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Chemical Wide-Area Decontamination, III: Barrier Polymers for Contamination Mitigation

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14. ABSTRACT
A wide-area decontaminant is needed to rapidly respond to and recover from potential chemical warfare agent release on exterior surfaces at transportation terminals and facilities such as runways and docks at airports and seaports. A novel hazard mitigation strategy was explored whereby water-based barrier polymers encapsulate the contamination and reduce the vapor and contact risks. An initial selection of widely available polymers was made, and polymer properties such as cure time and film thickness were measured on asphalt and concrete substrates. Fourier-transform infrared permeation measurements were attempted using a simulant, and approximate breakthrough curves were attained for each polymer. Efficacy at reducing the contact hazard of bis-(2-chloroethyl) sulfide and *O*-ethyl-*S*-(2-diisoproylaminoethyl) methyl phosphonothiolate (HD and VX, respectively) on concrete and asphalt was analyzed directly. After efficacy analysis, a cursory logistics analysis was performed to compare cost, storage, application, safety, and environmental profiles associated with use of each polymer. A list of polymers for further study is provided.

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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 no. CB10662. The work was started in January 2020 and completed in February 2021.

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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 no. CB10662. The work focused on decontamination of prototypical exterior materials found at airports and seaports after a chemical warfare agent (CWA) attack. This included exploring a novel technique for hazard mitigation, encapsulation of contaminated surfaces using barrier polymers. A variety of widely available water-soluble barrier polymers including dust suppressants, soil stabilizers, asphalt sealcoats, and stockpile sealants were considered.

Each of these barrier polymers was tested for permeability to the simulant methyl salicylate and for reduction in contact hazard. Three polymers were identified that could reasonably reduce the contact hazard of *O*-ethyl-*S*-(2-diisoproylaminoethyl) methyl phosphonothiolate (VX) on asphalt and concrete. Site-Lok (a cellulose-based stockpile sealant; manufactured by National Land Management; Phoenix, AZ), Grip-Flex (an asphalt sealcoat approved by the Federal Aviation Administration; manufactured by Grip-Flex Corporation; Philadelphia, PA), and Envirotac AW (a soil stabilizer used for roadway construction manufactured by Environmental Products and Applications; La Quinta, CA) all reduced the contact hazard by 90% or more. Reduction of contact hazard for HD on concrete was similar, however performance on asphalt was poor. Moreover, these reductions are modest in comparison to those found when using competing reactive technologies, such as Oxone and HTH.

Further analysis focused on the logistics of acquiring, storing, preparing, and applying these solutions at large scale. As all of the polymers are used commercially at large scale, little environmental, safety, or application concerns were found. This provides a distinct advantage over reactive technologies which generally have a higher environmental impact and are more difficult to acquire, store, and prepare. However, it was noted that vinylic and acrylic based polymers have short shelf lives and spoil upon freezing, increasing the difficulty of storage and stockpile management. Based on the results of this logistics analysis, the primary technologies recommended are Site-Lok and Grip-Flex, while Envirotac AW and Soiltac (Soilworks; Scottsdale, AZ) may be considered as alternatives.

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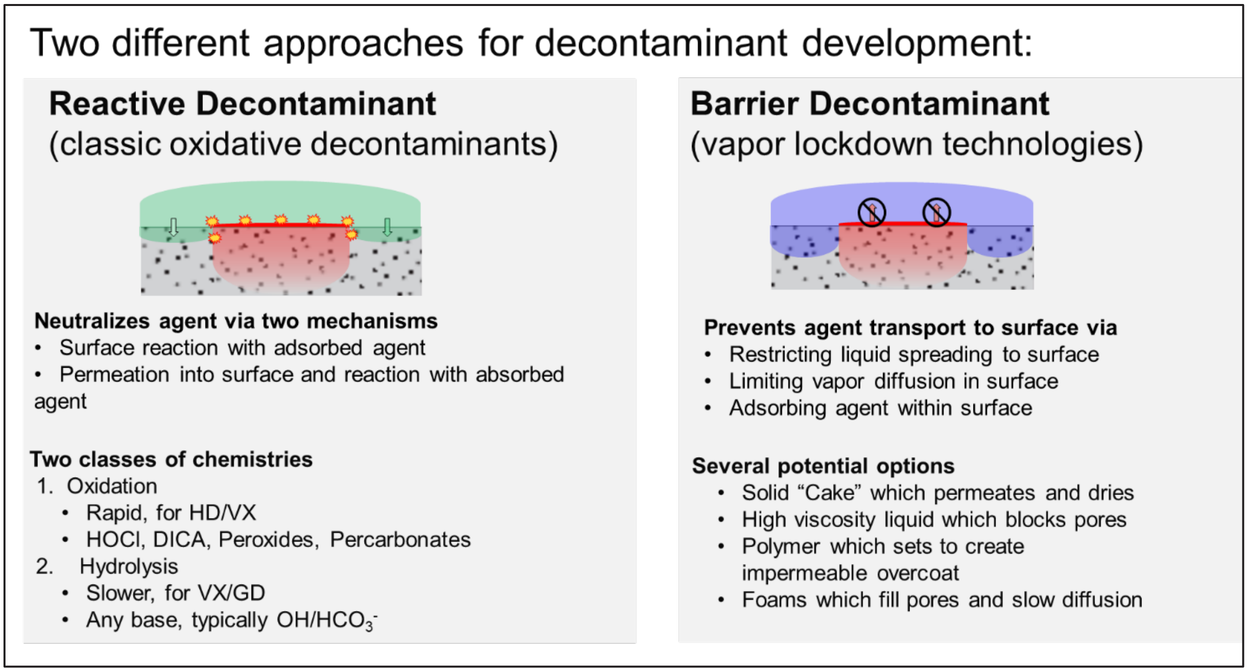
CHEMICAL WIDE-AREA DECONTAMINATION, III: BARRIER POLYMERS FOR DECONTAMINATION MITIGATION

1. APPROACHES FOR CHEMICAL WIDE-AREA DECONTAMINATION

1.1 Background

An effective decontaminant used in chemical wide-area decontamination (CWAD) applications enables rapid response and recovery after a chemical warfare agent (CWA) attack at an aerial port or seaport of debarkation (APOD and SPOD, respectively). 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 terrain hazard mitigation approach that is affordable at a large scale, compatible with current decontaminant applicators (e.g., M26, M12A1, and high-mobility decontamination systems), 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. Thus, there is a sizeable need for a CWAD technology that enables rapid response and recovery from a chemical weapons attack.

Reactive and barrier decontaminants are two approaches toward wide-area decontamination that were under consideration in the program, as shown in Figure 1. The primary focus of this report is the use of barrier polymer technologies for wide-area decontamination. 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. The barrier polymer may encapsulate the contamination and reduce the vapor and contact hazard posed by a chemical agent. These barrier decontaminants may provide a rapid short-term response and thereby allow for a reduction in mission-oriented protective posture to sustain operations. This novel decontamination approach has not been explored prior to this program.



Two different approaches for decontaminant development:

Reactive Decontaminant
(classic oxidative decontaminants)

Neutralizes agent via two mechanisms
- Surface reaction with adsorbed agent
- Permeation into surface and reaction with absorbed agent

Two classes of chemistries
1. Oxidation
    - Rapid, for HD/VX
    - HOCl, DICA, Peroxides, Percarbonates
2. Hydrolysis
    - Slower, for VX/GD
    - Any base, typically OH/HCO_3^-

Barrier Decontaminant
(vapor lockdown technologies)

Prevents agent transport to surface via
- Restricting liquid spreading to surface
- Limiting vapor diffusion in surface
- Adsorbing agent within surface

Several potential options
- Solid "Cake" which permeates and dries
- High viscosity liquid which blocks pores
- Polymer which sets to create impermeable overcoat
- Foams which fill pores and slow diffusion

Figure 1. Reactive and barrier hazard mitigation approaches. HD, bis(2-chloroethyl) sulfide (mustard gas); VX, *O*-ethyl-*S*-(2-diisoproylaminoethyl) methyl phosphonothiolate; GD, pinacolyl methyl phosphonofluoridate (soman); DICA, dichloroisocyanurate.

The other strategy is the use of traditional reactive decontaminant formulations, which can directly remove the contaminant through chemical reaction. This approach focused on the use of bulk commodity chemicals, such as oxidants and bases, as the basis for a formulation that can be readily prepared in the field. This approach was the subject of previous technical reports. 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 both barrier and reactive chemistries in coordination.

1.2 CWAD Development Approach

The experimental approach to developing an effective and fieldable wide-area decontaminant was divided into four distinct stages (Figure 2). Each stage was designed to advance the technology readiness level (TRL) as the program progressed. The level of analytical rigor is tailored to the needs of each development phase. In the early experiments, rapid, semiquantitative assessments are used to screen many different barrier polymer chemistries (Stage 1). After an initial down-selection, promising chemistries are evaluated to determine whether the decontaminant is safe, scalable, and logistically feasible (Stage 2). At this stage, one to three chemistries are selected for optimization. Optimization focuses on turning the chemistry into a fieldable approach, which includes determining the decontaminant concentration for preparation, identifying how to prepare the decontaminant, and quantifying the amount of decontaminant to be applied (Stage 3). These "stable configurations" are then evaluated and compared with each other and with current methods. The evaluation stage focuses on meeting key performance parameters for efficacy, material compatibility, and cost (Stage 4).

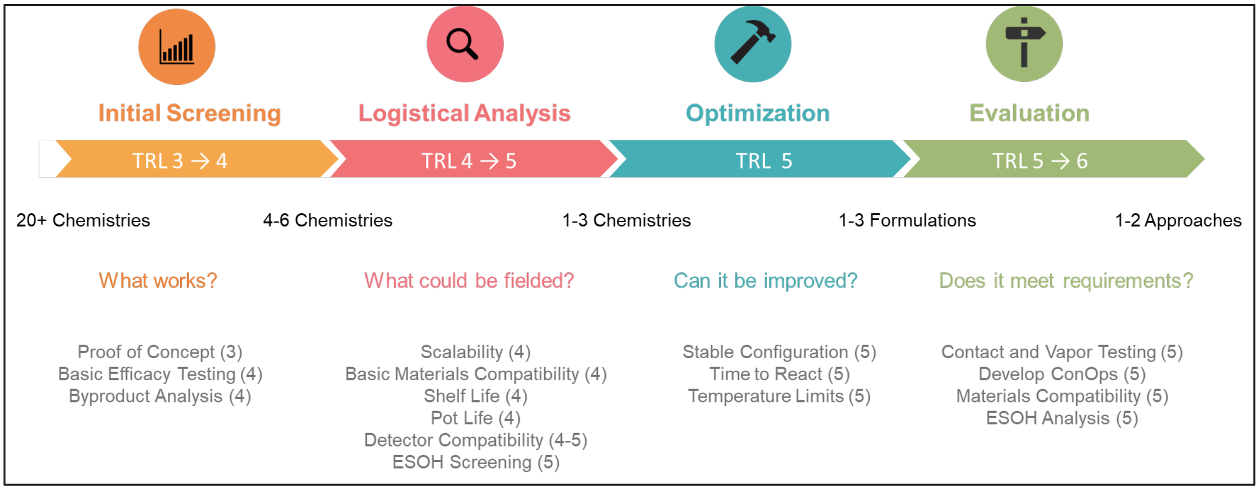


Figure 2. Developmental approach for CWAD development. ESOH, environmental, safety, and occupational health; ConOps, concept of operations.

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.

This report covers the screening (Stage 1) and logistics down-selection (Stage 2) for use of barrier polymers. Screening the efficacy of barrier polymers is more difficult than studying traditional reactive decontaminants. Reactive decontaminants reduce the overall level of contamination and can be assessed using traditional residual agent screening. However, barrier polymers directly reduce the contact and vapor hazards without any significant reduction in contaminant concentration within the originally contaminated surface. Efficacy must be assessed via contact testing, vapor testing, or both. Both of these test methods are more difficult and time-intensive than residual agent analysis and limit the throughput of testing. Because of this limitation, fewer barrier polymers were explored as compared to reactive components. Contact transfer hazard was the primary metric used to assess the efficacy of barrier polymers. This test assesses the amount of surface contamination that can be transferred following encapsulation of the contaminated surface using a barrier polymer. As traditional residual agent testing was not ideal for evaluation of the barrier polymers, contact testing was also conducted for the reactive decontaminants that were down-selected earlier in this program for use as a comparison of barrier technology efficacy. Vapor permeation testing was performed using simulants, but vapor off-gassing of agents was not directly measured.

Logistics analysis was performed as part of Stage 2 to aid in the selection of field-ready technologies. The logistical concerns of barrier polymers are unique as compared to traditional reactive decontaminants. This analysis focused on standard metrics such as cost, shelf-life, material compatibility, and safety. However, concerns unique to barrier polymers, such as cure time, ease of removal, and viscosity, were also considered.

This report provides an overview of the exploration of barrier polymers and highlights the initial stages of screening and logistics down-selection. The vapor permeation properties determined in this report along with the contact transfer results will be used to determine whether the barrier polymers studied provide protection from a contaminated surface. The final output is a list of barrier polymer technologies recommended for additional optimization and exploration. These technologies may be developed further into a primary method of contamination mitigation or used in conjunction with a reactive technology as part of an overall mitigation strategy.

2. MATERIAL SELECTION

Concrete and asphalt were chosen as the substrates for study (Figures 3 and 4), as these are the principle construction materials found at APODs and SPODs. 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. Both concrete and asphalt are highly variable materials, and their composition depends on local construction guidelines and availability of local materials.

These challenges are further complicated by laboratory constraints on size, cost, and reproducibility. Test coupons are needed that fit current testing apparatuses and are thin enough to be extracted easily. Materials also had to be prepared with a turnaround time of one month or less, to accommodate efficiency in cost and testing schedule. Most importantly, the ability to generate reproducible data is key to being able to identify differences in performance between different decontaminants and barrier polymers. Despite this, materials needed to be representative of the fielded materials that they are meant to replicate. Some variances are important to capture decontaminant evaluation, while others are not. In general, materials were selected to give a reproducible means of measuring the worst-case scenario. The following decisions reflect these trade-offs:

Large aggregate in the materials (e.g., larger stone and rock) should be avoided. Droplets falling on large aggregate do not permeate the material; thus, large aggregates are more easily decontaminated and do not necessarily yield a reproducibly representative measure of the material system. The use of large aggregate requires the use of thick coupons, which limits extraction efficiency and sample throughput.

Coupons must be thinner than ¼ in. Unless the contaminant breaks through the bottom of the coupon, thickness likely has little impact on decontaminant performance. Thinner coupons can be used with current test methods and are more easily extracted.

Lead time for acquisition of coupons must be short. Coupons must be prepared in less than one month. A turnaround time of less than one month was necessary to execute the project along the required timelines.

These guiding principles were used in the selection of concrete and asphalt coupons. Additional information on material selection can be found in technical report DEVCOM-CBC-TR-1699.[1]

Figure 3. (Left) Thick concrete coupon and (right) 1/8 in. thick calcium sulfoaluminate (CSA) quick-set coupon.

