



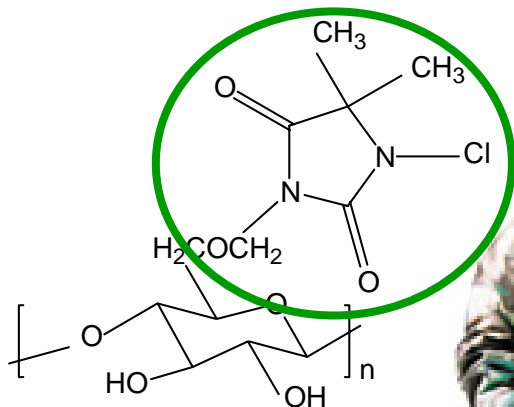
Reactive Materials Research for Self-Detoxifying CB Protective Clothing

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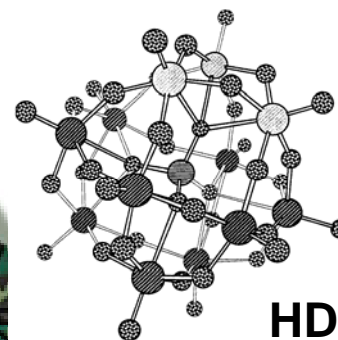
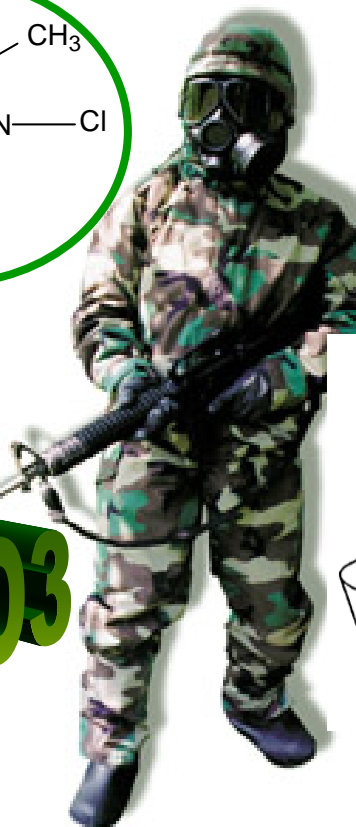
Concept

Place reactive materials in fabrics that detoxify
Contaminants on clothing within hours of exposure.

