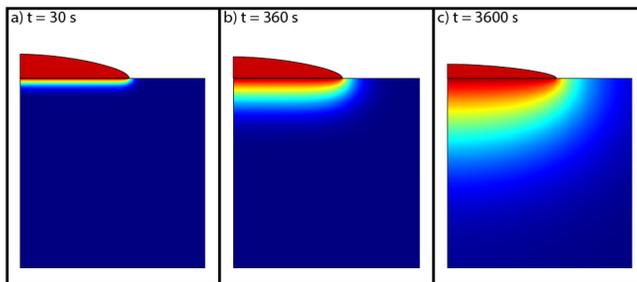


Mechanisms and Enhancement of VX Decontamination from Polymer Substrates above the Glass Transition Temperature

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Introduction

- A sessile liquid agent droplet can be absorbed into the substrate on which it resides via a solution-diffusion mechanism
- After the bulk liquid agent has been removed from the surface of the substrate, absorbed agent remains, which presents hazards due to evaporation and direct dermal contact
- Reducing the absorbed agent concentration to acceptable levels presents a challenge because the agent is not directly accessible to the reactive components of the decontaminant

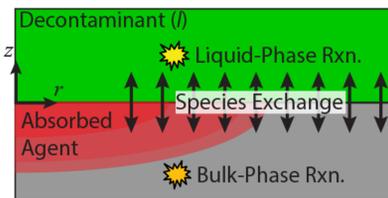


- This work showed that the efficacy of the decontamination process is not only determined by reaction rate
- The absorbed agent must be extracted into the liquid decontaminant for the reaction to occur, and this can be rate-limiting
- Furthermore, certain components can be added to a decontaminant formulation to increase the agent extraction rate

General Decontamination Model

Decontamination is described mathematically by a transport-reaction equation for each species in both liquid and polymer phases

- In general, all species including agent, decontaminant components, and byproducts must be accounted – a difficult problem
- The modeling framework provided a systematic framework that guided experimental study for the specific case of a silicone elastomer contaminated with VX and decontaminated with sodium hydroxide in water/methanol mixtures of varying composition



General Transport-Reaction Equation

$$\frac{\partial C_{i,p}}{\partial t} + \nabla \cdot (\mathbf{u}_p C_{i,p}) = -\nabla \cdot \mathbf{J}_{i,p} + \sum_j v_{ij} r_{j,p}$$

Thermodynamic Equilibrium at Interface

$$C_{i,s}(r, z=0, t) = \frac{C_{i,s,sat}}{C_{i,l,sat}} C_{i,l}(r, z=0, t)$$

Mass Conservation at Interface

$$D_{i,s} \left. \frac{\partial C_{i,s}}{\partial z} \right|_{z=0} = D_{i,l} \left. \frac{\partial C_{i,l}}{\partial z} \right|_{z=0}$$

Symbols

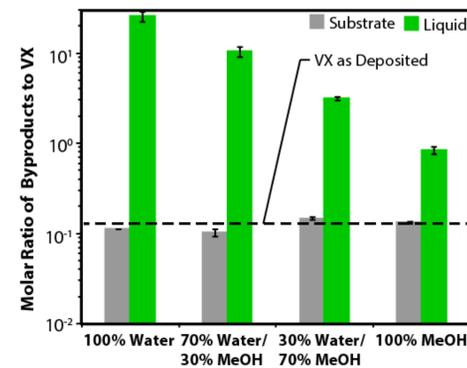
C = concentration of species
 J = diffusive mass flux vector
 r = reaction rate
 D = diffusivity

Subscripts

sat – refers to saturation
 i – refers to species i
 j – refers to reaction j

In What Phase Does Decontamination Reaction Occur?

- Allow a 2 uL droplet of VX to absorb into silicone substrate for 1 hr
- Expose contaminated substrates to 1000 mM NaOH dissolved in various water/methanol mixtures for 30 min
- Perform chemical analysis to determine the amount of VX and primary phosphorus containing byproducts EMPA and EA2192 separately for:
 - The decontaminant effluent (liquid)
 - The remaining absorbed chemicals in the silicone (substrate)

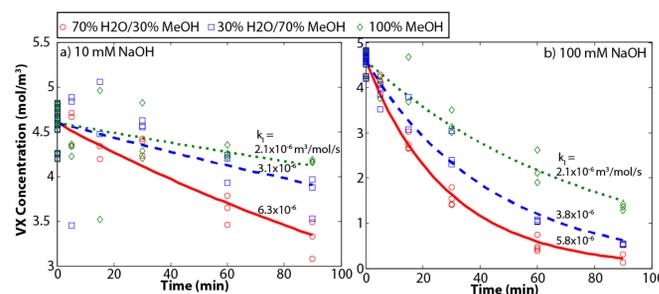


- Calculating the molar ratio of byproducts to VX in both the substrate and liquid phases showed:
 - The ratio was equivalent in the as-deposited VX droplet and in the substrate-phase after the decontamination process
 - The ratio was 1-2 orders of magnitude larger in the liquid-phase after decontamination

Highlights:

All decontamination reactions occur in the liquid-phase
VX must be extracted from the silicone for the reaction to proceed

