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**Effect of Using Stabilized VX on
Measurement of Agent Retention and
Decontamination Performance for Materials**

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PREFACE

The work described in this report was authorized under project number CB10409. This work was started in June 2018 and completed in September 2018.

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This report has been approved for public release.

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EFFECT OF USING STABILIZED VX ON MEASUREMENT OF AGENT RETENTION AND DECONTAMINATION PERFORMANCE FOR MATERIALS

1. PROJECT BACKGROUND AND OBJECTIVE

1.1 Introduction

There is a need to understand and predict how decontamination technologies will work on real assets in the field when contaminated with actual chemical weapons (i.e., not refined laboratory grade agents). Historical program results have shown the importance of accounting for agent purity and degradation in assessments of decontamination efficacy, especially for absorptive materials. Impurities in specific agent solutions can influence decontamination performance and potential exposure to personnel compared with high-purity agent, especially for materials susceptible to contaminant absorption. As an example, different vials of chemical agent standard analytical reference material (CASARM) and as-received munitions grade pinacolyl methyl phosphonofluoridate, bis-(2-chloroethyl) sulfide, and 2-(diisopropylamino)ethyl-*O*-ethyl methylphosphonothioate (VX) agents were used to contaminate the surfaces of aluminum and stainless steel, a polyurethane-based coating, and a silicone elastomeric material. A decontamination treatment using bleach was then applied to survey the effect of the agent purity on the measured decontamination performance relative to a soapy water immersion as a reference condition. Measurements of retained agent (RA) as a function of agent purity, material, and decontaminant treatment, as well as multi-touch contact transfer assessments, were used to evaluate agent purity influences in determining decontaminant performance evaluations.¹

In previous tests,² it was shown that the degree and types of interactions between a contaminant liquid and a surface can vary significantly as a function of the specific chemical composition of the liquid, and these interactions ultimately play a role in overall agent retention in the contaminated material. For example, when VX was deposited on impermeable surfaces at different temperatures, it underwent varying spreading behavior as a function of the specific composition of the liquid. As temperature increased, unstabilized VX degraded ($> \sim 35$ °C), and changes in the droplet shape indicated a change in the chemical composition. At elevated temperatures for 24 h, the droplet was no longer VX.² The degradation of VX was found to be sensitive to the concentrations of specific impurities in the original liquid droplet.

The principal focus of the study presented in this report was to determine the influence of a specific stabilizer for chemical warfare agents (CWAs), *N,N'*-diisopropylcarbodiimide (DICDI), on the decontamination efficacy measurements for VX that include a comparison of the results to measurements that were performed using CASARM grade agent. According to the *Military Specification, Chemical Agent, VX* (November 1964),³ the addition of DICDI to CASARM VX is used to prevent rapid degradation in storage.⁴ However, the vast majority of past work on decontamination evaluations involving agents like VX were performed using CASARM-grade sources. Brozena et al. characterized the temperature-resolved properties of DICDI.⁵ When stabilized agent is tested, factors such as how the addition of a stabilizer will affect measured decontaminant performance and how high temperatures will affect

the agent degradation rate need to be considered. In this study, as a complement to past work on nonrefined agent solutions and the spreading behavior of VX as a function of specific impurities, we aim to resolve the overall impact of the addition of a stabilizer to CASARM VX on RA measurements for military relevant materials.

1.2 Background

In the presence of water or acids, VX reacts to form ethyl methylphosphonic acid (EMPA) and a thiol. Over time, VX will react with the formed EMPA and generate VX-pyro, which will then react with the available water and degrade into two EMPA molecules.⁶ This reaction will then continue and speed up the degradation process in VX over time. Studies have shown that a 94.9% pure VX sample that was stored at 35 °C for over 3 weeks resulted in an increase of EMPA levels by 77% and a decrease in the purity of VX to 92.1%.⁷ However, the presence of DICDI in VX inhibited this autocatalytic reaction and acted as a scavenger for moisture and acids, which conceptually decreased the rate of VX degradation in storage. An important finding was that the DICDI inhibitor decomposed in the presence of water (i.e., acted as a scavenger) to form urea crystals but did not readily decompose in the absence of water (e.g., when the agent was in sealed storage).⁴

The overall objective of this work was to determine the degree to which CASARM VX with the addition of stabilizer DICDI and possibly sulfur (S) impacted decontaminant performance in CWA research studies. This report focuses on the effect of the stabilizer on CASARM VX in an evaluation of decontamination performance and the potential exposure to personnel, as compared with work performed using unstabilized VX. This type of work is especially relevant to any high-temperature testing, such as chemical hot air decontamination, where high temperatures are used to accelerate evaporation. For example, if the stabilizer inhibits agent degradation, the test results could vary significantly depending on whether stabilized or unstabilized agents were used. Additionally, researchers performing previous test programs have observed that VX rapidly degrades in its storage container (i.e., vial). Because the degradation may not have been observed before a given test, some test sessions have had to be repeated with “new” VX agent. If the stabilizer did not influence decontaminant performance, the stock agent could be stabilized to prevent the degradation of the agent and minimize the need for retesting. As a last perspective, if VX were used in the field, it would likely be stabilized. Therefore, this report also addresses whether the use of nonstabilized VX for testing would bias the decontamination results and cause an over- or underestimation of decontaminant performance or exposure potential.

2. MATERIALS, PROCESSES, AND METHODS

In this study, CASARM VX was used alone, mixed with DICDI (2.5%), and as a mixture with DICDI (2.5%) and sulfur (0.25%). (All percentages were calculated by weight.) The three solutions were created using a singular CASARM VX lot and purity that are listed in Table 1. Interference studies were performed to provide sample preparation requirements to confidently analyze contaminant–material–decontaminant interactions during panel studies.

Table 1. Purity and Grade for Agent Used as Stock to Create the Stabilized Testing Solutions

Agent	Vial No.	Purity (%)	Grade
VX	U-7165	94.2	CASARM

Three ampoules of VX-U-7165-CTF-N were combined in a tared 7 mL screw cap vial, and the weight was recorded (5.981 g). One 950 μ L aliquot was removed and transferred to a tared 4 mL vial, and the weight was recorded (1.902 g). This new item was identified with a vial number and referred to as CASARM VX for this study.

Next, 127.5 μ L of DICDI (99%, Sigma-Aldrich Company [St. Louis, MO], lot WXBC3897V) was added to the remaining VX (4.065 g), and the weight was recorded (4.164 g). One 950 μ L aliquot of this mixture was removed and transferred to a tared 4 mL vial, and the weight was recorded (1.895 g). This new item was identified with a vial number, recorded as containing 2.4 wt % DICDI, and referred to as VX+DICDI for this study.

Then, 5.62 mg of S (powder, 99.98%, Sigma-Aldrich, batch no. 11325MI) was added to a tared 4 mL vial. The remaining VX+DICDI was transferred to the vial, and the weight was recorded (2.209 g). This new item, which contained 2.4 wt % DICDI and 0.25 wt % S, was identified with a vial number and was referred as VX+DICDI+S for this study.

Three different materials were used, including impermeable materials (bare metals), permeable polymers (silicone), and a polyurethane coating material. The contamination of materials involved delivery of one 2 μ L droplet of agent (~ 1 g/m² contamination density) that was deposited at either 20 or 50 $^{\circ}$ C, with a subsequent droplet dwell (age) time on the material of 60 or 1440 min at the appropriate temperature. The rationale behind the extended dwell time stems from past results that showed evidence of evaporation or agent degradation at higher temperatures and extended dwell times. Further details on the handling of materials, as well as the methods employed for evaluation of RA in materials, were published by Lalain et al., (2011).⁸

Three different, representative decontamination processes were performed, including soapy water immersion, $\sim 6\%$ bleach, and a weathering condition, for evaluation of agent retention in polymeric materials as a function of agent type. The soapy water immersion treatment served as a baseline condition for removal of surface-bound agent with minimal extraction of absorbed agent. The bleach condition represented a typical reactive decontaminant. Both of these processes are depicted in Figure 1. The weathering condition (Figure 2), which is an extraction with no treatment, represented the amount of agent that was present at the start of the decontamination process.

