

Physical and Chemical Removal Options for Porous/Permeable Materials Contaminated with the Persistent Chemical Warfare Agent VX



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**Physical and Chemical Removal Options for Porous/Permeable
Materials Contaminated with the Persistent Chemical Warfare
Agent VX**

U.S. Environmental Protection Agency
Office of Research and Development
Center for Environmental Solutions and Emergency Response
Research Triangle Park, NC 27711

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EXECUTIVE SUMMARY

The U.S. Environmental Protection Agency (EPA) is responsible for preparing for, responding to, and recovering from threats to public health, welfare, or the environment caused by actual or potential hazardous materials incidents. Following either an accidental or intentional release of chemical warfare agents (CWAs), porous building materials and permeable coatings such as paints or sealants are likely to become contaminated. Residual CWA can then absorb into the materials, coatings, and into the material under such coatings. The reversal of the absorption process may not be possible or would likely take place at a rate significantly slower than the evaporation of CWAs from hard nonporous material surfaces. Further, absorbed CWA may become inaccessible to surface decontaminants applied as aqueous liquids due to the inability of these decontaminants to penetrate sufficiently into the material or coating. Thus, the best course of remediation of absorbed contamination may ultimately involve physical removal of the contaminated materials or coatings. The ideal physical removal process would eliminate the residual CWA entirely while simultaneously minimizing the amount of contaminated waste generated and maintaining the integrity of the item or structure from which the materials or coatings were removed. Following physical removal of contaminated materials and/or coatings, the item or structure could then be resurfaced and repainted as necessary and returned to service while the removed materials would be managed as waste according to federal, state, and local requirements.

The primary objective of this project was to quantitatively evaluate the efficacy of select physical removal technologies and determine the application conditions/methods necessary to decontaminate CWA-contaminated porous materials and permeable coatings through physical removal of the contaminated portions of the materials. Prior to testing, literature searches were performed to identify physical removal mechanisms that could be used to remove contaminated portions of porous materials and/or permeable coatings while simultaneously minimizing damage to the materials and generation of wastes that may be classified as hazardous waste. From the literature search results, grinding and chemical stripping were selected for further evaluation. Grinding was evaluated for efficacy in removal of contaminated portions of sealed concrete and limestone, and chemical stripping was evaluated for efficacy in removal of contaminated coatings from low-carbon steel and hardwood.

Bench scale studies were performed using neat O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate (VX) as the challenge CWA. The porous materials and permeable coatings were contaminated with a target 10 μL of VX (equivalent to a contaminant mass of 9.4 mg of VX). The VX was allowed to dwell on the surface of the materials for a period of 24 hours to allow for penetration into the materials. Following the 24-hour dwell period, the porous material and permeable coating coupon surfaces were sampled via wipe sampling to quantify residual, transferrable VX. Following wipe-sampling, the physical removal technologies under test were applied to remove the contaminated portions of the material coupons. Grinding was used to remove portions of sealed concrete and limestone at discrete 0.25 inch (in.) -thick depth

layers. Chemical stripper was applied to the coated steel and hardwood coupons to remove the paint/primer layers. Ground material removed from sealed concrete and limestone and coatings stripped from steel and hardwood were extracted with solvent, and extracts were analyzed via liquid chromatography-tandem mass spectrometry (LC-MS/MS) to quantify VX recovered from the removed materials. The surface of steel and wood coupons was also sampled via wipe sampling again following stripping.

Grinding Results:

Total percent of VX recovery from sealed concrete averaged only 8.5% compared to the associated VX spike control mean recovery. Average total percent recovery from limestone was markedly higher, at 47%. The major portion of the VX recovered from each sealed concrete and limestone coupon via application of the grinding technology was obtained in the topmost 0.25-in. of the material, to which the VX challenge was applied. Recoveries from the 2nd, 3rd and 4th grinded 0.25-in. layers decreased sharply to less than 1% of the spike control mean recovery in all cases except that of the 2nd limestone coupon, in which recoveries from the 3rd and 4th 0.25-in. ground layer samples remained as high as 5.8% and 5.4%, respectively. However, it cannot be discerned from the data whether lower detections in deeper layers are due to the absence of VX (i.e., VX did not penetrate past the topmost 0.25-in. layer), degradation of VX, or an inability to recover VX that is present. Thus, physical removal to a greater depth than just the topmost 0.25-in. of material may be necessary. While the data suggest that VX contamination in porous materials can be removed via application of grinding to remove contaminated portions of the materials, the generally low total recoveries as well as the relatively higher recoveries from deeper layers from the 2nd limestone coupon suggest that the necessary removal depths can be inconsistent.

Paint Stripper Results:

Generally, greater recoveries of VX were obtained from the painted steel than from painted wood coupons. Markedly less VX was recovered from the post-stripping wipe samples taken from the steel substrate, indicating that the majority of the VX contamination was removed by the first (pre-stripping) wipe and by removal of the permeable coating via application of the stripper. Assuming VX does not permeate into the steel substrate, the data suggest that remediation of VX-contaminated painted/coated steel via a combination of solvent wipe sampling and removal of the paint/coating via chemical stripping may be possible (though repeated solvent wipe sampling and application of the stripper may be required, depending on the required decontamination level). The lower total recoveries from painted wood samples as well as the higher recoveries from post-stripping wipe samples taken from the wood coupons suggest that VX may be permeating through the paint/coating layer and into the underlying permeable wood substrate. Such residual VX contamination could pose contact or vapor hazards

if the VX diffuses back to the surface of the wood or if the wood is cut, ground, or otherwise manipulated.

Waste Considerations:

Application of both the grinding and chemical stripping technologies generated wastes that retained measurable levels of VX. Such wastes included the porous materials removed by grinding and the permeable coatings removed from substrates via application of the chemical stripper. Both waste types would require collection and handling using appropriate PPE and managed appropriately as per federal, state, or local requirements. It must be noted that these wastes are likely regulated at the state level and it is crucial to discuss the management of these wastes prior to the time at which they are generated.

Once acceptable levels of decontamination are reached, concrete, limestone, and similar porous materials and nonporous substrates such as steel would likely be amenable to resurfacing or recoating and reuse following application of the grinding or chemical stripping technologies. An exception to this may be porous substrates from which permeable coatings are removed, such as the hardwood substrate which could be at risk of excessive damage if repeated chemical stripping applications or additional physical removal methods (beyond removal of the coating) are required to achieve acceptable levels of decontamination.

Health and Safety Considerations:

Grinding of porous materials such as concrete and limestone will result in dust formation. Dust mitigation will be required since small dust particles carrying agent contamination will likely become redistributed in the environment (and potentially transfer to other materials). Some of the potentially contaminated particulate matter may become an inhalation hazard.

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ATTACHMENT

Attachment A – Environmental Data

LIST OF ACRONYMS AND ABBREVIATIONS

AMC	Army Materiel Command
CASARM	Chemical Agent Standard Analytical Reference Material
CCDC	Combat Capabilities Development Command
CCV	Continuing Calibration Verification
CESER	Center for Environmental Solutions and Emergency Response (EPA)
cm	Centimeter(s)
cm ²	Square centimeter(s)
CoC	Chain of Custody
CoV	Coefficient of Variation
CWA	Chemical Warfare Agent
EPA	U.S. Environmental Protection Agency
FID	Flame ionization detector
GC	Gas Chromatography
g	Gram(s)
h	Hour(s)
HMRC	Hazardous Materials Research Center
HPLC	High Performance Liquid Chromatography
HSRP	Homeland Security Research Program
in.	Inch(es)
IPA	Isopropyl Alcohol
IS	Internal Standard
μL	Microliter(s)
L	Liter(s)
LC-MS/MS	Liquid Chromatography-Tandem Mass Spectrometry
LLOQ	Lower Limit of Quantitation
LRB	Laboratory Record Book
min	Minute(s)
mL	Milliliter(s)
mm	Millimeter(s)
MRM	Multiple reaction monitoring
NA	Not applicable
ng	Nanogram(s)
Pa	Pascal
PB	Procedural blank
PC	Positive control
PPE	Personal protective equipment
psi	Pounds per square inch
PTFE	polytetrafluoroethylene
QAPP	Quality Assurance Project Plan
r ²	Coefficient of determination
RDS	Research dilute solution
RDT&E	Research, development, test and evaluation
RH	Relative Humidity
RSD	Relative Standard Deviation
SC	Spike control
SS	Stainless Steel
TPCS	Test Parameter Control Sheet
TSA	Technical Systems Audit
VR	Russian VX

VX

O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate

1. INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is responsible for preparing for, responding to, and recovering from threats to public health, welfare, or the environment caused by actual or potential hazardous materials incidents. Hazardous materials include chemical, biological, and radiological substances, whether accidentally or intentionally released. The threat of a chemical agent release into the environment is driving EPA's Homeland Security Research Program (HSRP) to systematically evaluate potential decontamination technologies for chemical agents.

Following either an accidental or intentional release of chemical warfare agents (CWAs), many building materials, including porous building materials and/or permeable coatings such as paints or sealants are likely to become contaminated. Residual CWA can then absorb into the materials and coatings in a similar manner as how CWAs can permeate into and through gloves or other personnel protective equipment (PPE) [1]. The reversal of absorption may not be possible, and even if it is, would likely take place at a rate significantly slower than the evaporation of CWAs from hard nonporous material surfaces [2-4]. Further, absorbed CWA may become inaccessible to surface decontaminants applied as aqueous liquids due to the inability of the decontaminants to penetrate sufficiently into the material or coating [4].

Thus, the best course of remediation of absorbed contamination may involve physical removal of the contaminated materials or coatings. The ideal physical removal process would eliminate the residual CWA entirely while simultaneously minimizing the amount of contaminated waste generated and maintaining the integrity of the item or structure from which the materials or coatings were removed [5]. Following physical removal of contaminated materials and/or coatings, the item or structure could then be resurfaced as necessary and returned to service. EPA first responders have identified this high-priority knowledge gap for the HSRP to address.

1.1. Purpose

The purpose of this project was to determine the application conditions necessary and evaluate the efficacies of select methodologies for remediation of CWA-contaminated porous materials and permeable coatings through physical removal of the contaminated portions of the materials, while simultaneously minimizing the amount of hazardous wastes generated and maintaining the integrity of the surfaces or structures to which the technologies are applied.

1.2. Project Objectives

The primary objective of this project was to quantitatively evaluate the efficacy of select technologies to physically remove CWA-contaminated portions of select porous materials and permeable coatings through performance of bench scale laboratory studies using neat O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate (VX, CAS 50782-69-9) as the challenge CWA.

The fate and transport of VX in concrete has been studied in detail by many research groups. The general consensus is that while there is a measured fast degradation (half-life time of 2-3 hours) [6], this fast process may only apply to VX when present at very low concentrations. The presence of higher quantities as used in this study will lead to a prolonged persistence (weeks to months) of VX that permeated into the concrete [7].

Prior to the physical removal efficacy evaluations, technologies that were anticipated to be efficacious, generate minimal or no wastes, and minimize or eliminate irreparable damage were identified via searches of existing literature and secondary data. Physical removal technologies identified during the search were evaluated based on four primary characteristics, including:

- Anticipated or demonstrated efficacy of the technologies in removal of hazardous contamination through physical removal of the contaminated portions of a material.
- The types, quantities, and hazard designations of wastes generated from application of the technologies.
- The extent of irreparable damage caused (or anticipated to be caused) to surfaces/structures from application of the physical removal technologies (factors that impact the possibility, cost, and level of effort associated with resurfacing/restoring treated surfaces/structures and returning them to service).
- The application rate, ease-of-use, and personal protective equipment (PPE) and cost requirements associated with the technologies.

From the technologies identified during the literature searches, three were selected for physical removal efficacy evaluation during this project:

- Grinding was evaluated for efficacy in removal of VX-contaminated portions of sealed concrete and limestone.
- Chemical stripper was evaluated for efficacy in removal of VX-contaminated permeable coatings (paint and primer) from the surface of low-carbon steel and hardwood.
- Vapor-phase solvent extraction was selected for evaluation for efficacy in removal of VX contamination from both porous materials (sealed concrete and limestone) and permeable coatings (paint and primer applied to low-carbon steel and hardwood). However, technical difficulties associated with setup and application of the technology prevented a full evaluation within this project. Refer to Sections 2.2.3.4 and 3.1.1.4 for additional information.

Additionally, a method independent of the selected physical removal technologies, referred to as the “core sampling approach”, was developed and used for dissection of porous materials (sealed concrete and limestone) to quantify the extent of VX penetration/contamination as a function of depth. This core sampling experiment was conducted prior to the grinding tests and supported the depths to which porous materials were removed.

Refer to Sections 2.2.3.1 through 2.2.3.4 for additional information related to the physical removal technologies, the core sampling approach, and the application strategies used for each. Section 2.2.1 provides information related to the porous materials and permeable coatings used as test items.

Also, during the physical removal efficacy evaluation, quantities and types of hazardous (or potentially hazardous) wastes generated were assessed, as well as the extent of damage caused to the materials from application of the technologies. Waste generation assessments were quantitative where possible (waste volumes and CWA contamination levels) and otherwise qualitative (visual observations and descriptions of waste types). Damage extent to a material was qualitatively determined and included visual assessments and descriptions of damage caused.

1.3. Test Facility Description

All testing was performed at Battelle's Hazardous Materials Research Center (HMRC) located in West Jefferson, Ohio. The HMRC is certified to work with chemical surety material under a Provisioning Agreement with oversight by the U.S. Army Materiel Command (AMC; Provisioning Agreement Battelle-1). Wherever applicable and required, the reporting requirements for this agreement were followed.

1.4. Staff and Resources

Quantitative physical removal efficacy testing, associated methods demonstration testing, and qualitative assessments of waste generation and damage extent were completed using staff and resources from Battelle's HMRC (West Jefferson, OH) in consultation with the EPA's Center for Environmental Solutions and Emergency Response (CESER).

2. EXPERIMENTAL METHODS

2.1. Experimental Design

Project objectives were achieved through execution of physical removal efficacy tests, waste generation assessments, and material damage extent assessments. Generally, physical removal efficacy testing proceeded according to the following approach:

- Test articles of the porous materials and permeable coatings selected for evaluation were contaminated with VX, and the VX was allowed to dwell on the test article surface for a period of 24 hours. Environmental conditions during the dwell period were monitored but not controlled.
- Following the VX dwell period, test article surfaces were sampled via surface wipe-sampling to evaluate residual VX surface hazard following the dwell period.
- After wipe sampling, test articles were transferred into a test chamber, if required (core sampling approach and grinding technology), for application of the physical removal technology.
- The physical removal technology was then applied to remove the contaminated portions of the material.
- Samples of the porous material or permeable coating removed, samples of any waste generated, and samples taken from the physical removal technology itself (where applicable, e.g., wipe samples of the grinding wheel of the grinder) were analyzed via liquid chromatography-tandem mass spectrometry (LC-MS/MS) to quantify residual VX present in/on each.

During the project, test articles consisted of coupons of each of the porous materials or permeable coatings (coatings applied to a substrate material) selected for the evaluation. Exact coupon sizes for each material type were determined during assessments of the functionality of the physical removal technologies selected for testing. Coupons for all material types were sized adequately for proper application of the physical removal technologies. Refer to Section 2.2.1 for information on the porous materials and permeable coatings included in the evaluation.

Prior to physical removal efficacy testing, the experimental methods planned for use were demonstrated to ensure valid data would be generated. The experimental designs for each of these phases of testing, including technology functionality assessments, methods demonstration, physical removal efficacy testing, waste generation assessment, and damage extent assessment are described in the following subsections.

2.1.1. Methods Demonstration

2.1.1.1. Physical Removal Technology Functionality Assessments

Detailed descriptions of the application approaches for each of the physical removal technologies selected for evaluation as well as for the core sampling approach and for collection of wastes generated from application of the technologies are described in Sections 2.2.3.1 through 2.2.3.4. Prior to methods demonstration testing using VX, the functionality of each of the physical removal technologies selected for testing and of the core sampling approach were evaluated without VX present.

Coupon samples produced from application of each technology to each material type included ground material (via grinder applied to sealed concrete and limestone) and excised layer samples (“slices”) from material cores (via the core sampling approach applied to sealed concrete and limestone). Physical coupon samples were not collected/harvested from painted/coated materials following application of chemical stripper; rather, the treated surfaces of the materials were sampled via wipe sampling.

Waste samples produced from application of each technology to each material type included the dust created during excision of layer samples (“slices”) from material cores during application of the core sampling approach (Section 2.2.3.1) and the permeable coatings removed following application of chemical stripper to painted steel and wood coupons (Section 2.2.3.3). Separate waste samples were not collected during application of the grinding technology (the entirety of the ground material produced during application of the grinder was collected as the coupon sample).

Application of the vapor-phase solvent extraction technology to sealed concrete and limestone cores was planned to be followed by application of the core sampling approach to harvest coupon samples (successive depth layer “slices”) and waste samples (the dust produced during core sample cutting). As with application of chemical stripper, no physical coupon samples would be collected from painted materials following application of vapor-phase solvent extraction; rather, the surface of coupons would be sampled via wipe sampling. Condensed solvent collected during and following application of vapor-phase solvent extraction to all material types was planned for collection and analysis as well.

The form/nature of the coupon and waste samples collected from application of each technology to each of the materials is described/summarized in Table 1.

Table 1. Anticipated Nature of Coupon and Waste Samples

Physical Removal Technology	Material	Form/Nature of Coupon Samples	Form/Nature of Waste Samples
Core sampling approach ^A	Sealed concrete	Excised coupon sections ^A	Cutting dust
Core sampling approach ^A	Limestone	Excised coupon sections ^A	Cutting dust
Grinding	Sealed concrete	Ground material	Not Collected
Grinding	Limestone	Ground material	Not Collected
Vapor-phase solvent extraction	Sealed concrete	Excised coupon sections ^A	Cutting dust, collected solvent
Vapor-phase solvent extraction	Limestone	Excised coupon sections ^A	Cutting dust, collected solvent
Chemical Stripping	Painted steel	Post-treatment wipe sample	Stripped paint layer
Chemical Stripping	Painted hardwood	Post-treatment wipe sample	Stripped paint layer
Vapor-phase solvent extraction	Painted steel	Post-treatment wipe sample	Collected solvent
Vapor-phase solvent extraction	Painted hardwood	Post-treatment wipe sample	Collected solvent

NA = Not applicable ^A Refer to Section 2.2.3.1

To perform the physical removal technology functionality assessments, the technologies were applied to the porous materials and permeable coatings selected for the efficacy evaluations as described in Sections 2.2.3.1 through 2.2.3.4, using all identified equipment, procedures, and test samples. Functionality assessments of the core sampling approach and grinding technology took place in the test chamber, to assess the ergonomics and limitations associated with working with the technologies inside the chamber.

These preliminary assessments were intended to evaluate the adequacy of the planned approaches for application of each technology, assess “ease of use” for each technology/approach, and aid in refinement (as determined necessary) of the planned approaches for application of the technologies. Additional objectives of the functionality assessments included:

- Determination of the exact coupon sizes required for each porous material or permeable coating type included during physical removal efficacy testing efforts. Section 2.2.1 provides additional details (including coupon sizes) related to the porous materials and permeable coatings included in the evaluations.
- Determination/confirmation of the nature and dimensions of coupon samples obtained from the material coupons via application of the selected removal methods (e.g., volume/mass of ground solids; dimensions of core layer samples).
- Determination/confirmation of the nature and amount of wastes generated by the removal methods (e.g., volume/mass of sealed concrete and limestone cutting dust collected during application of the core sampling approach; size/amount and characteristics of the stripped paint layers; volume of condensed solvent collected during application of vapor-phase solvent extraction to porous materials and permeable coatings) and how the wastes would be collected most efficiently.
- Investigation of temperature increase in the materials during application of the core sampling approach.

- Application of the core sampling approach to excise layer samples from the sealed concrete and limestone material cores could generate heat and increase the temperature of the material.
- Following dissection of each core sample into individual coupon layer samples, the temperature of the coupon layer samples was measured using a calibrated non-contact infrared thermometer (9248T57, McMaster-Carr, Aurora, OH).
- Temperature of the material cores was also measured prior to application of the core sampling approach so that the increase in temperature due to application of the approach could be determined.

Additionally, the various coupon samples and waste samples produced for each material/technology combination (refer to Table 1) were retained for use during subsequent solvent extraction, wipe sampling, and waste sampling methods demonstration.

2.1.1.2. Sampling for Residual VX in Material Samples (Solvent Extraction)

As discussed in Section 2.1.1.1, the coupon samples generated during the physical removal technology functionality assessments were retained for use during testing to demonstrate the adequacy of the methods that were used to recover VX from the samples via solvent extraction. As identified in Table 1, such samples included:

- Excised layer samples obtained from sealed concrete and limestone cores following application of the core sampling approach.
- Ground sealed concrete and limestone material recovered from coupons following application of the grinding technology.

Replicate material core layer samples were each spiked in the center with 2 microliters (μL) of VX according to the procedures described in Section 2.2.2.2, and the VX was allowed to dwell on the material layer sample surface for either 30 minutes (min) or 24 hours. Although a challenge volume of 10 μL per coupon was used during physical removal efficacy testing and the VX depth penetration assessment, a challenge volume of 2 μL per replicate material core layer sample was used during solvent extraction method demonstration testing. At the time of the method demonstration, it was anticipated that 2 μL would be more representative of the amount of VX that would penetrate into the porous materials during the 24-hour dwell period and thus require extraction/recovery from the core layer samples (especially for deeper core layer samples). Coupon layer samples were placed on top of polytetrafluoroethylene (PTFE) disks during the VX dwell period. At the end of the 30-minute or 24-hour VX dwell period, the coupon layer samples were extracted individually with solvent according to procedures described in Section 2.2.5. The PTFE disks underneath each material core layer sample were extracted separately to determine if the VX applied to the samples migrated through the (target) 0.25-inch (in.) -thick core layer samples during the VX dwell period.

In addition to the sealed concrete and limestone core layer samples, stainless steel coupons (same surface dimensions as the coupon layer samples, i.e., round, 1.375-in. diameter coupons, but with a thickness of 24 gauge) were spiked with VX. The VX was allowed to dwell for the same duration as on the core layer samples, and the steel coupons were extracted with solvent alongside the core layer samples to act as a control material.

Ground sealed concrete and limestone samples were contained in glass jars (125 milliliters [mL] volume). Each sample of ground material was spiked with 2 μL of VX according to procedures described in Section 2.2.2.2, and the VX was allowed to dwell within the ground material for either 30 minutes or 24 hours. A challenge volume of 2 μL (as opposed to 10 μL for physical removal efficacy testing) was used for each ground material sample as it was anticipated that 2 μL would be more representative of the amount of VX that would penetrate into the porous materials during the 24-hour dwell period. Following the VX dwell period, the ground sealed concrete or limestone material in each jar was extracted with solvent according to procedures described in Section 2.2.5 (solvent was added directly to the jars containing the ground material samples).

In addition to the ground sealed concrete and limestone samples, 3-millimeter (mm) glass beads (10-310-1, Fisher Scientific, Pittsburgh, PA; approximately 61.4 grams [g] of beads per sample) were spiked with VX. The VX was allowed to dwell for the same duration as that on the ground material samples, and the beads were then extracted with solvent alongside the ground material test samples to act as a control material.

Isopropyl alcohol (IPA; A464-4, Fisher Scientific, Pittsburgh, PA) was evaluated as the core layer and ground material extraction solvent. IPA was selected because of its use to recover CWA via extraction from materials during previous studies [8] and because of its amenability for use with LC-MS/MS analysis.

Table 2 provides the matrix for solvent extraction method demonstration testing that was performed for this project.

Table 2. Solvent Extraction Method Demonstration Test Matrix

Material	Sample Form ^A	Sample Type	VX Challenge (μL)	Dwell Period	Replicates
Sealed concrete	Coupon layer sample ^B	Test sample	2	30 min	3
Sealed concrete	Coupon layer sample ^B	Test sample	2	24 hours	3
Sealed concrete	Coupon layer sample ^B	Procedural blank	NA	24 hours	1
Limestone	Coupon layer sample ^B	Test sample	2	30 min	3
Limestone	Coupon layer sample ^B	Test sample	2	24 hours	3
Limestone	Coupon layer sample ^B	Procedural blank	NA	24 hours	1
Stainless steel	Disk ^C	Positive control	2	30 min	3
Stainless steel	Disk ^C	Positive control	2	24 hours	3
Stainless steel	Disk ^C	Procedural blank	NA	24 hours	1
Sealed concrete	Ground material	Test sample	2	30 min	3
Sealed concrete	Ground material	Test sample	2	24 hours	3
Sealed concrete	Ground material	Procedural blank	NA	24 hours	1
Limestone	Ground material	Test sample	2	30 min	3
Limestone	Ground material	Test sample	2	24 hours	3
Limestone	Ground material	Procedural blank	NA	24 hours	1
Glass beads	Loose beads	Positive control	2	30 min	3
Glass beads	Loose beads	Positive control	2	24 hours	3
Glass beads	Loose beads	Procedural blank	NA	24 hours	1

^A Coupon layer samples and ground material samples retained following functionality assessments (refer to Section 2.1.1.1). Ground material masses collected are provided in Section 3.1.1.2.

^B Dimensions: 1.375 in. diameter, 0.25 in. thickness

^C Dimensions: 1.375 in. diameter, 24-gauge thickness

In addition to the test samples (core layer samples and ground material samples), a single procedural blank per material type/form was included (as indicated in Table 2). Procedural blanks for solvent extraction method demonstration testing consisted of core layer samples and ground material of the same porous material type as the associated test samples (sealed concrete and limestone) that were not spiked with VX but that were extracted with solvent and analyzed alongside the test samples. Additionally, three spike controls (SCs) were prepared to confirm the VX challenge application amount. SCs consisted of a spike of an equal volume of VX (2 μL) directly into extraction solvent. As discussed in Section 2.2.2.2, when spiked, VX was applied to the inside surface of the glass SC jar (rather than submerging the pipette tip into the solvent).

The coupon sample solvent extraction method would be deemed acceptable for use during subsequent physical removal efficacy evaluations if the mean recoveries from stainless steel (core layer sample controls) and glass beads (ground material sample controls) were within the range of 70% to 120% of the mean of the SC results with a coefficient of variation (CoV) between replicates of less than 30%.

Concrete has been shown to be capable of active degradation of penetrated/absorbed CWAs [3,9]. Data generated during previous studies [10] have demonstrated such difficulty in recovering VX spiked onto concrete surfaces using similar solvent extraction techniques. Further, while VX is commonly considered a persistent CWA (approximate vapor pressure of 0.09 pascals [Pa]), evaporation during the dwell period could still occur to some extent

(particularly during the 24-hour dwell period). While the propensity of limestone to degrade penetrated/absorbed VX in a manner similar to concrete is unknown, it was assumed for this testing that the evaporation rate of VX from limestone and concrete would be similar. Stainless steel and glass provided inert surfaces, and previous studies [11,12] have demonstrated the extractability of VX from the materials. Recoveries from stainless steel and glass provided an indication of the amount of VX lost to evaporation during the dwell period. As it was assumed that VX would not be absorbed or degraded by stainless steel or glass, comparison of the recoveries from sealed concrete and limestone (core layer samples and ground material) were compared to recoveries from stainless steel and glass to determine the amount of VX lost to entrapment within or degradation by the concrete and limestone matrices.

Results of solvent extraction method demonstration testing are provided in Section 3.1.2.

2.1.1.3. Sampling for Residual VX on Material Surfaces (Wipe Sampling)

The coupon surface (wipe) sampling methods developed for CWAs during work on previous EPA efforts [12] were evaluated for use in recovering residual surface VX contamination from the materials selected for testing during this project. Wipe sampling was used to assess residual VX surface hazard on the coupons following the 24-hour VX dwell period during physical removal efficacy testing (prior to application of the physical removal technologies) and was also applied to painted steel and painted hardwood following application of the chemical stripping technology to assess efficacy of the removal method (refer to Tables 1 and 6; wipe-sampling was also planned for use to quantify residual VX contamination following application of the vapor-phase solvent extraction technology).

Wipe sampling method demonstration testing focused on recovery of VX from the porous materials and permeable coatings selected for the physical removal efficacy evaluations. Stainless steel was included as a control material. The procedure and materials used for wipe sampling, including the specific wipe type that was used, are described in Section 2.2.4. Coupons of each porous material or permeable coating type were contaminated with 10 μ L of VX, and the VX was allowed to dwell on the surface of coupons for 24 hours. The 10- μ L VX challenge volume and 24-hour dwell period were used during physical removal efficacy testing. A challenge volume and VX dwell period of 10 μ L and 24 hours were used for the wipe sampling method demonstration testing to ensure a representative amount of VX was remaining/available on the surface of coupons at the time of wipe-sampling. This is in contrast to the 2 μ L VX challenge volume per sample discussed for solvent extraction method demonstration testing. Following the dwell period, coupons were wipe-sampled using the procedure described in Section 2.2.4. Each wipe was extracted individually in solvent according to procedures described in Section 2.2.5.

