Development and Application of Model for Decontamination of Polymer-Based Materials

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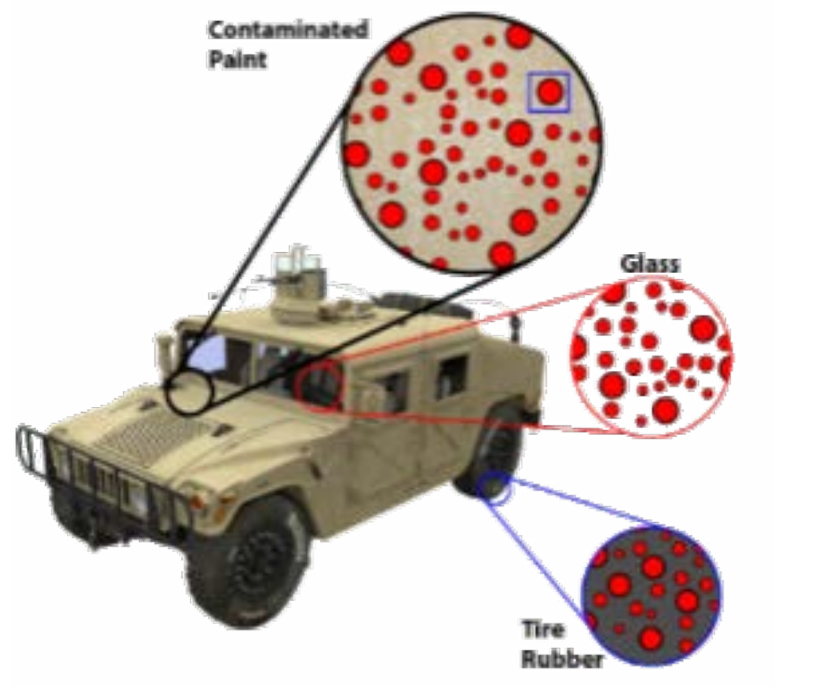
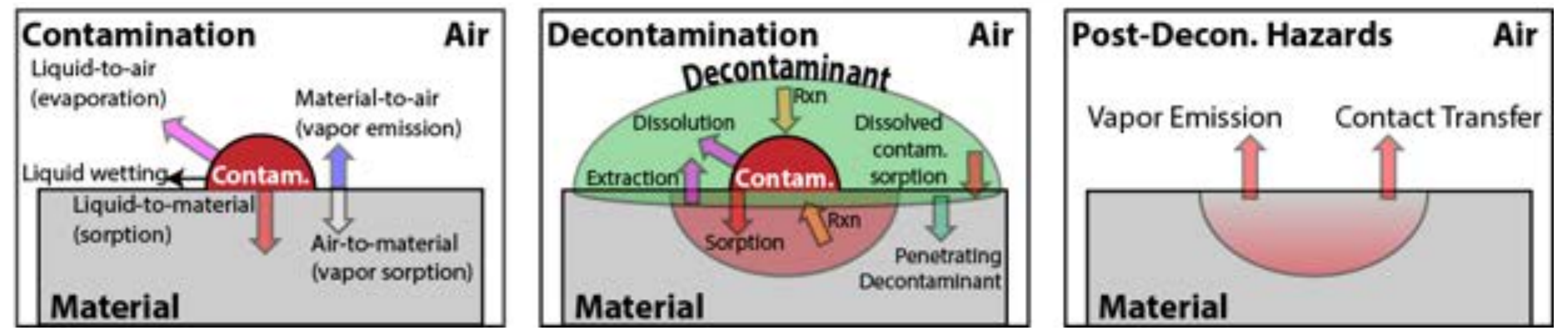
Abstract

- The ability to predict decontaminant performance fills critical gaps in testing since (1) it is often not possible to test over all operational conditions of interest, and (2) accurate models can provide insights into the mechanism of action and how modifying process parameters influences performance. To accomplish this, our model simulates all the physical and chemical processes that occur from the time a liquid agent droplet contacts the asset, through decontamination, and after the decontaminant is removed. For military coatings, the transport processes on the surface and in the bulk of the material are complex due to the irregular and heterogeneous nature of the material. This required development of high fidelity models for surface liquid spreading and diffusion in polymer-based materials to ensure accurate prediction. The process of designing experiments to obtain the necessary model parameters is described along with specific case studies varying the operating conditions and exploring scenarios not yet tested in the laboratory. Some examples include examining variations in the decontaminant thickness and timing of the decontamination process.

