Biological Treatment of High Explosives

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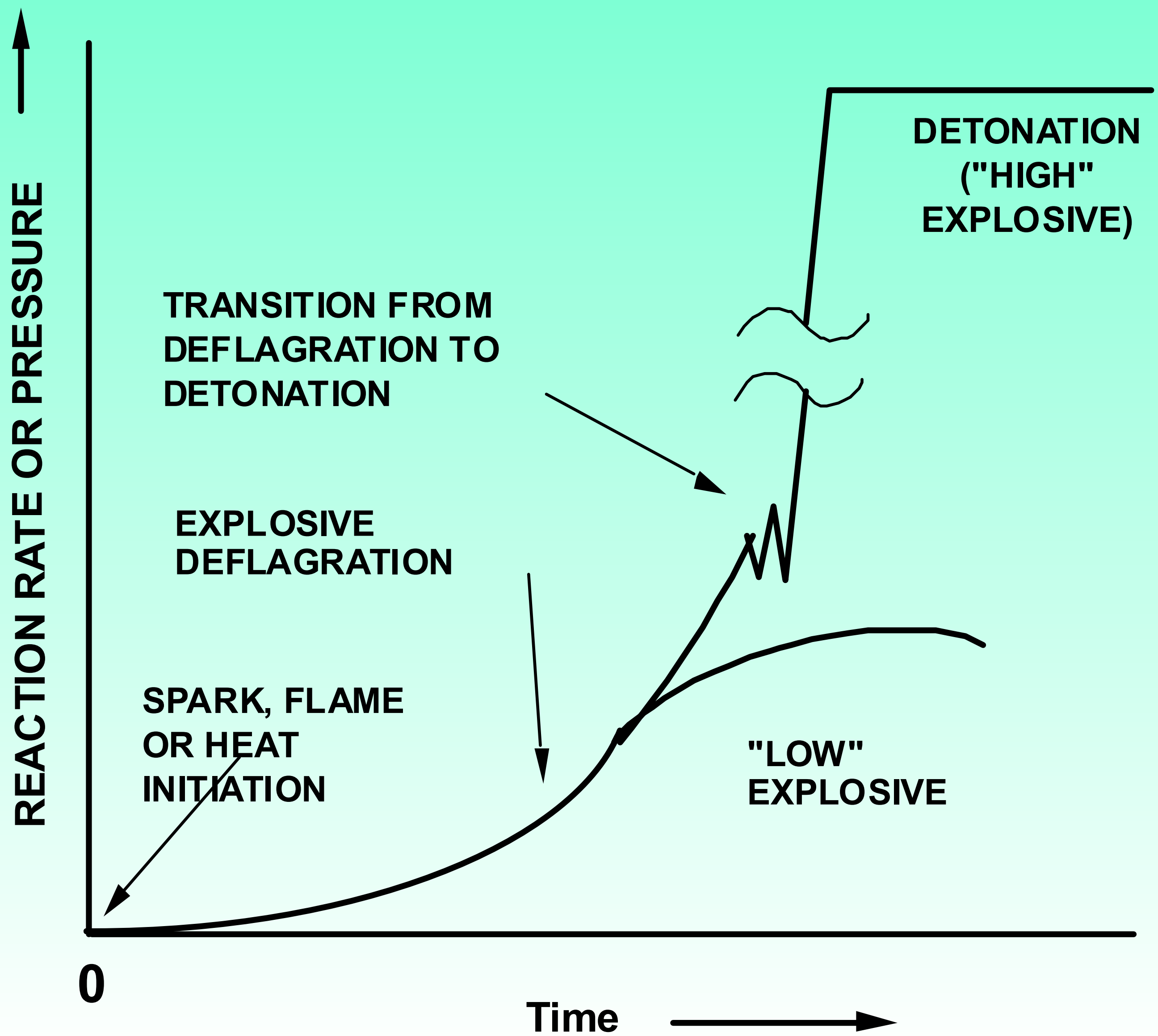
Outline

- Some information about explosives
  - Use, types, properties
- Biological treatment
- Treatment strategy
  - Carbon adsorption/desorption
- Mini-columns
- Mineralization
- Pilot Scale
- Conclusions

High Explosives

- Defined by their rate of reaction (high versus “low” or “normal” explosives)
- Some typical HEs - RDX, HMX, TNT, PETN, Ammonium-Nitrate
- Low Explosives - gunpowder, nitroglycerin

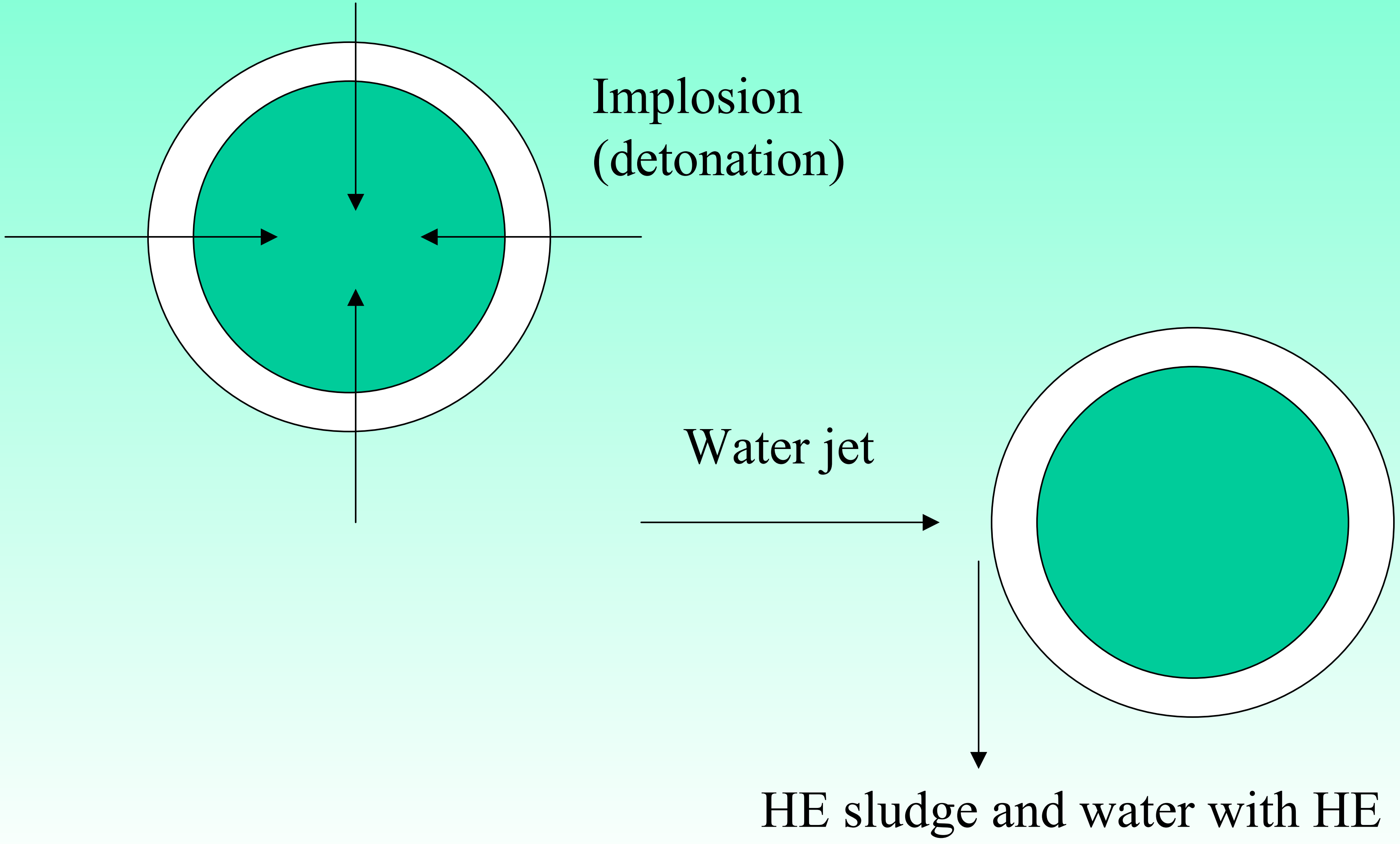
Pressure Curve



Usage

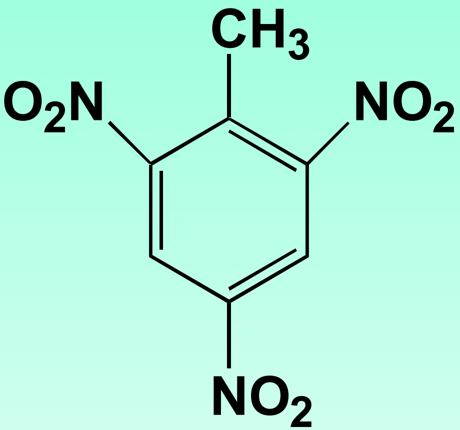
- Commercial blasting - coal mining, tunneling, road construction
- Military usage - bombs, artillery shells, various warheads
- Nuclear weapons - creates the implosion
- Some explosives had other uses, e.g., RDX used as rat poison

