State of the Science of Chemical Reduction and Oxidation of Chemical Agents

Webinar Presented to:

Military Munitions Support Services (M2S2)

Sponsored by U.S. Army Corps of Engineers

September 18, 2019

Presented by:

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Presentation Outline

- Current solutions and challenges
- Emerging alternative methods for CWA neutralization and destruction
- Chemical oxidation of CWAs case study
- Chemical reduction of Mustard (HD) case study
- Summary and conclusions

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Approaches for CWM Deactivation/Neutralization

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What are the Current Options?

1. Chemical Oxidation

- **Superchlorinated bleaches - solution or powder**
- **Anionic Oxidation**
- **Supercritical Water Oxidation**
- **Electrochemical Oxidation**
- **Hydrolysis (caustic) – hydrolysis of larger amounts of HD (>0.1 M) is a reversible process.**
- **Activated persulfate (L-GEL)**
- **Decon Green™ - hydrogen peroxide and a carbonate buffer as active ingredients**
- **Decon Green™ - Molybdate ion (MoO_4^{-2}) added to the decontaminant to catalyze the oxidation of HD**

2. Chemical Reduction

- MuniRem®
- Metal Catalysts

3. Thermal

- Baseline Incineration

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Current Solutions – CWA Deactivation & Neutralization

- Hydrolysis with Hot Water and Caustic
- Deactivation with MEA

Chemical Agent/Industrial Chemical	Reagent
S Mustard	Monoethanolamine (MEA) and water
Sarin	MEA and water
VX	MEA and aqueous Sodium Hydroxide
Phosgene	Aqueous Sodium Hydroxide

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Challenges with Hydrolysis and Monoethanolamine (MEA) Solutions

- Hydrolysis of CWA produces hazardous end-product
  - 99% of Mustard (HD) is converted to Thiodiglycol
  - Many impurities in HD not destroyed
  - pH is alkaline (RCRA violation)
  - Reaction is reversible under suitable conditions
  - Treatment of by-products prior to disposal of wastewater

- MEA treatment of CWA produces hazardous end-product
  - CWA is deactivated
  - By-products are toxic
  - Treatment of by-products required prior to disposal
  - Limited effectiveness in presence of explosives

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Criteria for Effective Chemical Neutralization of CWAs

1. Reagent should be stable over a wide range of temperatures
2. Effective over a wide pH range
3. Fast acting – possible free radical mediated reactions
4. Irreversible reactions
5. Non-hazardous degradation products

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Chemical Destruction of CWAs by Sulfoxyl Free Radicals

Source of Sulfoxyl Free Radicals:

- Sulfur Oxides

Types of Free Radicals:

- Chemical Oxidation → Activated Persulfate ($SO_4^{-}\bullet$)
- Chemical Reduction → Activated hydrosulfite ($SO_2^{-}\bullet$)

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Case Study
Lawrence Livermore National Laboratory

- Title: "**Direct Chemical Oxidation: Applications to Demilitarization and Decontamination**"
- Performers: John F. Cooper; Bryan Balazs; Patricia Lewis
- CWA Treated: "one-armed mustard" gas - thiodiethanol [(OHH2CCH2)2-S] and dimethylsulfoxide [(CH3)2-SO], non-toxic surrogates for hydrolyzed Mustard gas.
- Chemical Reagent: Oxidation at 90 degrees C using peroxydisulfate (persulfate) solutions.
- Effective persulfate based chemical oxidant formulated into a gel (L-Gel)

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Case Study
Lawrence Livermore National Laboratory

Oxidative decontamination of chemical and biological warfare agents using L-Gel

Ellen Raber*, Raymond McGuire

Environment Protection Department, Lawrence Livermore National Laboratory, University of California, P.O. Box 808, L-626, Livermore, CA 94551, USA

Received 22 August 2001; received in revised form 25 January 2002; accepted 11 February 2002

The new reagent, “L-Gel”, consists of an aqueous solution of a mild commercial oxidizer, OxoneTM, together with a commercial fumed silica gelling agent, Cab-O-Sil EH-5. L-Gel is non-toxic, environmentally friendly, relatively non-corrosive, maximizes contact time because of its thixotropic nature, clings to walls and ceilings, and does not harm carpets or painted surfaces. The new reagent also addresses the most demanding requirements for decontamination in the civilian sector, including availability, low maintenance, ease of application and deployment by a variety of dispersal mechanisms, minimal training and acceptable expense.

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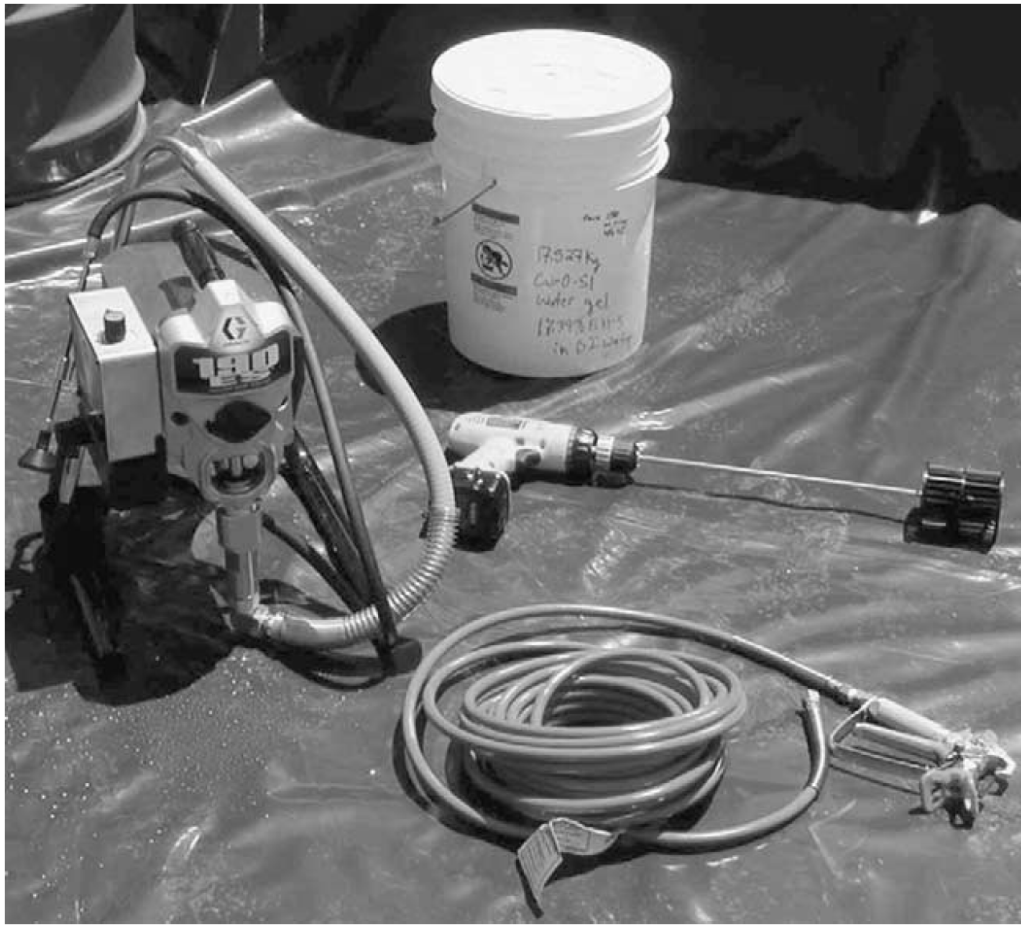
CWM/BWM Decontamination Equipment

