminant must either proceed to the initial oxidation to the sulfoxide or hydrolyze the alkyl halide sidechains to the resulting vinyl and hydroxyl groups. Moreover, HD has a reasonably high vapor pressure (~ 0.11 Torr at 25 °C), so weathering alone, especially in hotter climates, may provide a significant reduction in the remaining contaminant.

For decontamination of VX, the P-S bond must be cleaved, either through direct nucleophilic displacement (such as perhydrolysis/hydrolysis) or oxidation of the sulfur and subsequent hydrolysis. Of these potential mechanisms, perhydrolysis using oxidants such as hydrogen peroxide, peracetic acid, and hypochlorite are the most rapid.²⁸ Thus, the pH and protonation state of the oxidant should be considered carefully when formulating decontaminants. Due to the extremely low vapor pressure of VX ($\sim 7 \times 10^{-4}$ Torr at 25 °C), weathering provides little efficacy in removing this contaminant.

Based on these considerations, an initial selection of decontaminants was developed. Most currently fielded decontamination technologies are specialized for hardened military or individual equipment or for personnel. These technologies face scale-up limitations and restrict feasibility for large-scale CWAD applications due to prohibitively high cost, limited supply, environmental concerns, and difficulty in preparation. Therefore, initial decontaminant selection centered on technologies that were available in bulk and met the following criteria:

- effective: must reduce the vapor and contact hazards to personnel;
- available: must be available in bulk containers at reasonable prices;
- scalable: can be safely and easily prepared at 1000 gal scale; and
- sprayable: must be compatible with sprayer technologies.

As shown in Figure 5, five different decontamination classes were researched for additional consideration. Each approach focused on using simple, readily available chemistries. Furthermore, a number of different factors associated with possible reaction mechanisms (i.e., oxidation and hydrolysis) as well as agent–material–solvent interactions were taken into consideration when choosing the configurations of decontamination solutions.

Aqueous oxidant formulations fall in line with the traditional decontamination strategy of using oxidation as the principal decontamination mechanism for HD and VX. Decontamination of soman and other contaminants can be performed by a pH adjustment of the solution to facilitate alkaline hydrolysis. Initial considerations included hypochlorite-based oxidants (HTH or Dichlor), inorganic peroxides (Oxone or persulfates), and organic peroxides (oxidants). Approaches using hydrogen peroxide and peracetic acid were excluded from screening due to poor shelf life and air transport issues.

Although oxidants may be reactive with CWA in solution, aqueous decontaminants are not necessarily effective at extraction of hydrophobic agents such as HD. Moreover, aqueous decontaminants may not effectively permeate through oleophilic substrates such as asphalt, which actively repel water. For this reason, many decontaminant solutions are formulated, either with a cosolvent or a surfactant additive.²⁹ Most solvents are prohibitively expensive, flammable, or environmentally toxic at large scales. However, common aircraft deicers (Type II and Type IV) are typically 50–80% propylene glycol mixtures containing a colorant and a corrosion inhibitor.³⁰ Inclusion of propylene glycol as a cosolvent may increase decontaminant efficacy due to increased agent solubility and more rapid permeation through concrete and asphalt. Therefore, a select number of formulations were developed as mixtures of oxidants and bases in a propylene glycol/water mixture, mimicking a formulation prepared in aircraft deicer.

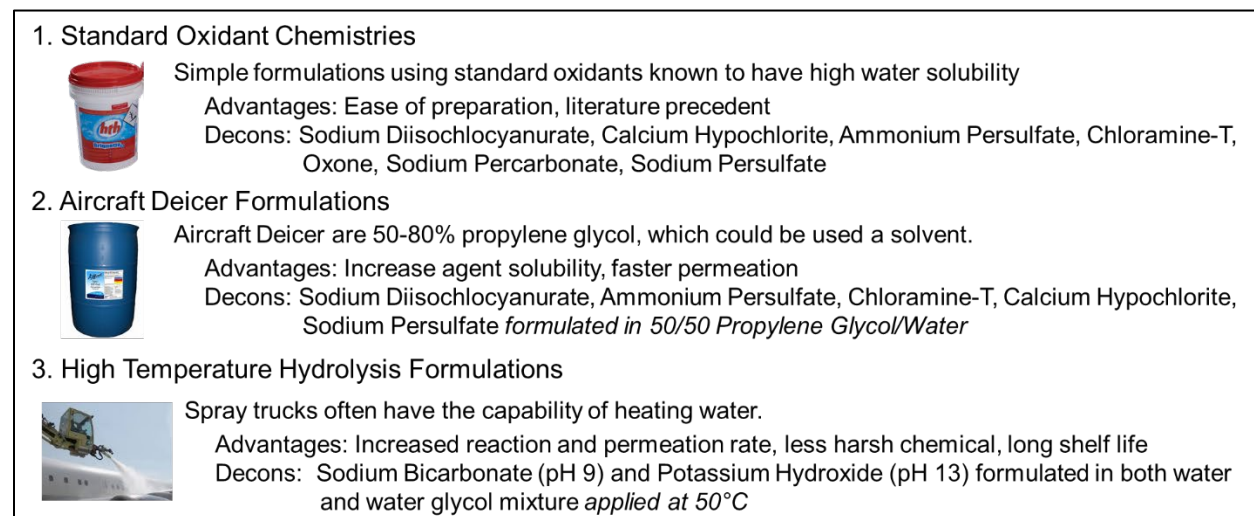


Figure 5. Reactive formulations under consideration for wide-area decontamination.

As an alternative to oxidant chemistries, hydrolysis-based decontaminants may prove to be effective at higher temperatures. Many sprayer technologies have the capability of heating aqueous mixtures, allowing a hot decontaminant solution to be applied. Increasing the decontaminant temperature increases the reaction and permeation rates through materials. Although hydrolysis of HD and VX is too slow at room temperature for effective decontamination, this reaction rate may be sufficient at higher temperatures. As a rule of thumb, the Arrhenius relationship suggests that most reactions double in rate for every 10 °C increase in

temperature. This relationship also holds for permeation of water through substrates like concrete.³¹ Thus, basic decontaminants such as potassium hydroxide, potassium carbonate, or sodium bicarbonate may be effective for longer interaction times when applied at high temperatures. When compared with oxidants, basic solutions have nearly infinite pot and shelf life and are typically easier to handle and prepare. The decontaminant application temperature can easily be increased by using a variety of current military and civilian liquid applicators (Figure 6). A mildly basic decontaminant applied at high temperature could provide adequate decontaminant efficacy with decreased cost and increased shelf life and material compatibility when compared with strong oxidants.

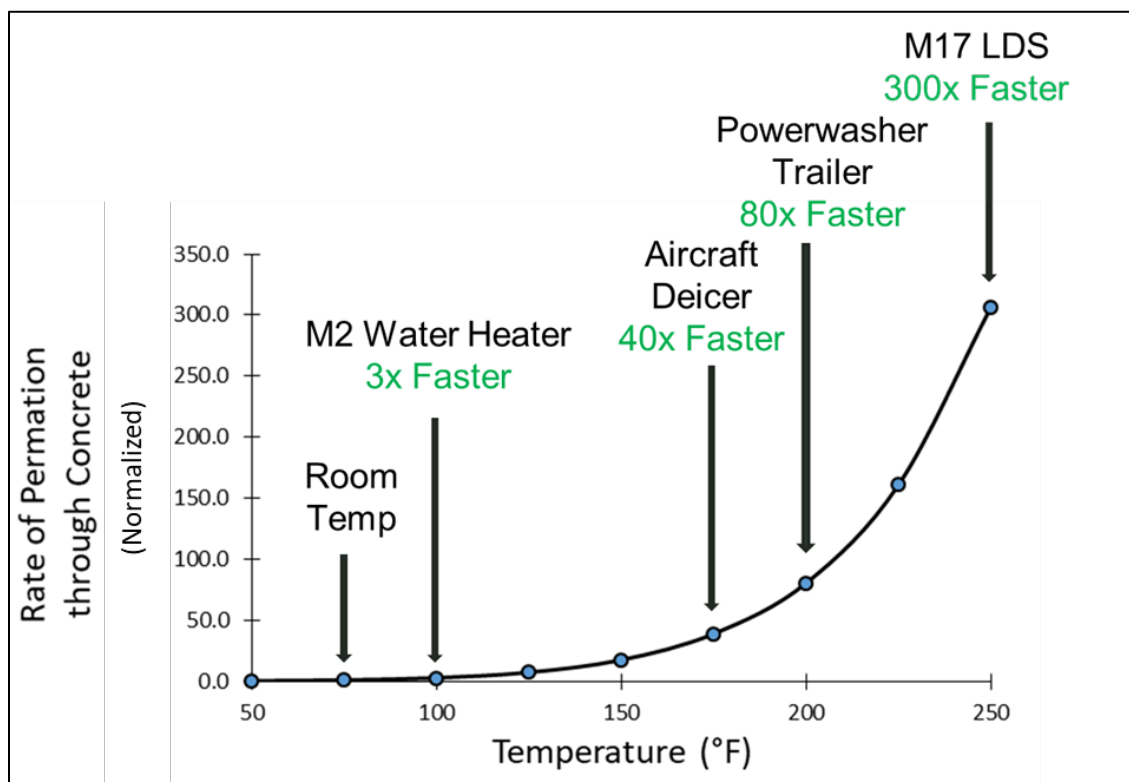


Figure 6. Arrhenius relationship for rate of permeation through concrete.

Several other formulations such as Clorox Bleach, Avion 50 Runway Rubber Remover, Sprayable Decontaminant Slurry, and Dahlgren Decon were tested in select conditions during this study. Although these decontaminants are likely too expensive to be prepared on a large scale, they provide performance benchmarks for comparison to currently fielded technologies.

3.2 Oxidant and Base Selection and Solubility Studies

An initial list of potential oxidants was selected based on shelf life, solubility, and availability. Water soluble oxidants were selected for strictly aqueous formulation, whereas solvent soluble oxidants were selected for use in a propylene glycol/water mixture. This mixture mimics formulation of a decontaminant solution using aircraft deicer solution. A list of potential oxidants and their mechanism of action, availability, and shelf life is provided in Figure 7. A variety of hypochlorite- and peroxide-releasing agents, inorganic peroxides, and organic peroxides was selected based on literature precedent and availability in bulk quantities.

Water Soluble Oxidative Decontaminants						
Chemical Name	Example	Mechanism	[Oxidant] in Saturated Soln	Shelf Stability	Availability ²	
Calcium hypochlorite	HTH	OCl-	1.9	2+ years	1	
Sodium hypochlorite	Bleach	OCl-	3.9	1 year	1	
Chloramine-T	Halamid	Releases OCl-	0.5	2 years	2	
Dichloroisocyanuric acid	Dichlor	Releases OCl-	1.8	5 years	1	
Hydrogen Peroxide	-	HOOH	miscible	6 months	1	
Sodium Perborate	-	Releases HOOH	0.3	1 year	3	
Sodium Percarbonate	OxiClean	Releases HOOH	1.4	6 months	2	
Peracetic Acid	-	Organic Peroxide	4.2	1+ years	2	
Peracetyl Borate	JGPD/Dahlgreen	Organic Peroxide	unknown	2+ years	4	
Potassium peroxymonosulfate	Oxone	Inorganic Peroxide	0.8	10+ years	1	
Sodium Persulfate	-	Inorganic Peroxide	2.3	3 years	2	
Ammonium persulfate	-	Inorganic Peroxide	3.5	1 year	2	

Solvent Soluble Oxidative Decontaminants						
Chemical Name	Example	Mechanism	Solubility in Organic Solvents	Strength ³	Shelf Stability	Availability ²
Trichloroisocyanuric acid	Trichlor	Releases HOCl	Good	1.3	2 years	1
Chloramine T	Halamid	Releases HOCl	Limited to Alcohols	0.4	2 years	2
Dichlorodimethylhydantoin	DCDMH	Releases HOCl	Good	0.9	3 years	3
Dibromodimethylhydantoin	DBDMH	Releases HOBr	Good	0.7	10 years	3
Hydrogen Peroxide	Peroxide	HOOH	Good but Reactive	2.9	6 months	1
Peracetic Acid	-	Organic Peroxide	Fair	1.3	1+ years	3
Potassium peroxymonosulfate	Oxone	Inorganic Peroxide	Aq. Solvent Blends	0.3	10+ years	1
Ammonium persulfate	-	Inorganic Peroxide	Good	0.5	1 year	2

¹Molar concentration (M) of available oxidant in a saturated aqueous solution; ²availability indexed as 1 = readily available in a store, 2 = easily purchasable online, 3 = ordered from specialty company, 4 = not commercially produced; ³Strength defined by molar concentration of available oxidant in a 0.1g/mL solution.

Figure 7. Image of the list of potential oxidative decontaminants.

Initial downselection of decontaminants was based on availability and shelf life. Hydrogen peroxide and peracetic acid were excluded due to poor shelf life and restrictions in air transport. Peracetyl borate, a component of a major commercial decontaminant formulation, is not available for bulk purchase and was therefore excluded.

The remaining decontaminants were screened for solubility (i.e., for use in either an aqueous- or deicer-based decontaminant formulation). Several bases were also included in the solubility screen. Solubility was measured in water, 30% propylene glycol/water and 50% propylene glycol/water (v/v). In addition, solubility was determined by adding solvent to a known mass of decontaminant at 20 °C until all solids were dissolved. The solubility results (Figure 8) allowed for a second downselection. Solubility drives the maximum decontaminant

concentration, which is the principal driving force in the rate of decontamination. Only decontaminant formulations with appreciable (>0.2M) solubility in water and propylene glycol/water mixtures were selected for further evaluation.

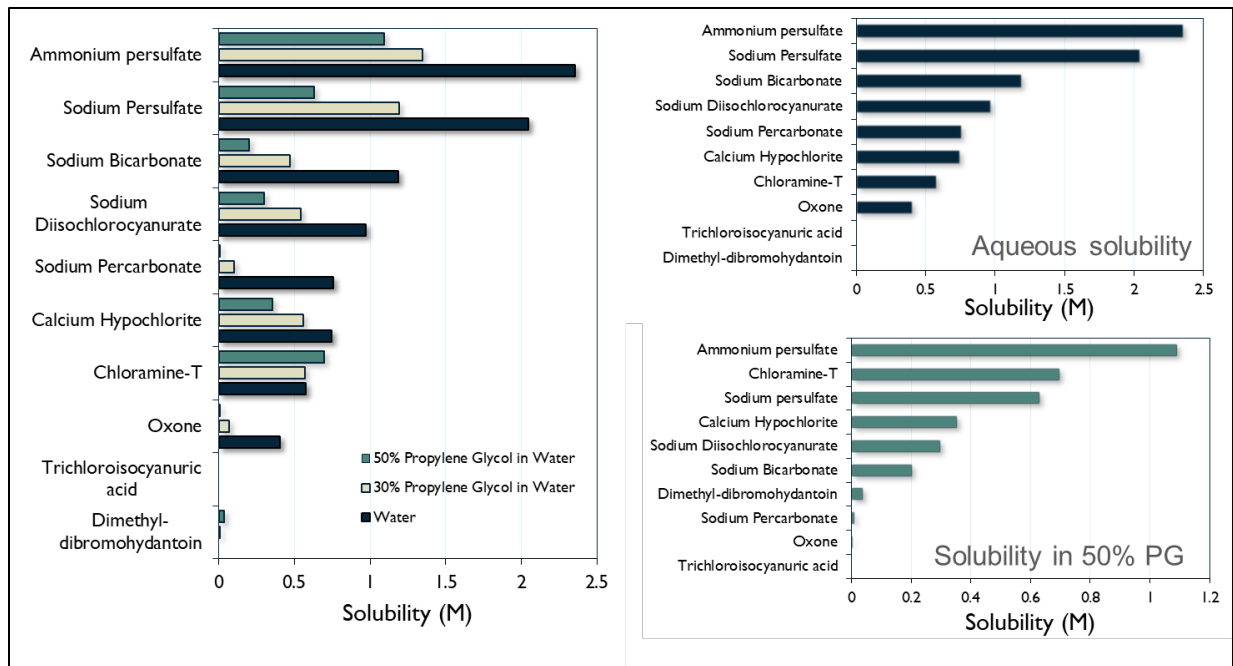


Figure 5. Solubility of candidate decontaminants in water and aqueous propylene glycol.

Several decontaminants, such as ammonium persulfate, chloramine-T, calcium hypochlorite, and sodium diisochlorocyanurate (Dichlor) displayed good solubility in water and the propylene glycol mixtures. Oxone and sodium percarbonate had excellent solubility in water but poor solubility in the glycol mixtures. Based on these results, an initial test matrix for screening was developed, including aqueous oxidants, deicer formulations, and high temperature hydrolytic decontaminants. Several inorganic bases (potassium hydroxide [KOH] and sodium bicarbonate) were selected for testing at elevated temperatures. Hot soapy water and Clorox Bleach were used as control decontaminants. This matrix is given in Table 1, outlining each of the decontaminant formulations, the concentration of the oxidant/base, and the decontaminant application temperature.

Table 1. Downselected Decontaminants for the Initial Efficacy Screen

No.	Chemical	Class	Mechanism	pH	[Decon] (M)	Temp	Solvent
1	Weathering only	Control	Evaporation	-	-	25	None
2	Hot soapy water	Control	Evaporation	7	-	40	Water
3	Bleach	Formulation	Hypochlorite	10+	-	25	Water
4	Ammonium persulfate	Aqueous oxidant	Inorganic peroxide	2	2.4	25	Water
5	Sodium persulfate	Aqueous oxidant	Inorganic peroxide	3	2.0	25	Water
6	Dichlor	Aqueous oxidant	Hypochlorite	6	1.0	25	Water
7	Sodium percarbonate	Aqueous oxidant	Hydrogen peroxide	10+	0.75	25	Water
8	Calcium hypochlorite	Aqueous oxidant	Hypochlorite	-	0.75	25	Water
9	Chloramine-T	Aqueous oxidant	Hypochlorite	6	0.60	25	Water
10	Oxone	Aqueous oxidant	Inorganic peroxide	3	0.40	25	Water
11	Ammonium persulfate	Organic oxidant	Inorganic peroxide	2	1.00	25	50% PG
12	Chloramine-T	Organic oxidant	Hypochlorite	6	0.70	25	50% PG
13	Sodium persulfate	Organic oxidant	Inorganic peroxide	3	0.60	25	50% PG
14	Calcium hypochlorite	Organic oxidant	Hypochlorite	-	0.35	25	50% PG
15	Dichlor	Organic oxidant	Hypochlorite	6	0.30	25	50% PG
16	KOH	Aqueous base	Hydrolysis	13+	14	40	Water
17	Sodium bicarbonate	Aqueous base	Hydrolysis	9	1.2	40	Water
18	KOH	Organic base	Hydrolysis	13+	14	40	50% PG
19	Sodium bicarbonate	Organic base	Hydrolysis	9	0.2	40	50% PG

PG, propylene glycol.