Model Overview

- Overall goal is to predict agent retention and vapor offgassing rate from an object after a decontamination process
- Need to simulate contamination and decontamination processes first because the final state of the system depends on its history
- Strategy is to deconstruct object into its component materials and simulate on the scale of a single droplet for each material and scale up to full-size





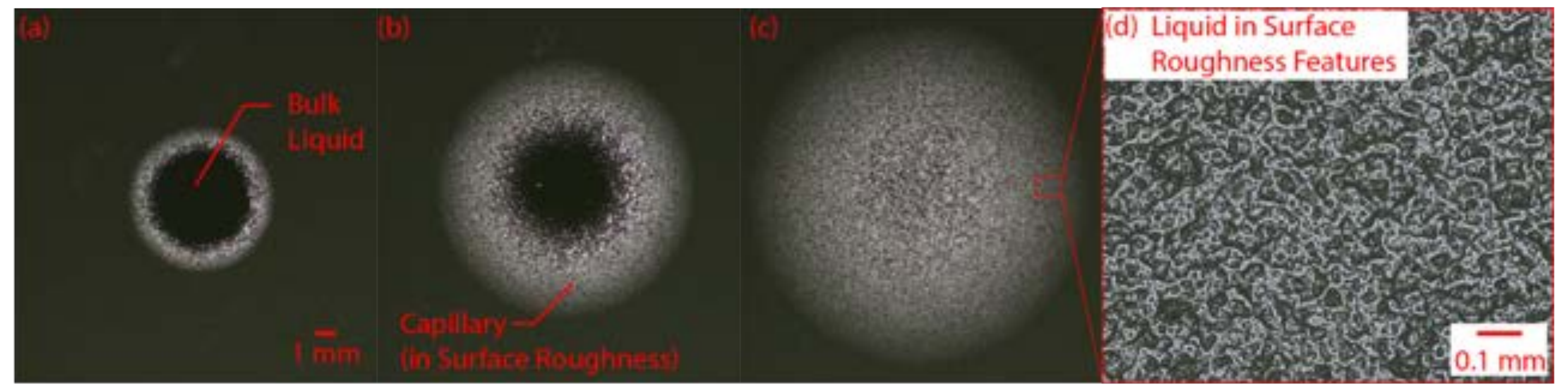
<u>Application areas</u>

- Test and Evaluation:
  - Enable exploration outside of tested parameter space without need for additional tests
  - Help with interpreting test results and most important factors to consider
- Operational Decision Making:
  - Informs when it would be safe to remove PPE and to minimize time in PPE
  - Can consider many different scenarios in short time
- Product Development
  - Identification of key performance parameters
  - Design tradeoffs and optimization

<u>Focus of This Work:</u>

- HD (sulfur mustard) and simulants on PU-coating
- Consider new decontaminant under development – zirconium hydroxide-based slurry
- Focus of model development is improved accuracy for liquid spreading on surface and multicomponent chemical diffusion in polymer-base of coating

