State of the Practice versus State of the Art in Chemical Oxidation / Reduction Technologies.

Presented by:

Mike Marley
Principal and Founder

Advances in Oxidation and Reduction Technologies for Remediation of DNAPL, LNAPL and Other Organic and Inorganic Contaminants (AORT), Atlanta, Georgia, USA, November 13-17, 2016.
Who am I?

- B.S. and M.S. Civil / Environmental Engineering; ABD - PhD studies Environmental Engineering – late 70’s – mid 80’s

- Have been focused on development, design and implementation of remediation technologies since early 1980’s
Discussion on State of the Art vs. State of the Practice

(primarily molded by pricing pressures)

- For majority of technologies developed the state of the practice diverged from the state of the art

- Pressure in the industry for low cost solutions is a major driver in the state of the practice
  - With the low cost driver, uncertainty in reaching the desired remedial goals can be high
  - This approach ultimately can result in higher cost to meet the remedial goals due to multiple remedy applications, failures and reevaluations

- For soil vapor extraction and air sparging, initial success is evident; however, it can take years of operation before system failure to meet remedial goals or system design limitations come to light

- For chemical oxidation and reduction, the failures and limitations are more likely to present themselves in the near-term
So the Question I Pose: Do we use the right balance of Engineering and Certainty of Success?

Choose any Technology

- **State of the Practice**
  - Initial low cost
  - Limited or “rule of thumb” design
  - Lower certainty of success
  - Ultimately highest cost?

- **State of the Art**
  - Potentially an initial higher cost
  - Appropriate testing and design
  - Higher certainty of success
Example: Soil Vapor Extraction Design

- SVE Designs:
  - Vacuum propagation? – State of the Practice
  - Clean air sweeps / pore volume exchanges? – State of the Art

- Recent examples:
  - Example 1 – Large Site in West
    - Inches of water vacuum throughout domain
    - 11 years of operation
    - Essentially ineffective
Example: Biostimulation with Oxygen Release Compounds

- Superfund Site: Mixed source / plume with chlorinated solvents and petroleum hydrocarbons
- Comparison of oxygen release products
  - Evaluated several oxygen release compounds on the market
  - Provided product vendors with site specific data and requested recommended dosing of product
  - Based on responses – tested all products at MAXIMUM dosage recommended
    * = some vendors recommended treatability testing to validate dosage assumption
- Not a product issue but an engineering design issue
Example: Oxygen Release Compounds

![Graph showing percent reduction in BTEX for different doses and compounds.](image-url)
Chemical Oxidation

- There are many ISCO technologies / products available – most common are:
  - Peroxide, Persulfate, Permanganate, Ozone
  - Many hybrids and packaged products

- Primary drivers for technology failure - rebound
  - Mass and architecture of target and non-target contaminants
    - Many sites have limited data to determine / estimate mass
    - ISCO is an oxidant mass to contaminant mass reaction technology
    - Characterization is key to estimate the mass with adequate certainty
  - Oxidant demand / stability with site-specific soils
  - Oxidant solution injection volume
  - Geology / soil permeability variability
    - Diffusion from impacted low permeability lenses
Example of Oxidant Stability Issue

North East Superfund Site

- Catalyzed hydrogen peroxide (CHP) selected by Army Corp. for treatment of chlorobenzenes in soil and groundwater

- Bench tested CHP and persulfate
  - CHP with stabilization agents failed due to instability
  - Iron activated persulfate was appropriate and cost-effective alternate

- Side by side pilots at site confirmed CHP failure (<1-foot ROI) and persulfate success

- Persulfate was applied successfully at pilot and full-scale
Oxidant Solution Injection Volume

Injection Volume vs. Pore Volume

- Lesser percent pore volume injected
  - Will primarily treat preferential pathways or limited radius from injection point
  - More dependent upon diffusion and groundwater transport

- Higher percent pore volume injected
  - Greater distribution via advective flow
  - Less dependent upon diffusion and groundwater transport

EPA Staff paper under review on this issue, expect publication end of 2016, beginning 2017

- Less volume = less oxidant = less cost - Certainty of success?
Geology / Soil Permeability Variability

Natural dissolution or treatment (SVE, P&T, ISCO, etc.)

