Treating 1,4-Dioxane with Activated Potassium Persulfate

RemTech 2021

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It’s Official!

PeroxyChem, LLC is now Evonik Active Oxygens, LLC

Evonik Soil & Groundwater Remediation

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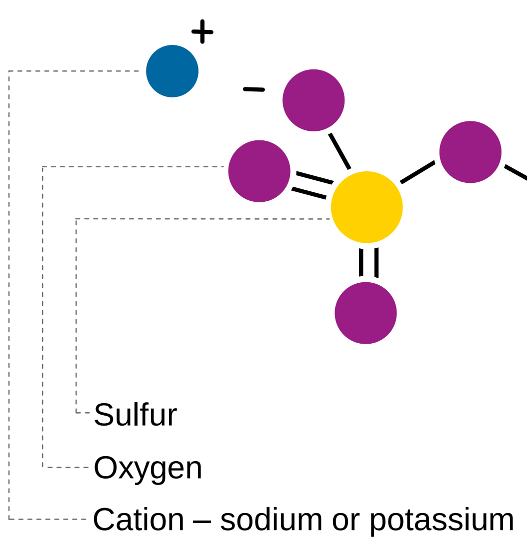
All Klozur® persulfates release the persulfate anion

- Sodium and potassium persulfate are used in environmental remediation applications
- A strong oxidant
- Activation results in the formation of oxidative and reductive radicals
- Applicable across a broad range of contaminants
- Extended subsurface lifetime (weeks to months)
- Little to no gas evolution



Free Radical Chemistry:
Persulfates produce free radicals in many diverse reaction situations

$$S_2O_8^{-2} + \text{activator} \longrightarrow SO_4^{\bullet -} + (SO_4^{\bullet -} \text{ or } SO_4^{-2})$$

Activation produces a radical which is more powerful and kinetically fast

Klozur® Persulfate Degradation Pathways

Oxidative

- Petroleum Hydrocarbons
- MGP Residuals
- BTEX
- PAHs
- Oxygenates
- 1,4-Dioxane

Either

- PCE, TCE, DCE and VC
- Chlorobenzenes
- Phenols
- Select Pesticides
- Select Fluorinated Compounds
- PCBs
- Select Energetics

Reductive

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

Activation Methods: Alkaline, Hydrogen Peroxide, and Heat

Activation Method: Iron Chelate

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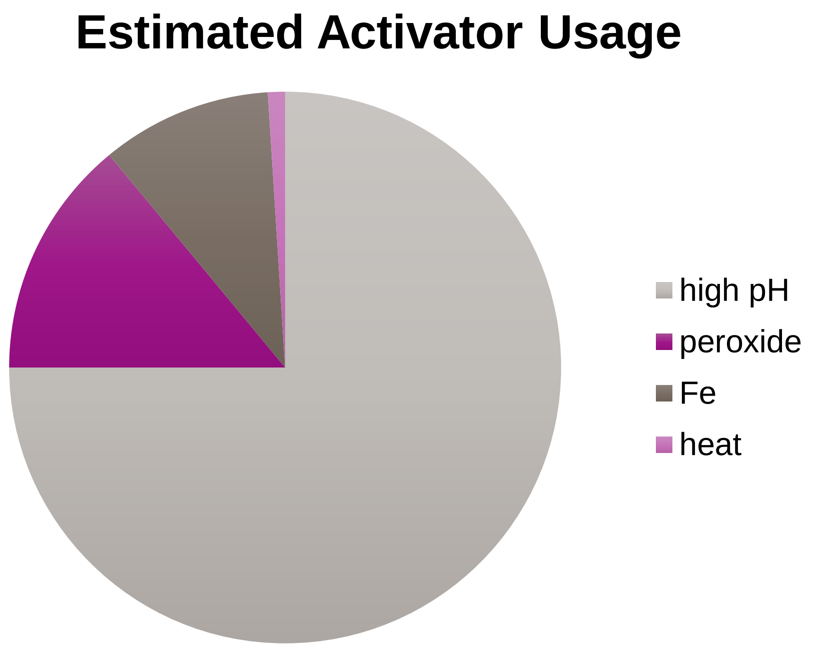
Klozur® Activation Technologies



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

- Alkaline Activation
  - More Compatible with carbon steel
  - Oxidants and reductants
- Klozur® One / Iron-Chelate Activated Persulfate
  - Chlorinated ethenes and petroleum hydrocarbons
  - Oxidative pathway
- Heat
  - Polishing step after thermal treatment
  - Oxidants and reductants
- Hydrogen Peroxide
  - Sites that benefit from rapid and vigorous reaction with both hydrogen peroxide and sodium persulfate
  - Oxidants and reductants