Commercially available equipment for L-Gel application includes a Graco Airless Electric Paint Sprayer.



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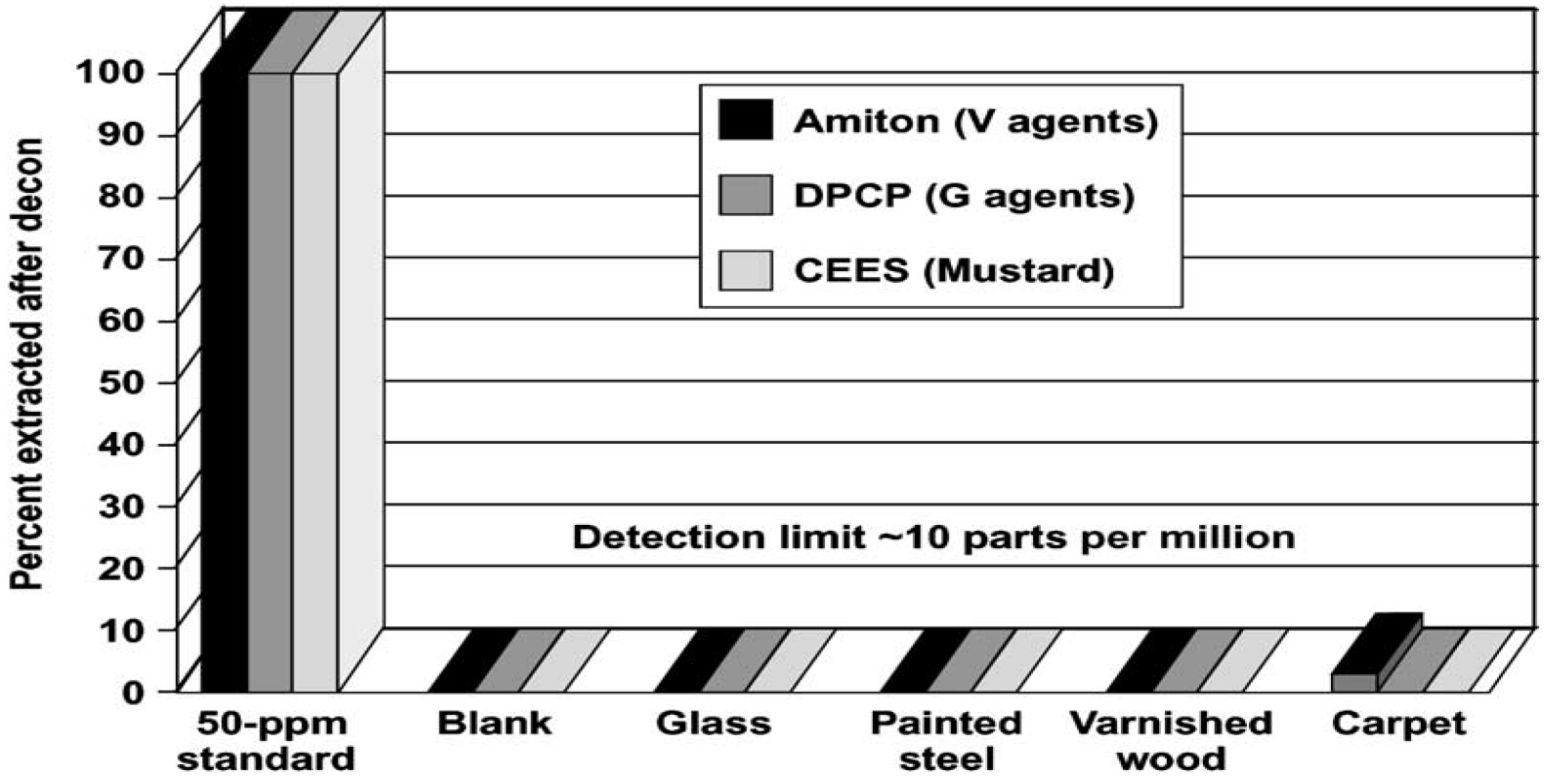
Results of Lawrence Livermore National Laboratory Study

Percent of extracted CW agent from substrates after decontamination, using GC–MS detection methods



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Independent laboratory and field testing of LLNL Gel

- Field testing at the Military Technical Institute of Protection, Brno, the Czech Republic (October 1998);

- Lab testing at Edgewood Chemical Biological Forensic Analytical Center (ECBC), Aberdeen Proving Ground, MD (November 1999);

- Lab testing with thickened agents at the Defence Evaluation and Research Agency (DERA), Porton Down, UK (October 1999).

