How to Improve ISCO Performance in Source Areas

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Presentation Overview

- ISCO Fundamentals
- Critical Aspects to Apply ISCO - Chemistry
  - Reagent dose
  - Establishing contact in the subsurface
  - Monitoring Program
- Improvements to ISCO performance – Field Application
- Conclusions

ISCO FUNDAMENTALS

What is ISCO

- In Situ Chemical Oxidation (ISCO)
  - Transform/degrade contamination in place in the subsurface

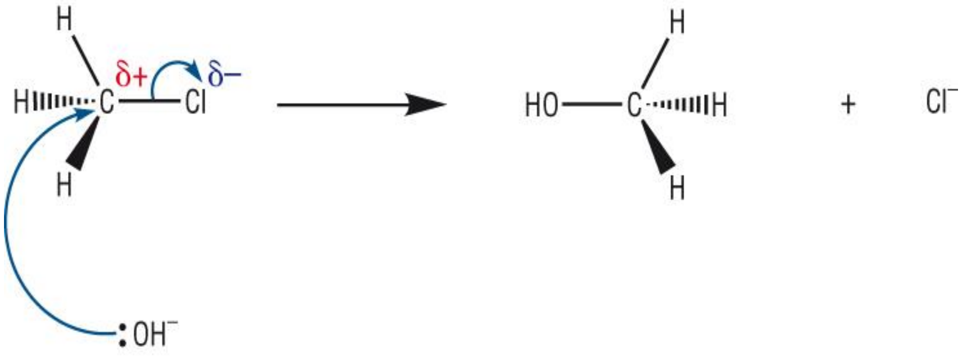
Massive supply of thermodynamically powerful electron acceptors

- Addition of chemicals that take electrons from, or oxidizing, contaminants of concern (COCs)

- Reductive (electron donating) and nucleophilic pathways are also present with certain technologies
  - Allows for treatment of multiple types of contaminants
  - Technology and activation method specific

Reaction Pathways

- Oxidative
  - Electrons are taken from contaminants $\rightarrow CO_2$
- Reductive
  - Electrons are donated to the contaminants $\rightarrow CH_4$
- Nucleophilic
  - Substitution reaction (electron neutral)



Common ISCO Technologies

- Common ISCO Technologies
  - Activated Persulfate
  - Hydrogen Peroxide
  - Permanganate
  - Ozone

Oxidant	Standard Reduction Potential (V)	Reference
Hydroxyl radical (OH•)	2.59	Siegrist et al.
Sulfate radical ($SO_4•^-$)	2.43	Siegrist et al.
Ozone	2.07	Siegrist et al.
Persulfate anion	2.01	Siegrist et al.
Hydrogen Peroxide	1.78	Siegrist et al.
Permanganate	1.68	Siegrist et al.
Chlorine (HOCl)	1.48	CRC (76th Ed)
Oxygen	1.23	CRC (76th Ed)
Oxygen	0.82	Eweis (1998)
Fe (III) reduction	0.77	CRC (76th Ed)
Nitrate reduction	0.36	Eweis (1998)
Sulfate reduction	-0.22	Eweis (1998)
Superoxide ($O_2•^-$)	-0.33	Siegrist et al.
ZVI	-0.45	CRC (76th Ed)

Hydrogen Peroxide: Key Characteristics

- Often referred:
  - Fenton's reagent
  - Catalyzed hydrogen peroxide
  - Catalyzed H_2O_2 Propagations
- Based on the decomposition of hydrogen peroxide
- Characteristics
  - Capable of degrading most types of contamination
  - Relatively inexpensive
  - Forms oxidants, reductants, and nucleophiles
  - Decomposes to water and oxygen
  - Persistence: Days to Weeks
- Common Issues
  - Sensitive to subsurface conditions (can decompose in minutes or persist for days)
    - If an issue, can impede successful distribution
  - Gas and heat evolution
    - Limits injection concentration
  - Hydroxyl radical can be scavenged by naturally occurring carbonates
- Current State
  - Stability
    - Stabilizers can be added with limited success
  - Gases can be captured
  - Injection concentration often limited to less than 12 percent hydrogen peroxide.

Permanganate: Key Characteristics

- Based on the reaction of permanganate forming manganese dioxide
  - Direct oxidative pathway

- Characteristics
  - Reactive with:
    - Chlorinated ethenes (TCE, PCE, etc), some PAHs, etc
    - Little to no reaction with many other compounds (chloromethanes, chloroethanes, benzene, MTBE, etc)
  - Kinetically aggressive reactions with chloroethenes
  - Sodium or potassium and manganese dioxide are typical end products
  - Potential persistence: months or longer

- Common Issues
  - Reactive in the field with a limited suite of compounds
  - Field solubility:
    - Potassium permanganate ~30 g/L
    - Sodium permanganate ~400 g/L (typical application < 200 g/L)
  - Manganese dioxide is a solid
  - Very stable, can persist for months to years, if oxidant demand is met

- Current State
  - Used to treat chlorinated ethene and some PAH sites.

