In Situ Chemical Oxidation (ISCO): System Design

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NEWMOA
In Situ Chemical Oxidation Workshop

March 15, 2011
Westford, Massachusetts

March 16, 2011
Danielson, Connecticut

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STRATEGIC. ENVIRONMENTAL. SOLUTIONS.

Big Picture of ISCO Design

Not all "ISCO" is created equal

- Variation in each ISCO technology
  - CHP, Pesulfate, Permanganate, and Ozone
- Variation in design and implementation
  - Thoroughly designed ISCO
  - Less well designed ISCO
  - Some guy with a bucket of something from Walgreens
- Variation in results and costs

Justification of ISCO Design

- Well Designed ISCO versus “Cookie Cutter” approach

- ISCO may be more design intensive than other technologies
  - Interaction of site specific geochemistry with ISCO technology process chemistry
  - Complex chemistry
  - Hazards associated with chemicals and application of chemicals

Critical Design Elements

- Technology Selection
  - Each has different properties
- Injection Strategy
  - Establish contact between a sufficient mass of oxidant with the contamination in the subsurface
- Monitoring
  - Process monitoring: Confirm reagent distribution
  - Performance monitoring: Quantify both the results of the ISCO application and the progress toward remedial goals

TECHNOLOGY SELECTION

Brief Technology Overview

- Primary oxidants include:
  - Hydrogen Peroxide (H_2O_2 becomes OH•, O_2^{-}•, HO_2^{-})
  - Permanganate (MnO_4^{-})
  - Iron Activated Persulfate ($S_2O_8^{2-}$ becomes SO_4^{-}•, OH•, O_2^{-}•)
  - Ozone

- Each technology behaves differently depending upon site soils/site conditions

Key Characteristics: CHP

• Activation:	Transition metal-can be stabilized
• Reactivity:	Most organic COC
• End products:	Oxygen and water
• Stability:	Minutes to days
• Cost:	Low
• "Pros":	Higher moles per pound
• "Cons":	Can autodecompose
	Gas and heat evolution
	Handling
	DHS listed >35%

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Key Characteristics: Permanganate

- Activation: No-direct oxidation
- Reactivity: Limited COCs (ethenes, etc)
- End products: Manganese dioxide
- Stability: Weeks to years
- Cost: Mid to high
- “Pros”: Kinetically fast reactions
- “Cons”: Potassium limited solubility

  Potassium listed with DHS

  Sodium highly reactive at 40%

  Can be limited by SOD

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Key Characteristics: Persulfate

- Activation: Iron (reduced TM) or alkaline
- Reactivity: Iron-many; alkaline most COCs
- End products: Sulfate and acid
- Stability: Days to months
- Cost: Mid-range
- "Pros": High solubility
- "Cons": Can be limited by SOD

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Key Characteristics: Ozone

• Phase:	Gas or aqueous
• Reactivity:	Acidic-many; alkaline most-COCs
• End products:	Oxygen and water
• Stability:	Low
• Cost:	Site dependent—mid to high
• “Pros”:	Treatment of unsaturated zone
• “Cons”:	Low solubility in water

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Oxidant Selection

LOW ← STABILITY → HIGH

LOW ← REACTIVITY → HIGH

Radicals

Hydroxyl Radicals ($OH\bullet$)

$H_2O_2 + Fe^{2+} \rightarrow OH\bullet + OH^- + Fe^{3+}$

$E^\circ = 2.80$ V

Sulfate Free Radical ($SO_4\bullet^-$)

$S_2O_8^{2-}$ + catalyst or heat $\rightarrow 2SO_4\bullet^-$

$E^\circ = 2.60$ V

Parent Oxidant Compounds

Ozone

$O_{3(g)} + 2H^+ + 2e^- \rightarrow O_{2(g)} + H_2O$

$E^\circ = 2.07$ V

Persulfate

$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$

$E^\circ = 2.01$ V

Hydrogen peroxide

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

$E^\circ = 1.78$ V

Permanganate

$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_{2(s)} + 2H_2O$

$E^\circ = 1.70$ V

Bench Tests

- Previously discussed
- "ISCO in a beaker"
- Assess potential failure mechanisms
- Provide:
  - Engineering parameters
  - Confirm effectiveness
- Useful in selecting technologies

INJECTION STRATEGY

Purpose of Injection Strategy

- Take what happened in the beaker and make it happen in the field
- The KEY to field scale up?
  - ***To establish contact between a sufficient mass of oxidant with the contamination for a sufficient duration of time***

Establishing Contact

- Critical Factors include:
  - Site characterization
  - Reagent transport
  - Contaminant mass, phase and distribution
  - Injection strategies
  - Additional design issues

Site Characterization

- Presented on earlier-an application can be no better than the site characterization
- ISCO is like artillery:
  - Need to know where to shoot
- Understand the site
- Poor characterization has several failure mechanisms:
  - Recontamination
  - Rebound

Reagent Transport

- ISCO has been applied successfully in a variety of geologies
- Design issues:
  - Non-target oxidant demand (identify on bench)
  - Geochemical interferences – interference with activation of oxidant (identify on bench)
  - Complex / heterogeneous subsurface (proper conceptual site model, ROI, oxidant selection, etc)
  - Limited hydraulic conductivities (injection flow rates, ROI)
  - Rapid groundwater flow rate (oxidant & activator selection)
  - Oxidant density effects (oxidant selection, injector placement, ROI)

