Environmental Solutions

PeroxyChem

Introducing Klozur® KP - an extended release ISCO persulfate reagent

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PeroxyChem

PeroxyChem Webinar Series
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Field-Proven Portfolio of Remediation Technologies Based on Sound Science

***In Situ* Chemical Oxidation**

1. Klozur® SP and KP
2. Klozur® CR

In Situ Chemical Reduction

3. EHC® Reagent
4. EHC® Liquid
5. Daramend® Reagent

Aerobic Bioremediation

6. Terramend® Reagent
7. PermeOx® Ultra

Metals Remediation

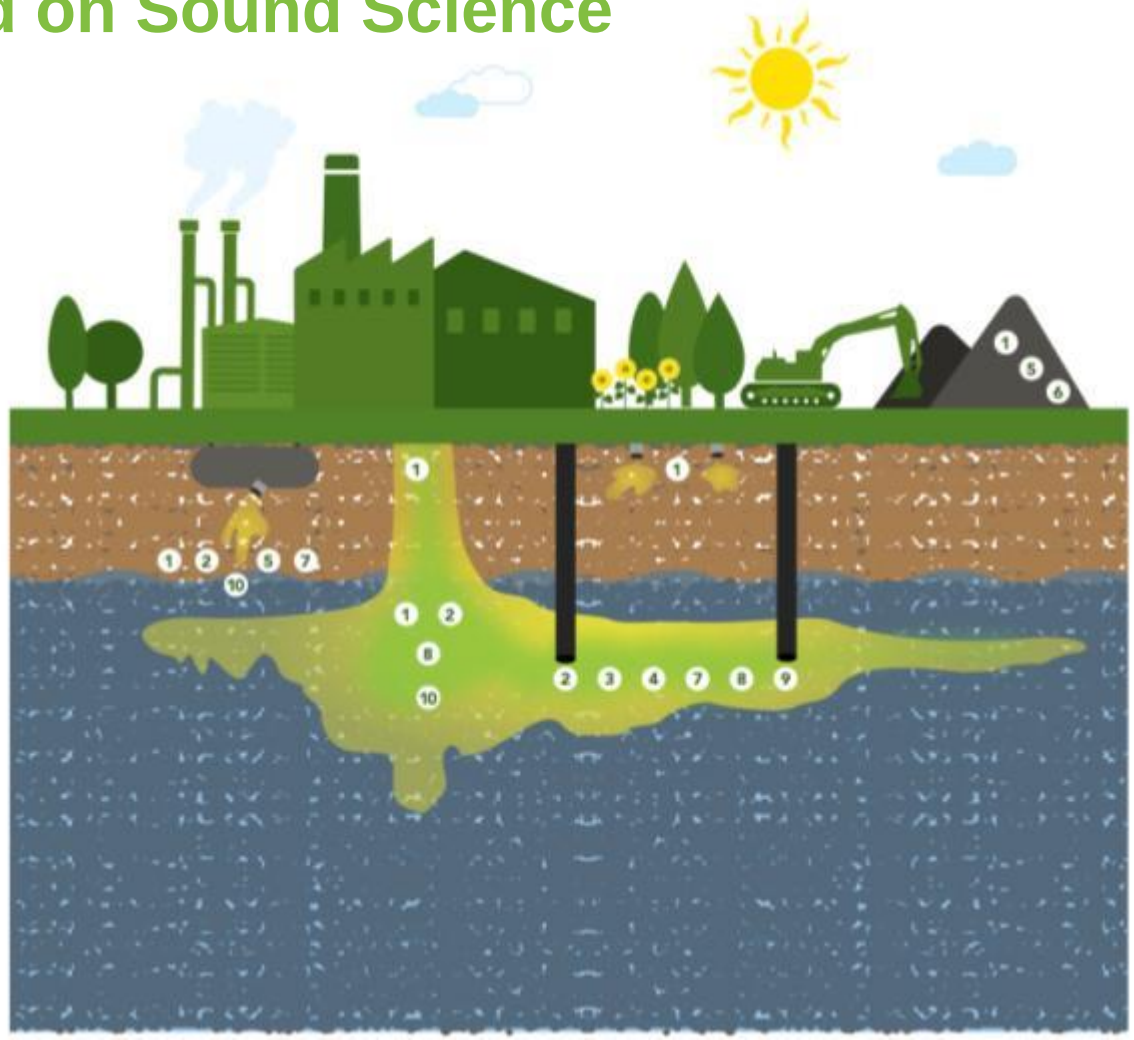
8. MetaFix® Reagent

Enhanced Reductive Dechlorination

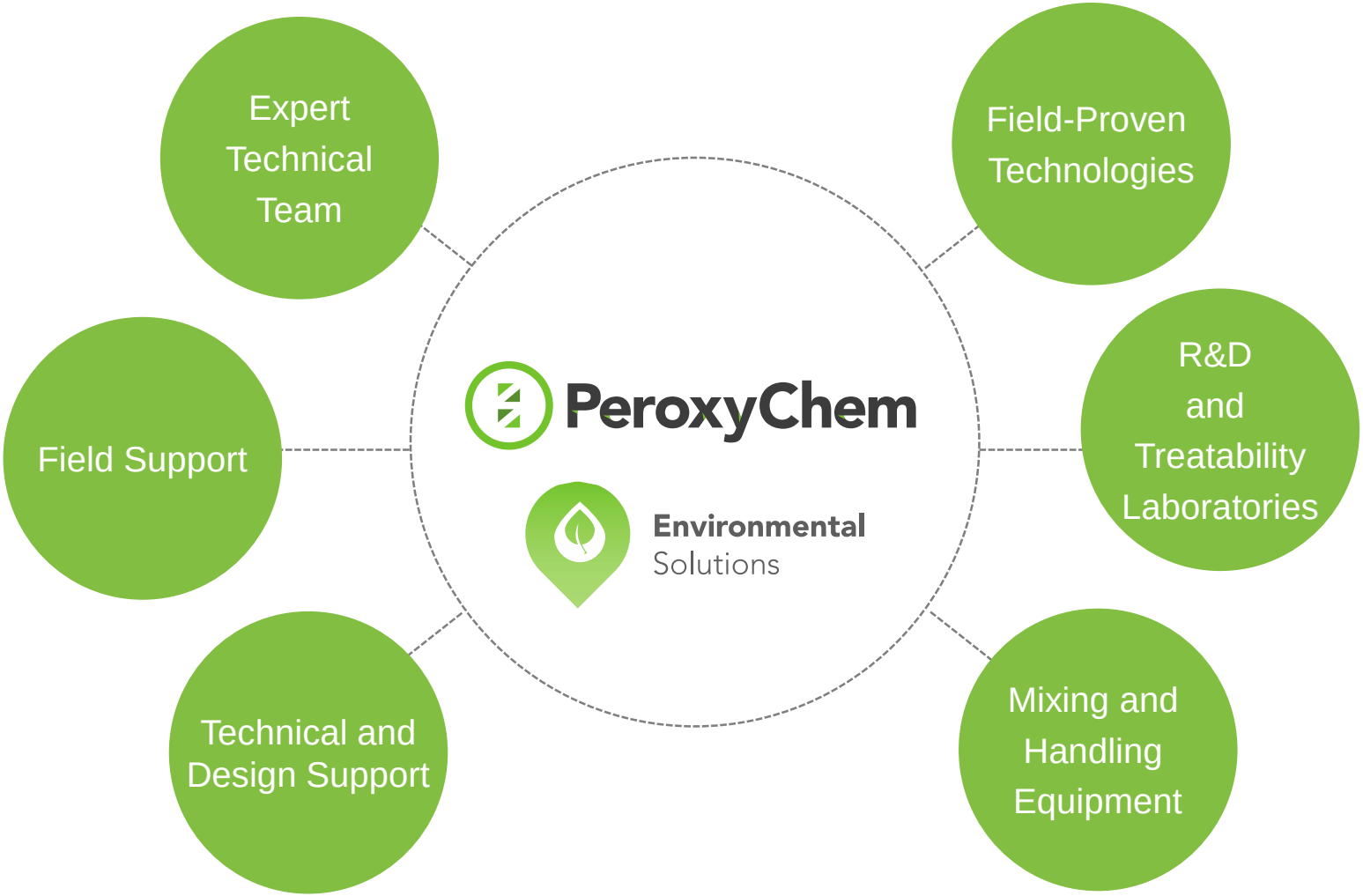
9. ELS™ Microemulsion

NAPL Stabilization/Mass Flux Reduction

10. ISGS™ Technology



Support We Provide



Presentation Outline

- Klozur Portfolio
- Klozur SP
- Klozur KP
  - Batch tests
  - Column test
  - Case Study
- Conclusions