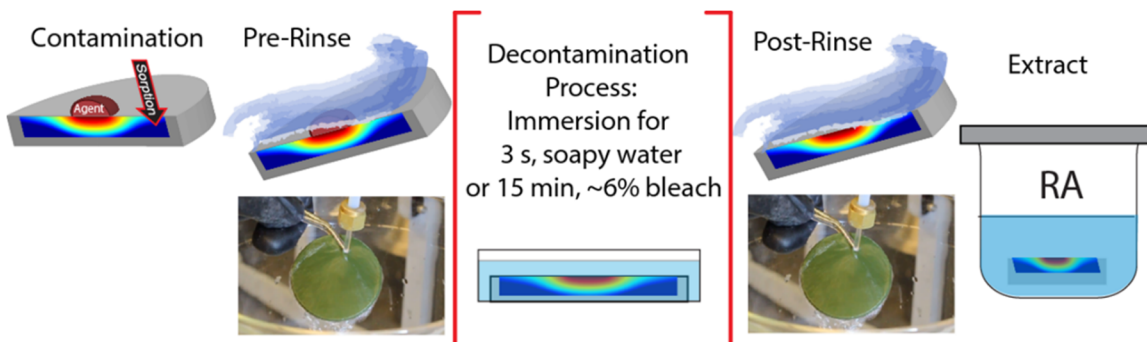


Figure 1. Process used for measurement of RA after soapy water or bleach treatments.

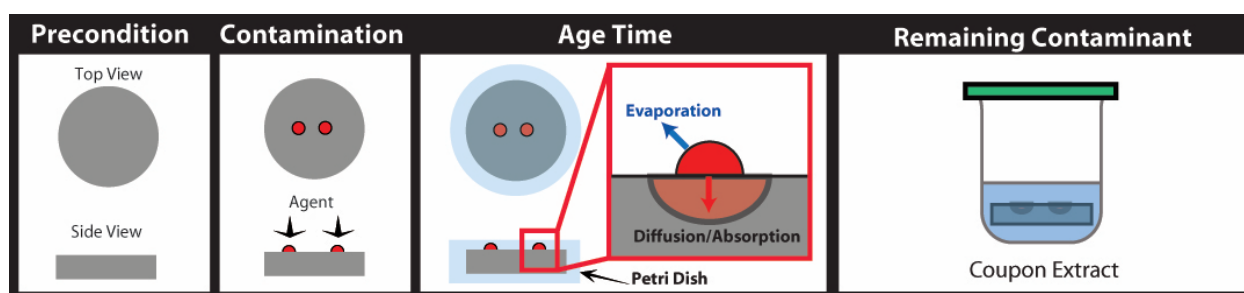


Figure 2. Process used for measuring RA after weathering.

All extractions were performed for 1 h in isopropyl alcohol that was aliquoted into an analytical vial and analyzed using liquid chromatography (LC) as a function of analyte for an RA evaluation. Extraction solution samples were quantified using LC with a mass spectrometer (Agilent Technologies [Santa Clara, CA] 1200/1290 series LC and Applied Biosystems [Carlsbad, CA] API5000/5500 triple-quadrupole mass spectrometer equipped with a TurboV ion source). Details on the use of chromatography platforms have been published by Shue et al., 2011.⁹ The test parameters are listed in Table 2.

Table 2. Overall Test Parameters

Setting	Values
Contaminants	CASARM VX, VX+DICDI, VX+DICDI+S
Contamination	One 2 μ L droplet each
Materials	Polyurethane paint, silicone elastomer, or impermeable metal (steel)
Dwell Time (min)	60 or 1440
Treatment	Weathering, soapy water immersion, or ~6% bleach
Replicates	Three
Environment	20 or 50 $^{\circ}$ C \pm 35% RH
Measurement	RA

3. RESULTS

3.1 Dose-Confirmation Samples (DCSs)

The decontamination test methodology indicates that the metric of starting challenge is defined as grams of liquid per square meter of material.⁸ DCSs quantify how much analyte is delivered to the panels. DCSs were collected to observe the impact of the addition of DICDI or DICDI+S on the distribution of VX and its byproducts at the same dosing volume.

A log difference (LD) calculation was used to compare the RA results, as defined by

$$LD = \log_{10} \frac{RA_{\text{test}}}{RA_{\text{reference}}} = \overline{\log_{10}(RA_{\text{test}})} - \overline{\log_{10}(RA_{\text{reference}})} \quad (1)$$

where

RA_{test} is mass measurement for test condition (ng); and

$RA_{\text{reference}}$ is mass measurement for reference condition (ng).

The details of the LD calculations are provided as Procedure 5 of the *Test Methodology Source Document*, and the error bars that were calculated from these results provided the 95% confidence interval on the difference.⁸ The LD was calculated across the agent types (CASARM VX served as the reference) using the mass from the DCS measurement. This research study took 3 days of testing over a 9 day period. DCSs were taken for each test to verify the dose distribution for each agent type and test day. Figure 3 shows the final mass of the five DCS samples taken for each agent type on each test day, along with an LD analysis comparing the two agent types with DICDI stabilizer to CASARM VX (without stabilizer). Although there were differences in the distribution of VX across the three agent types during some of the test days, the differences were relatively small in magnitude (i.e., <0.06 LD with respect to CASARM VX), which was not a significant difference in dosing distribution. The addition of DICDI or DICDI+S did not have a large impact on VX distribution at the same dosing amount (2 μL). Therefore, we can consider the quantity of VX delivered to each sample to be similar for all agent types across all the test days.

