DNAPLs: Above-Ground Remediation

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Microwave Technology for
Superfund Site Remediation
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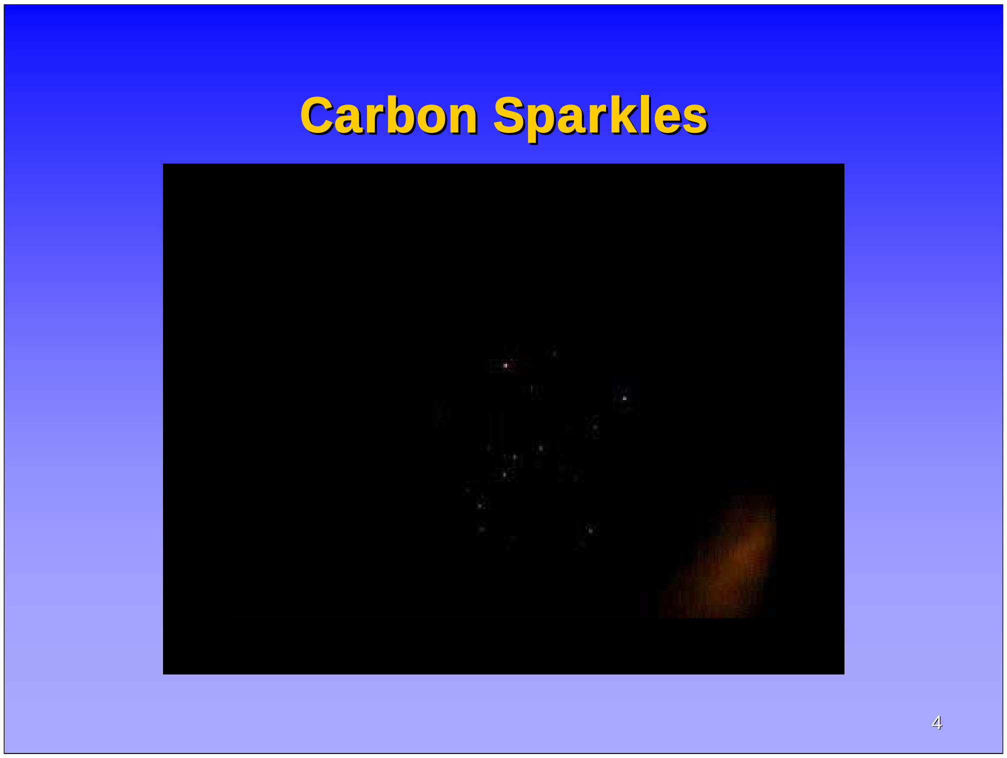
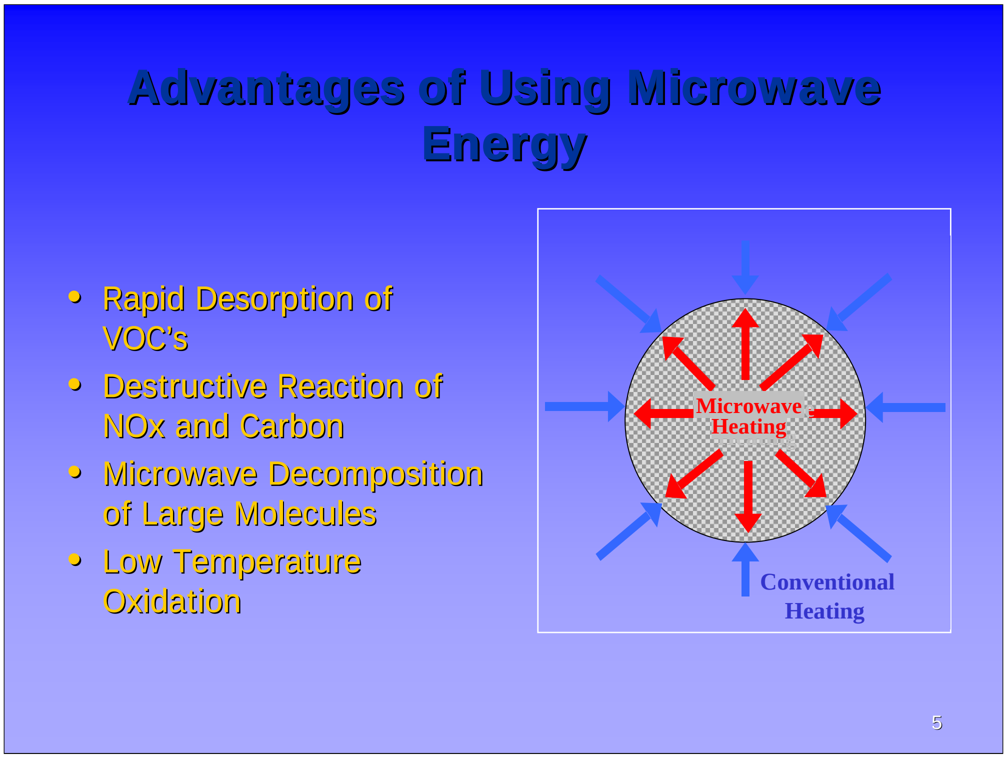
Reaction of Activated Carbon to Microwave Energy


Carbon Sparkles
4



1) Activated Carbon – VOC desorption
2) NOx & SOx– Chemical Reaction with Carbon
3) Decompose (because of heat) heavy molecules, when contacted with carbon and microwaves. – Waste rocket fuels
4) Carbon mixed with catalyst – causes low temp oxidation, chemical and biological warfare agents (or medical waste).

Microwave Induced Solvent Desorption

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Small Batch Regenerator

- 1,100 watt microwave oven

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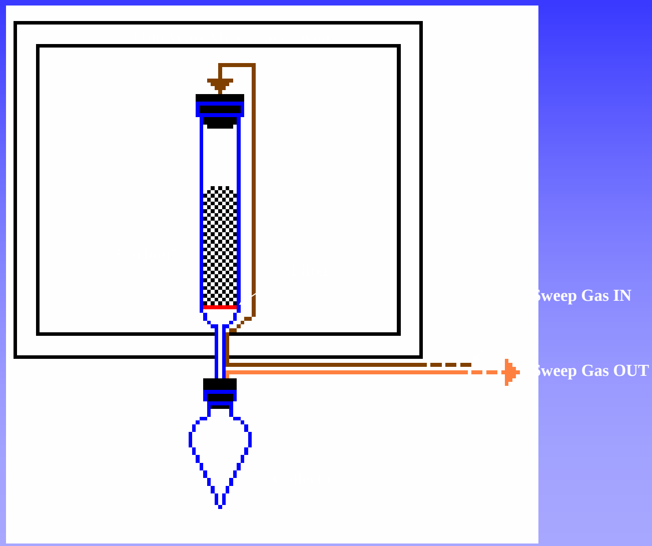
Small Batch Regenerator



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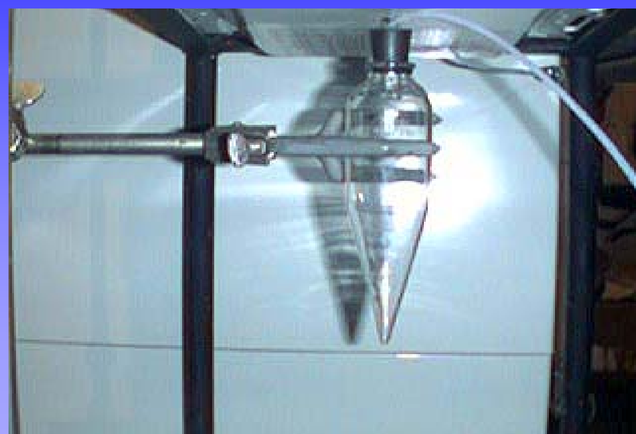
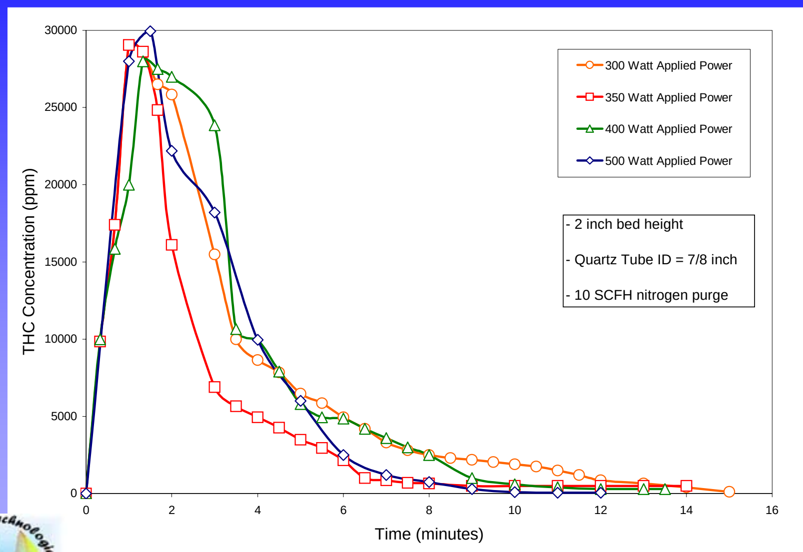
Regeneration of GAC

(Saturated with Gasoline)



Microwave-Induced Desorption



CHA Corporation

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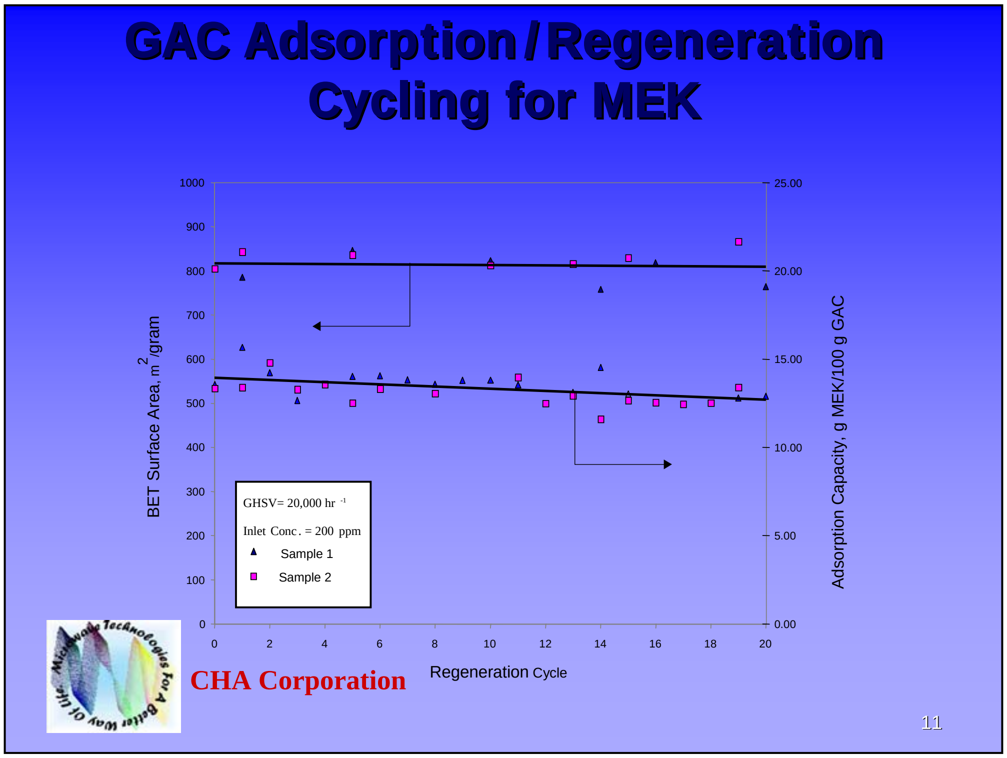

How many times can you regenerate carbon, without losing adsorption capability.

After about 7 cycles with steam, adsorption capacity decreased enough to replace carbon. Not the case with microwaves, still good after 20 cycles.

