An Update on Design Considerations for Activated Klozur® Persulfate Applications

Soil & Groundwater Remediation

Webinar | October 25, 2023

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Webinar Overview

- Update from 2015 Webinar
- Discuss options, key considerations and concerns regarding:
  - Site Characterization
  - Relevant Chemistry
  - Design
  - Application methods
  - Monitoring Programs

Courtesy of LEA (XDD, LLC)

How is Klozur® Persulfate Applied?

- Focus on establishing and maintaining contact (contact time)
- The most common methods:
  - Injection
  - Amendment to an open excavation
  - Soil mixing

ISCO Works by Establishing and Maintaining Contact between a sufficient mass of activated oxidant for the contaminant mass in the subsurface

Typically start with a box

- Target area
  - Length x width x height = Target Volume
- Understand what is within that box

Site Characterization

  - Contaminant type, phase, concentration and distribution
    - Uneven distribution may require designs for each area
  - Develop contaminant mass estimate
  - Groundwater direction, flux and velocity

Typically start with a box

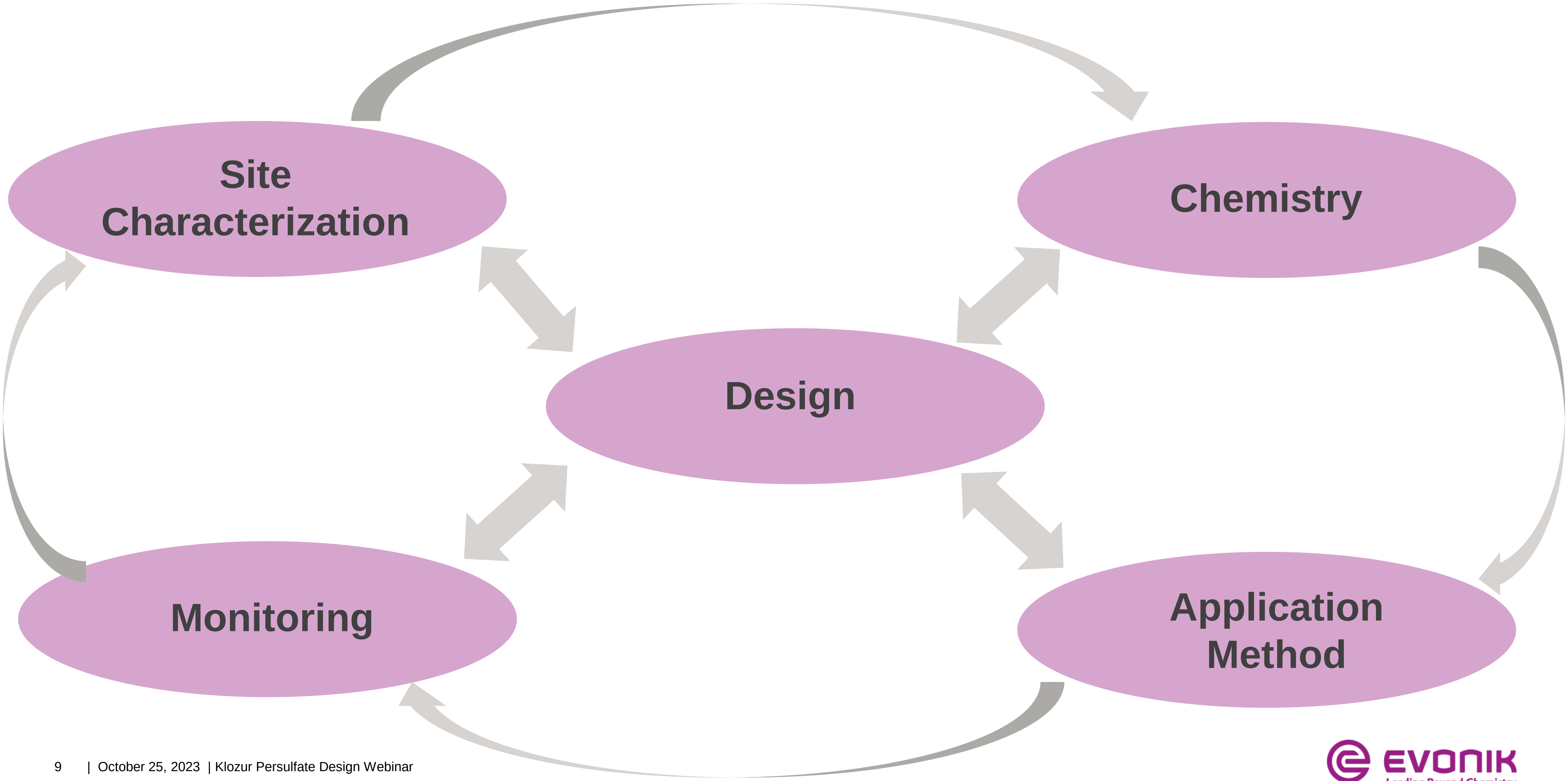
- Start asking yourself:
  - What technologies will treat my contaminants of concern?
  - How much mass of oxidant do I need to effectively treat the contaminant mass?
  - How do I establish and maintain contact of my activated persulfate with the mass of contaminant in the box?
  - How do I confirm the efficacy of the treatment and learn more about the site to improve any subsequent applications?

