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Effect of Thickener on Measurement of Simulant Retention and Decontamination Performance for Materials

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Decontamination technologies are generally tested under controlled, idealized laboratory environments with clean and uniform materials, high-purity agents, and single geometries. From an operational context, these conditions are often not met in the real world. Therefore, the magnitude of how these conditions affect the decontamination performance is relatively unknown and the results of laboratory tests may not be directly comparable to real-world decontamination scenarios. This report is part of a series of reports designed to provide details of the results from an investigation of issues such as the effects of agent purity, additives, and fouled surfaces. The focus herein is on how an additive (agent thickener) can cause a difference in the estimation of decontamination performance in terms of the remaining agent on an asset and contact transfer to an individual. This study used methyl salycilate as the contaminant. We also studied how and why there was such a drastic difference in decontaminant performance for specific scenarios when an agent thickener was present.

15. SUBJECT TERMS

Agent purity	Contact transfer	Decontamination performance	Thickener
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PREFACE

The work described in this report was authorized under project no. CB10409. The work was started in November 2017 and completed in March 2018. At the time this work was performed, the U.S. Army Combat Capabilities Development Command Chemical Biological Center (CCDC CBC) was known as the U.S. Army Edgewood Chemical Biological Center (ECBC).

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EFFECT OF THICKENER ON MEASUREMENT OF SIMULANT RETENTION AND DECONTAMINATION PERFORMANCE FOR MATERIALS

1. INTRODUCTION AND BACKGROUND

There is a need to understand and predict how decontamination technologies will perform on real assets when contaminated with actual chemical weapons systems. Numerous variables should be considered when attempting to capture multiple facets of operational context such as the purity of an agent, the presence of thickeners or stabilizers, the orientation of a surface (horizontal vs vertical), the fouling of an asset (dirty vs clean), and the type and distribution of materials. For example, it is known that chemical or agent transport changes depending on the type of material tested (e.g., polymer, metal, coating, etc.).[1] Consequently, to relate laboratory results to overall agent transport or retention in a full-scale asset, tests must account for the distribution of these materials on real assets. The same concept may apply to the purity of chemical agents because much of the small-scale laboratory testing employs contaminants that meet the requirements of a chemical agent standard analytical reference material,[2,3] which are high-purity agents that may not reflect actual chemical weapons systems. Because the presence of impurities and additives can affect the dominant mechanisms for chemical transport (i.e., material interactions, concentration, solubility, wetting, etc.),[4–7] it is essential to identify the degree of influence caused by these impurities to develop reliable experimental methodologies that can translate to field operations.

The goal of this study was to characterize how the presence of an agent thickener influences agent retention and decontaminant performance in materials found on military assets. Agent thickener is a compound that is sometimes added to a liquid agent to improve its persistence in the environment. Very little is known about how the inclusion of a thickener affects the contamination and decontamination processes. Thus, the retained agent (RA) values derived from a laboratory test with neat agent may not reflect the RA results from an asset contaminated with thickened agent. This study was designed to determine how the thickener influences agent retention, agent–material decontamination interactions, and decontaminant performance. This will enable the development of more robust methodologies that better reflect real-world situations.

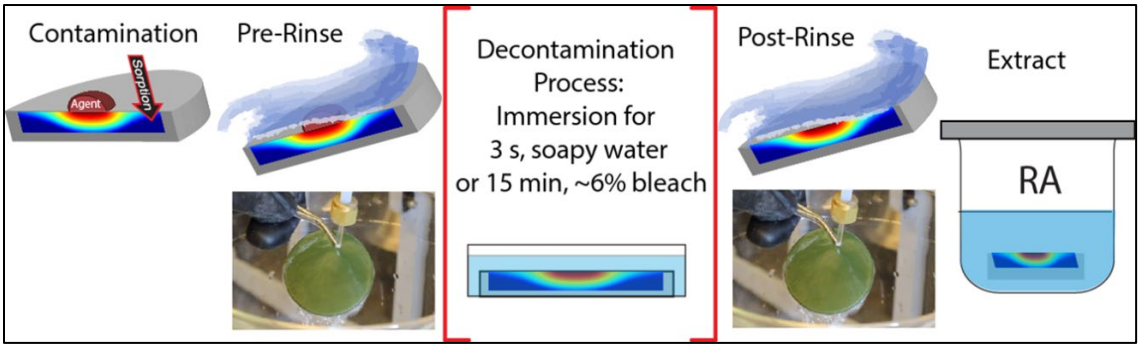

Figure 1. Treatment process used to characterize agent retention and decontaminant performance.

Panel tests using the standard Chemical Agent Resistance Method (CARM)[1,2] (shown in Figure 1) were conducted for the simulant methyl salicylate (MeS) to establish a reference RA result on different materials. These reference values were compared to the results of a panel test using polyacrylate-thickened MeS to evaluate the effectiveness of a typical decontamination procedure when thickener is present. The CARM method is generally used to determine the quantity of agent retained by a contaminated material. The process involves a soapy water immersion to obtain a baseline for comparison to results gathered with a decontaminant solution having active components (i.e., ~6% bleach). The difference in the amount of RA for each of these processes can be used to evaluate how effective the decontaminant is on a specific agent or simulant or in comparison with other decontaminant solutions.

In this study, the CARM was performed with three different simulant solutions that contained 0 (neat), 2, and 5% thickened MeS on two permeable materials (polyurethane [PU] paint and silicone) and one impermeable material (stainless steel). The addition of a thickener increases the viscosity, decreases the mole fraction of MeS in the solution, and potentially alters the liquid surface tension. These changes are likely to influence the adhesion of the liquid to the surface, droplet-spreading and spreading rate, evaporation rates, relative absorption rates into materials, and dissolution of the agent into the decontaminant phase.

For the soapy water immersion test, the increasing presence of thickener led to a decrease in overall rinse performance for all of the materials tested (i.e., thickener increases the amount of RA after the CARM process). This was partially attributed to the inability of the soapy water immersion procedure to completely remove the liquid droplet from the surface of the material. In contrast, the bleach decontamination procedure more effectively removed the liquid droplet, which resulted in no correlation between the amount of thickener and the decontaminant performance. Overall, if the decontaminant could dissolve or remove the thickened agent from the material surface, there were minimal differences in its performance. However, if the decontaminant could not dissolve or remove the thickener (e.g., soapy water immersion), there could be a significant difference in decontaminant performance. If the decontaminant is not tested against thickened agents, its effectiveness against such contaminants may not be known. Therefore, it is recommended that thickened agent testing be included in decontamination development efforts.

The dissolution rate of the thickened and neat MeS droplets into a decontaminant solution was measured by ultraviolet–visible (UV–vis) spectroscopy. Results suggested that the dissolution of a thickened MeS droplet into a decontaminant solution was slower than that of a neat MeS droplet. In addition, results showed that the rate of dissolution can be modulated by altering the composition of the decontamination solution (i.e., adding a cosolvent). To determine whether the contamination rate or amount absorbed into the material was affected by thickener, Fourier transform infrared–attenuated total reflection (FTIR–ATR) was employed to measure the breakthrough of MeS in polydimethylsiloxane (PDMS) membranes. Results showed that the uptake rates for thickened and nonthickened MeS were similar; however, the amount of absorbed MeS for the neat MeS test was slightly greater than that of the thickened MeS test. If it is assumed that the solubility of MeS was the same in both cases, this implies that the thickener does not influence the diffusion rate of MeS in the material, and the difference in total amount

absorbed is related to the concentration of MeS in the droplet (which is less for a thickened droplet). Overall, this study shows that the presence of a thickener affects the RA predicted from the performance of a traditional laboratory test.

2. MATERIALS

For all experiments, MeS (>99% ReagentPlus, Sigma-Aldrich; St. Louis, MO) was thickened with Acryloid K-125 standard thickener (lot 3-6326). A 2, 5, and 10 wt/wt % mixture was prepared and mixed on a roller for 5–7 days or until the thickener was completely dissolved. To ensure good mixing, thickener was slowly added to the MeS over the course of 3 h.

Standard coupons (2 in. diameter) were used for RA testing of PU paint, silicone, and steel. For the contamination rate measurement, PDMS samples were prepared using a standard preparation kit (Sylgard; DowDuPont, Inc.; Midland, MI). A 10:1 mixture of resin to curing agent was mixed and placed in a vacuum desiccator for 1 h to remove any air bubbles. The resin was cast in a shallow dish and cured overnight at 70 °C. Samples were cut to the desired size after deposition.

3. PANEL TESTING

Panel testing is an effective method to determine the amount of RA in or on a material after a specified amount of time and/or decontamination process. For the purposes of this report, RA refers to both the agent absorbed into the material and the residual liquid left on the interface (Figure 2). These data can then be applied to determine how effective a decontaminant is on specific agents or materials, how long a decontaminant should be applied, and whether or not the decontamination process is effective. These tests are designed to emulate real-world decontamination processes. To ensure an accurate representation, it is essential to determine how these results may change in the presence of an adulterant, such as a thickener. Current testing generally relies on results from neat agents (i.e., agents free from impurities or adulterants).

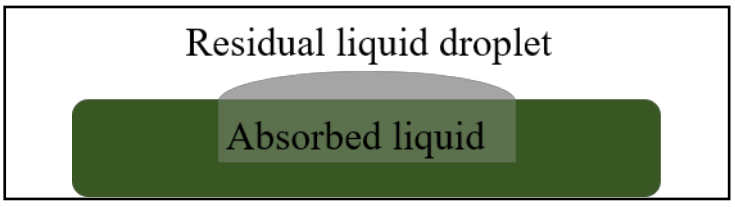

Figure 2. Depiction of remaining agent for the purposes of this report. Remaining agent includes both the liquid absorbed into the sample and the residual liquid droplet at the surface.

