

# NEWLY DEVELOPED COMPOSITE MEMBRANES BASED ON ROOM TEMPERATURE IONIC LIQUID FOR BARRIER FILMS

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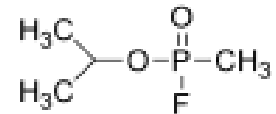


Dallas, TX  
November 19, 2009

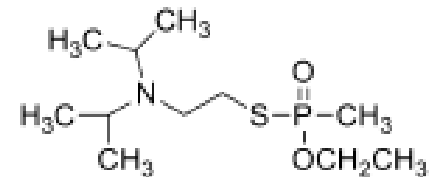
2009 CHEMICAL AND BIOLOGICAL DEFENSE SCIENCE  
AND TECHNOLOGY CONFERENCE

# Chemical Warfare Agents

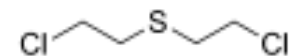
- Decontamination of Chemical Warfare Agents (CWA) is necessary
- Decontamination:
  - ▣ Hydrolysis
  - ▣ Nucleophile-Assisted Substitution
  - ▣ Oxidation
- Decontamination Media
  - ▣ Liquid
    - Solubility and Optimum reactivity
  - ▣ Solid
    - Ability to adsorb large amount of liquid agents
    - Reduce weight of decontaminant



**GB (sarin)**



**VX (V-agent)**



**HD (sulfur mustard)**

# Decontamination of CWA

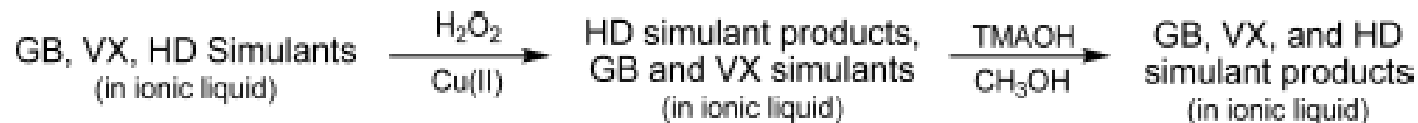
## □ Media

### ▣ Liquid

#### ■ Room Temperature Ionic Liquid (RTIL)

- RTIL: 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)

(Wilkes, J.S., et.al., Ind. Eng. Chem. Res., 2009, 48)



### ▣ Solid

#### ■ XE-555 (Rohm & Haas Company)

- Resin made of styrene/divinylbenzene copolymer with strong acid groups cation-exchange resin, and strong base anion-exchange resin

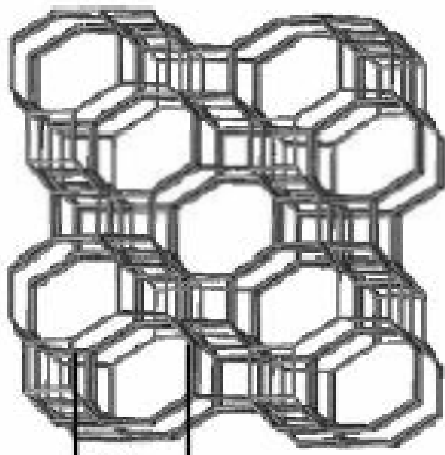
## □ Catalyst

### ▣ Metal Ion Catalyzed Hydrolysis

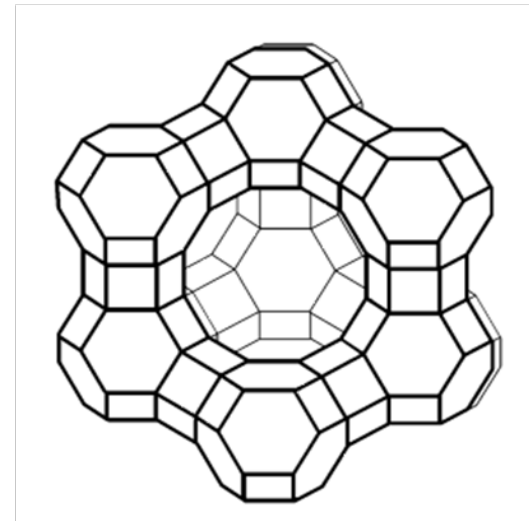
- $\text{Cu}^{+2}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^{+2}$