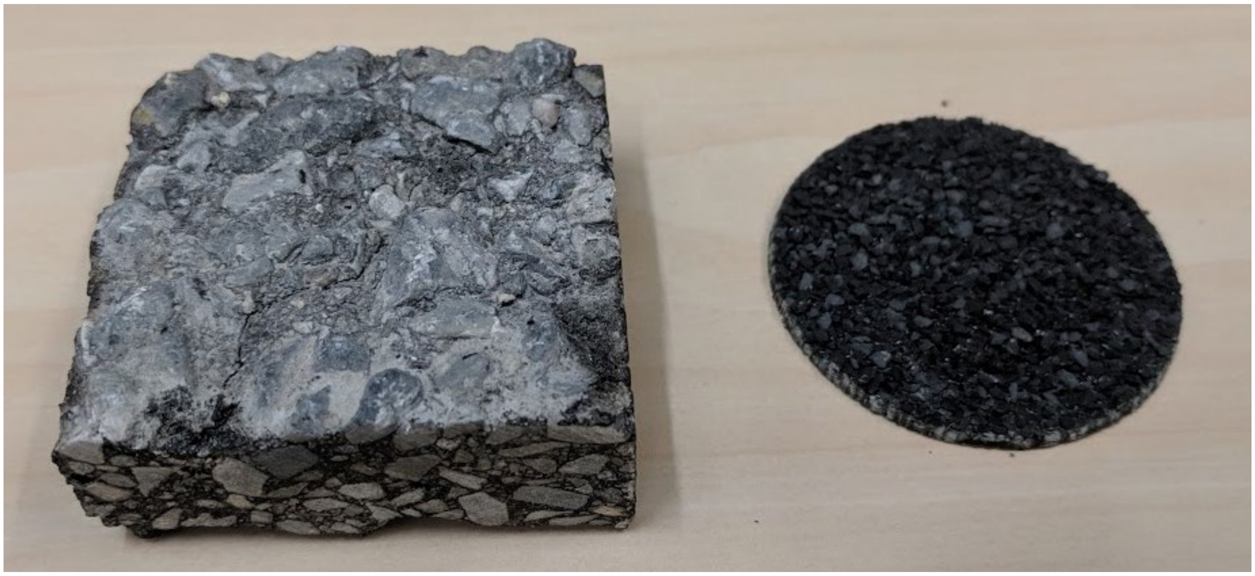


Figure 4. (Left) Thick asphalt sample from local roadway and (right) asphalt shingle coupon.

3. POLYMER SELECTION

3.1 Polymer Product Characteristics

Barrier polymers function to reduce the hazard to unprotected personnel by providing a physical barrier to prevent vapor and contact transfer from a contaminated surface. Initially applied as an aqueous solution, these chemicals cure with time and form a polymer coating over the concrete and asphalt surface. The hazard reduction by that coating depends on the coating thickness and the agent permeability of the specific polymer. The initial list of barrier chemistries was selected from commercial products used for large-scale applications such as soil stabilizers, stockpile sealants, and asphalt sealcoats. Products were selected based on the following criteria:

- available in 275 or 330 gal intermediate bulk containers;
- prepared in water and sprayable via a water truck;
- was previously used in large-scale government or military applications; and
- forms an overcoat within a 24 h cure period.

Based on these criteria, several products were selected. Grip-Flex (Grip-Flex Corporation; Philadelphia, PA) is a water-based bitumen emulsion typically used as an asphalt sealcoat that forms a black bitumen layer over the applied surface. Gorilla-Snot and Soiltac (both from Soilworks; Scottsdale, AZ) are soil stabilization chemicals that cure to form a clear vinyl polymer over the applied surface. Soiltac provides a higher density hydrophobic coating, whereas Gorilla-Snot has a lower density and is more water permeable. Envirotac AW (Environmental Products and Applications; La Quinta, CA) is an alternative acrylic-based soil dust suppressant that forms a transparent overcoat. PineBind (National Land Management; Phoenix, AZ) is a natural pine-pitch-based soil stabilizer that forms a slightly sticky yellow overcoat when applied. Site-Lok (National Land Management) is a stockpile sealant that is used to prevent wind erosion and dust-off of large stockpiles of sand, lime, and other bulk mining and construction materials. It is a methylcellulose-based polymer that cures rapidly to form a transparent overcoat. Figure 5 shows these polymer chemistries applied to aluminum coupons.

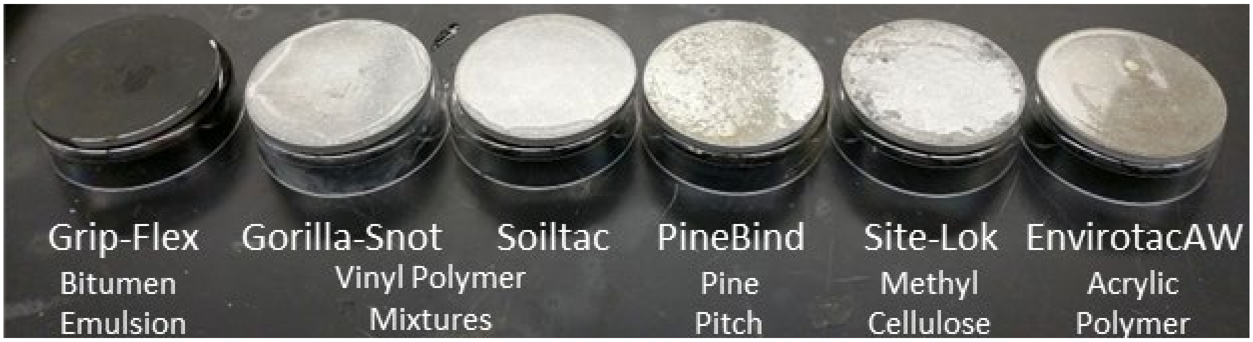


Figure 5. Application of different barrier decontaminant technologies (1 mL each) to 2 in. aluminum coupons.

3.2 Polymer Cure Time and Film Thickness

Film thickness, cure time, and application density are three connected properties that have an effect on the efficacy and logistical burden associated with using barrier polymers. Application density influences the coverage and film thickness of a given polymer. Initial studies show that ~0.5 mL/in.^{2} is required to completely coat a surface in a given polymer. This is demonstrated in Figure 6. Smaller application densities led to incomplete surface coverage, although the smaller amount may be sufficient with use of a different spray application apparatus or technique. Moreover, application density determines the film thickness of the polymer. The thickness and permeability of the polymer are what determine the duration of protection from a vapor hazard. Thicker, less-permeable films have longer breakthrough times than thinner, more-permeable films.

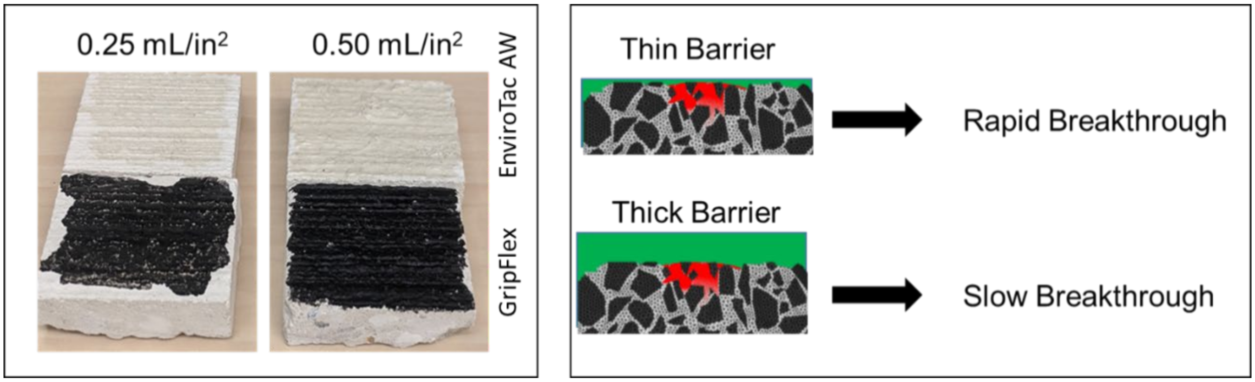


Figure 6. (Left) Application of barrier polymers at 0.25 and 0.5 mL/in.^{2} on concrete. Envirotac AW is shown at top, and Grip-Flex is shown at bottom. (Right) Influence of film thickness on breakthrough time.

An initial study was performed to determine how application density influences the final thickness of a barrier. Barrier polymers were applied to a stainless steel coupon of known thickness and were allowed to cure. After curing, the film thickness was determined using a micrometer. The results for five barrier polymers are shown in Figure 7. Readings for some polymers were highly variable due to uneven application. Both Grip-Flex and Soiltac exhibited predictable increases in film thickness as application density increased. Gorilla-Snot provided almost immeasurably thin films in every case.

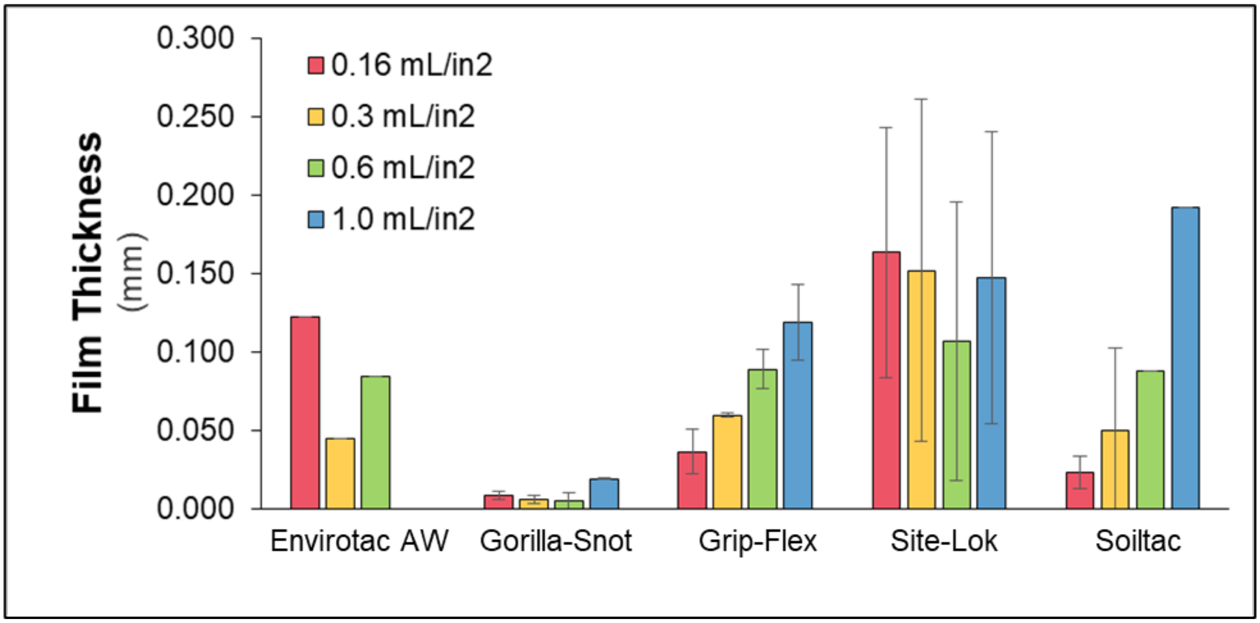


Figure 7. Film thickness as a function of application density for barrier polymers.

Another important parameter is cure time. Rapidly curing polymers are desired, as they allow a site to be useable much sooner after the barrier decontaminant is applied. Cure times depend on application density, the surface to which the polymer is applied, as well as the temperature and humidity in which the application takes place. Most of the polymers explored in this study are aqueous based and cure via water evaporation, which can be dependent of temperature and humidity conditions. Porous materials such as concrete have more rapid cure times because the surface-area-to-volume ratio increases as the liquid permeates via the pores. As shown in Figure 8, most barrier polymers cured within 2 h when applied to concrete, but required 3–6 h to cure on stainless steel. For this study, "cured" was defined as being dry to the touch or showing no remaining liquid water within the applied mass. In general, Grip-Flex and Envirotac AW were the fastest curing polymers on concrete; both cured within 20 min. Gorilla-Snot, an acrylic polymer, completely soaked into the material before it had cured.

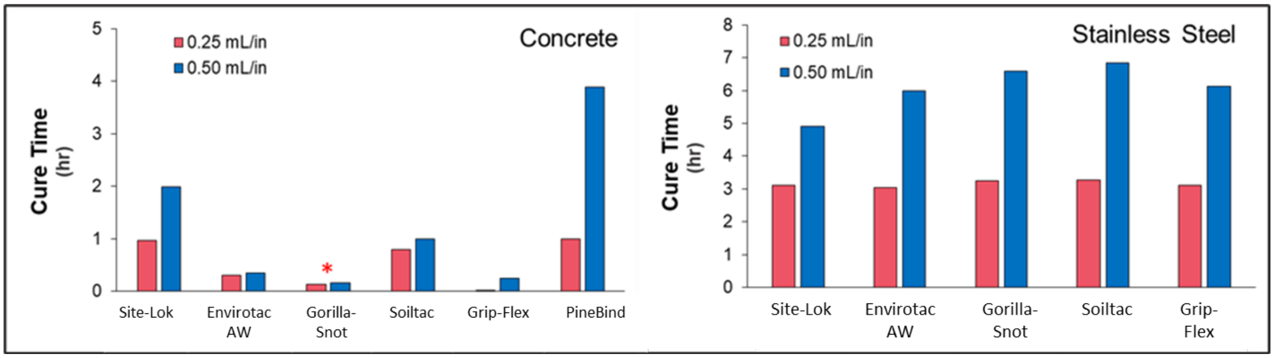
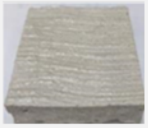
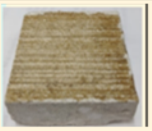


Figure 8. Cure times as a function of application density for (left) concrete and (right) stainless steel. *Polymer solution absorbed into the material before it cured.

A summary of these results is provided in Table 1. Generally, five of the six polymers tested had a film thickness of approximately 100 µm when applied at 0.6 mL/in.^{2} Cure times varied widely, but all polymers cured in less than 4 h on concrete.

Table 1. Barrier Polymers Selected for Permeability Studies

Product		Site-Lok	EnviroTac AW	Gorilla-Snot	Soiltac	Grip-Flex	PineBind
Image	-						
Polymer Type	-	Methyl Cellulose	Acrylic Polymer	Vinylic Polymer	Vinylic Polymer	Bitumen Emulsion	Pine Pitch
Film Thickenss	0.3mL/in^2 Steel	0.1mm	0.1mm	0.020mm	0.1mm	0.1mm	0.1mm
Cure Time	0.5mL/in^2 Concrete	2 hrs	20 min	Soaks @ 10 min	1 hr	15 min	4 hr
Notes		Viscous at 6:1, Shiny Coat	Rapid Cure, Hard Coat	No visible layer			Slightly sticky upon cure

4. VAPOR BREAKTHROUGH STUDIES USING FOURIER-TRANSFORM INFRARED (FTIR) SPECTROSCOPY

The breakthrough of contaminant vapor through the polymer barrier depends on the thickness and permeability of the polymer. The film thickness is a flexible parameter that can be controlled through the application density and the concentration of the polymer solution. Permeability is an intrinsic property that depends on the individual polymer chemistry, the extent of crosslinking, and other factors. For example, transport of contaminant vapor through highly cross-linked glassy polymers is likely significantly slower than transport through rubbery, porous polymers.

Previous methods were developed to determine the permeability of materials to agent vapors. Using FTIR spectroscopy, a crystal can be coated with a polymer material and exposed to agent vapor. The concentration of the agent vapor can be measured over time, which identifies how long it takes the agent vapor to break through the film. This breakthrough curve can be used to determine the permeability. The longer the vapor takes to penetrate the film, the lower the permeability. An example of a crystal coated in a barrier polymer (Envirotac AW) is shown in Figure 9.