3.1 Experimental Procedure for Panel Testing

The CARM was applied to determine the amount of RA in different types of material and is described in detail by Mantooth et al.[1] To contaminate panels of PU paint, silicone, and steel, 2 μL of the respective simulant (0, 2, or 5% thickened MeS) was placed on top of a panel and incubated for 60 min at ambient conditions. Photographs were taken at 5 and 60 min to determine the differences in the wetting properties of each panel material. Following contamination, samples were rinsed briefly in deionized (DI) water. Next, the panels were placed in 8 mL of a decontaminant solution for 3 s (soapy water) or 15 min (bleach), followed by a post-rinse with DI water. The RA was extracted from the decontaminated panel with 30 mL of isopropyl alcohol (IPA). Neat MeS was extracted from the panels within 60 min. However, the extraction of thickened MeS from the decontamination panels required an overnight incubation in the extraction solution. The increased extraction solution volume, 30 mL instead of 20 mL, and the extended extraction times were required to enable confident extraction of the thickened contaminant compared with that of neat contaminant. These times were estimated prior to experimentation by extraction efficiency tests that yielded 90% recovery.

The amount of MeS in the extraction solution was measured by gas chromatography–mass spectrometry (GC–MS). The instrument used in this study was an Agilent (Santa Clara, CA) model 6890 gas chromatograph with an Agilent model 5975C Inert XL mass selective detector. Sample introduction was performed through a multipurpose sampler (Gerstel, Inc.; Linthicum, MD). The Gerstel system included a cooled injection system (CIS) with Peltier cooling. A CIS-4 baffled deactivated liner, with no packing, was used in the Gerstel CIS. Helium was used as a carrier gas at an average linear velocity of 39 cm/s in solvent vent mode. All experiments used a capillary column with a bonded phase of 5% phenyl methylpolysiloxane (30 m × 0.25 mm) and a 1.00 μm film thickness.

3.2 Results from Panel Testing

Droplet-spreading on a solid material can change depending on the surface tension and viscosity of the liquid. This can influence the transport of the liquid into the solid material. Variations in agent droplet-spreading have been demonstrated in several studies for a wide selection of materials. The differences in the droplet-spreading of a 2 μL droplet of MeS in the presence of a thickener is shown in Figure 3 for PU paint, silicone, and steel. The spreading of the droplet was recorded after 5 and 60 min incubation periods. For neat MeS on PU paint after 5 min, a sessile droplet was observed with a distinctive outer ring. The outer ring is indicative of lateral capillary-spreading on a rough surface. The ratio (R) between the diameter of the sessile droplet and that of the outer ring was calculated to be 0.25 for neat MeS. When thickener was present, this ratio significantly increased to 0.95 for the 2% thickened MeS and to 0.88 for the 5% thickened MeS. After the 60 min incubation on PU paint, no sessile droplet was observed for neat MeS, and decreases in the ratios of MeS droplet diameters were observed for the 2% MeS droplet (R = 0.77) and for the 5% MeS droplet (R = 0.93). This suggested that the more viscous (thickened) solution resulted in a retardation of the droplet spread into the roughness features. Slower spreading was also observed for the silicone and steel panels with an increase in the amount of thickener; however, it was difficult to discern because of the colors of the panels.

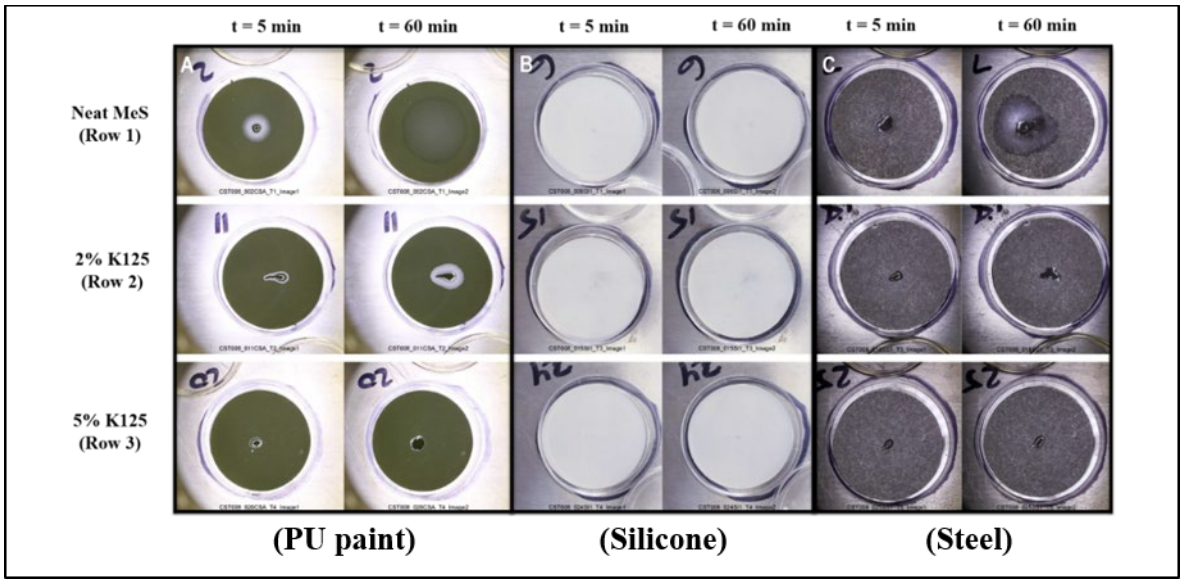

Figure 3. Comparison of droplet-spreading for thickened and neat MeS on three different materials: (A) PU paint, (B) silicone, and (C) steel. Two different spreading times (t) at 5 and 60 min are presented for each panel.

The amount of RA on contaminated panels after the decontamination process is shown in Figure 4A and B for 0, 2, and 5% thickened MeS. A log difference (LD) calculation was used to compare the RA results, as defined by

$$\mathrm{LD} = \log_{10}\frac{\mathrm{RA}_{\mathrm{test}}}{\mathrm{RA}_{\mathrm{reference}}} = \overline{\log_{10}(\mathrm{RA}_{\mathrm{test}})} - \overline{\log_{10}(\mathrm{RA}_{\mathrm{reference}})} \quad (1)$$

where

LD is log difference (unitless);
$\mathrm{RA}_{\mathrm{test}}$ is RA mass measurement for test condition (ng); and
$\mathrm{RA}_{\mathrm{reference}}$ is RA 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 calculated from these results provide the 95% confidence interval on the difference.[2] The upper portion of the graphs in Figure 4 represent the LD values relative to the neat agent (i.e., relative magnitude of difference between neat and thickened agent). For a soapy water immersion (Figure 4A), an increased amount of thickener resulted in a greater amount of RA for all three materials. *This suggests that as the percentage of thickener was increased, the soapy water immersion process became less effective at reducing RA*. This could be the result of a greater amount of residual droplet on the surface and/or a greater retention of agent in the material. Because the overall trend (increased thickener resulting in a greater RA) for the impermeable material (stainless steel) was the same as that of the permeable materials (PU paint and silicone), this finding was partly attributed to the decreased ability to successfully remove or dissolve the residual droplet from the material surface.

Photographs of the 2 μL droplet after the soapy water immersion for neat and thickened MeS, dyed with red dye (for contrast), are shown in Figure 4C. The darker red color for the thickened MeS indicates that some of the droplet was left behind after the rinse process, which corresponds with conclusions from the RA results. Figures 5–7 are expanded versions of Figure 4C that depict the progression of droplet removal for neat and thickened MeS using soapy water and bleach treatment processes. The lack of red dye tends to indicate a more complete removal of the MeS after decontamination.

Figure 4B shows the changes in RA results when the panels were immersed in a reactive decontaminant (bleach) for 15 min. There was no clear correlation between the RA results and the percentage of thickener used. For impermeable steel, less than 5,000 ng of MeS was detected for 0 and 2% thickener, and less than 100,000 ng of MeS was detected for 5% thickener. For soapy water, these values exceeded 100,000 ng of MeS in the 0 and 2% cases, and 1,000,000 ng of MeS for the 5% thickened sample. Overall, this suggests that the droplet was more successfully removed with bleach (15 min immersion) than with the soapy water immersion procedure (3 s rinse). Comparisons of the photographs of the contaminated panels after decontamination using bleach and soapy water in Figures 5–7 correspond with this observation. This could indicate that the decontaminant performance on thickened MeS had a greater dependence on the ability of the decontaminant solution to physically remove the liquid droplet from the surface (either by dissolution or force) than on the ability of the decontaminant to interact with the chemical simulant.