# Decontamination of CWA Using Zeolite as Catalyst

- Zeolite: porous polycrystalline materials
  - ▣ Framework: tetrahedral structure of aluminate, silicate
  - ▣ Non-framework: Typically Alkali cations
  - ▣ Pore size: ~3 - 7 Angstrom
  - ▣ High adsorption capacity
  - ▣ Catalytic potential



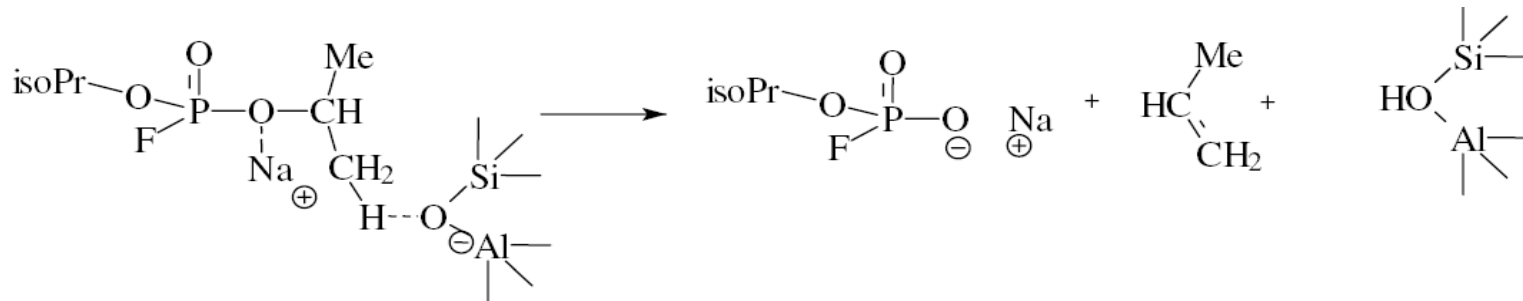
**0.38 nm** SAPO-34



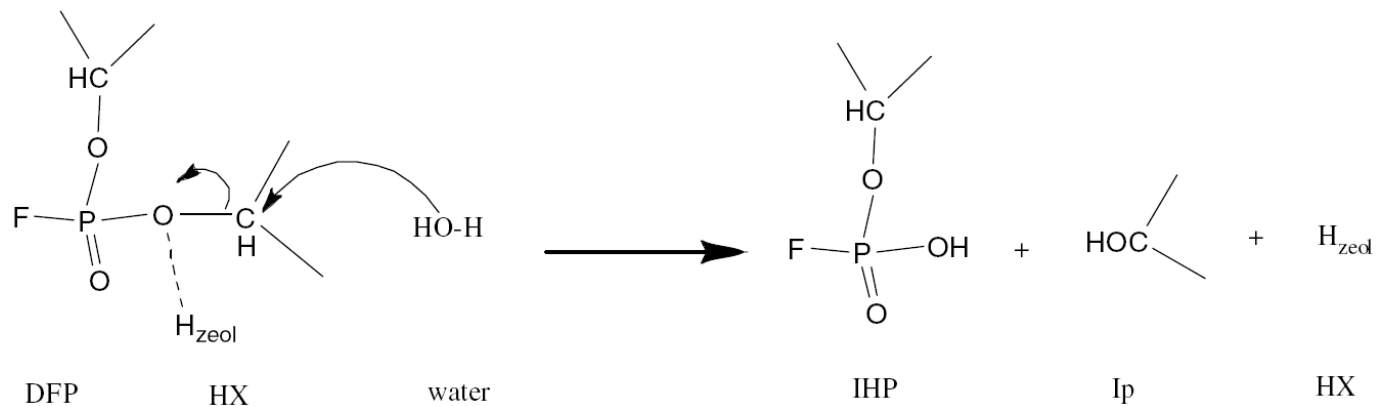
**0.74 nm** FAU (Y and X)

