

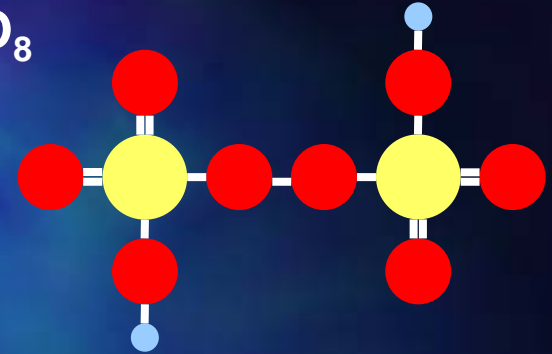
# **Novel Activation Technologies for Sodium Persulfate *In Situ* Chemical Oxidation**

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# Persulfate Oxidation Chemistry



Simplified Reaction



**Strong Oxidizer**

Persulfate anion:

*kinetically slow*



$$E^0 = 2.12 \text{ v}$$

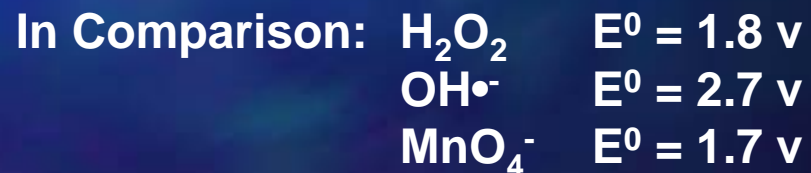


*need to activate*

**Sulfate radical:**



$$E^0 = \sim 2.6 \text{ v}$$



# Conventional Persulfate Activation

## Heat



Compounds with > 90% Decomposition Treat with Persulfate

20 °C	35 °C	45 °C
Toluene	Benzene	1,1,1-TCA
Ethylbenzene	Chlorobenzene	Chloroform
Xylene	1,2-DCE	Methylene Chloride
1,1-DCE	PCE	
1,2-Dichlorobenzene	TCE	
1,3-Dichlorobeneze	1,1-DCA	
1,2,4-Trichlorobenzene	1,2-DCA	
	MTBE	
	Vinyl Chloride	
	Carbon Tetrachloride	

Aqueous solutions - lab data; 72 hour

- **Advantage:** will oxidize all compounds of concern given enough thermal input
- **Disadvantage:** may be costly to apply in field applications

# Conventional Persulfate Activation

## Transition Metal Catalysis



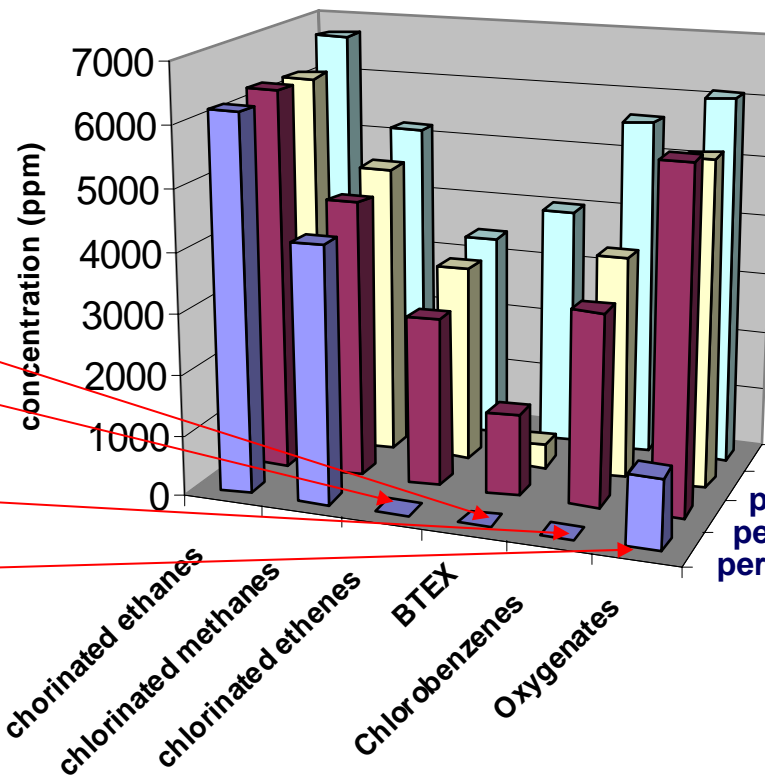
• Advantage:

BTEX

Chlorinated  
Ethenes

Chlorobenzenes

MTBE



Aqueous  
Room temp  
100 mg Fe / L  
2.5% persulfate  
21 days

control  
persulfate @ pH 8  
persulfate + Fe(II) @ pH 8  
persulfate + Fe(II) @ pH 2

• Disadvantage: precipitation of  $\text{Fe}(\text{OH})_3$  reduces availability of catalyst  
Remtech2006

# Novel Persulfate Activation

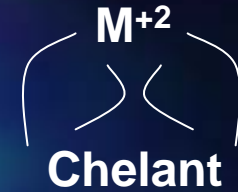
## Targets for Novel Technologies:

- Easy to apply in a variety of subsurface conditions
  - Transportable in a groundwater system
  - Increased reactivity of persulfate with a broad range of organic contaminants
- 
- Chelated metal catalysts
  - Hydrogen peroxide activation
  - High pH activation

# Novel Persulfate Activation

## Chelated Metal Catalysts

- enhance solubility and transportability in groundwater
- combinations of di- or tri- valent metals with chelants



### Examples:

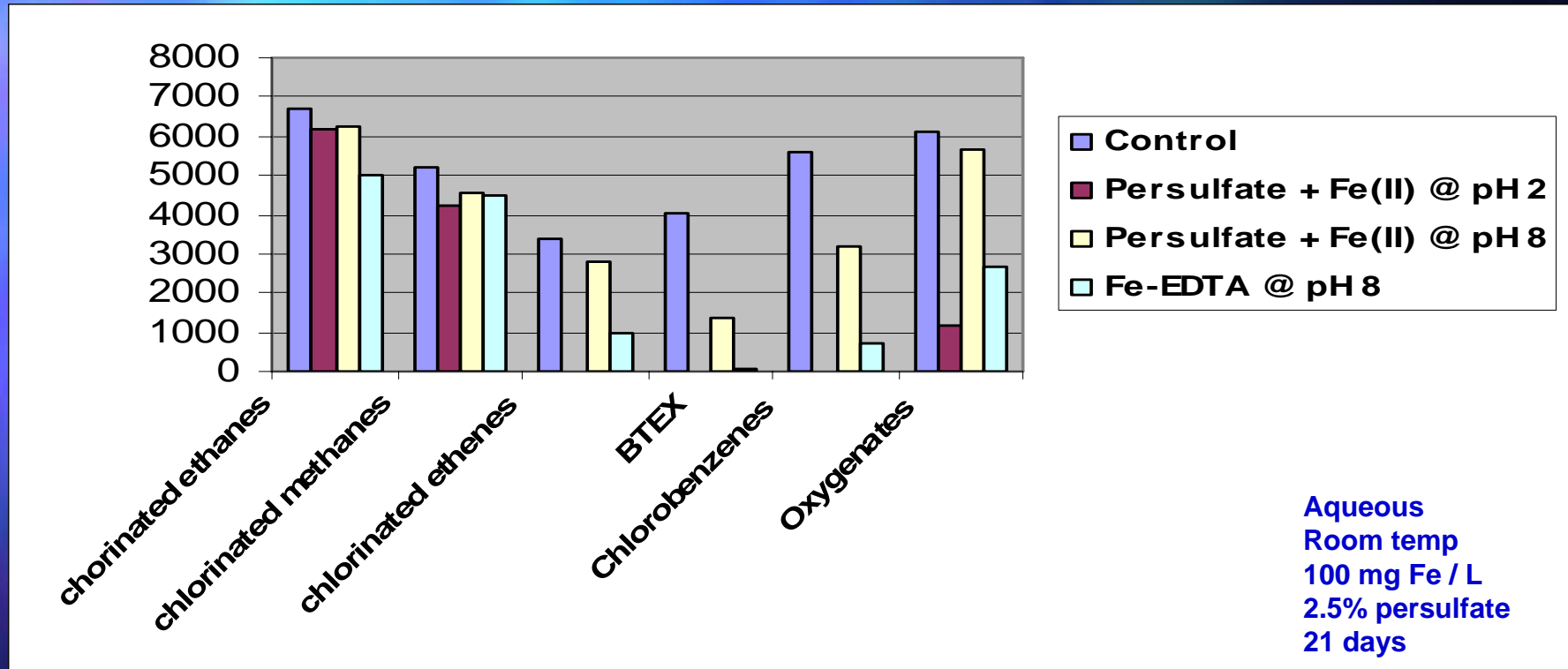
Fe (II)  
Fe (III)