IPA (A464-4, Fisher Scientific, Pittsburgh, PA) was evaluated as the wipe wetting and wipe extraction solvent. As during solvent extraction method demonstration testing, IPA was selected

because of its use to recover CWA via extraction from materials during previous studies [8] and because of its amenability for use with LC-MS/MS analysis.

Table 3 provides the matrix for wipe-sampling methods demonstration testing that was performed for this work.

Table 3. Wipe-Sampling Method Demonstration Test Matrix

Material	Sample Type	VX Challenge (μL)	Replicates ^A
Sealed concrete	Test coupon	10	3
	Procedural blank	NA	1
Limestone	Test coupon	10	3
	Procedural blank	NA	1
Painted steel	Test coupon	10	3
	Procedural blank	NA	1
Painted hardwood	Test coupon	10	3
	Procedural blank	NA	1
Stainless steel (control)	Test coupon	10	3
	Procedural blank	NA	1

^A Multiple wipe replicates may be obtained from a single coupon, depending on coupon size.

Multiple sections of a single coupon were spiked with VX to provide the required number of wipe sample replicates (each replicate area was spiked with 10 μL of VX). Figure 1 depicts the coupon spiking arrangement for obtaining multiple wipe replicates from a single coupon.

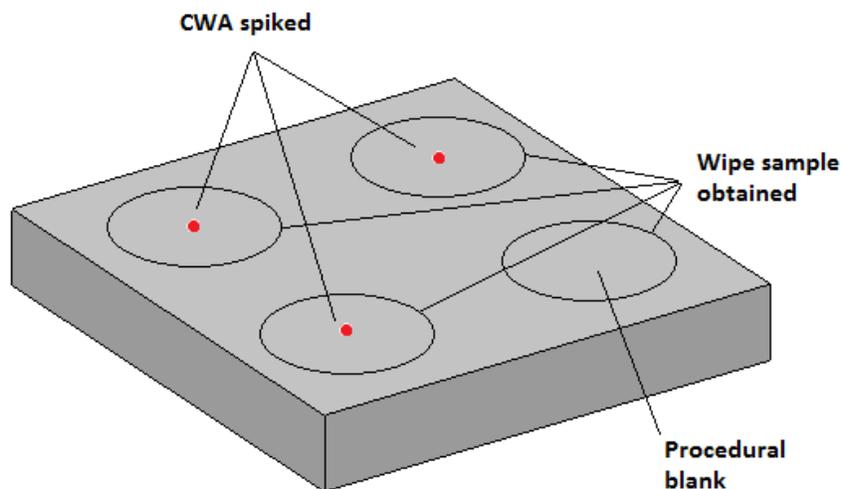


Figure 1. Single Coupon Spiking Arrangement for Multiple Wipe Replicates

In addition to the test coupons, a single procedural blank per material type was included (as indicated in Table 3). Procedural blanks for wipe-sampling method demonstration testing consisted of coupons of the same porous material or permeable coating and dimensions as the associated test coupons that were not spiked with VX but that were wipe-sampled and analyzed alongside the test coupons. Additionally, three SCs were prepared to confirm the VX challenge

application amount. SCs consisted of a spike of an equal volume of VX (10 μ L) directly into extraction solvent. As discussed in Section 2.2.2.2, when spiked, VX was applied to the inside surface of the glass SC jar (rather than submerging the pipette tip into the solvent).

The coupon wipe-sampling method would be deemed acceptable for use during subsequent physical removal efficacy evaluations if the mean wipe-sampling recoveries from stainless steel were within the range of 70% to 120% of the mean of the SC results with a CoV between replicates of less than 30%.

Data generated during previous studies [11] have demonstrated difficulty in recovering VX spiked onto concrete surfaces using solvent extraction techniques. Additionally, previous work [12] has demonstrated that VX spiked onto a paint layer applied to a substrate will absorb into the paint layer. For these reasons, difficulty in recovering VX from the surface of concrete, limestone, painted steel, and painted hardwood coupons via wipe sampling as described above was anticipated. Thus, only recovery from stainless steel as described above was considered when determining the effectiveness of the wipe sampling method for use during this project.

Results of wipe-sampling method demonstration testing are provided in Section 3.1.3.

2.1.1.4. Sampling for Residual VX in Generated Waste

As discussed in Section 2.1.1.1, the waste samples generated during the physical removal technology functionality assessments were retained for use during testing to demonstrate the methods that were used to recover VX from the wastes via solvent extraction. As identified in Table 1, such samples included:

- Cutting dust generated from application of the core sampling approach to excise layer samples from sealed concrete and limestone cores.
- The permeable coatings (paint and primer) removed from painted low-carbon steel and painted hardwood through application of the chemical stripper.

A method similar to that used to evaluate solvent extraction of VX from ground sealed concrete and limestone material was used to evaluate extraction of VX from the cutting dust generated during application of the core sampling method. Concrete and limestone cutting dust samples in glass jars (60 mL volume) were spiked with 2 μ L of VX according to procedures described in Section 2.2.2.2, and the VX was allowed to dwell for either 30 minutes or for 24 hours.

Following the dwell period, the cutting dust in each jar was extracted with solvent according to procedures described in Section 2.2.5 (solvent was added directly to the jars containing the dust samples).

As during the ground material solvent extraction method demonstration testing, 3 mm glass beads were used as a control/reference material (approximately 2.1 g of beads per sample). As discussed in Section 2.1.1.2, recovery from glass was intended to indicate the amount of VX lost to evaporation during the dwell period, and comparison of the recoveries obtained from sealed concrete and limestone cutting dust to the recovery obtained from the glass beads would be

indicative of the amount of VX lost to entrapment within or degradation by the concrete and limestone matrices.

Also, stripped permeable coatings (paint/primer) collected from application of chemical stripper were retained for use during testing to demonstrate that any VX present in the coatings could be accurately quantified via LC-MS/MS analysis. Stripped coatings collected following application of chemical stripper to the painted steel and painted hardwood materials were spiked with 2 μL of VX (spiked directly onto the stripped coatings sample). VX was allowed to dwell on the stripped coatings samples for either 30 minutes or for 24 hours. Following the dwell period, the spiked coatings samples were extracted in solvent. Extracts were then analyzed via LC-MS/MS. Analysis results were evaluated to ensure that the spiked VX could be adequately recovered from the coatings and that no interferences were present in the sample matrices from either the paint/primer or residual chemical stripper that would negatively affect analyses.

Table 4 provides the matrix for waste sampling method demonstration testing. As during coupon sample solvent extraction and wipe sampling method demonstration testing, IPA was evaluated as the extraction solvent for recovery of VX from the cutting dust and stripped coatings wastes generated during physical removal efficacy testing.

Table 4. Waste Sampling Method Demonstration Test Matrix

Material	Sample Form ^A	Sample Type	VX Challenge (μL)	VX Dwell Period	Replicates
Sealed concrete	Cutting dust	Test sample	2	30 min	3
Sealed concrete	Cutting dust	Test sample	2	24 hours	3
Sealed concrete	Cutting dust	Procedural blank	NA	24 hours	1
Limestone	Cutting dust	Test sample	2	30 min	3
Limestone	Cutting dust	Test sample	2	24 hours	3
Limestone	Cutting dust	Procedural blank	NA	24 hours	1
Glass beads	Loose beads (approximately 2.1 g)	Test sample (control material)	2	30 min	3
Glass beads	Loose beads (approximately 2.1 g)	Test sample (control material)	2	24 hours	3
Glass beads	Loose beads (approximately 2.1 g)	Procedural blank	NA	24 hours	1
Painted steel	Stripped paint	Test sample	2	30 min	3
Painted steel	Stripped paint	Test sample	2	24 hours	3
Painted steel	Stripped paint	Procedural blank	NA	24 hours	1
Painted hardwood	Stripped paint	Test sample	2	30 min	3
Painted hardwood	Stripped paint	Test sample	2	24 hours	3
Painted hardwood	Stripped paint	Procedural blank	NA	24 hours	1

^A Cutting dust samples and stripped paint samples retained following functionality assessments (refer to Section 2.1.1.1). Cutting dust masses collected are provided in Section 3.1.1.1.

In addition to the test samples and procedural blanks identified in Table 4, three SCs were prepared to confirm the VX challenge application amount. SCs consisted of a spike of an equal volume of VX (2 μL) directly into extraction solvent. As discussed in Section 2.2.2.2, when spiked, VX was applied to the inside surface of the glass SC jar (rather than submerging the pipette tip into the solvent).

Results of the waste sampling method demonstration testing are provided in Section 3.1.4.

As indicated in Table 1, application of the vapor-phase solvent extraction technology to the porous materials or permeable coatings was anticipated to produce condensed extraction solvent as a waste product. Retention of the solvent collected during the functionality assessment of vapor-phase solvent extraction on sealed concrete, limestone, painted steel, and painted hardwood was planned. Since vapor-phase solvent extraction was ultimately excluded from the physical removal efficacy test matrix (based on difficulties experienced with setup and application of the technology during functionality assessments), this portion of waste sampling method demonstration testing was not conducted.

2.1.1.5. VX Depth Penetration Assessment

The depths to which VX would penetrate each of the porous materials selected for evaluation during this project (sealed concrete and limestone) were evaluated. To determine these depths, the core sampling approach (an approach independent of the selected physical removal technologies) was developed and used for dissection of the porous materials to quantify the extent of VX penetration as a function of depth during the VX depth penetration assessment. Section 2.2.3.1 provides a description of the equipment and procedures that were used for the core sampling approach. The VX depth penetration assessment using the core sampling approach took place after functionality of the approach was assessed, and solvent extraction and wipe-sampling method demonstration testing had been completed, so that the VX depth penetration assessment results could be evaluated in light of the determined solvent extraction and wipe-sampling recovery efficiencies from the sealed concrete and limestone porous materials.

VX (10 μ L) was applied to sealed concrete and limestone core samples according to procedures described in Section 2.2.2.2. VX was applied in the center of the top surface of the cores. Following application, the VX was allowed to dwell on the surface of the cores according to procedures described in Section 2.2.2.3 and penetrate the material cores over the course of 24 hours.

Following the dwell period, the top (spiked) surfaces of the porous material cores were wipe-sampled according to the procedures demonstrated during wipe sampling methods development testing. Wipe samples were obtained from the entire area of the top surface of each core that was initially contaminated with VX.

Following wipe sampling, the core sampling approach was applied. The contaminated core samples were dissected into discrete layer samples. The individual layer samples were extracted separately in solvent, and each layer extract was analyzed via LC-MS/MS for VX. Analysis results were used to quantify the mass of VX that penetrated the material as a function of depth (in increments of approximately 0.25 in., based on VX recovery from each layer sample).

Table 5 provides the test matrix for the VX depth penetration assessment. Each core test sample replicate and procedural blank for each material type was sampled via wipe sampling following the VX dwell period (top, spiked surface), then dissected into five (5) discrete layer samples. For each discrete layer sample excised from the core (except for the 1st/topmost layer), the associated

cutting dust was collected and extracted with solvent and cutting dust extracts were analyzed via LC-MS/MS alongside the layer sample extracts.

Table 5. VX Depth Penetration Assessment Test Matrix

Material	Sample Type	Sample Form	VX Challenge (μL)	Dwell Period	Replicates
Sealed concrete	Test sample	Material core [^]	10	24 hours	3
Sealed concrete	Procedural blank	Material core [^]	NA	24 hours	1
Limestone	Test sample	Material core [^]	10	24 hours	3
Limestone	Procedural blank	Material core [^]	NA	24 hours	1

[^] Dimensions: 1.5 in. diameter, 2.0 in. thickness

In addition to the test samples and procedural blanks identified in Table 5, three SCs were prepared to confirm the VX challenge application amount. SCs consisted of a spike of an equal volume of VX (10 μL) directly into extraction solvent. When spiked, VX was applied to the inside surface of the glass SC jar (rather than submerging the pipette tip into the solvent).

Results of the VX depth penetration assessment are provided in Section 3.1.5.

2.1.2. Physical Removal Efficacy Evaluation

Coupons of the porous materials or permeable coatings (coatings applied to the low-carbon steel and hardwood substrates; coupon dimensions provided in Table 7) were contaminated with VX. VX was applied as a single 10-μL droplet. Following application, VX was allowed to dwell on the coupon surface for 24 hours to penetrate the porous material or permeable coating. Observations of the spreading/soaking/etc. nature of the VX after application were recorded on the test parameter control sheet (TPCS; refer to Section 4.4).

Following the dwell period, wipe samples were collected from each coupon surface prior to application of the physical removal methods to quantify residual VX surface hazard on the material (transferrable hazard that had not absorbed/permeated/penetrated into the material during the dwell period). Wipe samples were obtained using the procedures described in Section 2.2.4 that had been successfully demonstrated as described in Section 2.1.1.3.

Following wipe sampling, the selected physical removal technologies were applied as described in Sections 2.2.3.2 and 2.2.3.3 to obtain samples from the coupons (the form/nature of samples obtained depended on the material and physical removal technology applied). Generally, coupon samples (either ground material samples or post-technology application wipe samples) were collected from each coupon in the area below the location of VX contamination. Coupon samples were extracted in solvent and analyzed via LC-MS/MS to quantify VX in the samples. Wastes generated during removal (i.e., stripped coating layers) were collected, sampled and analyzed via LC-MS/MS to quantify VX in the waste. Wipe samples were collected from the parts of the removal technologies/equipment (as applicable, e.g., grinding wheel and deflector shield of the grinding approach) that contact the contaminated areas of the coupons, and the wipes were extracted in solvent and analyzed for VX.

Four (4) tests were executed to complete the physical removal efficacy test matrix. Each individual test involved evaluation of a single physical removal method and coupon material type, to avoid cross contamination of samples by any migrating chemicals or dusts and debris created during application of the physical removal technologies that could not be completely captured (for waste analysis). Table 6 summarizes and provides information for the four tests that were performed, including indication of the types of samples that were collected from replicate test coupons during each test.

Table 6. Physical Removal Efficacy Test Matrix

Material Type	Removal Method	Sample Type	VX Challenge	Pre-Application Wipe Sample	0.25 in. Depth Layer Samples	Post-Application Wipe Sample	Waste	Removal Technology	Replicates
Sealed Concrete	Grinding	Test sample	✓	✓	✓			✓	3
		Procedural blank		✓	✓			✓	1
Limestone	Grinding	Test sample	✓	✓	✓			✓	3
		Procedural blank		✓	✓			✓	1
Painted Steel	Chemical Stripping	Test sample	✓	✓		✓	✓		3
		Procedural blank		✓		✓	✓		1
	None	Positive Control	✓	✓		✓			1
Painted Hardwood	Chemical Stripping	Test sample	✓	✓		✓	✓		3
		Procedural blank		✓		✓	✓		1
	None	Positive Control	✓	✓		✓			1

Positive controls included in tests of the chemical stripping technology consisted of painted steel and hardwood material coupons that were contaminated with VX and sampled following the dwell period alongside the test coupons (via wipe sampling), but to which the chemical stripper was not applied.

Procedural blanks consisted of coupons that were tested alongside the test coupons, including the dwell, physical removal technology application, and sampling and analysis steps, but that were not contaminated with VX.

Three SC samples were prepared as well during each test by spiking VX (same volume as that applied to test coupons) directly into solvent to confirm the contamination amount applied to coupons.

Results from the four physical removal efficacy tests that were performed are provided in Sections 3.2 and 3.3.

2.1.3. Waste Generation Assessment

In addition to the quantitative measurements discussed in Sections 2.1.1.4, 2.2.3.1, and 2.2.3.3 (recovery of VX from core sample cutting dusts and stripped paint), the wastes generated during physical removal efficacy testing were characterized by nature (chunks, dust, stripped materials, etc.) and volume/weight.

2.1.4. Damage Extent Assessment

During the physical removal technology functionality assessments and following application of the technologies during physical removal efficacy testing, the appearance of coupons was

assessed and representative photographs of the damage portions of the materials (portions to which the technologies were applied) were taken.

2.2. Experimental Methods and Materials

Experimental methods and materials used to conduct the testing described in Sections 2.1.1 through 2.1.4 are described in the subsections below.

2.2.1. Porous Materials and Permeable Coatings

Porous material and permeable coating information is provided in Table 7. Information on the stainless steel and glass beads used as control samples during methods demonstration tests is provided in Table 7 also.

Coupons of the porous materials and permeable coatings used during the grinding and chemical stripper physical removal efficacy tests, respectively, were prepared and used at the dimensions provided in Table 7. Core samples of the two porous materials used during the VX depth penetration test were excised from coupons prior to testing. For both porous materials, core samples were 1.5-in. -diameter cylinders, with height dependent upon the original material coupon thickness. Limestone was not sealed prior to use. Concrete coupons (5.75 in. length by 5.75 in. width by 2 in. thick) were fabricated and allowed to cure for a period of five (5) days prior to sealing.

Table 7. Porous Materials and Permeable Coatings

Material	Description	Supplier	Coupon Dimensions	Preparation
Sealed concrete	Water repellent (Siloxane PD, PROSOCO, Lawrence, KS) sealed concrete (5 parts sand; 2 parts cement (Buzzi Unicem USA, Greencastle Plant, Greencastle, IN); custom preparation, sealed on all surfaces	Snowden Concrete Products, LLC, Cincinnati, OH	5.75 in. length 5.75 in. width 2 in. thick	Cleaned with dry air to remove loose dust
Limestone	Limestone pavers/cobbles	Roby Monuments London, OH	7.5 in. length 7.5 in. width 2.25 in. thick	Scrubbed with a water-wetted brush to remove grime/debris; dried in an oven at approx. 30.5°C for at least 24 hours
Painted steel	Low-Carbon Steel	McMaster-Carr Aurora, OH (6544K13)	7.5 in. length 7.5 in. width 22-gauge thickness (plus coating layer thickness)	1. Cut coupon to size 2. Applied coat of primer 3. Allowed to dry 4. Applied coat of paint 5. Allowed to dry 6. Cleaned using dry air to remove debris
	LATEX White Interior/Exterior Multi-Surface Primer, Sealer, and Stain Blocker	Home Depot (100096395)		
	High Performance Protective Enamel Gloss White Oil-Based Interior/Exterior Metal Paint	Home Depot (202067206)		
Painted Hardwood	Red Oak Hardwood	Lowe's (1054)	5.5 in. length 5.5 in. width 0.75 in. thickness (plus coating layer thickness)	1. Cut coupon to size 2. Applied coat of primer 3. Allowed to dry 4. Applied coat of paint 5. Allowed to dry 6. Cleaned using dry air to remove debris
	LATEX White Interior/Exterior Multi-Surface Primer, Sealer, and Stain Blocker	Home Depot (100096395)		
	High Performance Protective Enamel Gloss White Oil-Based Interior/Exterior Metal Paint	Home Depot (202067206)		
Stainless steel (control)	Type 304 stainless steel disks	Adept Products, Inc. West Jefferson, OH	1.375 in. dia. disk 24-gauge thickness	None
Glass beads (control)	Borosilicate glass beads	Fisher Scientific, Pittsburgh, PA (10-310-1)	3-mm dia. beads	None

2.2.2. Application of CWA

2.2.2.1. CWA

All quantities of VX used during this project were synthesized at Battelle's HMRC under Chemical Weapons Convention program guidelines, with accountability through the U.S. AMC. All VX used originated from the same synthesis lot. All VX was stored in the HMRC CWA vault in accordance with HMRC security and CWA storage policies until needed for testing.

Once prior to use during testing (prior to both methods demonstration and physical removal efficacy testing), purity of the VX was measured. Target purity for VX was $\geq 90\%$. A VX purity sample was prepared (900 $\mu\text{g}/\text{mL}$ concentration for VX) from the supply of neat VX available for use on the project. The purity sample was analyzed by gas chromatograph (GC)/flame ionization detector (FID) to determine the relative abundance of VX as determined by peak area and reported as percent purity. Impurities and composition can influence VX degradation rates.

Solvent blanks were used to correct for possible solvent contaminants. GC/FID method parameters for purity sample analysis are provided in Table 8.

Table 8. GC/FID VX Purity Sample Analysis Method Parameters

Parameter	Description ^A
Instrument	Hewlett Packard Model HP 6890 Gas Chromatograph equipped with FID and Model 7683 Automatic Sampler
Data System	Chromeleon 7 (Thermo Electron Corporation)
Column	Rtx-5 30 m x 0.25 μm x 0.25 mm or equivalent
Carrier Gas Flow Rate	1.5 mL/min
Injection Volume	0.10 μL
Column Temp	40 °C initial temperature, hold 2 min, 20 °C/min to 280 °C, hold 5 min
Injection Temperature	Cool on column (track oven temperature)
FID Temp	250 °C

Table 9 provides purity information for the VX used during each test.

Table 9. VX Purity by Test

Purity	Tests Used
92.7%	Solvent extraction, wipe-sampling, and waste sampling methods demonstration tests
93.1%	VX depth penetration test, all physical removal efficacy tests

2.2.2.2. Coupon Spiking

Coupons, core samples, and core layer samples were inspected visually prior to contamination with neat VX to ensure any samples with surface anomalies were not used. Neat VX was applied to each designated sample as a single 2- μL droplet using a 1- μL - to 10- μL -range Gilson™ MICROMAN™ E positive displacement pipette (FD10001G, Fisher Scientific, Pittsburgh, PA, or similar), or a single 10- μL droplet using a 3- μL - to 25- μL -range Gilson™ MICROMAN™ E positive displacement pipette (FD10002G, Fisher Scientific, Pittsburgh, PA, or similar). VX

droplets were generally placed in the center of samples (or in each coupon “quadrant” during the wipe sampling method demonstration test).

When spiking ground concrete and limestone coupon samples during coupon sample solvent extraction method demonstration testing, VX was applied to the ground material samples by submerging the tip of the positive displacement pipette into the ground material, ejecting VX into the material while the tip was submerged, and then using the pipette tip to “stir” the spiked VX into the material. This approach was intended to ensure adequate mixing and dispersal of the VX throughout the ground material. However, we observed that the dispensed liquid VX caused “clumping” of ground material and the “clumped” ground material would stick to the pipette tip, possibly preventing adequate dispersal and mixing of VX throughout the material. Refer to the solvent extraction methods demonstration results in Section 3.1.2 for further discussion. Following spiking each sample, the pipette tip used to spike/stir each sample was discarded (i.e., a new, unused tip was used to spike/stir each ground material sample).

A similar approach was initially used for spiking and mixing VX into the sealed concrete and limestone cutting dust during the waste sampling methods demonstration test as that used for the ground materials (VX was applied to the cutting dust by submerging the tip of the positive displacement pipette into the dust, ejecting VX while the tip was submerged, and then using the pipette tip to “stir” the spiked VX into the dust). The same “clumping” behavior was observed after the 1st cutting dust sample was spiked (i.e., liquid VX caused clumping of the cutting dust, and portions of the “clumped” dust sample stuck to the pipette tip; 1st sealed concrete dust sample; refer to the EPATO20-MD3 TPCS provided in Attachment B), so the spiked/“clumped” sample was discarded and a new sample was prepared and spiked using an alternative method. For the alternative cutting dust spiking method, the jar containing each dust sample was tilted to collect the dust to one side of the jar, exposing the bottom of the glass jar. VX was then applied to the bottom of the glass jar, and the jar was then closed and swirled by hand to mix the cutting dust and liquid VX droplet. The remaining sealed concrete and limestone cutting dust samples were then spiked using this alternative approach. Following spiking each sample, the pipette tip was discarded (i.e., a new, unused tip was used to spike each dust sample).

SC samples were prepared by delivering the same quantity of VX (2 or 10 μ L) directly into 20 mL of extraction solvent in a 60 mL glass extraction jar (same used for sample extraction), rather than onto a sample surface. When spiked, VX was applied to the inside surface of the glass SC jar (rather than submerging the pipette tip into the solvent). When extracted, SCs were processed in a manner similar to wipe, coupon, or waste sample extracts (that is, SCs were sonicated and aliquoted as described for test sample extracts in Section 2.2.5).

2.2.2.3. CWA Dwell Period

Following application of VX, the contaminated samples were allowed to remain undisturbed for a 30-minute or 24-hour CWA dwell period (depending on the test). During the dwell period, the samples were subjected to the ambient atmosphere within the test hood. Samples were left

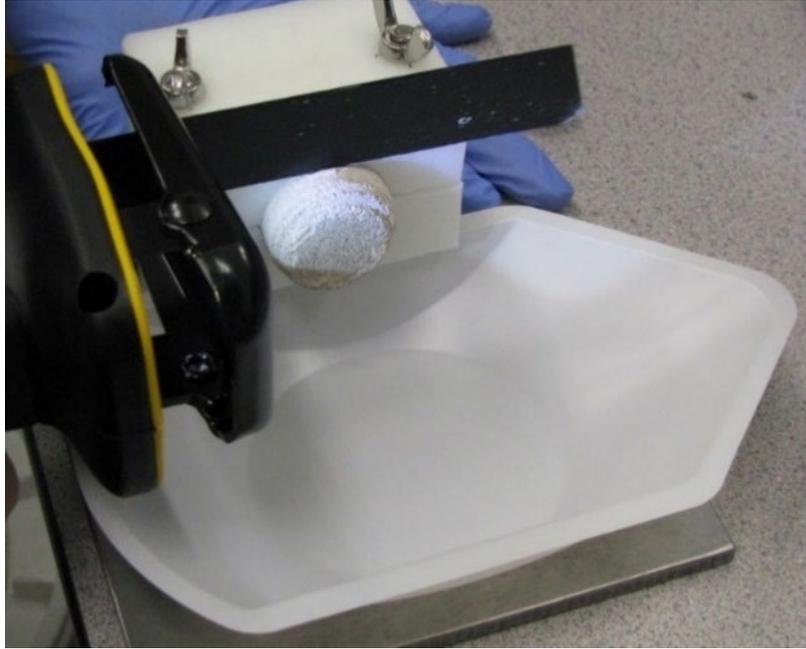
uncovered during the dwell period. Temperature and relative humidity (RH) of the sample environment within the hood were monitored and recorded but not controlled. RH was not expected to have an impact on evaporation or penetration of VX into the materials. Temperature and RH conditions within the hood were measured and recorded using a HOBO UX100 Datalogger (UX100-003, Onset® Computer Corporation, Bourne, MA) on each day of testing. Environmental data from each test are available as Attachment A.

2.2.3. Description and Application of Physical Removal Technologies

2.2.3.1. Core Sampling Approach

A method independent of the selected physical removal technologies was developed and used for dissection of porous materials (sealed concrete and limestone) to quantify the extent of VX penetration as a function of depth during the VX depth penetration assessment performed during methods demonstration.

A cordless drill/driver (1001592743, Home Depot, Columbus, OH, or similar) equipped with a 1.625 in.-diameter carbide hole saw (301697684, Home Depot, Columbus, OH, or similar) was used to excise 1.5 in.-diameter full-depth cylindrical core samples from coupons of each porous material. During the VX depth penetration assessment, the core samples were contaminated in the center of the top surface with VX, and the VX was allowed to dwell on the core surface for 24 hours (cores were oriented upright), after which the top (contaminated) surface of the core was wipe-sampled. Following wipe-sampling, the contaminated core was inserted into a holder with the bottom/uncontaminated surface of the core sample facing toward the front of the holder (Figure 2). A cordless reciprocating saw (1002338813, Home Depot, Columbus, OH, or similar) equipped with a diamond-tipped saw blade (1000683506, Home Depot, Columbus, OH, or similar) was then used to cut the core sample into discrete layer samples at (target) 0.25 in. depth increments. Layer samples were cut from the core beginning from the bottom/uncontaminated side of the core and progressing toward the top/contaminated side. The layer samples from the core were then extracted separately with solvent and layer sample extracts were analyzed via LC-MS/MS for VX. Cutting dust generated during use of the reciprocating saw (to dissect the core into individual slices) was collected in a tray placed underneath the core and retained for solvent extraction and analysis via LC-MS/MS for VX. No air monitoring was conducted to collect (contaminated) fine particulate matter which may have spread across a larger area.



**Figure 2. Core Sample Holder with Dust Collection Tray
(uncontaminated surface of core is visible)**

Figure 3 illustrates the overall core sampling approach used to obtain discrete depth layer samples of each porous material core to evaluate VX penetration into the material.