# Hydrolysis of CWA with Na-X Zeolite

- Hydrolysis of CWA via Na-X Zeolite without the presence of  $H_2O$

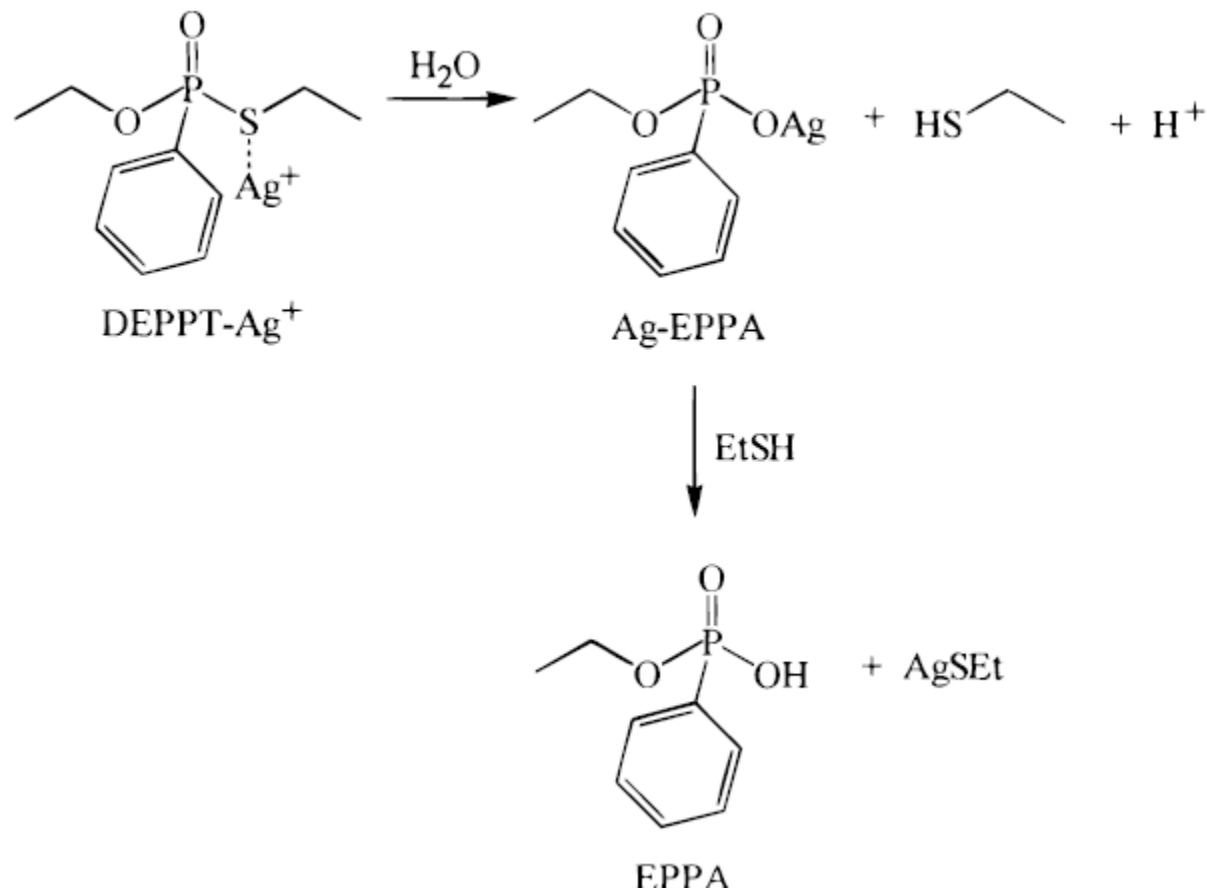


- Hydrolysis of VWA via Na-X Zeolite with presence of  $H_2O$

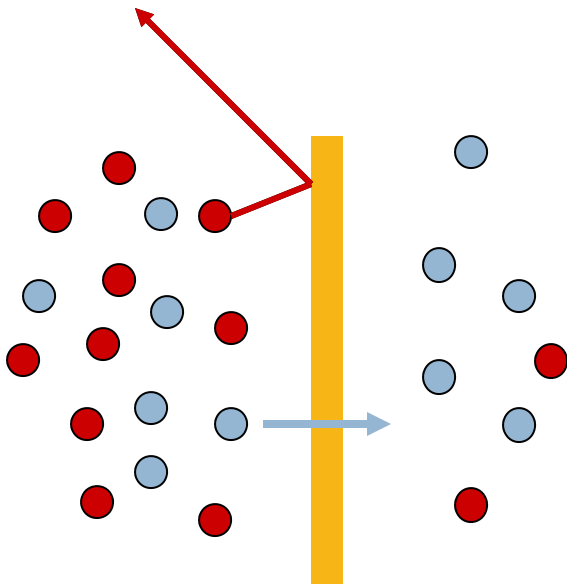


# Hydrolysis of CWA with Ag-Y Zeolite

## □ Hydrolysis