Klozur® Portfolio

KLOZUR® SP

- "Klozur" is now Klozur SP
- Based on environmental grade sodium persulfate

KLOZUR® KP

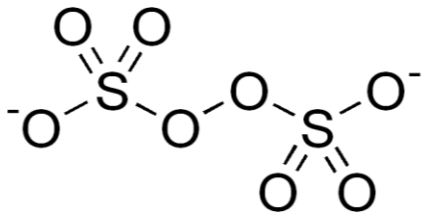
- Based on environmental grade potassium persulfate

KLOZUR® CR

- "Combined Remedy" with ISCO and ISB from a blend of Klozur SP and PermeOx Ultra

Klozur Portfolio

- All Klozur products release the persulfate anion:



Key Characteristics:

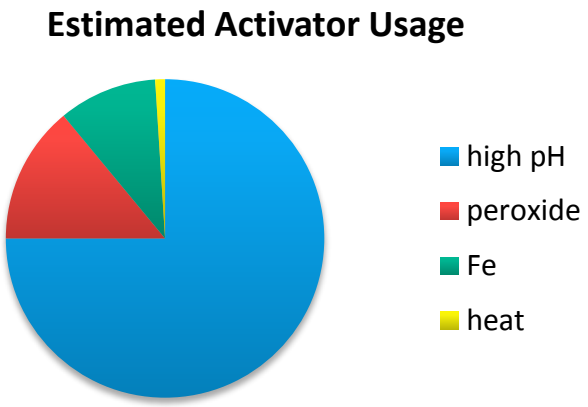
- A strong oxidant
- Applicable across a broad range of organic contaminants
- Extended subsurface lifetime (weeks to months)
- Little to no heat or gas evolution
- Activation results in the formation of radicals

Radical Formation Upon Activation

- Kinetically faster reacting radicals that are:
  - More powerful oxidants (SO_4• and OH•) than persulfate itself
  - Reductants (O_2•$^-$)
  - Nucleophiles (O_2•$^-$ and HO_2^-)

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)

PeroxyChem Activation Technologies



- Zero Valent Iron
  - Solid state activator
  - Oxidative pathway

Purchase of Klozur persulfate includes with it the grant of a limited license under PeroxyChem's patents covering the use of Klozur persulfate for environmental applications at no additional cost to the buyer

- Alkaline Activated Persulfate
  - Well suited for suited for most applications
  - Less corrosion on carbon steel
  - Reductants, oxidants and nucleophiles
- Iron-Chelate Activated Persulfate
  - Chlorinated ethenes and hydrocarbons
  - Oxidative pathway
- Heat
  - Complex sites
  - Polishing step after thermal treatment
  - Reductants, oxidants and nucleophiles
- Hydrogen Peroxide
  - Sites that benefit from vigorous reaction with both hydrogen peroxide and sodium persulfate
  - Reductants, oxidants and nucleophiles

Compounds Degraded by ISCO

Examples of Contaminants Destroyed by Klozur Persulfate

(not all ISCO reagents treat all compounds listed)

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

Others
Carbon disulfide
Aniline
1,4-Dioxane

TPH
BTEX
GRO
DRO
ORO
creosote

Oxygenates
MTBE
TBA

Perflourinated
Freon
PFOS
PFOA
PFBA

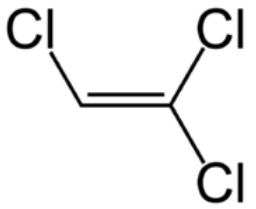
Chlorobenzenes
Chlorobenzene
Dichlorobenzene
Trichlorobenzene

Phenols
Phenol
Chlorophenols
Nitrophenols

PAHs
Anthracene
Benzopyrene
Styrene
Naphthalene
Pyrene
Chrysene
Trimethylbenzene

Pesticides
DDT
Chlordane
Heptachlor
Lindane
Toxaphene
MCPA
Bromoxynil

Energetics
Trinitrotoluene (TNT)
Dinitrotoluene (DNT)
RDX



Klozur SP

- Klozur® has been based on environmental grade sodium persulfate (SP)
- Thousands of successful applications around the world
- Common activation methods:
  - Oxidative Pathway
    - Iron (II) activated persulfate
  - Oxidative and Reductive Pathways
    - Alkaline, heat and hydrogen peroxide activation
- Contaminants treated:
  - Chlorinated ethenes, ethanes, benzenes, phenols, etc
  - Petroleum hydrocarbons: BTEX, PAHs, DRO, GRO, etc
  - Pesticides
  - Energetics (TNT, RDX, etc)
  - Others (1,4-dioxane, MTBE, etc.)

Klozur SP has a high solubility that is ideal for source area treatment.

Klozur KP

- Klozur KP based upon environmental grade potassium persulfate (KP)
- Primary differences to sodium persulfate
  - Solubility
  - K^+ vs. Na^+

Temperature (◦C)	Klozur SP		Klozur KP	
	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

Characteristic	SP	KP
Formula	$Na_2S_2O_8$	$K_2S_2O_8$
Molecular Weight	238.1	270.3
Crystal density (g/cc)	2.59	2.48
Color	White	White
Odor	None	None
Loose bulk density (g/cc)	1.12	1.30

Field Implementation

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

- Three ways of establishing contact:
  - Injection: Oxidant goes to the contamination (i.e. Source zone--Klozur SP)
  - Contaminant comes to Oxidant: (i.e. Permeable reactive barrier--Klozur KP)
  - Oxidant and contaminant are blended up together (Soil mixing---either Klozur SP or Klozur KP)

DISSOLUTION LIMITED RELEASE

Dissolution Limited Release

- Klozur KP's extended released is based upon its low solubility

- If Klozur KP is added in excess of low solubility limit, it will slowly dissolve to maintain persulfate concentrations at solubility limit