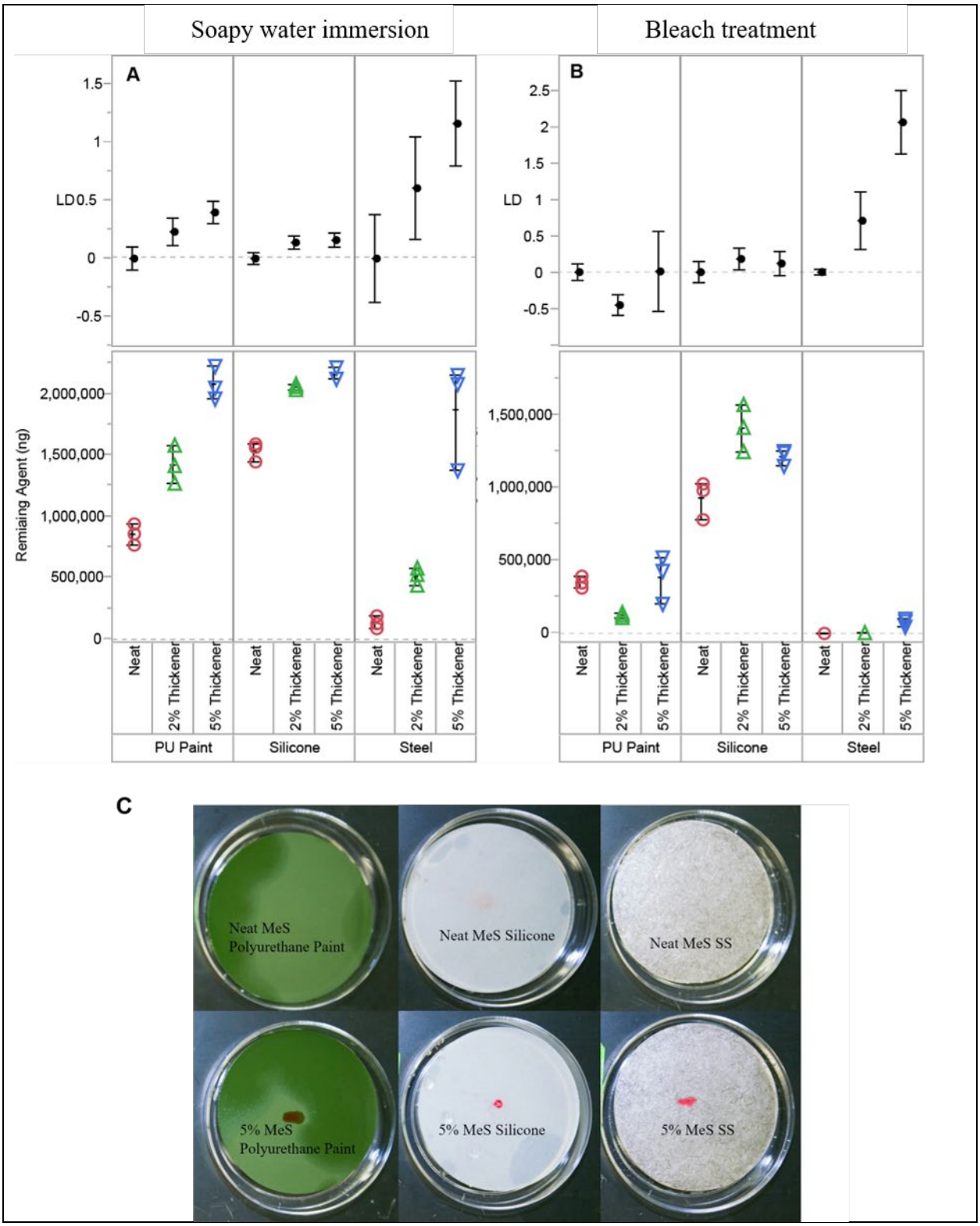

Figure 4. The amount of RA on various panels after a 60 min exposure to 0, 2, and 5% thickened MeS droplets after decontamination with (A) soapy water (3 s) and (B) 5% bleach (15 min). (C) Photographs of 0 and 5% thickened MeS on panels after soapy water rinse process.

Figure 5. Images of PU-coated panels contaminated with 0, 2, and 5% dyed MeS thickener and treated with soapy water or bleach.

Figure 6. Images of silicone panels contaminated with 0, 2, and 5% dyed MeS thickener and treated with soapy water or bleach.

Figure 7. Images of steel panels contaminated with 0, 2, and 5% dyed MeS thickener and treated with soapy water or bleach.

4. EVALUATION OF CONTAMINATION AND DISSOLUTION RATES

Although the panel tests provide insight into how the thickener affects the performance of the decontamination procedure, they do not clarify how the absorption mechanisms are affected by the thickener. Such absorption mechanisms could include contamination rate, rate of dissolution into a decontaminant solution, surface characteristics, and material interface, among others. A mechanistic understanding is necessary to devise suitable testing methods for the prediction of decontamination and contamination and for the design of effective decontamination procedures. For liquid-phase decontamination, agent dissolution into a decontamination solution can be a rate-limiting process.[8] This rate varies based on the chemical composition of the agent (i.e., the presence of adulterants or thickeners). Similarly, the contamination rate can help predict the amount of agent present after specific agent exposure times and lead to modifications of the decontamination procedures. Current methodologies, which were developed through asset decontamination testing using neat agents, may be insufficient to remove an agent in the presence of a thickener.

4.1 MeS Dissolution Rate

4.1.1 Experimental Procedure for MeS Dissolution Rate Testing

The dissolution rate of MeS was determined by suspending a droplet of the simulant in a solvent and measuring the change in total absorbance over time. The apparatus is shown in Figure 8. Briefly, a droplet of MeS (for three concentrations of 0, 2, and 5%) was suspended in a quartz cuvette containing 3 mL of solvent (water or water/methanol mixtures). The solution was constantly mixed with a magnetic stir bar located at the bottom of the cuvette. Deuterium light was directed through the bottom of the cuvette to an Ocean Optics (Dunedin, FL) spectrometer with fiber optic cables. To determine the rate of dissolution, the absorbance peak for MeS (centered at 312 nm) was monitored over time. To convert the absorbance value to concentration of MeS, a calibration sample was prepared using standards of MeS in MeOH (i.e., 1–6 µg/mL). The dissolution rate was determined via linear regression of the concentration values versus time. Using eq 1, rate values were normalized to the exposed surface area (SA) of the liquid droplet because the greater amount of thickener resulted in differences in surface tension and droplet shape.

$$SA = \frac{1}{2}\left[4 \times \pi \left(\frac{(\frac{1}{2}A)^{\rho}B^{\rho} + (\frac{1}{2}A)^{\rho}B^{\rho} + B^{2\rho}}{3}\right)\right] \quad (1)$$

where A is the short axis of the droplet, B is the long axis of the droplet, and ρ is the relative error from Knud Thomsen's formula (ρ = 1.6075). The equation is modified from the surface area of an ellipsoid.

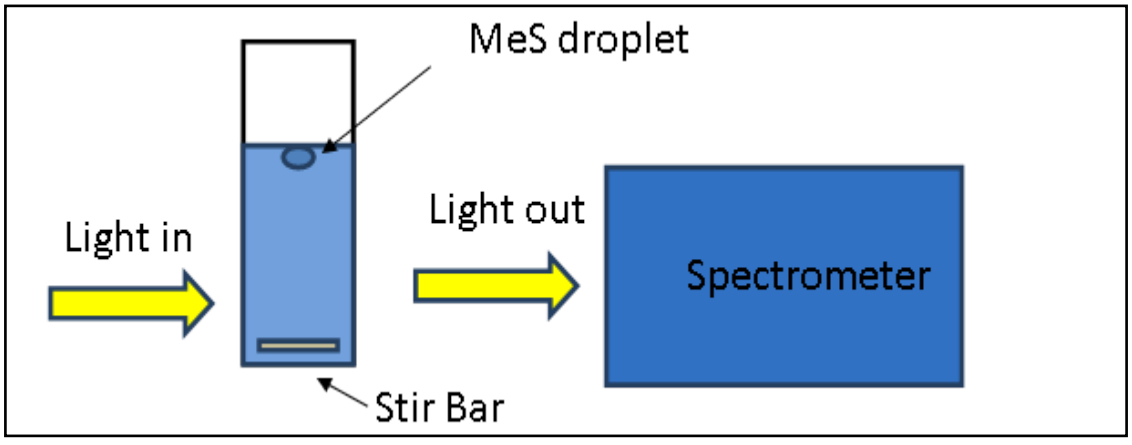

Figure 8. Schematic of apparatus to measure dissolution rate from droplets of simulant. The droplet is suspended in the cuvette as light is passed through the bottom of the cuvette to the spectrometer.

4.1.2 Results from MeS Dissolution Rate Testing

The dissolution rate of a liquid into a solution is particularly important when selecting a suitable decontamination solution. If the droplet will not dissolve into the decontaminant solution, it will be less effective in the overall decontamination. The rate of dissolution from a single droplet into a solvent (inset, Figure 9A) was monitored by UV–vis spectroscopy. Figure 9A shows the increasing absorbance (i.e., UV–vis spectra) of MeS from a 5% thickened droplet over time. The time scale progresses from blue to red in Figure 9A. Figure 9B depicts the rate calculated from the UV–vis spectra (µg/min) for 0, 2, 5, and 10% thickened MeS. An indirect relationship between the percentage of K-125 thickener and the rate of dissolution was observed. This finding suggests that an increased amount of thickener will decrease the rate at which a simulant or agent is dissolved into the decontaminant solution. This will ultimately reduce the effectiveness of the decontaminant. Consequently, to adequately remove the thickened agent, a more effective cosolvent and/or increased decontamination time may be required for thickened agents. *If formulation-development testing only used neat agent, the resulting formulation may not be optimized to handle thickened agents.*

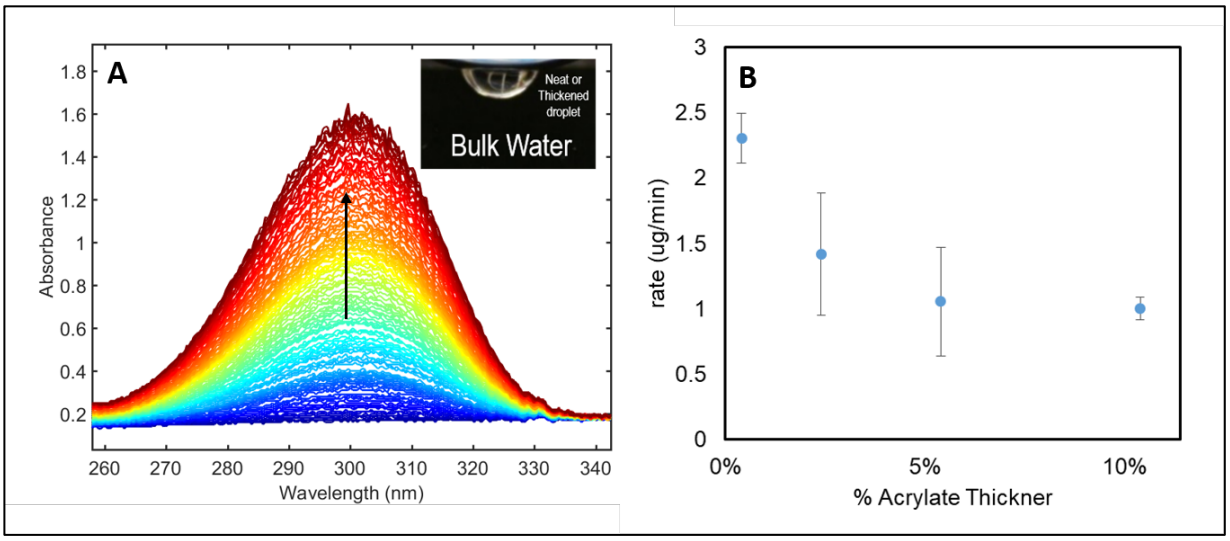

Figure 9. (A) MeS absorbance into bulk water solution for 5% droplet over time. Blue is for the initial spectra, and red is for the final spectra. The inset is a photograph of the droplet suspended in a cuvette containing bulk water. (B) The calculated rate of dissolution for MeS into water from droplets with 2, 5, and 10% acryloid thickener.