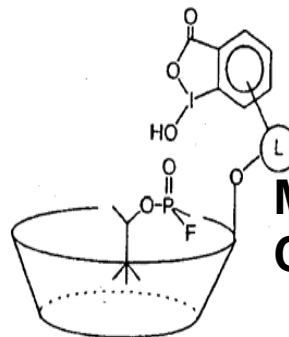


CHLORAMINE
Bactericide, Agent Decon

Nano Al₂O₃

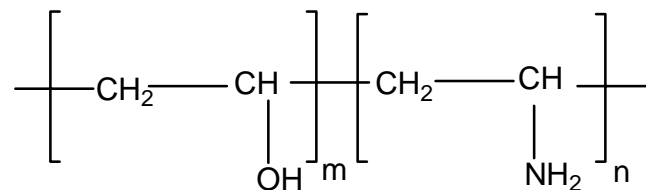


HD Catalyst



**Modified
Cyclodextrins**

Poly(vinyl)amines





Approach

Chloramides & Quats -Shell Fabric

Bio, HD, VX

Sporicide and Agent Decon, Water Repellancy

POM Catalysts – Liner Materials

HD

Carbon Surfaces

Polymer Film Surfaces

Nanoparticles – Attached to Fabrics,

HD, VX

Blended into Fibers

Particulate Absorbants

Reactive Permselective Membranes - Liners

G, VX



Nanoparticle Reaction Rate Studies

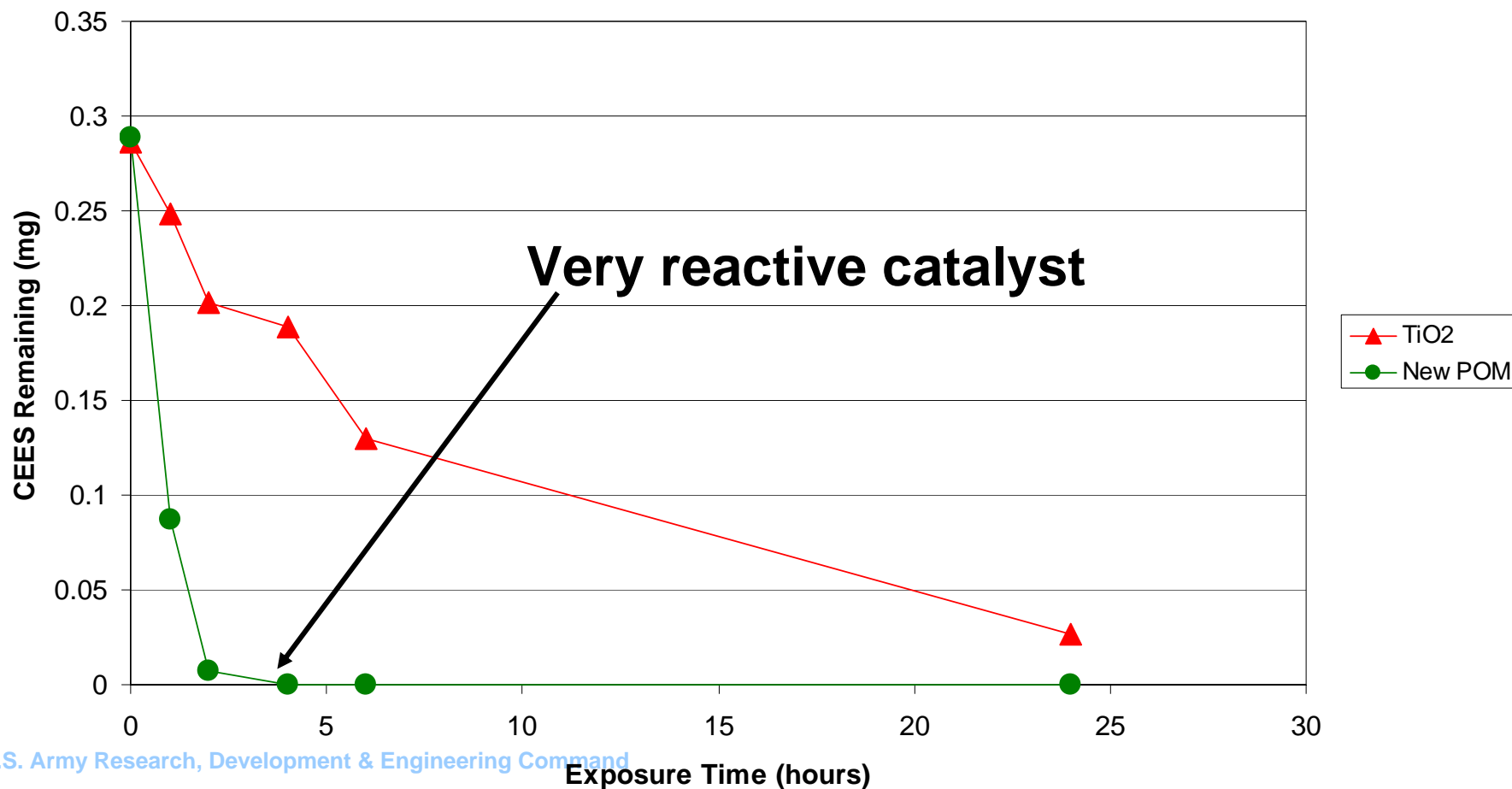
Depletion of 2-CEES

- In Solution
- In Vapor



Solution Depletion of 2-CEES

Nanoparticle TiO_2 vs POM Catalyst





Equilibrium Vapor Adsorption Measurements

ADSORBANT	% CEES Vapor Uptake
Carbon Spheres	56
NanoAl₂O₃ - PLUS	99
NanoAl₂O₃	10
NanoTiO₂	17



