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

Frank Sessa
FMC Corporation
Philadelphia, PA

Dalbir Sethi
FMC Corporation
Philadelphia, PA

Jean Pare
ChemCo
Quebec, CA

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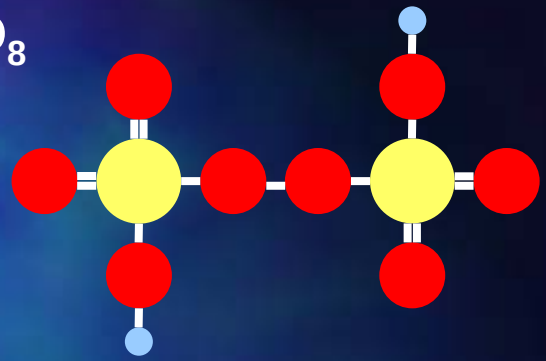
Power. Stability. Versatility.

Persulfate Oxidation Chemistry

$Na_2S_2O_8$



Simplified Reaction

Persulfate + CoC ⟶ CO_2 + H_2O

Strong Oxidizer **Persulfate anion:**

kinetically slow

$S_2O_8^{-2} + 2H^+ + 2e^- \rightarrow 2HSO_4^{-2}$ $E^0 = 2.12$ v

need to activate

Sulfate radical:

$SO_4^{\bullet -} + e^- \rightarrow SO_4^{-2}$ $E^0 = \sim 2.6$ v

In Comparison:

H_2O_2	$E^0 = 1.8$ v
$OH^{\bullet -}$	$E^0 = 2.7$ v
MnO_4^-	$E^0 = 1.7$ v

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Conventional Persulfate Activation

Heat

$S_2O_8^{-2}$ + heat ➔ 2 SO_4•

Compounds with > 90% Decomposition Treat with Persulfate

20 ºC	35 ºC	45 ºC
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

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Conventional Persulfate Activation