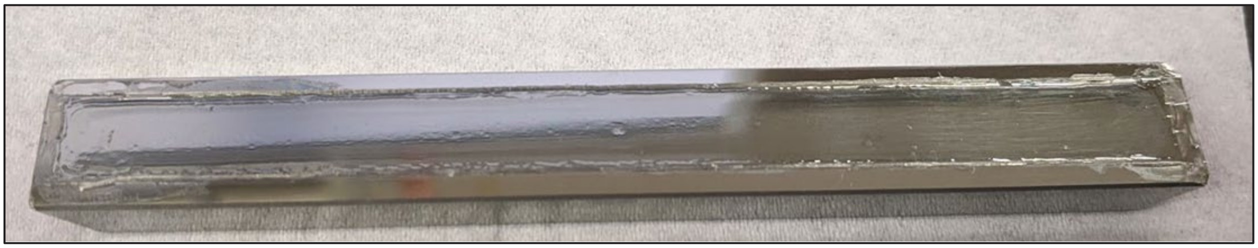


Figure 9. FTIR crystal coated with Envirotac AW.

In these studies, each of the barrier polymers was coated on an attenuated total reflectance germanium crystal, cured, and analyzed for breakthrough using the simulant methyl salicylate (MeS). The coating process shown in Figure 10 included a masked area of 250 µm generated using polymer tape, and the void was filled with 0.6 mL of the barrier polymer, diluted 6:1 with water. The polymer was allowed to cure at least 24 h. Film thickness was measured using optical microscopy.

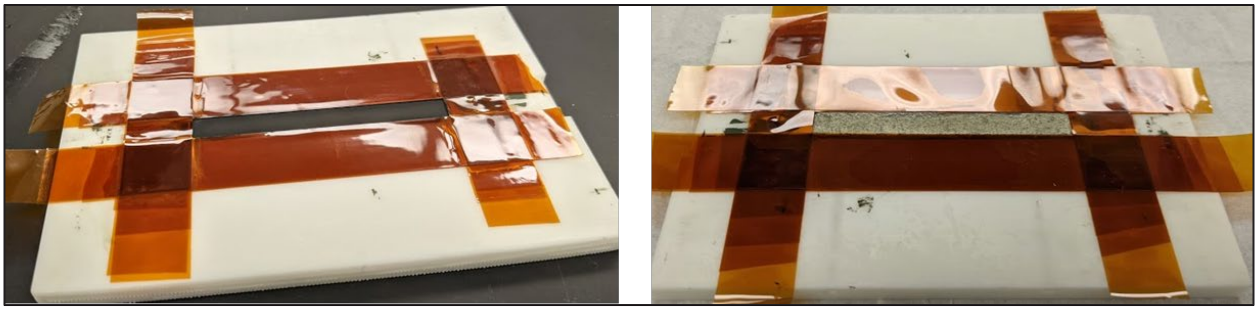


Figure 10. Coating FTIR crystals in (left) Grip-Flex and (right) PineBind using a masking method.

The cured polymer was placed in the FTIR instrument and exposed to a saturated stream of MeS at 38 °C. The increased temperature is necessary to generate a sufficient MeS concentration for the study, and to avoid MeS from condensing in the transfer lines. FTIR spectra were collected every 30 s and analyzed to identify the breakthrough curve. A graphic depicting the FTIR methodology is shown in Figure 11. This study tracked differences in the breakthrough time for MeS penetration through the polymers evaluated with FTIR assuming minimal chemical interactions between the penetrant and the material. Intensity for specific peak positions associated with MeS and polymers was considered, as opposed to absorbance band widths as well as shifts, which would be indicative of varying chemical interactions that influence measured vibrational modes.

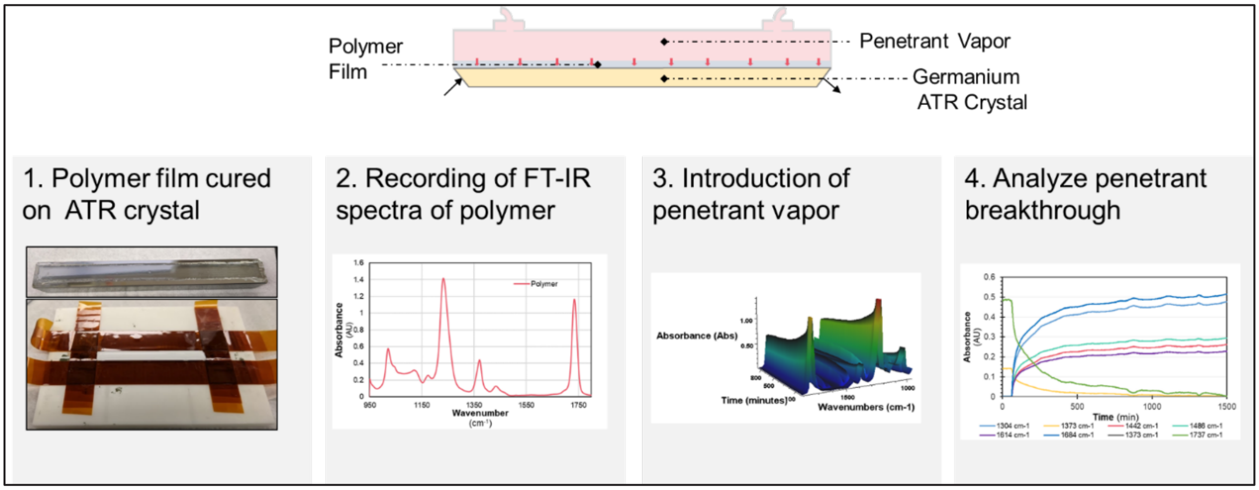


Figure 11. FTIR method for measuring penetrant breakthrough.

Spectra collected before exposure and after completed exposure were used to determine characteristic peaks that are associated with MeS. Characteristic peaks for MeS were identified at 1440, 1488, 1588, 1619, and 1680 cm^{-1}, as shown in Figure 12.

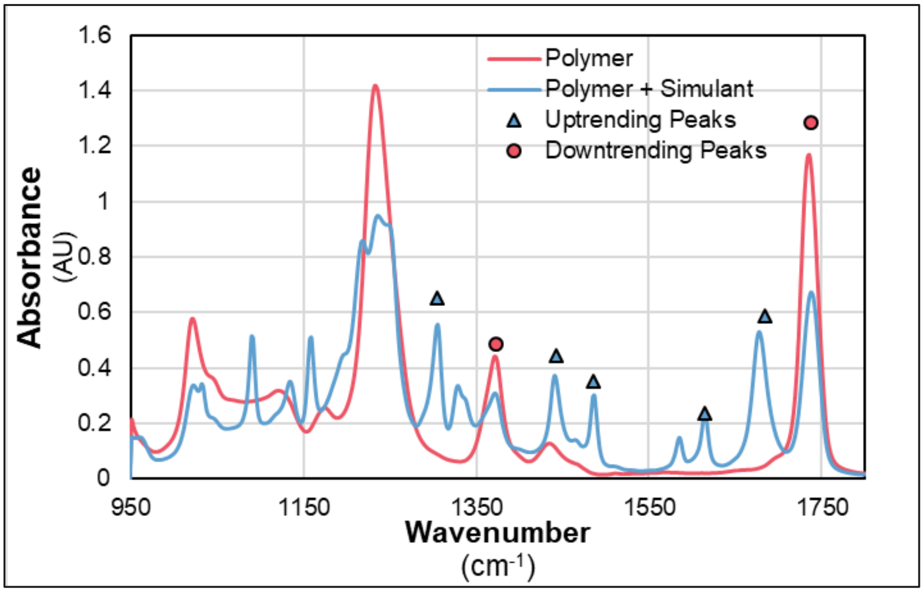


Figure 12. FTIR spectra for Envirotac AW before (red) and after MeS (blue) exposure. Peak determinations are highlighted.

Using the above method, breakthrough measurements were obtained for several of the barrier polymers using the HD simulant MeS as the penetrant of interest. MeS was chosen to evaluate the ability to measure penetrant breakthrough of these barrier polymers while being cost efficient. As shown in Figure 13, an FTIR crystal coated in the soil-stabilizing polymer Gorilla-Snot was exposed to MeS, and spectra were recorded for 24 h. The left side of Figure 13 displays the spectra for both the bare polymer prior to exposure (red spectra) as well as the polymer after full exposure to MeS (blue spectra). Several peaks appeared and several shrank upon exposure to MeS. The increasing peaks that are associated with MeS permeation include 1440, 1488, 1588, 1619, and 1680 cm^{-1}. As noted earlier, peak shifting may occur as a result of interactions within the polymer structure as the MeS interacts with the polymer. These specific interactions were not explored in this study. Future efforts could be used to expand knowledge of the specific polymer–chemical penetrant interactions. On the right side of Figure 13, the changes in peak intensity over time are normalized to the bare polymer spectra absorbance of the peaks of interest, where the polymer-associated peaks are set to 1 and the MeS-associated peaks are set to 0 at the beginning of measurements.

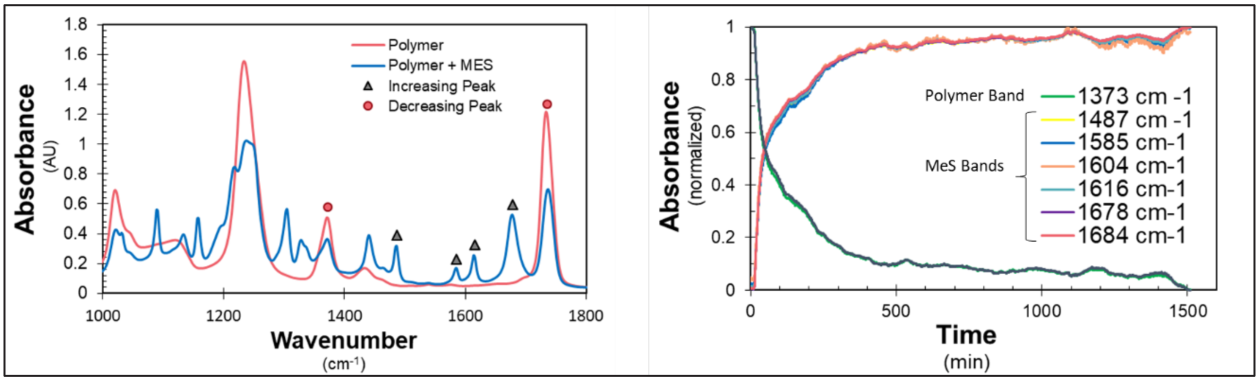


Figure 13. FTIR data of MeS breakthrough of Gorilla-Snot barrier polymer. (Left) Spectra for bare polymer prior to exposure (red) as well as after full exposure to MeS (blue). (Right) Changes in peak intensity over time are normalized to bare polymer spectra absorbance of peaks of interest. At the beginning of measurements, polymer-associated peaks were set to 1, and MeS-associated peaks were set to 0.

The peak around 1619 cm^{-1}, associated with MeS, was large and unobstructed by other polymer peaks across each barrier polymer studied. This specific peak was used as a reference to identify a general MeS breakthrough curve for each polymer (Figure 14). Figure 15 summarizes the calculated breakthrough time for each barrier polymer. No breakthrough was observed for PineBind or Site-Lok barriers after a 4000 min (66 h) MeS exposure. The next-longest breakthrough time was for Soiltac, followed by Grip-Flex, which prevented breakthrough for >16 and 2 h, respectively. Immediate breakthrough was observed for Envirotac AW and Gorilla-Snot barriers.

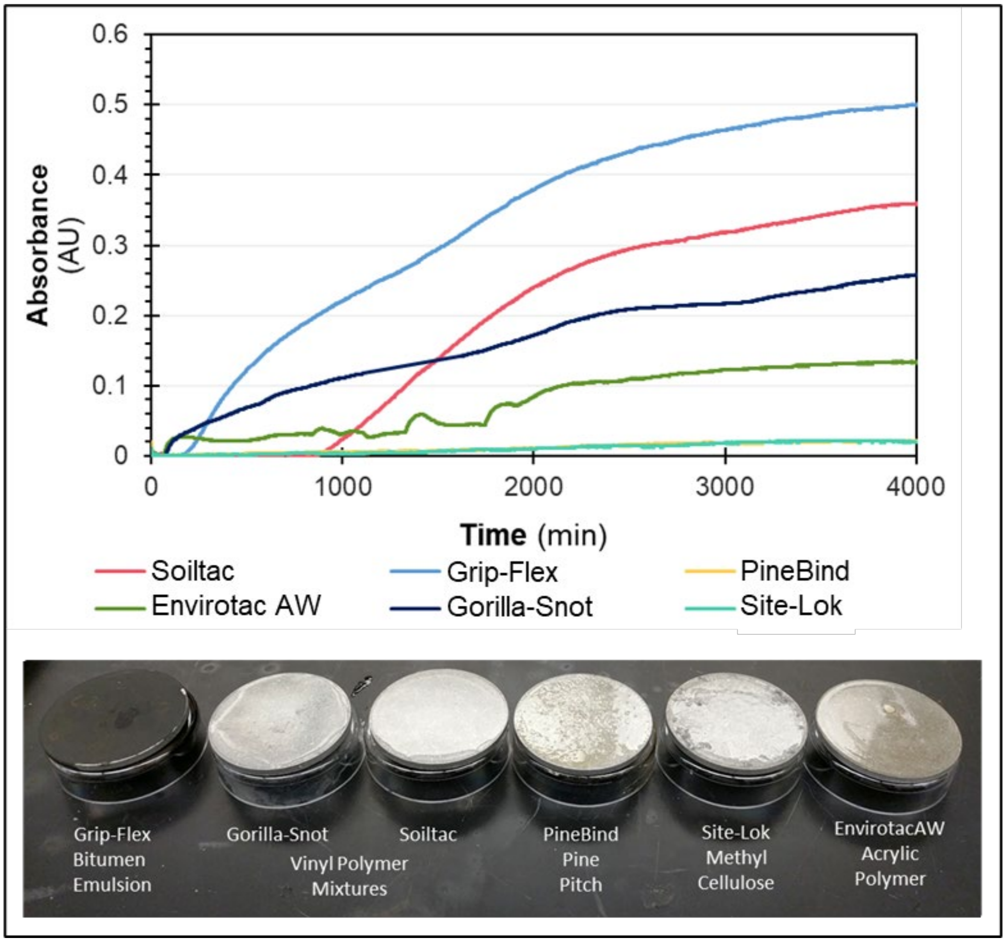


Figure 14. Absorbance over time of MeS peak at 1619 cm^{-1}
for each barrier polymer shown at bottom.

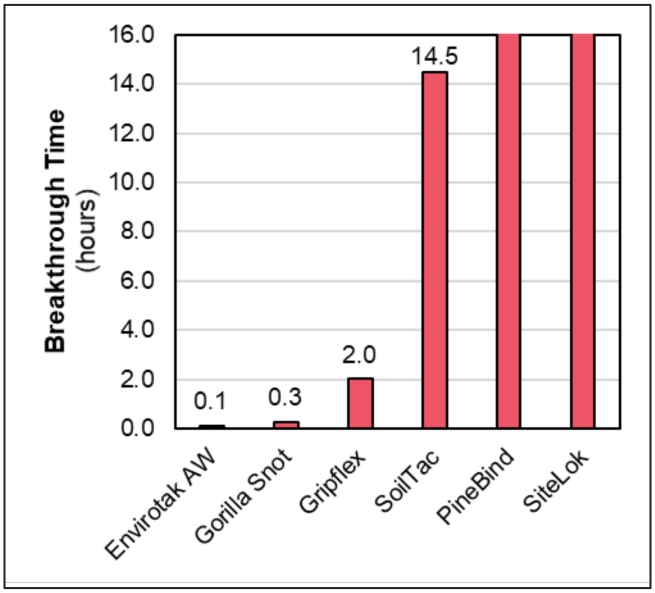


Figure 15. MeS breakthrough time through different barrier polymers.

