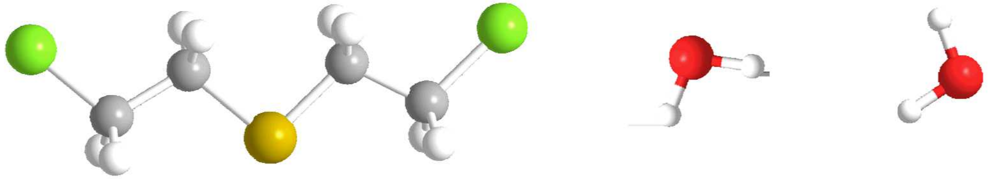
SAND2019-13538C

Systematic Optimization of High Activity Neutralization Materials for Bulk Chemical Agent Detoxification



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Detoxification is a fundamentally different process from decontamination

Several methods and chemistries have been developed to remediate chemical warfare agents or toxic industrial chemicals on a variety of surfaces.

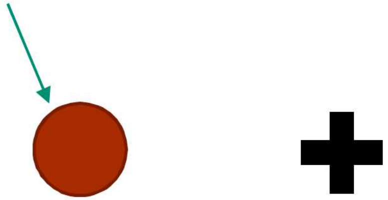
All of them share a common set of assumptions and practices:

1. The agent is a minority contaminant in a comparatively much larger system.
    - Eliminate toxicity posed by the agent while leaving the system (relatively) intact.
2. The precise quantity and location of agent is unknown.
    - Excess decontamination reagent is needed to ensure effective decontamination.
3. Many CWAs are poorly soluble in aqueous solution
    - Surfactants or substantial volumetric excess increase contact of the decontaminant with hydrophobic agents.

These practices are not practical for a bulk detoxification scenario

Detoxification of bulk chemicals requires specific considerations

Chemical agent comprises the majority or entirety of the system

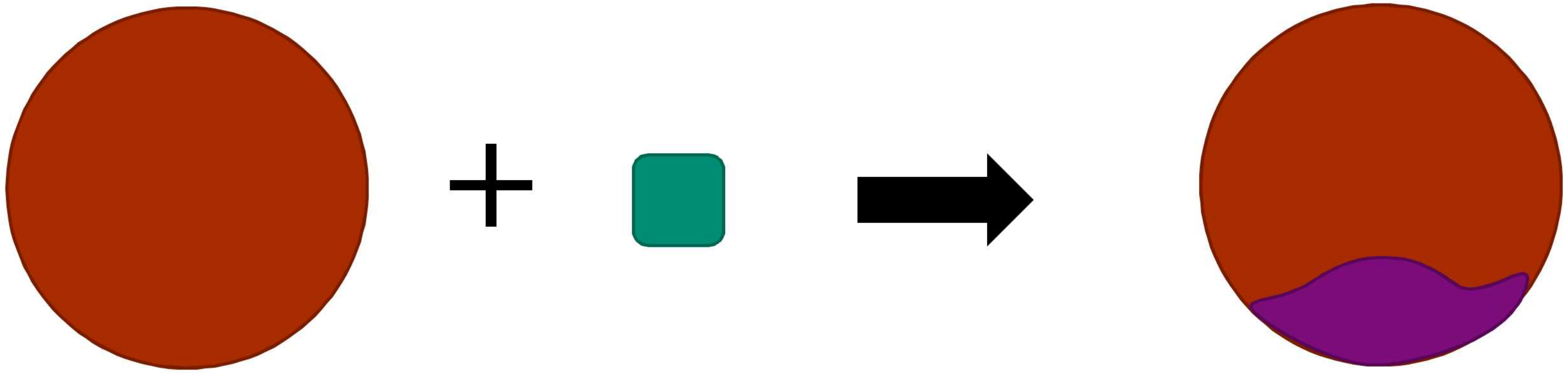


A smaller volume of more highly reactive reagents is needed for practical detoxification.