4. RESIDUAL AGENT TESTING METHODOLOGY

After an initial selection of decontaminant formulations, methods were developed to rapidly screen the decontaminants outlined in Section 3.2. These decontaminants were screened for efficacy against HD- and VX-contaminated concrete and asphalt. The aims of the screening study were threefold:

- (1) highlight potential decontaminant chemistries for use as CWAD decontaminants,
- (2) determine the agent–material combinations present in the largest mitigation challenges, and
- (3) provide an initial data set to direct subsequent downselection.

Analysis methods were developed to meet the requirements for screening. The aim was to ensure results were accurate enough to correctly identify high-performing decontaminants and provide an approximate estimate of decontaminant efficacy. This test was not designed to be an absolute measure of residual agent due to complexities in extraction of the matrix and quenching of the decontaminant solutions. Instead, these results provide a semi-quantitative picture of decontaminant efficacies against HD and VX.

The testing procedure was designed to mimic in-the-field conditions and still remain feasible for a laboratory study. All contamination steps were performed at room temperature. As shown in Figure 9, a 2 in. coupon of either concrete or bitumen sheet was

contaminated with a 5 μL drop of agent. This large contamination density (2.5 g/m^2) was selected to provide a more difficult decontamination challenge. The agent was aged on the coupon for 24 h, representing a one-day response time to a CWA attack. During this time, the agent permeated into the material and evaporated from the surface. Weathering reduced the mass of HD up to 70%, whereas the mass of VX remained largely unchanged.

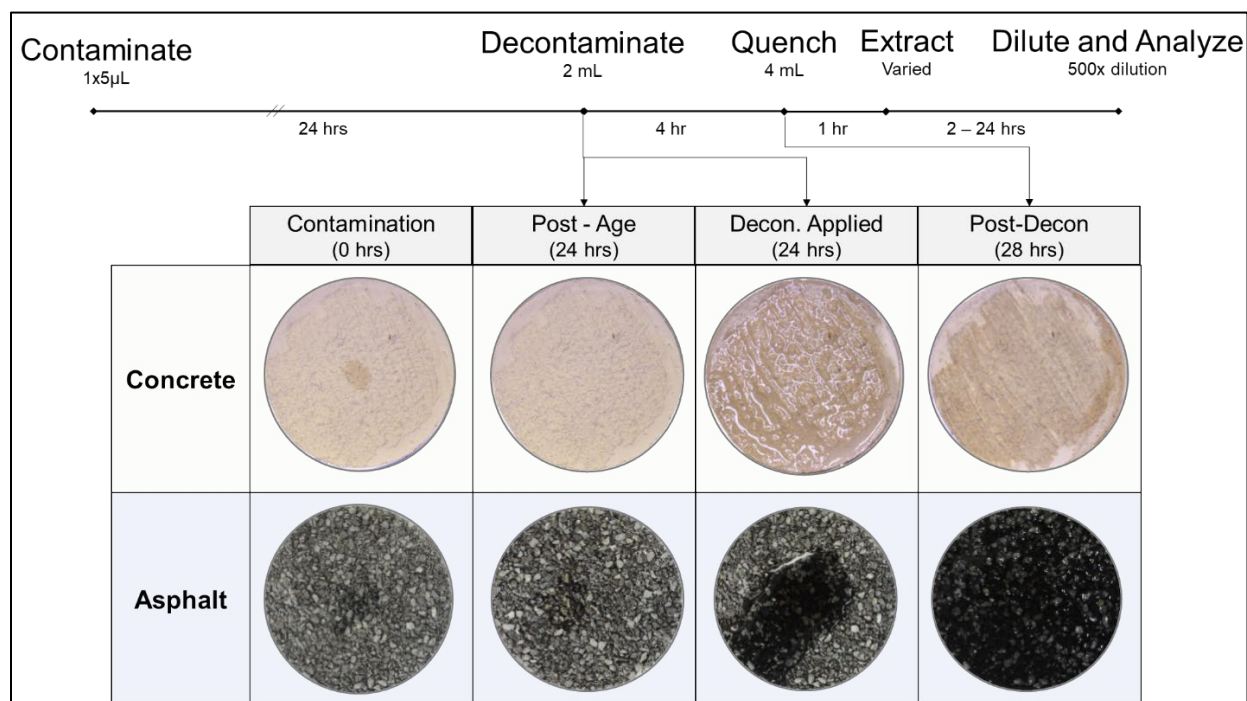


Figure 9. Testing procedure for initial decontaminant efficacy screening.

After aging was complete, the panels were treated with 2.0 mL of a freshly prepared decontaminant solution, which remained on the surface for 4 h. This procedure allowed for any decontaminant with a slower reaction rate and longer pot-life to perform well in the test. After this period, quench solution was added to prevent any additional reactivity from occurring within the extract. This procedure was effective for both VX and HD. The data from quench procedure development are provided in Appendix A. The quench components, sodium thiosulfate or tetrahydrothiophene (THT), act as a sacrificial-reducing agent. These reducing agents react rapidly with any remaining oxidant on and in the panel, thus halting the reaction. The quench components remained on the panel for 1 h, after which the panel was extracted. Extraction efficiency studies were performed to determine optimal extraction conditions, as described in Appendix B. Extraction of $>80\%$ of the agent was typical for the extraction methods used. The extraction solvents and extraction times are presented in Table 2.

Table 2. Extraction Methodologies for Residual Agent Studies

Agent	Substrate	Extraction Solvent	Extraction Volume (mL)	Extraction Time (h)
HD	Asphalt	ACN:CHCl ₃ (70/30)	20	2
	Concrete	CHCl ₃	40	24
VX	Asphalt	IPA:CHCl ₃ (70/30)	20	2
	Concrete	IPA	40	24

ACN, acetonitrile.

The extracts were then analyzed for residual agent using established GC-MS and LC-MS methods for HD and VX, respectively.³⁷ The results presented in the subsequent sections of this report were generated using this methodology.

5. DECONTAMINATION OF CONCRETE SURFACES

5.1 High-Throughput Screening Results

Initially, 19 decontaminants were tested for efficacy against HD and VX on CSA concrete coupons. The results from the decontaminant screening of HD and VX against concrete are shown in Figure 10. Average values are denoted by darkened circles, with grey representing control conditions, blue representing aqueous oxidant formulations, orange representing oxidant formulations in 50% propylene glycol, and green representing bases (hydrolysis) applied at 40 °C. The unfilled grey circles demonstrate the raw data points, which were collected in triplicate for each decontaminant. The data are plotted on a log scale of residual agent, which is the measured mass of agent remaining on the panel after decontamination.

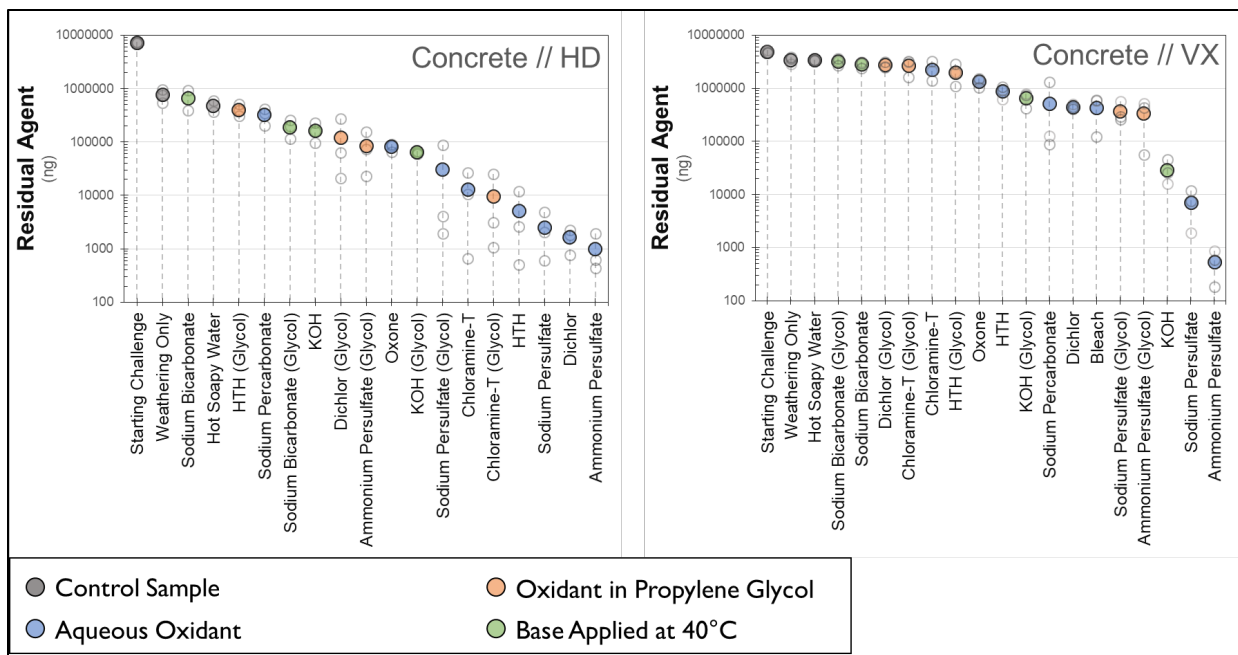


Figure 10. Initial screening results of HD (left) and VX (right) on CSA concrete coupons.

As described in Section 4, contaminant was applied to a coupon and aged for 24 h prior to decontamination. Decontaminant residence time was 4 h after which, the coupon was quenched and extracted. The temperature of the KOH solutions and sodium bicarbonate were at 40 °C when applied to surfaces. After application, the coupon was aged at room temperature, which allowed the decontaminant solution to cool down. All other decontaminants were applied at room temperature.

The data provided in Figure 10 show that weathering significantly reduces the starting challenge for HD but not for VX. This is due to the higher vapor pressure of HD, which significantly evaporates over the 24 h aging period. For HD, both the evaporative losses from weathering and the action of the decontaminant decrease the mass of agent in the coupon. To strictly focus on the influence of the decontaminant, performance compared with weathering controls is provided in Figure 11. The data are provided as a log difference plot, which allows for comparisons across orders of magnitude. For example, a log difference of 1 correlates to a 90% reduction, a log difference of 2 correlates to 99% reduction, and so forth.

The data show that several reactive chemistries are effective for the decontamination of concrete. The persulfate decontaminants provided the highest performance for HD and VX. KOH gave nearly a 99% reduction of both HD and VX when applied at 40 °C. Other notable decontaminants were Dichlor and HTH, which gave significant reduction in residual HD alongside a moderate reduction in VX. The results demonstrate that HD is typically more easily decontaminated from concrete than VX under these conditions. Finally, the use of propylene glycol cosolvent does not seem to increase decontaminant efficacy. This is likely due to decreased decontaminant concentration resulting from decreased solubility.

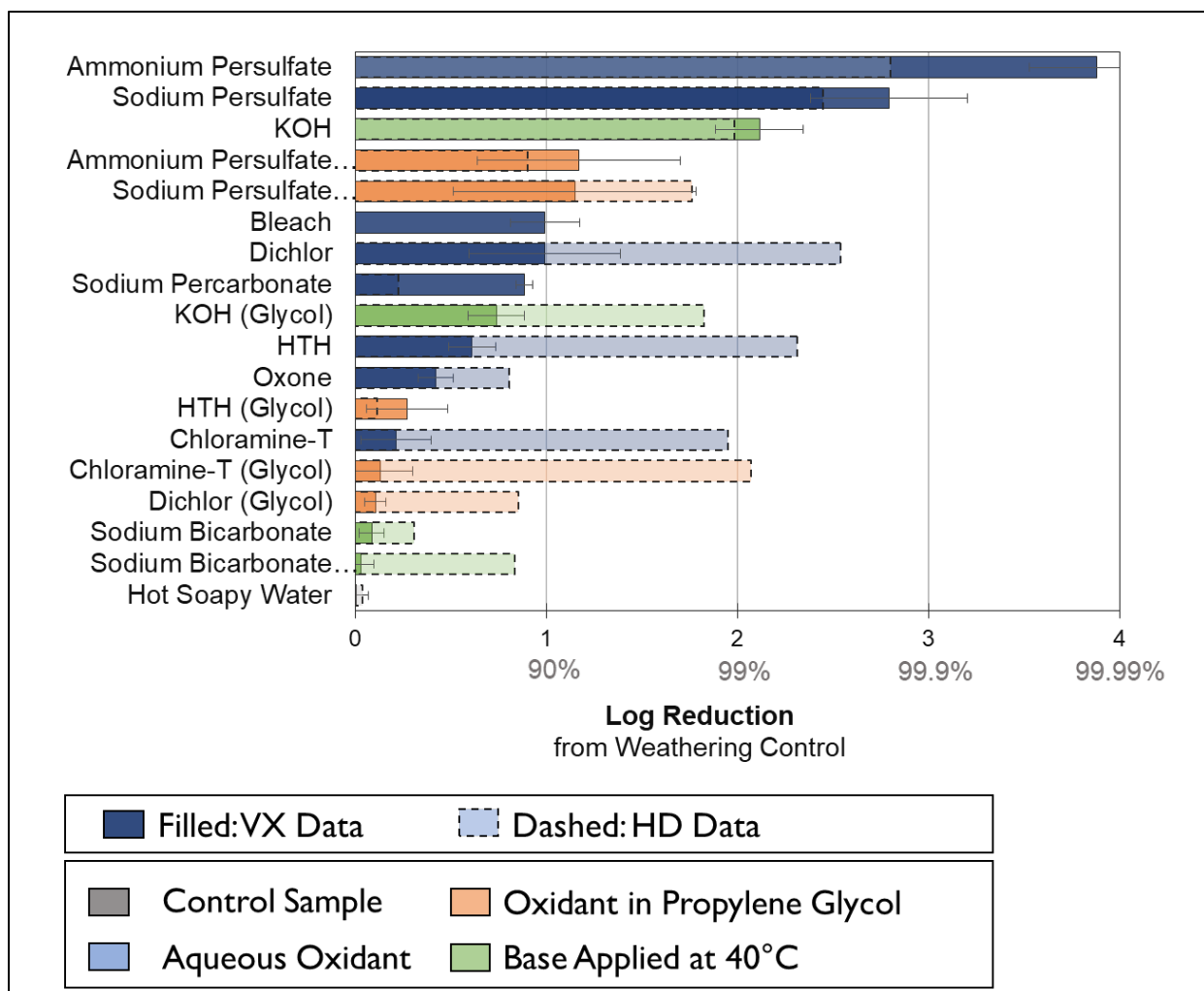


Figure 11. Decontaminant performance of HD and VX on CSA concrete compared with weathering controls.

The mechanism of action of each decontaminant can be proposed based on literature precedent and byproduct analysis. Most of the effective decontaminants in the system were simply hypochlorite-releasing agents, which led to a direct oxidation of the sulfur in both VX and HD (Figure 12). For VX, the oxidized P-S(O)₂ bond is rapidly cleaved to yield EMPA (ethyl methyl phosphonic acid) and DESH (diisopropylaminoethanethiol). For HD, the sulfur atom is rapidly oxidized to the sulfoxide and then slowly oxidized to the sulfone. Elimination of the alkyl chlorides may give further nontoxic products. This is the likely action mechanism of HTH, Chloramine-T, Dichlor, and bleach, which have been reported to generate hypochlorite (OCl) in aqueous solution. When in water, hypochlorite exists as the free anion at high pH (>8). The hypochlorite form, which is dominant in household bleach solutions, is relatively stable and has a moderate oxidation potential. At lower pH (<6), hypochlorous acid (HOCl) is formed. HOCl is more reactive, but also degrades as chlorine gas (Cl₂) is released. Dichlor and Chloramine-T have a pH of around 6.0 when dissolved in water and form HOCl as the active species.

The persulfate decontaminants likely act through an alternate mechanism. One possible pathway is the formation of a sulfate radical ($\text{SO}_4^{\cdot-}$) through either photochemical cleavage of peroxide bond or initiation from an electron donor such as Fe(II). The resulting highly reactive radical can then rapidly oxidize VX and HD. Another pathway is the formation of a peroxymonosulfate, the active ingredient in Oxone, through reaction with a hydroxide anion. The peroxy sulfate anion may react with the electrophilic sites on VX (phosphine) and HD (alkyl chloride) through a perhydrolysis mechanism similar to observed reactivity of alkaline hydrogen peroxide solutions.³²

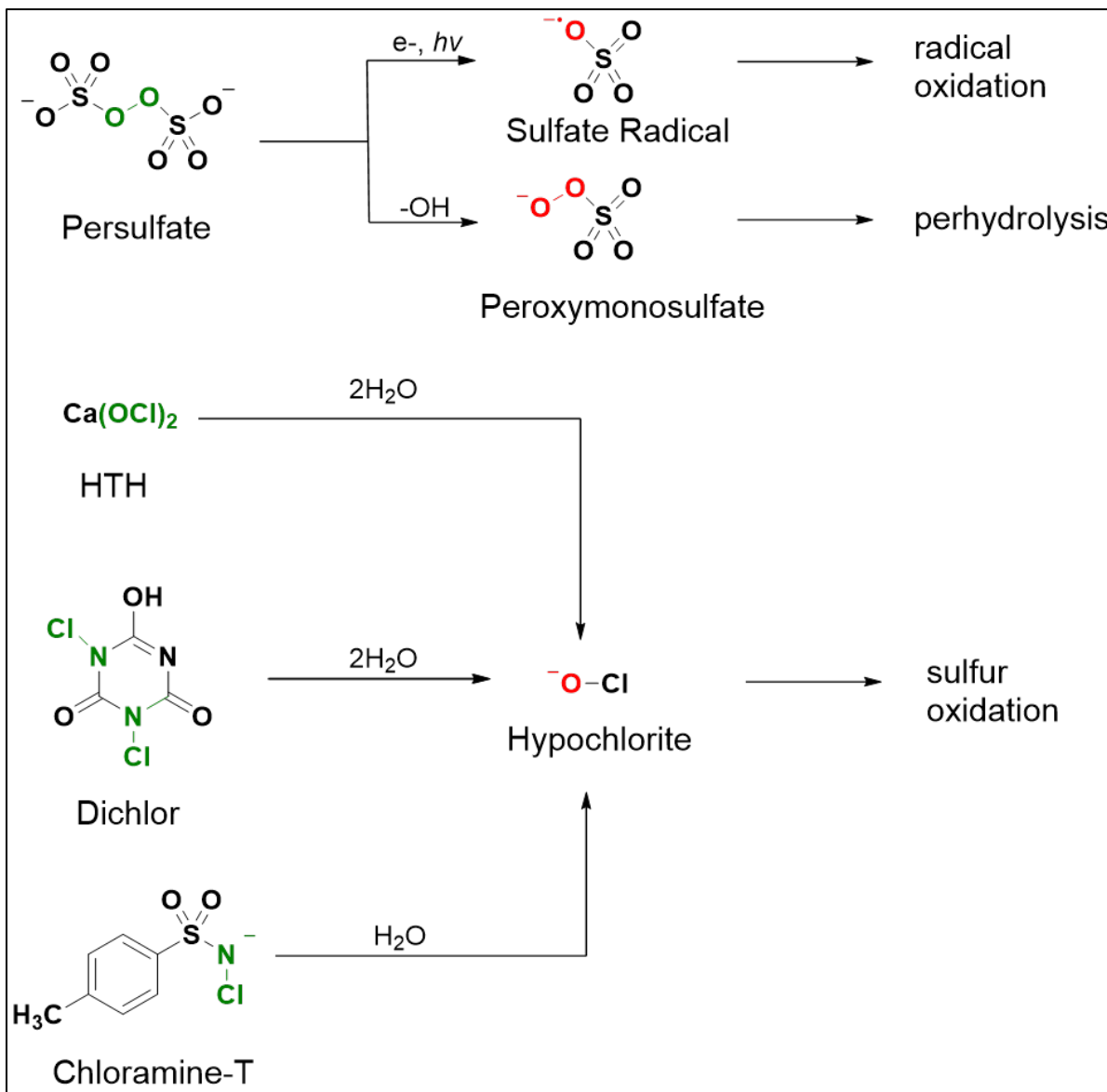


Figure 12. Likely mechanisms of select oxidant decontaminants on concrete.

