CATALYZED HYDROGEN PEROXIDE ACTIVATED SODIUM PERSULFATE REMEDIATION OF PETROLEUM AT AN ACTIVE FUEL STORAGE FACILITY

By:
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Project Challenge

- Site/operational issues
- Tight matrices & NAPL
- Regulatory permitting

Select technology to:
  - Efficiently and safely desorb contaminants
  - Optimize sequential treatment train
  - Eliminate rebound by rapid total mass destruction
# Saturated Zone Remediation (Groundwater AND Saturated Soil)

- Get it done.....now, cost-effectively and permanently
- Project drivers/motivators

<table>
<thead>
<tr>
<th>Driving Factor</th>
<th>Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost</td>
<td>Biological enhancements, mass transfer (SVE, sparging)</td>
</tr>
<tr>
<td>Time</td>
<td>In-Situ-Chemical Oxidation (ISCO)</td>
</tr>
<tr>
<td>Process Optimization (Life Cycle Cost &amp; Time)</td>
<td>Treatment train (combination of technologies including ISCO)</td>
</tr>
</tbody>
</table>
ISCO Process
Continuous Refinement

ISCO = introducing oxidizing reagents/chemicals into the subsurface to permanently destroy organic contaminants via active oxidation.

Steps for effective ISCO:
• Oxidant and Reagent Screening
• Oxidation Estimating Tool (OET; Modeling)
• Design Parameter Evaluation
• Field Application (Pilot; Full-Scale)
# Chemical Oxidant Screening

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Volts^{(1)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrofluoric Acid (HF)</td>
<td>3.0</td>
</tr>
<tr>
<td>Hydroxyl Radical (OH•)</td>
<td>2.7</td>
</tr>
<tr>
<td>Sulfate Radical (SO₄•)</td>
<td>2.6</td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>2.4</td>
</tr>
<tr>
<td>Sulfate (S₂O₈⁻²)</td>
<td>2.1</td>
</tr>
<tr>
<td>Hydrogen Peroxide (H₂O₂)</td>
<td>1.8</td>
</tr>
<tr>
<td>Permanganate (MnO₄⁻)</td>
<td>1.7</td>
</tr>
<tr>
<td>Chlorine (Cl₂)</td>
<td>1.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ISCO Technology</th>
<th>By Contaminant</th>
<th>Speed to Treat NAPL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BTEX</td>
<td>Chlorinated ethenes</td>
</tr>
<tr>
<td>FMC’s Klozur™</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>Activated Persulfate</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>Fenton’s Chemistry</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>Ozone</td>
<td>H</td>
<td>H</td>
</tr>
</tbody>
</table>

Legend:  
H – highly effective  
E – effective  
N – not effective
Activated Persulfate

• Persulfate can be activated several ways:
  - Presence of a transition metal
  - Heat (~95°F/35°C for benzene)
  - Hydrogen peroxide
  - High pH

• When combined with iron-catalyzed hydrogen peroxide, persulfate can be activated by several activation methods

• For sodium persulfate, sodium sulfate is a byproduct and it has a USEPA secondary maximum contaminant level of 250 ppm
Activated Sodium Persulfate Remediation Sites

- Industrial (active facilities; closed facilities)
- Fuel bulk storage and fuel distribution (pipeline)
- Gasoline Stations (active facilities; closed facilities)
- Commercial (office buildings, shopping centers)
- Residential (single family; multi-story/family)
- Active streets
Chemical Oxidant Goals and Process Optimization

• Goals
  - Enhance desorption
  - Persistent oxidation
  - Maximize oxidant radicals
  - Elimination of DNAPL
  - No rebound

• In-situ chemical oxidation technologies selected
  - Catalyzed hydrogen peroxide (CHP)
  - Activated sodium persulfate

• Methods
  - Induce groundwater flow/reagent dispersion
    - Temp < 180°F (82°C)
  - Real-time monitoring and reaction control/management
  - Maintain pressure < 10 psig
  - Manage reaction by controlled application of reagents
Overview of Selected Technologies

• Catalyzed hydrogen peroxide (simplified):
  $\text{H}_2\text{O}_2 + \text{Fe}^{+2} + \text{Contaminant} \rightarrow \text{acid} \quad \text{OH}^+ + \text{OH}^- + \text{Fe}^{+3} + \text{OH}^- + \text{Contaminant} \quad \text{CO}_2$

• Activated Persulfate (simplified):
  $\text{activation} \quad \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^- \cdot + \text{SO}_4^- \cdot + \text{e}^- + \text{Contaminant} \quad \text{SO}_4^{2-} + \text{CO}_2 + \text{H}_2\text{O}$

• Occurs effectively only in the saturated zone
Laboratory Treatability Test

• MECX’s Oxidation Estimating Tool (OET) is predictive empirical model to estimate overall oxidant demand (OD)

