



Activation of Klozur Persulfate to Create Oxidative and Reductive Treatment Pathways

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Outline

- Introduction to Klozur Persulfate
- Discussion of Activation Method
- Introduction to organic activation
- Case Study





Introduction to Activated Persulfate

Klozur® Persulfate is:

- Klozur SP: Highly soluble in water (significant oxidant mass in smaller volumes)
- Klozur KP: Low solubility, for extended release
- Klozur CR: Combined Remedy
- Activated persulfate anion:
 - A strong oxidant used for the destruction of contaminants in soil and groundwater
 - Aggressive and fast acting chemistry with little to no heat or gas evolution
 - Applicable across a broad range of organic contaminants



Klozur SP solubility of more than 500 g/L

Typically injected at 50 g/L to 250 g/L





Fundamental Chemistry

Persulfate anion kinetics are generally too slow for most contaminants. As a result, you must activate persulfate to form the sulfate radical.

Activated Persulfate

- produces radicals which are more powerful and kinetically fast
- PeroxyChem always recommends using an activator
- proper activation method is based on contaminant, site lithology, and hydrogeology
 Certain activators can also



Purchase of PeroxyChem's Klozur[®] Persulfate includes rights to practice the inventions covered by global patents in the purchase price of the product.





Why Activate?

- Formation of radicals that are:
 - More powerful oxidants
 (SO₄• and OH•) than
 persulfate itself
 - Reductants ($O_2 \bullet^-$)
 - Nucleophiles $(O_2 \bullet^- \text{ and } HO_2^-)$
 - Kinetically much faster reacting

Oxidant	Standard Reduction Potential (V)	Reference	
Hydroxyl radical (OH•)	2.59	Siegrist et al.	
Sulfate radical (SO₄• ⁻)	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 (O₂•¯)	-0.33	Siegrist et al.	
ZVI	-0.45	CRC (76th Ed)	



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 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







Activator Selection

- Alkaline Activated Persulfate
 - Well suited for suited for most applications
 - Favored for injection through DPT rods and in situ soil mixing
 - Reductants, oxidants and nucleophiles

Estimated Activator Usage



- Iron-Chelate Activated Persulfate
 - Chlorinated ethenes and hydrocarbons
 - Less contaminant mass
- Heat
 - Complex sites
 - Polishing step after thermal treatment
- Hydrogen Peroxide
 - Sites that benefit from vigorous reaction with both hydrogen peroxide and sodium persulfate





Iron-Chelate Activation

• Similar to Fenton's Reagent:

$$S_2O_8^{-2} + Fe (II) \rightarrow Fe (III) + SO_4^{-1} + SO_4^{-2}$$

 $S_2O_8^{-2} + e^- \rightarrow SO_4^{-1} + SO_4^{-2}$
 $O O e^-$
 $Na^+ O O S O^- Na^+$
 $O O O S O^- Na^+$

- Chelate needed to keep Fe (III) in solution
 - Would form solid precipitate if not chelated at pH>3
- 150 mg/L to 600 mg/L iron recommended
 - Chelates include EDTA, lactate and citrate anions





Heat Activation

Persulfate reaction with water:

 $S_2O_8^{-2} + H_2O \rightarrow 1/2O_2 + 2HSO_4^{-1}$

 Oxidation still occurs as pathway initiates with formation of sulfate radical.

 $S_2O_8^{-2} \rightarrow 2SO_4^{\bullet}$

- Temperatures from 35 °C to 50 °C recommended
 - 35 °C to 40 °C most common
- Reductive pathway observed with increasing temperature:
 - Carbon tetrachloride ~35 °C
 - 1,1,1-TCA ~45 ° C



Fig. 2. Effect of temperature on the oxidation of MTBE by persulfate. Inset: plot of $\ln k_1 \text{ vs } 1/T$ for E_a estimation using the Arrhenius equation. [MTBE]₀ ~ 0.06 mM; $[\text{Na}_2\text{S}_2\text{O}_8]_0 \sim 31.5$ mM; pH ~ 7; $I \sim 0.06$ M.

