Klozur® KP Applications Experience: Extended Release Chemical Oxidation

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September 19, 2018

Field-Proven Portfolio of Remediation Technologies Based on Sound Science

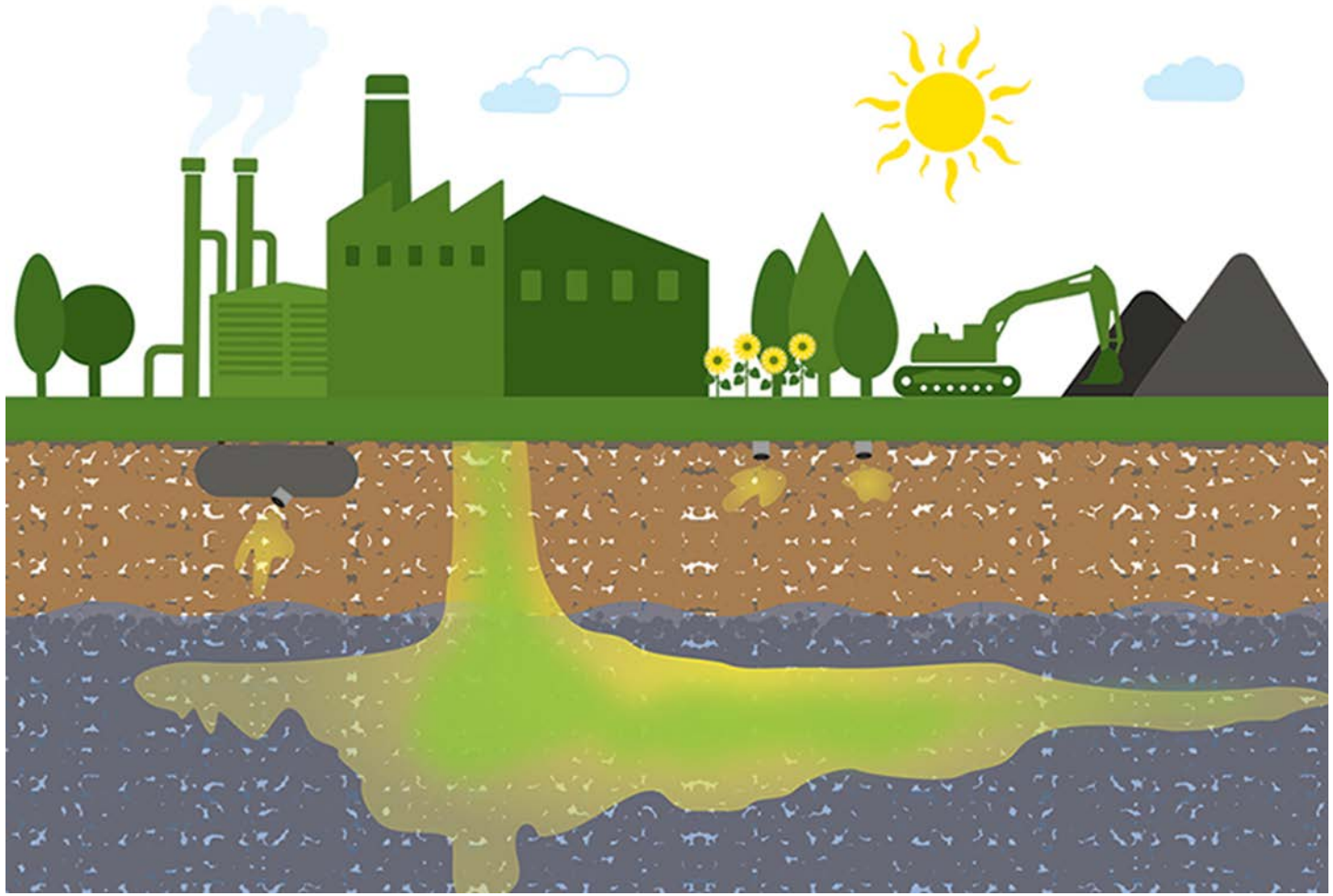
Chemical Oxidation
- Klozur® Persulfate Portfolio
- Hydrogen Peroxide

Chemical Reduction
- EHC® Reagent
- EHC® Liquid
- Daramend® Reagent
- Zero Valent Iron
- GeoForm™ Reagents

Aerobic Bioremediation
- Terramend® Reagent
- PermeOx® Ultra

Enhanced Reductive Dechlorination
- ELS® Microemulsion
- ELS® Concentrate

Metals Remediation
- MetaFix® Reagents



Outline

- Introduction to Klozur® persulfate

  KLOZUR® SP

  KLOZUR® KP

- Oxidative and reductive pathways from a single technology
- Bench and Case Studies
- General Overview of Klozur KP Applications

Klozur® Persulfates

KLOZUR® SP

- Environmental grade sodium persulfate

KLOZUR® KP

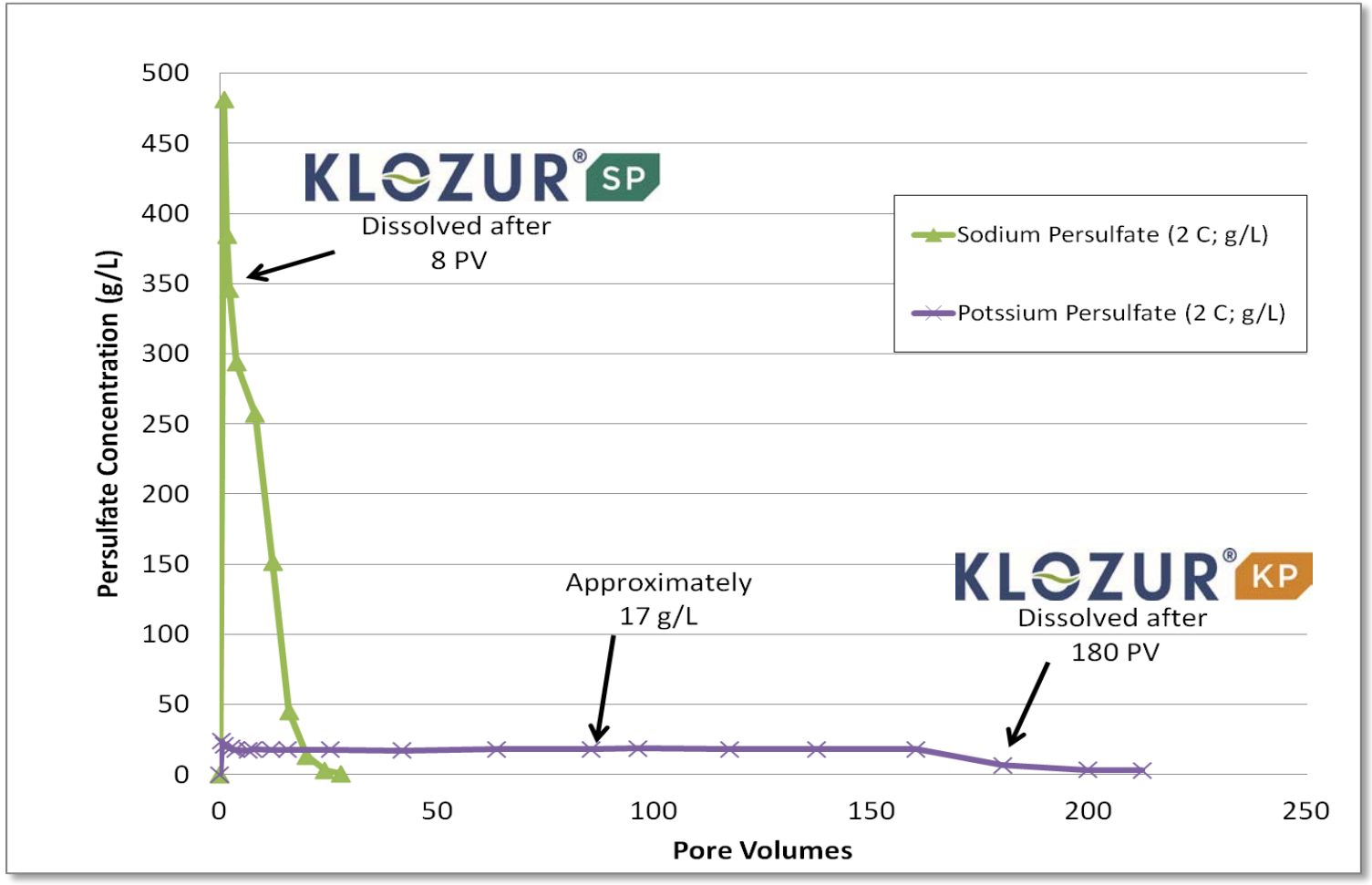
- Environmental grade potassium persulfate

Key Differences:
- Solubility
- Na^+ vs K^+ residual

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

Permeable Reactive Barrier: Column Study



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KLOZUR® SP

Classic: Applied at thousands of sites, the high solubility of Klozur SP is ideal for:

- Source zone treatment
  - Delivery of significant oxidative mass into the target area
  - Highly contaminated sites including non-aqueous phase liquids
  - High concentration applications

KLOZUR® KP

New: Low solubility and extended release can help address some of the previous technical challenges :

- Extended Release
  - Tight soils / clays – matrix diffusion
  - Permeable reactive barrier applications
  - Diffusive aqueous phase contaminants (plumes, aqueous phase contaminants, etc)

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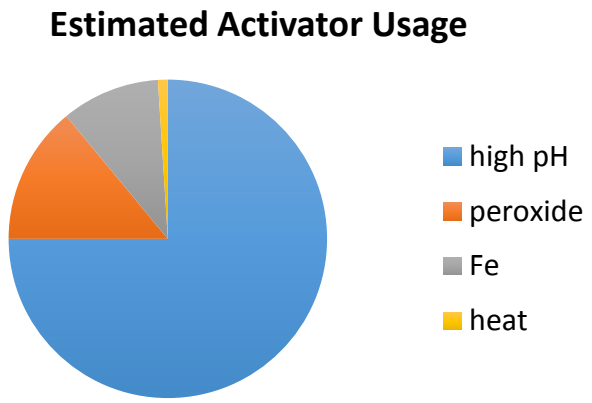