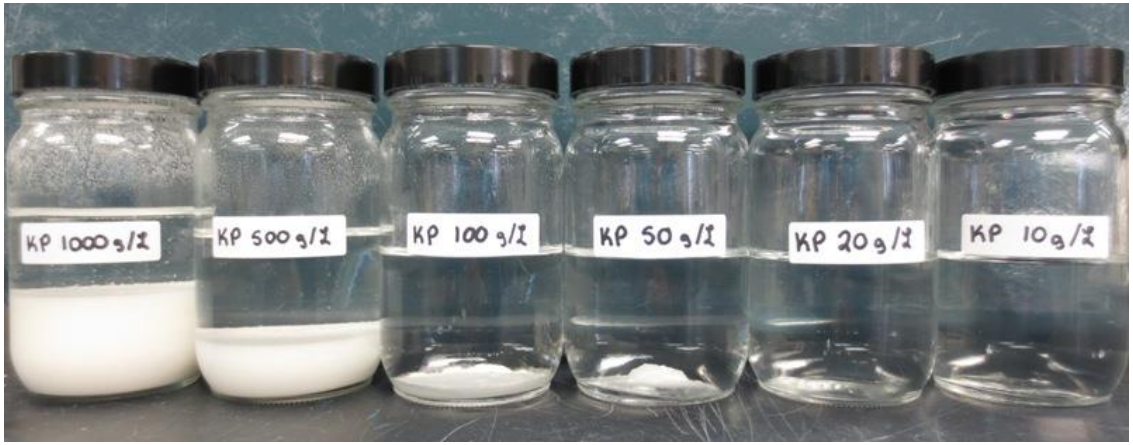
- Conceptual PRB:
  - 50 ft x 2 ft x 10 ft
    - 1,000 ft^3
    - 35% Porosity
    - **2,618 gal Pore Volume**
  - 25% KP and 75% sand
    - 25,000 lbs Klozur KP
  - Solubility limit of 35 g/L
    - 25,000 lbs = ~100,000 gal @ 35 g/L

38 Pore Volumes

Solubility Limited Release Static System

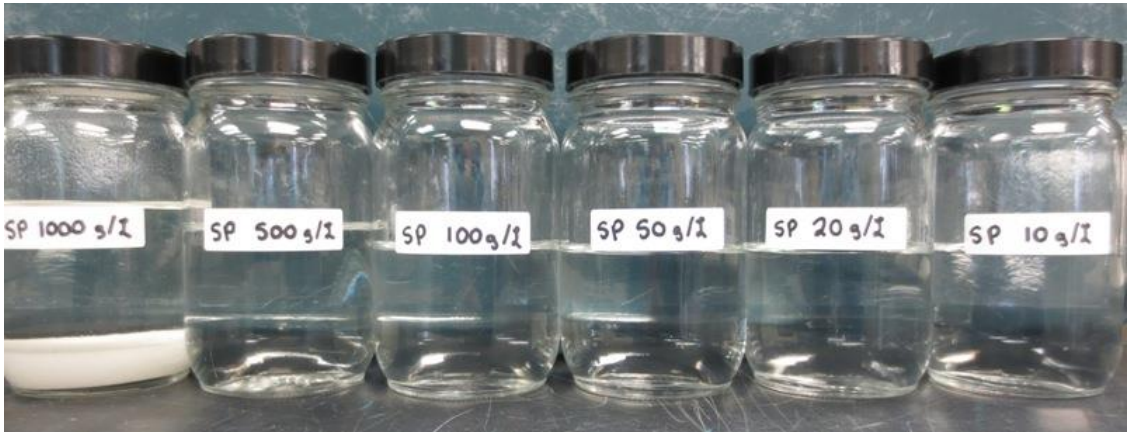
Reactors at ~20◦C

Klozur KP Solubility = 47 g/L



Reactors at ~20◦C

Klozur SP Solubility = 570 g/L



KP vs SP in Batch Reactors

- Batch reactors = static system
- May not illustrate differences between KP and SP

Klozur Soil Oxidant Demand Results

Klozur	Test Soil A (sandy silt)	Test Soil B (silty-clay)	Test Soil C (fine sand)
SP	2.8	3.4	1.3
KP	2.6	3.5	1.1

Courtsey of Jean Pare/Chemco. Presented at Remtech 2014.

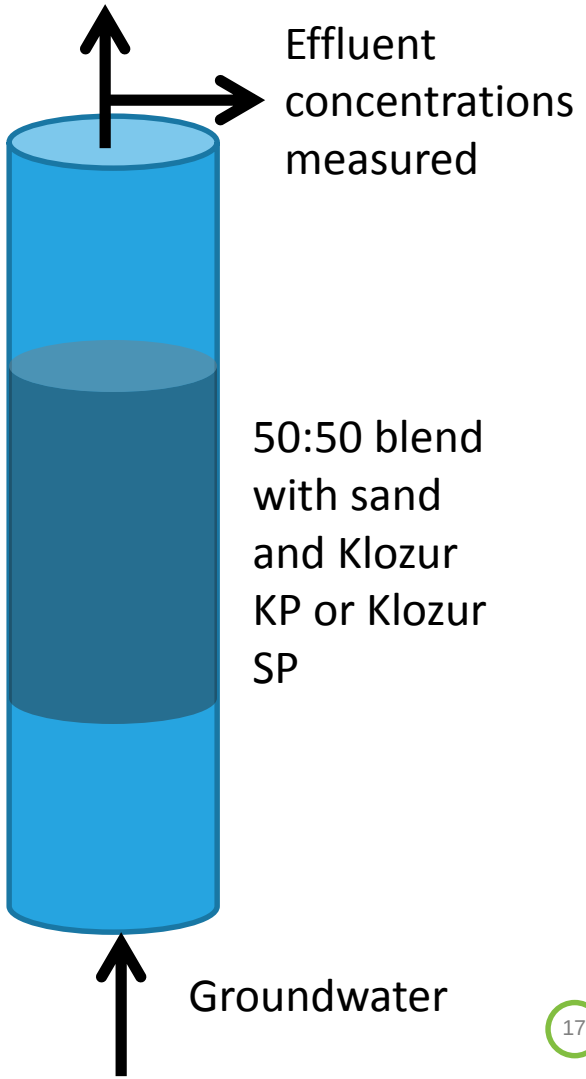
Alkaline Activated Klozur Treatability Results

Test condition	Test Soil A (sandy silt)		Test Soil B (silty-clay)			
	DRO (mg/Kg)	% Reduction	DRO (mg/Kg)	% Reduction	PAHs (mg/Kg)	% Reduction
Control	5,650		2,100		26.9	
SP	2,900	49%	1,440	31%	1.5	94%
KP	3,200	43%	1,020	51%	0.6	98%

Courtsey of Jean Pare/Chemco. Presented at Remtech 2014.