Liquid Spreading Model



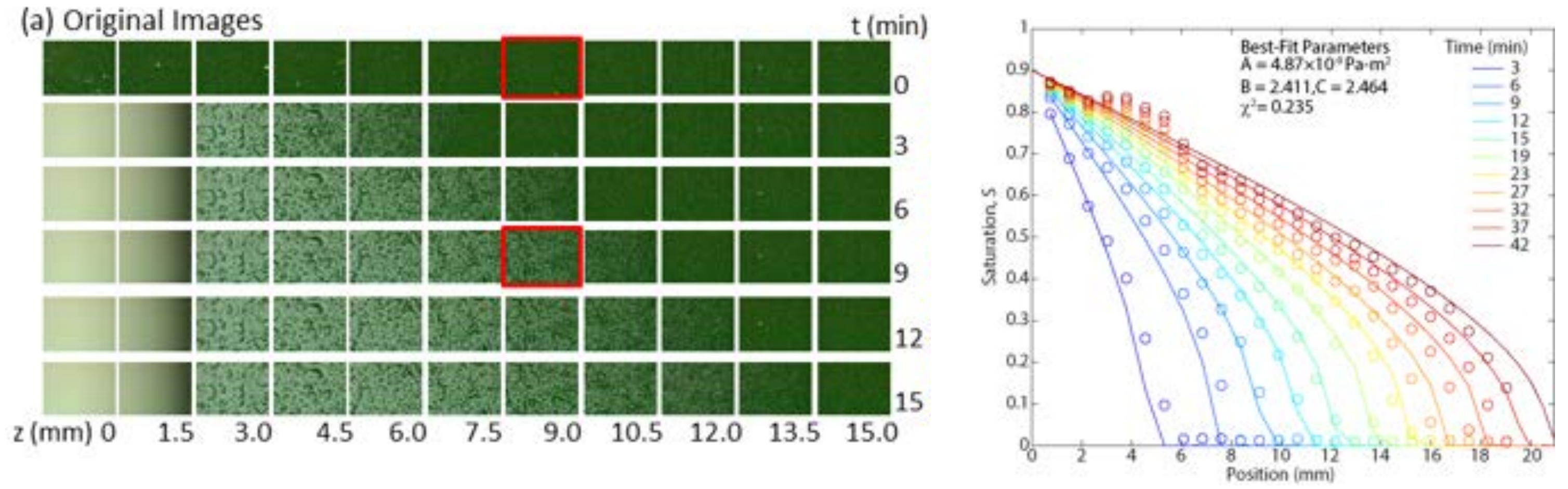
- Surface of PU-coating is rough and wetting liquids are pulled into surface roughness by capillary action, increasing the spreading rate
- Irregular nature of surface roughness results in a diffuse wetting front where the liquid surface coverage changes gradually over a finite area
- Spreading continues after bulk liquid imbibed

- Use model of Starov et al. (REF) for spreading over a thin porous substrate as a basis
- Use Richard's equation for unsaturated spreading via capillary action in surface roughness of material

Bulk Liquid: $\frac{dR}{dt} = v^+ - v^- \quad v^+ = 0.1\left(\frac{4V}{\pi}\right)^{0.3}\left(\frac{10\gamma}{\mu}\right)^{0.1}\frac{1}{(t+t_0)^{0.9}} \quad v^- = \frac{2}{3}\frac{\pi\delta\varepsilon R}{V}\int_0^\infty r\frac{\partial S}{\partial t}dr$

Capillary: $\varepsilon\frac{\partial S}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{K}{\mu}\frac{\partial p_c}{\partial S}\frac{\partial S}{\partial r}\right) \quad V = V_0 - \int_0^\infty 2\pi r\delta\varepsilon S dr$

- $K\frac{\partial p_c}{\partial S}$ is critical parameter determining spreading in surface roughness
- Can fit using experimental data for linear (1D) spreading, droplet (1D-axisymmetric) or surface topography
- Example shown is for silicone oil spreading linearly on PU-coating surface