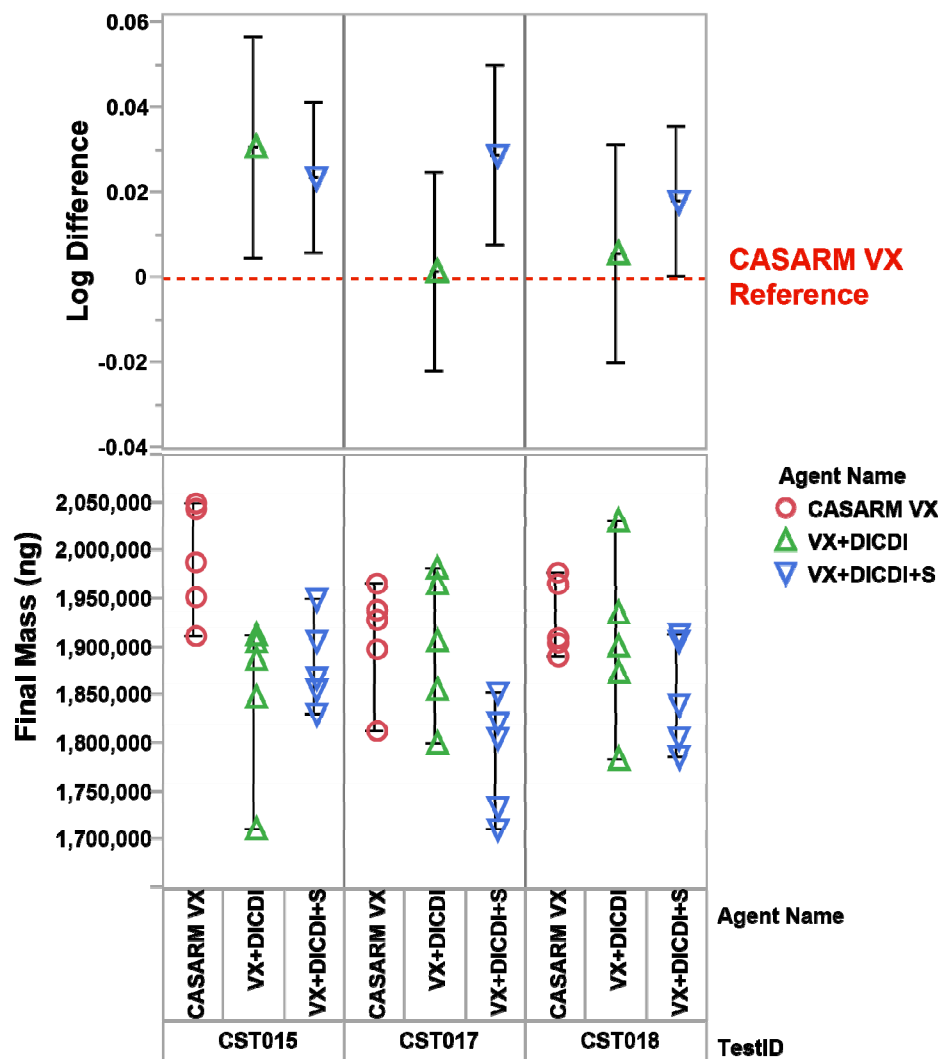


Figure 3. DCS samples taken across test days for three variations in the stability of VX. Error bars for LD indicate the 95% confidence interval on the difference.

VX solutions can contain many analytes and impurities.¹ The analytical methodology used in this study also tracks EA 2192 and EMPA. These two analytes are often responsible for the autocatalytic destruction of VX. Figure 4 shows the EMPA production for the three agent types. Although there was a difference in EMPA byproduct formation between agent types in comparison with the CASARM VX, the scale of these differences was too small to truly impact the distribution. EA 2192 was measured at or below the limit of quantification (0.66 ng/mL) for all three agent types on each day of testing. There were no differences in the byproduct distribution of EA 2192.

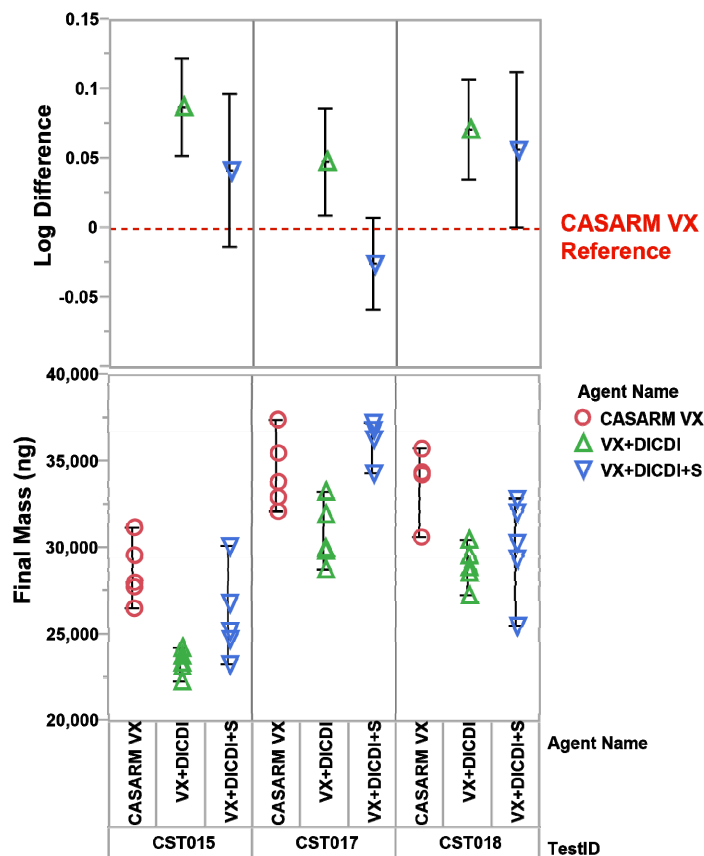


Figure 4. EMPA DCS results. Error bars for LD indicate the 95% confidence interval on the difference.

The addition of DICDI and S did not seem to alter the production of the byproducts or the distribution of VX, which verified that the distributions were considered comparable for this research study.

3.2 Liquid Spreading Results

Photography was used to capture any influences from the DICDI stabilizer and S on the liquid-spreading behavior of agent on impermeable and permeable materials. In all the cases, there was little-to-no variation in spread behavior between the three agent types for a given material. Figure 5 shows the results for sorptive materials (polyurethane coating and silicone), and Figure 6 shows the results for impermeable metal substrates (stainless steel).

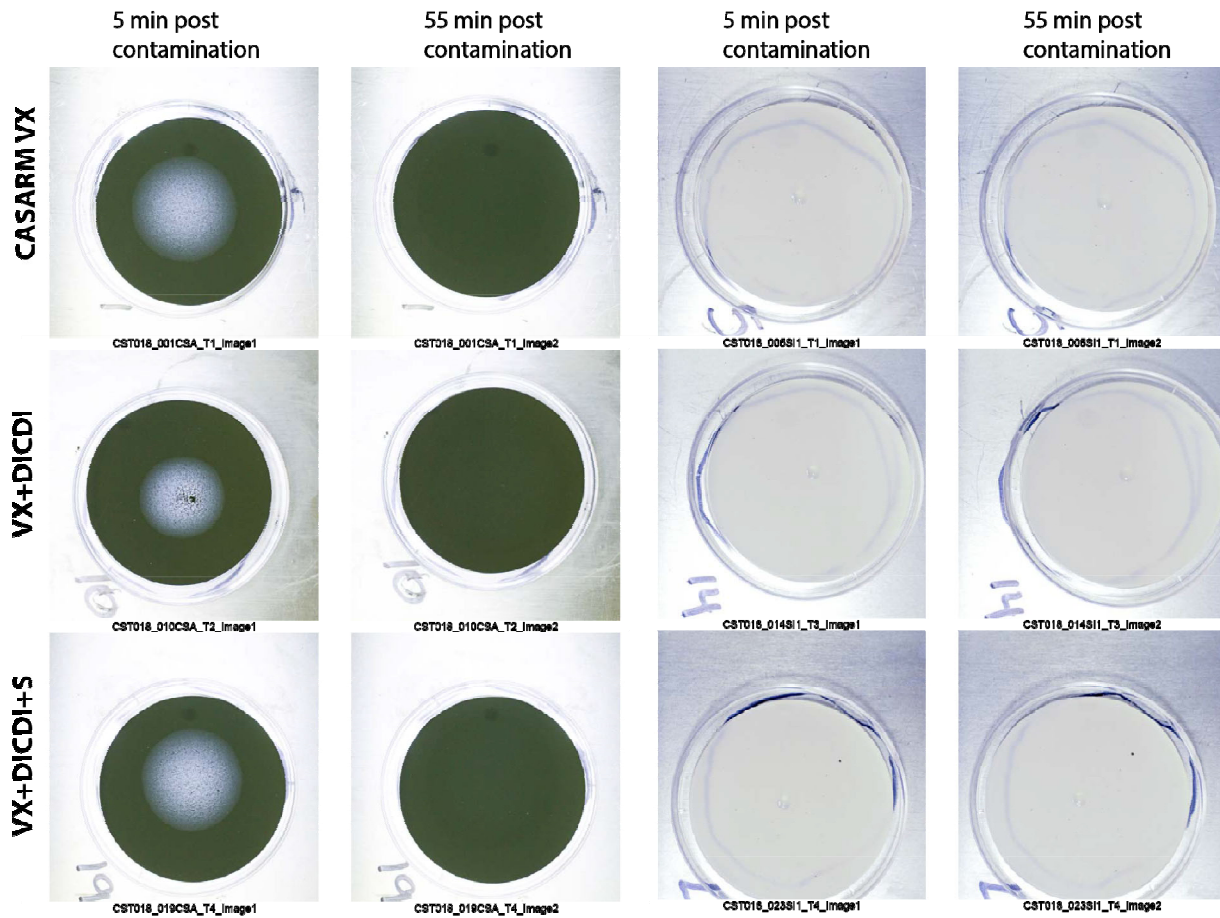


Figure 5. Photography of droplet spreading on polyurethane coating and silicone substrates. Comparison between 5 and 55 min after deposition shows no significant agent type-specific behavior within a given substrate material.