EDTA  
Citrate  
Catechol  
Polyphosphate  
Glycolic acid  
NTA  
THQ

# Novel Persulfate Activation

## Chelated Metal Catalysts



- **Advantages:** improved performance at neutral pH's on chlorinated ethenes, BTEX, chlorobenzenes and oxygenates
- **Disadvantages:** not effective on chlorinated ethanes or methanes

# Novel Persulfate Activation

## Hydrogen Peroxide Activation



- multi-radical attack
- removal of SOD by peroxide

### Degradation of Contaminants with Persulfate + Peroxide

Contaminant (mg/L)	Time 0	Day 8
1,1-DCE	4.5	0.1
TCE	2.8	Non Detectable
1,1-DCA	1.1	Non Detectable
1,1,-TCA	12.0	0.6

Room temp  
Aqueous soln

2 g persulfate  
8 mL 12.5% H<sub>2</sub>O<sub>2</sub>

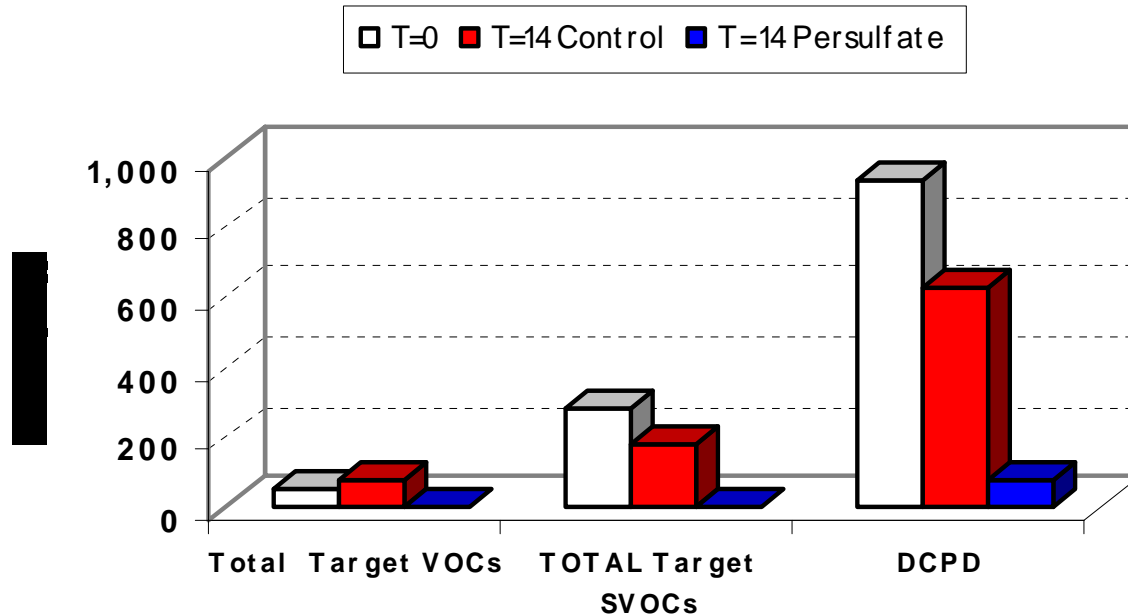
100 g of solution

Data from ORIN RT

# Novel Persulfate Activation

## Hydrogen Peroxide Activation

Oxidation of MGP Residuals



data from  
ERM

400 g soil from MGP site  
1.08 L distilled water

1.5 g / L sodium persulfate  
120 mL of 50% peroxide

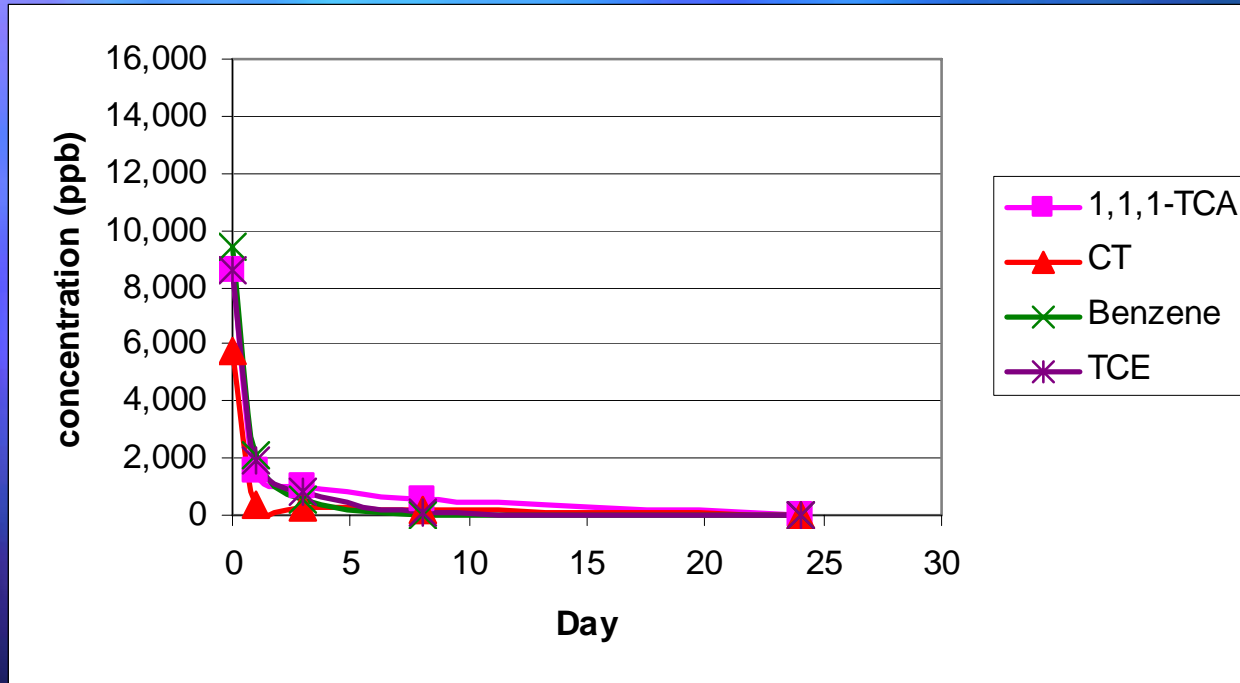
Remtech2006

VOC's: BTEX, styrene  
SVOC's: 3 – 5 ring PAHs  
DCPD: dicyclopentadiene

# Novel Persulfate Activation

## Hydrogen Peroxide Activation

### Decomposition of Contaminants by Persulfate + Peroxide



Room temp  
300 mL water  
150 g soil  
(KMnO<sub>4</sub> SOD 9 – 13 g / kg)