of DEPPT catalyzed by Ag-Y

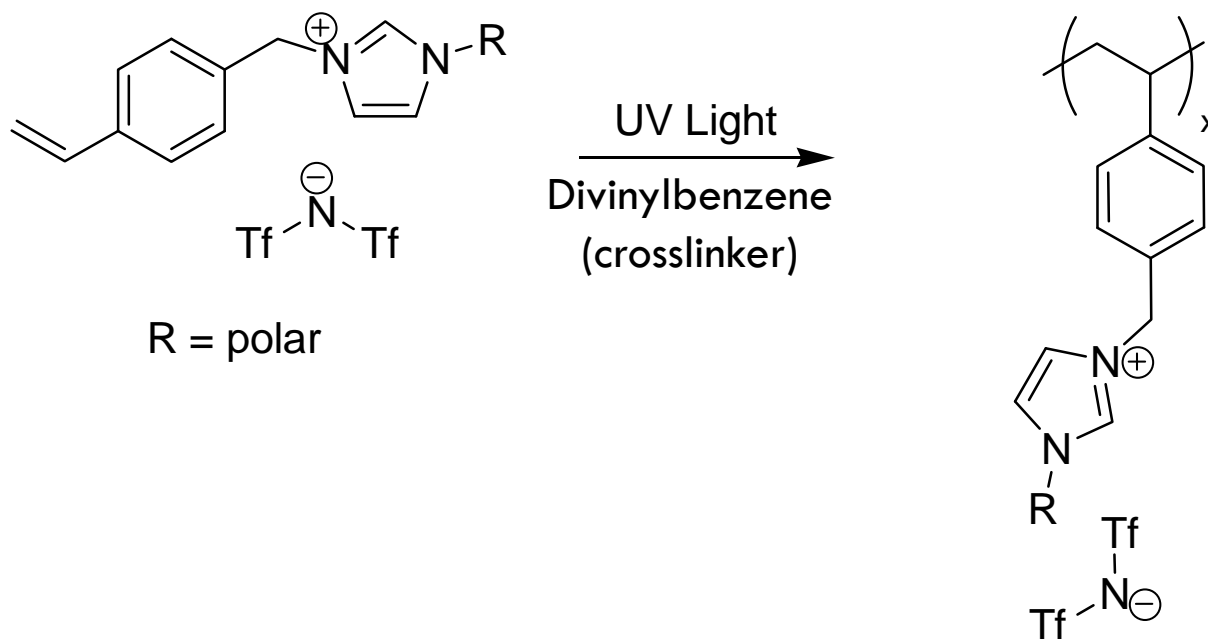


# Objective



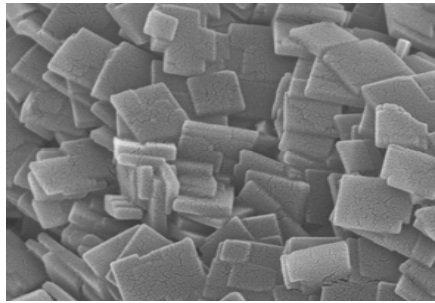
- Develop a breathable membrane
  - Transport  $\text{H}_2\text{O}$
  - Block CWA
- Organic/Inorganic Composite Membrane
  - Zeolite : catalyst
  - Polymerizable Ionic Liquid (poly(RTIL))

