In Situ Chemical Oxidation (ISCO) Overview

NEWMOA 2025 Workshops

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Soil & Groundwater | Persulfates

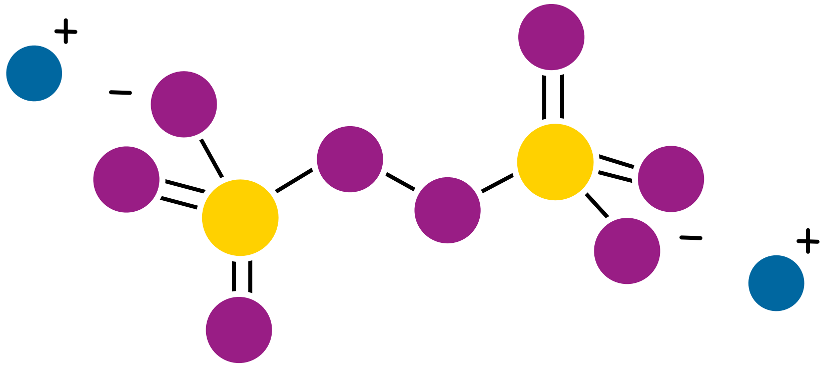
Overview

- ISCO Reagents
- Applicable Contaminants
- Soil Mixing Approaches
- Favorable vs Unfavorable Site Conditions
- Data Needs (Before, During and After)
- Implementation Logistics
- Recommendations and Lessons Learned

What is ISCO?

- In Situ Chemical Oxidation (ISCO)
  - Transform/degrade organic contamination in the subsurface
- Addition of chemicals that take electrons from, or oxidize, contaminants of concern
- Reductive (electron donating) pathways are also present with certain technologies
  - Allows for treatment of multiple types of contaminants
  - Technology specific and activation method dependent

Massive supply of thermodynamically powerful electron acceptors



Why ISCO?

- **Effective:**
  – ISCO can treat a wide assortment of contaminants of concern (COCs)
- **Cost:**
  – Many situations where ISCO is the most cost effective remedy
- **Time:**
  – Can provide results quickly, usually within weeks to months of an application
  – Other ISCO reagents can persist for years allowing for extended treatment conditions
- **Flexible:**
  – Can do smaller focused (hot spot) treatments, optimize treatment with multiple applications, or otherwise apply ISCO in a variety of manners
- **Contaminant Mass:**
  – Dose of ISCO reagents can be optimized to treat very high or relatively low levels of contamination
- **Ease:**
  – ISCO is among the most popular remediation technologies with experience consultants and contractors around the world

Common ISCO “Oxidants”

- Hydrogen peroxide (H_2O_2; liquid amendment)
  – Activated to form hydroxyl radical (oxidant) and superoxide radical anion (reductant)
- Persulfate ($Na_2S_2O_8$/$K_2S_2O_8$; powder, dissolved, solid slurry)
  – Activated to form hydroxyl and sulfate radicals (oxidants) and superoxide radical anion (reductant)
- Permanganate (Na/$KMnO_4$; powder, dissolved, solid slurry)
  – Non-radical-Direct reaction
  – Oxidative pathway
- Ozone (gas, will dissolve)
  – Typically oxidant only, but can decompose at high pH to form radicals

Product Selection Process

1. Technical efficacy
   - Does it Contaminant (Yes or No)?
2. Remediation Kinetics
   - How quickly will it work?
3. Application method
4. Mass per Application/Number of Applications
5. Total Cost

Assume Site Characteristics are well understood

- **Remediation Goals/Timeframe**
- **Soil/GW Characteristics**
- **Contaminant Characteristics**

Reagents have Characteristics too!
Important Characteristics of ISCO Technologies

- How do you match an ISCO technology to your given site:
  - Thermodynamics
    - Reactivity with contaminants
  - Kinetics
    - Rate of reaction with contaminants
  - Persistence: How long will regent be active
    - Stability
    - Solubility/Extended Release
  - Mass per application
    - Target and non-target demands
  - Other factors: Color, etc

Courtesy of Lauderner

Technical Efficacy

Will the Oxidant React with the Contaminant

YES

Or

NO

Pathways: Oxidative vs Reductive Pathways

- Oxidative Pathway:
  - Electrons are taken from the contaminant moving organic contaminants to carbon dioxide
  - Oxidants serve as electron acceptors

- Reductive Pathway:
  - Electrons are donated to the contaminant moving organic contaminants toward methane/ethane
  - Reductants serve as electron donors

- Persulfate is typically activated to form radicals
  - Alkaline Activation (Furman et al, 2010):

$$S_2O_8^{2-} + 2H_2O \rightarrow HO_2^- + 2SO_4^{2-} + 3\,H^+$$

$$HO_2^- + S_2O_8^{2-} \rightarrow SO_4{\bullet}^- + SO_4^{2-} + H^+ + O_2{\bullet}^-$$

$$SO_4{\bullet}^- + OH^- \rightarrow OH{\bullet} + SO_4^{2-}$$

(note: $H_2O_2 \leftrightarrow HO_2^- + H^+$ $pK_a = 11.7$)

Thermodynamics

- Hydrogen peroxide: Oxidative and Reductive Pathways
  - Hydroxyl Radical and Superoxide Radical Anion
- Persulfate: Oxidative and (proper activation) Reductive Pathways
  - Sulfate and Hydroxyl Radicals and Superoxide Radical Anion
- Permanganate: Oxidative pathway
  - Direct oxidation
- Ozone:
  - Typically oxidant only, but can decompose at high pH to form radicals

Electron Tower: Half Reactions	
Reagent	**Standard Reduction Potential (V)**
Hydroxyl radical ($OH\cdot$)	2.59
Sulfate radical ($SO_4\cdot^-$)	2.43
Ozone	2.07
Persulfate anion	2.01
Hydrogen Peroxide	1.78
Permanganate	1.68
Oxygen	1.23
Sulfate	0.17
Hydrogen (H_2)	0.0
Superoxide ($O_2\cdot^-$)	-0.33
ZVI	-0.45

Notes: 1. Siegrist et al. (2011), 2. CRC (76th Edition)

Contaminants Treated

Oxidative	Either	Reductive
Petroleum Hydrocarbons	PCE, TCE, DCE and VC	Carbon Tetrachloride
MGP Residuals	Chlorobenzenes	1,1,1-Trichloroethane
BTEX	Chlorophenols	Dichloroethanes
PAHs	Select Pesticides	Select Pesticides
Oxygenates	Select Fluorinated Compounds	Select Energetics
	PCBs	