5.2 Influence of pH and Temperature on Base Catalyzed Hydrolysis of VX

The initial screening identified KOH as an effective decontaminant on concrete for VX, achieving 99% decontamination when compared with the weathering control. In this case, the KOH solution was applied at 40 °C. However, the concentration of KOH was extremely high (14M). This extremely high concentration would likely be impractical in the field, as the highly caustic solution could cause chemical burns and would be difficult to prepare due to the large heat of mixing. Therefore, a screening test was developed to address this issue and answer the following questions:

- could VX be decontaminated using basic hydrolysis at a decreased pH,
- how does temperature increase the efficacy of basic hydrolysis, and
- how much EA2192 is formed at varied temperatures and pH?

Using buffered solutions as decontaminants, the reactivity of VX in concrete was measured using the protocol outlined in Section 4. Buffered solutions at pH 9–12 and 14 (1M) were applied to VX-contaminated concrete panels. Sodium carbonate/bicarbonate buffers were used at pH 9–11, and sodium phosphate buffers were used at pH 12. Buffering concentration was 0.9M. After the buffers were applied to the panel at 40, 50, 60, and 70 °C, the panel was aged for 4 h at room temperature. Additional solutions were prepared at 7 and 14M KOH. Residual agent and formation of EA 2192 were measured, as shown in Figure 13.

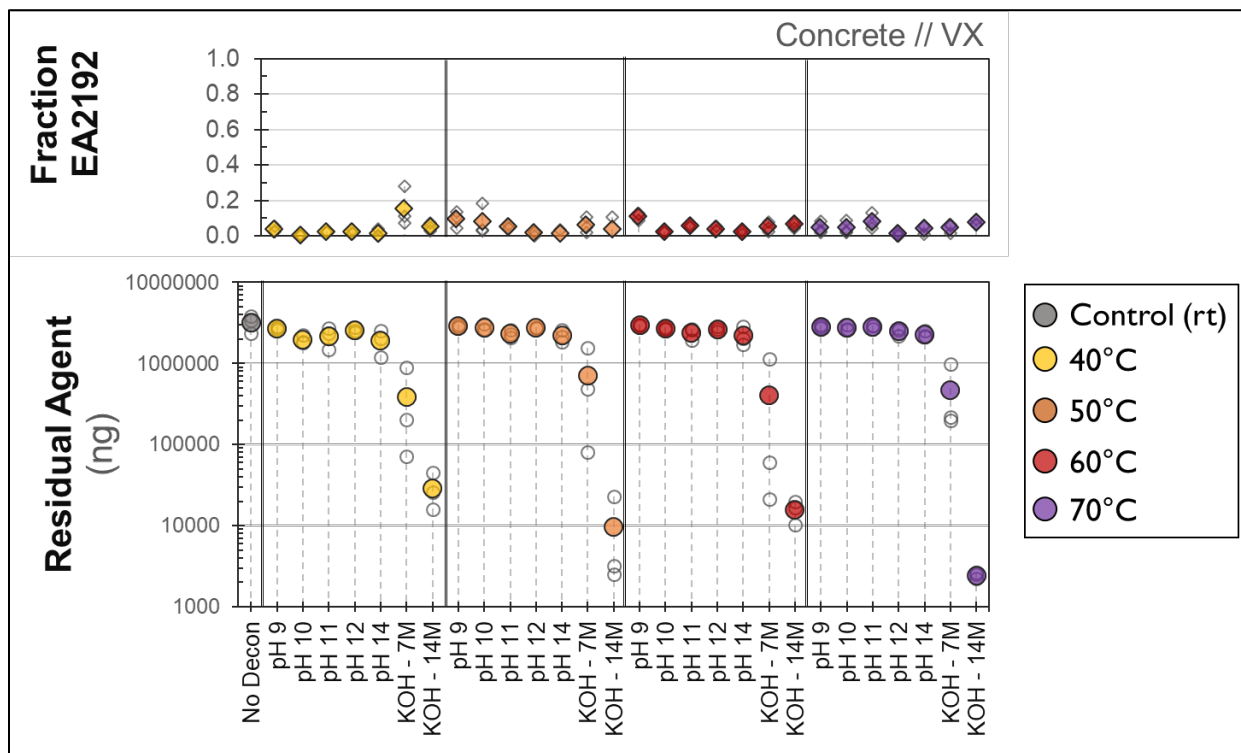


Figure 6. pH and temperature screening of VX on concrete.

Little reactivity was seen at pH 14 or below, regardless of the temperature. In all cases, less than 20% of the reacted VX formed the toxic byproduct EA 2192. As shown in Figure 14, significant reactivity was only seen using the 7M and 14M KOH solutions when compared with weathering controls. Increasing the decontaminant application temperature appeared to have little impact on efficacy. It is likely that either (a) the decontaminant cools to room temperature before the increased temperature has any effect or (b) the rate of decontamination is controlled by a temperature-independent process. Moreover, increasing temperature had no measureable effect on EA 2192 formation although this was difficult to detect.

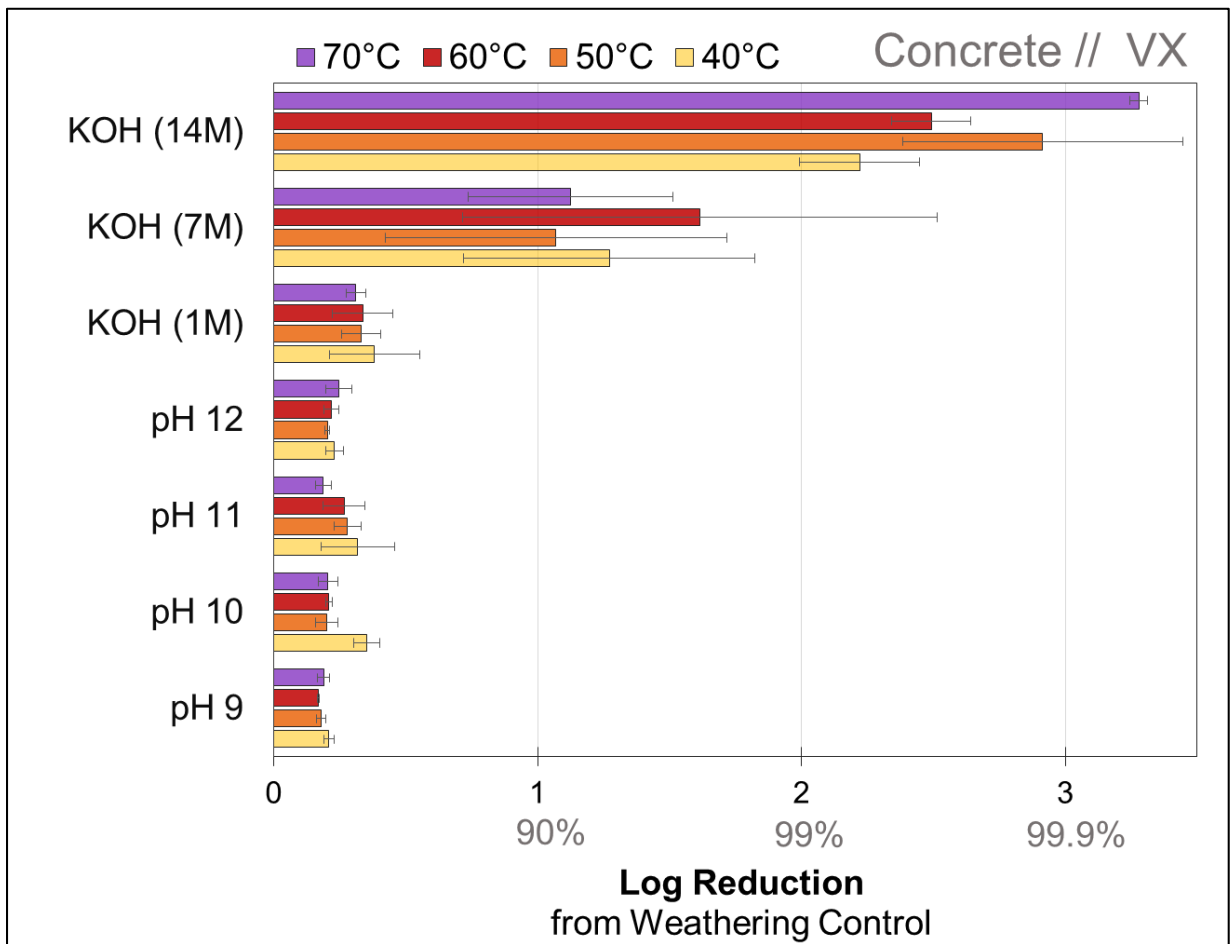


Figure 14. Efficacy of basic decontaminants against VX on concrete compared with weathering controls.

5.3 Cost-Benefit Analysis of Concrete Decontamination

The initial screening identified several options for concrete decontamination. A first cost-benefit analysis was performed to compare the pricing, logistics, and efficacy of each of the potential decontaminants, as shown in Figure 15. The decontaminants, ammonium persulfate, sodium persulfate, Dichlor, KOH, and HTH, were selected due to their moderate-to-high efficacy against VX and HD. Oxone was also included (at both tested concentrations) due to its potential use on asphalt. Pricing was based on the bulk prices given on Alibaba (Hangzhou, China). Although Alibaba is not a viable supplier for the Department of Defense, the website was a reasonable source for estimating the price of bulk commodity chemicals. All chemicals listed were available at the ton scale or greater from multiple vendors.

Based on the concentrations of the decontaminant and its price per kilogram, an estimated price for filling a 1000 tank pumping unit (TPU) on a light medium tactical vehicle was provided. Driving at 2.5 mph and spraying at 77 GPM (recommended for the M12A1 terrain decontamination spray bar developed by the U.S. Army), this would cover roughly a 30 yard × 0.5 mile area, in approximately 13 min. The total coverage area would be ~85,000 ft². This correlates roughly with application density used in the panel studies.

Logistics such as shelf life, pot life, resale market, and environmental concerns will also be of great importance in decontaminant downselection. Approximate estimates of these values were made based on a cursory literature search. Persulfates in particular have a variable shelf life. Stored completely dry, persulfate salts have a nearly limitless shelf life but can degrade over the course of months when wet.

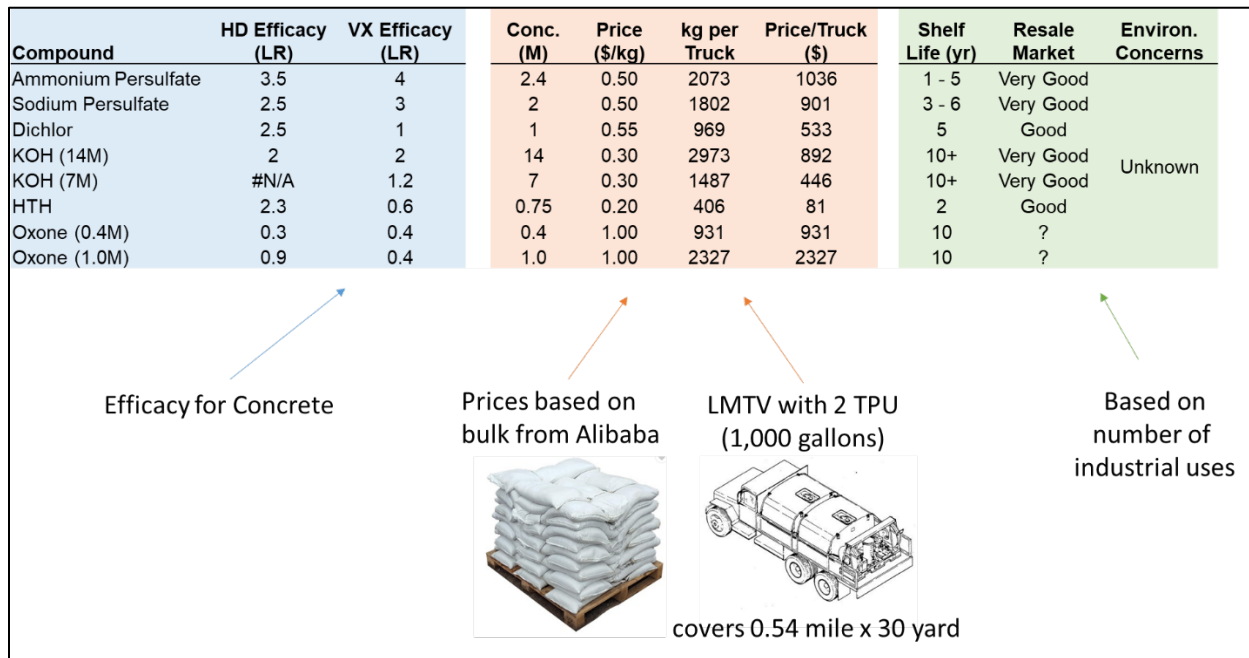


Figure 15. Analysis of efficacy, cost, pricing, and logistics for each of the selected decontaminants.

A further cost-benefit analysis is provided in Figure 16. These plots compared the efficacy of the decontaminant against HD and VX as opposed to the cost of filling one 1000 gal TPU with decontaminant. Ammonium persulfate is the most efficacious decontaminant. However, if only one log reduction is required, more inexpensive decontaminants such as Dichlor, KOH, and HTH may be feasible.

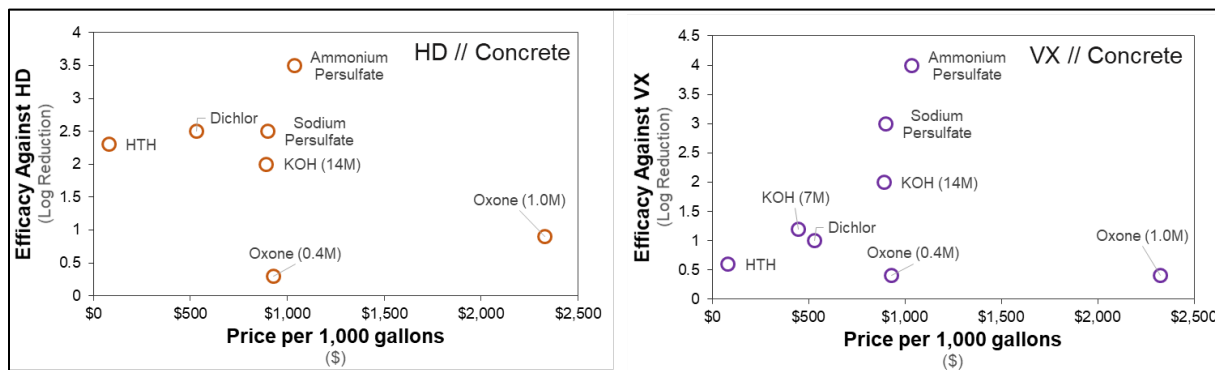


Figure 16. Cost-benefit analysis for decontamination of HD and VX on concrete.

This analysis was only performed using the efficacy of decontamination on concrete, but similar analyses may be performed to compare both barrier and reactive decontaminants on asphalt. In addition, there is a large amount of room for optimization based on performance requirements. Decontaminant efficacy may be increased through increased application temperature and number of applications. Cost can be decreased by decreasing decontaminant spray density and concentration. This type of analysis can also be used to compare logistics to fielded decontaminants such as DF200 and Dahlgren Decon.

6. DECONTAMINATION OF ASPHALT SURFACES

6.1 High-Throughput Screening Results

The 19 decontaminants tested for efficacy against HD and VX were used to decontaminate bitumen sheets, a surrogate for asphalt. The results from the decontaminant screen of HD and VX against concrete are shown in Figure 17. Average values are indicated by darkened circles, with grey representing control conditions, blue representing aqueous oxidant formulations, orange representing oxidant formulations in 50% propylene glycol, and green representing bases applied at 40 °C. The unfilled grey circles demonstrate the raw data points, which were collected in triplicate for each decontaminant. The data are plotted on a log scale of residual agent, which is the measured mass of agent remaining on the panel after decontamination.