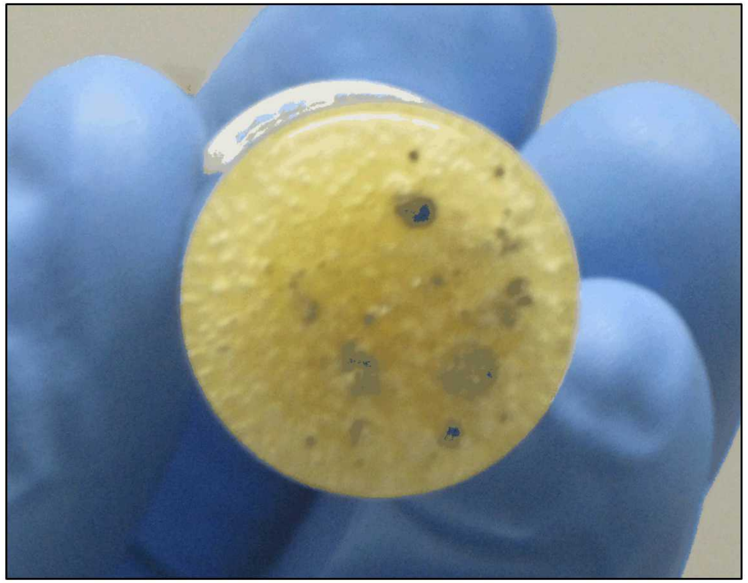
Since great excesses are not used, physical mixing and solubility of the reagent becomes a more significant issue.

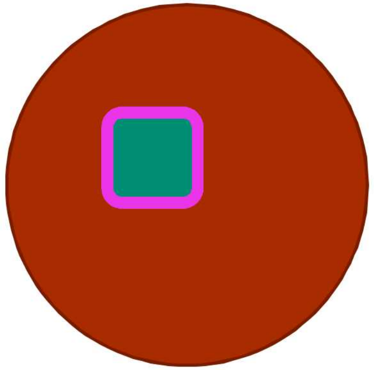
Treatment with a substantial excess of mild reagents is not feasible.

Under bulk conditions, the agent itself is the reaction solvent



As the reaction progresses, products accumulate and change the distribution of agent and reactants.





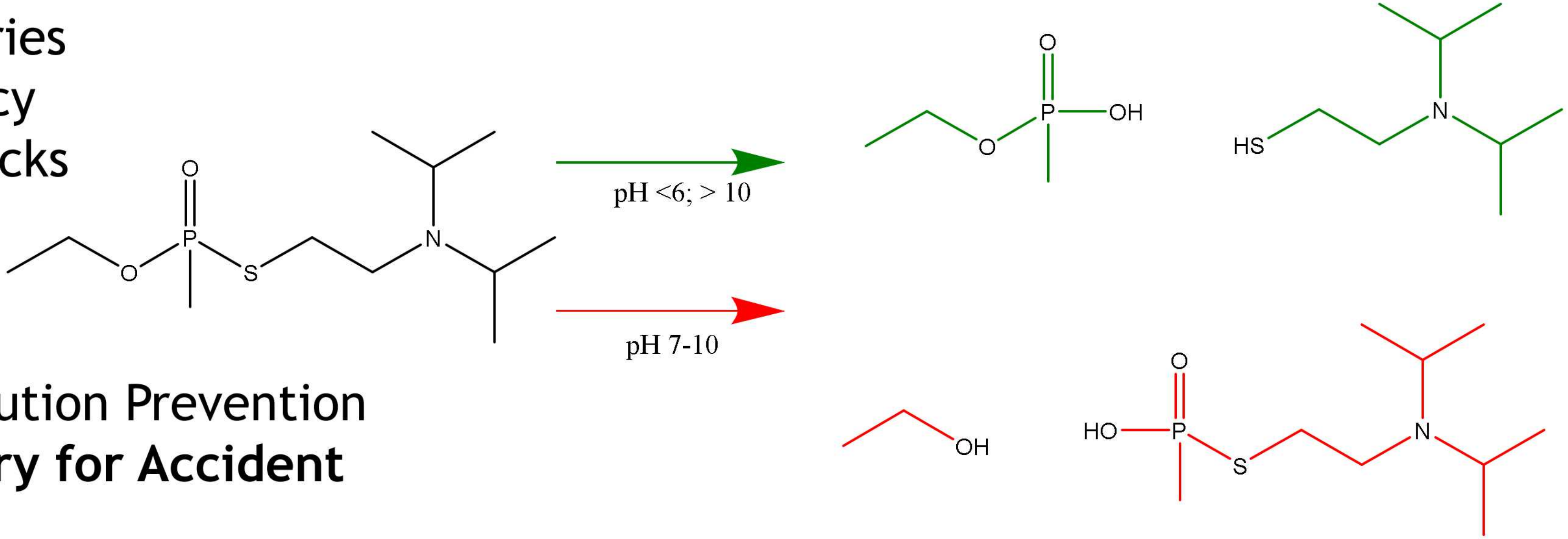
Products may passivate the reactant, limiting overall reaction

