Application of Alkaline Activated Persulfate and Evaluation of Treatment Residuals

Remediation of Chlorinated and Recalcitrant Compounds
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“After ISCO, What Then?”

- Side-effects of In-Situ Chemical Oxidation (ISCO)
- Common questions:
  - Will biological treatment be possible after ISCO?
  - Will pH recover?
  - Will metals be mobilized?
Alkaline Activated Persulfate (AAP):
- Typically activation occurs at pH > 10.5
- Auto-decomposition reaction forms two sulfate radicals:
  \[ S_2O_8^{2-} \rightarrow 2 \text{SO}_4^{-} \]
- Add sodium hydroxide [NaOH] to raise pH
- Overcome base soil buffering capacity and acid [H⁺] production during oxidant reaction
Theory: Side-Effects of ISCO

- Change in pH

- Mobilization (or precipitation) of metals caused by:
  - pH effects
  - Change in redox conditions (oxidation/reduction of metals)

- Transformation
  - Example: Cr(III) to Cr (VI), etc.
Theory: Attenuation Mechanisms

- **Buffering capacity:**
  - Redox (electron donors/acceptors)
  - pH buffering

- **Solid-surface interactions and ion exchange:**
  - Negative surface charges (influenced by pH)
  - Metal oxides \([\text{MnO}_x], [\text{FeO}_x]\)

- **Mineral dissolution-precipitation reactions:**
  - Calcite \([\text{CaCO}_3]\), gypsum \([\text{CaSO}_4]\), etc.

- **Dilution**
The Problem: Solvent Contamination

- **Source Area:**
  - 30 x 60 feet area
  - 15 feet thick
  - ~1,000 CY

- Located beneath active manufacturing plant

- **Treatment Goal:**
  - Reduce groundwater to below 1 mg/L in source
  - Goal based on protection of downgradient receptor

<table>
<thead>
<tr>
<th>Compound</th>
<th>Historical Max. Conc. (ug/L)</th>
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<tbody>
<tr>
<td>1,1,1-TCA</td>
<td>101,000</td>
</tr>
<tr>
<td>PCE</td>
<td>20,000</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>3,000</td>
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</tbody>
</table>
Site Map

GW Flow Direction

ISCO Treatment Area*

(*wells located between PZ-269 and PZ-264 A/B are not shown for clarity, including PZ-275, PZ-277, PZ-278, PZ-279, and PZ-281)
The Solution: ISCO Treatment

• Selected AAP for safety reasons
  – Greater in-situ stability
  – Reduced potential for gas evolution

• Evaluated AAP on bench scale
  – Soil buffering capacity
  – 2 to 4 g NaOH/Kg Soil

  ❖ NaOH Mass < Soil Buffering Capacity + acid generated by persulfate reaction

• Two injection events

  ❖ 31,000 Kg Klozur (sodium persulfate)
  ❖ 15,300 Kg Sodium Hydroxide (NaOH)

  ❖ NaOH dose was equivalent to total NaOH demand
ISCO Equipment/Construction

- Engineered small, mobile system
- Multiple wells injected into simultaneously
Long Term Monitoring Results - VOCs

- 2-3 Orders Magnitude Reduction
- Target compounds remain below 1 mg/L
  (as of Oct 2010 sampling round)
What About the Treatment Residuals?

- **Added significant amount of NaOH:**
  - pH...will it recover?

- **Persulfate → Sulfate:**
  - Sulfate formed, will it attenuate?

- **Metals:**
  - Mobilization of As, Cr and other metals?
Aquifer pH: Treatment Area 2008

Average ORP: Pre-ISCO = -90 mV; During ISCO = -234 mV; Post ISCO: = -150 mV
Aquifer pH: Treatment Area 2010

Post ISCO ORP (2010) = -117 mV

I mean pH REALLY slowly rebounding...
**Residual Effects: Metals (2008)**

- Significant but temporary increases in Al, Cr, and As
- Levels trending downwards within target area
- Consistent with pH-Eh diagrams

All Concentrations in ug/L
Residual Effects: Metals (2010)

- Cr and As attenuated
- Al appears to be slightly increasing as of 2010, but still low

All Concentrations in ug/L

- Precipitation of Fe and Mn occurred
- No significant rebound through 2008
- Behavior is consistent with pH-Eh diagrams

All Concentrations in ug/L
Residual Effects: Metals (2010)

- Iron is rebounding
  - this is also happening downgradient...
  - More on that later..

- Manganese still low

All Concentrations in ug/L
Have Impacts Migrated Downgradient?

In 2008 Predicted that groundwater from ISCO Area should have reached closest downgradient well by then

Migration Calculations:
- Groundwater Velocity = 120 ft/yr
- Travel Time = 290 days to nearest downgradient well
- Over 1 year since injection completed

Concentrations in mg/L

Legend
- Arsenic - July 2008
- Degreaser FIs

ISCO Treatment Area

GW Flow Direction

Approx. 95 Feet

PZ-284 0.0057
PZ-258 0.0402
PZ-283 0.187
PZ-264B 17.1
PZ-264A 13.4
PZ-269 1.15
Downgradient Water Parameters (2008, One Year After Treatment)

*Comparison of upgradient wells (left of dashed line) to downgradient wells (right of dashed line), one year after ISCO

All Concentrations in ug/L
Have Impacts Migrated? (2-3 Years Later)

In 2009 Sulfate concentrations began rising at PZ-283, approx. 2 years after ISCO treatment.

Revised Migration Calculations:
- Groundwater Velocity = ~50 ft/yr
- Travel Time = ~ 2 years to nearest downgradient well

Concentrations in mg/L

Legend
- Arsenic - July 2008
- Degreaser Pits

GW Flow Direction

ISCO Treatment Area
Sulfate Concentrations After Treatment

2008 – One Year After*

- Sulfate flushed out of target area
- Sulfate arrives at PZ-283 in 2010
- If Sulfate migrated...did Arsenic and Chromium too?

2010 – Three Years After*

*Comparison of upgradient wells (left of dashed line) to downgradient wells (right of dashed line), 1 and 3 years after ISCO treatment

All Concentrations in ug/L
Downgradient Water Parameters (2010, 3 Years After Treatment)

*Comparison of upgradient wells (left of dashed line) to downgradient wells (right of dashed line), one year after ISCO*

All Concentrations in ug/L

- Fe at 385,000 ug/L (higher than baseline)
- Mn still at Baseline levels, no changes
- Cr still at Baseline levels
Downgradient Effects?

- **pH:**
  - pH remains elevated in source area, but no impact downgradient
  - Mass balance on NaOH buffer vs. soil buffering capacity
    - Buffering capacity approximately equal to dosage applied
    - No downgradient effect, but pH in treatment area will take long time to recover

- **Metals:**
  - As, Cr, etc. were elevated in source after treatment, but attenuated
  - No evidence of migration of As, Cr out of source area
  - Naturally occurring dissolved Fe, Mn precipitated in source area

- **Sulfate Migration:**
  - Interesting spike in iron concentrations, coinciding with sulfate arrival downgradient
  - May enhance anaerobic biodegradation (not evaluated yet)
Conclusions

• Treatment successful for solvent contamination

• **Metals Migration:**
  – No evidence of metals migration beyond treated areas
  – NaOH dosage balanced with buffering capacity, pH not impacted downgradient

• **Sulfate Migration:**
  – May enhance anaerobic biodegradation
  – Secondary MCLs

• **Site-specific, attenuation reactions**
  – In this case, metals behaved as expected (Eh-pH)
  – ISCO bench testing can help
Thank You!

For More Information
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