Early/mid stage NAPL spill site

Late stage NAPL spill site

Ground water fluctuation

Effects of Treatment on Flux

Key Oxidant Characteristics Needed
- Higher concentrations – potassium permanganate problematic / limited solubility
- Slower reaction kinetics – peroxide and ozone problematic / no diffusion into LKZ
### Persulfate Treated Dissolved Source Tank

#### Diagram Description:
- Dissolved source mass ≈ 0.9 g

#### Table:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Control Tank</th>
<th>Experimental Tank</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher K sand (cm/s)</td>
<td>6x10^-2</td>
<td></td>
</tr>
<tr>
<td>Lower K sand (cm/s)</td>
<td>8x10^-5</td>
<td></td>
</tr>
<tr>
<td>Velocity (ft./d)</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>Pre treatment stage (d)</td>
<td>239</td>
<td>26</td>
</tr>
<tr>
<td>Treatment stage (d)</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>Post treatment stage (d)</td>
<td>0</td>
<td>203</td>
</tr>
<tr>
<td>Na$_2$S$_2$O$_8$ (g/L)</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Baseline Source Dissolved Condition (mg/L)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MTBE</td>
<td>37</td>
<td>41</td>
</tr>
<tr>
<td>Benzene</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>Toluene</td>
<td>20</td>
<td>26</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td>P-Xylene</td>
<td>7</td>
<td>8</td>
</tr>
</tbody>
</table>
Flux Reduction: Dissolved Source

- Benzene
- Toluene
- Ethylbenzene
- P-Xylene

Normalized Flux vs. Days

Control Tank
Treated Tank
Treated Tank <DL

Normalized to -21 d (4 days from start of flow)

= Active treatment period
Persulfate Treated LNAPL Source Tank

- LNAPL source mass ≈ 76-82 g

<table>
<thead>
<tr>
<th>Compounds</th>
<th>*NAPL Zone mg/kg-soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>98</td>
</tr>
<tr>
<td>Toluene</td>
<td>600</td>
</tr>
<tr>
<td>Octane</td>
<td>3800</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>620</td>
</tr>
<tr>
<td>P-Xylene</td>
<td>640</td>
</tr>
<tr>
<td>O-Xylene</td>
<td>650</td>
</tr>
<tr>
<td>n-Propyl</td>
<td>570</td>
</tr>
<tr>
<td>1,3,5 TMB</td>
<td>310</td>
</tr>
<tr>
<td>Total</td>
<td>7400</td>
</tr>
</tbody>
</table>

*Samples were collected from remaining sand after tank was packed.
Treatment Stages

10% w/w Na$_2$S$_2$O$_8$ in high K
19 g/L NaOH in high K

First treatment event
Rebound
Second treatment event
Normalized Dissolved Emissions

[from NAPL source; normalized to t=24 d results]

- Benzene control
- Toluene control
- Octane control
- Ethylbenzene control
- P-Xylene Control
- O-Xylene control
- N-Propylbenzene Control
- 1,3,5 TMB control

First treatment event

Second treatment
Research Conclusions

- **Dissolved Persulfate**
  - Long-term emission reduction of 63% for MTBE and 95-99% from a dissolved BTEX source
  - Persulfate diffused 10 cm in 14 d (active treatment period) and ≥ 40 cm after 135 d

- **NAPL Base Activated Persulfate**
  - Long-term emission reduction of 60-73% (except octane which was 14%)
  - Persulfate diffused 4-18 cm during active treatment period
Example ISCO Site: In Situ New York, NY

Petroleum Hydrocarbons Treatment with ISCO

- Characterization of target BTEX, additional TPH in silty sands

- Treatability Study
  - Tested multiple oxidants
  - Determined target and non target oxidant demand of soils
  - Alkaline activated persulfate selected

- Six days of chemical injection
  - Oxidant loading based on bench testing results
  - Approximately 70% pore space injection volume

- Site closed by NYSDEC
  - 92 to 95% groundwater concentration reduction
  - > 99% reduction of BTEX, DRO + GRO on soils
Question: Do we use the right balance of Engineering and Certainty of Success?

Mike Marley
Marley @XDD-LLC.COM
1-800-486-4411
www.XDD-LLC.COM