Thermal Desorption GC/MS

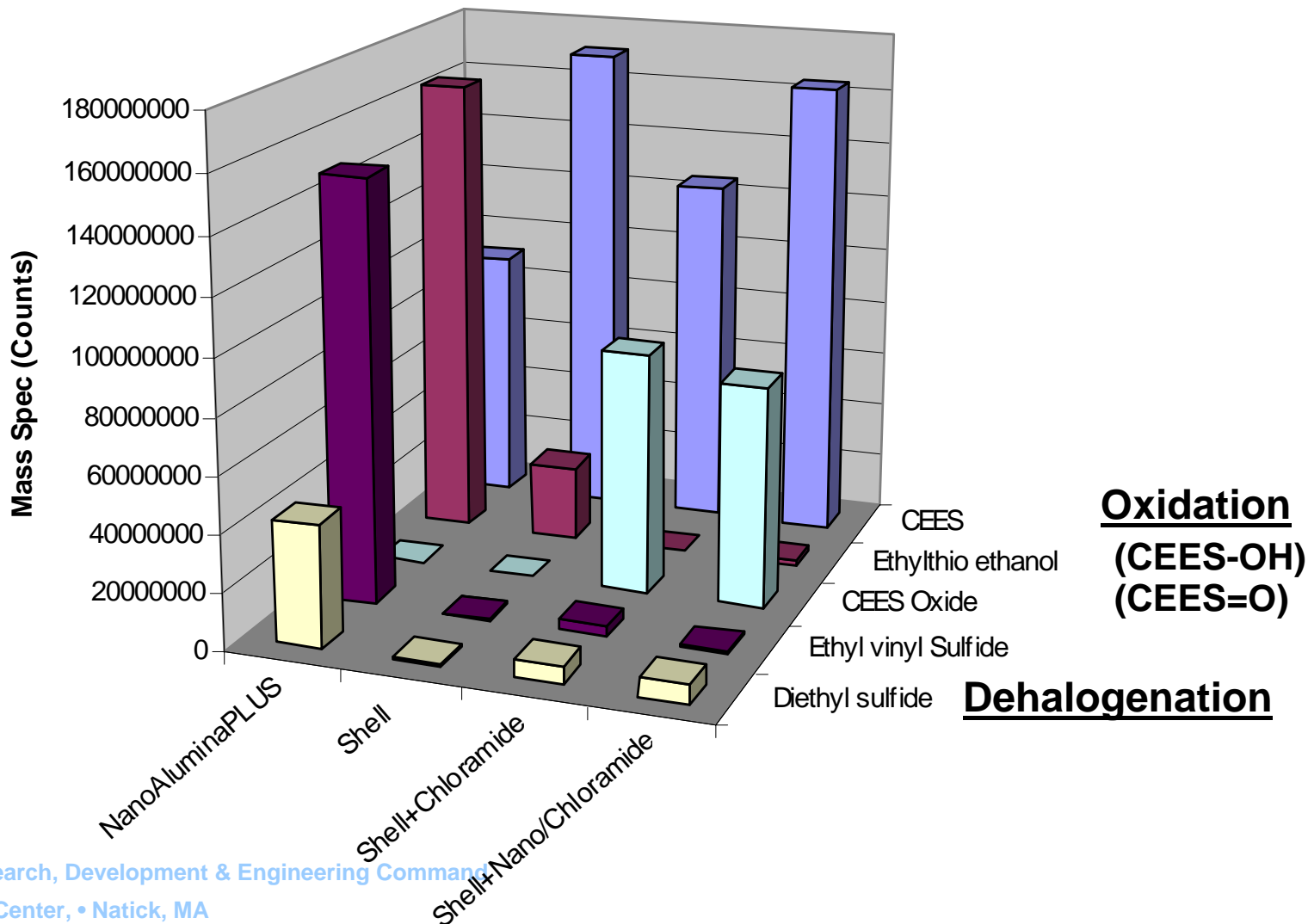
Sample in Tube



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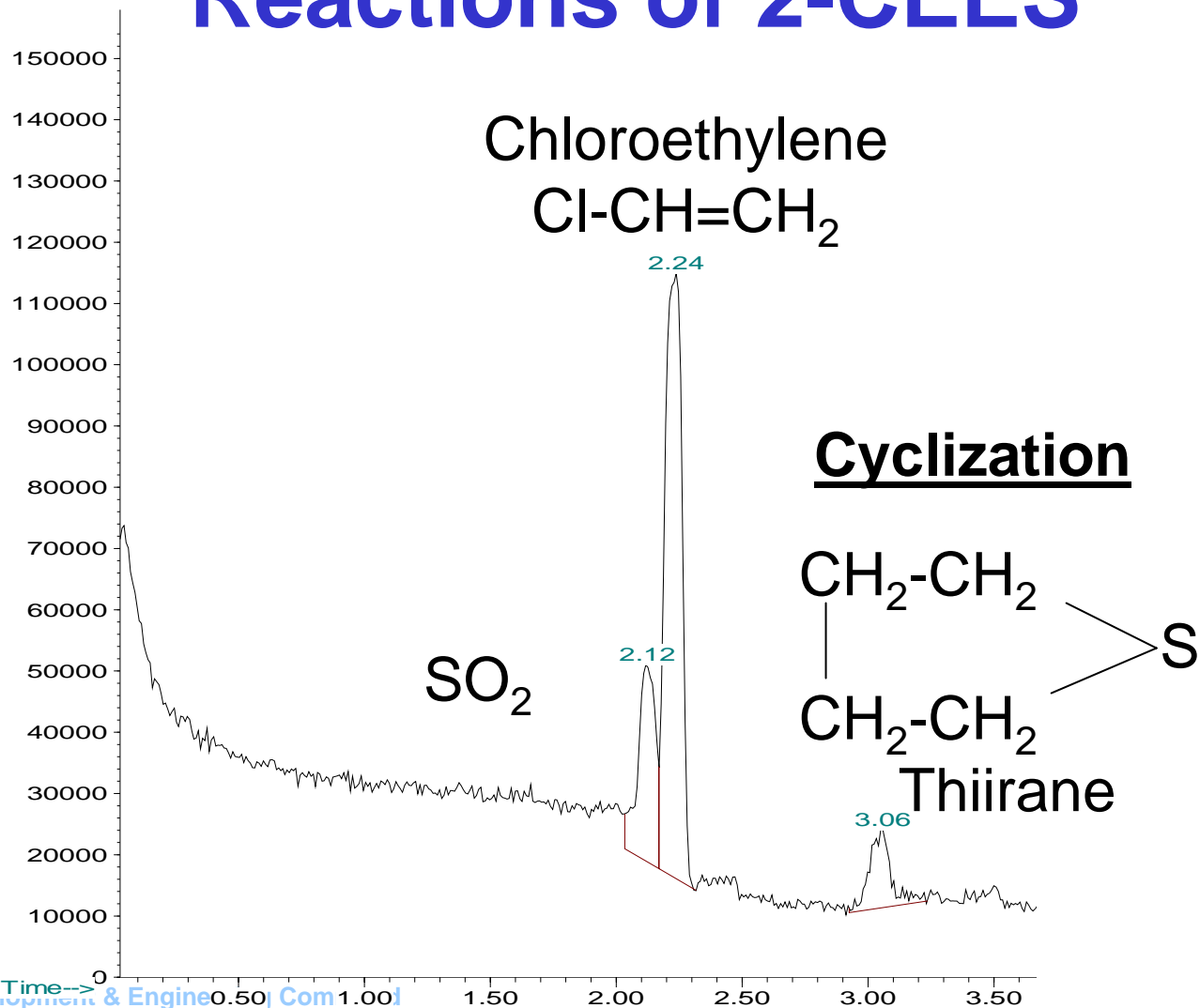


Depletion of CEES Formation of Products



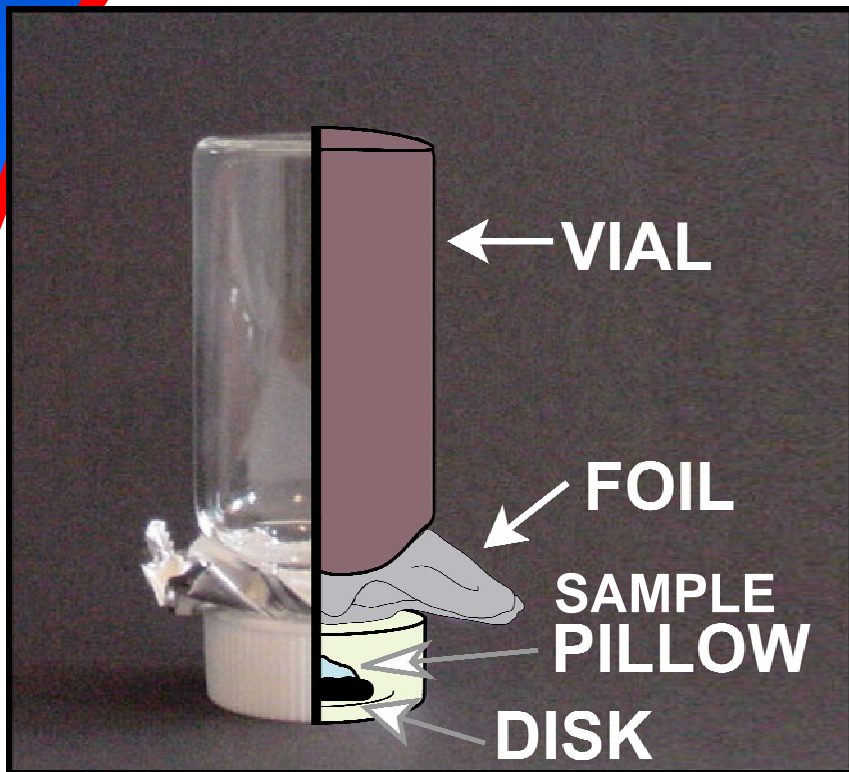


Some Products from Oxidation Reactions of 2-CEES





NMR (HRMAS) Sample preparation



Vapor chamber for exposing catalyst to vaporous agent/simulant



4 mm HRMAS rotor for examining small volumes of sample (< 100 µl)