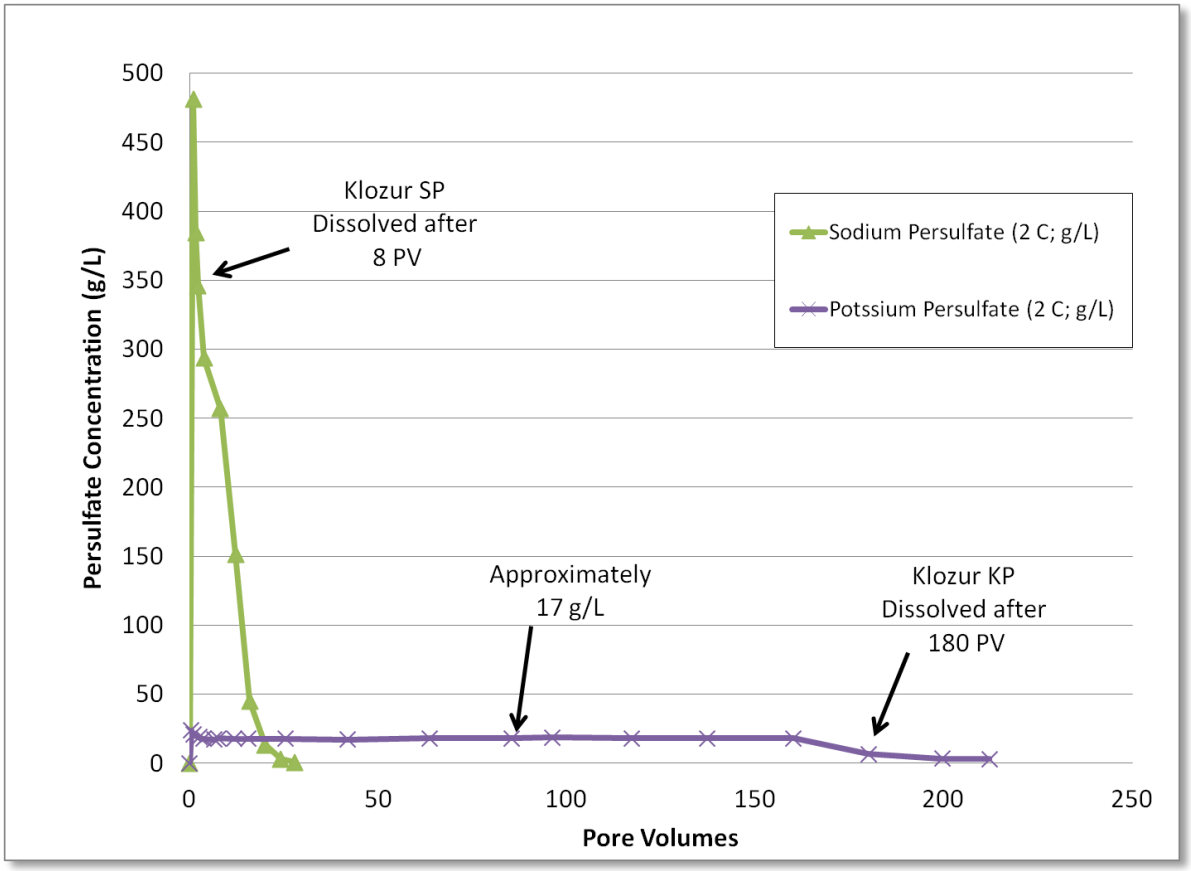
Solubility Limited Release Dynamic System

- Column Study:
  - 12 inch columns
    - 6 inch section of 50:50 blend of sand and either Klozur KP or Klozur SP
    - Targeting 300 g of oxidant
    - 3 inch sand above and below
  - Four columns
    - 2 °C :
      - Klozur SP
      - Klozur KP
    - 20 °C
      - Klozur SP
      - Klozur KP



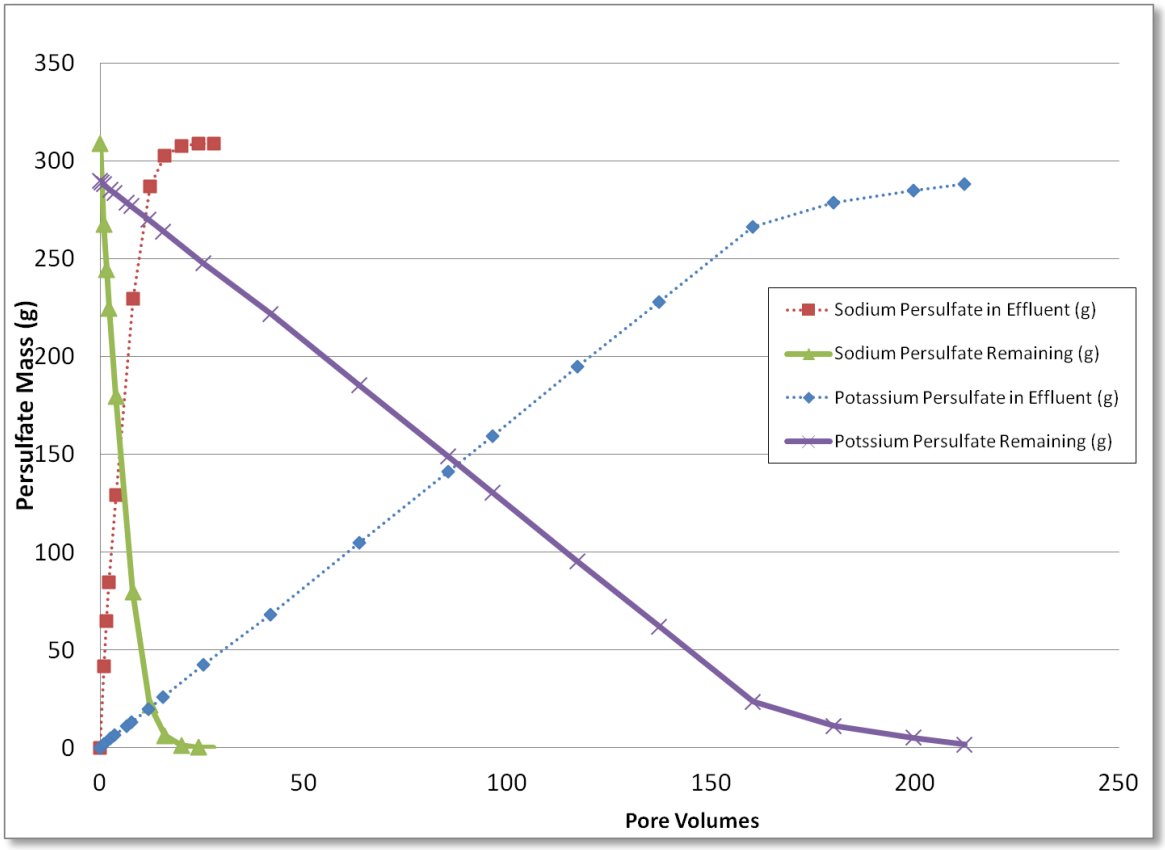
Column Study (2°C)
Effluent Persulfate Concentration

- Dissolution of Persulfate
  - 2 ◦C
- Klozur SP
  - Peak at theoretical maximum
- Klozur KP
  - Sustained at theoretical maximum



