



# **U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND CHEMICAL BIOLOGICAL CENTER**

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**CCDC CBC-TN-085**

## **Extraction and Quenching Procedures for HD and VX on Concrete and Asphalt Substrates**

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**RESEARCH AND TECHNOLOGY DIRECTORATE**

**June 2020**

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## **PREFACE**

The work described in this technical note was authorized under project number CB10662. This work was started in January 2019 and completed in February 2020. At the time this work was performed, the U.S. Army Combat Capabilities Development Command Chemical Biological Center (CCDC CBC; Aberdeen Proving Ground, MD) was known as the U.S. Army Edgewood Chemical Biological Center (ECBC).

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## **EXTRACTION AND QUENCHING PROCEDURES FOR HD AND VX ON CONCRETE AND ASPHALT SUBSTRATES**

### **1. SUMMARY**

Analysis of the post-decontamination concentration of Chemical Warfare Agents (CWAs) requires development of analytical methods. The substrates here were calcium sulfoaluminate (CSA) concrete coupons or asphalt roofing shingles. Coupons were 1/8" thick and 2" in diameter. Thicker test materials may need to be crushed to give reasonable extraction efficiency. A summary of the findings is provided below.

#### **Extraction Results**

- HD was extracted from concrete using Chloroform over a 24 hour period.
- VX was extracted from concrete using Isopropanol (IPA) over a 24 hour period.
- Use of very non-polar solvents (Hexane or Chloroform) stripped all the of the coal tar from asphalt substrates and made analysis difficult. Polarity was adjusted by adding acetone.
- HD was extracted from asphalt using an Acetone:Chloroform mixture (70/30) over 3 hours.
- VX was extracted from asphalt using an Acetone:Isopropanol mixture (70/30) over 3 hours.