Achieving effective detoxification requires a highly efficient approach

The 12 Principles of Green Chemistry are guidelines to achieve the greatest product output while minimizing detrimental environmental impact.

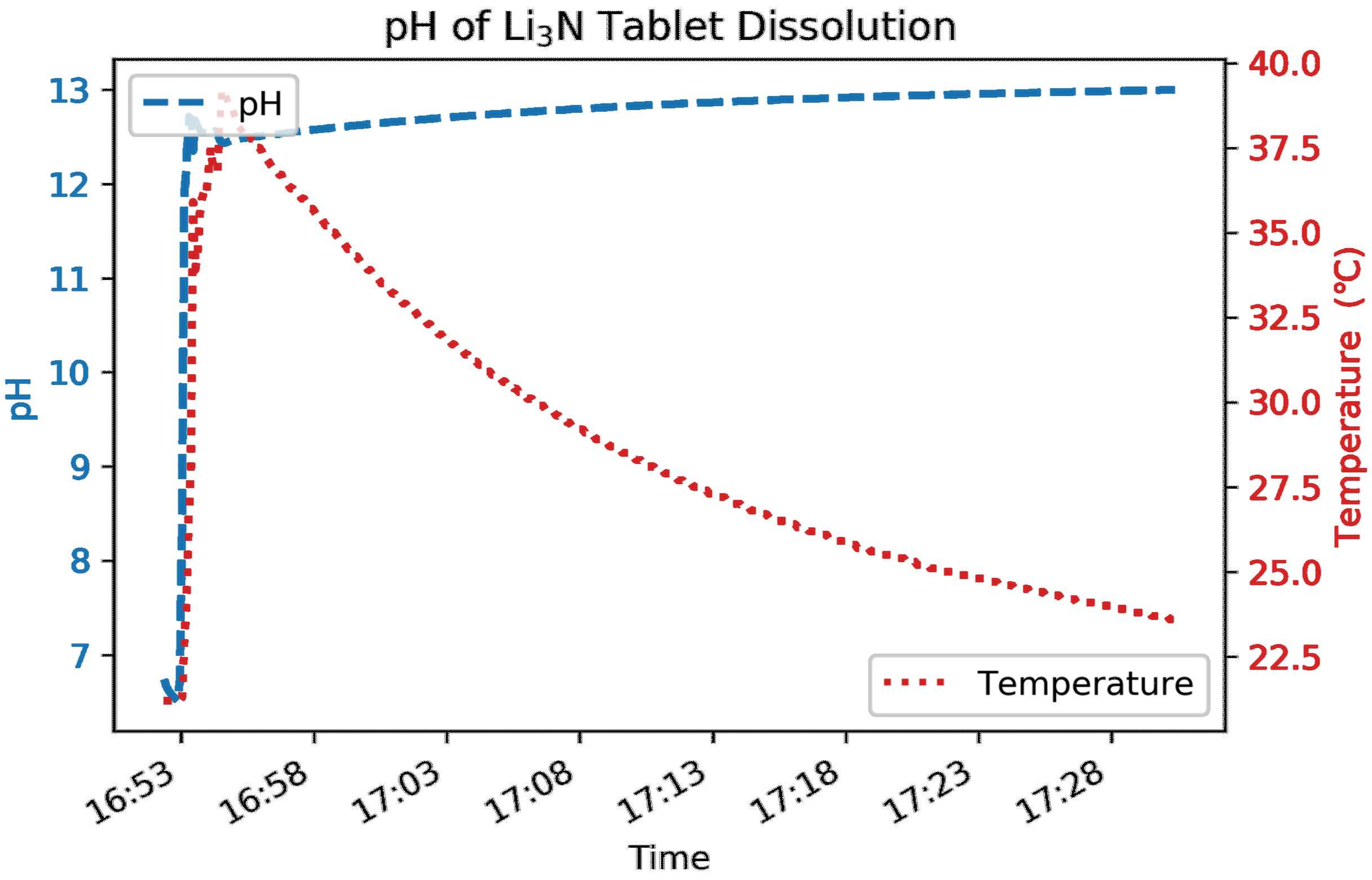
Lump of mustard (HD) recovered by fishing in the Baltic Sea
Missiaen *et al.*, *Science of The Total Environment* **2010**, *408* (17), 3536-3553.