These results may not be directly translated to efficacy on a real-world matrix such as asphalt and concrete because the polymers cure and spread differently on the FTIR crystal than on concrete or asphalt. Concrete has a porous network that may help to spread the polymer over the surface, leading to a more rapid cure time. The simulant MeS was also used as opposed to a CWA such as HD, which may have different chemical interactions with the barrier polymers. These results serve as a proof of concept that barrier polymer technologies may be evaluated for vapor permeability using this method to determine efficacy against vapor hazards in a CWAD scenario. Further method refinement and vapor flux studies are needed to confirm these trends.

5. CONTACT HAZARD TESTING

5.1 Background

A primary aim of a CWAD is to prevent contamination from being transferred to vehicles and personnel traveling through the contaminated area. The purposes of the contact investigations are (1) to determine how the potential contact hazard changes as the agent weathers, and (2) to understand how the use of barrier polymers may reduce this contact transfer hazard through contaminant encapsulation. The initial focus of this effort was on asphalt surfaces followed by concrete; the asphalt proved the most difficult to decontaminate using reactive decontaminants.

The contact transfer test method is designed to measure the contaminant present on a material surface and in the immediate subsurface after hazard mitigation, which could pose a hazard through contact transfer to skin. A contact sampler (typically latex) is a surrogate for human skin. The contact sampler is used to collect the residual agent from the test article surface. A contact test event is called a “touch”. A touch is characterized by contact area, contact pressure, and contact duration. The contact sampler is extracted to determine the contact transfer mass as a function of touch, which in turn can be used to determine a contact transfer rate. Contact transfer testing can provide a source term, typically given as a mass of agent per unit area or per drop, per contact duration.

Contact sampling can be performed as either a single- or multi-touch event. For single-touch events, the surface is sampled only once for a prescribed period of time, and analysis is typically performed immediately after the touch ends. Single-touch events provide information on the contact transfer of a surface at a single point in time. Information that can be obtained from a single-touch event is limited, is not generally useful in distinguishing between bulk and diffusive transfer processes nor the change in contact transfer as a function of time, and should be used with full understanding of the limitations of the insight that can be obtained. In multi-touch events, the surface is sampled multiple times (using a fresh contact sampler per touch) over a pre-established time frame. If information regarding the change in contact transfer over time irrespective of previous touches is desired, different areas of the surface (or different panels) should be sampled only once at pre-established time intervals. If the contribution of previous touches is to be accounted for, multi-touch events should sample the same area (panel) at pre-established time intervals. Multi-touch events are recommended when test objectives include the characterization of both bulk and diffusive transfer and discrimination between the two or characterization of the anticipated health effects resulting from operational use of assets.

5.2 Development of Contact Testing Methodology for Asphalt

5.2.1 Substrate Determination

Initial contact testing was conducted to compare asphalt shingles to real-world asphalt panels. A 20 µL contamination challenge was introduced to either a 2 in. diameter asphalt roofing shingle or a 2 in. asphalt block cut from a local roadway. The samples were aged for 5 or 60 min before being sampled for 30 s with a latex contact sampler. As shown in Figure 16, at the 60 min age time, similar results were obtained for both the shingle and asphalt block. However, at the 5 min age, roughly one order of magnitude less mass was pulled from the asphalt block. This was likely because of poorer initial spreading on the asphalt block. For future studies, the asphalt shingle was chosen for several reasons:

- The asphalt shingle provided more reproducible data.
- The asphalt shingle is less expensive.
- The shingle is easier to handle for high-replicate studies (less waste).
- The asphalt shingle reliably provides an equal or overestimation of the contact hazard posed.

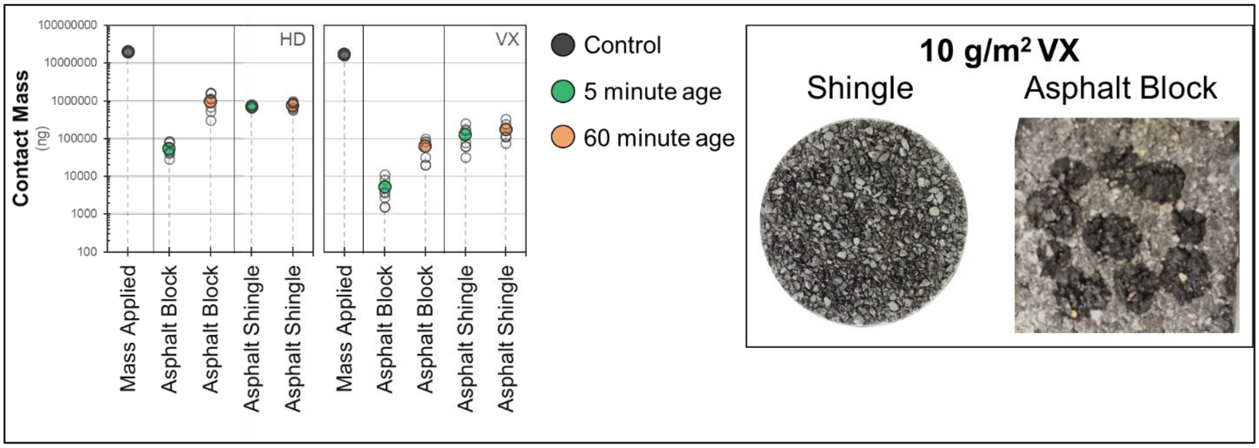


Figure 16. Comparison of contact transfer data for asphalt shingle and asphalt block.

5.2.2 Contact Sampler Determination

An original interest was to evaluate the rollover hazard on asphalt and concrete. The rollover hazard is the measurement of the amount of contaminant transferred to a tire while it traverses a contaminated concrete or asphalt surface. However, contact hazard measurements are highly variable and require high replicate numbers for statistical certainty, and the rollover method was very low throughput. Therefore, a traditional measure of contact hazard using latex samplers was used. Latex samplers are highly absorbent and will readily absorb the contaminant available on the panel surface. This provides a good measure of the surface-bound contaminant available for transfer and an upper bound to the contact risk posed to a vehicle or person traversing the area. The latex sampler method reveals a worst-case scenario, as latex is likely to absorb more chemical agent over the sampling period as compared to a short rollover contact with a rubber sampler.

5.2.3 Contact Time Determination

The influence of contact duration was probed by first contaminating a panel, aging the panel for 60 min, and then placing the latex contact sampler and a weight on a panel for 30 s, 2 min, 5 min, or 15 min touches. After this initial touch, a second 15 min touch was performed to determine whether any residual agent was accessible on the surface after the first touch (Figure 17). As shown in Figure 18, increasing the contact duration consistently increased the contact transferred mass for VX. The mass collected on the second touch was consistently equal to or lower than the first touch mass, suggesting that the rate of transfer was less than or equal to the transfer rate seen in the 5 and 15 min first touch. The remaining mass available for the second touch was influenced slightly by the duration of the first touch, suggesting that the length of the first touch influences how much mass is left on the surface. These effects diminished if the first touch was 5 min or longer, which suggests that a 5 min touch would be sufficient to identify differences in barrier polymer encapsulation as a function of changes in the contact transfer rate at a 5 min contact duration. For this reason, a single 5 min touch was used for all subsequent studies.

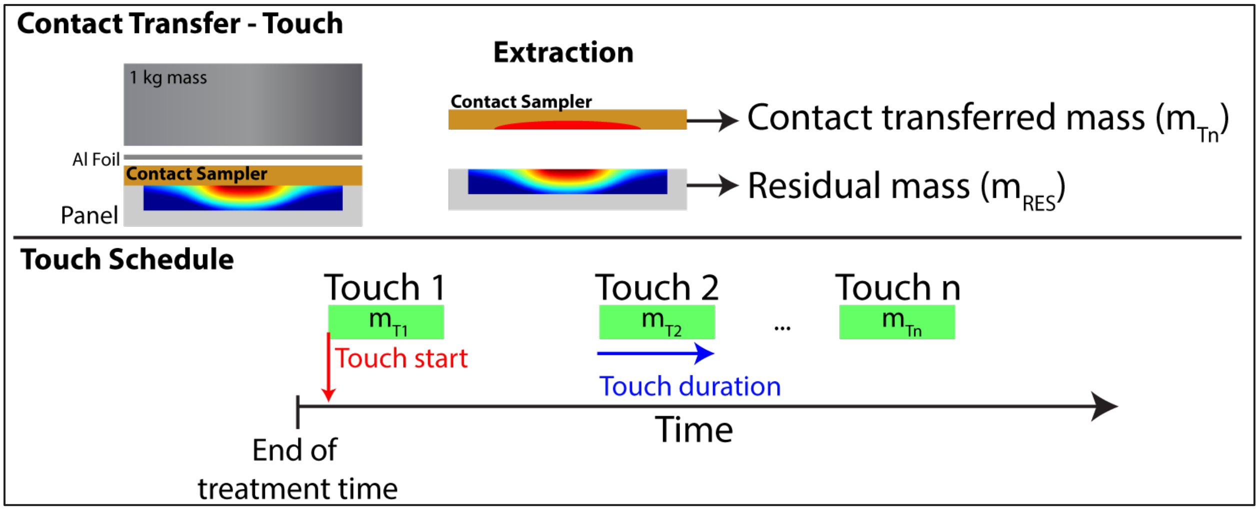


Figure 17. Contact transfer test procedures.

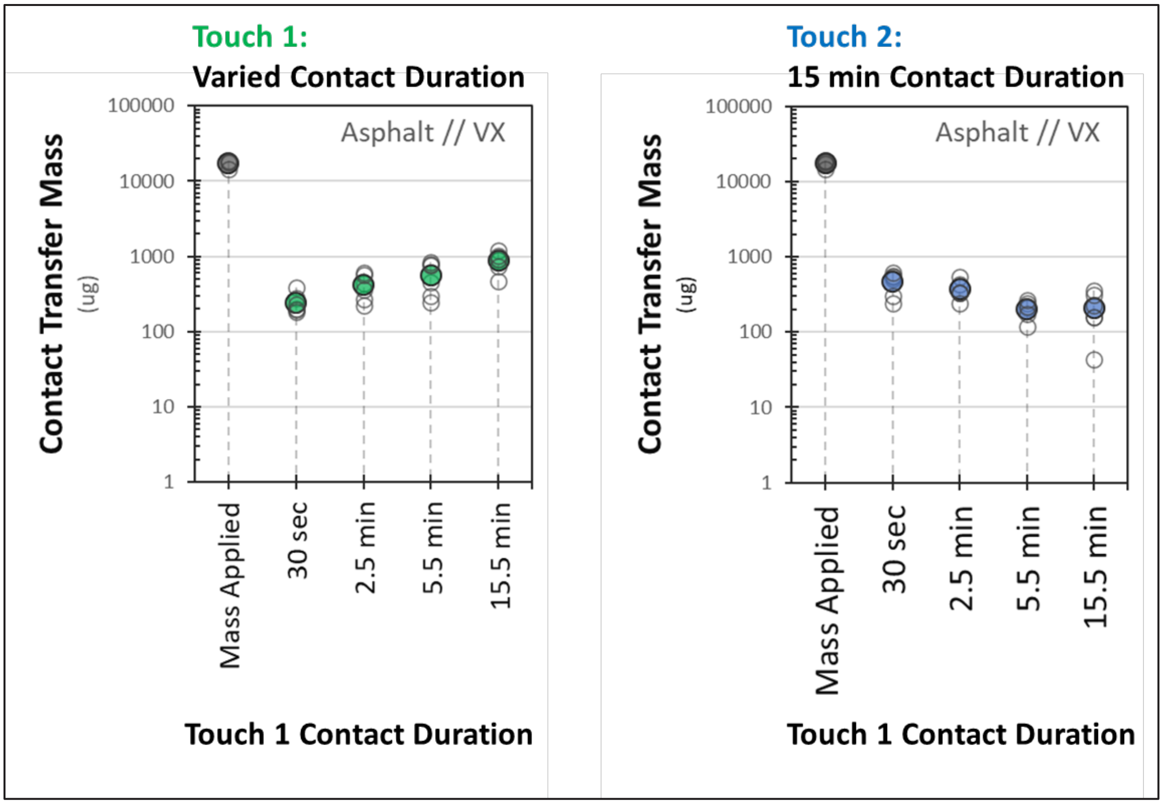


Figure 18. Influence of contact duration on transfer mass for VX on asphalt.

A similar trend was observed for HD, as shown in Figure 19. Contact transferred mass increased as the duration of the first touch increased. However, the duration of the first touch had little influence on the sampled mass of the second touch, which suggests that the surface bulk had been removed via the first touch and the contact transfer rate at the second touch was similar regardless of the first touch duration. Thus, any touch longer than 30 s should be adequate to remove surface HD from the coupon. For consistency, a 5 min contact duration was selected for all HD contact studies.

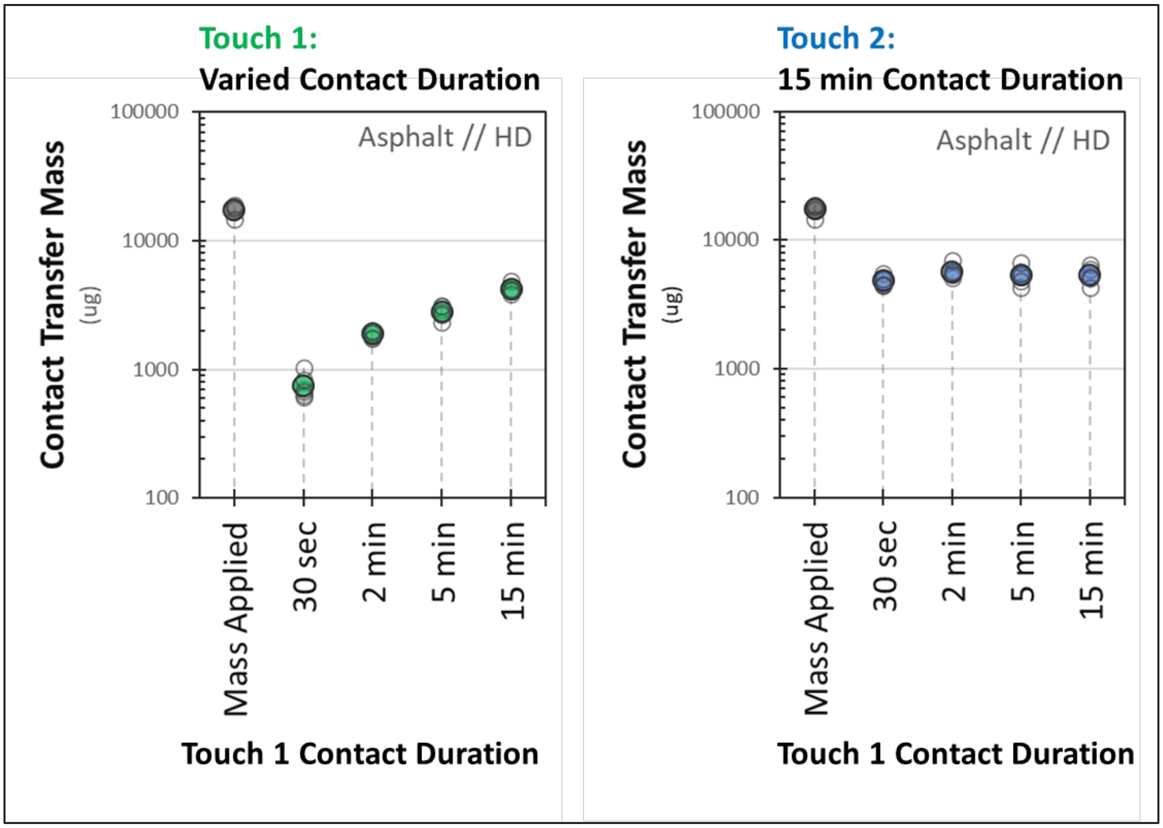


Figure 19. Influence of contact duration on transfer mass for HD on asphalt.