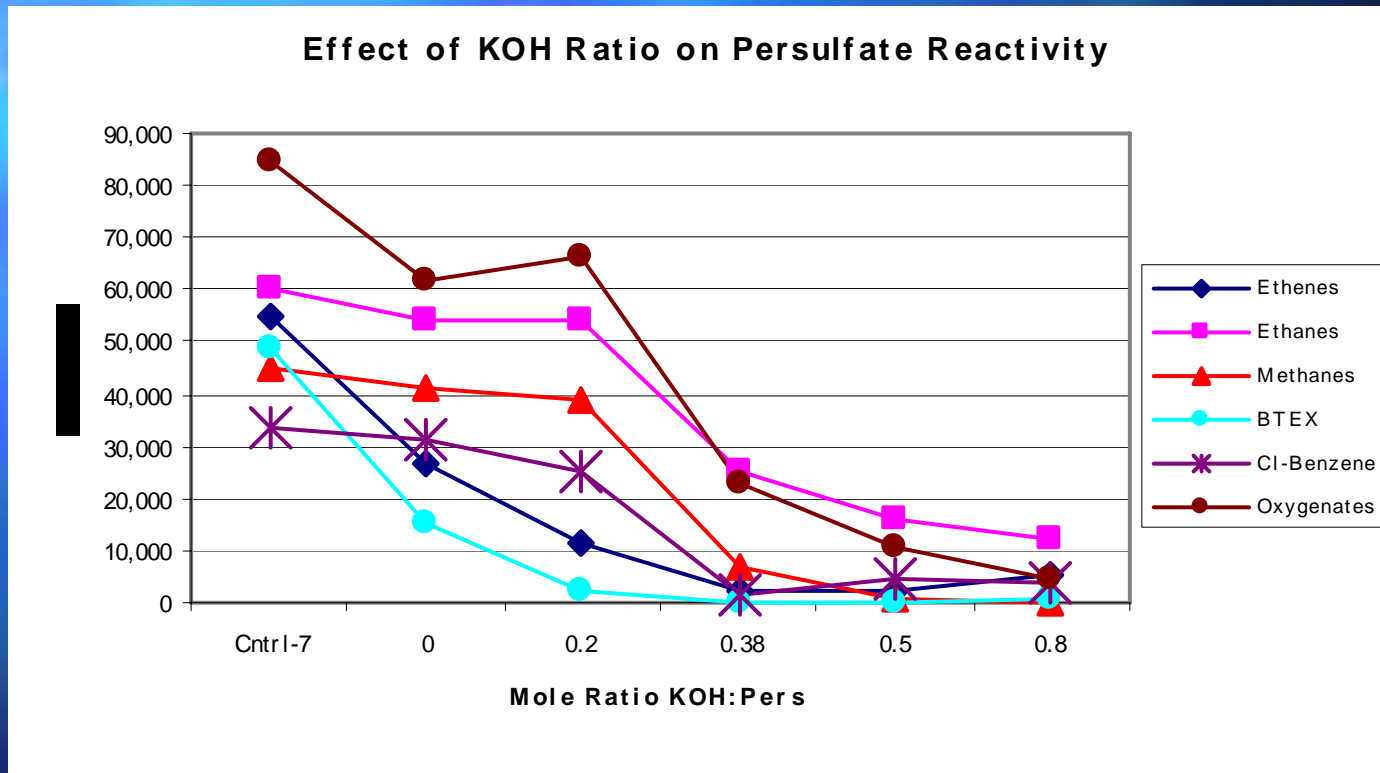
5 g/L sodium persulfate  
50 g 17.5% peroxide