- ❑**Prevention**
- ❑**Atom Economy**
- ❑Less Hazardous Chemical Syntheses
- ❑**Designing Safer Chemicals***
- ❑Safer Solvents and Auxiliaries
- ❑Design for Energy Efficiency
- ❑Use of Renewable Feedstocks
- ❑**Reduce Derivatives***
- ❑Catalysis
- ❑Design for Degradation
- ❑Real-time analysis for Pollution Prevention
- ❑**Inherently Safer Chemistry for Accident Prevention**



*This effort is to *decompose* existing materials into a less toxic form. The concepts are still valid, but are approached differently.

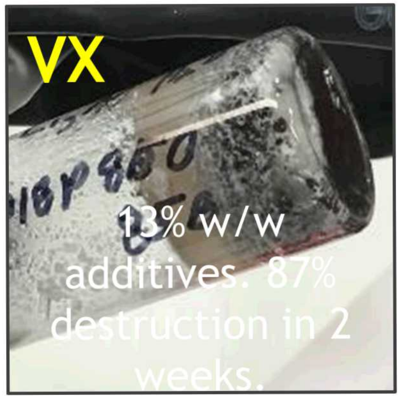
Synergistic benefits of Li_3N compared to LiOH and NH_3



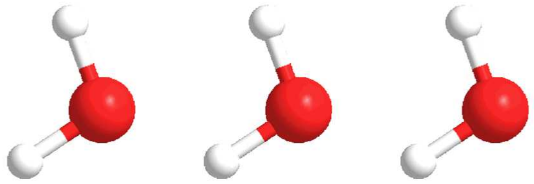
$$Li_3N + 3H_2O \xrightarrow{\text{exothermic}} 3LiOH + NH_3$$

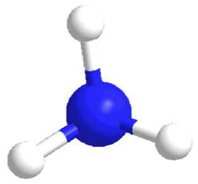
Live Agent Tests in Small Scale

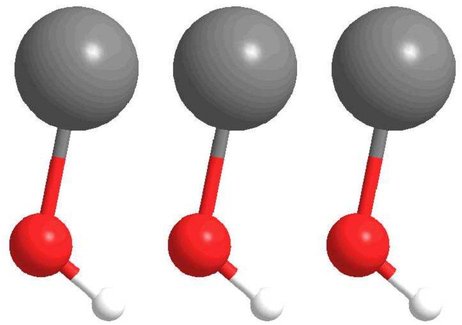
Agent	RXN Vol (mL)	Additive Quantity (% vol)	Agent Remaining with Time
GB	10	13	9% (1 day)
GD	10	13	<0.4% (5 days)
VX	10	13	14% (13 days)
VX	100	18	17% (5 days)
QL	10	18	ND (7 day)
DF	10	19	16% (7 days)