DOE Application – Plutonium Pits



Explosives

TNT



(2,4,6-Trinitrotoluene)

RDX

(Hexahydro-1,3,5-trinitro-1,3,5-triazine; *R*oyal *D*emolition e*X*plosive)

HMX

(Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; *H*igh *M*elting e*X*plosive)

RDX Properties

CAS Reg. No.	121-82-4
Molecular Weight	222.26
Empirical Formula	$C_3H_6N_6O_6$
Crystal form	white orthothombic crystals
Melting Point	204°C
Vapor Pressure (25°C)	4.03×10^{-9}
Heat of Fusion	38.26 cal/g
Ignition temperature	229°C

Aqueous solubility	in g/100g solvent
Water	0.006 (25°C)
Chloroform	0.008 (20°C)
Toluene	0.02 (20°C)
Benzene	0.05 (20°C)
Ether	0.055 (20°C)
Ethanol	0.11 (20°C)
Ethyl acetate	1.5 (20°C)
Acetonitrile	5.5 (25°C)
Acetone	8.2 (25°C)

Health Hazards

- RDX
  - a hazardous waste (EPA)
  - Health Advisory by EPA
    - 2 μg/L for lifetime exposure for adults in drinking water
  - A possible human carcinogen (Class C)
- HMX
  - a hazardous waste (EPA)
  - Health Advisory (1989) - Class D Carcinogen

Explosives Contamination

- Munitions production over the past years led to widespread and persistent contamination at government facilities.
- The current emphasis on demilitarization.
- Past methods for disposal include dumping in lagoons, at landfills, open burning.
- RDX and HMX pose risks to human health, and can be toxic to aquatic and terrestrial organisms.
- Thousands acres of highly toxic soils and groundwaters need to be cleaned up.

Existing Technology for Treatment

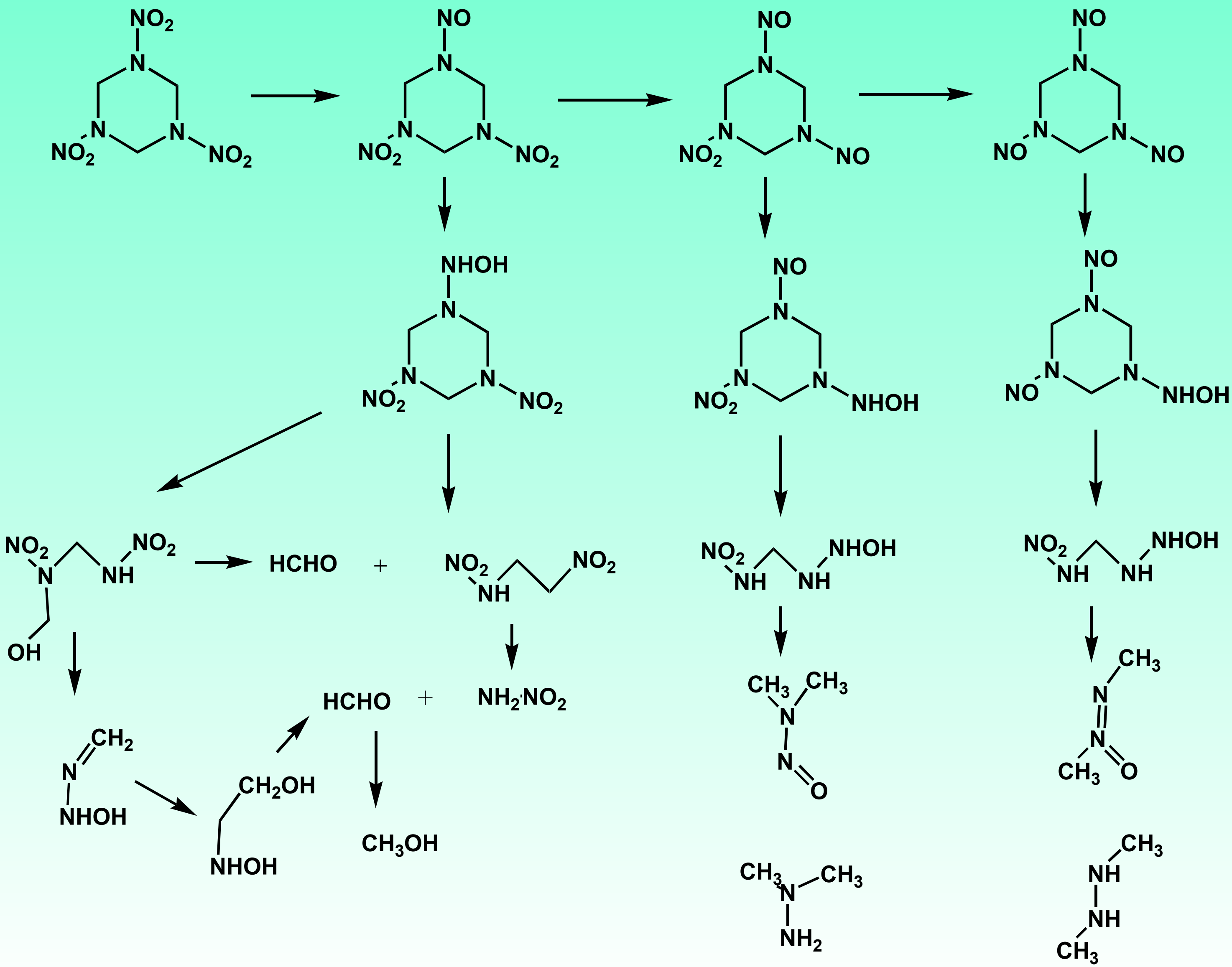
- Physical
  - Incineration
  - Excavation
  - Adsorption
- Biological
  - Aerobic
  - Anaerobic
  - Composting
- Chemical
  - Hydrolysis + Biological treatment
  - Advanced oxidation

RDX/HMX Research

- Aerobic treatment (unsuccessful)
- Anaerobic degradation
- Advanced oxidation (Fenton's reagent)
- Carbon adsorption followed by:
  - Alkaline hydrolysis (also for TNT) followed by biological treatment
  - Anoxic degradation
- Multicomponent carbon adsorption
- (bibliography attached to handout)

Anaerobic Biotransformation of RDX

(McCormick *et al.*, 1981)



CoSubstrates

(typical batch results)

- Gratuitous degradation
- Organism transforms or degrades a compound, but does not use it for growth
- Used in chlorinated solvent degradation (methane degrading bacteria)