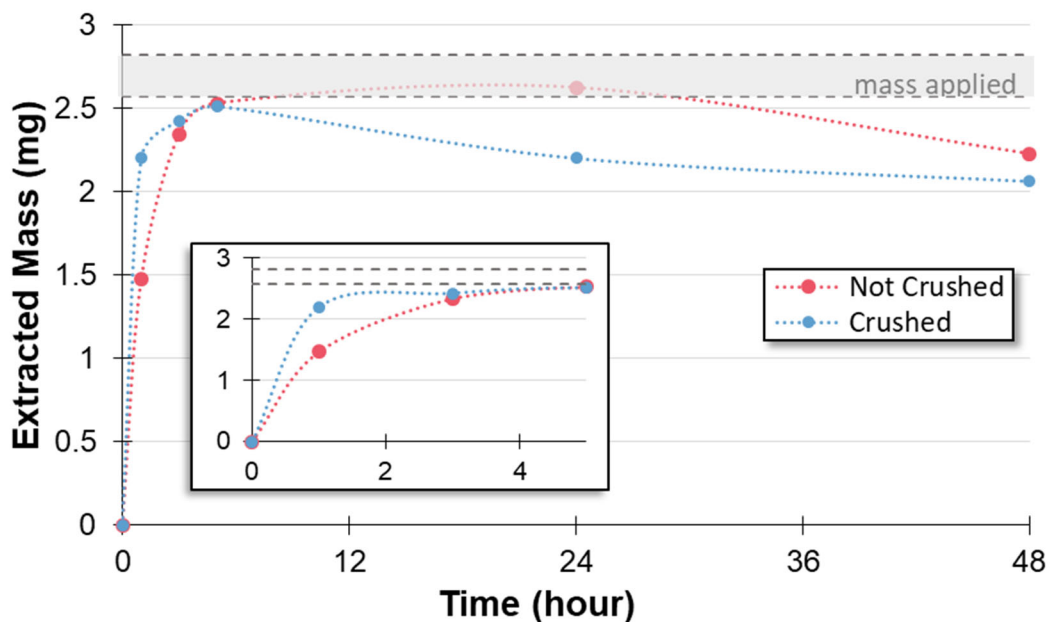
#### **Quenching Results**

- Sodium Thiosulfate and Sodium Sulfite reacted with HD on concrete.
- Some decontaminants would self-quench as the active ingredient degraded over the course of 4 hours (notably Oxone, Percarbonate, Persulfate, and Chloramine-T)
- A 4mL Saturated Sodium Thiosulfate could quench a concrete surface containing 2mL of Saturated Dichlor, HTH (High Test Hypochlorite), Persulfate, Bleach, Oxone, and Percarbonate
- A 2mL solution of 4M tetrahydrothiophene (THT) could quench a concrete surface containing 2mL of saturated Oxone, HTH, Dichlor and Persulfate.

## 2. EXTRACTION METHOD DEVELOPMENT

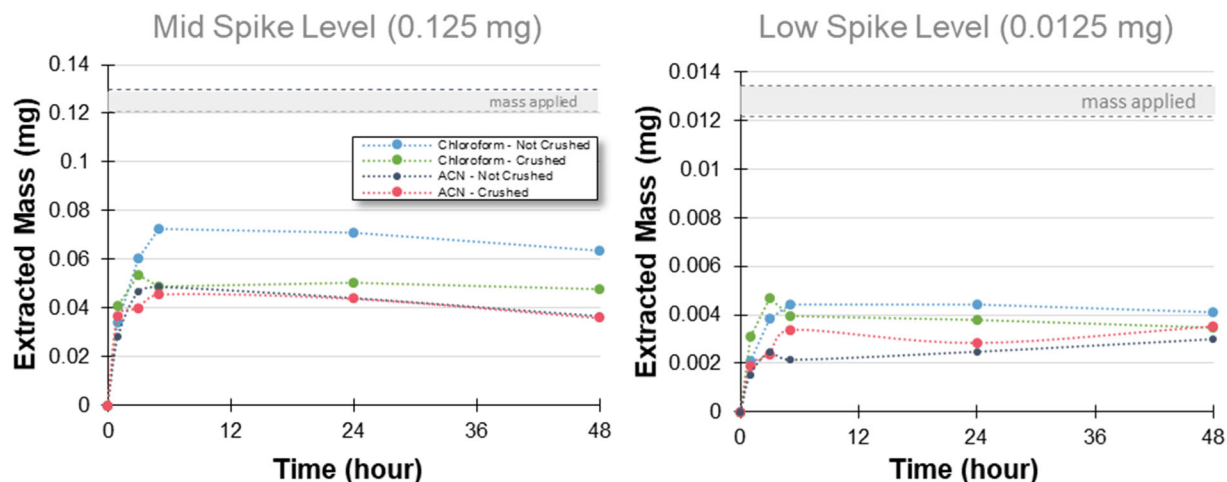
### 2.1 Extraction of HD from Concrete.

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



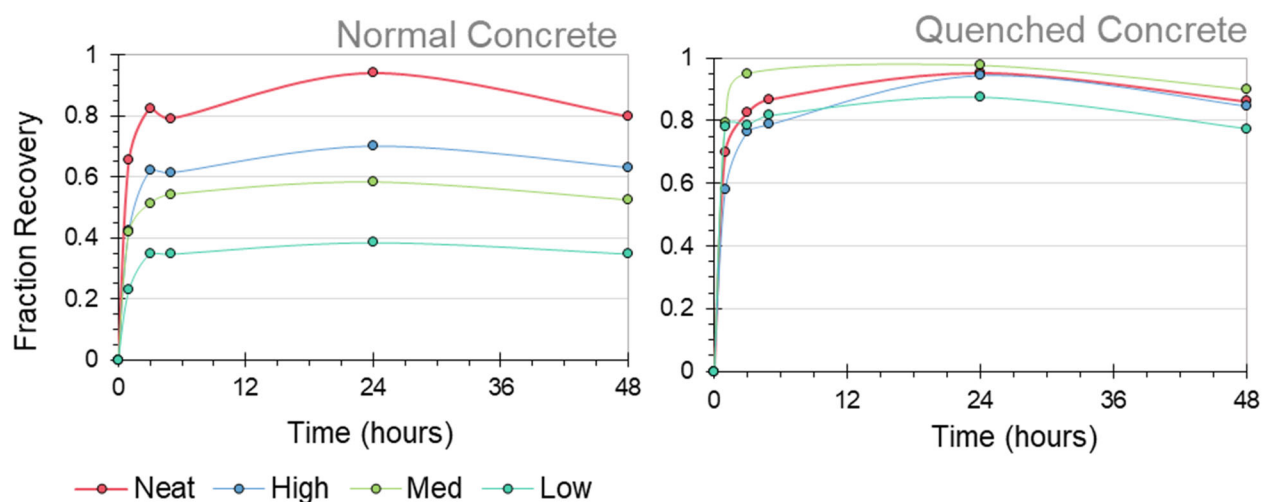
**Figure 1.** Comparison of crushed vs. non-crushed concrete for extraction of HD with  $\text{CHCl}_3$ .