- Zero Valent Iron
  - Solid state activator
  - Oxidative pathway

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 most applications
  - More compatible with carbon steel
  - Oxidants and reductants
- Iron-Chelate Activated Persulfate
  - Chlorinated ethenes and hydrocarbons
  - Oxidative pathway
- Heat
  - Complex sites
  - Polishing step after thermal treatment
  - Oxidants and reductants
- Hydrogen Peroxide
  - Sites that benefit from vigorous reaction with both hydrogen peroxide and sodium persulfate
  - Oxidants and reductants

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Activation of Persulfate

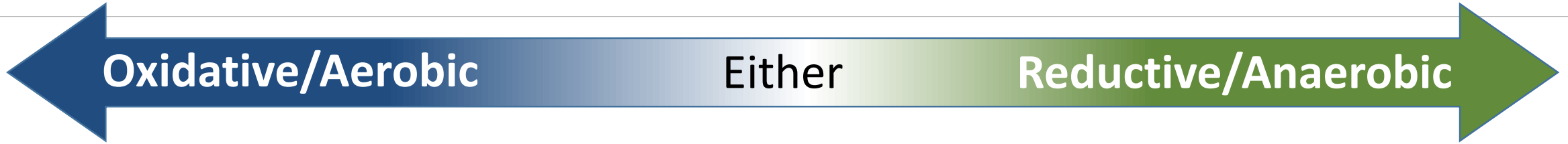
Sodium Persulfate:

- Aqueous phase oxidant – aqueous phase activators
  - NaOH (alkaline)
  - Fe / Fe-chelate
  - Hydrogen peroxide
  - Heat

Potassium Persulfate:

- Solid/extended release oxidant – **Solid/extended release activators**
  - **Hydrated lime-$Ca(OH)_2$ (alkaline)**
  - Zero Valent Iron (ZVI)
    - Separate trench (down gradient)

Degradation Pathways



Oxidative/Aerobic

- Petroleum Hydrocarbons
- BTEX
- PAHs
- Oxygenates
- **1,4-dioxane**

Either

- Chlorinated Ethenes
- Chlorobenzenes
- Phenols
- Select Pesticides
- Select Fluorinated Compounds
- PCBs
- Select Energetics
- **Dichloroethenes**

Reductive/Anaerobic

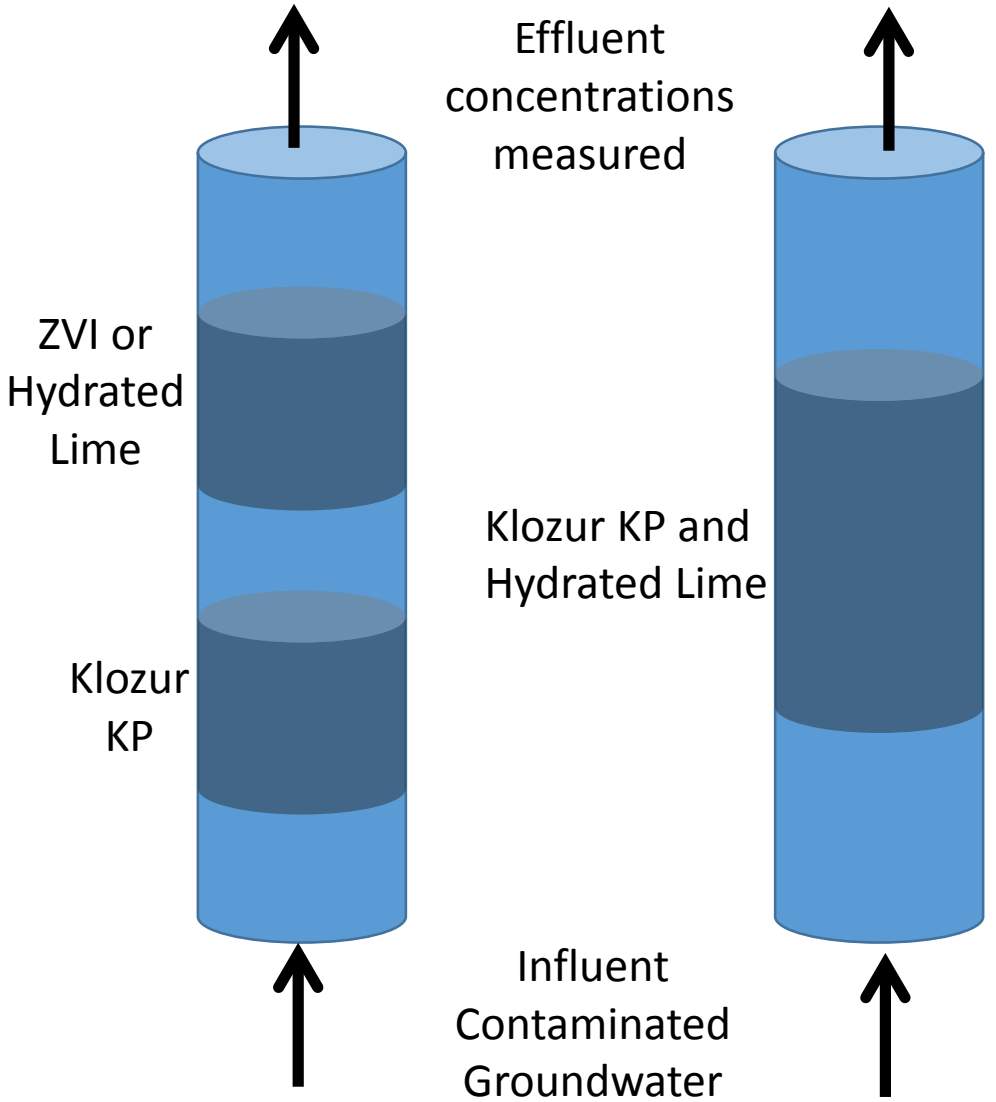
- Select Pesticides
- Select Energetics
- Carbon Tetrachloride
- 1,1,1-Trichloroethane
- **Dichloroethanes**

Select Bench and Case Studies

- Site 1: Weston Solutions Superfund site in the New England
- Site 2: ERM Private site located in the Pacific Northwest
- Site 3: AECOM Former manufacturing facility located in Northeast
- Site 4: Jacobs Former oil well servicing facility

Treatability Column

- Up flow column reactors:
  - Klozur KP and Hydrated Lime [$Ca(OH)_2$] mixed together
  - Klozur KP and ZVI in separate sections due to incompatibilities
- Columns run at 20 °C
- Continuous feed of contaminated site groundwater



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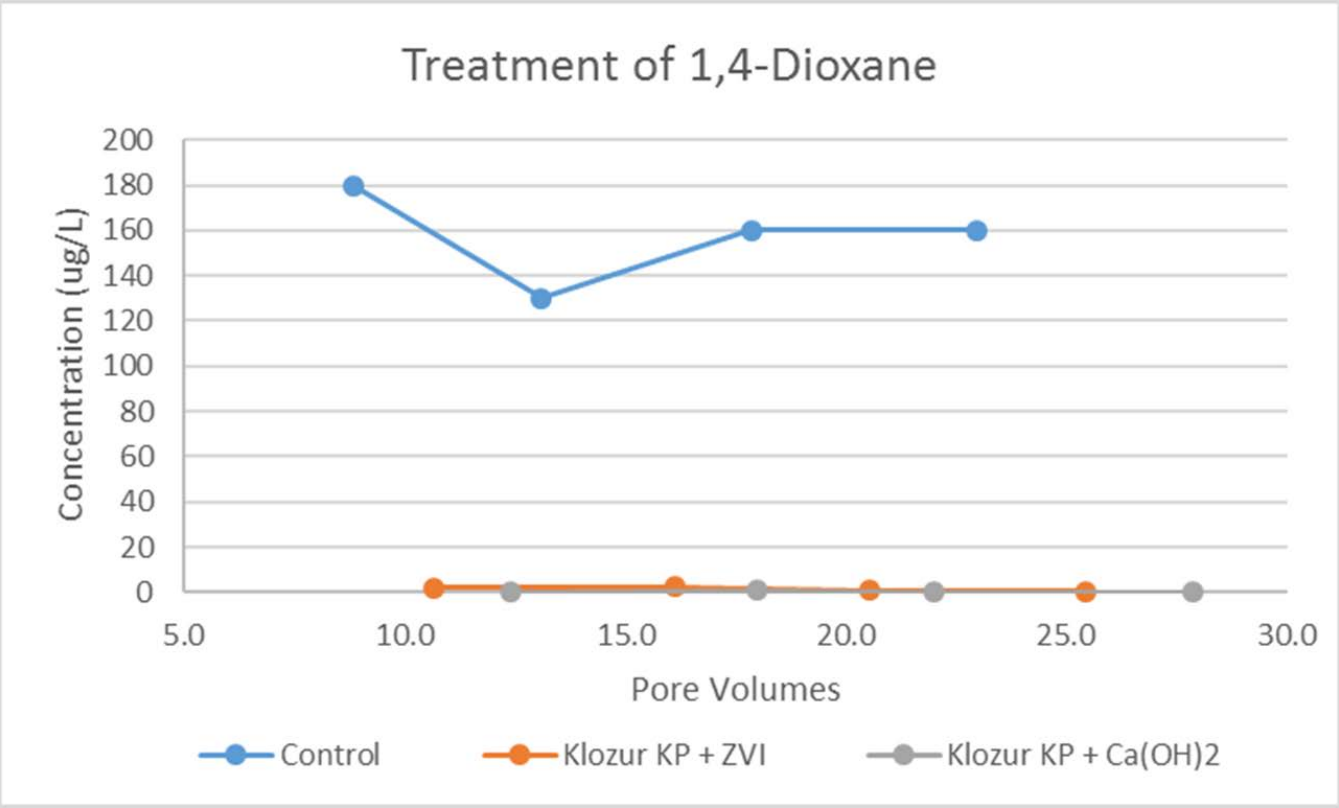
Site 1: New England Superfund Site

- Consultant: Weston Solutions
- Former chemical waste storage and bulking facility
- Residual 1,4-dioxane and 1,1,1-Trichloroethane (1,1,1-TCA) daughter products
  - 1,1-Dichloroethane (1,1-DCA)
  - 1,2-Dichloroethane (1,2-DCA)
  - 1,1-Dichloroethene (1,1-DCE)
- Soil matrix of clay till was bench tested. Site includes sand lenses.