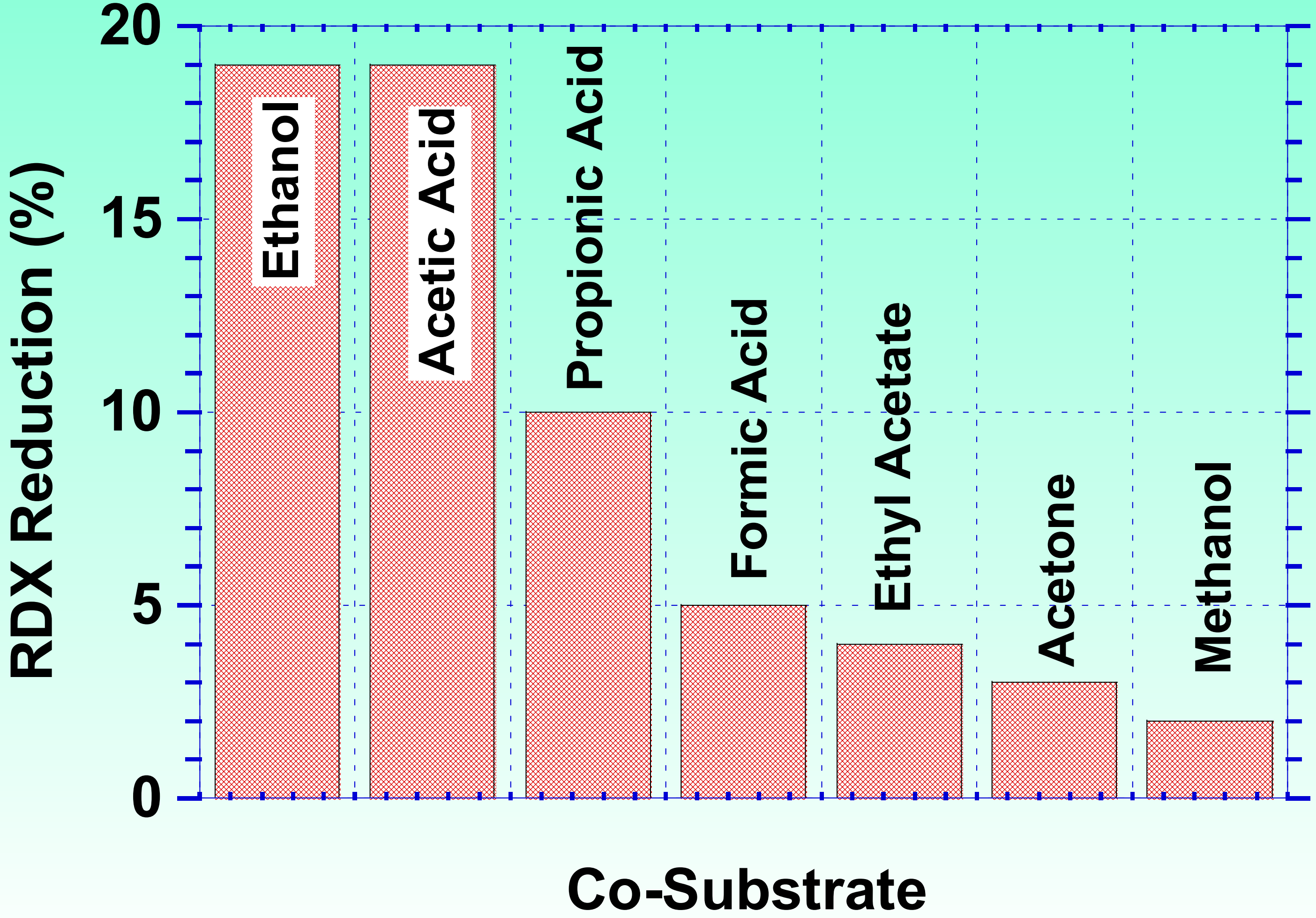
Batch Experiments to Determine Electron Acceptors and CoSubstrates

- Performed a series of incubations
- Different electron acceptors (e.g., NO_2, NO_3, SO_4 etc.) and substrates
- Measured disappearance of RDX and later HMX
- Eventually arriving at relative efficiencies for a wide range of conditions

Conclusions of Batch Studies

- High efficiencies are possible
- CoSubstrate concentrations too high for practical application
- Not suitable for groundwater (pump and treat) applications due to the remaining cosubstrate and biological byproducts

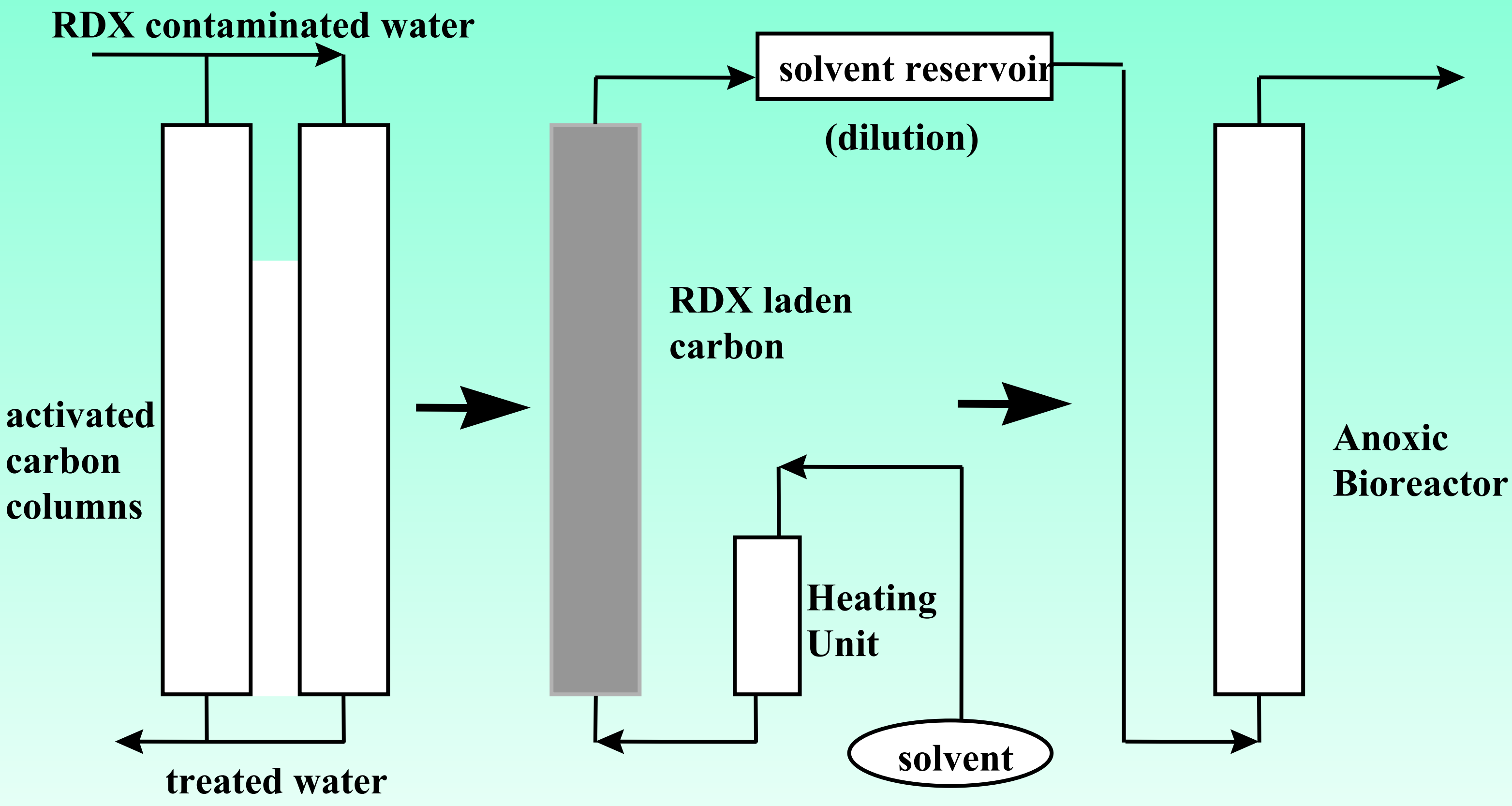
CoSubstrate Selection



How to Use CoSubstrates in a Practical System

- Cannot afford the substrates in dilute systems
- Excess substrate represents a treatment problem
- Could not for example, reinject treated groundwaters after cosubstrate addition
- Need to separate and concentrate HE from bulk flow streams