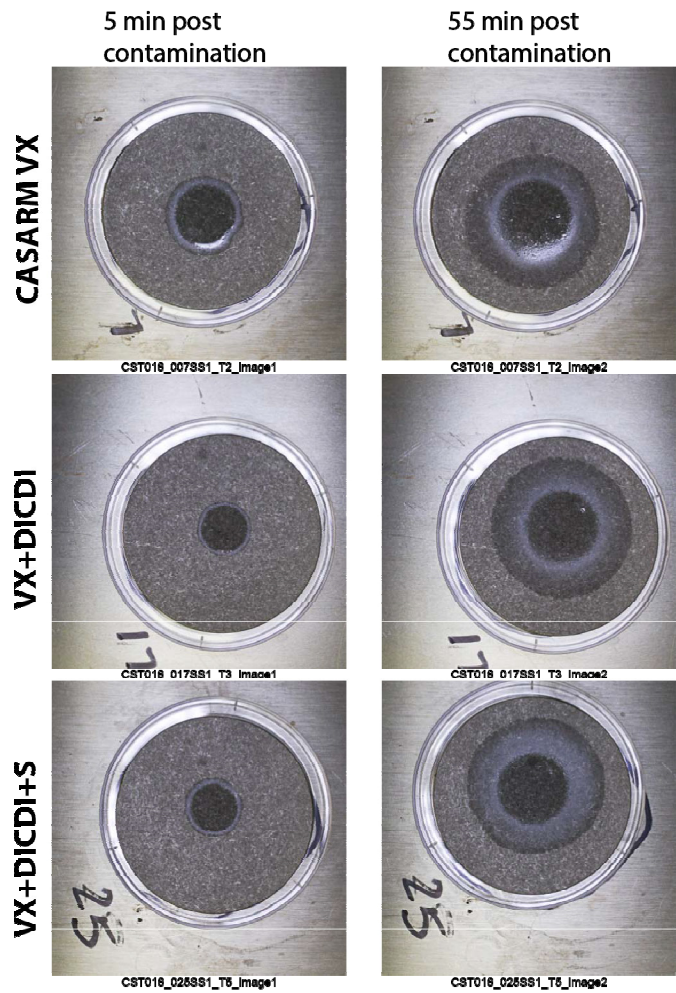


Figure 6. Photography of droplet spreading on a stainless steel paint coating. Comparison between 5 and 55 min after deposition shows no significant agent purity-specific behavior within a given substrate material.

3.3 RA Measurements

RA measurements are simple, robust indicators of possible agent vapor and contact source terms that are presented by contaminated material because those source terms are directly dependent on the mass of chemical retained by a material. If there are variations in RA due to the introduction of DICDI stabilizer, the vapor and contact source terms are likely to be different as well.

The soapy water immersion technique removes bulk contaminant from the surface of materials with minimal disruption to the absorbed agent. This process provides a baseline for the amount of agent retained by materials, which essentially represents the decontamination challenge. To verify whether the addition of DICDI stabilizer has an effect on agent retention in materials, a study was performed using a 60 min agent residence time at 50 °C. Conducting the

measurements at an elevated temperature provided the greatest opportunity to observe an effect of stabilizer inclusion.

The RA and LD results for impermeable metal substrates are shown in Figure 7. The DICDI stabilizer or S had no influence on RA, as shown in the similar results from all three agent solutions; in other words, the spread in LD included zero with CASARM VX as the reference condition. This indicated that the addition of a stabilizer to the agent did not alter (i.e., strengthen or weaken) the chemical interactions that dictated the adhesion of the agent to the metal surface.

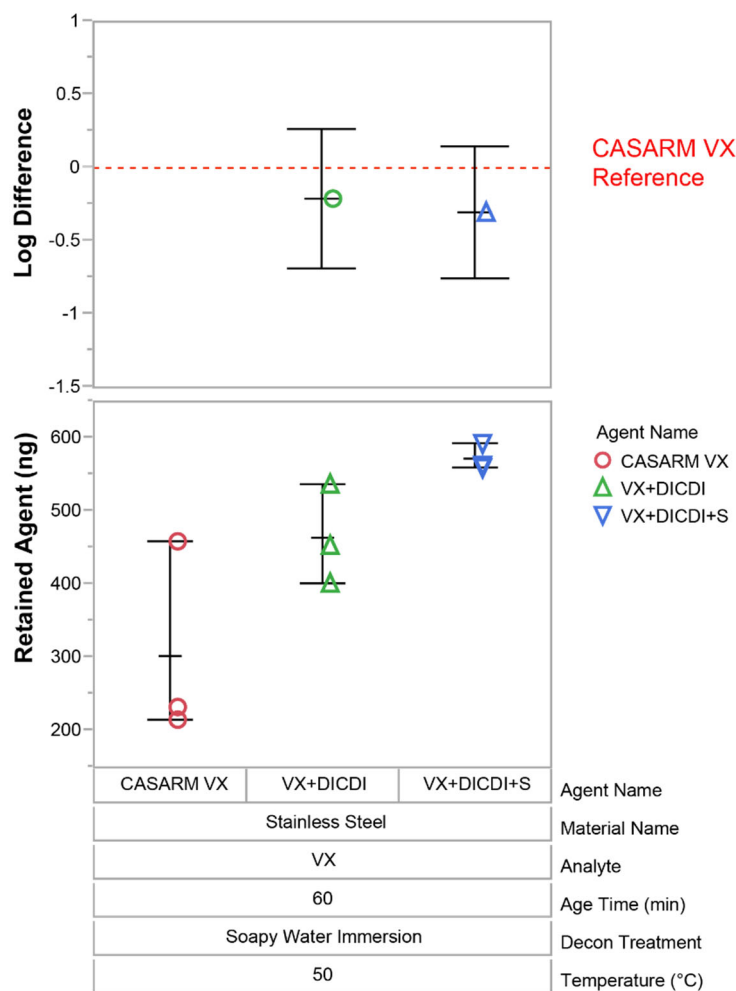


Figure 7. RA results for impermeable, metal substrates, including the LD for soapy water treatments. Error bars for LD indicate the 95% confidence interval on the difference.

Figure 8 presents the RA results for contamination of absorptive, polymeric materials. The only case where there was a statistically significant difference in RA relative to CASARM VX (i.e., spread in LD did not include zero) was for VX+DICDI+S on the polyurethane coating. However, the magnitude of the difference was relatively small (<0.1 LD), and it can be reasonably assumed that this agent type was still comparable to the other tested

agent types with respect to agent retention. Essentially, the DICDI stabilizer did not have an impact on agent retention in these two different polymeric materials.