Contaminant/Decontaminant Diffusion in Polymer

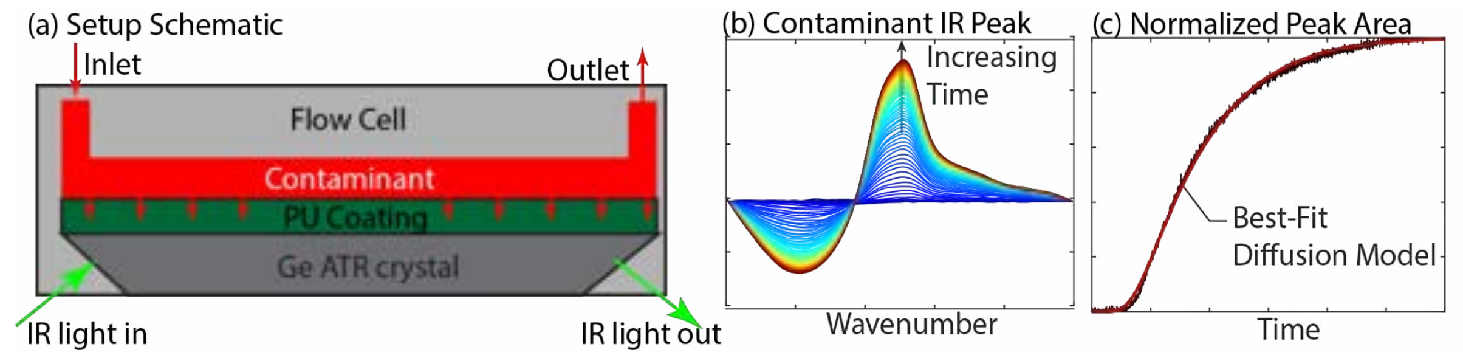
- Polymer is glassy at room temperature and undergoes transition as chemical absorbs
- Need to account for changes in polymer stress (σ), modulus (E) and viscosity (Type equation here.) as chemical absorbs
- Use model of Wu and Peppas (REF) as basis for model

$$\frac{\partial\phi_{c,m}}{\partial t} = (1-\phi_{c,m})\frac{\partial}{\partial z}\left[D_{c,m}(1-\phi_{c,m})\frac{\partial\phi_{c,m}}{\partial z} + \frac{D_c\bar{V}_c\phi_{c,m}}{RT(1-2\chi_{cm}\phi_{c,m})}\frac{\partial\sigma}{\partial z}\right]$$

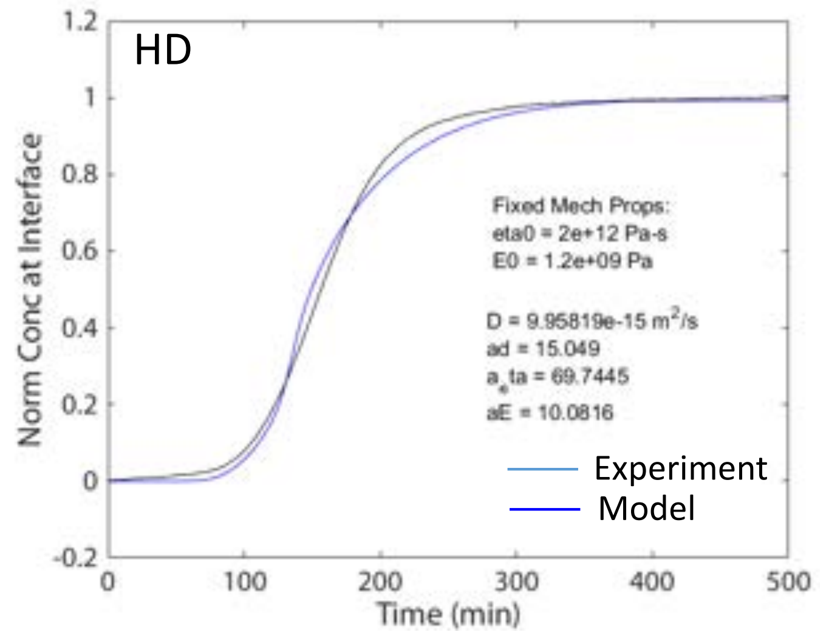
$$\frac{\partial\sigma}{\partial t} = -\frac{\sigma}{\eta/E} + \frac{E}{(1-\phi_{c,m})^2}\frac{\partial\phi_{c,m}}{\partial t}$$