# Polymerizable RTIL



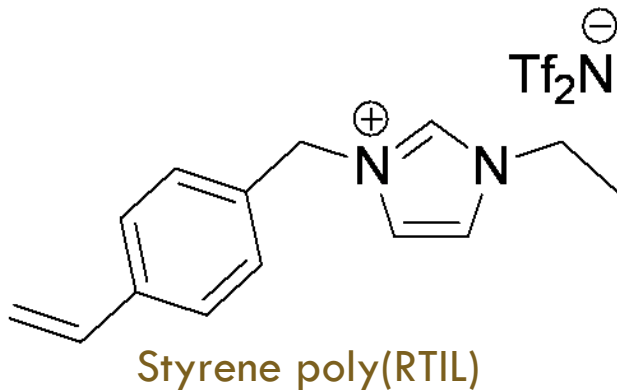
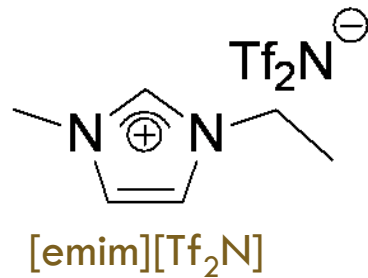
- ❑ Monomer version of ionic liquids were previously synthesized
- ❑ A membrane based on poly(RTIL) was fabricated

