# Fate of 2-Chloro Ethyl Ethyl Sulfide on 13X Molecular Sieve Adsorbent

## Implications for Regenerative Filtration

2003 Joint Scientific Conference on Chemical & Biological Defense Research

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# Introduction

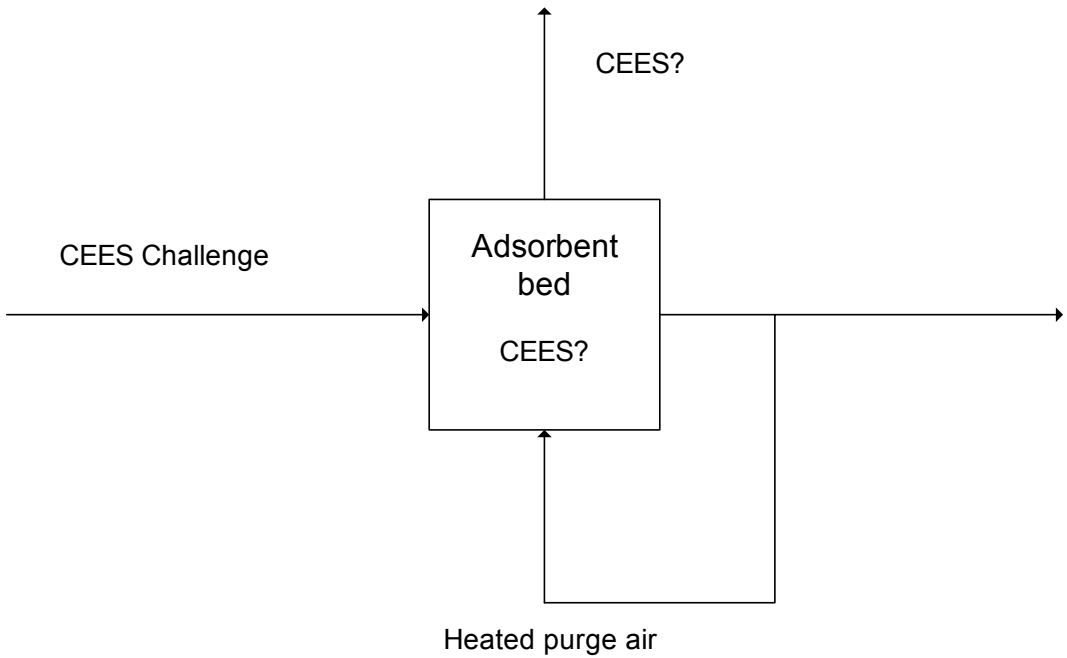
- Regenerative filtration technology offers the promise of greater capacity and breadth of chemical protection than the currently fielded single pass filtration technology.

- Many past and current regenerative filtration prototypes utilize zeolite adsorbents such as 13X molecular sieve.

- The current carbon based adsorbent knowledge base must be expanded to include adsorbate-adsorbent interaction under regenerative filtration conditions.

# Objective

- Evaluate the behavior of 2-chloro ethyl ethyl sulfide (CEES), a mustard (HD) simulant, on 13X molecular sieve under thermal regeneration conditions.



# Approach

- Expose a packed bed of 13X to a vapor challenge of CEES until it reaches saturation.
- Purge the saturated bed with reverse flow and introduce step-wise heating.
- Evaluate at conditions relevant to regenerative filtration.
  - Examine effect of preloaded water.
  - High face velocity (several times that of M48).
  - Restrained adsorbent bed.

# Experimental

Preparation of 13X adsorbent

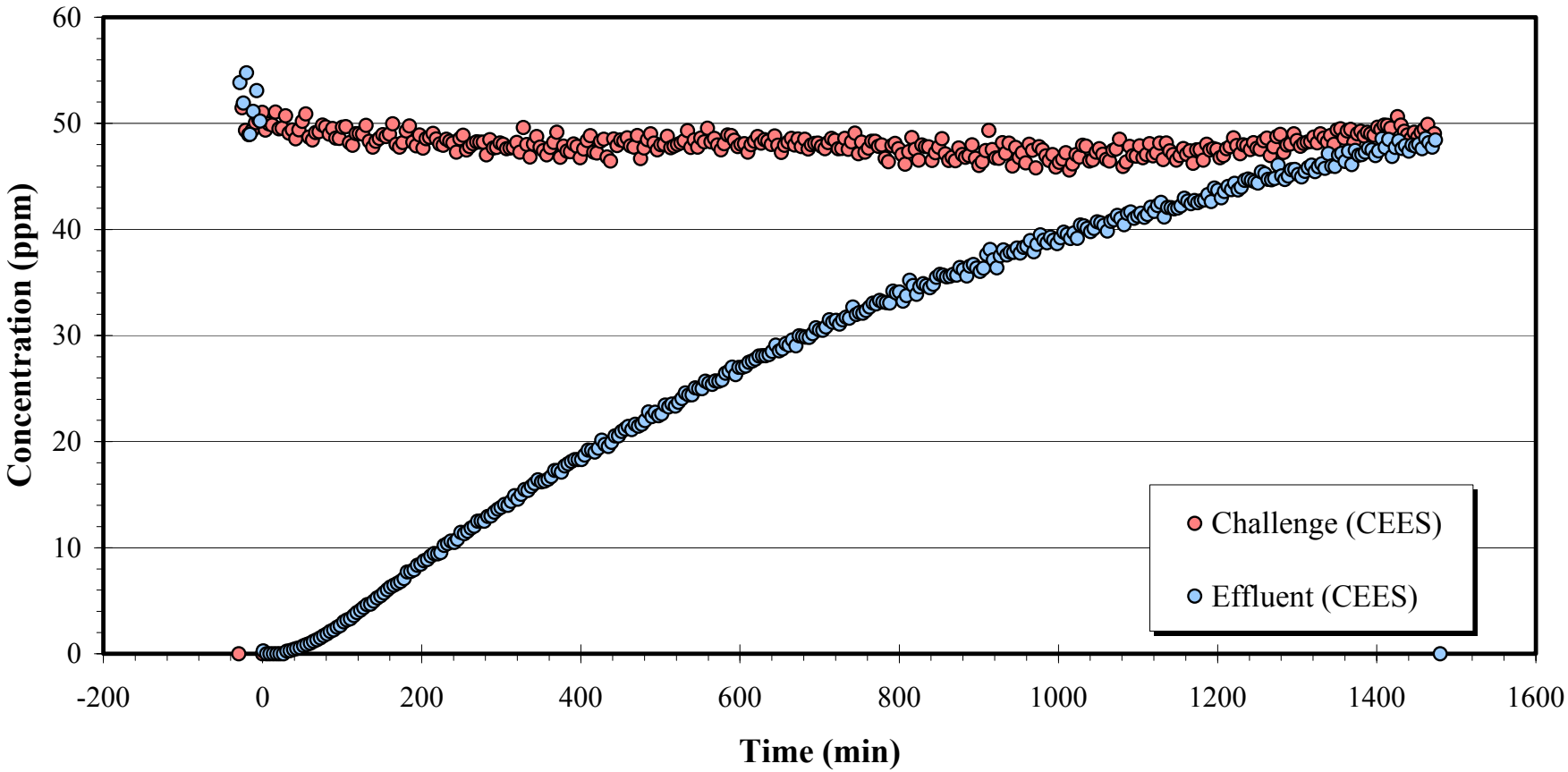
| | |
|---|---|
| CEES feed concentration | 200 mg/$m^3$ (43 ppm) |
| Temperature | 50 C |
| Bed depth | 3 cm |
| Flow rate | 50 LPM (21.1 C, 1 atm) |
| Face velocity | 51.8 cm/s |
| Dew point | <-80 C to 0 C |