Site 1: Treatment of 1,4-Dioxane



1,4-Dioxane treated by oxidative pathway

- Treated to below the detection limit by both ZVI and hydrated lime activated persulfate
- Persisted for theoretical design period

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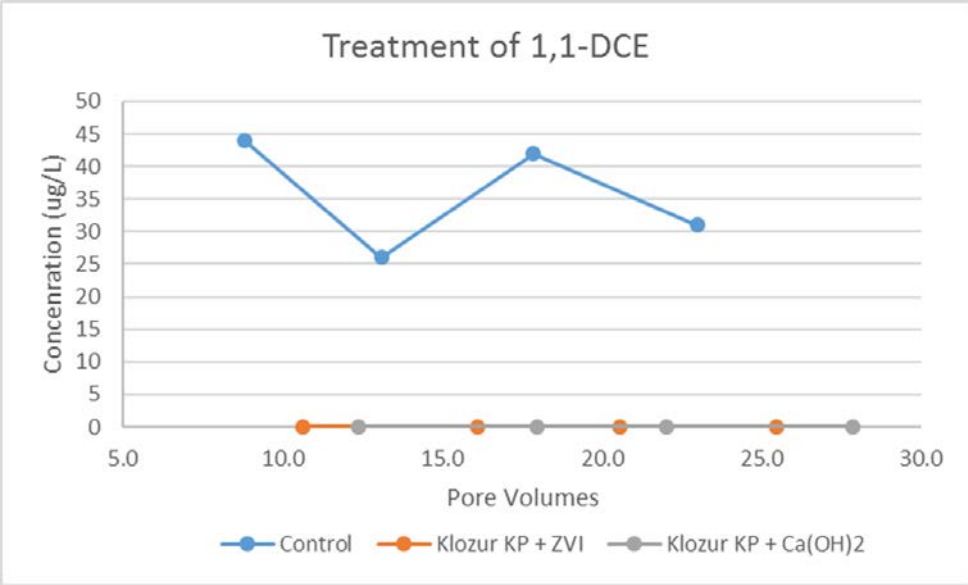
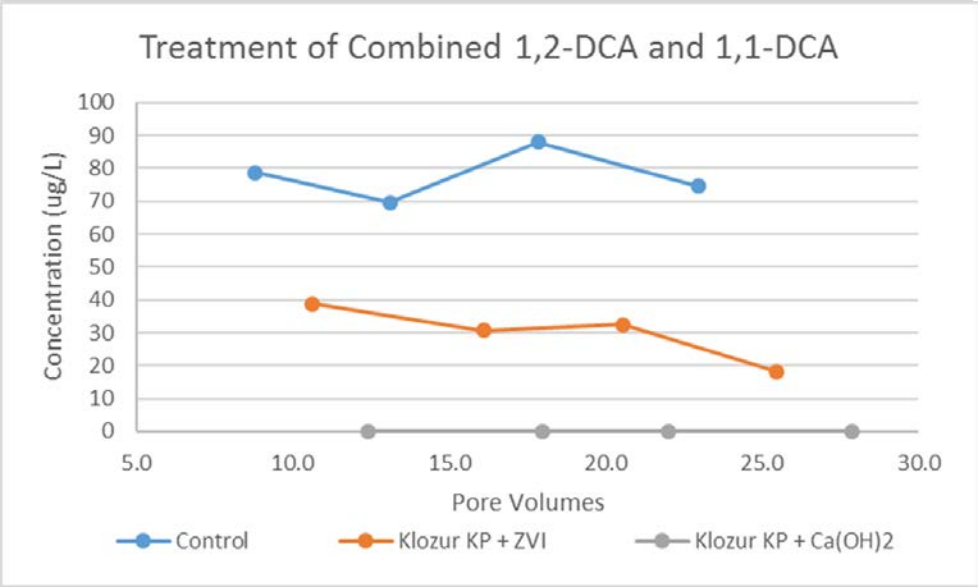
Site 1: Treatment of CVOCs

- DCE can be treated by both oxidative and reductive pathway
- DCAs are primarily treated by a reductive pathway
  - Treated to below the detection limit by hydrated lime activated persulfate
  - Partial reduction by ZVI activated persulfate





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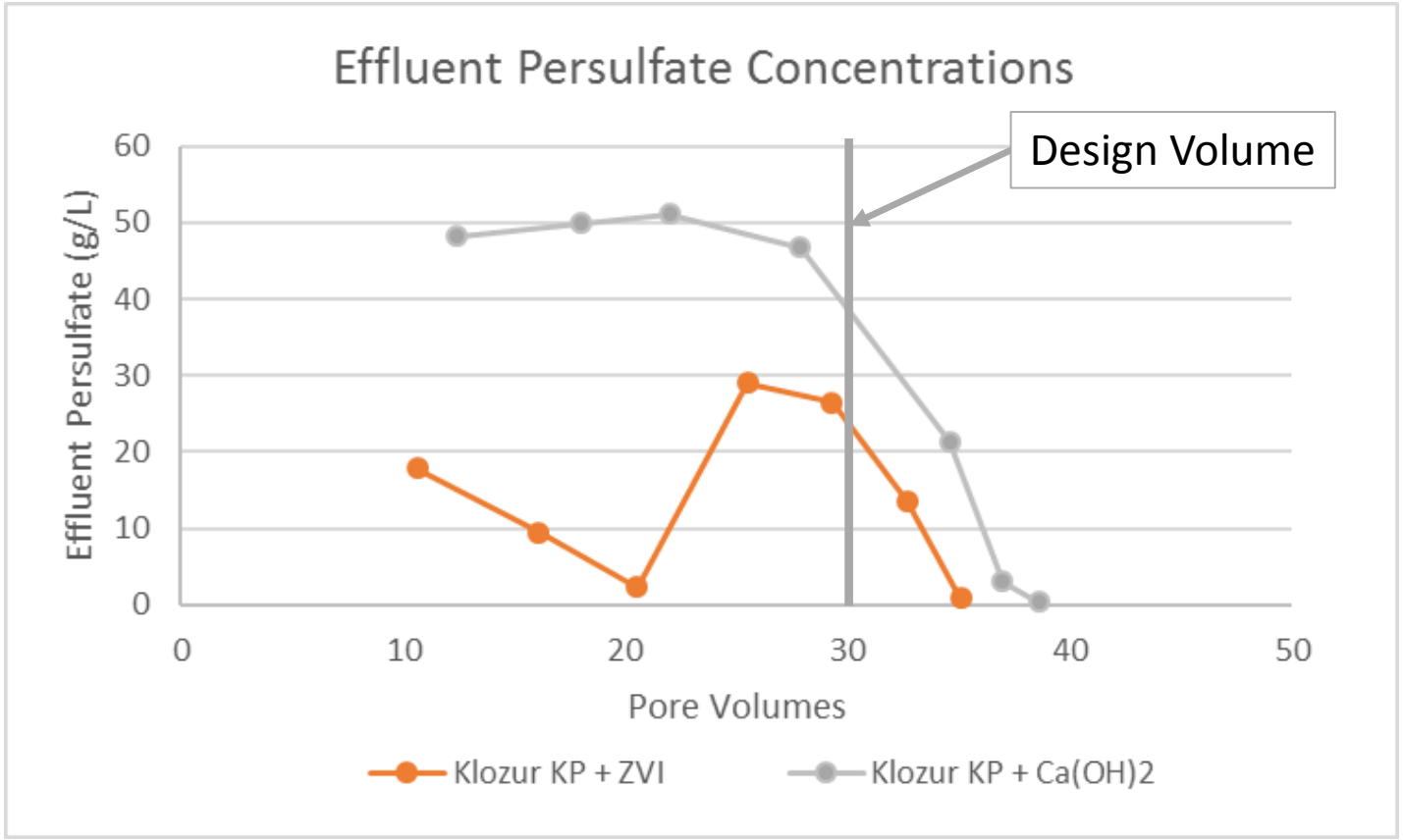
Site 1: Extended Release of Klozur KP

- Klozur KP persisted in both reactors for longer than the design period
  - Hydrated lime lasted longest
  - ZVI activation showed more consumption of persulfate, but effective treatment for design life



