Transport of Persistent Chemical Warfare Agents HD and VX into Porous Materials and Permeable Layers

Practical data for remediation of contaminated building materials

Purpose

The Organisation for the Prohibition of Chemical Weapons (OPCW) continues to investigate the alleged use of chemical weapons around the world. The use of chemical warfare agents (CWAs) on the battlefield has a long history. More recent (since 2012) use has occurred in Syria, Malaysia, the United Kingdom, and Russia [1-4]. Two CWAs, the nerve agent VX and blister agent sulfur mustard (HD), are of great concern due to their high toxicity and high persistence in the environment. This brief compiles data from several recent U.S. Environmental Protection Agency (EPA) bench-scale studies [5-10] that assessed the fate and transport of these two chemicals, each studied separately, into porous and/or permeable materials. This summary provides decision-makers with practical information on the expected degree of absorption/permeation of VX or HD (VX/HD) into several types of materials following a chemical incident resulting in the release of the CWA to the environment. This practical information will inform the remediation strategy for the reopening of contaminated buildings or infrastructure.

Background

EPA's Homeland Security Research Program conducts research to help on-scene coordinators and decision-makers minimize human health effects and environmental impacts following the release of a CWA. A release of a persistent CWA inside a building would result in its deposition onto a large variety of materials ranging from nonporous, impermeable materials to those with varying degrees of porosity leading to permeation of the agent into and potentially through the material.

Definitions and Descriptions

Permeation can occur in two main ways. First, a material may be porous, meaning that it contains void spaces (spaces not occupied by the atomic/molecular framework that make up the structure). Bulk VX/HD liquid can enter these pores by capillary action, just like a paper towel absorbs water. Second, for some materials like certain polymers, the large polymer molecules are close enough together that they do not form pores, but VX/HD molecules can move through them via forces of diffusion, i.e., to move from a place of high concentration to a place of low concentration, because the VX/HD are essentially soluble in the polymers. It is like a drop of food coloring as it dissolves in and spreads through a glass of water. Permeation of VX/HD into building materials can occur as a combination of these two processes, depending on the building material. For example, liquid VX/HD can enter the pore structure and move some depth into the material, all the while adsorbing onto the surface of the material and diffusing through it.

To simplify resulting complexities, for purposes of discussion, designing experiments, and practically applying the resulting data, it is useful to group materials via common characteristics. Figure 1 illustrates such a grouping, including common materials falling into groups that need to be considered in a remediation strategy following a CWA incident. A brief description of each material group follows.

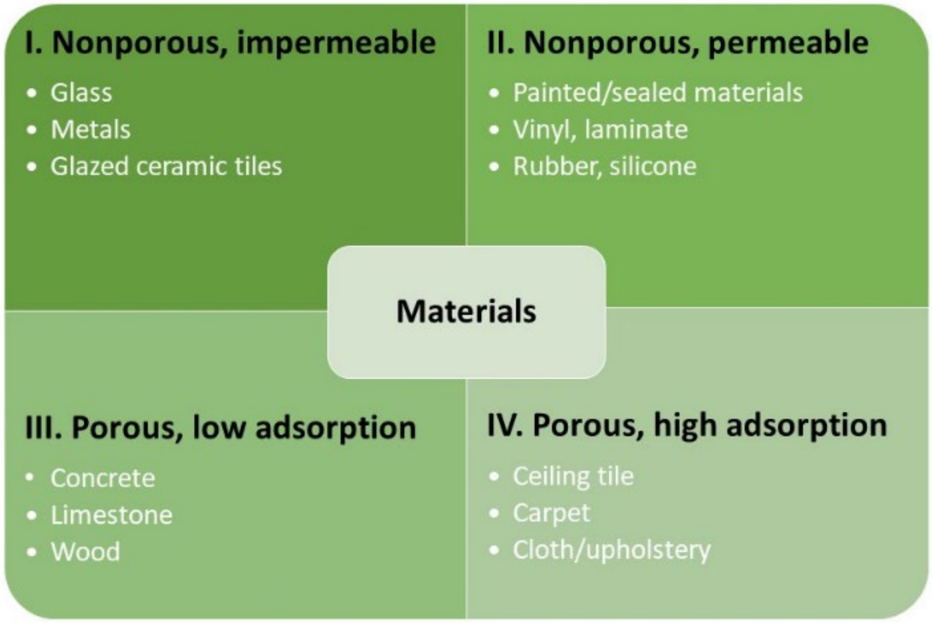

Figure 1. Generic grouping of commonly used building materials based on their interaction with VX/HD.