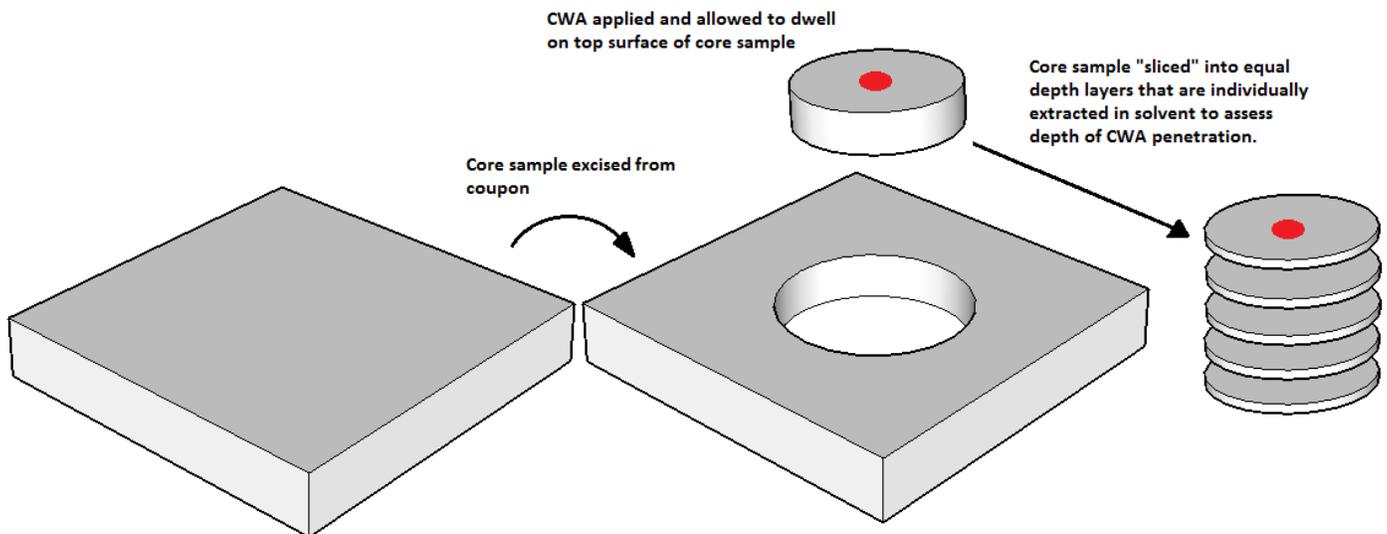


Figure 3. Porous Material Core Sampling Approach

Figure 4 illustrates the approach used to dissect each individual material core to harvest the discrete layer samples.

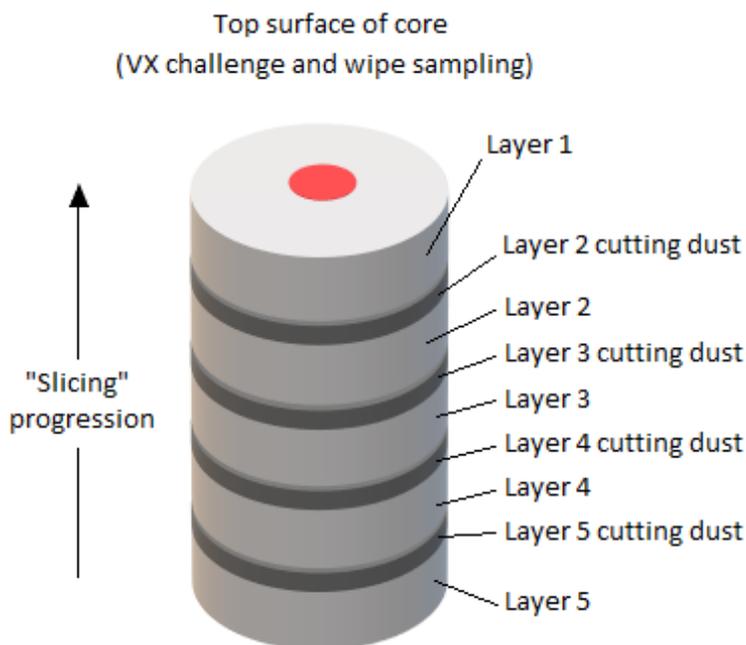


Figure 4. Core Sampling Dissection

Once the core had been cut into discrete layer samples, a wipe sample was obtained from the reciprocating saw blade. The wipe covered the full surface of the blade. The blade was then replaced prior to cutting the next core sample (i.e., each blade was used to cut only a single core into layer samples).

2.2.3.2. Grinding

Grinding is a commonly used approach for surface layer removal in which coarse-grained abrasives in the form of grinding wheels or surfacing disks are applied to a material. The rotating wheel abrades the material, grinding it and removing surface layers. During this project, an angle grinder (DeWalt 11 amp corded, 4.5 in. small angle grinder, 1001672186, Home Depot, Columbus, OH, or similar) equipped with a fine-grit diamond grinding wheel (203061023, Home Depot, Columbus, OH, or similar) was used.

Following application of VX, the 24-hour dwell period, and the initial coupon wipe sample, the grinder was applied to the coupon surface to remove material to a target depth of 0.25 in. Removal to this depth was achieved using a stepwise approach, wherein the grinder was applied to remove material across a wide area of the coupon surface to a depth visually less than 0.25 in. After the first “pass”, the achieved removal depth was measured to gauge the additional material that needed to be removed via reapplication of the grinder (a second “pass”) to reach a final 0.25 in. depth. Once the final depth of approx. 0.25 in. had been achieved across the removed area of the coupon surface, the aggregate ground material removed was collected and retained for solvent extraction and analysis via LC-MS/MS to quantify VX in the removed material. Prior to

solvent extraction, the mass of ground material removed in the depth layer sample was determined gravimetrically.

Following removal of the first 0.25 in.-depth layer sample, the grinding wheel was sampled via wipe sampling, and the wipe was extracted with solvent and analyzed via LC-MS/MS to assess VX contamination transferred to the grinding wheel. The wipe sample obtained from the wheel covered the full surface of the wheel that contacted the coupon during grinding.

The above approach was then repeated to remove an additional (second) 0.25 in. depth layer sample (thus to a cumulative target depth of 0.5 in. from the original coupon surface). The area of the coupon over which the grinder was applied to collect the second (and subsequent) 0.25 in.-depth layer sample was slightly less than the area of the first (or previous) 0.25 in.-depth layer sample. Following collection of each successive depth layer sample after the second, the grinding wheel was wiped using a solvent-soaked wipe, but the wipe was not extracted with solvent and analyzed (i.e., the wipe was used only to clean the wheel between collection of the second and third, and subsequent, depth layer samples).

The general approach for collecting 0.25 in.-depth layer samples from the porous material coupons is illustrated in Figure 5.

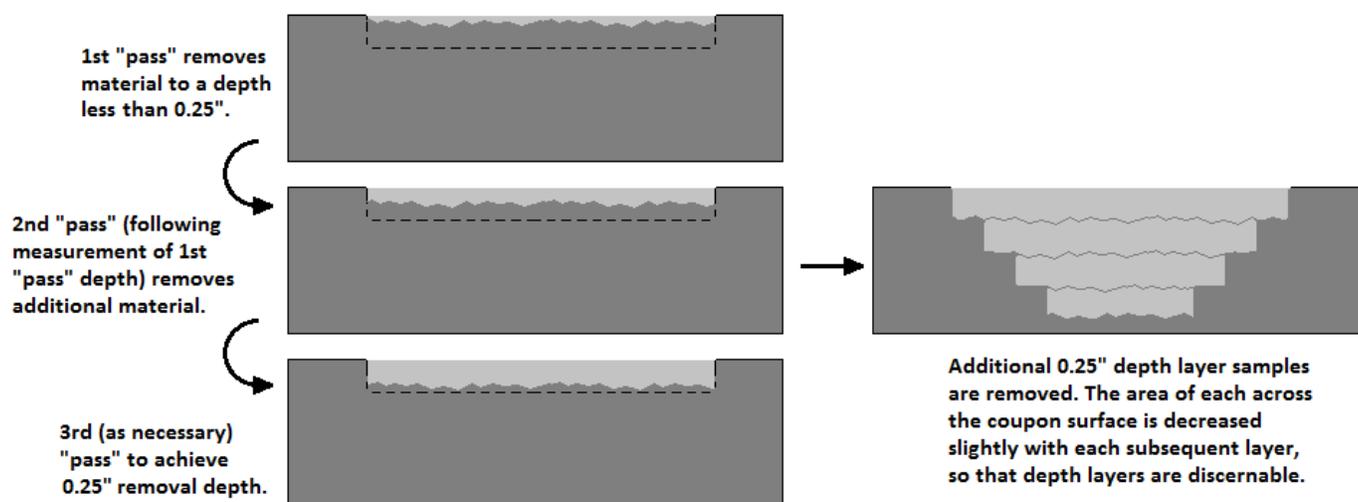


Figure 5. Approach for Depth Layer Sample Collection via Grinding

Coupon setup for application of the grinder involved orientation of the coupon upright on a side within the test chamber using an aluminum easel. Figure 6 depicts a sealed concrete coupon on the aluminum easel.

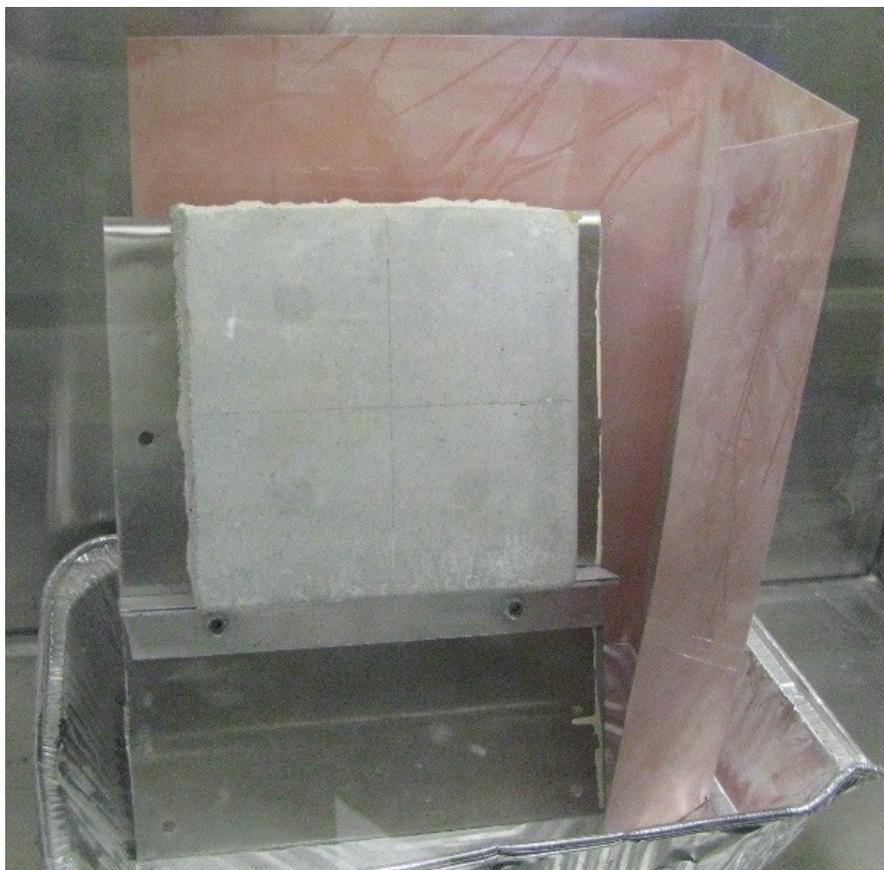


Figure 6. Concrete Coupon on Aluminum Easel

Figure 6 also shows that a deflector shield was positioned to the right of the coupon. When the grinder was applied, ground material removed from the surface of the coupon was thrown by the grinding wheel against the deflector shield and directed downward into an aluminum collection pan. Once a depth layer sample of 0.25 in. had been removed, the ground material collected in the aluminum collection pan was extracted with solvent according to procedures described in Section 2.2.5, and the extract was analyzed via LC-MS/MS for VX. Similar to the grinding wheel, the inside surface of the deflector shield that was contacted by removed ground material was sampled via wipe sampling following removal of the first depth layer sample, and the wipe was extracted with solvent and analyzed via LC-MS/MS. The deflector shield was also wiped between collection of the second and third, and subsequent, depth layer samples, but these wipes were not extracted and analyzed for VX (i.e., wipe sampling was performed only to clean the inner surface of the deflector shield between replicates to reduce/eliminate the potential for cross-contamination).

2.2.3.3. Chemical Stripping

Klean-Strip® KS-3 Premium finish/paint stripper (100144685, Home Depot, Columbus, OH, or similar) is a dichloromethane-based stripper. It is a thickened semi-paste that can be applied via brushing and is intended to cling to vertical surfaces without running or dripping.

Following application of VX, the 24-hour dwell period, and the initial coupon wipe sample, 1 mL of the chemical stripper was applied directly to the permeable coating (primer/paint) on coupons using an Eppendorf Repeater M4 Pipette (14-287-150, Fisher Scientific, Pittsburgh, PA). The stripper was then manually spread across an area with diameter of approx. 1.375 in. using a ½ in.-width brush (7237T84, McMaster-Carr, Aurora, OH), centered over the area of the coupon that was contaminated with VX (or in the center of the coupon in the case of procedural blanks). Following application, the stripper was allowed to dwell on the coating for 30 minutes (manufacturer-recommended contact time). After 30 minutes, the coating was visually assessed. If the coating did not appear to be detached from the steel or hardwood material (as evidenced by a “bubbled” or “swollen” appearance of the paint/primer), the stripper was allowed to dwell and react with the coating for an additional 15 minutes (total 45-minute stripper dwell period). The total chemical stripper residence time on the coating surface was recorded on the TPCS.

Once the coating layer appeared to be visibly detached from the steel or hardwood material, the coating was stripped from the material using a 2 in.-width plastic joint knife (3546A421, McMaster-Carr, Aurora, OH). Generally, the coating was removed as a single, solid piece (a “bubbled” or “swollen” section of degraded paint/primer) that was physically scraped away from the material. The stripped coating (potentially containing VX) was collected, extracted with solvent, and analyzed for VX via LC-MS/MS.

2.2.3.4. Vapor-Phase Solvent Extraction

Vapor-phase solvent extraction is a physical removal technology that involves vaporization of an organic solvent with a low boiling point so that the vaporized solvent will circulate within a building (or similar enclosed space). As they are circulated, the vapors permeate into porous building materials, where they condense, solubilize contaminants, and then diffuse outward. Condensed solvent containing the removed contaminants is then decontaminated using a separate approach.

As discussed in Section 1.2, vapor-phase solvent extraction was selected following the literature search for evaluation for efficacy in removal of VX contamination from both porous materials and permeable coatings. As vapor-phase solvent extraction is primarily designed for application in buildings and similar large, enclosed spaces, a modified, laboratory-scaled approach was conceptualized and intended for use during this project. As discussed in Section 2.1.1.1, the conceptualized apparatus and approach for application of vapor-phase solvent extraction were evaluated during the technology functionality assessments conducted during the methods demonstration phase of the project. The apparatus and test stand setup that were evaluated for application of the vapor-phase solvent extraction physical removal technology are depicted in Figure 7.

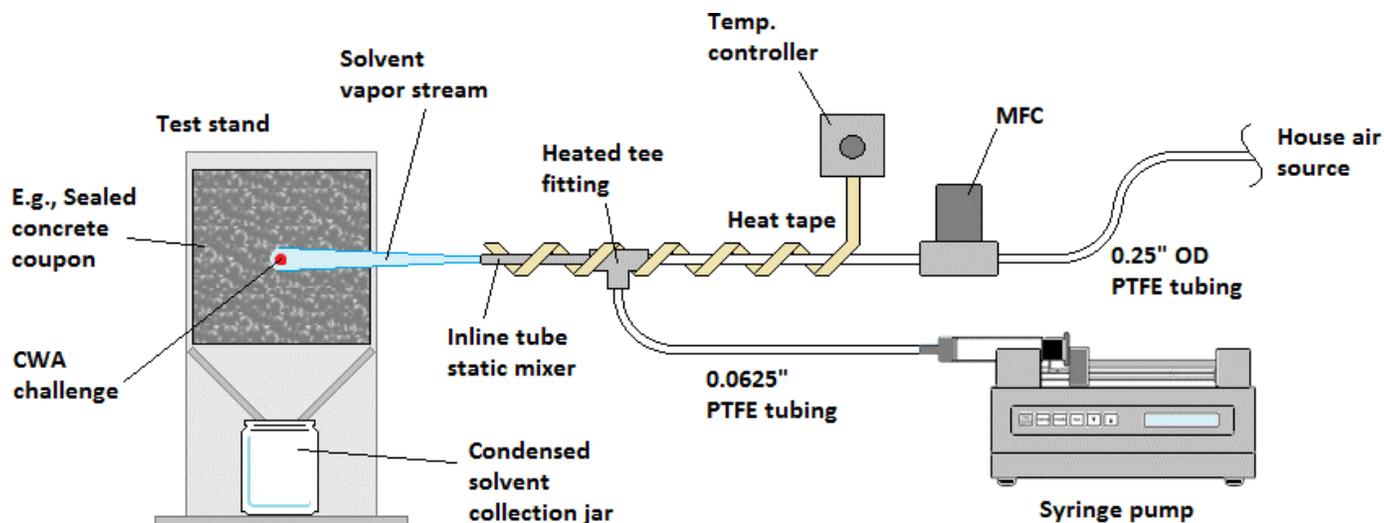


Figure 7. Vapor-Phase Solvent Extraction Apparatus

Clean, dried house air (regulated to 20 pounds per square inch [psi]) was supplied to a mass flow controller that set the flow rate of the airstream to approximately 300 mL/min. The air stream coupled with an infusion (via a syringe pump) of solvent (acetone, A929-4, Fisher Scientific, Pittsburgh, PA) at a tee fitting. Heat tape (VV-03106-32, Cole Parmer, Vernon Hills, IL) was used to heat the tee fitting and air supply tubing to vaporize the acetone (heated to above the boiling point of the solvent). The vaporized acetone would then be carried by the airstream through an inline static mixer (3530K43, McMaster-Carr, Aurora, OH).

It was planned that following application of VX, the 24-hour dwell period, and the initial coupon wipe sample, the test or control coupon would be set into a test stand that would orient the coupon in an upright position. The solvent vapor stream from the static mixer would then be directed onto the contaminated area of the coupon (or the center of the coupon in the case of procedural blanks). The solvent vapor stream would be allowed to impact the coupon surface for a period of 2.5 hours. The syringe pump would be set to infuse solvent into the airstream at a rate of 150 μ L/min. Thus, the total amount of solvent vaporized would be approx. 22.5 mL.

As the solvent vapor stream impacted the coupon surface, it was expected that solvent would either: (1) migrate into the porous materials, (2) be deflected off the coupon and dissipate into the air, or (3) condense on the coupon surface, run down, and drip from the bottom edge of the coupon. Solvent vapor that deflected off the coupon surface and into the air would not be collected. Solvent that condensed on the coupon surface and ran downward would be collected for analysis. The design of the test stand included channels that would direct condensed solvent into a graduated glass collection vessel below the coupon. The collection vessel would be kept on dry ice to keep the condensed, collected solvent cold to minimize evaporation during the 2.5-hour vapor-phase solvent extraction application. It was suspected that solvent that penetrated (spiked) porous materials would either carry penetrated CWA farther into the coupon or would allow for migration of penetrated CWA out of the coupon. It was assumed that CWA that

migrated back out of the coupon through the penetrated solvent would be carried by condensed solvent running down the surface of the coupon into the collection vessel below. At the end of 2.5-hour vapor-phase solvent extraction application, the volume of condensed solvent collected in the vessel would be recorded. The solvent would then be analyzed via LC-MS/MS for VX.

Following solvent vapor treatment, the core sampling approach would be used to dissect and sample the treated porous materials (sealed concrete and limestone). Permeable coatings (painted steel and painted hardwood) would be wipe-sampled a second time, following the first wipe collected prior to solvent vapor treatment.

During the technology functionality assessment of the vapor-phase solvent extraction apparatus, operating conditions/parameters to produce a viable solvent vapor stream could not be determined using the apparatus as conceptualized (setup as depicted in Figure 7). Initial revisions of the apparatus setup were unsuccessful in generating a useable solvent vapor stream. Budget and schedule limitations of the project then precluded further development of the technology, so vapor-phase solvent extraction was not carried forward into further methods demonstration test phases or into physical removal efficacy testing. Refer to Section 3.1.1.4 for additional information.

2.2.4. Coupon Surface (Wipe) Sampling for VX

The wipe sampling method used during this project was consistent with a method developed and used during a previous EPA study [12] to sample transferable/residual CWA on the surface of materials. Leveraging the wipe-sampling methods development testing conducted during the previous work, the wipe sampling method used during this project included the following details:

- Wipes were lint-free 2 in. × 2 in. (5 centimeters [cm] × 5 cm) four-ply rayon/polyester blend (gauze) sponges (22-037-921, Fisher Scientific, Pittsburgh, PA).
- The same solvent selected for coupon sample and waste sample extraction (IPA) was used as the wipe wetting and wipe extraction solvent.
- Wipes were wetted with 1.5 mL of solvent. This volume of solvent added to this particular wipe was determined to be an amount that is approximately half-saturating for the wipe, as determined gravimetrically by weighing three wipes before and after soaking the wipes in solvent (half of the amount of solvent remaining on the wipe 30 seconds after immersion in solvent and hanging vertically to allow excess solvent to drip off) [12].
- Each coupon was wiped using four horizontal and four vertical strokes (using the same wipe) over an area of no larger than approximately 100 square centimeters (cm²; adjusted as necessary based on wipe sampling a coupon or a core sample) centered on the area of the coupon/core that was contaminated with VX. Adequate overlap between strokes occurred so that the entire 100 cm² (or as adjusted) area was wiped. The leading edge of the wipe was maintained between passes. The wipe was folded, as necessary, for manageability during wipe sampling. Figure 8 depicts the wipe pattern that was used.

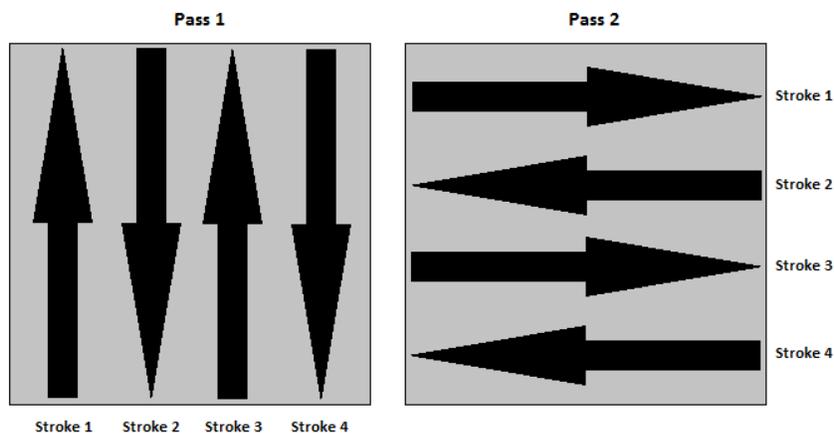


Figure 8. Wipe Pattern

Following collection, wipes were extracted in solvent in the same manner as coupon samples and waste samples, using the same solvent as that used to wet the wipes IPA. Wipe extracts were then analyzed for VX by LC-MS/MS.

2.2.5. Extraction of VX from Wipe, Coupon, and Waste Samples

All core layer samples, wipe samples, and waste samples (cutting dust and stripped paint) were extracted by placing each into a separate 60-mL glass jar (05-719-257, Fisher Scientific, Pittsburgh, PA, or similar) containing extraction solvent (IPA). Ground material samples were placed into a 125-mL glass jar (05-719-57, Fisher Scientific, Pittsburgh, PA, or similar). SCs, wipe samples, core layer samples, core sampling cutting dust, and stripped coating samples were extracted with 20 mL of solvent. Ground material samples were extracted with 80 mL of solvent. PTFE disks included during the solvent extraction method demonstration test were extracted with 10 mL of solvent. These jars and these volumes of solvent were sufficient to submerge all sample types fully in the extraction solvent.

Following addition of coupon samples, wipe samples, or waste samples to the extraction solvent within each jar, the jars were swirled by hand for approximately 5-10 seconds and placed into a sonicator (15-336-103, Fisher Scientific, Pittsburgh, PA, or similar). Extraction jars were sonicated at 40 - 60 kilohertz for 10 min. Within 30 min of completing this process, aliquots of approximately 0.5 mL from each extraction jar were transferred to individual analysis sample vials (21140 [vial], 24670 [cap], Fisher Scientific [Restek Corp.], Hanover Park, IL 60133) and sealed. Samples that were not analyzed the same day were stored at -20 ± 10 °C.

2.3. Analytical Methods

Coupon, wipe, and waste sample extracts were analyzed using LC-MS/MS to quantify the amount of residual VX present. An AB SCIEX 5500 triple quadrupole MS (SCIEX, Framingham, MA) coupled to a Shimadzu 20 XR series LC (Shimadzu, Columbia, MD) was used for sample analysis. VX was quantitated in sample extracts using a reversed-phase high performance liquid chromatography (HPLC) method and multiple reaction monitoring (MRM). MRM provides high specificity and sensitivity and is typically used in quantitative applications.

The MRM transition with the best signal-to-noise ratio is usually selected for quantitation. VR (Russian VX; nominal concentration 0.5 nanograms [ng]/mL) was used as the internal standard (IS) for quantitation of VX, and was added to calibration standards, controls, and test samples just prior to LC-MS/MS analysis (specifically, a solution of VR in water was used as the diluent for dilution of samples prior to analysis). The VR used during this project was a Chemical Agent Standard Analytical Reference Material (CASARM) obtained from the U.S. Army Combat Capabilities Development Command (CCDC) Chemical Biological Center. Table 10 provides the ion transitions that were used for detection and quantitation of VX.

Table 10. Analyte Ion Transitions

Analyte	Precursor Ion	Product Ion Quantifier
VX	268	128
VR	268	100

The lower limit of quantitation for VX (i.e., the lowest concentration standard used in the calibration curve) was 0.010 ng/mL, which was above, but near, the instrument detection limit of the LC-MS/MS.

The concentration of VX in the samples was interpolated using the VX area/IS area ratio and the regression equation generated from the calibration standards. Samples that were quantitated below the lowest calibration standard concentration (< 0.010 ng/mL), or displayed area counts below the area counts of the lowest concentration on the calibration curve, were reported as less than the lower limit of quantitation (LLOQ; e.g., < 0.010 ng/mL). The less-than-the-LLOQ value was corrected to account for any sample dilution factor (minimum of 10-fold). Samples that were quantitated above the highest calibration standard (2.0 ng/mL) were diluted (i.e., a new analytical sample was prepared from the original extract using a higher dilution factor) and reanalyzed. Refer to Section 4.2.2 for LC-MS/MS calibration details. All data were reported to two significant figures. LC-MS/MS parameters that were used for analyses are provided in Table 11.

Table 11. LC-MS/MS Conditions for VX Analysis

Parameter	Description	
Ionization Mode and Polarity	Electrospray Ionization, Positive Mode	
HPLC Column	Restek Allure PFPP, 2.1 x 50 mm, 5 μ m, (part no. 9169552)	
Column Temperature	Ambient	
Mobile Phase	A: 2 mM Formic Acid/2 mM Ammonium Formate in Water B: 2 mM Formic Acid/2 mM Ammonium Formate in Methanol	
Mobile Phase Gradient	Time (minutes)	%B
	0.0	20
	1.0	20
	2.0	100
	4.0	100
	4.1	20
Flow Rate	Ramp from 0.5 to 0.7 mL/min from 1.0 to 2.0 minutes	
	Ramp from 0.7 to 0.5 mL/min from 4.0 to 4.1 minutes	

Parameter	Description
	0.5 mL/min for all remaining method segments
Injection Volume	2 - 50 μ L
Run Time	4.5 minutes

Samples (in IPA) were diluted a minimum of 10-fold prior to LC-MS/MS analysis. Higher dilution factors were used based on the concentration of VX in the samples. Sample dilutions were performed using calibrated positive displacement pipettes and were documented on the sample chain of custody (CoC) forms (refer to Section 4.3), the laboratory record book (LRB), and the raw analysis data files.