Activated Persulfate: Key Characteristics

- Based on the decomposition of the persulfate anion

- Characteristics
  - Most kinetically viable and powerful reactions depend upon activation.
  - Depending upon activation method- capable of degrading most types of contamination
    - Can form oxidants, reductants, and nucleophiles
  - Relatively inexpensive
  - Sodium and sulfate are typical end products
  - Persistence: Weeks to Months

- Activation
  - Alkaline, hydrogen peroxide, and heat form oxidative, reductive and nucleophilic pathways
  - Iron forms oxidative only pathway

- Common Issues
  - Generates acid during decomposition

- Current State
  - If exceeding soils natural buffering capacity, alkaline activation is used to off set acid formation
  - Typically injected at 50-250 g/L

Active Industrial Site

- PCE, 1,1,1-TCA, and 1,4-dioxane (DNAPL source)
- AAP does not produce gas during treatment
- Treated with two applications totaling 31,000 Kg Klozur®
  - 25 g Klozur per Kg soil
- Remedial goal of less than 1 mg/L for each contaminant

Contaminants	Average Contaminant Concentrations (µg/L)			
	Baseline	Post 1st Application	Post 2nd Application	Total Percent Reduction
PCE	11,987	4,819	113	99.1
1,1,1-TCA	8,736	5,698	64	99.3
1,4-Dioxane	410	1,029	165	59.8

Courtesy of XDD, LLC

ISCO DESIGN AND IMPLEMENTATION

Key to Success for Field Applications

- Highly efficient reactions are known to take place on the laboratory scale
  - 100% contact between ISCO and contamination

- Scale up to the field:

ISCO works by establishing contact between a sufficient mass of activated oxidant with the contaminant mass in the subsurface, for a sufficient time.

- Critical Aspects
  - Oxidant Mass
  - Establishing Contact
  - Monitoring Program

Design Failures

- Most likely due to:
  - Not enough material was used
  - Not enough material was placed in the correct location
  - Improper design

Tacoma Narrows Bridge prior to its collapse

Approaches for each of these topics for ISCO will be discussed

OXIDANT MASS

Design of Field Applications

Developing a sufficient mass of oxidant:

1. Target demand
   a) Contaminant type
   b) Mass in GW, on soil, or in NAPL phases
2. Non-target demand
3. Uncertainties and variability
   a) Target demand
   b) Non-target demand
   c) Contaminant distribution
   d) Desorption or back diffusion rates of mass sorbed to soil
4. Remedial goals

Calculating Proper Oxidant Dose

- Basic formula-Oxidant Mass:

  $[(CM_{Soil} + CM_{GW} + CM_{NAPL}) \times Ratio + SOD * Soil\ Mass] \times S.F.$

  Where:

  - CM_{Soil} = Contaminant mass in the soil phase
  - CM_{GW} = Contaminant mass in the groundwater phase
  - CM_{NAPL} = Contaminant mass in the NAPL phase
  - Ratio = Degradation or stoichiometric ratio of oxidant needed to treat a unit mass of contaminant
  - SOD = Soil Oxidant Demand (g Oxidant per Kg Soil)
  - S.F. = Safety Factor

Oxidant Mass: Detailed Assumptions

$[(CM_{Soil} + CM_{GW} + CM_{NAPL}) \times Ratio \quad + SOD \times Soil\ Mass] \times S.F.$

- Average or maximum concentrations?
- NAPL
- Stoichiometric vs empirical ratios ?
- Soil Density?
- Non-target demand?

Soil Type	Bulk Density Range (lbs/ft3)		
	lower	upper	variation
compacted sandy loam	100	125	25%
compacted clay loam	90	110	22%
compacted glacial till	120	140	17%
undisturbed subsurface soil	90	140	56%

Hydrogen Peroxide has potentially significant autodecomposition mechanism that has to be considered

- Safety Factor?
  - Conservative design, unknowns, variables, and uncertainties

Math is great, but….

- First cut design use estimates for:
  - Target Demand
  - Non-target demand
  - Uncertainties
- Other ways of determining dose:
  - Total oxidant demand tests
  - Detailed bench tests

- Thermodynamics (something will happen) vs kinetics (how quickly something will happen)
  - Minimum injection concentrations:
    - Approximately 40 to 50 g/L
  - Minimum concentrations in the subsurface:
    - Approximately 20 to 30 g/L

High COC Source Mass

- Technology specific
- ISCO:
  - Oxidant mass
  - Injection volume
  - Flexible approach
  - Injection network density
  - Multiple applications
  - Robust monitoring program

- If needed:

