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Environmental Solutions

Design Consideration for Activated Klozur® Persulfate Field Applications

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Who We Were…

PeroxyChem

New Name.
Decades of Experience.

1980's
Hydrogen Peroxide Applications

1999
First Application of PermeOx® Plus

2004
Launch of Klozur® Persulfate

2006
Launch of Klozur® CR

2007
FMC offers Klozur Demand Testing

2011
FMC acquired Adventus

2014
FMC Corporation divested the Peroxygens Group, **PeroxyChem was founded**

1988
WR Grace Remediation R&D Program

1994
First Application of Daramend® Reagent

2002
Adventus Remediation Technologies was formed via WR Grace Divestiture

2003
First Application of EHC® Reagent

2004
EnviroMetal Technologies Acquired by Adventus

2012
FMC Environmental Solutions Division Formed

Field-Proven Portfolio of Remediation Technologies Based on Sound Science

***In Situ* Chemical Oxidation**

1. Klozur® persulfate
2. Klozur® CR

In Situ Chemical Reduction

3. EHC®
4. EHC® Liquid
5. Daramend®

Aerobic Bioremediation

6. Terramend®
7. PermeOx® Ultra

Immobilization/Stabilization

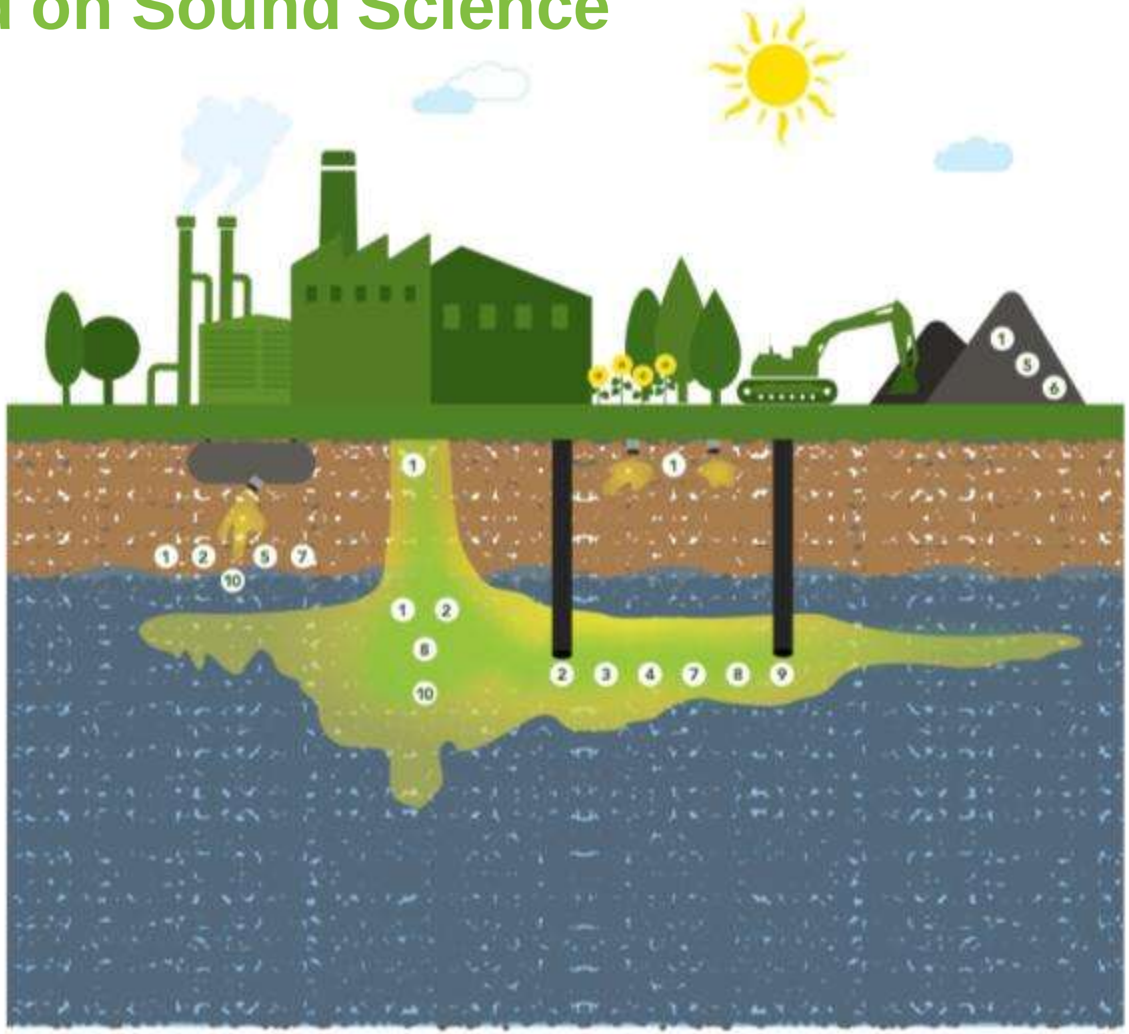
8. EHC® Metals and MetaFix™

Enhanced Reductive Dechlorination

9. ELS™

NAPL Stabilization/Mass Flux Reduction

10. ISGS™



Support We Provide

Klozur® Specific Support Services

- Mixing & Injection Equipment
- Bench Scale Tests
- Klozur® Field Test Kits
  - Measure persulfate in the field
- Klozur® Stabilization Kits
  - Quench residual persulfate prior to analysis

IN SITU CHEMICAL OXIDATION

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What is ISCO

