Remediation Technology Symposium (RemTech) 2012

In-Situ Chemical Oxidation (ISCO) Using Ozone Sparging for Treatment of Petroleum Hydrocarbon-Impacted Groundwater

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Presentation Overview

- Site Background
- Remedial Process Optimization
- Bench Scale Testing
- Capture Zone Analysis
- Pilot Test - In-Situ Chemical Oxidation (ISCO) Using Ozone


Site Background – Nature and Extent of Impacts

- Former Natural Gas processing station (1961 to late 1980’s)

- Chemicals of Concern identified in saturated zone:
  - Gasoline Range Organics (GRO)
  - Diesel Range Organics (DRO)
  - Motor Oil Range Organics (ORO)
  - Benzene, toluene, ethylbenzene, and xylenes (BTEX)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>GRO (µg/L)</th>
<th>DRO (µg/L)</th>
<th>ORO (µg/L)</th>
<th>Benzene (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td>1,600</td>
<td>5,000</td>
<td>770</td>
<td>25</td>
</tr>
<tr>
<td>Clean-up Levels</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>1</td>
</tr>
</tbody>
</table>

*Groundwater concentrations from 2011 Annual monitoring report.*
Site Background – Previous Relevant Activities

- **1999**: Vapor Intrusion Study
- **2005**: ORC Injection Study
- **2007**: Remedial Process Optimization
- **2009**: ISCO Bench Test

Additional Activities:
- **1999 - 2012**: Groundwater Extraction
- **2001 - 2006**: Soil Vapor Extraction/Air Sparging Remediation
- **2009**: ISCO Bench Test
- **2010**: ISCO Pilot Test
- **Targeted: 2013**: Full Scale ISCO Implementation
Remedial Process Optimization – Recommendations

- Both the AS/SVE system and the groundwater extraction system have reached the practical limits of COC mass removal and COC concentration reduction and will not produce significant additional COC mass removal.
- Shut down the groundwater extraction system
- Monitor the off-site groundwater concentrations
- Conduct an in-situ chemical oxidation (ISCO) Pilot Study - Study onsite conditions to evaluate the best ISCO product and approach (potassium permanganate, persulfate, ozone, etc.)
Bench Test
Bench Test Activities

- Collected soil from 12 to 26 feet bgs (8 kg total) in boring B-29
- Collected groundwater from MW-2 (24 L total)
- Homogenized samples
- Established six reactor studies to evaluate COC degradation, secondary impacts, and ozone demand
Bench Scale Test - Conclusions

- Ozone effective in removing DRO (primary COC) in impacted groundwater
- DRO removal in saturated soil appeared to be desorption/dissolution limited
- Ozone off-gas ~ 21 mg/L (a 30% ozone consumption within the reactors)
- Ozone demand of 8 to 12 mg ozone/ mg TPH
- Secondary by-products identified as hexavalent chromium, nitrate, bromate
Bench Scale Test - Recommendations

- Conduct pilot test to determine operating pressure and flow rate and estimate radius of influence (ROI) of ozone sparging system

- Ozone sparging should be pulsed to maximize ROI, minimize off-gassing, and maximize the use of ozone since COC removal in saturated soil appears to be desorption/dissolution limited

- Monitor attenuation of identified secondary COCs
Capture Zone Analysis

Approximate Plume Size

LEGEND:

6 Flowline Captured by Extraction Well (Travel Time = 6 months)
6.90 Simulated Water Contour Level
Capture Zone Analysis

Property Line
ISCO Ozone Pilot Test Approach

- Short-Term Ozone Sparge Test – determine appropriate injection pressure and flow rate, estimate injection pulse frequency and ROI

- Long-Term Ozone Sparging Test – evaluate the COC removal efficiency, secondary groundwater impacts, and off-gas emissions

- Post Sparging Monitoring – evaluate the COC rebound and attenuation of secondary groundwater impacts
### Treatment Zone Monitoring Well Network

<table>
<thead>
<tr>
<th>Well ID</th>
<th>Media Monitored</th>
</tr>
</thead>
<tbody>
<tr>
<td>EW-1</td>
<td>Groundwater – Performance</td>
</tr>
<tr>
<td>EW-3</td>
<td>Groundwater – Performance</td>
</tr>
<tr>
<td>EW-5</td>
<td>Groundwater – Performance</td>
</tr>
<tr>
<td>MW-2</td>
<td>Groundwater – Performance</td>
</tr>
<tr>
<td>MW-5</td>
<td>Groundwater – Performance</td>
</tr>
<tr>
<td>NMP-1-W</td>
<td>Groundwater – Performance</td>
</tr>
<tr>
<td>SV-1</td>
<td>Soil Vapor - Performance</td>
</tr>
<tr>
<td>SV-2</td>
<td>Soil Vapor - Performance</td>
</tr>
<tr>
<td>SV-3</td>
<td>Soil Vapor - Compliance</td>
</tr>
<tr>
<td>SV-4</td>
<td>Soil Vapor - Compliance</td>
</tr>
<tr>
<td>SV-5</td>
<td>Soil Vapor - Compliance</td>
</tr>
<tr>
<td>NMP-1-S</td>
<td>Soil Vapor - Performance</td>
</tr>
<tr>
<td>V-5</td>
<td>Soil Vapor - Performance</td>
</tr>
<tr>
<td>V-9</td>
<td>Soil Vapor - Performance</td>
</tr>
<tr>
<td>NMP-1-D</td>
<td>Soil Vapor - Performance</td>
</tr>
</tbody>
</table>
## Short Term Ozone Sparge Test