Site 1: Summary

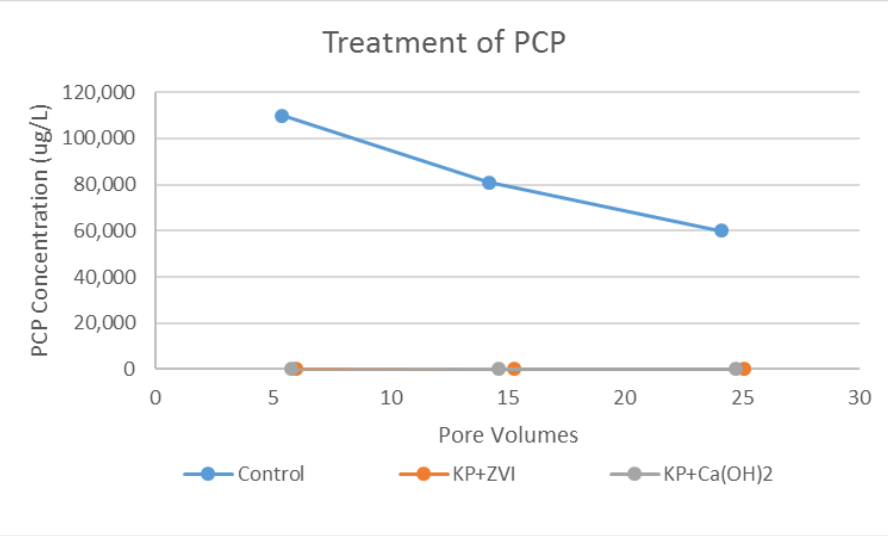
- Klozur KP:
  - Persisted as designed
  - Alkaline activation
    - Oxidative and reductive pathway
    - Treatment of all three contaminants
  - ZVI activation
    - Primarily oxidative pathway
    - Treatment of 1,4-dioxane and DCE
    - Limited treatment of DCA

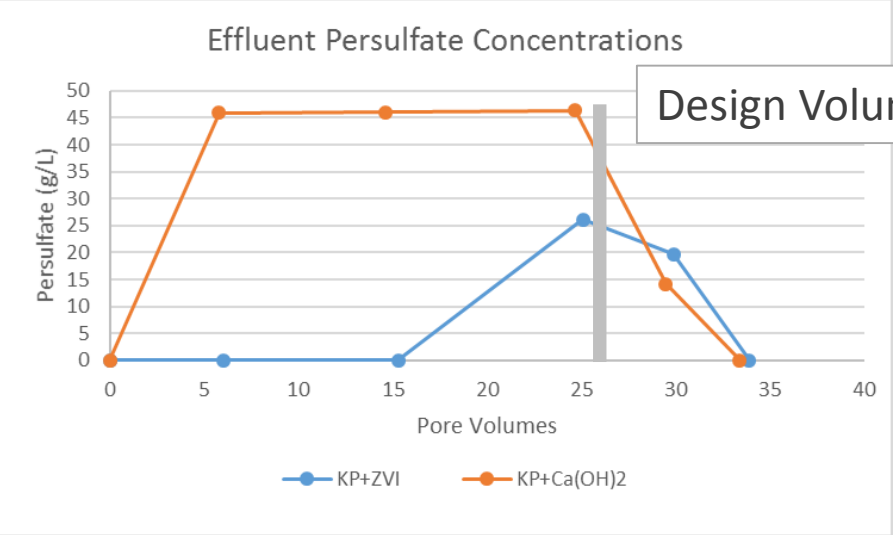
- Evaluating natural attenuation. Treatment with Klozur KP is an alternative if natural attenuation is not successful

Site 2: Pacific Northwest Site

- Consultant: ERM
- Former wood treatment facility
- Residuals include PAHs, TPH, and Pentachlorophenol
  - Pentachlorophenol (PCP) primary COC at proposed PRB boundary
- Soil matrix: Sand lens below a confining silt lens

Site 2: Treatment of Pentachlorophenol





- Concentrations reduced by greater than 99.9% passing through both ZVI and hydrated lime activated persulfate systems
  - Influent was spiked
- Treated via oxidative and reductive pathway
  - Reductive pathway beneficial in dechlorinating PCP
- KP persisted to design volume
- Field pilot test on going September 2018

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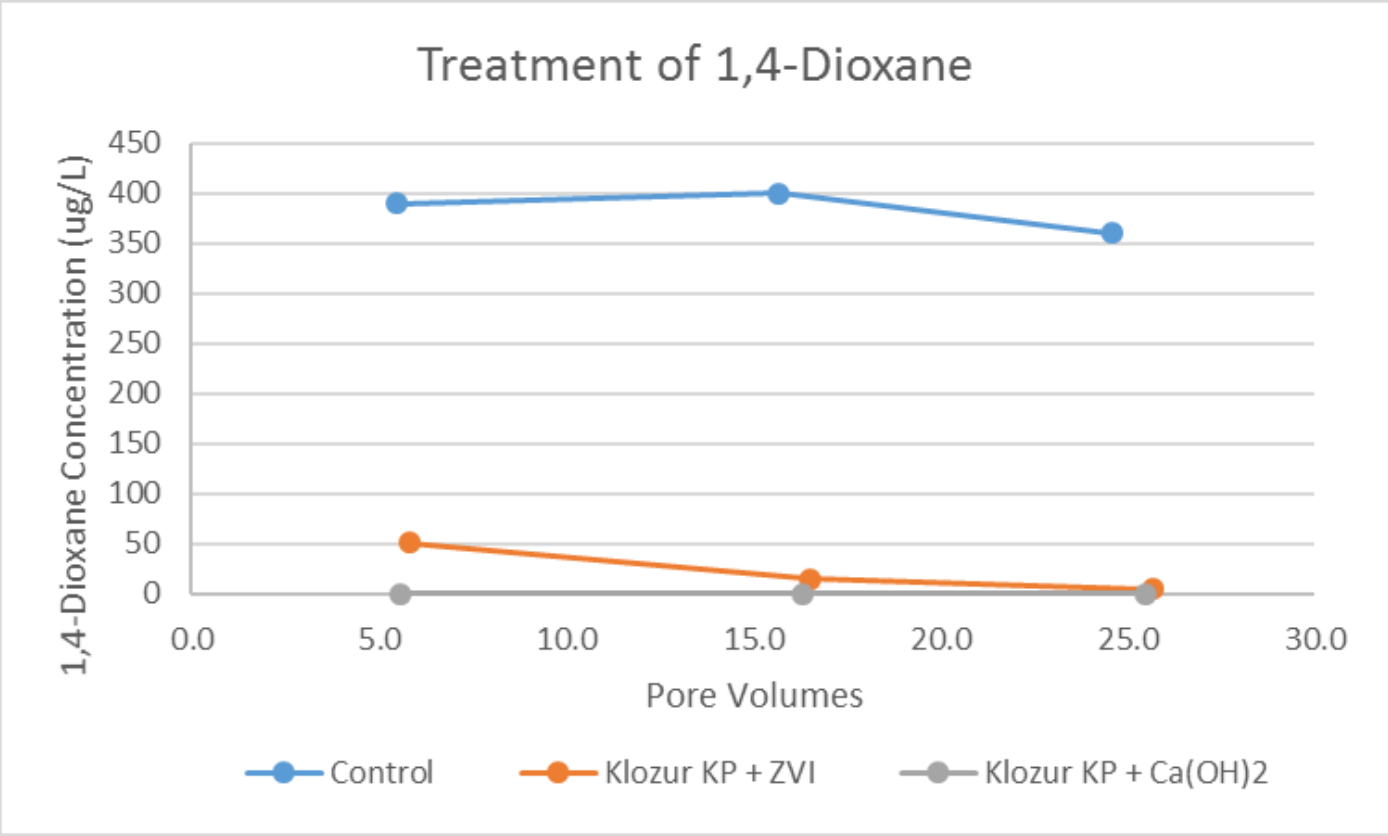
Site 3: Former Industrial Facility in the Northeast

- Consultant: AECOM
- Residual 1,4-dioxane, TCA , and TCA daughter products
  - 1,1,1-Trichloroethane and 1,1,2-Trichloroethane (TCAs)
  - 1,1-DCA and 1,2-DCA
  - 1,1-DCE
- Silty soils with sand lenses

Site 3: Treatment of 1,4-Dioxane



1,4-Dioxane treated by oxidative pathway

- Treated to below the detection limit by hydrated lime activated persulfate
- Up to 98.7% reduction in column activated with ZVI

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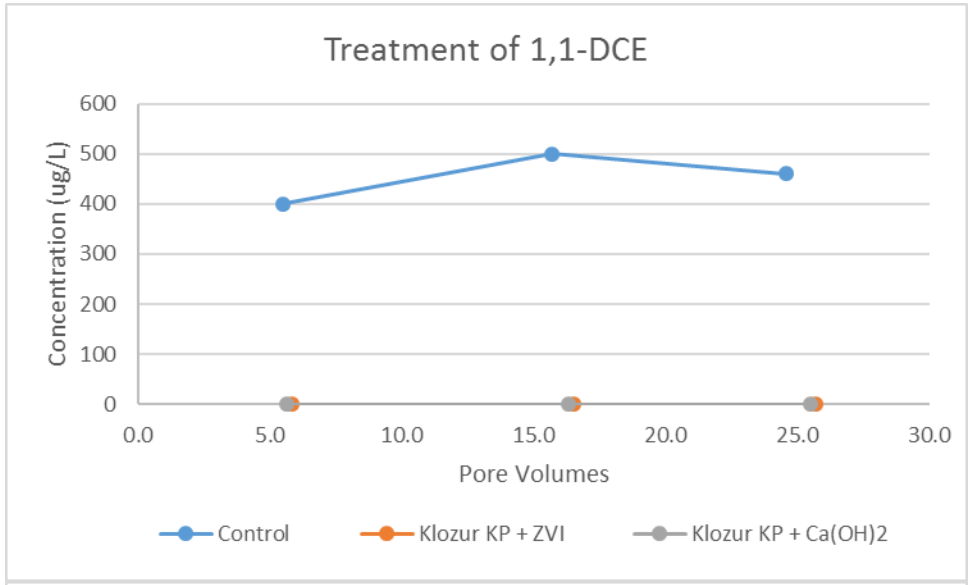
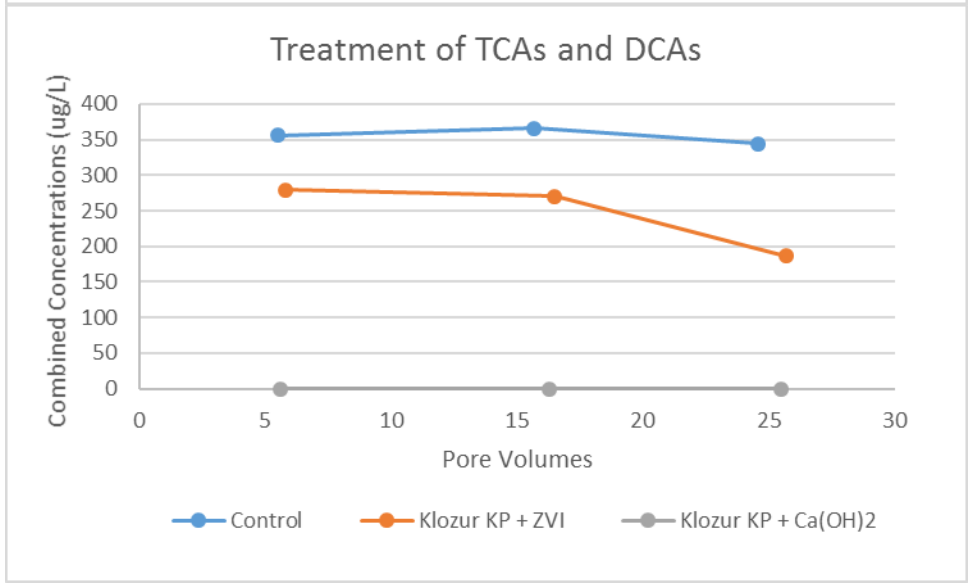
Site 3: Treatment of CVOCs