• Stochiometry is only a small fraction of the actual oxidant required for ISCO

• Treatability test is run on several formulations to develop an efficiency curve and confirm OD

• The primary purposes of the OET are:
  1. To determine the reactivity of the site media
  2. To select the optimum reagent formulation
  3. To observe site-specific reactions
Persulfate Safety

- All oxidizing chemicals require careful handling/use.
- Equipment compatibility (stainless steel ideal)
- Other metals (i.e., iron) cause decomposition
- pH of persulfate solutions decrease over time, and may drop <2
- PPE: eyewear, gloves, chemical resistant shoes, respiratory (dust)
- Storage (dry media): cool dry storage area until use
- Store (liquid solution): in vented vessels
Site Background

- Lithology: clay with silt and sand lenses
- Dissolved plume size: 9,000 ft² (~840 m²)
- Free-phase petroleum/NAPL plume size: 2,800 ft² (~260 m²)
- Depth to target treatment zone: 4 ft (1.2 m)? 8 ft (2.4 m)? 17 ft (5.2)?
- Treatment zone vertical thickness: 10 ft (3 m)
- Unpaved area
- Immediately adjacent to full and active gasoline bulk fuel storage tank
## Understanding Site Lithology

### Soil Description Table

<table>
<thead>
<tr>
<th>DEPTH FEET</th>
<th>SOIL DESCRIPTION</th>
<th>SAMPLE NUMBER</th>
<th>SAMPLE TYPE</th>
<th>CVIA (ppm)</th>
<th>REMARKS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Dark brown sandy silt Loamy (CL)</td>
<td>1</td>
<td>CT</td>
<td>&gt; 1,000</td>
<td>Strong gasoline odors 0-2 feet</td>
</tr>
<tr>
<td>2.5</td>
<td></td>
<td>2</td>
<td></td>
<td>&gt; 1,000</td>
<td></td>
</tr>
<tr>
<td>5.8</td>
<td>Red orange and gray beached/sandy sand</td>
<td>1</td>
<td></td>
<td>&gt; 0.095</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td></td>
<td>&gt; 0.095</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>Tan and gray sandy clay (CL)</td>
<td>5</td>
<td></td>
<td>&gt; 0.095</td>
<td>Odors decrease 9 feet - 10 feet Strong odors 10 feet - 12 feet</td>
</tr>
<tr>
<td>12.5</td>
<td>Tan and red clayey sandy clay (CL)</td>
<td>6</td>
<td></td>
<td>&gt; 1.002</td>
<td></td>
</tr>
<tr>
<td>15.9</td>
<td>Tan and red sandy clay (CL) with iocronite and some large quartz particles</td>
<td>7</td>
<td></td>
<td>&gt; 1.002</td>
<td></td>
</tr>
<tr>
<td>17.5</td>
<td>Tan and orange sandy sandstone (CP) unconsolidated</td>
<td>9</td>
<td></td>
<td>600</td>
<td>Water on roots at 17 feet</td>
</tr>
<tr>
<td>20.0</td>
<td>Tan and red sandy loamy sandstone with sand</td>
<td>10</td>
<td></td>
<td>150</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>11</td>
<td>CT</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>22.0</td>
<td></td>
<td>12</td>
<td></td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>Bottom of boring at 25 feet</td>
<td>13</td>
<td></td>
<td>23</td>
<td></td>
</tr>
</tbody>
</table>

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**Actual NAPL/contaminant zone**

**Zone erroneously identified as ISCO target prior to MECX review**

**Site Characterization Screened Zone**
Initial Application/Field Pilot

- Application of reagents to 8 wells
- 10-day application
- Total mass destruction of 84%
- Effective treatment radius of 7-17 ft (2.1-5.2 m)
- No disruption to on-site business operations
MEC\textsuperscript{x} ISCO Reagent Delivery

Critical Controls:
- Pressure
- Temperature
- Flow Rate
- Concentration

MEC\textsuperscript{x} Reagent Distribution Manifold

MEC\textsuperscript{x} ISCO Wellhead
MEC\textsuperscript{x} Temperature Monitoring
Full-Scale Application

- Application of reagents simultaneously to 92 wells
- Single 28-day application
- Effective treatment radius of up to 16 ft (4.9 m) in dissolved and 8 ft (2.4 m) in NAPL
- No disruption to on-site business operations
Treatment Area D Site Plan
Treatment Area D
Daily Temperature Trend

- Peak Temperature (172.3 °F)
- Soil is becoming contaminated
- NAPL Encountered
- Stop daily oxidizer
- Begin daily oxidizer

MECX, LP
www.mecx.net
A Service-Disabled Veteran Owned Small Business
Application Cycle Temperature
Dissolved Concentrations

- Benzene
- MTRF

MECX ISCO APPLICATION
Pre/Post Mass Distribution

Overall Mass Reduction: 88%
QUESTIONS?

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