

# Mechanisms and Enhancement of VX Decontamination from Rubbery Polymer Substrates

M. J. Varady, Ph.D.<sup>1</sup>, T. P. Pearl, Ph.D.<sup>1</sup>, S. M. Stevenson<sup>2</sup>, B. A. Mantooth, Ph.D.<sup>2</sup>  
(1) OptiMetrics, Inc., (2) U.S. Army Edgewood Chemical Biological Center

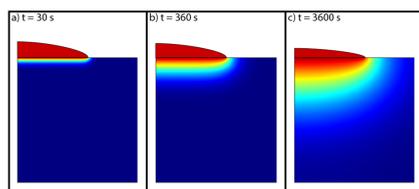
## Abstract

Successful recovery of an asset after contamination with a chemical warfare agent (CWA) requires that the decontamination technology neutralizes the CWA so that vapor inhalation and contact exposure hazards fall below established toxicological limits. Effective decontamination is an especially difficult challenge for materials that absorb the CWA because the agent becomes less accessible to the subsequently applied liquid-phase decontaminant. This work studied the specific transport and reaction mechanisms involved during the decontamination process for the case of O-ethyl S-[2-(diisopropyl-amino)ethyl] methylphosphonothioate (VX) absorbed in a silicone elastomer substrate. Several ratios of water/methanol blends were used as solvent carriers for NaOH as the reactive ingredient in the decontaminant. A primary result of this study was the determination that negligible reactive decontamination occurs within the subsurface of the polymer regardless of the formulation used.

Rather, it is shown experimentally that the rate limiting process for decontamination of VX from a silicone elastomer substrate is extraction into the liquid-phase decontaminant on its surface. It is further demonstrated that the solvent carrier can penetrate the polymer substrate, increasing the transport rate of VX from the silicone into the liquid-phase decontaminant, thus enhancing the decontamination efficacy. The transport rate enhancement is directly correlated to the water/methanol ratio used in the solvent carrier of the decontaminant. Physics-based models of the transport and reaction processes occurring during decontamination are developed and predictions compare favorably to experimental results. These results lay the groundwork for the rational design of more effective decontaminant solutions for absorbing materials using combined basic physical understanding and corresponding models for guiding effective decontaminant formulation in the laboratory. Such decontaminant formulation efforts should focus on the ability to extract agent compounds from substrates in addition to confirming liquid-phase reactivity.

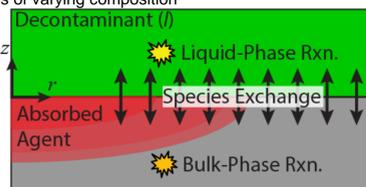
## Contamination of Absorbing Materials and Resulting Hazards

- 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



## General Model of Decontamination

- In most decontamination processes, a liquid-phase solution is applied to the surface of the contaminated material
- Mathematically, the decontamination process is described by a transport-reaction equation for each species present in the system
- This framework is used to guide a systematic experimental investigation of the decontamination of the specific case of silicone elastomer contaminated with VX and decontaminated with sodium hydroxide in water/methanol mixtures of varying composition



M. J. Varady et al., JPC Lett, submitted (2015)

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

### Equilibrium at Interface:

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

### Mass Conservation at Interface:

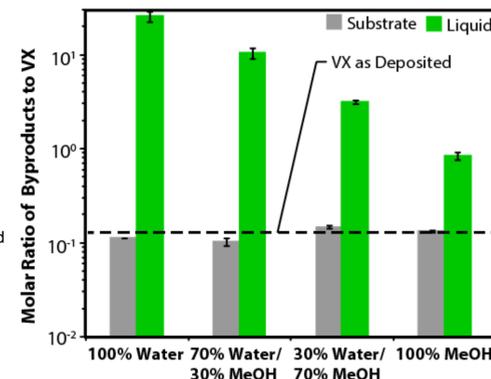
$$D_{i,s} \left. \frac{\partial C_{i,s}}{\partial z} \right|_{z=0} = D_{i,l} \left. \frac{\partial C_{i,l}}{\partial z} \right|_{z=0}$$