- In Situ Chemical Oxidation (ISCO)
- Addition of chemicals to the soil and groundwater that react with a wide variety of chemicals of concern (COCs) by taking electrons from, or oxidizing, those COCs
- Oxidative, reductive and nucleophilic pathways have also been shown to be effective under certain conditions

Why ISCO?

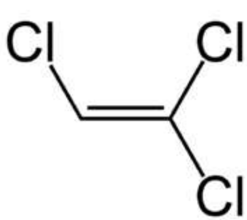
- Many in situ remediation technologies to choose from, why pick ISCO?
  - **Cost**: Often the lowest cost alternative
  - **Time**: Provides results quickly, usually within weeks to months of an application
  - **Effectiveness**: ISCO can treat a wide assortment of typical COCs
  - **Contaminant Mass**: ISCO can treat a wide variety of contaminant concentrations including heavily impacted areas that may inhibit bioremediation

Introduction to Klozur® Persulfate

Examples of Contaminants Destroyed by Klozur Persulfate

Chlorinated Solvents
PCE, TCE, DCE
TCA, DCA
Vinyl chloride
Carbon tetrachloride
Chloroform
Chloroethane
Chloromethane
Dichloropropane
Trichloropropane
Methylene chloride

Others
Carbon disulfide
Aniline
PVA/ TNT / DNT



TPH
BTEX
GRO
DRO
ORO
creosote

Oxygenates
MTBE
TBA

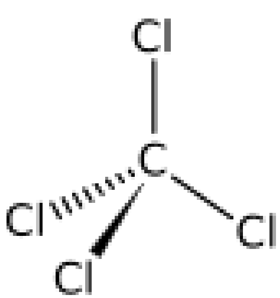
Perflourinated
Freon
PFOS
PFOA
PFBA

Chlorobenzenes
Chlorobenzene
Dichlorobenzene
trichlorobenzene

Phenols
phenol
Pentachlorophenol
nitrophenol

PAHs
Anthracene
Benzopyrene
Styrene
Naphthalene
Pyrene
Chrysene
trimethylbenzene

Pesticides
DDT
Chlordane
Heptachlor
Lindane
Toxaphene
MCPA
Bromoxynil



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Introduction to Klozur® Persulfate

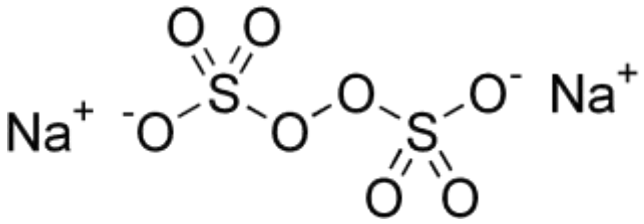
Klozur® Persulfate is:

- Based on the sodium persulfate molecule
- A strong oxidant used for the destruction of contaminants in soil and groundwater
- Aggressive and fast acting chemistry with extended subsurface lifetime (weeks to months) and little to no heat or gas evolution
- Applicable across a broad range of organic contaminants
- Highly soluble in water (significant oxidant mass is smaller volumes)

Field solubility of more than 500 g/L possible

Fundamental Chemistry

- Klozur® Activated Persulfate is based upon the persulfate anion:



- Persulfate is a peroxygen, and similar to hydrogen peroxide, it can be split at the O-O bond forming the sulfate radical:

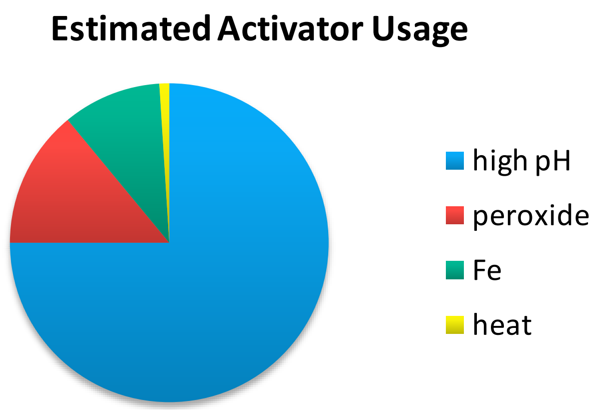
$$^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^{-} \rightarrow {}^{-}O_3S\text{-}O\bullet \quad \bullet O\text{-}SO_3^{-}$$

Radical Formation

- Common activation methods include:
  - Alkaline activation
    - ($OH\bullet$, $SO_4\bullet^-$, $O_2\bullet^-$)
  - Nascent iron, iron or iron chelate activation
    - ($SO_4\bullet^-$)
  - Heat activation
    - (Temperature dependent: $OH\bullet$, $SO_4\bullet^-$, $O_2\bullet^-$)
  - Hydrogen peroxide activation
    - ($OH\bullet$, $SO_4\bullet^-$, $O_2\bullet^-$)

Oxidant	Standard Reduction Potential (V)	Reference
Hydroxyl radical ($OH\bullet$)	2.59	Siegrist et al.
Sulfate radical ($SO_4\bullet^-$)	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 ($O_2\bullet^-$)	-0.33	Siegrist et al.
ZVI	-0.45	CRC (76th Ed)

Activator Selection



- Alkaline Activated Persulfate
  - Premier activation method
  - Best suited for most applications
- Iron or Iron-Chelate Activated Persulfate
  - Chlorinated ethenes and hydrocarbons
  - Less contaminant mass
- Heat
  - Complex sites
  - Polishing step after thermal treatment
- Hydrogen Peroxide
  - Sites that benefit from vigorous reaction with both hydrogen peroxide and sodium persulfate

CONSIDERATIONS FOR DESIGNING KLOZUR® PERSULFATE FIELD APPLICATIONS

Design Considerations

- Goal:
  - Help have success implementing Klozur Persulfate
- Considerations
  - Each site is unique
  - Many ways to accomplish a successful field event
  - Uncertainty is a common factor with in situ remediation

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Field Applications

- Reactions are known to take place on the laboratory scale
  - Key is scaling up the laboratory scale results into the field