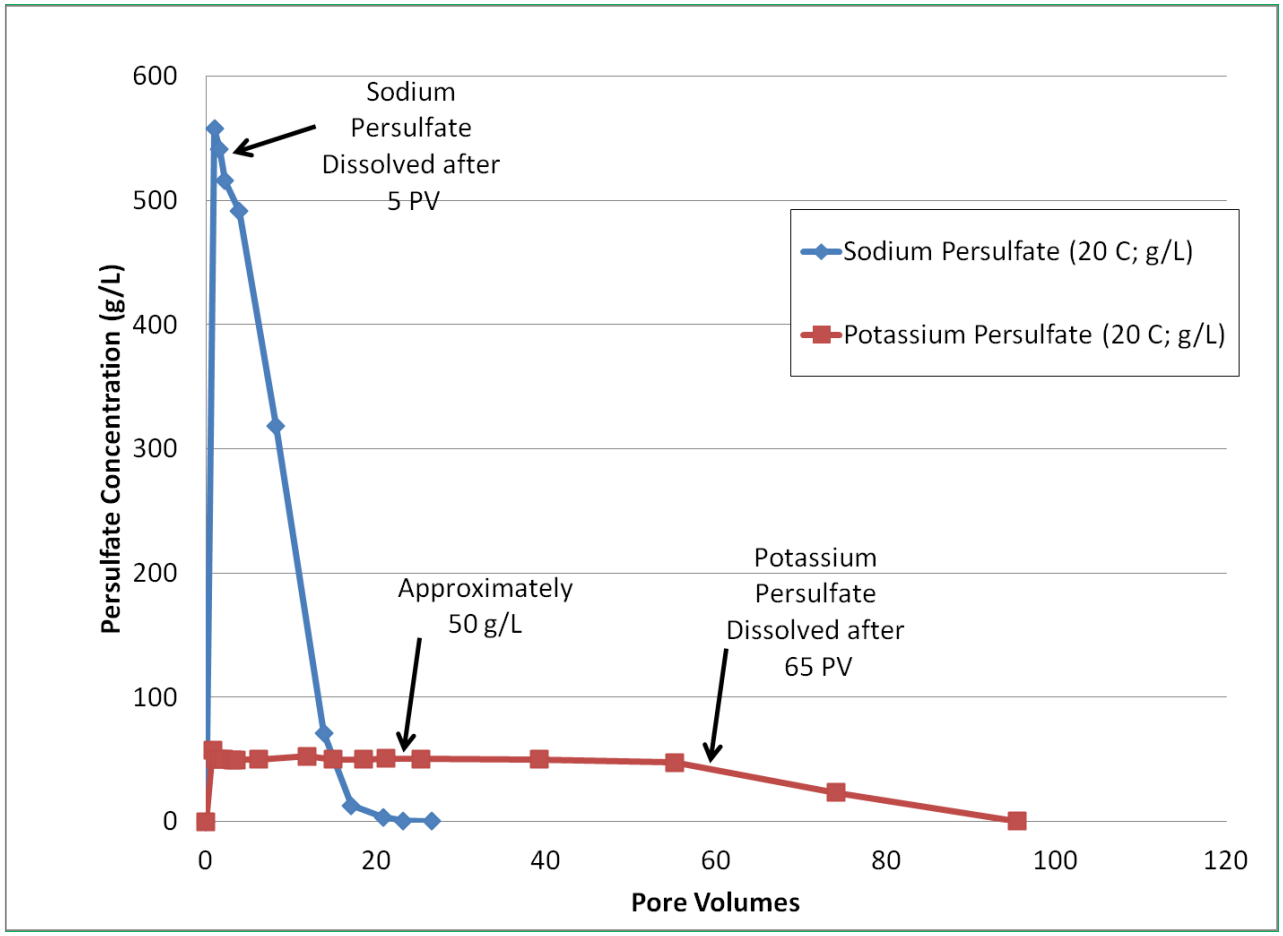
Column Study (2°C)
Residual Persulfate Solids in Column

- Dissolution of Persulfate
  - 2 ◦C
- Rate of decline in residual persulfate mass linear with Pore Volumes



Column Study (20°C) Effluent Persulfate Concentration

- Dissolution of Persulfate
  - 20-25 ◦C
- Klozur SP
  - Peak at theoretical maximum
- Klozur KP
  - Sustained at theoretical maximum



Environmental Solutions

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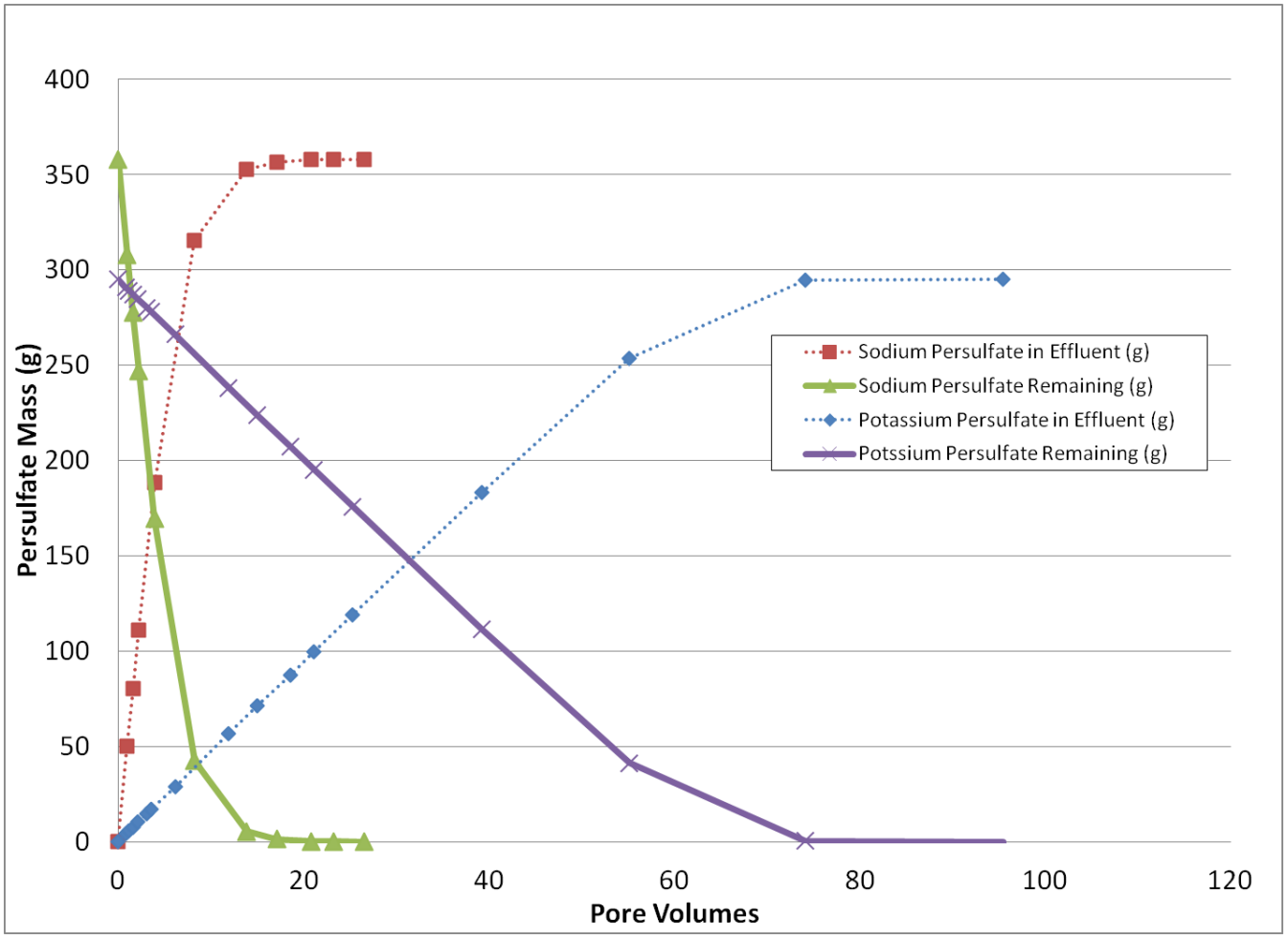
Column Study (20°C)
Residual Persulfate Solids in Column

- Dissolution of Persulfate
  - 20-25 ◦C
- Rate of decline in residual persulfate mass linear with Pore Volumes



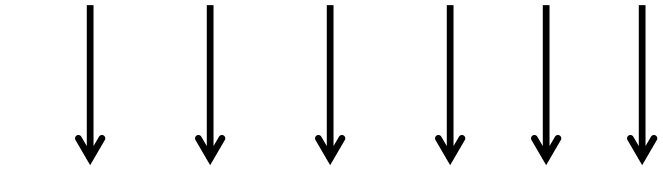
Dissolution Study Key Conclusions

- Klozur KP maintained theoretical maximum concentration for most of study
- Rate of release of Klozur KP linear with groundwater flux (pore volumes)
- Key variables for determining longevity of solubility limited release:
  - Ideal:
    - Mass of KP present
    - Volume of groundwater contacted
      - Groundwater flow velocity or flux
    - Temperature
  - Site factors:
    - Target and non-target demand
    - Decomposition

Conceptual Permeable Reactive Barrier

- Permeable Reactive Barrier (PRB)
- Conceptual Design of Gate
  - 50 ft wide, 10 ft high, 5 ft deep
  - ~50% w/w KP
  - 150,000 lbs KP