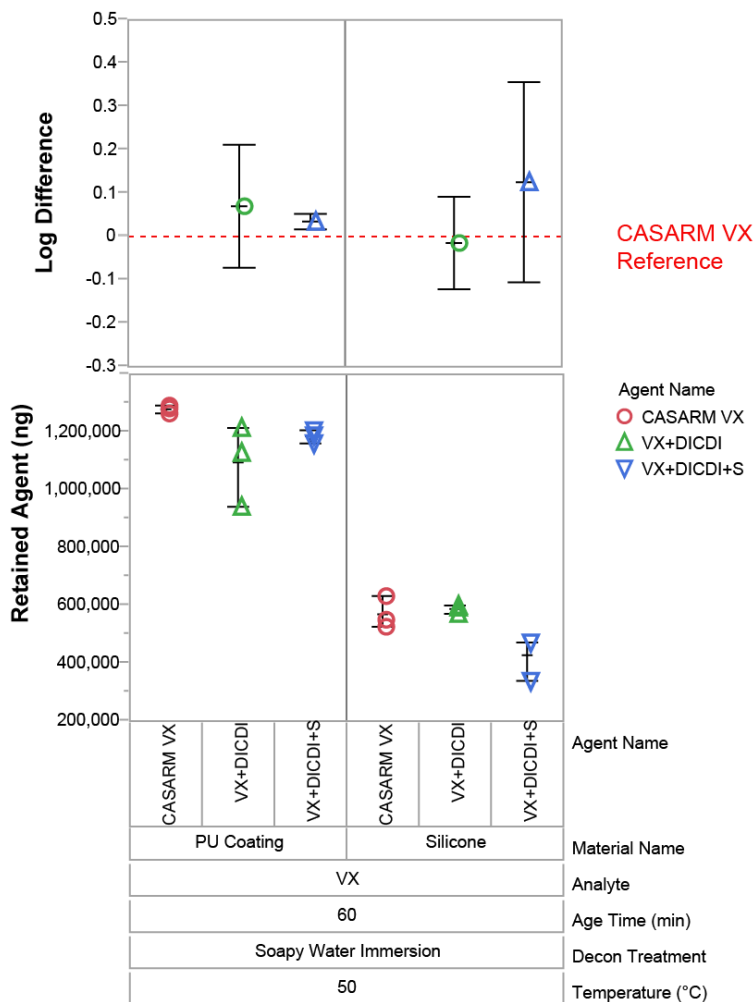


Figure 8. RA results for two different polymeric materials, i.e., polyurethane paint and silicone elastomer, including the LD for soapy water treatments. Error bars for LD indicate the 95% confidence interval on the difference.

One of the primary objectives of this analysis was to determine if the addition of DICDI stabilizer to CASARM VX would impact the agent retention in materials during testing. The results in Figures 7 and 8 demonstrate that *both the absolute values of the RA and the LD for comparisons of stabilized VX relative to CASARM VX were unaffected by the addition of DICDI or S.*

3.4 Decontaminant Relative Performance

The addition of DICDI to CASARM VX could extend the shelf-life of stored VX. However, stabilized CASARM VX is used, the decontamination performance measurements should not be biased by the inclusion of a stabilizer. RA testing was performed at 50 °C using a 60 min contaminant dwell time, along with 20 and 50 °C studies performed using a 1440 min (24 h) contaminant dwell time. The RA study at the shorter dwell time involved both permeable and impermeable materials. However, the silicone material was not tested during the extended dwell time studies due to challenges encountered while extracting the VX from silicone after extended contamination durations (e.g., after 24 h). The data for the extended dwell time focused on the testing of polyurethane coating and steel materials.

3.4.1 RA: 60 min Contamination Duration

RA and LD data for the 60 min contaminant dwell time at 50 °C on the impermeable stainless steel are shown in Figure 9. LD data show the comparison between the decontamination processes of soapy water immersion versus bleach. The results indicate that for each agent type, bleach removed more agent from the material surface compared with soapy water immersion. The decontaminant treatments performed similarly for both the CASARM VX and VX+DICDI+S. The bleach-treated panels dosed with VX+DICDI showed a significant decrease in RA on the impermeable surface. The results for bleach, as compared with the reference soapy water immersion for contamination with VX+DICDI, had an LD greater than 2, and the bleach condition for the other two agent types (CASRM VX and VX+DICDI+S) had an LD of ~1. Other than this one case, there was no significant difference in decontaminant relative performance between agent types for impermeable stainless steel. Although the LD calculation for the case of VX+DICDI on stainless steel was larger than that of the other combinations, this was because of the very low absolute magnitude of RA (~3 ng) for the bleach test. This was statistically significant, but the differences between the absolute magnitudes of the RA for bleach decontamination across the agent types were not remarkably different (~30 vs ~3 ng).

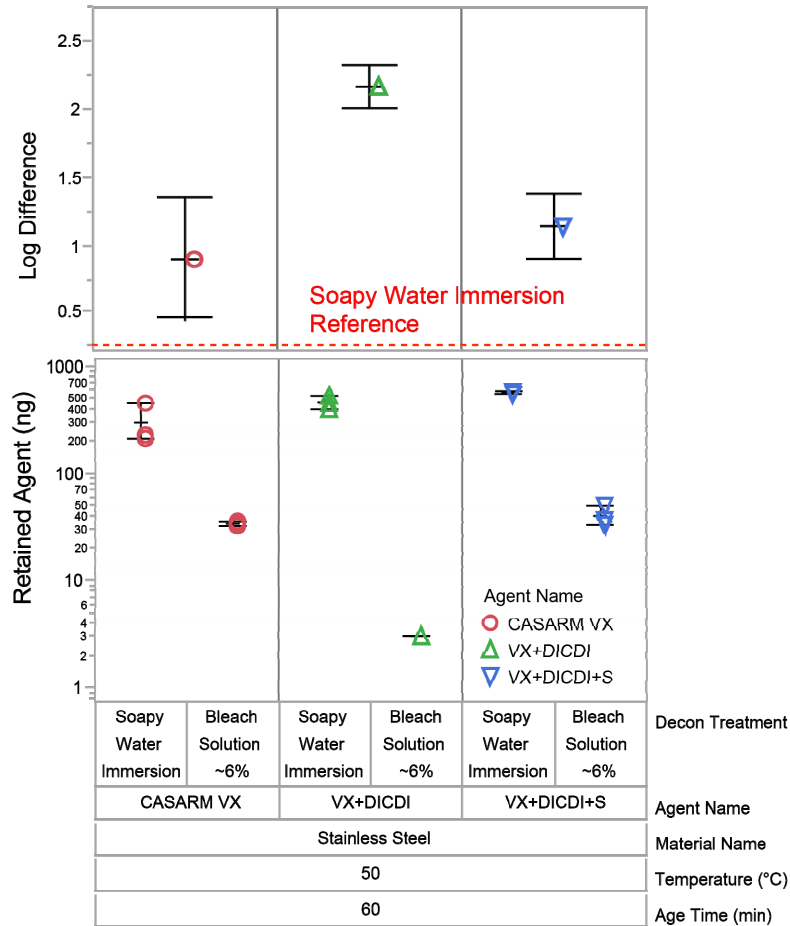


Figure 9. RA results for stainless steel at 50 °C with a 60 min contaminant dwell time after soapy water immersion and bleach decontaminant treatments. Error bars for LD indicate the 95% confidence interval on the difference.