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



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

In order to determine whether the poor mass recovery was a result of reactivity, an extraction efficiency test was run using quenched concrete. The quenched concrete was treated with a solution of acetic acid, so that the pH of the concrete surface was  $\sim 7$ . The quench conditions were determined by titration of a crushed concrete slurry in water with acetic acid. As shown in Figure 3, greater than 80% extraction of the quenched concrete solution was achieved after 24 hours. Recoveries were poor for the non-quenched concrete, due to reactivity during the age time. This demonstrates that HD can be reasonably extracted from a panel after 24 hours using  $\text{CHCl}_3$ .



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

## 2.2 Extraction of VX from Concrete

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

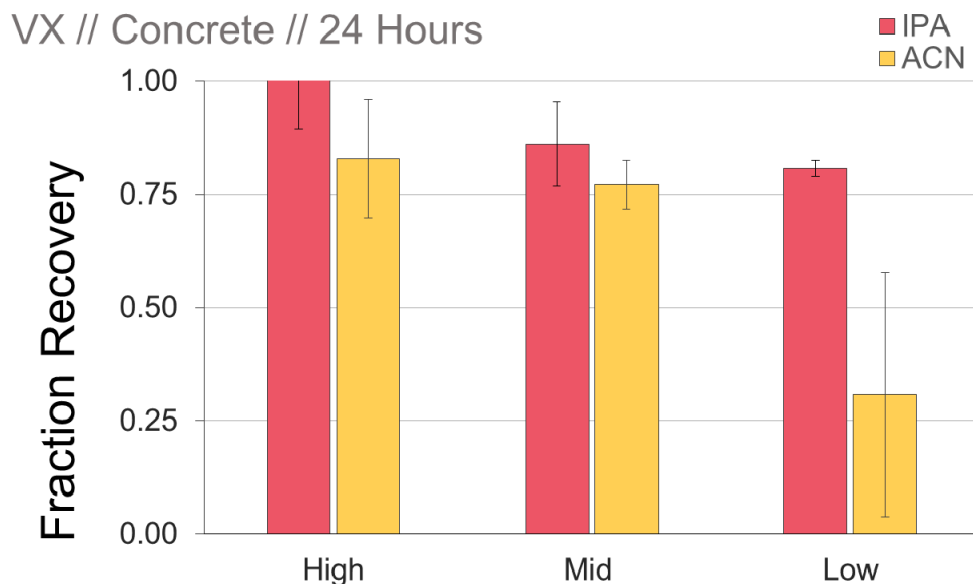
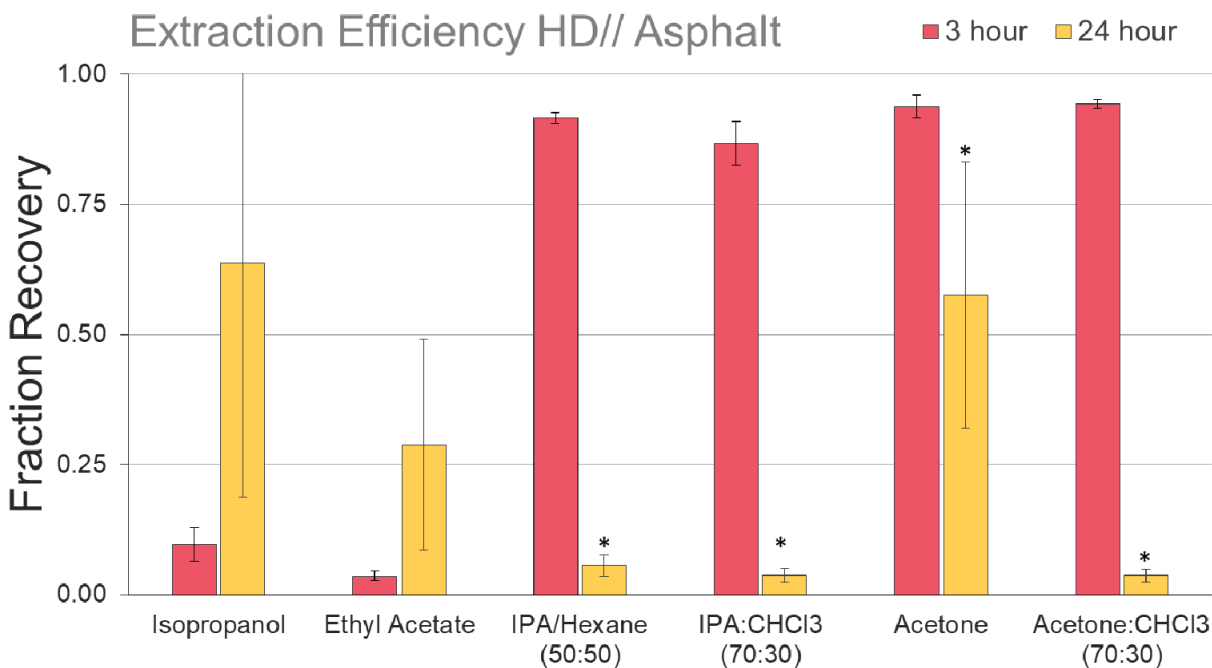


