

In Situ Chemical Oxidation (ISCO): System Design

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Big Picture of ISCO Design

Not all “ISCO” is created equal

- Variation in each ISCO technology
 - CHP, Persulfate, 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



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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 $\text{OH}\cdot$, $\text{O}_2^{-\cdot}$, HO_2^-)
 - Permanganate (MnO_4^-)
 - Iron Activated Persulfate ($\text{S}_2\text{O}_8^{2-}$ becomes $\text{SO}_4^{-\cdot}$, $\text{OH}\cdot$, $\text{O}_2^{-\cdot}$)
 - 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%

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

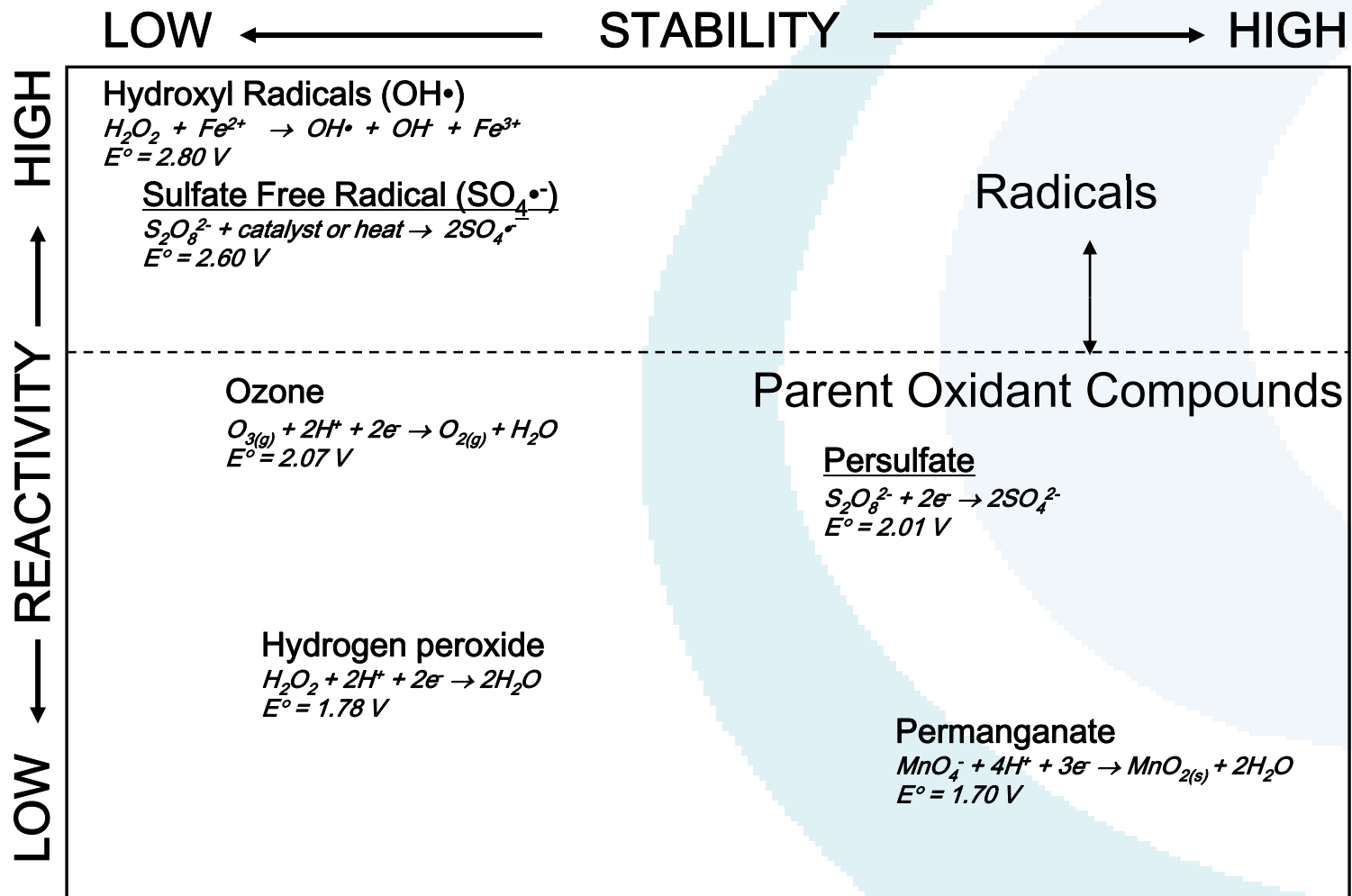
Key Characteristics: Persulfate

- 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

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

Oxidant Selection



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)

Contaminant Mass

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

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

- Typical ISCO reactions:

- TCE with persulfate



- Benzene with peroxide



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

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%



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



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

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

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

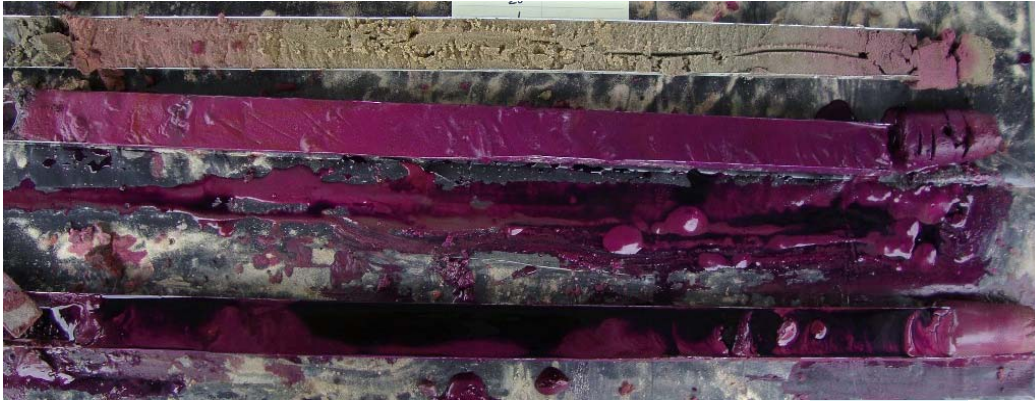
- **What it is:**
 - Mixing soils from core or visually similar section to obtain a composite sample for analysis
- **What it does:**
 - Provides a more comparable analysis for mass determination and treatment effectiveness
 - May not meet regulatory requirements in many states

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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