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

Field Applications

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

Field Applications

Sufficient Mass

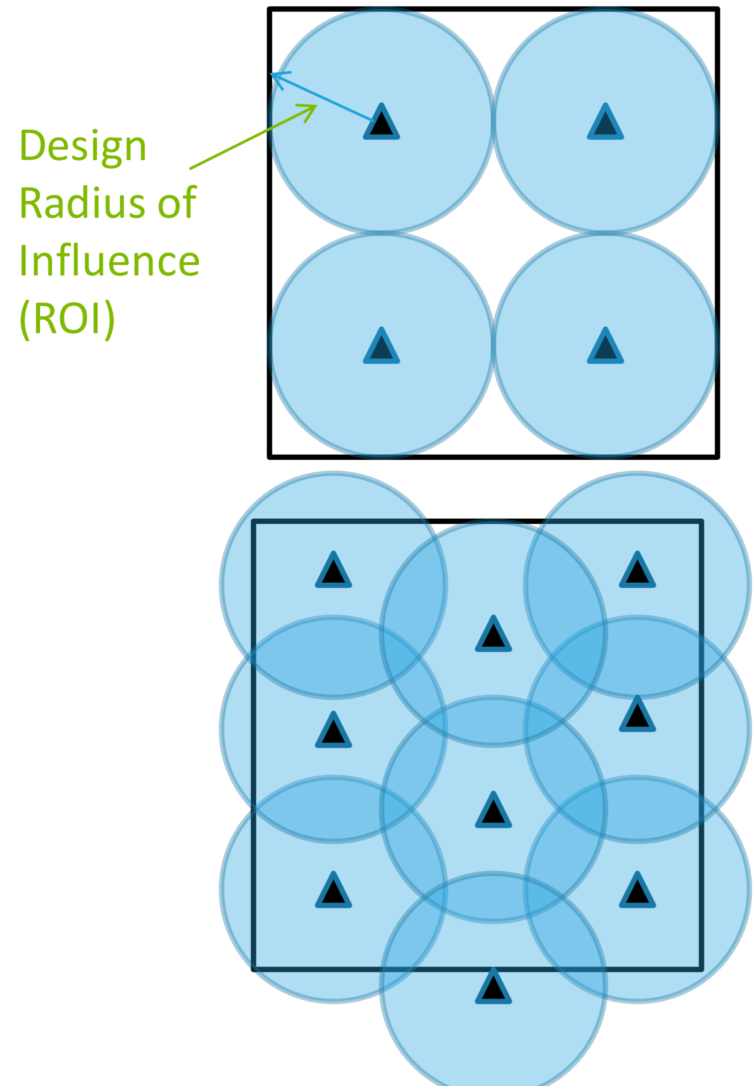
- Oxidant
  - Total Contaminant Mass
  - Non-target demand
    - Target Volume
  - Degradation ratio
  - Confidence of Treatment
    - Safety Factors
- Activator
  - Varies with activator

Establishing Contact

- Site Geology
- Contaminant Distribution
  - Injection location placement (vertical and horizontal)
- Injection Volume
  - Effective vs Total Porosity
- Injection Point
  - Spacing/Density
  - Vertical Interval
  - Injection ROI vs Design ROI
- Injection Strategy
- Groundwater Velocity

Target Area

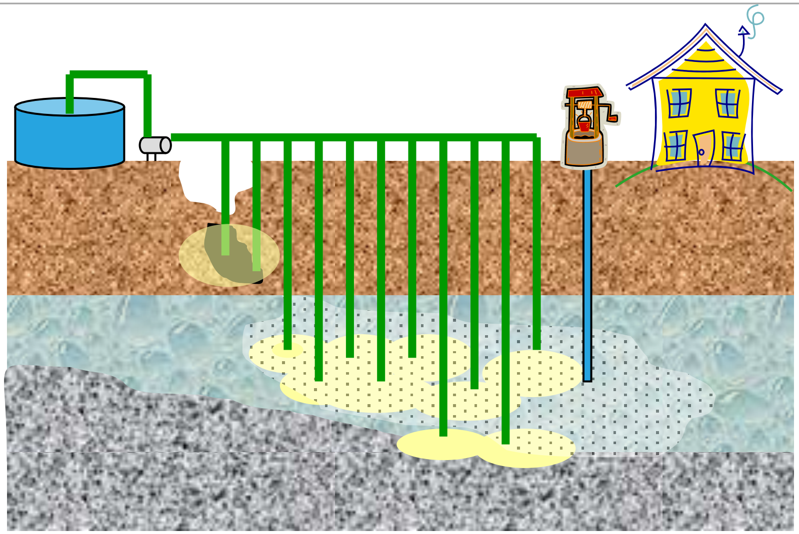
- Design Target Area:
  - Based on a box
  - Sum ROI of injection points
- Considerations
  - Overlapping ROI
  - ROI outside of the box
  - Distance “on center”
  - Impacts on:
    - Injection Volume
    - Oxidant Mass