Bring the hammer

But careful with hydrogen peroxide

ESTABLISHING CONTACT

Design of Field Applications

Establishing contact between the oxidant and contamination

1. Site geology
2. Contaminant distribution
3. Reagent distribution
4. Injection
   a) Strategy
   b) Volume (total and as a function of design ROI)
   c) Network
5. Contact time as a function of groundwater velocity
6. Multiple injection events

Establishing Contact

- Common strategies to establish contact between the oxidant and the contamination in the subsurface
  - In situ shallow and deep soil mixing
  - Amendments to excavations
  - In situ injection strategies

In Situ Mixing





- Divide site into cells (e.g 10’x10’) and lifts (e.g. 5’)
- Goal = homogenous target zone.
- Can establish contact even with low permeable soils
  - Can address matrix back diffusion issues
  - Function of mixing time per cell
- Keys to implementation:
  - Correct dose and uniformity of blend within each cell
  - Balance % pore volume mixed for contact versus post mixing compaction requirements
- Base of excavation can also be mixed

In Situ Soil Blending

Conditioning Soil with Lime

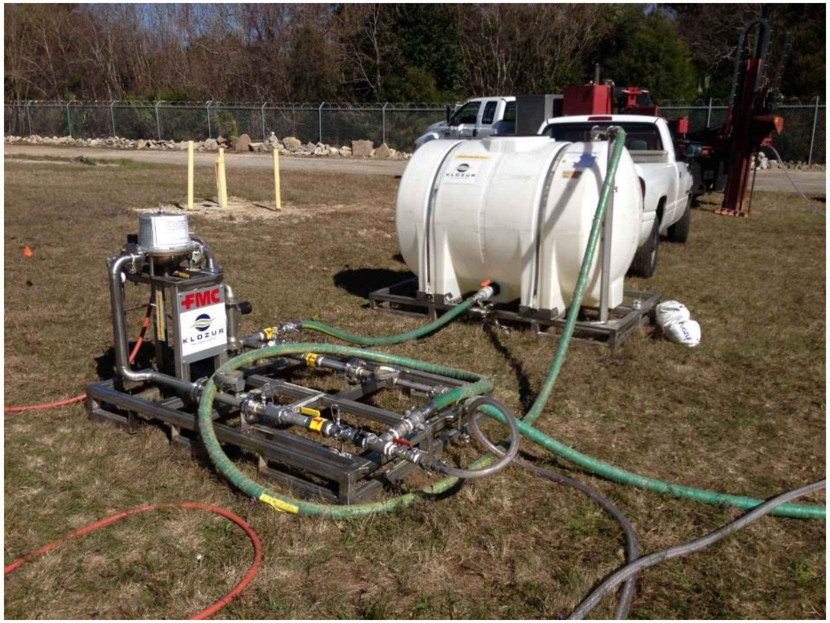
Thorough Incorporation

Courtesy of Exo Tech

Injection Strategies

- Direct Injection
  - Injection through injection point either direct push or fixed injection wells.
- Recirculation
  - Injection through injection point coupled with extraction through separate extraction points
- Pull/Push
  - Extract a volume of groundwater from a point, amend with reagents, and reinject into the same point
- Flow Down
  - Inject reagents to let groundwater advection transport the reagents to the target area