Hydrogen Peroxide; Alkaline or Hydrogen Peroxide Activated Persulfate

Iron Chelate Activated Persulfate

Permanganate*

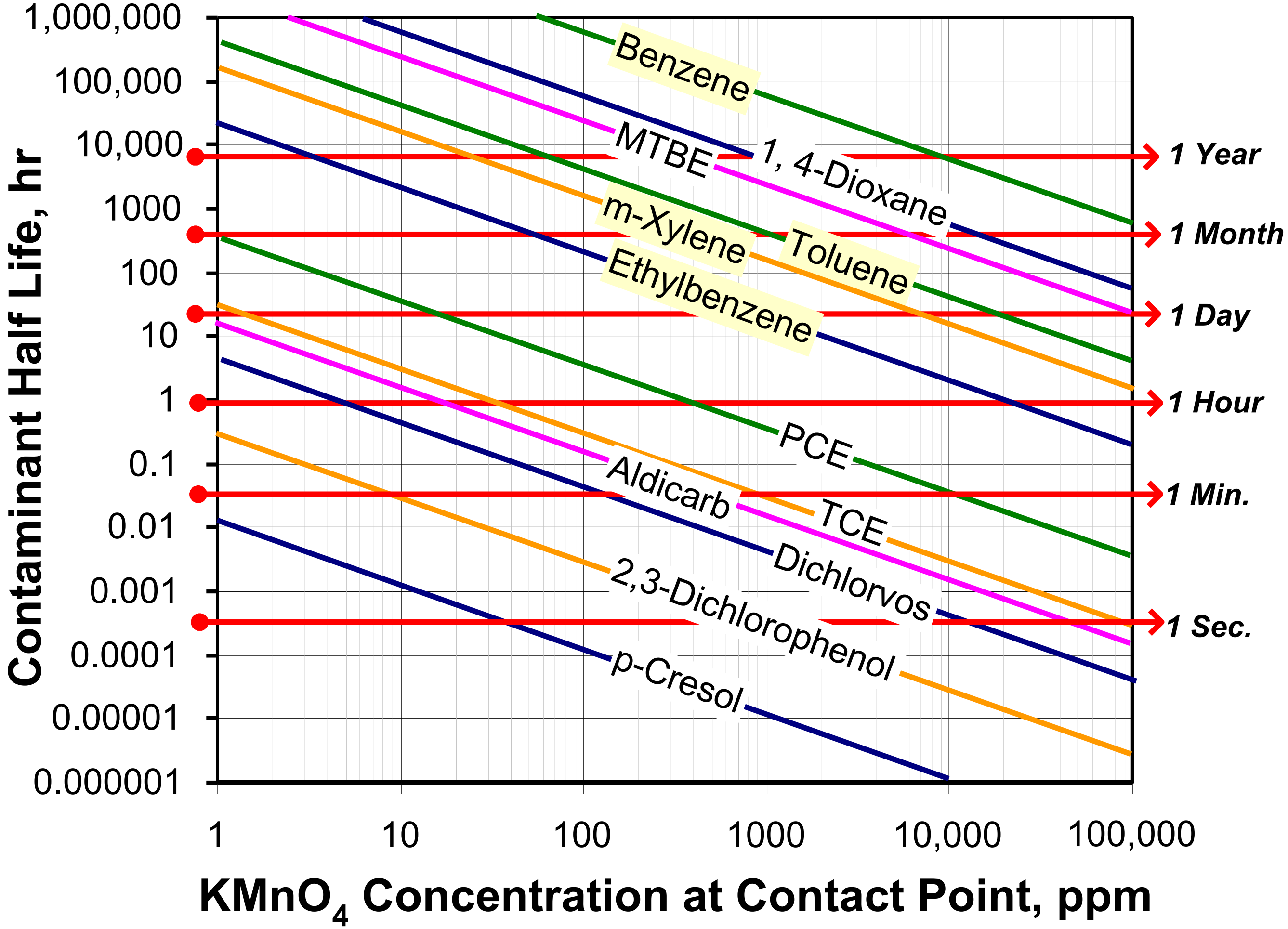
Ozone**

*Permanganate is primarily reactive with chlorinated ethenes

**Ozone can have a reductive pathway at high pH

Sometimes More than "Yes/No"…it depends

- Radicals react within nanoseconds
  - Radical based chemistries are about distributing parent compound and creating radicals at point of contamination
- Permanganate is direct oxidation
  - Concentration based kinetics
  - >99% treatment ~7 half lives