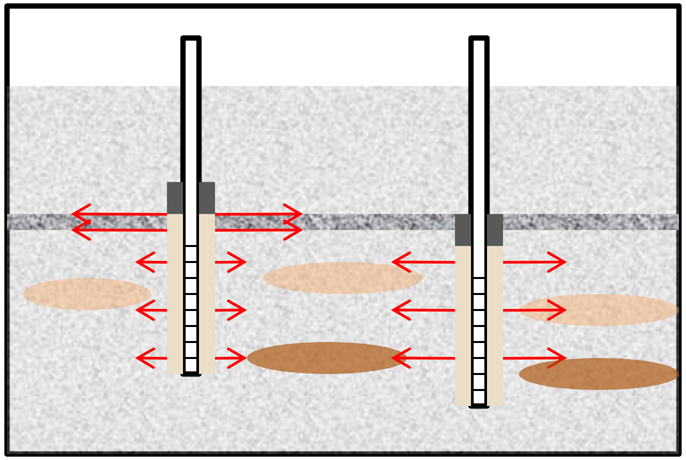


Target Interval

- Vertical interval to be targeted with injection
  - Impacts volume to be treated

- Considerations:
  - Contaminant distribution over interval
  - Preferential pathways within target interval
  - Sand pack vs screen interval





Oxidant Mass: Contaminant Mass Estimate

- Contaminant Mass Phase:
  - Groundwater (mg/L)
  - Soil (mg/Kg)
  - Non-aqueous phase liquid (NAPL) (lbs or kgs)

- Total contaminant mass needs to be considered in the design
  - Sum the estimated mass in each phase in areas to be treated with ISCO

- Analytical data preferred but can use partitioning coefficients to estimate between soil and groundwater
  - $K_d = K_{oc} * f_{oc}$ = (Conc on Soils)/(Conc in GW)
    - Issues as you approach saturation

K_d = Partitioning or distribution coefficient of contaminants in a natural system
K_{oc} = Organic carbon partition coefficient
F_{oc} = Fraction of organic carbon

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Persulfate Stoichiometry

Persulfate Oxidation Principles:

Taking of e- is the oxidative step

$$S_2O_8^{-2} + 2H^+ + 2e^- \rightarrow 2HSO_4^{-1}$$

persulfate anion

Examples

Note acid formation

$$15\ S_2O_8^{-2} + C_6H_6 + 12\ H_2O \rightarrow 6\ CO_2 + 30\ HSO_4^{-1}$$

benzene

45 lb / lb

$$2\ S_2O_8^{-2} + C_2Cl_4 + 4\ H_2O \rightarrow 2\ CO_2 + 4\ Cl^- + 4\ H^+ + 4\ HSO_4^{-1}$$

PCE

3 lb / lb

Oxidant Mass: Non-Target Demand

- Sufficient oxidant is needed to account for non-target demand
  - Soil Oxidant Demand (SOD)
    - Reduced metals in mineralogy
    - Naturally occurring organics
  - Demand associated with the contamination that may not be target demand
    - e.g. DRO or GRO (non-target) associated with BTEX (target)

Estimating Oxidant Mass

- Basic Calculations:
  - Targeted Contaminant Mass:

    Contaminant Mass[1] – Remedial Goal = Target Mass
  - Theoretical:

    Target Mass x Stoichiometric Ratio[2]
    + SOD x Soil Mass
    Required Oxidant
  - Laboratory Based[3]:

    Target Mass x Degradation Ratio
    Required Oxidant

1. Designers may elect to use maximum or average concentrations depending upon contact strategy.
2. Effective destruction of TPH compounds with less than the stoichiometric ratio has been observed.
3. SOD sometimes included with degradation ratio to estimate required oxidant. For example, if field contaminant concentrations are less than those tested in laboratory.