Treatment Strategy

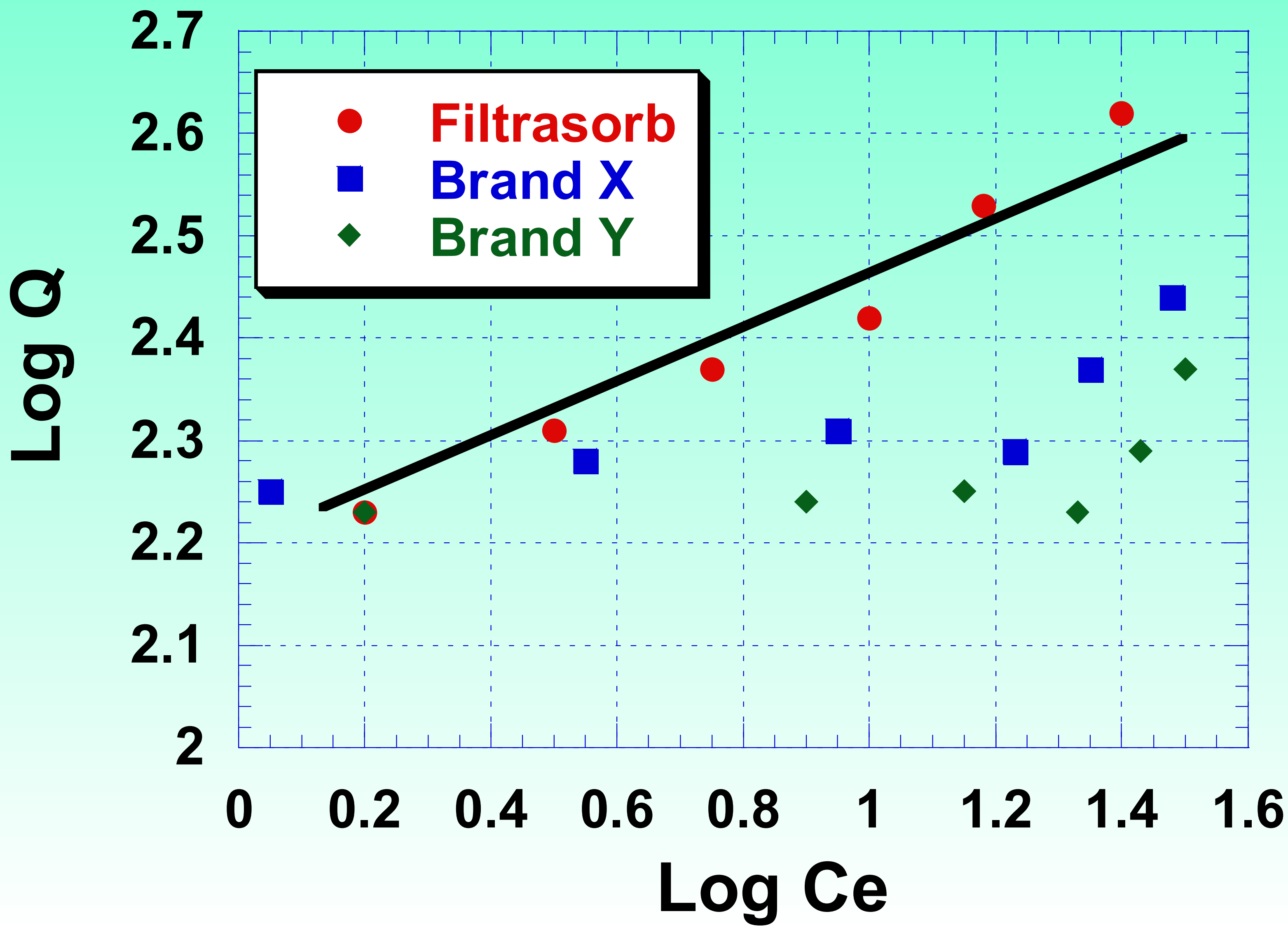


Step 1: Activated carbon adsorption

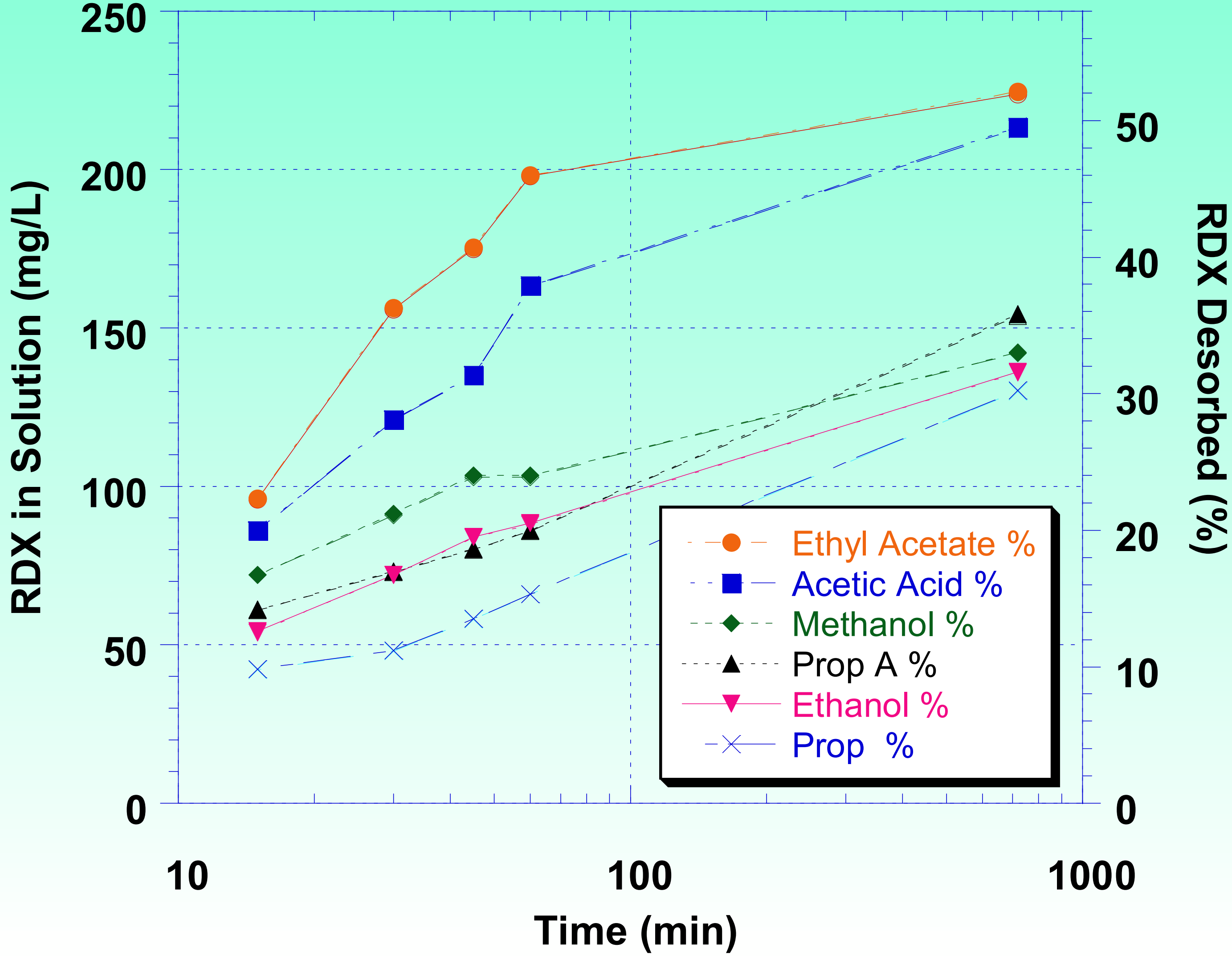
Step 2: Laden carbon desorption with organic solvents