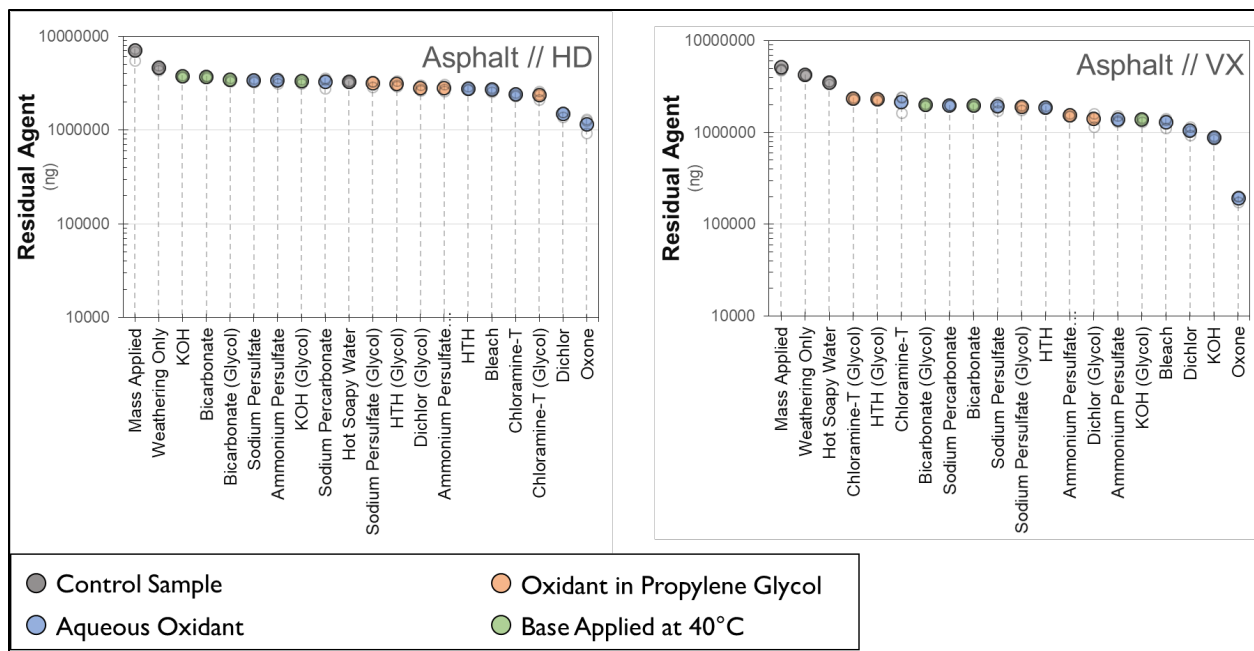


Figure 17. Initial screening results of HD (left) and VX (right) on asphalt sheets.

In general, decontaminant performance of both agents on asphalt was poor. Oxone was the most effective decontaminant for both HD and VX, but it only gave a ~70% reduction in HD concentration. Compared with that of concrete, significantly less HD was lost due to weathering during the 24 h aging time. This is likely due to the strong sorption of HD into the bitumen layer of asphalt or decreased matrix reactivity when compared with that of concrete.

Decreased decontaminant performance on asphalt coupons is likely a result of poor mass transport. Bitumen, which acts as a binder in asphalt, is extremely nonpolar. Therefore, it is likely that both HD and VX readily dissolve into the hydrophobic bitumen layer and cannot be accessed by the aqueous decontaminant. Propylene glycol (a polar solvent) does not appear to help extract the agent out of the nonpolar bitumen layer. With the exception of VX and Oxone, all decontaminants gave less than one log reduction when compared with the weathering control (Figure 18).

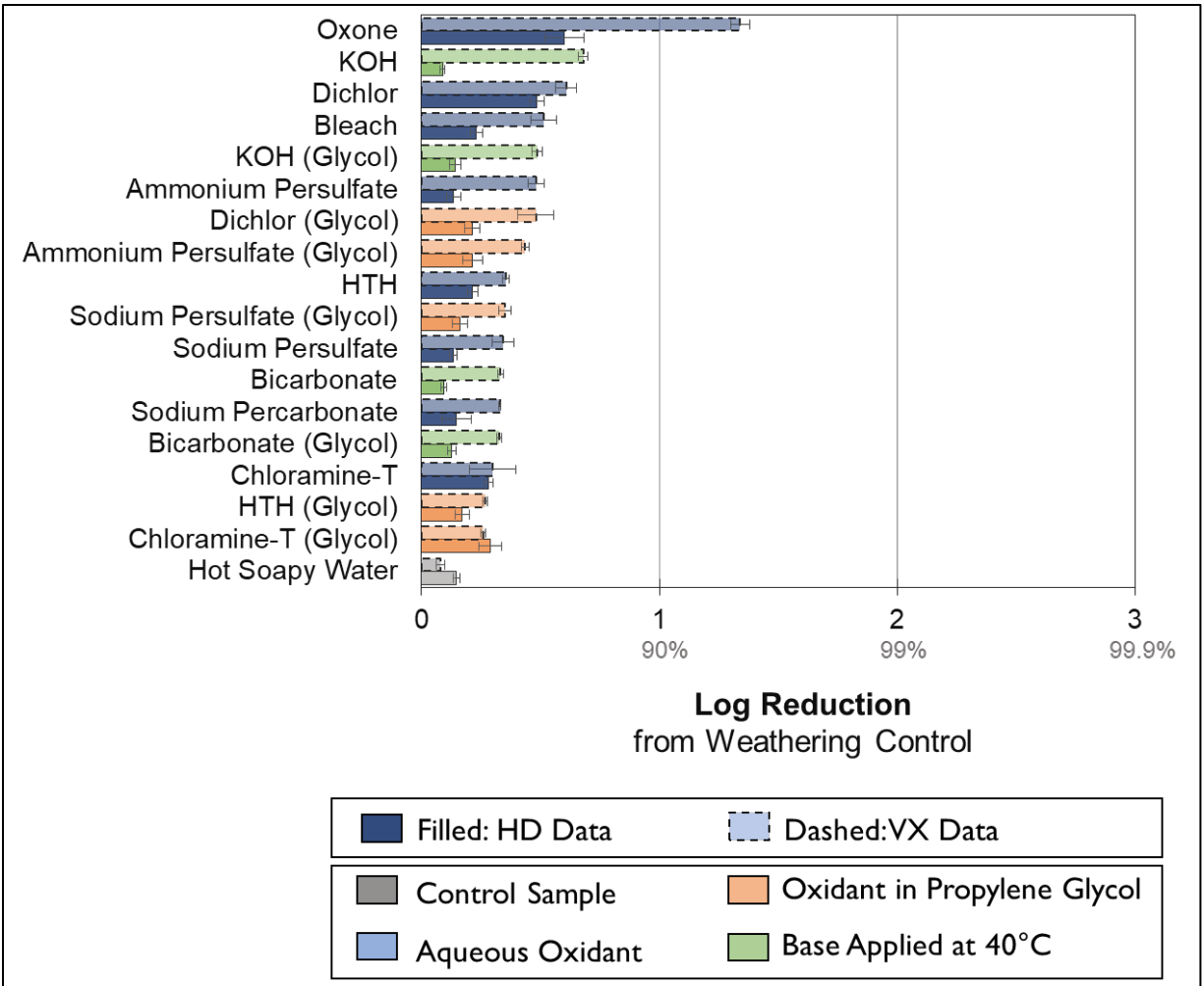


Figure 18. Decontaminant performance vs weathering controls on asphalt sheets.

The hydrophobic nature of the asphalt binder can be seen in the images displayed in Figure 19. Ammonium persulfate was a highly reactive decontaminant in the concrete studies and thus, it was also anticipated to perform well on asphalt. However, the images show that the persulfate solution remained as a bead on top of the asphalt matrix and could not permeate into the material. Ammonium persulfate, like most of the aqueous decontaminants, could not access the contaminant dissolved in the bitumen coating. Oxone was the only decontaminant that appeared to readily permeate into the material during the 4 h aging period. However, only modest reductions in agent mass were seen using Oxone. Increasing decontaminant performance may rely on the use of increased temperature or addition of surfactants/cosolvents to increase permeation into the material.

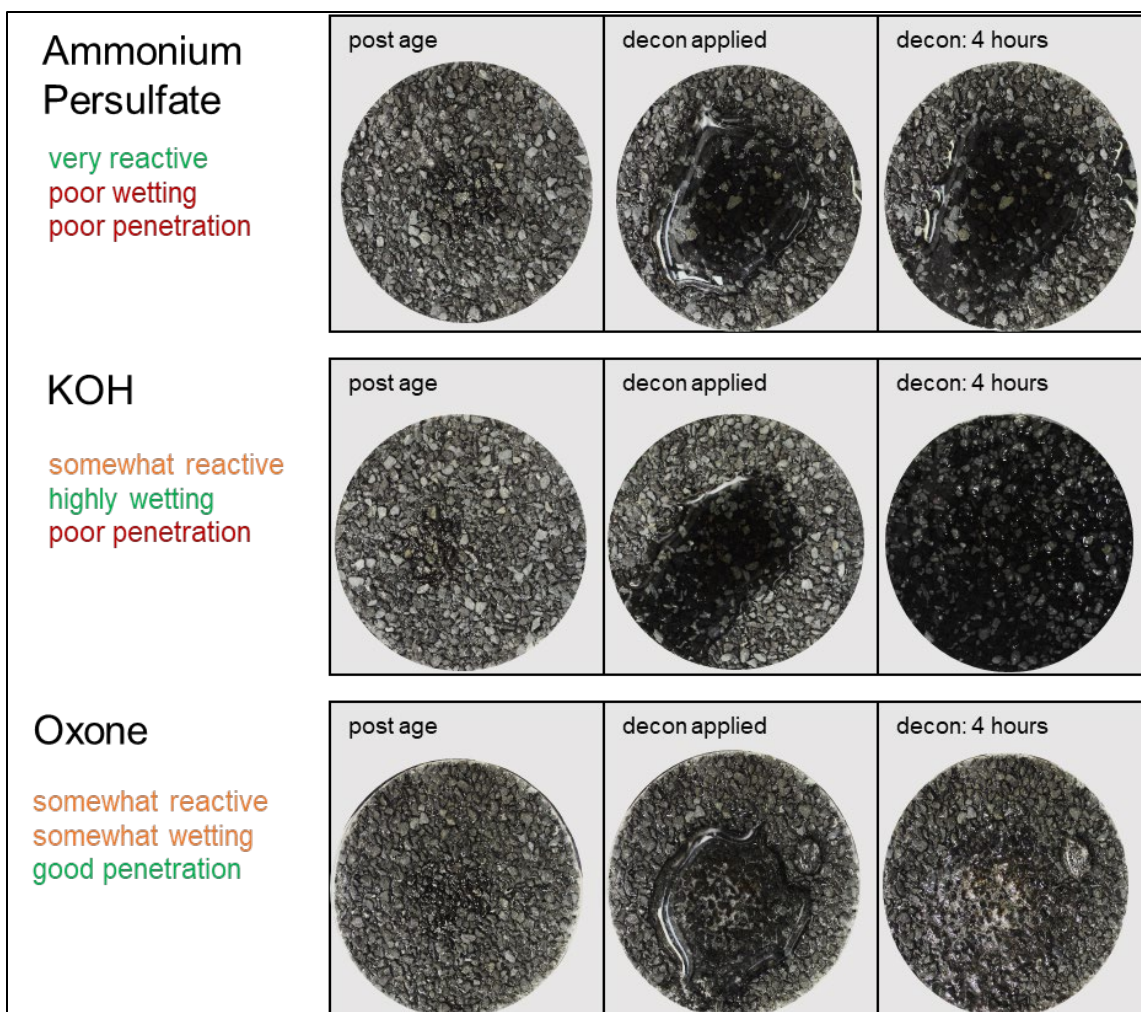


Figure 19. Images from the decontamination of bitumen sheets.

6.2 Optimization of Decontaminant Efficacy on Asphalt

Decontaminant screening revealed that few decontaminants gave reasonable efficacy on asphalt sheets. Of these decontaminants, Oxone yielded the best results. An experiment was designed to test several strategies for increasing decontaminant performance on asphalt.

The first strategy was to increase the concentration of Oxone. Oxone is a triple, salt-containing, one active ingredient (potassium peroxydisulfate, $\text{K}_2\text{S}_2\text{O}_8$) and two inactive salts (potassium sulfate, K_2SO_4 and potassium bisulfate KHSO_4), as shown in Figure 20. The initial screening was performed at the solubility limit of the Oxone triple salt, that is, all three components are soluble. Increasing the concentration past this point would result in a slurry, but the concentration of the active peroxy species could increase if the solubility were higher than the solubility of the triple salt. Therefore, an experiment was performed using a $2.5\times$ more concentrated solution of Oxone (for a final concentration of 1.0M), in the attempt to increase efficacy.

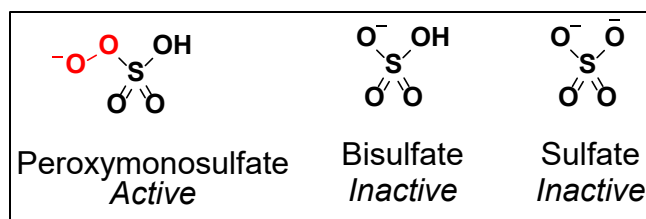


Figure 20. Principal components of Oxone triple salts.

The second strategy was to utilize the reactive decontaminants, Dichlor, ammonium persulfate, and KOH, at higher temperatures to see if increasing temperature would increase performance. Increasing temperature increases permeation rate in asphalt²⁶ and thus, could enable access of the decontaminant solution to the agent absorbed within the bitumen layer. All three of these decontaminants proved effective at decontaminating HD and VX on concrete.

The final strategy was the use of surfactants to help facilitate extraction of agent from bitumen into the water layer, which allows for reaction with the decontaminant. Surfactants were chosen to form oil and water emulsions. Previous studies show that surfactants with a hydrophobic-lipophilic balance (HLB) number of 12–14 best solubilized HD.³² Two surfactants, Tween 21 and Tergitol 15-S-9, were chosen and used as 8% solutions based on this work. Both surfactants had an HLB number of 13.

Results for the optimization of Oxone are given in Figure 21. For HD, modest improvements are shown. Increasing the temperature appeared to give very slight increases in efficacy, but efficacy remained below 90%. Similarly, addition of Tergitol had minor affect when the decontaminant was applied at 40 °C. (The influence was little.) At 60 °C, Tween and Oxone reacted to form a paste, which likely hampered reactivity. Overall, the influence of temperature and surfactant seemed minimal and was mostly obscured by the high variability in the data. In the case of VX, increasing temperature and concentration had no influence on reactivity. Only a slight increase in reactivity on asphalt was seen at 60 °C when compared with that of room temperature.

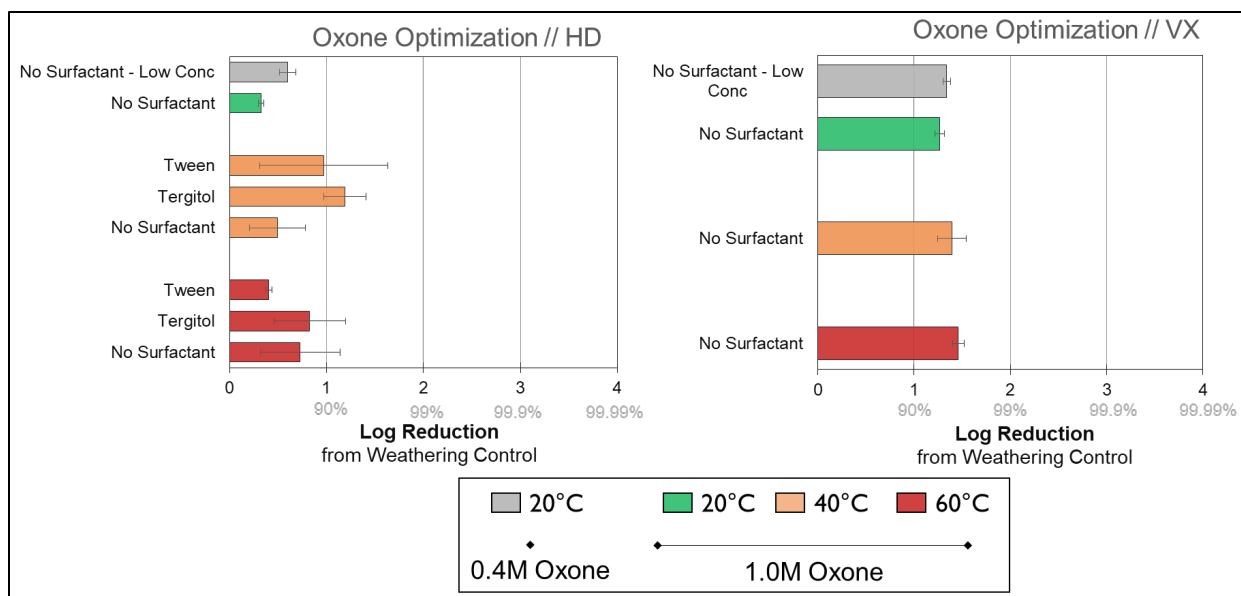


Figure 21. Influence of increased concentration, temperature, and surfactant loading on the efficacy of Oxone on asphalt.

In addition, a temperature optimization study was performed using KOH and HD, as shown in Figure 22. At RT and 40 °C, KOH had little efficacy of HD on asphalt. Increasing the decontaminant application temperature to 60 °C gave increased efficacy, but still only a slight reduction (~50%) in HD concentration was seen. The addition of Tergitol-S-15 helped with the spreading of the decontaminant, but this did not lead to an increase in performance. The KOH and Tween mixture formed a thick paste, which did not easily spread and gave lower performance when compared with that of the surfactant free mixtures. KOH does not seem to be a viable decontaminant for HD on asphalt.

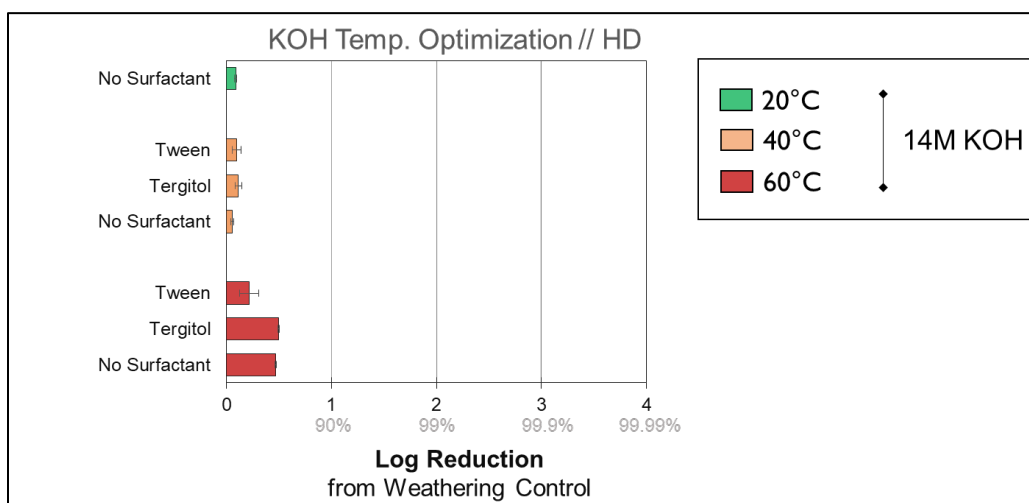


Figure 22. KOH optimization study with HD on asphalt, increasing temperature and surfactant.