- DCE can be treated by both oxidative and reductive pathway
- TCA/DCA are primarily treated by a reductive pathway
  - Treated to below the detection limit by hydrated lime activated persulfate
  - Partial reduction by ZVI activated persulfate





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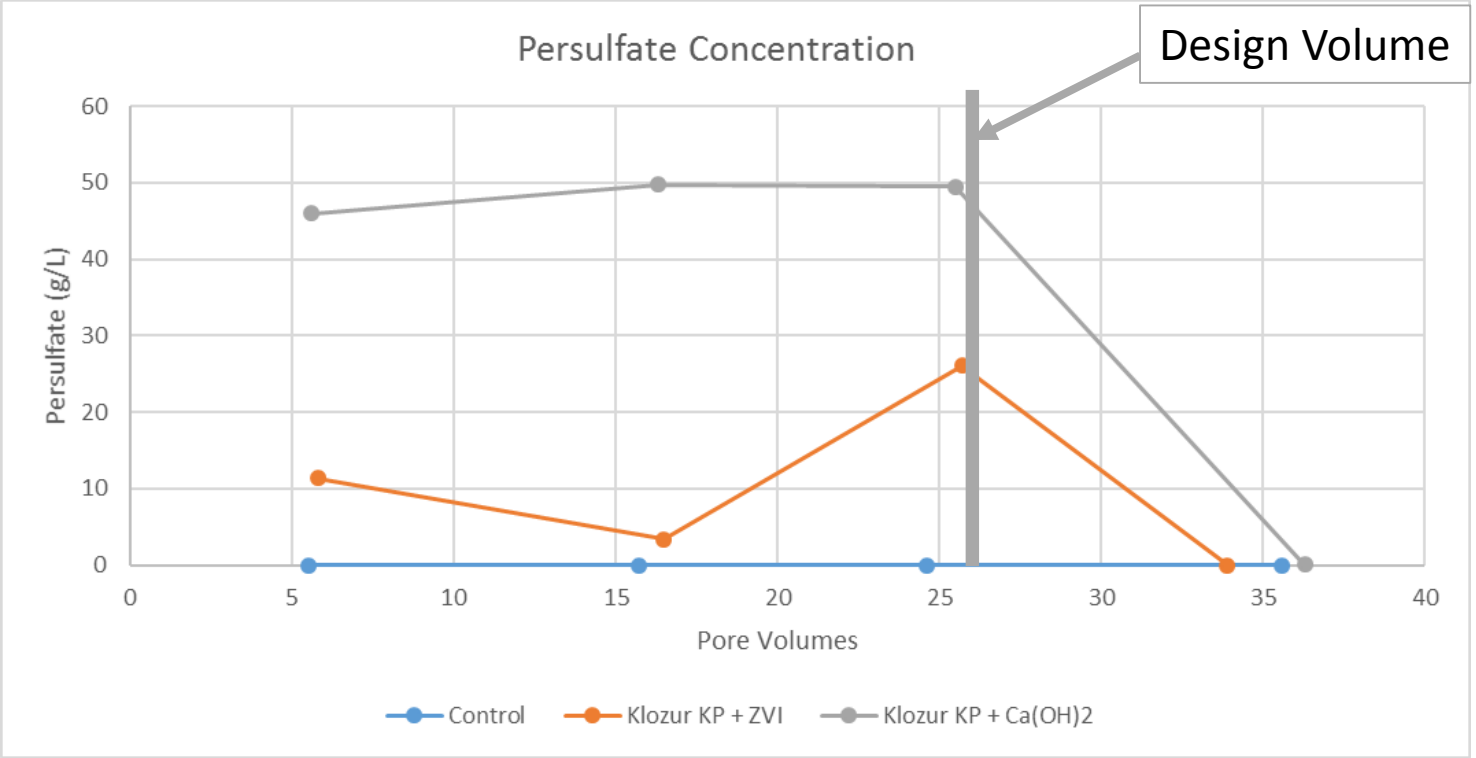
Site 3: Extended Release of Klozur KP

- Klozur KP is thought to have persisted in both reactors for longer than the design period



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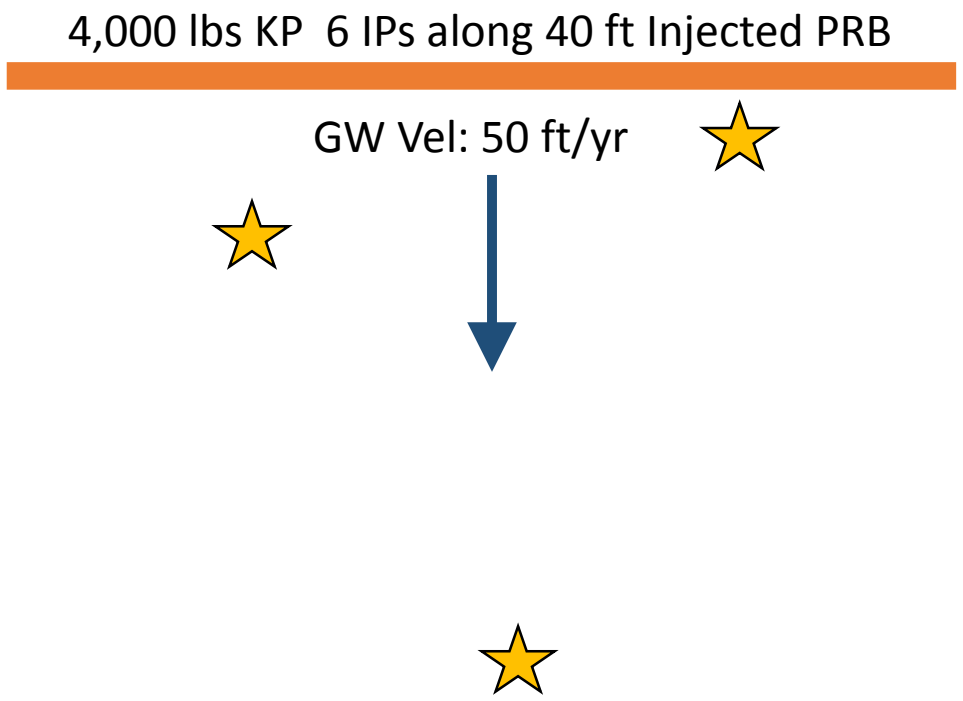
Site 3: Pilot Study

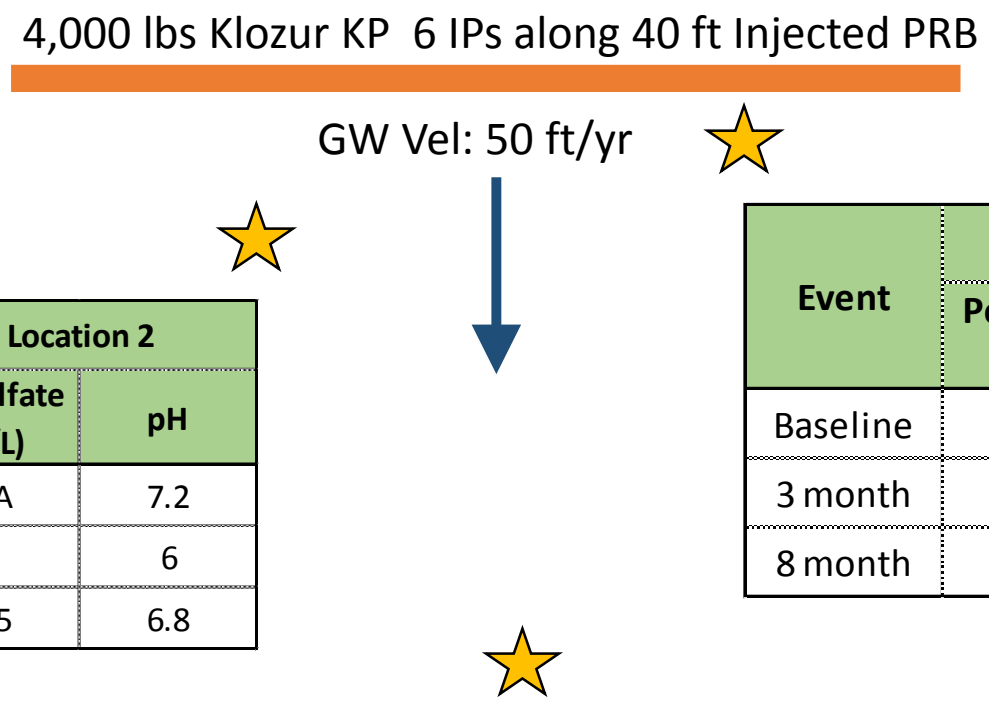
- Pilot Conducted Early December 2017

- Injected PRB (40 ft)
  - Solid slurry
  - 6 DPT points
  - 20 to 30 ft bgs
  - Designed for 6 month persistence