2.4. Calculations

Diluted test, control, and blank wipe sample, coupon sample (core layers or ground material), and waste sample (cutting dust or stripped coating) extract concentrations were provided in units of ng of VX per mL of extract by the LC-MS/MS Analyst® software (ver. 1.7, SCIEX, Framingham, MA) through comparison of VX and IS peak areas to the calibration curve. After correction of extract concentrations for dilutions performed prior to analyses, mass recovered from the samples via extraction was determined according to Equation 1:

$$Mass_{Rec} = \frac{Conc_{Ext} \times Vol_{Ext}}{1000} \quad (1)$$

where:

$Mass_{Rec}$ = CWA mass recovered from the sample (μ g)

$Conc_{Ext}$ = Sample extract concentration provided by the LC-MS/MS software (ng/mL)

Vol_{Ext} = Volume of extraction solvent (mL)

Total mass recovered from test, control, or blank coupons or cores was the sum of the masses recovered from wipe samples taken from the coupons or cores, from extraction of coupon samples in solvent (core layers or ground material layers), and from extraction of waste samples (cutting dust or stripped coating). Multiple wipe and/or coupon samples contributed to the total mass recovered from coupons or cores (depending on the test; e.g., wipe samples were taken from the coupon, grinder, and deflector shield, and multiple ground material layer samples were collected during application of the grinding technology to a single coupon). Total mass was calculated according to Equation 2:

$$Mass_{Tot} = Mass_{Rec(wipe)} + Mass_{Rec(coupon)} + Mass_{Rec(waste)} \quad (2)$$

where:

$Mass_{Tot}$ = Total CWA mass recovered from the coupon or core (μ g)

$Mass_{Rec(wipe)}$ = CWA mass recovered from the wipe(s) (μ g)

$Mass_{Rec (coupon)} = \text{CWA mass recovered from the coupon sample(s)} (\mu\text{g})$

$Mass_{Rec (waste)} = \text{CWA mass recovered from the waste sample(s)} (\mu\text{g})$

Percent recovery was calculated for each individual test coupon or core according to Equation 3:

$$Recovery = \left(\frac{Mass_{Tot}}{Mass_{SCAvg}} \right) \times 100\% \quad (3)$$

where:

$Mass_{SCAvg} = \text{Average CWA mass recovered from the SCs} (\mu\text{g})$

$Mass_{Tot} = \text{Total CWA mass recovered from the coupon} (\mu\text{g})$

3. RESULTS

3.1. Methods Demonstration

3.1.1. Physical Removal Technology Functionality Assessment Results

3.1.1.1. Core Sampling Approach

The method planned initially for application of the core sampling approach involved contamination of sealed concrete and limestone coupons with VX (10- μ L droplet spiked at the center of the coupon) prior to application of the approach. After the 24-hour dwell period, core samples would then be excised from the coupons underneath the area of the coupon to which VX was applied. Following excision of the core, the core would be sliced into discrete layer samples to assess depth of VX penetration into the material. This initially planned approach was evaluated during the technology functionality assessment of the core sampling approach (performed prior to testing without VX present).

Method

Limestone (8 in. length by 8 in. width by 2.25 in. thick) or sealed concrete (12 in. length by 12 in. width by 2 in. thick) coupons were placed vertically in a holder inside the test chamber with a weigh dish placed under the coupon to collect cutting dust (refer to Figure 9). A drill (1001592743, Home Depot, Columbus, OH) with a 1.5 in.-diameter carbide hole saw bit (301697689, Home Depot, Columbus, OH) was used to drill a 1.375 in.-diameter core sample out of the coupon. An infrared thermometer (9248T57, McMaster-Carr, Aurora, OH) was used to measure the surface temperature of each coupon before and after core excision. The core sample was then inserted into a nylon block/holder for slicing, with a weigh dish placed underneath to collect cutting dust (refer to Figure 10). A reciprocating saw (1002338813, Home Depot, Columbus, OH) with a 6 in. diamond grit saw blade (1000683506, Home Depot, Columbus, OH) was used to slice the core into 0.25 in. thick slices. The infrared thermometer was again used to measure the temperature of the core before and after slicing. After slicing, the cutting dust collected in the dish was poured into a sample jar and the mass of dust was determined gravimetrically. A ruler was used to measure the thickness of each slice.



Figure 9. Core Excision Setup



Figure 10. Core Slicing Setup

Results

A core sample was excised from sealed concrete in 22 minutes. Temperature of the sealed concrete coupon prior to excision of the core was 72.1°F as measured on the top surface of the coupon. Temperature of the core following excision from the coupon was 93°F at the top of the core and 110°F at the bottom of the core.

Difficulty was experienced with starting the coring process as the drill/hole saw had a tendency to “travel” on the coupon surface until some depth was achieved (the pilot bit typically used with a hole saw could not be used since during normal testing the area drilled by the pilot bit would be the VX-contaminated area of the coupon). The coupon was removed from the chamber and a circular groove/score was pre-drilled into the surface. After approximately 6 minutes of drilling, the operator became fatigued and the angle of the drill shifted causing a (approximately) 0.25 in.-thick piece of the core to break off (still inside the coupon), as depicted in Figure 11.



Figure 11. Broken Core

At that point, a 2nd operator continued the coring process. Multiple times during drilling, the operator lost control of the drill due to ergonomics and positioning and also to the hole saw becoming seized within the coupon, leading to concerns regarding the safety of application of the method within the test chamber on coupons that would be contaminated with VX during physical removal efficacy testing. By the time the operator finished drilling through the material, the hole

saw bit had again become seized within the coupon. The coupon had to be removed from the chamber to remove the hole saw bit. The excised core was also stuck inside the hole saw bit and operators had to use a screwdriver to remove the core sample from the hole saw. An attempt was made to pre-drill/score another coupon but was unsuccessful as the hole saw bit had become dull from use during the first core sampling.

Given the complications and safety concerns described above, it was decided that the core sampling approach would not be applied as initially planned during the VX depth penetration assessment and physical removal efficacy testing (wherein the coupon is spiked with VX prior to coring, and the hole saw is used to excise a core from the contaminated coupon). Alternatively, pre-excised core samples would be used; i.e., core samples were obtained from uncontaminated coupons prior to testing, and the cores would be spiked and treated using the technologies (rather than spiking coupons and obtaining core samples from the contaminated portion of the coupons after the dwell period). Because pre-excised cores would be used, the nominal core sample diameter (for the VX depth penetration assessment) was increased to 1.5 in. (excised using a 1.625 in.-diameter carbide hole saw bit, 301697684, Home Depot, Columbus, OH).

Additional 1.375 in.-diameter core samples were prepared outside the lab for preparation of layer samples for solvent extraction method demonstration testing. The temperature of the core was measured during drilling (once with the used, dull hole saw bit for concrete and limestone and once with a new bit for concrete). An increase in temperature was observed and results are provided in Table 12. Photographs of the core samples excised from limestone and sealed concrete are provided in Figure 12. Such temperature increase was also observed in other studies and resulted in thermal degradation of VX [13].

Table 12. Temperature Increase for Core Excision using Drill Press

Material	Start Temp (°F)	Temp at ¼ in. Depth (°F)	Temp at ½ in. Depth (°F)	Temp at 1 in. Depth (°F)	Temp at 2 in. Depth (°F)
Limestone (old bit)	61.7	Not measured	Not measured	151.6	145.3
Concrete (old bit)	67.8	141.0	145.5	196.1	179.1
Concrete (new bit)	68.2	91.1	109.1	174.9	163.7



Figure 12. Cores Excised from Limestone (left) and Sealed Concrete (right)

The time required to slice the core samples, temperature changes, and collected cutting dust masses are provided in Table 13 for limestone and Table 14 for sealed concrete. The thickness of the resulting slices for limestone and sealed concrete are provided in Table 15. Both materials were amenable to slicing using the method described in Section 2.2.3.1. Representative photographs of core sample slices are provided in Figure 13 and associated cutting dust samples are provided in Figure 14.

Table 13. Limestone Core Slicing Results

Core	Slice	Slicing Time (min)	Start Temp (°F)	End Temp (°F)	Cutting Dust Mass (g)
1	1	10	72.1	93.5	2.85
	2	3	93.5	97.3	2.73
	3	3	97.3	97.8	2.66
	4	2	97.8	107.9	2.18
	5	3	107.9	121.8	2.66
	6	2	105.1	110.3	2.92
2	1	4	81.9	98.0	2.41
	2	2	98.0	104.6	2.07
	3	1	104.6	97.8	2.43
Average					2.55

Table 14. Sealed Concrete Core Slicing Results

Core	Slice	Slicing Time (min)	Start Temp (°F)	End Temp (°F)	Cutting Dust Mass (g)
1	1	5	81.6	114	8.69 ^A
	2	2	89	124	
	3	3	94	120	
2	1	2	78.1	80.8	1.39
	2	3	80.8	83.8	1.85
	3	3	83.8	93.8	1.66
	4	2	93.8	105.3	1.90
3	1	1	82.1	101.3	1.09
	2	3	76.1	90.3	1.25
	3	2	90.3	106.9	1.70
	4	3	106.9	117.5	1.66
Average					1.56

^A Cutting dust from all three slices was combined (data not used for average calculation).

Table 15. Slice Thickness Results

Rep	Concrete Thickness (inches)	Limestone Thickness (inches)
1	0.25	0.25
2	0.25	0.25
3	0.25	0.25
4	0.25	0.25
5	0.25	0.25
6	0.375	0.19
7	0.25	0.31
8	0.25	0.31
9	0.25	0.25
10	0.25	0.25
11	0.50 ^A	-
12	0.375 ^A	-
Average	0.29	0.26

^A Remaining end of cores



Figure 13. Core Slices from Limestone (left) and Sealed Concrete (right)



Figure 14. Cutting Dust from Limestone (left) and Sealed Concrete (right)

3.1.1.2. Grinding

The method planned initially for application of the grinding technology involved use of a vacuum dust shroud (302674944, Home Depot, Columbus, OH) attached to the grinder to collect ground material as it was removed from the coupon. This initially planned approach was evaluated during the technology functionality assessment of the grinding technology (performed prior to testing without VX present).

Method

Difficulty was experienced with application of the grinding technology using the method initially planned that incorporated a vacuum dust shroud attached to the grinder to collect the ground material that was produced. Difficulties experienced included:

- Operators were unable to orient the grinder against the coupon as necessary so that the grinding wheel contacted the material properly, due to the position and shape of the vacuum shroud attachment.
- When attempts were made to orient the grinder to obtain successively deeper ¼ in. depth-layer samples, the vacuum shroud attachment could not be interfaced properly with the surface of the coupon and vacuum was lost, leading to loss of the ground material sample.
- When a means for collecting the ground material sample using the vacuum shroud was added to the setup (i.e., a capture vessel installed in-line between the shroud and vacuum source), vacuum suction strength was lost and was inadequate to collect the ground material sample.
- The high speed of the grinder exacerbated loss of ground material sample, given the above discussed inability to adequately contain and capture ground material via vacuum.

Due to the issues summarized above, the method for application of the grinding technology was revised. Limestone (8 in. length by 8 in. width by 2.25 in. thick) or sealed concrete (12 in. length by 12 in. width by 2 in. thick) coupons were placed inside the test chamber. The coupons were leaned against the back of the chamber and, if necessary, to prevent them from slipping forward, placed on a PTFE block. A sheet of aluminum foil with folded sides was placed under the coupon to collect the removed/ground material. An aluminum shield was placed inside the foil to the right of the coupon to deflect and collect the ground material (refer to Figure 15).

An angle grinder (1001672186, Home Depot, Columbus, OH) fitted with a diamond cup grinding wheel (203061023, Home Depot, Columbus, OH) was connected to an adjustable autotransformer (W5MT3, Variac®, General Radio Company) to slow the grinding speed. Using the grinder, a section of the coupon was ground down at 0.25 in. depth increments. The depth of each grind was measured using a ruler (refer to Figure 16). After grinding, the ground material deflected by the shield and collected in the foil was poured into a sample jar and the mass collected was determined gravimetrically.

An infrared thermometer (9248T57, McMaster-Carr Part, Aurora, OH) was used to measure the surface temperature of each coupon before and after grinding.

A wet/dry vacuum (648846002842, Home Depot, Columbus, OH) was connected to the top of the chamber to draw and capture the fine grinding dust created that was not captured/redirected by the shield to the right of the coupon (this fine grinding dust was thus not included with the ground material sample collected for each grinding pass).



Figure 15. Grinding Setup

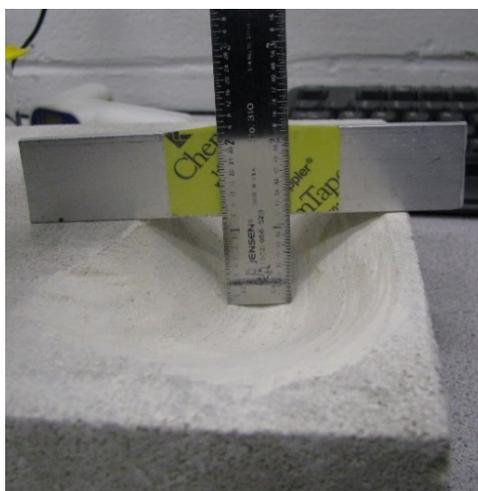


Figure 16. Depth Measurement

Results

The depth reached after each grinding pass, temperature difference between before and after grinding, and the mass of ground material collected for each depth layer are provided in Table 16 for limestone and in Table 17 for sealed concrete.

Table 16. Limestone Grinding Results

Coupon	Layer	Target Depth	Temp Diff (°F)	Grinding Time (min)	1 st Grind Pass Depth (in.)	2 nd Grind Pass Depth (in.)	3 rd Grind Pass Depth (in.)	Ground Material Mass (g)
1	1	¼	-0.3	8	1/8	1/8 - 1/4	¼	36.34
	2	½	0.4	9	3/8-1/2	½	N/A	60.03
	3	¾	1.2	5	¾	N/A	N/A	59.80
	4	1	0.9	11	1	N/A	N/A	57.72
2	1	¼	0.7	6	1/8	¼	N/A	55.60
	2	½	-1.1	12	3/8	½	N/A	67.07
	3	¾	1.7	8	5/8	¾	N/A	59.51
Average								56.58

Table 17. Sealed Concrete Grinding Results

Coupon	Layer	Target Depth (in.)	Temp Diff (°F)	Grinding Time (min)	1 st Grind Pass Depth (in.)	2 nd Grind Pass Depth (in.)	3 rd Grind Pass Depth (in.)	Ground Material Mass (g)
1	1	¼	1.1	8	3/16	¼	N/A	68.66
	2	½	0.3	10	3/8	½	N/A	66.68
	3	¾	3.2	8	5/8	¾	N/A	68.56
	4	1	0.8	6	1	N/A	N/A	62.77
2	1	¼	2.4	6	¼	N/A	N/A	56.70
	2	½	2.5	7	½	N/A	N/A	68.05
	3	¾	2.7	7	5/8	¾	N/A	71.72
Average								66.16

Both materials were amenable to grinding using the method described above. As the ground material was ejected from the grinding wheel toward the right side of the setup (due to the nature of operation of the grinder), the material was deflected/directed downward by the shield and collected in the foil underneath the coupon. As mentioned, fine dust generated during grinding was not captured as part of the sample collected for each grinding pass. After the first few grinding applications, a sturdier aluminum baking dish (8.13 in. by 12.25 in., 551537495, Walmart, Columbus, OH) that was better able to capture the ground material was used instead of the folded aluminum sheet. Additionally, an aluminum easel was fabricated and used to hold the coupons in place during grinding, which provided increased stability and better orientation of the coupon (Figure 6). The size of the limestone coupons was much preferred over the larger sealed concrete coupons, which were very difficult to maneuver inside the test chamber, so the size of the concrete coupons was reduced to 5.75 in. by 5.75 in. for physical removal efficacy testing. The reduced size allowed for proper application of the grinding technology while allowing for simpler and safer manipulation of the sealed concrete coupons within the chamber.

**Figure 17. Limestone Ground to 0.25 in. (left) and 1 in. (right)**

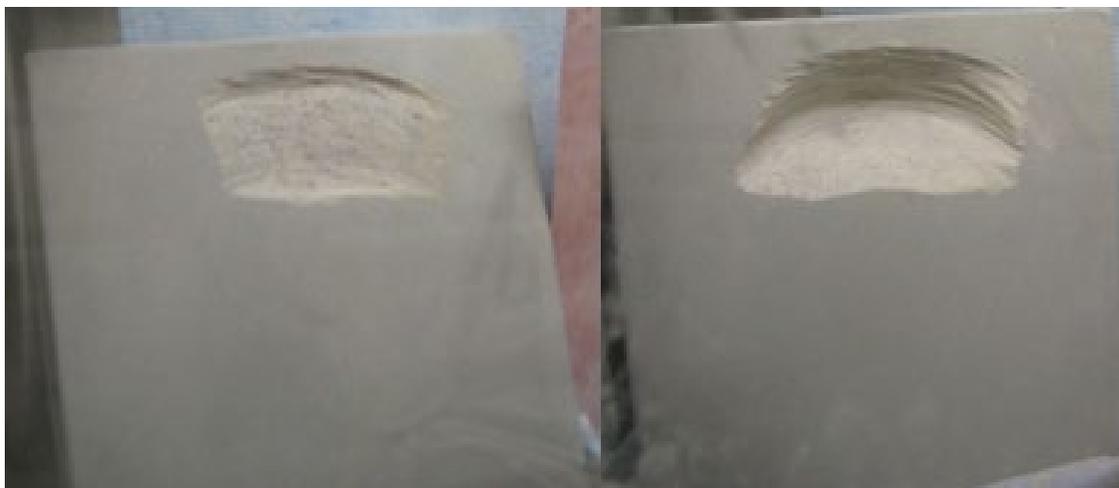


Figure 18. Sealed Concrete Ground to 0.25 in. (left) and 1 in. (right)



Figure 19. Ground Material

3.1.1.3. Chemical Stripping

Method

Chemical stripper (Klean Strip GKS3 KS-3 Premium Paint Stripper) was pipetted onto the coated surface of each material using an Eppendorf Repeater M4 Pipette (14-287-150, Fisher Scientific, Pittsburgh, PA). The chemical stripper was then either manually spread across an approximately 1.375 in. area using a ½ in. brush (7237T84, McMaster-Carr, Aurora, OH) or allowed to spread out on its own. The chemical stripper was allowed to dwell on the surface of each material for a total 45 minutes (initial 30-minute dwell, then an additional 15-minute dwell determined necessary based on visual inspection of the stripping progress, per manufacturer directions). A 2 in. disposable putty knife (3546A421, McMaster-Carr, Aurora, OH) was then used to scrape the coating from the surface of each material and the coating removed was collected into a sample jar.

Results

The spread diameters for each of the different application methods are summarized in Table 18.

Table 18. Chemical Stripper Application Methods and Spread Results

Material	Paint Stripper Volume	Stripper Brushed (Y/N)	Spread Diameter (in.)
Painted Steel	1 mL	Y	1.375
	1.5 mL	N	1.25
	2 mL	N	1.375
Painted Wood	1 mL	Y	1.375
	2 mL	N	1.5

For all replicates, the paint started to “bubble up” almost immediately after the chemical stripper was applied to the materials. The treated paint was easily removed from all replicates after the dwell time (Figure 20). The brushed replicates had a slightly cleaner surface (i.e., more complete removal of paint, based on subjective visual assessment) after scraping (Figure 21 and Figure 22). Generally, a greater volume of residual paint stripper was observed on unbrushed replicates after the dwell period (Figure 23 and Figure 24).

The method of pipetting 1 mL of chemical stripper onto coupons accompanied by brushing produced the best results, defined as most complete removal of paint (again, subjective visual assessment) using the least volume of chemical stripper. This method was then used to produce additional replicate samples for the remainder of the method demonstration testing (solvent extraction of VX from the stripped paint [waste sampling]).



Figure 20. Coating Removal

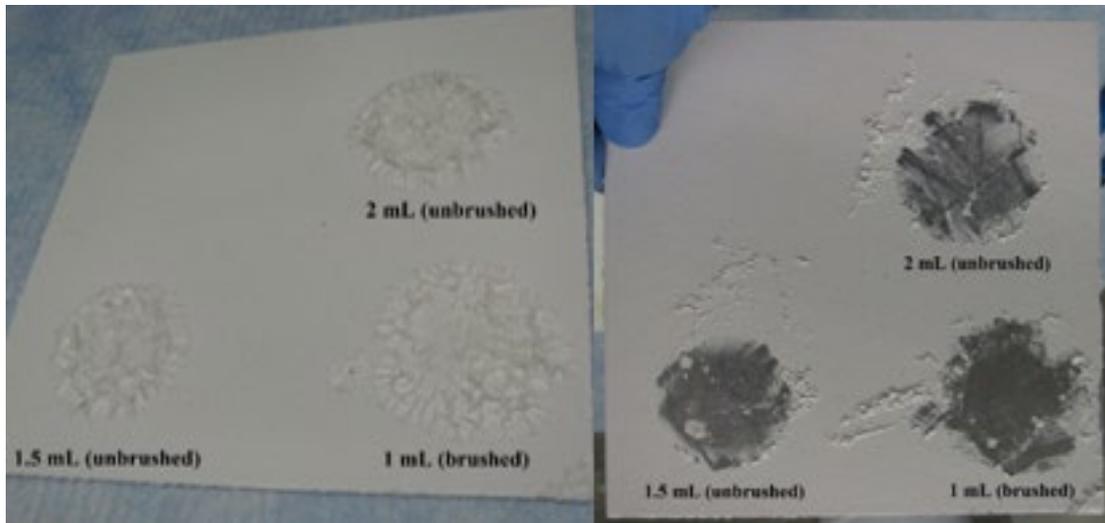


Figure 21. Coated Steel Before (left) and After Scraping (right)



Figure 22. Coated Wood Before (left) and After Scraping (right)



Figure 23. Collected Coating Using 1 mL Application with Brushing



Figure 24. Collected Coating Using 1.5 mL Application without Brushing

3.1.1.4. Vapor-Phase Solvent Extraction

Operating conditions/parameters to produce a viable solvent vapor stream could not be determined using the vapor-phase solvent extraction test apparatus as conceptualized (setup as depicted in Figure 7) or using revised apparatus setups described below. Budget and schedule limitations of the project then precluded further development of the technology, so vapor-phase solvent extraction was not carried forward into further methods demonstration test phases or into physical removal efficacy testing.

Method

A limestone (8 in. length by 8 in. width by 2.25 in. thick) coupon was placed vertically in a holder in the test chamber (same coupon holder used for the initially planned application method for the core sampling approach; see Figure 9). A 20-mL scintillation vial with a funnel inserted was placed underneath the holder and dry ice was packed around the vial (Figure 25).

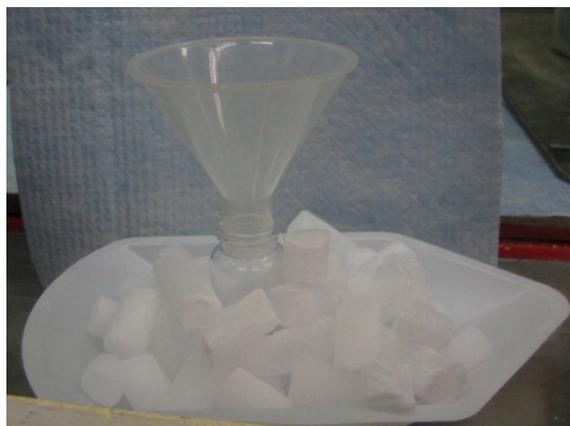


Figure 25. Vial for Solvent Collection

The vapor-phase solvent extraction technology was set up as described in Section 2.2.3.4 and depicted in Figure 7. The end of the inline static tube mixer (from which the solvent vapor stream would be ejected) was attached to a bulkhead fitting installed in the side of the test chamber, and the limestone coupon in the holder was oriented in front of the tube mixer opening (outlet).

The heat tape affixed to the tee fitting and tube mixer was turned on and the temperature of the system was increased so that the temperature of the tee fitting measured approximately 250°F and the temperature at the end of the tube mixer was approximately 150°F. Conditioned (clean, dried) house air was supplied through the system at approximately 300 mL/min. Acetone was then infused into the airstream at the heated tee fitting using a syringe pump at a rate of 375 $\mu\text{L}/\text{min}$ (a 60-minute infusion duration would thus result in a total infused solvent volume of 22.5 mL).

Results

No solvent vapor was visible from the outlet of the tube mixer. Furthermore, after several minutes, no condensed solvent was observed to collect on the surface of the coupon. Brown Kraft paper and M8 Chemical Detector paper were also held against the outlet end of the tube mixer for periods of up to approximately 60 minutes, but no visible collection of condensed solvent or darkening (wetting) of the Kraft or M8 paper were observed. The acetone infusion rate was increased incrementally from 375 $\mu\text{L}/\text{min}$ to up to 4.5 mL/min while the supply airflow rate through the system was also increased incrementally from 300 mL/min to up to 1.9 L/min. No combination of airflow rate and acetone infusion rate was identified that resulted in a visible solvent vapor stream from the end of the tube mixer or in formation of condensed solvent droplets on the surface of the coupon, Kraft paper, or M8 paper (though lower airflow rates and higher acetone infusion rates did result in liquid acetone dripping from the end of the tube mixer).

Alternative setups were assembled and evaluated as well. These included:

- Elimination of the static tube mixer. The heated tee was attached directly to the bulkhead fitting at the side of the test chamber. The intent of this revised setup was to minimize the distance between the heated tee and the point at which the solvent vapor stream would be ejected and prevent loss of vapor to condensation within cooler portions of the system.
- Revision of the system design. Rather than generating solvent vapor via infusion of liquid acetone into a heated tee fitting, a 1-liter (L) glass beaker filled with approximately 500 mL of acetone was submerged in a second glass beaker containing water. The water was heated to approximately 100°F (using heat tape wrapped around the outside of the second/outer beaker) to act as a heated jacket. Conditioned (cleaned, dried) house air was then bubbled into the heated acetone (various flowrates from 2 to 5 L/min were evaluated). The solvent vapor generated in the headspace was then directed into the test chamber via the bulkhead and the vapor stream was directed at the limestone coupon. Figure 26 provides a schematic of the revised vapor-phase solvent extraction setup that was evaluated.

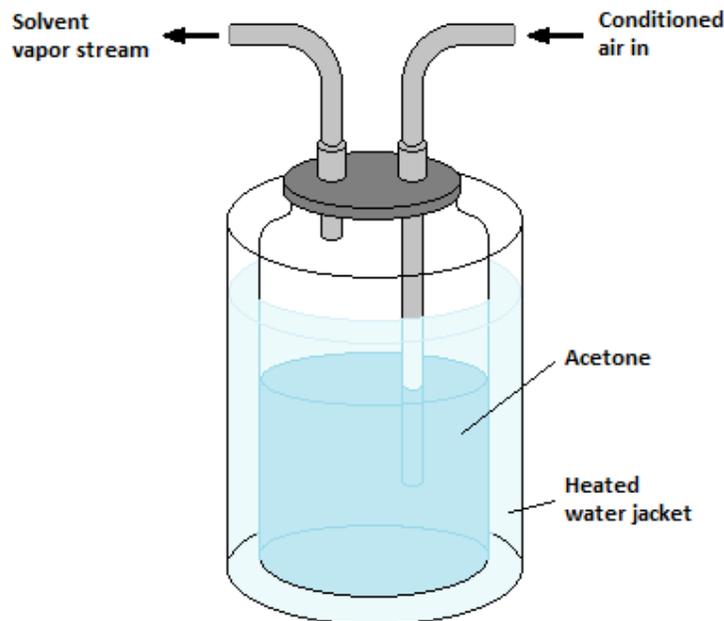


Figure 26. Revised Vapor-Phase Solvent Extraction Test Setup

Neither of these alternative setups produced visible solvent vapor streams or resulted in collection of condensed solvent droplets or formation of wetted areas on the test coupon, Kraft paper, or M8 paper.

3.1.2. Solvent Extraction Method Demonstration Results

The methods used for recovery of VX from coupon samples (core layer samples and ground material samples) were demonstrated experimentally prior to the start of physical removal efficacy testing to verify the adequacy of the methods. A single test was conducted using core layer and ground material samples of each porous material type (sealed concrete and limestone; produced during the technology functionality assessments of the grinding and core sampling approaches) to evaluate recovery of VX via solvent extraction for all anticipated coupon sample types after VX dwell periods of both 30 minutes and 24 hours. Testing was conducted as described in Section 2.1.1.2.

Stainless steel coupons and glass bead samples were included in the test matrix to serve as nonporous, inert positive control samples for core layer samples and ground material samples, respectively. Positive controls were spiked with VX and then subsequently extracted after VX dwell periods of 30 minutes and 24 hours.

Spike control recovery results are provided in Table 19. VX recovery results from the stainless steel and glass bead positive control samples are provided in Tables 20 and 21. A single procedural blank of each material type was included during the test as well. VX was detected in all procedural blank extracts except for the ground limestone material procedural blank, but all detections were within specification (Table 43).