Estimating Oxidant Mass

- Considerations:
  - Calculation estimate the minimum oxidant mass required.
  - Oxidant to be lost outside of the target area
  - Accuracy of estimates:
    - Contaminant mass
    - Non-target demand (SOD)
  - Contaminant Mass (average vs maximum)
    - Reagents are injection uniformly
    - Contaminants are often not distributed uniform
    - Could lead to overdosing of some areas and underdosing of others

- Potential options:
  - Address considerations directly
  - Apply a safety factor onto the oxidant mass calculations

Estimating Activator Mass

- Estimating Klozur Persulfate Activator:
  - Iron-EDTA
    - Target 150 mg/L to 600 mg/L of iron in solution
    - Higher concentrations of iron for:
      - Higher concentrations of persulfate
      - Faster subsurface kinetics (not always needed)
  - Alkaline

Base Buffer Capacity x Soil Mass to be contacted
<u>+ 2 moles NaOH per mole of Klozur Persulfate</u>
Required Mass of Sodium Hydroxide (or equivalent)

Estimating Activator Mass

- Hydrogen Peroxide
  - 1 to 10 moles of hydrogen peroxide per mole of sodium persulfate
  - Recommended to be determined on a bench test
    - Potential use of stabilizers for the hydrogen peroxide
- Heat
  - Raise temperature into range where persulfate is known to degrade contaminants of concern
  - Steam, ERH, etc used to heat subsurface

ESTABLISHING CONTACT

Site Geology and Contaminant Phase

- Understanding where injected reagents are likely to flow
- Contaminant distribution
  - Ability to establish contact
  - Low volume/high concentration injections have had success in low permeable soils
- Contaminant Phase
  - Groundwater
  - Soils
  - NAPL—contact a function of surface area

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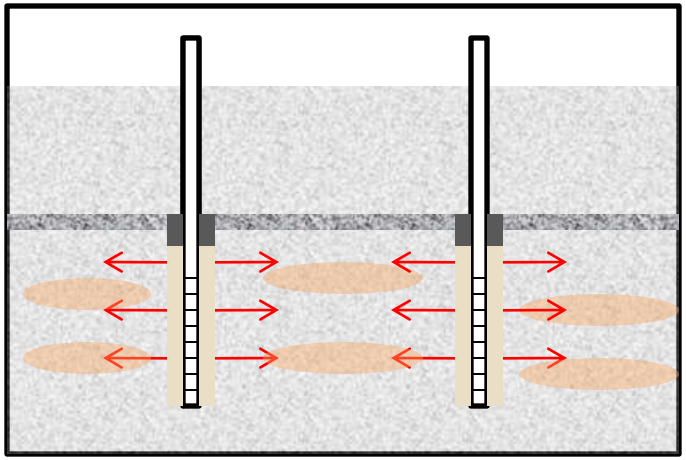
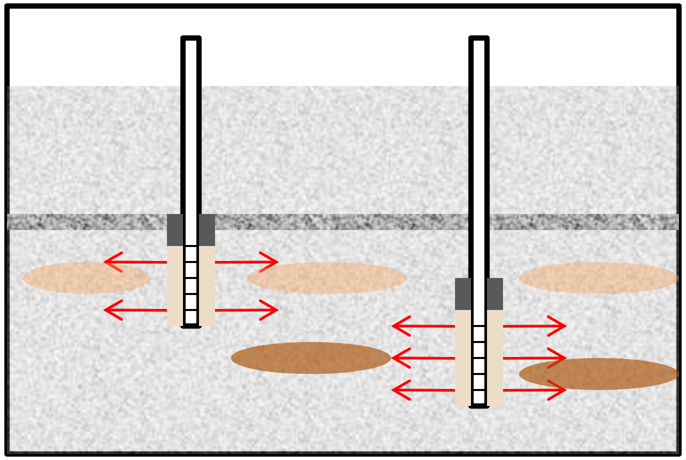
Contaminant Distribution

- Uniform contaminant distribution
  - Uniform distribution of oxidant solution
- Hetergeneous contaminant distribution can be selectively targeted by varying:
  - Injection concentration
  - Injection volume
  - Multiple applications
  - Key is to get sufficient oxidant to contact contaminant mass
- Age and area of contamination
  - Source area vs Plume
  - Old vs less old





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Injection Volume

- Volume injected key to achieving distribution and establishing contact with contamination
  - Advection from injection
  - Advection from groundwater flow
  - Diffusion/dispersion
- Type of Pore Volume
  - Total – Total void/pore space
  - Effective - Porosity available for fluid flow
- Typical Fraction of Pore Volume:
  - 0.3 to 1 pore volumes is typical for permeable soils
  - 0.01 to 0.2 pore volumes is typical for tight soils and fractured bedrock