Step3: Biological degradation

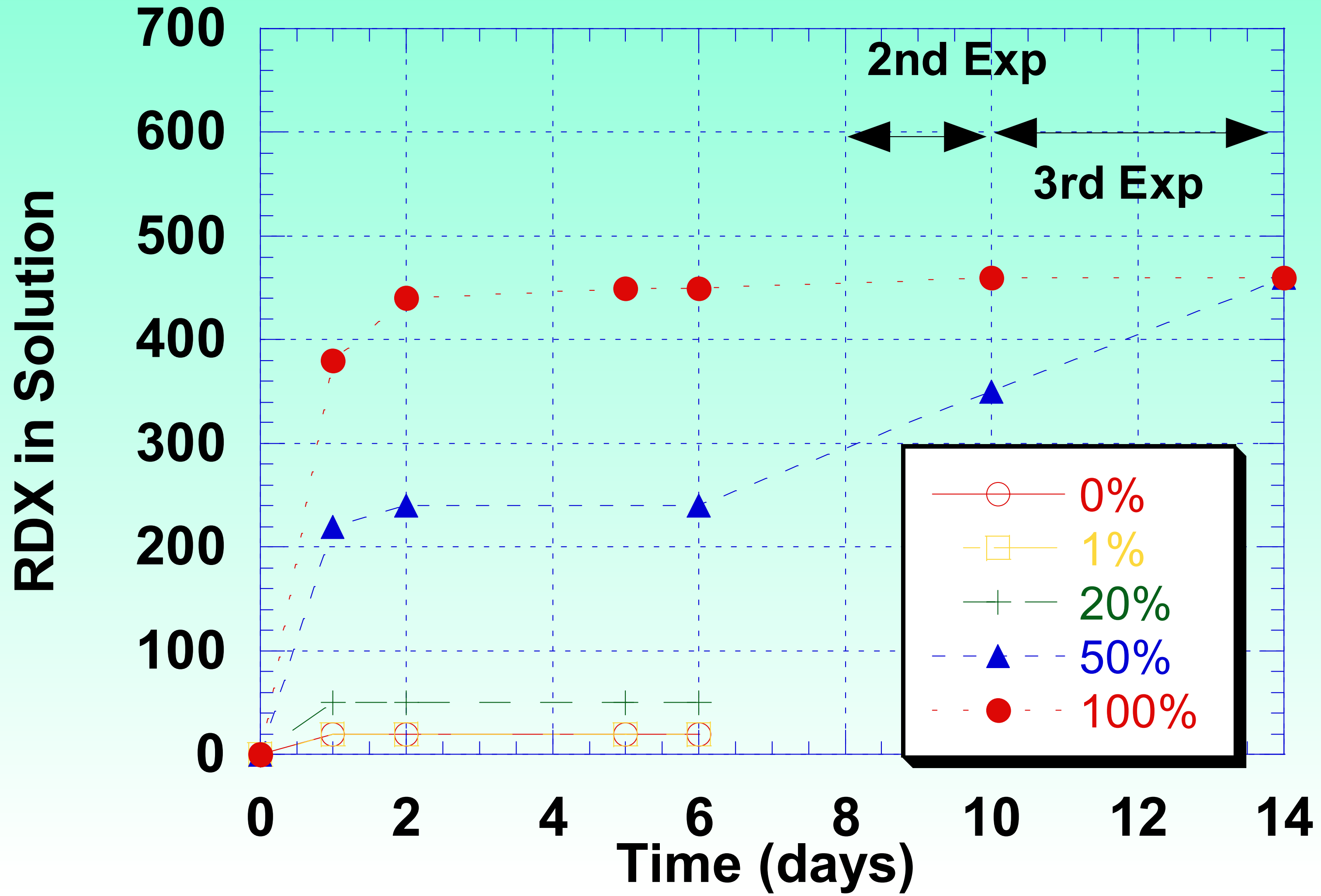
Isotherms


Filtrasorb
Brand X
Brand Y
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2
Log Q
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Log Ce

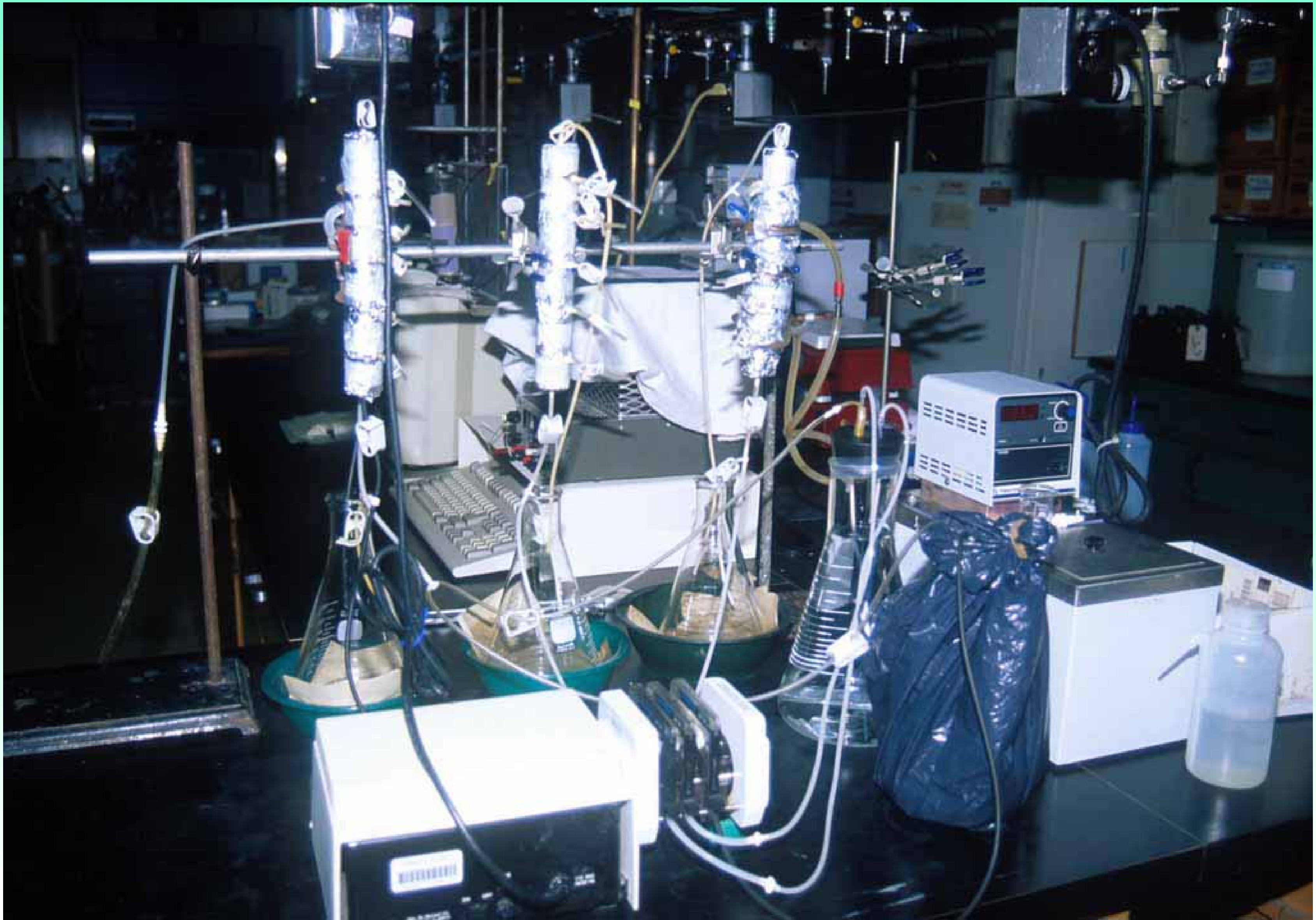
Solvent Selection



Desorption Results



Mini Columns (1 in diameter)