# Experimental

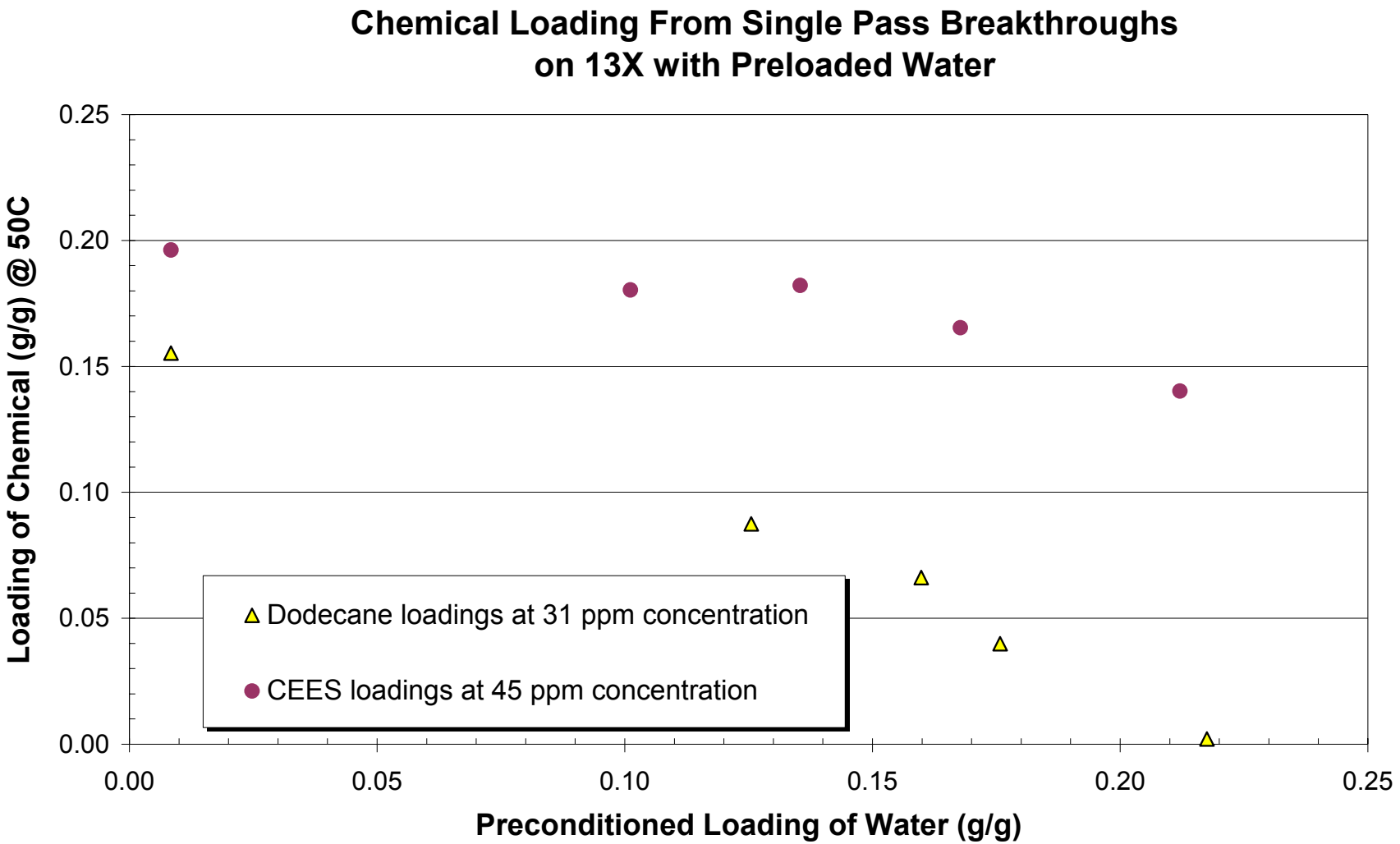
Purge of 13X adsorbent

| | |
|---|---|
| Temperature | 50 C to 125 C |
| Bed depth | 3 cm |
| Flow rate | 25 LPM (21.1 C, 1 atm) |
| Face velocity | 25.8 cm/s @ 50 C |
| Dew point | <-80 C |

# Results


Breakthrough of CEES on 13X Adsorbent
43 ppm CEES challenge, 51.8 cm/s velocity, 3 cm bed depth, <-80 C dew point
Concentration (ppm)
60
50
40
30
20
10
0
-200
0
200
400
600
800
1000
1200
1400
1600
Time (min)
Challenge (CEES)
Effluent (CEES)

# Results


Chemical Loading From Single Pass Breakthroughs
on 13X with Preloaded Water
Loading of Chemical (g/g) @ 50C
0.25
0.20
0.15
0.10
0.05
0.00
0.00
0.05
0.10
0.15
0.20
0.25
Preconditioned Loading of Water (g/g)
Dodecane loadings at 31 ppm concentration
CEES loadings at 45 ppm concentration

