

Persistence of Chemical Warfare Agent VX on Building Material Surfaces

PURPOSE

Chemical warfare agents (CWAs) comprise several chemical classes of which “nerve” agents are compounds of concern due to their extremely high toxicity. Various nerve agents have recently been identified as used in Middle East conflicts [1], as well as in attacks against individuals in the United Kingdom [2] and Malaysia [3]. The nerve agent VX (O-ethyl S-(2-[diisopropylamino]ethyl) methylphosphonothioate) is highly persistent – lasting days to weeks on surfaces under commonly encountered environmental conditions. VX is one of the most toxic nerve agents and can be introduced into the body by inhalation, ingestion, skin contact, or eye contact. This brief provides a summary of two recent U.S. Environmental Protection Agency (EPA) bench-scale studies assessing the persistence of VX on various building material surfaces [4,5]. This overview provides decision-makers with practical information on the expected persistency of VX following a chemical incident, which will inform the remediation strategy prior to reopening contaminated buildings or infrastructure.

INTRODUCTION

EPA’s mission is to protect human health and the environment. EPA is also the primary federal agency responsible for remediation of indoor and outdoor areas at locations in which CWAs might be released. Therefore, in support of EPA’s mission in this area, EPA’s Homeland Security Research Program conducts research to help on-scene coordinators and decision-makers minimize environmental impacts and human health effects following the release of a chemical agent. Limited data exist on the actual persistence of nerve agent VX on building materials. EPA conducted bench-scale studies to evaluate the VX persistence on various building materials, and as a function of temperature and of presence/absence of air flow. VX amounts on these materials were measured over a period of up to five weeks post-contamination. One study also evaluated the potential distribution of VX vapor to other materials that could act as sinks [4].

VX PERSISTENCE RESEARCH

The VX persistency is high [6] because of its low vapor pressure (8.8×10^{-4} mm Hg at 25 °C) and its oily liquid form. VX evaporates slowly and is expected to last days to weeks on surfaces. The persistence of the neat agent is expected to be dependent on material type and environmental conditions. Therefore, persistence should be considered in the overall remediation objectives following a chemical release. The studies in this brief assessed the influence of temperature on the persistence of VX on ten different materials, including the porous/permeable materials that are frequently encountered in indoor environments. The persistence studies measured VX remaining on surfaces through some of the prevalent processes in an indoor environment (e.g., evaporation, degradation and other physical or

chemical interactions) over the course of a five-week period. Testing was conducted at three different temperatures (10 °C, 25 °C, and 35 °C), which represent a range of conditions that might be encountered in an evacuated abandoned indoor environment following a VX release. Other environmental conditions such as relative humidity (RH) at 40%, and air flow associated with a specific air exchange rate (none or one air exchange per hour) were held constant during the testing. Silanized glass served as a nonporous reference material.

EXPERIMENTAL METHODS

Material coupons (excised samples) of 4.0 cm × 2.5 cm were each spiked with 2 microliters (μL) of neat VX, which is equivalent to an initial average surface concentration of 2.2 g/m². After a contact period between VX and a material (ranging from 30 minutes to 35 days, depending on temperature), remaining VX was extracted from the material coupons and residual mass was quantified via gas chromatography /mass spectrometry (GC/MS). Table 1 shows the types and function of materials that were included in the VX persistence studies and their qualitative permeability by water and oil/octanol. Materials that are generally more permeable can be expected to exhibit longer VX persistency due to penetration and adherence of agent to the material.