## Chemical Reaction in Liquid and Polymer Substrate Phases

- In general, chemical reactions can proceed in both the polymer substrate and the liquid phases
- To assess where reaction was occurring, the decontamination process was carried out on VX contaminated silicone substrates using 1000 mM NaOH solutions in various mixtures of water/methanol

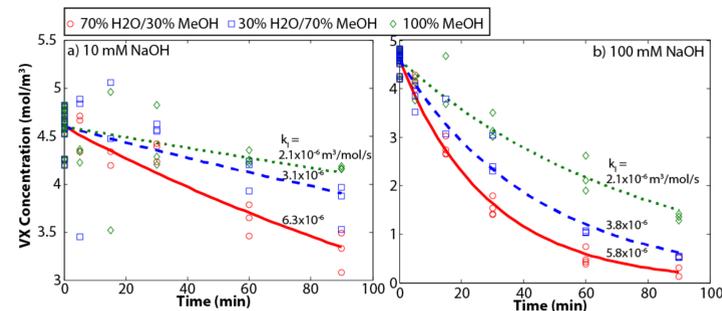
### Procedure

- A 2  $\mu$ L droplet of VX was deposited on a silicone disc (5.08 cm diameter, 3 mm thickness)
- VX droplet resided on surface for 60 minutes, then was washed off
- Substrates prepared in this manner were immersed in four different decontaminant solutions of 1000 mM NaOH in 100% water, 70%/30% water/methanol, 30%/70% water/methanol, and 100% methanol for 30 minutes
- After the decontamination process, the silicone substrate was extracted in isopropyl alcohol to capture the residual VX and byproducts
- The amount of VX and the primary P containing byproducts, EMPA and EA2192, were quantified using LC/MS/MS
- Quantification was performed for both the extractant and the decontaminant solution
- The molar ratio of the byproducts to VX compared to a reference gives a measure of the extent of chemical reaction
- The molar ratio of reaction byproducts to VX in the silicone substrate was approximately equivalent to that in the liquid VX droplet deposited at the start of the contamination process
- The molar ratio of reaction byproducts to VX in the decontaminant was significantly higher
- All chemical reactions during decontamination occur in the liquid-phase
- VX must be extracted from the silicone into the liquid decontaminant solution for reaction to proceed



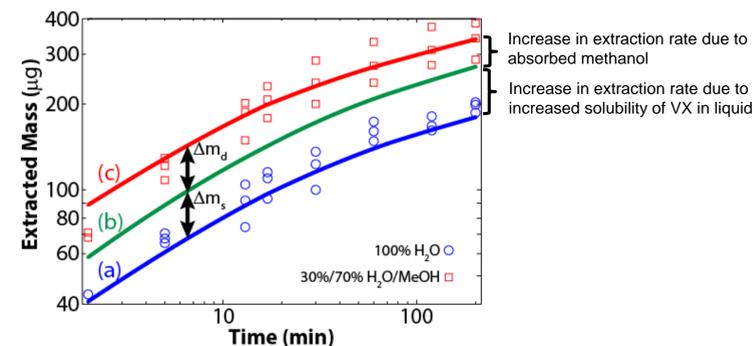
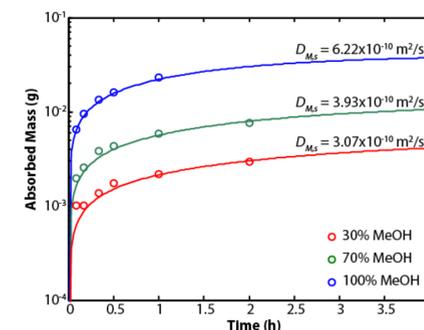
### Liquid-Phase Reaction Kinetics

Experiments were performed to monitor the disappearance of VX in a liquid-phase mixture with NaOH and fit to a second-order rate law.