I. Nonporous, impermeable materials

VX/HD present on materials such as glass and various metals are expected to remain on the nonporous, impermeable surface from which they (slowly) evaporate or possibly degrade via natural attenuation.

II. Nonporous, permeable materials

Painted and/or sealed surfaces fall in the category of nonporous materials. Such paints and sealants are intended to prevent water absorption into the porous material behind or below it (e.g., painted drywall or sealed concrete, wood). However, VX/HD, being oily substances, may behave differently than water because paint or sealant layers are permeable to VX/HD [5] via diffusion. Painted surfaces account for 60% to 70% of exposed surfaces in residences [11]. Once this occurs, VX/HD can slowly evaporate from these (painted) materials, remain in the permeable paint/sealant layers, or diffuse into the underlying porous and even more absorptive material. Organic materials such as rubber, silicone, vinyl or laminate also fall into this category, as VX/HD can diffuse into these materials, too. If these organic materials are thick enough and the VX/HD have permeated far enough into the material, it may take a very long time for them to diffuse back out. Then, these materials become reservoirs for VX/HD, potentially presenting long-term remediation challenges.

III. Porous, low adsorption materials

Liquid HD/VX can penetrate quickly (seconds, minutes) into porous materials such as unsealed concrete or limestone. The penetration depth into a porous material, movement across the substrate, and possible chemical degradation reactions with the surrounding matrix will impact the remediation strategy. In the absence of degradation processes, VX/HD may reside within a porous material for periods of time that can exceed the time they would be present on a nonporous surface. Hence, the materials become reservoirs of VX/HD, with associated remediation challenges. For materials in this category, the VX/HD are not expected to adsorb and diffuse through the material but remain on the interior surface of the pores, meaning that they potentially can be physically dislodged from the pores.

IV. Porous, high adsorption materials

Materials in this category may be the most difficult to remediate and may be candidates for disposal. Namely, the VX/HD not only penetrates the porous structure but then diffuses into the material. Thus, remediation techniques must overcome both mechanisms, which can be technically complex or uneconomical. Many of the materials in this category are polymeric materials manufactured in a manner that they are also porous. For example, carpets and clothes can be composed of natural or synthetic polymer fibers, which are processed to have desirable touch-and-feel properties, which coincidentally can increase porosity of these materials. The fate and transport of VX/HD for this group of materials will be part of future studies.

Experimental Methods

EPA studied the transport of VX/HD when applied to several porous and to painted and sealed materials. VX (O-ethyl S-[2-(diisopropylamino)ethyl] methyl-phosphonothioate) is highly persistent [12] with a vapor pressure of 7×10^{-4} mm Hg at 20 °C and oily appearance. HD [bis(2-chloroethyl)sulfide] is less persistent with a vapor pressure of 0.072 mm Hg at 25 °C [13]. The experimental designs of the EPA studies are described briefly here. Contamination occurred in each study by application of a single droplet of chemical agent (typically 1 or 2 µL volume across these studies) onto these materials.

Study A [5] investigated the permeation of VX/HD into three different paint types and two types of sealants. This included measurement of the partitioning of the chemical into the permeable paints/sealants and underlying simulated porous material as function of time (up to 48 h for HD and 72 h for VX) (Figure 2).

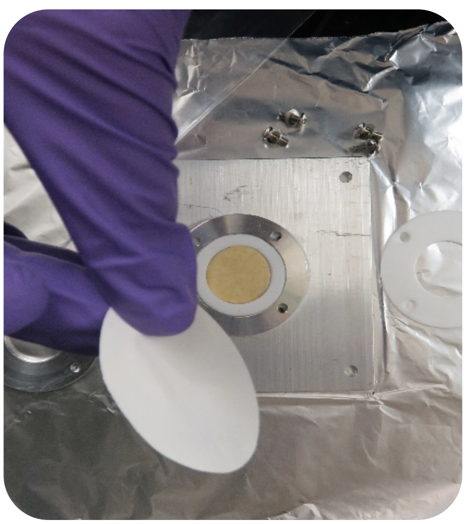

Figure 2. Setup with paint layer and solid phase extraction disk below the layer.

Study B [6] assessed the level of VX permeation into limestone as a porous inorganic material and into sealed concrete as a nonporous organic barrier to a porous inorganic material.