Figure 10 shows the RA data gathered from the polyurethane coating and silicone materials after a 60 min contaminant dwell time at 50 °C and subsequent decontamination. Soapy water immersion was used as the reference condition for the LD calculation. Within each material and across agent types, the bleach decontamination method reduced the amount of RA in the material as compared with the soapy water reference treatment. The reduction in RA was also consistent across agent types. *The addition of DICDI and S did not negatively or positively impact the measured decontamination performance and absolute value of RA for these materials.*

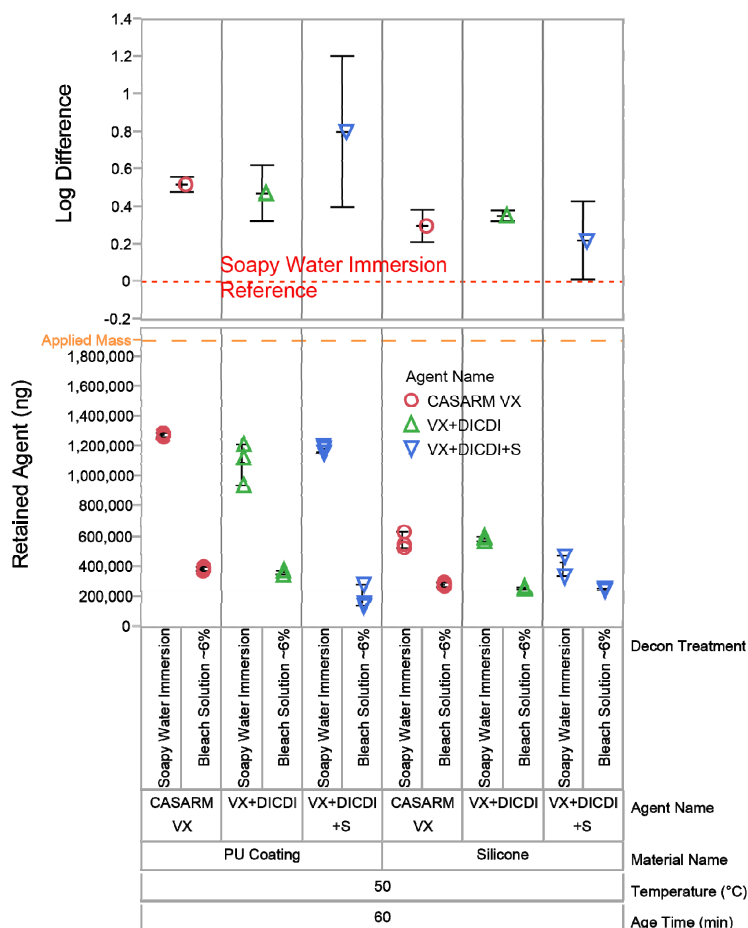


Figure 10. RA results for polyurethane coating and silicone at 50 °C with a 60 min contaminant dwell time after soapy water immersion and bleach decontaminant treatments. Error bars for LD indicate the 95% confidence interval on the difference.

3.4.2 RA: 24 h Dwell Time Study

Previous research studies on unstabilized VX showed that degradation or evaporation of the VX analyte occurred at elevated temperatures.² Weathering controls (extraction performed immediately after a 24 h contaminant dwell time with no further treatment) were added to the 1440 min study to account for VX loss due to higher temperatures and degradation over time. The weathering controls show how much VX remains on or in a material after 24 h at 20 and 50 °C across agent types. The purpose of these controls was to establish whether the addition of DICDI and S impact the evaporation or degradation rate of VX.

Figures 11 and 12 show RA measurements from weathering for 24 h at 20 and 50 °C compared with the DCS samples (applied mass) on the impermeable stainless steel (designated SS1) and the polyurethane coating material (designated PU). The change in detected mass of VX between the DCS samples and RA indicate agent mass loss due to evaporation and degradation. For both materials, all agent types resulted in similar changes in RA after weathering; the addition of a stabilizer did not influence the disappearance of VX over 24 h.

Temperature, did play a major role in RA over 24 h. After a 24 h contaminant dwell time at 20 °C, stainless steel materials showed an average reduction in starting challenge of 43% across agent types. The contaminated polyurethane coating material at 20 °C over 24 h of weathering showed an average of 26% reduction in starting challenge across agent types. The 50 °C studies showed a >2 log reduction ($\geq 99\%$) in applied agent mass from evaporation or degradation after 24 h of weathering at the set temperature. This occurred across all agent and material types. These results indicate that elevated temperatures acted as an effective decontaminant for VX-contaminated materials, regardless of the presence of the DICDI stabilizer. These data also provide us with the level of contaminant on materials before the start of the prospective decontamination treatments. In this case, materials tested at 20 °C retained 300× more contaminant mass than did those tested at 50 °C before decontaminant treatments were applied, or alternatively, 99.9% of the agent was gone when the decontaminant was applied.

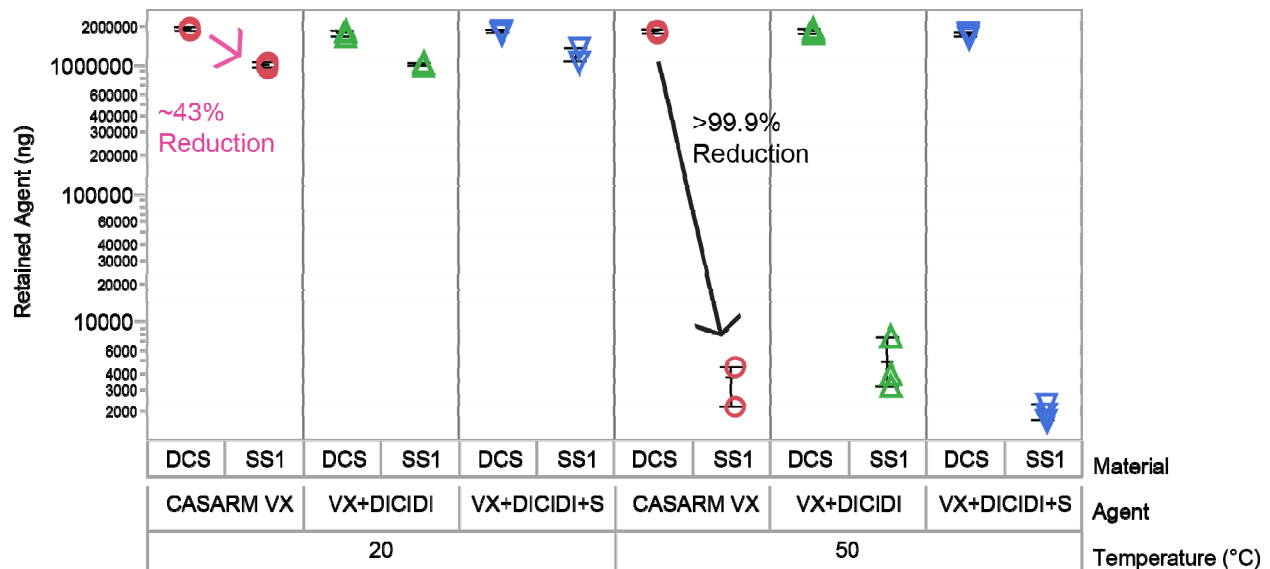


Figure 11. VX mass recovered from steel after 24 h compared to mass applied (i.e., DCS).

