



*Using Potassium Klozur Persulfate as an Extended
Release Oxidant and Permeable Reactive Barrier*



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SMART Remediation
Ottawa, ON
February 16, 2017

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Presentation Outline

- Klozur Portfolio
- 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

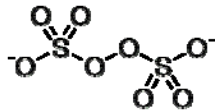
KLOZUR® CR

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

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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

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Radical Formation Upon Activation

- Kinetically faster reacting radicals that are:
 - More powerful oxidants ($\text{SO}_4\bullet$ and $\text{OH}\bullet$) than persulfate itself
 - Reductants ($\text{O}_2\bullet^-$)
 - Nucleophiles ($\text{O}_2\bullet^-$ and HO_2^-)

Oxidant	Standard Reduction Potential (V)	Reference
Hydroxyl radical ($\text{OH}\bullet$)	2.59	Siegrist et al.
Sulfate radical ($\text{SO}_4\bullet$)	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 ($\text{O}_2\bullet^-$)	-0.33	Siegrist et al.
ZVI	-0.45	CRC (76th Ed)

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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:

- **Oxidant goes to the contamination** (i.e. Injection in a source zone--Klozur SP)
- **Contaminant comes to Oxidant** (i.e. Permeable reactive barrier--Klozur KP)
- **Oxidant and contaminant are blended together** (Soil mixing---either Klozur SP or Klozur KP)

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Klozur KP (Potassium Persulfate)

- 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 ₂ S ₂ O ₈	K ₂ S ₂ O 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

Activation of Klozur KP

Klozur SP:

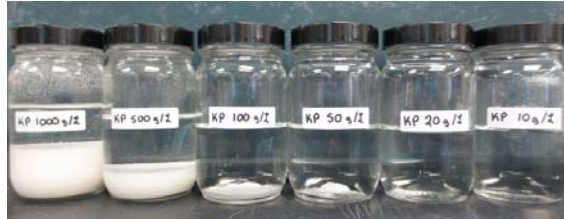
- Aqueous phase oxidant – aqueous phase activators
 - NaOH (alkaline)
 - Fe:Chelate
 - Hydrogen peroxide
 - Heat

Klozur KP:

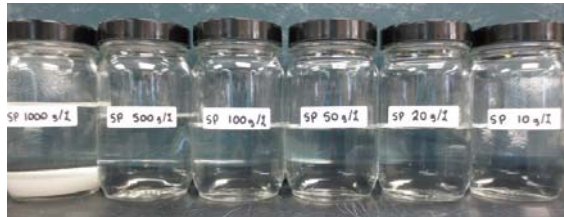
- Solid/extended release oxidant – **Solid/extended release activators**
 - PermeOx Ultra (alkaline)
 - Hydrated lime-Ca(OH)₂
 - Zero Valent Iron (ZVI)

Solubility Limited Release Static System

Reactors at ~20°C
Klozur KP Solubility
 = 47 g/L



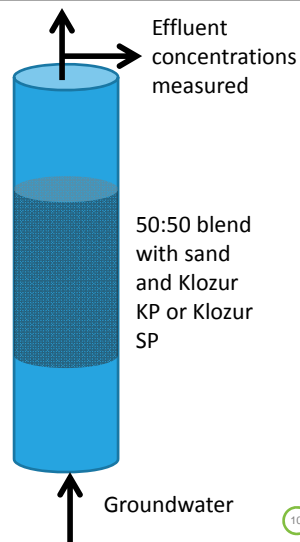
Reactors at ~20°C
Klozur SP Solubility
 = 570 g/L



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Solubility Limited Release Dynamic System

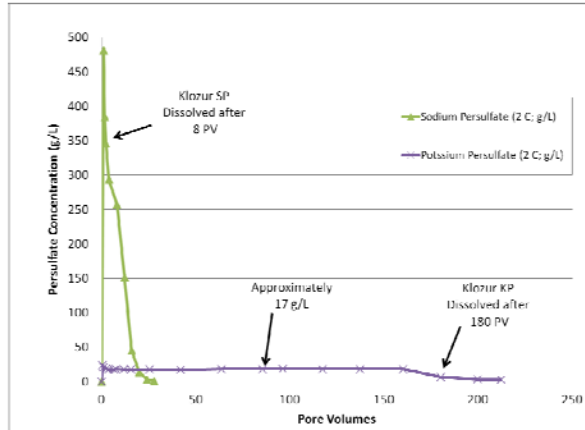
- Column Study:
 - 30 cm columns
 - 15 cm section of 50:50 blend of sand and either Klozur KP or Klozur SP
 - Targeting 300 g of oxidant
 - 7.5 cm sand above and below
 - Four columns
 - 2 °C :
 - Klozur SP
 - Klozur KP
 - 20 °C
 - Klozur SP
 - Klozur KP



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Column Study (2°C) Effluent Persulfate Concentration

