23\textsuperscript{th} International Petroleum Environmental Conference

Upgradient Persulfate Injection and Downgradient Ozone Sparging to Accelerate Closure of a Petroleum Hydrocarbon-Impacted Site

November 9, 2016
Authors and Presenter

- Parsons’ Authors:
  - Jim Leu, PhD, PE
  - Michelle Morales, EIT

- Parsons’ Presenter:
  Jim Leu, PhD, PE
  Jim.Leu@parsons.com
Presentation Overview

- Site Background
- Groundwater Modeling
  - Capture Zone Analysis (MODFLOW)
  - By-products Impacts Evaluation (MT3D)
- Upgradient Persulfate Injection
  - Injection and Monitoring Program
  - Geotechnical Monitoring
- Downgradient Ozone Sparging
  - Pilot Test
  - Interaction with Persulfate
TPH Site Background

- Former natural gas processing station (1960 to 1980s)
- Interbedded layers of sand and silty sand (0 to 30 ft bgs)
- Shallow unconfined zone (15 to 30 ft bgs)
- Chemicals of concern

<table>
<thead>
<tr>
<th>Matrix</th>
<th>GRO (µg/L)</th>
<th>DRO (µg/L)</th>
<th>ORO (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upgradient GW (µg/L)</td>
<td>3,500</td>
<td>3,700</td>
<td>440</td>
</tr>
<tr>
<td>Downgradient GW (µg/L)</td>
<td>3,500</td>
<td>5,600</td>
<td>520</td>
</tr>
<tr>
<td>Clean-up Levels (µg/L)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Chronology of Key TPH Site Events

1999 – vapor intrusion study

2001 to 2006 – soil vapor extraction/air sparging remediation

2005 – ORC injection study

2007 – remedial process optimization

2009 – ozone bench test

2010 – ozone pilot test

2012 – ISCO bench test

1999 to 2013 – groundwater extraction

2012 – ISCO bench test

2013 to 2014 – Full-scale ISCO implementation

2015 – NFA request
Persulfate Injection and Ozone Sparging

- Persulfate ROI
- Ozone Sparging ROI
- Oxygen Sparging ROI

GW Flow
MODFLOW – Capture Zone

**Existing 5 EWs at 3 gpm**

**Proposed 2 EWs at 3 gpm**
MT3D – Predicted TDS Impact Distribution

One month after

Nine months after
MT3D – Predicted TDS Concentration at EW-5
Vertical/Angle Drilling and Injection

**Vertical Drilling/Injection**
- Open field
- Points: 6
- Depth: 15 to 23 feet vertical

**Angle Drilling/Injection**
- Below the building
- Points: 6
- Angles: 10 to 20 degrees
- Depth: 14 to 21 feet vertical
Geotechnical Monitoring Results

- **Visual inspection:** No observable changes
- **Crack monitoring**
  - No expansion or extension of existing cracks
- **Settlement monitoring**
  - Differential settlement less than 1%
  - Total settlement less than 0.5 inches
**Pilot Test Injection Specifications**

- Injection well: 2
- Pressure: 5.5 to 6.0 psi
- Flow rate: 3.5 cfm per well
- Equivalent to ~ 2 lb $O_3$/day
- ROI ~ 20 feet
- Injection time: 60 minutes
Pilot Test Results – DRO Concentration

Groundwater Concentration of TPHd in Treatment Zone Wells

Injection start

Injection end

Date


DRO 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 and Hexavalent Chromium)
Full-scale Ozone Sparging Implementation
Full-scale Ozone Injection Implementation

- Injection wells: 6
  - Ozone sparging wells: 4
  - Oxygen sparging wells: 2
- Injection pressure: 12 to 25 psi
- Sparge flow rate: 6.8 cfm per well
- Ozone capacity: 27 ppd
- ROI: 20 feet based on DO and ORP measurements
- Treatment monitoring wells: 8
- Transition and compliance wells: 10
Groundwater Monitoring Well Locations
Persulfate Injection Contingency Plan

- Trigger: TDS concentrations at transition wells (TW-2, TW-3) exceed 20% of baseline concentration continuously for 3 times

- Response: Initiate GWETS at extraction wells
Groundwater Monitoring Well Locations
Ozone Treatment Wells – Conductivity

Conductivity (umhos/cm)

Sample Date

MW-2 MW-3 MW-5 EW-1 EW-2 EW-6 V-11 V-13 TW-2 TW-3
Ozone Treatment Wells – ORP

Sample Date

MW-2  MW-3  MW-5  EW-1  EW-2  EW-6  V-11  V-13  TW-2  TW-3
GRO Results

Prior to remediation

One year after remediation
95% removal after rebound
DRO Results

Prior to remediation

One year after remediation
65% removal after rebound
MW-2 Chromatography – Polar Compounds

DRO

DRO with Silica Gel Cleanup
BIOSCREEN – Polar Compounds Biodegradation in MW-2

5 years

10 years

20 years
Conclusions

- Successfully destroys COCs in saturated zone
- Byproduct impacts
  - Injected chemicals (TDS, sulfate) captured
  - Oxidized chemicals (Cr(VI), BrO$_3^-$) contained
- Interaction monitoring parameters
  - pH – decreased
  - Conductivity – increased
  - ORP – increased
Questions