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Klozur® Persulfate
Differences between Sodium and Potassium Persulfates

KLOZUR® SP

- Environmental Grade Sodium Persulfate

KLOZUR® KP

- Environmental Grade Potassium Persulfate

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

Temperature	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

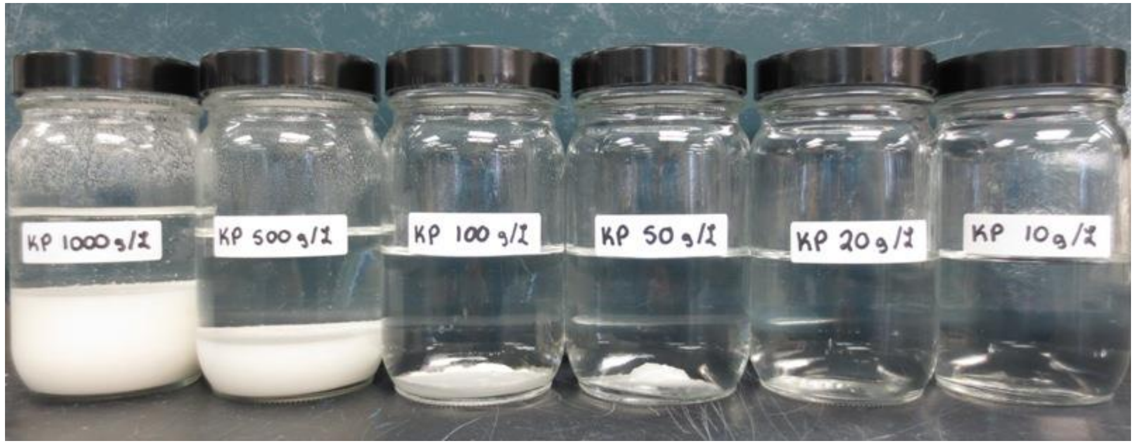
Characteristic	Klozur® SP	Klozur® KP
Formula	$Na_2S_2O_8$	$K_2S_2O_8$
Molecular Weight	238.1	270.3
Color	White	White
Loose Bulk Density (g/cc)	1.12	1.30

Klozur® Persulfate

Solubility Limited Release: Static System

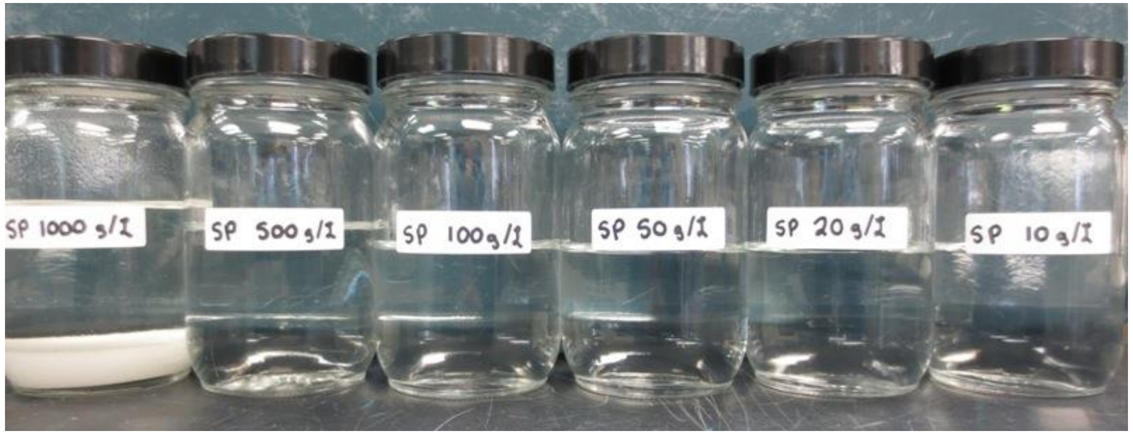
Reactors at ~20◦C

Klozur KP Solubility = 47 g/L



Reactors at ~20◦C

Klozur SP Solubility = 570 g/L



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Klozur® Persulfate
Dissolution Column Study