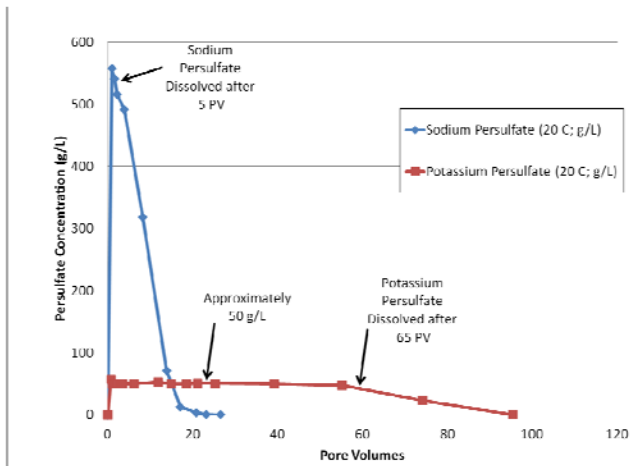
- Dissolution of Persulfate
 - 2 °C
- Klozur SP
 - Peak at theoretical maximum
- Klozur KP
 - Sustained at theoretical maximum



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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



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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

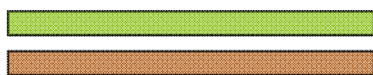
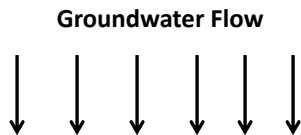
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Conceptual Permeable Reactive Barrier

- Permeable Reactive Barrier (PRB)
- Conceptual Design of Gate
 - 30 m wide, 3 m high, and 1 m deep
 - 43,500 Kg KP
 - 15% ePorosity

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 Seepage Velocity (m/yr)	3	879	667	523	411	328
	10	264	200	157	123	98
	20	132	100	78	62	49
	30	88	67	52	41	33
	60	44	33	26	21	16
150	18	13	10	8	7	



KP PRB
Activator PRB

Does not consider potential "site" factors

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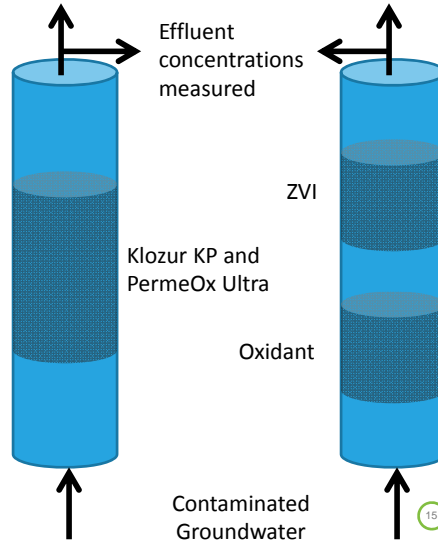
Treatability Column

Column Study:

- 30 cm 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

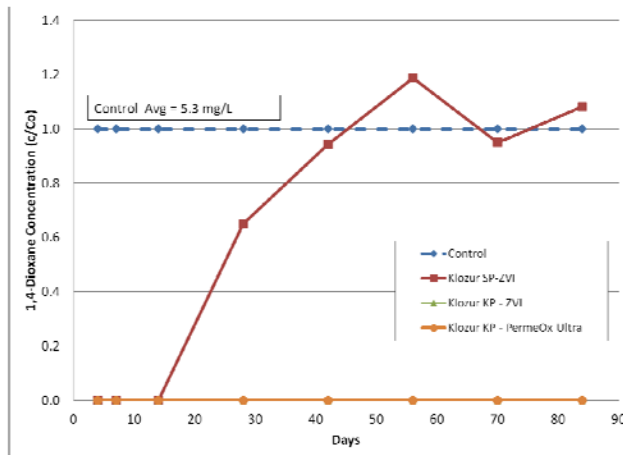


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Treatment of 1,4-Dioxane

- Klozur KP columns non-detect throughout experiment

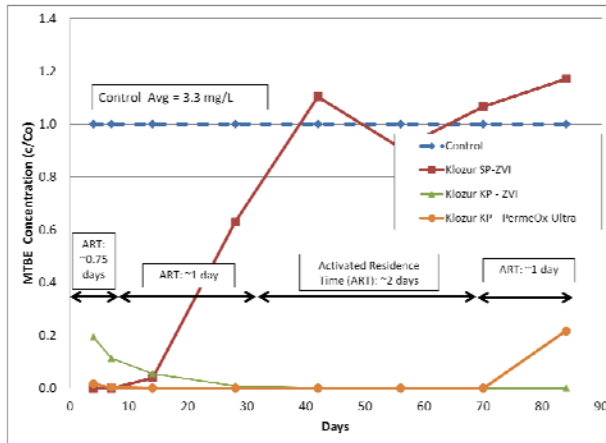
- Klozur SP breakthrough between Day 14 and Day 28



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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



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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

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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

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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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