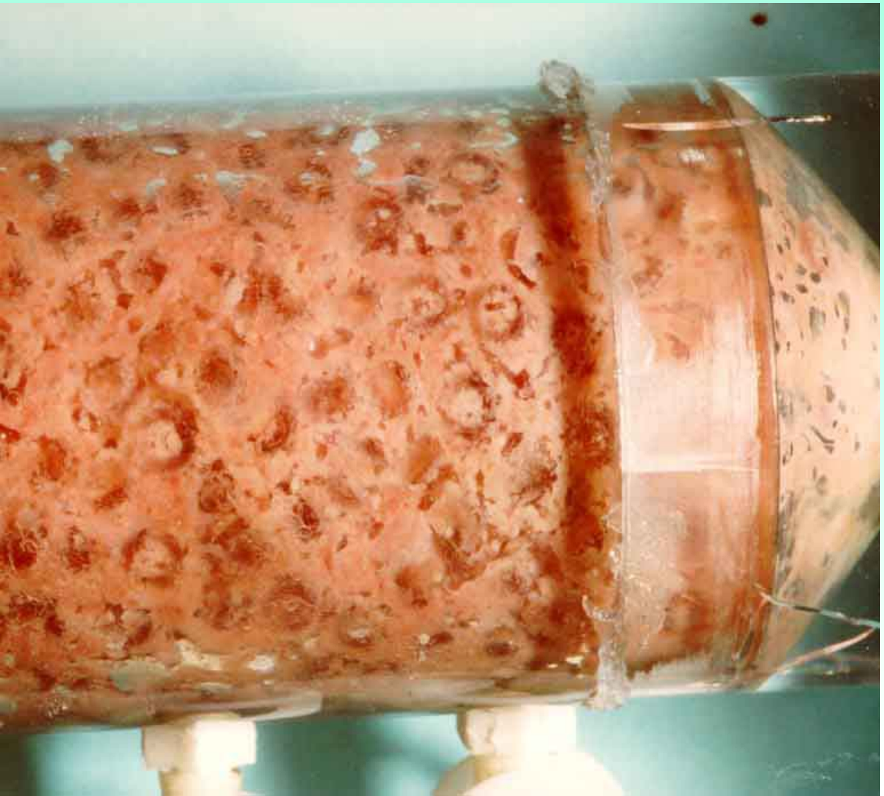


Column Packing

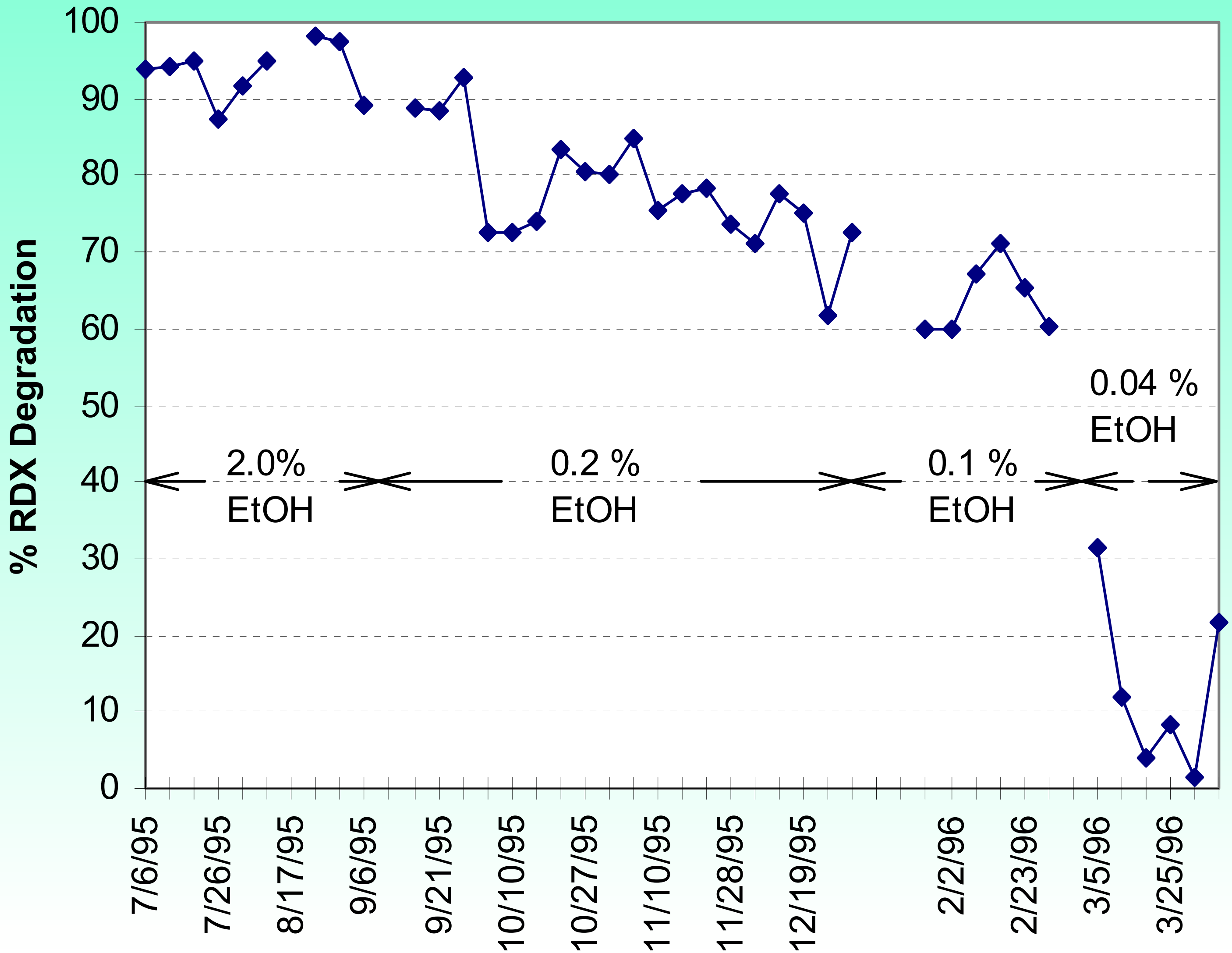
Rings from silicon tubing

Rings from Tygon tubing

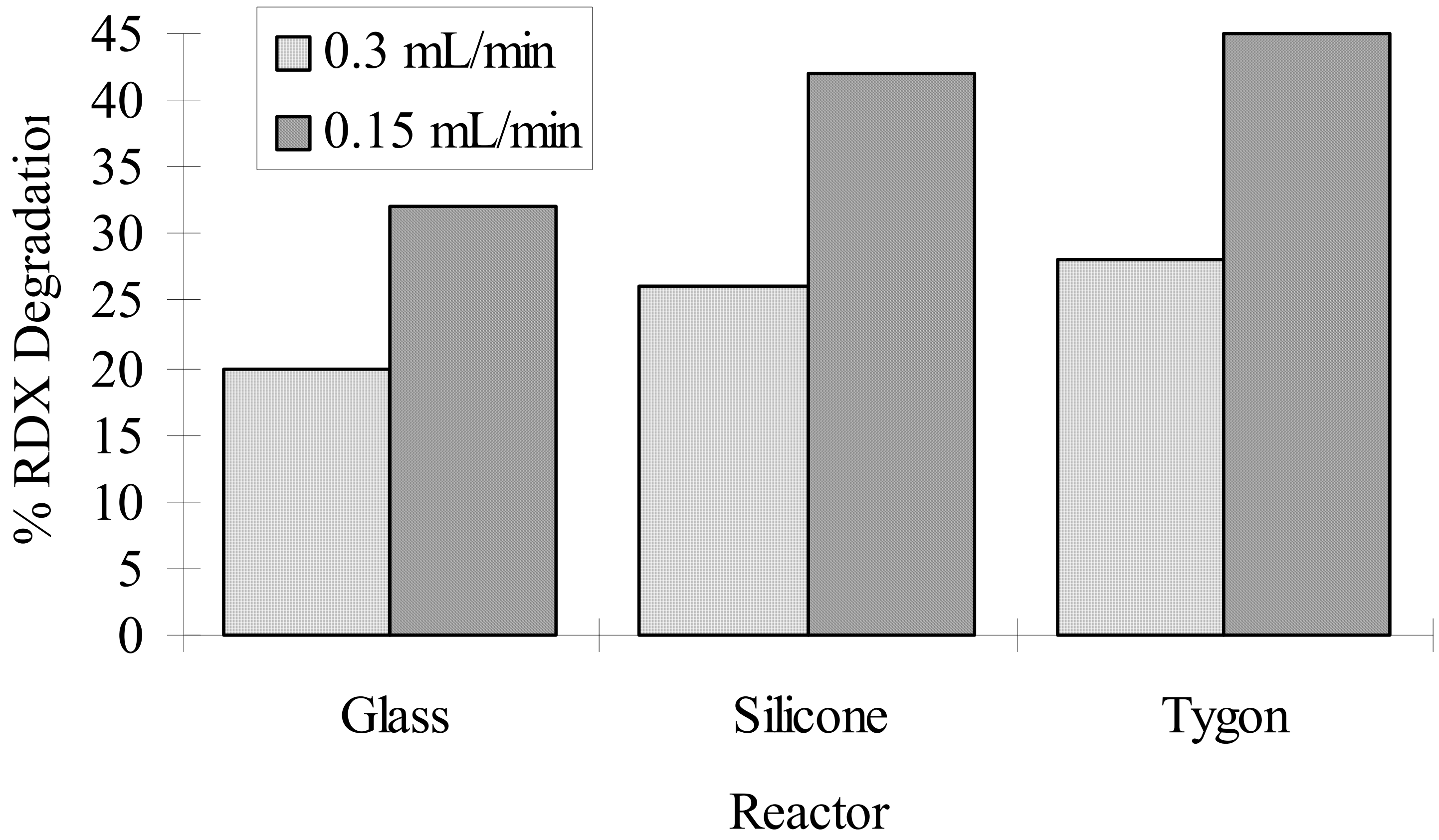
BioMass



EtOH Concentration Effect



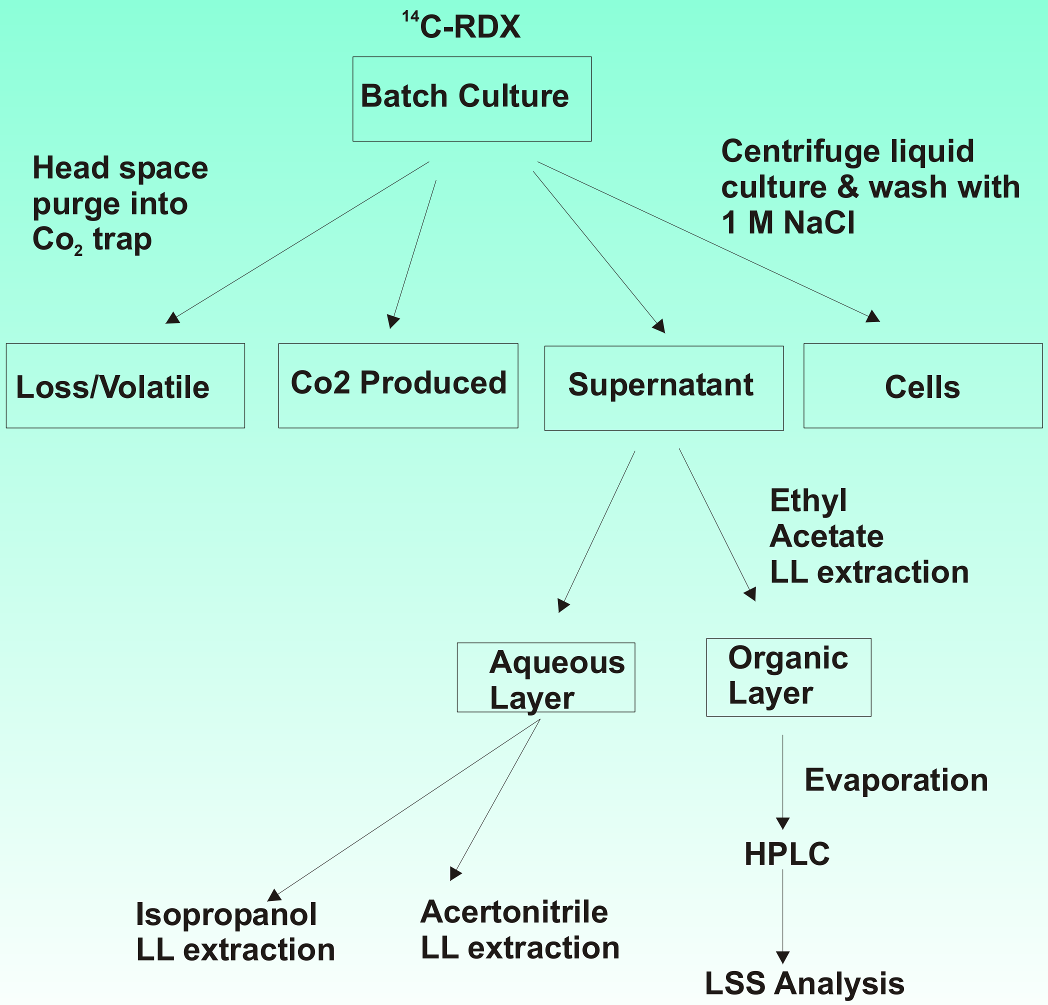
Effects of Packing and Retention Time



Mineralization

- Need to document not only the disappearance of the parent compound (RDX) but also the end products
- Some end products are worse than the parents (e.g. nitrosoamines)
- ^{14}C studies using RDX purified by HPLC