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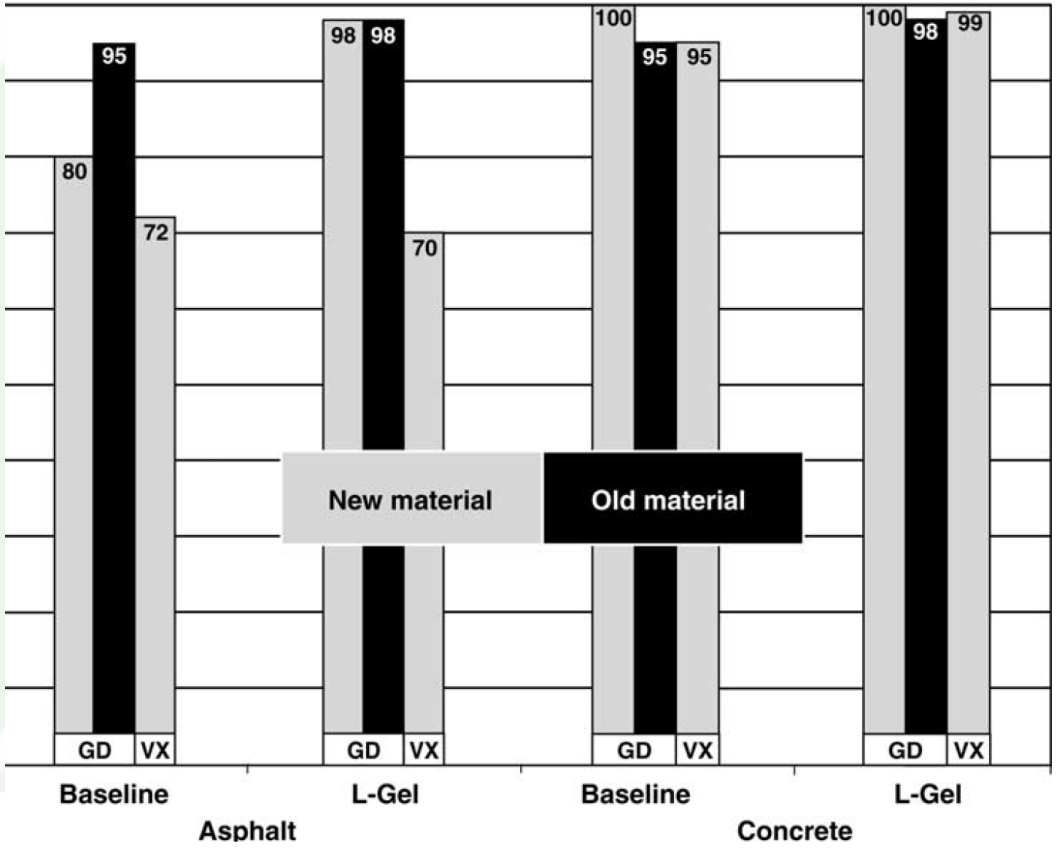
Results - Biological Agent Decontamination Test

Field testing with real CW agents on concrete and asphalt substrates showed that the L-Gel system was as effective or more effective against VX and GD than the baseline US military method using HTH. VX was only tested on new materials.



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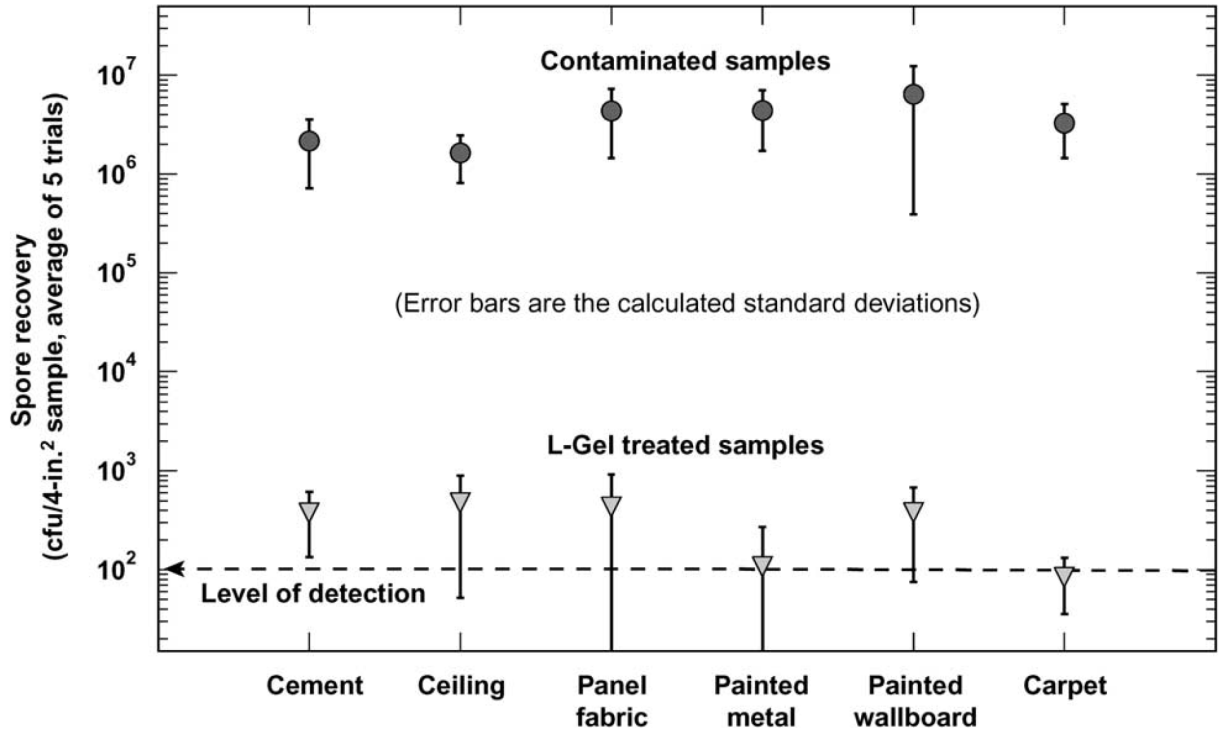
Results - Biological Agent Decontamination Test

Results of field tests on six materials contaminated with BG spores before and after application of decontamination gel.
BG spores were reduced by an average of 99.988% by the decon gel.



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Chemical Reduction - MuniRem Case Study

RESULTS FROM PROOF-OF-CONCEPT EVALUATION STUDY TITLED "MICRO-SCALE EVALUATION OF MUNIREM REAGENTS FOR THE DEMILITARIZATION OF SULFUR MUSTARD"

MuniRem reagent evaluation was independently performed by the United States Department of Defense at its Non-Stockpile Department, Edgewood, MD.