Kinetics

Time

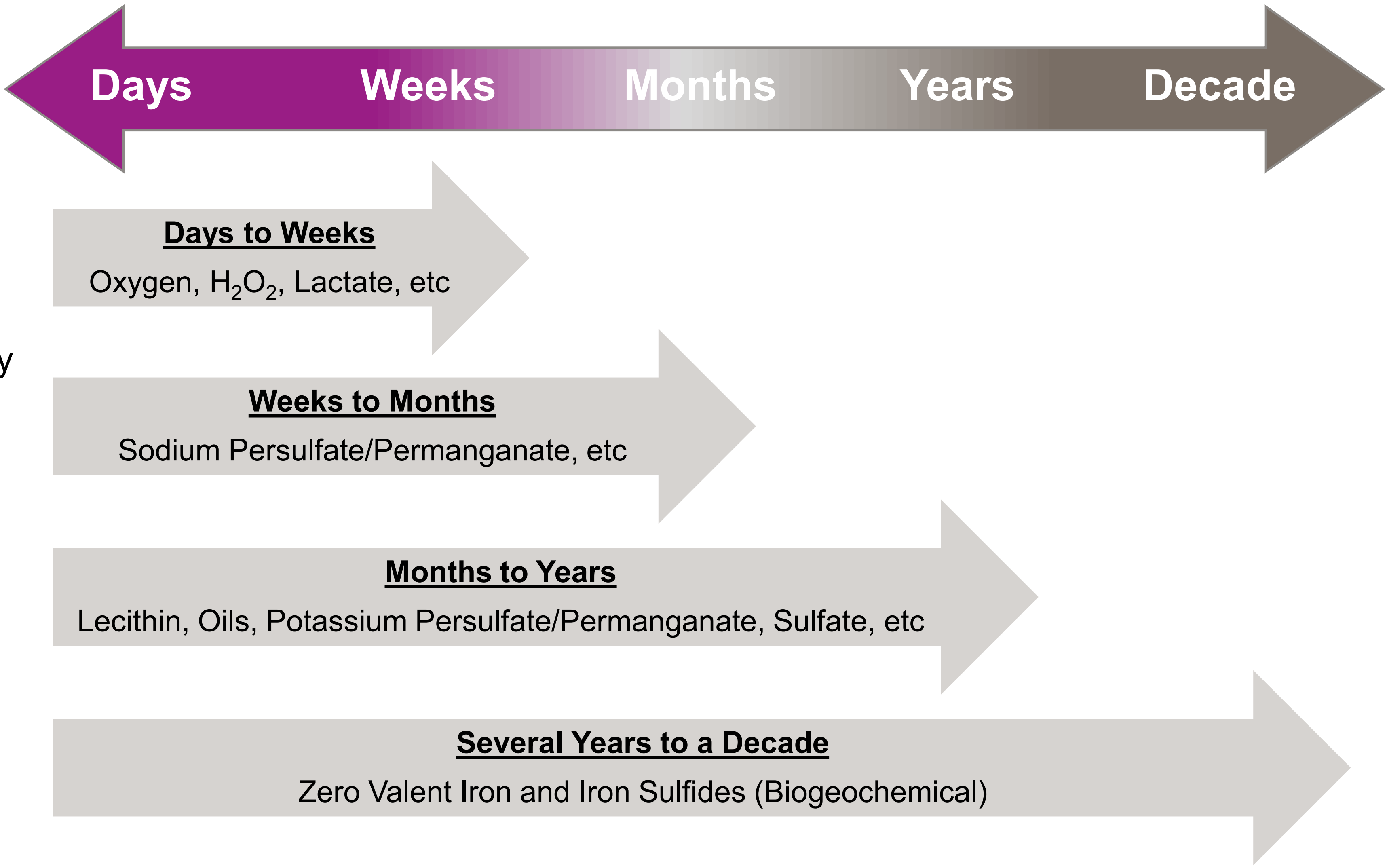
Longevity


Courtesy of LEA (XDD, LLC)

Reagents have Characteristics Too!!
Potential Reagent Longevity

- Solid, low solubility and oil-based reagents tend to persist longer than soluble reagents
  - More soluble reagents will migrate with groundwater
- Presence of demand affects longevity
  - Excess demand decreases longevity
  - Less demand extends longevity
- Mechanisms to longevity
  - Low solubility
  - Fermentation
  - Corrosion

Longevity Buckets



Oxidants: Available at time of Application vs Extended Release

- Available:
  - When you want all oxidant available at injection
    - Source zones, high oxidant demands, etc.

PCB	Day 56 PCB % Reduction			
	Klozur® SP		Klozur® KP	
	Low	High	Low	High
Arochlor 1254	12%	26%	53%	53%

- Extended Release:
    - Permeable Reactive Barriers (PRBs)
    - Back diffusion from low permeable soils
    - Low solubility contaminants
    - Low contaminant concentrations
  - High groundwater velocity

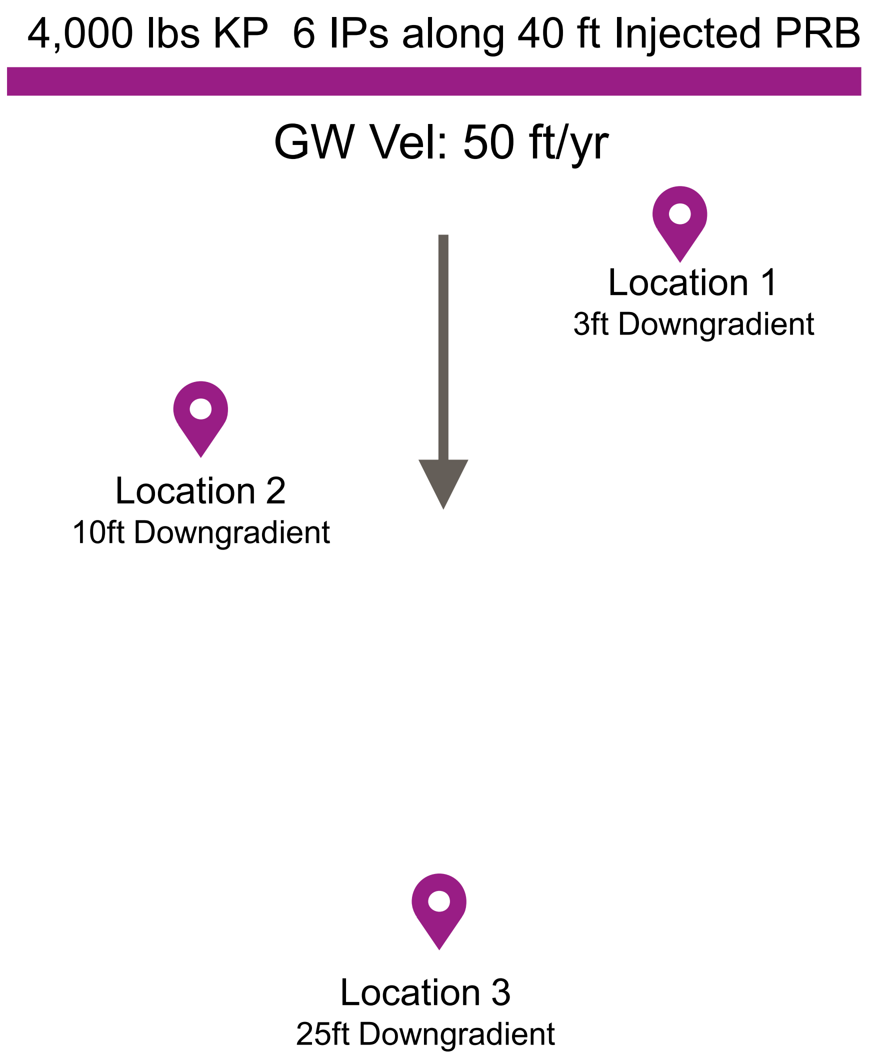
Klozur KP Solid Slurry Fracture

Courtesy of FRx/Brown & Caldwell

Understanding Oxidants: Persistence

Characteristic	Hydrogen Peroxide	Permanganate	Persulfate	Ozone
Autodecomposition	Yes: Transition Metals, temperature, etc	Very very very slow	Yes: Slow	Yes
Typical Persistence Range	Minutes to Days	If dosed above demand, has been observed to persist for years	Once Dissolved: Days to Months Potassium Persulfate Solid: Months to Year	Dissolved in water: Minutes Gas phase: Days
Lessons Learned	Stabilization and bench testing to confirm longevity	Often slightly underdosed to avoid persistent oxidant	Slow autodecompostion allows for distribution, Importance of effective activation	Majority of ozone mass distributed is typically in gas form

Klozur® KP Case Study - 1,4-Dioxane
Treatment Results



Event	Location 1: Contaminant Concentrations (µg/L)				
	DCA	DCE	1,4-Dioxane	VOCs*	Reduction VOCs (%)
Baseline	21	40	30	115	0%
3 Month	0.2	ND	ND	0.2	99.8%
6 Month	0.2	ND	ND	0.2	99.8%