Injection Volume

- Additional Considerations:
  - Preferential pathways
  - Earlier injected reagents likely to encounter more demand for the oxidant
    - Over inject (safety factor on injection volume)
    - Higher concentration of oxidant for earlier injected reagents
  - Overlapping ROIs
  - Density driven migration
    - Used to target contamination
    - Density increases with concentration

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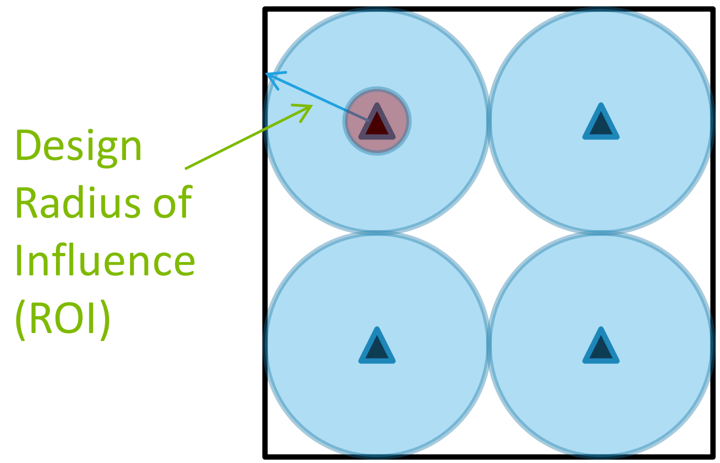
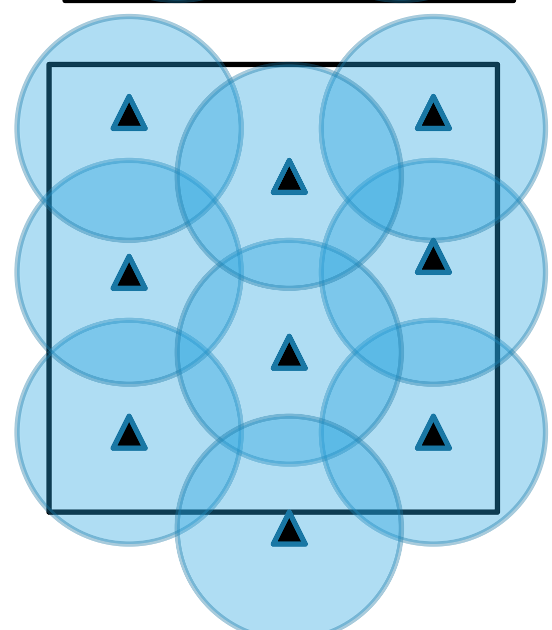
Injection Point Network

- Injection Point Density
- Overlapping ROIs
- Vertical Interval
- Design ROI vs Injection ROI
- Accounting for mass outside the target area
- Distance "on center"