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Chemical Destruction of Mustard Case Study

CONTRACT #: W912PP-10-P-0034

RESULTS PRESENTED ARE OBTAINED FROM PROOF-OF-CONCEPT TEST DATA FOR TESTS CONDUCTED AT NON-STOCKPILE LABORATORY, EDGEWOOD (2010)

Liquid HD

HD Solids

Liquid and Solid HD from 4.2-inch Mortar by Dr. Yu Chu Yang (Chief Scientist, PM ACWA)

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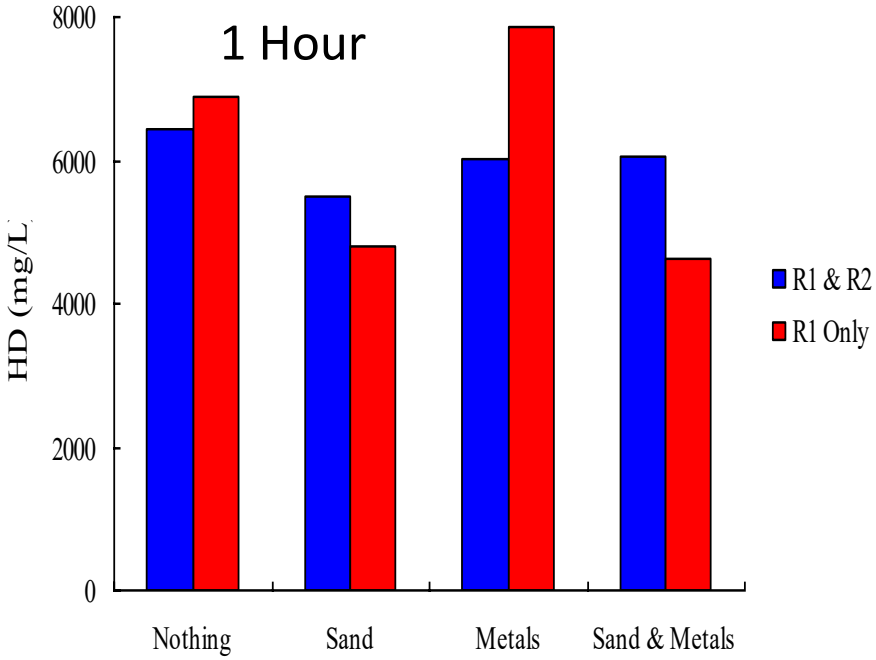
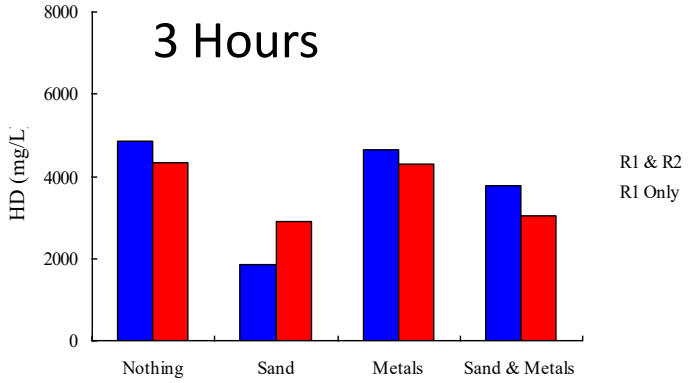
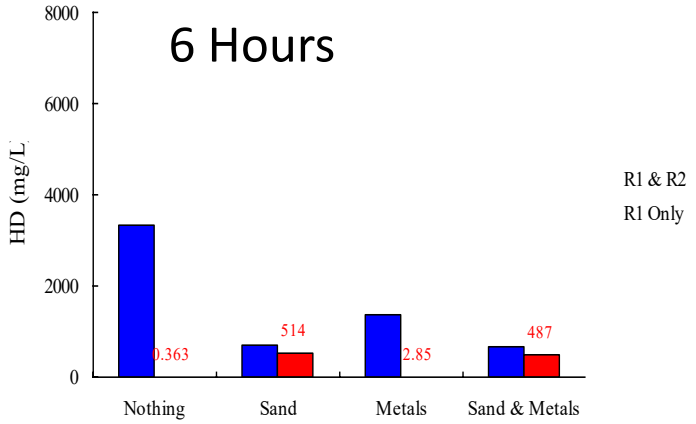
Neutralization of Mustard (HD) with MuniRem Reagent

- ✓ Nothing = Homogeneous Solution of MuniRem; no solids added.
- ✓ Sand and Metal (Iron) was added to simulate real scenario
- ✓ Initial Concentration of Mustard = 18,500 mg/L
- ✓ Results for: 1 hour; 3 hours; **6 hours**







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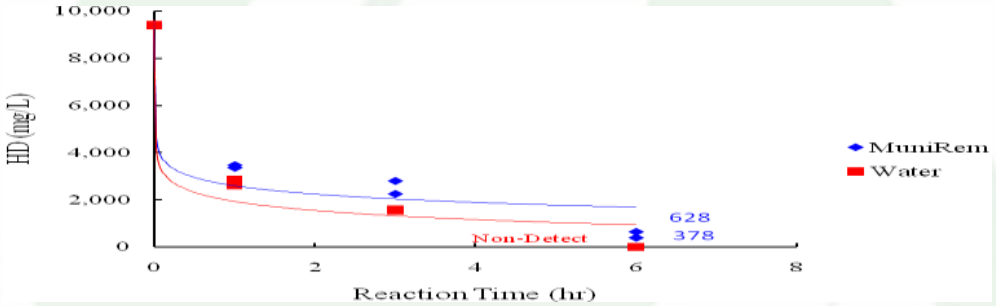
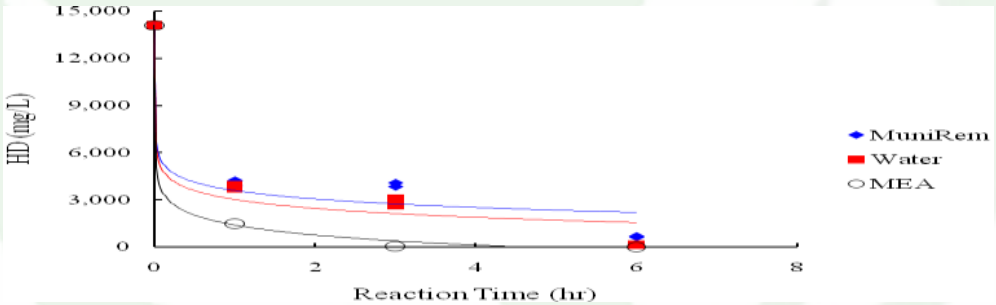
Rate of Destruction of HD by MuniRem Reagent vs. Hydrolysis by Water & Deactivation by MEA



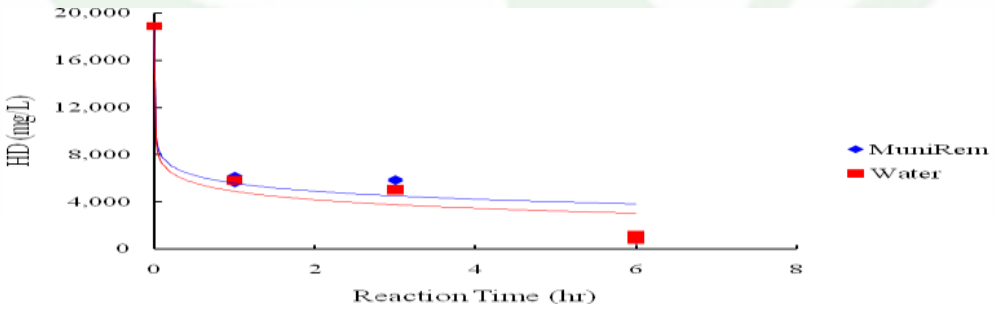
Initial = 40 uL (9,000 mg/L)