Advantages of Microwave Unit

- Does not require a long startup period
- Does not produce any air emission or wastewater
- Requires much smaller space than conventional technologies
- Can be easily installed on a trailer or skid
- Recovers PERC and other solvents and fuels for recycle
- Eliminate greenhouse gas production
- Cost-effective means to replace currently operating catalytic oxidizers

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Potential Applications

- Recover gasoline and other fuel vapors generated during the loading of fuel tankers at bulk fuel terminals
- Recover and recycle fuel, solvents, and other chemicals from soil vapors produced during remediation operations of contaminated sites including old gas stations
- Recover and recycle PERC and other solvents used in dry cleaning and part washing as well as painting operations

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Field Demonstration of Microwave Technology at Former McClellan Air Force Base in Sacramento California (NIEHS SBIR Phase I Program)

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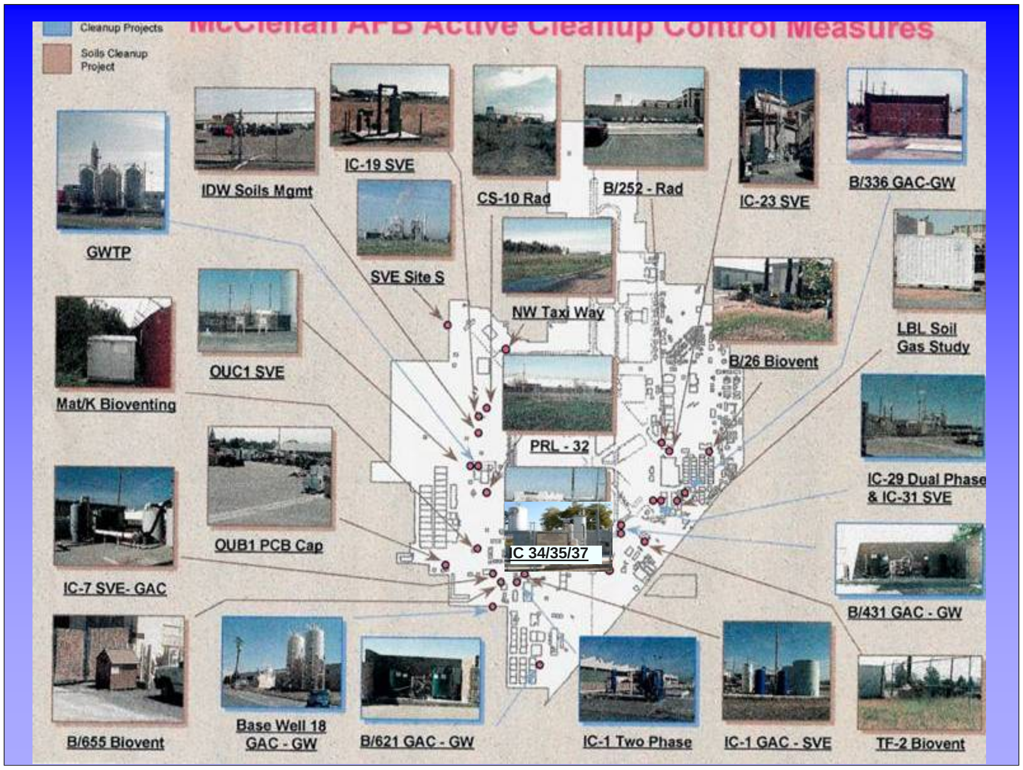
McClellan AFB Active Cleanup Control Measures
Cleanup Projects
Soils Cleanup Project
GWTP
IDW Soils Mgmt
IC-19 SVE
CS-10 Rad
B/252 - Rad
IC-23 SVE
B/336 GAC-GW
SVE Site S
NW Taxi Way
LBL Soil Gas Study
B/26 Biovent
OUC1 SVE
Mat/K Bioventing
PRL - 32
IC-29 Dual Phase & IC-31 SVE
OUB1 PCB Cap
IC 34/35/37
IC-7 SVE- GAC
B/431 GAC - GW
B/655 Biovent
Base Well 18 GAC - GW
B/621 GAC - GW
IC-1 Two Phase
IC-1 GAC - SVE
TF-2 Biovent


Specific Aims
• Operate the prototype microwave unit at McClellan IC 34/35/37 FTO site for two months to regenerate carbon on-site and recover solvents, fuels and other chemicals contained in the soil vapors
• Demonstrate that microwave technology can be a cost-effective solution for the treatment of soil vapors
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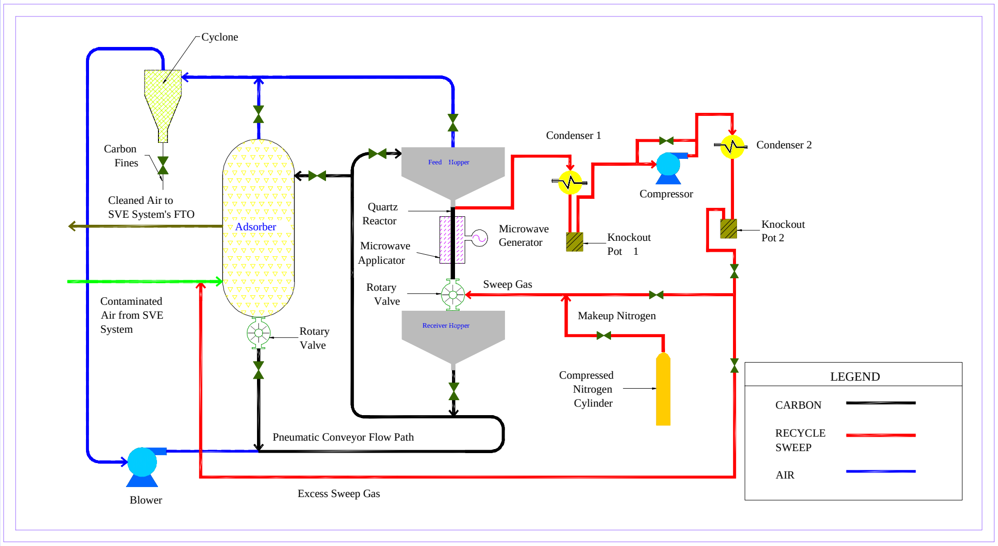
Prototype Microwave Reactor System



Front View of IC 34/35/37 FTO Facility

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Overall View of Microwave Reactor System Setup

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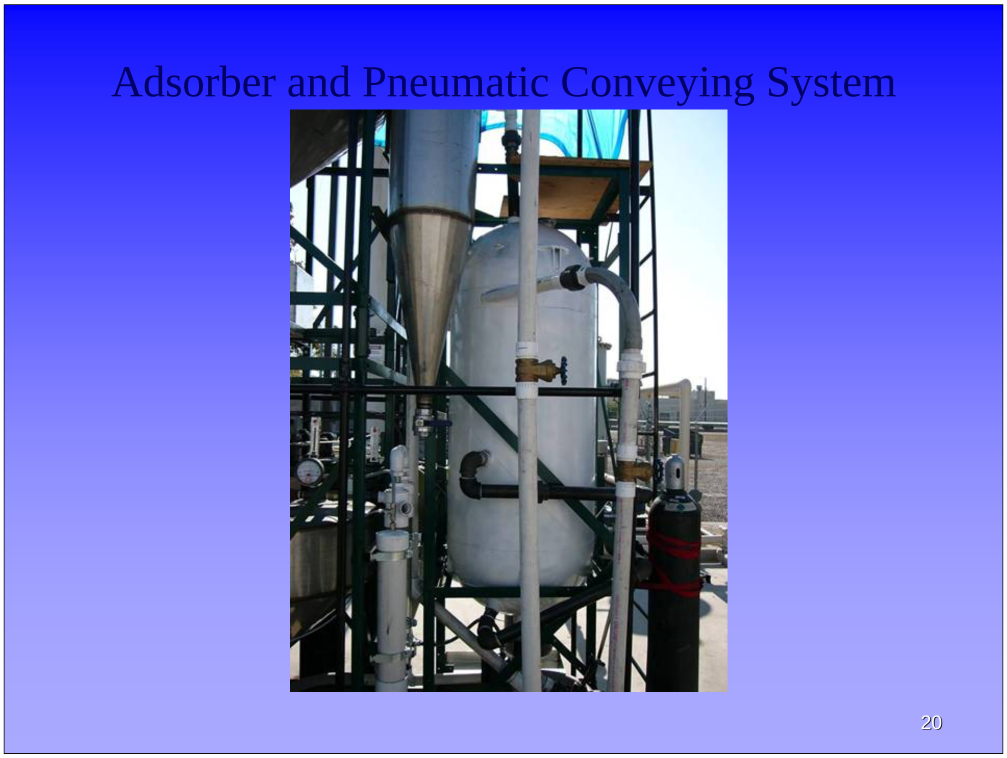
Adsorber and Pneumatic Conveying System
20

Multimode-Cavity, Tuning Device and Top Hopper

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Bottom Hopper and Multimode-Cavity

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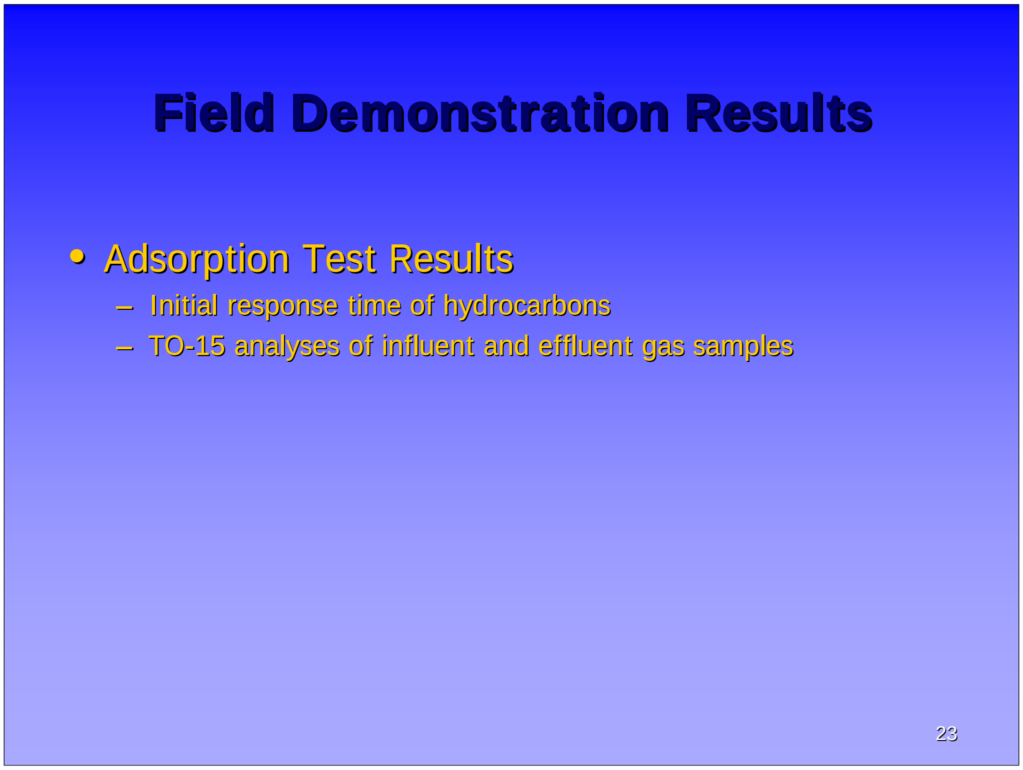
Field Demonstration Results
• Adsorption Test Results
– Initial response time of hydrocarbons
– TO-15 analyses of influent and effluent gas samples
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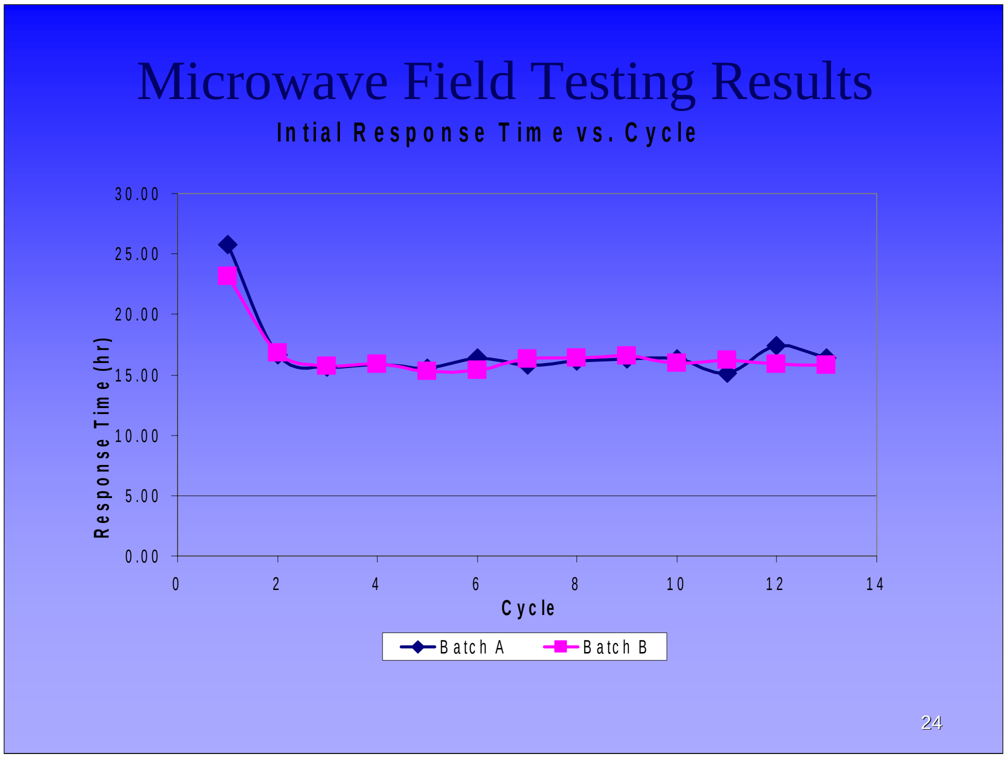
Microwave Field Testing Results
Intial Response Time vs. Cycle
Response Time (hr)
30.00
25.00
20.00
15.00
10.00
5.00
0.00
0
2
4
6
8
10
12
14
Cycle
Batch A
Batch B
24