- Advantages: broad applicability including chlorinated ethanes and methanes

# Novel Persulfate Activation

## Alkaline Activation

- pH > 10



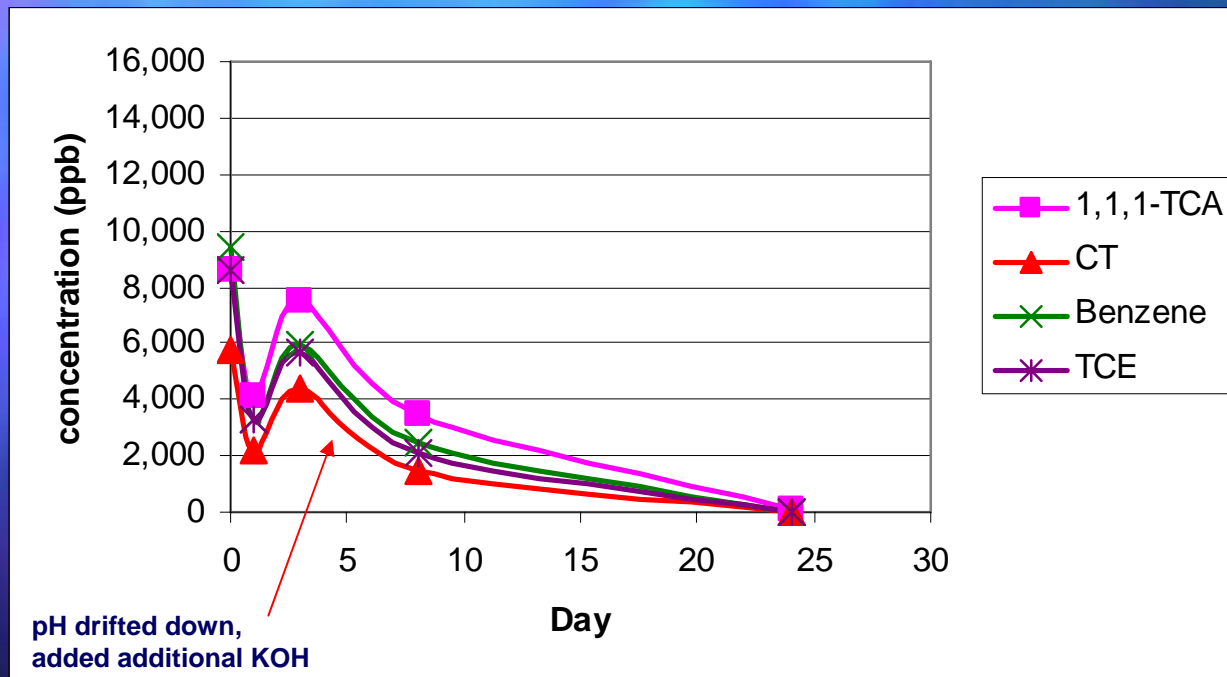
Room temperature  
Aqueous solutions  
7 days  
Analyzed by GC-MS

25 g/L sodium persulfate  
KOH as pH modifier

# Novel Persulfate Activation

## Alkaline Activation

### Decomposition of Contaminants by Alkaline Activation



Room temp  
300 mL water  
150 g soil  
(KMnO<sub>4</sub> SOD 9 – 13 g / kg)