For chemical decontamination, a cosolvent is often used to increase the solubility of the agent into the decontaminant solution. It is generally unknown whether the effectiveness of the decontaminant changes based on the composition of the agent. To evaluate the effect of a cosolvent when thickener is present, the rate of dissolution was determined for neat MeS and for 10% thickened MeS in water/methanol mixtures ranging from 10 to 40% MeOH. Figure 10A depicts the effect of solvent composition on the shape of the droplet (i.e., exposed surface area). For comparative purposes, neat MeS is shown at the top of Figure 10, and 10% thickened MeS is depicted at the bottom. To correct for the differences in exposed areas, the calculated rates were

normalized to the surface area of the MeS droplet. Figure 10B represents the normalized rates of MeS dissolution in the water/solvent mixtures. The brown line represents dissolution from the neat MeS droplet, and the red line indicates dissolution from the droplet containing 10% K-125. For the neat MeS, there was no observable trend in the rate of dissolution with different solvent compositions. However, for the thickened agent, as the MeOH was increased, the MeS dissolution rate also increased. This demonstrated that the composition of the decontaminant solution can affect the time it takes for the agent to dissolve into solution. Similar to testing for rate of dissolution, if the formulation or testing efforts only involve neat agent, the resulting formulation may not be optimized to deal with thickened agents.

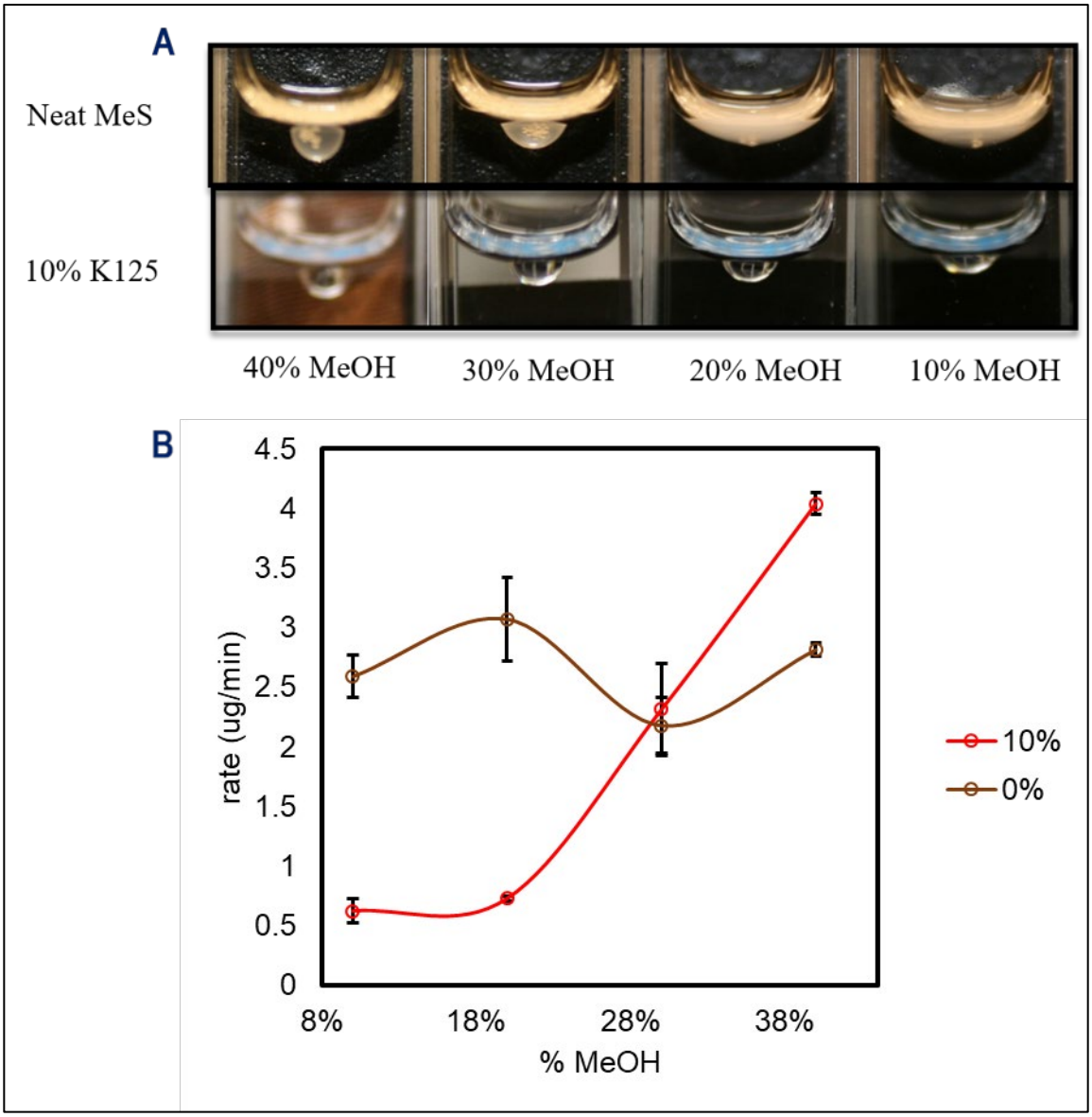

Figure 10. (A) The effect of solution composition on the shape of the suspended droplet, and (B) the normalized rate of dissolution of 0 and 10% thickened MeS in different water/methanol solutions.

4.2 MeS Rate of Absorption

4.2.1 Experimental Procedure for MeS Rate of Absorption Testing

An important factor for decontamination performance is how much of the contaminant is absorbed into the material.[8] An analysis was conducted to quantify how neat versus thickened MeS absorbs into a polymer to determine if the presence of the thickener influences the absorption rate. PDMS was selected as the polymer because the experimental technique requires the ability to cast a thin film of material onto the internal reflecting element (IRE) to conduct breakthrough measurements. PDMS is similar in chemistry and transport characteristics to the silicone polymer used in panel testing. The breakthrough measurement indicates the time-resolved concentration of analyte on the back surface of the material. If the thickener influences the absorption rate, it will produce a different trend in the time-resolved breakthrough measurement.

The rate of absorption of MeS into PDMS films was determined by a modified FTIR–ATR method that was described by Santos et al.[9] ATR is a sample introduction system for FTIR that passes through an IRE and reflects it back into an infrared (IR) spectrometer. In this particular configuration (Golden Gate ATR with a diamond IRE; Specac Limited; Orpington, U.K.), solids (e.g., polymer films, powders, etc.) or liquids placed directly on top of the IRE will absorb light before it is reflected back into the spectrometer due to an evanescent wave that extends 2 μm into the interface of the prism with the sample. To analyze the breakthrough of MeS through PDMS, a 0.5 cm film of PDMS was placed on the diamond IRE. A flow cell containing a pressure anvil was placed on top of the PDMS film, and the flow cell was filled with either 0 or 5% thickened MeS. As the MeS absorbed into the polymer, an absorption peak representing MeS (centered at 1486 cm^{-1}) was monitored over time until an equilibrium was reached. The measurement was repeated twice to evaluate reproducibility. The apparatus is depicted in Figure 11.

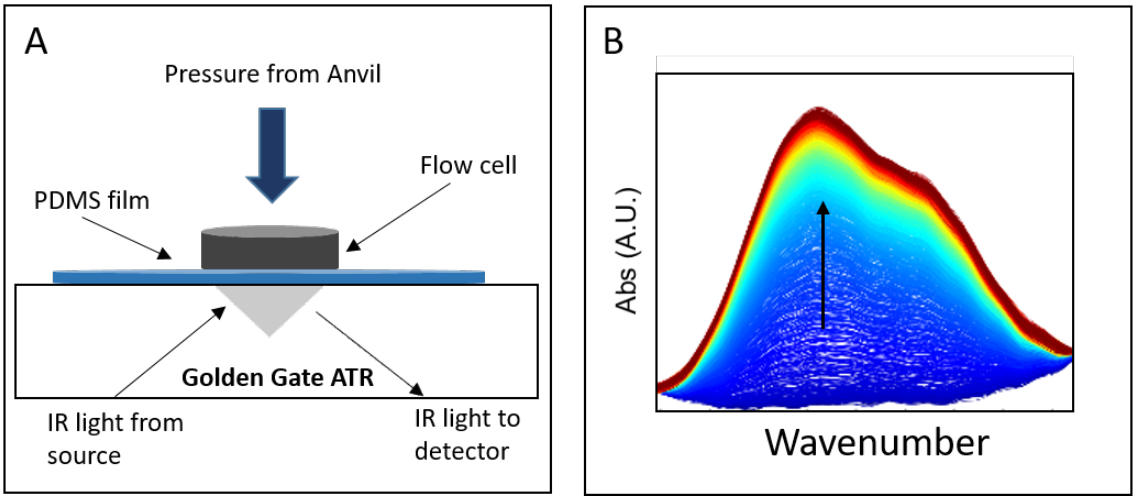

Figure 11. (A) Schematic of flow cell apparatus. A PDMS film is placed between a flow cell and the Golden Gate ATR (equipped with a diamond IRE). The flow cell is filled with the liquid of interest (0 or 5% thickened MeS), and a breakthrough curve (time vs absorbance) is generated by monitoring the area under the curve or maximum intensity of a specific peak. (B) An example of an absorbance peak monitored over time.