Field Demonstration Results

- Microwave Regeneration Tests
  - Hydrocarbon liquid recovered from each regeneration
  - Repeated regeneration
  - Regeneration without sweep gas recycle

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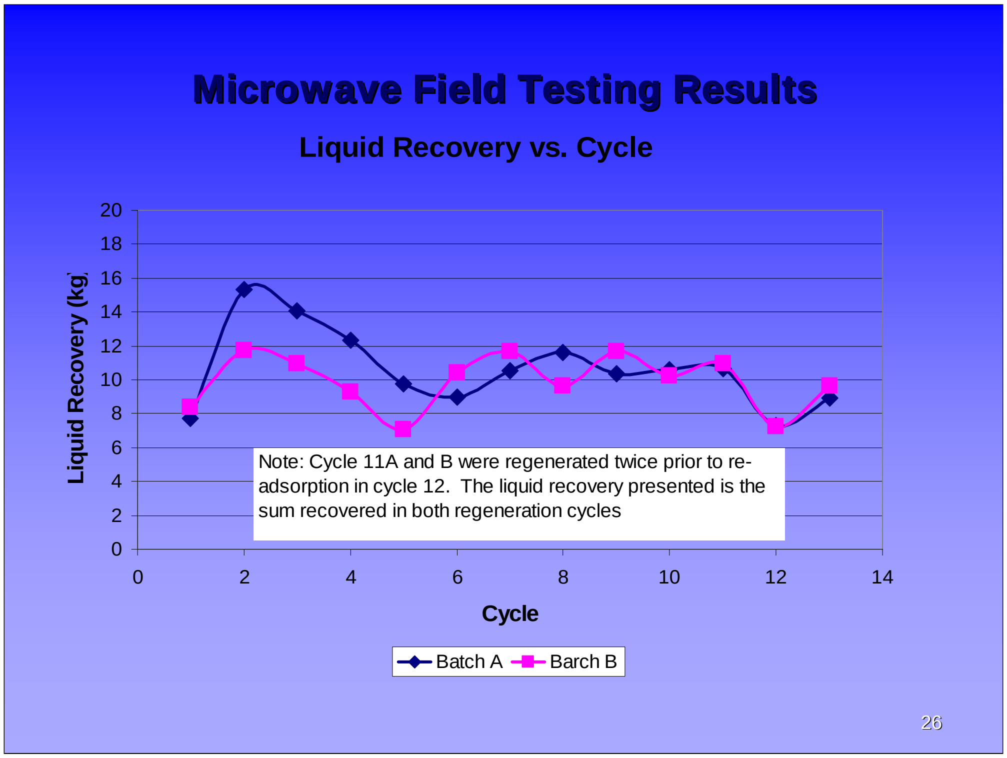
Microwave Field Testing Results
Liquid Recovery vs. Cycle
Liquid Recovery (kg)
Cycle
Note: Cycle 11A and B were regenerated twice prior to re-adsorption in cycle 12. The liquid recovery presented is the sum recovered in both regeneration cycles
Batch A
Barch B
26

Liquid Recovered During Microwave Regeneration

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Recovered Liquid

- Trichloroethane = 3.2 mole%
- Hydrocarbons
  - C5 – C8 = 21.3 mole%
  - C8 – C10+ = 75.5 mole%
- Specific Gravity = 0.787
- JP fuel Specific Gravity = 0.75 – 0.80

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GAC Balance

GAC Added	Batch A	Batch B
9/24/2003	200 lb	
9/27/2003		200 lb
10/16/2003		24.92 lb
11/20/2003	15.25 lb	
Total	**215.25 lb**	**224.92**
GAC Removed	**Batch A**	**Batch B**
Fines	7.83	6.72
End of Testing	208.47	216.24
Total	**216.22**	**222.96**
Difference	**0.45%**	**-0.87%**

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Tests After Field Testing

- Measure Adsorption Capacity of GAC after 13th Adsorption/Regeneration Cycle
- Determine the Effect of Sweep Gas Velocity on the GAC Regeneration Efficiency
- Determined Size Distribution of GAC after 13th Adsorption/Regeneration Cycle

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Adsorption Capacity (gHC/100g carbon)

- Batch A after 13th Regeneration = 22.0
- Batch B after 13th Regeneration = 22.0
- Fresh Carbon = 29.0

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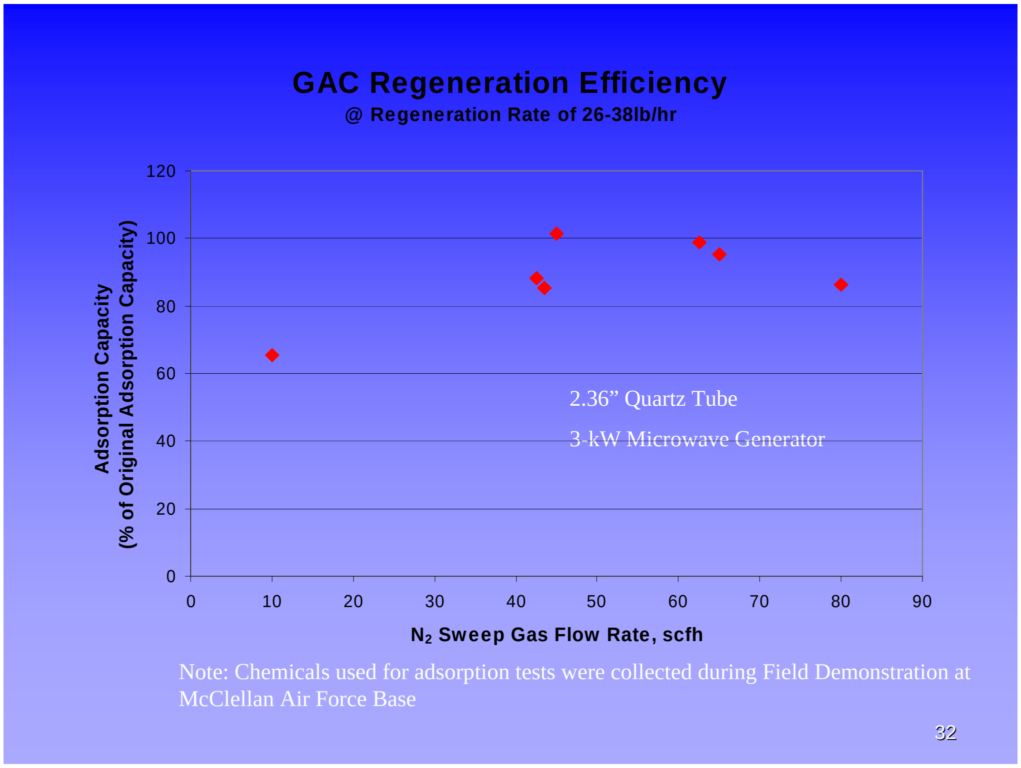
GAC Regeneration Efficiency
@ Regeneration Rate of 26-38lb/hr
Adsorption Capacity
(% of Original Adsorption Capacity)
120
100
80
60
40
20
0
0
10
20
30
40
50
60
70
80
90
N2 Sweep Gas Flow Rate, scfh
2.36" Quartz Tube
3-kW Microwave Generator
Note: Chemicals used for adsorption tests were collected during Field Demonstration at McClellan Air Force Base
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GAC Size Analysis

Sieve Analysis			
	Fresh GAC	Batch A	Batch B
+20 mesh	0.1%	3.9%	3.6%
+10 mesh	99.6%	95.9%	96.3%
+3 mesh	0.4%	0.1%	0.1%

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NIEHS SBIR Phase II Program

- Design and Construct a 50-kg/hr Mobile Microwave Unit
- Field Demonstration of Mobile Microwave Unit
  - Chlorinated Solvent Contaminated Site
  - Fuel Contaminated Site (Fuel depot or gas station)
  - Dry Cleaning Facility
- Characterize and Purify Recovered Solvents and Fuels

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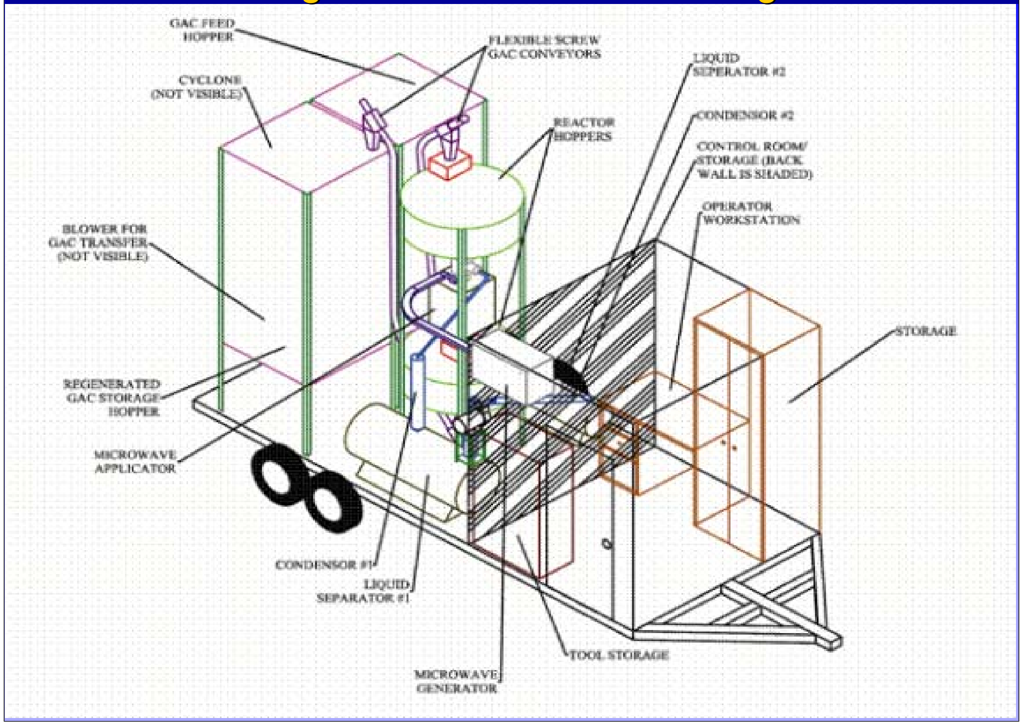
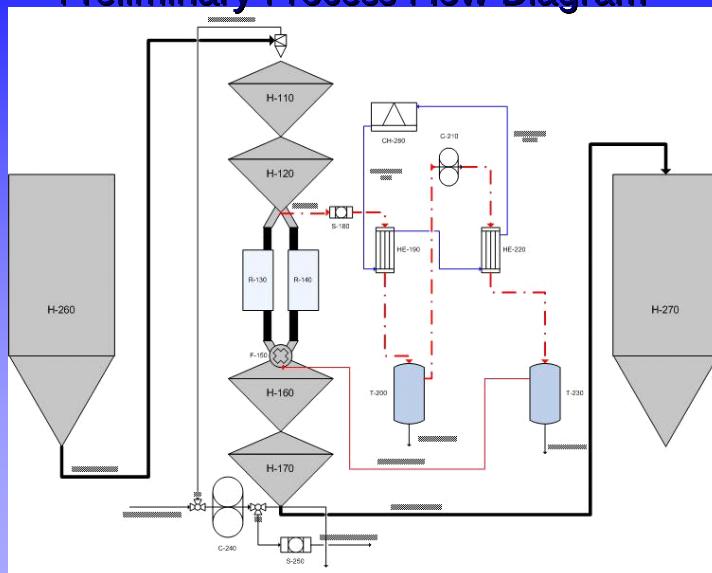
Mobile 50-kg/hr Microwave Carbon Regenerator



Preliminary Process Flow Diagram



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Experimental Work Required to Build a 50-kg/hr Mobile Unit