5 g/L sodium persulfate  
0.01 mol / L KOH

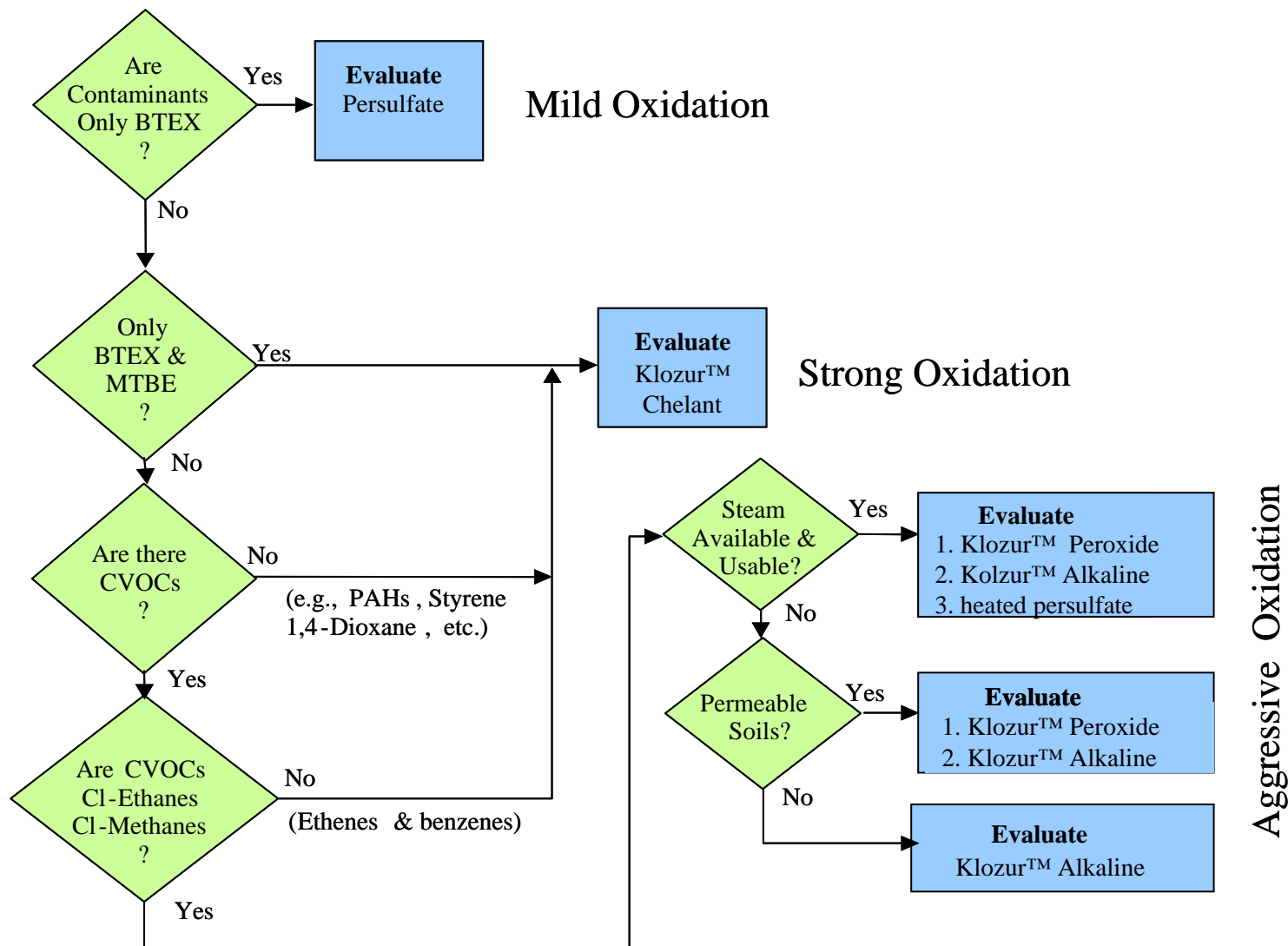
- Advantages: broad applicability including chlorinated ethanes and methanes

# Selection of Activation Technology

## Efficacy Matrix

Technology	BTEX	chlorinated ethenes	chlorinated ethanes	MTBE	PCB	1,4-dioxane
Un-activated Sodium Persulfate	Y	N	N	N	N	N
Sodium Persulfate + Fe(II)	Y	Y	N	Y	?	Y
Sodium Persulfate + Heat	Y	Y	Y	Y	Y	Y
Persulfate with Chelated Metals	Y	Y	N	Y	?	Y
Persulfate with Hydrogen Peroxide Activation	Y	Y	Y	Y	?	Y
Persulfate with Alkaline Activation	Y	Y	Y	Y	Y	Y

# Selection of Activation Technology



# Acknowledgements

- Richard Brown ERM
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