Studies C [7] and D [8] (as summarized in [9]) addressed the persistence of VX as function of temperature and material. This study did not measure whether the amount of VX remained on the surface or whether it permeated or absorbed into the material. Instead, it provided information how much of VX remained with the coupon (the extracted sample of the material being tested) after specific time.

Study E [10] was a decontamination study and was not designed to focus on the fate and transport of VX/HD. However, the positive controls that were part of this study provided insight in the fate and transport by measurement of the remaining VX/HD mass on the surface (surface wipe sample) and mass held by the porous or permeable material (extraction of the full material after the surface wipe sampling).

Results

Table 1 summarizes the expected percent of VX/HD that can be detected on the surface (as determined via surface wipe sampling) 24 h (unless noted otherwise) after the contamination occurs. Also noted, where applicable, is how much of the VX/HD migrated into the material (full material extraction) and how much was recovered from the underlying material (Studies A and E) or within the first 0.25-inch depth (Study B) or held by the material itself (Studies C and D). Table 2 provides additional information associated with the paints and sealants in Table 1. Prior to the fate and transport studies, surface wipe sampling methods and material extraction methods were verified, as applicable, on their high efficiency to sample VX/HD from all materials.

Table 1. Surfaces, Materials, Function, Properties, and Percent Recoveries for VX and for Sulfur Mustard (HD) after 24 h.

Surface	Subsurface Material	Function	Water Permeability Top Layer	Oil Permeability Top Layer	VX percent on surface and in other layers or material after 24 h	HD percent on surface and in other layers or material after 24 h	Study ID (Table 2)	Ref.
I. Nonporous, impermeable materials								
Glass	Same		None	None	65% (coupon)	*Not included in test*		7
Galvanized metal	Same	HVAC ductwork			48% (coupon)	*Not included in test*		7
Glazed Ceramic Tile		Wall, floors			18% (coupon)	*Not included in test*		7
Glass					73% (coupon)	*Not included in test*		8
Glazed Ceramic Tile		Wall, floors			74%	120% [5 h], <0.5% [76 h]		9
Glass	Same				94%	61% [5 h], <0.5% [76 h]		9
Stainless Steel	Same				79% 57% 89%	*Not included in test* 40%, 0.12% [48 h] 31%, 0.01% [48 h]		6 5 5
II. Nonporous, permeable materials								
Paint - Latex Flat [i] **Paint - Latex Semi-Gloss [ii]** **Paint - Oil-Based [iii]**	Steel	Surrogate for nonporous material	Low-Medium	Low	42%; 15% in latex flat 17%; 30% in latex semi-gloss 26%; 8% in oil-based layer	4%; 76% in latex flat 3%; 89% in latex semi-gloss 8%; 40% in oil-based layer	A1	5
Paint - Latex Flat [i]	SPE disk	Surrogate for porous material			30%; 25%; 8% on surface; in paint; and in SPE	0.7%; 33%; 61% on surface; in paint; and in SPE	A2	5
Paint -Latex Semi-Gloss [ii]	SPE disk	Surrogate for porous material			18%; 40%; 4% on surface; in paint; and in SPE	0.5%; 27%; 67% on surface; in paint; and in SPE	A3	5
Paint - Oil Based [iii]	SPE disk	Surrogate for porous material			15%; 18%; 2% on surface; in paint; and in SPE	0.3%; 27%; 48% on surface; in paint; and in SPE	A4	5
Paint - Primer & Oil-Based	Steel	Building material			58% (surface)	*Not included in test*	B1	6
Paint - Primer & Oil-Based	Hardwood	Building material			42% (surface)	*Not included in test*	B2	6
Paint - Primer & Latex Flat	Drywall	Wall material			NA; 69% (coupon)	*Not included in test*	C1	7
Sealant - Epoxy **Sealant - Polyurethane**	Steel	Surrogate for nonporous material	None	Low	23%; 37% in epoxy 16%; 35% in polyurethane	9%; 13% in epoxy 7%; 57% in polyurethane	A5	5
Sealant - Epoxy	SPE disk	Surrogate for porous material			58%; 22%; 0% on surface; in sealant; and in SPE	1%; 14%;21% on surface; in sealant; and in SPE	A6	5