- Conduct a series of experiments to develop the design for microwave reactor configuration capable of regenerating 50-kg/hr activated carbon
- Design and construct supporting systems on the trailer

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New Slotted Waveguide
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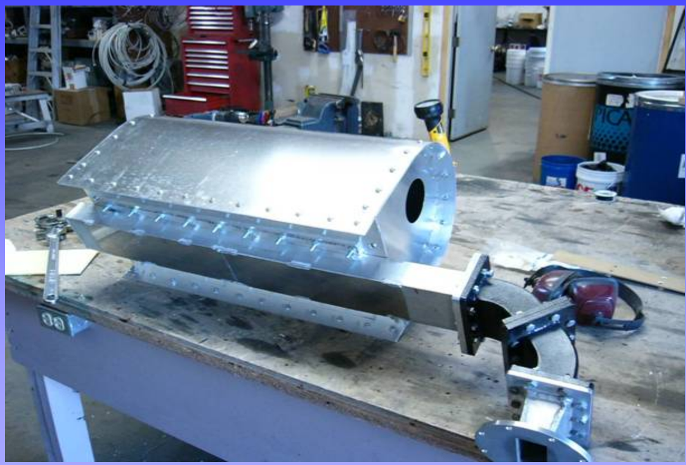
Slotted Waveguide In Mailbox Cavity



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Inside View of New Applicator System

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Advantages of New Applicator System

- Slotted Waveguide Distributes Energy Along the Length of the Tube
- Curved Cavity Wall Reflects Energy Back Toward the Tube

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Scale-up Test System
Completed Test System

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Laboratory Adsorber

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Scale Up Testing Results

Test	Carbon Rate (lb/hr)	Power (kW)	Sweep Gas (SCFH)	% Recovery
1A	35	3	90	98
1B	35	3	60	96
2A	35	3.5	90	99
2B	40	3.5	85	97
3A	40	3.5	70	98
3B	40	4.5	80	98
4A	40	4	80	101
4B	45	4	70	98
5A	45	4.5	85	102
5B	50	4.5	55	109
6A	50	5	80	101
6B	50	5	35	108
7A	50	5	80	102

“Note” %Recovery = (Fresh GAC wt./Reg. GAC wt.)x100

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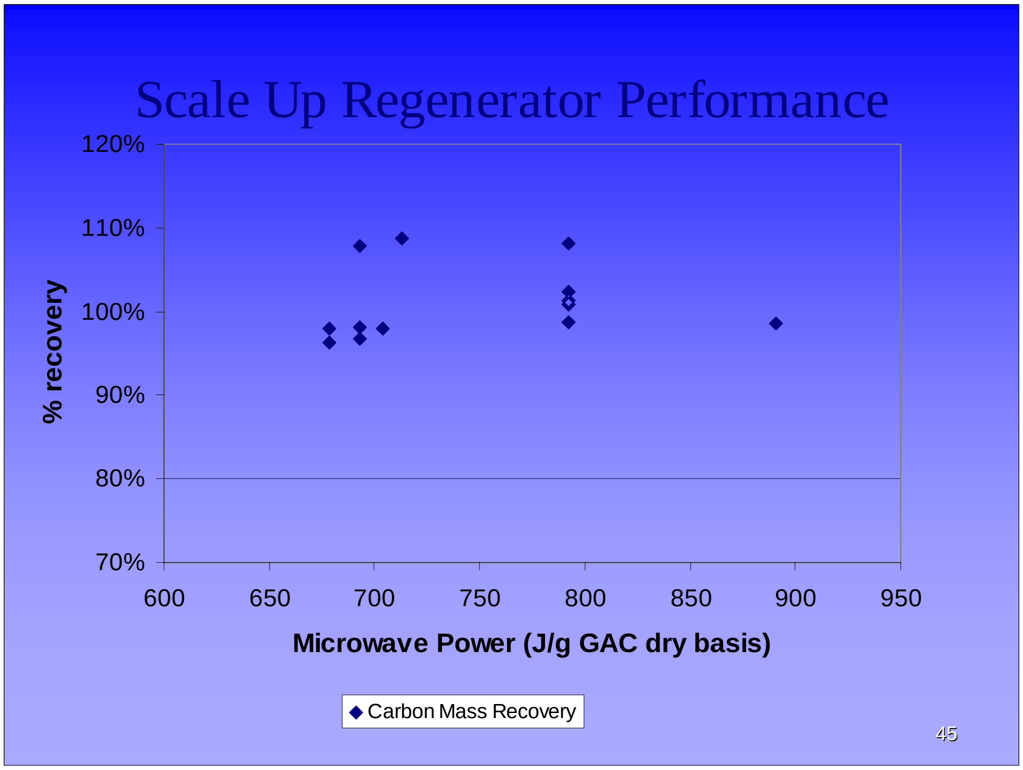
Scale Up Regenerator Performance
120%
110%
100%
90%
80%
70%
% recovery
600
650
700
750
800
850
900
950
Microwave Power (J/g GAC dry basis)
Carbon Mass Recovery
45

Additional Field Testing At McClellan Air Force Base (IC19 and OUD Site, Chlorinated Solvents)

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Annual Cost Savings, dollars

Item	Quantity Savings	Cost savings, $
Natural Gas	188,431 therm	131,902
Electricity	418,522 kwh	37,667
Wastewater	4.756 M gallons	10,608
Utility water	5.67 M gallons	3,061
GAC changeouts		120,000
Labor and supplies		100,740
Total Annual Savings		**403,978**

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Prepare Field Testing at Former McClellan AFB

- Build a Shelter to protect microwave equipment from rain
- Modify previous microwave unit to allow
  - Carbon transportation from/to the portable adsorber
  - Higher recycle gas flow rate
  - Isolate the system from the adsorption unit
  - Install the automatic shutdown system in the microwave generator

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Microwave Unit at McClellan AFB

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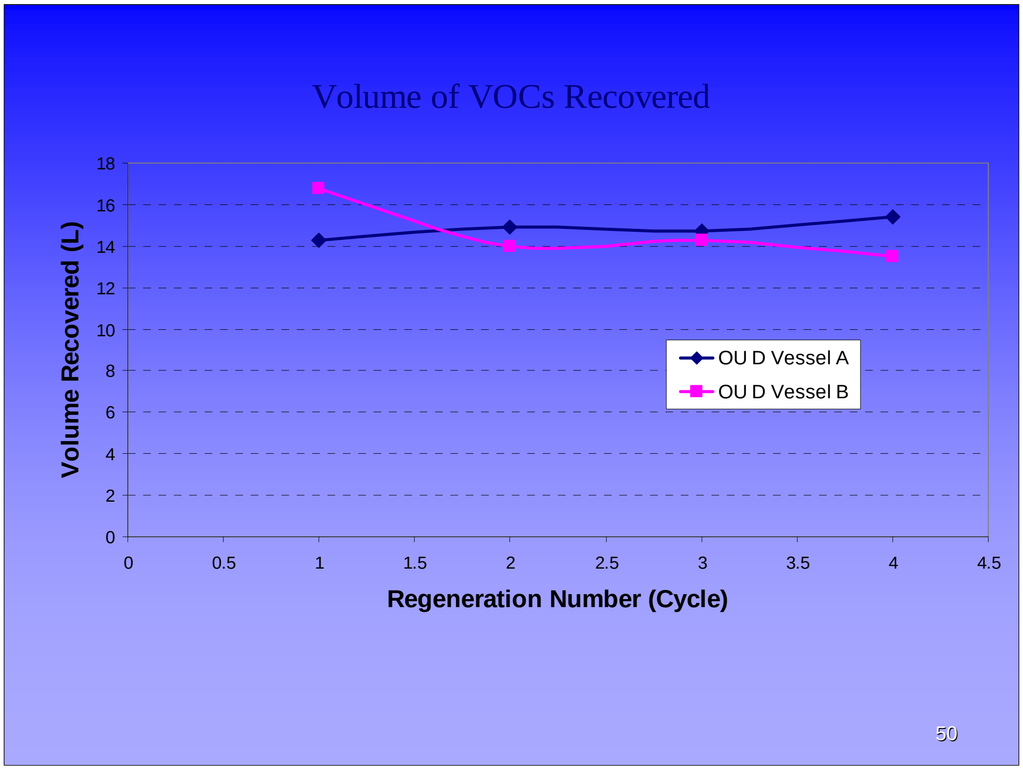
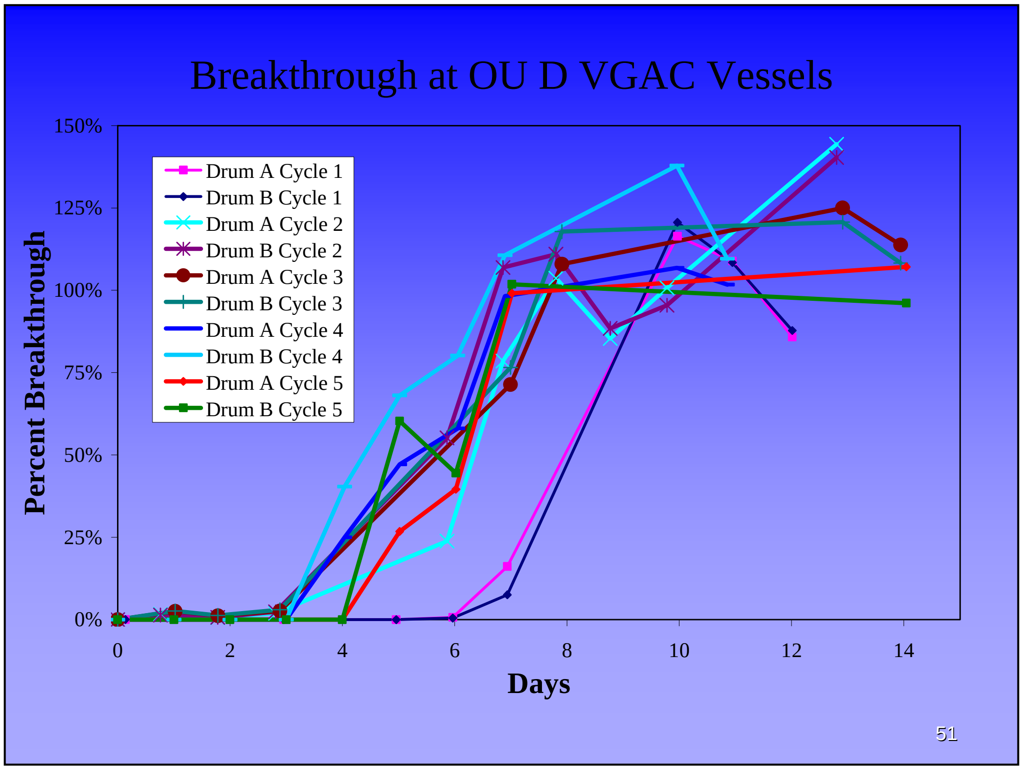

Volume of VOCs Recovered
Volume Recovered (L)
18
16
14
12
10
8
6
4
2
0
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
Regeneration Number (Cycle)
OU D Vessel A
OU D Vessel B
50



Breakthrough at OU D VGAC Vessels
Percent Breakthrough
150%
125%
100%
75%
50%
25%
0%
0
2
4
6
8
10
12
14
Days
Drum A Cycle 1
Drum B Cycle 1
Drum A Cycle 2
Drum B Cycle 2
Drum A Cycle 3
Drum B Cycle 3
Drum A Cycle 4
Drum B Cycle 4
Drum A Cycle 5
Drum B Cycle 5
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Dry Cleaning Facility

- Purpose
  - To remove PERC by the activated carbon from dry cleaner's vented air
  - To demonstrate the feasibility of recovering PERC from saturated carbon by microwaves
- Test Location
  - Deluxe Cleaners and Tailors
    1614 House Ave.
    Cheyenne, WY

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Carbon Regeneration

Fresh GAC, kg	37.2	37.7
GAC after saturation, kg	49.5	44.1
GAC after regeneration, kg	38.4	37.0
Liquid recovered, kg	5.65	4.96

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Recovered PERC After Water Extraction (PERC is Bottom Layer)