^1H 1D Spectra Reaction Kinetics

CEES Peaks at 2.8 and 2.6 disappear
upon vapor exposure to nano- Al_2O_3

2.8 2.6

4.5 hrs

10.4 hrs

24.6 hrs

27.8 hrs

63.3 hrs

71.4 hrs

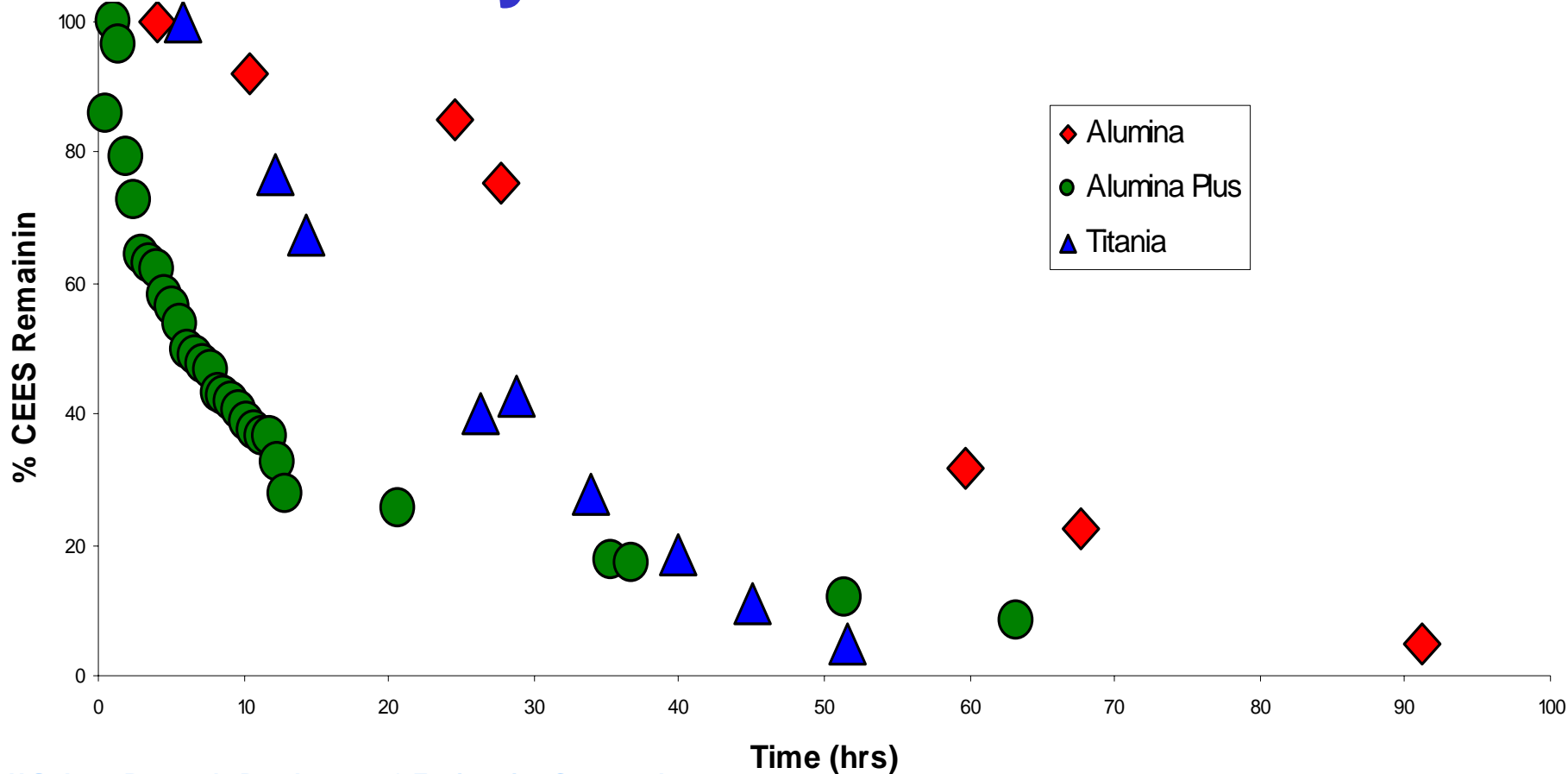
94.8 hrs

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5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



Normalized 2-CEES Degradation Kinetics By Solid State NMR





Rate of CEES Vapor Depletion in HRMAS NMR Studies

	Rate % CEES/hr	Activity <u>mgCEES/24hr</u> mgNanoparticle
NanoAl ₂ O ₃	0.83	0.020
NanoTiO ₂	2.3	0.094
NanoAl ₂ O ₃ -PLUS	3.1	0.74*