Groundwater Flow



KP PRB

Activator PRB

Conceptual "Ideal" Persistence of the Extended Release KP

Conceptual Klozur KP Persistence (months)						
	Temp (◦C)	5	10	15	20	25
	Solubility (g/L)	22	29	37	47	59
Groundwater Velocity (ft/yr)	10	262	199	156	123	98
	25	105	80	62	49	39
	50	52	40	31	25	20
	75	35	27	21	16	13
	100	26	20	16	12	10
	500	5	4	3	2	2

Does not consider potential "site" factors

Activation of Klozur KP

Klozur SP:

- Aqueous phase oxidant – aqueous phase activators
  - NaOH (alkaline)
  - Fe:Chelate
  - Hydrogen peroxide
  - Heat

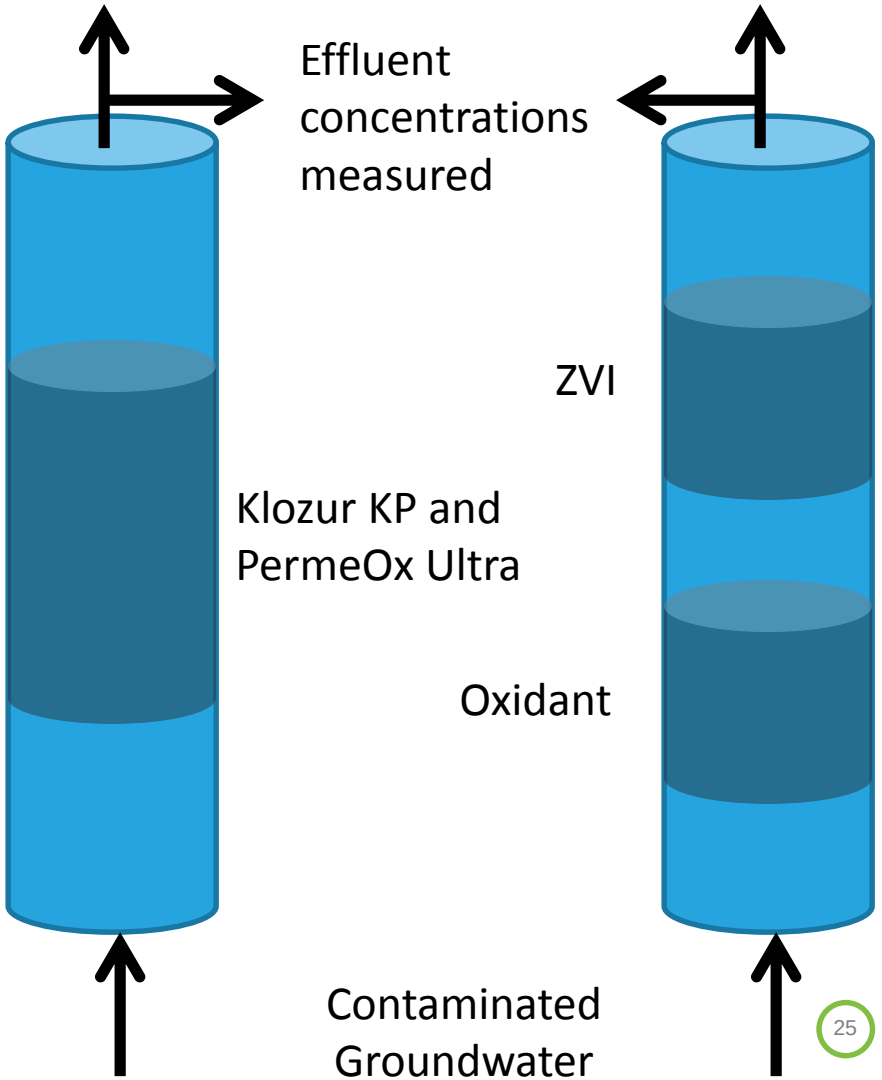
Klozur KP:

- Solid/extended release oxidant – **Solid/extended release activators**
  - PermeOx Ultra (alkaline)
  - Hydrated lime-$Ca(OH)_2$
  - Zero Valent Iron (ZVI)

Treatability Column

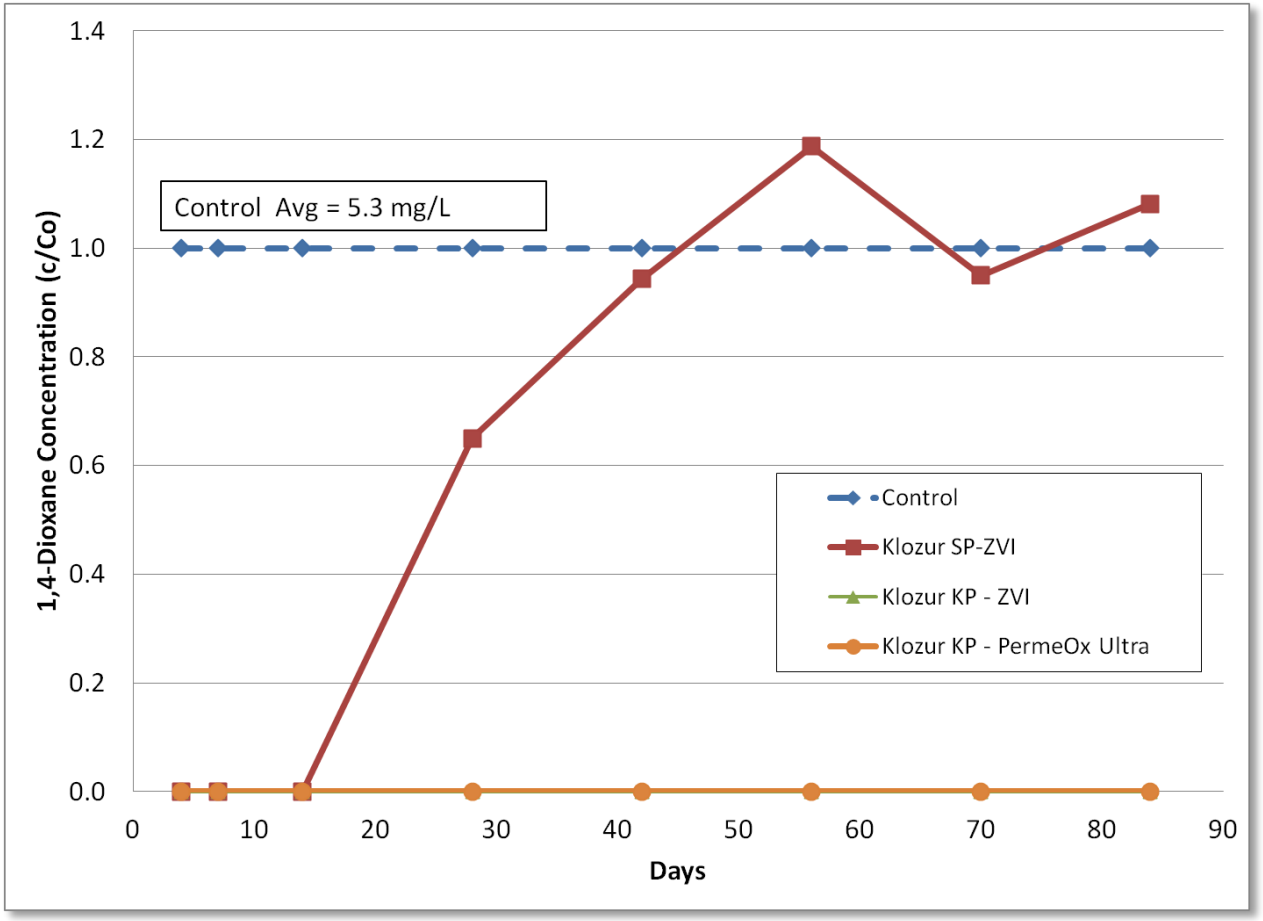
Column Study:

- 12 inch columns
  - 50:50 blend of sand and either Klozur KP or Klozur SP. Targeting 150 g of oxidant
  - Sand above and below
- Four columns (20 °C)
  - Control (sand only)
  - Klozur SP
    - ZVI
  - Klozur KP
    - ZVI
    - PermeOx® Ultra
- Continuous feed of contaminated groundwater



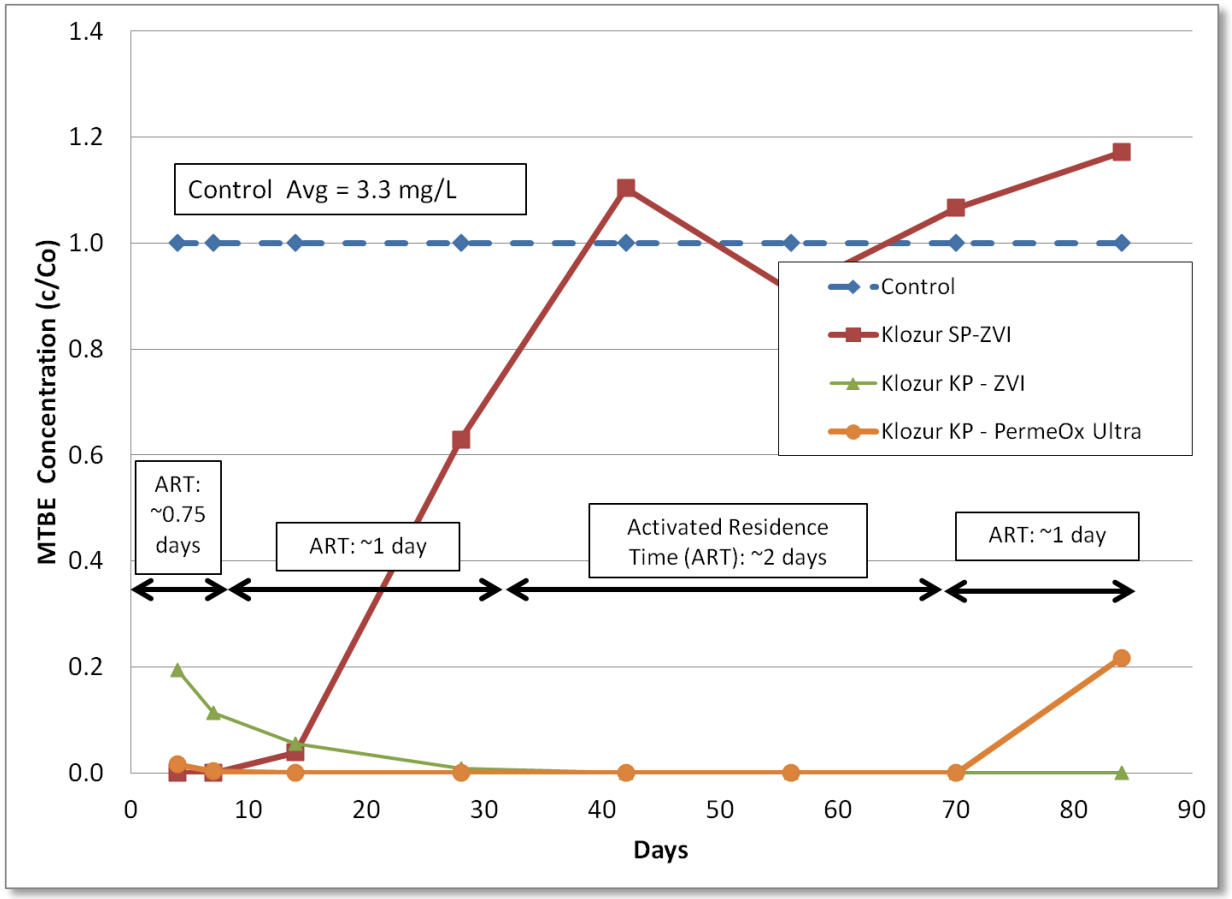
Treatment of 1,4-Dioxane

- Klozur KP columns non-detect throughout experiment
- Klozur SP breakthrough between Day 14 and Day 28



Treatment of MTBE

- MTBE treated to ND in KP-ZVI columns with ~2 day residence time
- Klozur SP breakthrough between Day 7 and Day 14
- ART = Estimated hydraulic residence time in the ZVI activated interval. Flow rate through column



Potential Applications

K^+ vs. Na^+

- Certain sites have limits on sodium
- Potassium persulfate would be alternative
  - Higher solubility at higher temperatures

Benefit from Extended Release

- Permeable reactive barriers
  - Funnel and Gate
- Low permeable soils
  - Low groundwater flux
- In situ soil mixing

Field Applications of KP

- Primarily applied in Canada and Europe
  - ~12 Applications
  - Mostly emplacement
  - Activated:
    - Iron-chelate
    - Alkaline
- Rationale
  - Easy of emplacement
  - Potassium residual
  - Longevity over SP
- Aquifer materials
  - Clay
  - Sand
  - Bedrock

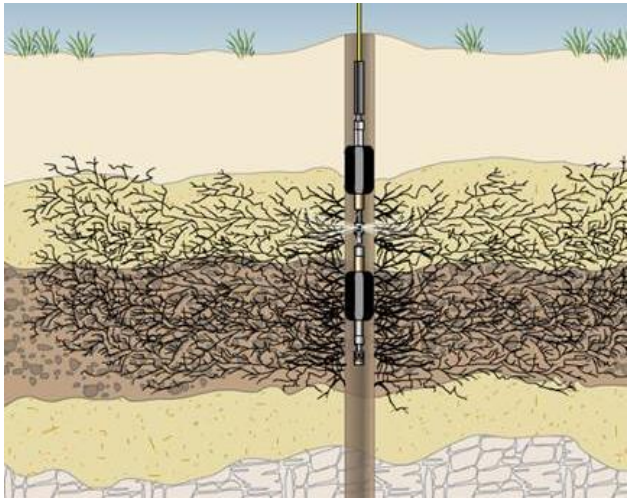
Conceptual Implementation Approaches

- Constructed Permeable Reactive Barrier
  - Ditch/trench tool
  - Excavator

- In Situ Soil Mixing
  - KP, SP or blend
  - Slaked lime or NaOH activator

Conceptual Implementation Approaches

- Expected loadings through emplacement/ fracturing technologies
  - Hydraulic
    - 50-100 lbs per linear foot
  - Specialized Hydraulic
    - 1,000-4,000+ lbs per fracture
  - Pneumatic
    - ~300-500 lbs per vertical foot



Extended Release Persulfate

- Dissolution Limited Release
  - Rate of release of persulfate maintains steady concentration in aquifer
  - Can be distributed within aquifer using:
    - Emplacement strategies
    - Soil Mixing
  - Cost per lb
- Encapsulated (wax) SP-Matrix Limited Release
  - Rate of release of persulfate limited by matrix:
    - Concentration in aquifer
  - Mass
    - Concentration in aquifer
  - Distribution:
    - Boreholes
    - Soil Mixing