Surface	Subsurface Material	Function	Water Permeability Top Layer	Oil Permeability Top Layer	VX percent on surface and in other layers or material after 24 h	HD percent on surface and in other layers or material after 24 h	Study ID (Table 2)	Ref.
Sealant - Polyurethane	SPE disk	Surrogate for porous material			11%; 57%; 10% on surface; in sealant; and in SPE	0.2%; 26%; 73% on surface; in sealant; and in SPE	A7	5
Sealant- Silane/Siloxane	Concrete	Protective flooring material			0.3-0.8%; 8-14% in top 1/4“	*Not included in test*	B3	6
Sealant- Silane/Siloxane	Concrete	Protective flooring material			NA; 6% (coupon)	*Not included in test*	C2	7
Sealant- Silane/Siloxane	Sandstone	Used as surrogate for porous material			NA; 29% (coupon)	27% (coupon 5 h), 2.2% (coupon 76 h),	E1	10
Rubber	Same	Escalator handrail, wall base molding	Low	Low-Medium	56% (coupon)	*Not included in test*		8
					77% (coupon)	130% (coupon 5 h), 130% (coupon 76 h)*		10
HDPE Plastic	Same	Water pipes, liner	Low	Low	92% (coupon)	*Not included in test*		8
III. Porous, low adsorption materials								
Limestone	Same	Building material	High	Medium-High	0.41% (surface) 0.2-0.4%; 11-43% in top 1/4“	*Not included in test*		6
Unsealed Concrete	Same	Walls, floors			0.8% (surface) 13% (coupon)	*Not included in test*		6 8
Plywood	Same	Subfloor material	Medium-High	Medium-High	62% (coupon)	*Not included in test*		8
IV. Porous, high adsorption materials								
Ceiling Tile	Same	Dropped ceiling	High	Medium-High	81% (coupon)	*Not included in test*		8

*: Recoveries biased high due to significant interferences in ion chromatograms
coupon: the extracted sample of the material being tested, HDPE: high-density polyethylene, SPE: solid phase extraction

Table 2. Additional Data for Paints and Sealants.

Study ID	Reference	Top Surface	Specifics	Product Information	Notes
A1	5	Painted Steel	Latex Flat Latex Semi-Gloss Paint - Oil-Based	See info for specific paints below (A2, A3, and A4)	
A2	5	Paint Layer	Latex Flat	Behr® Premium Plus Ultra-Pure White Flat Zero VOC Interior Paint	Free standing paint layer
A3	5	Paint Layer	Latex Semi-Gloss	Behr® Premium Plus Ultra-Pure White Semi-Gloss Zero VOC Interior Paint	Free standing paint layer
A4	5	Paint Layer	Paint - Oil-Based	Rust-Oleum® Professional High Performance White Gloss Oil-Based Enamel Interior/Exterior Paint	Free standing paint layer
A5	5	Sealed Steel	Epoxy-based Polyurethane-based	See info for specific sealants below (A6, A7)	
A6	5	Sealant Layer	Epoxy-based	Rust-Oleum® 5300 System Water-Based Epoxy in White, Gloss Finish with Activator	Free standing sealant layer
A7	5	Sealant Layer	Polyurethane-based	Rust-Oleum® 6711 System Water-Based Polyurethane, Clear	Free standing sealant layer
B1	6	Painted steel	Primer + Oil-based metal paint	Latex White Interior/Exterior Multi-Surface Primer, Sealer, and Stain Blocker + High Performance Protective Enamel Gloss White Oil-Based Interior/Exterior Metal Paint	
B2	6	Painted hardwood	Primer + Oil-based metal paint	Latex White Interior/Exterior Multi-Surface Primer, Sealer, and Stain Blocker + High Performance Protective Enamel Gloss White Oil-Based Interior/Exterior Metal Paint	Same paint was used for consistency with study ID B1
B3	6	Sealed concrete	Siloxane Sealant	Sure Klean® Weather Seal Siloxane PD (predilute)	
C1	7	Painted drywall	Latex primer + Latex Flat	KILZ® latex primer + Behr® Premium Plus Interior Flat White Latex Paint	
C2	7	Sealed concrete	Siloxane Sealant	Sure Klean® Weather Seal Siloxane PD	
E1	10	Sealed Sandstone	Siloxane Sealant	Sure Klean® Weather Seal Siloxane PD	

Impact of VX/HD Transport into Materials on Sampling, Decontamination and Waste Management

The observed transport of VX/HD into porous and/or permeable materials will impact the environmental sampling of these agents during the consequence management phase following an incident. The impact described below on surface wipe sampling is derived from bench-scale surface wipe sampling approaches, which were effective in the experiments but are not fully verified field sampling methods. Further, most of the efficacious decontaminants that are capable to degrade VX/HD are water based. Hence, it is likely that any transport of decontaminants into a porous material that would degrade the agent within the material will differ significantly in magnitude and mechanism in comparison to the transport of these oily chemicals. Specific impacts on sampling, decontamination, and waste management are summarized here.