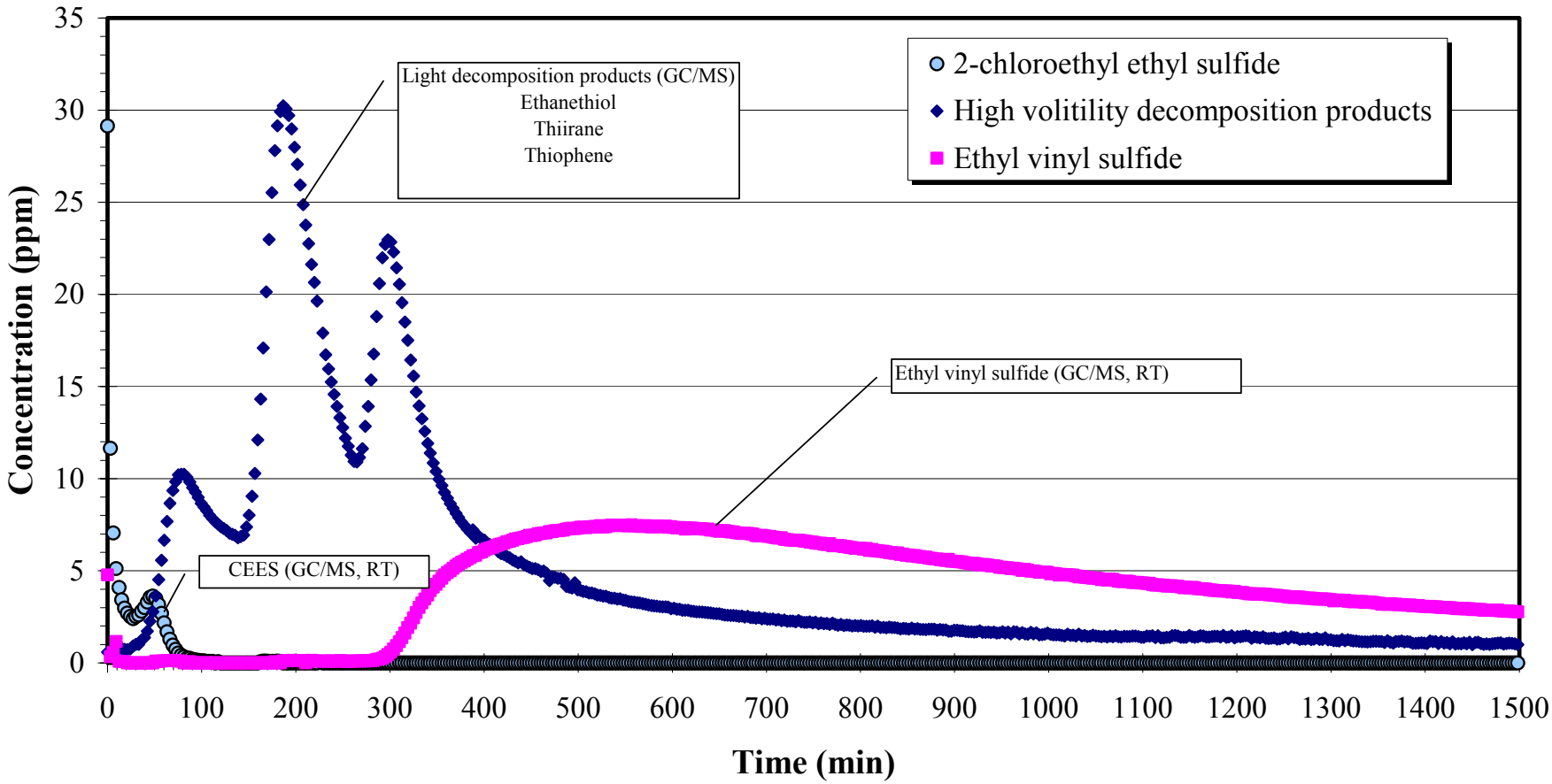
# Results

- Identification of purge components
  - Sample 1
    - GC FID
      - One low retention time peak, no other detectable peaks
    - GC/MS suggests presence of following compounds
      - Ethanethiol
      - Thiirane
      - Thiophene
      - Diethyl sulfide
      - Diethyl disulfide (oxidation product of ethanethiol)
      - CEES
  - Sample 2
    - GC FID
      - CEES peak and two unidentified peaks
    - GC/MS suggests presence of following compounds
      - Ethyl vinyl sulfide
      - CEES
    - Confirmed presence of ethyl vinyl sulfide by matching retention time and response with standard.