***30 g/m² of nanoAl₂O₃-PLUS needed to meet current protection requirements. 100 g/m² of nanoTiO₂ needed.**

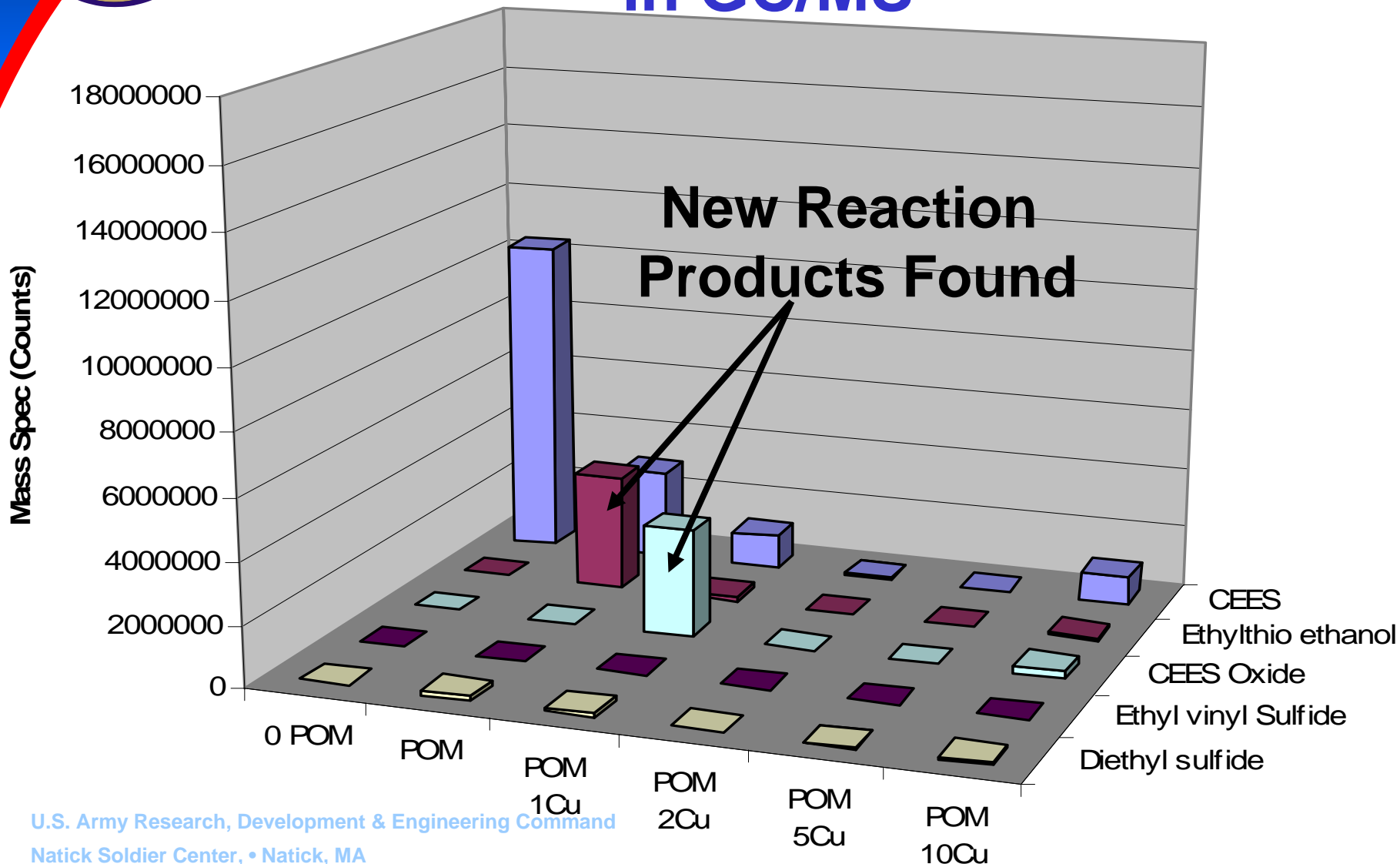


POM Catalyst Reactions with 2-CEES

- POM on Carbon Surface**
- Effect of Copper Content**

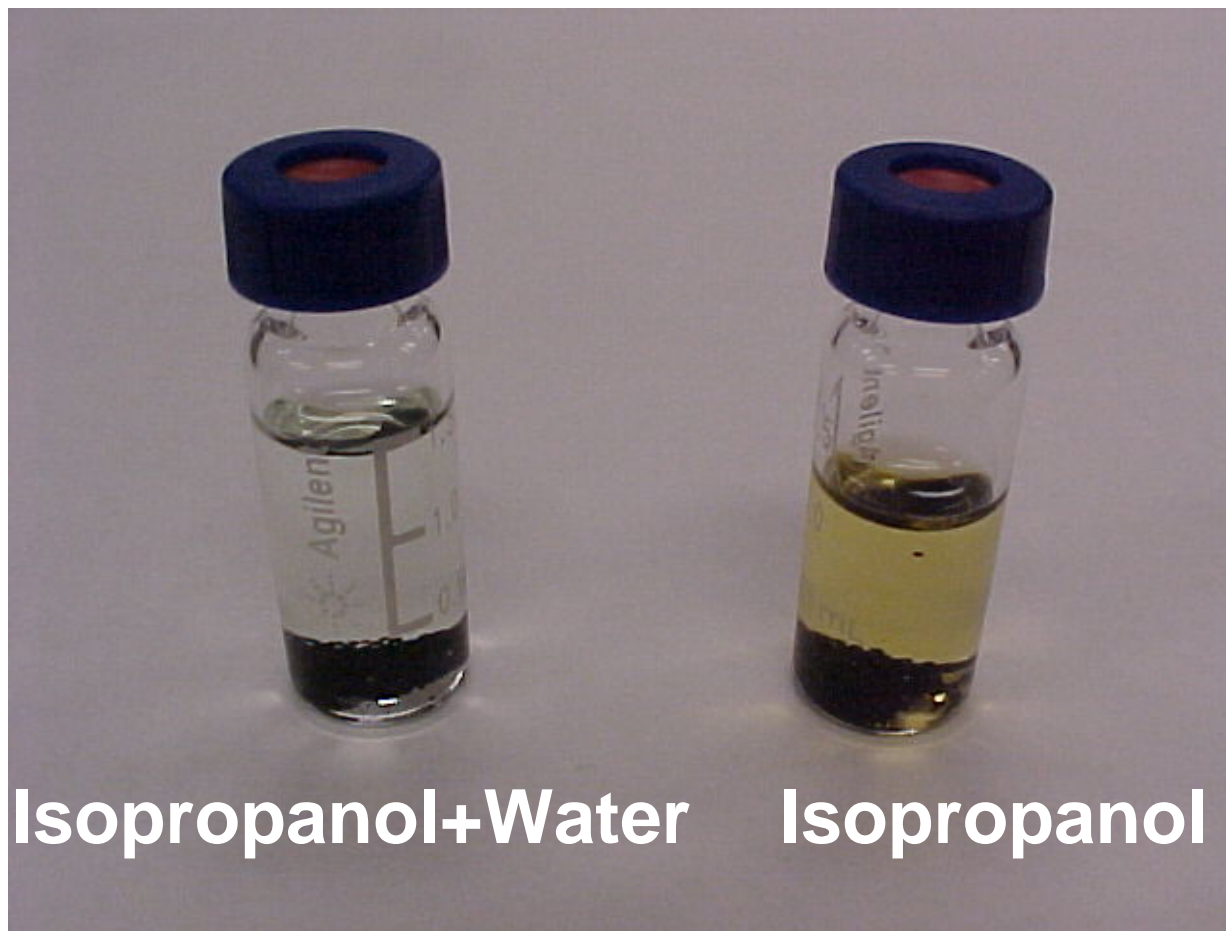


POM/Carbon Reduces 2-CEES in GC/MS





Reaction Product from Carbon/POM + 2-CEES

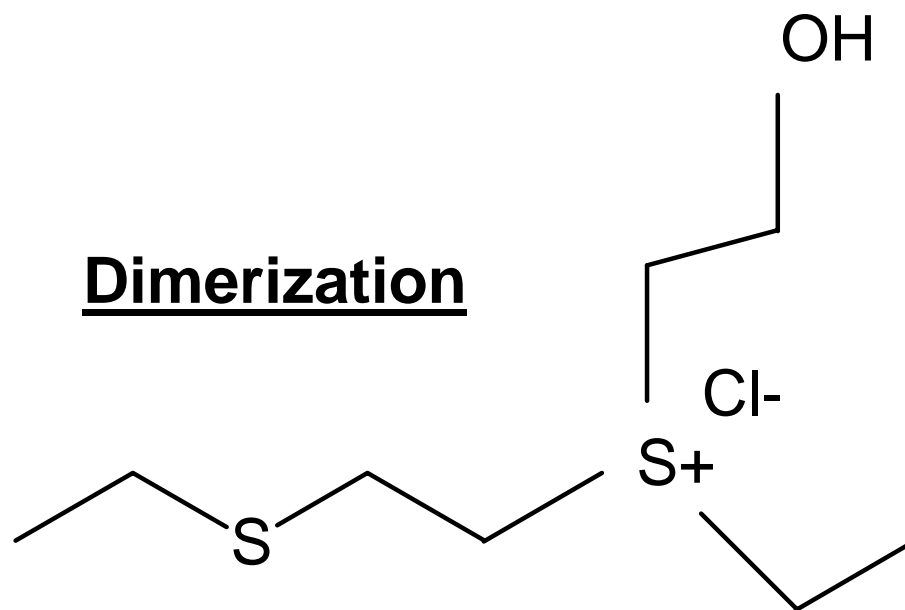


Isopropanol+Water

Isopropanol



Dimer of 2-CEES from Oxidation Reaction