Transition Metal Catalysis

$S_2O_8^{-2} + M^{+2} \rightarrow M^{+3} + SO_4^{-2} + SO_4\bullet$

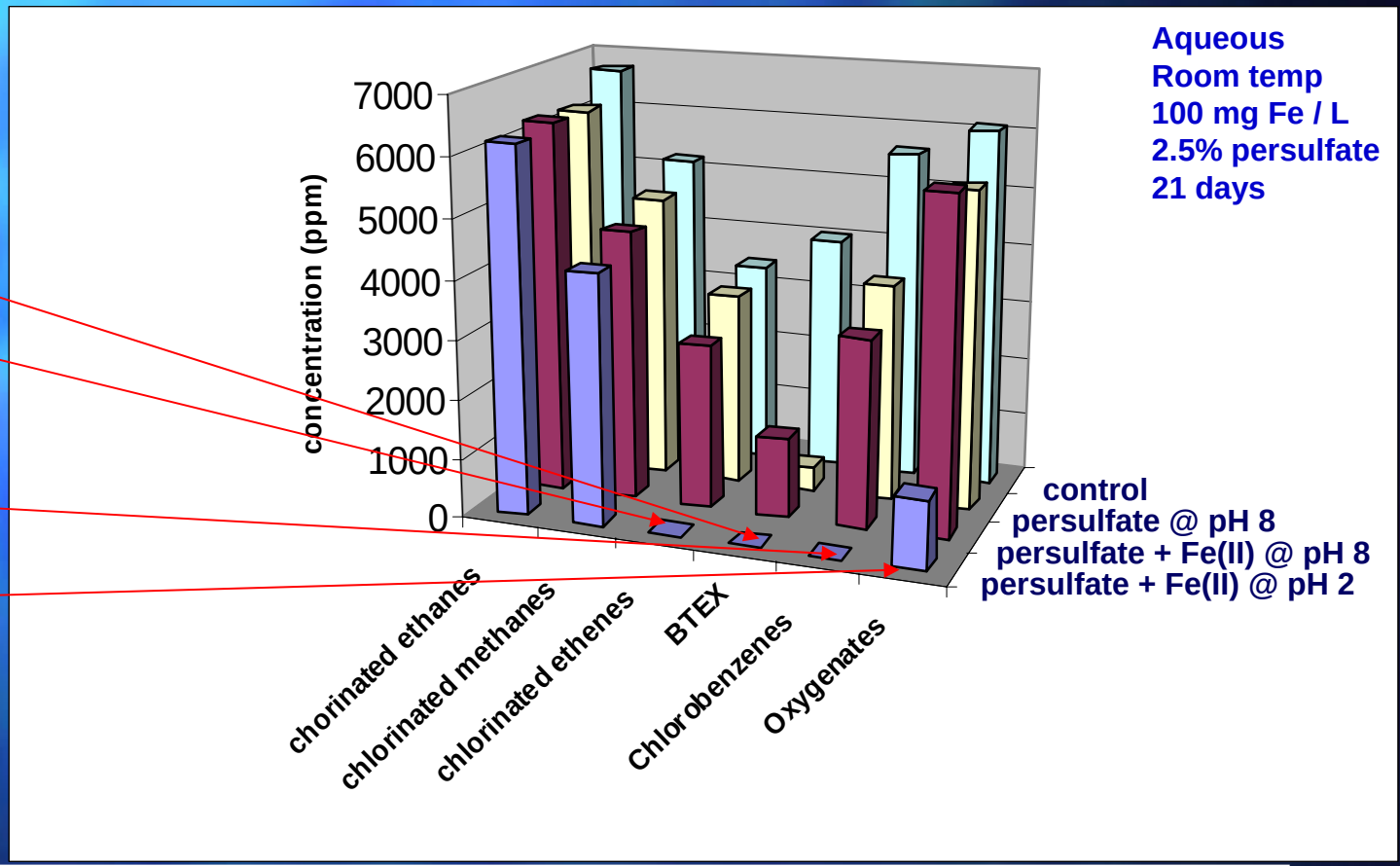
- Advantage:

BTEX

Chlorinated Ethenes

Chlorobenzenes

MTBE



- Disadvantage: precipitation of $Fe(OH)_3$ reduces availability of catalyst

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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**

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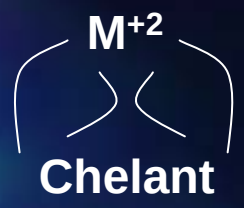
Novel Persulfate Activation

Chelated Metal Catalysts



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

Examples:

Fe (II)	⟷	EDTA
Fe (III)		Citrate
		Catechol
		Polyphosphate
		Glycolic acid
		NTA
		THQ