MEA forms Hazardous Waste



Initial = 60 uL (14,000 mg/L)

MEA forms Hazardous Waste



Initial = 80 uL (18,500 mg/L)

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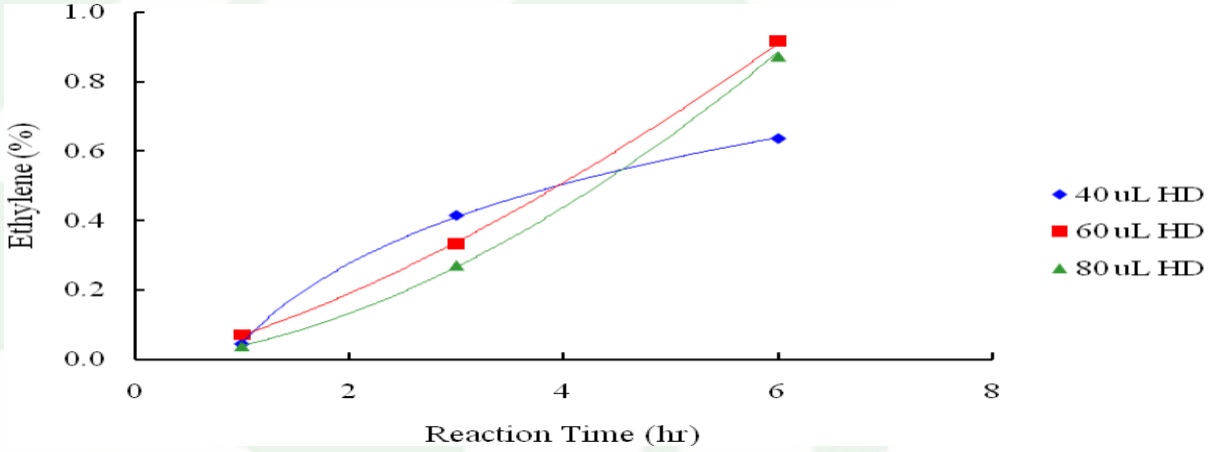
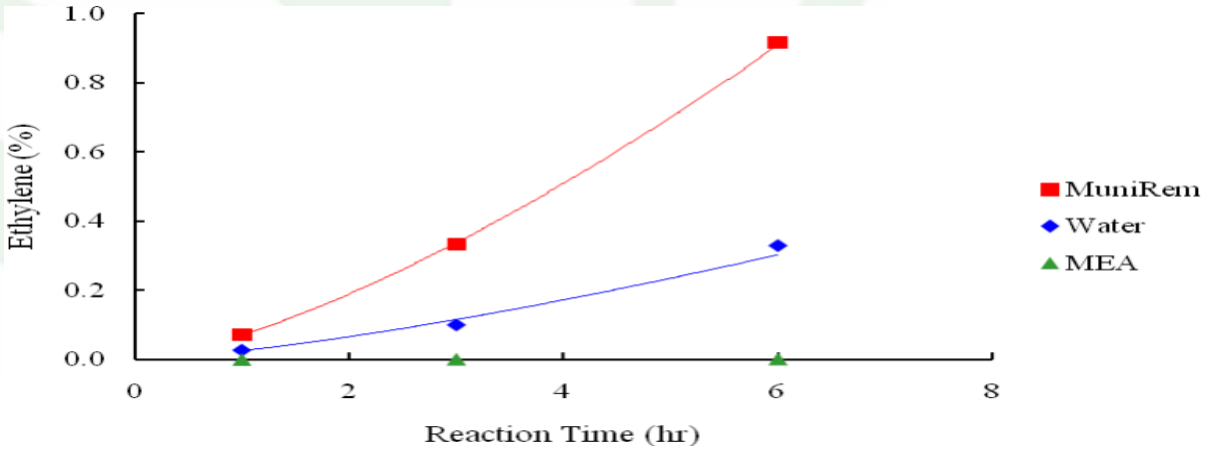
Mustard (HD) Destruction by MuniRem
Ethylene Gas Production as a Function of Time