Chemistry

Design

Application Method

Monitoring Program


Site Characterization
Chemistry
Design
Monitoring
Application Method

Site Characterization: Understand what is happening in the box

- Many sites are characterized from a risk perspective

Common information needed for a site to characterize for design

- Formation:
  - Soil type vs bedrock
  - Water content: Saturated, unsaturated and smear zones
  - Heterogeneity between soil types
    - Same soil type can have heterogeneity
  - Parameters:
    - Soil bulk density, hydraulic conductivity, porosity, effective porosity, and 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

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/m3)		
	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

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Chemistry

Klozur® Portfolio: What they are

KLOZUR® SP

Environmental grade, high purity (>99%) sodium persulfate (SP)

KLOZUR® KP

Environmental grade, high purity (>98%) potassium persulfate (KP)

KLOZUR® ONE

95% Klozur® SP and 5% built in activator

- Iron-chelate and organic acid activated persulfate

KLOZUR® CR

A 50/50 blend of Klozur® SP and PermeOx® Ultra engineered calcium peroxide.

- Alkaline and hydrogen peroxide activated persulfate

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Activators

- Persulfate is activated to form more powerful oxidative and reductive radicals

Activation Method	Liquid	Solid	Treatment Pathways	Comments
Alkaline	25% NaOH	$Ca(OH)_2$ Calcium peroxide	Oxidative & Reductive	More compatible with carbon steel
Klozur® One	Built in (Organic acid and Iron-chelate)	--	Oxidative	All-in-One
Iron chelate	Fe-EDTA Fe-Citrate Fe-Lactate	--	Oxidative	Recent challenges procuring Fe-chelates
Hydrogen Peroxide	Hydrogen Peroxide	Calcium peroxide	Oxidative & Reductive	Powerful but limitations with H_2O_2
ZVI	--	Zero Valent Iron	Oxidative	Caution with exothermic nature

Chemistry: Activation and Degradation Pathways

Oxidative | Either | Reductive

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
1,4-Dioxane	PCBs	

Alkaline or Hydrogen Peroxide Activated Persulfate

Klozur® One and Iron Activated Persulfate

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Contaminant Physical Properties

- Contaminant chemistry can be critical in both treatability and in establishing contact
- Establishing contact:
  - Contaminant can be in non-aqueous phase
    - Non-aqueous phase liquid
    - Partitioned onto soils
  - Solubility
    - If primarily in aqueous phase, may be displaced by injection strategy
      - Consider: Permeable reactive barrier, soil mixing or solid slurry reagents

$$K_d = Koc * foc = \frac{Soil\ (\frac{g}{Kg})}{GW\ (\frac{g}{L})}$$

Contaminant	EPA* K_{oc}	F_{oc}	Contaminant Distribution (%)	
			GW	Soil
1,4-Dioxane	17	0.005	70%	30%
1,1,1-TCA	110		27%	73%
1,2-DCA	38		51%	49%
1,1-DCA	53		43%	57%
DCE	38		51%	49%
Benzene	59		40%	60%
Toluene	182		18%	82%
Ethylbenzene	363		10%	90%
Xylene	386		9%	91%
TCE	166		19%	81%
Carbon Tetrachloride	174		19%	81%
1,2-Dichlorobenzene	617		6%	94%
Dieldrin	21,380		0%	100%
Note:	1. Assuming 1.5 g/cm^3 soil bulk density and effective pore volume of 0.15			

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Oxidants have characteristics too!

- Sodium persulfate has higher solubility
  - Entirely available at time of application
- Potassium persulfate has much lower solubility
  - Applied as solid slurry and will slowly dissolve over time due to limited solubility
- Both dissolve to release the persulfate anion
  - Once dissolved, tends to persist for 1-8 weeks

Temperature	Klozur® SP $Na_2S_2O_8$		Klozur® KP $K_2S_2O_8$	
(℃)	wt%	g/L	wt%	g/L
0	36.5	480	1.6	17
10	40.1	540	2.6	29
20	41.8	570	4.5	47
25	42.3	580	5.7	59

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When to Use Lower Solubility/Solid Slurry Oxidants?

- High Solubility: When you want all oxidant available at injection. Source zones, high oxidant demands, etc.
- Lower Solubility:
  – Treating Aqueous Phase Contaminants
    – Permeable Reactive Barriers (PRBs)
    – Source zones
  – Longer Contact Time
    – Low permeable soils
    – Low solubility contaminants
    – Low contaminant concentrations
  – High groundwater velocity

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

Klozur KP Solid Slurry Fracture

Courtesy of FRx/Brown & Caldwell

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Klozur® Portfolio: What they do

KLOZUR® SP

When you want oxidant available at time of application.

- Source areas
- Highly contaminated soils
- Alkaline activation helps protect carbon steel (DPT/soil mixing)

KLOZUR® KP

When you want extended release of the oxidant.

- Permeable reactive barriers (PRBs)
- Low permeable soils
- Low to moderate contaminant concentrations
- Applied as a solid slurry

KLOZUR® ONE

Ease of application, all-in-one activator with Klozur® SP.

- Fully soluble
- Source areas
- Highly contaminated soils

KLOZUR® CR

Combined remedy.

- ISCO and bioremediation
- Low to moderate levels of contamination
  - Primarily petroleum hydrocarbons
- Source zones and plumes