# Fabrication of Zeolite – poly(RTIL)s Composite Membranes

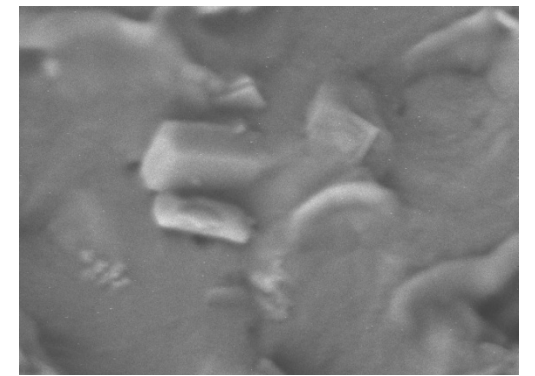


SAPO-34

100 nm



UV light  
crosslinker

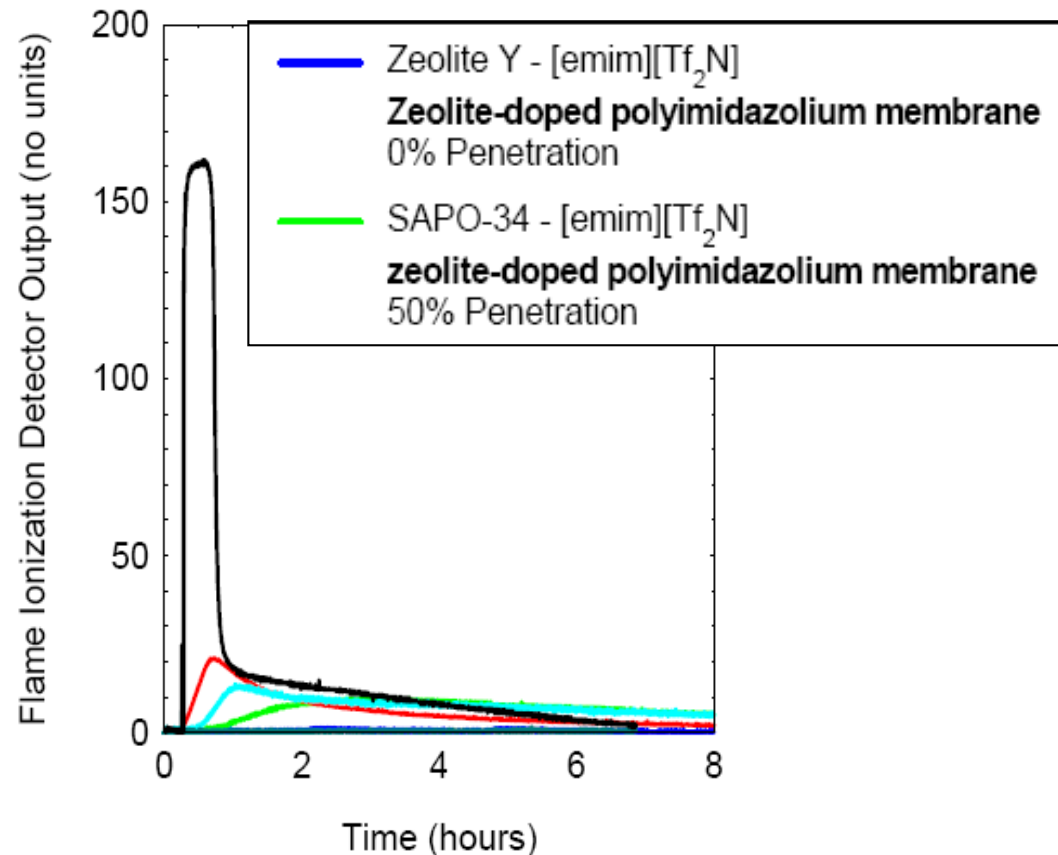
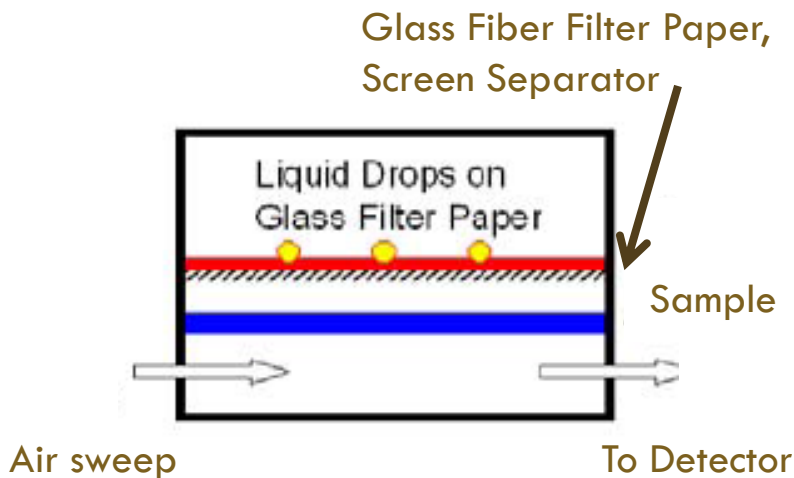