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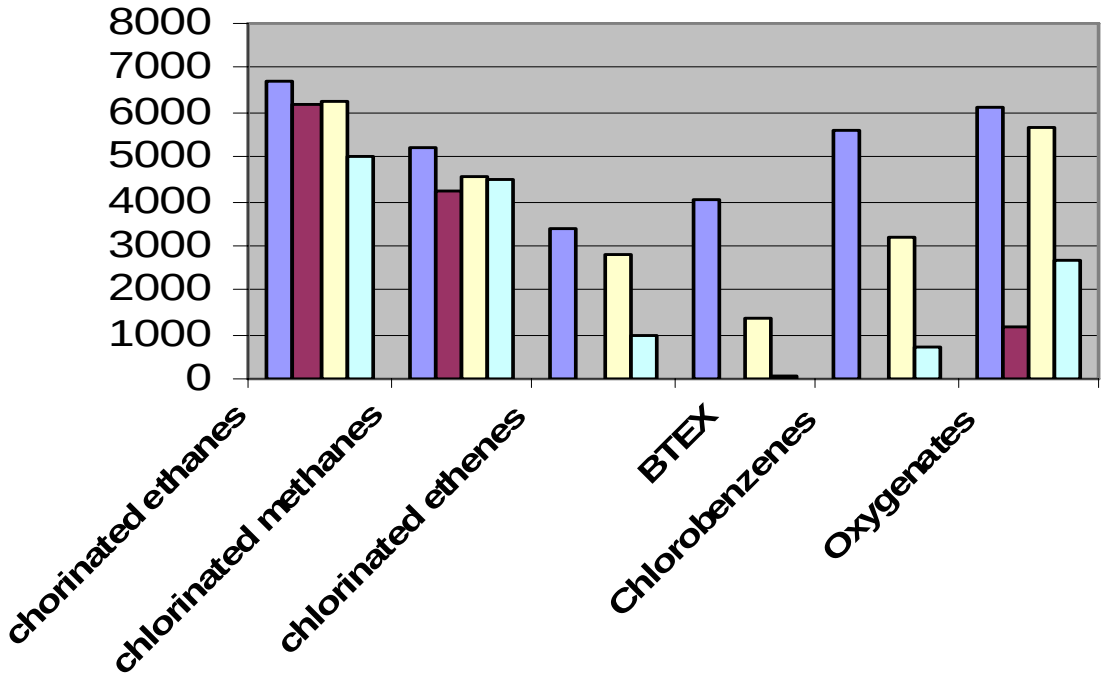
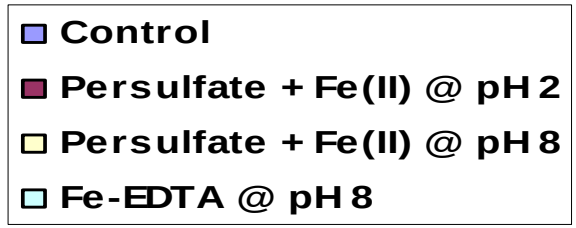
Chelated Metal Catalysts





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

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

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Novel Persulfate Activation

Hydrogen Peroxide Activation

$S_2O_8^{-2} + H_2O_2 \rightarrow SO_4\bullet + 2OH^*$

- 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% H2O2

100 g of solution

Data from ORIN RT

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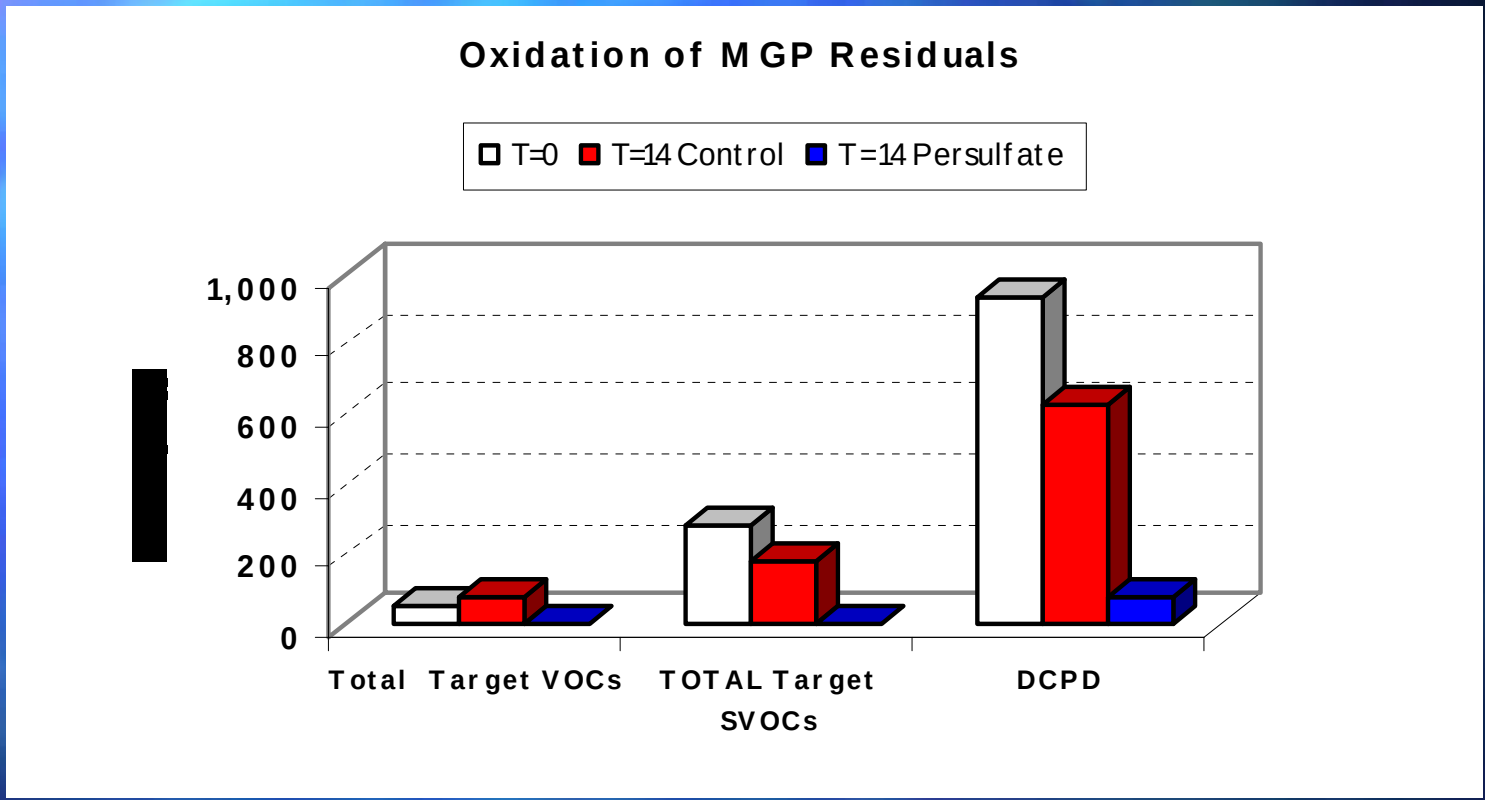
Hydrogen Peroxide Activation