In Situ Injection



Klozur™ Sodium Persulfate Injection Wells

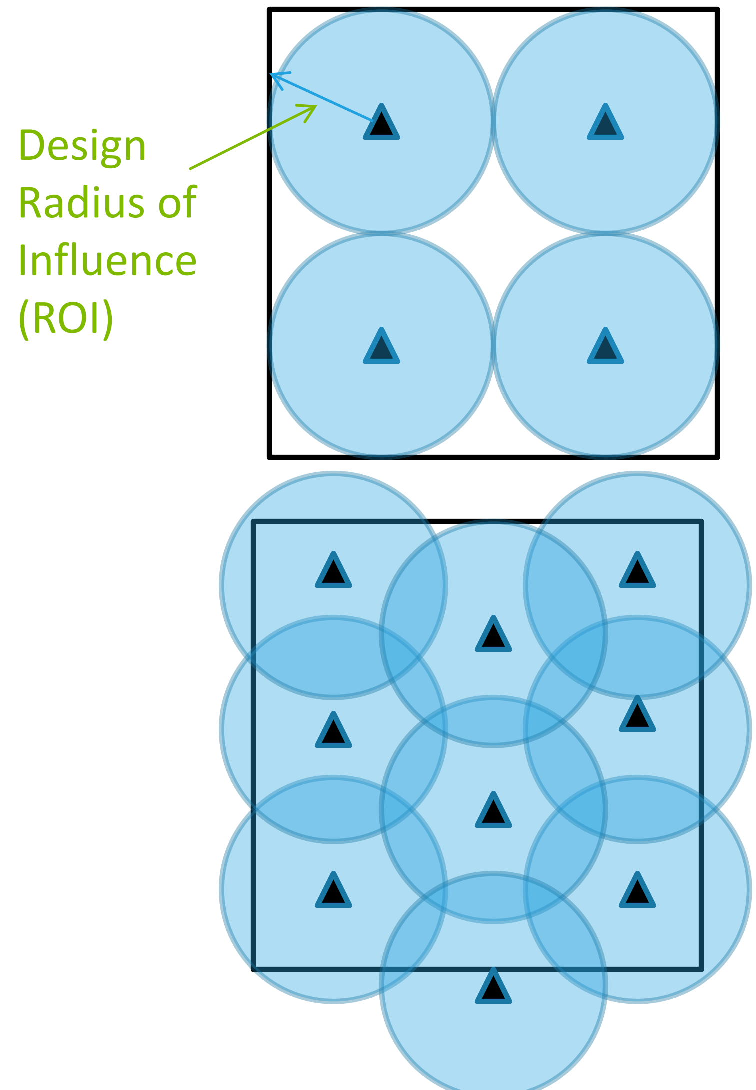
Klozur Injection

Injection Well Operation

Activated Klozur Reaction with Hydraulic Fluid

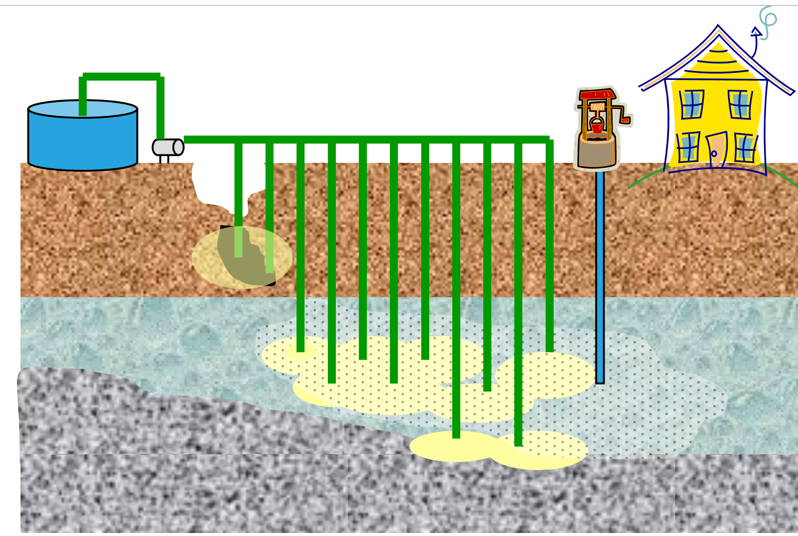
Injection Network

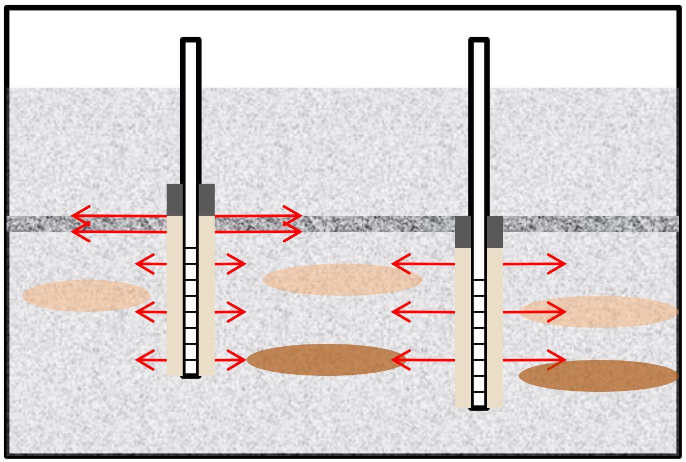
- Injection point density
- Overlapping design ROIs
  - Avoid gaps
- Accounting for mass outside the target area
- Distance "on center"
- Groundwater velocity (seepage velocity) can distort "circles"
  - Modified "flow down" strategy: Tighter spacing between points and longer spacing between rows
  - ROI must account for advection within the time the oxidants are reactive



Target Interval

- Considerations:
  - Contaminant distribution over interval
  - Preferential pathways within target interval
  - Frac or rely on diffusion from transmissive zones
  - Use of high resolution evaluation
    - E.x. feet of NAPL in well can be from very thin lens