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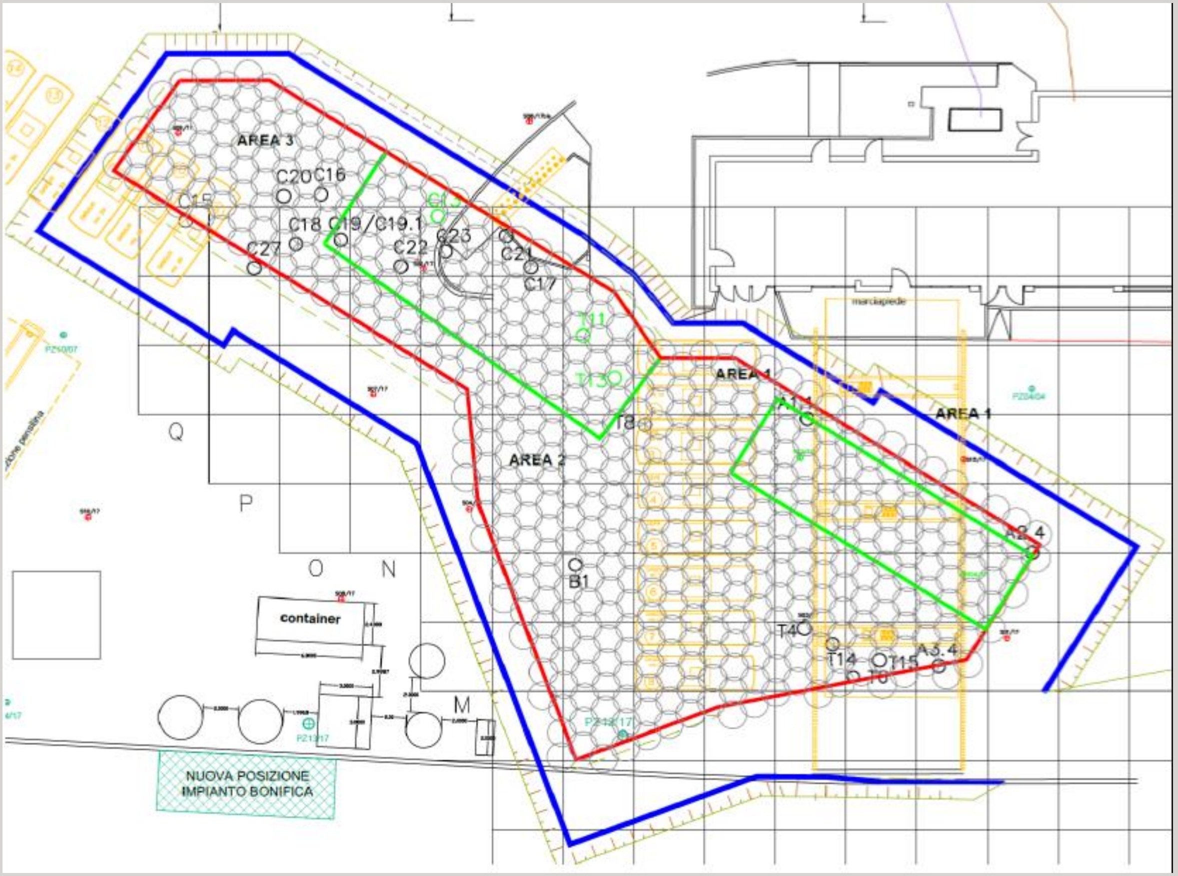
Design Considerations



Courtesy of Ladurner

Basic Target Area Oxidant Calculations

- Most ISCO designs need to address the contamination inside the target volume

- Basic assumption
  - Persulfate will distribute and react as intended within target zone
    - Groundwater flow
    - Injection

- Persulfate anion typically persists 1 to 8 weeks in field conditions
  - Many Soil Oxidant Demand (SOD) tests only run 2 days
  - Evonik's KDT (our SOD test) is run 7 days

Estimating Oxidant Mass: Basic Steps

1. Estimating Oxidant Demands
   – Target Demand from Contamination
   – Non-Target Demand
     – Natural organics or reduced metals on soils
     – Demand of contamination that may not be "Target" (i.e. non-BTEX petroleum hydrocarbons)

2. Apply Safety Factors

3. Confirm viability of implementation
   – Minimum and maximum concentrations
   – Varies with application method

Step 1: Estimating Oxidant Demand

Basic formula-Oxidant Mass:

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

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

Stoichiometric Ratio: Theoretical
Degradation Ratio: Empirical

Oxidant required for each contaminant is individual calculated and then summed

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Step 2: Apply Safety Factors

- Safety Factors:
  - Needed for uncertainties in reagent distribution, contaminant mass estimate, contaminant distribution, etc
  - If phase transfer limited (i.e. with some NAPLs/low solubility/high K_{oc} contaminants), either higher S.F. or longer lasting oxidant, such as Klozur® KP, may be needed.
  - Increase confidence in desired outcome

Common Safety Factors

Contaminant Concentrations:

- High: ~1.1 to ~1.5x
- Low: ~1.5 to ~4x

Adjusted to meet desired minimums or at the discretion of design engineers and stakeholders

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Step 3: Design Check

- Minimum recommended concentrations
  - Injection concentration
    - 40 to 50 g/L
  - Target pore volume
    - 10 to 25 g/L
- Injection strategy Maximum Concentration
    - Klozur® SP: 250 g/L
      - Crystal formation with NaOH/Flexibility in field
    - Klozur® One: 200 g/L
      - Rate of decomposition
- Typical injection concentrations
  - 50 to 250 g/L Klozur® SP
  - 50 to 200 g/L Klozur® One

- Soil Mixing
  - Minimum: ~0.5% w Persulfate/w soil
  - Maximum: as needed (but testing recommended if considering above 10% w/w soil)
  - Typical soil mixing:
    - 1 to 5% w/w with soil
- Klozur® KP
  - Can be difficult to inject solid slurry when injection volume is greater than 10% of pore volume

Multiple Application Strategy

- Reasons for a multiple application strategy include:
  - **Mass required for treatment is greater than can be delivered in a single application**
  - Remedial goals are multiple orders of magnitude lower than initial concentrations
  - Evaluative (Iterative) approach: Monitoring between applications can be used to refine future applications
    - Using each application as a diagnostic tool
    - Minimizes initial commitment allowing for further site assessment
  - Injection locations can be adjusted between events

- Potential issues with multiple application strategy
  - Partial treatment of contaminants may cause concern

Mass Estimate: Klozur® One

- Design as if the application was Klozur® SP
- Adjust for fact that Klozur® One is 95% Klozur® SP
- Activator is built in
- Klozur® One = One
  - Tank
  - Pump
  - Design number

Courtesy of TTE Consultants and Heijmans Infra B.V.