Event	Location 2: Contaminant Concentrations (µg/L)				
	DCA	DCE	1,4-Dioxane	VOCs*	Reduction VOCs (%)
Baseline	44	72	55	184	0%
3 Month	10	11	ND	26	86%
6 Month	16	ND	16	34	82%

Event	Location 3: Contaminant Concentrations (µg/L)				
	DCA	DCE	1,4-Dioxane	VOCs*	Reduction VOCs (%)
Baseline	89	270	200	610	0%
3 Month	46	82	69	216	65%
6 Month	63	30	110	230	62%

*Detected VOCs not including acetone

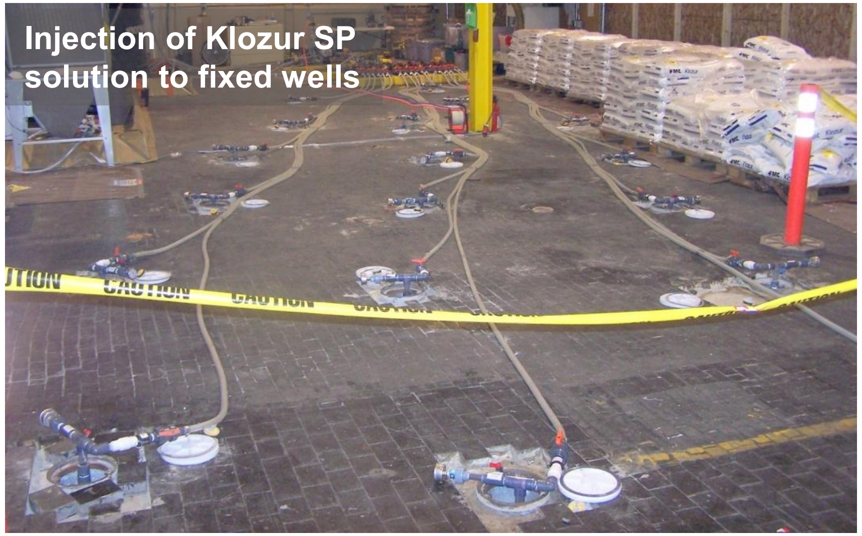
Application Methods

Keys to Success

- Focus on establishing and maintaining contact (contact time)
- Understanding the:
  - Site
  - Contaminants
  - Key characteristics of the technologies
  - Application methods

Transformative Technologies Work by Establishing and Maintaining Contact between a sufficient mass of activated oxidant for the contaminant mass in the subsurface

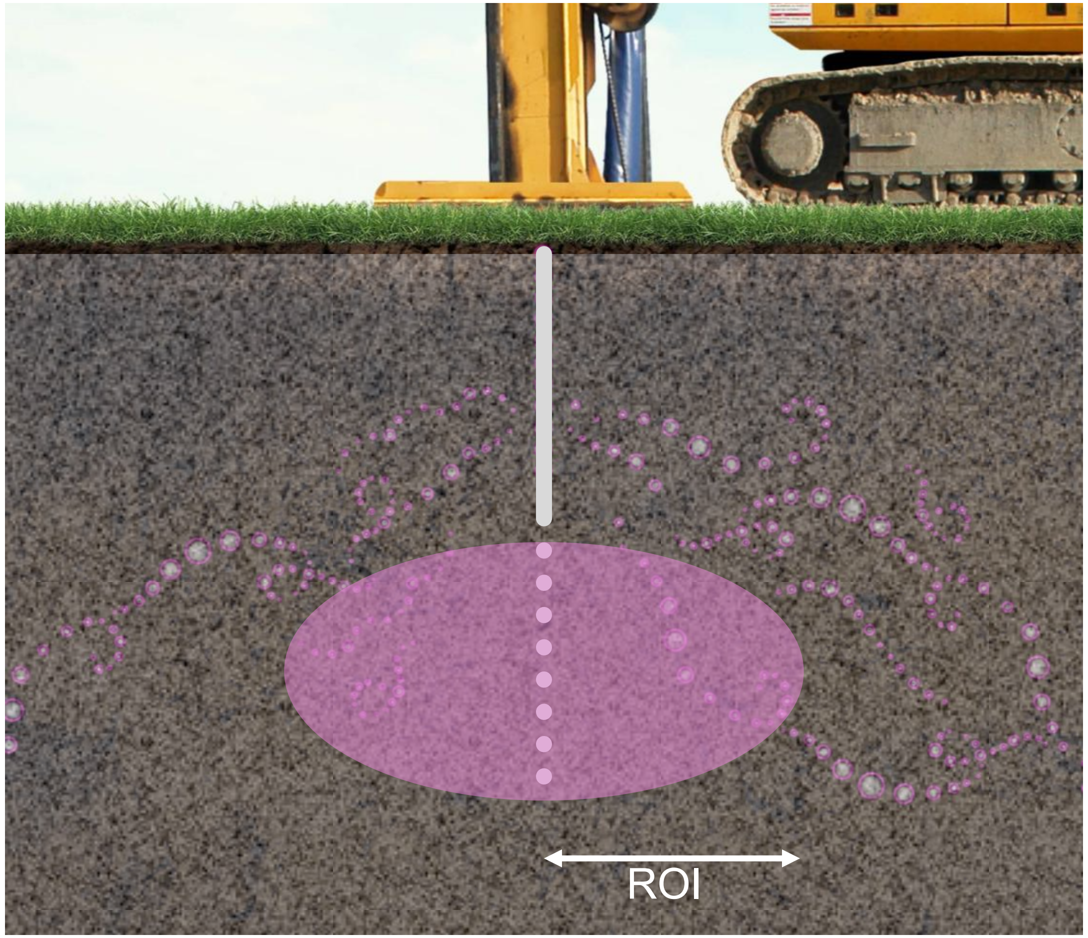
Common ISCO Application Methods



- **Injection:**
  - Soluble substrates (Klozur SP): Fixed wells, DPT, recirculation
  - Solid reagents (Klozur KP): High pressure injection of slurry (DPT/TAM-tubes/fracturing)
  - Less intrusive to site activities / low footprint
- **Soil Mixing:**
  - Uniform placement / high dose
  - Ideal for source areas and tight soils, incl. vadose zone treatment
  - Excavator, mixing heads, or large diameter augers