4.2.2 Results from MeS Rate of Absorption Testing

The total amount and rate at which an agent diffuses and absorbs into a material (i.e., contamination and breakthrough rate) can give insight into how an additive (such as agent thickener) changes the material–agent interactions. This can lead to variations in the decontaminant performance, such as the time it takes for complete extraction or how much of the decontaminant it takes for complete decontamination. To determine the breakthrough rate, the contamination area is kept constant to remove the effects of surface coverage (e.g., spreading variations, as observed in Figure 3). Breakthrough curves (time vs peak area) are depicted in Figure 12 for 0 and 5% thickened MeS (red and blue lines, respectively). In general, the slope of the curve is related to the diffusion rate, and the equilibrium peak area is related to the total absorbed concentration of MeS in the polymer film (via Beer's law). For both the 0 and 5% thickened MeS, the absorption rate was approximately the same; however, the total absorbed concentration of MeS into the polymer was different. For the thickened contaminant, the amount of MeS absorbed into the polymer was less than that for neat MeS. Because the absorption rate is the same for both neat and thickened MeS, the differences in the total amount of MeS absorbed (i.e., saturation) may be related to the decreased concentration of MeS in the polyacrylate-thickened contaminant. This could indicate that the solubility of MeS into PDMS is the same when thickener is present, and the amount of MeS absorbed is related to the concentration of the MeS in the droplet. Thickener decreases the mole fraction (i.e., concentration) of MeS in the droplet. Overall, the polyacrylate thickener had minimal influence on absorption rate into the material.

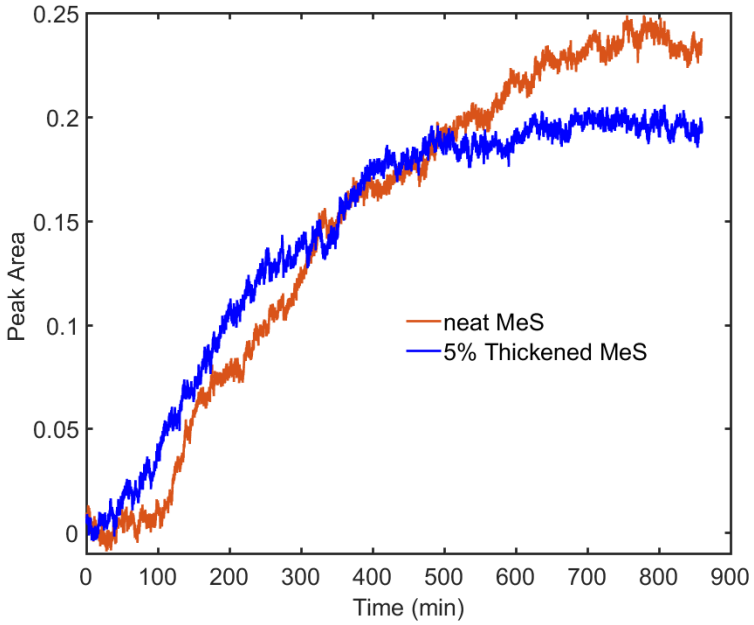

Figure 12. Breakthrough of 0% MeS (red line) and 5% thickened MeS (blue line) in PDMS-free films.

5. CONTACT TRANSFER

Contact transfer is a typical test performed to assess the amount of agent that will be transferred via contact after a contamination and decontamination process has occurred. In a typical multi-touch contact transfer test, several touches are applied to a single panel, and the amount transferred to a latex contact sampler is measured for each of the touches. There are two primary mechanisms by which contact transfer may occur, as illustrated in Figure 13. Diffusive transfer occurs when absorbed agent diffuses from the substrate material into the contact sampler over time and will only occur for absorptive materials. Squeeze-flow occurs when there is liquid on the surface of the material (Figure 13B). Application of the contact sampler squeezes the liquid across the surface, and when the sampler is pulled away, some quantity of liquid sticks to the sampler and some remains on the material.[10] Squeeze-flow happens very rapidly (i.e., several seconds or less) and is a result of the fluid properties of agent (e.g., viscosity, surface tension, and adhesion to the materials). The images in Figures 5–7 show that the red-dyed MeS tends to remain on the surface, especially in the case of thickened agent. Results described in Section 3.2 suggest that when thickener is present, the amount of RA can be increased up to 2× for a soapy water immersion process. This was attributed to an inadequate removal of the droplet from the surface via physical force or dissolution. Consequently, for contract transfer, it is expected that a greater rate of surface-bound agent will result in the transfer of a greater amount of contaminant.

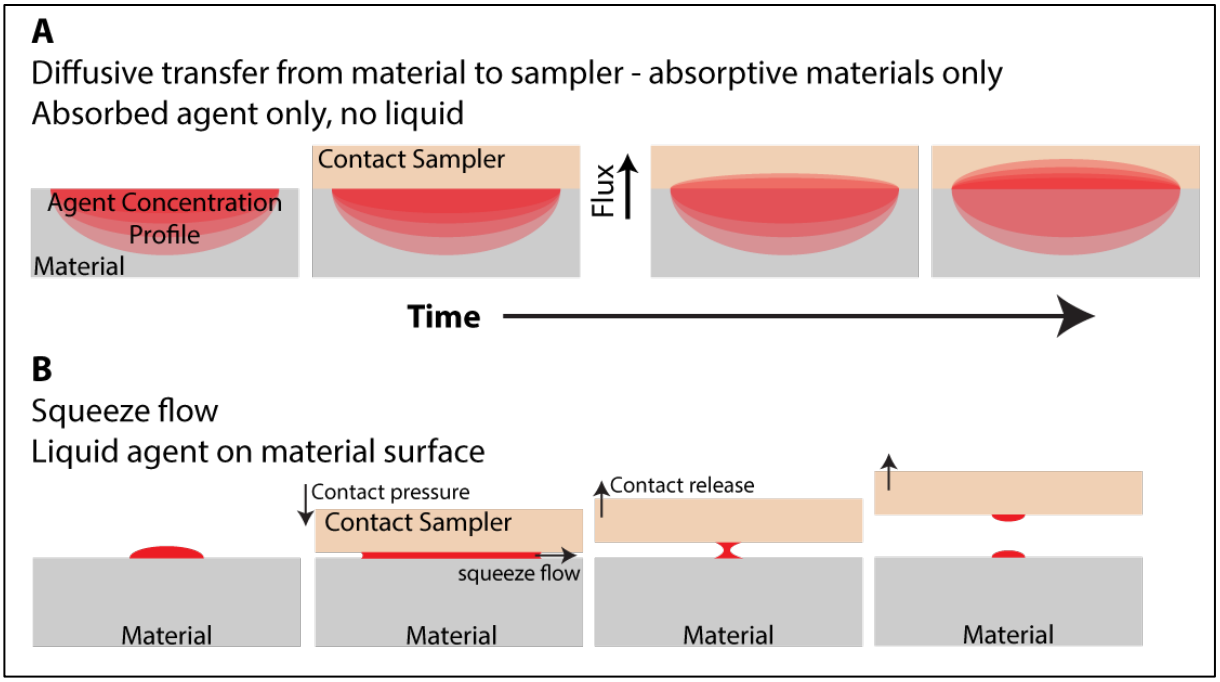

Figure 13. Mechanisms of contact transfer including (A) diffusive transport and (B) squeeze-flow transfer. Note that both mechanisms can occur simultaneously.

5.1 Experimental Procedure for Contact Transfer

Multi-touch contact transfer experiments were conducted for PU paint and steel. The touch schedule, which indicates when contact samplers are placed in contact with the substrate and the duration of the touch, is shown in Table 1. Similar to RA tests, panels of PU paint and steel were contaminated with 2 µL droplets of 0 and 5% thickened MeS. The droplets incubated on the panel surface for 60 min. After the contamination, the samples were rinsed with 20 mL of DI water and placed in 8 mL of a decontaminant solution for 3 s (soapy water) or 15 min (bleach), followed by a post-rinse with 20 mL of DI water. Previously, soapy water was used as a baseline treatment condition to remove the surface-bound liquid and represent only the RA on the panel; however, the results from Section 4 indicated that the process was less effective at removing the thickened agent droplet. Therefore, for reference, a panel was also prepared with no post-treatment (i.e., no rinse, no decontaminant) to indicate how much MeS mass could be transferred if significant quantities of liquid chemical were on the material surface. For a typical touch sample, latex contact samplers were placed in contact with the substrate, and a 1 kg weight was placed on top of the sampler for a specific touch duration (Table 1). The latex was then removed and extracted. The process was repeated to provide three touches (T1, T2, and T3) for each panel. A more detailed description of the test setup is available in the 2011 report by Lalain et al.[2] All samples were extracted in IPA overnight, and the solutions were analyzed by GC (Section 3.1 includes GC parameters). The contact transfer panels were also extracted for residual agent (RES) after the touch sampling had been performed.

Table 1. Touch Schedule for Contact Transfer Test

Touch No.	Touch Start Time (min)	Touch Duration (min)	Rationale
1	1	0.03	Short duration is likely to sample only squeeze-flow types of transfer
2	1.03	~5	Longer duration allows for combination of squeeze-flow and diffusive transfer
3	60	~5	Longer duration allows for combination of squeeze-flow and diffusive transfer

5.2 Identifying Surface-Bound Liquid

As illustrated in the previous examples, agent thickener is expected to result in an increased amount of bulk liquid remaining on a surface of a panel after a treatment process. Due to the nature of an RA test, it is difficult to experimentally differentiate between agent that is absorbed into the material and agent that remains as a bulk liquid on the surface of the material. An appropriately designed contact-sampling experiment can potentially assist in the differentiation between these types of retention. The analysis in this section focuses on the no-treatment reference condition and the soapy water immersion treatment to help identify surface-bound liquids.