Monitoring Well 2	Parameter	6-Sept 2019	24-Sept 2019	21-Oct 2019	21-Nov 2019
depth: 4.5 meters below ground level	PCE (µg/l)	<50	<1	<1	<1
	TCE (µg/l)	14,000	2.4	<1	<1
	DCE (µg/l)	<50	1.4	1.4	1.4
	VC (µg/l)	<100	<2	<2	<2
	Sodium (mg/l)	13	n.a.	3,900	2,600
	Sulfate (mg/l)	30	n.a.	1,300	1,400

99.6% of TCE pollution destroyed.
Site closure with no further action required

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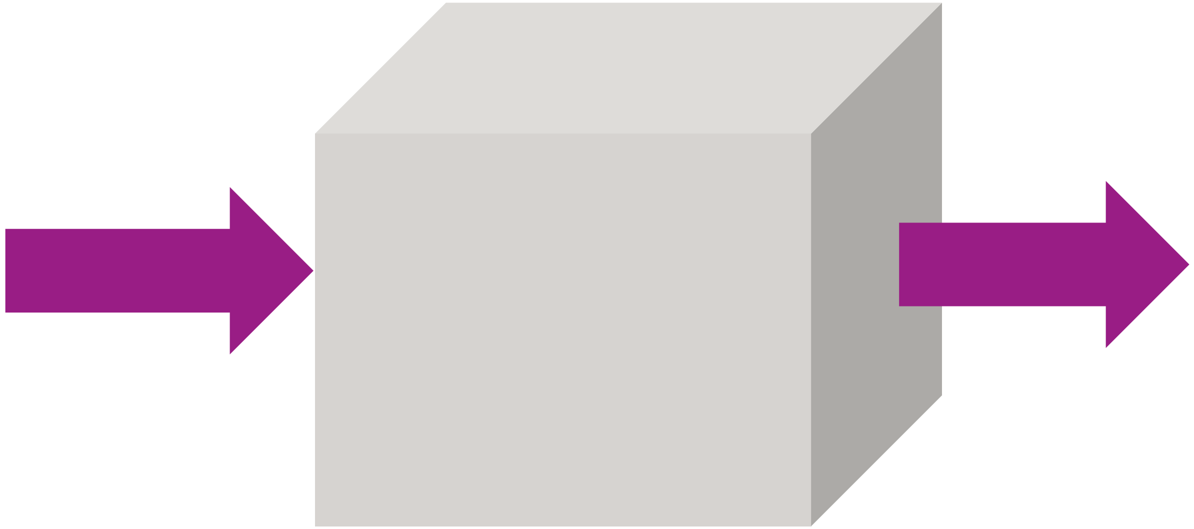
Mass Estimate: Klozur® KP

- Treating the target volume

- Depending on objectives:
  - Need to account for oxidant demand fluxing into box
  - Need to account for Klozur KP fluxing out of the box



Need sufficient oxidant for oxidant demand entering treatment volume

Need sufficient oxidant knowing oxidant will dissolve and flux out of treatment volume

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KP calculations

- Groundwater flux:

  Q = A x ePV x V

- Influent demand:
  - Target demand:

KP (mass) = Q (volume/time) x T (time) x Contaminant Concentration (mass/volume) x ratio x S.F.

  - Non-target demand: Use actual data or approximation, such as COD

KP (mass) = Q (volume/time) x T (time) x COD (mass/volume) x ratio x S.F.

- Effluent oxidant migration:

KP (mass) = Q (volume/time) x T (time) x KP concentration (mass/volume)