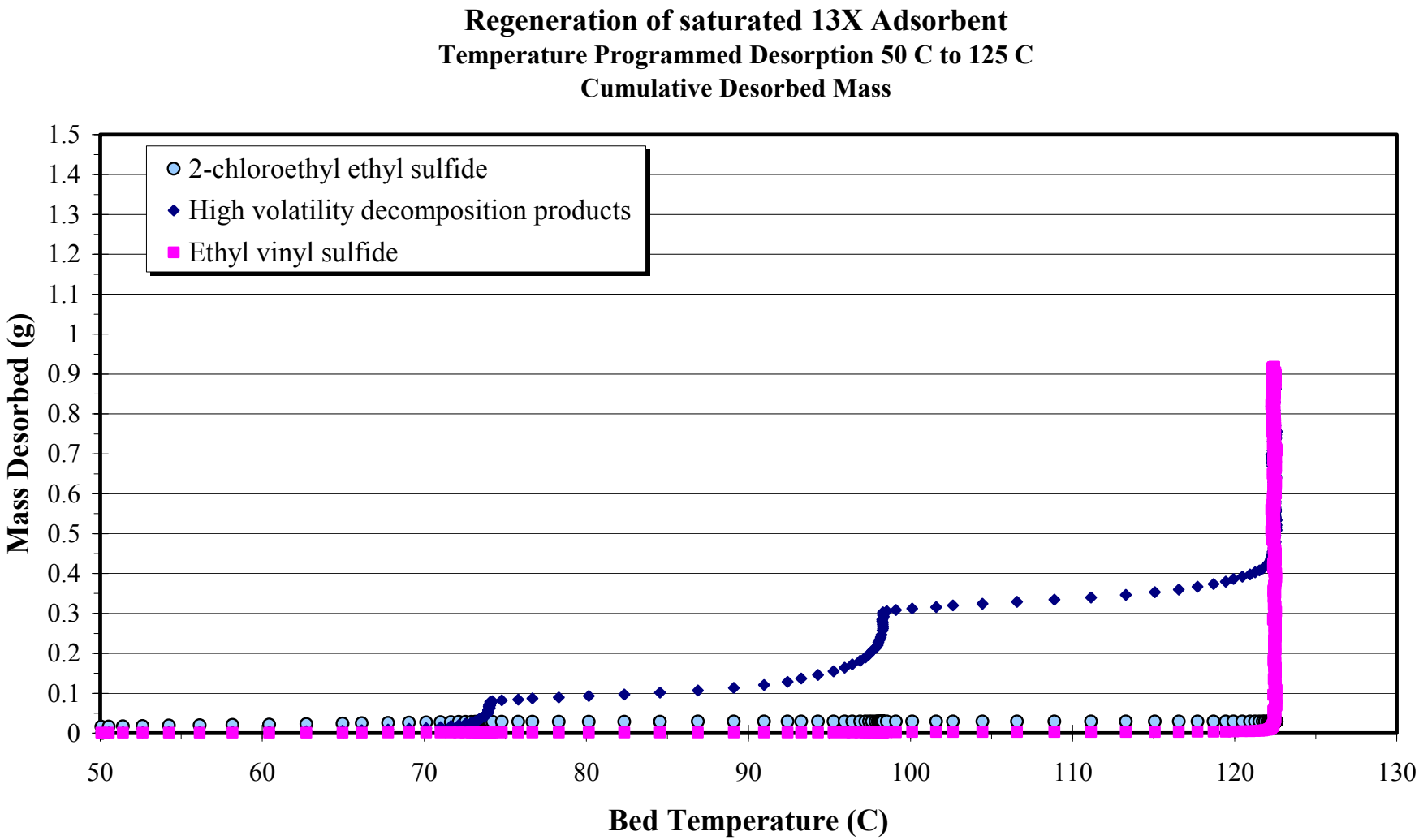
# Results

**Regeneration of saturated 13X adsorbent**

**Temperature Programmed Desorption 50 to 125 C**



# Results

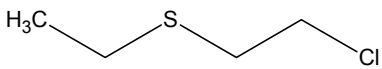

Regeneration of saturated 13X Adsorbent
Temperature Programmed Desorption 50 C to 125 C
Cumulative Desorbed Mass
2-chloroethyl ethyl sulfide
High volatility decomposition products
Ethyl vinyl sulfide
Mass Desorbed (g)
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
60
70
80
90
100
110
120
130
Bed Temperature (C)

# Results

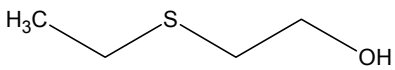
Mass balance

| Dew Point | Mass loaded (g) | CEES recovered (g) | Reaction products (g) | Total recovery (%) | Mass balance (%) |
|---|---|---|---|---|---|
| < -80 C | 7.40 | 0.04 | 2.59 | 36 | 99 |
| -40 C | 6.81 | 0.06 | 2.01 | 31 | 100 |
| -20 C | 6.24 | 0.03 | 2.37 | 38 | 101 |

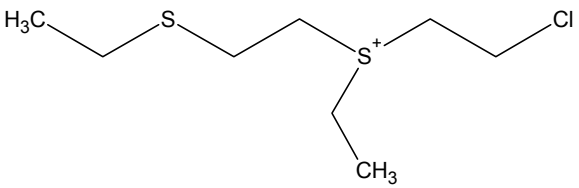
# Results



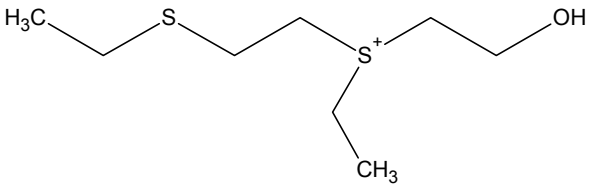

2-chloroethyl ethyl sulfide




HCl $H_2O$



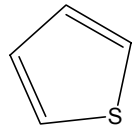

(2-chloroethyl)(ethyl)[2-(ethylthio)ethyl]sulfonium



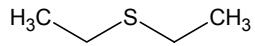

ethyl[2-(ethylthio)ethyl](2-hydroxyethyl)sulfonium

CEES and potential hydrolysis products

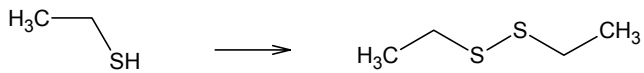

thiirane




thiophene




diethyl sulfide

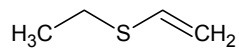



ethanethiol

diethyl disulfide

Maximum generation 95-120 C

Maximum generation 122 C




ethyl vinyl sulfide

Decomposition products

# Summary

- One decomposition product identified: ethyl vinyl sulfide.
  - Requires a 122 C bed temperature for desorption.
  - Purges at long times with first order kinetics.
- Several other possible desorption products suggested by data.
  - GC FID method does not allow resolution of 0.64 min RT peak.
  - Possible products are fragments or cyclic derivatives of CEES.
  - Temperature at which the desorption concentration peaks, rises with increased preloaded water (95-120 C).
  - Purges at long times with second order kinetics.

# Conclusions

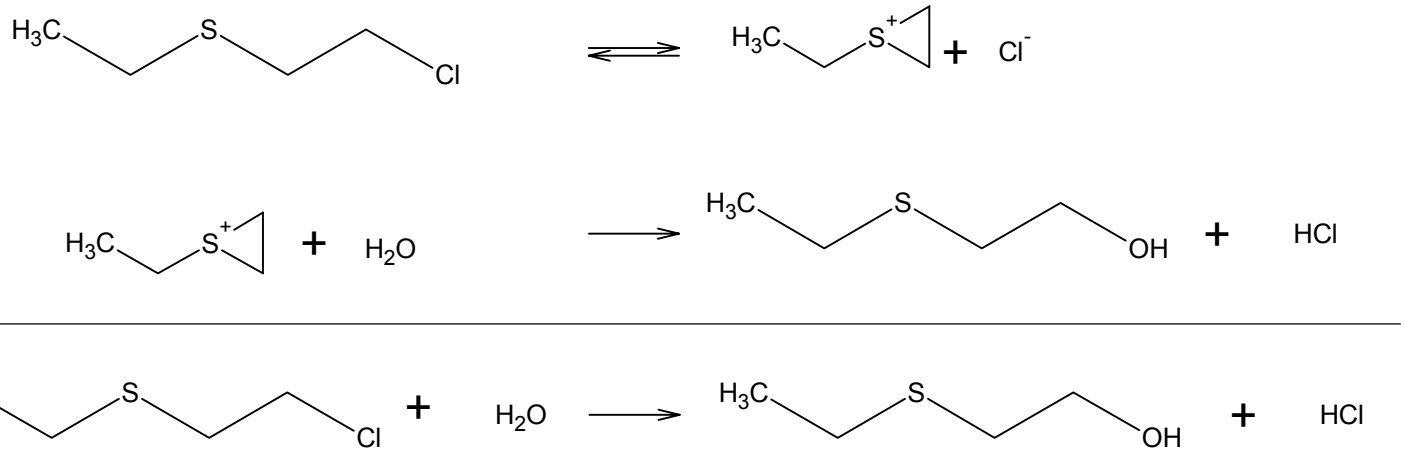
- CEES undergoes hydrolysis and decomposition under conditions relevant to regenerative filtration on 13X adsorbent.
- Less than 1% of loaded CEES is purged as CEES, which is <2% of the total purge mass.
- 13X adsorbent is not fully regenerated when tested with CEES under the test conditions (<50%).
- Future work
  - Test mustard under similar conditions.
    - Literature suggests mustard may be less reactive but produce analogous (mustard chemistry) decomposition products.
  - Design apparatus for screening desorption properties (reactivity, dynamics, equilibrium) for regenerative filtration adsorbent candidates under a wide variety of conditions. This would be an important engineering tool for regenerative filtration system design.