If the agent is absorbed into the material, it is expected that the contact transport mechanism will be diffusive (Figure 13A). In this case, the contact-transferred mass should increase with the duration of agent contact as agent migrates from the substrate to the sampler. If the agent is a surface-bound liquid, it is expected that squeeze-flow would be the dominant mechanism for contact transfer (Figure 13B). In general, this is a rapid process that exhibits minimal time-dependence. Unlike diffusive transfer, each subsequent touch should remove a portion of the agent, which would result in a diminishing contact-transferred mass for each touch. To isolate the squeeze-flow mechanism, stainless steel was selected as an impermeable material. Examples of the touch-transferred MeS mass and relative touch-transferred MeS mass are provided in Figure 14. The total mass is the sum of T1 + T2 + T3 + RES. It must be noted that T2, for neat MeS with no treatment, was compromised during testing, and the total mass for this condition is unavailable. The no-treatment and soapy water immersion treatment processes produced similar results for neat and thickened agent on steel. In the case of neat agent, this could indicate that there is little liquid MeS remaining on the panel due to evaporation before the treatment process. In the case of thickened MeS, where evaporation was less of a concern, the similarity of the results may indicate that a soapy water immersion is not effective at removing surface-bound liquids of thickened MeS.

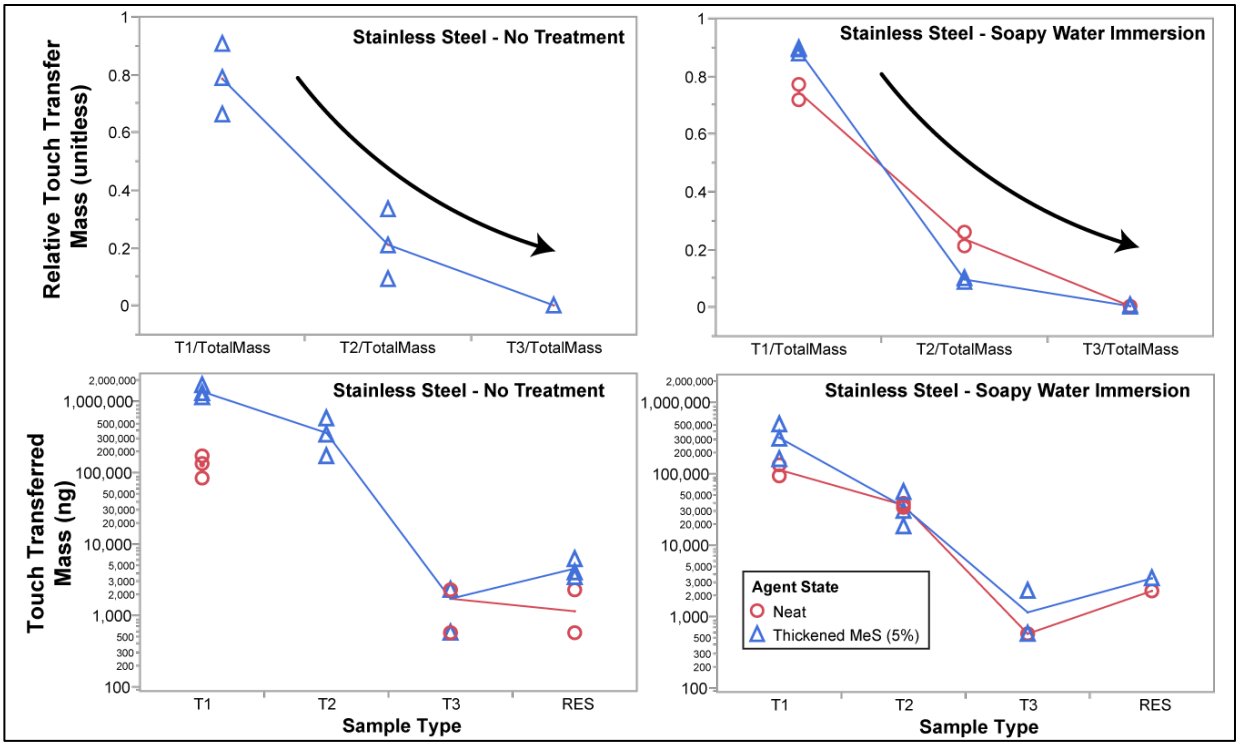

Figure 14. (Top) relative touch-transferred MeS mass and (bottom) contact-transferred MeS mass from stainless steel for no treatment and soapy water immersion.

The data in Figure 14 show how the relative touch-transferred MeS mass decreases for each touch, as the quantity of agent retained by the panel diminishes with each touch. In this case, the touch trend for thickened agent behaved approximately similar to that for the neat agent. The most significant differences occurred during T1, where more of the thickened MeS agent was transferred, as compared with that of neat MeS. After the three touches, the RES agent was relatively small (~2000 ng), which indicated that the touches had removed the majority of MeS from the material, and further touches should not result in significant contact transfer.

In contrast, the test results obtained using PU coating revealed different trends for contact transfer than did those produced using stainless steel (Figure 15). Because PU is an absorptive coating, it is possible that some of the MeS was absorbed, some remained as a bulk liquid on the panel surface, and some evaporated. Evaluation of the panel images for neat MeS in Figure 3, shows that there was less liquid present on the panel surface, which indicates that most of the neat agent either absorbed or evaporated from the material. For thickened agent, which did not spread out, there was still a substantial quantity of liquid on the surface. The large variations in surface-bound liquid were probably responsible for the differences observed in the contact transfer results for thickened and neat MeS. For the no-treatment and soapy water immersion treatment conditions, the thickened MeS contact-transferred mass for the T1 (3 s contact duration) touch was much greater than the contact-transferred mass for neat MeS. This can be attributed, at least in part, to a greater amount of surface-bound liquid in the case of thickened MeS, where squeeze-flow transfer was the dominant mechanism.

For the T2 (300 s duration) contact transfer test, the stainless steel panel exhibited decreasing MeS mass for each touch. However, tests performed with the PU coating produced a contact-transferred MeS mass for the T2 touch that was similar to or greater than that obtained for the T1 test. This indicates that T2 test results were from a combination of squeeze-flow transfer of any residual liquid and diffusive transfer. The results from the T3 test were less in all cases than those of the previous two touches, likely because the substrate of MeS was depleted for both thickened and neat contamination. The sudden, sharp mass decrease from the T2 to T3 tests for thickened MeS could indicate that the majority of the surface-bound MeS liquid was removed by the T2 touch sample.

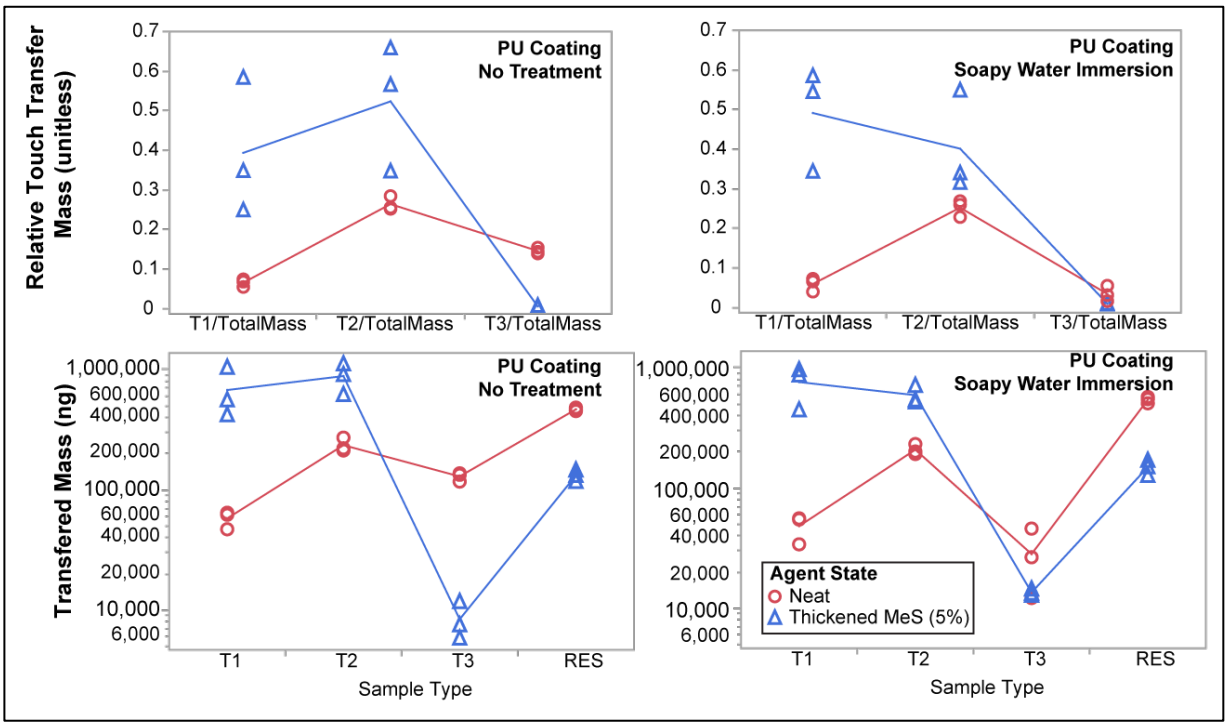

Figure 15. Contact-transferred mass and relative touch-transferred mass for PU coating.

The T3 (300 s duration) contact transfer test results for the thickened MeS using both treatment processes (no-treatment and soapy water immersion conditions) were significantly less than those observed using neat MeS. It is possible that this occurred because the neat MeS spread to a greater extent on the panel compared with thickened MeS (Figure 3). This would result in more contaminated area interaction with the decontaminant for the neat agent. A similar rationale could be applied to the larger RES value for neat versus thickened agent.

