Source Area MIP Investigation and Pilot-Scale Groundwater Remediation Using Activated Persulfate*

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Abstract

Background/Objectives. AECOM performed a pilot test at a site in Southern California to assess the applicability and effectiveness of in situ chemical oxidation (ISCO) using activated persulfate for treating residual gasoline free product and high concentrations of dissolved-phase petroleum hydrocarbons as gasoline, BTEX, and MTBE. A former leaking UST, which was removed in 1995, was the apparent source of soil and groundwater impacts at the site. Several site investigations were performed in the late 1990s and interim remedial actions were performed at the source area in the early 2000s.

Approach/Procedures. The pilot test was performed in 2010, starting with a membrane interface probe (MIP) investigation to characterize the lithology and total VOCs in the source area in high-resolution. The MIP results were then used to design the ISCO injection grid. Soil and groundwater samples were collected for a bench-scale study to evaluate the total oxidant demand (TOD) of three persulfate activation methods (iron, alkaline, and peroxide). The TOD results were then used to choose the most cost-effective activator and calculate reagent mass and volume.

6,600 lbs of sodium persulfate were mixed with 660 pounds of iron EDTA and water before being injected across the top 10 feet of the saturated zone using direct-push methods. Five groundwater monitoring events were performed: baseline and 1, 2, 3, and 6 months following the injection, to track changes in geochemical conditions, assess the distribution of injected reagent, and evaluate changes in VOC and metal concentrations.

Results/Conclusions. The MIP results indicated that the source in the unsaturated zone is beneath the former UST and sorbed onto tight silty soils. There is also a significant mass in the saturated zone set in more permeable/sandy soils. The bench-scale study indicated high TODs for alkaline and peroxide activation methods (approximately 20 grams of oxidant per kilogram of saturated soil [g/kg]) and a lower TOD for iron activation (4.8 g/kg).

Persulfate distribution and oxidation were achieved within the injection zone and as far as 20 feet cross-gradient and 35 feet downgradient of the
injection zone. Iron-activated persulfate was effective in reducing concentrations of dissolved-phase VOCs and enhancing free-phase desorption and dissolution. Concentration rebound was observed indicating that repeated injections would be required to achieve a sustained cleanup of the source area saturated zone.
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Problem Statement

Identification of release and contamination from aeronautical hydrocarbon release using active and passive remediation technologies: Evaluate 5,030-gallon gasoline underground storage tank

Remediation Program Goal

Reduction of the impact of gas and gasoline to acceptable risk-based levels.

Technical Objectives

- Mixed hydrocarbon characterization
- Pore water and groundwater analysis
- Groundwater modeling
- Ongoing groundwater monitoring since 2003

Pilot Test Technical Approach

- Bench-scale study using oxidant reaction vessels
- Pressure / Flow rate: 10 – 90 psi / 2.5 gpm (9.5 lpm)
- Injection interval: Vertical interval: 23’ – 33’ (7 – 10 m) bgs
- Total solution volume: Total BTEX = 2,300 mg/kg
- Sodium persulfate: Klozur™ sodium persulfate 6,600 lbs (3,000 kg)
- Solution concentrations: 11% – 20% by weight

Groundwater Results – Source Area

- Iron-activated sodium persulfate was effective in reducing concentrations of dissolved-phase COCs and enhancing free-phase desorption and dissolution in the source area.

Iron-Activated Persulfate Injection

- Concentrations of dissolved-phase COCs decreased significantly compared to baseline (50%-79%).

Injection Summary

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Pilot Test Conclusions

- Groundwater results from oxidant reaction vessel and pilot-scale monitoring confirmed the potential and practicality of using activated persulfate in the vadose zone and saturated zone.
- The initial effects of oxidation were exhibited as free-phase dissolution of MTBE followed by benzene (and gasoline-range hydrocarbons) desorption/dissolution in the source area, consistent with the expectations of the bench-scale study.
- ORP substantially increased following the injection indicating the presence of persulfate.
- ORP then gradually decreased thereafter indicating the gradual depletion of persulfate.

Bench-Scale Study

- Concentration reductions:
  - Total BTEX = 2,300 mg/kg
  - TPHg = 15,000 mg/kg
  - Total VOCs - 15’ bgs (center of vadose zone source)
  - Total VOCs - 25’ bgs (2’ below groundwater surface)

- Extent and magnitude:
  - Total BTEX = 1,400 mg/kg
  - TPHg = 9,000 mg/kg
  - Total VOCs -15’ bgs
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- Sorbed to tight silty soils
- ~30’ by 15’ (~10 m by 5 m) beneath the former UST
- Membrane Interface Probe (MIP) investigation
- In Groundwater
- Bench-Scale Study

- Iron-activated persulfate injection
- Injection Summary
- Pilot Test Conclusions
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Overview of ISCO

In Situ Chemical Oxidation

Chemical oxidation is a remediation technology that introduces oxidants to the contaminated subsurface by injection or mechanical mixing. Physical placement of the chemicals into the subsurface is referred to as in situ chemical oxidation (ISCO).

Effective chemical oxidation may be achieved using a strong oxidant only, or in combination with other chemicals that function as catalysts. The oxidants chemically react with contaminants, and convert them to non-toxic end products such as carbon dioxide and water.

In situ chemical oxidation is an attractive option at many hazardous waste sites, because:

- Complete contaminant destruction is possible
- Rapid treatment times are achievable
- It is a green and sustainable remedial option
- It is an innovative remedy, compatible with mechanical and biological cleanup approaches

Although a chemical oxidation reaction is relatively simple, not all oxidants react effectively with any given contaminant; therefore, selection of the appropriate oxidant is critical to successfully achieving the remediation endpoint.

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### Oxidant and Reactions

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Reactive Species</th>
<th>Form</th>
<th>Persistence (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanganate</td>
<td>MnO₂</td>
<td>powder/liquid</td>
<td>&gt;3 months</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>H₂O₂</td>
<td>liquid</td>
<td>minutes-hours</td>
</tr>
<tr>
<td>Ozone</td>
<td>O₃</td>
<td>gas</td>
<td>minutes-hours</td>
</tr>
<tr>
<td>Persulfate</td>
<td>SO₄²⁻</td>
<td>powder/liquid</td>
<td>hours-weeks</td>
</tr>
</tbody>
</table>

### Oxidant and Electrode Potential (V (2))

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Electrode Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanganate</td>
<td>1.7 V (permanganate ion)</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>1.8 V (hydrogen peroxide)</td>
</tr>
<tr>
<td>Ozone</td>
<td>2.1 V (ozone)</td>
</tr>
<tr>
<td>Persulfate</td>
<td>2.1 V (persulfate)</td>
</tr>
</tbody>
</table>

(1) Persistence of the oxidant varies depending on site-specific conditions. Durations specified here are based on general observations.

(2) Oxidants in parentheses; reduction potential is negative.