Introduction of time element allows for designing extended release

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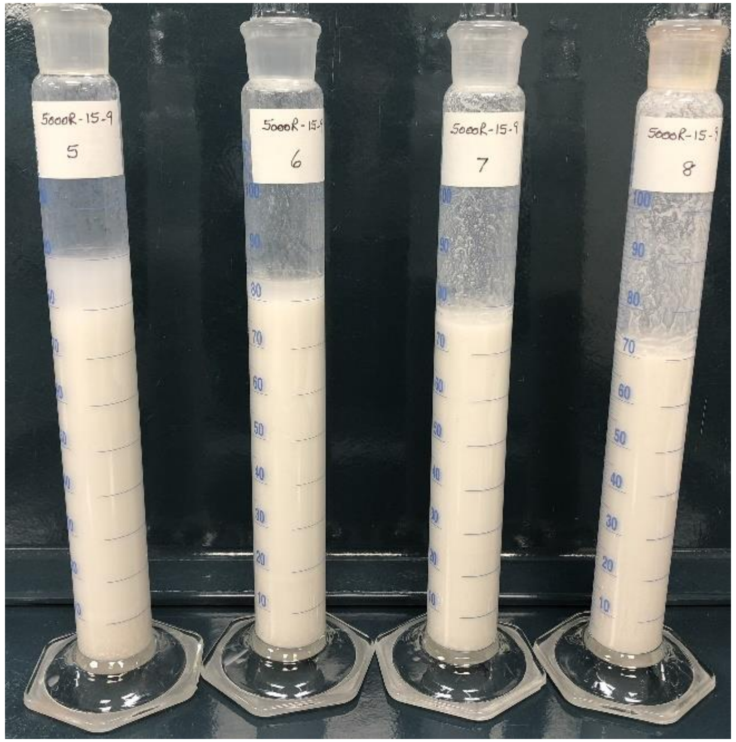
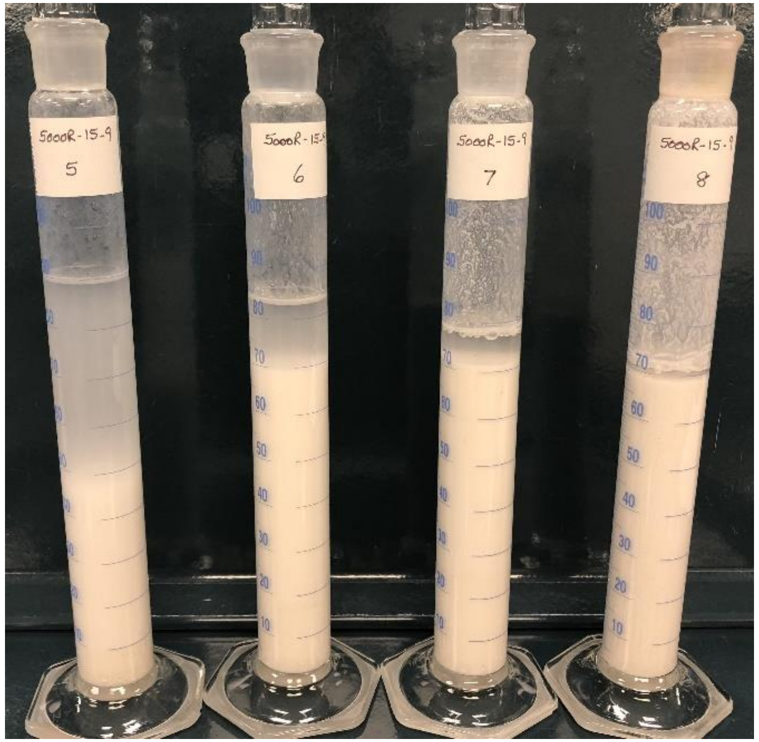
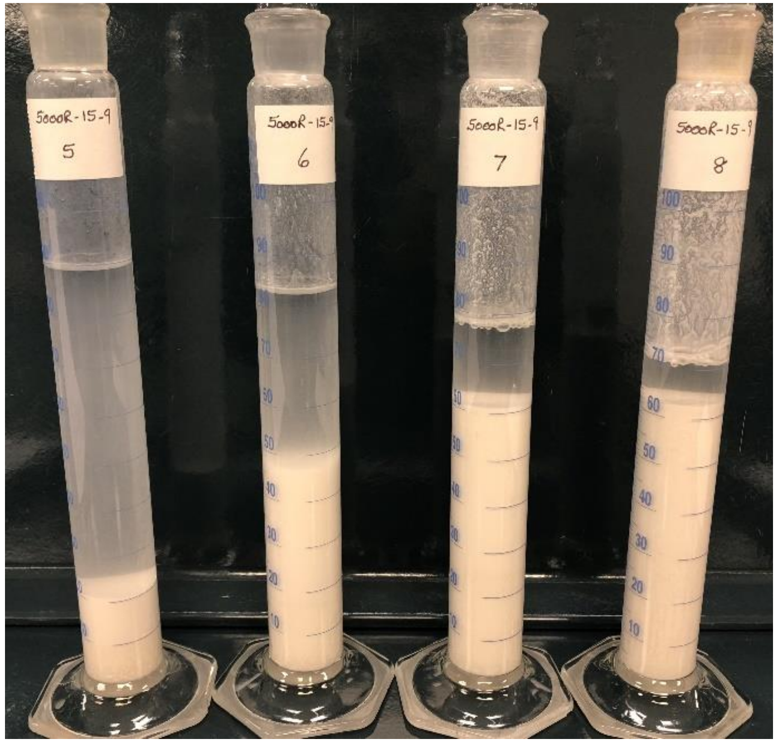
KP Activation/Slurry settling



Time 1 min



Time 5 min



Time 15 min

Klozur® KP and Hydrated Lime

Left to right: 20%, 30%, 40% and 50% solids

Recommended

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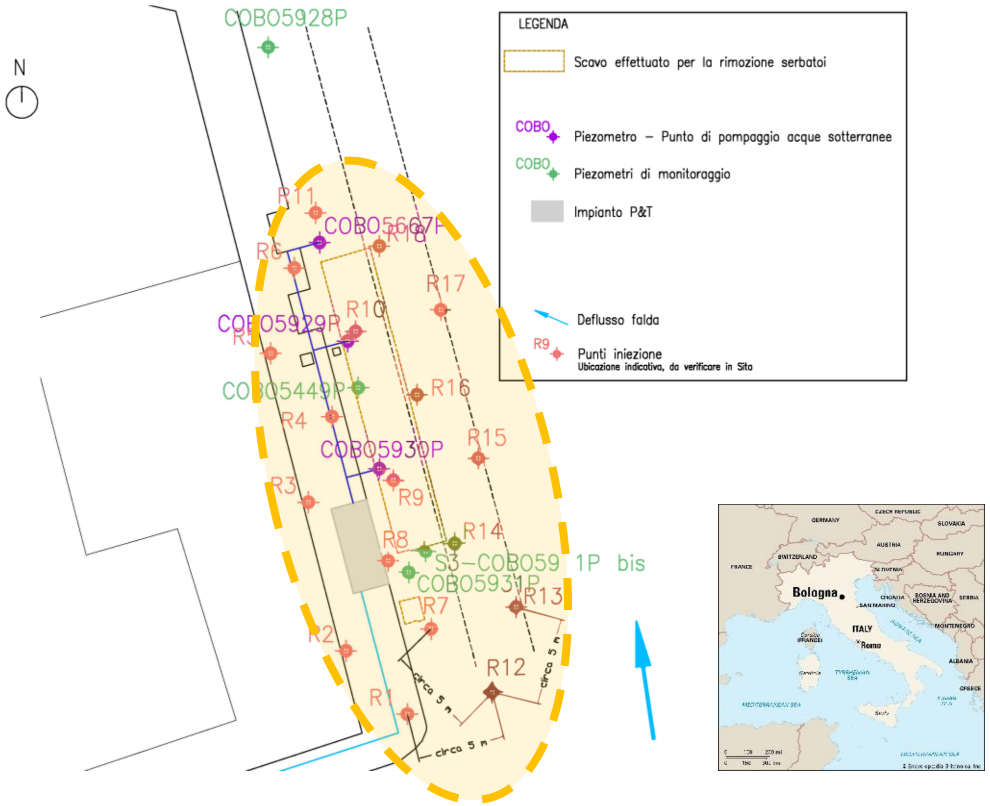
Klozur® CR