Historically, the soapy water immersion treatment process was developed to remove bulk and surface-bound liquid contaminants from a surface and leave behind only absorbed contaminant. The development of this technique was focused on the use of pure or neat contaminants. The aforementioned results indicated that the soapy water immersion treatment process may not remove all of the surface-bound liquid for thickened contaminants, as was seen

with the significantly greater T1 test transferred mass values for thickened compared with neat MeS. This could imply that the treatment process may not remove surface-bound liquid for contaminants with low water solubility and/or high viscosity.

Overall, these results showed how contact transfer testing can indicate if a contaminant could be surface-bound. For impermeable materials (steel), there was a rapid decrease in contact-transferred mass that was independent of contact duration. For absorptive materials, the trend of contact transfer was dependent on contact duration (differences between T1 and T2). The results for panels with PU coating that were tested using the soapy water immersion technique tended to indicate that this treatment process did not remove surface-bound liquid for the thickened MeS.

5.3 Contact Transfer with Bleach Treatment

The next analysis includes the evaluation of an active decontamination treatment using bleach on neat and thickened MeS, in contrast with the results from the other treatment processes. The RA results presented in Section 3.2 showed that bleach treatment on steel was very effective at removing the majority of neat and thickened MeS from the material. The results in Figure 16 show a similar trend for the contact transfer data. The magnitude of the contact transfer results are much less for bleach treatment compared with the soapy water immersion procedure. Almost all detectable quantities of neat MeS were removed from the steel panel when bleach was used. This resulted in limit of quantification (LOQ) results for all but two touch samples. The addition of thickener to the MeS resulted in small but quantifiable amounts of contact transfer for the first three touches. This indicated that the bleach was effective at removing most of the thickened MeS (soapy water immersion T1 test results were on the order of 100,000 ng of MeS). It is possible that this smaller quantity of MeS could be the effect of the thickener alone or in combination with defects and roughness in the material, as shown in Figure 17. For both neat and thickened MeS after the three touches, all of the contaminant was removed, as shown by the RES values near the LOQ. In comparison with soapy water immersion, the bleach was very effective at removing both neat and thickened MeS from steel.

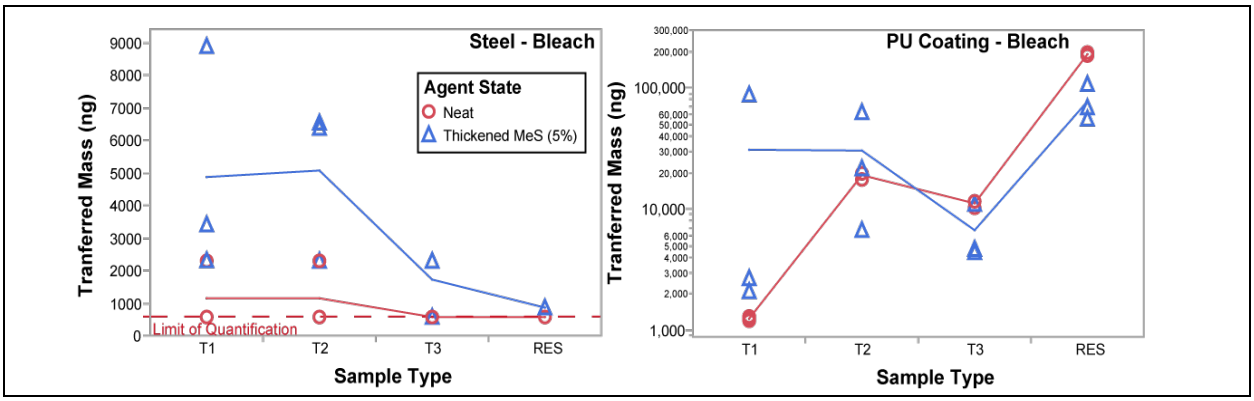

Figure 16. Contact-transferred MeS test results for bleach treatment on (left) steel and (right) PU coating. Dashed red line corresponds to the LOQ.

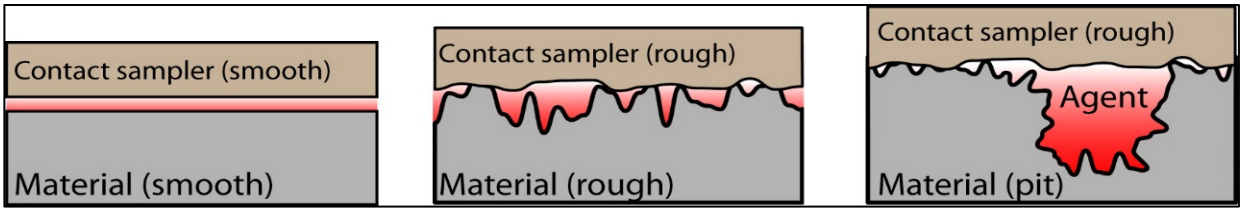

Figure 17. Illustration of how surface roughness could influence contact-transferred mass.

Because PU is absorptive, it is possible to have both squeeze-flow from bulk liquid and diffusive transfer from absorbed MeS. The effectiveness of the bleach treatment process in reducing the T1 values (quantified in Section 5.4) for both neat and thickened MeS from the PU coating (Figure 16) suggests that the bleach process removes the surface-bound liquid. This result was also observed for the impermeable material, stainless steel. In addition, like steel, the thickened MeS on PU resulted in more contact transfer during the T1 test than did the neat MeS. There was little difference in the absolute values from the T2 and T3 tests on PU with bleach treatment for both neat and thickened MeS. This suggests that there was not as much surface-bound liquid after the decontamination treatment due to the effective removal by bleach, and/or the T1 contact test removed most of the surface-bound liquid. The observed RES values for neat MeS were greater than the RES values for thickened MeS. This can be attributed to a greater amount of absorption into the PU material, which resulted from a greater amount of spreading for the neat MeS (more surface coverage leads to more absorbed mass). Overall, bleach significantly reduced the contact-transferred mass and RES values for both neat and thickened MeS on PU.

5.4 Comparison of Neat and Thickened MeS for Contact Transfer

For each decontamination treatment, the results for each contact transfer test type (e.g., T1, T2, and RES) were compared for neat and thickened MeS using an LD calculation. The results for stainless steel are provided in Figure 18. The LD indicates the order of magnitude difference in response due to the addition of the thickener. A value of 1 indicates that 10× more agent was detected for thickened MeS compared with neat MeS for a given sample. Considering the concepts of surface-bound liquid, the largest differences were observed for the T1 contact transfer test in which the most surface-bound liquid was likely to be sampled. In general, thickened and neat MeS provided similar results within the experimental uncertainty, but the thickened MeS resulted in slightly greater transferred mass values.

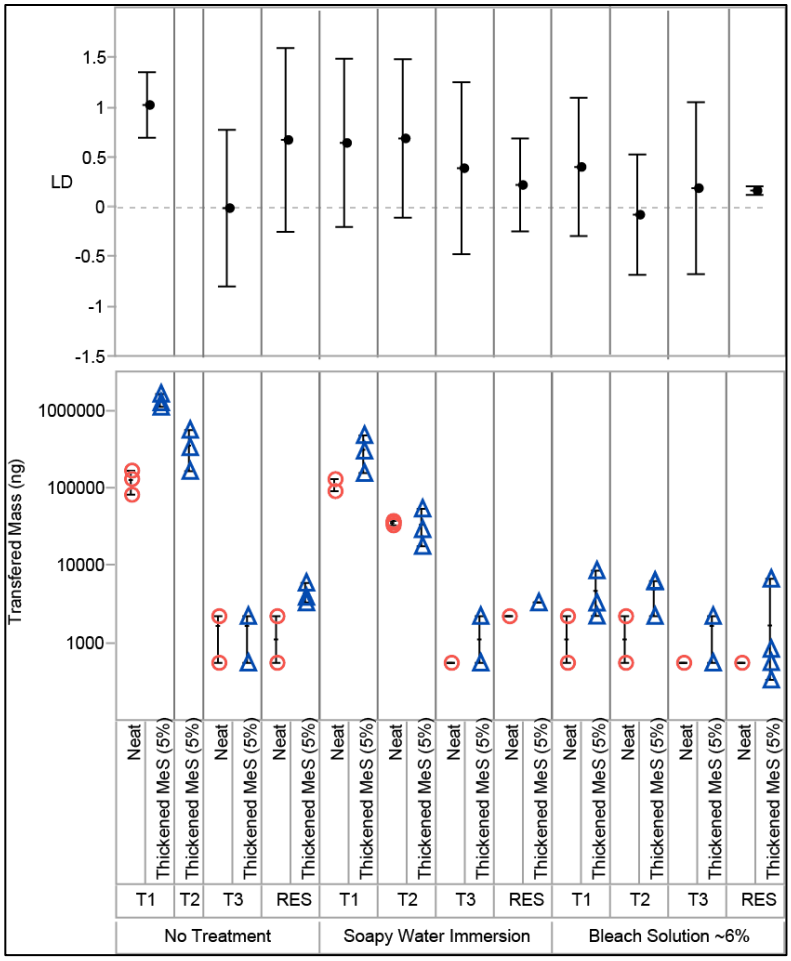

Figure 18. Results of contact transfer testing on stainless steel for neat and thickened MeS decontaminated using the soapy water treatment and using no treatment. LD was calculated using neat MeS as the reference condition.

The contact transfer results for the PU coating are shown in Figure 19. Several trends are apparent from these data. First, for the T1 touches there were significant differences of about 1 LD between results using neat and thickened MeS with no treatment and soapy water immersion treatments. As previously discussed, these results can be attributed to the presence of more surface-bound liquid with the use of thickened MeS. For decontamination with bleach, there was significant variability in which the mass found for two of the three replicates of the thickened MeS was only slightly greater than that of the neat MeS. Contrasting the soapy water immersion and bleach test results showed that some decontamination treatments may be significantly influenced by the presence of thickener, but *if the decontaminant can dissolve or react with the thickened contaminant, the contaminant can be removed from the material*.