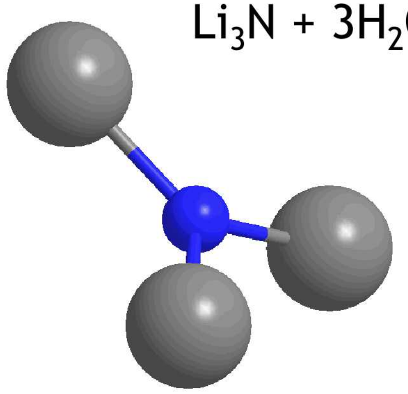
Atom Economy





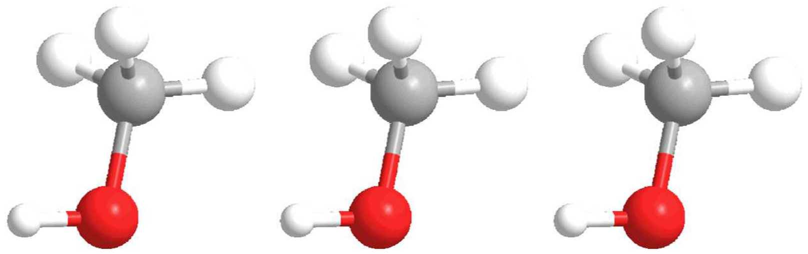


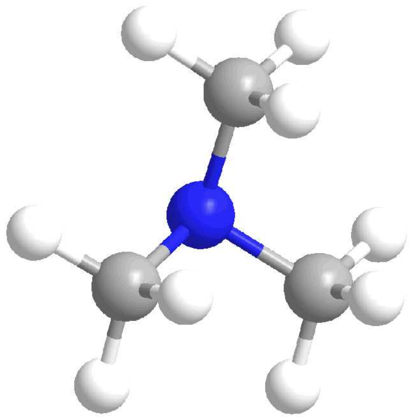
$Li_3N + 3H_2O \rightarrow 3LiOH + NH_3$ (g)

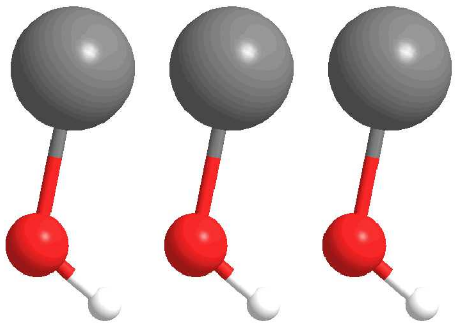


The logistics of transporting reagents to detoxify CWAs can be challenging. Making efficient use out of every atom becomes essential to minimize transportation burden.

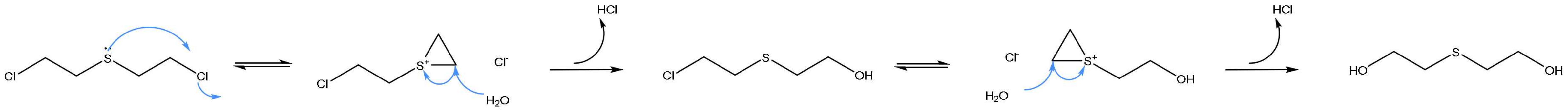
$Li_3N + 3CH_3OH \rightarrow 3LiOH + (CH_3)_3N$ (l)