5.3 Comparison of Barrier and Reactive Decontaminants on Asphalt Substrates

Using the Section 5.2 discussion as guidance for determination of contact transfer methods, the efficacy of barrier polymers at reducing contact transfer via contaminant permeation was studied. Previous reports explored the efficacy of reactive decontaminants to reduce the contamination in or on concrete and asphalt. In addition to evaluation of the efficacy of the barrier polymer to reduce contact transfer, several reactive decontaminants were also evaluated for their efficacy to reduce the contact transfer hazard. These reactive decontaminants can be used as a point of comparison to the barrier polymers when determining which contamination mitigation strategy is best for a given scenario. In this study, the panels were contaminated at a large contamination density (10 g/m^2) and aged for 24 h. This larger contamination density was used to allow for the creation of sufficient signal to determine differences in efficacy of the various barrier polymers and reactive decontaminants. After contaminant aging, a barrier or reactive decontaminant was applied, which remained on the surface for 6 h. After the decontaminant residence time, a contact sample was collected using a latex sampler that was applied for 5.5 min. It was determined that contact samplers could be analyzed without significant analytical interference; however, in some cases, it was necessary to quench the reactive samples. This was done by addition of 10 mM tetrahydrothiophene (THT), a sacrificial reductant, to the contact sampler extraction solvent. This quench stopped any reaction that was still occurring between the reactive decontaminant and the transferred contaminant. Further information on the development of quench procedures and analytical interference is provided in technical note DEVCOM CBC-TN-085.[2] Testing parameter details are provided in Table 2.

Table 2. Parameters for Asphalt Contact Testing

Parameter	Value
Contaminants	VX, HD
Contamination density	10 g/m^2
Contaminant residence time	24 h, unless otherwise specified
Material	Bitumen asphalt sheets, 2 in. diameter
Decontaminants or barrier polymers	Oxone (0.4 M), Oxone with 8% Tergitol (1.0 M, applied at 60 °C), dichloroisocyanuric acid (Dichlor; 1.0 M), ammonium persulfate (2.4 M), high-test hypochlorite (HTH; 0.75 M), potassium hydroxide (14 M, applied at 60 °C), Envirotac AW, Site-Lok, Soiltac, PineBind, Grip-Flex, Gorilla-Snot
Decontaminant residence time	6 h, unless otherwise specified
Decontaminant volume	2.0 mL
Decontaminant application temperature	Room temperature, unless otherwise specified
Contact sampler material	Latex
Contact duration	5.5 min
Contact mass	1 kg
Contact extraction solvent	Isopropyl alcohol with 40 mM THT (VX) $CHCl_3$ with 40 mM THT (HD)

This methodology allowed us to analyze the effectiveness of barrier polymers at reducing the contact hazard. The data provide relative comparisons of the effectiveness of each polymer and can be used for down-selection when combined with vapor permeation data to identify a best-performing barrier polymer. Moreover, this methodology allows for barrier polymer efficacy to be directly compared with reactive decontaminant effectiveness, thereby helping us to discern which method is most efficacious with regard to contact transfer. This evaluation was performed on asphalt substrates first, as asphalt lacked an effective reactive decontaminant solution for reducing the contaminant hazard. Several reactive decontaminants proved effective on concrete substrates, which made it a lower priority for a barrier polymer.

Efficacy was compared for six barrier polymers and six reactive decontaminants using the contact test method described herein. The amounts of contact transfer for each studied polymer and for select reactive decontaminants are shown in Figure 20. Several of the barrier polymers provided a modest change (50% reduction) in contact transfer, including Site-Lok LX100 and Envirotac AW. Grip-Flex and Soiltac provided little reduction in contact transfer when compared to an untreated, weathered asphalt sample. Moreover, decontaminants such as KOH and PineBind actually caused increased contact transfer. This was likely because they assist in extraction of the contaminant from the panel (without reactivity) or they increase the effectiveness of contact transfer on wet versus dry surfaces. PineBind forms a sticky film until it has fully cured. This may result in the contaminant being initially absorbed and then readily transferred during a touch.

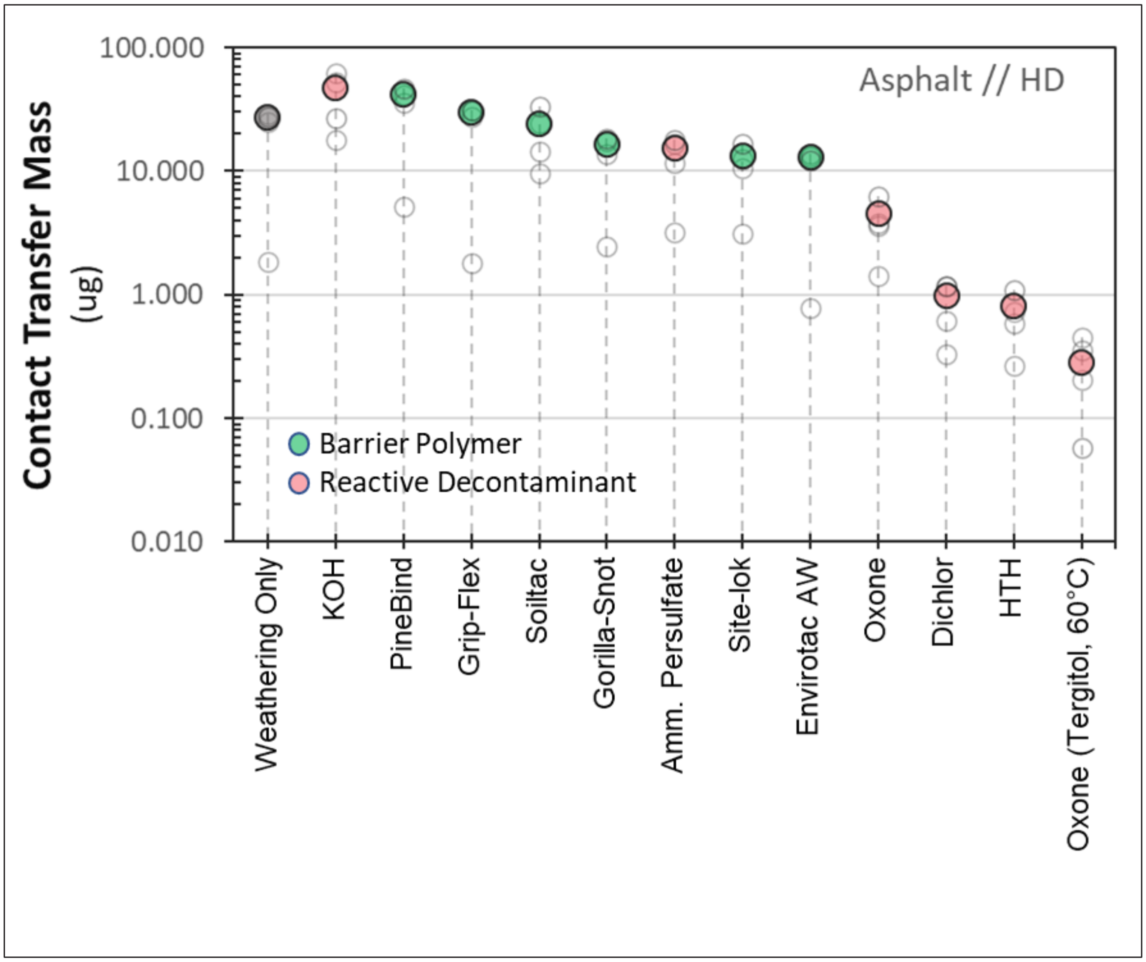
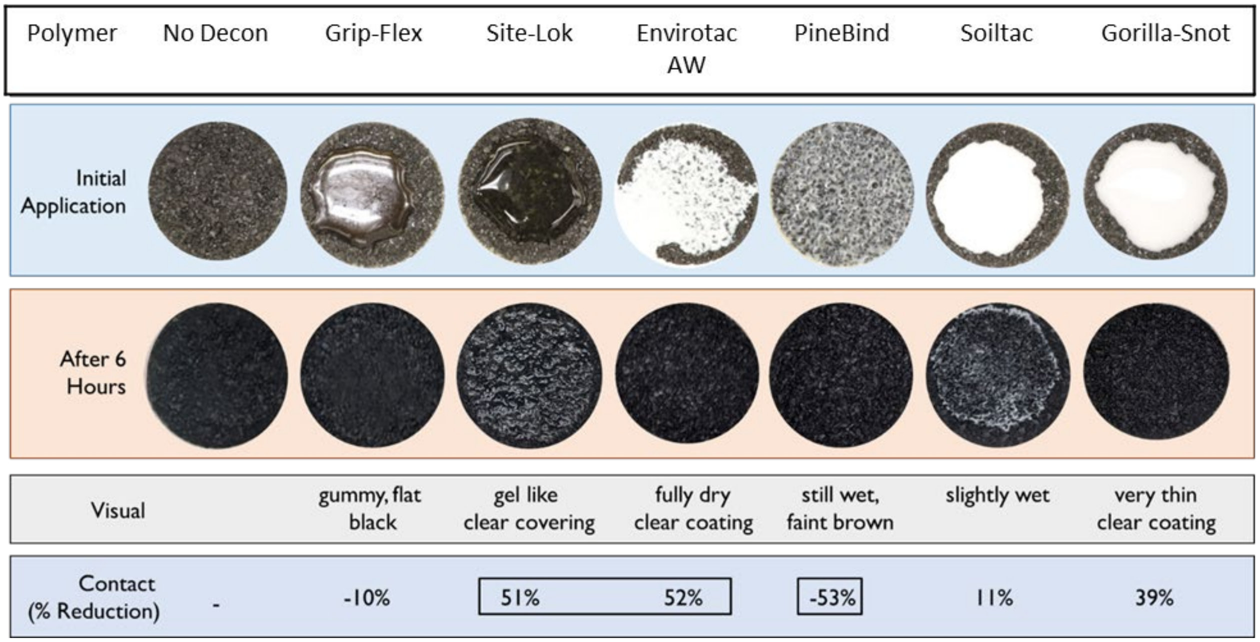


Figure 20. Contact transfer hazard for HD (10 g/m^2) on asphalt after 24 h age and 6 h decontaminant residence time.

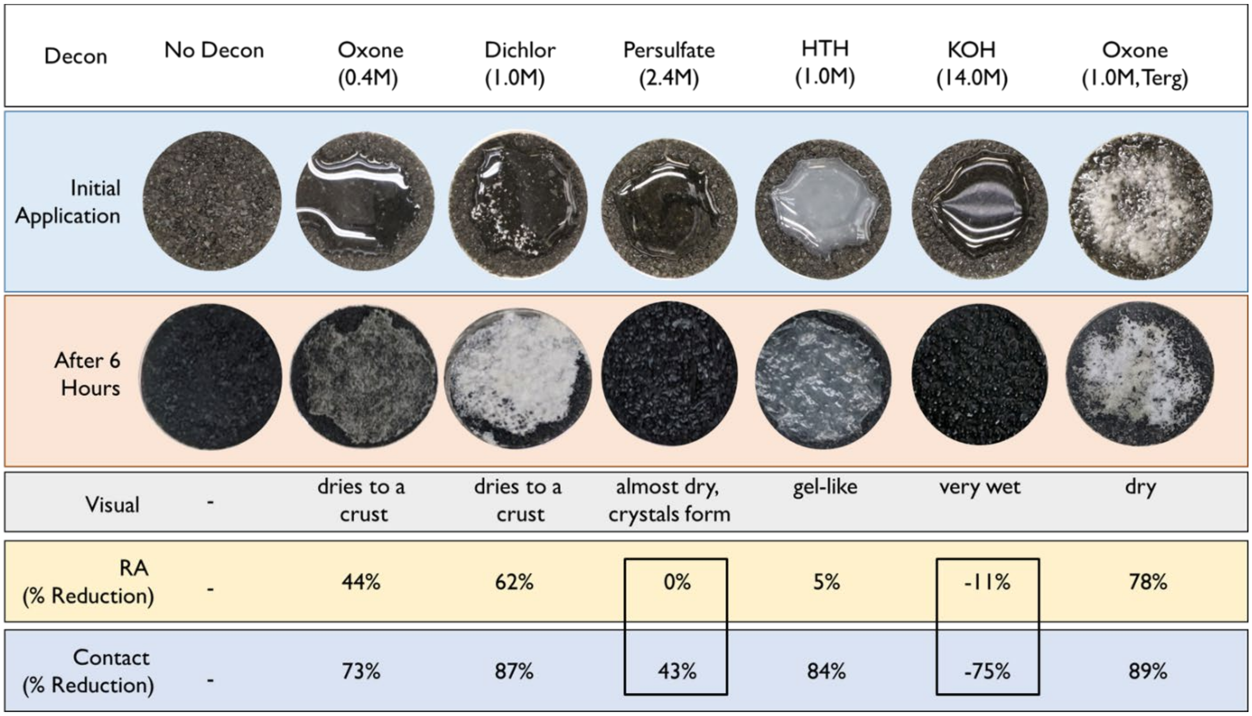
One hypothesis for the poor performance of barrier polymers was that the solutions were not given enough time to cure, which resulted in creation of a gummy or wet surface that increased contact transfer. This idea is supported by photographs of test panels, as shown in Figure 21. In particular, PineBind remained wet on the surface, while Grip-Flex had a gummy, undried appearance. Both of these polymers increased, rather than decreased, contact transfer; likely the wet surface increased the effective contact area, or it served to extract the contaminant and bring it to the surface to be made available for contact transfer.



Polymer	No Decon	Grip-Flex	Site-Lok	Envirotac AW	PineBind	Soiltac	Gorilla-Snot
Visual		gummy, flat black	gel like clear covering	fully dry clear coating	still wet, faint brown	slightly wet	very thin clear coating
Contact (% Reduction)	-	-10%	51%	52%	-53%	11%	39%

Figure 21. Images of barrier polymers applied to contaminated asphalt panels upon application and after a 6 h residence time.

These results contrast with those for the reactive decontaminants, which dried fully (with the exception of KOH). This dried decontaminant layer provided additional reduction in contact hazard, as shown in Figure 22. Being hygroscopic, KOH maintained a wet surface and was shown to increase contact transfer, similar to the uncured barrier polymers.



Decon	No Decon	Oxone (0.4M)	Dichlor (1.0M)	Persulfate (2.4M)	HTH (1.0M)	KOH (14.0M)	Oxone (1.0M, Terg)
Initial Application							
After 6 Hours							
Visual	-	dries to a crust	dries to a crust	almost dry, crystals form	gel-like	very wet	dry
RA (% Reduction)	-	44%	62%	0%	5%	-11%	78%
Contact (% Reduction)	-	73%	87%	43%	84%	-75%	89%

Figure 22. Images of reactive decontaminants applied to contaminated asphalt panels upon application and after a 6 h residence time.

To see whether increasing cure time would lead to increased performance of barrier polymers, an additional test was performed for HD on asphalt. In this experiment, decontaminant residence time was increased to a full 24 h, to allow polymers sufficient time to cure. To accommodate the testing schedule, the contaminant residence time was decreased from 24 to 6 h. The results of this study are shown in Figure 23. In general, the performance of the poorest-performing barrier polymers increased: PineBind, Grip-Flex, and Soiltac all showed significantly less contact transfer with the longer cure time. This likely confirms the hypothesis that these polymers had insufficiently cured at the time of prior testing. However, increased cure time had little effect on performance of the highest-performing barrier polymers, such as Site-Lok LX100 and Envirotac AW.