Figure 4. Extraction of VX from CSA concrete coupons.

## 2.3 Extraction of HD from Asphalt

Previous literature has demonstrated that extraction of chemical agents from asphalt is particularly troublesome. Both HD and VX are reasonably non-polar, and therefore quite soluble in the bitumen (coal tar) binder found within asphalt. Bitumen can be dissolved in non-polar organic solvents such as hexane and chloroform, but the large amount of dissolved bitumen can lead to matrix interference, injector clogging, and other analytical issues. For this reason, a broad number of extraction solvents were screened after a 2 hour aging period, using moderately non polar solvents or mixtures of polar and non-polar solvents. As shown in Figure 5, this screen identified four solvents which gave ~90% extraction efficiency after 3 hours. However, the 24 hour samples gave low responses, likely due to analytical interference from the extracted matrix. Visually, the 24 hour matrices from this mixture were sludgy, dark black mixtures that were difficult to filter and analyze. After some analytical optimization, 70/30 Acetone:CHCl<sub>3</sub> was selected as the ideal extraction solvent based on interference and additional extraction studies performed at an age time of 24 hours. This solvent mixture gave greater than 85% extraction efficiency for mid (1.0 mg) and high (6.4 mg) dose levels. Low level analysis was difficult due to evaporation of the agent. Panels were dosed with 6.4 mg of VX, aged