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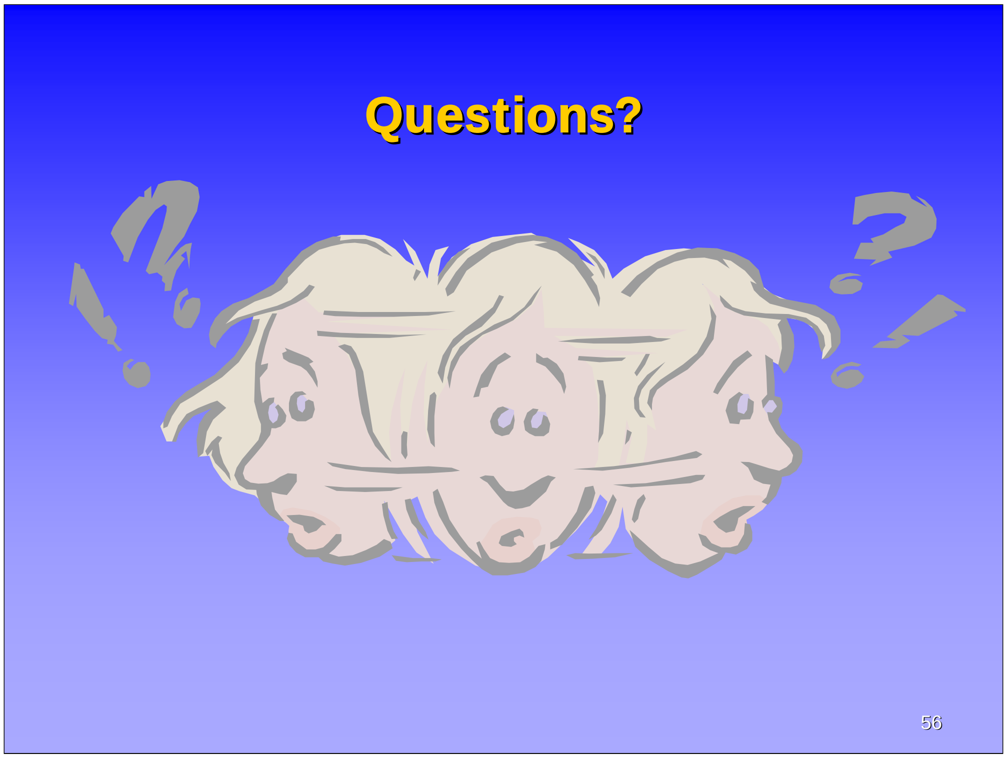
Questions?
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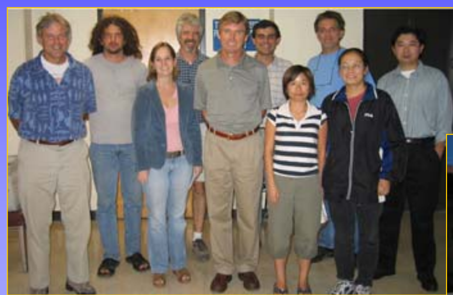
Innovative Technologies for Destruction of Chlorinated Solvents

Departments of Chemical & Environmental Engineering
Atmospheric Sciences
The University of Arizona, Tucson, AZ

- Dr. Robert Arnold
- Dr. Eric Betterton
- Dr. Wendell Ela
- Dr. Eduardo Saez

- Brian Barbaris
- Kate Candillo
- Xiumin Ju
- Cary Leung
- Ozer Orbay
- Lei Wang
- Rohit Tripathi



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Systems Summary

Zero-valent metals	Complete, e.g., *Env. Sci. Technol.*, *34*, 804-811 (2000)
Electrolytic reduction (conventional cell)	Complete, e.g., *Ind. Eng. Chem. Res.,* 43 (25), 7965 -7974 (2004); *Ind. Eng. Chem. Res.* 43, 913-923 (2004)
Electrolytic oxidation (conventional cell)	Complete, e.g., *J. Appl. Electrochem.*, 961–970, 29 (1999)
Continuous-flow electrolytic reactor (1-dimensional)	Complete, manuscript prepared
Continuous-flow electrolytic reactor (2-dimensional)	In progress - manuscript in preparation
Modified fuel cell reactor	In progress, e.g., *Env. Sci. Technol.,* 35, 4320-4326 (2001)
Photo-initiated dehalogenation in 2-solvent system	Complete, e.g., *Env. Sci. Technol.*, *34*, 1229-1233 (2000); *Water Res.* 38, 2791-2 (2004); *Environ. Sci. Technol.*, 39, 2262-2266 (2005)
Membrane air stripping reactor	Complete, e.g., *J. Env. Eng.* 130, 1232-1241 (2004)
Redox catalysis	In progress

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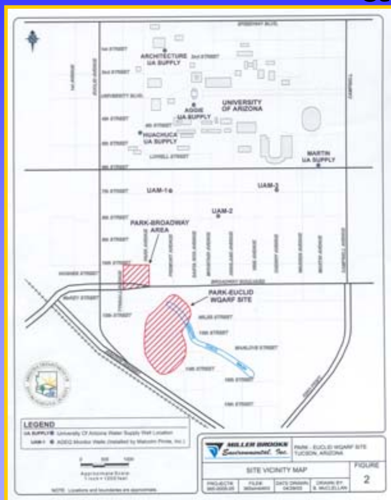
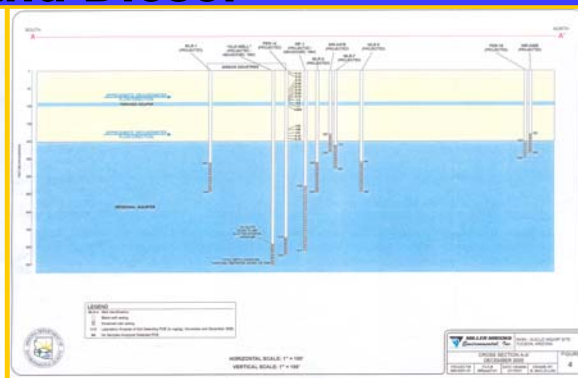
Park-Euclid WQRF Site: PCE, TCE and Diesel





Typical Soil Vapor Analysis

PCE ≈ 300 ppmv

TCE ≈ 30 ppmv

cis-1,2-DCE ≈ 3 ppmv

O_2 ≈ 18% v/v

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Redox Catalytic Destruction:
Oxidative and Reductive Dehalogenation

- $PCE + 5H_2 \xrightarrow{\text{catalyst}} C_2H_6 + 4HCl$
- $2PCE + 3C_3H_8 \xrightarrow{\text{catalyst}} 2C_2H_6 + 2HCl + 9C$
- $C_2H_6 + 3/2O_2 \xrightarrow{\text{catalyst}} 2CO_2 + 3H_2O$
- $2H_2 + O_2 \xrightarrow{\text{catalyst}} 2H_2O$
- $2HCl + ½\, O_2 \xrightarrow{\text{catalyst}} H_2O + Cl_2$

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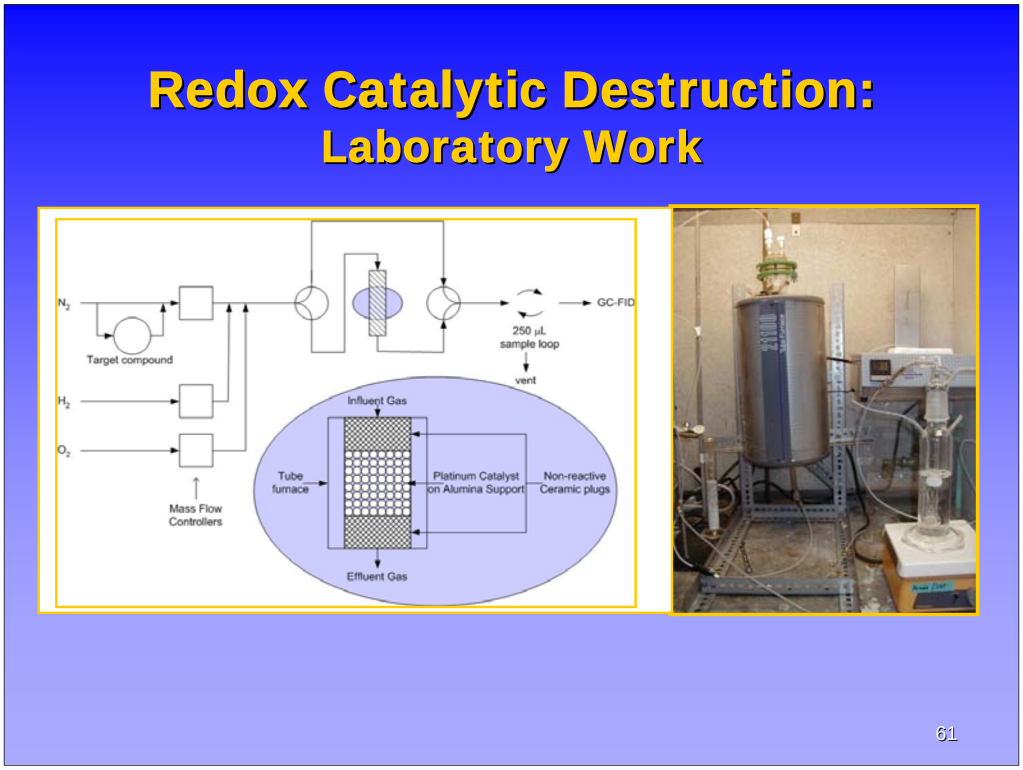
Redox Catalytic Destruction:
Laboratory Work
N2
Target compound
H2
O2
Mass Flow Controllers
250 µL sample loop
GC-FID
vent
Influent Gas
Tube furnace
Platinum Catalyst on Alumina Support
Non-reactive Ceramic plugs
Effluent Gas
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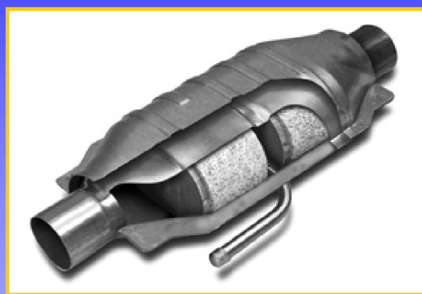
Catalytic Converter



- 2 alumina honeycomb monolith support s (2" long x 4.7" major axis 3.15" minor axis).
- Pt/Rh or Pd/Rh with cerium/zirconium oxygen storage additives.
- Surface area = 4400 m^2
- Normal automotive flow rate: 20 cfm to 300 cfm.
- Minimum temperature for 50% activity = 415 ^0C

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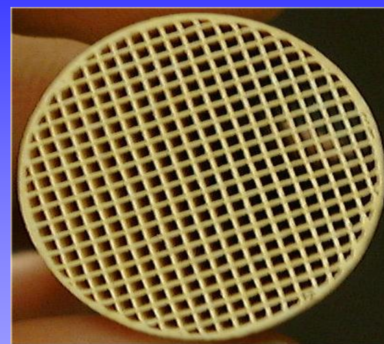
Ceramic Honeycomb Support



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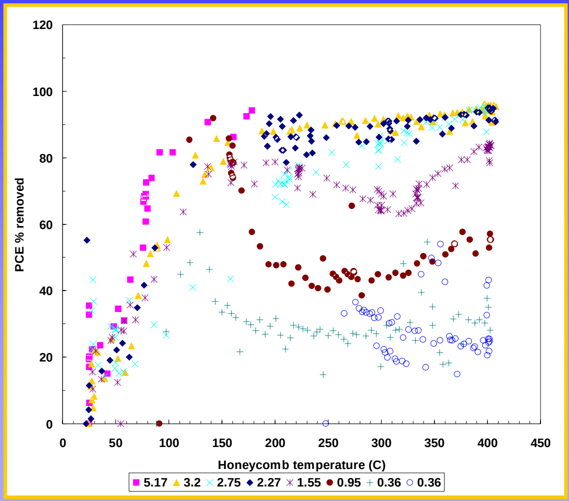
PCE Removal: Laboratory T and H_2/O_2 Ratio

(500 mL/min, 1.2 s retention)



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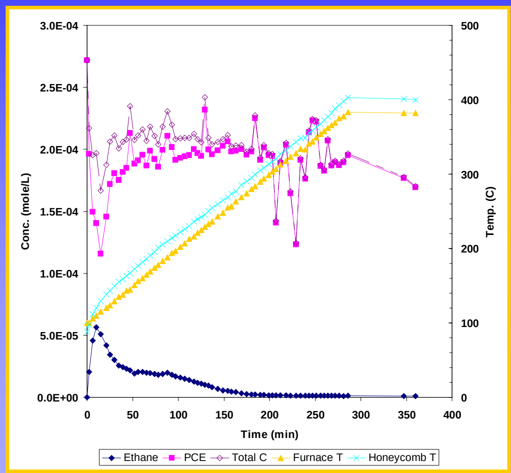
PCE Removal: Laboratory T vs. Ethane

(8.64 mL/min H_2, 25 mL/min O_2, 500 T mL/min, 1.2 s retention)