The influence of temperature on the decontaminant efficacy of Dichlor and ammonium persulfate was studied. The results are given in Figure 23. The concentration of Dichlor and ammonium persulfate were kept constant at 1.0M and 2.6M, respectively. In the case of HD, increasing the application temperature of ammonium persulfate to 40 °C had little influence on reactivity. Increasing the temperature of Dichlor gave greater efficacy at 40 °C but decreased efficacy at 60 °C, which was likely due to a decreased pot life. There is slight evidence that the addition of 8% Tergitol may increase the efficacy of Dichlor on asphalt at 60 °C, but this is obscured by the high variability in the results. In the case of VX, no significant increase in efficacy was seen for either decontaminant as a result of temperature increase.

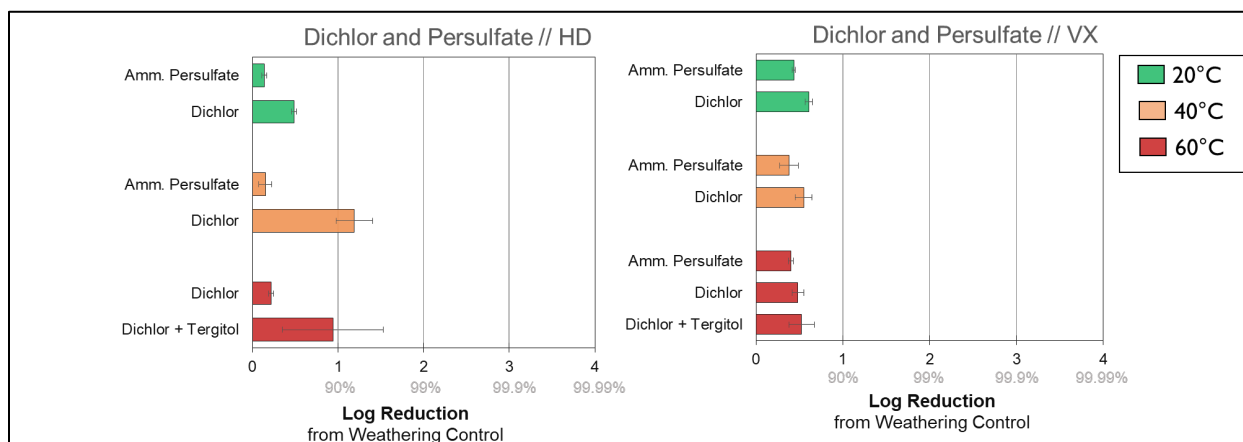


Figure 23. Influence of temperature and surfactant on the efficacy of Dichlor and ammonium persulfate on asphalt.

These results showed that decontaminant options for asphalt are highly limited. For VX, Oxone was the only decontaminant with >90% effectiveness. Similarly, Oxone was the only functional decontaminant for HD on asphalt when applied at 40 °C with a Tergitol surfactant. Previous studies have demonstrated that decontaminant efficacy against VX increases for certain oxidants when pH is raised. By raising the pH of the solution above the pK_a of the oxidant, a deprotonated peroxy anion can undergo perhydrolysis or SN_2 nucleophilic attack of the phosphorous center. Perhydrolysis is typically more rapid than oxidation, and displacement of the sulfur leads to faster decontamination. This effect is most pronounced with small peroxides, namely hydrogen peroxide, but has been shown for other peroxy species as well.³² Ammonium persulfate, Oxone, and Dichlor were prepared as basic solutions (pH 13-14) through the addition of KOH to a final concentration of 1M. These solutions were then applied to VX-contaminated panels to see if increasing pH increased efficacy.

Increasing the pH of oxidant solutions did not increase the efficacy of any of the decontaminant formulations. As shown in Figure 24, the basic oxidant solutions had similar or even lower efficacy than the unbuffered solutions. KOH may increase the degradation rate of the oxidant in solution and thus, decrease the concentration of active oxidant in solution. Overall, this was not an effective means at increasing decontaminant efficacy.

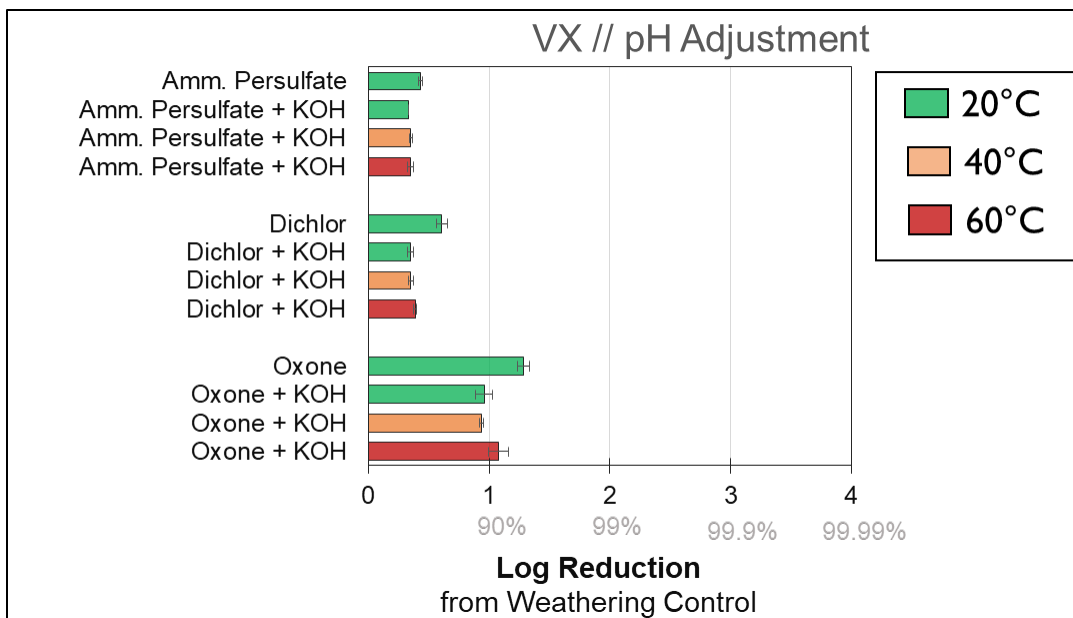


Figure 24. Influence of high pH oxidant solutions on decontamination of VX on asphalt sheets.

Another optimization approach was to perform two decontaminant treatments. It is possible that an initial Oxone treatment may prepare the surface for another decontaminant process. The idea is that if the hydrophobicity of the bitumen layer decreases upon exposure to Oxone, subsequent decontaminant treatments would be more effective. To test this, an initial treatment with Oxone was performed and then followed by another decontaminant after 2 h. The overall efficacy was measured after 4 h and compared with a single decontaminant treatment. As shown in Figure 25, this approach did not increase reactivity over a single Oxone treatment.

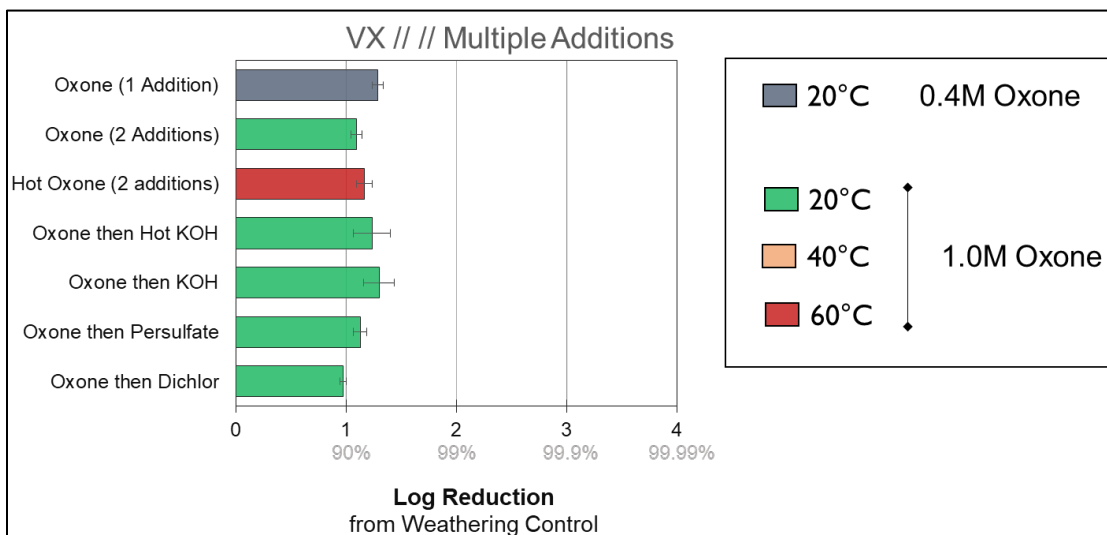


Figure 25. Influence of multiple treatments on decontamination of VX on asphalt sheets.

Because of the lack of efficacy from most reactive decontaminants, the use of alternative decontaminants such as Dahlgren Decon and Sprayable Decontaminant Slurry were investigated. Both of these products failed to give >90% reduction in contaminant on bitumen sheets for HD and VX. A summary of the performance of commercial products in comparison with the top performers on bitumen sheets is provided in Figure 26.

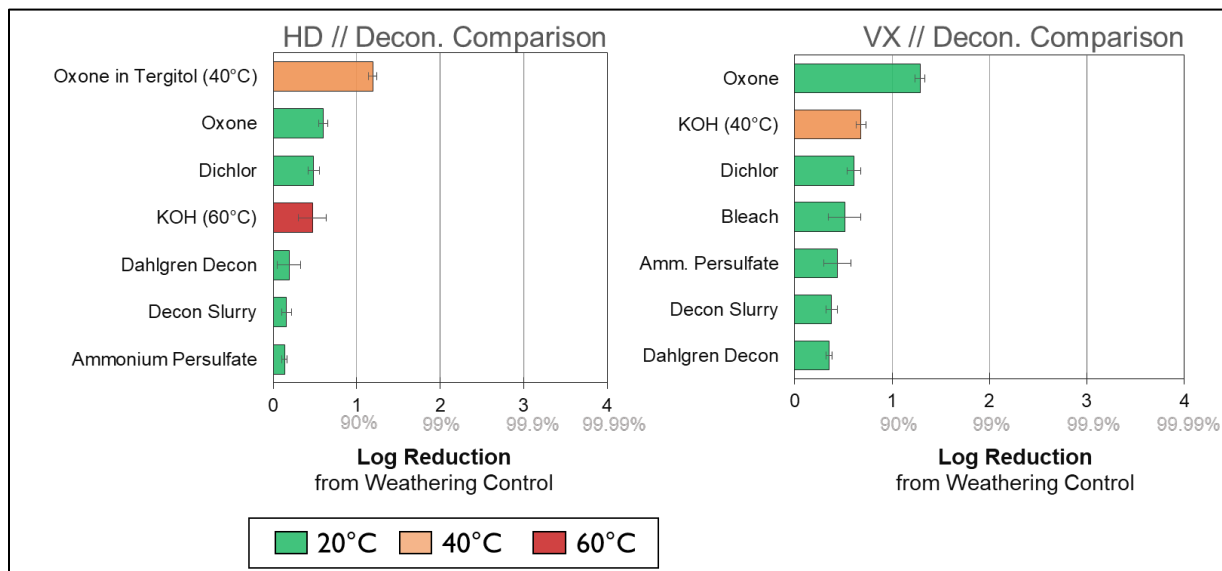


Figure 26. Summary of decontaminant efficacy on bitumen sheets with top performers and commercial products.

6.3 Cost-Benefit Analysis of Asphalt Decontamination

Screening and optimization efforts gave limited options for the decontamination of HD and VX from asphalt (Figure 27). A cost-benefit analysis was performed to compare the pricing, logistics, and efficacy of each of the potential asphalt decontaminants, as shown in Table 3. Oxone was by far the highest performer, reducing the agent concentration by 90%. Other performers, including commercial technologies such as bleach and Dahlgren, gave poor efficacy. From a logistics and cost standpoint, Oxone gives the highest performance on both agents at comparable or slightly increased cost. Dichlor and KOH are also decontaminant options, which may be used as dual-use concrete and asphalt decontaminants. It is likely a dual hazard mitigation approach may be considered in cases where a reactive decontaminant is applied prior to a barrier polymer. This strategy may be needed to yield clearance levels for reduction in MOPP levels.

Table 3. Logistics Analysis of Asphalt Decontaminants

Efficacy			Pricing				Logistics		
Compound	HD Efficacy (LR)	VX Efficacy (LR)	Conc. (M)	Price (\$/kg)	kg per Truck	Price/Truck (\$)	Shelf Life (yr)	Resale Market	Environ. Concerns
Ammonium Persulfate	0.14	0.44	2.4	0.50	2073	1036	1 - 5	Very Good	
Dahlgren	0.19	0.35	-	-	-	19000	1	None	
Dichlor	0.49	0.61	1	0.55	969	533	5	Good	
KOH	0.47	0.68	13	0.30	2761	828	10+	Very Good	Unknown
Bleach	N.D.	0.51	-	-	-	900	1 - 2	Good	
Oxone (0.4M)	0.6	1.29	0.4	1.00	931	931	10	Poor	
Oxone (1.0M)	1.19	N.D.	1.0	1.00	2327	2327	10	Poor	

-, not available.

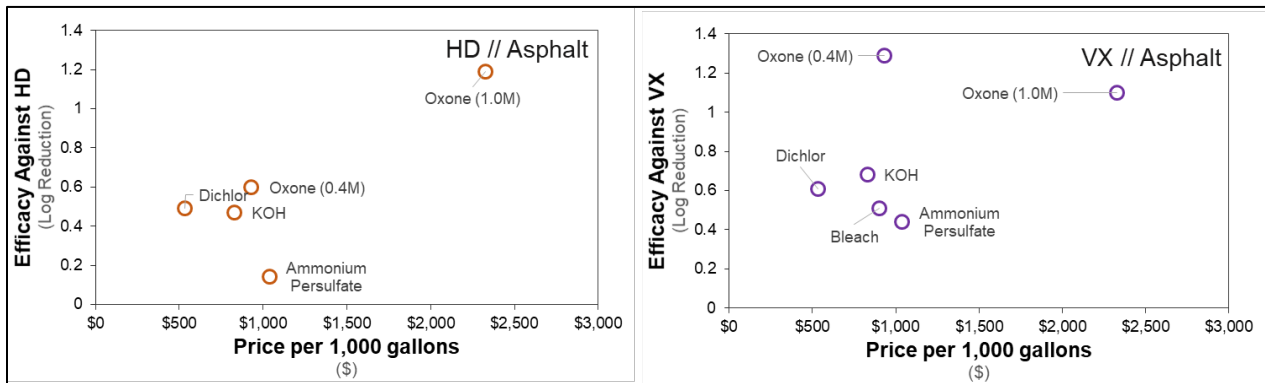


Figure 27. Cost-benefit analysis of asphalt decontaminants.

7. DISCUSSION AND DECONTAMINANT DOWNSELECTION

7.1 Discussion of Performance Requirements

Wide-area decontamination provides a unique challenge for decontaminant development. Previous decontaminants have focused on the decontamination of personnel protective equipment (PPE) and vehicles. In these cases, decontaminant performance criteria are stringent and often require 99.9% (2 log) reduction or greater in agent mass. In addition, army doctrine was centered around thorough decontamination, using specialized personnel and equipment. For wide-area decontamination, requirements may need to be considered differently, based on different operational context and changes in army doctrine.

7.1.1 Different Operational Context

The decontamination of protective equipment, vehicles, and personnel must be thorough to ensure that the warfighter is not at risk for post-decontamination exposure. After all, warfighters have prolonged and frequent contact with their weapons, uniforms, and the vehicles they travel in. However, warfighters and civilians travelling through a contaminated airport or seaport will only have fleeting, limited contact with the area. The primary purpose is to ensure that no significant vapor exposure occurs as warfighters traverse contaminated areas and that contamination is not transferred to vehicles and personnel. Therefore, a decontaminant, which reduces the hazard by 70%, may be sufficient to meet these goals.

7.1.2 Changes in Guiding Doctrine

More recent doctrine has focused on maintaining operational tempo in the battlefield and exploiting CBRN contamination rather than avoiding it. Based on this doctrine, a rapidly deployable 70% effective solution may be preferable to a 99.9% effective solution that slows operations by days to weeks. Moreover, decontamination is considered as being part of a larger hazard mitigation strategy. Therefore, it may not need to be the only battlefield solution to CBRN contamination. Small preparatory steps, such as covering key areas and assets with a protective covering, may reduce contamination by 50–70%. An initial rinse prior to the decontaminant application may reduce contamination by another 50%. A decontaminant, which may only be moderately effective without these steps, could reduce the hazard to below detectable levels. Viewing decontamination as just one step in hazard mitigation reduces the burden placed on a decontamination technology.

These influences should be considered when evaluating the performance of a wide-area decontaminant. This study highlighted several decontaminants with exceptional performance (99% or greater). It also highlighted many decontaminants with 50–90% performance. In previous programs, 70% performance may have been considered poor efficacy, and the decontaminant may have been dismissed. However, a logistically feasible, rapidly deployable 70% solution may be more than sufficient to allow warfighters and civilians to safely transit through a contaminated airport or seaport. It is also important to consider that a relatively high starting challenge (2.5 g/m^2) was used in this study, and performance may be greater at lower starting challenges. In addition, these studies used long aging times, thereby giving the agent time to absorb into the material and increase the difficulty in decontamination. Performance may also be greater at shorter aging times when the agent is more accessible to the decontaminant solution.

7.2 Summary of Results

Screening and optimization studies highlighted that reactive decontaminants can be highly effective on concrete but have limited efficacy on asphalt. Log difference plots are provided in Figure 28. On concrete, several decontaminant chemistries, including persulfates, KOH, and Dichlor, provided 99.9% or greater chemical reduction.