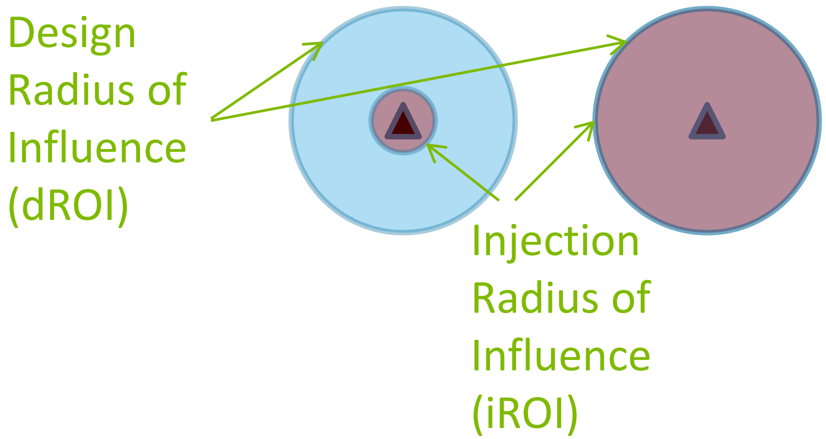


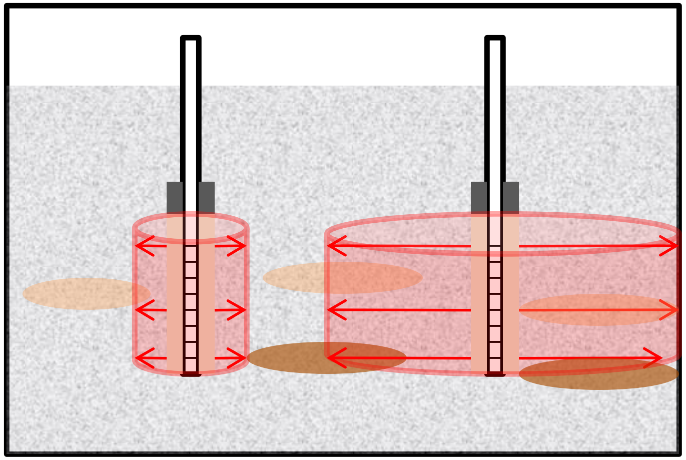
Injection Volume

- Reagents have to be distributed within subsurface in order to establish contact
  - Distribution should be evaluated on pilot test (horizontal and vertical)

- Effective pore volume
  - Portion of the pore volume that is mobile (e.g. 1 to 30%)
  - Consider injection volume as a percent of the effective pore volume to support ROI calculations

- Primary distribution mechanisms include:
  - Advection from injection
  - Advection from groundwater flow (velocity)

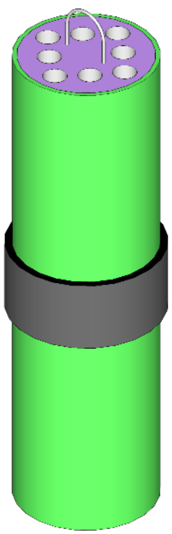




What If: Source Mass Inaccessible?

- Under an active production unit or facility.
- Under road or highway.
- Pipeline leak.
- Utility corridor – fiber optic lines.
- Indoor air quality issues.

Source Remediation using Flux Cartridges – A New Technology under Development



Replaceable treatment cartridge containing permeable reactive materials.
International Patent Pending by Ai-Remedial Systems, LLC (Ai-RS).

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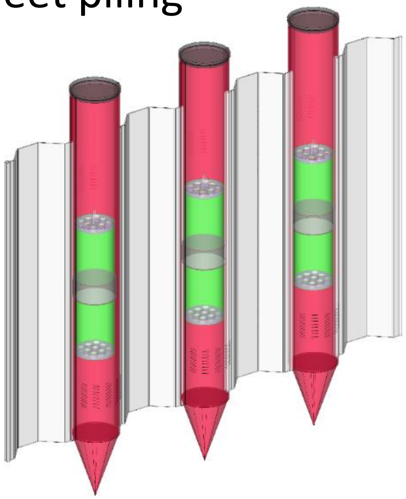
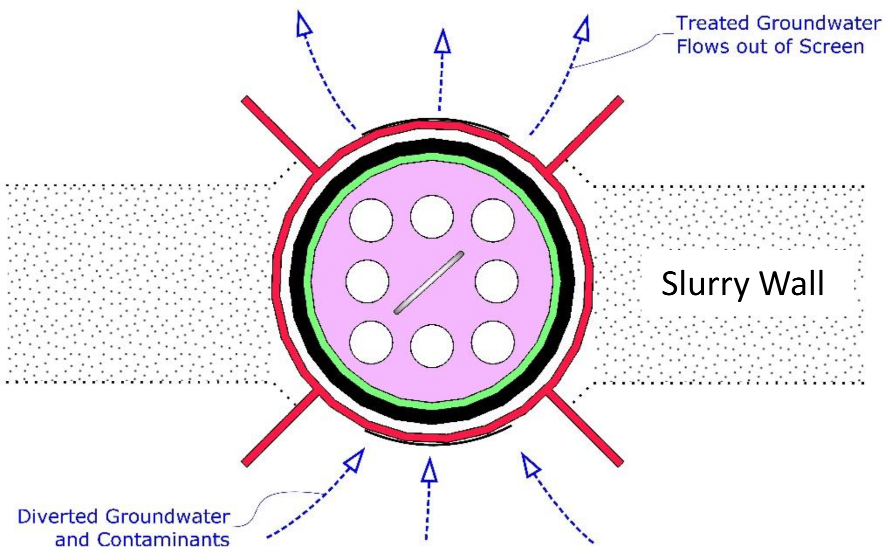
Flexible Installation Options

Option 1. Filter Piles (red) driven in ground and connected to conventional sheet piling



Option 2. Plan view of Filter Pile installed in a slurry wall



Note: Replaceable cartridges shown in green casings, with purple perforated lids, and black inflatable seals.