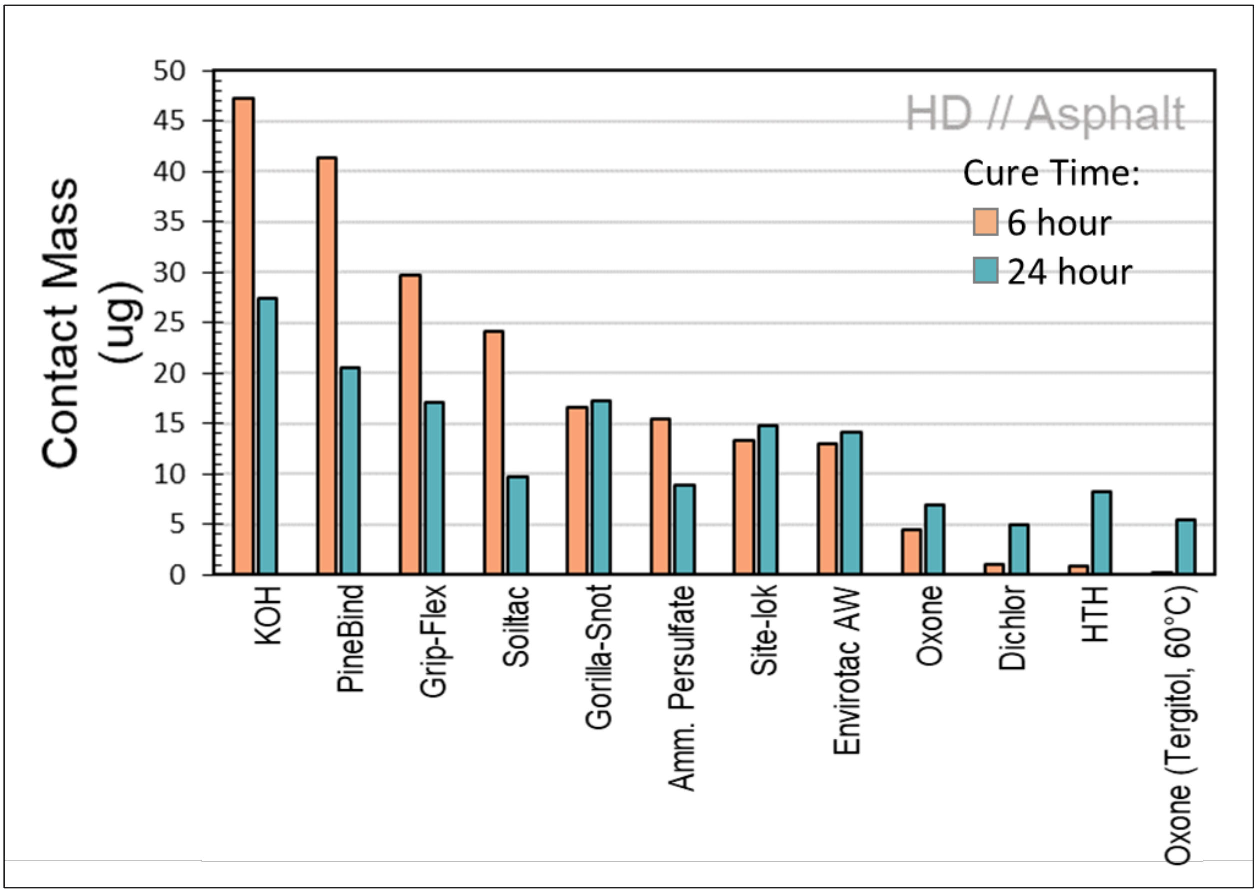


Figure 23. Comparison of 6 versus 24 h cure times for barrier and reactive decontaminants.

Distinct differences were observed during investigation of the contact hazard from VX on asphalt. VX had a significantly higher contact hazard than HD at the 24 h age time for untreated samples. VX has a lower vapor pressure, and thus little contaminant is removed via off-gassing and evaporation during the 24 h contaminant age time. VX may absorb into asphalt to a greater extent than HD and be less available at the surface for contact transfer.

Despite a higher initial contact hazard, this hazard was readily mitigated by several of the technologies investigated. As shown in Figure 24, nearly all reactive decontaminants and barrier polymers significantly reduced the contact hazard. All of the barrier polymers investigated showed significant improvement, and all provided at least a 90% reduction in contact hazard. Reactive decontaminants significantly outperformed barrier polymers and provided a 99% or greater reduction in contact hazard. The exception was Dichlor, which performed extremely poorly against VX on asphalt.

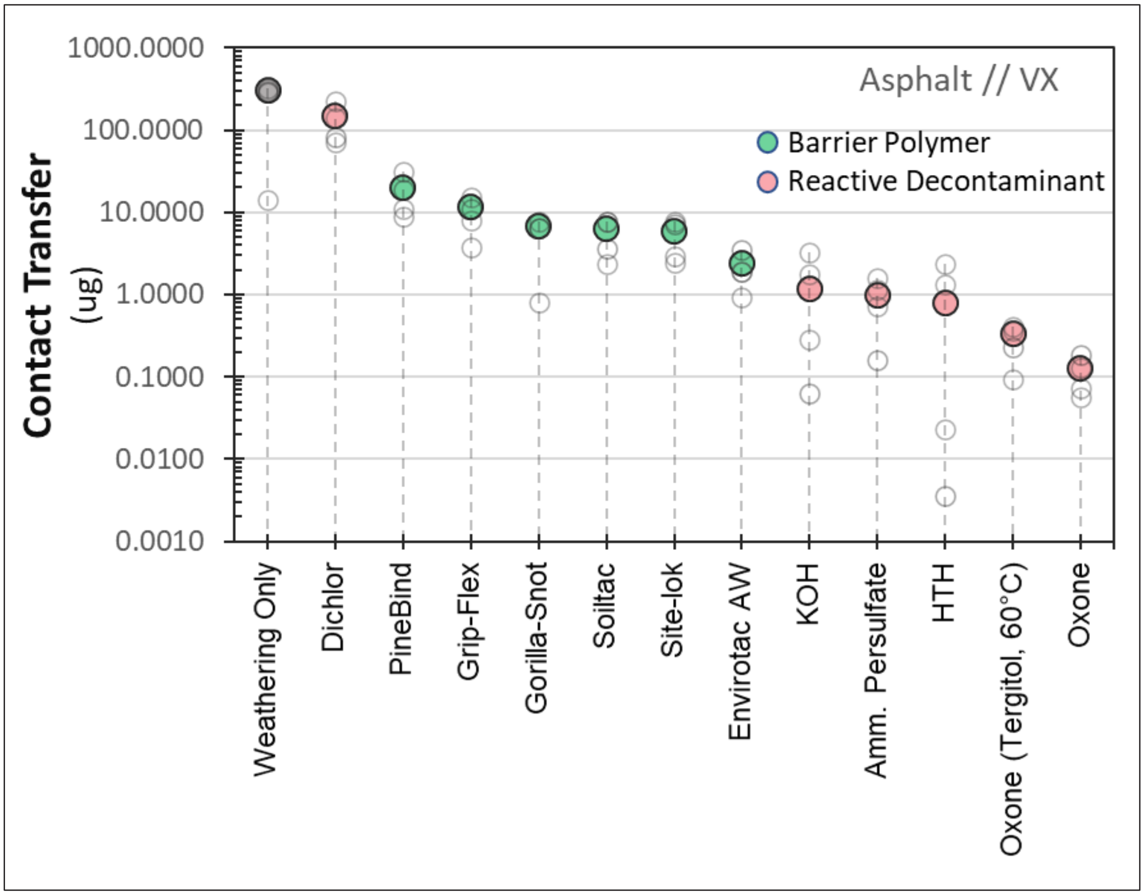


Figure 24. Contact transfer for VX (10 g/m^2) on asphalt.

Grip-Flex and PineBind exhibited the lowest performance among barrier polymers, providing an approximately 95% reduction in contact transfer. This may have been due to partial curing of the polymer, as was observed in the previous HD study. Soiltac, Gorilla-Snot, and Site-Lok all exhibited an approximately 98% reduction in contact transfer. Envirotac AW was the best-performing polymer, and it reduced the contact hazard by >99%. Similar to the results for HD on asphalt, the reactive decontaminants showed increased efficacy as compared to the barrier polymers. This was likely a result of the twofold effect of reactivity and crust formation that is discussed in DEVCOM CBC-TR-1699.[1] This twofold effect shows that because of the reactivity of the decontaminants, the contaminant available for contact transfer was reduced to a greater extent than was observed with use of the encapsulation nonreactive method by the barrier polymers.

The results for both HD and VX are summarized in Figure 25 as contact mass. These results reinforce the finding that VX had a higher contact transfer than HD when no treatment was applied. However, both barrier polymers and reactive decontaminants were more effective at reducing the contact transfer on VX than on HD. In every case, the post-treatment contact mass was smaller for VX than it was for HD, although generally, the transferred mass was within an order of magnitude. Site-Lok and Envirotac AW were the most effective polymers at limiting penetration of contaminant from the asphalt.

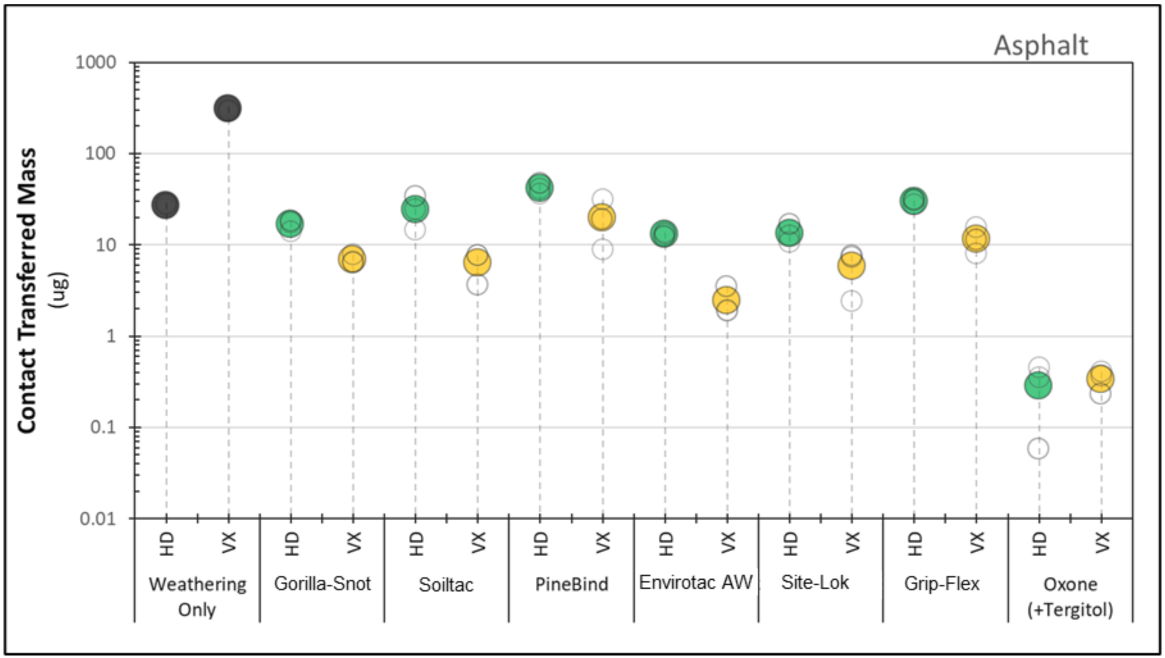


Figure 25. Contact transferred mass for HD (green) and VX (yellow) at 10 g/m^2 on asphalt.

5.4 Comparison of Barrier and Reactive Decontaminants on Concrete Substrates

Further studies were carried out to determine the efficacy of barrier polymers at preventing contact transfer on concrete substrates. Concrete is a significantly different matrix than asphalt. Concrete is porous and facilitates transfer of the water-based polymer throughout the material. Porous transport facilitates faster cure times, but it also results in polymer transfer into the material. This is in stark contrast to the hydrophobic asphalt surface, wherein the aqueous polymer solution remains on the surface and does not permeate significantly into the material prior to curing. Concrete is also basic and may exhibit mild reactivity toward some of the contaminants over longer duration.

The conditions of this study match those of the previous studies performed on asphalt in Section 5.3. Contamination density was maintained at 10 g/m^2 to allow a large dynamic range for performance analysis. Polymers were permitted to reside on the surface for 6 h to give adequate time for the polymer to cure. Contact testing was performed on all decontaminants. All polymers were prepared at a 6:1 dilution ratio. The testing parameters are listed in Table 3.

Table 3. Parameters for Concrete Contact Testing

Parameter	**Value**
Contaminants	VX, HD
Contamination density	10 g/m^2
Contaminant residence time	24 h
Material	Concrete (CSA with sand aggregate)
Decontaminants	Oxone (0.4 M), Oxone with 8% Tergitol (1.0 M, applied at 60 °C), Dichlor (1.0 M), ammonium persulfate (2.4 M), HTH (0.75 M), KOH (14 M, applied at 60 °C), Envirotac AW, Site-Lok, Soiltac, PineBind, Grip-Flex, Gorilla-Snot
Decontaminant residence time	6 h
Decontaminant volume	2.0 mL
Decontaminant application temperature	Room temperature, unless otherwise specified
Contact sampler material	Latex
Contact duration	5.5 min
Contact mass	1 kg
Contact extraction solvent	Isopropyl alcohol with 40 mM THT (VX) $CHCl_3$ with 40 mM THT (HD)

Contact testing data for HD on concrete is provided in Figure 26. The no-treatment condition yielded ~18 µg of transferred HD, which was similar to the amount transferred on the asphalt. Grip-Flex was the most effective polymer on concrete; it reduced the contact mass to approximately 0.1 µg, which represents a 99% reduction. Site-Lok, Soiltac, Envirotac AW, and Grip-Flex reduced contact transfer by 95% or more. Oxidative reactive decontaminants were all highly effective and reduced the contact hazard down to level-of-quantitation limits. This data shows that barrier polymers and reactive decontaminants are all viable options for remediation of the HD contact hazard on concrete.

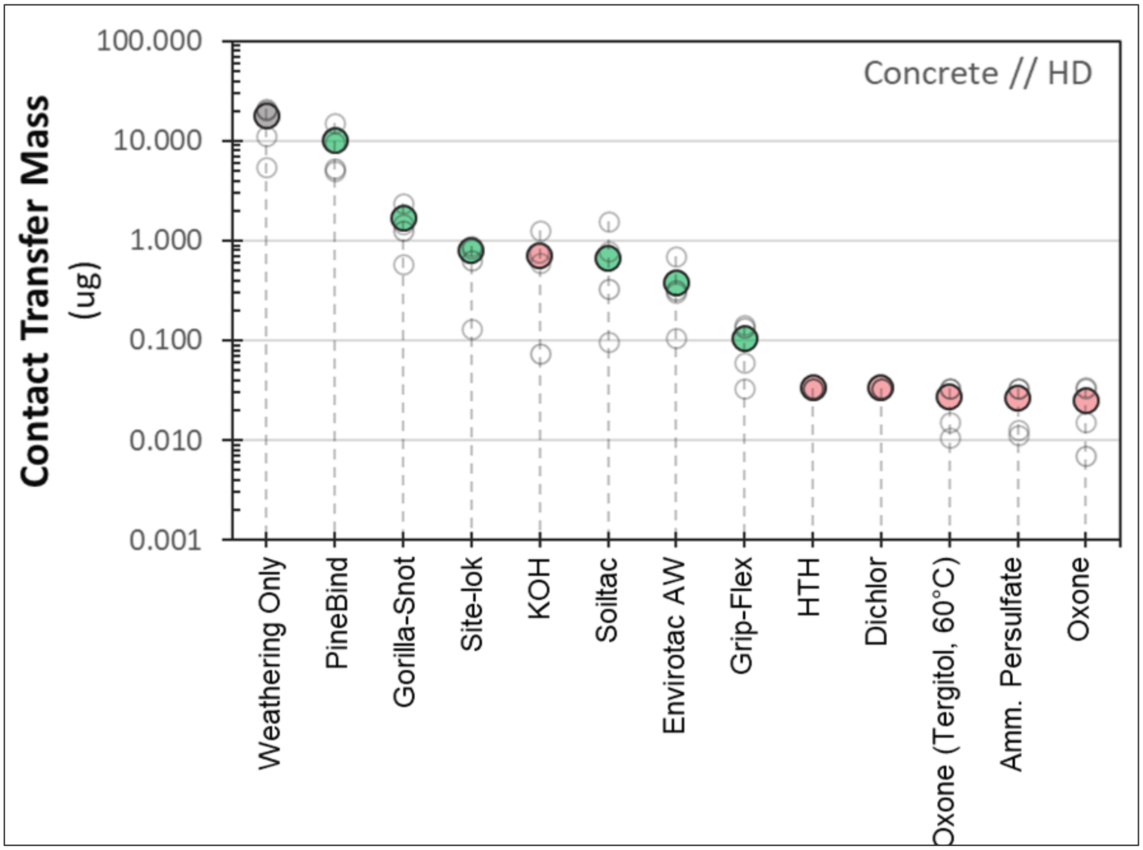


Figure 26. Contact transfer barrier polymers (green) and reactive decontaminants (red) for HD and concrete.