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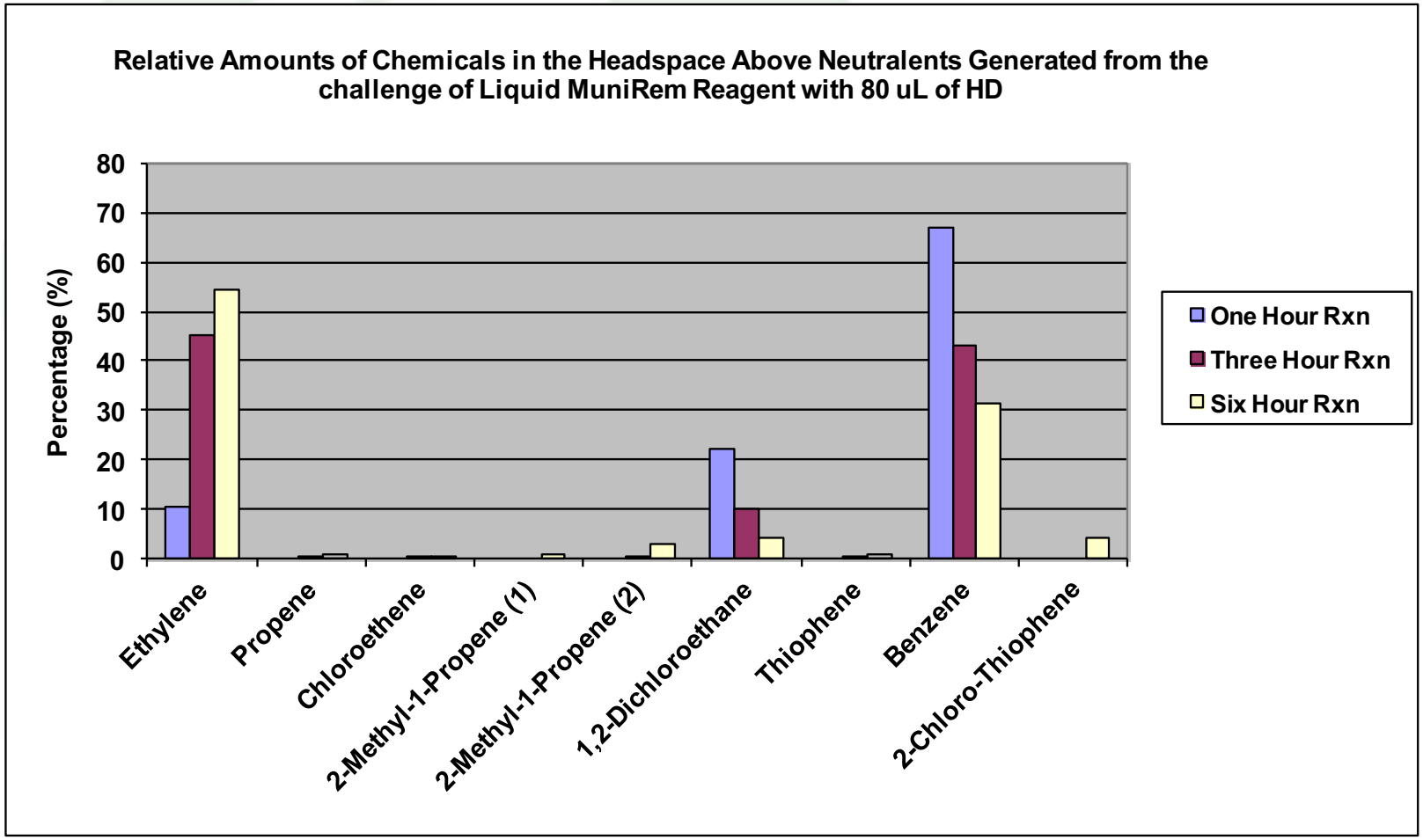
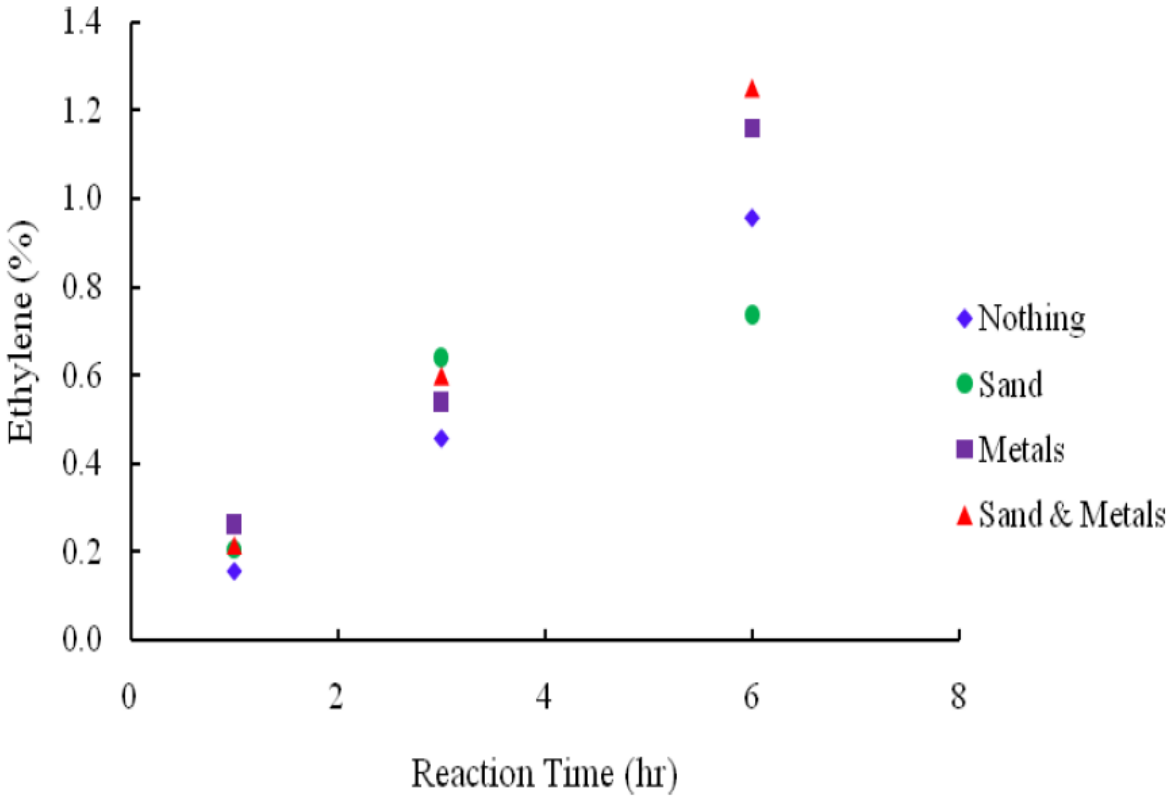
What is Headspace of Neat Mustard Destroyed by MuniRem Reagent?



Quantitative Measurements of Ethylene End-Product in the Headspace of MuniRem Treated Mustard (HD)



- Nothing = MuniRem Solution Only
- Sand = MuniRem solution + Sand as Impurity
- Metals = MuniRem solution + Metals (Fe oxides) as Impurity
- Metals = MuniRem solution + Sand & Metals as Impurity

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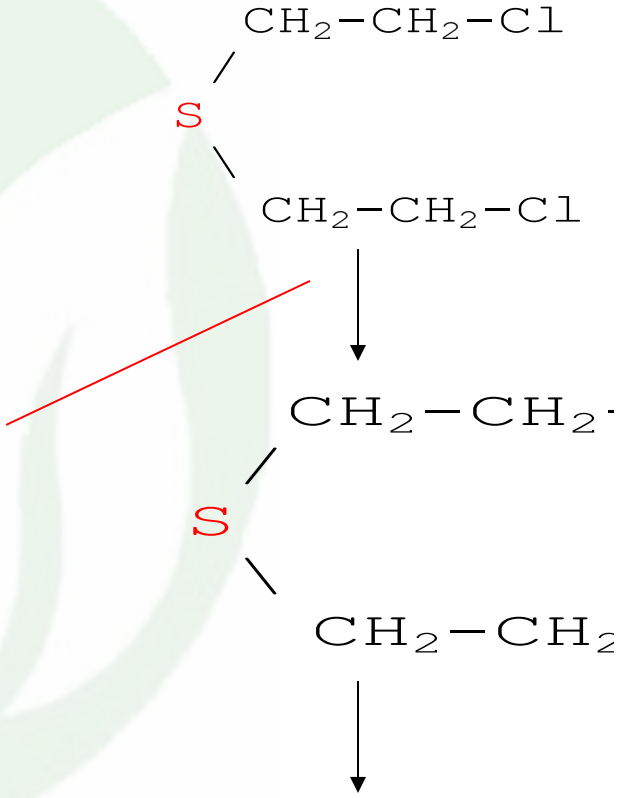
Reaction Pathway
Chemical Reduction of HD to Ethylene