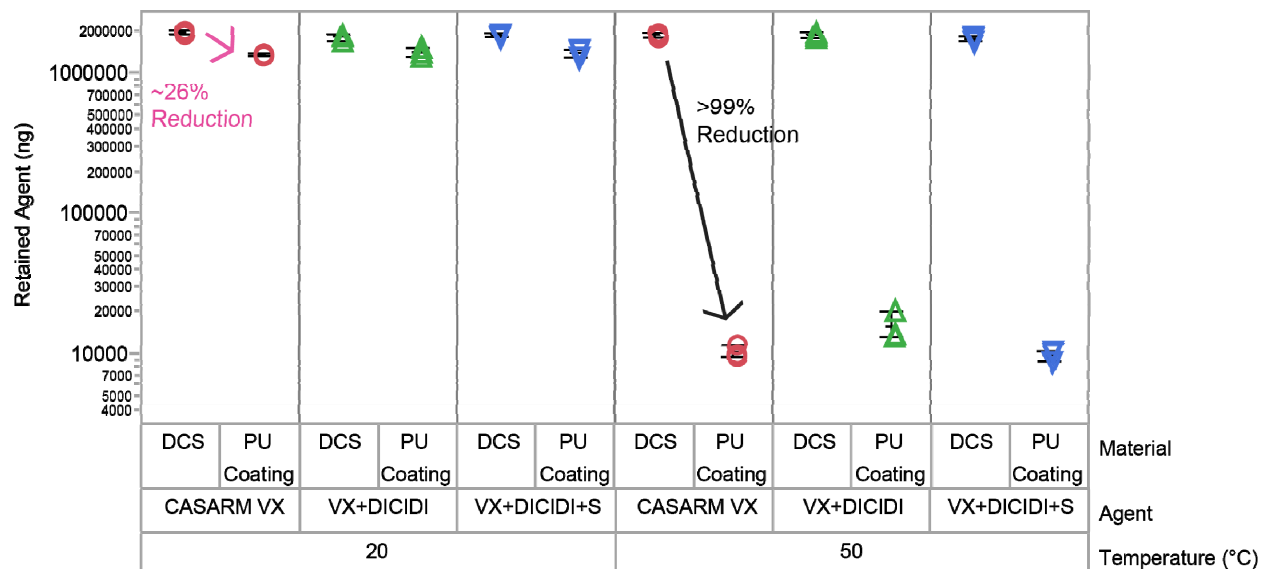


Figure 12. VX mass recovered from polyurethane coating after 24 h compared to mass applied (i.e., DCS).

Figures 13 and 14 depict the weathering and decontamination treatment results for stainless steel and the polyurethane coating material, respectively, at 20 °C. After a 24 h contaminant dwell time, the bulk of contaminant was removed from the surface of materials using a soapy water treatment, whereas a larger percentage of contaminant was removed using bleach across both material types. There was no measurable impact on decontaminant performance due to the addition of DICDI stabilizer or S. All the agent types showed similar data after the use of decontamination treatments, which implied that DICDI and S could be used for CWA research studies without biasing the measured decontamination performance at the 20 °C condition.

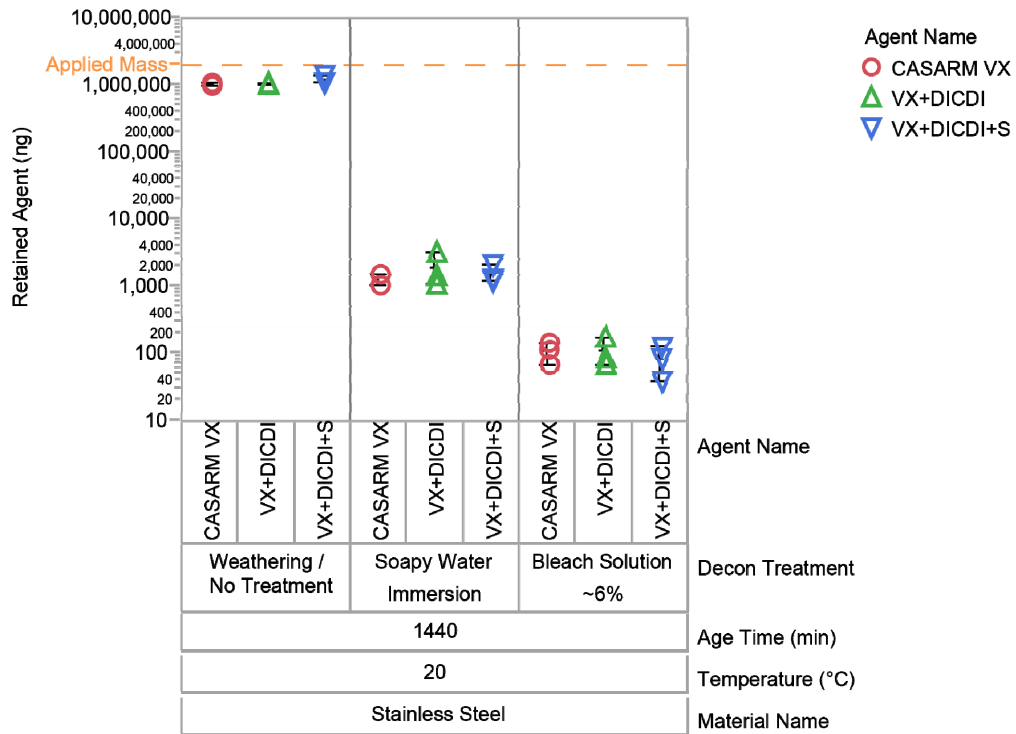


Figure 13. RA results for stainless steel at 20 °C after 1440 min dwell time.

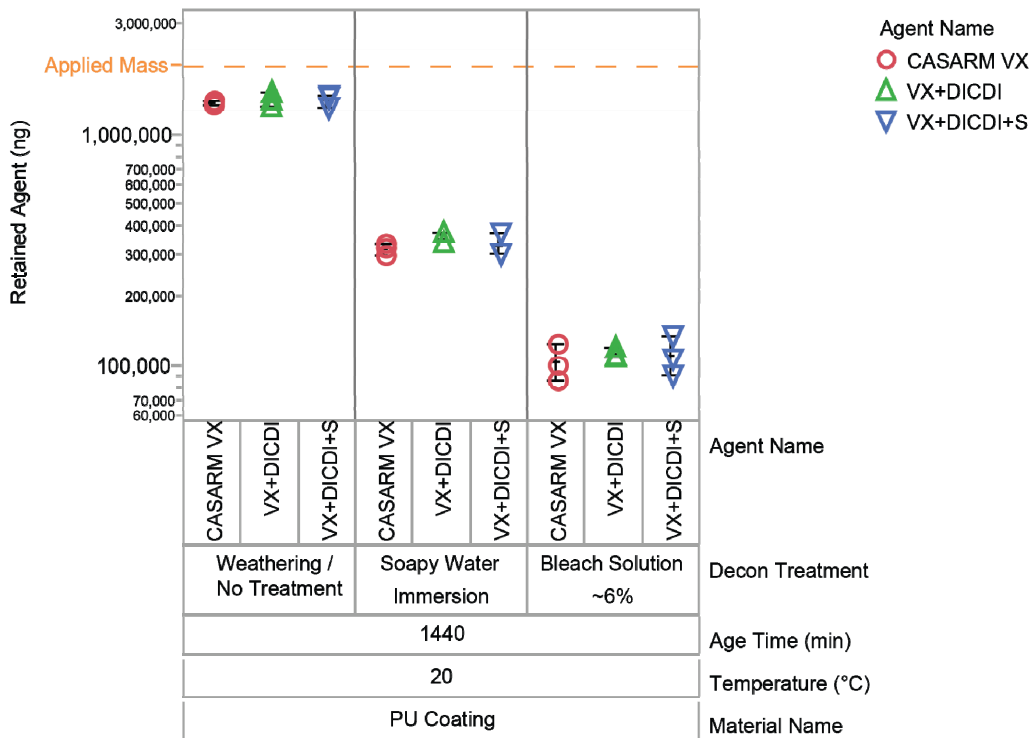


Figure 14. RA results for polyurethane coating material at 20 °C after 1440 min dwell time.