100 nm

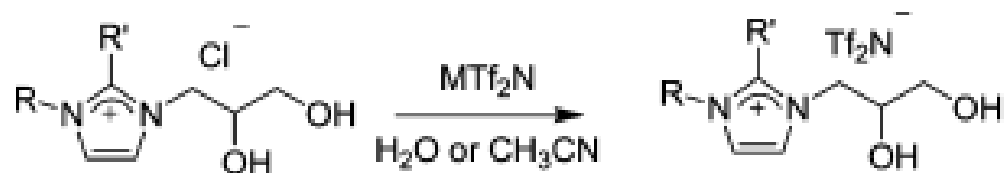
10 wt% of SAPO-34 &  
(80-20)wt% of styrene  
poly(RTIL) and [emim][Tf<sub>2</sub>N]

# CEES & H<sub>2</sub>O Transport of Na-Y Zeolite / Styrene-methyl poly(RTILs) Composite

- Styrene-methyl poly(RTIL) –zeolite (10wt%) – [emim][Tf<sub>2</sub>N] composite
- Membrane was tested by Phillip Gibson at Natick
- No penetration of CEES, but poor water transport



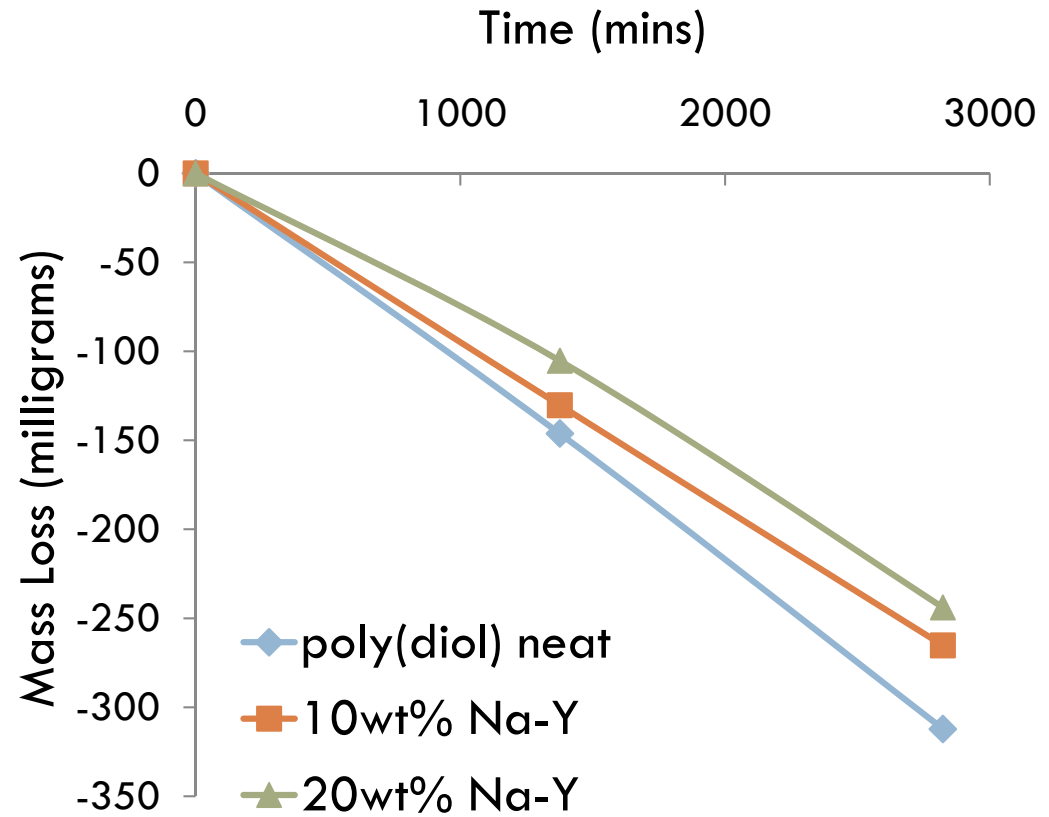
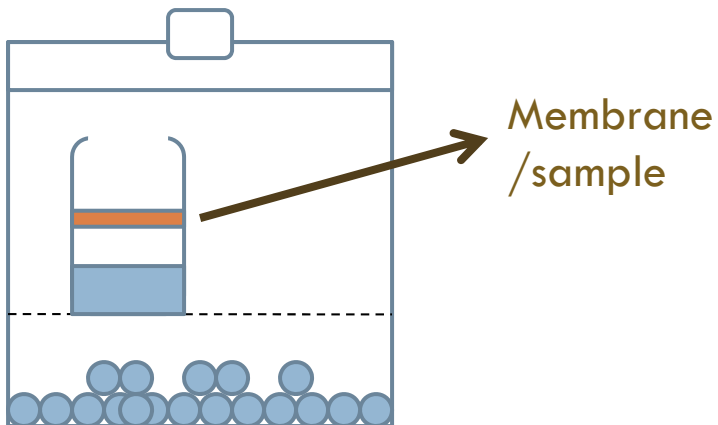
# Diol-RTIL with Tunable Water Miscibility



R	R'	Solvent/M	H <sub>2</sub> O Miscible
Me	H	CH <sub>3</sub> CN/K	Yes
Me	Me	H <sub>2</sub> O/Li	No
Et	H	CH <sub>3</sub> CN/K	Yes
Pr	H	H <sub>2</sub> O/Li	No
Bu	H	H <sub>2</sub> O/Li	No
Bn	H	H <sub>2</sub> O/Li	No

# H<sub>2</sub>O Transport Experiment

- The mass loss of water in the sample cell was measured in a closed desiccator over time



# H<sub>2</sub>O Permeability of Composite Membranes

Solution – Diffusion Mechanism :

$$P_i = J_i \frac{l}{\Delta p_i}$$

P: Permeability

J: Flux

l: Membrane Thickness

$\Delta p$ : Driving force (pressure change)

