In Situ Chemical Oxidation of Gasoline Compounds Using Persulfate

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In Situ Chemical Oxidation (ISCO)

Contemporary oxidants
- Potassium Permanganate (KMnO$_4$)
- Hydrogen Peroxide (H$_2$O$_2$)
- Sodium Persulfate (Na$_2$S$_2$O$_8$)

• Oxidant choice
  - Interaction with aquifer materials
  - Reactivity with organic compounds
Oxidant Choice

- MnO$_4^-$ (Permanganate)
  - High TOC/reductant => High NOD
    - Unproductive oxidant consumption
  - Ineffective against PHCs etc.
Oxidant Choice

- $\text{H}_2\text{O}_2$ (Hydrogen Peroxide)
  - Enhanced decomposition rates
  - Limited radius of influence
Oxidant Choice

• $\text{S}_2\text{O}_8^{2-}$ (Persulfate)
  – Limited and contradictory literature
  – Complex oxidation/activation chemistry
    • Potentially complex interaction with aquifer materials on activation
    • Newest activation schemes
      – $\text{H}_2\text{O}_2$, High pH, Chelated Ferrous
Persulfate

– High oxidation potential on activation
  \( (E^\circ = 2.6 \text{ V}) \)

– Potentially widespread reactivity

– High aqueous solubility (~550 g/L)
ISCO Applications

Understanding Persulfate

– Persistence in aquifer media
  • Activation strategies: Natural, H₂O₂, Fe(II), pH

– Oxidation of prevalent target organics (PHCs)
Objective 1: Persistence

• Function of
  – Auto-decomposition
  – Reactions with non-target chemicals in soil
  – Interaction with activating agents
Overview of Investigations

– Bench-scale (7 aquifer materials)
  • Batch Tests (1 and 20 g/L)
  • Column Tests
– Pilot-scale (CFB Borden)
  • Push-Pull Tests
Batch Reactor

- 100 mL H$_2$O
- 100 g aquifer material
- 100 mL persulfate solution (1 and 20 g/L)
- Persulfate spike
- 100 g aquifer material
Batch Tests

Temporal sampling for persulfate, pH

Pre and post-oxidation analyses for COD
Batch Results (1 g/L)
Batch Results (1 g/L)

![Graph showing batch results with time in days on the x-axis and C/C₀ on the y-axis. The graph compares Control, DNTS, and LSU treatments.](image)
Batch Results (1 g/L)

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>C/Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
</tr>
<tr>
<td>4</td>
<td>0.6</td>
</tr>
<tr>
<td>6</td>
<td>0.4</td>
</tr>
<tr>
<td>8</td>
<td>0.2</td>
</tr>
</tbody>
</table>

- Borden: 16 days
- DNTS: 174 days
- LAAPLSU: 174 days
- MAAPNIROPUSU: 174 days
- Control: 16 days
Batch Results (20 g/L)

Time (days)

C/C₀

153 days
COD Reduction

COD (g O₂/Kg aquifer material)

- Preoxidation
- Postoxidation (1 g/L)
- Postoxidation (20 g/L)

Borden  DNTS  LAAP  LSU  MAAP  NIROP  USU

COD (g O₂/Kg aquifer material)
Effect on pH

1 g/L

20 g/L

Time (days)

pH

Time (days)
## Summary of kinetic data

<table>
<thead>
<tr>
<th>Aquifer Material</th>
<th>Half-life, $t_{1/2}$ (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 g/L</td>
</tr>
<tr>
<td>Borden</td>
<td>174</td>
</tr>
<tr>
<td>DNTS</td>
<td>117</td>
</tr>
<tr>
<td>LAAP</td>
<td>185</td>
</tr>
<tr>
<td>LSU</td>
<td>16</td>
</tr>
<tr>
<td>MAAP</td>
<td>188</td>
</tr>
<tr>
<td>NIROP</td>
<td>36</td>
</tr>
<tr>
<td>USU</td>
<td>78</td>
</tr>
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</table>
## Degradation Rate Controlling Factors

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$k_{\text{obs}} = f$ (TOC, Fe-Amor)</th>
<th>$R^2 = 0.92$</th>
<th>$k_{\text{obs}} = f$ (COD)</th>
<th>$R^2 = 0.95$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 g/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 g/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Concentration of persulfate
- Exposure time
- Dissolution and exposure of minerals due to $H^+$ production
Objective 2: Treatability of Gasoline

• To evaluate utility of persulfate in treatment of gasoline compounds i.e.
  – Effectiveness at two persulfate concentrations
  – Effectiveness and efficiency using different persulfate activation strategies
    • Chelated Fe(II)
    • $\text{H}_2\text{O}_2$
    • Natural (aquifer materials)
Gasoline compounds