Liquid Injection via fixed wells or screened tip

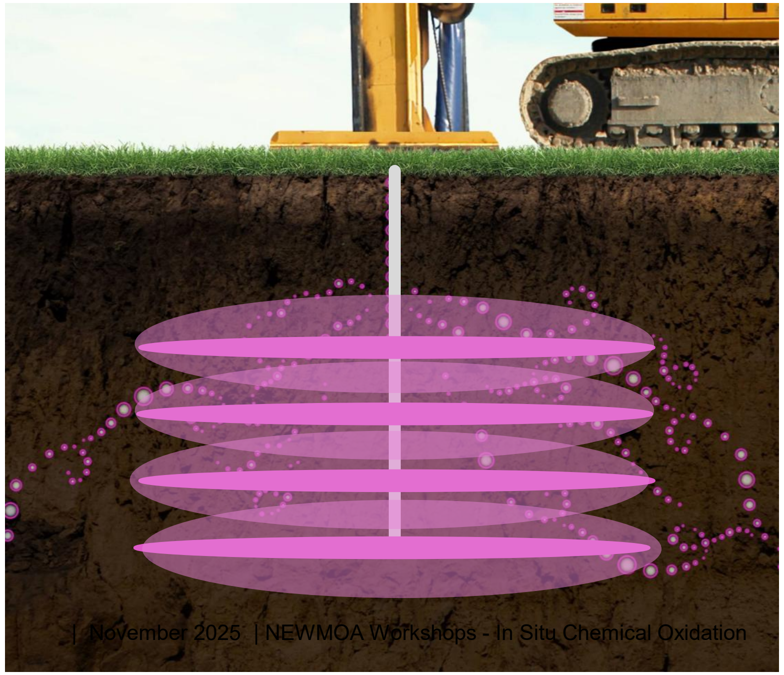
- Fully Soluble Oxidants Only
- Recommended for more permeable soils
- Radius of influence (ROI) is going to be a function of the injection volume and effective pore volume
  - Typically, 50-100% of the effective pore volume targeted within the target ROI

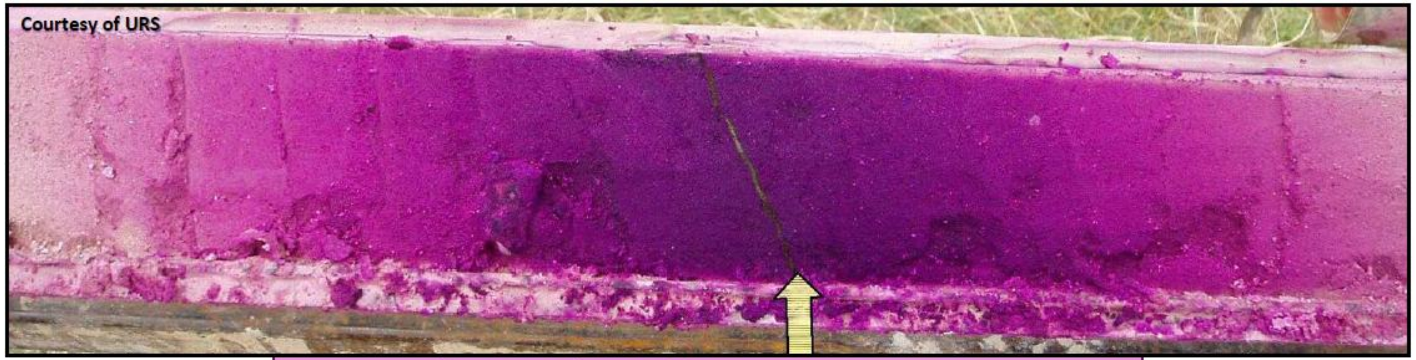


Specialized Hydraulic Fracturing

1. Solid reagents – Potassium Persulfate, Potassium Persulfate, Calcium Peroxide
2. Injection via direct push or open bore holes using packers
3. ROI up to >5 m, Depths up to >20 m bgs

Potassium Persulfate + Hydrated Lime





Potassium Permanganate

In Situ Soil Mixing

- Establishes contact:
  - Mechanical mixing
    - Augers, excavators, rotating heads, etc
    - Modern tools can inject reagents at depth
  - Homogenizes soil and contaminant
    - Minimizes impact of site heterogeneity
    - Low permeable material

- High reagent doses more easily applied
  - 0.5 to 5 percent Klozur® SP typical
  - Higher dosages can be applied

- Easily combined with in situ stabilization/solidification (ISS) technologies

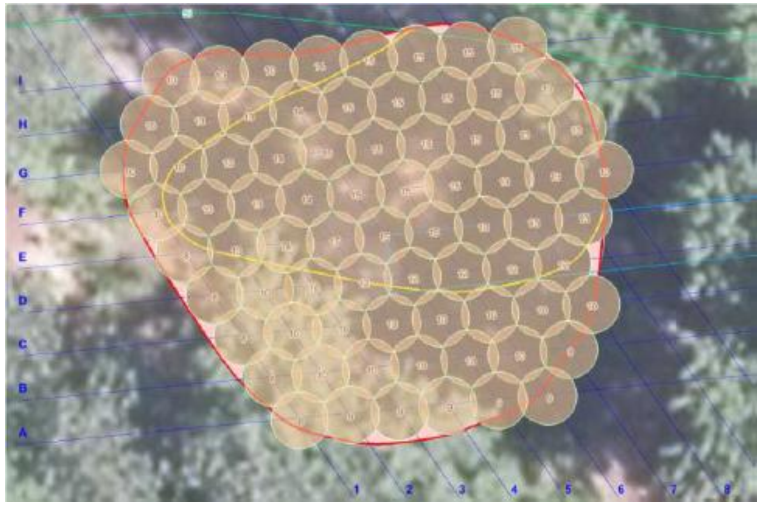
Courtesy of Stockholm Stad

Courtesy of Bill Lang

Courtesy of Jacobs

Combined Remedy: ISCO-ISS

- Remedy in a single application combining:
  - Alkaline activated Klozur® persulfate
  - In situ Solidification and Stabilization (ISS)
    - Portland cement
    - Blast Furnace Slag



Courtesy of COWI, Geosyntec, and Capital Region of Denmark

- In single soil mixing application
  - Degrades contamination (ISCO)
  - Solidifies remaining contamination (ISS)
  - Lowers leachate concentrations (ISCO and ISS)
  - Provides competent soils for future site activities and redevelopment