## Interaction of Solvent with Polymer Substrate

- Although increased methanol concentration decreases the liquid-phase reaction rate, VX is more soluble in methanol than in water, which can increase the extraction rate
- Additionally, methanol is absorbed by the silicone elastomer, which can alter the diffusivity of VX
- Gravimetric uptake experiments were performed to quantify the dynamics and equilibrium of absorption of pure methanol, pure water, and mixtures
- Equilibrium experiments provided the saturation concentration of the liquids in the silicone
- Dynamic experiments provided the diffusivity of methanol in the silicone
- Extraction of absorbed VX from a silicone panel proceed more quickly for a water/methanol mixture compared to pure water



- Modeling the extraction process shows that the solubility alone cannot account for the observed difference in extraction dynamics
- The absorbed methanol must increase the diffusivity of VX in silicone
- A linear relationship between VX diffusivity and absorbed methanol concentration is assumed

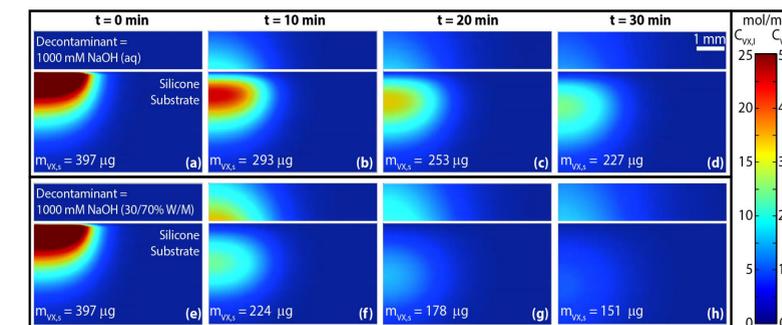
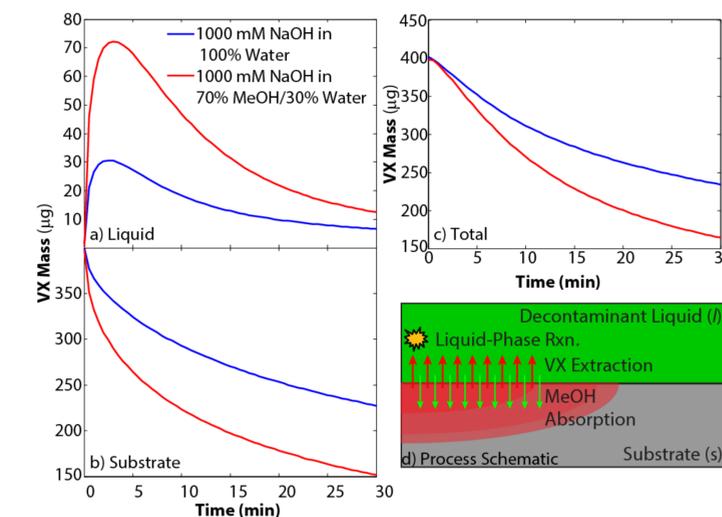
## Determination of Model Parameters

- Due to logistical constraints, gravimetric uptake experiments could not be performed to obtain saturation concentration and diffusivity of VX in silicone
- Instead a model of the extraction process was fit to experimental data for extraction of VX from silicone in pure water
- The normalized error,  $\chi^2$ , between experimental results and model predictions is minimized using the Levenberg-Marquardt algorithm, yielding the optimum values of parameters

$$\chi^2 = \frac{m_{VX,J,exp}^2(t_i) - m_{VX,J,mod}^2(t_i, C_{VX,s,ss}, D_{VX,s}^0)}{\sigma^2}$$

## Model Predictions

- Determining the model parameters allows predictions to be made
- In addition to providing the total amount of VX in both liquid and substrate phases over the course of the decontamination process, the VX spatial distribution can also be tracked



## Conclusions

- Decontamination of a silicone substrate contaminated with VX proceeds by extraction of VX followed by reaction in the liquid-phase
- The rate of agent extraction is an important metric; reactivity cannot be the only criterion by which a decontaminant is assessed when used on absorbing materials
- The extraction rate can be increased by including species that absorb into the substrate and increase the diffusivity of the agent

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