Table 1: Materials Used in VX Persistence Studies

Material	Study Reference*	Function	Water Permeability	Oil Permeability
Sealed concrete	4	Flooring material	None	Low
Galvanized metal	4	HVAC ductwork	None	None
Painted drywall	4	Wall material	Low-Medium	Low
Glazed ceramic tile	4	Wall, floors	None-Low	None-Low
Silanized glass	4,5	Reference Material	None-Low	None
Unsealed concrete	5	Walls, floors	High	Medium-High
Plywood	5	Subfloor material	Medium-High	Medium-High
Rubber	5	Escalator handrail	Low	Low-Medium
HDPE* plastic	5	Water pipes, liner	None-Low	None-Low
Ceiling tile	5	Dropped ceiling	High	Medium-High

Acronyms: HDPE, High-Density Polyethylene; HVAC, heating, ventilation, and air conditioning. *: Full references are at the end of the brief.

SHORT TERM (<30 MINUTES) INTERACTION OF VX WITH MATERIALS

Experimental results for the shortest contact time of VX with any material (30 minutes) in this study yielded a noticeable difference in VX amounts recovered. Whereas recovery after immediate (less than 5 minutes) extraction of VX was higher than 70% across all 10 materials (except for unsealed concrete, 17%) [5], Figure 1 shows that of the ten materials included in this study, two materials (unsealed and sealed concrete) had significantly less VX recovered in comparison to any of the other eight materials, indicating a high absorption rate into the material, strong adherence to the material, or chemical degradation by these two materials in comparison to the other materials. The absorption of VX into this

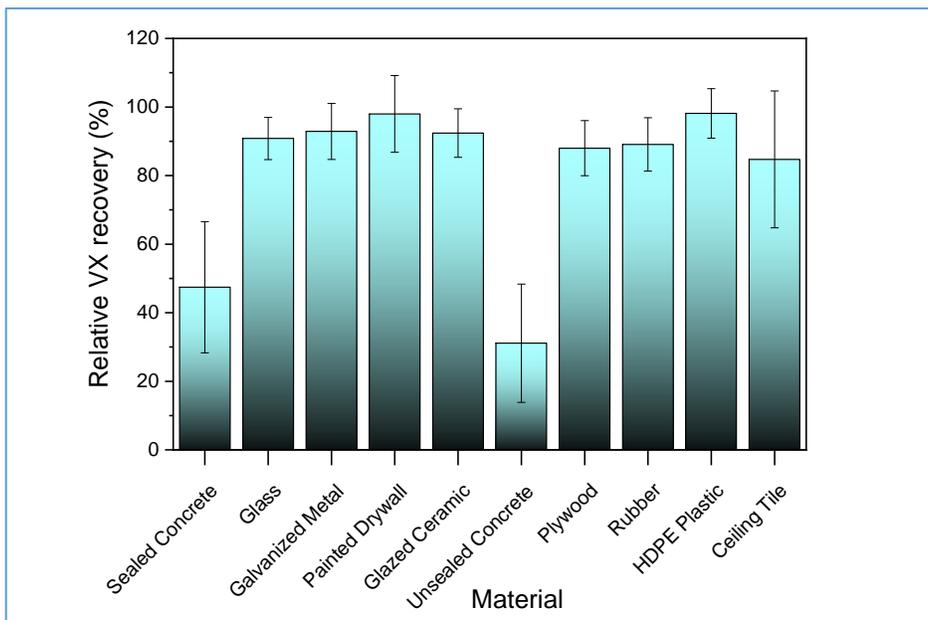


Figure 1. Relative recovered mass of VX after 30 minutes contact time with material

sealant has been observed previously [7]. The porous characteristics of unsealed concrete are known to allow for absorption and likely degradation of VX [8], depending on concrete age and type. Neither the absorption or degradation process was further investigated as part of this VX persistence study. Following an actual incident involving VX, sealed and unsealed concrete should therefore be considered as sinks of VX with an associated difficulty in measuring the remaining amount of VX within these two materials. Hence, the presence of residual VX associated with these materials as observed by, for example, wipe sampling may be biased low. The remaining liquid VX on the surface of sealed and unsealed concrete evaporates in a manner similar to the evaporation of VX from other surfaces.