Former MGP Site in Stockholm being Redeveloped into Residential Area

Client: City of Stockholm

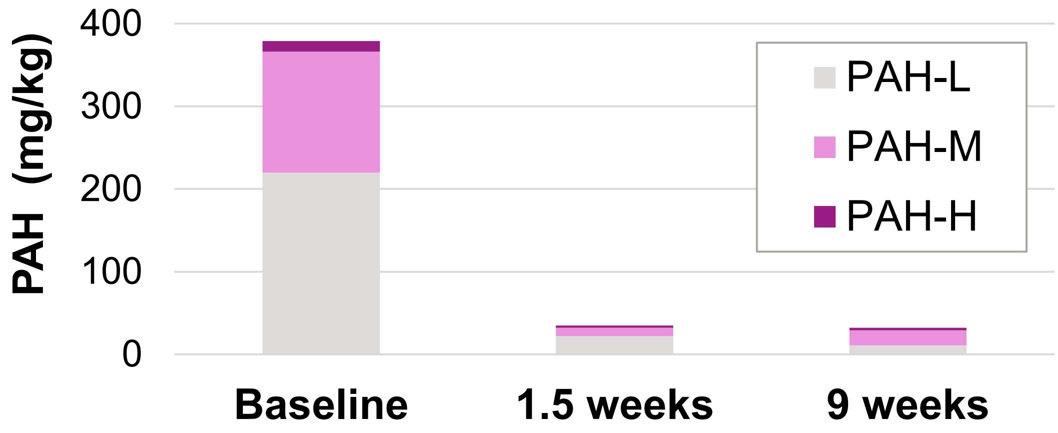
Contractor: PEAB / ARKIL

Treatment Volume: 50,000 m^3 clay layer

Remedial Goals: Prevent vapor intrusion to planned buildings via combination of stabilization and contaminant reduction

Reagent dose:
•1.8wt% Klozur SP
•4-8 wt% Slag cement

Klozur SP, cement and water applied using large diameter auger



- ~95% reduction in PAH-L
- ~90% reduction in PAH-M
- ~80% reduction in PAH-H
- Higher % reduction in lower molecular weight fractions.
- All samples below remedial goal of 250 mg/kg

Reference: Uppföljning av föroreningshalter i pelare efter stabilisering och kemisk oxidation av lera (ISS-ISCO), Golder, Jan 2022

Understanding the Oxidants: Oxidant dose per Application

Characteristic	Hydrogen Peroxide	Permanganate	Persulfate	Ozone
Liquid Injection	Limited by heat and gas evolution: <10% common	Potassium: ~30 g/L Sodium: ~200 g/L	Sodium: 50 to 250 g/L common	Limited by mass in gas and solubility in water (mg/L)
Solid Slurry Injection	NA	~1 to 1.5% w/w with soil		NA
Soil Mixing	Limited by heat and gas evolution	High Concentrations	High Concentrations (5 to 10% w/w soil)	NA
Permeable Reactive Barrier	Continuous injection	Continuous injection or solid slurry of potassium permanganate	Continuous injection or solid slurry of potassium persulfate	Ozone Sparging Systems

Favorable vs Unfavorable Site Conditions

Favorable Conditions

Charlie Munger:
"Invert, always Invert"

"How do I keep these pilots safe?"
or better question:
"How would I kill these pilots"
…and avoid those conditions

Unfavorable Conditions

- Industry has worked for ~25 years to overcome and address issues with Unfavorable Conditions:
  - **Extremely high contaminant concentrations**: Limited by what can practically be applied
  - **Low contaminant concentrations**: Counterintuitively, often leads to excessive oxidant demand and higher costs compared to competition
  - **High non-target demand**: Can make cost ineffective and inhibit treatment
  - **Establishing contact difficult**: Evolution in application methods help, but still critical to establish contact
    - Significant NAPL: Combines both of the above; 1) extreme concentration; and 2) Issues with establishing contact (dissolution limited treatment)
    - High K_{oc}/Low solubility contaminants: Can be desorption limited
    - Rapid GW velocities: Reagent flow out of target zone
  - **Contaminant limited or no reactivity:** PFSAs (i.e. PFOS); some pesticides, etc.

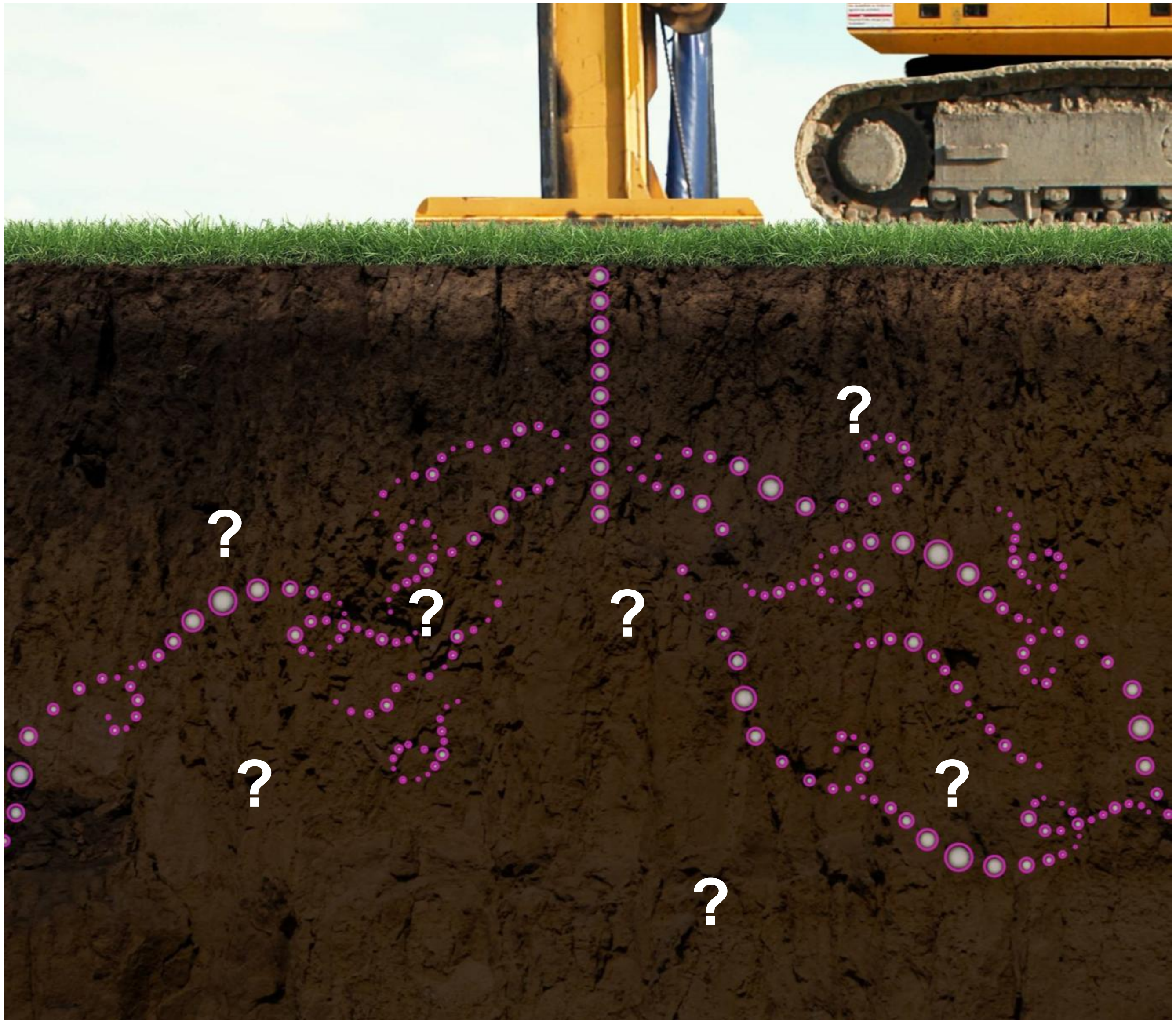
Favorable Conditions: Part 2

- Oxidant capable to treating contaminant: YES
- We can establish sufficient contact between oxidant and contaminant: YES
- Remediation timeframe matches oxidant: YES
  - Available at once-source zone
  - PRB: Bubbles from ozone, KP, PP
  - Dissolution/desorption will occur
- Contaminant demand can be met in reasonable number of applications: YES
- Other technologies are not more cost effective: YES