Table 19. Solvent Extraction, Spike Controls

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs target)	Avg (µg)	Avg % vs Target	St Dev	%RSD
Spike Control 1	90500	1810	97%	1809	97%	11	0.62%
Spike Control 2	91000	1820	97%				
Spike Control 3	89880	1798	96%				

Table 20. Solvent Extraction, Stainless Steel Positive Controls

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)	Avg (µg)	Avg % vs SC Avg	St Dev	%RSD
SS PC 1 (30 min)	83470	1669	92%	1851	102%	268	14%
SS PC 2 (30 min)	107900	2158	119%				
SS PC 3 (30 min)	86240	1725	95%				
SS PC 1 (24 h)	96780	1936	107%	1806	100%	250	14%
SS PC 2 (24 h)	98260	1965	109%				
SS PC 3 (24 h)	75910	1518	84%				

SS = Stainless Steel; PC = Positive Control; SC = Spike Control

Table 21. Solvent Extraction, Glass Bead Positive Controls

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)	Avg (µg)	Avg % vs SC Avg	St Dev	%RSD
Glass Beads PC 1 (30 min)	30000	2400	133%	2636	146%	269	10%
Glass Beads PC 2 (30 min)	32230	2578	143%				
Glass Beads PC 3 (30 min)	36610	2929	162%				
Glass Beads PC 1 (24 h)	29800	2384	132%	2277	126%	111	4.9%
Glass Beads PC 2 (24 h)	27020	2162	119%				
Glass Beads PC 3 (24 h)	28580	2286	126%				

PC = Positive Control; SC = Spike Control

As discussed in Section 2.1.1.2, the coupon sample solvent extraction method would be deemed acceptable for use during subsequent physical removal efficacy evaluations if the mean recoveries from stainless steel positive controls and glass bead positive controls were within the range of 70% to 120% of the mean of the SC results with a relative standard deviation (RSD) between replicates of less than 30%. Recoveries from stainless steel at both VX dwell periods met this requirement.

Average recovery of VX from the glass beads was higher than the criterion defined in Section 2.1.1.2 of 70% to 120% of the spike control average, with average recoveries of 146% at 30 minutes and 126% at 24 hours. RSD in both cases was within specification (10% at 30 minutes, 4.9% at 24 hours). No immediately attributable cause for the high recoveries from the glass beads was available, but we speculated that the beads may have been exposed to additional VX (past the 2 µL spiked into the beads) due to the manner in which the beads were spiked. The tip of the positive displacement pipettor used to spike the glass bead positive controls was submerged into a vial containing VX to draw up the 2 µL to be spiked. The end of the pipettor tip was touched to an absorbent wipe to ensure excess VX drips/droplets hanging to the tip were removed, but the remaining exterior of the tip was not wiped off. The tip was then inserted into the beads and the VX expelled from the tip. The tip was then used to mix the spiked VX into the

beads. We suspect that VX still present on the outside surface of the pipettor tip (from drawing VX into the tip) was transferred to the glass beads, leading to higher recoveries.

VX recoveries from sealed concrete and limestone core layer samples via solvent extraction after VX dwell periods of 30 minutes and 24 hours are provided in Table 22. As described in Section 2.1.1.2, PTFE disks were placed below the core layer samples during the VX dwell periods to assess for VX breakthrough (i.e., VX migrating through the 0.25 in.-thick core layer samples) during the dwell periods. PTFE disks were extracted in solvent and analyzed via LC-MS/MS alongside the core layer samples. Recoveries from PTFE disks are provided in Table 22 as well.

Table 22. Solvent Extraction, Core Layer Samples

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs Pos avg)	Avg (µg)	Avg % vs Pos Avg	St Dev	%RSD
Concrete Core Layer (30 min) 1	22110	442	24%	411	22%	28	6.8%
Concrete Core Layer (30 min) 2	19410	388	21%				
Concrete Core Layer (30 min) 3	20150	403	22%				
Concrete Core Layer (24 h) 1	9982	200	11%	182	10%	22	12%
Concrete Core Layer (24 h) 2	7839	157	8.7%				
Concrete Core Layer (24 h) 3	9439	189	10%				
Concrete Core Layer (30 min) 1 - PTFE	0.36	0.004	0.0002%	0.003	0.0002%	0.002	62%
Concrete Core Layer (30 min) 2 - PTFE	0.51	0.005	0.0003%				
Concrete Core Layer (30 min) 3 - PTFE	0.11	0.001	0.0001%				
Concrete Core Layer (24 h) 1 - PTFE	1.9	0.02	0.001%	0.02	0.001%	0.004	23%
Concrete Core Layer (24 h) 2 - PTFE	2.2	0.02	0.001%				
Concrete Core Layer (24 h) 3 - PTFE	1.4	0.01	0.001%				
Limestone Core Layer (30 min) 1	18010	360	19%	362	20%	84	23%
Limestone Core Layer (30 min) 2	13920	278	15%				
Limestone Core Layer (30 min) 3	22320	446	24%				
Limestone Core Layer (24 h) 1	7497	150	8.3%	133	7.4%	28	21%
Limestone Core Layer (24 h) 2	5063	101	5.6%				
Limestone Core Layer (24 h) 3	7398	148	8.2%				
Limestone Core Layer (30 min) 1 - PTFE	0.67	0.01	0.0003%	0.01	0.0003%	0.003	44%
Limestone Core Layer (30 min) 2 - PTFE	0.44	0.004	0.0002%				
Limestone Core Layer (30 min) 3 - PTFE	1.1	0.01	0.0004%				
Limestone Core Layer (24 h) 1 - PTFE	0.96	0.01	0.0004%	0.01	0.0005%	0.01	48%
Limestone Core Layer (24 h) 2 - PTFE	0.68	0.01	0.0003%				
Limestone Core Layer (24 h) 3 - PTFE	1.7	0.02	0.001%				

Average recoveries of VX from the sealed concrete and limestone core layer samples at 30 minutes were 22% and 20%, respectively. Average recoveries at 24 hours were lower at 10% (sealed concrete) and 7.4% (limestone). Such recoveries from these materials appeared to be generally consistent with previously acquired data [10] for solvent extraction recovery of CWAs from concrete and with studies that have shown that concrete is capable of active degradation of penetrated/absorbed CWAs [9].

VX recoveries from sealed concrete and limestone ground material samples via solvent extraction after VX dwell periods of 30 minutes and 24 hours are provided in Table 23.

Table 23. Solvent Extraction, Ground Material Samples

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs Pos avg)	Avg (µg)	Avg % vs Pos Avg	St Dev	%RSD
Concrete Ground Material (30 min) 1	23740	1899	72%	1070	41%	949	89%
Concrete Ground Material (30 min) 2	15950	1276	48%				
Concrete Ground Material (30 min) 3	449	36	1.4%				
Concrete Ground Material (24 h) 1	17850	1428	63%	560	25%	759	136%
Concrete Ground Material (24 h) 2	235	19	0.82%				
Concrete Ground Material (24 h) 3	2921	234	10%				
Limestone Ground Material (30 min) 1	22350	1788	68%	1361	52%	1068	78%
Limestone Ground Material (30 min) 2	1815	145	5.5%				
Limestone Ground Material (30 min) 3	26860	2149	82%				
Limestone Ground Material (24 h) 1	27780	2222	98%	2157	95%	78	3.6%
Limestone Ground Material (24 h) 2	27230	2178	96%				
Limestone Ground Material (24 h) 3	25890	2071	91%				

Recovery of VX from ground sealed concrete ranged from 0.82% to 72%. Average recovery at 30 minutes was 41% and at 24 hours was 25%, and RSDs were high at 89% (30 minutes) and 136% (24 hours). The test was conducted as described in Section 2.1.1.2. Samples were spiked as described in Section 2.2.2.2 in that VX was spiked into the ground material, and the pipettor tip was then used to mix the spiked VX into the ground material. Use of this approach caused the ground material to “clump” and “stick” to the pipettor tip. Attempts were made to remove the stuck material from the tip into the extraction jar but based on the data it appears that this approach was incomplete and inconsistent. Thus, recoveries from ground sealed concrete are likely impacted by the amount of “clumped” or “stuck” material that was able to be removed from the pipette tip. Recoveries from ground limestone after a VX dwell period of 30 minutes also appeared to have been impacted by this issue of “clumping” VX/ground material. Oddly though, average recovery of VX from ground limestone at 24 hours was 95% with only 3.6% RSD. No explanation could be determined for why the “clumping” and “sticking” issue impacted recoveries from ground sealed concrete (both dwell times) and ground limestone after 30 minutes but did not affect recovery from ground limestone after a 24-hour dwell period.

Figure 27 summarizes average VX mass recoveries via solvent extraction after dwell periods of 30 minutes and 24 hours from the core layer and ground material coupon samples of sealed concrete and limestone. Figure 28 summarizes average percent recoveries. Given the known difficulty associated with recovery of CWA from concrete [9,10] (and likely similar materials), the suspected cause of the higher-than-specification recoveries from the glass bead positive controls, and the acceptable recoveries from the stainless steel positive controls, the solvent extraction method was used as evaluated during method demonstration testing during subsequent physical removal efficacy tests (i.e., the method was not revised or altered from that described in Section 2.2.5 based on the results of method demonstration testing).

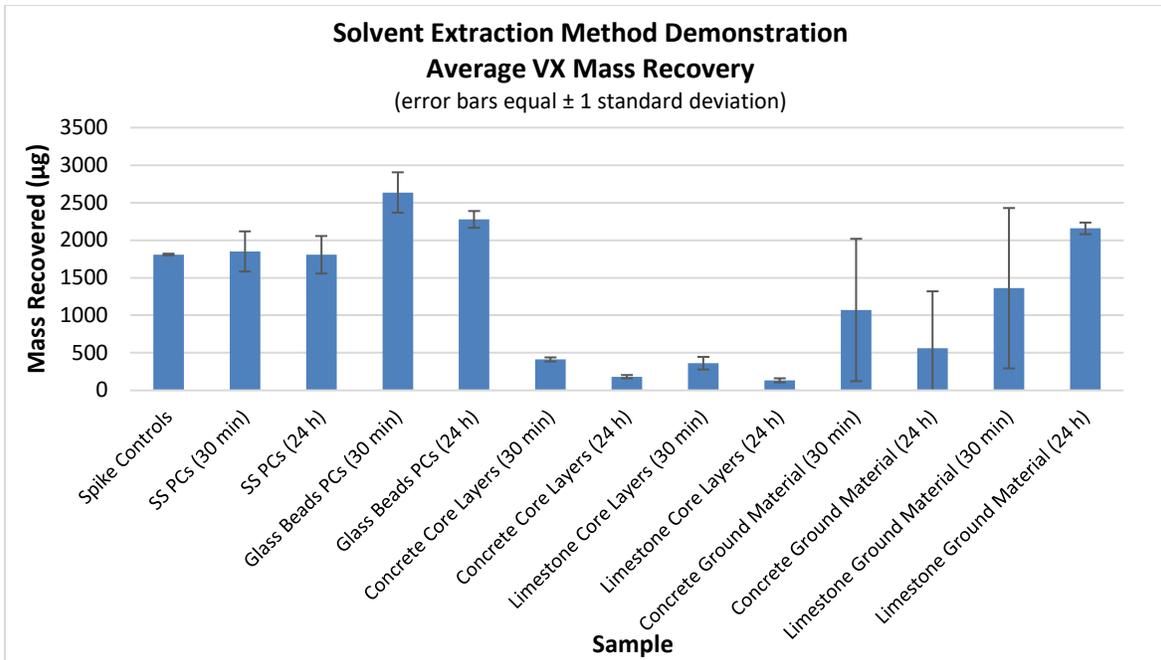


Figure 27. Solvent Extraction, Average Mass Recovery

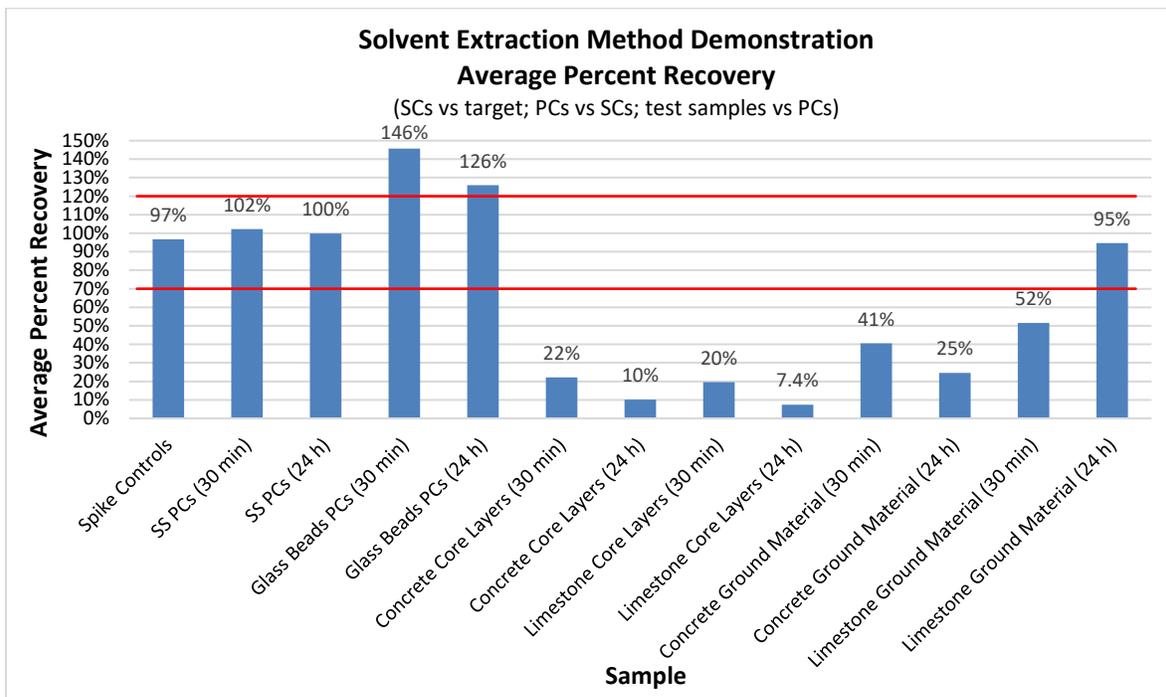


Figure 28. Solvent Extraction, Average Percent Recovery

3.1.3. Wipe Sampling Method Demonstration Results

A single test to assess the adequacy of the wipe sampling method was performed. VX (10 µL) was applied to coupons of sealed concrete, limestone, painted steel, and painted wood and allowed to dwell on the surface of coupons for 24 hours. Stainless steel coupons were spiked

with VX as well to serve as positive controls. Following the dwell period, wipe samples were collected from the coupons.

Spike control recovery results are provided in Table 24.

Table 24. Wipe Sampling, Spike Controls

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs target)	Avg (µg)	Avg % vs Target	St Dev	%RSD
Spike Control 1	517500	10350	111%	10000	107%	336	3.4%
Spike Control 2	484000	9680	104%				
Spike Control 3	498500	9970	107%				

VX recoveries from the stainless-steel positive control samples are provided in Table 25.

Table 25. Wipe Sampling, Stainless Steel Positive Controls

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)	Avg (µg)	Avg % vs SC Avg	St Dev	%RSD
Stainless Steel Wipe 1	363700	7783	78%	7867	79%	230	2.9%
Stainless Steel Wipe 2	359400	7691	77%				
Stainless Steel Wipe 3	379800	8128	81%				

SC = Spike Control

VX recoveries via wipe-sampling from the porous materials and permeable coatings are provided in Table 26. Average VX mass recoveries are summarized in Figure 29. Average percent recoveries are summarized in Figure 30.

Table 26. Wipe Sampling Results

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs Pos avg)	Avg (µg)	Avg % vs Pos Avg	St Dev	%RSD
Concrete Wipe 1	2509	54	0.68%	60	0.77%	5.9	9.7%
Concrete Wipe 2	2993	64	0.81%				
Concrete Wipe 3	2977	64	0.81%				
Limestone Wipe 1	1781	38	0.48%	32	0.41%	5.4	17%
Limestone Wipe 2	1446	31	0.39%				
Limestone Wipe 3	1282	27	0.35%				
Painted Steel Wipe 1	184000	3938	50%	4586	58%	852	19%
Painted Steel Wipe 2	199500	4269	54%				
Painted Steel Wipe 3	259400	5551	71%				
Painted Wood Wipe 1	172500	3692	47%	3293	42%	357	11%
Painted Wood Wipe 2	149000	3189	41%				
Painted Wood Wipe 3	140200	3000	38%				

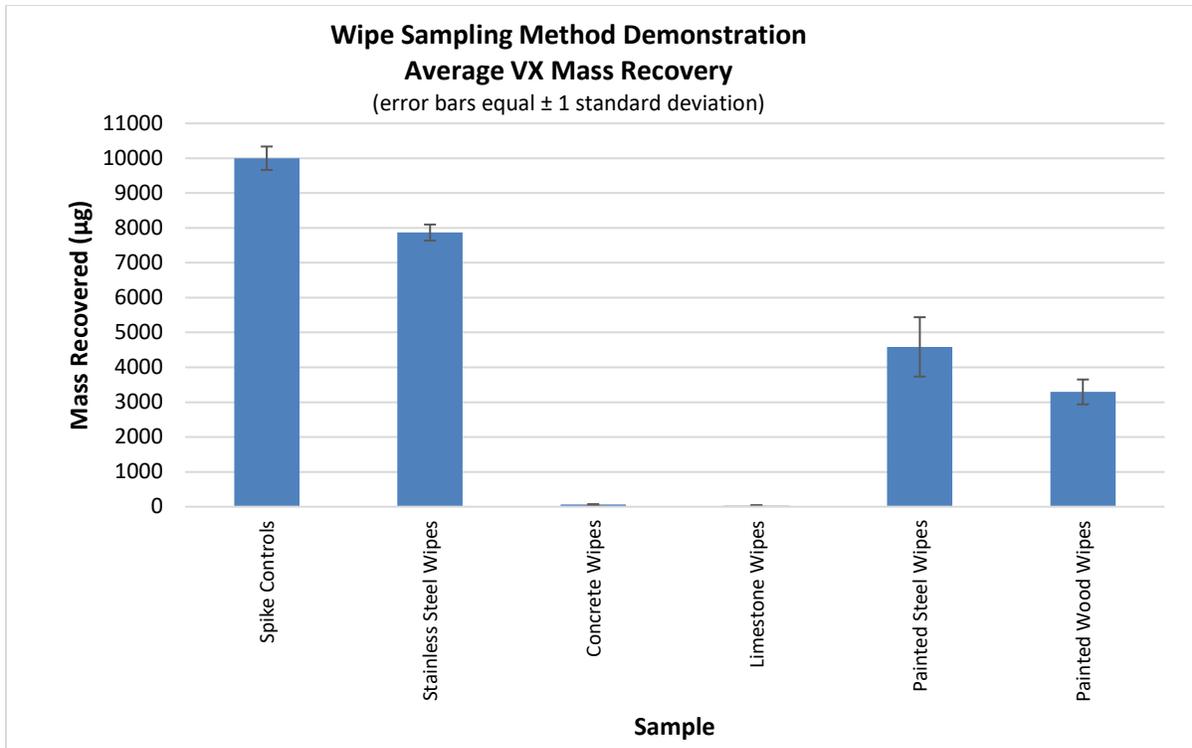


Figure 29. Wipe Sampling, Average Mass Recovery

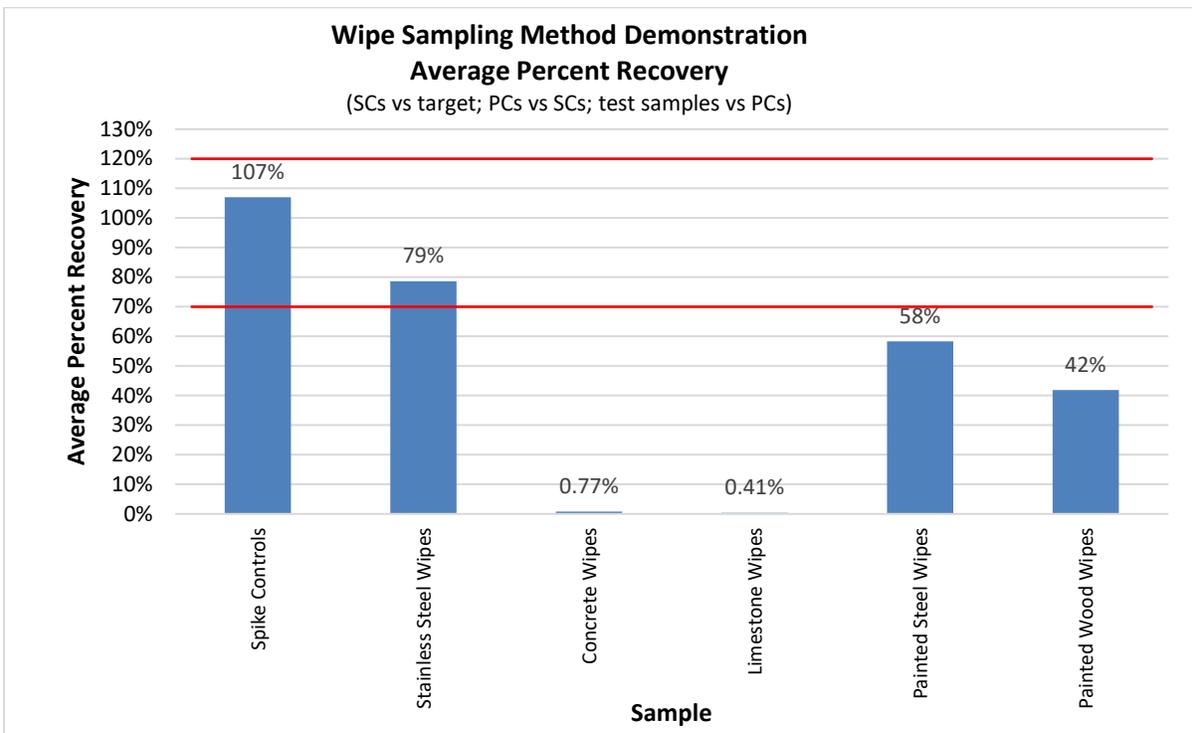


Figure 30. Wipe Sampling, Average Percent Recovery

The coupon wipe-sampling method would be deemed acceptable for use during subsequent physical removal efficacy evaluations if the mean wipe-sampling recovery from the stainless-steel positive controls was within the range of 70% to 120% of the mean of the SC results with an RSD between replicates of less than 30%. Average percent recovery from the stainless-steel positive controls via wipe-sampling was 79% with an RSD of 2.9%, so the recovery criterion was met.

Data generated during previous studies [10] have demonstrated difficulty in recovering VX spiked onto concrete surfaces using solvent extraction techniques. Additionally, previous work [11] has demonstrated that VX spiked onto a paint layer applied to a substrate will absorb into the paint layer. The data generated during wipe-sampling method demonstration testing conducted during this project were consistent with these findings, as average percent recoveries measured only 0.77% from sealed concrete, 0.41% from limestone, 58% from painted steel, and 42% from painted wood (compared to the stainless-steel positive controls). Despite these low recoveries, the wipe sampling method was deemed adequate for use during subsequent physical removal efficacy testing given that the criterion for recovery from stainless steel was met, as discussed above.

3.1.4. Waste Sampling Results

The methods that would be used for recovery of VX from wastes generated during application of the physical removal technologies were experimentally evaluated prior to physical removal efficacy testing. Samples of the wastes produced during the technology functionality assessments (sealed concrete and limestone cutting dusts produced from application of the core sampling approach, and coatings stripped from steel and hardwood from application of the chemical stripper) were spiked with VX and allowed to dwell for 30 minutes or 24 hours. Following the specified dwell period, waste samples were extracted with solvent. As during ground material solvent extraction method demonstration testing, glass bead samples were used as positive controls at both dwell periods.

Spike control recovery results are provided in Table 27.

Table 27. Waste Sampling, Spike Controls

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs target)	Avg (µg)	Avg % vs Target	St Dev	%RSD
Spike Control 1	97320	1946	104%	1856	99%	86	4.6%
Spike Control 2	88770	1775	95%				
Spike Control 3	92300	1846	99%				

VX recoveries from the glass bead positive control samples at both dwell periods are provided in Table 28. Average percent VX recovery via solvent extraction from the glass bead positive controls (vs the spike control mean) after a dwell period of 30 minutes was 108% with an RSD of 10%. Average percent recovery after a dwell period of 24 hours was lower. However, at only 51% with an RSD of 18%. The amount of glass beads used for the positive control samples was based on the average mass of the cutting dust samples collected during the technology

functionality assessments and used during the waste sampling method demonstration test. Approximately 2.1 g of glass beads were used for each positive control sample. This number/amount/volume of beads did not cover the bottom of the 60 mL extraction jar fully (i.e., the beads formed a single “layer” across the bottom of the jar). Although VX is considered a persistent hazard (vapor pressure of 0.09 Pa), it is suspected that the beads provided a greater evaporative surface area (i.e., thinner “coat” of VX on/across the beads, as opposed to a single droplet), and a greater amount of VX was lost via evaporation during the 24-hour dwell period.

Table 28. Waste Sampling, Glass Bead Positive Controls

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)	Avg (µg)	Avg % vs SC Avg	St Dev	%RSD
Glass Beads PC 1 (30 min)	112000	2240	121%	2002	108%	206	10%
Glass Beads PC 2 (30 min)	93940	1879	101%				
Glass Beads PC 3 (30 min)	94390	1888	102%				
Glass Beads PC 1 (24 h)	57490	1150	62%	956	51%	173	18%
Glass Beads PC 2 (24 h)	40920	818	44%				
Glass Beads PC 3 (24 h)	44950	899	48%				

PC = Positive Control; SC = Spike Control

VX mass recoveries and percent recoveries from sealed concrete and limestone cutting dust samples are provided in Table 29. Percent recoveries were determined via comparison to the glass bead positive control mean for each dwell period. Given the lower recoveries obtained from glass beads at the 24-hour dwell period, percent recovery from sealed concrete and limestone cutting dust samples at 24 hours were also determined via comparison to the spike control mean recovery.

Table 29. Waste Sampling, Cutting Dust Recovery

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs Pos avg)	Avg (µg)	Avg % vs Pos Avg	St Dev	%RSD	% Recovery (vs SC avg) ^A	Avg % vs SC Avg
Concrete Cutting Dust (30 min) 1	95080	1902	95%	1982	99%	125	6.3%	-	-
Concrete Cutting Dust (30 min) 2	106300	2126	106%						
Concrete Cutting Dust (30 min) 3	95880	1918	96%						
Concrete Cutting Dust (24 h) 1	79200	1584	166%	1755	184%	150	8.5%	85%	95%
Concrete Cutting Dust (24 h) 2	90870	1817	190%						
Concrete Cutting Dust (24 h) 3	93130	1863	195%						
Limestone Cutting Dust (30 min) 1	97960	1959	98%	1961	98%	47	2.4%	-	-
Limestone Cutting Dust (30 min) 2	100400	2008	100%						
Limestone Cutting Dust (30 min) 3	95740	1915	96%						
Limestone Cutting Dust (24 h) 1	104300	2086	218%	1980	207%	172	8.7%	112%	107%
Limestone Cutting Dust (24 h) 2	103600	2072	217%						
Limestone Cutting Dust (24 h) 3	89050	1781	186%						

SC = Spike Control

^A Compared also to SC avg because of lower recovery from glass beads at 24 hours

VX mass recoveries and percent recoveries from permeable coatings stripped from steel and hardwood are provided in Table 30. Average percent recoveries from coatings stripped from steel and hardwood after a 30-minute VX dwell period (vs the spike control mean recovery) were 95% and 91%, respectively. Average percent recoveries from coatings stripped from steel and hardwood after a 24-hour dwell period were lower at 65% and 82%, respectively. The lower recoveries after the longer dwell period are consistent with findings from previous studies

demonstrating that VX spiked onto a paint layer applied to a substrate will absorb into the paint layer [12], if the absorption decreases “extractability” of VX from the paint in some manner.

Table 30. Waste Sampling, Stripped Coating Recovery

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)	Avg (µg)	Avg % vs SC Avg	St Dev	%RSD
Stripped Paint Steel (30 min) 1	97850	1957	105%	1767	95%	212	12%
Stripped Paint Steel (30 min) 2	90220	1804	97%				
Stripped Paint Steel (30 min) 3	76920	1538	83%				
Stripped Paint Steel (24 h) 1	36620	732	39%	1198	65%	467	39%
Stripped Paint Steel (24 h) 2	83330	1667	90%				
Stripped Paint Steel (24 h) 3	59760	1195	64%				
Stripped Paint Wood (30 min) 1	85610	1712	92%	1686	91%	78	4.6%
Stripped Paint Wood (30 min) 2	87370	1747	94%				
Stripped Paint Wood (30 min) 3	79940	1599	86%				
Stripped Paint Wood (24 h) 1	86660	1733	93%	1518	82%	206	14%
Stripped Paint Wood (24 h) 2	66160	1323	71%				
Stripped Paint Wood (24 h) 3	74930	1499	81%				

SC = Spike Control

Average VX mass recoveries from cutting dust and stripped coating samples are summarized in Figure 31. Average percent recoveries are summarized in Figure 32.