CEES

Vapor Diffusion Studies

**Thick vs Thin Supported
Selectively Permeable Films**

Reactive

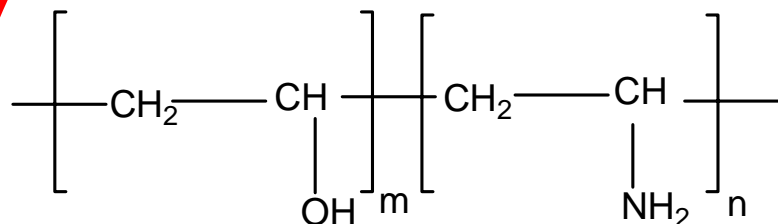
PVAM (polyvinyl amine-co-vinyl alcohol)

Non-Reactive

Nafion, Membrane C, Membrane T



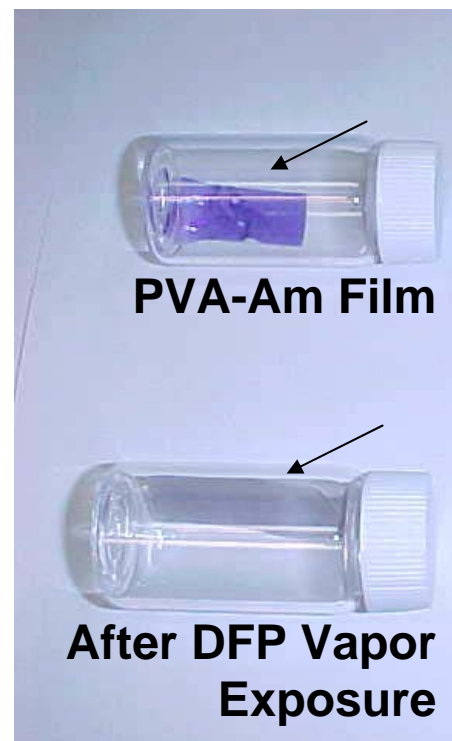
Reactive Selectively Permeable Membranes



Polyvinyl alcohol-co-amine, PVA-Am

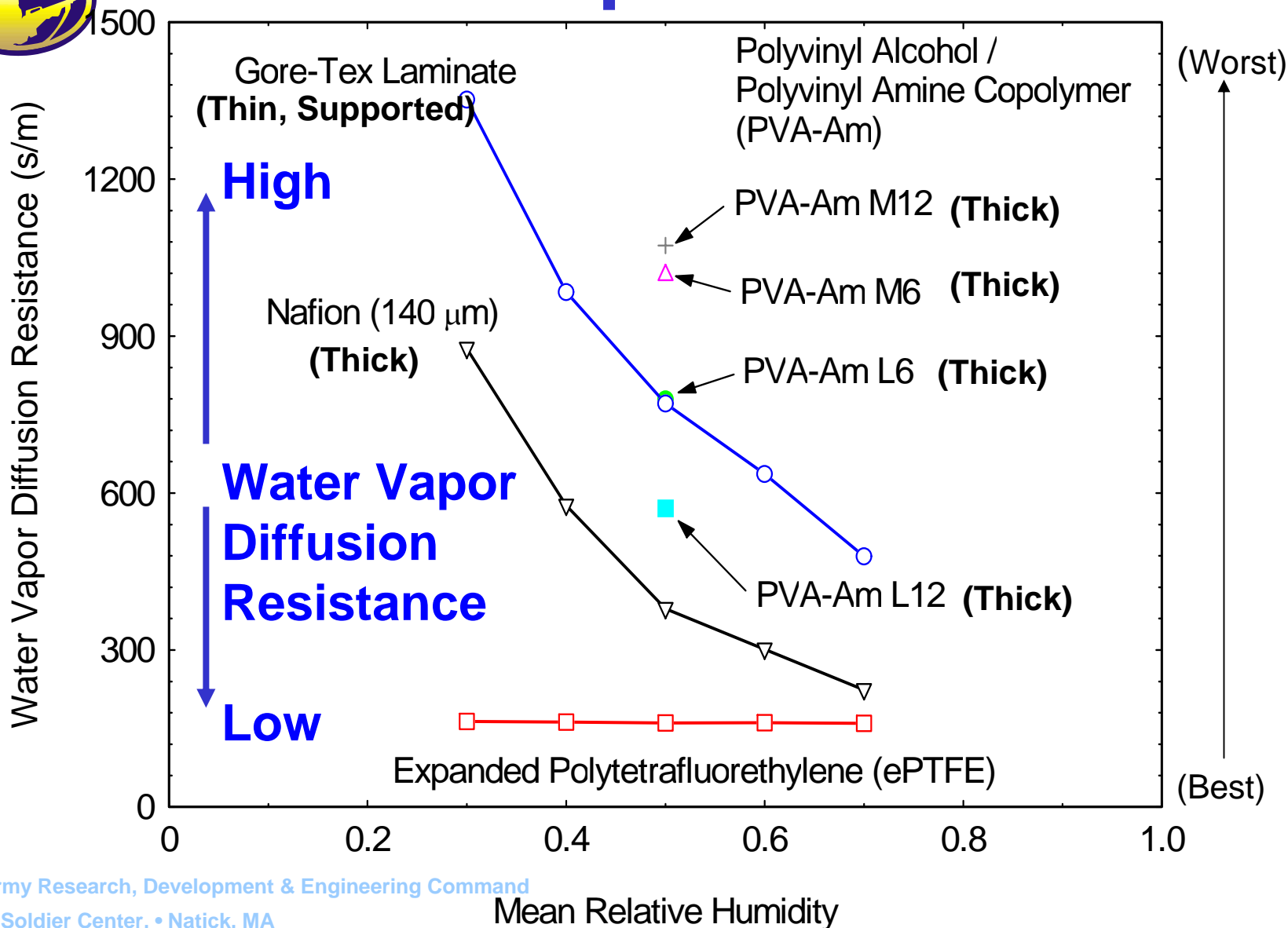
PVA-Am Film Hydrolyzes
DFP, G-agent Simulant

(Seen by pH indicator).