• Prevalence, persistence and toxicity
  – Benzene, Toluene, Ethylbenzene, Xylenes (BTEX)
  – Trimethylbenzenes (TMBs)
  – Naphthalene

• Petroleum hydrocarbon fractions
  – F1 \((C_6 - C_{10})\)
  – F2 \((C_{10} - C_{16})\)
  – TPH (Total Petroleum Hydrocarbons)
Treatments

API Standard Gasoline @ ~25 mg/L
- Control

- Unactivated System
  - 1 or 20 g/L Persulfate

- Activated System @ 20 g/L Persulfate
  - Peroxide
    - 0.1 or 1.0 mol $\text{H}_2\text{O}_2$/mol $\text{S}_2\text{O}_8^{2-}$
  - Chelated Fe (II) (w/ Citric acid 1:1 molar ratio)
    - 150 or 600 mg/L Fe(II)
  - Natural
    - Two aquifer materials: Borden, LSU
Batch Reactor Systems (Aqueous)

19 mL aqueous solution

• Gasoline ~25 mg/L

• Persulfate @ 1 or 20 g/L

and

• Peroxide – 0.1 or 1.0 mol \( \text{H}_2\text{O}_2/\text{mol S}_2\text{O}_8^{2-} \)

or

• Chelated Fe(II) – 150 or 600 mg/L
Batch Reactor Systems (Solids)

- 30 mL aqueous solution
  - Gasoline ~25 mg/L
  - Persulfate @ 20 g/L

- 30 g soil mass
  - Borden or LSU-LC34
Benzene Results

![Graph showing benzene results over time.](image)

- **C/C₀** represents the ratio of current concentration to initial concentration.
- **Time (days)** is plotted on the x-axis, ranging from 0 to 30 days.
- **Control** line indicates the trend of benzene concentration over time with error bars.
Benzene Results

The graph shows the concentration of benzene (C/C₀) over time (in days) for two conditions: Control and 1 g/L. The bars indicate the mean with error bars representing the standard deviation.
Benzene Results

- **Time (days)**: 0, 1, 0.2, 0.4, 0.6, 0.8, 1, 1.2
- **C/C_0**:
  - Control: 1 g/L, 20 g/L

The graph shows the concentration ratio (C/C_0) over time (days) for different concentrations and time points.
Benzene Results

![Graph showing benzene results over time for different concentrations of peroxyde.]
Benzene Results

![Graph showing benzene results over time with different conditions: Control, 20 g/L, 20 g/L and 0.1 Peroxide, 20 g/L and 1.0 Peroxide. The graph plots C/C₀ against Time (days).]
Benzene Results

Control
20 g/L
20 g/L and 150 mg/L Fe(II)
20 g/L and 600 mg/L Fe(II)
Benzene Results

![Graph showing the concentration of benzene over time for different conditions: Control, 20 g/L, Control Borden, and Borden. The graph plots time in days on the x-axis and concentration ratio (C/C₀) on the y-axis.](image-url)
**Benzene Results**

![Graph showing the decrease of Benzene concentration over time for different conditions.](image)

- **Time (days)**
- **C/C₀**

Conditions:
- **Control**
- **1 g/L**
- **20 g/L**
- **0.1 Peroxide**
- **20 g/L and 0.1 Peroxide**
- **1.0 Peroxide**
- **20 g/L and 1.0 Peroxide**
- **20 g/L and 150 mg/L Fe(II)**
- **20 g/L and 600 mg/L Fe(II)**
- **Control Borden**
- **Borden**
- **Control LSU**
- **LSU**
Benzene Results

![Graph showing the results of benzene degradation over time for different concentrations and treatments.](Graph.png)
Benzene Results

![Graph showing the decline of benzene concentration over time for various conditions.](image-url)
Toluene Results

![Toluene Results Graph]

- **Control** Borden
- 1 g/L
- 20 g/L
- 0.1 Peroxide
- 20 g/L and 0.1 Peroxide
- 1.0 Peroxide
- 20 g/L and 1.0 Peroxide
- 20 g/L and 150 mg/L Fe(II)
- 20 g/L and 600 mg/L Fe(II)
- Control Borden
- Borden
- Control LSU
- LSU

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</tr>
<tr>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>0.6</td>
<td>0.05</td>
</tr>
<tr>
<td>0.8</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Toluene Results

![Graph showing Toluene Results with various conditions and control groups.](image)
Ethylbenzene Results

Time (days)