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

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

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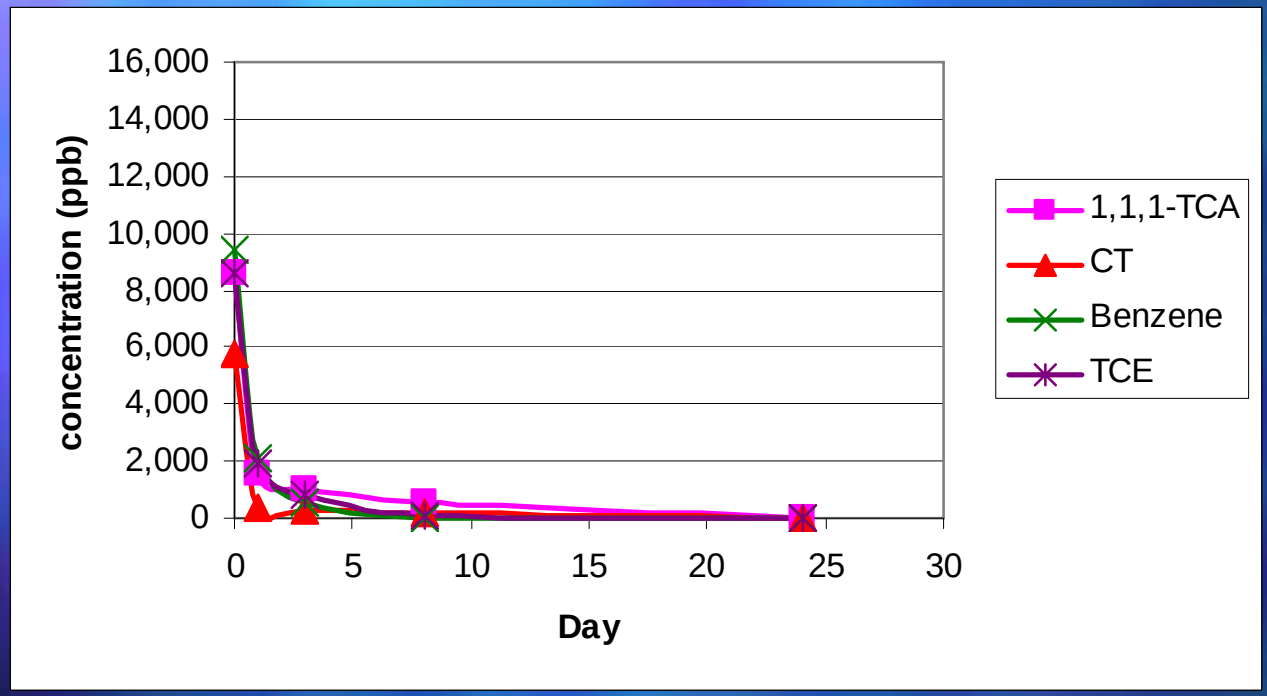
Hydrogen Peroxide Activation