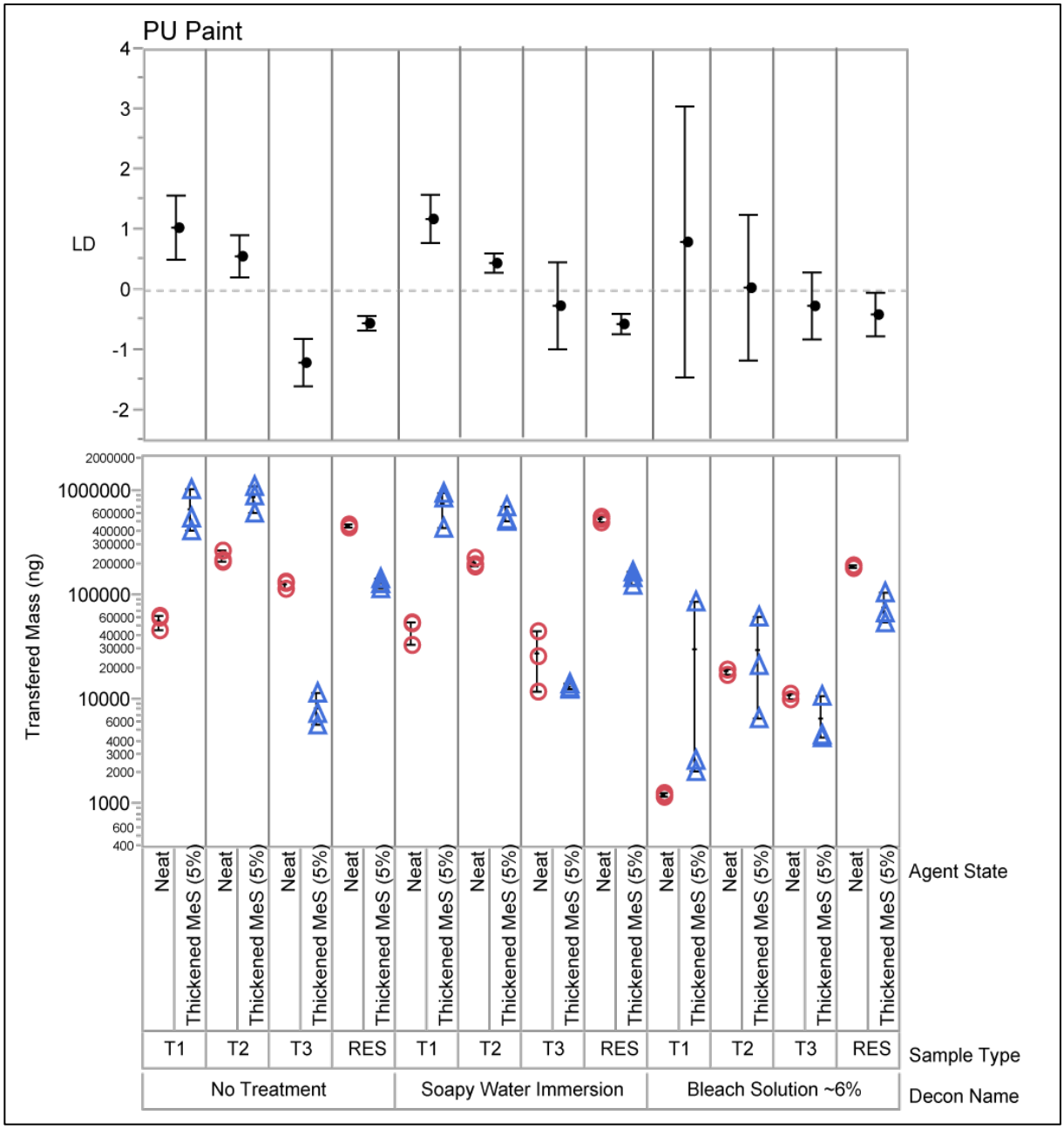

Figure 19. Results of contact transfer tests with neat and thickened MeS decontaminated using the bleach and soapy water treatment processes on PU paint. LD was calculated using neat MeS as the reference condition.

The comparison of T2 touch test data obtained using no treatment and soapy water immersion for the decontamination of MeS on the PU coating shows the differences between the two techniques to be smaller, likely because the T1 touch test removed most of the surface-bound liquid. This is very similar to the bleach data obtained for the T2 touch test potentially because the bleach removed much more of the thickened surface-bound MeS. The data obtained from the T3 and RES testing show different trends for all applied treatment

processes. The data from tests performed using neat MeS had greater remaining mass values, as compared with those from the thickened MeS testing, which resulted in negative LD values. It is possible that this could be due to a difference in the contaminated area where the neat MeS spread across the surface, which allowed for more absorption into the material, but the thickened MeS remained as a more sessile drop (Figure 3). The T1 and T2 touch tests did not show this trend, possibly because the surface-bound liquid could have dominated the signal of contact-transferred mass. This could indicate that the quantity of surface-bound liquid may not be strongly correlated with the spread of the liquid and the resulting contaminated area of the droplet.

Overall, the data show that thickener can change various aspects of the type of agent retention and the effectiveness of some treatment processes for the removal of the contaminant. The presence of thickener can influence how the contaminant spreads on the material (Figure 3) and how a decontaminant can physically remove the contaminant from a material (Figure 7). These changes in agent distribution and surface-bound versus absorbed liquid can result in significantly different contact transfer trends (Figure 19). An agent thickener can result in 10× more or 10× less mass transfer, depending on the context of the test.

6. DISCUSSION AND CONCLUSIONS

In conclusion, this study demonstrated that the presence of a thickener can significantly influence the effectiveness of a decontamination process, and therefore, must be considered when drawing correlations between laboratory tests and real-world situations. The major findings for each section are as follows:

(1) Panel Tests: Variations in the RA results obtained during panel tests suggest that one of the primary reasons for an increase in the RA with the presence of thickener is the ability of the decontamination procedure to effectively remove the liquid agent droplet (either by physical force or dissolution). Evidence of this was found by comparing the decontamination effectiveness of two different post-contamination treatments (soapy water and bleach). For the soapy water decontaminant, the thickened MeS droplet was not effectively removed, and therefore, a direct increase in the amount of remaining agent and percentage of thickener was observed. For the bleach decontaminant, no correlation between percentage of remaining agent and the presence of a thickener was observed, which was attributed to a smaller amount of residual liquid on the surface for all materials tested.

(2) Dissolution Rate: UV–vis measurements of the dissolution rate by a suspended droplet method indicated an indirect relationship between the amount of thickener added and the rate at which MeS dissolved into a water solution. These tests ultimately showed that when thickener is present, the dissolution of MeS is reduced up to 2.25×. Additionally, the presence of a cosolvent in the water accelerated the dissolution for the

thickened droplet; therefore, the dissolution rate could be potentially modulated by changing the water/cosolvent ratio.

(3) Material Absorption Rate: FTIR–ATR measurements of the chemical breakthrough of MeS (thickened and neat) into PDMS revealed no difference in the rate of absorption; only the maximum amount of MeS that was absorbed into the film. This suggests that (assuming the contact area is the same) the diffusion rate of MeS into the film is likely related to the concentration because the thickened droplet is effectively lower in concentration than the neat MeS.

(4) Contact Transfer: The trends observed for the contact transfer tests with 5% thickened and neat MeS corresponded with the conclusions obtained from the RA panel tests. The ineffectiveness of the soapy water treatment in the removal of surface-bound liquid for thickened agent resulted in larger transferred mass values than were obtained for the same test with neat MeS. When neat MeS was used, the surface-bound liquid was more effectively removed by soapy water. This was attributed to the greater amount of squeeze-flow transfer. In the case of the bleach decontaminant treatment (i.e., where the surface-bound liquid was effectively removed in both cases), neat and thickened agent behaved similarly. The exception was that the RES values observed for the PU coating were greater for neat MeS than for thickened MeS. This was attributed, at least in part, to the presence of more absorbed agent, which was likely due to greater droplet-spreading (i.e., more area of the panel was exposed to agent during contamination).

Ultimately, these results showed that a discrepancy exists between neat and thickened MeS in typical agent tests (RA and contact transfer). This inconsistency is related to the ability to physically remove and dissolve the simulant into the decontamination solution. For the soapy water immersion decontamination technique, the RA can be up to 2× greater for thickened MeS than for neat MeS due to the ineffective removal of the droplet. Consequently this leads to increased agent transferred during a contact transfer test. The dissolution rate of the MeS into a solution is reduced in the presence of thickener (up to 2.25×) but can be increased by the addition of a cosolvent. Finally, because the contamination rate for a constant surface area is the same for neat and thickened MeS, the amount of agent absorbed into a material (not surface-bound) will be dominated by the concentration of MeS in the droplet and the surface coverage (i.e., surface-spreading) of the droplet. These issues must be considered to relate common laboratory tests to real-world situations where agent thickener is used to improve the agent persistence in the environment. To enable the development of optimal hazard mitigation technologies, these data indicate that testing and formulating agents with thickeners may be important to provide optimal performance in fielded technologies.

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ACRONYMS AND ABBREVIATIONS

ATR	attenuated total reflection
CARM	Chemical Agent Resistance Method
CIS	cooled injection system
DI	deionized (water)
FTIR	Fourier transform infrared
GC	gas chromatography
IPA	isopropyl alcohol
IR	infrared
IRE	internal reflection element
LD	log difference
LOQ	limit of quantification
MeS	methyl salicylate
MS	mass spectrometry
PDMS	polydimethylsiloxane
PU	polyurethane
R	ratio
RA	retained agent
RES	residual agent
t	time
UV–vis	ultraviolet–visible

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