Huang et al (2002) Chemosphere, 413-420

Often used as a polishing step following a thermal remediation application





Alkaline Activation

• Persulfate reaction with water (Furman et al., ES&T, 2010):

$$S_2O_8^{2-} + 2H_2O \xrightarrow{OH^-} HO_2^{-} + 2SO_4^{2-} + 3 H^+$$
$$HO_2^{-} + S_2O_8^{2-} \rightarrow SO_4^{-} + SO_4^{2-} + H^+ + O_2^{-}$$
$$SO_4^{-} + OH^- \rightarrow OH^{-} + SO_4^{2-}$$

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(note: H_2O_2 \leftrightarrow HO_2^- + H^+ pK_a = 11.7)
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- pH > 10.5 = Reaction results in the transient oxygen species of SO₄•⁻, OH•, O₂•⁻, and HO₂⁻
- Alkaline Demand:
 - Natural buffering capacity of site soils (Base Buffering Capacity or BBC)
 - 2:1 molar ratio (OH⁻:Persulfate)





Hydrogen Peroxide Activation

- Hydrogen Peroxide Activation: $H_2O_2 + S_2O_8^{2-} \rightarrow SO_4^{--} + SO_4^{2-} + 2H^+ + O_2^{--}$
- Commonly applied in range of 1:1 to 10:1 (H₂O₂:Persulfate)
 - 5:1 Ratio most common
 - Reaction more vigorous when transition metals present
- Potential to stabilize hydrogen peroxide to increase subsurface persistence

Solutions New Activation Method--Organic Activation

 Organic molecules are thought to donate electron to persulfate



- Not all organics well suited to this task
 - Persulfate anion without activation will react very slowly or not at all with many organics
- On surface, very similar to iron-chelate activation
 - One electron transfer mechanism
 - Typically only sulfate radical
 - Little to mitigate acid formation

Patent Pending Technology





Organic Activation

- More detailed analysis
 - May allow for better control over rate of activation
 - Potential to completely consume persulfate in given time frame
 - Help in creation of biogeochemical conditions
 - Reductant pathway under increasingly alkaline conditions
 - Allows for treatment of contaminants such as 1,1,1-TCA and carbon tetrachloride
 - May help in difficult to treat compounds
 - Ease of use benefits



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[•] Third Party Bench Test Looking at Treating Carbon Tetrachloride Site



- MFR Chelated iron and hydrogen peroxide (aka Modified Fenton's reagent)
- MASP MFR with persulfate
- GBASP Organic and alkaline activated persulfate

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MGP Site in Illinois, USA

Results:

- Contaminant:
 - ~17,000 mg/Kg TPH
 - ~45,000 μg/L Benzene
 - ~140 µg/L Naphthalene
- Remedial goals:
 - TPH to less than 9,000 mg/Kg
 - Reduce benzene in groundwater by greater than 90 percent
- Applied 21,000 Kgs of AAP to site over 3 applications
 - 32 g Klozur per Kg soil



MMW-05 Groundwater Data

percent

Less than 2,500 mg/Kg TPH

reduced by greater than 98

Benzene in groundwater

- State of Illinois issue a **No**

Further Action letter

Active Industrial Site

- PCE, 1,1,1-TCA, and 1,4dioxane (DNAPL source)
- AAP does not produce gas during treatment
- Treated with two applications totaling 31,000 Kg Klozur[®]
 - 25 g Klozur per Kg soil
- Remedial goal of less than 1 mg/L for each contaminant

Contaminants	Average Contaminant Concentrations (µg/L)				
	Baseline	Post 1st Application	Post 2nd Application	Total Percent Reduction	
PCE	11,987	4,819	113	99.1	
1,1,1-TCA	8,736	5,698	64	99.3	
1,4-Dioxane	410	1,029	165	59.8	











Summary

- Activated persulfate is a very effective remediation technology
- Persulfate anion can be activated by:
 - Alkalinity (pH > 10.5)
 - Iron chelates
 - Heat
 - Hydrogen peroxide
 - Organics





Summary

- Oxidative Pathway:
 - Radicals: Hydroxyl and Sulfate Radicals
 - Contaminants: cVOCs, TPH, PAHs, Energetics, etc.
- Reductive Pathway:
 - Radicals: Superoxide
 - Contaminants: Carbon Tetrachloride, 1,1,1 TCA, Energetics, degradation products, etc





Questions





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