International Patent Pending (Ai-RS)

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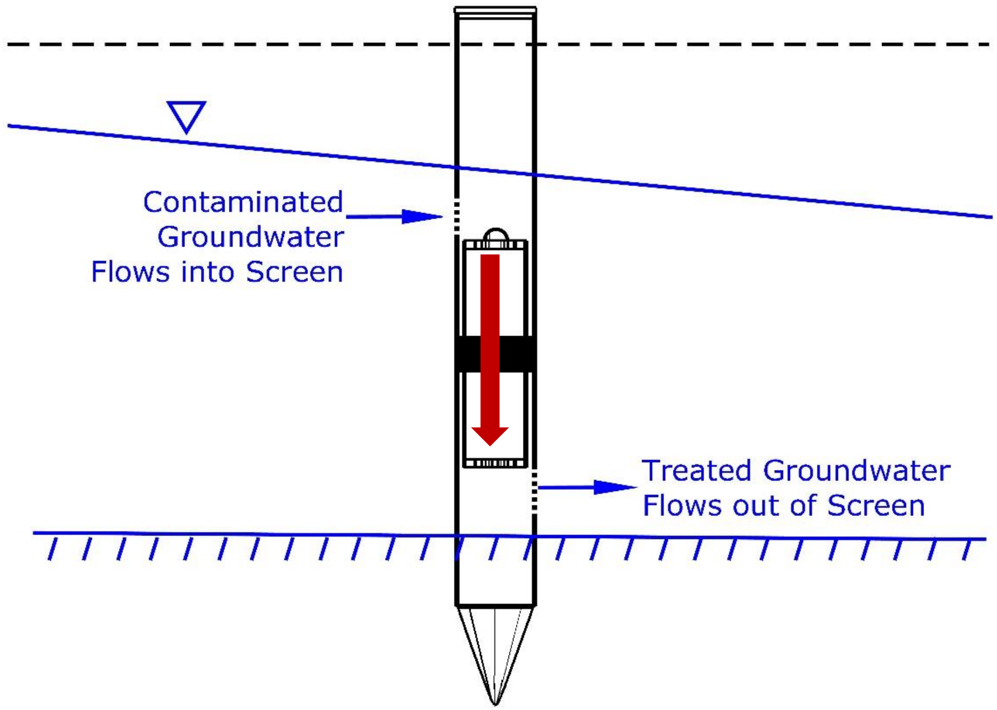
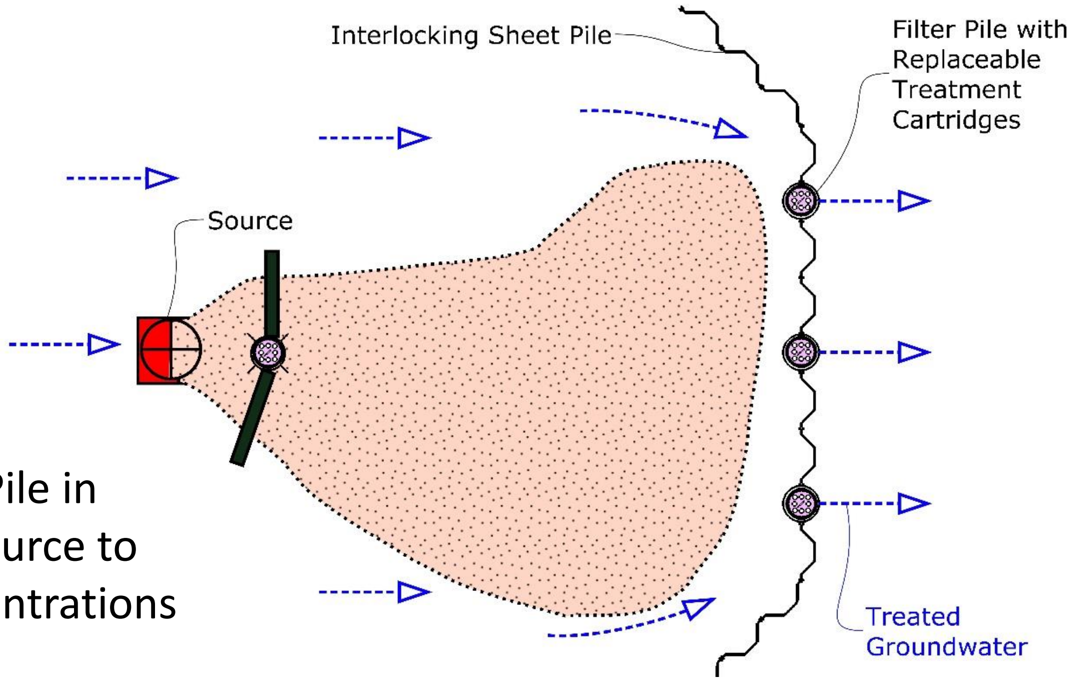
How it Works



Note: Contaminated groundwater flows from higher hydraulic head through screen in Filter Pile and into treatment cartridge. Inflated seal (black) prevents contaminated groundwater (red) from bypassing treatment inside replaceable cartridge. Treated groundwater flows out downgradient screen in Filter Pile.