- Reductive Dechlorination
- Catalyzed by MuniRem



CH_2=CH_2 + S^{2-} (formation of metal sulfide)

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INCORPORATION OF MUNIREM INTO EXISTING DEMILITARIZATION SYSTEMS

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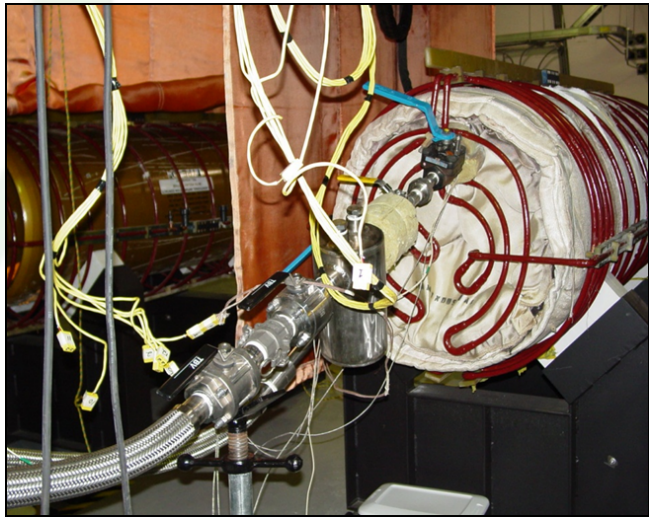
Demilitarization Solutions

- Explosive Destruction System (EDS)
- Donovan Chamber – TC-25
- Thermal Heating Station for Decontamination One Ton Container



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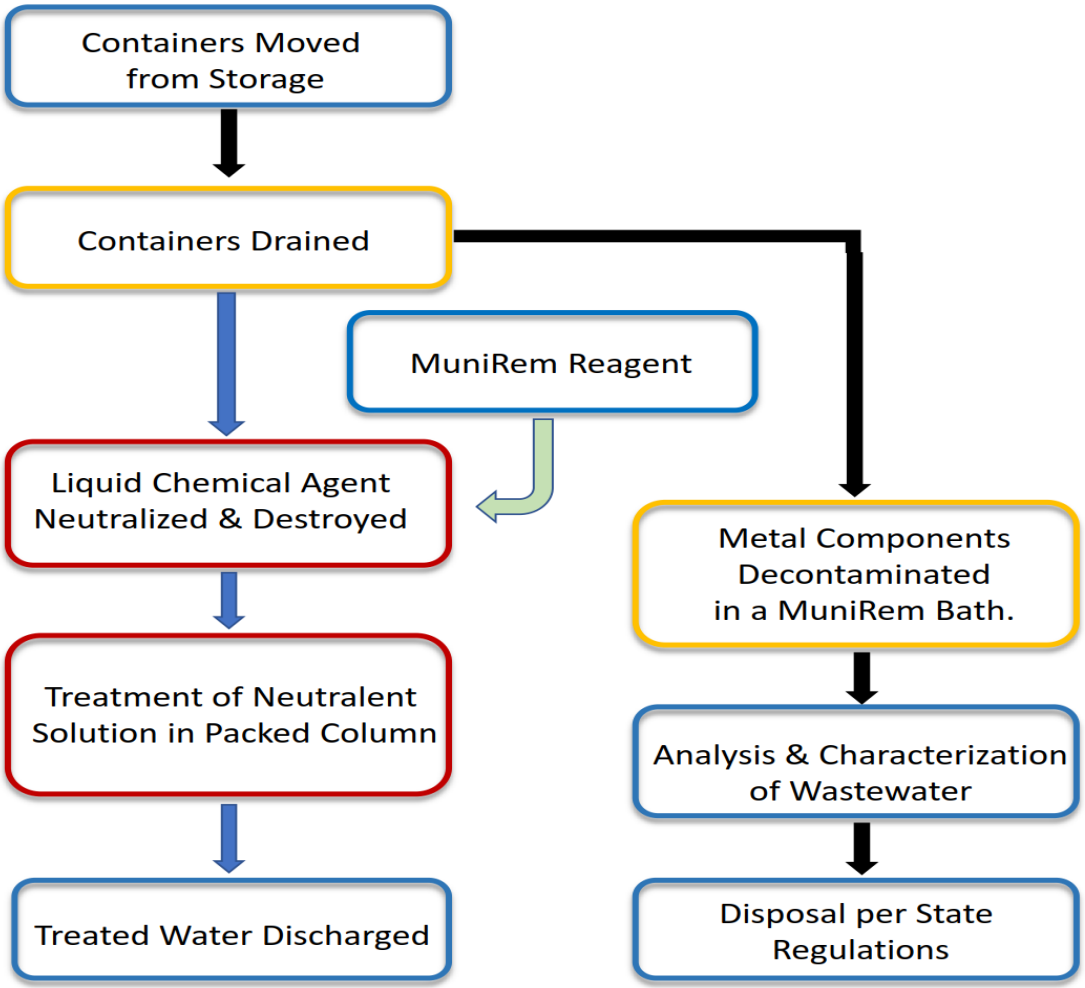
Flow Chart – Chemical Agent Neutralization Process