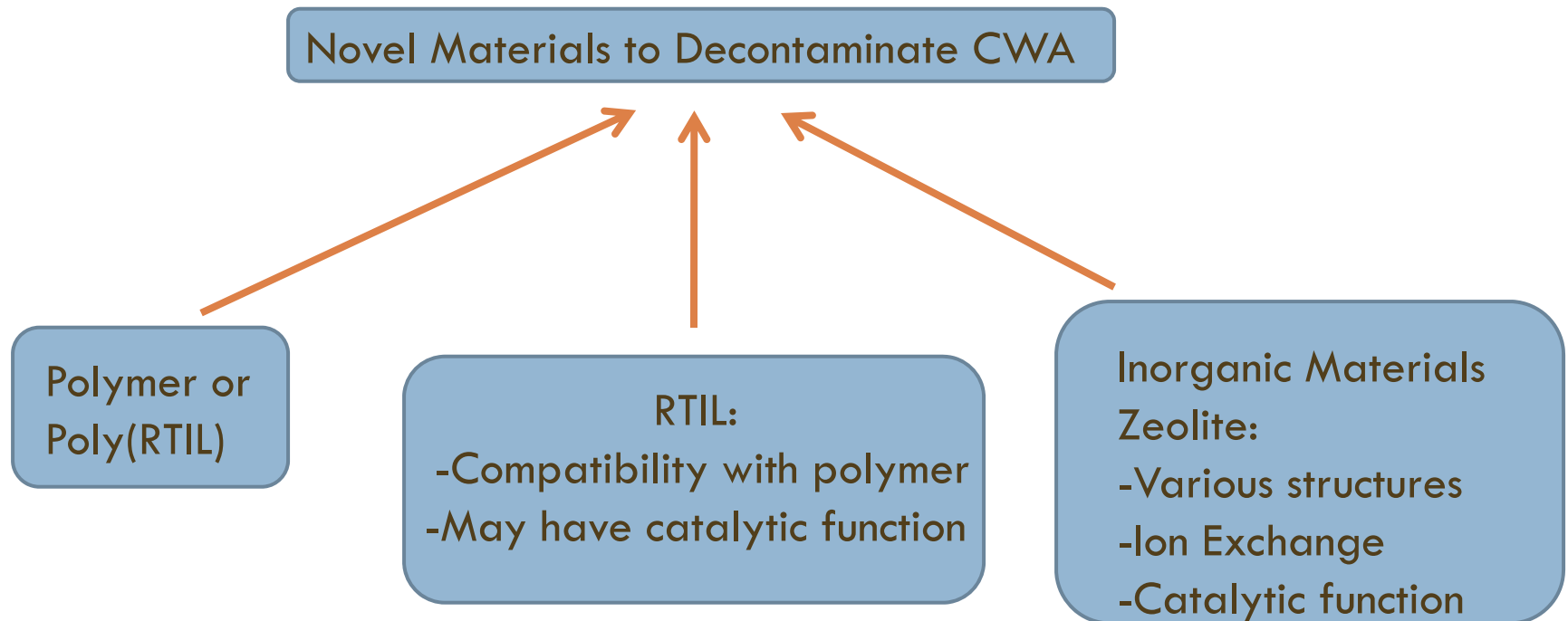
- The permeability was calculated using solution-diffusion mechanism without normalizing it with the driving force
- Addition of Na-Y doesn't not decrease water permeability → Na-Y zeolite is hydrophilic

Sample	P
	(gram H <sub>2</sub> O/m/hr)
poly(diols) neat	0.008
10wt% Na-Y	0.018
20wt% Na-Y	0.039

The membrane was sent to be tested for CEES transport

# Looking Forward

- There may not be a single material which would be able to decontaminate all the type of CWAs
- But we may be able to combine several systems to provide one (composite structure)



# Summary

- Poly(RTILs) – Zeolite composite membranes were successfully fabricated which show good barrier properties for CEES
  - ▣ future research will focus on adjusting the type and amount of each component to optimize both the CWA barrier and water transport properties
- The Zeolite may have decontaminated CEES as previously shown in the literature
  - ▣ future study is needed to verify this reaction
- Poly(RTILs) – Zeolite composite membranes with poly(diols) showed good water permeability
  - ▣ Na-Y zeolite is hydrophilic and does not show a decrease in permeability of water

# Acknowledgment

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- Phillip Gibson and Heidi Gibson for CWA test
- Defense Threat Reduction Agency (DTRA),  
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