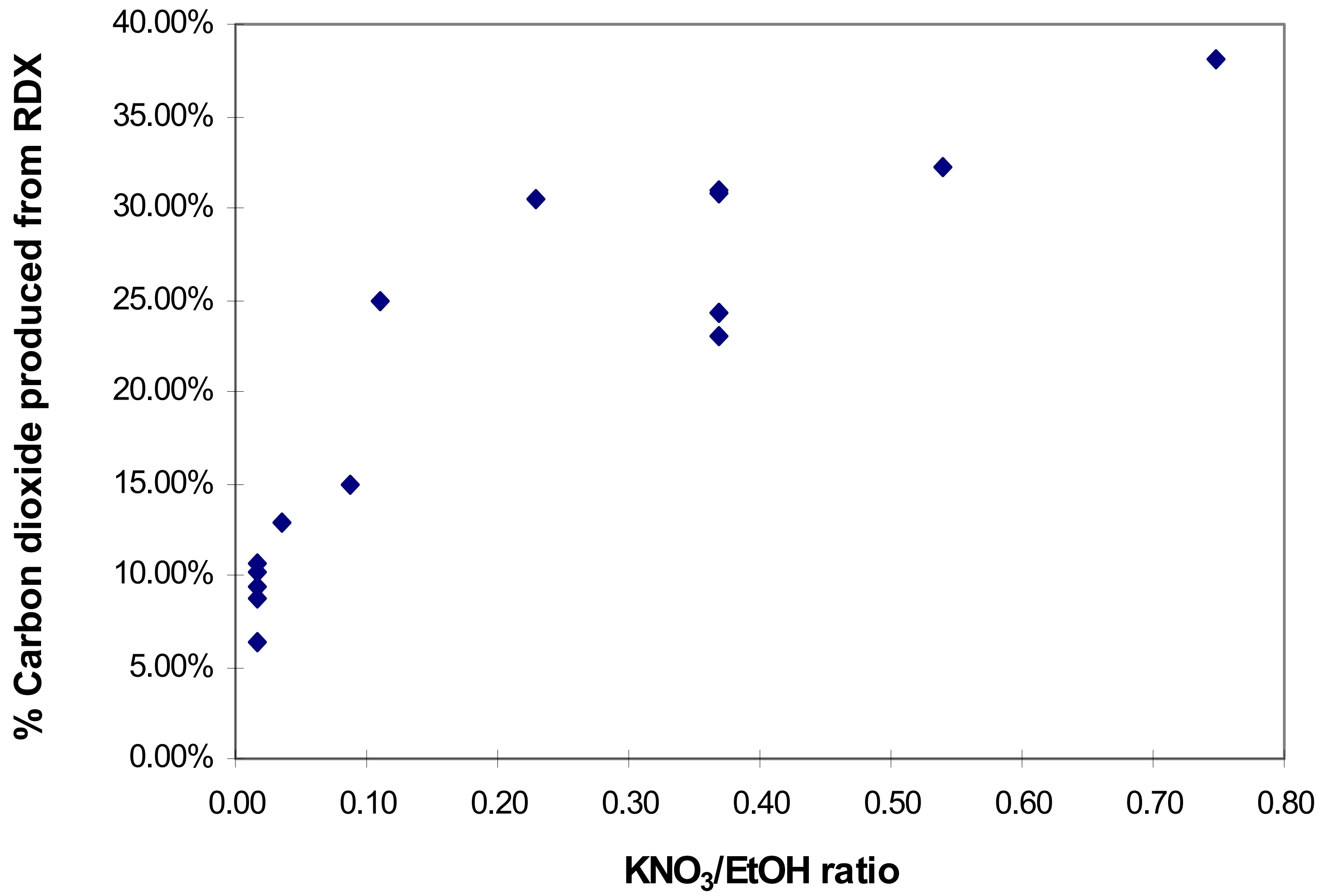
^{14}C Labeled Studies



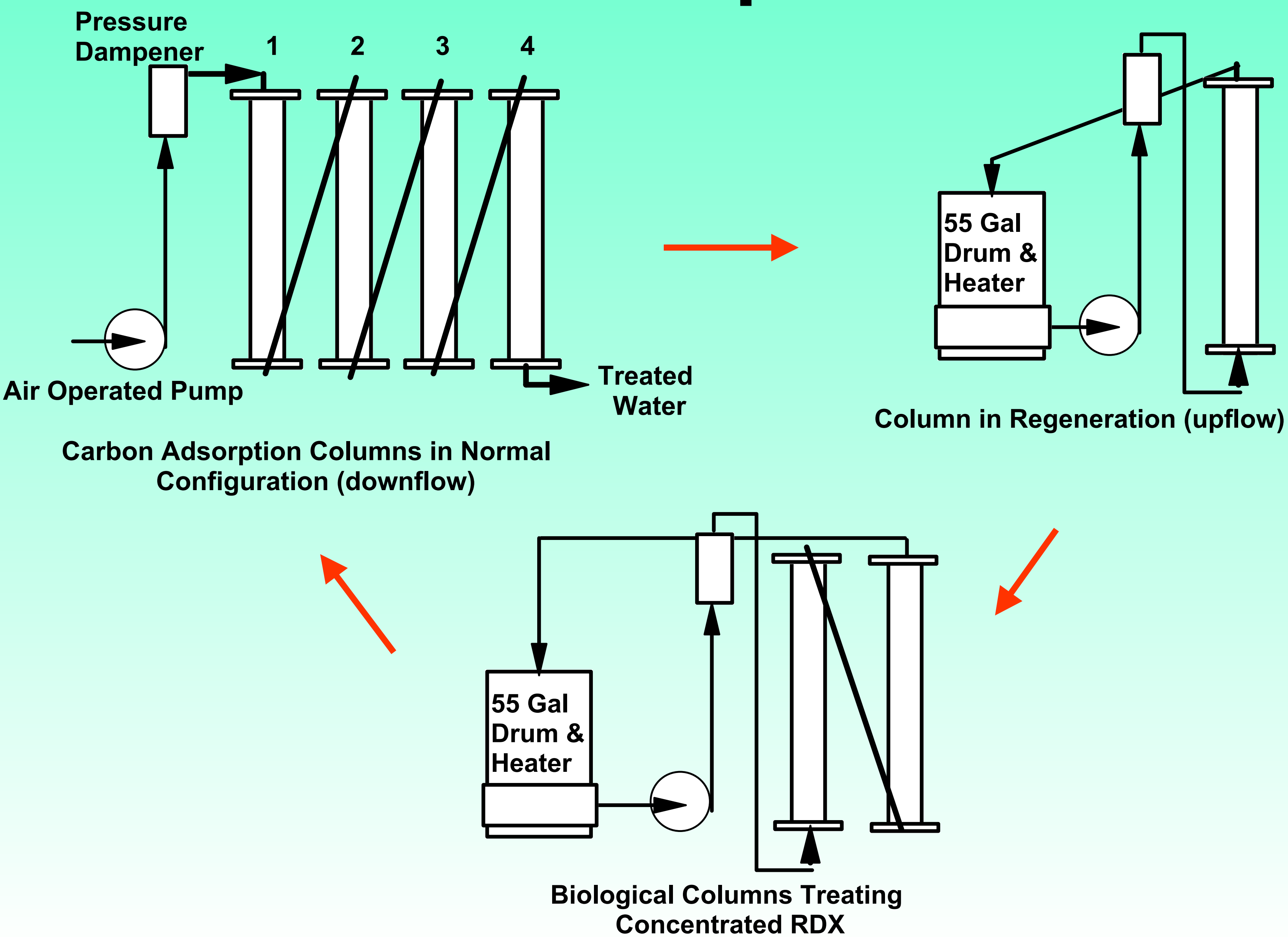
Label Results

- Mono, di and tri nitrosoamines were briefly observed and quickly disappeared
- Low molecular weight, polar byproducts were observed
- Varying amounts of CO_2 observed
- Batch studies over varying time periods with greater amounts of NO_3 showed more CO_2 production and less soluble byproduct
- Up to 38% carbon recovered as CO_2

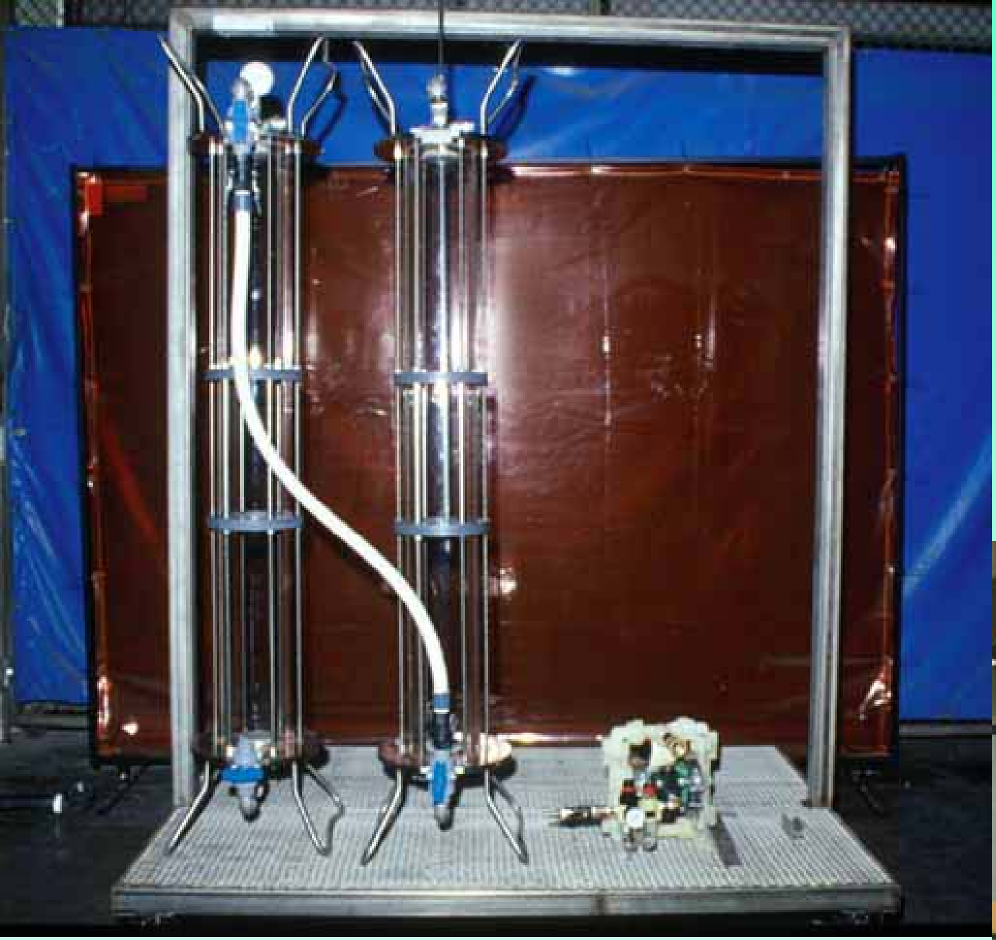
KNO3/EtOH


% Carbon dioxide produced from RDX
40.00%
35.00%
30.00%
25.00%
20.00%
15.00%
10.00%
5.00%
0.00%
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
KNO3/EtOH ratio

Column Operation



Six Inch Columns



Column Media

Conclusions

- RDX treatment via carbon adsorption/desorption and anoxic biological treatment possible
- Conclusive evidence for RDX mineralization
- Demonstration at pilot scale for demil processing wastewaters
- Opportunities for other sites
- Probably not as efficient or as economical as our alkaline hydrolysis strategy