- Dissolution of Persulfate

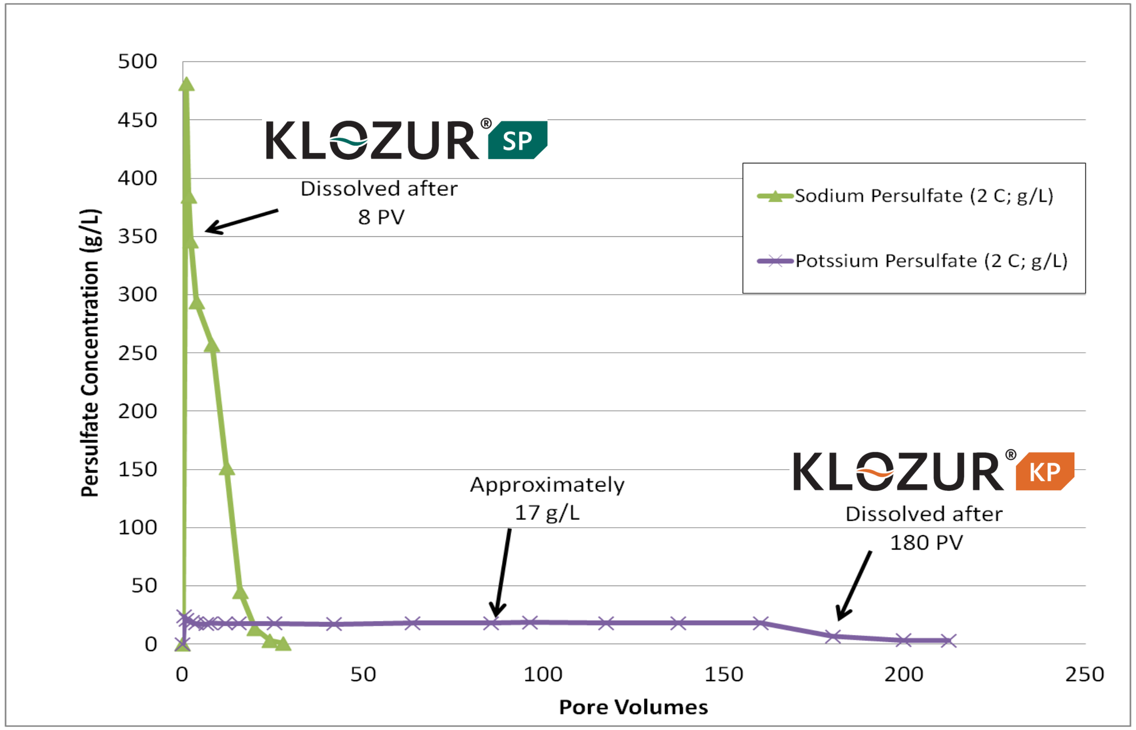
  - 2 ◦C

- Klozur SP

  - Peak at theoretical maximum

- Klozur KP

  - Sustained at theoretical maximum



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Klozur® Persulfate
Common Activators

Klozur® SP	Klozur® KP
▪ Alkaline Activation ▪ Injection: 25% NaOH ▪ Soil Mixing: 25% NaOH, $Ca(OH)_2$, Portland cement	▪ Alkaline Activation ▪ Slurry Injection: $Ca(OH)_2$ ▪ Soil Mixing: 25% NaOH, $Ca(OH)_2$, Portland cement
▪ Iron chelate Activators ▪ Fe-citrate, Fe-lactate, FeEDTA	▪ Zero Valent Iron ▪ Separate, down gradient ▪ Vigorous reaction with persulfate

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Why is 1,4-Dioxane different from other contaminants?

It *REALLY* likes water…

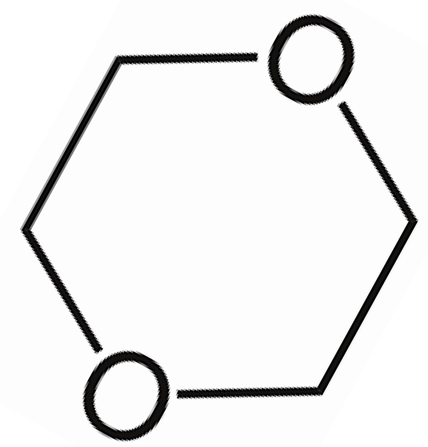
- Polar compound
- Once in water, it wants to stay there

Its often co-mingled with other contaminants that have very different characteristics.

- TCE
- 1,1,1-TCA

Partitioning coefficients:

- Log K_{ow} = -0.27
- K_{oc} = 17
- Henry's Coefficent: 4.8 x 10^{-6} atm m^3/mole



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Why is 1,4-Dioxane Different

Soil-Groundwater Partitioning

Assuming F_{oc} of 0.005 (5,000 mg/Kg):

- 1,4-Dioxane is usually primarily in the aqueous phase
  - Some K_{oc} estimates lower than 17 which would result in higher percentage in aqueous phase
- Other contaminants are primarily sorbed to soil
- K_d is the soil/groundwater distribution coefficient.