We Avoided The Pitfalls

Data Needs

Before, During and After



Site Characterization: Understand what is happening in the Target Volume

- Formation:
  - Soil type
    - Clay, sand, silt, bedrock, etc
    - Heterogeneity between/within soil types
  - Water content: Saturated, unsaturated and smear zones
  - Key parameters:
    - Soil bulk density
    - Hydraulic conductivity
    - Porosity and effective porosity
    - Fraction organic carbon (F_{oc})

- Groundwater velocity/flux and direction
- Preferential flow paths
- Contaminant distribution (often at interface of low and high transmissive zones)
- Contaminant types, phase, concentration, and distribution

Contaminants commonly treated in source areas, secondary source areas, plume, property boundaries and fractured rock

Best Practices: Understanding Your Site

- Use site specific data: Not assumptions
  - Porosity, effective porosity, soil bulk density, hydraulic conductivity, etc
- Assess each soil type in target area
- Assess for changes within each soil type

Soil Type	Hydraulic Conductivity (cm/sec)		
	Upper	Lower	OoM
Gravel	10^{1}	10^{-2}	3
Sand	10^{-1}	10^{-5}	5
Silt	10^{-4}	10^{-6}	2
Clay	10^{-6}	10^{-9}	3

Fetter, 3rd Edition, Applied Hydrogeology

Soil Type	Bulk Density Range (kg/m^3)		
	Upper	Lower	% Diff
Clays	1 600	1 000	60%
Sands	1 800	1 200	50%

Watts (1997) Hazardous Wastes: Sources, Pathways and Receptors

Always best to have site specific data
and
Understand that there are natural variations in each soil type

Monitoring Program

- Should be design to answer specific questions.
- Ask good questions, get good answers
- Ask unclear question, you may get unclear answers

Potential Monitoring Program

	Baseline Monitoring	Application Monitoring	Distribution Monitoring	Performance Monitoring
	To set a baseline to compare against	During application	Immediately post application	Typically, 4-10 weeks post application
Contaminants	x			x
Fraction Organic Carbon, foc	x			x
Persulfate		x	x	x
Sodium/Potassium/Activator Ions	x		x	x
Sulfate	x		x	x
Electric Conductivity	x	x	x	x
ORP	x	x	x	x
pH	x	x	x	x
DOC	x			x

Summary: Proper Monitoring can Support Better Site Understanding

Monitoring

- Residual oxidant
- Geochemical parameters (conductivity, ORP, and pH)
- Common cations and anion
  - Sodium/potassium, oxygen, Mn, calcium and/or sulfate
- Dissolved organic carbon
- Total organic carbon on soil
- Contaminant concentrations

- Reagent distribution
- Aquifer flow paths and flow velocities
- Reagent longevity
- Residence time of reagents within the target area
- Recontamination vs. rebound
- Potential for secondary treatment methods such as anaerobic oxidation
- Contaminant distribution/residual hotspots

Implementation Logistics

Courtesy of Lauderner

“No one thing that we do is very hard.

What is hard is getting all 800 things that need to be done

done properly and in the correct sequence.

---A very very very very wise man

Ok…it was me.

Implementation Logistics: Example-Injection System

- Injection locations (horizontal and vertical-accounting for topography)
- Injection wells (design, contractor, materials, etc)
- Injection system (assembled, tested, backup, etc)
- Reagent(s) (quantities, suppliers, delivery schedule, pickups/disposal, etc)
- Dilution water source
- Reagent batching system
- Tank(s): storage, batch
- Office, Porta potty, Hand Wash Station, Injection System Cover, generators, air compressors, and storage (need proper storage for reagents)
- Health and Safety: HASP, JHA, showers, eye wash, first aide station(s), staged PPE, etc
- Spill Control: Secondary containment, pathway identification, drain controls, pumps, tanks, protocols
- Notifications: Fire department, regulators, town officials, etc
- Monitoring: Baseline, application, post-application, etc

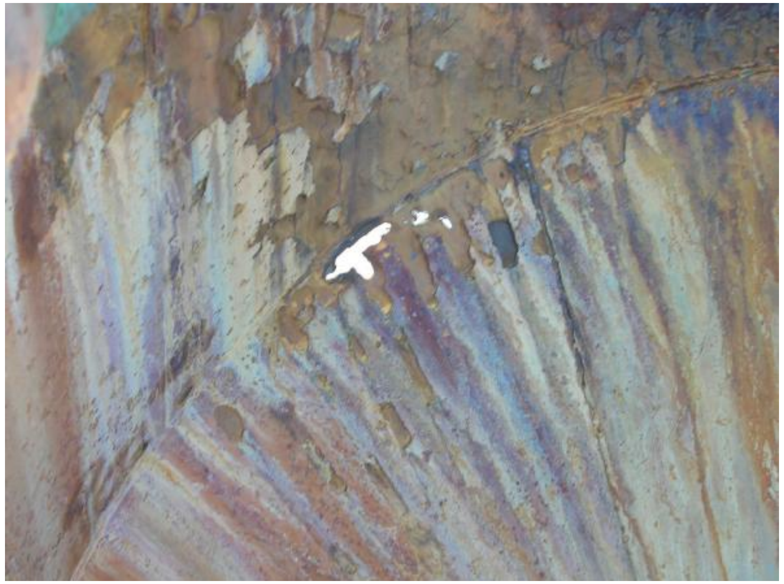
Typical Path for an ISCO Project

- Intended to Prove Concept, Generate Design Parameters, and Answer Questions
  - Bench Test
    - Design parameters (Buffer capacities, soil oxidant demands, etc)
    - Treatment Efficacy
- Pilot
  - Often used to confirm treatment efficacy
  - Best used:
    - Test ability to establish contact of given strategy
    - Develop field specific design parameters (production rates, injection pressures, radius of influence, etc)
- Full Scale Application