- 50% Klozur® SP
  - Design can be similar to alkaline activated persulfate
  - Residual sulfate can result in anaerobic oxidation if conditions becomes sufficiently reducing

- 50% PermeOx® Ultra
  - ~180 mg O_2 released per g PermeOx® Ultra
  - Follow typical aerobic bioremediation design

- 2022 Klozur® CR webinar available at:

  www.Evonik.com/remediation



Confidential Former Petrol Station

Bologna, Italy

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Activator Design

- Alkaline:
  - Base buffer capacity x Soil mass to be contacted
  - 2 moles NaOH (or equivalent) per mole of persulfate

- Klozur® One: Activator built in

- Klozur® CR: Activator built in

- Hydrogen peroxide:
  - 1 to 10 moles of hydrogen peroxide per mole of sodium persulfate
  - Caution regarding gas and heat evolution from hydrogen peroxide
  - Hydrogen peroxide may have different persistence/distribution compared to sodium persulfate

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Application Methods

Courtesy of Bill Lang

Example Application Methods for Reagent Emplacement

Injection via Direct Push

Injection/Recirculation via fixed wells

Soil mixing using buckets

Excavation backfill

Soil mixing using Augers

Soil mixing using specialized tools

Soil mixing using tillers

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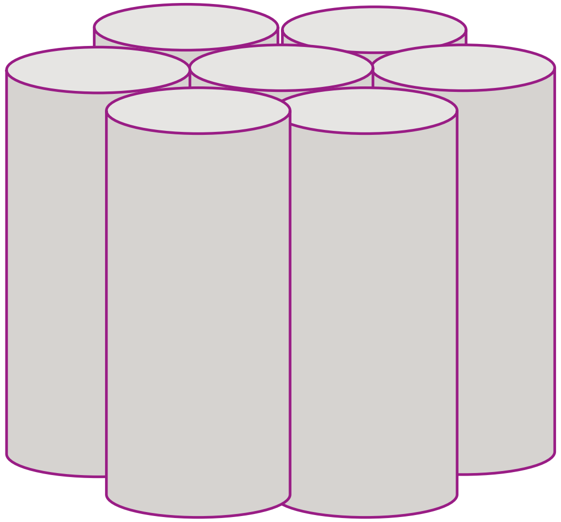
Application: Boxes vs Overlapping Radius of Influences

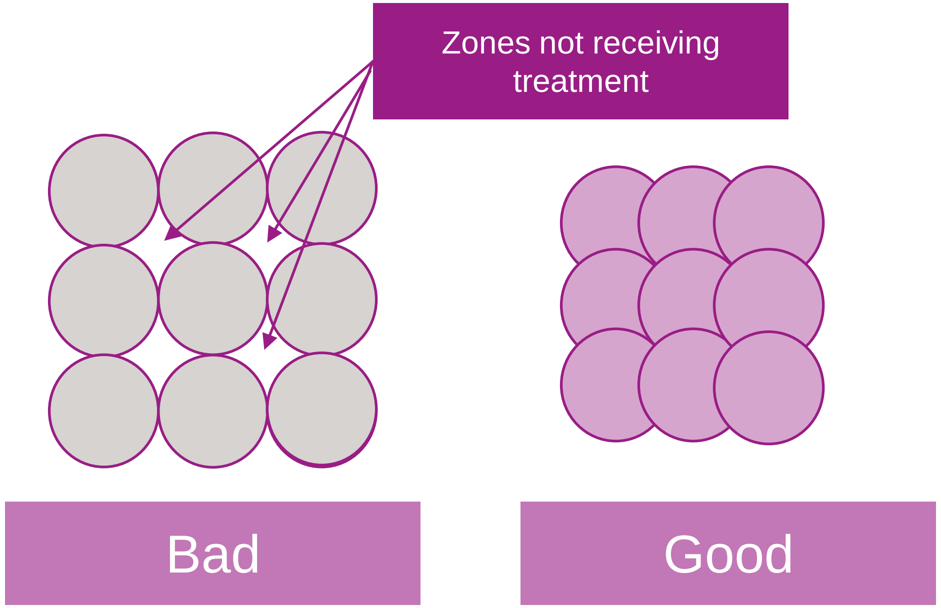
- Box design:
  - Excavations
  - Soil mixing with mixing heads or excavator buckets