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

Contaminant	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
2. EPA Technical Fact Sheet: 1,4-Dioxane, Nov 2017 https://semspub.epa.gov/work/HQ/175223.pdf on 9/23/2021

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Establishing Contact

- Contaminant partitioning between soil and groundwater largely dependent upon fraction of organic carbon on soil (F_{oc})
- 1,4-Dioxane tends to be in aqueous phase more than other contaminants

Contaminant	K_{oc}	F_{oc} = 0.02			F_{oc} = 0.005			F_{oc} = 0.0001		
		K_d	Contaminant Distribution (%)		K_d	Contaminant Distribution (%)		K_d	Contaminant Distribution (%)	
			GW	Soil		GW	Soil		GW	Soil
1,4-Dioxane	17	0.34	**37%**	63%	0.08	**70%**	30%	0.00	**99%**	1%
TCE	166	3.32	6%	94%	0.83	19%	81%	0.02	92%	8%
1,1,1-TCA	110	2.20	8%	**92%**	0.55	27%	**73%**	0.01	95%	**5%**
DCE	38	0.76	21%	79%	0.19	51%	49%	0.00	98%	2%
1,1-DCA	53	1.07	16%	84%	0.27	43%	57%	0.01	97%	3%
1,2-DCA	38	0.76	21%	79%	0.19	51%	49%	0.00	98%	2%