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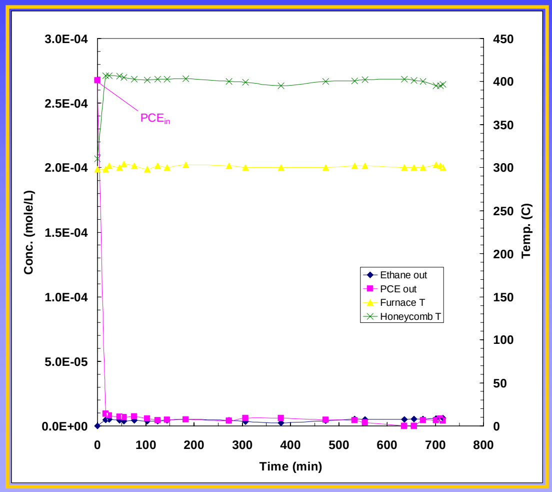
Redox Catalyst: PCE Destruction

(300 C; 500 mL/min total flow, 50 mL/min H_2, 25 mL/min O2, 1.2 s retention time



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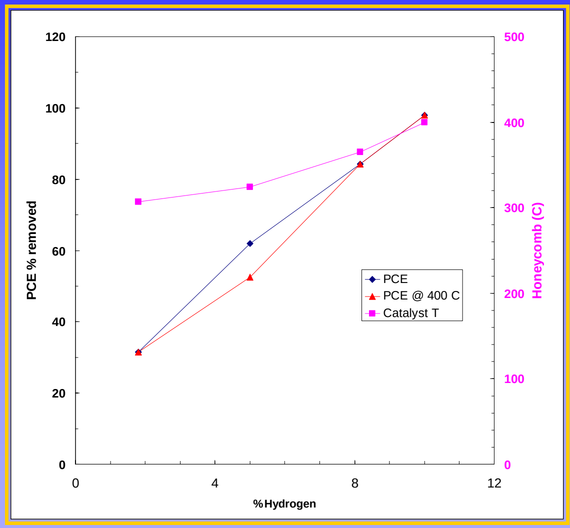
Redox Catalyst: PCE Reduction H-Effects



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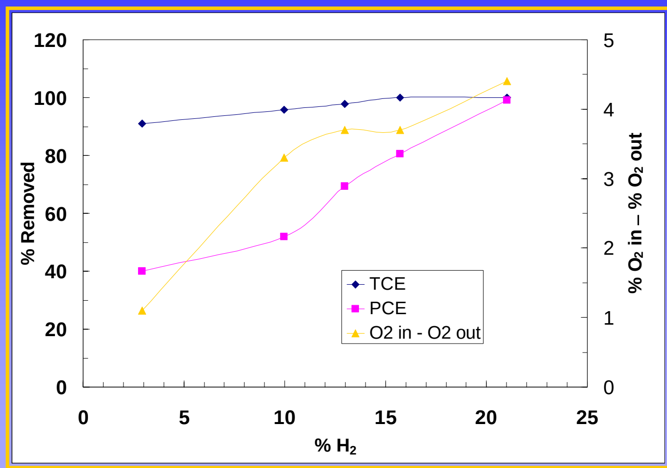
PCE Removal: Park-Euclid

(H_2 and O_2)



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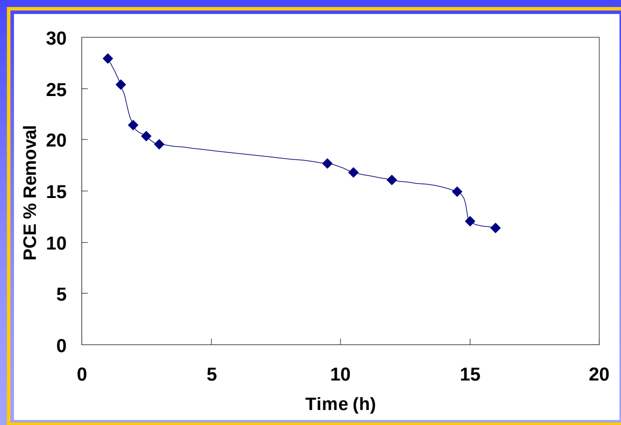
Catalyst Poisoning: Oxidative

450 ^{0}C, O_2 =21%, Pd/Rh Catalyst



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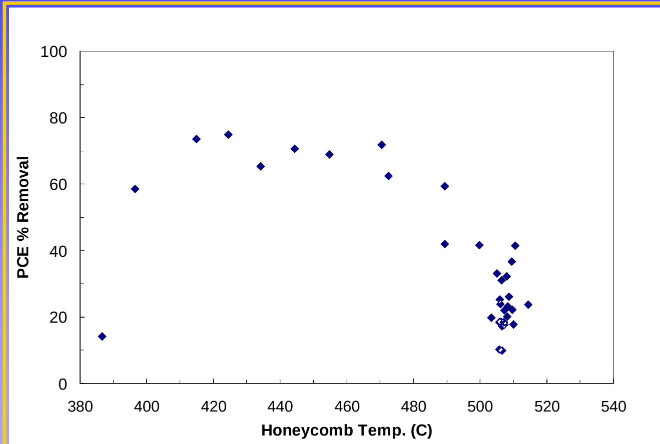
Catalyst Poisoning: Reductive

(propane, O_2= 0 %; residence time:1.08 s, run time:410 min



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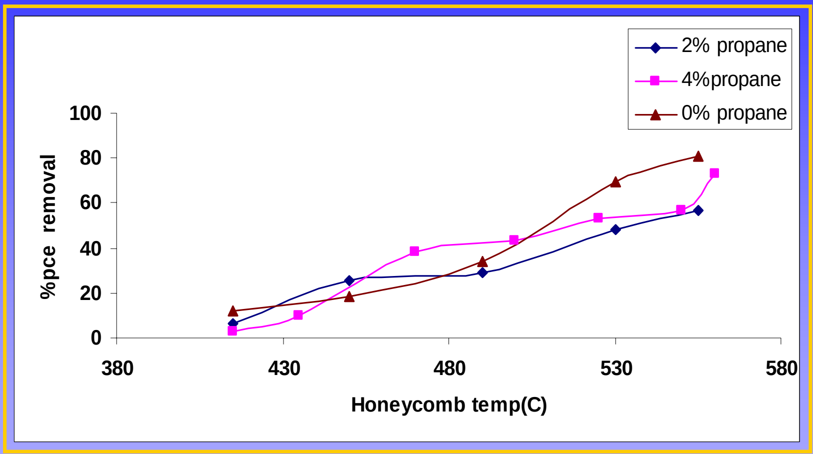
Redox Catalyst: PCE with propane

($21\% \ O_2$)



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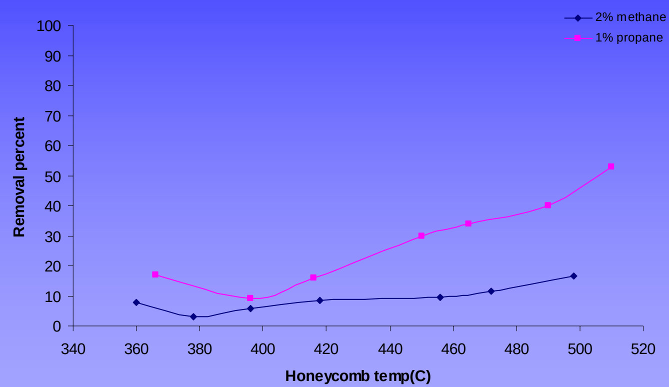
Redox Catalyst: Methane vs. Propane and T

(21% O_2)



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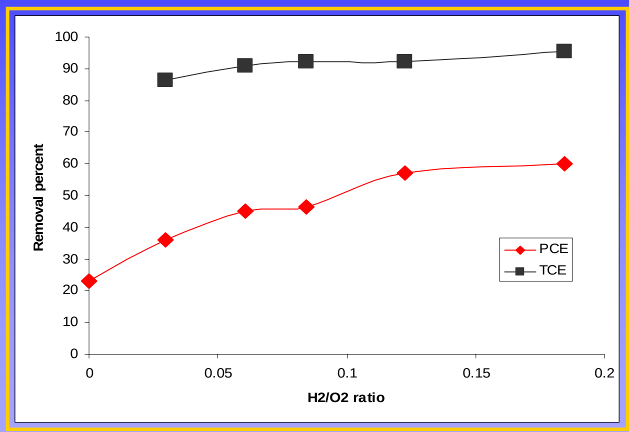
Redox Catalyst: PCE and TCE with H_2/O_2 ratio

($410\ ^0C$)