LONG-TERM (>30 MIN) INTERACTION OF VX WITH MATERIALS

The amount of VX recovered from all surfaces was found to diminish with time. Despite the low volatility, VX slowly dissipates from all surfaces via evaporation. Further, absorption of VX into some of the porous/permeable materials (from which it cannot be recovered via solvent extraction) and possible chemical reactions with the surface result in a loss in the amount of recovered VX. Figure 2 shows the relative VX mass (compared to VX spike controls) recovered from ten building materials as a function of the contact time of VX on the surface after application at 25 °C (initial VX mass, 2200 µg/material) and a condition of one air exchange per hour. Excluding the two concrete materials with a high affinity to absorb or react with VX on a short timescale, the fastest loss in recovered VX mass was observed for glazed ceramic tile while the slowest loss in VX mass recovery occurred from the rubber material. These rates are consistent with glazed ceramic tile as a nonporous material while rubber may absorb some of the VX, which would slow the overall evaporation rate. It should be noted that all

materials may degrade over time leading to changes in permeability. For example, weathering of ceramic tile tends to lead to micro-fractures in the glaze while rubber would become inelastic and brittle.

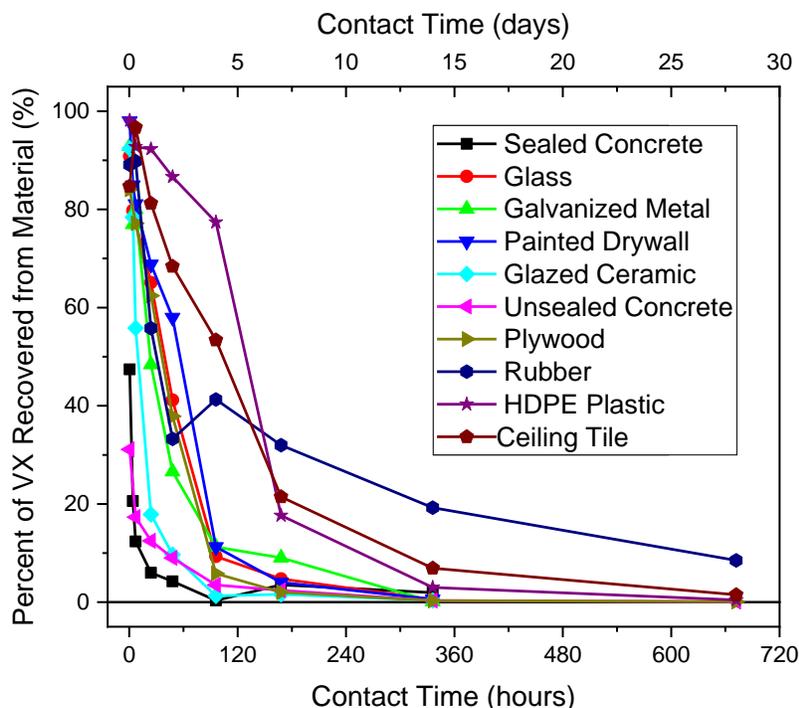


Figure 2: Dissipation of VX from materials as function of contact time at 25 °C

FITTING OF EXPERIMENTAL DISSIPATION DATA

The time dependence of the loss in recovered VX mass from these building materials can be plotted to calculate the rates in the loss of recovered VX. The observed dependence in recovered VX amounts as a function of contact time with the material surface were fitted to a pseudo first-order kinetic process. The resulting pseudo-first order half-lives from the fit to the experimental data and the calculated 99% loss times are tabulated in Table 2 for all three tested temperatures (10, 25, and 35 °C) and one air exchange per hour.

Table 2: Fitted half-life and derived 99% dissipation times for VX from surfaces at 10, 25 and 35 °C.