<table>
<thead>
<tr>
<th>Well</th>
<th>Injection Time (hours)</th>
<th>% Ozone by weight</th>
<th>Pressure (psi)</th>
<th>Flow Rate (cfm)</th>
<th>Concentration (g/m³)</th>
<th>Ozone Delivered (lbs/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS-1</td>
<td>8</td>
<td>0.56</td>
<td>4.5-5.5</td>
<td>2.5</td>
<td>7.2</td>
<td>1.62</td>
</tr>
<tr>
<td>OS-1</td>
<td>7</td>
<td>0.55</td>
<td>6.0-6.5</td>
<td>2.5-3.0</td>
<td>6.8</td>
<td>1.50</td>
</tr>
</tbody>
</table>

### Monitoring Specifics

- Four rounds soil gas
  - O₃, VOCs, O₂, CO₂, CH₄
- Three rounds groundwater
  - DO, dissolved O₃, ORP, pH, temperature, well head pressure, depth to water
Ozone Sparging Test

Long-Term Injection Specifics

- 2 months of injection
  - ~12.8 g/m³
  - 5.5 to 6.0 psi
  - 3.5 cfm
  - Equivalent to ~4 lb O₃/day (2 lb O₃/day to each injection well)
  - ROI ~20 ft
  - Alternating pulse period 60 minutes

Monitoring Specifics

- O&M site visits – two times a week
- GW and SG monitoring
- Inspected for leaks, proper injection parameters, fugitive emission monitoring
Long-Term Ozone Sparging Test - Results

- Concentrations of GRO and BTEX inside treatment zone typically non-detect;

- Concentrations of DRO had a decreasing trend with notable decreases;

- Concentrations of secondary impacts increased in the treatment zone to above water quality objectives
  - Hexavalent chromium as high as 44 μg/L (WQO 2 μg/L)
  - Bromate as high as 110 μg/L (WQO 10 μg/L)

- Increasing trends of ORP and DO in field measurements in the treatment zone during injection indicates an increased state of oxidation during injection.
Pilot Test Results - Groundwater COCs

Groundwater Concentration of TPHd in Treatment Zone Wells

- Injection Start
- Injection End

Date

TPHd Concentration (ug/L)


EW-1 MW-4 EW-5 NMP-1 MW-5 EW-3 Cleanup Level (TPHd 100 ug/L)
Pilot Test Results - Secondary Impacts: Bromate

Groundwater Concentration of Bromate in NMP-1

Injection Start

Injection End
Pilot Test Results - Secondary Impacts: Cr$^{+6}$

**Groundwater Concentration of Hexavalent Chromium in NMP-1**

- Injection Start: 12/8/2010
- Injection End: 2/6/2011

Date: 11/18/2010 to 5/17/2011
## Pilot Test Results – Soil Sampling

### Pre-Pilot and Post-Pilot Soil Concentrations

<table>
<thead>
<tr>
<th>Location</th>
<th>Depth (ft bgs)</th>
<th>Date</th>
<th>GRO (mg/kg)</th>
<th>DRO (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OS-1</td>
<td>17</td>
<td>9/1/2010</td>
<td>340</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2/23/2011</td>
<td>ND</td>
<td>26</td>
</tr>
<tr>
<td>NMP-1</td>
<td>15.5</td>
<td>9/2/2010</td>
<td>ND</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2/23/2011</td>
<td>ND</td>
<td>6.7</td>
</tr>
<tr>
<td>NMP-1</td>
<td>20</td>
<td>9/2/2010</td>
<td>ND</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2/23/2011</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>
COC Removal and Rebound

- Concentrations of GRO and BTEX inside treatment zone typically non-detect.
- Concentrations of DRO had a decreasing trend with notable decreases.

<table>
<thead>
<tr>
<th>Well</th>
<th>Baseline (μg/L)</th>
<th>Post-Injection (μg/L)</th>
<th>Rebound (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP-1</td>
<td>200</td>
<td>ND</td>
<td>460</td>
</tr>
<tr>
<td>EW-1</td>
<td>170</td>
<td>ND</td>
<td>88</td>
</tr>
<tr>
<td>EW-5</td>
<td>13,000</td>
<td>430</td>
<td>490</td>
</tr>
</tbody>
</table>
Secondary Contaminants

- Hexavalent Chromium and bromate detected in only NMP-1.
  - Increased above water quality objectives of 2 µg/L and 10 µg/L respectively

- Hexavalent Chromium decreased more than 50% the first month and each month thereafter to reach baseline levels in three months

- Bromate decreased more rapidly and was near baseline levels in one month
Conclusions – Overall

- ISCO using ozone successfully destroys COCs in saturated zone.
- Ozone injection should be targeted to areas that experience large rebound.
- Groundwater secondary impacts attenuated to their background levels without any secondary treatment.
- Ozone/VOCs did not impact offsite residence and can be contained within treatment zone by controlling injection rate without initiating a mobile SVE system.
- This technology is fit for this site and can be scaled up.
- Materials selection is very important!
Injection Locations (View to the SE)
Injection Locations (View to the NW)
Questions

Thank You