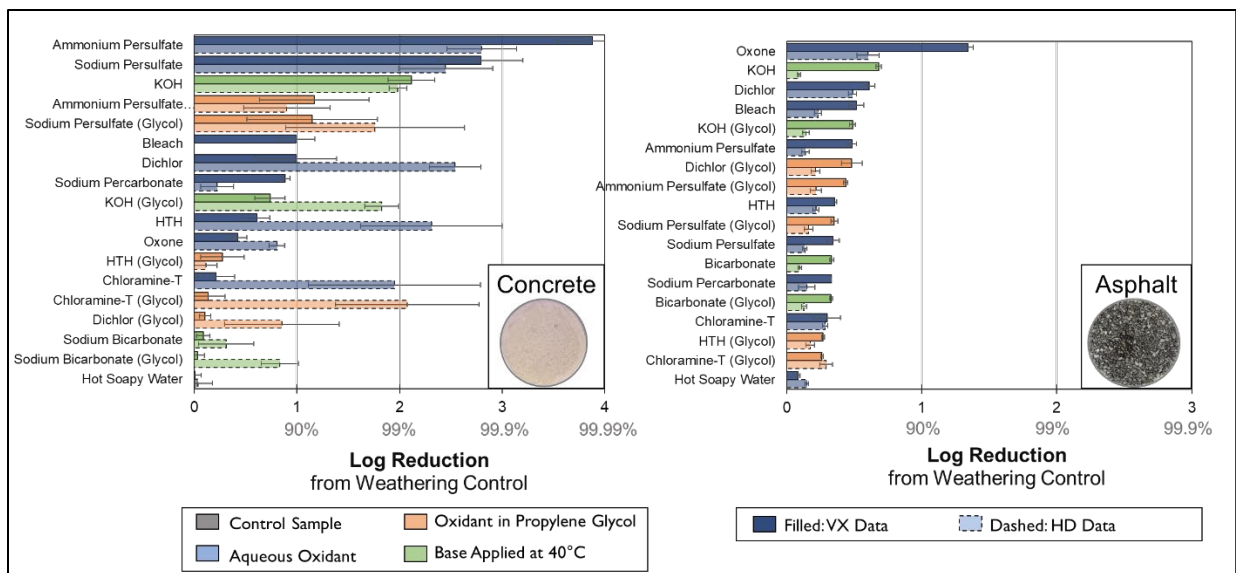


Figure 28. Reactive screening results, log difference vs weathering.

The following five decontaminants either have excellent efficacy on concrete or moderate efficacy on both asphalt and concrete:

- ammonium/sodium persulfate,
- Dichlor,
- HTH,
- KOH, and
- Oxone

Asphalt has been shown to be the most challenging substrate to decontaminate. Optimization of performance on asphalt has so far only led to slight improvements in efficacy. Increasing decontaminant application temperature, inclusion of surfactants, pH adjustment of the decontaminant formulation, use of a propylene glycol cosolvents, and multiple decontaminant treatments had little to no effect on decontaminant performance. This study was not an exhaustive screening of all potential decontamination options. However, the initial screening and optimization effort failed to find any decontaminants, which could reach 99% reduction of HD or VX (at the starting challenge of 2.5 g/m²). The difficulty of decontaminating asphalt was further supported by the poor efficacy of Dahlgren Decon and Decon Slurry, two highly successful decontaminant formulations used in other applications. Each decontaminant faced the mass transfer problem of extracting agent from a highly hydrophobic bitumen layer using an aqueous decontaminant. A successful reactive decontaminant may require the use of an organic, nonpolar solvent and a phase-transfer catalyst to reach 2 log reduction.

However, while no decontaminants reached 99.9% reduction, modest reductions of 50–70% in agent mass were considered reasonable for the five decontaminants selected.

Log reduction plots are useful for comparing order of magnitude performance differences among decontaminants. A strict fraction reduction plot helps highlight

decontaminants with moderate efficacy (50–80%). The fraction reduction comparison with weathering controls is given in Figure 29.

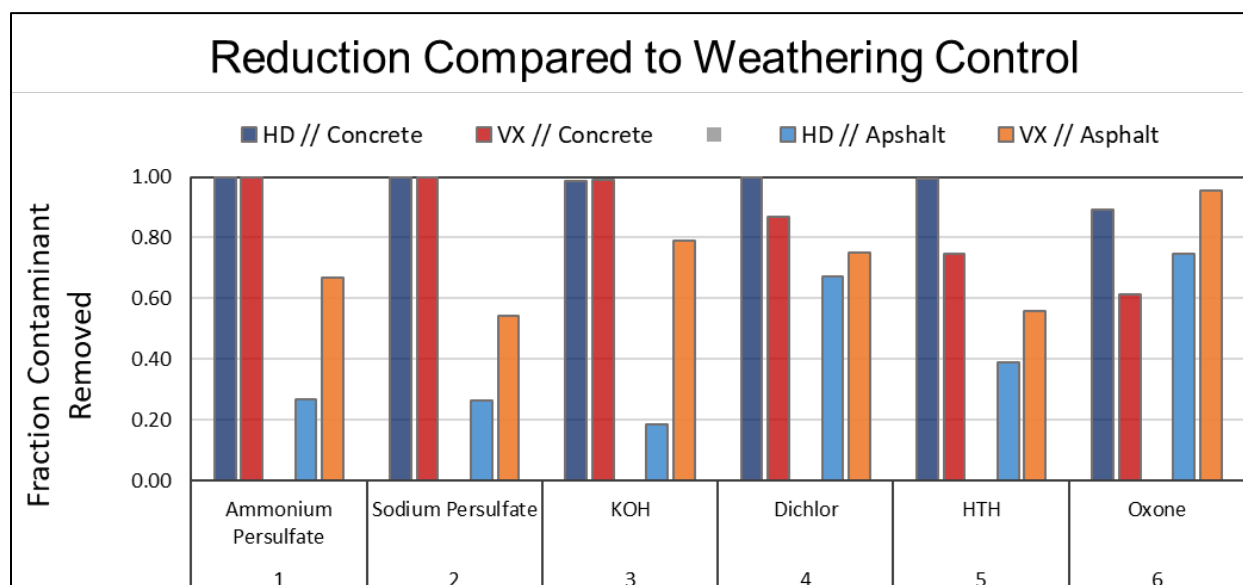


Figure 29. Fraction contaminant removed and compared with weathering controls for downselected decontaminants.

These results show that ammonium persulfate, sodium persulfate, and KOH give excellent performance on concrete for both HD and VX, but have poor to moderate efficacy on asphalt substrates. Other decontaminants, such as Dichlor and Oxone, give moderate reductions (60–80%) across all agents and substrates. It is important to note that the reductions shown in Figure 29 are compared with the weathering control and not the initial starting challenge. Weathering alone leads to 20–80% reductions, depending on the agent and substrate. The combined effect between decontamination and weathering is shown in Figure 30.

The simpler solution may be to separate the problem into specific decontaminant solutions for each substrate: reactive decontaminants for concrete and barrier polymer technologies for asphalt. Barrier polymers are currently used on a large scale for soil stabilization, dust suppression, asphalt sealcoating, and stockpile sealing. This approach is likely more expensive and logistically more difficult but may be the only option for reasonable hazard mitigation on asphalt. Future investigations will determine the efficacy of these barrier polymers for mitigating vapor and contact hazard on asphalt.

A hybrid approach may be to first apply a reactive decontaminant to both concrete and asphalt before applying a barrier polymer to asphalt. This simplifies the need for specialized equipment and protocols depending on the surface. Further testing will be performed to assess the validity of this approach.

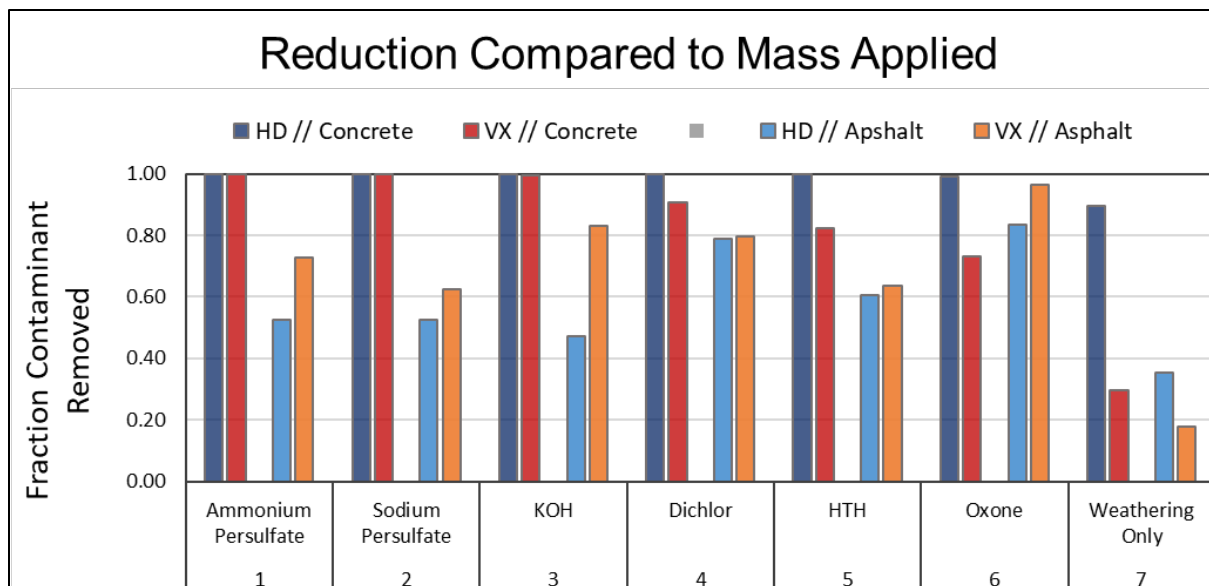


Figure 30. Fraction reduction compared with mass applied for downselected decontaminants.

7.3 Downselected Decontaminants

For this study, the five downselected decontaminants were persulfate, hydroxide, Dichlor, HTH, and Oxone. Persulfate and KOH proved to be highly effective on concrete but gave poor to modest performance on asphalt (20–60%). Dichlor was a good all-around performer, giving >60% reduction on all agents and substrates evaluated. HTH was typically outperformed by Dichlor, persulfate, and hydroxide but may prove to be the most cost-effective option. Oxone was the strongest performer on asphalt and gave a modest performance on concrete. Each of these decontaminant chemistries offers distinct advantages and disadvantages Table 4.

Table 4. Analysis of Downselected Decontaminants

Decontaminant	Conc.	Efficacy Concrete	Efficacy Asphalt	Pros	Cons
Persulfate	1.0 to 2.6M	HD: Highly Effective VX: Highly Effective	HD: Poorly Effective VX: Somewhat Effective	<ul style="list-style-type: none"> • Most Effective Concrete Decontaminant • Reasonable price (\$1.00/gal) • Prior use in environmental cleanup 	<ul style="list-style-type: none"> • Etchant: Potentially corrosive • Short shelf life when wet • Poor asphalt efficacy
KOH	14.0M	HD: Effective VX: Effective	HD: Not Effective VX: Somewhat Effective	<ul style="list-style-type: none"> • Likely highly effective for G-Series and other compounds 	<ul style="list-style-type: none"> • Very corrosive • Little promise for optimization • Highly exothermic when mixed • Poor asphalt efficacy
Dichlor	1.0M	HD: Effective VX: Somewhat Effective	HD: Somewhat Effective VX: Somewhat Effective	<ul style="list-style-type: none"> • Inexpensive, readily available 	<ul style="list-style-type: none"> • Moderate performance against VX
HTH	1.0M	HD: Effective VX: Somewhat Effective	HD: Somewhat Effective VX: Somewhat Effective	<ul style="list-style-type: none"> • Already fielded as decontaminant • Very inexpensive 	<ul style="list-style-type: none"> • Poor efficacy on VX and concrete • Poor efficacy on asphalt
Oxone	0.4 to 1.0M	HD: Effective VX: Somewhat Effective	HD: Somewhat Effective VX: Somewhat Effective	<ul style="list-style-type: none"> • Only decontaminant effective on asphalt • Long shelf life 	<ul style="list-style-type: none"> • May react with asphalt surface • Expensive

Decontaminant efficacy was used as the primary downselection criteria for these studies. Considerations such as availability, material compatibility, pot life, shelf life, safety, scalability, and environmental toxicity are also important in developing an effective decontaminant. A summary of the decontaminants, their measured efficacy, supply sources, and likely substitutes are given in Figure 31.

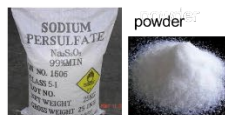














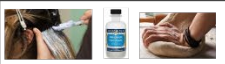









Sodium Persulfate	Dichlor	HTH	Potassium Hydroxide	Oxone
 powder 	 granular 	 granular tablets 	 pellets flakes 	 powder 
 99.9% Effective on Concrete Poorly Effective on Asphalt	 90 - 99% Effective on Concrete ~70% effective on Asphalt	 70-90% Effective on Concrete Poorly Effective on Asphalt	 90+% Effective on Concrete Poorly Effective on Asphalt	 60+% Effective on Concrete 90% effective on asphalt
 Used as hair bleach, in baking, to etch circuit boards	 Used as pool shock	 Used as pool shock, water treatment	 Used for food cleaning, descaling, water treatment	 Used as non-chlorine pool shock
Available in bulk from chemical suppliers 	Available in bulk from pool supply stores 	Available in bulk from pool supply stores 	Available in bulk from chemical suppliers 	Available in bulk from pool supply/chemical suppliers 
Substitutes: Ammonium Persulfates	Also known as sodium diisochlorocyanurate	Also known as calcium hypochlorite	Substitutes: Sodium Hydroxide (Caustic, Lye)	Also known as potassium peroxymonosulfate, MPS

Figure 31. Summary of downselected reactive wide-area decontaminant chemistries.

The persulfates were the most effective decontaminants on concrete, giving 99.9% reduction at a 2.5 g/m² starting challenge. Two persulfates were studied: ammonium and sodium persulfate. Both chemicals likely operate by the same mechanism of action; they differ only in aqueous solubility. Ammonium salt is slightly more soluble (2.6M) than sodium salt (2.0M). The concentrations that were used correlate to a 54 and 48% solution in water for ammonium and sodium persulfate, respectively. These concentrations could be reduced with further optimization. Persulfates can either react through a radical mechanism or through in-situ formation of the peroxymonosulfate (Figure 32). Persulfates are used as industrial etchants in soil remediation and as dough conditioner in baking and hair bleaches. The ability to etch metals may lead to material compatibility issues with sprayer systems, but this has not been tested. Toxicity studies show that persulfate solutions used in cosmetic formulations are largely safe. Persulfates have a long shelf life when dry but decompose within several weeks when wet.

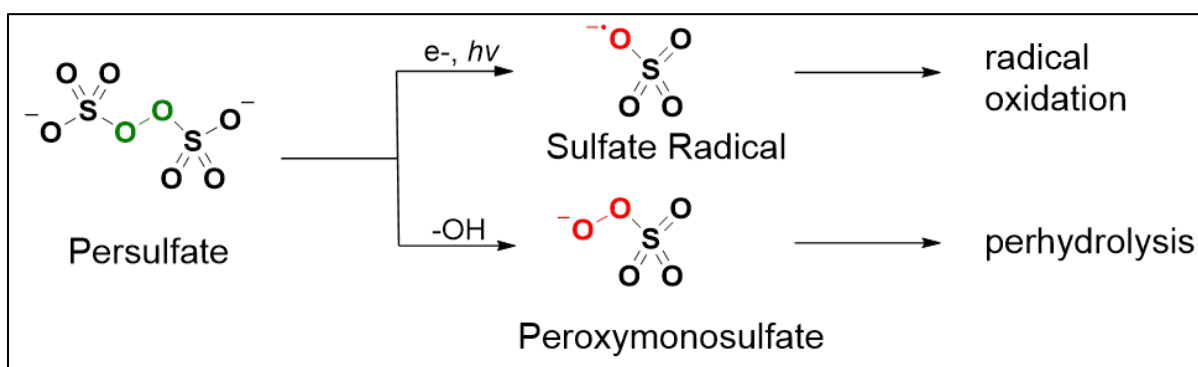


Figure 32. Proposed mechanism of action for persulfate decontamination.

KOH is a common base. It provided 99 and 80% reductions as starting challenges for VX and HD on concrete, respectively. The KOH decontaminant performed poorly with VX on asphalt, giving only 18% efficacy. A high concentration (14M) was required for effective decontamination, with reduced concentrations giving decreased performance. The effective formulation was a concentrated 78% solution in water. Increasing the decontaminant application temperature had little influence on decontaminant efficacy. The mechanism of action is basic hydrolysis for HD and VX, forming thiodiglycol adducts for HD and mostly EMPA for VX. Further studies showed that only 1–8% of EA 2192 is formed when using KOH to decontaminate VX on concrete. KOH is used in a large number of industrial, agricultural, and commercial applications. Sodium hydroxide (also known as lye or caustic soda) is likely an acceptable substitute for KOH because it is more readily available and less expensive. One main concern is the potential for strong basic solutions to easily cause chemical burns. Although some efficacy was seen using the 39% solution, this solution is still likely extremely caustic. Whereas this can be safely handled with PPE, runoff may pose a threat to personnel, sensitive equipment, and the environment. Moreover, preparation of such a highly concentrated solution produces a large amount of heat, which may make it difficult to mix the solution on a large scale.

Dichlor produces hypochlorite and hypochlorous acid when dissolved in water. On concrete, Dichlor reduced the starting challenge by 99% for HD and 90% for VX. A modest 50–70% reduction was found on asphalt. The concentration tested was 1.0M, which is approximately a 25% solution in water. Although not as effective as KOH or persulfate on concrete substrates, Dichlor provides an additional option if these decontaminants are not feasible due to logistical concerns. Dichlor is widely available as a chlorine pool shock chemical and is roughly half as expensive as ammonium or sodium persulfate. Dichlor is a strong oxidizer and forms a weakly acidic (pH 6) solution in water. Therefore, it is likely more compatible with sprayer materials than highly caustic solutions of bleach or hydroxide. Dichlor has a reasonably long shelf life although it is incompatible with acidic chemicals. A mixture of Dichlor with acidic chemicals results in the formation of toxic chlorine vapors.

HTH is also a potential decontaminant. A 10% slurry of HTH was used, as this concentration is typically recommended for other decontaminant applications. Calcium hypochlorite is a direct source of the hypochlorite and can directly oxidize both HD and VX in a similar manner to bleach. HTH was the least expensive decontaminant option. It cost roughly \$400 to fill a 1000 gal of TPU with decontaminant solution. However, the HTH performance was moderate, and HTH was typically outperformed by Oxone and Dichlor on asphalt and persulfates and KOH on concrete. This decrease in performance may be offset by its low cost and ease of acquisition.