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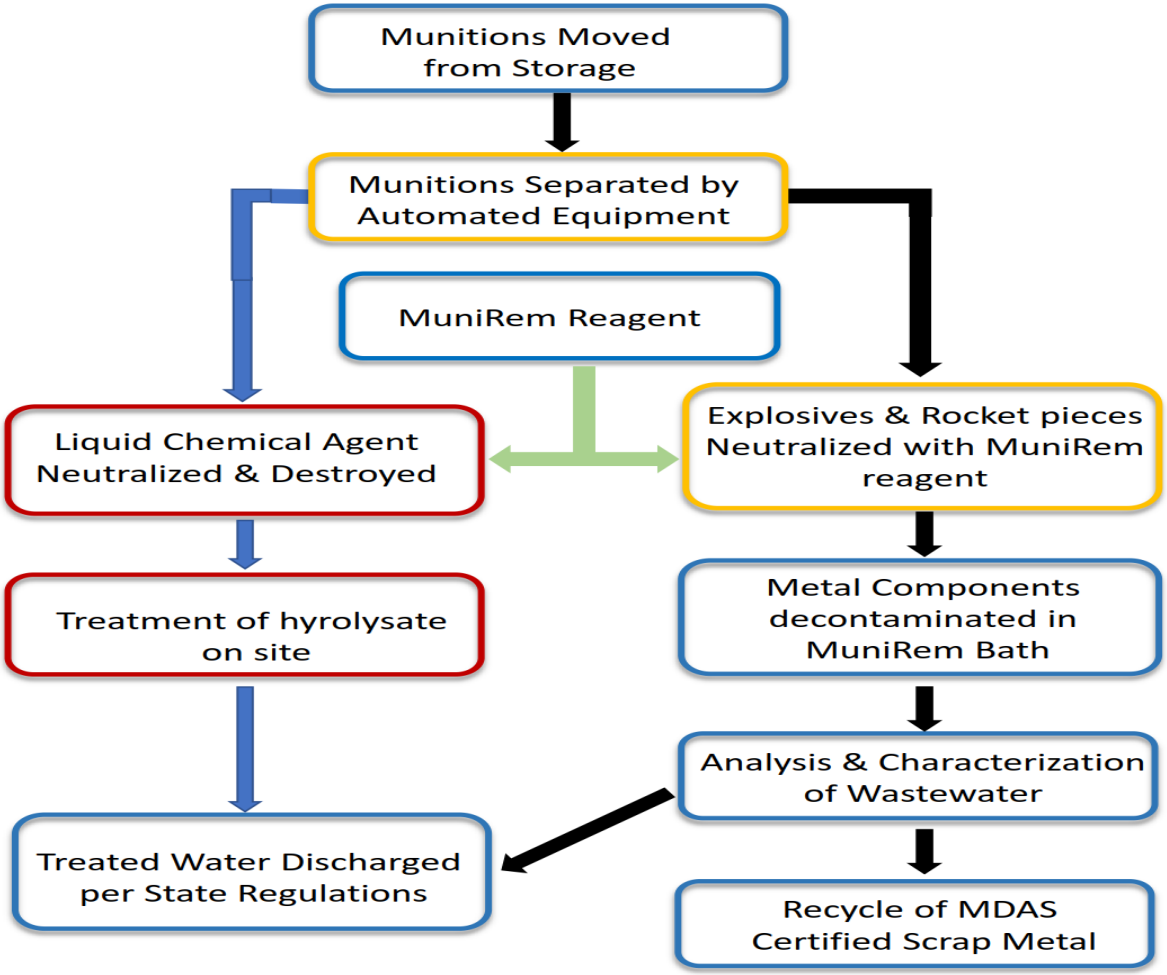
Flow Chart - Chemical Agent & Explosives Neutralization Process



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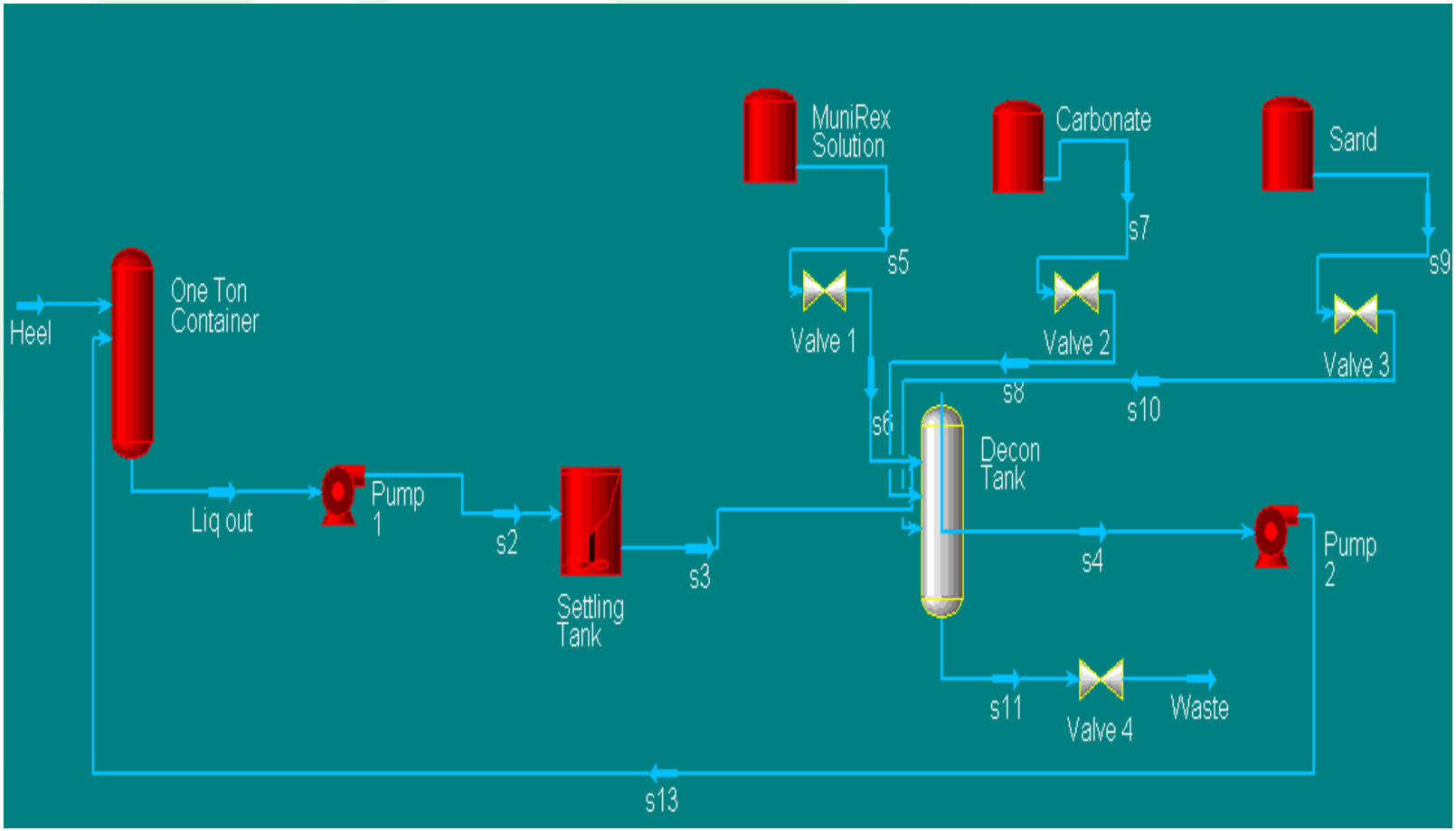
Schematic of Closed Loop Decontamination of One Ton Steel Containers



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Conclusions

- Chemical neutralization and destruction of CWA to non-hazardous end products is feasible.
- Sulfur Oxides based neutralents offer the most promise.
- An optimized MuniRem reagent soon to be commercialized.
- Effective chemical neutralents require less capital equipment costs.

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Your Questions Are Appreciated

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