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Novel Activation Technologies for Sodium Persulfate

*In Situ* Chemical Oxidation

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Persulfate Oxidation Chemistry

Strong Oxidizer

Persulfate anion:

\[ \text{S}_2\text{O}_8^{2-} + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{HSO}_4^{-2} \]

\[ E^0 = 2.12 \text{ v} \]

In Comparison:

- \( \text{H}_2\text{O}_2 \) \( E^0 = 1.8 \text{ v} \)
- \( \text{OH}^{-} \) \( E^0 = 2.7 \text{ v} \)
- \( \text{MnO}_4^{-} \) \( E^0 = 1.7 \text{ v} \)

Sulfate radical:

\[ \text{SO}_4^{\cdot-} + \text{e}^- \rightarrow \text{SO}_4^{2-} \]

\[ E^0 = \sim 2.6 \text{ v} \]

Simplified Reaction

Persulfate + CoC → CO\(_2\) + H\(_2\)O

kinetically slow

need to activate
**Conventional Persulfate Activation**

**Heat**

\[ S_{2}O_{8}^{2-} + \text{heat} \rightarrow 2 \text{SO}_{4}^{2-} \]

**Compounds with > 90% Decomposition** Treat with Persulfate

<table>
<thead>
<tr>
<th>20 ºC</th>
<th>35 ºC</th>
<th>45 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>Benzene</td>
<td>1,1,1-TCA</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>Chlorobenzene</td>
<td>Chloroform</td>
</tr>
<tr>
<td>Xylene</td>
<td>1,2-DCE</td>
<td>Methylene Chloride</td>
</tr>
<tr>
<td>1,1-DCE</td>
<td>PCE</td>
<td></td>
</tr>
<tr>
<td>1,2-Dichlorobenzene</td>
<td>TCE</td>
<td></td>
</tr>
<tr>
<td>1,3-Dichlorobenzene</td>
<td>1,1-DCA</td>
<td></td>
</tr>
<tr>
<td>1,2,4-Trichlorobenzene</td>
<td>1,2-DCA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MTBE</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vinyl Chloride</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carbon Tetrachloride</td>
<td></td>
</tr>
</tbody>
</table>

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

\[ \text{S}_2\text{O}_8^{2-} + \text{M}^{2+} \rightarrow \text{M}^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{•} \]

- **Advantage:**
  - BTEX
  - Chlorinated Ethenes
  - Chlorobenzenes
  - MTBE

- **Disadvantage:** precipitation of \( \text{Fe(OH)}_3 \) reduces availability of catalyst

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

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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
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
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

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Novel Persulfate Activation

Hydrogen Peroxide Activation

$S_{2}O_{8}^{2-} + H_{2}O_{2} \rightarrow SO_{4}^{+} + 2OH^{*}$

- multi-radical attack
- removal of SOD by peroxide

<table>
<thead>
<tr>
<th>Contaminant (mg/L)</th>
<th>Time 0</th>
<th>Day 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1-DCE</td>
<td>4.5</td>
<td>0.1</td>
</tr>
<tr>
<td>TCE</td>
<td>2.8</td>
<td>Non Detectable</td>
</tr>
<tr>
<td>1,1-DCA</td>
<td>1.1</td>
<td>Non Detectable</td>
</tr>
<tr>
<td>1,1-TCA</td>
<td>12.0</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Degradation of Contaminants with Persulfate + Peroxide

- Room temp
- Aqueous soln
- 2 g persulfate
- 8 mL 12.5% H2O2
- 100 g of solution

Data from ORIN RT

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**Novel Persulfate Activation**

**Hydrogen Peroxide Activation**

**Oxidation of MGP Residuals**

- **T=0**
- **T=14 Control**
- **T=14 Persulfate**

**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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Novel Persulfate Activation

Hydrogen Peroxide Activation

Decomposition of Contaminants by Persulfate + Peroxide

- Advantages: broad applicability including chlorinated ethanes and methanes

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

5 g/L sodium persulfate
50 g 17.5% peroxide
Novel Persulfate Activation

Alkaline Activation
• pH > 10

Effect of KOH Ratio on Persulfate Reactivity

Room temperature
Aqueous solutions
7 days
25 g/L sodium persulfate
KOH as pH modifier
Analyzed by GC-MS
Novel Persulfate Activation

Alkaline Activation

Decomposition of Contaminants by Alkaline Activation

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

Room temp
300 mL water
150 g soil
(KMnO4 SOD 9 – 13 g / kg)
5 g/L sodium persulfate
0.01 mol / L KOH

pH drifted down, added additional KOH
# Selection of Activation Technology

## Efficacy Matrix

<table>
<thead>
<tr>
<th>Technology</th>
<th>BTEX</th>
<th>chlorinated ethenes</th>
<th>chlorinated ethanes</th>
<th>MTBE</th>
<th>PCB</th>
<th>1,4-dioxane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-activated Sodium Persulfate</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>Sodium Persulfate + Fe(II)</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
<td>?</td>
<td>Y</td>
</tr>
<tr>
<td>Sodium Persulfate + Heat</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Persulfate with Chelated Metals</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
<td>?</td>
<td>Y</td>
</tr>
<tr>
<td>Persulfate with Hydrogen Peroxide Activation</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>?</td>
<td>Y</td>
</tr>
<tr>
<td>Persulfate with Alkaline Activation</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
</tbody>
</table>
Selection of Activation Technology

Are Contaminants Only BTEX?

- Yes: Evaluate Persulfate
- No: Only BTEX & MTBE?
  - Yes: Evaluate Klozur™ Chelant
  - No: Are there CVOCs?
    - Yes: Are CVOCs Cl-Ethanes Cl-Methanes?
      - Yes: Evaluate Klozur™ Peroxide
      - No: Permeable Soils?
    - No: (e.g., PAHs, Styrene, 1,4-Dioxane, etc.)

Mild Oxidation

Strong Oxidation

Evaluate 1. Klozur™ Peroxide
2. Klozur™ Alkaline
3. heated persulfate

Evaluate Klozur™ Alkaline

Evaluate Klozur™ Alkaline

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