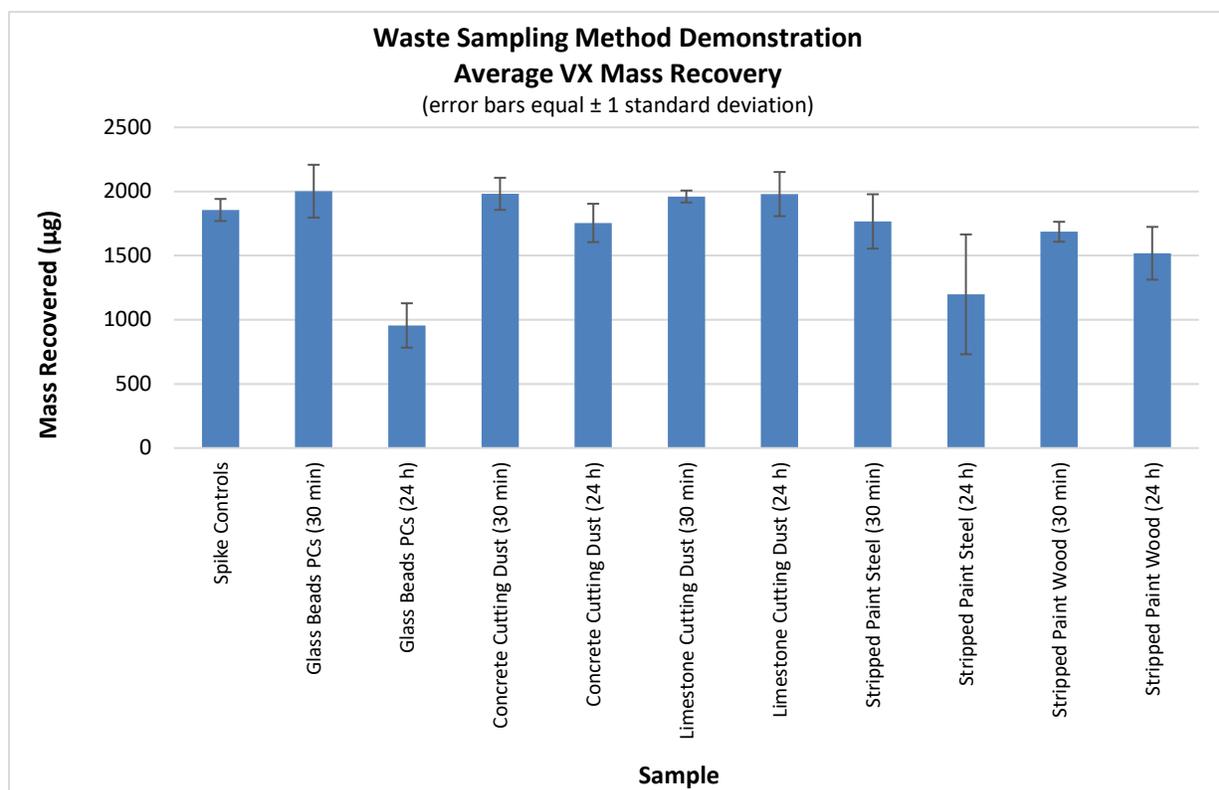


Figure 31. Waste Sampling, Average Mass Recovery

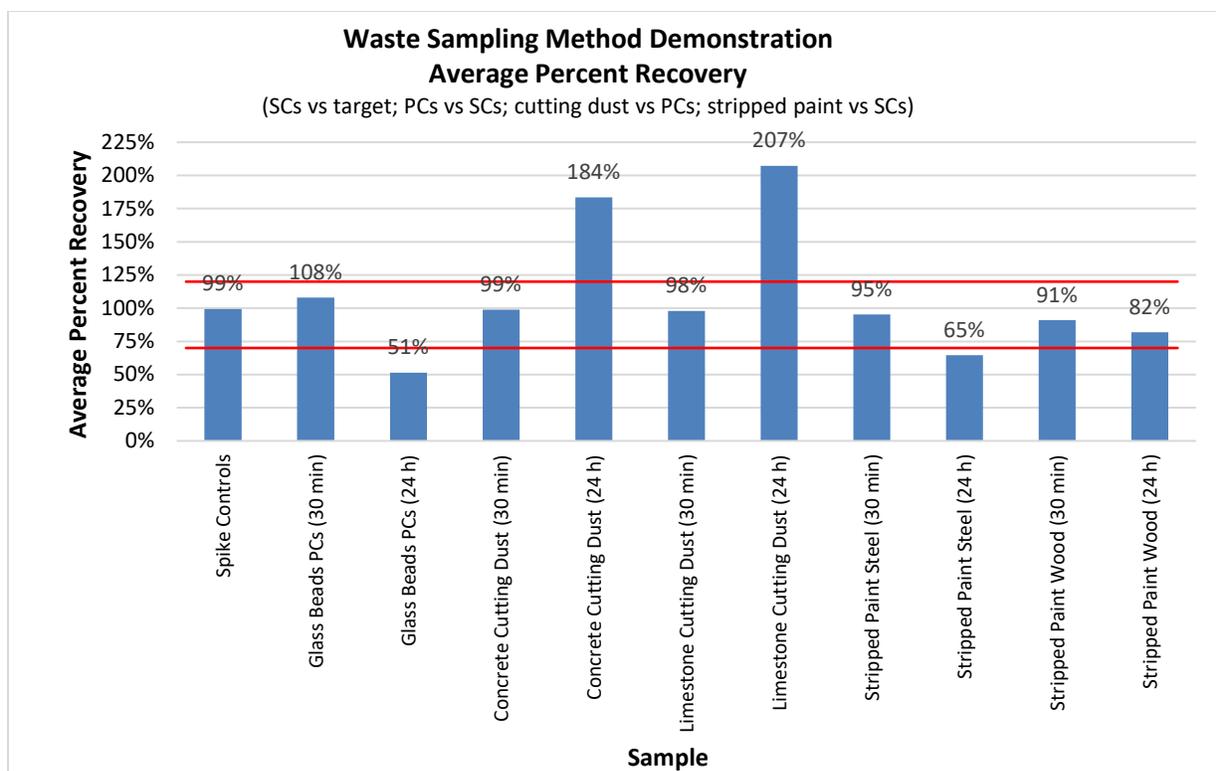


Figure 32. Waste Sampling, Average Percent Recovery

3.1.5. VX Depth Penetration Assessment Results

The core sampling approach was used to assess the depth to which VX penetrates the porous materials selected for physical removal efficacy evaluations. Core samples were excised from sealed concrete and limestone coupons, the cores were spiked with 10 μL of VX (center of top surface of each core sample), and the VX was allowed to penetrate into the cores for a period of 24 hours. Following the 24-hour dwell period, the core sampling approach was applied to separate the core samples into 0.25 in.-thick layers that were individually extracted in solvent. VX depth penetration into the cores was then assessed based on recovery of VX from the individual core layer samples.

Spike control recovery results are provided in Table 31.

Table 31. VX Depth Penetration Assessment, Spike Controls

Sample Description	Extract Conc. (ng/mL)	Mass (μg)	% Recovery (vs target)	Avg (μg)	Avg % vs Target	St Dev	%RSD
Spike Control 1	435400	8708	86%	8445	84%	493	5.8%
Spike Control 2	393800	7876	78%				
Spike Control 3	437500	8750	87%				

VX mass recovery and percent recovery results for each limestone core sample included during the VX depth penetration assessment are provided in Table 32. Mass recovery and percent recovery results for sealed concrete core samples are provided in Table 33. Mass recovery results from all core samples are also summarized in Figure 33.

Table 32. VX Depth Penetration Assessment, Limestone Recovery

Sample Description	Limestone Core 1			Limestone Core 2			Limestone Core 3			Avg Mass (µg)	Avg Mass % Recovery (vs SC Avg)	St Dev	%RSD
	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)				
Wipe	1806	39	0.46%	1744	37	0.44%	853	18	0.22%	31	0.37%	11	36%
Layer 1	43150	863	10%	42710	854	10%	51110	1022	12%	913	11%	95	10%
Cutting Dust 2	0.55	0.01	0.0001%	18	0.36	0.004%	1.1	0.02	0.0003%	0.13	0.002%	0.20	152%
Layer 2	1.1	0.02	0.0003%	4.1	0.08	0.001%	7.3	0.15	0.002%	0.08	0.001%	0.06	75%
Cutting Dust 3	<0.10	<0.002	<0.00002%	<0.10	<0.002	<0.00002%	0.11	0.002	0.00003%	0.002	0.00002%	0.0001	6.9%
Layer 3	0.68	0.01	0.0002%	0.84	0.02	0.0002%	3.9	0.08	0.001%	0.04	0.0004%	0.04	99.9%
Cutting Dust 4	<0.10	<0.002	<0.00002%	0.10	0.002	0.00002%	0.12	0.002	0.00003%	0.002	0.00003%	0.0003	12%
Layer 4	0.28	0.01	0.0001%	0.25	0.01	0.0001%	2.1	0.04	0.0005%	0.02	0.0002%	0.02	121%
Cutting Dust 5	<0.10	<0.002	<0.00002%	<0.10	<0.002	<0.00002%	<0.10	<0.002	<0.00002%	0.002	0.00002%	0.00	0.00%
Layer 5	<0.10	<0.002	<0.00002%	<0.10	<0.002	<0.00002%	0.30	0.01	0.0001%	0.003	0.00004%	0.002	70%
Blade Wipe	0.41	0.01	0.0001%	0.38	0.01	0.0001%	0.54	0.01	0.0001%	0.01	0.0001%	0.002	19%
Total Mass	NA	902	11%	NA	892	11%	NA	1041	12%	945	11%	83	8.8%

Table 33. VX Depth Penetration Assessment, Sealed Concrete Recovery

Sample Description	Sealed Concrete Core 1			Sealed Concrete Core 2			Sealed Concrete Core 3			Avg Mass (µg)	Avg Mass % Recovery (vs SC Avg)	St Dev	%RSD
	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)				
Wipe	2704	58	0.69%	2845	61	0.72%	1979	42	0.50%	54	0.64%	9.9	19%
Layer 1	67960	1359	16%	56630	1133	13%	47790	956	11%	1149	14%	202	18%
Cutting Dust 2	No sample ^A			1.1	0.02	0.0003%	0.42	0.01	0.0001%	0.02	0.0002%	0.01	65%
Layer 2	No sample ^A			0.59	0.01	0.0001%	0.73	0.01	0.0002%	0.01	0.0002%	0.002	15%
Cutting Dust 3	0.52	0.01	0.0001%	0.54	0.01	0.0001%	0.23	0.005	0.0001%	0.01	0.0001%	0.004	41%
Layer 3	0.63	0.01	0.0001%	1.0	0.02	0.0002%	0.51	0.01	0.0001%	0.01	0.0002%	0.005	37%
Cutting Dust 4	0.16	0.003	0.00004%	0.39	0.01	0.0001%	0.17	0.003	0.00004%	0.005	0.0001%	0.003	55%
Layer 4	0.47	0.01	0.0001%	0.55	0.01	0.0001%	0.17	0.003	0.00004%	0.01	0.0001%	0.004	50%
Cutting Dust 5	<0.10	<0.002	<0.00002%	0.28	0.01	0.0001%	0.34	0.01	0.0001%	0.005	0.0001%	0.003	52%
Layer 5	0.22	0.004	0.0001%	0.28	0.01	0.0001%	<0.10	<0.002	<0.00002%	0.004	0.00005%	0.002	46%
Blade Wipe	0.34	0.01	0.0001%	0.22	0.005	0.0001%	0.11	0.002	0.00003%	0.005	0.0001%	0.002	51%
Total Mass	NA	1417	16.8%	NA	1194	14%	NA	998	12%	1203	14%	210	17%

^A Only four (4) layers were cut and collected. No "Layer 2" or "Cutting Dust 2" samples.

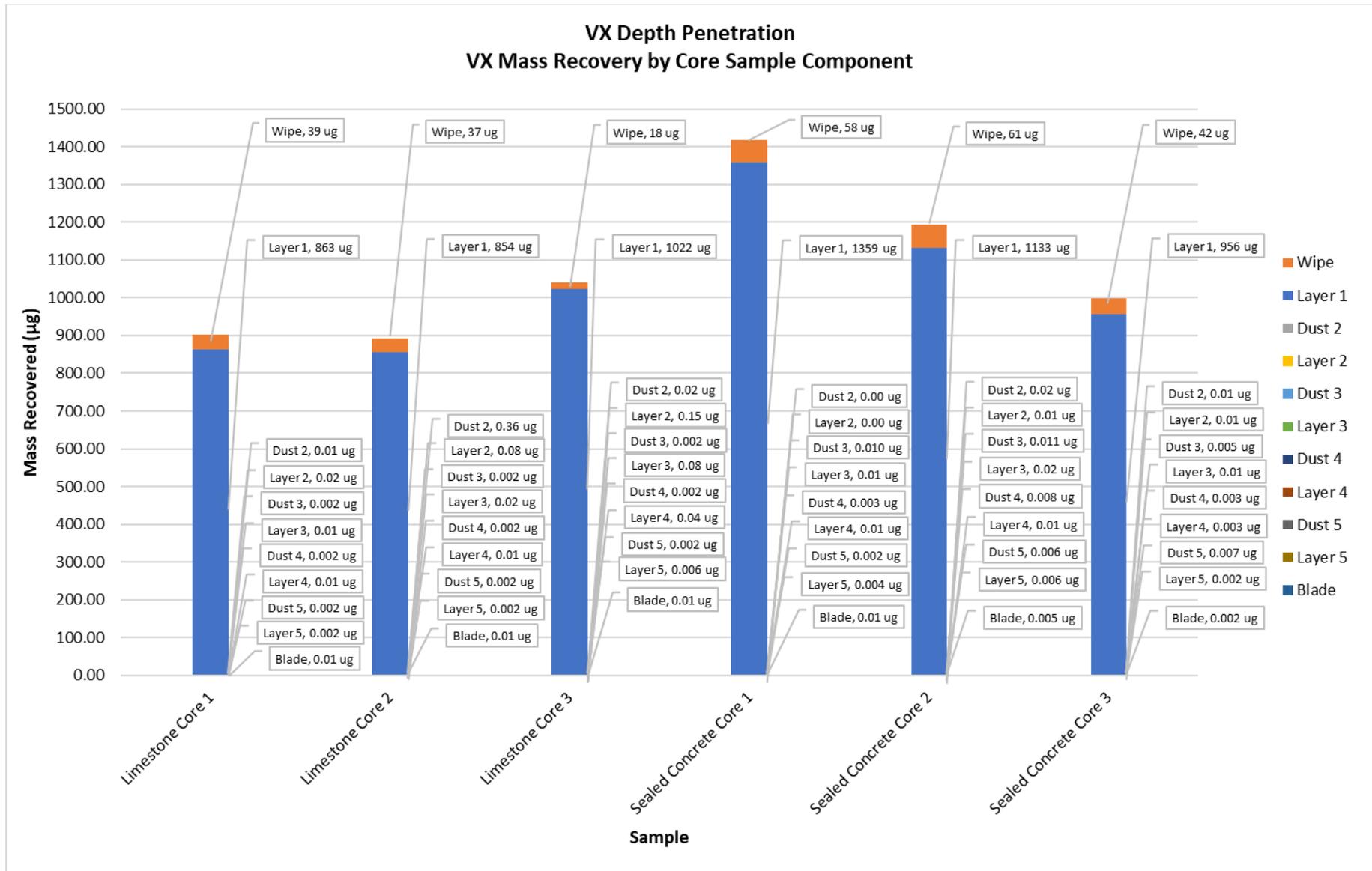


Figure 33. VX Depth Penetration Assessment, VX Mass Recovery by Component

Generally, total recoveries from core samples (sum of the masses recovered from each core layer, the cutting dusts collected during “slicing” of each layer from the core, and wipe samples obtained from the top of the core following the 24-hour dwell period and from the blade following application of the core sampling approach) were low compared to the associated spike control mean recoveries, measuring only 11% average total recovery from limestone cores and 14% average total recovery from sealed concrete cores.

The majority of VX recovered from each core sample was obtained from solvent extraction of the 1st layer sample (the “topmost” layer of the core that was initially contaminated with VX). The next highest recovery from each core sample was obtained via the wipe sample taken from the top surface of the core following the 24-hour dwell period (prior to application of the core sampling approach). VX mass recoveries from the core layer and cutting dust samples collected below the 1st/topmost layer (layer and cutting dust samples 2 through 5) drop off significantly, indicating that either VX does not penetrate into the materials past the topmost approximately 0.25 in. depth (via gravity, over the course of 24 hours), or VX becomes increasingly unrecoverable or degrades as it penetrates farther than approximately 0.25 in. into the materials. The low recoveries are also consistent with [10] and potentially attributable to previously implied degradation of VX on concrete due to the presence of basic catalytic sites [6,7,9]. Such degradation may even be enhanced at elevated material temperatures as observed during the cutting of the concrete slices.

3.2. Physical Removal Efficacy Results – Grinding

Sealed concrete and limestone coupons were contaminated with 10 µL of VX (single 10-µL droplet applied in the center of the top surface of the coupon), and the VX was allowed to dwell on the surface of the coupon for 24 hours. Following the 24-hour dwell period, the surface of the coupon was sampled via wipe sampling, then the grinding technology was applied to collect successive 0.25 in. depth layer samples from the coupon.

Spike control recovery results from the grinding tests are provided in Table 34.

Table 34. Grinding, Spike Controls

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs target)	Avg (µg)	Avg % vs Target	St Dev	%RSD
SC1 (sealed conc. test)	470400	9408	93%	9163	91%	213	2.3%
SC2 (sealed conc. test)	452800	9056	90%				
SC3 (sealed conc. test)	451200	9024	89%				
SC1 (limestone test)	434700	8694	86%	8694	86%	220	2.5%
SC2 (limestone test)	423700	8474	84%				
SC3 (limestone test)	445700	8914	88%				

The mass of each ground layer sample that was collected through application of the grinding technology was determined gravimetrically. Sealed concrete and limestone ground layer masses are provided in Tables 35 and 36.

Table 35. Sealed Concrete, Ground Layer Masses

Sample Description	Coupon 1 Mass (g)	Coupon 2 Mass (g)	Coupon 3 Mass (g)	PB Mass (g)
Sealed Concrete Ground layer 1	33.3	52.4	57.3	40.5
Sealed Concrete Ground layer 2	74.4	51.2	56.4	46.8
Sealed Concrete Ground layer 3	81.3	84.6	73.5	46.5
Sealed Concrete Ground layer 4	72.8	45.5	43.8	26.8
Avg	65.5	58.4	57.8	40.2
St Dev	21.7	17.7	12.2	9.4
%RSD	33%	30%	21%	23%
Total Mass	261.8	233.7	231.0	160.6

PB = Procedural blank

Table 36. Limestone, Ground Layer Masses

Sample Description	Coupon 1 Mass (g)	Coupon 2 Mass (g)	Coupon 3 Mass (g)	PB Mass (g)
Limestone Ground layer 1	25.6	64.3	47.1	72.8
Limestone Ground layer 2	50.0	None ^A	43.6	92.6
Limestone Ground layer 3	38.3	51.7	52.7	87.0
Limestone Ground layer 4	42.0	55.6	43.6	72.5
Avg	39.0	57.2	46.8	81.2
St Dev	10.2	6.5	4.3	10.2
%RSD	26%	11%	9%	13%
Total Mass	155.9	171.6	187.0	324.9

PB = Procedural blank

^A Inadvertently ground deeper than target 1/4 in. for 1st layer; no sample for 2nd layer, since already ground to 1/2 in.

VX mass recovery and percent recovery results for the wipe and ground layer samples collected from each sealed concrete coupon included during grinding technology physical removal efficacy testing are provided in Table 37. Mass recovery and percent recovery results for the wipe and ground layer samples collected from limestone coupons are provided in Table 38. Wipe sample and ground layer sample mass recovery results from all coupons are also summarized in Figure 34.

Table 37. Grinding, Sealed Concrete Recovery

Sample Description	Sealed Concrete Coupon 1			Sealed Concrete Coupon 2			Sealed Concrete Coupon 3			Avg Mass (µg)	Avg Mass % Recovery (vs SC Avg)	St Dev	%RSD
	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)				
Coupon Wipe	1732	37	0.40%	1609	34	0.38%	1001	21	0.23%	31	0.34%	8.4	27%
Grinder Wipe	8.8	0.19	0.002%	7.6	0.16	0.002%	3.1	0.07	0.001%	0.14	0.002%	0.06	47%
Shield Wipe	21	0.46	0.01%	167	3.6	0.04%	69	1.5	0.02%	1.8	0.02%	1.6	86%
Ground layer 1	5500	440	4.8%	17940	1435	16%	4351	348	3.8%	741	8.1%	603	81%
Ground layer 2	43	3.4	0.04%	66	5.3	0.06%	36	2.9	0.03%	3.9	0.04%	1.3	33%
Ground layer 3	24	1.9	0.02%	25	2.0	0.02%	24	1.9	0.02%	2.0	0.02%	0.07	3.5%
Ground layer 4	5.8	0.47	0.01%	17	1.4	0.01%	14	1.2	0.01%	1.0	0.01%	0.47	47%
Total Mass	NA	484	5.3%	NA	1482	16%	NA	377	4.1%	781	8.5%	610	78%

Table 38. Grinding, Limestone Recovery

Sample Description	Limestone Coupon 1			Limestone Coupon 2			Limestone Coupon 3			Avg Mass (µg)	Avg Mass % Recovery (vs SC Avg)	St Dev	%RSD
	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)				
Coupon Wipe	1466	31	0.36%	930	20	0.23%	571	12	0.14%	21	0.24%	9.6	46%
Grinder Wipe	228	4.9	0.06%	184	3.9	0.05%	215	4.6	0.05%	4.5	0.05%	0.48	11%
Shield Wipe	150	3.2	0.04%	58	1.2	0.01%	373	8.0	0.09%	4.1	0.05%	3.5	84%
Ground layer 1	47730	3818	44%	35810	2865	33%	55080	4406	51%	3697	43%	778	21%
Ground layer 2	323	26	0.30%	None ^A			176	14	0.16%	20	0.23%	8.3	42%
Ground layer 3	139	11	0.13%	6339	507	5.8%	12	0.98	0.01%	173	2.0%	289	167%
Ground layer 4	28	2.2	0.03%	5823	466	5.4%	5.5	0.44	0.01%	156	1.8%	268	172%
Total Mass	NA	3897	45%	NA	3863	44%	NA	4447	51%	4069	47%	328	8.1%

^A Inadvertently ground deeper than target 1/4 in. for 1st layer; no sample for 2nd layer, since already ground to 1/2 in.

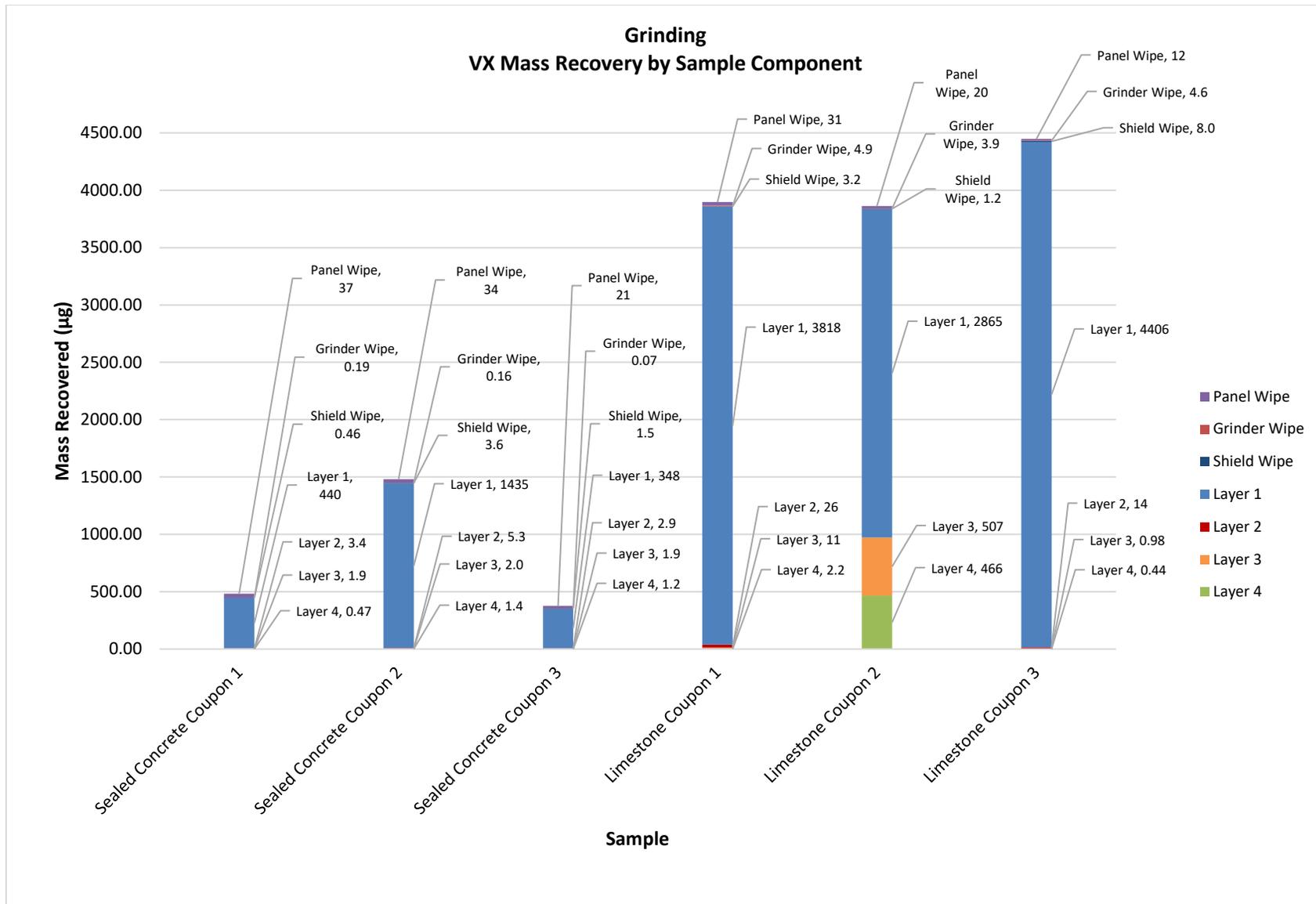


Figure 34. Grinding, VX Mass Recovery by Component

The majority of VX recovered from each coupon (both sealed concrete and limestone) was obtained in the 1st ground layer sample. Total percent recovery (sum of the masses recovered via wipe samples taken from the top surface of the coupon following the 24-hour dwell period, the wheel of the grinder, and from the inside surface of the deflector shield, and from solvent extraction of all four ground layer samples) averaged only 8.5% (vs the associated spike control mean) from sealed concrete. Average total percent recovery from limestone was markedly higher, at 47% of the associated spike control mean recovery. The higher recovery from ground limestone is consistent with the results of the ground material solvent extraction method demonstration testing, during which an average 25% recovery of VX from sealed concrete was obtained following a 24-hour dwell period, compared to an average 95% recovery of VX from ground limestone after a 24-hour dwell period.

Total mass recovery from the 2nd sealed concrete coupon was markedly higher than the total mass recovered from the 1st and 3rd sealed concrete coupons. No readily attributable cause was noted or could be determined for the difference in total recovery from the 2nd coupon versus from the 1st and 3rd coupons.

The next highest recovery from each coupon (both sealed concrete and limestone) was obtained from the wipe sample taken from the top surface of the coupon following the 24-hour dwell period (prior to application of the grinding technology), except in the case of the 2nd limestone coupon. Markedly higher masses of VX were recovered from extraction of the 3rd and 4th ground layer samples taken from the 2nd limestone coupon than from the 3rd and 4th ground layer samples taken from other coupons, suggesting that VX had penetrated more deeply into the 2nd limestone coupon than into other coupons (or alternatively, that VX that had penetrated deeply into the 2nd coupon was more amenable to recovery via grinding and solvent extraction than from similarly deep layers from other coupons). No observations or anomalies were noted during testing that would explain the higher recoveries from the 3rd and 4th ground layer samples collected from the 2nd limestone coupon. It was discussed that since limestone is a porous material, it may be possible that the porosity of the material throughout the full coupon is inhomogeneous, and areas may exist within the material wherein there are relatively higher and relatively lower abundances of pores within the material matrix. It was discussed that VX may have been applied to the 2nd limestone coupon over an area of higher porosity compared to the 1st and 3rd limestone coupons.

3.3. Physical Removal Efficacy Results – Chemical Stripping

Painted steel and painted hardwood coupons were contaminated with 10 µL of VX (single 10-µL droplet applied in the center of the top surface of the coupon, equivalent to 9.4 mg of VX) and the VX dwelled on the surface of the coupon for 24 hours. Following the 24-hour dwell period, the surface of the coupon was sampled via wipe sampling, then chemical stripper was applied. Following the chemical stripper contact period (total 45 minutes), the paint/coating stripped from the surface of the coupons was scraped and collected, the stripped coating samples were extracted with solvent, and repeat wipe samples were taken from the surface of the coupons.

Spike control recovery results from the chemical stripping tests are provided in Table 39.