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Contaminant Mass

- *Sufficient mass of oxidant* for the mass of contaminant in a given volume of soil to meet project goals.

$$\text{Oxidant Mass} \geq \begin{array}{l}\text{Contaminant demand} \\ + \text{SOD/NOD} \\ + \text{Auto-decomposition}\end{array}$$

- Typical ISCO reactions:
  - TCE with persulfate

$$3\ S_2O_8^{-2} + C_2HCl_3 + 4\ H_2O \rightarrow 2\ CO_2 + 6\ HSO_4^{-} + 3\ HCl$$

  - Benzene with peroxide

$$15\ H_2O_2 + C_6H_6 \rightarrow 6\ CO_2 + 18\ H_2O$$

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Contaminant Phase and Distribution

Contaminant Phase

- Aqueous
- Soil
- Residual on Soil
- NAPL

Contaminant Distribution

- Heterogeneous lenses
- Homogeneous zone
- Different phases in different areas

Baseline

IP2 8-12

IP2 12-16

Post-application

IP2 9-13

IP2 13-17

Injection Strategies

- Strategy is designed to match the site, contaminant, budget and remedial goal
- Common Strategies
  - Direct injection (conventional and flow down)
  - Recirculation
  - Pull-Push
  - Push – Pull
- Strategy may change during treatment or between phases

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Contaminant Phase and Injection Strategies

Contaminant	Average Concentration (μg/L)	Organic carbon fraction in soil f_{oc} (%)	Calculated Concentration on Soil (μg/Kg)	Mass in GW (%)	Mass on Soil (%)
VC	1,000	0.1	2	**99%**	**1%**
DCE	1,000	0.1	49	**78%**	**22%**
TCE	1,000	0.1	126	**57%**	**43%**
VC	1,000	0.5	12	**93%**	**7%**
DCE	1,000	0.5	245	**41%**	**59%**
TCE	1,000	0.5	630	**21%**	**79%**
VC	1,000	1	25	**87%**	**13%**
DCE	1,000	1	490	**26%**	**74%**
TCE	1,000	1	1,260	**12%**	**88%**

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Additional Design Issues

- 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

- Injection Concentration / # Applications
  - Higher concentrations / applications help ensure contact with *sufficient oxidant*

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MONITORING PROGRAM

Monitoring Program

- Monitoring program typically underappreciated but critical aspect to implementation of ISCO

- Key Factors:
  - Monitoring Objectives
  - Soil vs. Groundwater Sampling
  - Soil Sampling Strategies

Monitoring Objectives

- Implementation Process
  - Examples: reagent distribution, injection volumes, pressures, etc.
- ISCO event
  - Example: contaminant mass
- Progress toward site remedial goals
  - Example: groundwater concentrations

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Soil vs. Groundwater Sampling

- Monitor contaminant phase that contributes to the intended remedial goal:
  - Mass reduction on soils or NAPL: Monitor soils
  - High concentrations in GW: Monitor soils and GW
  - Low concentrations in GW: Monitor GW

- Investigation wells vs ISCO monitoring wells
  - Investigation well screen intervals may or may not correlate with target interval
  - ISCO monitoring wells screen interval should be entirely within target interval

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Soil Sampling Strategies

Grab Samples

- **What it is:**
  - Discrete sample selected from cores based on visual or screening tool
- **What it does:**
  - Typically meets regulatory requirements in many states
  - Can provide negative or positive bias on performance based on sample selection approach

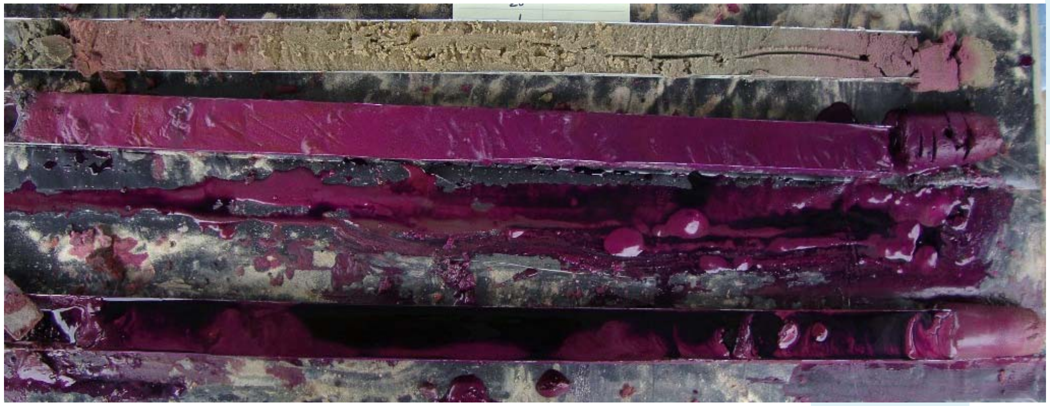
Composite Samples

- **What it is:**
  - Mixing soils from core or visually similar section to obtain a composite sample for analysis
- **What it does:**
  - Provides a more comparable analysis for mass determination and treatment effectiveness
  - May not meet regulatory requirements in many states

Summary

- ISCO is a complex remedial technology
- Key Design Elements
  - Oxidant Selection
  - Injection Strategy
  - Monitoring Program
- Different level of design effort likely results in different probability of success

Questions?



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