# Acknowledgements


- US Army Edgewood Chemical Biological Center
  - Alex Balboa
  - Leonard Buettner
  - Michael Causey
- Guild Associates, Inc.
  - Roy Brown
  - James Kotary
- Geo-Centers, Inc.
  - Kathy Matson

# Background

- Hydrolysis of 2-chloroethyl ethyl sulfide in solution*

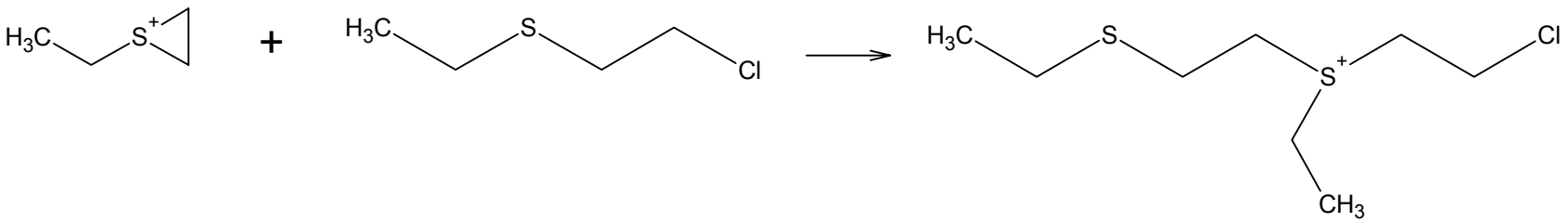



  - First order kinetics dominate when CEES is infinitely dilute.
  - Major hydrolysis products are HEES and HCl.

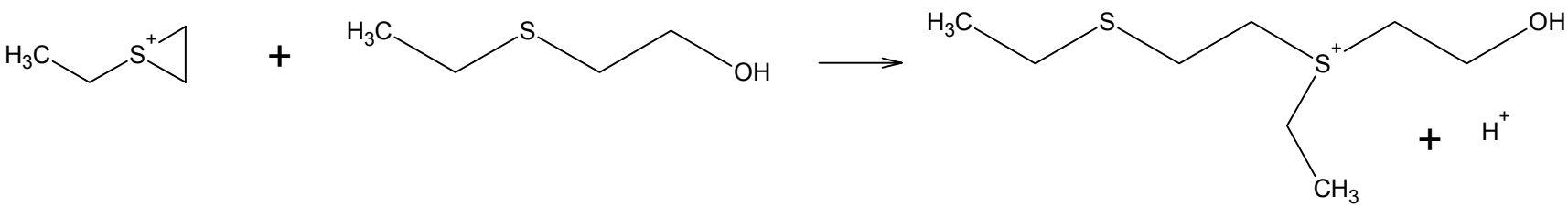
* Yang, Y., et al., "Mechanisms of Interactions of 2-chloroethyl sulfides with Water.", CRDEC-SP-88013, Nov 1987

# Background

- Hydrolysis of 2-chloroethyl ethyl sulfide in solution.
  - For higher concentrations of CEES, reaction proceeds to equilibrium of CEES, HEES, and EHT.