Table 39. Chemical Stripping, Spike Controls

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs target)	Avg (µg)	Avg % vs Target	St Dev	%RSD
SC1 (painted steel test)	423200	8464	84%	8911	88%	823	9.2%
SC2 (painted steel test)	493000	9860	98%				
SC3 (painted steel test)	420400	8408	83%				
SC1 (painted wood test)	451000	9020	89%	8562	85%	573	6.7%
SC2 (painted wood test)	396000	7920	79%				
SC3 (painted wood test)	437300	8746	87%				

Positive controls included in tests of the chemical stripping technology consisted of painted steel and hardwood material coupons that were contaminated with VX and sampled following the dwell period alongside the test coupons (via wipe sampling), but to which the chemical stripper was not applied (two wipe samples were collected from the surface of positive controls (pre and post-wipes, consistent with and alongside the test coupons), but without application of chemical stripper between the wipe samples, in contrast to the test coupons). Painted steel and painted hardwood positive control recovery results are provided in Table 40.

Table 40. Chemical Stripping, Positive Control Recovery

Sample Description	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs SC avg)
Painted Steel PC Pre-Wipe	332900	7124	80%
Painted Steel PC Post-Wipe	66570	1425	16%
Painted Steel PC Total Mass	NA	8549	96%
Painted Wood PC Pre-Wipe	106100	2271	27%
Painted Wood PC Post-Wipe	69350	1484	17%
Painted Wood PC Total Mass	NA	3755	44%

VX mass recovery and percent recovery results for the pre-stripping and post-stripping wipe samples and stripped coating solvent extraction samples collected from each painted steel coupon included during chemical stripping technology physical removal efficacy testing are provided in Table 41. Mass recovery and percent recovery results for the pre-stripping and post-stripping wipe samples and stripped coating solvent extraction samples collected from painted hardwood coupons are provided in Table 42. Wipe sample and stripped coating extraction sample mass recovery results from all coupons are also summarized in Figure 35. Generally, greater recoveries of VX were obtained from the painted steel coupons, which is suspected to be due mostly to migration of VX through the coating layer and into the underlying wood substrate (consistent with previous findings [12]).

Table 41. Chemical Stripping, Painted Steel Recovery

Sample Description	Painted Steel Coupon 1			Painted Steel Coupon 2			Painted Steel Coupon 3			Avg Mass (µg)	Avg Mass % Recovery (vs PC)	St Dev	%RSD
	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs PC)	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs PC)	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs PC)				
Pre-Wipe	226900	4856	68%	249400	5337	75%	194500	4162	58%	4785	67%	591	12%
Post-Wipe	5309	114	8.0%	5607	120	8.4%	6814	146	10%	126	8.9%	17	13%
Stripped Paint	103400	2068	NA	89860	1797	NA	149500	2990	NA	2285	NA	625	27%
Total Mass	NA	7037	82%	NA	7254	85%	NA	7298	85%	7197	84%	140	1.9%

Table 42. Chemical Stripping, Painted Wood Recovery

Sample Description	Painted Wood Coupon 1			Painted Wood Coupon 2			Painted Wood Coupon 3			Avg Mass (µg)	Avg Mass % Recovery (vs PC)	St Dev	%RSD
	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs PC)	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs PC)	Extract Conc. (ng/mL)	Mass (µg)	% Recovery (vs PC)				
Pre-Wipe	158200	3385	149%	74730	1599	70%	61500	1316	58%	2100	93%	1122	53%
Post-Wipe	12030	257	17%	17430	373	25%	14890	319	21%	316	21%	58	18%
Stripped Paint	88490	1770	NA	127200	2544	NA	118500	2370	NA	2228	NA	406	18%
Total Mass	NA	5413	144%	NA	4516	120%	NA	4005	107%	4645	124%	713	15%

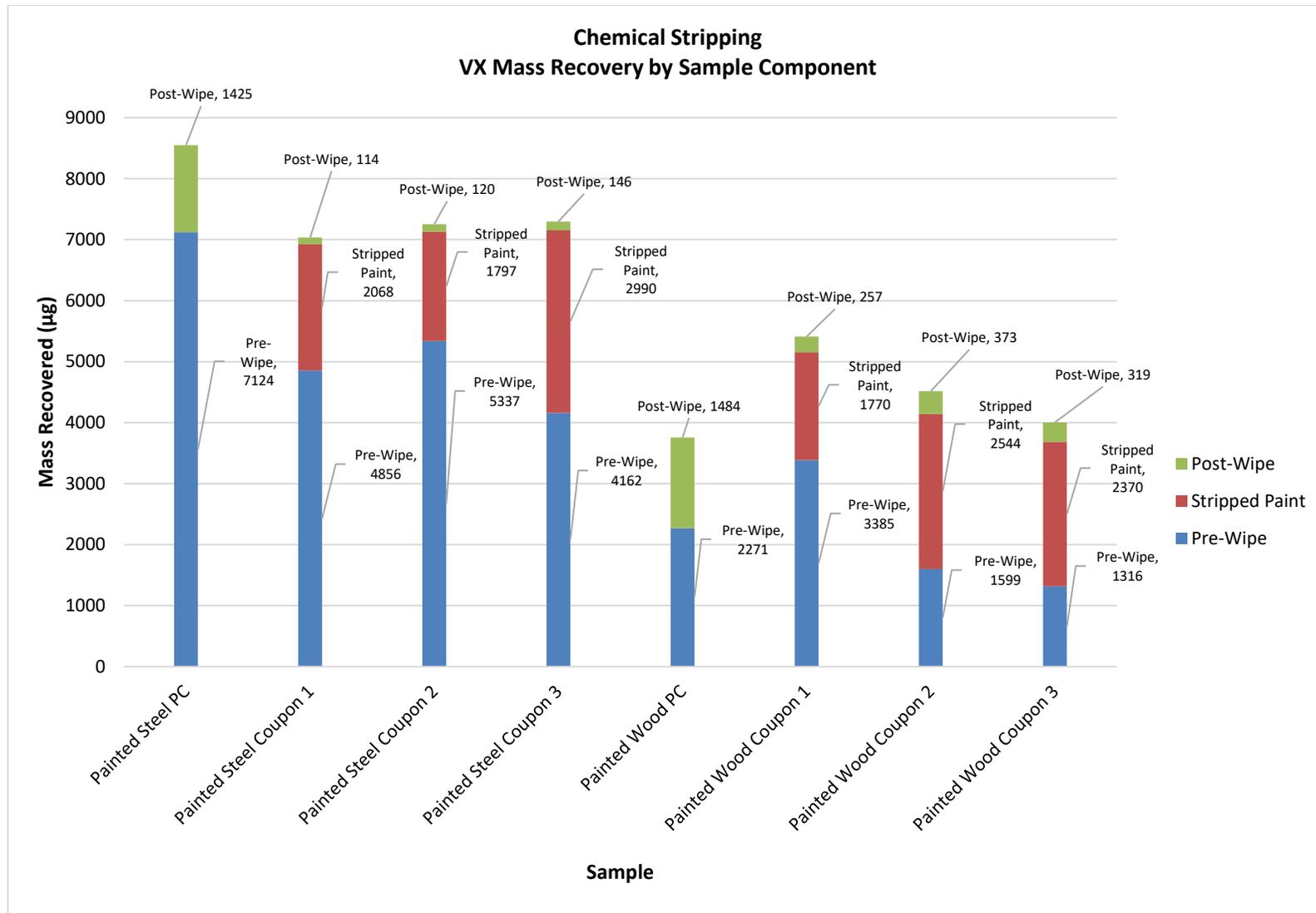


Figure 35. Chemical Stripping, VX Mass Recovery by Component

3.4. Waste Generation Assessment Results

Grinding

As the physical removal efficacy test results provided in Section 3.2 show, VX was recovered in the sealed concrete and limestone ground material removed from coupons, thus potentially requiring treatment (e.g., via incineration) prior to disposal. Application of the grinding technology to an area of approximately 100 cm² to a total depth of approximately 1 in. produced average total ground material masses of 221.8 g from sealed concrete and 209.9 g from limestone (Tables 35 and 36). While the large majority of VX recovered from coupons by application of the grinding technology was recovered in the topmost 0.25 in.-thick layer collected, it cannot be discerned from the data produced during this testing whether lower detections in deeper layers are due to the absence of VX (i.e., VX did not penetrate past the topmost 0.25 in. layer), degradation of VX, or an inability to recover VX that is present (given the low recovery efficiency of the solvent extraction method used to recover VX from ground concrete and from ground limestone after a 30-minute dwell period). Thus, physical removal to a greater depth than just the topmost 0.25 in. of material would likely be considered necessary, and application of a grinding approach similar to the method used here to surface areas much larger than the approximately 100 cm² used during this testing would generate a proportionally larger amount of ground material waste, all of which might require treatment prior to disposal.

Application of the grinding technology using the procedure developed for this testing created both coarse ground material that was collected at each discrete 0.25 in. depth layer (using the deflector shield and aluminum collection pan underneath the coupon) as well as fine dust that was not captured within/redirected by the deflector shield. A wet/dry vacuum was attached to the top of the test chamber in which grinding operations took place to attempt to draw in and collect the fine dust, but this approach was only partially successful, leaving a portion of the fine dust uncollected/uncontained. Attempts were made to use a vacuum shroud to collect the ground material, but difficulties were experienced that precluded its use. In a field application of a grinding approach to remove larger areas of sealed concrete or limestone (and likely other porous material types) contaminated with CWAs or other hazardous compounds, similar fine, airborne dusts would likely also be generated. Many grinding and cutting technologies incorporate attachments for application of water (e.g., mist, spray, or similar) to wet the ground materials produced and reduce airborne dusts, but adequate PPE, including respiratory protection, would be necessary. Management of these wastes are typically regulated at the state level, and the appropriate regulatory authorities should be contacted to discuss waste management practices including waste acceptance criteria for any treatment or disposal facility accepting these materials.

Chemical Stripper

Klean-Strip® KS-3 Premium finish/paint stripper is a thickened semi-paste that can be applied via brushing and is intended to cling to vertical surfaces without running or dripping. During the

functionality assessment of the Klean-Strip® KS-3 Premium stripper, the stripper was absorbed into the coating following application and “lifted” the coating from the substrate, leaving behind minimal liquid residue. The stripped coating layer was then generally easily removed from the substrate surface via scraping with a 2 in. plastic joint knife (although not completely removed in the case of the hardwood substrate, as can be seen in Figure 22). Repeated applications of the stripper would likely be required in some cases to achieve adequately thorough removal of coatings, and complete removal may not be possible for some substrates (e.g., very porous surfaces). As can be seen from the physical removal efficacy test results provided in Section 3.3, VX was recovered in the stripped coating samples, revealing that contamination is retained in coatings stripped using the technology and collection and disposal of stripped coatings would require use of appropriate PPE and post-removal decontamination or waste treatment methodologies.

3.5. Damage Extent Assessment Results

Grinding

Application of the grinding technology to remove sealed concrete and limestone to a depth of approximately 1 in. across an area of approximately 100 cm² left superficial void spaces in sealed concrete and limestone coupons that were, generally, smooth across the surface and not of an excessively odd or inaccessible shape (subjective, visual assessment). Refer to Figures 17, 18, and Figures 36 and 37 below. Based on the findings and observations from this testing, surfaces to which similar grinding technologies have been applied would be amenable to resurfacing.



Figure 36. Ground Sealed Concrete Coupon

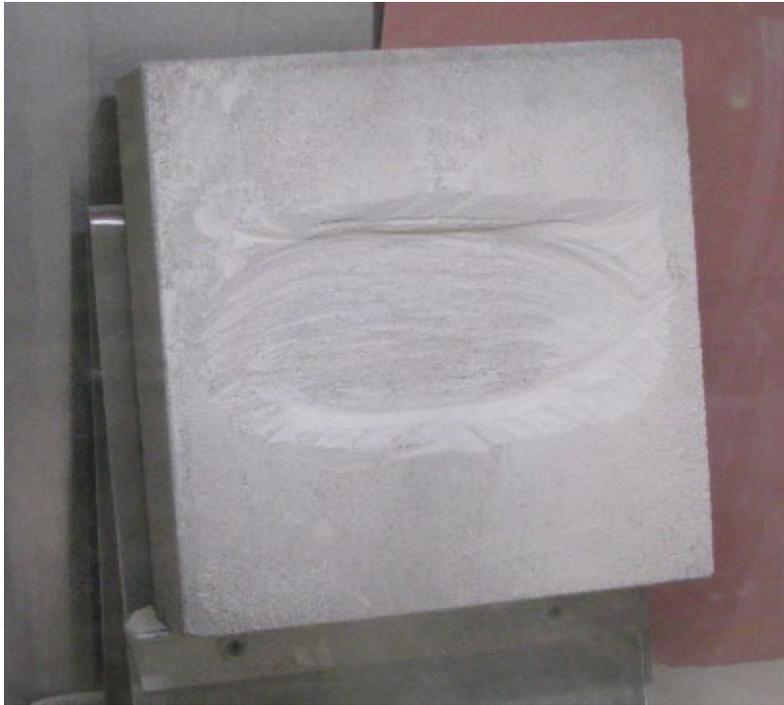


Figure 37. Ground Limestone Coupon

Chemical Stripper

As can be seen in Figures 21, 22 and Figures 38 and 39 below, a single application of the chemical stripper technology to paint/primer on low-carbon steel and hardwood appeared to achieve removal of a large portion of the coating layers without excessive damage to the underlying substrates.



Figure 38. Stripped Coating, Steel



Figure 39. Stripped Coating, Hardwood

Most likely for low-carbon steel, or other similar substrates (e.g., stainless steel), repeated applications of the stripper could be performed to achieve increasingly higher levels of physical removal efficacy still without excessive damage to the material, allowing for the surface to be restored/repainted once acceptable levels of decontamination are achieved. Conversely, repeated applications of the chemical stripper technology to hardwood (or similar substrates that are not as inherently resistant to damage as steel substrates) may cause softening, hardening, discoloration, or other damage. Furthermore, acceptable levels of decontamination by physical removal via chemical stripping may not be achievable for porous substrates, such as hardwood. In these cases, portions of the substrate itself may require removal, obviously leading to much greater levels of damage to the surface which might preclude resurfacing and reuse.

4. QUALITY ASSURANCE/QUALITY CONTROL

Quality objectives and performance criteria described in the sections below provide the requirements used for determining the adequacy of data generated during this project. Methods were considered acceptable and valid data were assumed if the data quality objectives for the test measurements were met, and the Technical Systems Audit (TSA), Performance Evaluation (PE), and data quality audits demonstrated acceptable results, as described in Sections 4.5, 4.6, and 4.7. Accuracy was ensured by the calibration of the instruments. The PE audits further confirmed that valid data were generated.

4.1. Data Quality Indicators

Data quality indicators and results are provided in Table 43. In general, the data quality indicator results were acceptable per the Quality Assurance Project Plan (QAPP) including checks of the measurement methods for temperature, RH, time, volume, and VX recovery from blank samples and spike controls. Attainment of these data quality indicator results limited the amount of error introduced into the evaluation results.

Table 43. Data Quality Indicators and Results

Parameter	Measurement Method	Data Quality Indicators	Results
Temperature (°C)	HOBO UX100 Datalogger	Compare against calibrated thermometer once before testing; agree $\pm 1^\circ\text{C}$ through 60 minutes.	The HOBO UX100 datalogger used during the project remained within 0.04°C of the calibrated reference through one hour.
Relative Humidity (%)	HOBO UX100 Datalogger	Compare against calibrated hygrometer once before testing; agree $\pm 10\%$ through 60 minutes.	The HOBO UX100 datalogger used during the project remained within 5.26% of the calibrated reference through one hour.
Time (sec)	Timer/data logger	Compare to time provided at NIST.time.gov once before testing; agree ± 2 second/hour.	No difference was observed between the timer and NIST.time.gov after one hour.
Volume (μL)	Calibrated pipette (CWA delivery)	Checked for accuracy and repeatability one time before use by determining the mass of water delivered. Acceptable if the range of observed masses for five droplets is $\pm 10\%$ of expected.	Two pipettes used for VX application were checked: <ul style="list-style-type: none"> • 1 to 10 μL range Gilson pipette, error ranged from 0.17% to 4.83 % of theoretical • 3 to 25 μL range Gilson pipette, error ranged from 2.83% to 4.83 % of theoretical
VX in Procedural Blank Sample Extracts ($\mu\text{g/mL}$)	Extraction, LC-MS/MS	Procedural blanks (coupons without applied agent that are processed alongside test coupons) should have less than 1% of the average SC amount.	No VX outside the stated criteria was measured in any procedural blank sample extracts throughout testing. Refer to Section 3 for complete test results.
VX in SC Extracts ($\mu\text{g/mL}$)	LC-MS/MS	The mean of the SCs included with each test should be within 80% to 120% of the target application and have a CoV of $< 30\%$ between replicates.	Spike control means throughout testing were within specification. Refer to Section 3 for complete test results.

4.2. Instrument Calibration

4.2.1. Calibration Schedules

Instrumentation needed for the investigation was maintained and operated according to the quality and safety requirements and documentation of Battelle's HMRC. Except for the LC-MS/MS, all instruments utilized during the project were calibrated as stipulated by the manufacturer or, at a minimum, annually. The LC-MS/MS was calibrated as described in Section 4.2.2. Table 44 provides calibration schedules for instruments that were used during the evaluation.

Table 44. Equipment Calibration Schedule

Equipment	Frequency
Calibrated pipette and repeating dispenser/syringe	Prior to the investigation and annually thereafter.
Calibrated UX100 HOBO Hygrometer/Thermometer	Prior to the investigation by the manufacturer.
Timer	Prior to the investigation by the manufacturer.
LC-MS/MS	Beginning of each batch of test samples (calibration curve) and a calibration verification standard after every ten samples.

4.2.2. LC-MS/MS Calibration

Neat VX was used to create calibration standards (concentrations corrected for percent purity) encompassing the appropriate analysis range. The expiration date for VX calibration standards was six months. The expiration date for VX continuing calibration verifications (CCVs) was one month. A seven (7)-point calibration for VX was used with a lower calibration level of 0.010 ng/mL and an upper limit of 2.0 ng/mL. A linear or quadratic regression (specified in the raw data product) was used to describe the data with $1/x^2$ weighting. The origin was not included for regression. The coefficient of determination (r^2) from the regression analysis of the calibration standards was required to be ≥ 0.990 . Limits were also placed on the percent bias (Equation 4) observed in the standards.

$$\text{Bias} = \left(\frac{E_V - O_V}{E_V} \right) \times 100\% \quad (4)$$

where: E_V = expected value from calibration curve

O_V = observed value from standard

The percent bias for the low standard was required to be less than or equal to 25%, and the percent bias for the remaining standards was required to be less than or equal to 15%. The signal-to-noise ratio of the lowest calibration standard was required to be approximately 3:1 at minimum. Retention time for each target compound (VX) and IS in each injection was reviewed to confirm that it was within ± 0.1 minutes of the retention time for the same components in the mid-level calibration standard. Solvent blank and double blank samples were included during analytical runs and were analyzed to confirm that no VX carryover was occurring, and no significant analyte signal was originating from the IS. Solvent blank sample analysis results were required to be below the value of the lowest calibration standard.

Independently prepared CCV standards were analyzed prior to sample analysis, following every ten test/control samples (not including blanks), and at the end of each set of samples. Two CCV

concentrations were used, one of which was equal to the low calibration standard (0.010 ng/mL) and the other within the calibration range (1.0 ng/mL). CCV response was required to be within 25% of the nominal concentration for the 0.010 ng/mL CCV and within 15% of the nominal concentration for the 1.0 ng/mL CCV.

Calibration standards and CCVs were matched to the samples undergoing analysis as closely as possible. For example, IPA samples prepared for analysis by a 10-fold dilution in water were quantitated by standards and CCVs prepared in 10% IPA.

The area of VR IS in the test samples was compared to that in the nearest passing calibration standard or passing CCV. VR area in the test samples was required to fall within 50% to 200% of the area of the IS in the calibration standard or CCV to which it was compared (criteria per EPA Method 8000D [14]). It was assumed that any test sample matrix would affect analysis of VX and VR IS in a similar manner. Given that assumption, IS response variability within the range of 50% to 200% of that of the nearest passing calibration standard or CCV was considered acceptable and IS was assumed to be properly compensating for similar effects on VX response due to sample matrices.

Table 45 summarizes LC-MS/MS analysis performance parameters and acceptance criteria.

Table 45. LC-MS/MS Performance Parameters and Acceptance Criteria

Parameter	Criterion
Coefficient of determination (r^2)	≥ 0.990
% Bias for the lowest calibration standard	$\leq 25\%$
% Bias for remaining calibration standards (except lowest standard)	$\leq 15\%$
Solvent blank samples	< lowest calibration standard
% Bias for the lowest CCV	$\leq 25\%$
% Bias for remaining CCVs (except lowest CCV)	$\leq 15\%$
Signal-to-noise ratio for the lowest calibration standard	Minimum of 3:1
Retention time for target compound and IS	± 0.1 min. as same compounds in mid-level calibration standard
VR IS area in samples	50% to 200% area of nearest passing calibration standard or passing CCV

4.3. Sample Handling and Custody

At all times during the project, protocols required by the U.S. Army were followed in the movement and use of VX and Research, Development, Test, and Evaluation (RDT&E) Dilute Solutions (RDS) within the HMRC. CoC forms were used to ensure that test samples generated during the project were traceable throughout all phases of testing.

4.4. Technical Systems Audit

A Quality Assurance (QA) Officer performed a TSA during the VX depth penetration method demonstration test. The purpose of the TSA was to ensure that testing was performed in accordance with the QAPP. The QA Officer reviewed the investigation methods, compared test procedures to those specified in the QAPP (and the associated amendments), and reviewed data acquisition and handling procedures. The QA Officer did not identify any findings that required corrective action.

4.5. Performance Evaluation Audits

PE audits, summarized in Table 46, addressed those reference measurements that factored into the data used in quantitative analysis during the project, including volume and time measurements and LC-MS/MS calibration and performance. The volume of VX dispensed correlated directly with the mass of VX in the wipe, coupon layer, and waste sample extracts. Volume of solvent used to extract samples directly impacted measured concentrations. The measured time that VX was allowed to remain in contact with the coupons directly influenced depth of VX penetration and extent of VX spread. Calibration of the LC-MS/MS and IS recovery provided confidence that the analysis system was providing accurate data.

Temperature and RH were measured and recorded on each day of testing, but not monitored or controlled. Therefore, no PE audit of these parameters was performed. See Attachment A for a summary table of measured temperature and RH ranges.

Table 46. Performance Evaluation Audit Results

Parameter	Audit Procedure	Required Tolerance	Results
Volume (mL, μ L)	Pipettes were checked for accuracy and repeatability one time before use by determining the mass of water delivered. The pipette was acceptable if the range of observed masses for five droplets is $\pm 10\%$ of expected.	$\pm 10\%$	Two pipettes used for VX application were checked: <ul style="list-style-type: none"> • 1 to 10 μL range Gilson pipette, error ranged from 0.17% to 4.83 % of theoretical • 3 to 25 μL range Gilson pipette, error ranged from 2.83% to 4.83 % of theoretical
Time (sec)	Compare to time provided at NIST.time.gov once before testing; agree ± 2 second/hour.	± 2 sec/hour	No difference was observed between the timer and NIST.time.gov after one hour.
VX in SC Extracts (μ g/mL)	Use LC-MS/MS to determine mass of agent delivered as a 2- or 10- μ L droplet into extraction solvent and compare to target application level.	$\geq 80\%$ of spike target; $\leq 120\%$ of spike target; $\leq 30\%$ CoV	Spike control means throughout testing were within specification.
LC-MS/MS VX Calibration Standards (%)	Verify all standards and CCVs used to calibrate and confirm calibration of the LC-MS/MS system used for analysis fall within the requirements provided in Section 4.2.2.	Refer to Table 45	All standards and CCVs were within specification for all reported data.

4.6. Data Quality Audit

Validation of the data included verification of the completeness of the data, compliance with the acceptance criteria in the QAPP, recalculation checks, and tracing of the data from instrument outputs through the final report. The data were reviewed to verify completeness and ensure the data were valid and met the acceptance criteria of the QAPP. One hundred percent (100%) of all data was reviewed prior to use in calculations, and data manipulation was completed before the data quality audit.

The QA Manager, operating independently of the laboratory testing effort, audited approximately 10% of the data generated during testing. The QA Manager traced the data from initial acquisition through reduction and to final reporting. All data analysis calculations were checked. Through the data quality audit, the TSA, and the review of the draft and final reports,

the Battelle QA Manager ensured that data generated during the project were valid, meeting the requirements of the QAPP.

5. SUMMARY

The primary objective of this project was to quantitatively evaluate the efficacy of select technologies and determine the application conditions/methods necessary to decontaminate CWA-contaminated porous materials and permeable coatings through physical removal of the contaminated portions of the materials.

Prior to testing, literature searches were performed to identify technologies that could be used to physically remove contaminated portions of porous materials and/or permeable coatings while simultaneously minimizing damage to the materials and generation of hazardous wastes. From the literature search results, grinding and chemical stripping were selected for evaluation. Grinding was evaluated for efficacy in removal of contaminated portions of sealed concrete and limestone and chemical stripping was evaluated for efficacy in removal of contaminated coatings from low-carbon steel and hardwood.

Bench scale studies were performed using neat VX as the challenge CWA. The porous materials and permeable coatings were contaminated with VX and the VX was dwelled on the surface of the materials for a period of 24 hours to allow the VX to penetrate the materials. Following the 24-hour dwell period, the porous material and permeable coating coupon surfaces were sampled via wipe sampling to quantify residual, transferable VX. Following wipe-sampling, the physical removal technologies under test were applied to remove the contaminated portions of the material coupons. Grinding was used to remove portions of sealed concrete and limestone at discrete 0.25 in.-thick depth layers. Chemical stripper was applied to the coated steel and hardwood coupons to remove the paint/primer layers. Ground material removed from sealed concrete and limestone and coatings stripped from steel and hardwood were extracted with solvent, and extracts were analyzed via LC-MS/MS to quantify VX recovered from the removed materials. The surface of steel and wood coupons were also sampled via wipe sampling again following stripping.

A method independent of the selected physical removal technologies was also developed and used for dissection of porous materials (sealed concrete and limestone) to quantify the extent of VX penetration into the porous materials as a function of depth. The core sampling approach involved excision of 1.5 in. diameter cylindrical core samples from coupons of sealed concrete and limestone that were contaminated on the top surface with VX. Following a 24-hour VX dwell period, the contaminated surfaces of the core samples were sampled via wipe sampling. The core samples were then dissected into discrete 0.25 in.-thick layer samples that were extracted individually with solvent, and extracts were analyzed via LC-MS/MS. Analysis results were then used to determine the depth to which VX had penetrated the cores over the course of the 24-hour dwell period, based on the amount of VX recovered from each core layer sample.

Prior to physical removal efficacy testing and VX depth penetration testing (using the core sampling approach), the methods used for solvent extraction of coupon, wipe, and waste samples, and for wipe sampling of coupon surfaces were evaluated. Results of methods demonstration testing are summarized in Figures 40, 41, and 42.