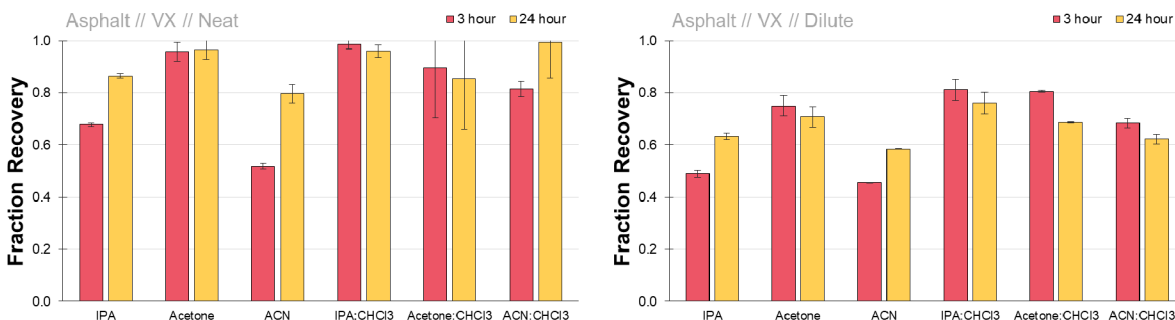
2 hours, and extracted using 20 mL of solvent. Extracted mass analyzed by aliquots after 3 hours and 24 hours.



**Figure 5.** Extraction solvent screen of HD on bitumen sheets. \* indicate likely analytical interference issues due to matrix.

## 2.4 Extraction of VX from Asphalt

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



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

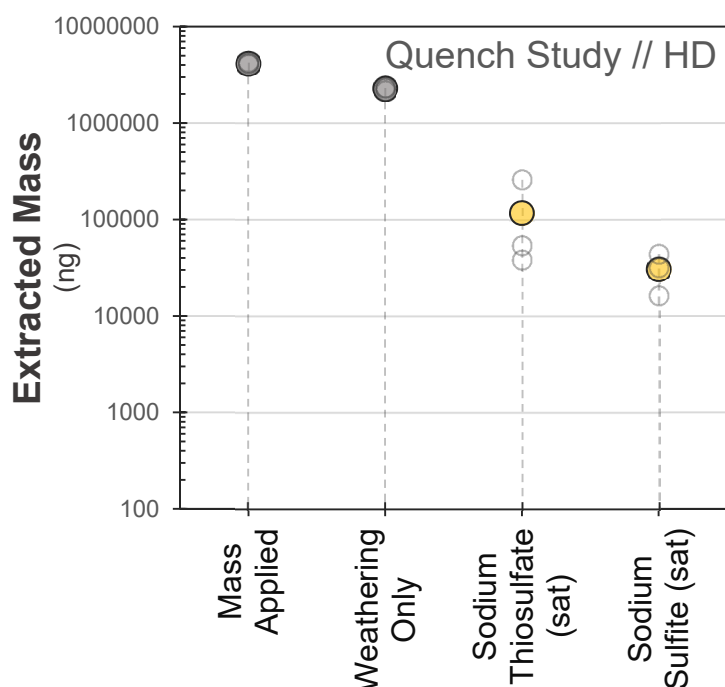
### 3. QUENCHING METHOD DEVELOPMENT

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

### 3.1 HD Quench Methodology

Quenching of bases was straightforward. KOH and Bicarbonate were neutralized using acetic acid. The concentration of acetic acid was selected based on the amount of base added to coupon, such that a 1:1 molar ratio of base to acetic acid was used.