Persistence and Distribution

- Reagents:
  - Klozur KP
  - Klozur SP
  - Hydrated Lime
  - 25% NaOH
- Monitoring wells downgradient in targeted vertical interval:
  - Location 1 (~3 ft)
  - Location 2 (~10 ft)
  - Location 3 (~25 ft)



Event	Location 2	
	Persulfate (g/L)	pH
Baseline	NA	7.2
3 month	3	6
8 month	2.5	6.8

Event	Location 1	
	Persulfate (g/L)	pH
Baseline	NA	6.9
3 month	7.2	12
8 month	14.2	12

Event	Location 3	
	Persulfate (g/L)	pH
Baseline	NA	7.2
3 month	NA	NA
8 month	8	6.5

Site 3: Treatment

4,000 lbs Klozur KP 6 IPs along 40 ft Injected PRB

GW Vel: 50 ft/yr

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%

* Detected VOCs not including acetone

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%

* Detected VOCs not including acetone

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

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Site 3: Summary

- Bench test:
  - Successful treatment in columns
  - Klozur KP persisted as expected

Full Scale:
Implemented August 2018
Three transections
Designed to last ~1 yr

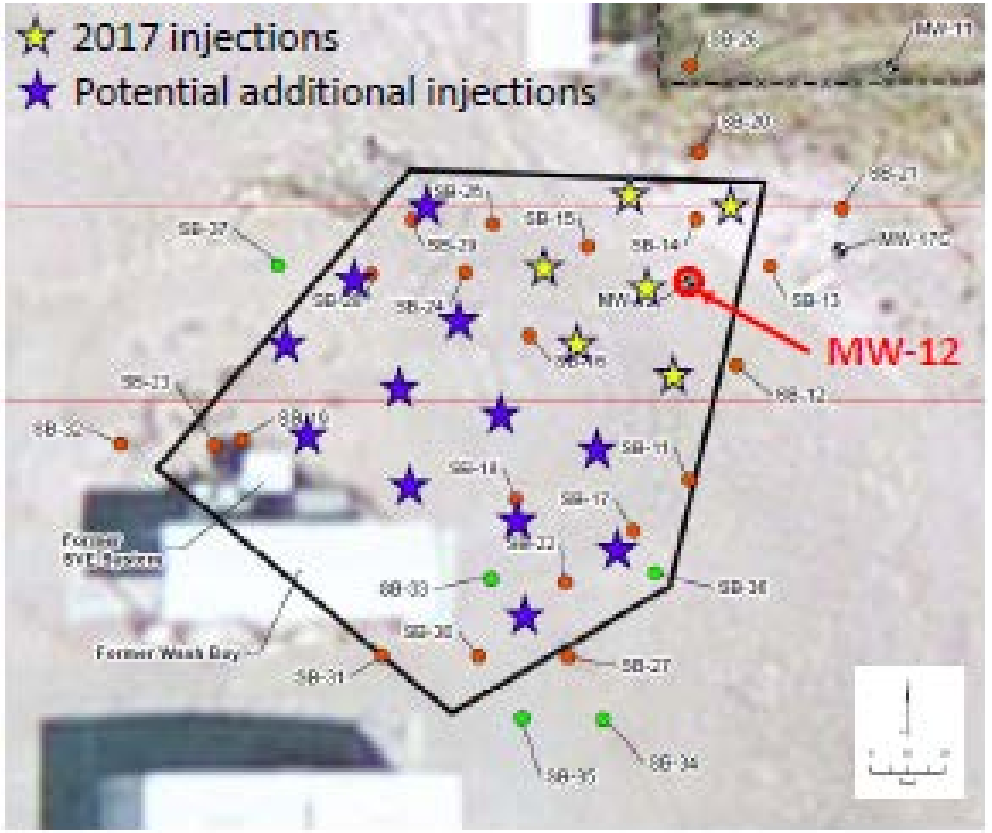
- Pilot study:
  - Klozur KP persisted longer than designed (safety factor + lower temperature)
  - Resulted in 99-100% reduction at PRB, less reduction as you move downgradient from PRB
  - Oxidative and reductive pathways observed in field
    - 1,4-dioxane and TCA/DCA treated in a single application

Site 4: Southwest USA

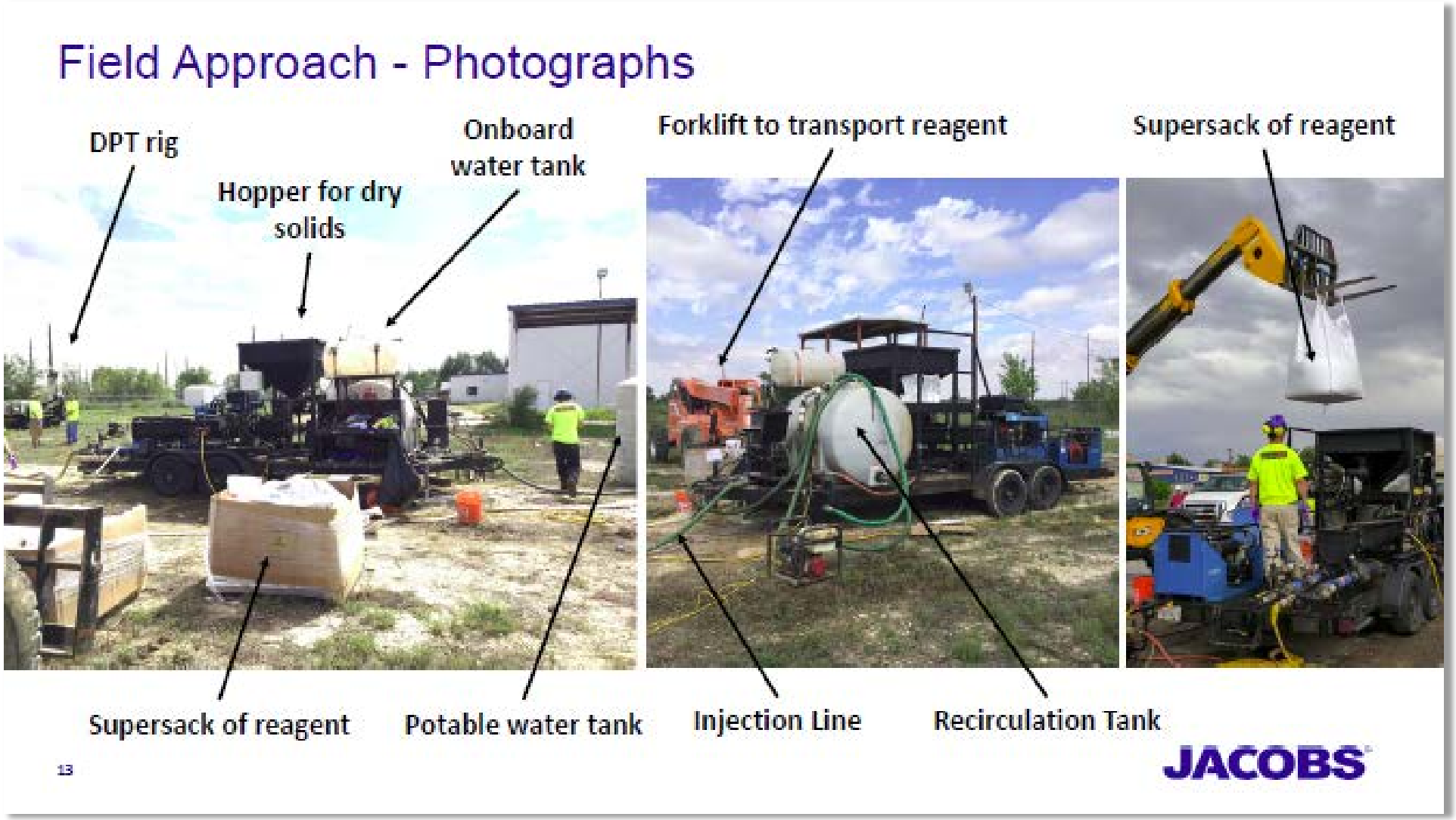
- Consultant Jacobs
- Presented Session B9 Battelle Palm Springs (2018)
- Former oil well servicing facility
- Prior remedies sufficiently treated most of the site
  - Source: Excavation and SVE
  - Plume: Recirculation with P&T and ISCO
- Low permeable soils (silt, silty clay, clay) with gypsum/carbonate rubble
- Polishing Application in Source Area: Concentrations above goals persisted at MW-12
  - DCA, DCE, PCE, Benzene, and Naphthalene
- Goal: No further Action
- Bench
  - 2 g Klozur SP/Kg soil
  - Very high base buffer capacity
  - Selected iron activated persulfate (IAP)
    - ERD following if needed for DCA