Figures 15 and 16 depict the weathering and decontamination treatment results for stainless steel and the polyurethane coating material, respectively, at 50 °C. After a 24 h contaminant dwell time, $\geq 99.9\%$ of the applied agent mass was lost because of evaporation or degradation on both materials across all agent types. DICDI stabilizer did not prevent the breakdown of VX at high temperatures. On stainless steel panels, any remaining contaminant on the surface was removed using the soapy water immersion technique. On these panels, bleach performed similarly to the soapy water immersion technique due to the impermeable nature of the material (no absorbed agent). On the polyurethane coating material, no significant difference was seen between decontaminant treatments. The bulk of the contaminant was removed in the weathering process, and soapy water immersion and bleach were unable to further reduce the remaining contaminant in the material.

There was no impact on measured decontaminant performance due to the addition of DICDI stabilizer or S. All the agent types showed significantly similar data after the use of decontaminant treatments, which implies that DICDI stabilizer and S could be used for CWA research studies without affecting the measured decontaminant performance at 50 °C.

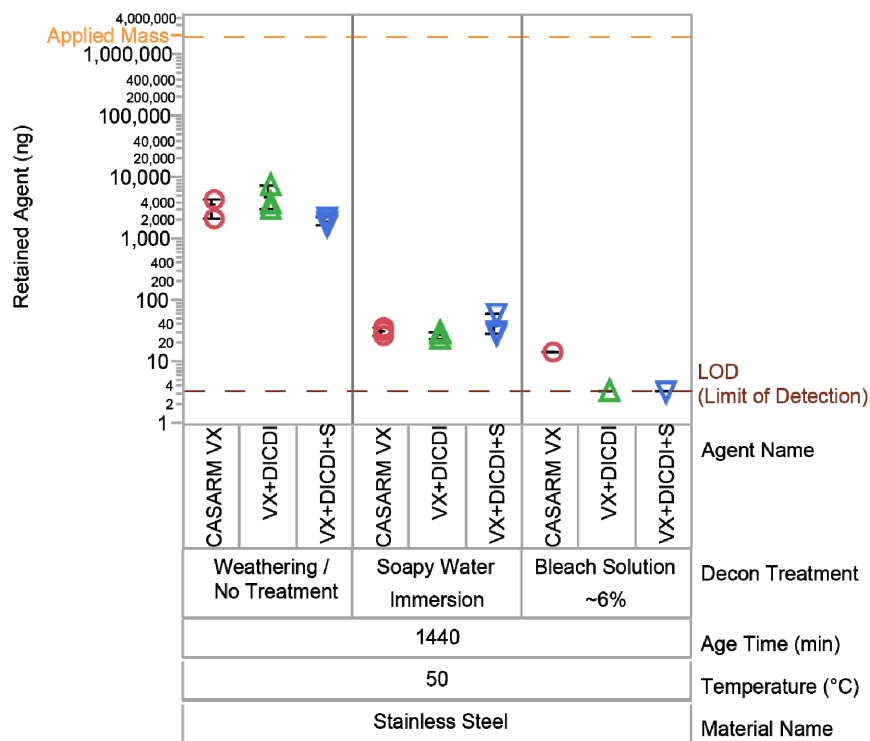


Figure 15. RA results for stainless steel at 50 °C after 1440 min dwell time.

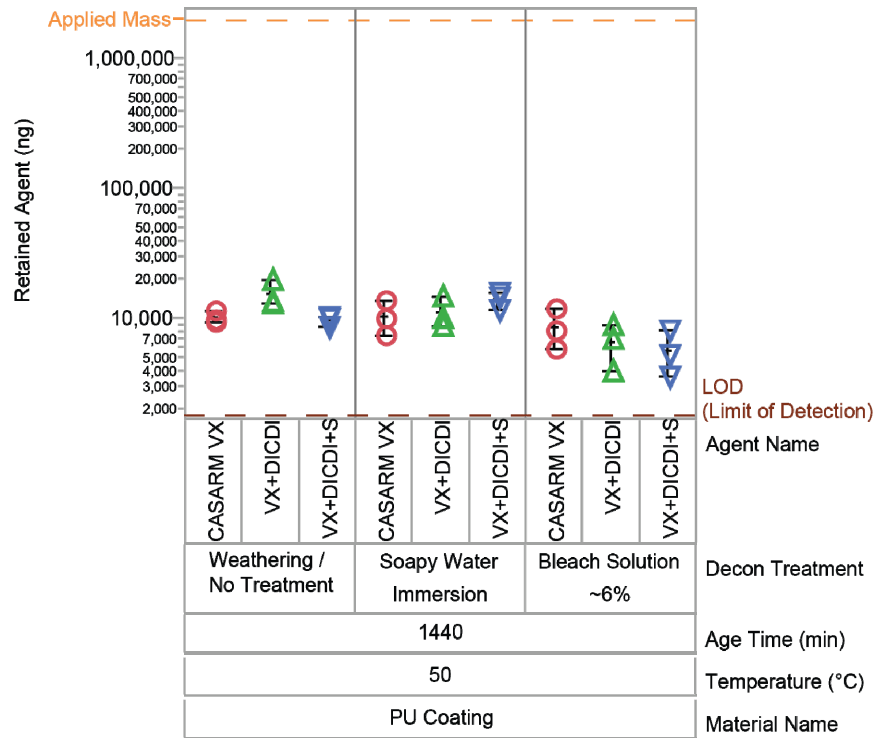


Figure 16. RA results for polyurethane coating material at 50 °C after 1440 min dwell time.

4. CONCLUSIONS

This report presented results on the impact of a chemical stabilizer (DICDI) on measured decontamination performance for a set of military relevant materials that were contaminated with VX. The same lot of CASARM VX was divided into three vials (CASARM VX, VX+DICDI, and VX+DICDI+S), and these three solutions were used to contaminate the surfaces of stainless steel, a polyurethane-based coating, and a silicone elastomeric material. Decontaminant treatments with and without stabilizer were then applied to survey the impact of DICDI stabilizer on measured decontamination performance against CASARM VX. Measurements of RA as a function of VX distribution, tested materials, and decontaminant treatments were used to evaluate the influence of DICDI stabilizer in determining decontaminant performance evaluations. The main conclusions of this study are as follows:

1. The addition of a DICDI stabilizer and S to CASARM VX did not affect the distribution of VX and VX byproducts at the same dosing volume.
2. Liquid spreading on materials was consistent across agent types on impermeable materials (bare metals) or permeable polymers (silicone) and a polyurethane coating material.

3. Agent retention on the polyurethane coating varied for VX+DICDI+S when compared with the CASARM VX alone but on a very small scale (<0.1 LD). In no other occurrence did the stabilizer show any impact on agent retention of materials.
4. Overall, RA measurements after 60 or 1440 min of contaminant dwell times at 20 or 50 °C were not positively or negatively impacted by the presence of DICDI or S.
5. Exposure to elevated temperatures for a 24 h time period reduced the agent starting challenge present on impermeable and sorptive materials by $\geq 99\%$, which was attributable to evaporation or degradation of VX from the material. This reduction in the mass of agent should be considered when characterizing decontaminant performance.

This study showed that stabilized CASARM VX can be used for CWA research or testing due to the consistency of these results with those produced using unstabilized CASARM VX, which has been the typical agent grade used for VX decontamination sciences research and testing. Therefore, the storage life of CASARM VX may be extended by adding DICDI as a stabilizer with no resulting influence on any measured decontamination performance.

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ACRONYMS AND ABBREVIATIONS

CASARM	chemical agent standard analytical reference material
CWA	chemical warfare agent
DCS	dose-confirmation sample
DICDI	<i>N,N'</i> -diisopropylcarbodiimide
EMPA	ethyl methylphosphonic acid
LC	liquid chromatography
LD	log difference
RA	retained agent
VX	2-(diisopropylamino)ethyl- <i>O</i> -ethyl methylphosphonothioate

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