Material	10 °C		25 °C		35 °C	
	Half life ± SD (hours)	99% loss in recovered VX ± SD (days)	Half life ± SD (hours)	99% loss in recovered VX ± SD (days)	Half life ± SD (hours)	99% loss in recovered VX ± SD (days)
Glazed Ceramic	66 ± 4.7	18 ± 1.3	13 ± 1.3	3.5 ± 0.4	6.1 ± 0.47	1.7 ± 0.13
Sealed Concrete ¹	72 ± 19	20 ± 5.4	14 ± 2.9	3.9 ± 0.8	5.1 ± 0.88	1.4 ± 0.24
Galvanized Metal	111 ± 22	31 ± 6.2	23 ± 3.3	6.4 ± 0.9	7.7 ± 0.62	2.1 ± 0.17
Glass	181 ± 28	50 ± 7.8	30 ± 2.4	8.4 ± 0.7	7.3 ± 0.47	2.0 ± 0.13
Plywood	153 ± 6.9	42 ± 1.9	31 ± 2.7	8.5 ± 0.8	12 ± 1.4	3.4 ± 0.39
Painted Drywall	215 ± 18	60 ± 5.0	35 ± 3.3	9.8 ± 0.9	10 ± 1.5	2.8 ± 0.42
Unsealed Concrete ²	150 ± 35	41 ± 9.7	46 ± 5.2	12.8 ± 1.4	18 ± 1.0	5.0 ± 0.29
HDPE Plastic	486 ± 98	135 ± 27	81 ± 11	22.4 ± 3.1	27 ± 2.3	7.5 ± 0.64
Ceiling Tile	418 ± 37	116 ± 10	93 ± 6.7	25.6 ± 1.8	35 ± 0.81	9.6 ± 0.23
Rubber	79 ± 17	22 ± 4.8	118 ± 23	32.6 ± 6.5	48 ± 5.6	13 ± 1.5

SD: Standard Deviation in in the pseudo-first order fit to the experimental data. HDPE: High density polyethylene.

¹: VX permeates through sealant; less than 47% extracted from sealed concrete after 30 min.

²: VX absorbs into concrete; less than 17% extracted from unsealed concrete after 30 min.

As is evident from Figure 3, VX dissipation half-lives from all surfaces were found to be strongly dependent on (inverse of) temperature with an average reduction in half-life times by a factor eight to twelve across materials when comparing data collected at 10 and 35 °C, with a relatively minor