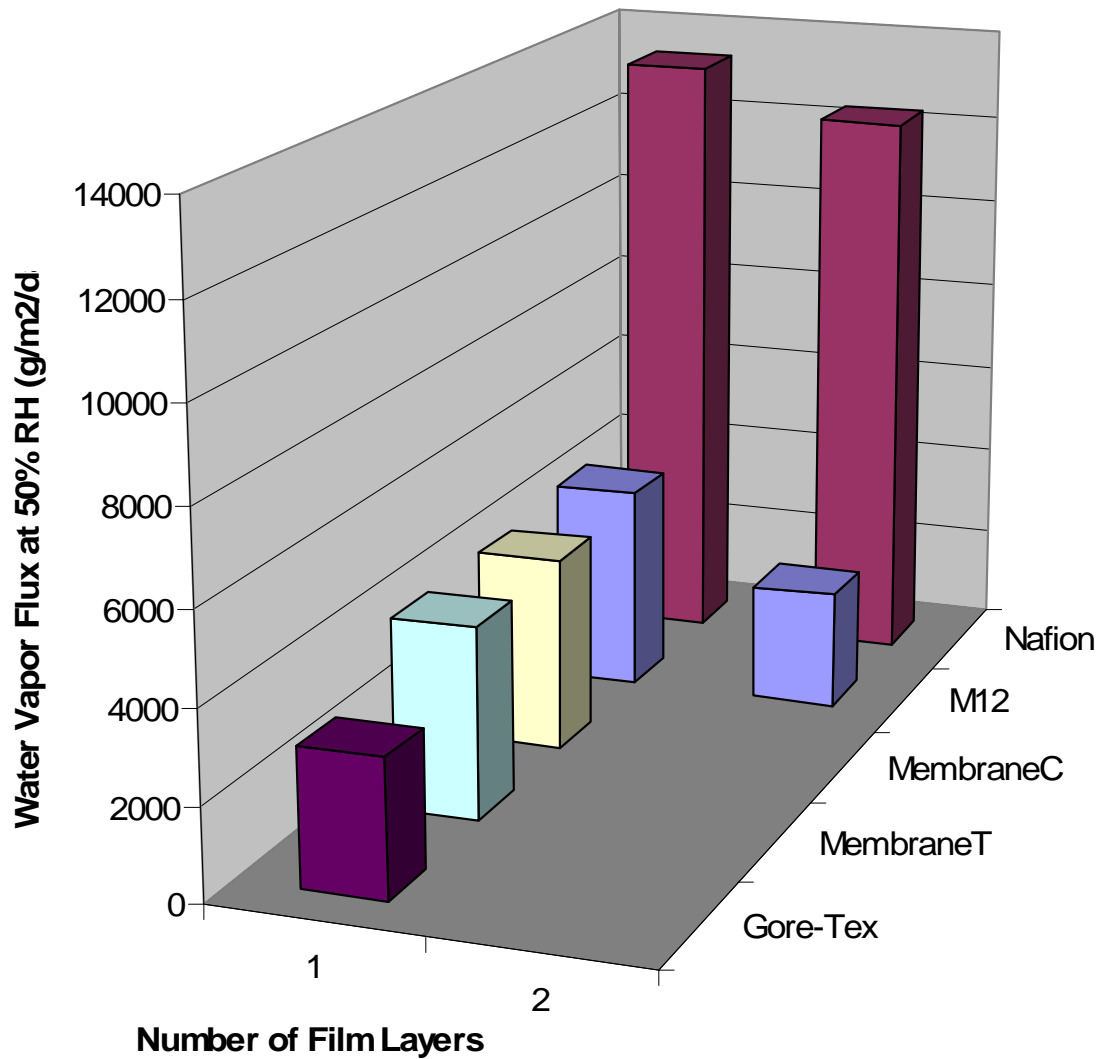
Water Vapor Diffusion





Water Vapor Diffusion

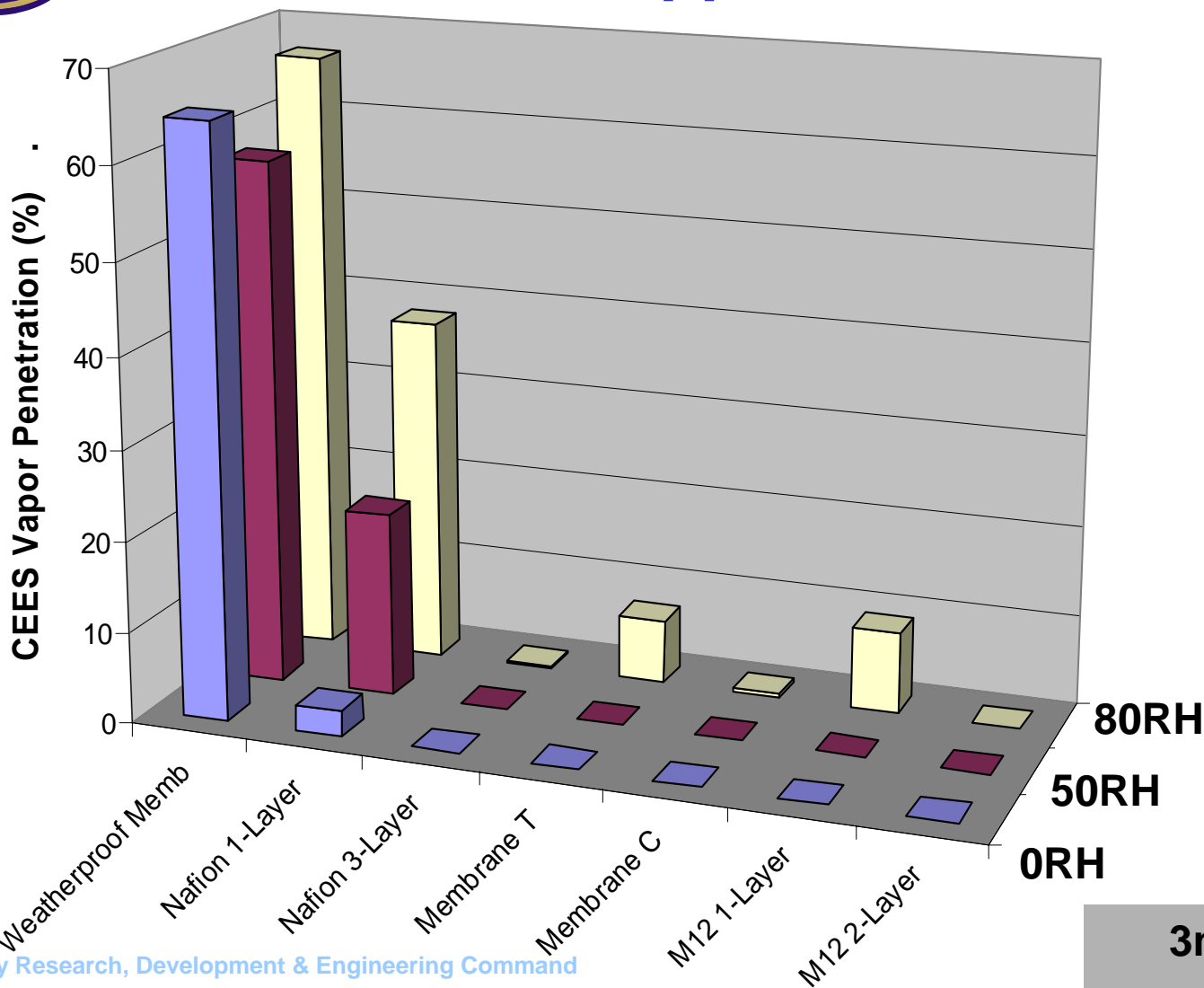
Thin, Supported Films





CEES Vapor Diffusion

Thin, Supported Films



**3mg CEES
applied**



Conclusions

Chloramide-treated fabrics break down 2-CEES in solution and in vapor challenge tests.

One of the major by-products was the nontoxic sulfoxide. Other by-products include dimers.

Chloramides bound to nanoparticles of alumina were reactive, but not as active as the chloramides alone.



Conclusions

NanoAl₂O₃-PLUS more adsorptive than activated carbon.

NMR found that NanoAl₂O₃-PLUS depleted 2-CEES at a rate of 0.74 mgCEES/mgNanoparticle/day.

A fabric weight of 1-33 grams per square meter of NanoAl₂O₃-PLUS needed to meet the 1mg/cm²/day protection requirement for clothing systems.

100 gsm of nanoTiO₂ would be needed for protective fabrics to meet Chemical Protection requirements.



Conclusions