I. Nonporous, impermeable materials

VX/HD present on materials in the nonporous, impermeable group remain on the nonporous or impermeable surface. Wear and tear over time may make these materials porous. Cracks in glazed ceramic tile are known to result in the transport of chemicals into the clay material. The rate of evaporation will determine the amount of agent remaining [see reference 9 for VX].

Sampling: Wipe sampling methods can recover agent on the surface. High surface wipe sampling efficiencies can be achieved that will lead to more accurate level of agent contamination characterization.

Decontamination and Waste Management: These types of surfaces can be relatively straightforward to clean/decontaminate. They are expected to remain in place and would not enter the waste stream.

II. Nonporous, permeable materials

The observed transfer of VX/HD into a paint or sealant and into a potentially more porous material below or behind it (like drywall behind paint) complicates remediation of such material or such combination of materials. The degree to which this permeation occurs depends on the chemical and physical properties of both agents and the paint/sealant type and sheen. The rate of permeation may exceed the evaporation rate. No data have been collected for rubber to determine how much of the recovered agent in a coupon extract can be attributed to the amount on the surface versus the amount permeated into the material. High recoveries after 24 h suggest that VX may have substantially permeated the substrate.

Sampling: Surface wipe sampling of these type of painted or sealed surfaces may not recover the actual amount of agent present and may even lead to false negatives on the presence of an agent. Surface wipe sampling of materials such as rubber is expected to recover the non-permeated agent remaining on the surface, but not VX/HD that has diffused into the material.

Decontamination and Waste Management: Full decontamination of the permeable paint or sealant layers is expected to be complex considering the inability of water-based decontaminants to react with the agents in the paint or sealant layer. Modifications to decontamination approaches would be required to be confident that the agent in the paint or sealant has degraded. For bulk materials such as rubber, residual VX/HD post-decontamination may diffuse back to the surface from which it would volatilize and become an airborne and contact hazard. Currently, decontamination of these types of materials is difficult and often cost prohibitive. In many cases, they may become part of the waste stream.

III. Porous, low adsorption materials

Low recoveries of VX (no direct information for HD available) demonstrate the penetration into porous materials. Degradation (of VX) through interactions with the material should not be excluded either, especially for more materials known to be reactive with VX, such as concrete.

Sampling: Surface wipe sampling of these surfaces may detect low or minimal VX/HD on the surface. Most of the VX/HD would not be accessible to a surface wipe. The VX/HD would slowly diffuse back to the surface and volatilize from the substrate.

Decontamination and Waste Management: Applied decontaminants may not be able to reach deeper into pores because the pores are occupied by the VX/HD and will have limited efficacy. Physical removal of top layers containing the agent may be possible without loss in integrity of the material [10]. Currently, decontamination of these materials is difficult and often cost prohibitive. In many cases, they may become part of the waste stream. Less waste would be generated if only layers of materials (containing the VX/HD) are removed.

IV. Porous, high adsorption materials

Transport studies for this group of materials have been limited. Impacts on sampling, decontamination and waste management are expected to be like those porous, low adsorption materials described under III) and are not repeated here.

Limitations of Studies

- All transport studies were conducted with representative, new, and clean surfaces and materials. Soiling, degradation, hardening, cracking or other deteriorations by wear and tear over time would impact the transport and permeation of the VX/HD into a material. For instance, deep cracks or fissures that might occur during normal wear and tear of originally less permeable surface (like a glazed ceramic tile) could result in unexpected transport of agent into the material.
- Other paints or sealants are expected to behave differently than described here, based on the large variations between the limited numbers of these products investigated in these studies.
- Unsealed concrete is an example of a frequently encountered porous and reactive material. The transport and observed degradation of VX/HD on/in unsealed concrete is complex and is not discussed in detail in this brief. The provided transport data for unsealed concrete complements information already in the literature.

Contacts

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