Oxone is an inorganic peroxide, which readily oxidizes HD and VX. Oxone is mostly sold as a triple salt, a shelf stable mixture of three different components (Figure 33). Oxone is typically used as a non-chlorine pool shock chemical, but it is also used in industrial applications as an oxidant. Oxone provided the best performance on asphalt when compared with any other decontaminant formulation tested. It also performed moderately well on concrete substrates yielding 90% reduction of HD and 60% reduction of VX. These results could be further optimized. Modest increases in efficacy could be seen on asphalt by increasing the decontaminant application temperature and adding a surfactant. Increasing the concentration of Oxone may have slightly increased efficacy, but it also greatly increased the cost of the decontaminant application.

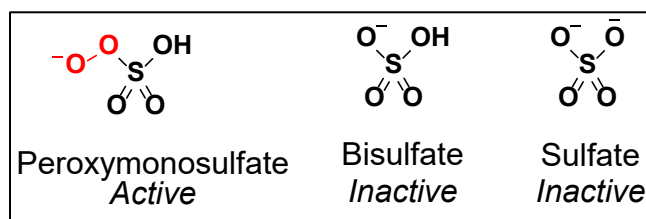


Figure 33. Principal components of Oxone triple salts.

In general, persulfate and KOH are the best options for concrete decontamination. Dichlor and Oxone provide moderate across the board efficacy for both concrete and asphalt. HTH provides an inexpensive and logistically simple option but at the cost of performance. However, efficacy is not the only consideration in the decontaminant process, and additional options will have to be considered in the downselection step. Future studies will be focused on a logistics analysis of these downselected formulations. The following considerations will be studied over the next several quarters for the reactive decontaminants:

- Scalability: can the decontaminant be prepared safely and easily on a large scale?
- Shelf life: how long can the decontaminant be stored?
- Pot life: how long does the decontaminant remain active after mixing?
- Environmental safety: will the decontaminant pose a significant threat to local environments?
- Detector compatibility: can detectors still function in the presence of the decontaminant?
- Material compatibility: will the decontaminant corrode the decontaminant applicator and PPE with which it comes into contact?

These issues will be studied to further downselect this list to 1–3 potential chemistries. These chemistries will be optimized to produce final effective formulations. The focus will be on minimizing decontaminant concentration while maintaining performance. The final stable configurations will be further tested and evaluated.

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LITERATURE CITED

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ACRONYMS AND ABBREVIATIONS

ACN	acetonitrile
APOD	airport of disembarkation
CHCl ₃	chloroform
CSA	calcium sulfoaluminate
CWA	chemical warfare agent
CWAD	chemical wide-area decontaminant
DESH	diisopropylaminoethanethiol
Dichlor	sodium dichloroisocyanurate
EA 2192	diisopropylaminoethyl methyl thiolo-phosphonate
EMPA	ethyl methyl phosphonic acid
HCP	hardened cement paste
HD	bis(2-chloroethyl) sulfide, mustard gas
HLB	hydrophobic–lipophilic balance
HTH	high test hypochlorite
KOH	potassium hydroxide
KPP	key performance parameter
MOPP	mission oriented protective posture
NMR	nuclear magnetic resonance
PG	propylene glycol
PPE	personnel protective equipment
SPOD	seaport of disembarkation
TPU	tank pumping unit
TRL	technology readiness level
VX	ethyl N-2-diisopropylaminoethyl methylphosphonothiolate
w/c	water to cement

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APPENDIX A: EXTRACTION METHODOLOGY

A.1 Extraction of HD from Concrete

A dynamic extraction efficiency test was performed to determine an appropriate extraction method for bis(2-chloroethyl) sulfide (HD) from 1/8 in. concrete coupons. Based on literature precedent, chloroform (CHCl_3) and acetonitrile were chosen as the initial solvents. Previous studies have shown that crushing concrete increases extraction rate and overall extraction efficiency. Therefore, initial studies tested both crushed and non-crushed concrete coupons. Moreover, extraction may be efficient for large concentrations of contaminant but may be less efficient for low levels of contaminant, so three different spike levels were tested. The initial results at the high-spike level (Figure A-1) show that crushing the concrete leads to a more rapid initial extraction; however, over time, it leads to a decrease in extracted mass. This decrease is likely a result of reactivity, as the highly basic concrete may slowly hydrolyze HD in solution. Crushing the concrete greatly increases the surface area and leads to increase in the rate of this mass transport (surface area driven) process.

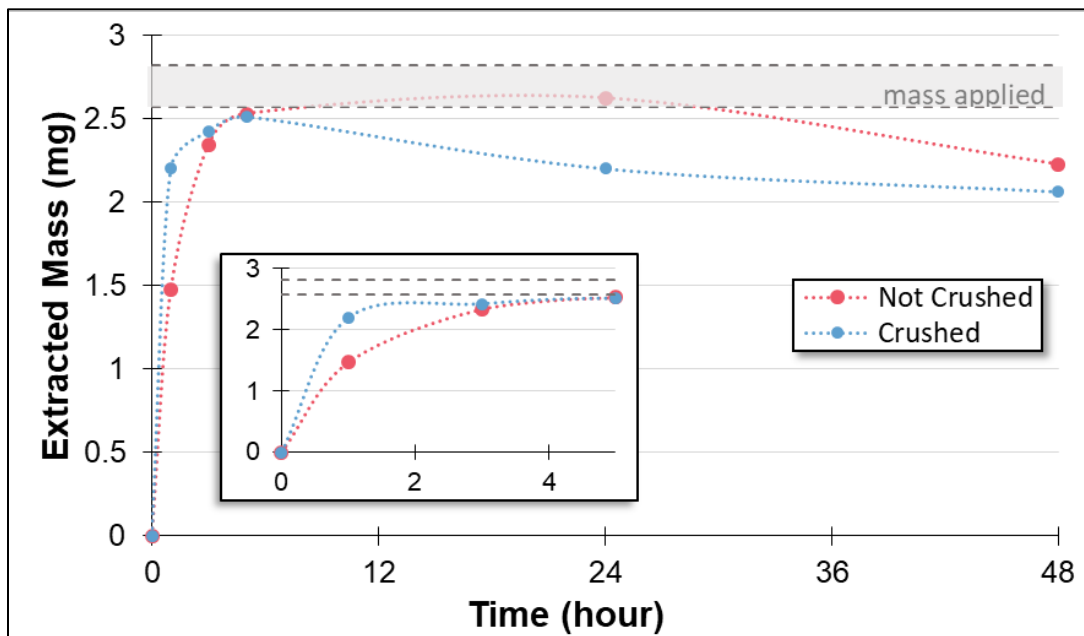


Figure A-1. Comparison of crushed vs non-crushed concrete for extraction of HD with CHCl_3 .

This effect was seen to a greater extent at the low and mid-spike levels, as shown in Figure A-2. Poor recovery (20–60%) was seen for the acetonitrile and CHCl_3 samples. CHCl_3 proved the superior extraction solvent, but the recoveries were poor. Degradation was seen after 48 h in all of the crushed samples. It was unclear whether the low mass recovery was a result of reactivity with concrete or poor extraction efficiency.

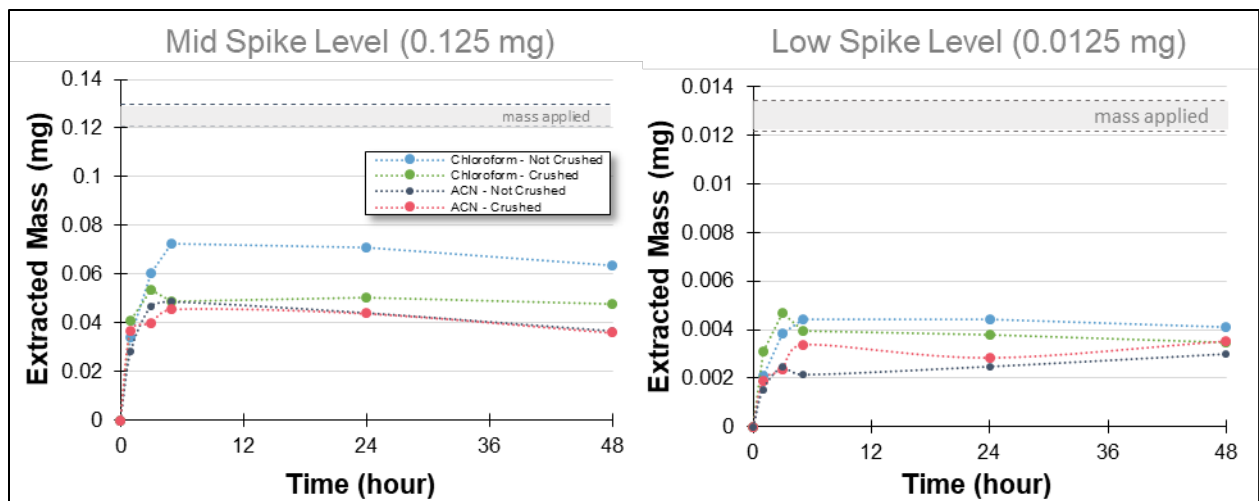


Figure A-2. Extraction of HD from concrete coupons for crushed and uncrushed coupons.

To determine whether the poor mass recovery was a result of reactivity, an extraction efficiency test was run using quenched concrete, which was treated with a solution of acetic acid, so that the pH of the concrete surface was ~ 7 . The quench conditions were determined by titration of a crushed concrete slurry in water with acetic acid. As shown in Figure A-3, $>80\%$ extraction of the quenched concrete solution was achieved after 24 h. Recoveries were poor for the non-quenched concrete due to reactivity during the aging process. This demonstrates that HD can be reasonably extracted from a panel after 24 h using CHCl_3 .

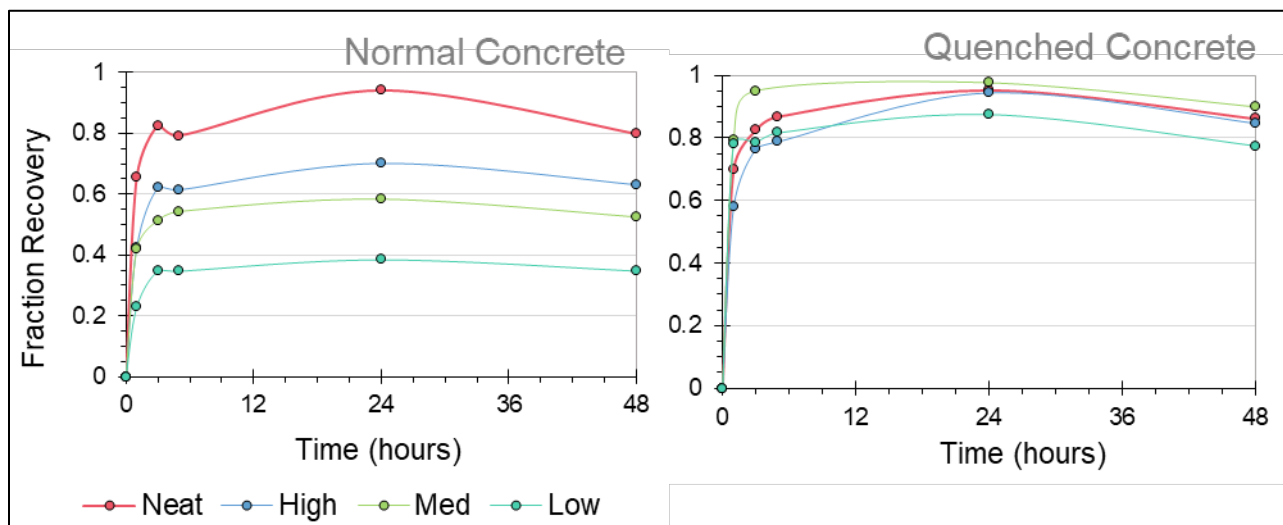


Figure A-3. Fraction recovery of a normal (left) and quenched (right) concrete coupon.

A.2 Extraction of Ethyl N-2-Diisopropylaminoethyl Methylphosphonothiolate (VX) from Concrete

Extraction of VX from concrete proved more straightforward. Based on literature precedent, both isopropanol (IPA) and acetonitrile (ACN) were tested as extraction solvents. As shown in Figure A-4, IPA gave acceptable (>80% extraction) of VX after 24 h for all the spike levels tested. Coupons were treated with 5.0 (high), 1.5 (mid) or 0.1 mg (low) doses of VX, aged for 2 h, and extracted with 40 mL of IPA (red) or ACN (yellow). Recoveries after 24 h are provided below.

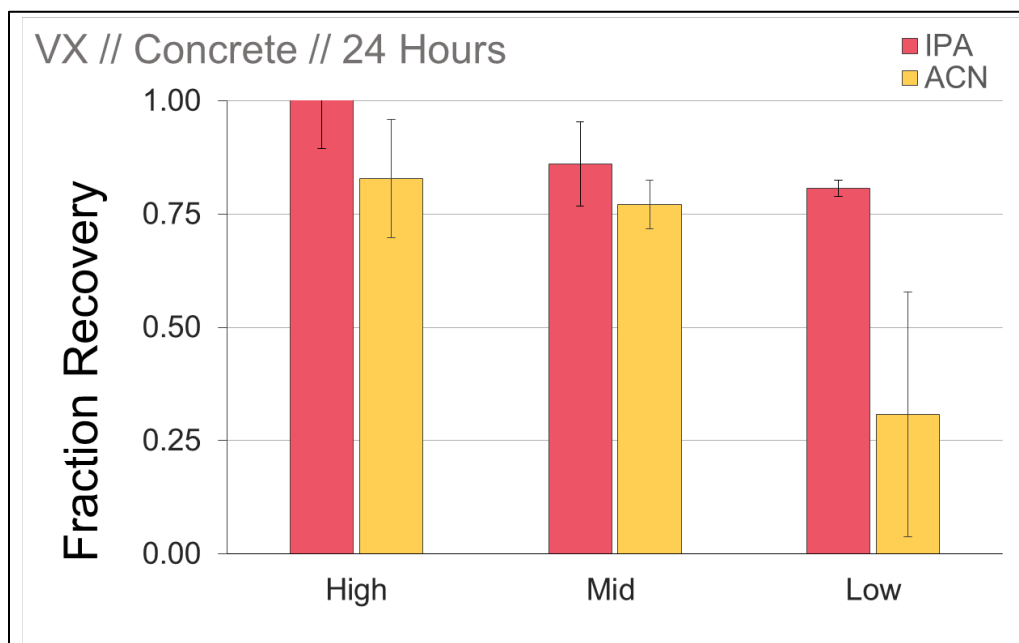


Figure A-4. Extraction of VX from CSA concrete coupons.

A.3 Extraction of HD from Asphalt

Previous literature has demonstrated that extraction of chemical agents from asphalt is particularly troublesome. Both HD and VX are reasonably nonpolar and therefore, quite soluble in the bitumen (coal tar) binder found within asphalt. Bitumen can be dissolved in nonpolar organic solvents such as hexane and CHCl_3 , but a large amount of dissolved bitumen can lead to matrix interference, injector clogging, and other analytical issues. For this reason, a broad number of extraction solvents were screened after a 2 h aging period, using moderately nonpolar solvents or mixtures of polar and nonpolar solvents. As shown in Figure A-5, this screening identified four solvents, which yielded ~90% extraction efficiency after 3 h. However, the 24 h samples gave low responses, likely due to analytical interference from the extracted matrix. Visually, the 24 h matrices from this solution were sludgy, dark black mixtures that were difficult to filter and analyze. After some analytical optimization, a 70/30 ratio of $\text{ACN}:\text{CHCl}_3$ was selected as the ideal extraction solvent based on interference and additional extraction studies performed at an age time of 24 h. This solvent mixture gave >85% extraction efficiency

for mid (1.0) and high (6.4 mg) dose levels. Low level analysis was difficult due to evaporation of the agent. Panels were dosed with 6.4 mg of VX, aged 2 h, and extracted using 20 mL of solvent. Extracted mass was analyzed by aliquots after 3 and 24 h time periods.

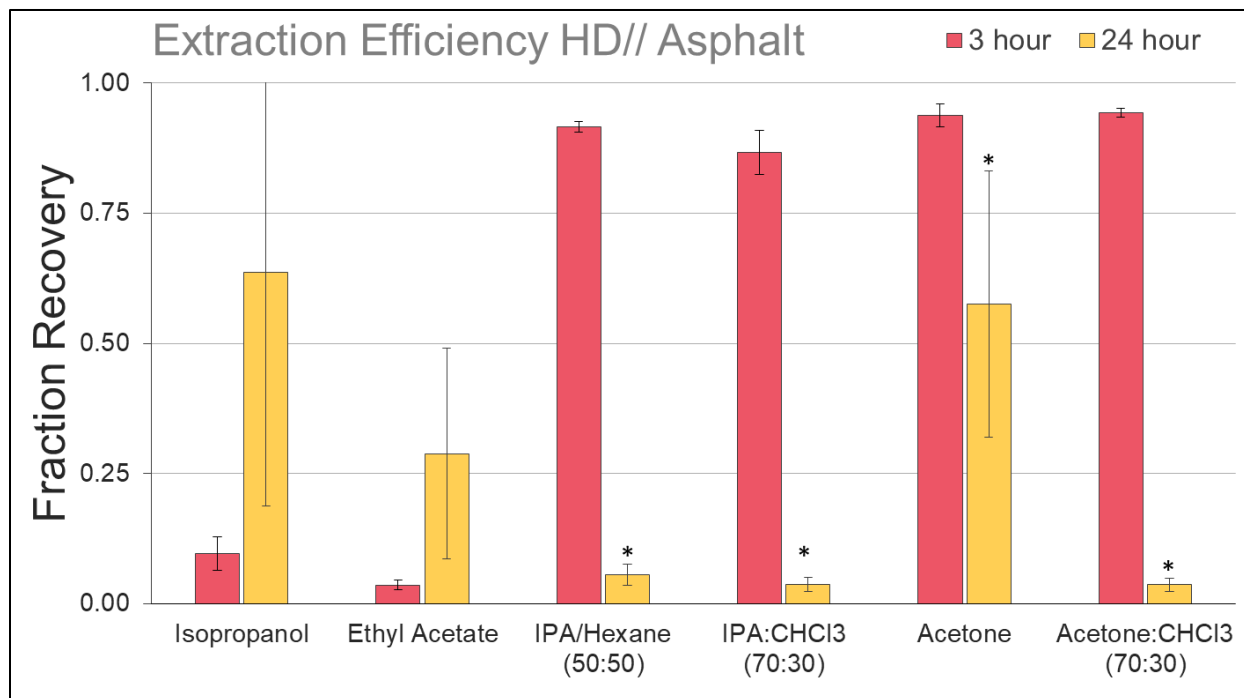


Figure A-5. Extraction solvent screen of HD on bitumen sheets. (*Indicates likely analytical interference issues due to matrix.)