Establishing Contact

KLOZUR® SP
Aqueous Reagents

"Solid" Contaminants

Injection Strategy

Aqueous Contaminants

KLOZUR® KP
"Solid" Reagents

PRB Strategy

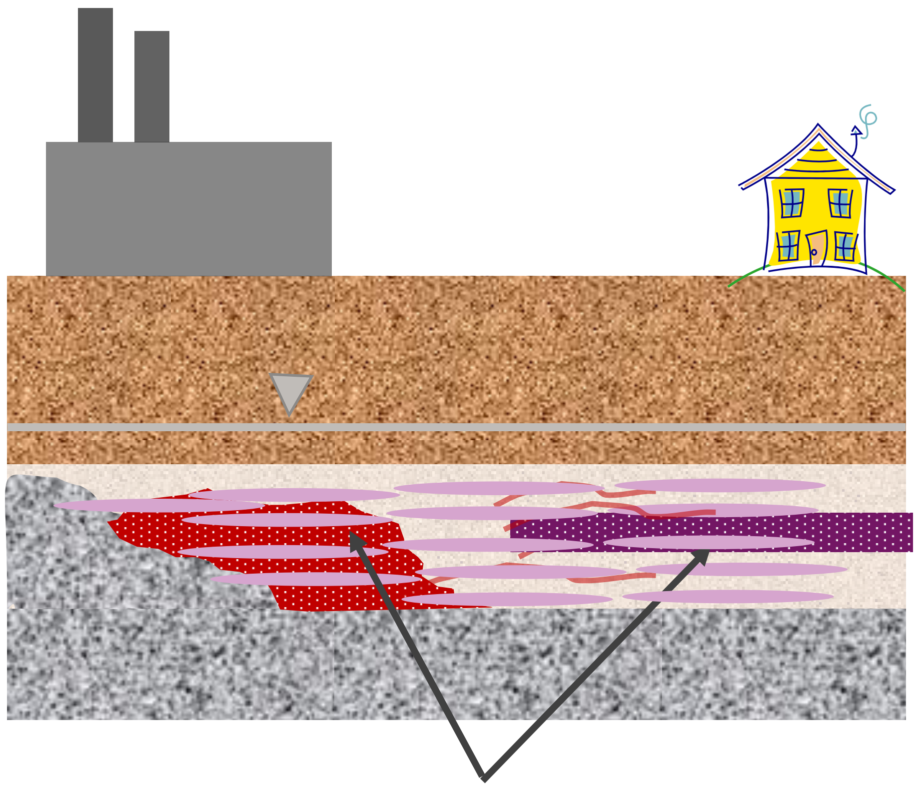
Aqueous and Solid Reagents

Aqueous and "Solid" Contaminants

Soil Mixing

Fracture in a Grid or PRB Injection

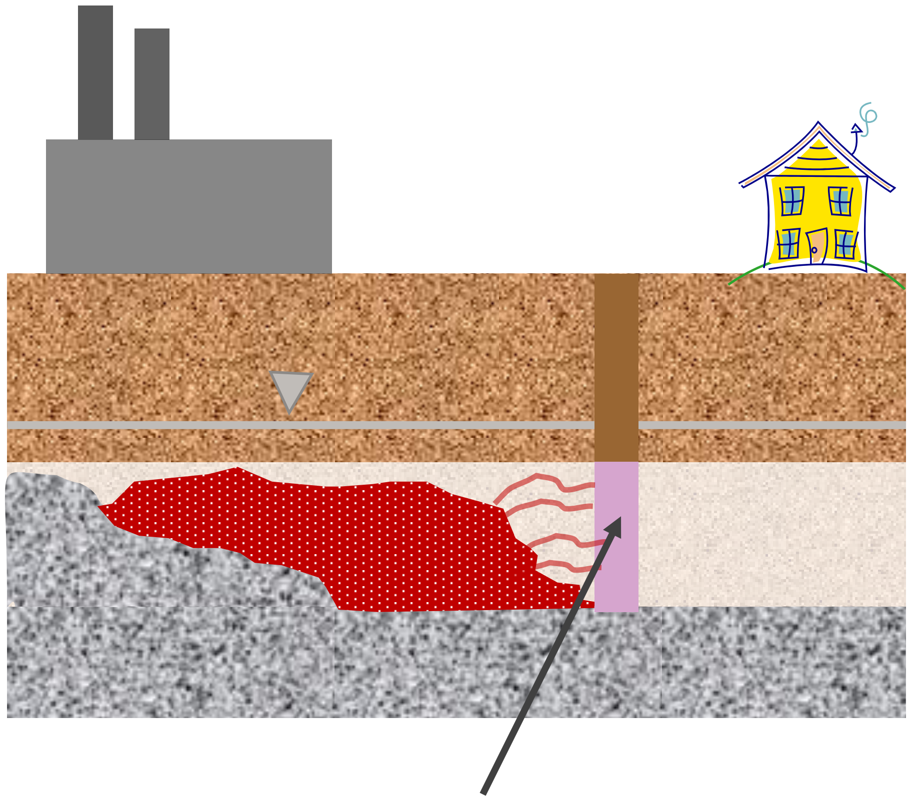
Grid Application



KLOZUR® KP

Hydrated lime activator (typical)

Permeable Reactive Barrier (PRB)



KLOZUR® KP

Hydrated lime activator (typical)

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Soil Mixing Strategy

- Establishes contact
  - Typically, more rapid treatment
- Low permeable material
- Minimizes impact of site heterogeneity
- Homogenizes soil and contaminant
- Can be combined with ISS

Courtesy of Bill Lang

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Case Study:
Treatment of 1,4-Dioxane with Klozur® KP

1,4-Dioxane Case Study
Former Industrial Facility in the Northeast

- Consultant: AECOM
- Injection Contractor: Pilot-ERFS; Full Scale-ISOTEC
- 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
- Klozur® KP PRB selected to establish contact with aqueous phase reagents

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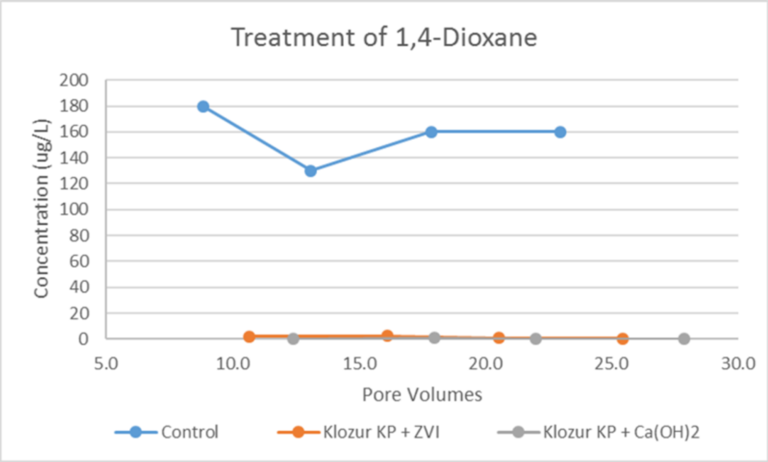
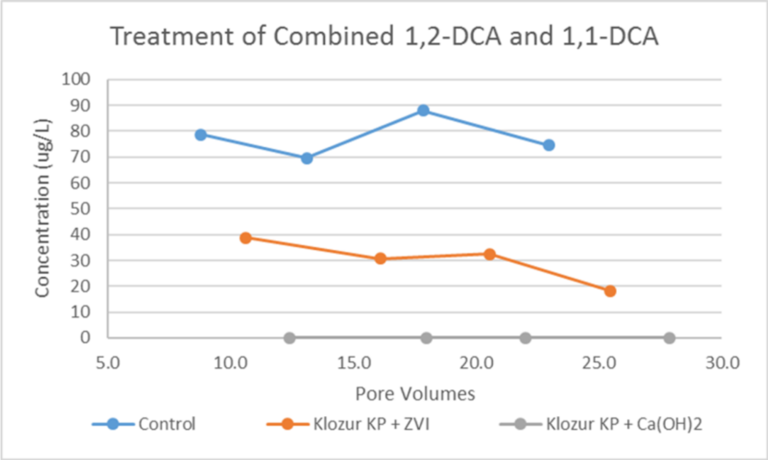
1,4-Dioxane Case Study
Klozur® KP Bench Test

