Chemical Based Neutralization of Neat Chemical Warfare Agents

Mark K Kinnan [1], David J McGarvey [2], Todd M Alam [1], William R Creasy [3]

[1] Sandia National Laboratories; [2] Edgewood Chemical Biological Center; [3] Leidos, Inc., supporting ECBC

Motivation

In situ neutralization and polymerization of neat Chemical Warfare Agents (CWAs) could be performed in the existing CWA storage container via wet chemical approaches using minimal quantities of chemical based reactive materials. This approach does not require sophisticated equipment, fuel to power generators, electricity to power equipment, or large quantities of decontaminating materials. By utilizing the CWA storage container as the reaction vessel, the amount of logistical resources could be significantly reduced. Fewer personnel are required since no sophisticated equipment needs to be set up, configured, or operated. Chemical based bulk CWA neutralization chemistries offer advantages such as:

- broad spectrum capabilities,
- readily fieldable,
- off the shelf reactive materials,
- easy to transport,
- irreversible neutralization,
- no mixing required,
- rapidly deployable in a warzone,
- covert neutralization if desired,
- performed at room temperature.

Employing the CWA storage container as the reaction vessel enables the capability to add materials to multiple containers in a short period of time as opposed to processing one container at a time for typical batch reactor approaches.

Goal

Identify one or two chemistries that are effective at rapidly neutralizing and gelling a variety of different chemical weapons such as GB, HD, and VX.

Bulk Agent Challenges

Designing chemistries for destruction of neat chemical agents is a challenge. There are many interrelated factors that come into play, see Figure 1. For example, in some scenarios it may be necessary to neutralize bulk agent as quickly as possible. In this case, it may be necessary to use a chemical pathway that requires more material and/or material that is difficult to handle (e.g., air sensitive). In other cases, the reactive material may be stable in air/moisture environments but require higher quantities of materials to achieve high levels of destruction over longer periods of time.

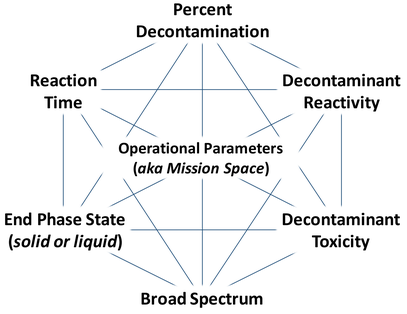

Figure 1. Interdependence of bulk decontamination

Agents and Simulants

The chemical agents and simulants used in this research are depicted in Figure 2.

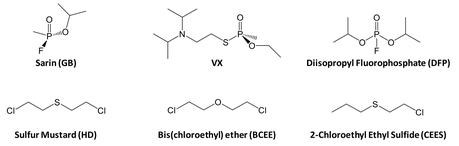

Figure 2. Chemical structures of agents and simulants

Discussion

Two chemistries are presented here that demonstrated effective destruction of GB, HD, and VX at milliliter reaction volumes. These chemistries were first designed and optimized using simulants (at SNL) to gain an understanding on their anticipated behavior when tested on agents (at ECBC). The first chemistry described below utilized lithium aluminum hydride ($LiAlH_4$) and the second utilized lithium nitride (Li_3N).

$LiAlH_4$ is effective at rapid destruction of GB and VX. Using approximately 7% by volume $LiAlH_4$ to GB, 27% of the GB was destroyed right after mixing. Near complete gelling was observed over the course of several minutes. Unfortunately, reactions using $LiAlH_4$ only exhibited immediate reactivity and did not continue destroying agent with time. Additional testing revealed HD was also destroyed using $LiAlH_4$. Over several hours a physical change was observed, and the mixture appeared to thicken and gel.

Discussion Cont.

Li_3N was also demonstrated to be effective on destruction of GB and HD. After adding Li_3N to neat chemical agent/simulant, a small amount of water was added that reacted with the Li_3N in solution to form LiOH that likely reacted with the agent/simulant. Using 21% volume additive ($Li_3N + H_2O$), 50% neutralization of bulk GB occurred in 10 minutes with gelation occurring within 6 hours. 99% neutralization was observed in approximately 2 days. Using 36% volume additive, HD was gelled over the course of a day.

Figure 3. Reaction of (left) VX + $LiAlH_4$ and (right) HD + Li_3N + H_2O

Analysis Challenges

A challenge associated with performing neat simulant/agent reactions was monitoring the kinetics and breakdown of the chemicals. The reactions began as neat liquid solutions in an NMR rotor. Reactive materials are added to the NMR rotor and monitored. As time elapsed the reactions transformed from liquid to solid making it difficult to observe solid based reaction products using liquid based NMR probes. Molecules that cannot freely tumble in solution cannot be observed in a typical liquids NMR experiment. Solid product was scooped out of NMR rotor or vials and analyzed via solid state NMR.

Conclusion

We are reporting on two chemistries that exhibited rapid and effective neutralization and gelation of chemical agents at milliliter reaction volumes: lithium aluminum hydride and lithium nitride. The chemistries offered broad spectrum destruction in short periods of time. Destruction was verified by NMR as decreases of the agent bands and/or generation of new peaks.

Next Steps

Both chemistries have been demonstrated to be effective at rapidly neutralizing chemical agents. Scaling up testing to significantly larger volumes (tens of milliliters to liters) will require research in order to develop approaches to be able to safely and effectively deliver the chemistries to the neat agent.

Disclaimer

The reactions described in this research are extremely dangerous. These reactions were carried out by trained and qualified personnel.

Acknowledgements

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Contact

Mark Kinnan, (505) 284-6903, mkkinna@sandia.gov