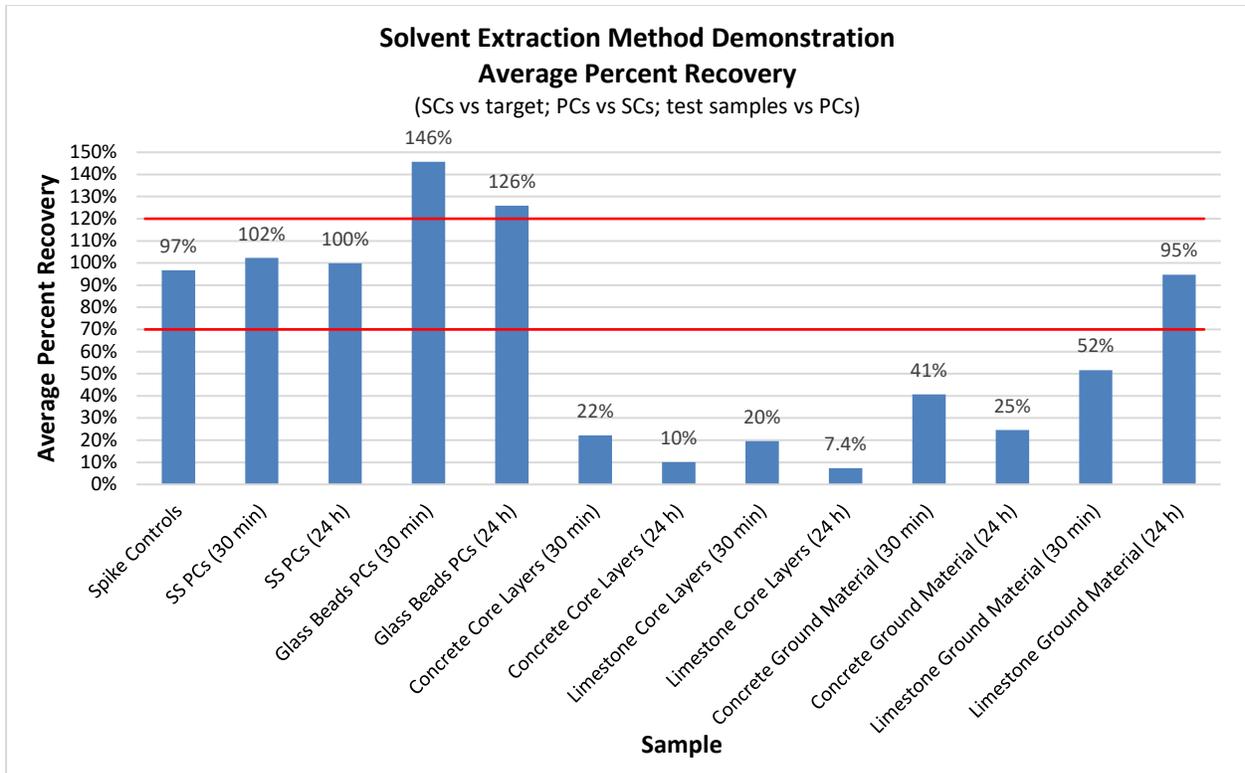


Figure 40. Solvent Extraction, Average Percent Recovery

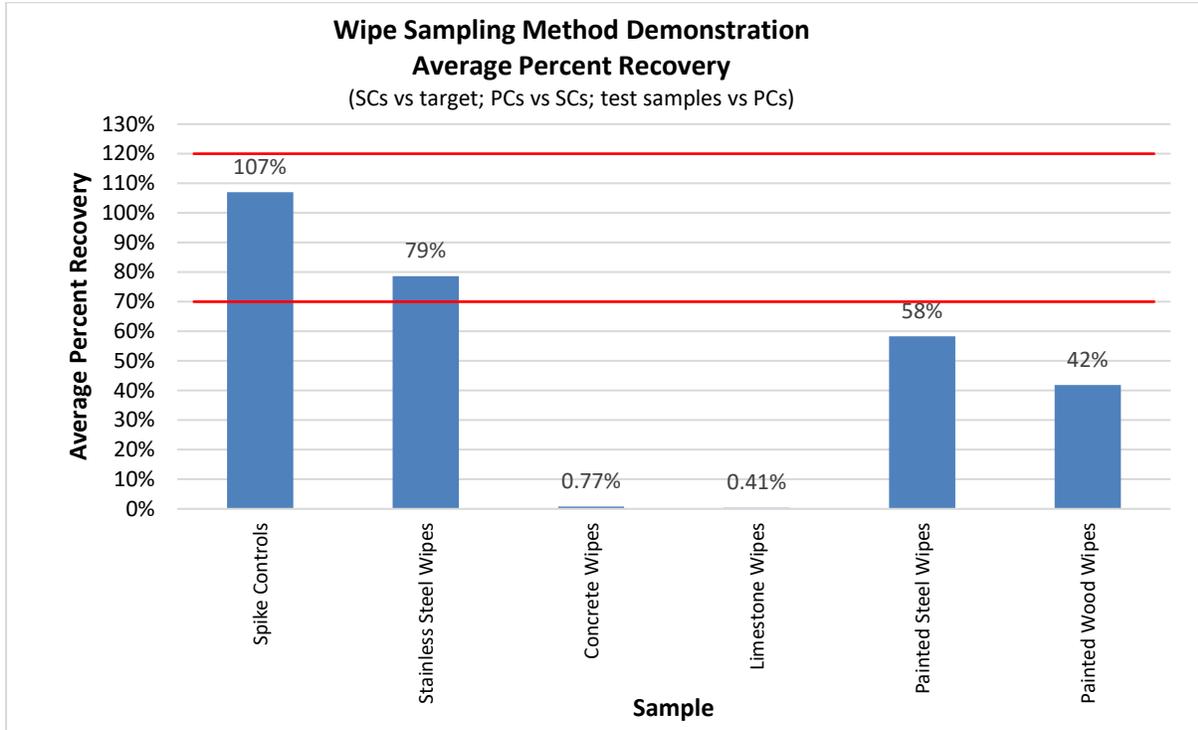


Figure 41. Wipe Sampling, Average Percent Recovery

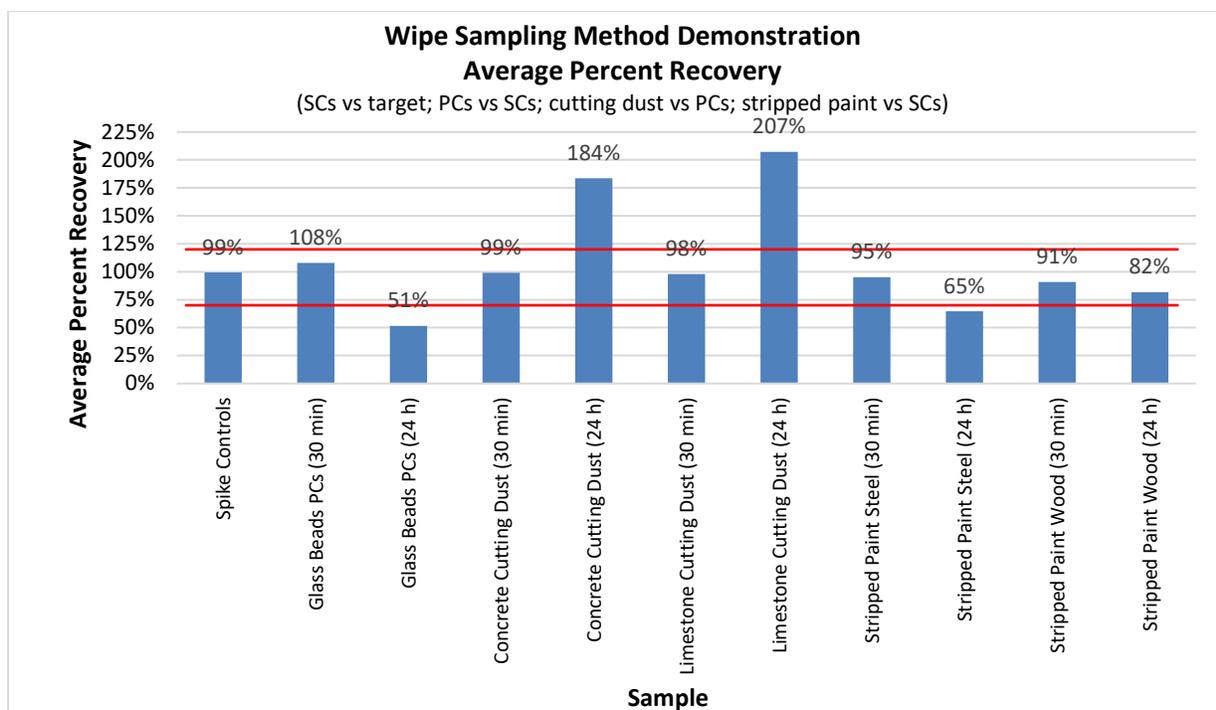


Figure 42. Waste Sampling, Average Percent Recovery

VX recovery criteria in coupon samples (ground material and core layer samples), wipe samples, and waste samples (cutting dust and stripped coating samples) were 70% to 120% of the associated spike control mean recovery with an RSD between replicates of $\leq 30\%$. Acceptable recoveries from waste samples were achieved using the solvent extraction method demonstrated during the project (submersion in IPA with sonication), but generally lower recoveries were obtained when using the method to recover VX from coupon samples. Generally lower recoveries ($< 70\%$ acceptance criterion) were obtained also using the wipe sampling method that was demonstrated. The lower recoveries are generally consistent, though, with previous studies that describe similar difficulties with recovery of CWAs from similar materials [3] as well as degradation of CWAs in material matrices [2,6,7].

Results of the VX depth penetration assessment using the core sampling approach are summarized in Figure 43. Generally, total recoveries from core samples were low compared to the associated spike control mean recoveries, measuring only 11% average recovery from limestone cores and 14% average recovery from sealed concrete cores. The majority of VX recovered from each core sample was obtained from solvent extraction of the 1st layer sample (the “topmost” layer of the core that was initially contaminated with VX). The next highest recovery from each core sample was obtained via the wipe sample taken from the top surface of the core. VX mass recoveries suggest that either VX does not penetrate into the materials past the topmost approximately 0.25 in. depth (via gravity-driven diffusion over the course of 24 hours), or VX becomes increasingly unrecoverable or degrades as it penetrates farther than approximately 0.25 in. into the materials. The low recoveries are also consistent with [3] and

potentially attributable to previously implied degradation of VX on concrete due to the presence of basic catalytic sites [2].

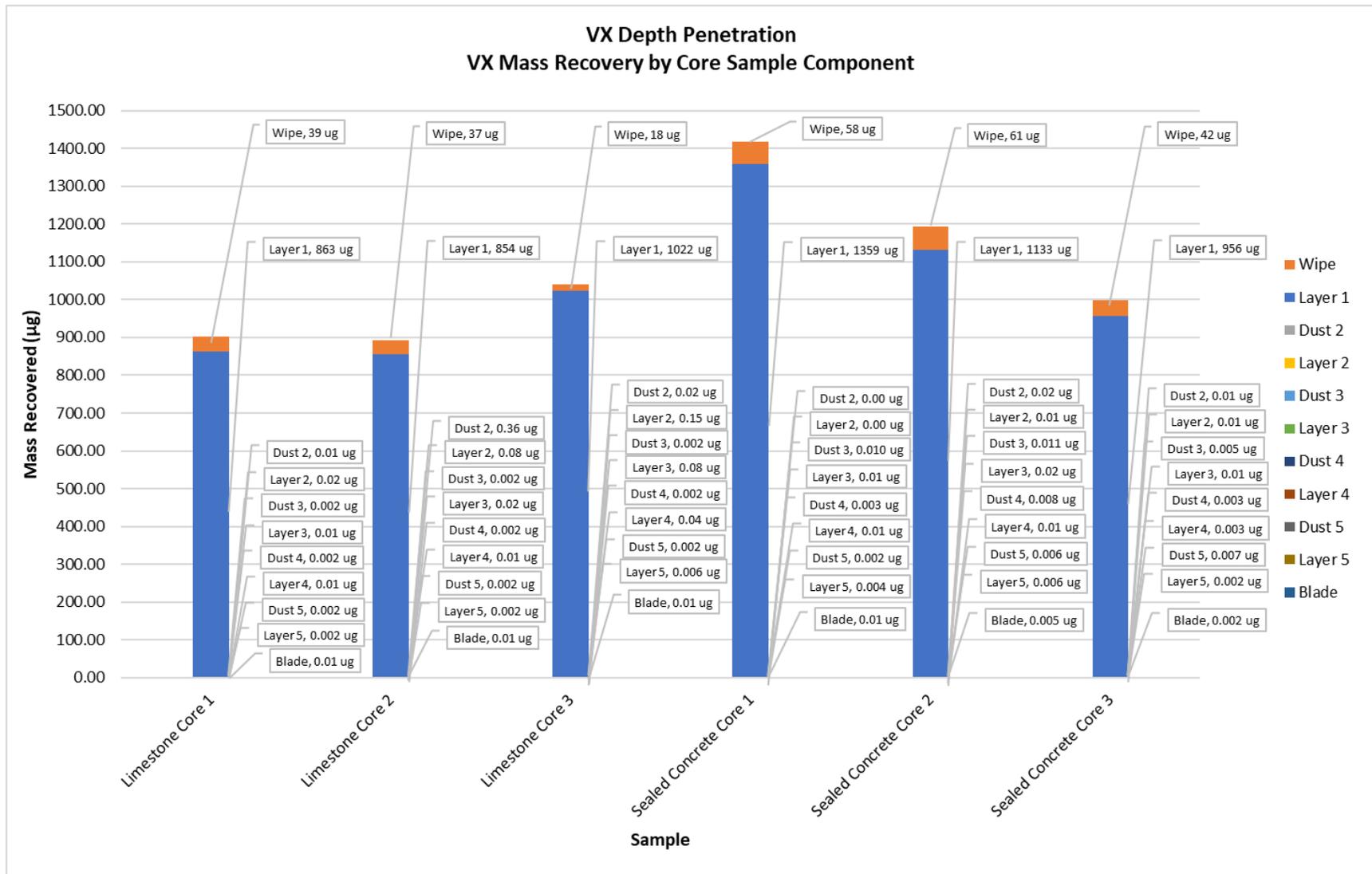


Figure 43. VX Depth Penetration Assessment, VX Mass Recovery by Component

As during the VX depth penetration assessment, the major portion of the VX recovered from each sealed concrete and limestone coupon via application of the grinding technology was obtained in the 1st ground layer sample (the topmost 0.25 in. of the material, to which the VX challenge was applied). Total percent recovery averaged only 8.5% (versus the associated spike control mean) from sealed concrete. Average total percent recovery from limestone was markedly higher, at 47% of the associated spike control mean recovery. The higher recovery from ground limestone is consistent with the results of ground material solvent extraction method demonstration testing, during which an average 25% recovery of VX from sealed concrete was obtained following a 24-hour dwell period, compared to an average 95% recovery of VX from ground limestone after a 24-hour dwell period. After the 1st ground layer sample, recoveries then decreased sharply to less than 1% of the spike control mean recovery in all cases except that of the 2nd limestone coupon, in which recoveries from the 3rd and 4th 0.25 in. ground layer samples remained as high as 5.8% and 5.4%, respectively. Results from the assessments that were conducted of physical removal efficacy via grinding are summarized in Figure 44.

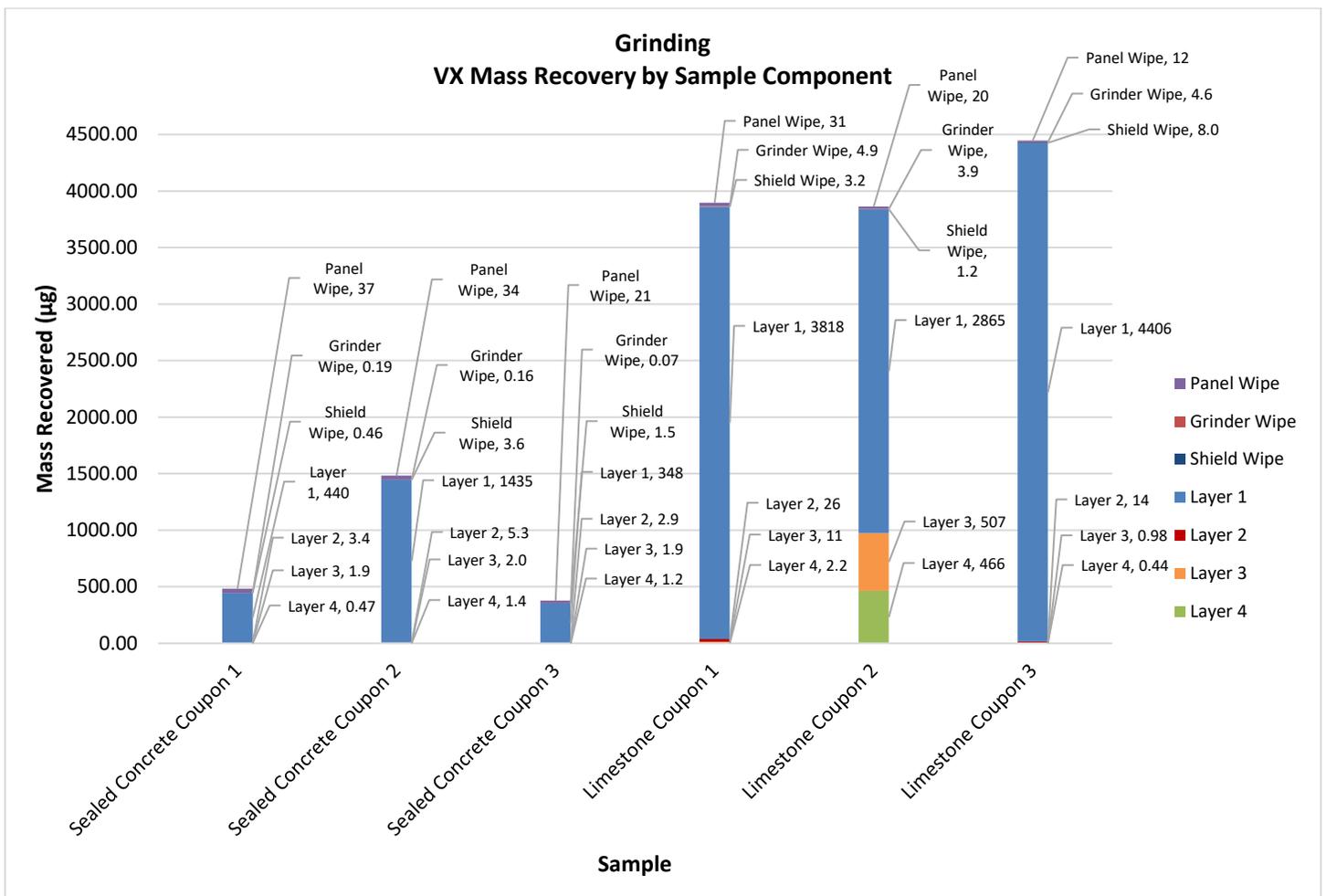


Figure 44. Grinding, VX Mass Recovery by Component

It cannot be discerned from the data whether lower detections in deeper layers are due to the absence of VX (i.e., VX did not penetrate past the topmost 0.25 in. layer), degradation of VX, or an inability to recover VX that is present. Thus, in a field-application of grinding to remove contamination, physical removal to a greater depth than just the topmost 0.25 in. of material is likely necessary. While the data suggest that VX contamination in porous materials can be removed via application of grinding to remove contaminated portions of the materials, the generally low total recoveries as well as the relatively higher recoveries from deeper layers from the 2nd limestone coupon suggest that the depths necessary for removal to safe (i.e., nonhazardous) levels can be inconsistent.

Wipe sampling and stripped coating extraction sample mass recovery results from all painted steel and painted wood coupons are summarized in Figure 45. Generally, greater recoveries of VX (as compared to mean positive control recoveries) were obtained from the painted steel coupons.

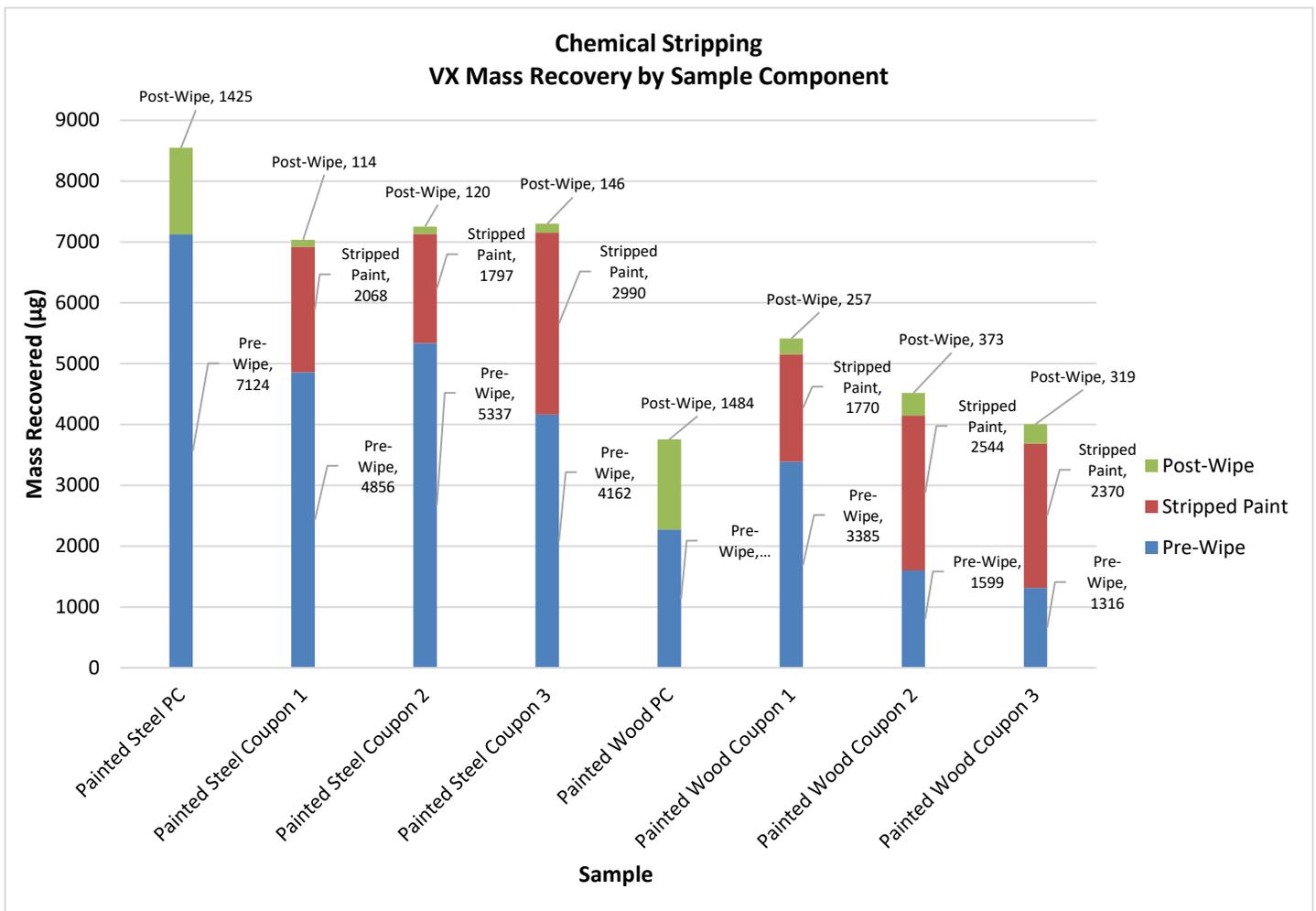


Figure 45. Chemical Stripping, VX Mass Recovery by Component

Markedly less VX was recovered from wipe samples taken from the coupons following removal of the paint/coating layer from the steel substrate via application of chemical stripper, indicating that the majority of the VX contamination was removed by the first (pre-stripping) wipe and by removal of the permeable coating via application of the stripper. The data suggest that remediation of VX-contaminated painted/coated steel via a combination of solvent wipe sampling (i.e., wipe sampling with solvent-soaked wipes) and removal of the paint/coating via chemical stripping may be possible. This assumes that VX does not permeate into the steel substrate (given that it's a non-porous, relatively inert material). A repeated solvent wipe sampling and application of the chemical stripper may be required, depending on the required decontamination level. The lower total recoveries from painted wood samples as well as the higher recoveries from post-stripping wipe samples taken from the wood coupons suggest that VX may have permeated through the paint/coating layer and into the underlying permeable wood substrate. Such residual VX contamination could potentially pose contact or vapor hazards later if the VX diffuses back to the surface of the wood or if the wood is cut, ground, or otherwise manipulated.

The grinding technology and the core sampling approach were applied to both porous materials (sealed concrete and limestone). Application of both physical removal/sampling methods produced depth layer samples at 0.25 in. increments into the material samples to which they were applied. Also, prior to application of both the grinding technology and the core sampling approach, the surfaces of coupons/cores were sampled via wipe sampling.

Figure 46 provides VX mass recovered by the surface wipe and in each successive depth layer sample collected from sealed concrete and limestone coupons/core samples. As Figure 46 shows, the largest amount of VX recovered from both material types using both removal/sampling methods was obtained in the first 0.25 in.-thick depth layer sample (either core layer sample or grinding layer sample). Based on visual assessment of Figure 46, it appears that generally similar total amounts of VX were recovered from sealed concrete and limestone core samples via application of the core sampling approach and from sealed concrete coupons via application of the grinding technology, but significantly greater VX was recovered from limestone coupons via application of the grinding technology.

Both grinding and chemical stripping, as applied to porous materials and permeable coatings during this project, generate wastes that retain hazardous contaminants and would require collection and handling using appropriate PPE and decontamination to acceptable levels prior to disposal. Further, dust mitigation will be required since small dust particles carrying agent contamination would likely become redistributed in the environment (and potentially transfer to other materials). Some of the potentially contaminated particulate matter may become an inhalation hazard.

The porous materials and permeable coating substrates evaluated during this project would likely be amenable to resurfacing and reuse following application of the grinding and chemical stripping technologies to remove contaminated portions of the materials, except in the case of the

hardwood permeable coating substrate which could be at risk of excessive damage if repeated chemical stripping applications or additional physical removal methods (beyond removal of the coating) are required to achieve acceptable levels of decontamination..

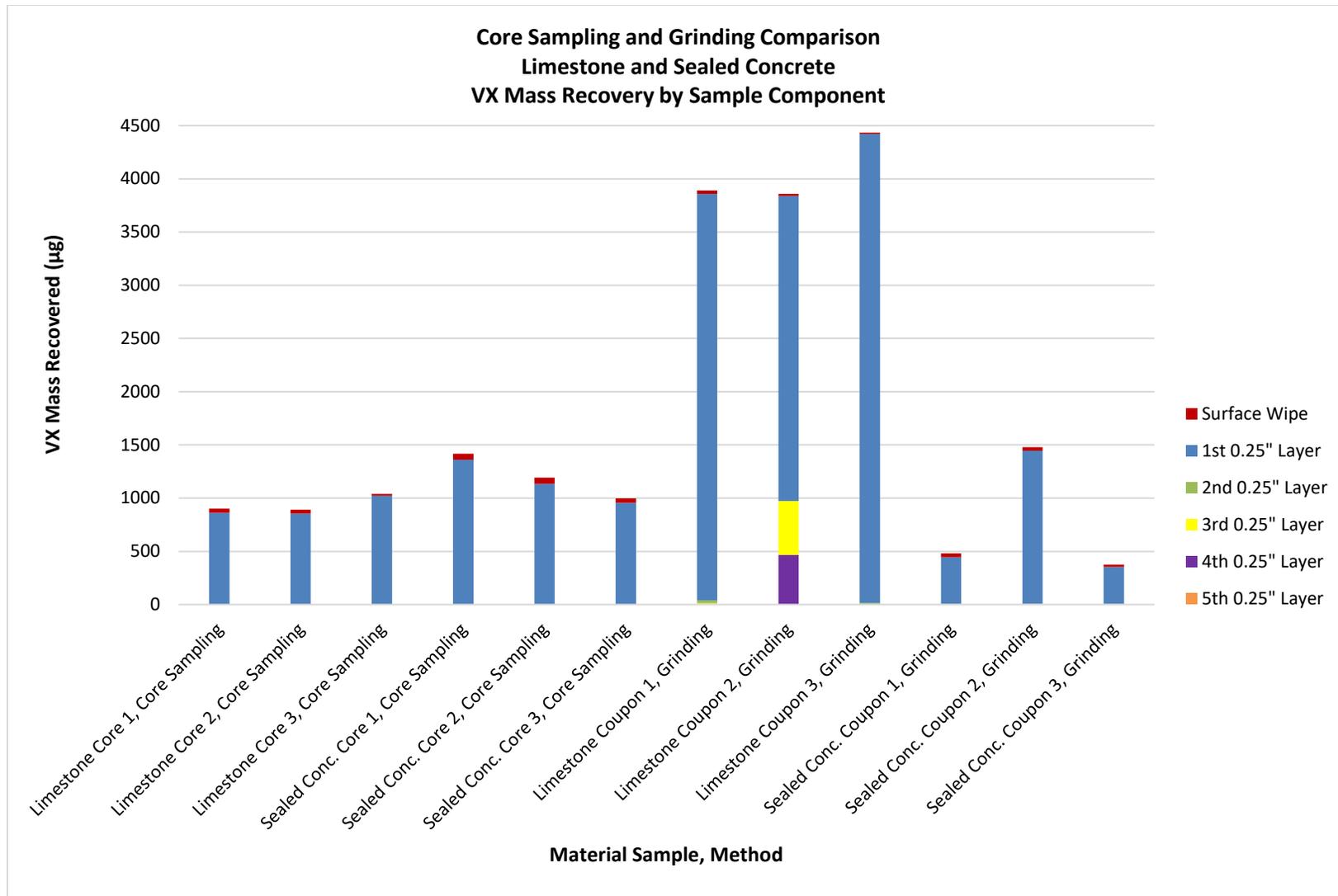


Figure 46. Limestone and Sealed Conc. Recovery, Grinding vs Core Sampling Comparison

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ATTACHMENT A – ENVIRONMENTAL DATA

Activity	Temperature Range (°C)	RH Range (%)
Solvent Extraction, Wipe Sampling, and Waste Sampling Method Development	21.0-23.0	15-16
VX Depth Penetration Assessment	22.0-24.0	40-45
Physical Removal: Concrete Grinding	21.5-22.5	40-45
Physical Removal: Limestone Grinding	21.0-22.0	40-45
Physical Removal: Chemical Stripping	22.0-23.0	42-47



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