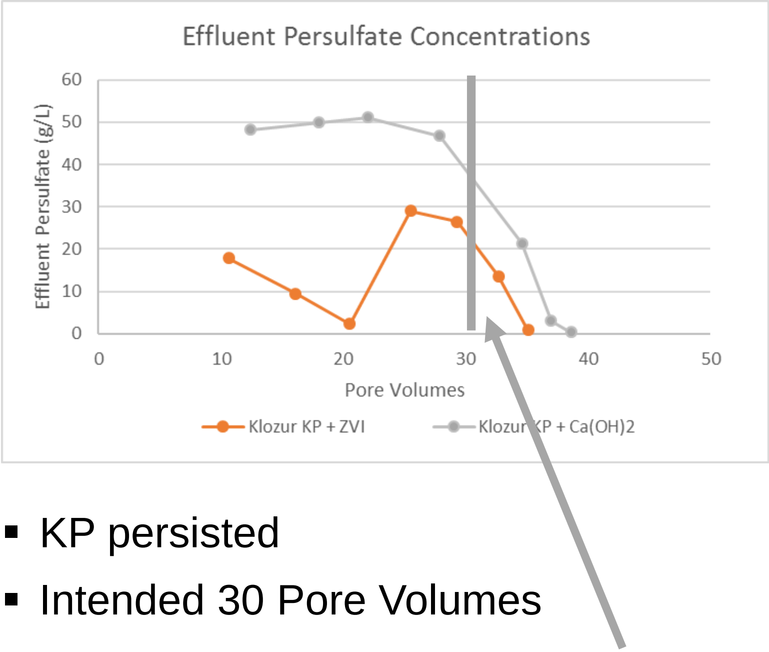
Oxidative Pathway	Reductive Pathway	KP Persisted



- 1,4-Dioxane



- DCA(s)