A similar trend was observed for VX on concrete, as shown in Figure 27. The no-treatment control exhibited significantly lower contact transfer on concrete (71 µg) compared to asphalt (306 µg). As observed with HD, Grip-Flex provided the largest reduction in contact mass of the barrier polymers on concrete, and reduced the contact hazard to 0.87 µg, which was a 98% reduction. These results were closely matched by those for Envirotac AW and Site-Lok. As observed in previous trials, oxidative decontaminants provided a significant reduction in contact transferred mass, reducing the transfer to below the limit of detection.

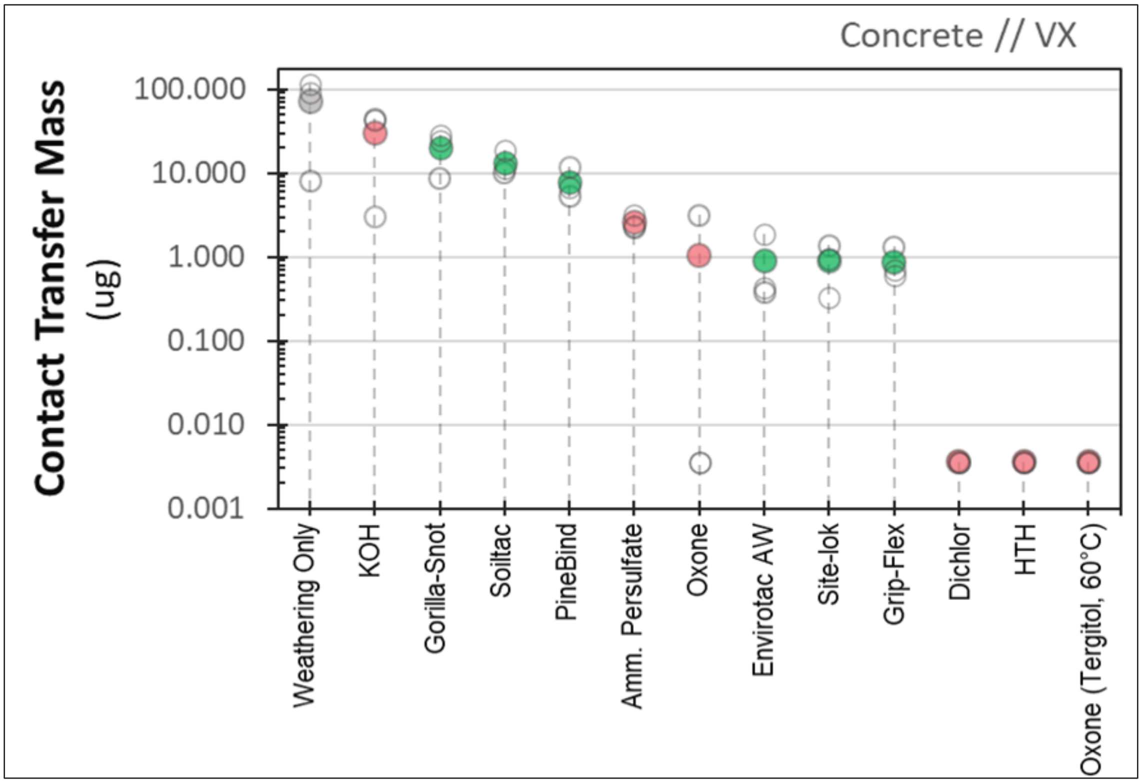


Figure 27. Contact transfer barrier polymers (green) and reactive decontaminants (red) for VX and concrete.

Figure 28 is a summary of the contact transfer results for the tested barrier polymers on concrete. As was observed with asphalt, the no-treatment controls were significantly higher for VX than for HD. However, the HD contact transfer was easily reduced by a variety of barrier polymers and reactive decontaminants. VX was also mitigated by a select few barrier polymers, notably Envirotac AW, Grip-Flex, and Site-Lok LX100. Grip-Flex was the best performer on concrete for both HD and VX.

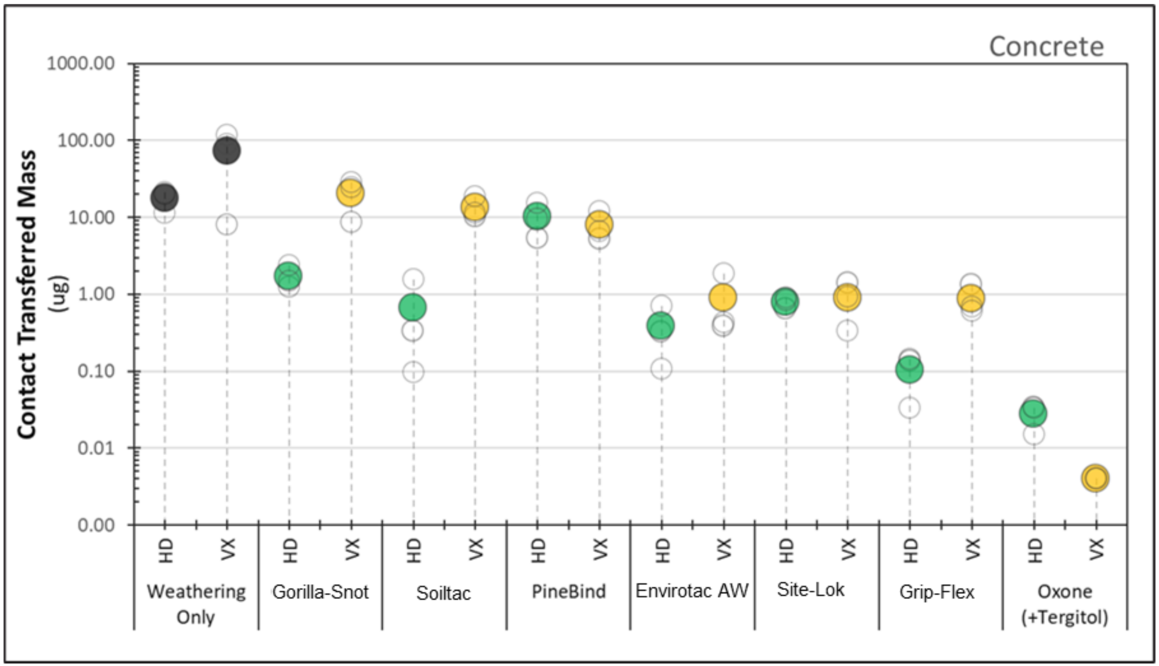


Figure 28. Residual agent data at 10 g/m^2 for concrete with reactive decontaminants.

6. LOGISTICS ANALYSIS OF BARRIER POLYMERS

The second stage in this work was the investigation of logistics associated with use of the barrier polymers. Some of the metrics used, such as material compatibility, shelf life, and cost, are common concerns associated with both barrier polymers and reactive decontaminants. Some concerns, such as polymer removal, are unique to the barrier polymers. Overall, this study investigated the logistical burden associated with the acquisition, application, and safety of each of the given polymers. No laboratory testing was performed, as all data provided was obtained from safety data sheets, protocol documents, or other vendor-provided documents. With initial efficacy studies complete using contact transfer, a logistics analysis of the barrier polymers was performed. This analysis looked at logistical concerns with the acquisition, application, and safety of each barrier polymer. Acquisition analysis looked at cost, shelf life, storage temperature, and presence of a DoD national stock number (NSN). Application analysis examined pot life, stability in seawater, cure time, and potential removal. The safety review looked at chemical compatibility alongside a cursory environmental, safety, and occupational health (ESOH) analysis.

The cost of the barrier polymer technology is likely one of the most important logistical concerns when selecting a wide-area decontaminant. The true cost of a barrier polymer can be measured in different ways, including the purchase cost, the cost per area decontaminated, and the lifecycle cost. The cost analysis is summarized in Table 4. In addition to the cost analysis for the barrier polymers, a cost analysis is included for currently fielded super tropical bleach (STB) and one of the down-selected reactive decontaminants from this program.

Table 4. Cost Analysis of Barrier Polymers

	Cost ($/gallon)	Shelf Life (yrs)	Batch Cost ($/447 gal)	Area Covered (acre/batch)	Area Cost ($/acre)	Lifecycle Cost ($/acre·year)
SiteLok LX100	2.00	3	$ 894.00	0.42	$ 2,128.57	$ 709.52
EnviroTac AW	1.50	0.5 - 1	$ 670.50	0.42	$ 1,596.43	$ 3,192.86
GripFlex	2.00	2+	$ 894.00	0.42	$ 2,128.57	$ 1,064.29
SoilTac	1.50	1**	$ 670.50	0.42	$ 1,596.43	$ 1,596.43
Gorilla Snot	0.48	0.25	$ 216.05	0.42	$ 514.40	$ 2,057.62
PineBind	1.13	3+	$ 502.88	0.42	$ 1,197.32	$ 399.11
Oxone (low)	$ 4.93	10	$ 2,205.89	1.20	$ 1,838.24	$ 183.82
Oxone (high)	$ 9.03	10	$ 4,036.89	0.84	$ 4,780.83	$ 478.08
STB	$ 10.47	5	$ 4,678.38	0.34	$ 13,568.65	$ 2,713.73

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Most Desirable ---------→ Least Desirable

Cost was estimated by examining the single-use cost (cost per gallon) for acquisition of the barrier polymer or as a lifecycle cost (cost per acre per year). Single-use cost may help to determine the viability for a single use, where a barrier polymer is not prestaged or stored. As shown in Figure 29, as compared to the reactive technologies, all of the barrier polymers are significantly cheaper to purchase for a single use. However, lifecycle cost may be used in situations where decontaminant is purchased and stored in anticipation of use. This cursory analysis was performed by dividing the cost per acre by the shelf life of the decontaminant. Oxone has a much longer shelf life than most water-based polymers and thus has a significantly lower life-cycle cost.

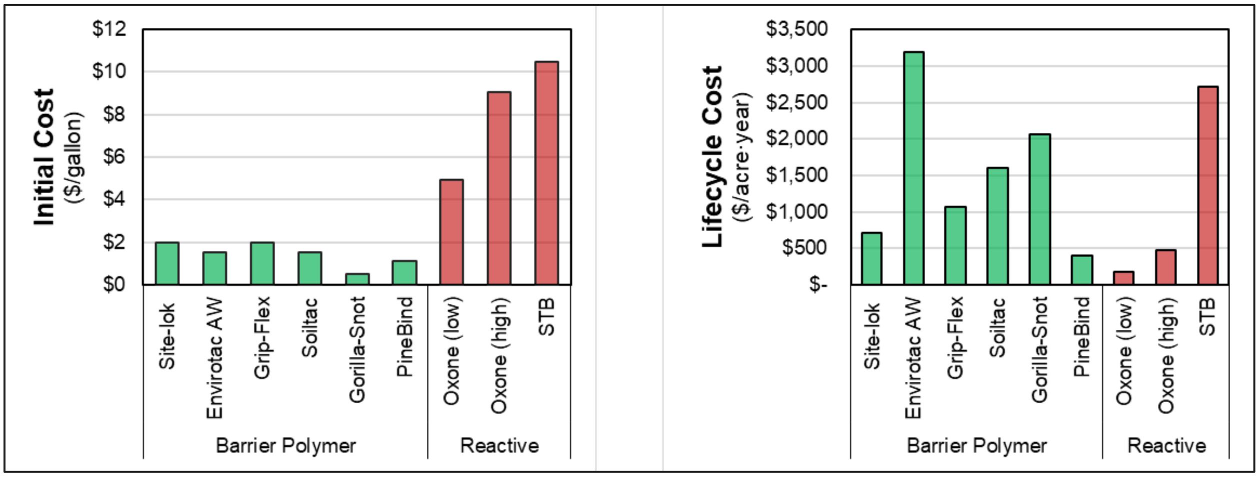

Figure 29. Cost metrics for selected barrier polymers.

Cost can also be compared to efficacy using cost-efficacy plots, such as those provided in Figure 30. These plots demonstrate that reactive solutions are typically the best trade-off between cost and efficacy when looking at lifecycle cost. Some formulations, such as Site-Lok and Grip-Flex, provide reasonable value for moderate performance.

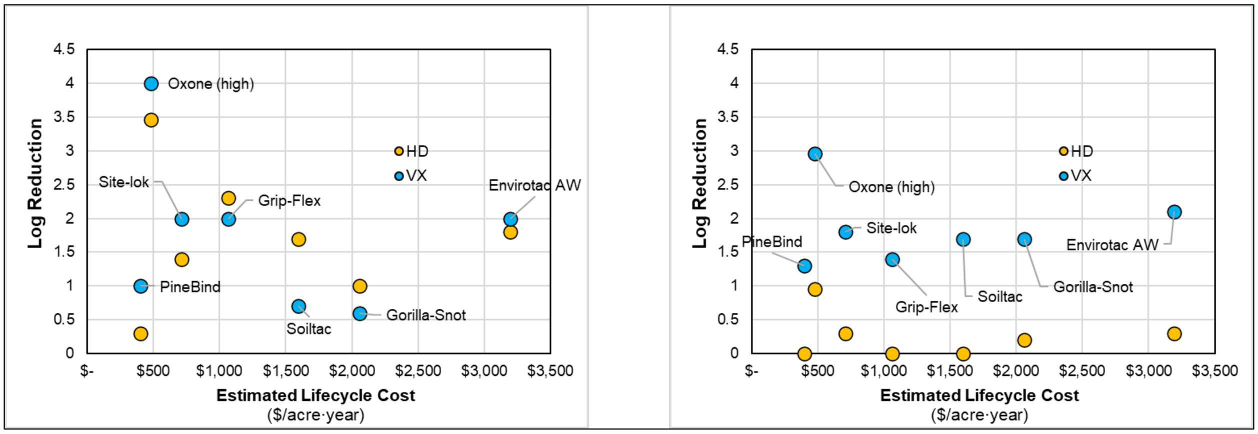

Figure 30. Cost-efficacy plots comparing reduction in contact hazard to cost for (left) concrete and (right) asphalt for VX (blue) and HD (yellow).