Site 4: Field Application Design

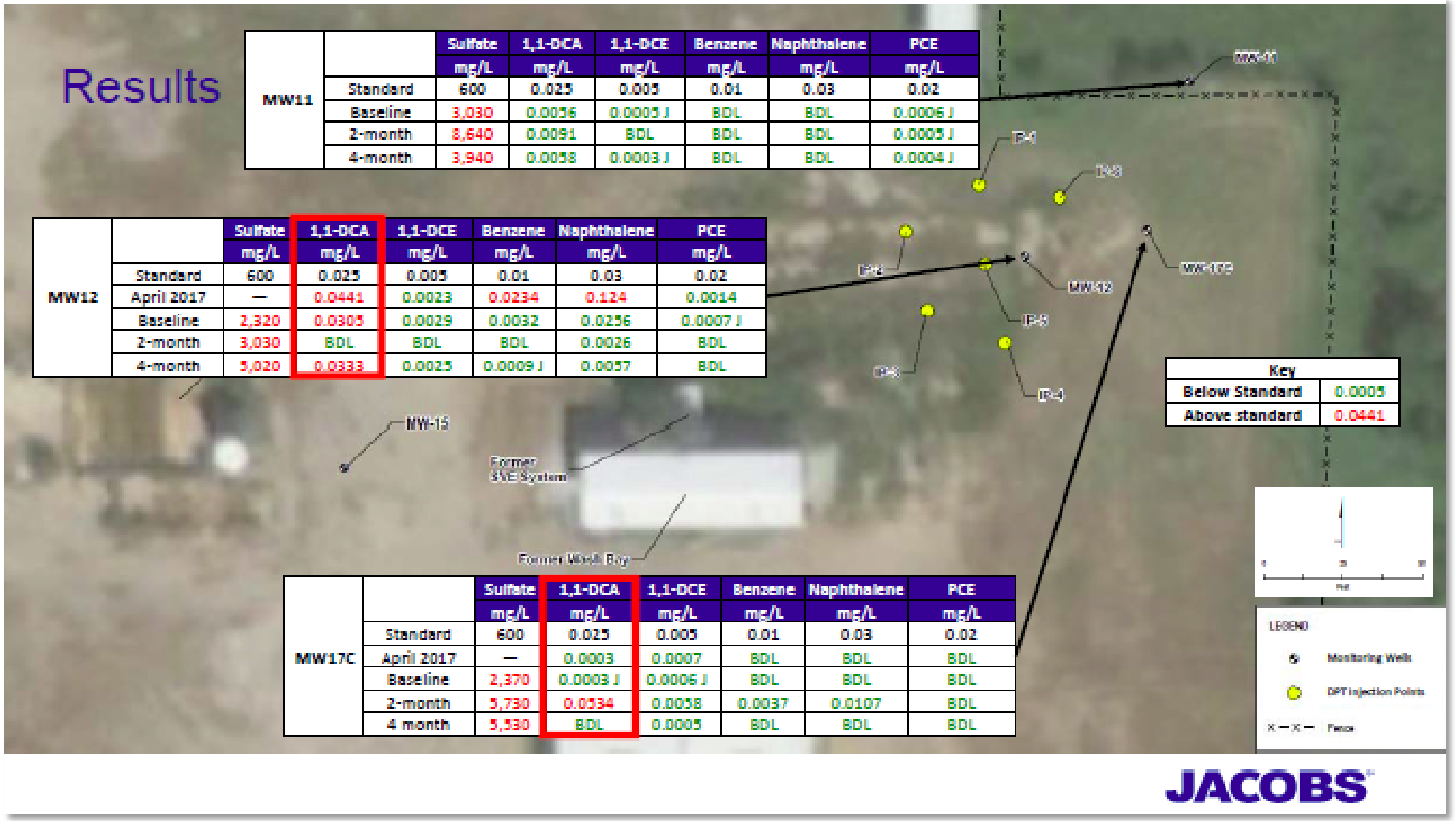
- Work completed by FRx
- 24 fractures (4 fractures per location)
  - Klozur SP: 1,800 lbs
  - Klozur KP: 9,000 lbs
  - Chelated Iron
  - Carrier fluid
  - Chase water



Site 4: Field Application



Site 4: Results



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Site 4: Summary

- Successful targeting of
  - Low concentration COCs
  - Low permeable soils
- Rapid application
  - 2 day field event
  - Results favorable at 2 months
- Used
  - Klozur SP for rapid treatment
  - Klozur KP for extended release
- Concentrations of COCs expecting treatment are BDL
- DCA may persist (lack of reductive pathway for IAP)
  - If persists may be polished with ERD/organic substrate

Bench and Case Study Summary

- Klozur KP is an extended release persulfate that is being used for permeable reactive barriers, low permeable soils, and soil mixing
- Extended release of Klozur KP
- Klozur KP and Klozur SP and be combined in a single application to take advantage of their different characteristics
- Alkaline activated persulfate creates oxidative and reductive pathways, which can be used to treat comingled contaminant plumes such as 1,4-dioxane, TCA, and DCAs.

Klozur KP Application Details

- Factors influencing oxidant mass
  - Klozur KP
  - Klozur SP
- Slurry concentrations
- Settling of solid slurries
- General guidance for common applications

Factors Influencing Oxidant Mass

- Application area
  - Target on soil, groundwater and NAPL
  - Non-target on soil
  - Safety Factor

- Extended release of persulfate anion with GW flux
  - Dissolve to maintain theoretical solubility limit
  - Influent target demand
  - Influent non-target demand
  - Minimize initial dissolution of Klozur KP
  - Safety Factor

Klozur KP or Klozur SP

- Application area
  - Target on soil, groundwater and NAPL
  - Non-target on soil
  - Safety Factor

KLOZUR® SP
KLOZUR® KP

- Extended release of persulfate anion with GW flux
  - Dissolve to maintain theoretical solubility limit
  - Influent target demand
  - Influent non-target demand

KLOZUR® KP

  - Minimize initial dissolution of Klozur KP

KLOZUR® SP

  - Safety Factor

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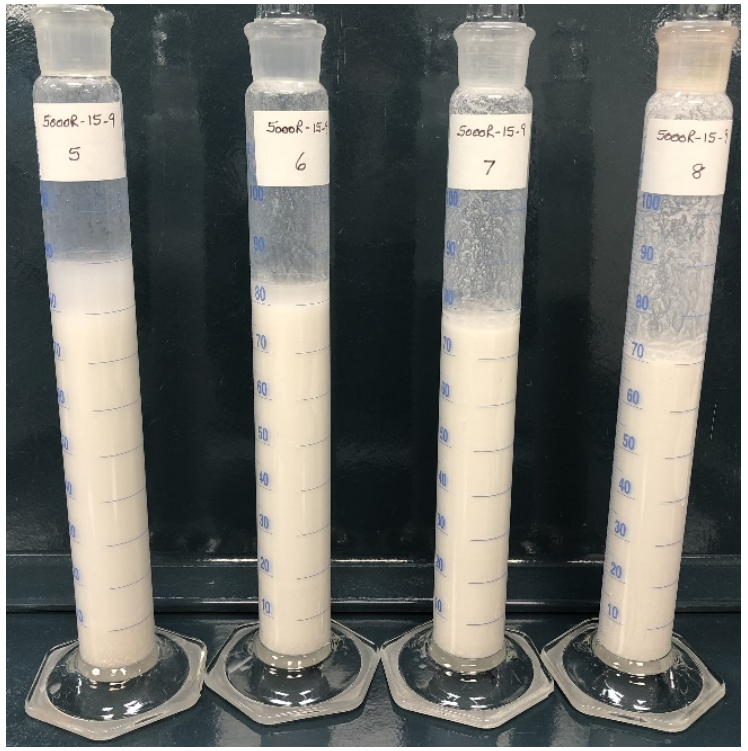
Klozur KP Slurries

- Slurries include:
  - Klozur KP
  - Klozur SP
  - Hydrated Lime
- Percent Solids
  - 25 percent to 50 percent
- Small batches. Inject within 4 hrs of batching