A.4 Extraction of VX from Asphalt

As with HD, VX extraction from asphalt relies on the use of a sufficiently nonpolar solvent to extract the agent and avoids being too nonpolar as to completely dissolve the matrix and lead to interference issues. As shown in Figure A-6, three solvent systems were identified that could extract at least 80% of the mass of VX after a 24 h age time. Of these solvent systems, a 70/30 mixture of IPA and CHCl₃ was used because of favorable interference results. An extraction time of 3 h was selected to better fit the testing schedule.

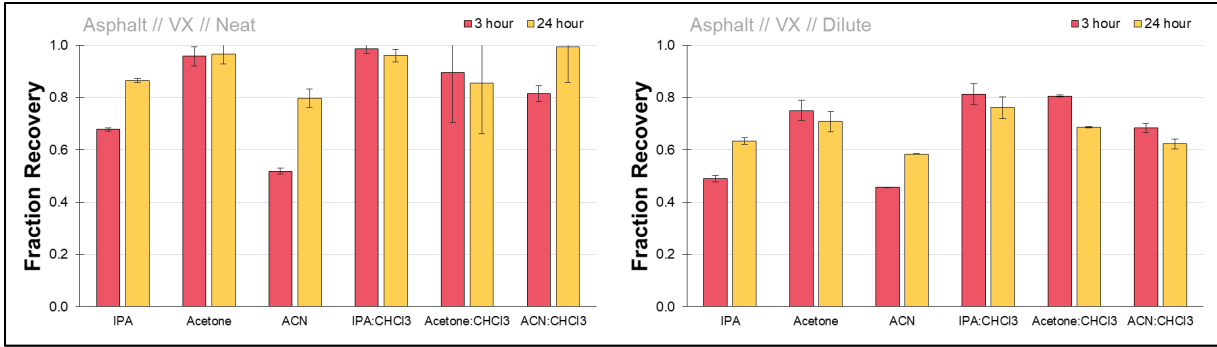


Figure A-6. Extraction of VX from bitumen asphalt sheets using a variety of solvents.

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APPENDIX B: QUENCH METHODOLOGY

To correctly report decontaminant performance, it was essential that the reactive components in the decontaminant were quenched prior to extraction. In the absence of a quench, a reactive decontaminant could reduce the mass of chemical agent in the panel, either due to mass transport issues or poor reactivity in aqueous media. It may be possible that although the decontaminant is non-reactive in a material, it may be reactive when the agent and the decontaminant solution are extracted into an organic solvent. If the remaining agent is determined by analyzing the organic solvent extract, improper quenching may give a low agent concentration in the extract, which can be falsely attributed to decontaminant performance. For this reason, a quenching study was designed to ensure that no reactivity occurred in the extract after the panel was quenched. In this study, a decontaminant was placed on a panel, aged for 4 h (same residence time as the screening experiments), and then, a saturated solution of sodium thiosulfate or tetrahydrothiophene (oxidative decons) or acetic acid (basic decontaminants) was added. After 1 h, the panel was placed in an extract solvent that had been spiked with chemical agent. The concentration of the extract was monitored over time to determine if any reactivity occurred within the extract solvent. This methodology was developed after initial studies showed that 1 h quench time was sufficient and that sodium thiosulfate (VX) and tetrahydrothiophene (HD) could be analyzed without interference issues.

B.1 HD Quench Methodology

Quenching of bases was straightforward. Potassium hydroxide (KOH) and Bicarbonate were neutralized using acetic acid. The concentration of acetic acid was selected based on the amount of base added to coupon in such a way that a 1/1 molar ratio of base to acetic acid was used.

Initially, sodium thiosulfate was selected as a quench for oxidative decontaminants. This was found to effectively neutralize all of the oxidative decontaminants after it was added as a saturated solution. However, a review of the literature found that sodium thiosulfate could be reactive towards HD. Sodium thiosulfate not only acts as a reducing agent but can also act as an α nucleophile and react with electrophilic sites such as the sulfonium adduct in HD. The reactivity of sodium thiosulfate with HD was confirmed experimentally. A concrete coupon was dosed with 3 μ L of HD and aged for 6 h. After aging, 4 mL of a saturated solution of sodium thiosulfate or sodium sulfite was added. After 1 h residence time, the quench was removed and the panel was extracted with isopropanol. As shown in Figure B-1, the addition of sodium thiosulfate led to a nearly order of magnitude reduction in the extracted mass. The effect was even more pronounced with sodium sulfite, which gave nearly two orders reduction. This is distinct evidence that sodium thiosulfate reacts with HD in concrete.

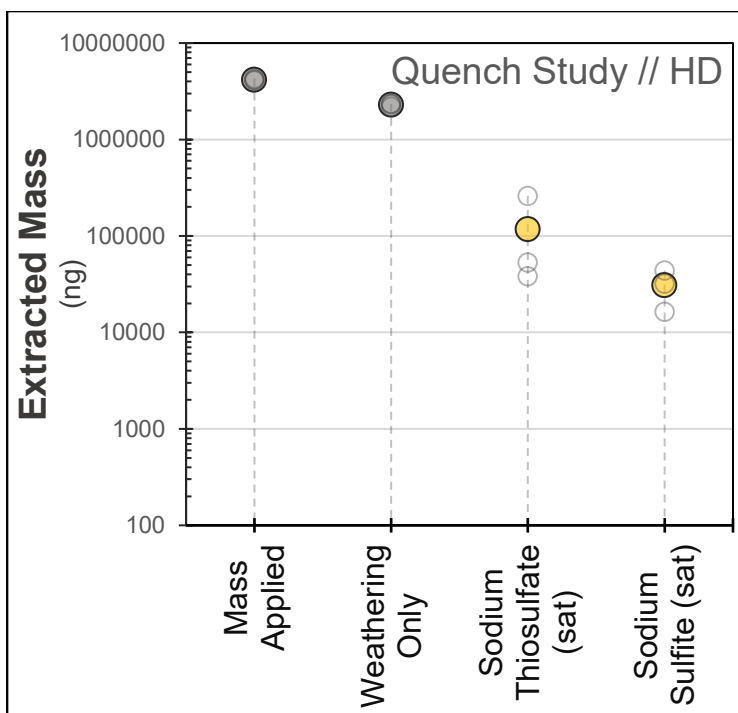


Figure B-1. Test for reactivity with HD with sodium thiosulfate and sodium sulfate on a concrete substrate.

An additional study was performed to see if a quench was even necessary given the long decontaminant residence time. It is possible that the decontaminant may completely decompose or react with the matrix over the course of the 4 h residence time, so it may not be necessary to quench the substrate prior to extraction. This was examined by a quench test, which has been outlined in previous reports. In this test, decontaminant was added to a panel and aged for 4 h. An extraction solvent spiked with HD was then added, and the concentration in the extract was monitored over time (at 1, 3, and 24 h). If the decontaminant is quenched, then the concentration should remain stable in the extract. If the decontaminant continues to react with contaminant in the extract, the concentration will drop over time.

As shown in Figure B-2, the panels containing water, ammonium persulfate, sodium percarbonate, chloramine-T and Oxone self-quenched prior to the addition of the extraction solvent. The concentration in the extraction solvent remained stable over the 24 h time period. However, bleach, HTH, and Dichlor continued to react after the extraction solvent had been added, thus demonstrating that an additional quench process is needed.

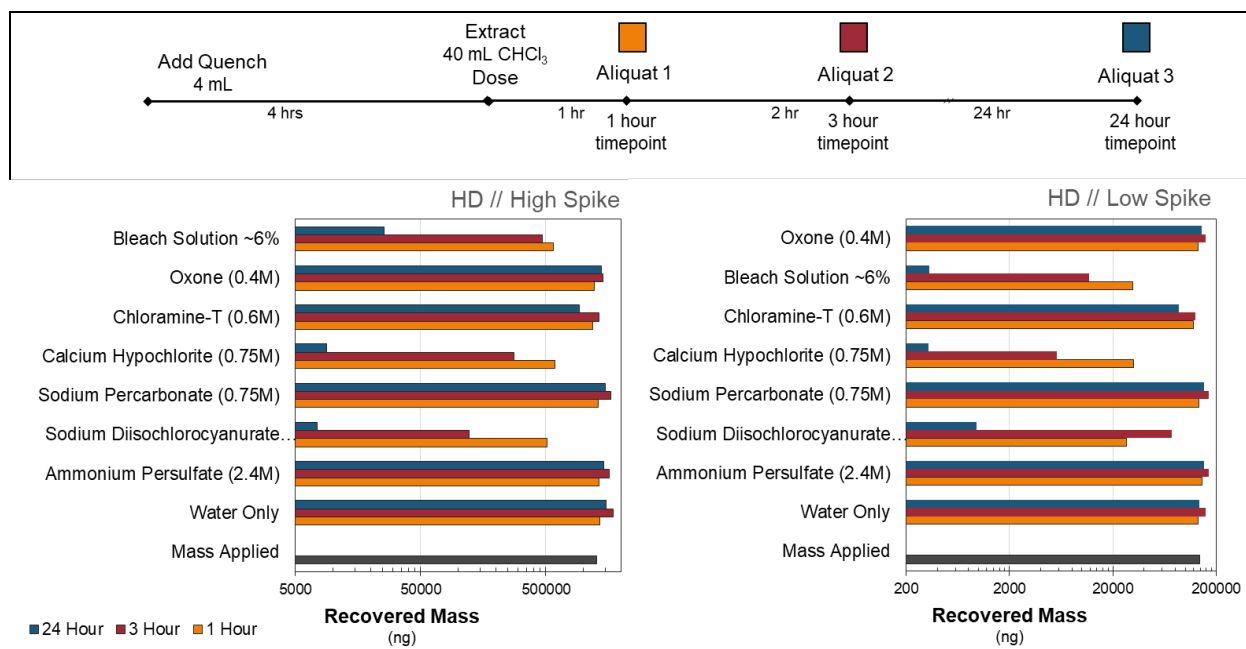


Figure B-2. Self-quench test for HD and concrete at high- (left) and low-spike levels (right).

Tetrahydrothiophene (THT) was tested as a sacrificial reductant to quench HTH, bleach, and Dichlor. THT is readily oxidized to form sulfolane, a polar solvent. In a similar quench test, THT was found to effectively quench Dichlor and HTH and had moderate efficacy at quenching bleach. Results from this study are given in Figure B-3. For this study, 2 mL of 4M THT were used, but later studies confirmed that 0.75 mL of 7M THT also gave effective quenching. This methodology was used as the updated quench methodology for any following studies. Quench only controls were carried through subsequent studies to ensure that the quench reacted with the contaminant in the panel. Interference studies demonstrated that THT could be used with current analytical methods.

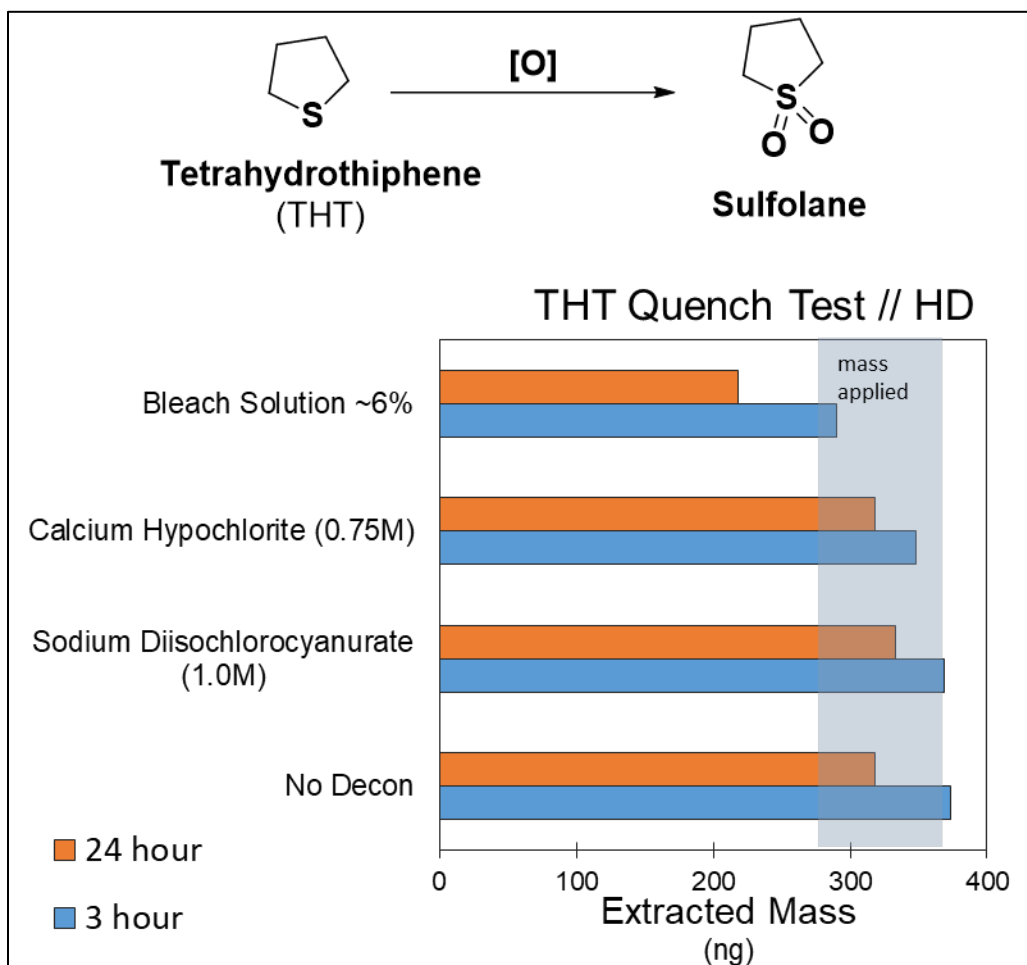


Figure B-3. THT quench test. Decontaminant was quenched after 4 h with 2 mL of 4M THT in MeOH. (One hour after the addition of quench, the solution was spiked with a dilute solution of HD, and the concentration was measured after 3 h [blue] and 24 h [orange] time periods.)

B.2 VX Quench Methodology

It was found that only minimal reactivity occurred between sodium thiosulfate and VX. Therefore, sodium thiosulfate was used as a quench for all VX studies. A 4 mL aliquot of saturated sodium thiosulfate was added to each coupon at the end of the decontaminant aging time (typically 4 h). The coupon was removed from the quenching solution (if any remained) and then was extracted using isopropanol (concrete). The extract was immediately spiked with 1 mg of VX and allowed to sit in the extraction solvent for 24 h. The post-quench mass recovered was measured after 24 h. As shown in Figure B-4, all tested configurations fell within the expected mass delivered, within error. Both HTH and KOH had evidence of some small amounts of reactivity based on EMPA detected within the extraction mixture, but this was <1% of the applied mass. Tests were only performed on concrete matrices, as decontaminant permeation was much more substantial within these matrices. If the quench was sufficient to

permeate into concrete and react with any remaining oxidant, it was likely sufficient to react with decontaminants on asphalt, which showed little evidence of permeation into the material.

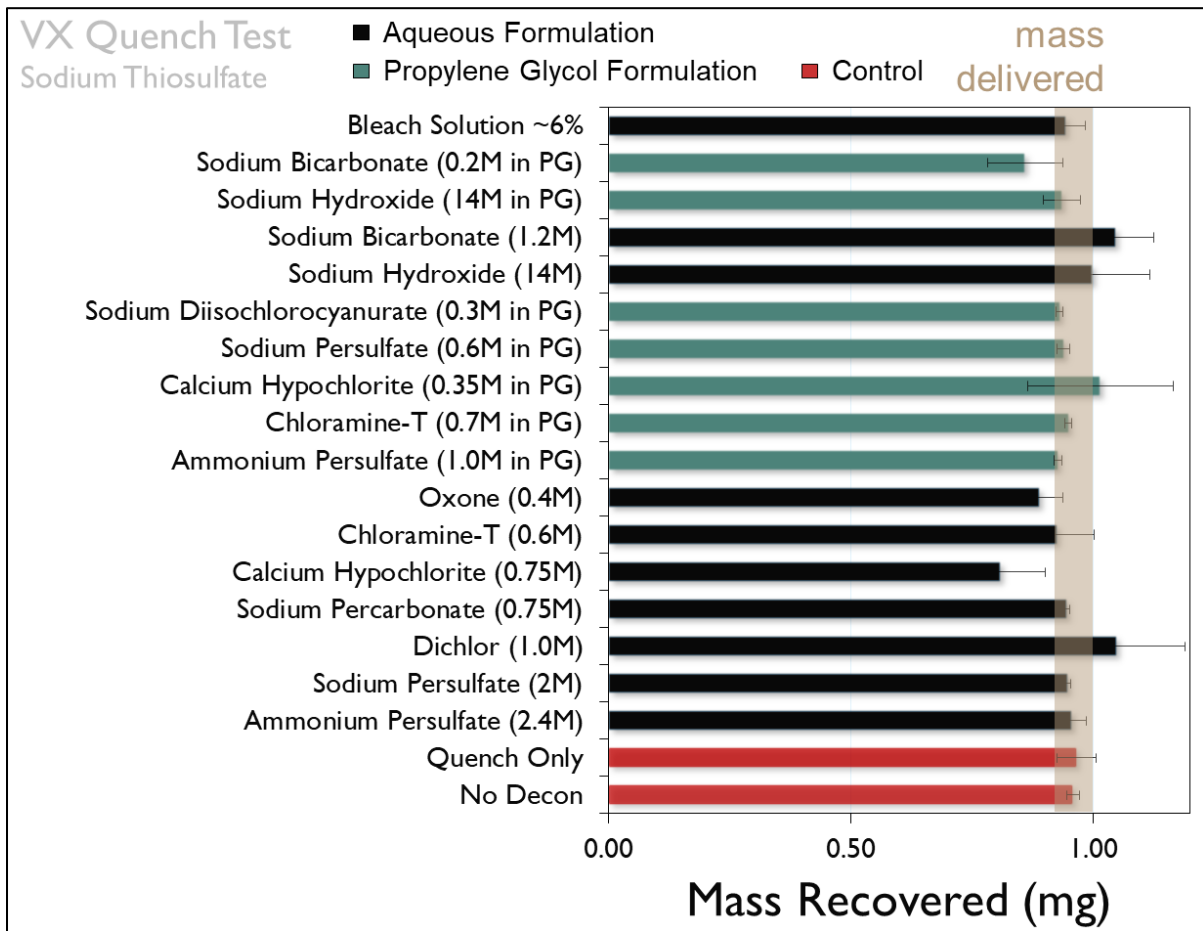


Figure B-4. Quench test using VX on concrete.

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