Decomposition of Contaminants by Persulfate + Peroxide



Room temp
300 mL water
150 g soil
(KMnO4 SOD 9 – 13 g / kg)

5 g/L sodium persulfate
50 g 17.5% peroxide

- **Advantages: broad applicability including chlorinated ethanes and methanes**

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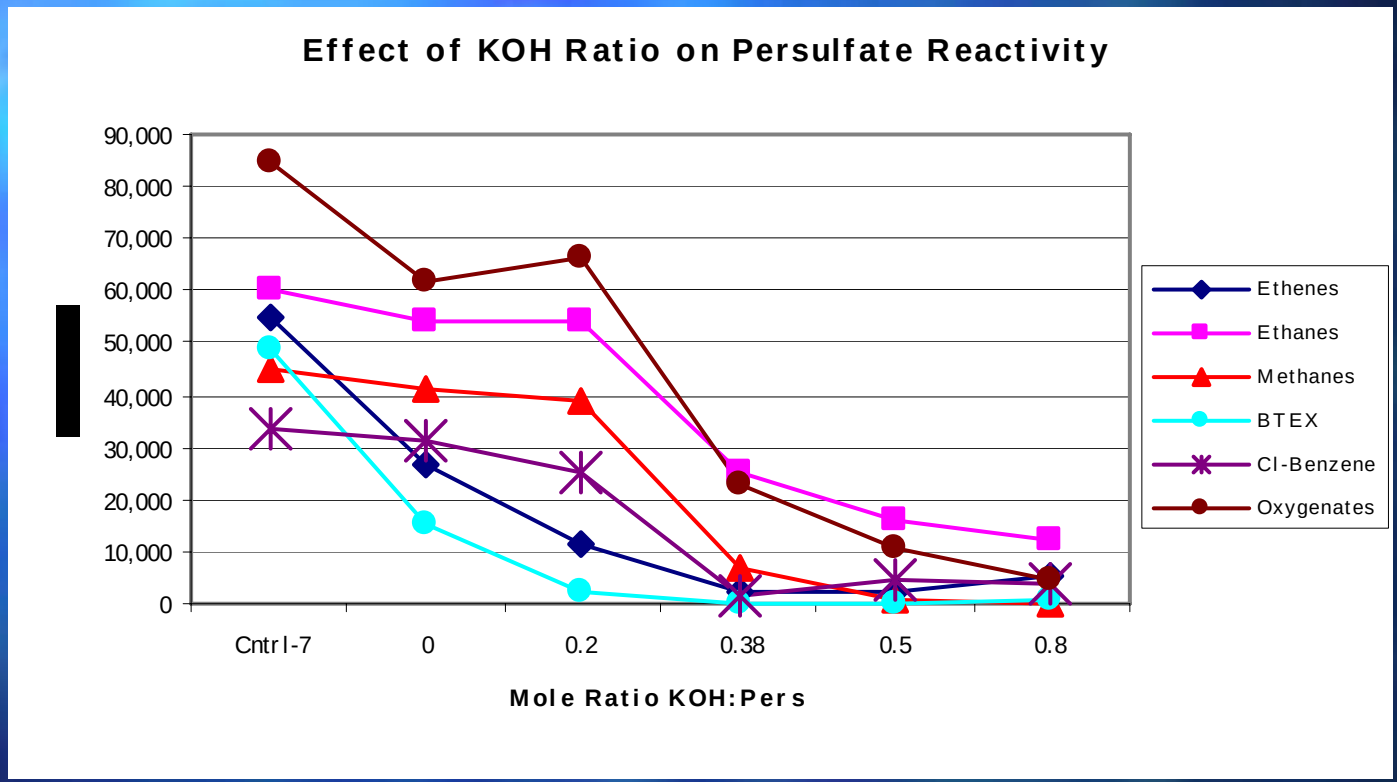
Novel Persulfate Activation