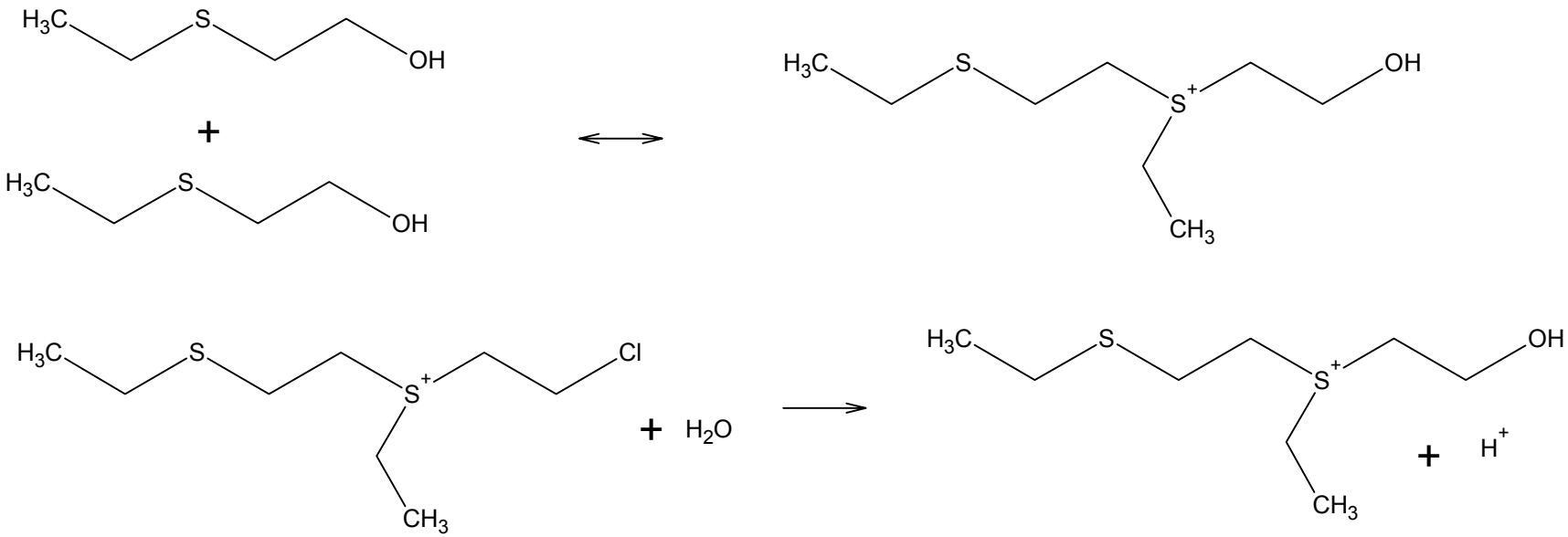

(2-chloroethyl)(ethyl)[2-(ethylthio)ethyl]sulfonium




ethyl[2-(ethylthio)ethyl](2-hydroxyethyl)sulfonium

# Background

- Hydrolysis of 2-chloroethyl ethyl sulfide in solution.
  - For higher concentrations of CEES, reaction proceeds to equilibrium of CEES, HEES, and EHT.



# Background

| | **CEES** $CH_3CH_2SCH_2CH_2Cl$ | **Mustard** $S(CH_2CH_2Cl)_2$ |
|---|---|---|
| Molecular weight | 124.6 | 159.1 |
| Boiling point | 157.1 C | 227.8 C |
| Specific gravity | 1.07 @ 25 C | 1.27 @ 20 C |
| Water solubility* | $4.85 * 10^{-2}$ M | $4.44 * 10^{-3}$ M |
| Hydrolysis products | HCl, HEES, EHT, sulfonium salts | HCl, CH, TG, sulfonium salts |

* Yang, Y. et al., "Solubility Properties and Rates of Solution of Mustard Gas and 2-Chloroethyl ethyl sulfide", CRDEC-TR-88043, February 1988

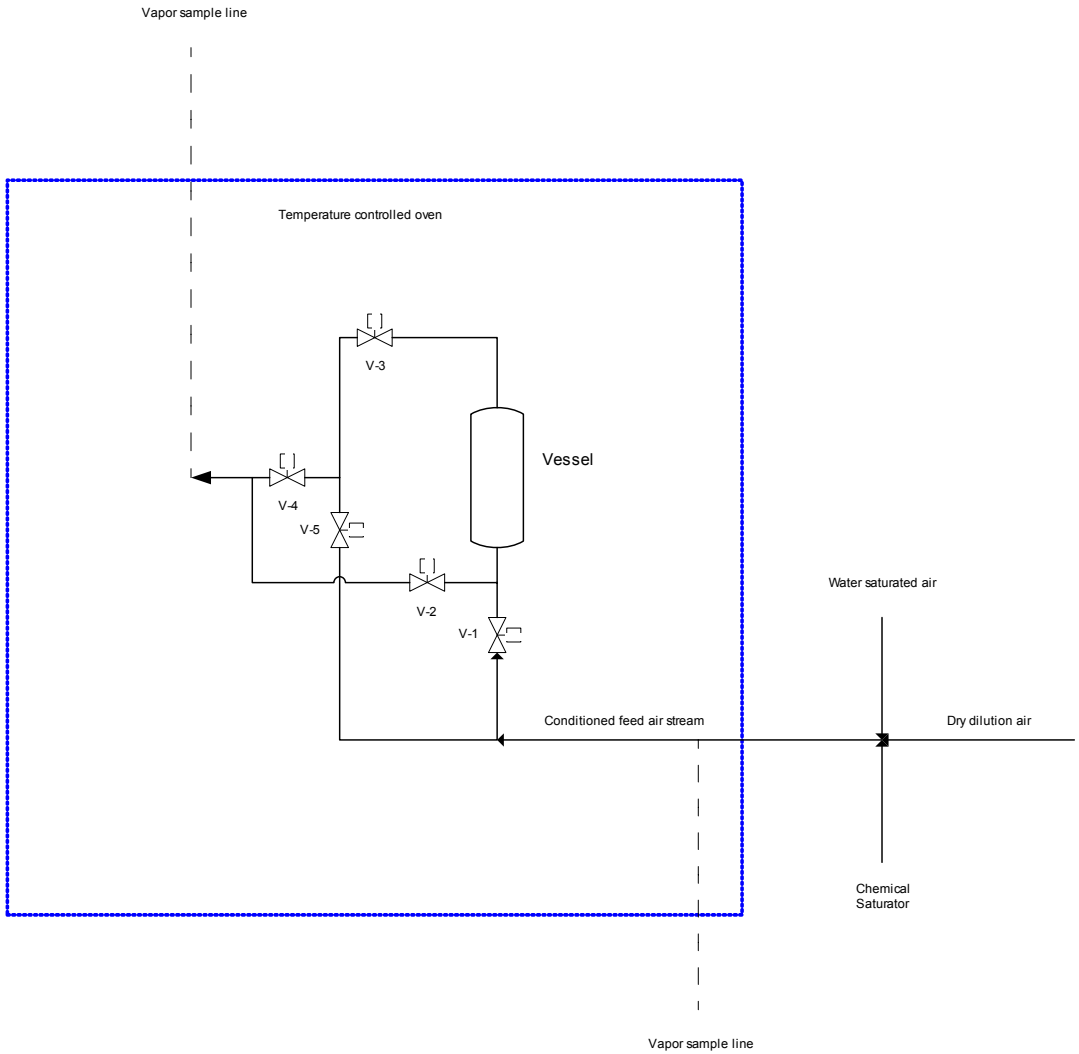
# Background

- Behavior of neat HD on NaY (13X)* [room temp]
  - HD + $H_2O$ → CH + TG → CH-TG
- Thermal desorption of HD from CSC carbon**
  - Combination of hydrolysis and thermal decomposition
  - Decomposition products 1,2 dichloroethane, 2-chloroethanol, 1,4 thioxane, 1,4 dithiane, sulfides, ethers
  - Only low level concentrations examined.

* Wagner, G.W., Bartram, P. W., "Reactions of VX, HD, and Their Simulants with NaY and AgY Zeolites. Desulfurization of VX on AgY.", Langmuir. 1999, 15, 8113-8118

** Karwacki, C. J., et al., "Effect of Temperature on the Desorption and Decomposition of HD from Activated Carbon.", ERDEC-TR-555, Dec 1998.