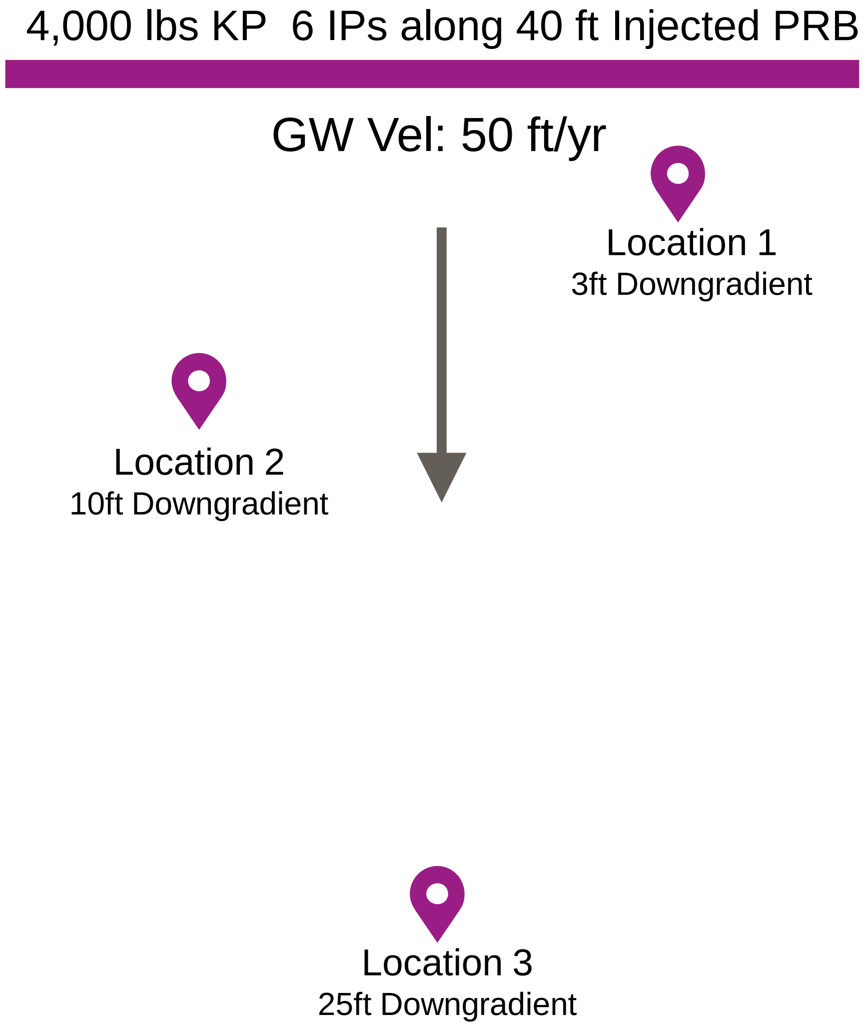


- KP persisted
- Intended 30 Pore Volumes

Design Volume

1,4-Dioxane Case Study
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
- Reagents:
  - Klozur® KP
  - Klozur ® SP
  - Hydrated Lime
  - 25% NaOH



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

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

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

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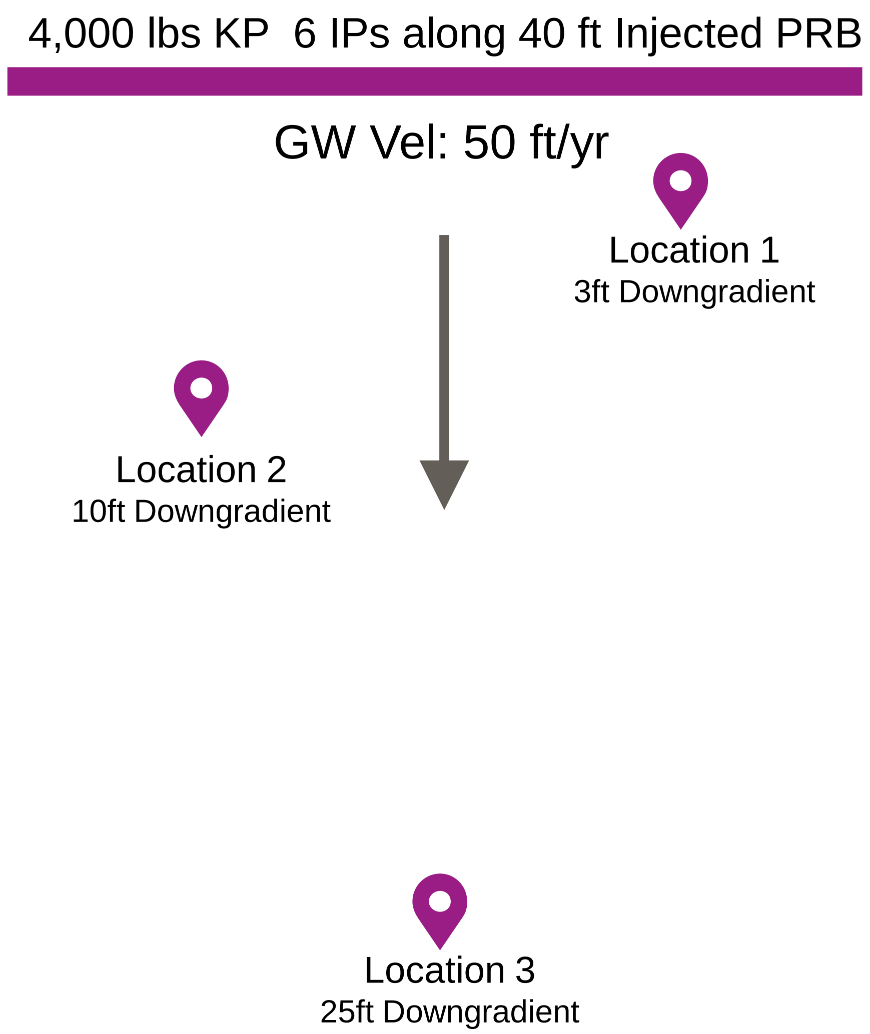
1,4-Dioxane Case Study