Carbon-bound POMs faster than free POM in the decomposition of 2-CEES.

Carbon-bound POMs can be optimized with Cu to increase depletion of 2-CEES by 7x.

Copper-containing POMs completely neutralize 2-CEES in 30 min. Produce CEES-oxide (sulfoxide) product.



Conclusions

Thin supported PVAM films have high water vapor permeation, similar to commercial permselective membranes C and T.

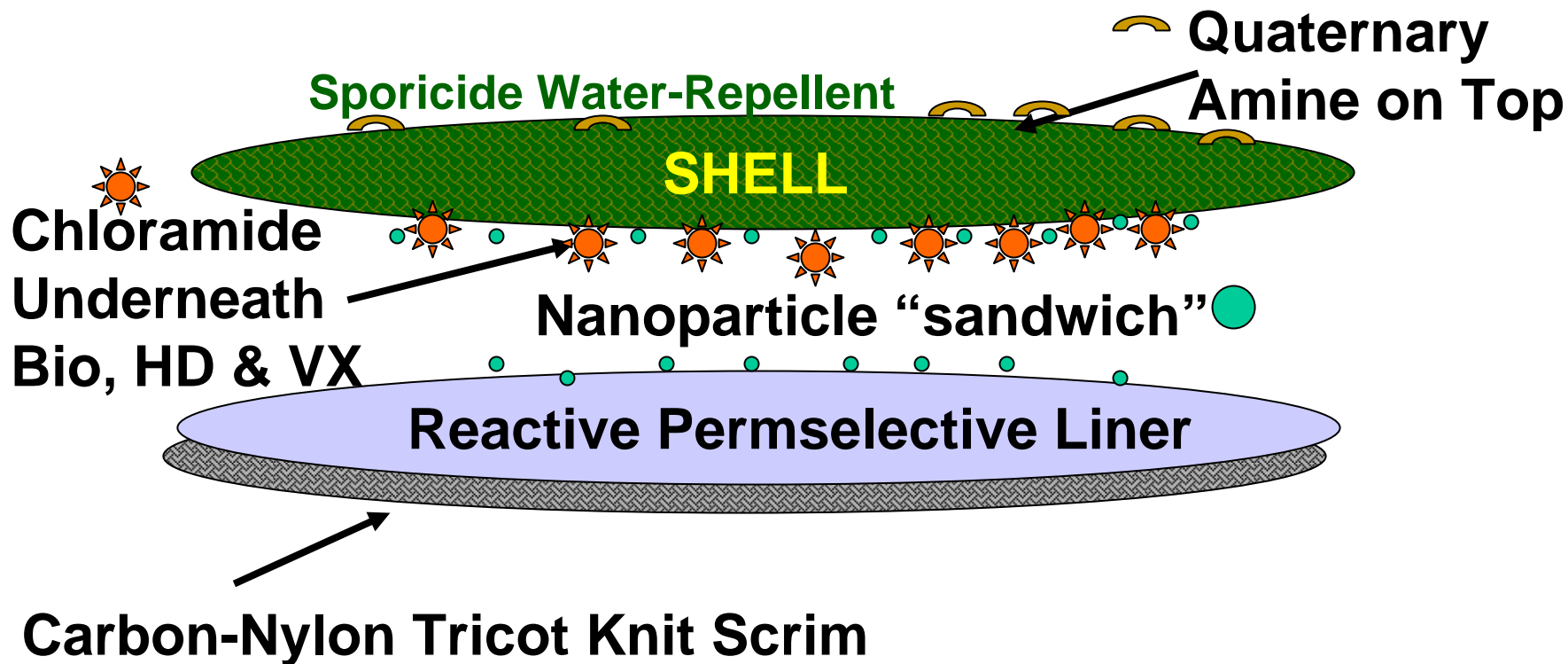
Thin supported Nafion has the highest water vapor permeation.

Thin supported Nafion and MembraneC allow CEES penetration above 50RH

Thin supported PVAM films and MembraneT block CEES below 80RH.



Reactive Fabric System Design





Acknowledgements

Professor Craig Hill and Dr. Nelya Okun, Emory University for POM Catalysts

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Phil Gibson, Joel Carlson, John Walker at Natick

U.S. Army Research, Development & Engineering Command

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