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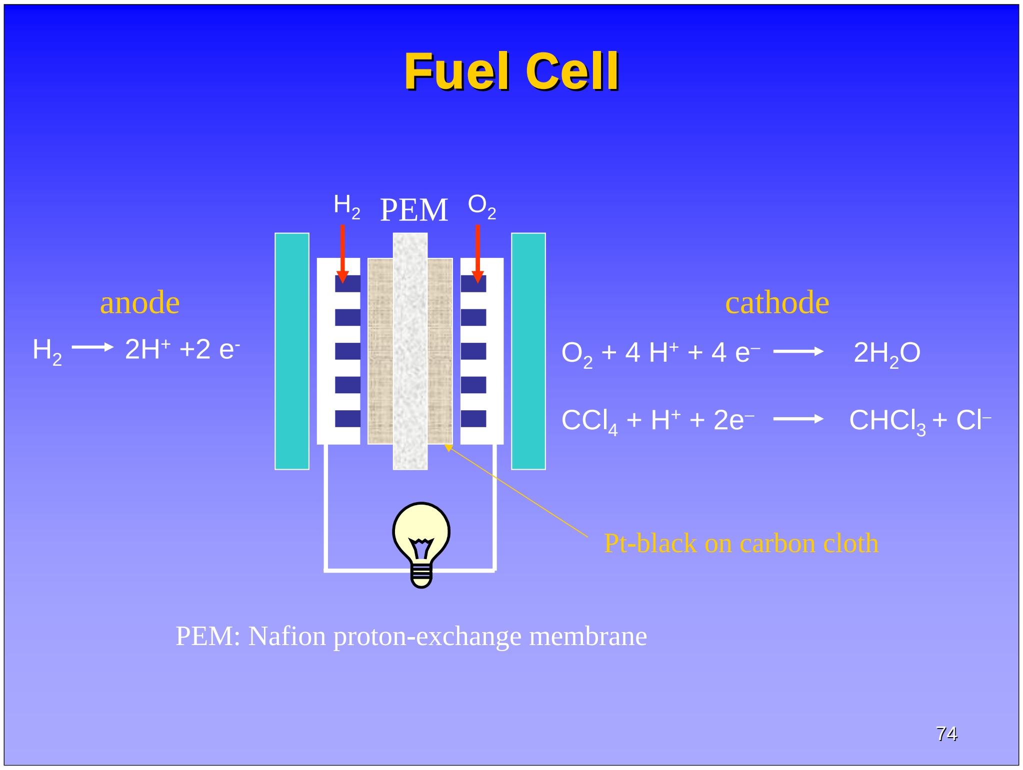
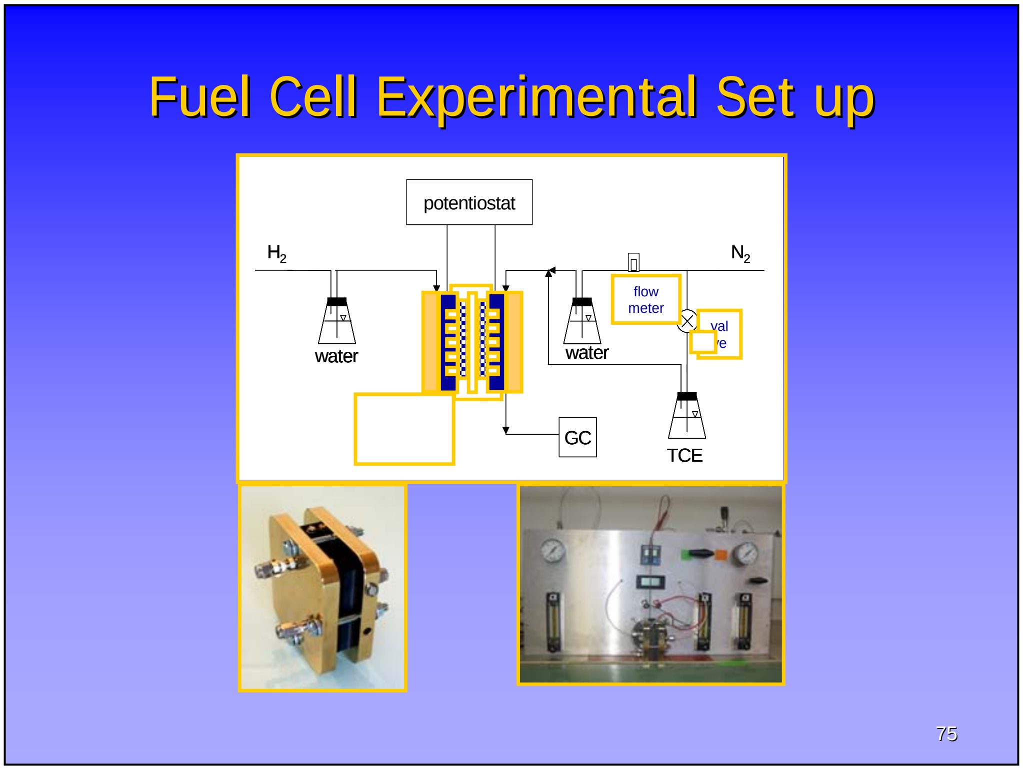
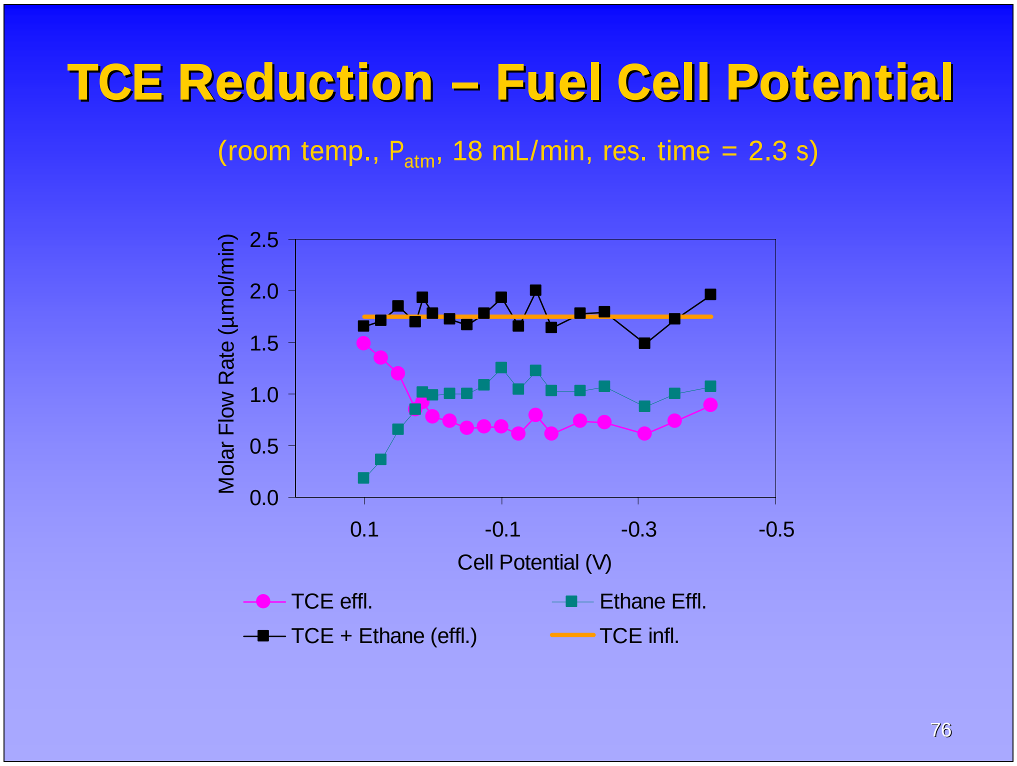
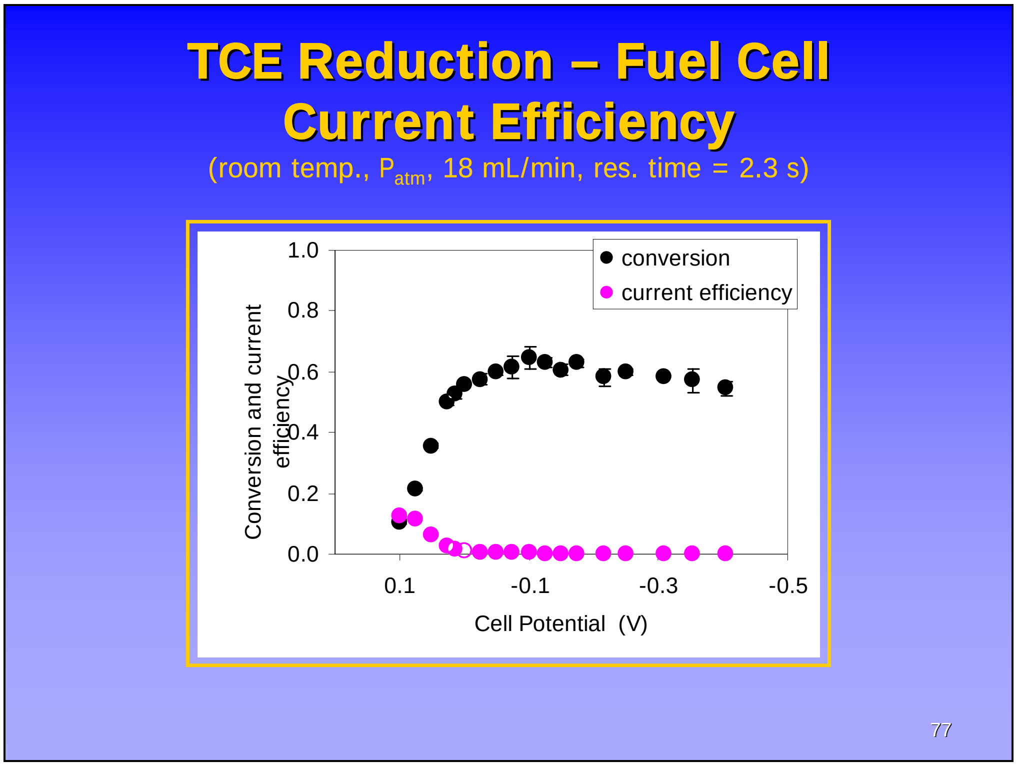

Fuel Cell
H$_2$
PEM
O$_2$
anode
$H_2 \longrightarrow 2H^+ + 2e^-$
cathode
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$
$CCl_4 + H^+ + 2e^- \longrightarrow CHCl_3 + Cl^-$
Pt-black on carbon cloth
PEM: Nafion proton-exchange membrane
74


Fuel Cell Experimental Set up
potentiostat
H2
N2
water
flow
meter
water
GC
TCE
75

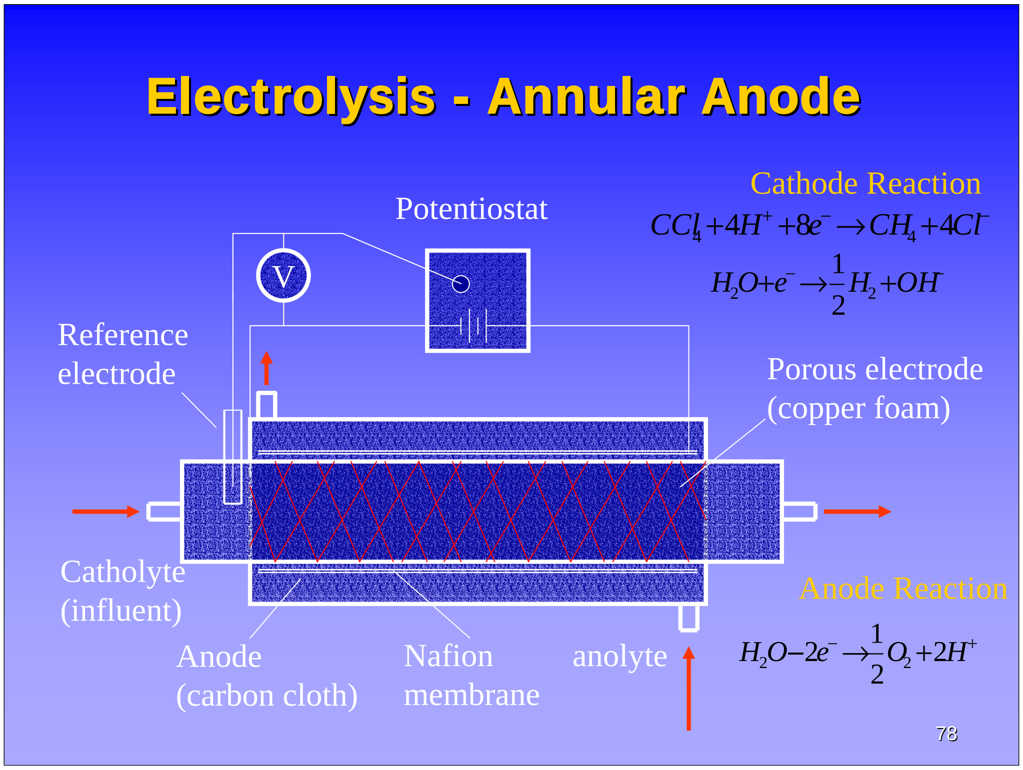


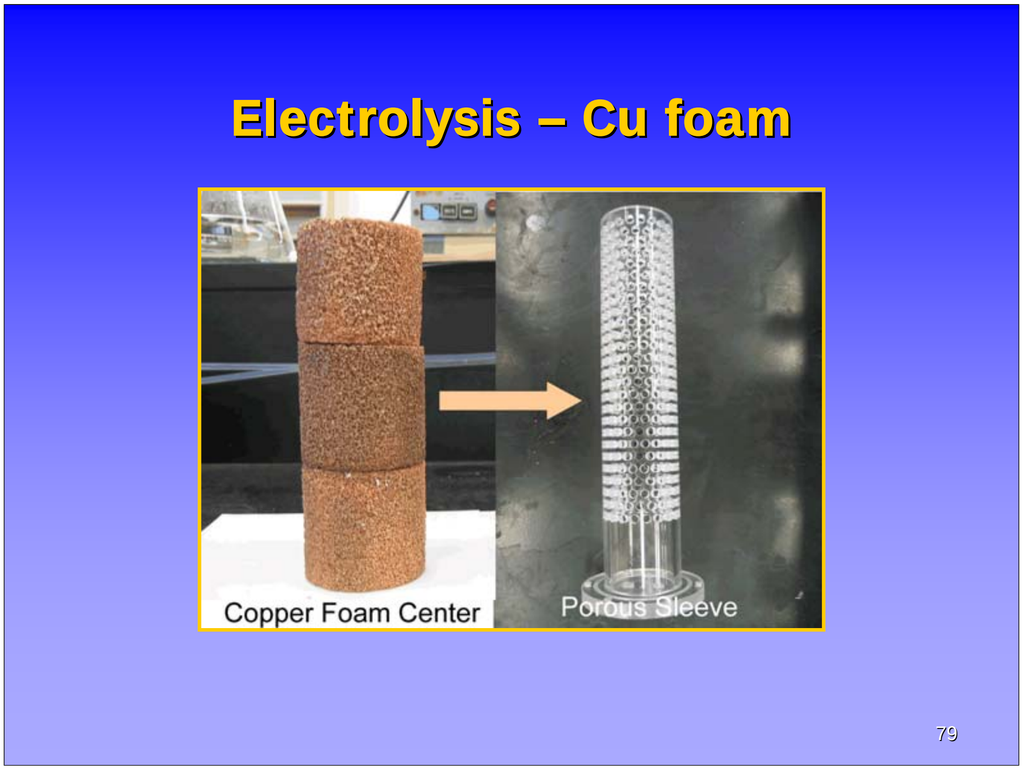
This slide showed an experiment conducted under room temperature, atmospheric pressure, inlet flow rate 18 ml/min, TCE concentration of 2500ppmv. The left graph showed TCE and reaction product concentration in the effluent. TCE concentration was reduced monotonically with respect to cell potential. Ethane as the product of TCE degradation increased to a maxima, and then decreased with respect to cell potential. This was caused by increase of flow rate due to hydrogen evolution in the cathode. No Chlorinated intermediates were detected.

The right graph showed the molar flow rate of TCE and ethane and the sum of two in the effluent. The solid red line represented the inlet TCE molar flow rate. We can see that a good mass balance was obtained here, and thus proved that ethane was the major product of TCE degradation. The variation of effluent data around inlet data probably due to experimental error.