Alkaline Activation

- pH > 10



Room temperature
Aqueous solutions
7 days
Analyzed by GC-MS

25 g/L sodium persulfate
KOH as pH modifier

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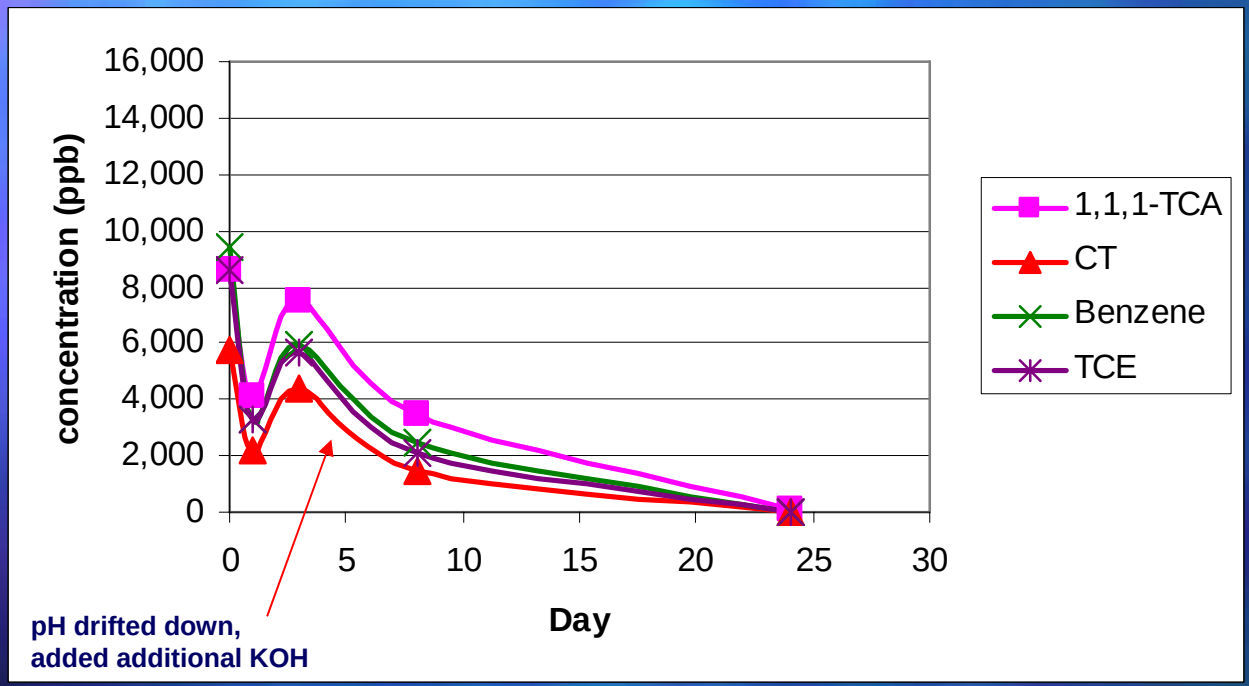
Novel Persulfate Activation

Alkaline Activation

Decomposition of Contaminants by Alkaline Activation



Room temp
300 mL water
150 g soil
(KMnO4 SOD 9 – 13 g / kg)