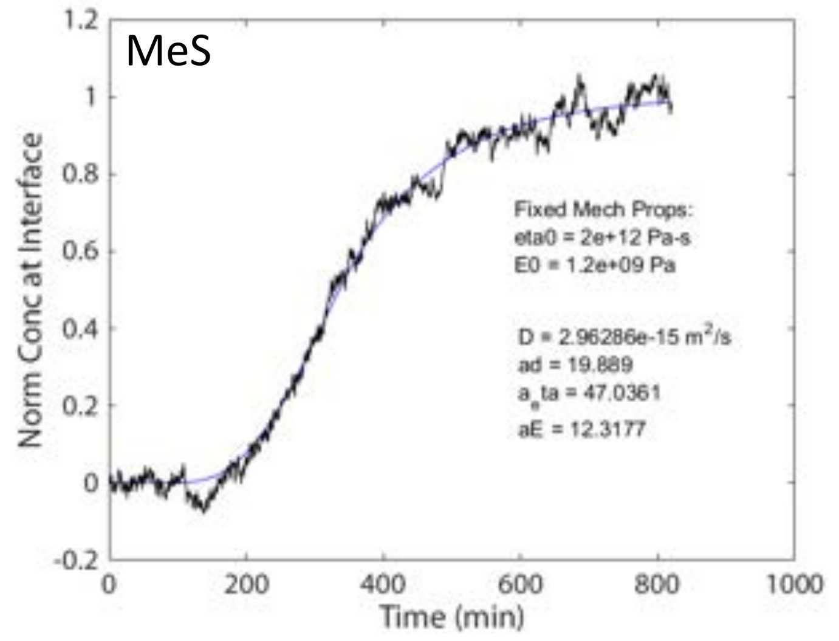
- Assume diffusivity, modulus, and viscosity vary exponentially with chemical volume fraction in polymer

$$D_{c,m} = \boxed{D_{c,m0}}\exp(\boxed{a_d}\phi_c) \quad E = E_0\exp(-\boxed{a_E}\phi_c) \quad \eta = \eta_0\exp(-\boxed{a_\eta}\phi_c)$$



- Use IR-based technique to obtain breakthrough dynamics curve
- Cast PU-coating on ATR crystal and monitor IR spectrum as chemical absorbs into PU coating
- Get chemical concentration vs. time at coating/crystal interface
- Fit model parameters using experimental data





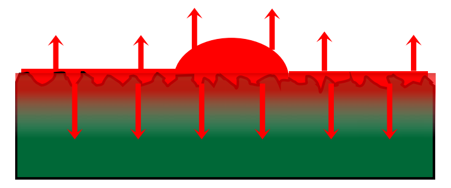
- Data and fits shown for HD and methyl salicylate (MeS)
- HD diffuses significantly faster than MeS
- Also performed experiments to determine diffusivity of decontaminant solvent and multicomponent contaminant-solvent diffusion in PU coating
- Future work – directly measure modulus and viscosity of polymer as a function of chemical absorption using quartz crystal microbalance (QCM) and dynamic mechanical analysis (DMA)

