ISCO Re-Engineered

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Lets Set the Stage

- Chemical oxidation is a long-standing treatment technology with a proven track record
  - first aid
  - water treatment
- Fenton’s reactions and ozone were early pioneers for oxidant remediation, with permanganate and persulfate following suit
- ISCO for contaminant remediation has a checkered past, and no one ISCO approach has gained a preferred status
What’s the Problem?

• I believe a big obstacle is expectations!
  – ISCO is marketed as a quick remedy – and it can be

> In Situ Chemical Oxidation (ISCO) with sodium permanganate and potassium permanganate is a safe, cost-effective and rapid remediation technology for the treatment of VOCs (e.g. PCE, TCE, DCE VC etc.) in groundwater, soils and sediments.

  – Practitioners believe that they can predict ISCO volume needs
    • if you know your contaminant mass
    • if you know your flow characteristics (ROI)
    • if you can get good contact
  – In practice, application is more art than science
Re-Engineered In What Way?

• Realign how we think of ISCO
  – preferred use of the remedial technology
  – short-term vs. long-term expectations

• Reconsider data/monitoring needs
  – decrease reliance on NOD/SOD/TOD testing and contaminant mass calculations
  – increase focus on performance monitoring using key parameters like oxidation potential
  – use caution in over-interpreting color in wells

• Methods of application
Rebound

- A typical response to ISCO at sites which include low K materials, concentrated source areas, and DNAPL
  - we are all aware of the excellent literature and research related to matrix diffusion
  - add complexity of spills maturity
  - and consider site heterogeneity
  - don’t necessarily expect that a quick application of ISCO will reverse decades of penetration

Krembs et al.
- 62% of sites had rebound
- Of those, half the wells within the treatment zone exhibited rebound

* Courtesy of Dr. Tom Sales
• 60-80% reductions for injection-based remedies
• ISCO rapidly destroys chloroethenes, but has important limitations
• ISCO has been a marginally successful source treatment
• Reactants are short-lived
• May disrupt natural attenuation
• Sorbed mass may be released
• One study found average maximum decreases if 55%
Typical Batch Injection

- CVOCs decrease after each batch
- May note Mn, MnO4-, chlorides or purple color inc.
- DO or ORP may bounce around
- Low chemical data density compared to potential geochemical changes
Client/Regulator Perspective

- Is this the right remedy for the site?
- Why does it keep rebounding?
- Are you simply pushing contaminants around?
- How much longer will this take?
- You want how much more money?
- Will we really get to closure?
- Can you guarantee a fixed price?
So, Re-Engineer ISCO

- Limit rebound, and lower the cost of ISCO
- Reduce batch injection labor, which is about 50% of injection cost
- Maybe simply add oxidant until done
  - try considering ISCO as a long-term remedy approach
  - eliminates guess work of oxidant mass needed
  - avoids need to evaluate NOD
  - mechanize injection to reduce consultant costs, put $ to the remedy
- Need to address
  - having enough storage volume
  - security
  - potential health and safety issues
## How?

<table>
<thead>
<tr>
<th>Concern/Issue</th>
<th>Mitigation</th>
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<tbody>
<tr>
<td>Limit Rebound</td>
<td>• Promote and maintain a reactive treatment environment sufficient to degrade contaminants</td>
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<td></td>
<td>• Reduce storage requirements by injecting higher concentrations</td>
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<td></td>
<td>• Reduce injection volumes accordingly</td>
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<tr>
<td>Reduce Labor/Costs</td>
<td>• Mechanize injections</td>
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<td></td>
<td>• Use instrumentation for real-time monitoring</td>
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<tr>
<td>Chemical Storage</td>
<td>• Include shelters appropriate to location</td>
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<tr>
<td>Security</td>
<td>• Reduced contact, but at higher concentrations</td>
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“Reactive Treatment”

• Simple addition of an oxidant may not show benefits because of
  – lack of contact (hydraulics)
  – insufficient volume (scope, cost)
  – insufficient concentration
• There is a threshold point for each site – and I propose that it is based on achieving a suitable oxidation potential.
• Once that threshold is achieved, it needs to be maintained until treatment is accomplished.
• Time needed to maintain that environment is variable, and may be long.
One Option - LVCOI

• Considering Low Volume Chemical Oxidant Injection (LVCOI) as a long-term option allows for management of process and costs
• Avoid the cyclic environment associated with batch injections using
  – more frequent applications, or
  – continuous injection
• Avoid concerns of hydraulically pushing contaminants away from the high concentration areas using lower volumes
“LVCOI”

• LVCOI is based on the consistent application of oxidant to reach and maintain a reactive degradation environment
  – the amount and frequency of injection is site dependent
  – the amount and frequency can be assessed monitoring the oxidation front

• About 10 years of site experience support this approach
  – dramatic improvements have been observed in some source zones
  – impacts have been documented significant distances from injection locations
  – observed slow but steady improvements in low K materials
Initiating LVCOI

- Initial pilot test data resulted in less than optimal results
- Change in consultants
- LVCOI implemented during 2009
  - remote site
  - long-term outlook
  - source area application
  - delayed ORP response
Reviewing LVCOI Data

- Common data trends illustrate an initial decline, then plateau in concentration
- ORP has a higher plateau, then some rise
- Many wells have an ORP plateau at about 150-200 mV
- Mn data is inconsistent from site-to-site, likely related to metals Eh-pH mineralization
Impact of Low K
Impact of Low K

- Less common – data trends don’t illustrate an initial decline then plateau in concentration
- ORP has a higher plateau, then some rise
- ORP plateaus at about 350 mV for approximately 2 years, but wells remained clear
- Note no decrease in TCE
Impact of Low K

• Less common – data trends don’t illustrate an initial decline then plateau in concentration
• ORP has a higher plateau, then some rise
• ORP plateaus at about 350 mV for approximately 2 years, but wells remained clear

Time frame for previous photos
Paired Deeper Well

- Although the deeper well responded sooner than its shallow partner, the same trends formed.
- At this location, ORP had to increase to about 600 mV to achieve meaningful TCE degradation.
LVCOI vs Batch Injection

• The long-term chemical trends collected from high- and low-K sites demonstrate the necessity of achieving and holding an elevated ORP for considerable periods of time

• Batch injections won’t maintain reactive oxidation conditions at sites that have separate phase or appreciable mass sorbed into low K materials due to
  – consumption of the oxidant
  – hydraulic migration
  – insufficient chemical gradient to reach sorbed contaminants
How Much ORP is Needed?

- Data to date does not definitively answer this question, but suggest elevated ORPs of 250-600 are required.
Not a Typical ROI

35 m

406 m

828 m

GW Flow
LVCOI Benefits

• Long-term approach has cash flow benefits
• LVCOI reduces consultant field time
• Allows for data trends to develop, improving interpretation of remedy success
• Improved remedy success for low-K materials
ISCO Re-Engineered – Questions?

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Evolution of Application