Klozur KP Summary

- Extended
  - Target
    - Groundwater plumes (1,4-dioxane, MTBE, etc)
    - Low permeable soils
    - Potassium residual
  - PRBs require periodic replenishment of:
    - Klozur KP
    - Activator
      - Extended release
- Critical Information:
  - Groundwater flux
    - Hydraulic conductivity
    - Hydraulic gradient
  - Aquifer temperature
  - Aqueous phase demand
    - Target
    - Non-target (COD, etc)
  - Depth to target interval

CASE STUDY

Case Study

- Former industrial sites in Germany
- Former drum area
- Contaminants: Naphthalene and BTEX
- Contaminants mainly in low permeable sandstone up to 12 m bgs
- Pump & treat not practical and not possible for excavation
- Preferred approach was hydraulically placed ISCO technology

Courtesy of Riskcom

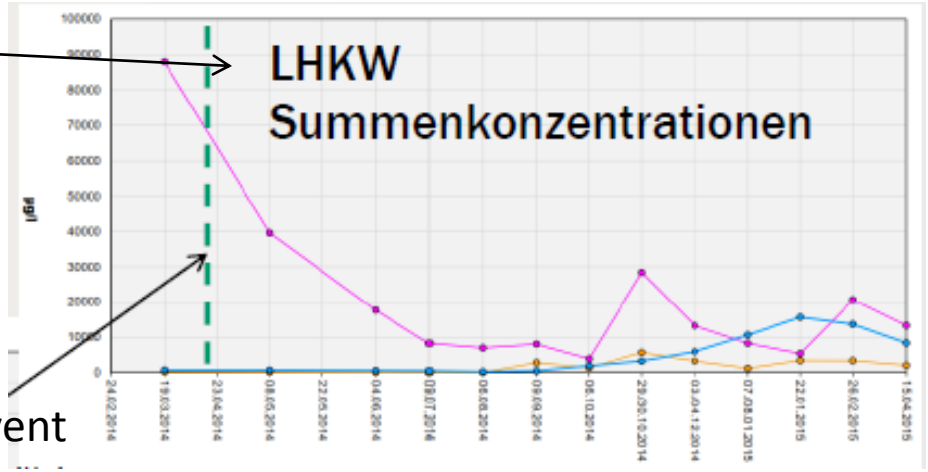
Case Study

- Pilot Project:
  - Targeted 7 to 11 m bgs
  - Heavy GW impacts
  - Emplaced KP 15 specific lifts in 3 injection location (5 per location)
  - Total of 1,350 kg KP with 200 kg of ferrous lactate

Courtesy of Riskcom

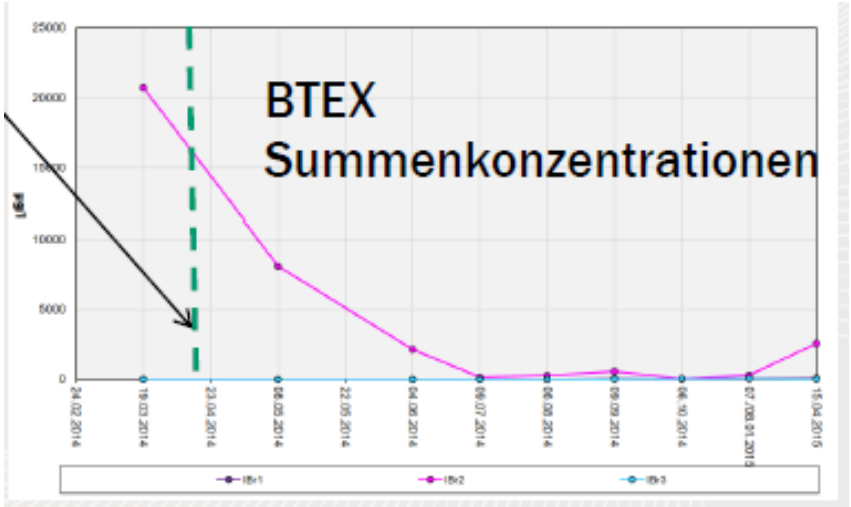
Long Term Monitoring Results

cVOCs



Pilot Test Event

Pilot Test Event



Courtesy of Riskcom

Results and Conclusions

- 1 Year Post Application Monitoring
- Successful distribution of KP and activator over a 200 m^2 area (2,152 ft^2) with 3 injection locations
- Activated Klozur KP resulted in up to 99% treatment of Target COCs

Date	Contaminant (mg/L)				
	PCE	TCE	cDCE	BTEX	PAH
3/19/2014	13,000	22,000	52,000	20,713	98
10/7/2014	8	23	3,800	47	5
Percent Reduction	99.9%	99.9%	92.7%	99.8%	94.5%
4/15/2015	4	6	13,000	2,570	104
Percent Reduction	99.97%	99.97%	75.0%	87.6%	-5.3%

Courtesy of Riskcom

Conclusions

- Sodium persulfate (SP) still works!!!
- Potassium persulfate (KP) offers an alternative to sodium persulfate (SP)
  - Both form the powerful oxidant persulfate anion
- Unique characteristics of KP:
  - Lower solubility
  - K^+ vs Na^+
- Column studies indicate consistent rate of release of persulfate anion maintaining a constant concentration consistent with theoretical solubility limit
- Column studies show successful activation and treatment of aqueous contaminants 1,4-dioxane and MTBE

Conclusions

- KLOZUR® SP When oxidant is pushed into formation to attack contamination
  - Source zone treatment

- KLOZUR® KP When contaminant is coming to the oxidant or when you want extended contact
  - Permeable reactive barriers
  - Low permeable soils

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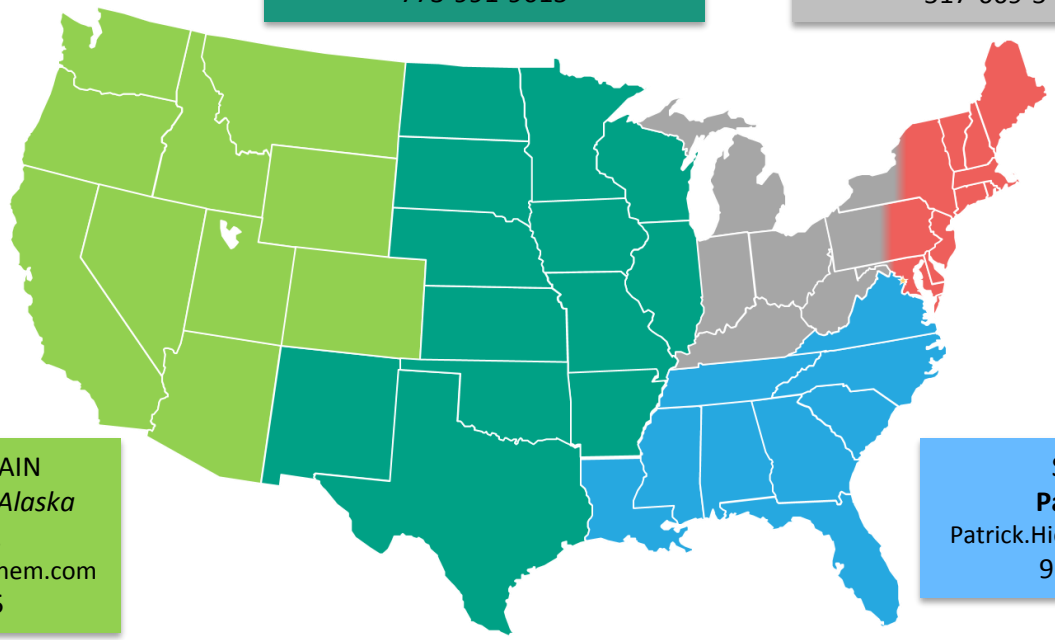

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