C/C₀

Control
1 g/L
20 g/L
0.1 Peroxide
20 g/L and 0.1 Peroxide
1.0 Peroxide
20 g/L and 1.0 Peroxide
20 g/L and 150 mg/L Fe(II)
20 g/L and 600 mg/L Fe(II)
Control Borden
Borden
Control LSU
LSU
Xylenes Results

**o Xylene**

**m,p Xylene**

- Control
- 1 g/L
- 20 g/L
- 0.1 Peroxide
- 20 g/L and 0.1 Peroxide
- 1.0 Peroxide
- 20 g/L and 1.0 Peroxide
- 20 g/L and 150 mg/L Fe(II)
- 20 g/L and 600 mg/L Fe(II)
- Control Borden
- Borden
- Control LSU
- LSU
Xylenes Results

**o Xylene**

- Control
- 1 g/L
- 20 g/L
- 0.1 Peroxide
- 20 g/L and 0.1 Peroxide
- 1.0 Peroxide
- 20 g/L and 1.0 Peroxide
- 20 g/L and 150 mg/L Fe(II)
- 20 g/L and 600 mg/L Fe(II)
- Control Borden
- Borden
- Control LSU
- LSU

**m,p Xylene**

- Control
- 1 g/L
- 20 g/L
- 0.1 Peroxide
- 20 g/L and 0.1 Peroxide
- 1.0 Peroxide
- 20 g/L and 1.0 Peroxide
- 20 g/L and 150 mg/L Fe(II)
- 20 g/L and 600 mg/L Fe(II)
- Control Borden
- Borden
- Control LSU
- LSU

- C/Co
- Time (days)
TMB Results

1,2,3 - Trimethylbenzene

Control
1g/L
20 g/L
0.1 Peroxide
20 g/L and 0.1 Peroxide
1.0 Peroxide
20 g/L and 1.0 Peroxide
20 g/L and 150 mg/L Fe(II)
20 g/L and 600 mg/L Fe(II)
Control Borden
Borden
Control LSU
LSU
TMB Results

1,2,3 - Trimethylbenzene

- Control
- Control Borden
- Control LSU
- 1 g/L
- 20 g/L
- 0.1 Peroxide
- 20 g/L and 0.1 Peroxide
- 1.0 Peroxide
- 20 g/L and 1.0 Peroxide
- 20 g/L and 150 mg/L Fe(II)
- 20 g/L and 600 mg/L Fe(II)

C/C₀ vs Time (days)
Naphthalene Results

![Graph showing the effect of various treatments on naphthalene concentrations over time. The x-axis represents time in days, ranging from 0 to 30, and the y-axis represents the ratio of naphthalene concentration (C/C₀) ranging from 0 to 1.2. The graph includes lines for different treatments such as Control, 1 g/L, 20 g/L, 0.1 Peroxide, 20 g/L and 0.1 Peroxide, 1.0 Peroxide, 20 g/L and 1.0 Peroxide, 20 g/L and 150 mg/L Fe(II), 20 g/L and 600 mg/L Fe(II), Control Borden, Borden, Control LSU, and LSU. Each treatment is represented by a different color and marker, allowing for easy comparison of results.]
Bulk Petroleum Hydrocarbon Fractions Results

F1  C₆ - C₁₀
Bulk Petroleum Hydrocarbon Fractions Results

F2 C_{10} - C_{16}
Bulk Petroleum Hydrocarbon Fractions Results

F2  \( C_{10} - C_{16} \)
Total Petroleum Hydrocarbons (TPH) Results

![Graph showing TPH results over time for different treatments.]

- **Control**
- **1 g/L**
- **20 g/L**
- **0.1 Peroxide**
- **20 g/L and 0.1 Peroxide**
- **1.0 Peroxide**
- **20 g/L and 1.0 Peroxide**
- **20 g/L and 150 mg/L Fe(II)**
- **20 g/L and 600 mg/L Fe(II)**
- **Control Borden**
- **Borden**
- **Control LSU**
- **LSU**
Conclusions

• Persulfate appears to follow first order degradation in presence of aquifer materials
  – More stable at higher concentration

• Rate constants are highly correlated with reductive properties (COD, Fe-Amor, TOC)
Conclusions

• Unactivated persulfate at high concentration (~20 g/L) is capable of oxidizing gasoline compounds

• Activation of persulfate by peroxide and chelated ferrous iron enhances the oxidation rates in general
Conclusions

• Chelated ferrous produced the best results for BTEX, TMBs and F1 oxidation
  – F2 treatment was not effective

• Optimal molar ratio of peroxide to persulfate may be required for maximizing oxidation of gasoline
Conclusions

- F1 fraction was readily oxidizable
- F2 fraction stalled after nearly 60% oxidation
Acknowledgements

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