- Colum/cylinder design:
  - Injection strategies
  - Soil mixing with augers



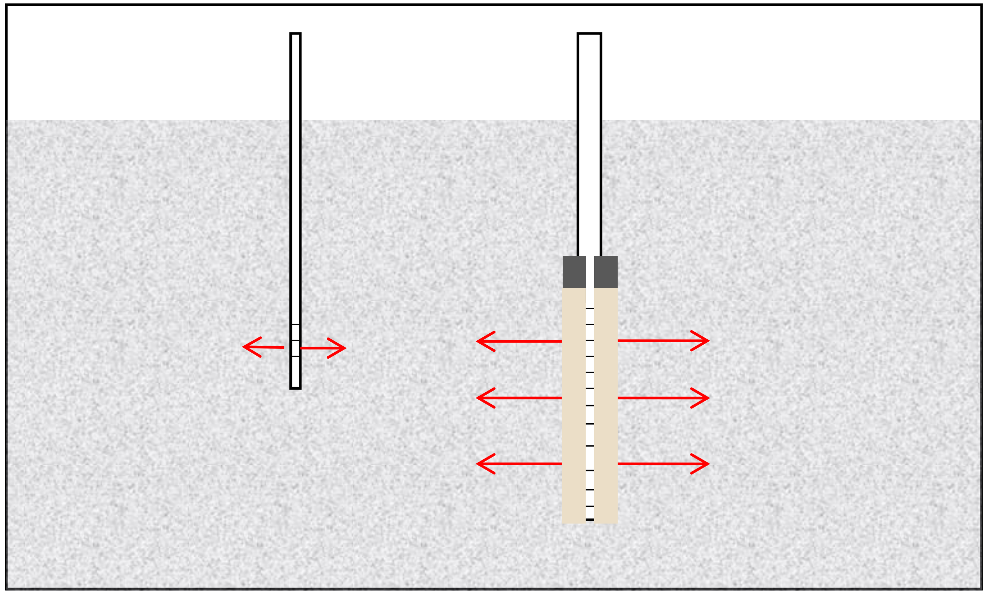
Cylinder Design: Overlapping ROIs

- Overlapping ROIs
  - Necessary to prevent dead zones
  - Should consider adjusting Safety Factor for oxidant
  - Typically need 17 to 20% overlap



Liquid Reagent Injection

- Liquid Injection Strategy with Klozur® SP
  - Typically a cylinder design
  - Dissolved reagents injected through DPT or fixed wells
    - Effective at treating preferential flow paths with some diffusion into secondary pathways
  - Injection volume
    - 50% to 100% of effective pore volume recommended



Injection Volume (gal)	Radius of Influence (ft)		Injection Volume (L)	Radius of Influence (m)
100	1.9		500	0.6
300	3.3		1 000	0.9
500	4.2		3 000	1.5
1 000	6.0		6 000	2.2
2 000	8.4		10 000	2.8
4 000	11.9		15 000	3.5
8 000	16.8		20 000	4.0
ePV - 20%; Screen height - 6 ft or 2 m, cylindrical distribution				

Injection Strategy: Lessons Learned

- Inadequate injection volume can lead to inadequate reagent distribution
  - Evonik recommends 50 to 100% of an effective pore volume

- Reagents follow the path of least resistance, not always as desired

- Tends to:
  - Treat preferential pathways:
    - Be careful to emplace in less permeable zones if they include contamination
    - Back diffusion
  - Treat regions closer to injection location: Can stagger injection locations
    - Fixed points: more volume vs DPT easier to stagger. Can combine both approaches

Injection Strategy: Lessons Learned

- Daylighting of reagents:
  - Previous boreholes from soil sampling—care to properly close (use tremie vs pouring bentonite from surface)
  - Up annulus of well—use pre-pack well screens or Tremie bentonite grout slurry instead of pouring bentonite from surface

- Movement of regent with groundwater:
  - Care to have reagents stay within treatment zone while persulfate is decomposing

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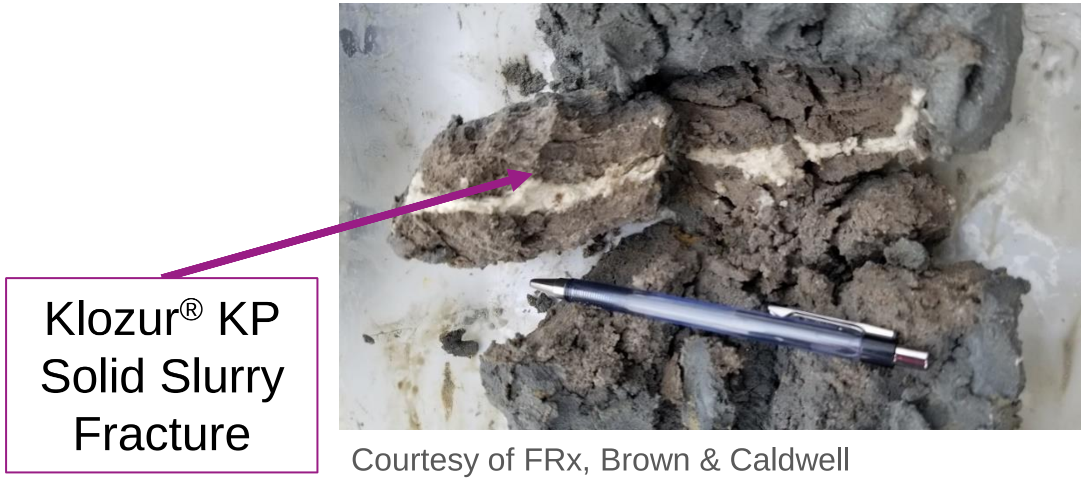
Solid Slurry Injection

- Solid-Slurry Injection Strategy with Klozur® KP, Klozur® CR or PermeOx® Ultra
  - Cylinder design
  - Solid slurry of reagents injected, usually through DPT
    - Used to inject extended release oxidants
      - Smaller injection volumes = less displacement
        - ~10% of a pore volume (maximum)
      - Extended persistence allows for treatment of low solubility contaminants and diffusion into low permeable units