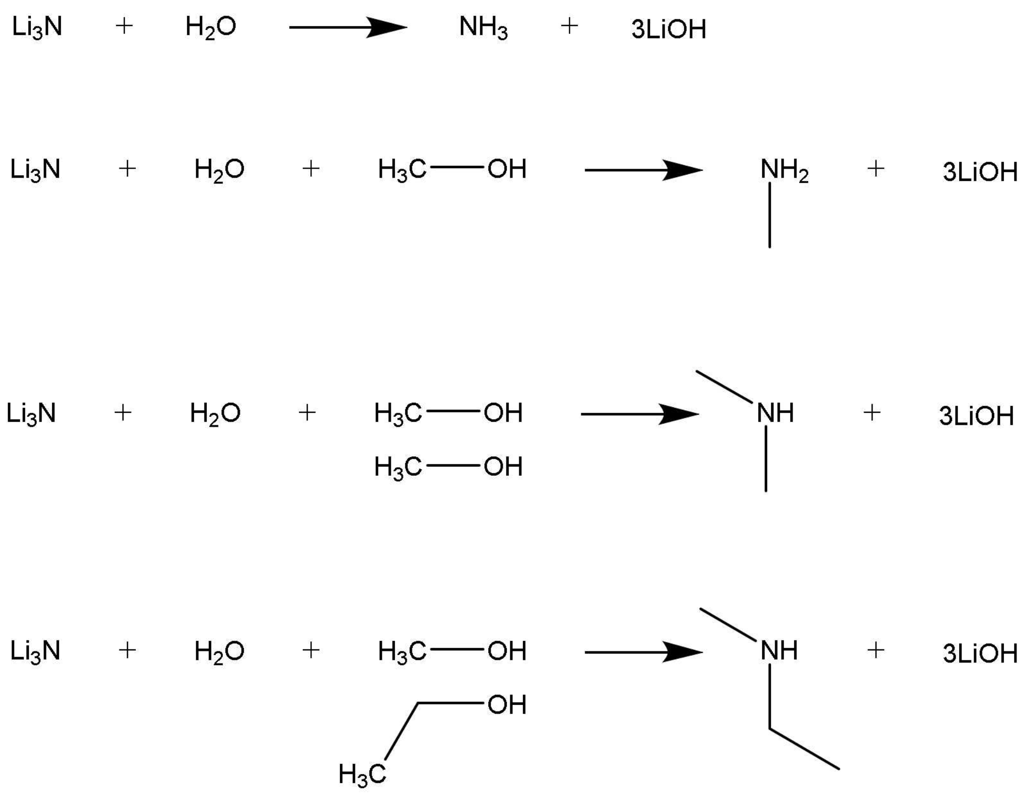




Challenges specific to HD



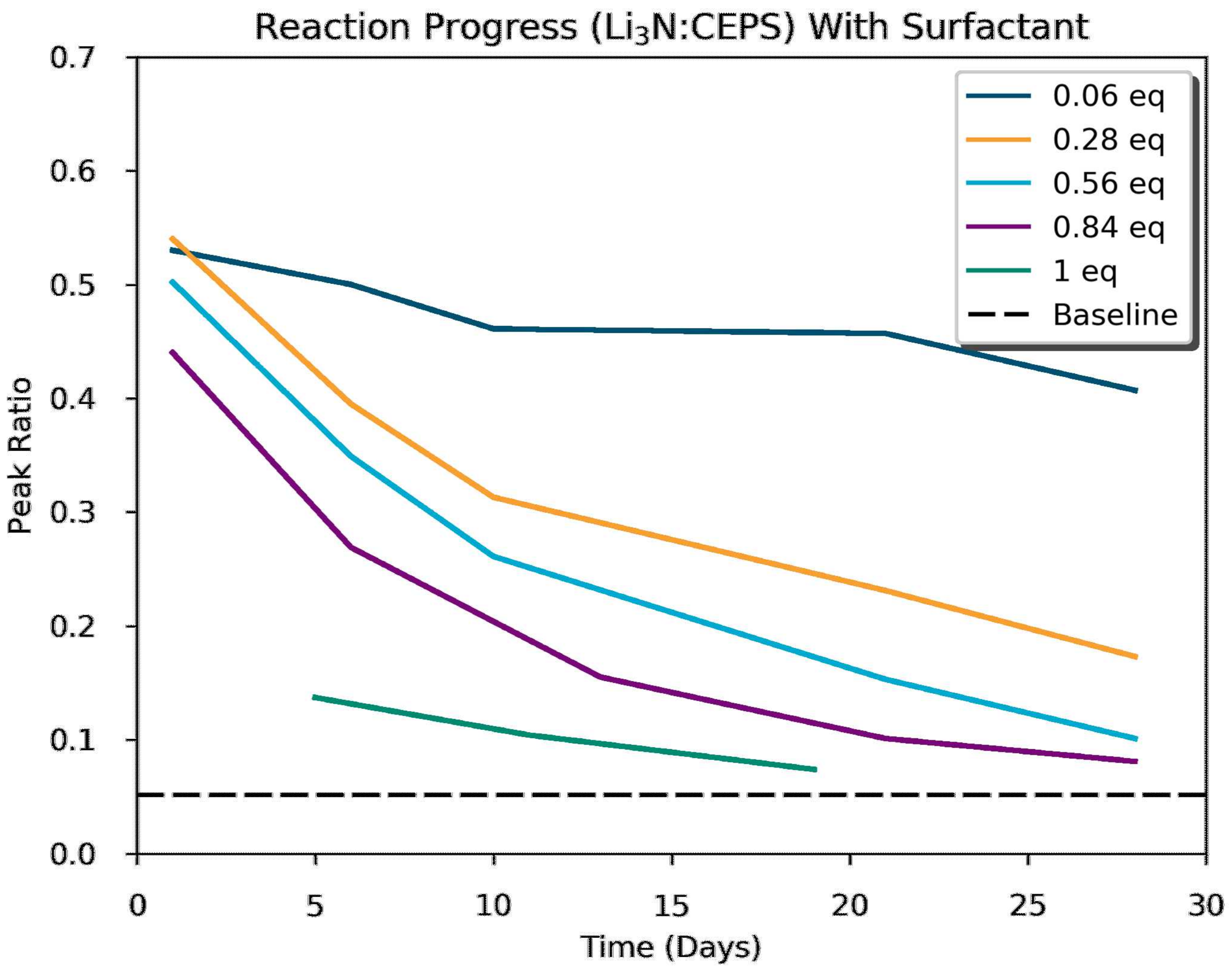
HD hydrolyzes easily under optimal conditions, but is very insoluble in aqueous solution.

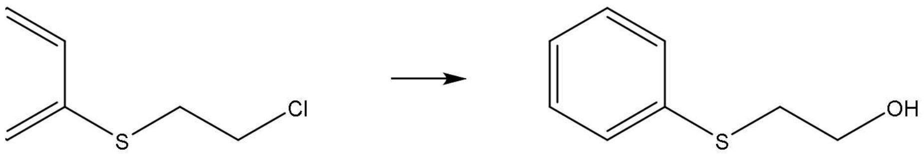


Tailoring the solvent used to initiate Li_3N reaction provides control over the reactants produced.

Larger aliphatic alcohols reduce the reaction rate.

Cooperative effect of high pH and ammonia production





ɔichiometric Li_3N is still reactive, but not t. Since there is not enough NH_3 to fully (slower) hydrolysis is likely taking

ʀequires a surfactant to disperse surrogate

Summary

- Detoxification of bulk scale CWAs ($Volume_{CWA}$ > $Volume_{neutralization\ reagent}$) is challenging.
- The agent, neutralization reagent, and breakdown products must be collectively optimized.
- Applying green chemistry practices provides the needed efficiency perspective.
- Li_3N, a pyrophoric material, provides multifunctional detoxification efficacy.