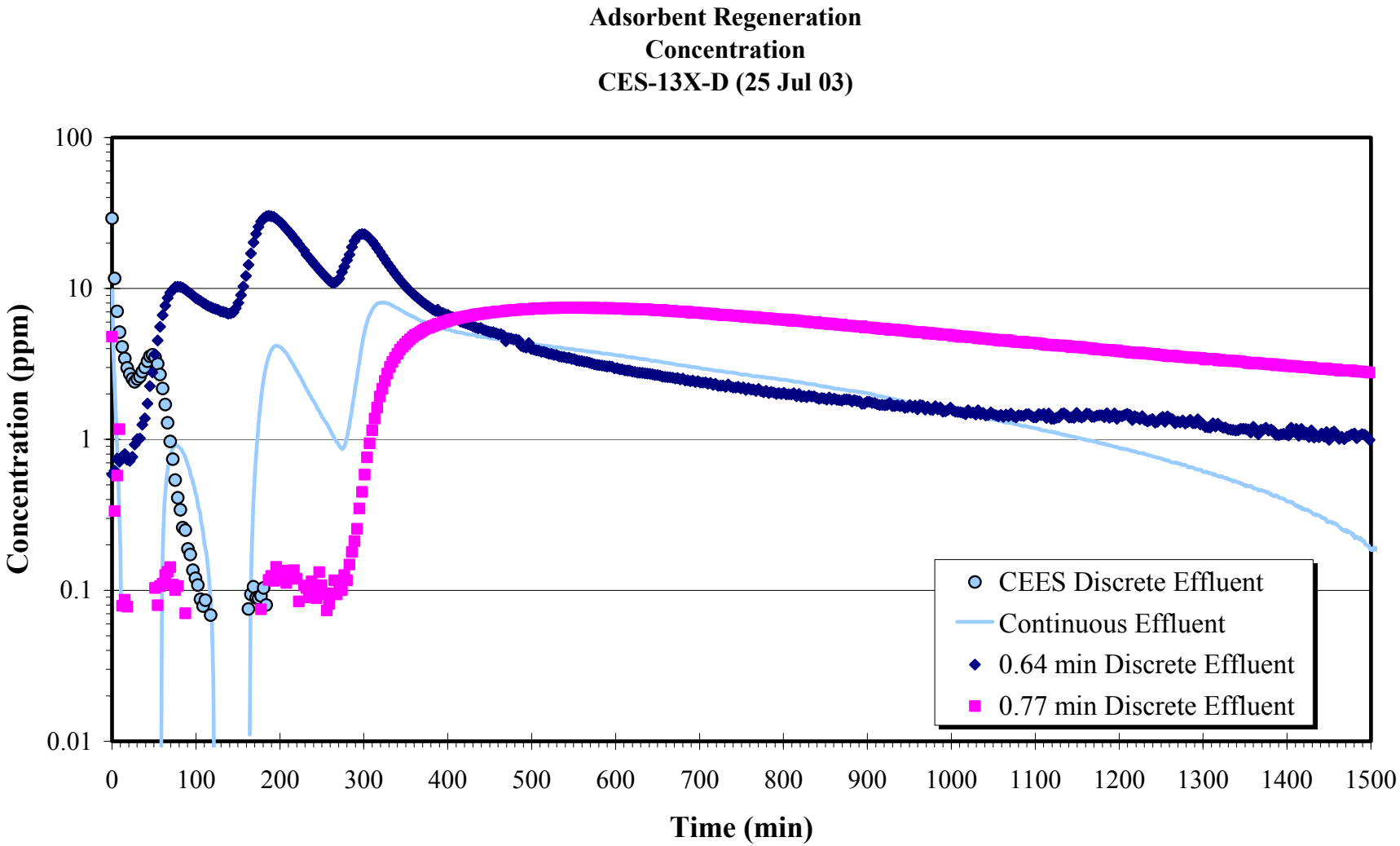
# Experimental



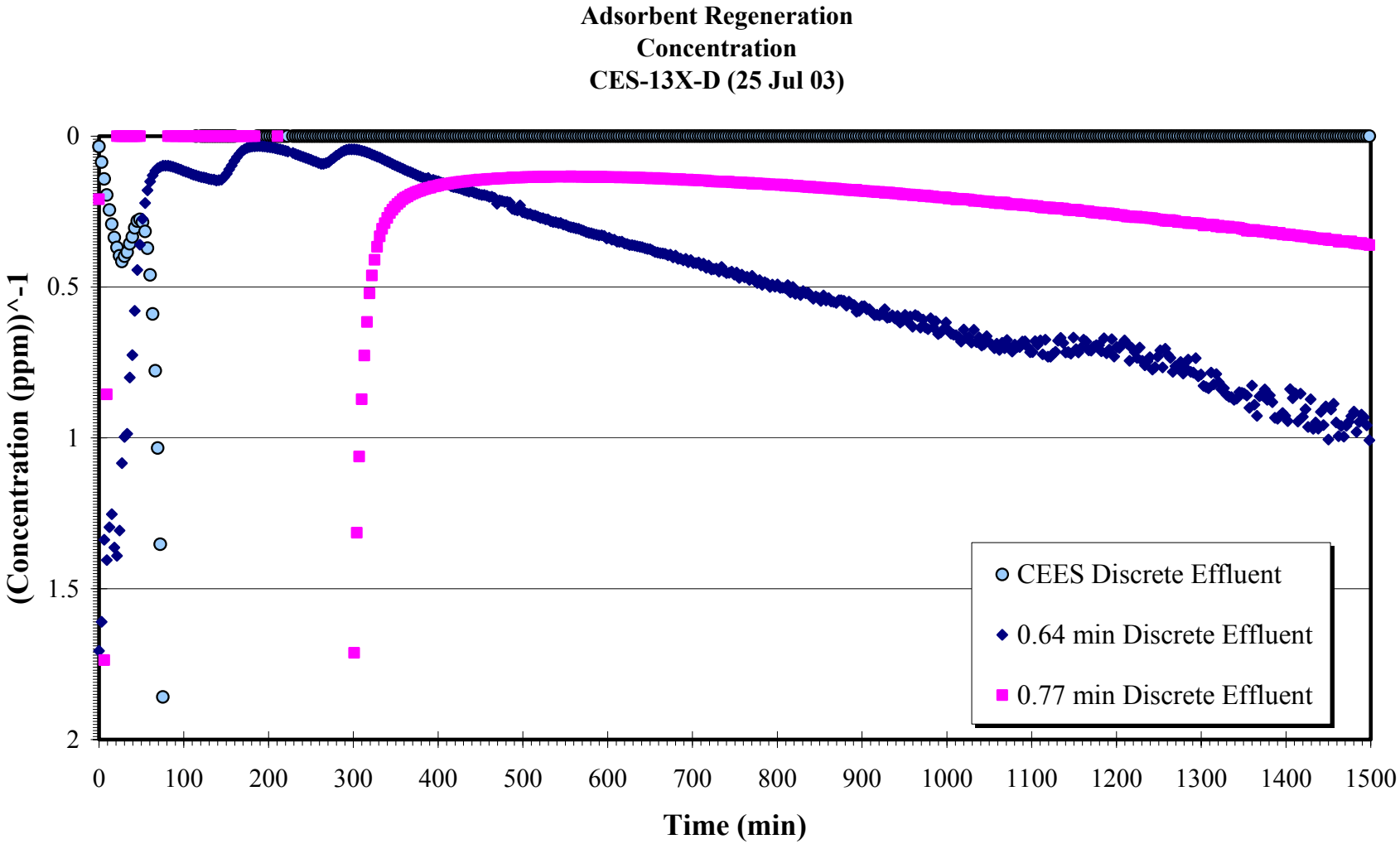
# Experimental

- Analytical equipment.
  - Preparation and purge of adsorbent bed.
    - Continuous feed and effluent signal.
      - Direct FID voltage output.
    - Discrete feed and effluent signal.
      - GC fid, 110 c.
      - HP-1701 column (14%-cyanopropyl-phenyl)-methylpolysiloxane).
  - Sampling of bagged purge effluent.
    - Transfer at 25 C at 500 ml/min on Tenax.
    - Desorb contents to GC/MS with FID detector.

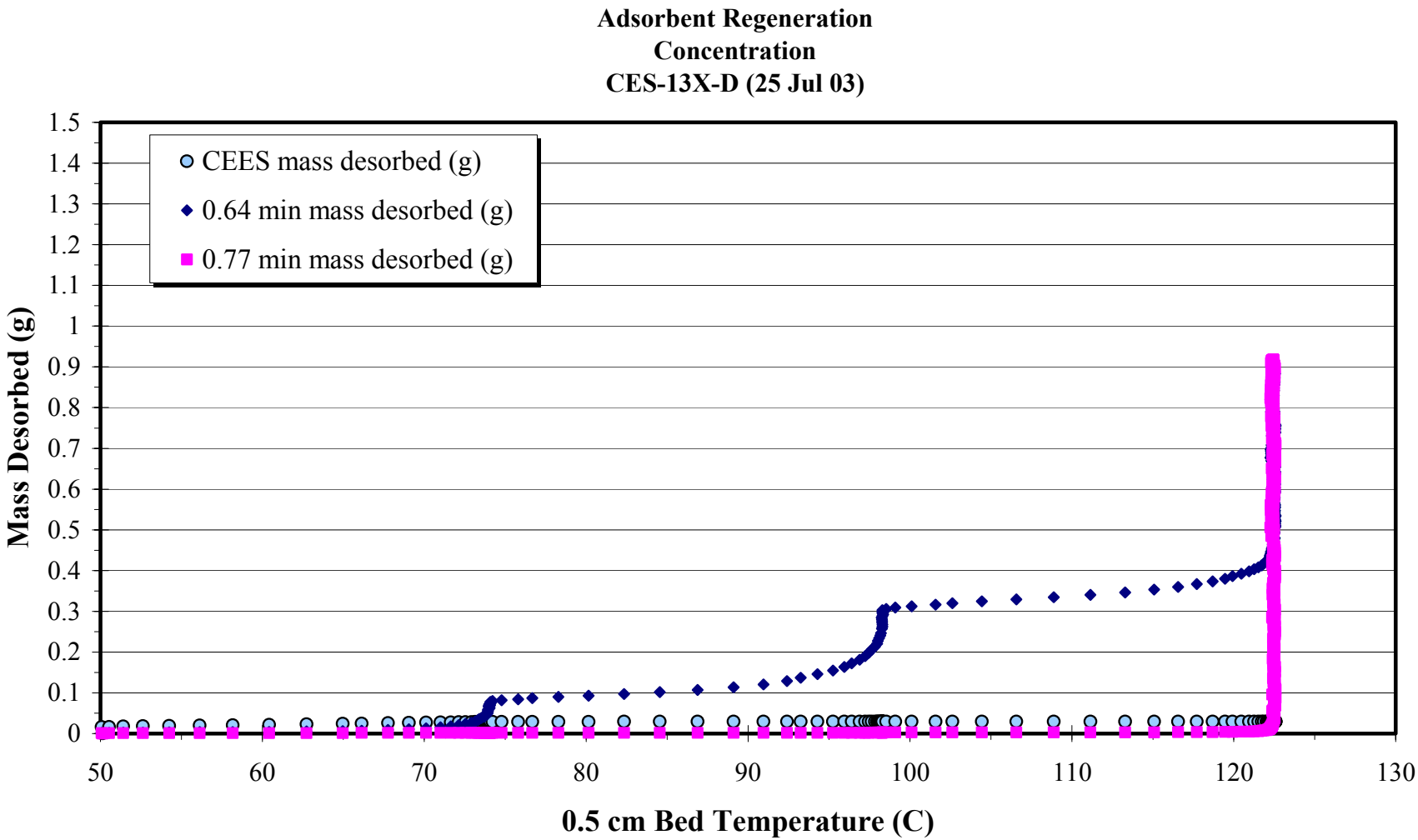
# Results


Adsorbent Regeneration
Concentration
CES-13X-D (25 Jul 03)
Concentration (ppm)
100
10
1
0.1
0.01
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
Time (min)
CEES Discrete Effluent
Continuous Effluent
0.64 min Discrete Effluent
0.77 min Discrete Effluent

# Results


Adsorbent Regeneration
Concentration
CES-13X-D (25 Jul 03)
(Concentration (ppm))^-1
0
0.5
1
1.5
2
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
Time (min)
CEES Discrete Effluent
0.64 min Discrete Effluent
0.77 min Discrete Effluent

# Results


Adsorbent Regeneration
Concentration
CES-13X-D (25 Jul 03)
CEES mass desorbed (g)
0.64 min mass desorbed (g)
0.77 min mass desorbed (g)
Mass Desorbed (g)
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
60
70
80
90
100
110
120
130
0.5 cm Bed Temperature (C)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