International Patent Pending (Ai-RS)

Source and/or Downgradient Control



Example 1. Filter Pile in slurry wall near source to treat higher concentrations

Example 2. Filter Piles connected to sheet piling further downgradient to control leading edge of dissolved plume

International Patent Pending (Ai-RS)

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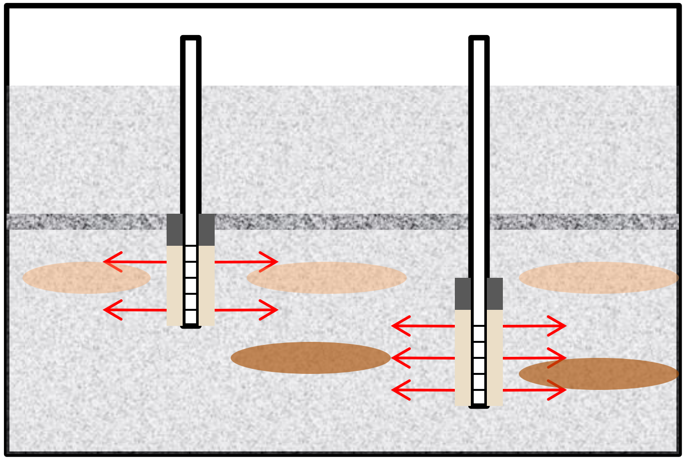
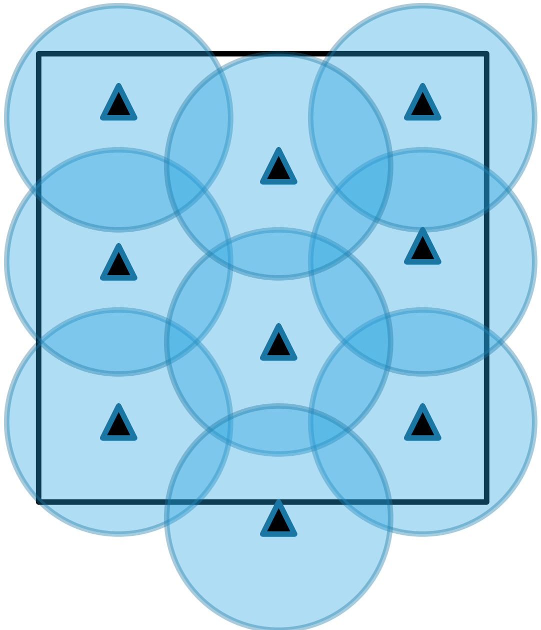
OTHER CONSIDERATIONS

Subdivide the Target Volume

- Divide the site into mass or lithogical subsets
  - Establish contact between sufficient mass of oxidant for the contamination
  - Method of establishing contact or injection rates, pressures, etc, may change based upon geology



- Injection concentration or volume can be varied to deliver appropriate mass of oxidant into each subsection



Number of Applications

- Many designs utilize a multiple application strategy. Reasons for a multiple application strategy include:
  - Injection volume and number of applications used to maintain practical reagent injection concentrations
  - Evaluative (Iterative) approach: Monitoring between applications can be used to refine target area
    - Diagnostic for highly contaminated areas
    - Minimizes initial commitment allowing for further site assessment
    - Optimize events to reduce remediation target volume or troubleshoot areas not responding per design
  - Injection locations can be staggered between events

- Potential issues with a multiple application strategy
  - Preferential treatment of non-target demand changes partitioning between soil and groundwater – interim results
  - Partial treatment of COCs

Field Application

Desired Path

- Path
  - Bench scale tests – performed by qualified practitioners
    - Design parameters
  - Design Optimization (Pilot scale tests)
    - Reagent distribution
  - Full scale applications
  - Achievement of goals or transition to another technology as part of a treatment train approach

Expectations

- Evaluation of several common remedial technologies showed field results of up to 99%
- Mass reduction
  - Will depend upon
    - Dosage/ability to contact contamination
    - Initial concentrations
- Typically 80 to 99 percent per successful application
- Multiple applications and, potentially, multiple technologies are typically necessary for greater than 1 to 2 order of magnitude reductions