Model Case Studies

Baseline case

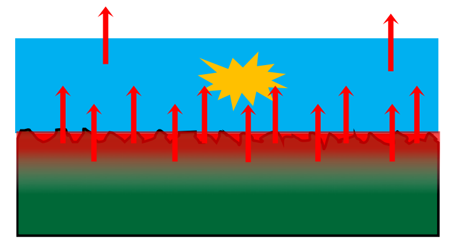
<u>Contamination</u>

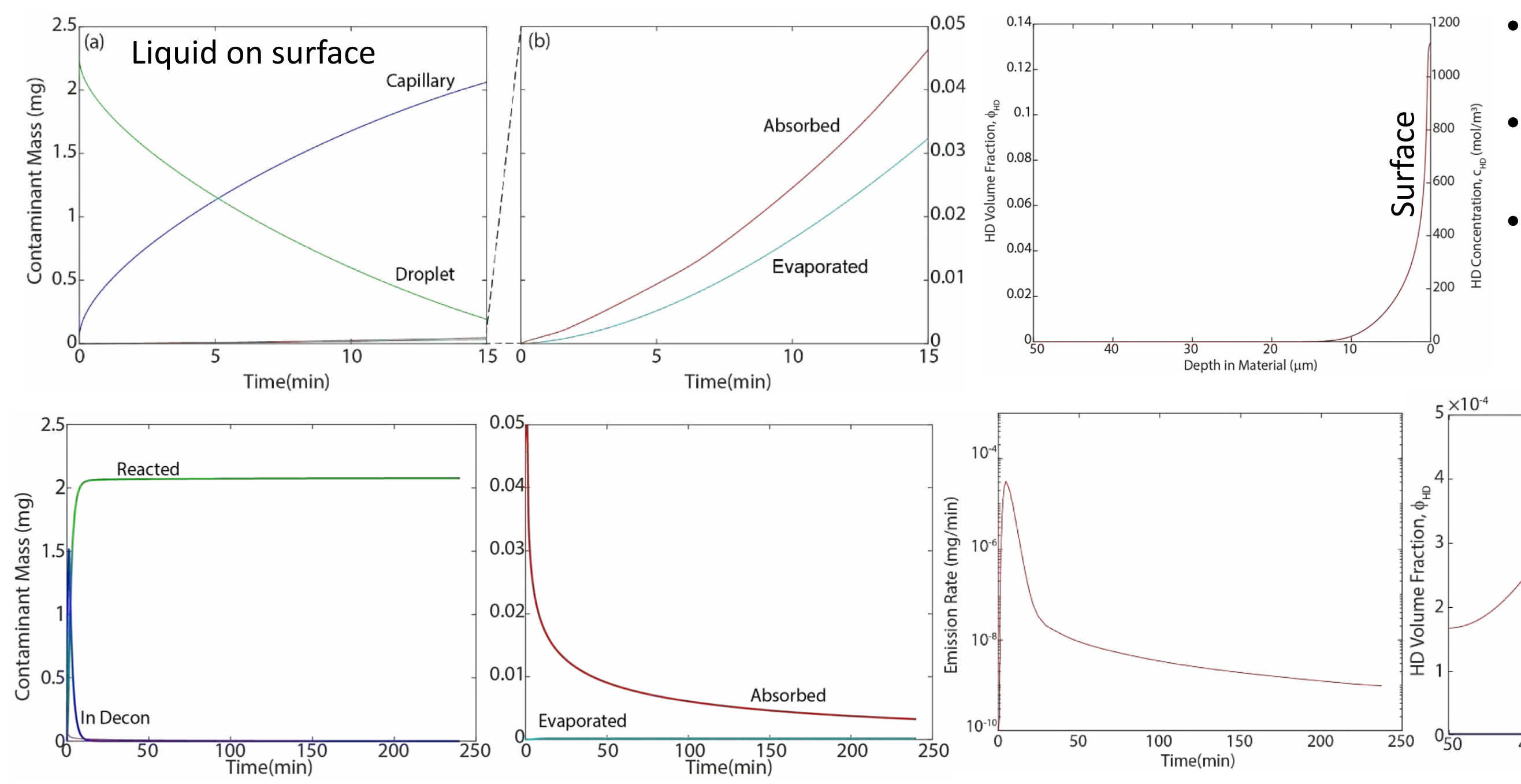
Single 2 μL drop of HD on PU coating



<u>Decontamination</u>

0.5 mm layer of Decon



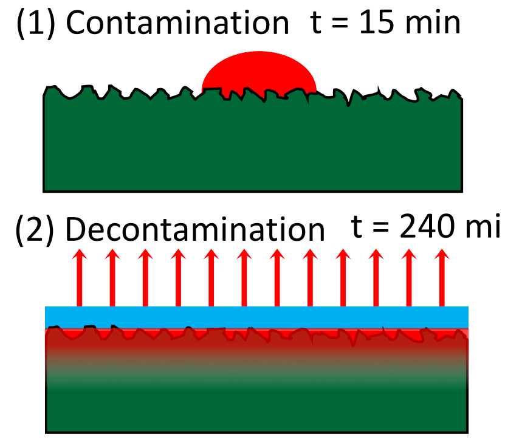


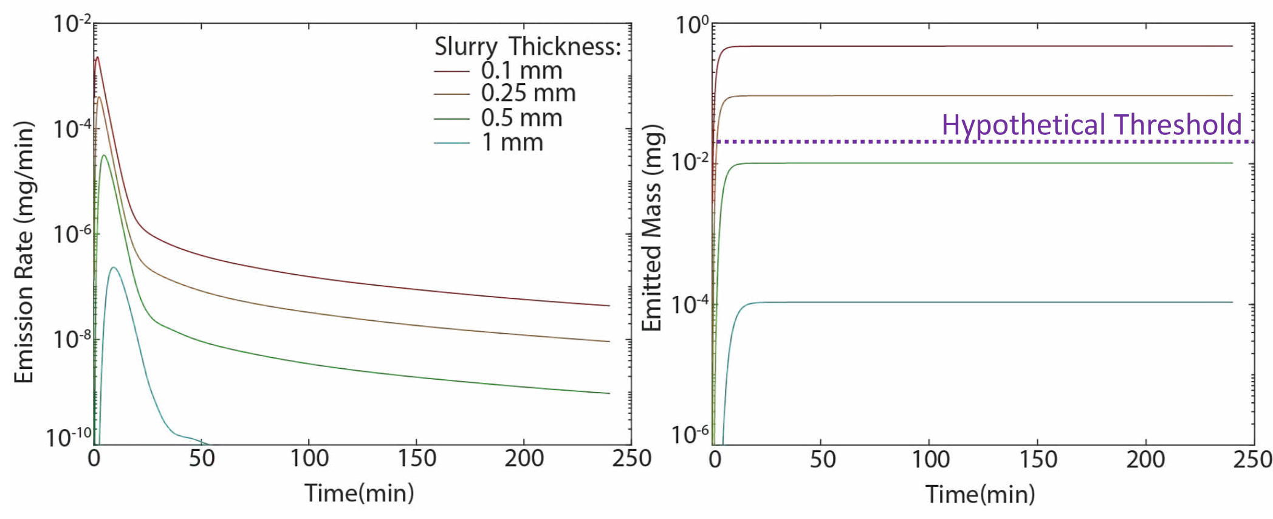
- Can see how much/ where contaminant is at any time
- Liquid contaminant on surface quickly reacted
- Contaminant absorbed in material presents lower level, longer term hazard as it slowly offgasses

Effect of Decon Thickness

(1) Contamination t = 15 min

(2) Decontamination t = 240 min





- Vary thickness of decon layer and see how vapor emission rate and total emitted mass is influenced
- Factor of 10 change in thickness results in multiple order of magnitude change in emission
- If there is a threshold emission level determined by health effects/operational impact, a minimum thickness could be determined
- Example of how model can be used in product development