Klozur KP Settling Tests

Time 0
Klozur KP Only



Time 1 min
Klozur KP and Hydrated Lime

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

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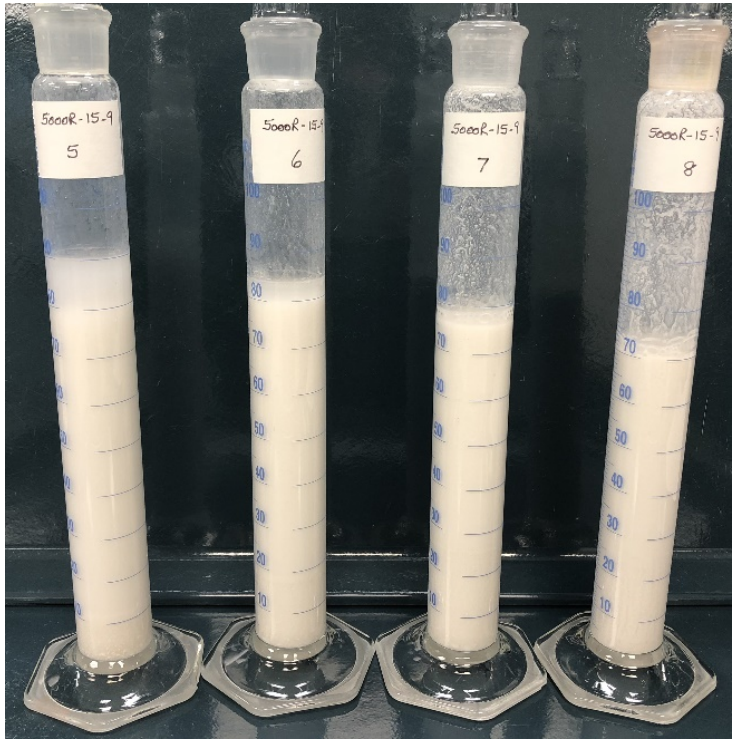
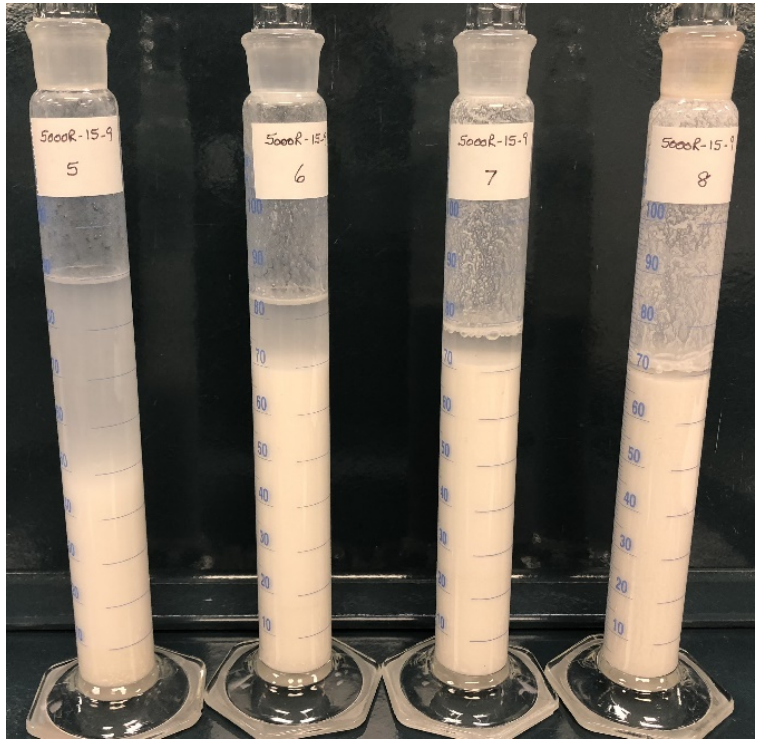
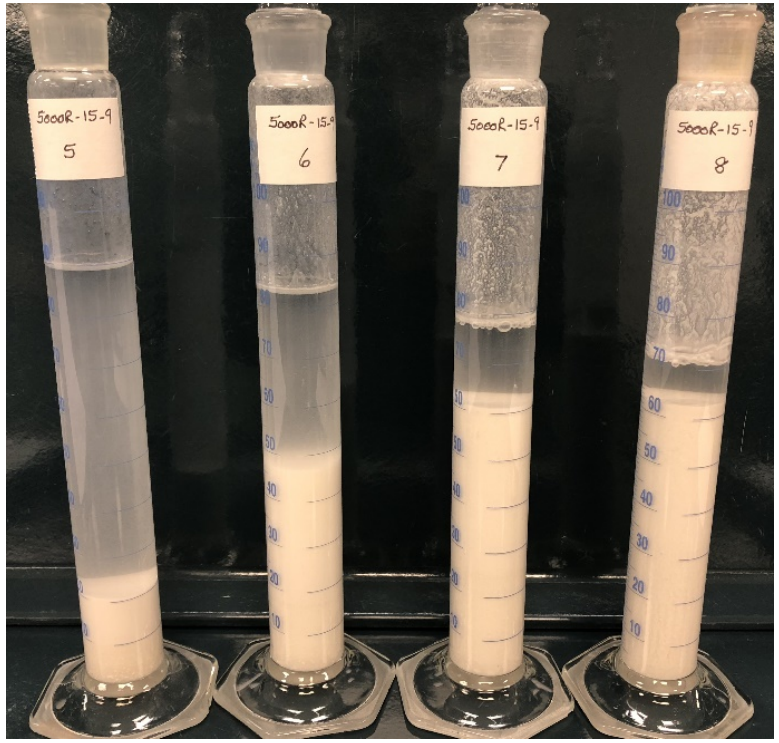
Klozur KP Settling Tests



Time 1 min



Time 5 min



Time 15 min

Klozur KP and Hydrated Lime

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

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Permeable Reactive Barriers

- Injected PRBs
  - Application
    - DPT rods (stingers)
    - Specialized injection tooling
  - Application range:
    - Maximum (w/w solids to soil):
      - Sand: ~2.5% (10% PV)
      - Clay: ~1.5 %
    - Typical 0.5-1.5% w/w
- Trench PRBs
  - Application
    - Slurries and dry mix
    - Soil mix or sand blend
  - Application range:
    - Typically 5-20% reagents
    - Higher possible, but watch for settling
  - Trench stabilization
    - May be needed depending on trench characteristics
    - Specialized physical applicators to minimize contact

Soil Mixing

- Klozur SP:
  - Initial treatment
  - 4-8 week persistence typical
  - 25% NaOH or hydrated lime to activate
  - Areas of elevated concentrations
  - ISCO – ISS
    - If sufficient Portland cement is added to quickly solidify and dry matrix, Klozur SP is recommended.
- Klozur KP:
  - Extended release
  - Months to years
    - Will dissolve to maintain concentration (persistence depends on dose)
  - Typically for less than 1,000 mg/Kg
    - Will dissolve as oxidant is consumed negating benefit of extended release
  - Hydrated lime to activate

Applications ranges:
1 to 10% w/w typical

Low Permeable Soils

- Solid slurry injection
  - Klozur SP for initial rapid treatment, migration into preferential pathways
  - Klozur KP for extended treatment
- Activator
  - 25% NaOH or hydrated lime for Klozur SP
    - Maintain elevated pH to protect equipment
  - Hydrated lime for Klozur KP

Traditional Klozur SP:
Low volume-high concentration application

Difficult to Treat Contaminants

- Extended release may be better for certain contaminants
  - Highly sorbed
  - Low solubility

- Example:
  - PCBs

Contaminant	Solubility (mg/L)	K_{ow}
1,4-Dioxane	miscible	0.53
Benzene	~1,800	135
TCE	~1,300	513
PCBs (1242)	0.24	398,100

Conclusion

- Klozur KP's unique physical characteristics (low solubility) opens ISCO to new types of applications
  - Klozur SP: Source Area
  - Klozur KP: PRBs, low permeable soils, etc
- Builds off same powerful chemistry expanding the versatility of activated Klozur persulfate
- Versatility expanded by activation methods that can create both oxidative and reductive pathways (alkaline, heat, and H_2O_2)

Questions

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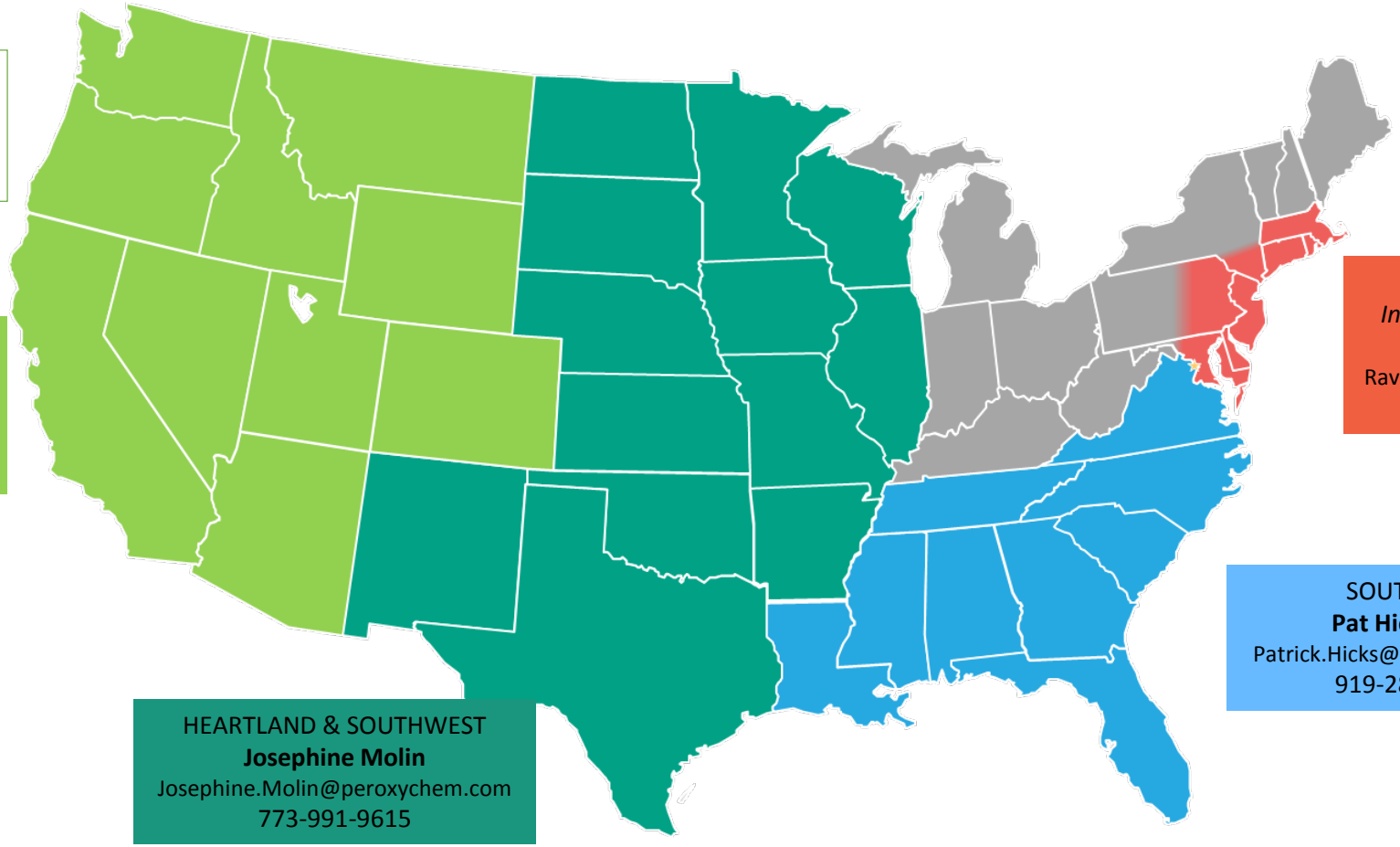

MIDWEST &
EASTERN GREAT LAKES
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Additional Klozur KP Resources

- Original webinar:
  - http://www.peroxychem.com/remedationwebinars

- www.Klozur.com
  - SDS
  - Product Brochure
  - Technical Documentation
    - Application Guide