MONITORING PROGRAM

Monitoring Programs

- Critical aspect to ISCO design
- Objectives
  - Progress toward remedial goals
  - Assessing effectiveness of ISCO application
- Monitoring Phase
  - Soil and groundwater typical
  - Phase monitored may be different for each objective
  - Progress of ISCO best measured by total mass reduced (GW mass plus Soil mass)
  - HRSC as additional line of evidence on mass reduction considering variability in soil analysis.
- Soil
  - Discrete/grab
  - Composite
- Frequency
  - Allow time:
    - ISCO to react
    - Groundwater, soil and NAPL re-equilibrate
    - Can have biotic activity following ISCO
  - Minimum 2-3 months post application recommended
  - Multiple monitoring events recommended to determine new equilibrium
- Parameters
  - Contaminant
  - Residual oxidant
  - Geochemical parameters
    - DO, temperature, conductivity, pH, ORP
  - Others, as needed

Monitoring

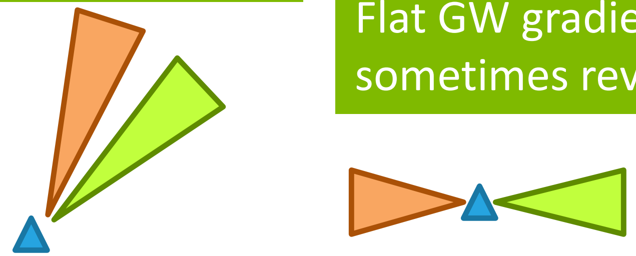
- Key design parameters
  - SOD, BBC, soil density, porosity, foc, hydraulic conductivity, contaminant distribution, groundwater/seepage velocity, groundwater direction with seasons, soil matrix, and degree of heterogeneity.
- Baseline
  - Contaminants of concern in soil and groundwater
  - HRSC
  - Foc
- Monitoring during application
  - Injection parameters, reagent distribution, injection solution chemistry,etc
- Post application monitoring
  - Contaminants of concern in soil and groundwater
  - HRSC
  - Presence/absence of NAPL
  - Foc, etc

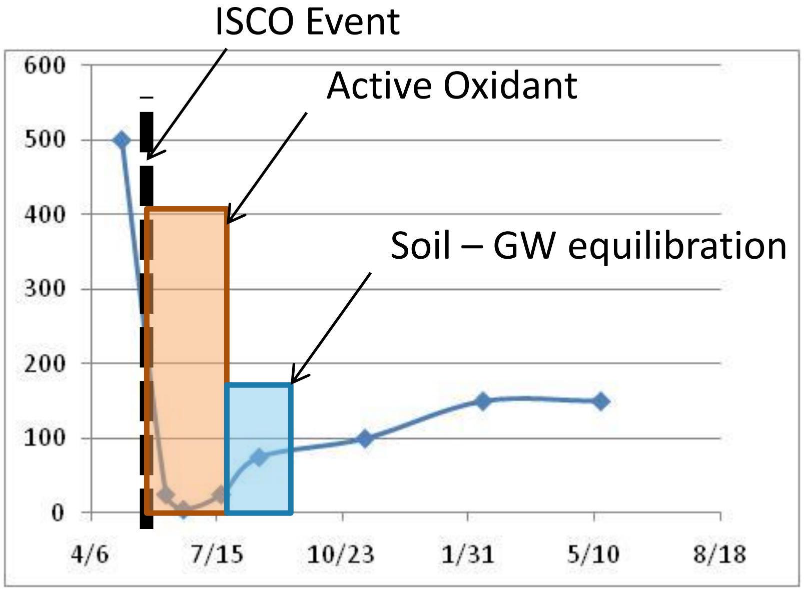
Design of Field Applications

- What does the data actually represent
  - Groundwater velocity and direction
  - Active reagent solution
  - Equilibrium

Slight shift in GW direction

Flat GW gradients sometimes reverse





SUMMARY

Recommended Practices

- Technologies based on ISCO materials have been proven to work.
  - ISCO applied at thousands to tens of thousands of sites

- Recommended practices for application design and monitoring program:
  - Design
    - Consider all aspects in determining the proper oxidant mass
      - Target demand, non-target demand, and variables to be addressed with conservative design or safety factor
    - Establish sufficient contact between the oxidant and contamination in the subsurface
      - Distribution through injection event
      - Distribution effects from groundwater/seepage velocity
    - Consider impacts of groundwater/seepage velocity
    - Flexible approach as needed
      - More is learned with each site visit
    - Successful implementation of the design:
      - Experienced implementation team
      - Proper H&S
  - Monitoring
    - Develop monitoring program that fits site needs and requirements
    - Wait for new equilibrium to be established between soil and GW for final GW results
    - Emphasis on soil data. Sufficient grab samples or composite samples
    - Measuring Foc to understand relationship of partitioning between soil and groundwater
    - Use of high resolution data to assess site

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Comments and Questions are Welcome!

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