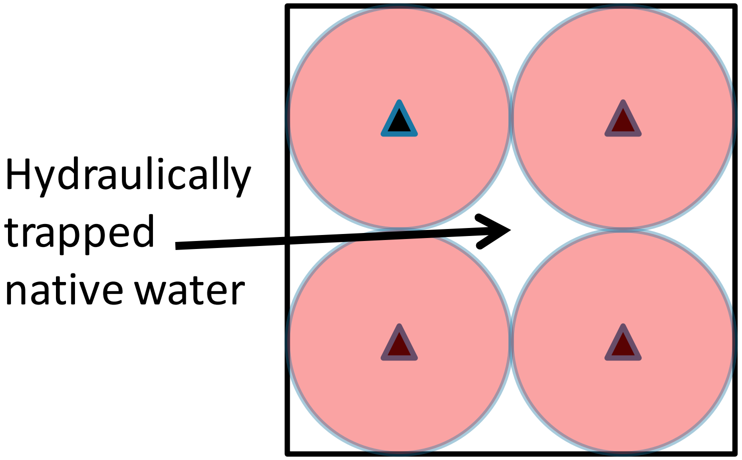


Common Injection Strategies

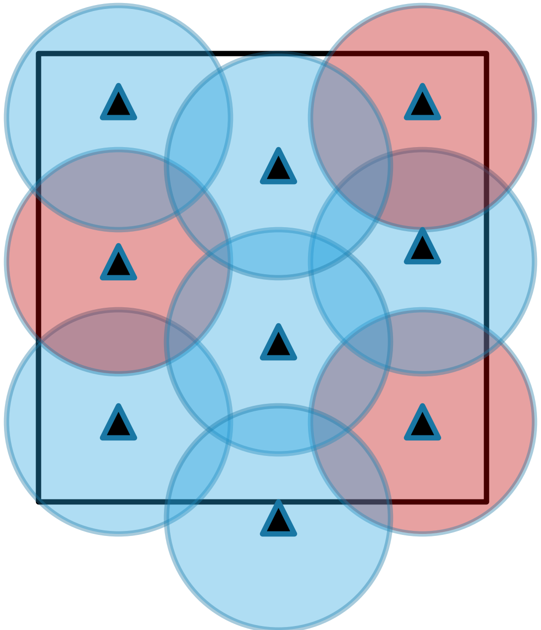
- Direct Injection
  - Injection through injection point
- Recirculation
  - Injection through injection point coupled with extraction through separate extraction points
- Pull/Push
  - Extract a volume of groundwater from a point, amend with reagents, and reinject into the same point
- Push/Pull
  - Inject reagents into a point and then extract the reagents from the same point (used for pilot tests)
- Flow Down
  - Inject reagents to let groundwater advection transport the reagents to the target area

Injection Strategy

- Native water, if trapped, can create a hydraulic barrier to prevent reagents from equally distribution



- Inject with a strategy that allows pathways for displaced water to flow



Oxidant Concentration

- Injection Concentration
  - 50 g/L to 250 g/L is typical
  - Higher Concentrations:
    - Lower permeable material/Fractured Bedrock (less accessible injection volume)
    - High contaminant mass
    - Aggressive treatment
  - Lower Concentrations
    - Larger injection volumes
    - Lower contaminant concentrations

- Subsurface Concentration
  - Concentration of oxidant in an entire pore volume
  - 20 g/L to 250 g/L is typical
  - Concentration largely depends on
    - Mass of contaminants
    - Aggressiveness of treatment

Number of Applications

- Injection volume and number of applications used to maintain practical reagent injection concentrations

- Monitoring between applications can be used to refine target area
  - Diagnostic for highly contaminated areas

Additional Design Considerations

- Injection Rate
- Injection Pressure
- Number of Simultaneous Injection Points
- Work hours
  - Sufficient light
- Delivery Schedule
- Reagent Batching

Summary: Bench Test

- Bench tests can be used to estimate design parameters including:
  - Soil oxidant demand
  - Total oxidant demand
  - Degradation ratio
  - Base buffering capacity (Alkaline activation)

Summary: Key Design Parameters

Sufficient Oxidant

- Target Area, Interval and Volume
- Contaminant Mass
  - Avg vs maximum
  - Distribution
- Stoichiometric ratio
- Degradation ratio
- Non-target demand
- Safety Factors
  - Non-target demand
  - Contaminant mass
  - Mass outside target area
- Sufficient activator
  - Base buffering capacity
  - etc

Establishing Contact

- Injection point density
- Design Radius of Influence
  - Overlapping ROIs
- Injection volume
  - % of pore volume
  - % of radius of influence
- Injection strategy
- Groundwater velocity
- Contaminant distribution
  - Compared to site geology
- Multiple applications

Summary: Basic Steps to a Design

1. Develop cross section of target interval with detailed geologic and contaminant information
2. Bench test soils representative of target area
3. Decide how best to target the contamination and establish contact between a sufficient mass of activated oxidant and the contaminant (potentially on well by well basis)
    1. Mass of oxidant and activator
    2. Injection strategy and volume
4. Develop monitoring program that will show success of treatment as well as progress toward remedial goals

Conclusion

- Activated Klozur persulfate is a common, highly successful ISCO technology capable to treating most organic contaminants of concern
- Common keys to success: Establishing contact of sufficient activated oxidant mass with the contamination
- Bench tests can be used to determine key design parameters

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Thank You - Questions

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