Liquid-Phase Reaction Kinetics



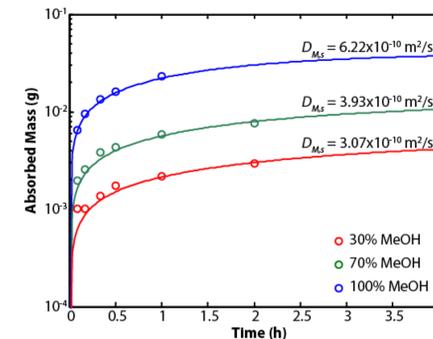
- Agitated mixtures of 4 mM VX with 10 or 100 mM NaOH dissolved in various water/methanol blends were sampled at various times
- The data were fit to 2nd order reaction kinetics (1st order in both VX and NaOH)

Highlight:

Increasing the ratio of methanol in the mixture decreased reaction rate

Solvent-Polymer Interaction

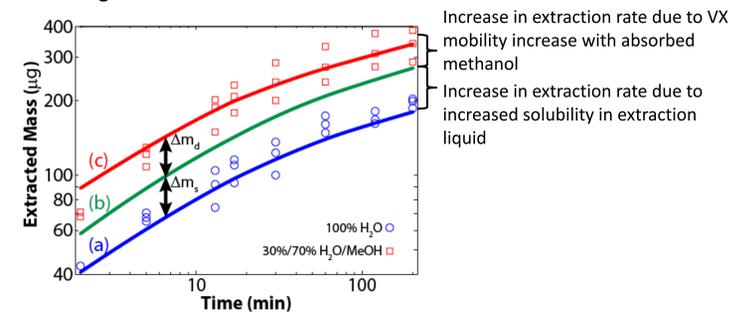
- Methanol slowed reaction in the liquid-phase, but it also absorbed into the substrate
- The rate and equilibrium amount absorbed were determined using gravimetric uptake measurements for pure water, pure methanol, and mixtures



- This data was used to determine the diffusivity and saturation concentration of water and methanol needed for the mathematical model of decontamination

Extraction Rate in Water vs. Water/Methanol Mixtures

- Silicone substrates equivalently contaminated with VX were placed in well-stirred baths of water (blue circles) and 30%/70% v/v water methanol mixture (red squares)
- Sampling the VX concentration as a function of time produced the following extraction curves:



- Modeling the extraction process in water produced good agreement with experiment: **curve (a)**
- Modeling the extraction process in the water/methanol mixture underpredicted the observed extraction rate: **curve (b)**

Highlight:

The VX diffusivity in silicone increases in the presence of absorbed methanol

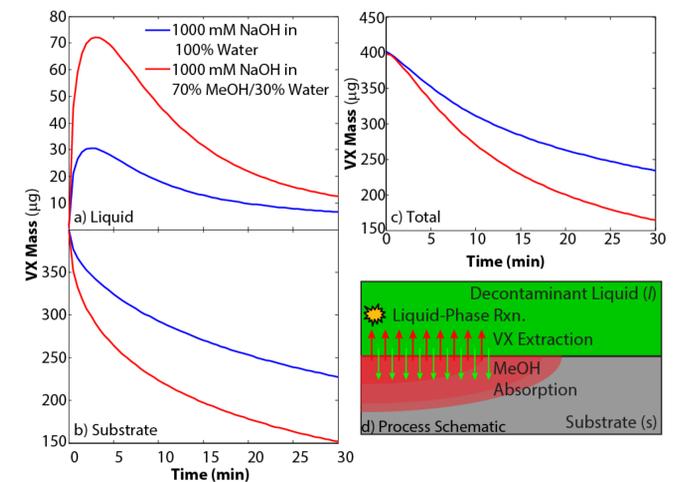
- Assuming the VX diffusivity is linearly proportional to the local methanol concentration in the silicone, the parameter α was fit to produce **curve (c)**, which matched the experimental extraction data

$$D_{VX} = D_{VX}^0 + \alpha C_{MeOH,s}$$

Fit to match experimental data

Model Predictions

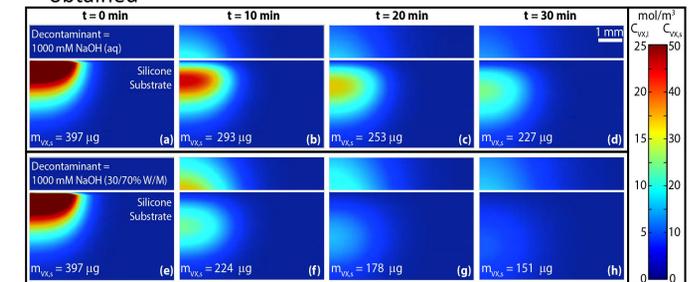
- Determination of the model parameters allowed predictions to be made under a wider variety of conditions
- Tracked the total amount of VX in both liquid and polymer phases over time



Highlight:

Although reaction is slower in liquid-phase, addition of methanol speeds VX extraction so that net effect is overall faster decontamination

- The detailed spatial distribution of VX in each phase can also be obtained



Conclusions

- Decontamination of VX from silicone proceeded by extraction followed by reaction in the liquid-phase
- Reactivity cannot be the sole metric used for determining decontaminant efficacy for absorbing substrates
- The extraction rate (and thus decontamination rate) was increased by addition of species that interact with the polymer and contaminant to enhance transport

Acknowledgments

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