Other acquisition concerns such as shelf life, storage, and availability can have a significant impact on logistics. As shown in Table 5, vinylic and acrylic polymers have short shelf lives and are ruined upon freezing. Thus, storage and stockpile maintenance are significant concerns for these polymers. However, because of their use in dust control and temporary roadway construction, these items are commonly stored by the U.S. Government. These polymers can be easily acquired and have assigned NSNs. Nonacrylic polymers, namely Site-Lok, Grip-Flex, and PineBind, have longer shelf lives and do not have significant issues with freezing. However, use of these materials is more limited, and these items do not have assigned NSNs.

Table 5. Storage and Procurement Logistics of Barrier Polymers

	Polymer Type	**Shelf Life (years)**	**Storage Temperature**	**DoD NSN**
Site-Lok	Methylcellulose (HPMC)	3+	Does not freeze (–50 °F)	None
Grip-Flex	Bitumen	2+	Freezing can lower coating longevity	None
PineBind	Pine pitch	3+	Freezes but can be thawed	None
Gorilla-Snot	Vinylic	0.25	Do not freeze	6850-01-542-5389
Envirotac AW	Acrylic	0.5–1	Do not freeze	6850-01-538-3162
Soiltac	Vinylic	1	Do not freeze	6850-01-519-4708

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Most Desirable ----------→ Least Desirable

Another concern is associated with polymer application and removal. Based on data provided by the various manufacturers, application parameters such as preparation in seawater, pot life, cure time, and removal were examined for each of the polymers. As shown in Table 6, Only Site-Lok, Soiltac, and Envirotac AW could be prepared in seawater. Pot lives for all polymers were at least 12 h. Every polymer except for PineBind cures in less than 2 h. These conditions are likely sufficient for each of the barrier polymers in a possible operational context. Most polymers could not be removed without the use of solvents, with the exception of Site-Lok, which could be removed using water and vacuum trucks. The removal of these barriers would warrant the need for other remediation efforts, as the potential exists for new contamination hazards to occur during and after the removal process. Those hazards are not explored in this effort.

Table 6. Logistics of Barrier Polymer Application

	Polymer Type	Seawater Preparation?	Pot Life	Cure Time	Removal
Site-Lok	Methylcellulose (HPMC)	Yes	1+ month	1–2 h	Possible (water, vacuum truck)
Soiltac	Vinylic	Yes	12 h	1–2 h	Difficult, requires solvents
Envirotac AW	Acrylic	Possible, not recommended	72 h	<30 min	Unknown
Grip-Flex	Bitumen	Likely no	Unknown	<30 min	Not possible
Gorilla-Snot	Vinylic	No	12 h	<15 min	Difficult, requires solvents
PineBind	Pine pitch	No	1+ month	1–4 h	Not possible

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Most Desirable ----------→ Least Desirable

Overall, application and safety concerns were minimal for each of the polymers studied. These polymer products have been applied and used at large scale in prior U.S. Government applications and protocols for application are established. Similarly, these products were formulated and evaluated for occupational health and environmental impact. From a safety perspective, all of the polymers studied produce relatively benign health effects and are significantly safer than using reactive oxidants. Therefore, shelf life and storage limitations have the largest impact on the logistics profile of each barrier polymer. Vinylic polymers and acrylic polymers had a short shelf and spoiled upon freezing. Site-Lok, Envirotac, and Grip-Flex all had significantly longer shelf lives and could be frozen. From these results, the nonvinylic polymers are recommended for further study based on the logistics profile. The exception to this is Soiltac, which has recently been formulated as a solid powder. This new formulation may overcome some of the logistics concerns with shelf life and storage; further testing is needed to confirm efficacy. A complete summary of the logistics analysis is given in Table 7.

Table 7. Logistics Analysis of Barrier Polymers

	Acquisition				Application				Safety	
	Cost ($/gal)	Shelf Life (years)	Storage Temp.	DoD NSN	Seawater Preparation?	Pot Life	Cure Time	Removal	ESOH	Chemical Composition
Site-Lok	2.00*	3+	Does not freeze	No	Yes	1+ month	1–2 h	Possible	Safe	Safe
Envirotac AW	1.50	0.5	Do not freeze	Yes	Possible	72 h	<30 min	Unknown	Safe (limited studies)	Avoid degreasers, lime
Grip-Flex	2.00	2+	Can freeze	No	Likely no	Unknown	<30 min	Not possible	Safe	Safe
Soiltrac	1.50	1†	Do not freeze	Yes	Yes	12 h	1–2 h	Requires solvents	Safe	Safe
Gorilla-Snot	0.48	0.25	Do not freeze	Yes	No	12 h	<15 min	Requires solvents	Safe	Safe
PineBind	1.13	3+	Can freeze	No	No	1+ month	1–4 h	Not possible	Safe	Safe

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Most Desirable ----------→ Least Desirable

*Cost will likely be reduced, will be used at a higher dilution factor.

†A powered version is available that has a longer shelf life and is significantly easier to prepare and apply.

7. SUMMARY AND DOWN-SELECTION

The final selection of recommended polymers is based on logistics and efficacy analyses. A ranking of polymer efficacy based on the reduction in contact hazard is provided in Table 8. The vapor penetration data was not used in the overall ranking of the barrier polymers because a simulant was used, and the substrates were of sufficiently different material that it would not be equitable to compare vapor breakthrough of the barriers for the purpose of down-selection. Further study of vapor hazards is necessary to verify efficacy of barrier polymers against potential vapor hazards. All of the polymers struggled with reducing the contact transfer mass of HD on asphalt, which was also a challenge for the reactive decontaminants. However, Envirotac AW, Site-Lok, and Grip-Flex all reduce the contact transfer mass of the other material–contaminant pairs by 95% or more. Soiltac performs well against VX on asphalt and HD on concrete and also provides modest performance against VX on concrete.

Table 8. Log Reduction in Contact Hazard for Barrier Polymer Versus Weathering Controls

Rank	Polymer	Asphalt		Concrete	
		HD	VX	HD	VX
1 (best)	Envirotac AW	0.32	2.12	1.78	2.03
2	Site-Lok	0.32	1.77	1.35	1.98
3	Grip-Flex	–0.04	1.44	2.29	1.94
4	Soiltac	0.07	1.71	1.68	0.74
5	Gorilla-Snot	0.21	1.65	1.03	0.60
6 (worst)	PineBind	–0.18	1.25	0.28	0.98

Most Desirable ----------→ Least Desirable

Logistics analysis showed that most of the polymers had similar application and safety profiles, as shown in Table 9. The largest defining factors were shelf life and storage constraints. Vinylic and acrylic polymers had short shelf lives and spoiled upon freezing, which increased the difficulty of storage and inventory management. Polymers of other materials tended to have longer shelf lives and could withstand freezing storage temperatures. For this reason, Site-Lok, Grip-Flex, and PineBind were recommended based on their logistics profile.

Table 9. Summary of Logistics Analysis of Barrier Polymers

		Polymer	Acquisition	Application	Safety
Recommend	Site-Lok	Methylcellulose	Long shelf life, does not freeze	Seawater preparation, moderate cure	Safe
	Grip-Flex	Bitumen	Long shelf life, can be frozen	No seawater preparation, short cure	Safe
	PineBind	Pine pitch	Long shelf life, can be frozen	No seawater preparation, long cure	Safe
No	Envirotac AW	Vinylic	Short shelf life, freezes	No seawater preparation, short cure	Safe
	Soiltac	Acrylic	Short shelf life, freezes	Can prepare in seawater, short cure time	Safe
	Gorilla-Snot	Acrylic	Short shelf life, freezes	no seawater preparation, short cure	Safe

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Most Desirable ----------→ Least Desirable

From the combination of contact transfer efficacy and logistics analysis, the top performer was Site-Lok. Site-Lok is preferred over the slightly more efficacious Envirotac AW because of logistical constraints: Envirotac AW cannot be stored at freezing temperatures.

The overall top performer was Site-Lok (sold by National Land Management). This methylcellulose polymer is a stockpile sealant composed of biodegradable and environmentally friendly monomers. The polymer has a long shelf life, does not freeze, can be prepared in saltwater, and is the only polymer that has any possibility of removal from the surface once it is applied. Site-Lok formerly had a NSN number, which could be reinstated. This polymer was tested at a 6:1 dilution ratio, which resulted in a viscous liquid. Spraying may require further dilution, which may decrease efficacy; however, it would also drive down cost. With rain, this polymer "self-heals" by reactivating and curing. Rain events may lead to off-gassing, which would warrant further study if this polymer were selected.

Grip-Flex is an asphalt sealcoat composed of a water-based bitumen emulsion. This product is approved for use at airfields and was designed to meet Federal Aviation Administration (FAA) specifications. The water-based spray seal can be applied alone, but it is often mixed with aggregate for microsurfacing. As part of a requirement for airfield use, it has also passed environmental water-leach tests. Although this product may be applied using a terrain decontamination spray bar, spraying to meet FAA requirements may require specialized equipment and personnel. This product has a moderate shelf life (2+ years) and can be frozen, although freezing will affect the durability of the final coating. This product is typically used undiluted, but these studies investigated the use at a 6:1 dilution ratio. Use of the undiluted product will drive up cost, but may lead to increased performance. The use of the product by the U.S. Air Force likely means it is available to the DoD, but no NSN was provided. This product likely cannot be prepared in seawater, and it leaves a dark or black coating on any surface it is sprayed on.

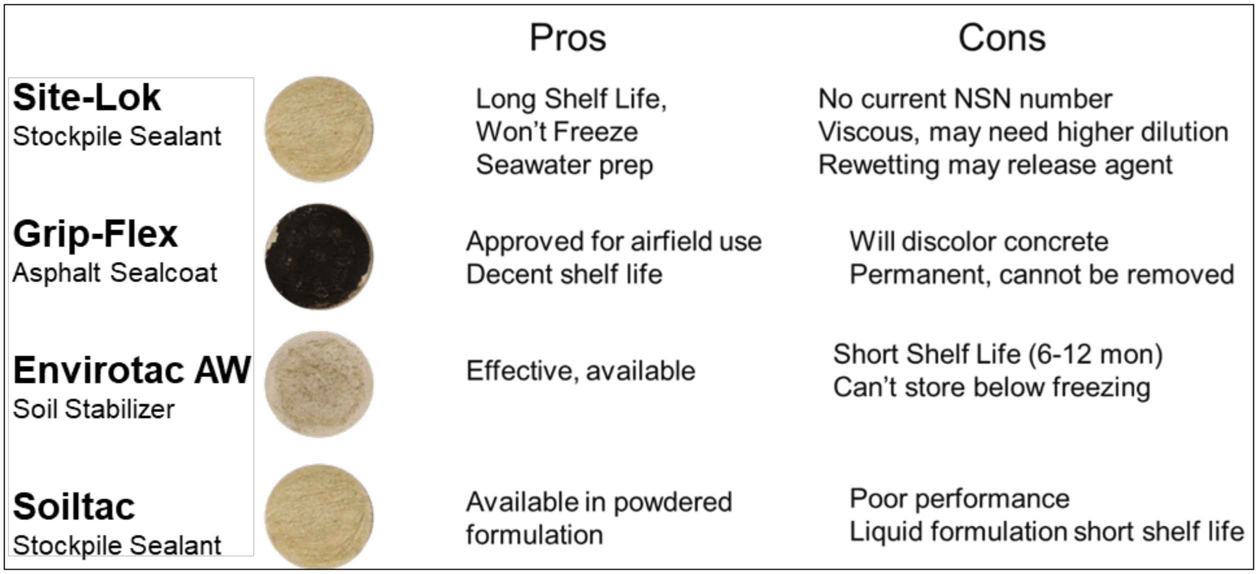
The soil stabilizer Envirotac AW was another high-performing barrier polymer. This more-standard acrylic polymer suffers from a short shelf life (6 months to a year) and cannot be frozen. Envirotac AW is one of several polymers produced by Environmental Products and Applications and is formulated specifically for durability. Other polymers produced by this manufacturer include standard (Envirotac II), concentrated (Envirotac SC), and economy-grade (Earth Glue) formulations. Envirotac II has been used by the Marines at Twentynine Palms, CA and has a DoD NSN. Although it is quite effective, this polymer is limited by a short shelf life and is not recommended for use with seawater.

Soiltac is a vinylic polymer used as a soil stabilizer. This polymer is a "prime product" that has been used for road construction in Afghanistan. Soiltac cures by evaporation and dries to give a colorless coating. The product had limited efficacy on VX and concrete as compared to Grip-Flex, Site-Lok, and Enivrotac AW. It has a short shelf life and cannot be frozen. However, Soiltac can be prepared with seawater and has an assigned DoD NSN. It is available in a powdered form, which conveys the benefits of a very long shelf life and lower shipping weight and storage cost. The availability of the powdered version is one reason this polymer can still be recommended for consideration as a wide-area encapsulant.

Gorilla-Snot is an economy version of Soiltac, and is also a vinylic-based soil stabilizer. This product is the least expensive by far, costing less than 50 cents per gallon of diluted product. The polymer itself resembles paint primer, and it dries to form a clear coating. However, Gorilla-Snot exhibited limited performance in the contact transfer test and has an extremely short shelf life. Moreover, this polymer cannot be frozen and cannot be prepared in seawater. Although it is commonly used and readily available, Gorilla-Snot cannot be recommended because of the poor efficacy results and its short shelf life.

PineBind is a natural pine pitch-based polymer used as general-purpose binder. It can be used for soil stabilization or as a binder for larger aggregates. Although PineBind has been used in environmental remediation efforts, it is not effective on concrete or asphalt for purposes of encapsulation. The polymer leaves behind a sticky residue that may also transfer to vehicles and personnel traveling over an area. It has excellent cost and shelf life considerations; however, this polymer cannot be recommended because of its poor performance in contact transfer tests.

The aforementioned studies demonstrate that several barrier polymers may be considered for further study, as listed in Figure 31. Site-Lok has a long shelf life, can be prepared in seawater, and will not freeze in storage, but it may have availability and rewetting issues. Grip-Flex is approved for airfield use and has a moderate shelf life, but it is permanent and non-removable. Envirotac AW is effective and readily available, but it has a short shelf life and can freeze in storage. Soiltac has an extremely short shelf life, but alternative formulations using powered polymer may have significant logistical advantages. This program has provided the initial data set to demonstrate the use of barrier polymers as an orthogonal technique for CWA remediation on asphalt and concrete. Further screening, optimization, and durability studies are needed to advance the viability of this approach. However, most of these products are commercially available and purchasable by the DoD and could be readily acquired and used given existing infrastructure.



	Pros	Cons
Site-Lok Stockpile Sealant	Long Shelf Life, Won't Freeze Seawater prep	No current NSN number Viscous, may need higher dilution Rewetting may release agent
Grip-Flex Asphalt Sealcoat	Approved for airfield use Decent shelf life	Will discolor concrete Permanent, cannot be removed
Envirotac AW Soil Stabilizer	Effective, available	Short Shelf Life (6-12 mon) Can't store below freezing
Soiltac Stockpile Sealant	Available in powdered formulation	Poor performance Liquid formulation short shelf life

Figure 31. Final recommendation of barrier polymers for further study.

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ACRONYMS AND ABBREVIATIONS

APOD	airport of disembarkation
CSA	calcium sulfoaluminate
CWA	chemical warfare agent
CWAD	chemical wide-area decontaminant
ESOH	environmental, safety, and occupational health
FAA	Federal Aviation Administration
FTIR	Fourier-transform infrared
GD	pinacolyl methyl phosphonofluoridate, soman
HD	bis(2-chloroethyl) sulfide, mustard gas
HTH	high-test hypochlorite
MeS	methyl salicylate
SPOD	seaport of disembarkation
STB	super tropical bleach
THT	tetrahydrothiophene
TRL	technology readiness level
USAF	U.S. Air Force
VX	*O*-ethyl-*S*-(2-diisoproylaminoethyl) methyl phosphonothiolate

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