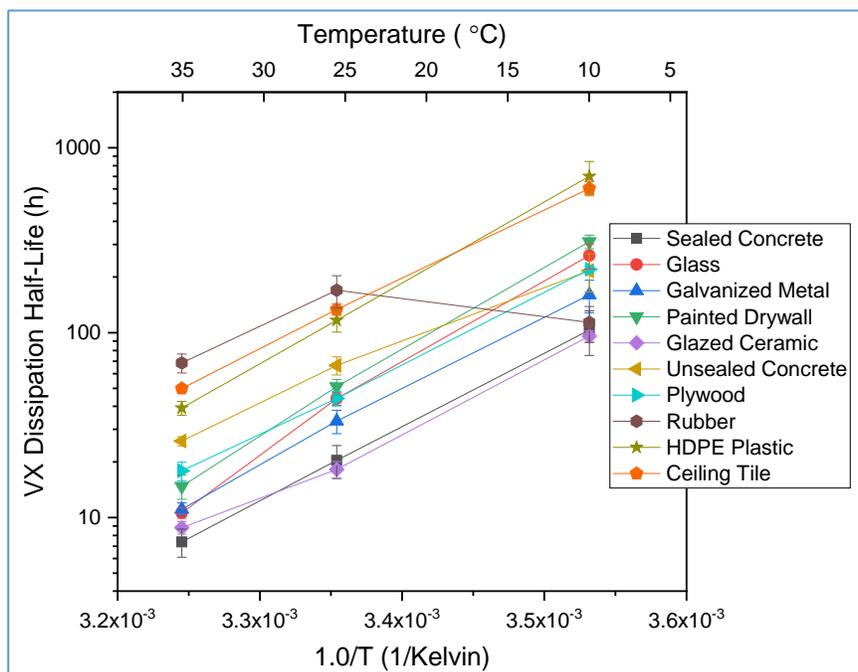


Figure 3. VX dissipation half-life as function of temperature

additional material dependence. One noticeable exception was for the rubber material for which the fitted VX dissipation half-life at 10 °C was found to be shorter than at 25 °C. This difference is attributed to an inexplicable anomaly in the recovered amounts of VX for the rubber material after 7 and 14 days [5] at 10 °C, resulting in a poor quality of the pseudo-first order fit to the experimental data sets at these two temperatures. Rates (except for rubber) followed the Arrhenius equation for the temperature dependence in (dissipation) rate constants,

$$k = A \times e^{\frac{-E_a}{RT}} \quad [1]$$

where k is the (dissipation) rate constant, T is the absolute temperature, A is a constant, E_a is the activation energy for the dissipation of VX and R is the universal gas constant. The near equal slopes of the curves in Figure 3 shows that the activation energy, which is associated with the heat of evaporation, is only somewhat dependent on the material, suggesting that the VX dissipation is independent of the material and dominated by the evaporation from the initial VX liquid droplet on the material.

IMPACT OF A LACK OF AIR EXCHANGE ON DISSIPATION OF VX AT 25 °C

VX persistence data were collected in a subset of five building materials at 25 °C without an air exchange present [4]. In this study, using an approximately 200 L volume chamber, half-life times for the persistence of VX on these materials were found not to be statistically significantly different from the persistence half-lives for VX in the presence of one air exchange on the same materials.

MIGRATION OF VX TO OTHER SURFACES

The potential distribution of VX via movement of its vapor from contaminated materials to other initially noncontaminated materials (leather upholstery, high density polyethylene, painted metal, desk laminate, and cubicle divider cloth) was investigated through extraction of these materials that were placed near the contaminated material (glass). After a seven-day contact period of VX with the glass materials, the spiked glass coupons had a mean VX recovery of approximately 2% of the initially spiked VX amount, which is similar to the reported mass recovered after seven days in other VX persistence experiments. After seven days, VX was also recovered from leather upholstery, high density polyethylene, and cubicle divider cloth (mean VX recoveries were $\leq 0.2\%$ of initial amount). VX was not recovered from painted metal or desk laminate. The highest VX amount recovered from an unspiked coupon was 0.25% of the amount of VX spiked for a cubicle divider cloth material. This observed migration of VX vapor may be biased low. Measurement of the material-specific extraction efficiencies for VX were beyond the scope of this study to characterize the precision and accuracy of the analysis of the various coupon materials and may, therefore, underestimate the VX amount measured on these surfaces due to the volatilization of VX from the contaminated material. This limited study provides strong evidence that some distribution of VX to initially uncontaminated materials occurs, and these materials may become sinks and would also require decontamination.

IMPACT OF VX ATTENUATION ON REMEDIATION ACTIVITIES

Starting with a 2.2 g/m² surface concentration of VX, the 99% dissipation time implies that 22 mg/m² or 2.2 µg/cm² would remain on a surface after 4 to 33 days across all materials at 25 °C, with shorter times at higher temperatures and longer times at lower temperatures. This residual surface concentration is expected to be significantly higher than a cleanup goal surface concentration value. As a comparison,

the preliminary remediation goal (PRG), risk-based goal for surfaces contaminated with VX as calculated via EPA's Risk Assessment Guide for Superfund (RAGS) methodologies [9] is approximately 10,000 times lower. Although these PRGs may not be the ultimate clearance goal for VX remediation, the significant difference between the residual amount of VX observed at the end (4-5 weeks) of these dissipation tests and the PRG indicates that the attenuation of VX by itself is not an effective approach for remediating a contaminated site. Decontamination approaches may likely be needed to remediate a VX contaminated area. Waste generated from remediation activities is likely to contain residual VX. Further, volatilization of VX will lead to elevated air concentrations and to the spread of the contaminant.

DISCLAIMER

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