Courtesy of FRx, Brown & Caldwell

Excavation backfill

- Klozur® persulfates are commonly used as a backfill amendment
  - Box design
  - Used to treat residual contamination following excavation
  - Often soil mixed into the top of remaining soil or added with backfill

- Common application

Confidential Client-Alaska

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

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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

- 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

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Soil Mixing Lessons Learned

- Need for complete mixing
  - Clumps could still include contamination in their center
- Especially with ISCO-ISS, track soil mixing volume
  - Migration after application not likely
- Manage water content
  - Water is important component as both binder (ISS) and persulfate consume water
  - Vadose vs saturated zones
- Chemical compatibility
- Equipment designed to handle dry reagent susceptible to even minor clumps

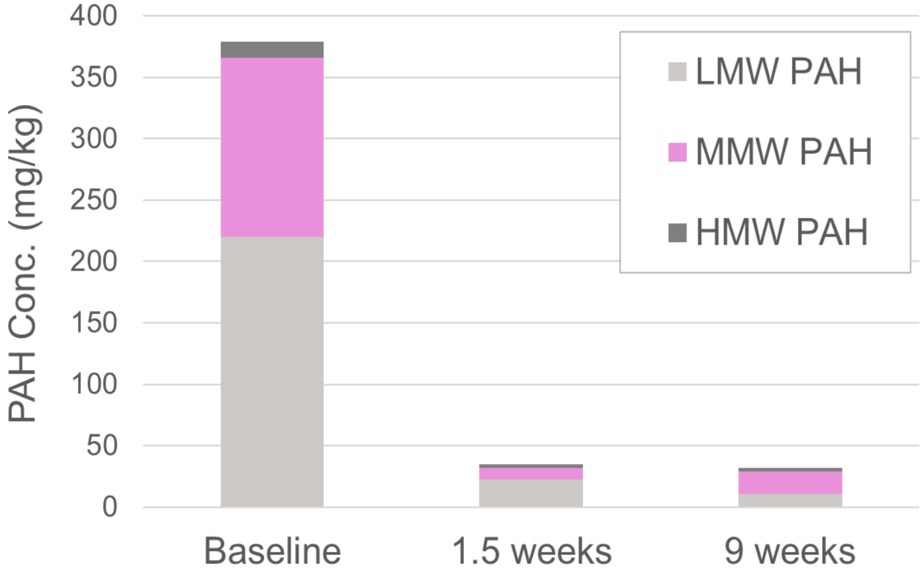
One Site: Two solutions

Area 1:

- NAPL level MGP Residuals in Clay
- Goals: Vapor intrusion and construction

Solution: ISCO-ISS with Klozur SP

Remedial Goals Achieved



Area 2:

- MGP Residuals is sands and gravels
- Below clay (>7 m bgs)
- Goals: Low final concentrations

Solution: Fixed well injection with Klozur® SP and Klozur® KP

Application #2 underway

Remedial Goals Achieved in most locations

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

Monitoring

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Monitoring Programs

- Site investigation

- Development of Design Parameters:
  - Bench Tests
  - Pilot test

- Field Applications
  - Performance monitoring
  - Progress monitoring

Monitoring programs should be developed to answer specific questions regarding the site and application

Klozur Persulfate “Fingerprint” or “Signature”

- Active reagent solution = Quantified active persulfate

- Reagent Solution
  - – Geochemical parameters:
    - – Residual ions result in increased **Electrical Conductivity**
    - – Klozur caustic should increase **pH**
    - – In absence of caustic, Klozur Persulfate should decrease **pH**
    - – Klozur Persulfate should increase **ORP**
  - – Analytical
    - – Analytes can be directly measured
      - – Ratio of sodium/potassium to sulfate changes if sulfate is not conservative

Approximate Residual Ratios

Compound	Na^+	K^+	SO_4^{2-}	Ca^{2+}
SP	19%		81%	
KP		29%	71%	
NaOH	57.5%			
HL				54%

* Residuals may not be conservative (sulfate, calcium, etc)

Monitoring Lessons Learned

- Groundwater velocity
  - Rapid moving groundwater can recontaminate a site shortly after the application
- ISCO is a mass reduction technology; best to compare total mass balance (soil and groundwater)
  - Treatment of NAPL/high concentrations may have similar groundwater concentrations
  - "Rebound" is sometimes a shift from soil to aqueous phase due to change in F_{oc}

$$K_d = Koc * foc = \frac{Soil\ (\frac{g}{Kg})}{GW\ (\frac{g}{L})}$$

- Monitoring location placement: Have locations where treatment is expected as well as less likely
- Fraction of organic carbon (F_{oc}) will change, best to monitor
- Monitoring well screen should be within treatment interval

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Summary

- ISCO has evolved over almost 40 years of practice
  - Over 20 years of persulfate applications
  - Success requires design and execution in each critical element:
    - Site Characterization, Chemistry, Design, Application and Monitoring

Select Oxidant to Match Site/Contaminant Characteristics

Klozur® Reagent	Liquid Injection	Solid Slurry Injection	Soil Mixing	Reactive Pathway	Key Characteristics
Klozur® SP	Yes		Preferred-Alkaline	Oxidative and reductive[1]	All oxidant available at time of application—Source area/ISCO-ISS
Klozur® One	Yes		Not Recommended	Oxidative	All-in-one built in activator SP Easy of use
Klozur® KP		Yes	Occasional-Alkaline	Oxidative and reductive[1]	Extended release of persulfate anion
Klozur® CR		Yes	Preferred	Oxidative and reductive[1]	Combined remedy: ISCO followed by bioremedation

1. Reductive pathway with certain activation methods

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Questions?

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Soil & Groundwater Remediation

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Brant Smith

Director of Technology

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