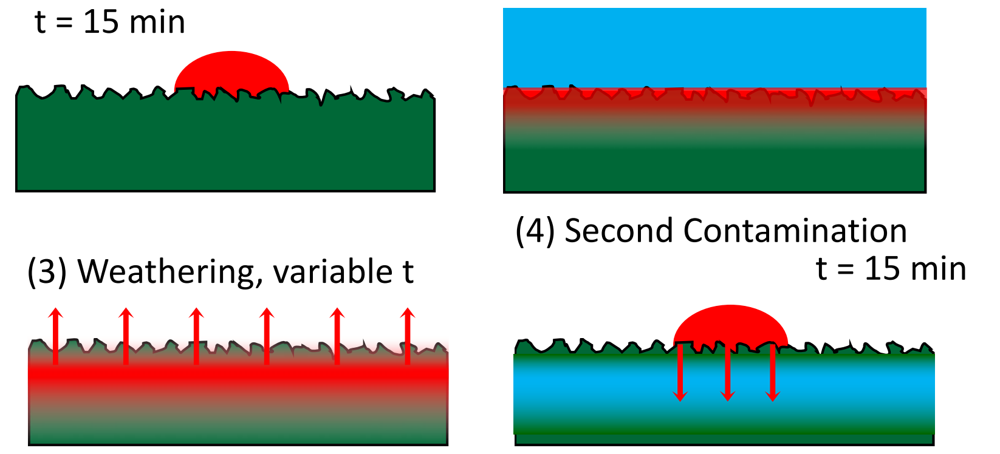
Secondary Contamination

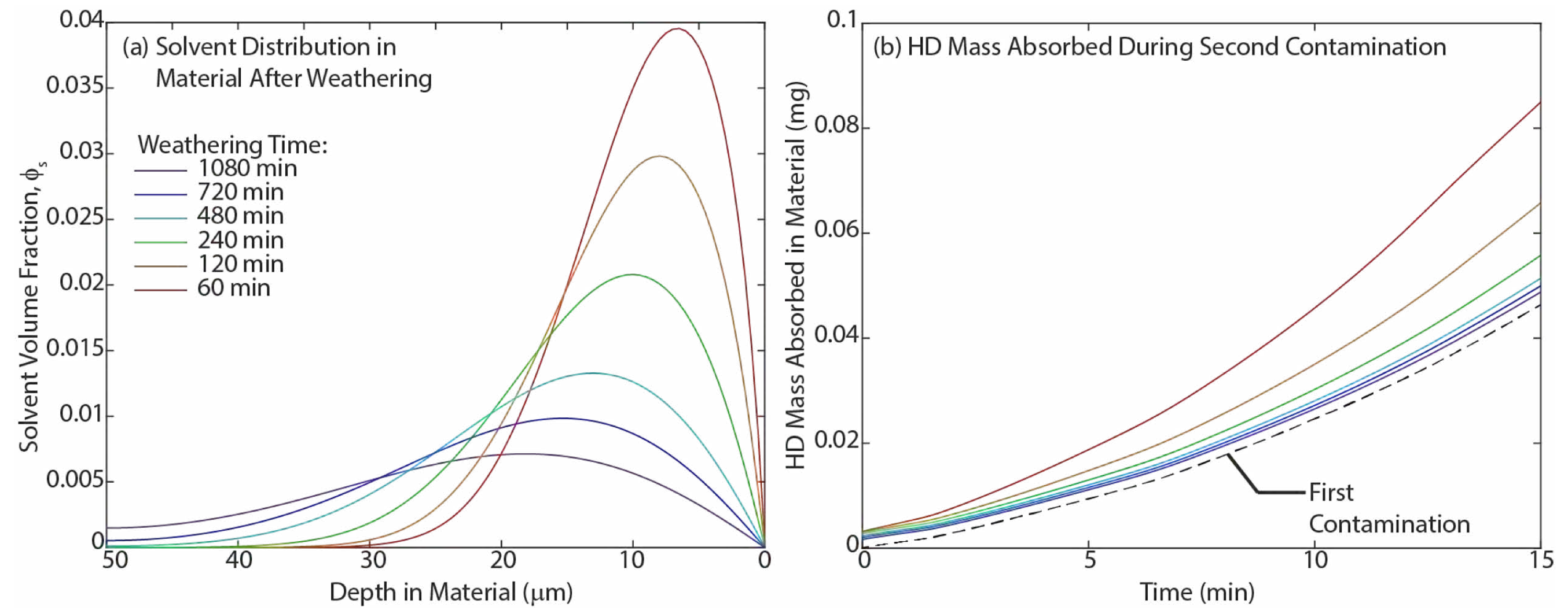
(1) Contamination t = 15 min

(2) Decontamination t = 240 min

(3) Weathering, variable t

(4) Second Contamination t = 15 min





- Solvent from decon formulation absorbs into the PU coating, aiding extraction of the contaminant
- Residual absorbed solvent could also make PU coating more susceptible to a subsequent, second contamination
- More HD absorbed on second contamination, but decreases as more time allowed for solvent to desorb

Conclusions

- Uses physics-based models on the scale of a single droplet to predict vapor emission rate and scales up to full object
- Can be used in product development, test and evaluation, operational decision making
- Improved model accuracy and performed model parameter estimation to incorporate ability to predict decon performance
- Examined several key factors in decon performance including timing, thickness, starting challenge, multiple contaminations
- Many potential applications of model from development of new decon technologies to answering questions about products that are already fielded

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