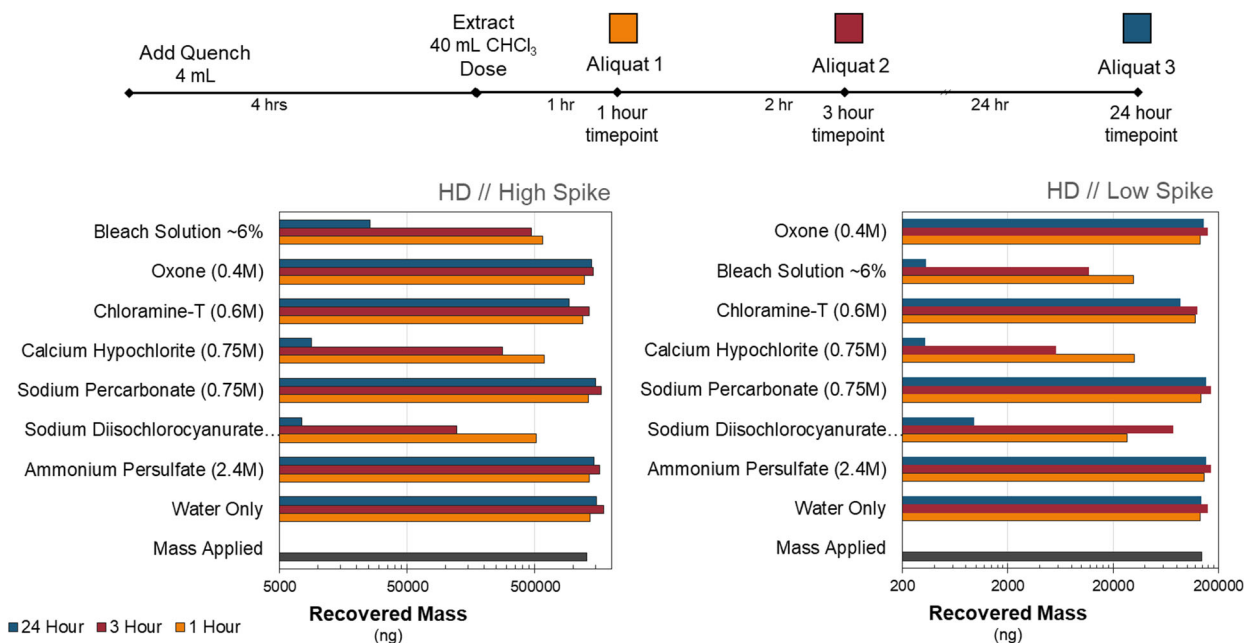
Initially, sodium thiosulfate was selected as a quench for oxidative decontaminants. This was found to effectively neutralize all of the oxidative decontaminants when added as a saturated solution. However, a review of the literature found that sodium thiosulfate could be reactive towards HD. Sodium thiosulfate not only acts as a reducing agent, but can also act as an  $\alpha$  nucleophile and react with electrophilic sites, such as the sulfonium adduct in HD. The reactivity of sodium thiosulfate with HD was confirmed experimentally. A concrete coupon was dosed with 3 $\mu$ L of HD and aged for six hours. After aging, 4mL of a saturated solution of sodium thiosulfate or sodium sulfite was added. After one hour residence time, the quench was removed and the panel was extracted with isopropanol. As shown in Figure 7, the addition of sodium thiosulfate led to a nearly order of magnitude reduction in the extracted mass. The effect was even more pronounced with sodium sulfite, giving nearly two orders reduction. This is distinct evidence that sodium thiosulfate reacts with HD in concrete.