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%

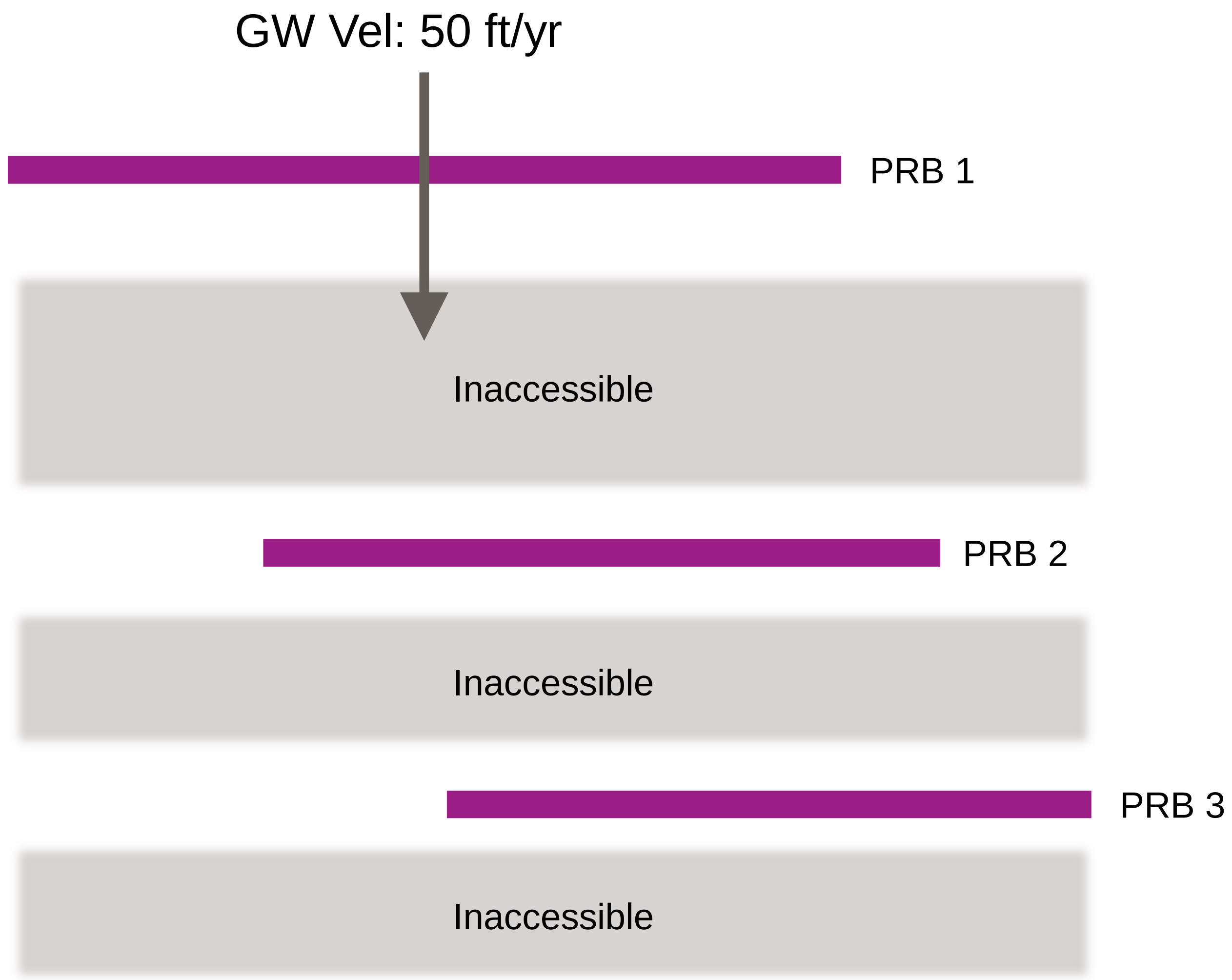
Event	Location 2: Contaminant Concentrations (µg/L)				
	DCA	DCE	1,4-Dioxane	VOCs*	Reduction VOCs (%)
Baseline	44	72	55	184	0%
3 Month	10	11	ND	26	86%
6 Month	16	ND	16	34	82%

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

1,4-Dioxane Case Study
Full Scale

- Ongoing
- Three transects/PRBs
- Largely targeting 1,4-dioxane
- Cut off source long enough and clean inaccessible zones



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Summary

1. 1,4-Dioxane and common comingled contaminants have been successfully treated by alkaline activated persulfate

2. 1,4-Dioxane prefers aqueous phase compared to most common contaminants

    - Keys to establishing contact

3. Klozur® KP can be used as solid-state oxidant to treat aqueous phase contaminants

4. Klozur® SP can still be used if contact can be established

Questions?

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