5 g/L sodium persulfate
0.01 mol / L KOH

- **Advantages: broad applicability including chlorinated ethanes and methanes**

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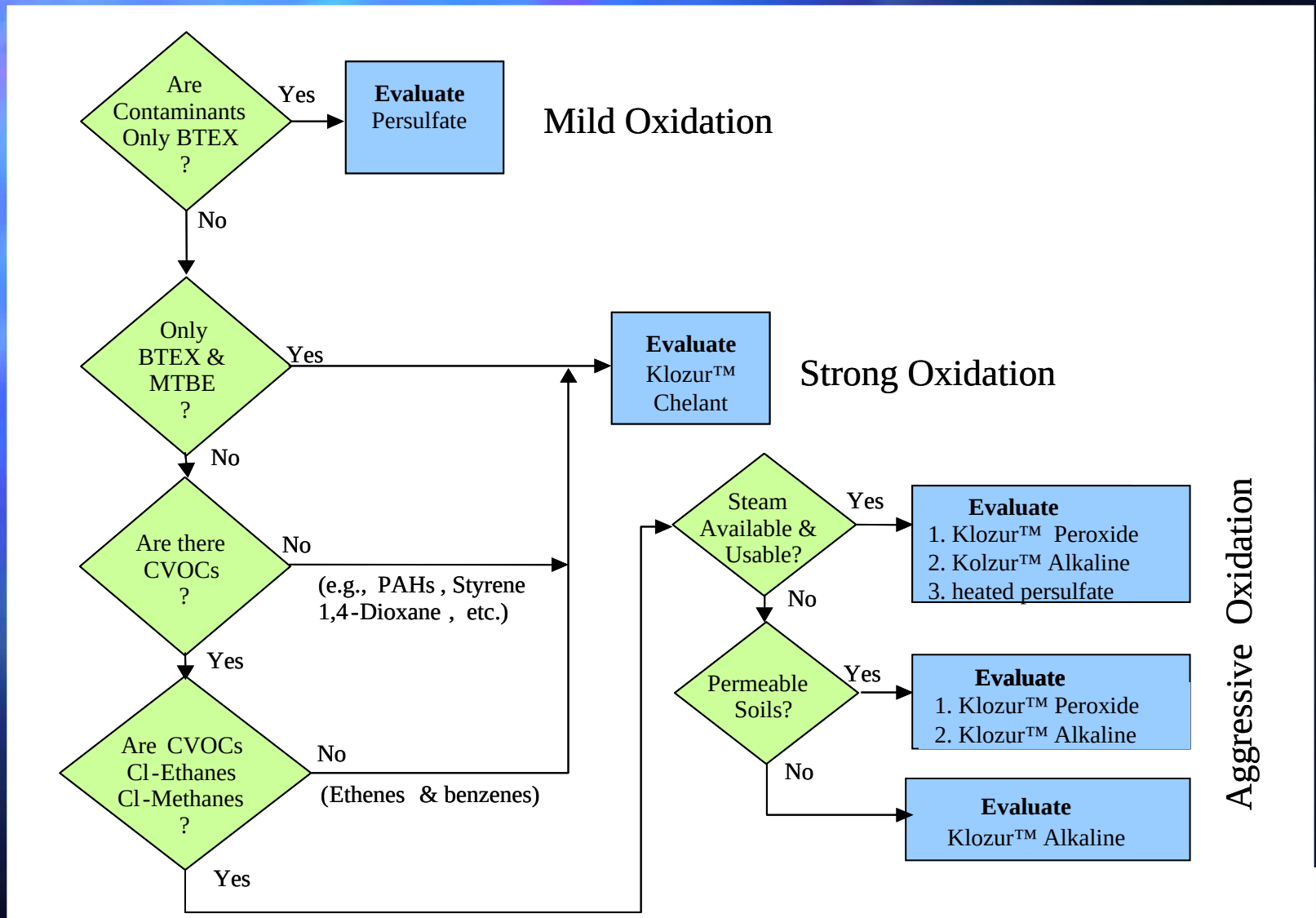
Selection of Activation Technology

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



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