**Figure 7.** Test for reactivity with HD with sodium thiosulfate and sodium sulfite on a concrete substrate.

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

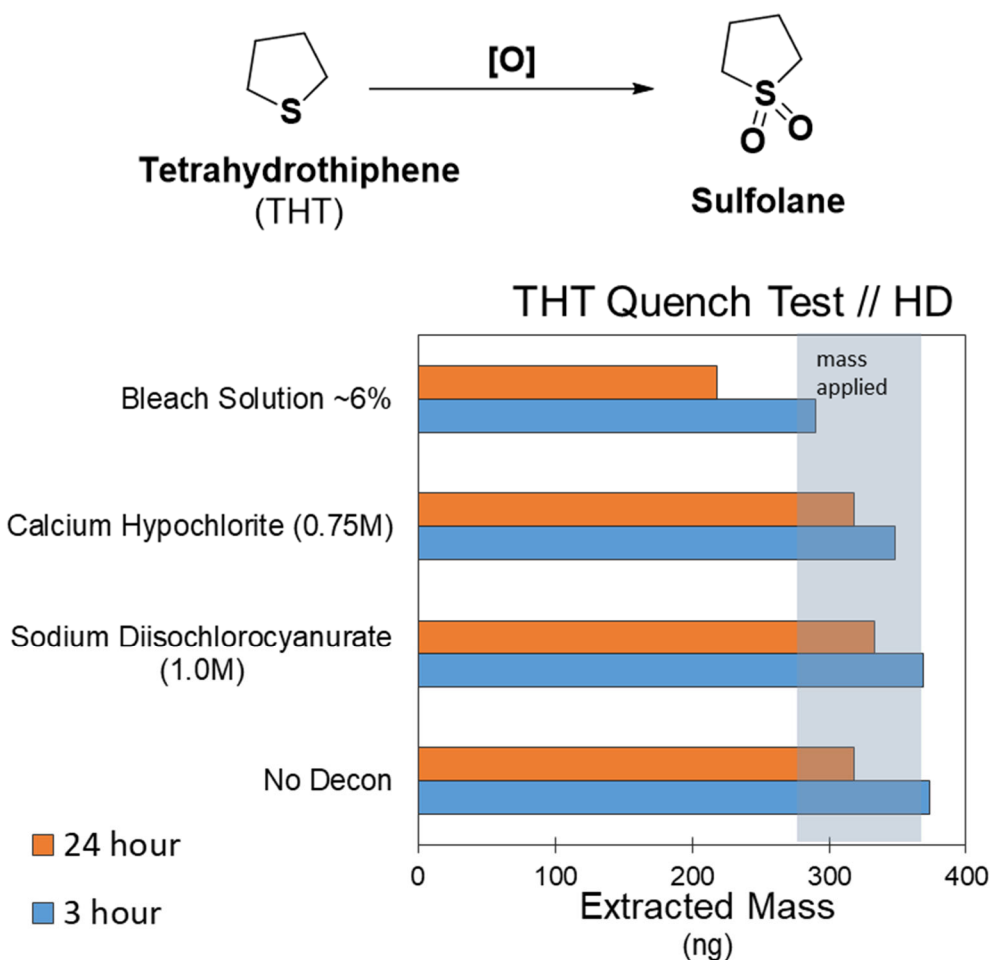
As shown in Figure 8, the panels containing Water, Ammonium Persulfate, Sodium Percarbonate, Chloramine-T and Oxone self-quenched prior to addition of the extraction solvent. The concentration in the extraction solvent remained stable over the 24 hour time period. However, Bleach, HTH, and Dichlor continued to react after the extraction solvent had been added, demonstrating that an additional quench process is needed.



**Figure 8.** Self-quench test for HD and concrete at high spike level (left) and low spike level (right).

Tetrahydrothiophene (THT) was tested as a sacrificial reductant to quench HTH, bleach and Dichlor. THT is readily oxidized to form sulfolane, a polar solvent. In a similar quench test, THT was found to effectively quench Dichlor and HTH, and had moderate efficacy at quenching bleach. Results from this study are given in Figure 9. For this study, 2mL of 4M THT were used, but later studies confirmed that 0.75mL of 7M THT also gave effective quenching. This methodology was used as the updated quench methodology for any following studies. Quench only controls were carried through subsequent studies to ensure no that the quench was reacting with the contaminant in the panel. Interference studies demonstrated that THT could be used with current analytical methods.





**Figure 9.** THT quench test. Decontaminant was quenched after 4 hours with 2 mL of 4M THT in MeOH. One hour after quench addition, solution was spiked with a dilute solution of HD and the concentration was measured after 3 hours (blue) and 24 hours (orange).