Lessons Learned and Recommendations

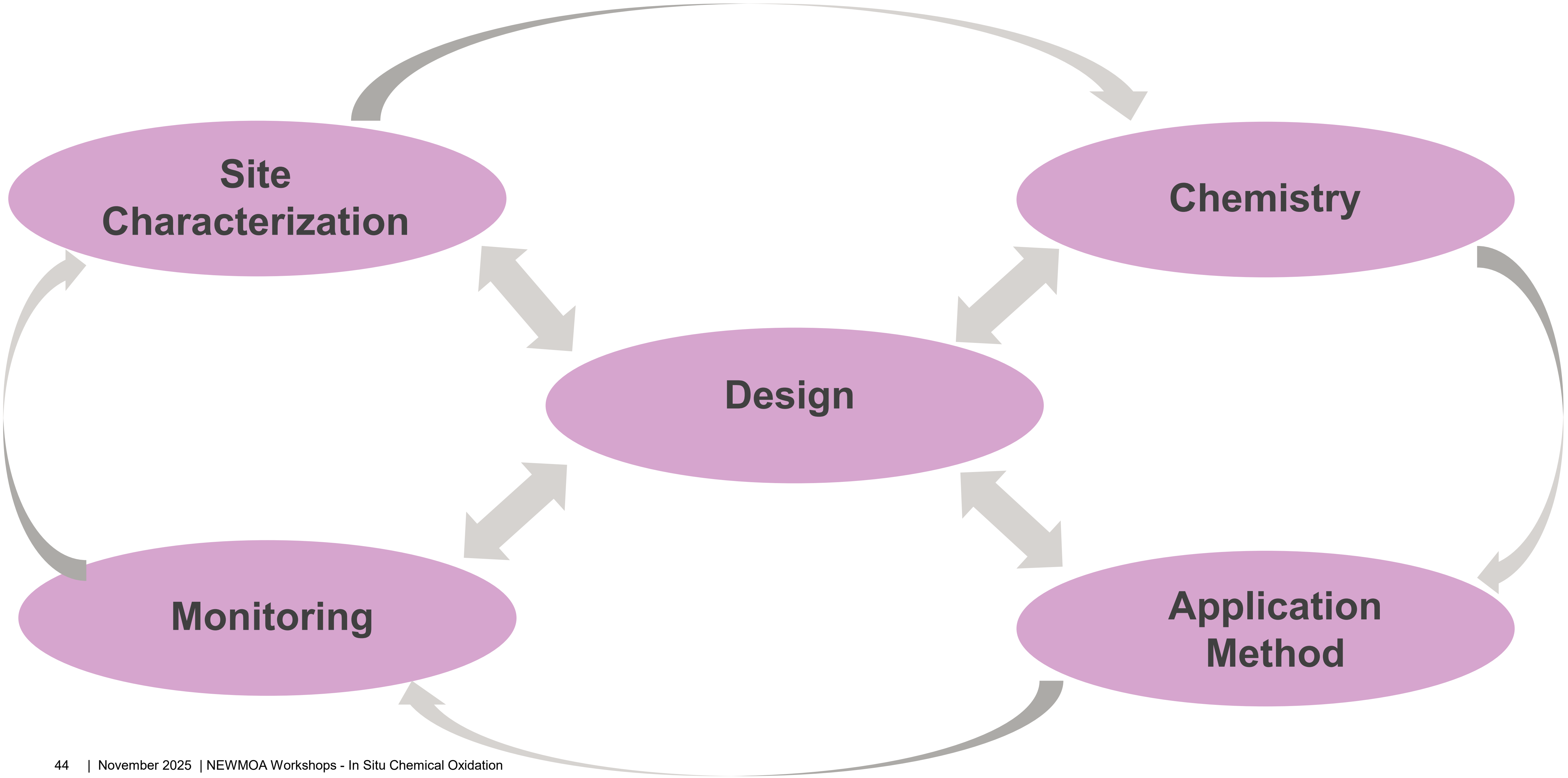
Lessons Learned

- Compatible materials
- Water is an important component of mixture
- Behavior of Sediments is very different from “upland” soils



Lessons Learned

- Soil Oxidant Demand/Non-target Demand: Used to not be quantified.
- Injection Volumes: Some still inject small volumes, more common to target 50-100% of the effective porosity
- Large ROIs: Save on injection well installation costs, but have issues with injection volumes and preferential flow paths
- Large Vertical Target Intervals: Issues with preferential flow paths
- Matching screen intervals between Monitoring and Injection Locations
- Rebound vs Recontamination: Be mindful of upgradient contamination and GW flow velocities
- Contaminant partitioning: Understanding mass balance (soil/NAPL/GW) vs just aqueous GW concentrations
- Combined remedies: Understand the evolving situation at your site and use the appropriate technology
- Flexibility: Being able to adapt to new or unforeseen conditions. Do not trap yourself.
- Insanity: Do not do the same thing over and over again and expect a different result


Site Characterization
Chemistry
Design
Monitoring
Application Method

Combining Key Characteristics

- Site Characteristics
  - Groundwater velocity
  - Soil/Formation/Matrix type
  - Access
  - Remedial goals
  - Remediation timeline
- Contaminant Characteristics
  - Phase
  - Solubility
  - Partitioning (K_{oc})
  - Distribution/Concentration
  - Mass

- ISCO Chemistry
  - Oxidative and Reductive Pathway
  - All oxidant available at once vs Extended Release
  - Contaminant K_{oc}
  - Mass to be applied
  - Cost
  - Aerobic bio after ISCO
    - Klozur CR
  - Anaerobic bio after ISCO
    - Sulfate reduction after persulfate
    - DOC

- Application Methods/Establishing Contact
- Monitoring Programs

Best Practices for Designing and Applying In Situ Chemical Oxidation (ISCO)

- **<u>Site:</u>** Understanding details, goals, and objectives of each site.
- **<u>Chemistry</u>:** Is the contaminant degraded by activated the oxidant?
- **<u>Design</u>:** Is there sufficient oxidant mass to react with non-target demand and the contaminant mass?
  - Safety factors
- **<u>Application</u>**: How will the persulfate chemistry establish contact with the contamination in the subsurface?
- **<u>Monitoring Program</u>**: Designed to answer key questions regarding the ISCO application

<u>Current Best Practices</u>

Understanding Key Characteristics of Each Facet of a Remedy and Combining them in the Most Advantageous Way for Your Site

- Chemistry
- Site
- Contaminant
- Application Method

Use Monitoring Program to Inform the Design, Understand the Application, and Confirm Progress toward Remedial goals.

Questions

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Leading Beyond Chemistry