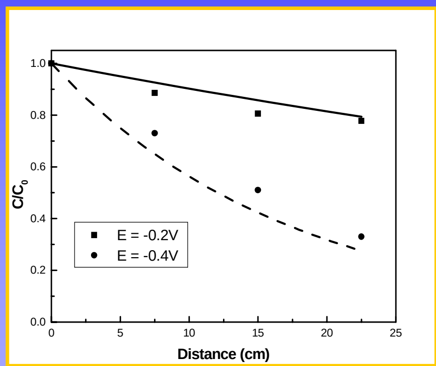
Here in this graph the current efficiency was plotted with respect to cell potential, and TCE conversion was also plotted. Current efficiency here is defined as the ratio of the current used for TCE reduction to total current. As you can see, the current efficiency is relatively low due to large amount of hydrogen generated.


Electrolysis - Annular Anode
Cathode Reaction
$CCl_4 + 4H^+ + 8e^- \rightarrow CH_4 + 4Cl^-$
$H_2O + e^- \rightarrow \frac{1}{2} H_2 + OH^-$
Potentiostat
V
Reference electrode
Porous electrode (copper foam)
Catholyte (influent)
Anode Reaction
$H_2O - 2e^- \rightarrow \frac{1}{2} O_2 + 2H^+$
Anode (carbon cloth)
Nafion membrane
anolyte
78

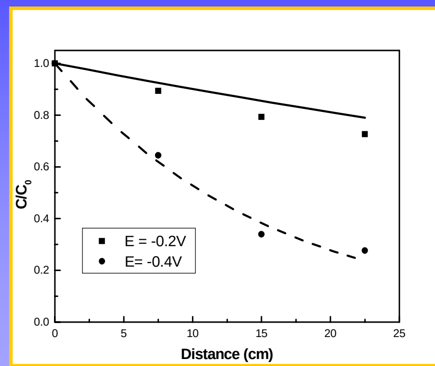

Electrolysis – Cu foam
Copper Foam Center
Porous Sleeve
79

CT Electrolysis: Applied Potential and Conductivity

(velocity = 0.0349 cm/s, cathode = 22.5 cm)



Conductivity = 0.067 S/m (tap water)

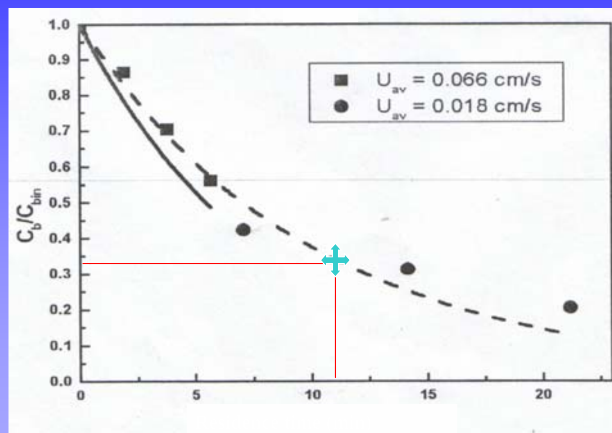


Conductivity = 2.7 S/m

80

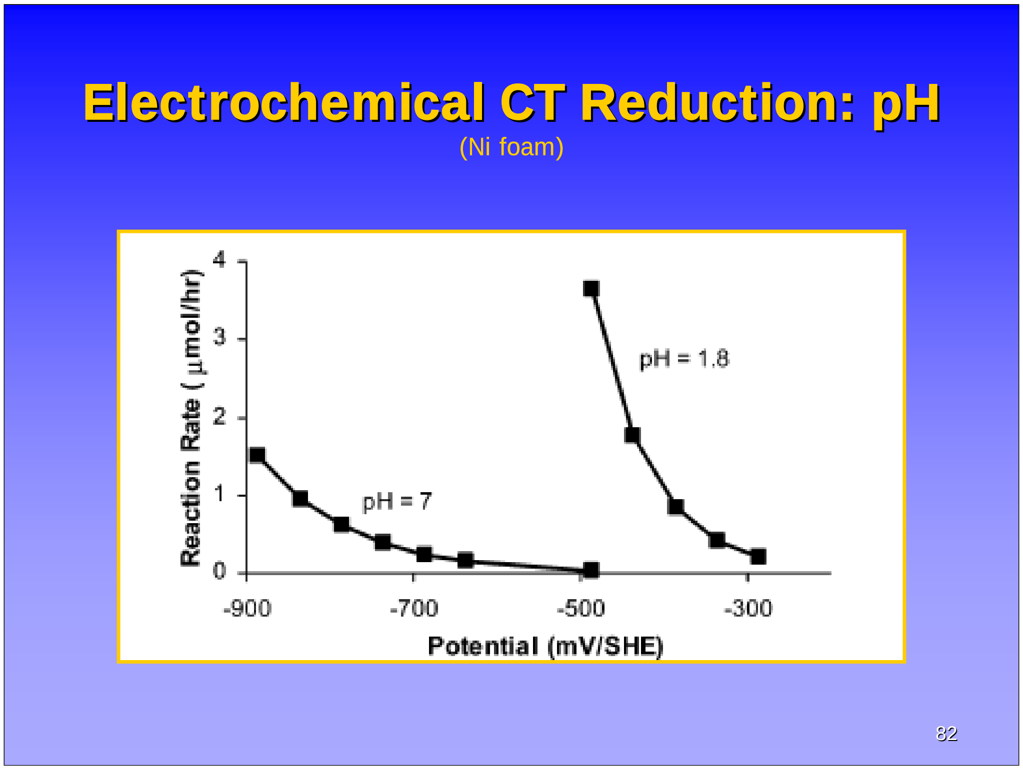
CT Electrolysis: Applied Potential and Conductivity

cathode = 22.5 cm; -0.4 V; 0.05 S/m; solid and dashed lines correspond to mathematical model

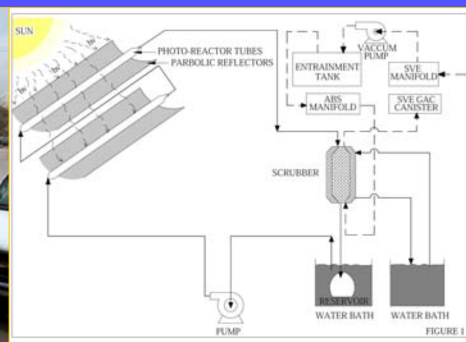


C_{bin}--Inlet concentration. C_b—Bulk concentration

81


Electrochemical CT Reduction: pH
(Ni foam)
Reaction Rate (µmol/hr)
4
3
2
1
0
-900
-700
-500
-300
Potential (mV/SHE)
pH = 1.8
pH = 7
82

Photochemical Treatment at Park-Euclid Site



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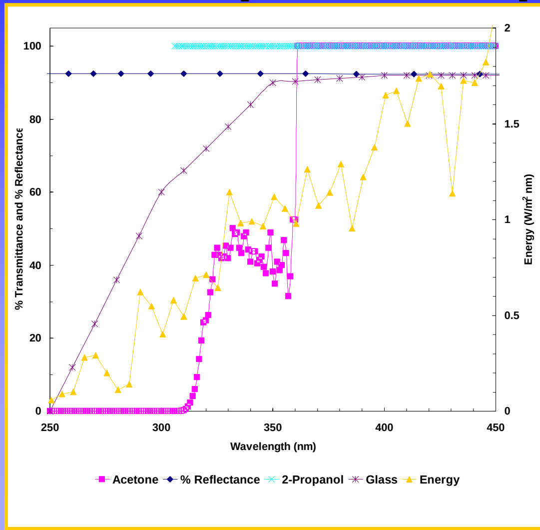
Photochemical Treatment: PCE at Park-Euclid Spectral Properties



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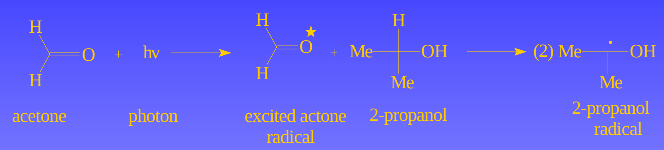
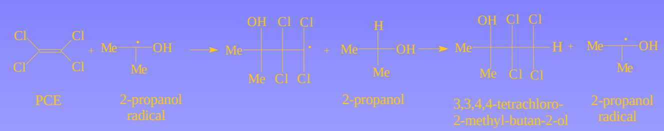
Photochemical Mechanism



Acetone in its excited state, extracts a hydrogen atom from a suitable donor, such as 2-propanol, producing a highly reduced 2-propanol radical that is capable of reducing a variety of halogenated targets.



1. Alkene-radical chemistry suggests that the 2-propanol radical may add to the chlorinated alkene to produce a chloro-methyl alcohol (3,3,4,4-tetrachloro-2-methyl-butan-2-ol).

2. Data also support electron donation to PCE and/or the chloro-methyl alcohol by the 2-propanol radical accompanied by chloride elimination, similar to carbon tetrachloride mechanism (Betterton et al., *ES&T* 2000).

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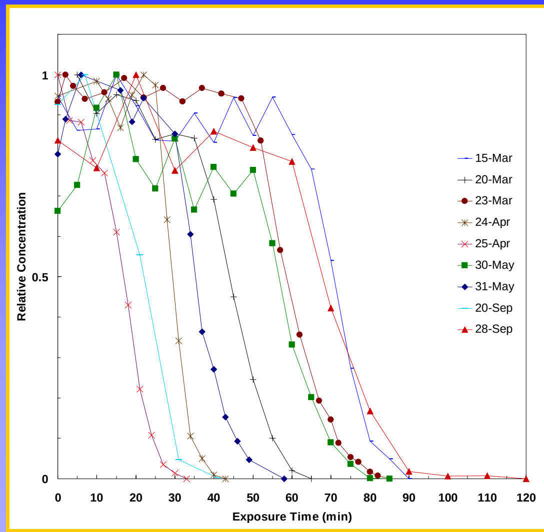
PCE Photochemical Treatment: Park-Euclid



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Summary

- Catalyzed thermochemical reduction is feasible – H_2 costs may be high but propane may be viable substitute.
- Electrolytic reduction of chlorinated solvents appears feasible using annular anode/cathode – even in low-conductivity water.
- Gas-phase treatment of solvents is fast using fuel cell – system requires scale up/additional design work.
- Photocatalytic system effective but scale up for volatile liquids may be unattractive.

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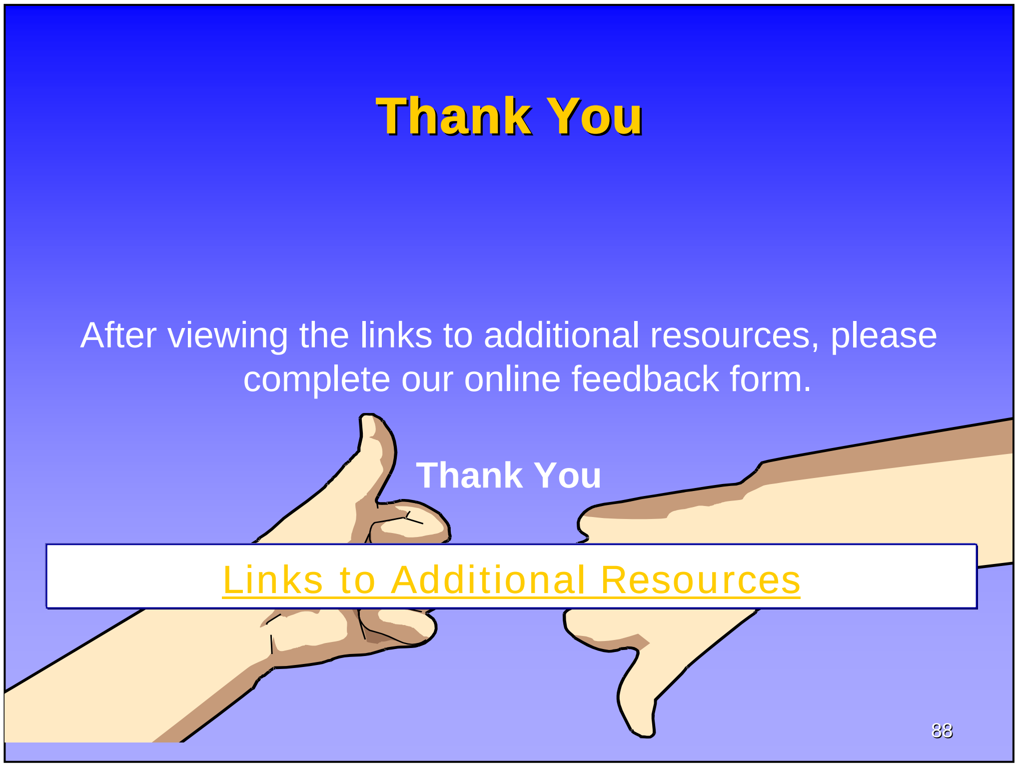
Thank You
After viewing the links to additional resources, please complete our online feedback form.
Thank You
Links to Additional Resources
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