### 3.2 VX Quench Methodology

It was found that only minimal reactivity occurred between sodium thiosulfate and VX. Therefore, sodium thiosulfate was used as a quench for all VX studies. A four mL aliquot of saturated sodium thiosulfate was added to each coupon at the end of the decontaminant age time (typically 4 hours). The coupon was removed from the quenching solution (if any remained) and then was extracted using isopropanol (concrete). The extract was immediately spiked with 1mg of VX and allowed to sit in the extraction solvent for 24 hours. The post-quench mass recovered was measured after 24 hours. As shown in Figure 10, all tested configurations fell within the expected mass delivered, within error. Both HTH and KOH had evidence of some small amount of reactivity, based on EMPA detected within the extraction mixture, but this was <1% of the applied mass. Tests were only performed on concrete matrices, as decontaminant permeation was much more substantial within these matrices. If the quench was sufficient to permeate into concrete and react with any remaining oxidant, it was likely sufficient to react with decontaminants on asphalt, which showed little evidence of permeation into the material.

# VX Quench Test

## Sodium Thiosulfate

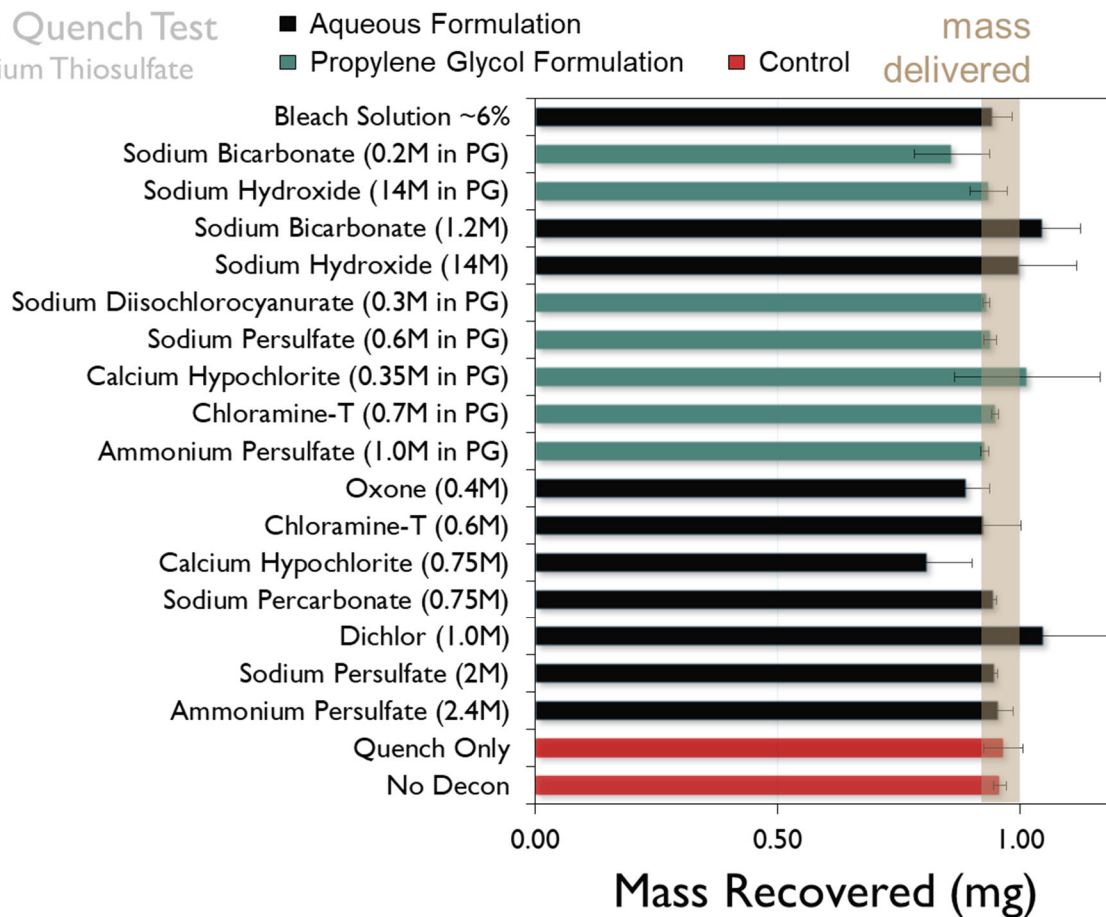


Figure 10. Quench test using VX on concrete.

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