Chemical Oxidation Update: New Method for Activating Persulfate

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PeroxyChem

SMART Remediation
Toronto, ON
January 28, 2016

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Outline

- Klozur Persulfate
- Current Activation Methods
  - Oxidative and Reductive Pathways
- New Activation Method
  - Oxidative Pathways
  - Reductive Pathways
- Summary and Conclusions

KLOZUR PERSULFATE

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Introduction to Klozur® Persulfate

Klozur® Persulfate is:

- Based on the sodium persulfate molecule:
  - A strong oxidant used for the destruction of contaminants in soil and groundwater
  - Highly soluble in water (significant oxidant mass is smaller volumes)
- Aggressive and fast acting chemistry with extended subsurface lifetime (weeks to months) and little to no heat or gas evolution
- Applicable across a broad range of organic contaminants

Field solubility of more than 500 g/L possible

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Why Activate?

- Formation of radicals that are:
  - More powerful oxidants (SO_4• and OH•) than persulfate itself
  - Reductants (O_2•$^-$)
  - Nucleophiles (O_2•$^-$ and HO_2^-)
  - Kinetically much faster reacting
- Two primary methods of activations:
  - Donation of an electron
  - Reactions with water

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)

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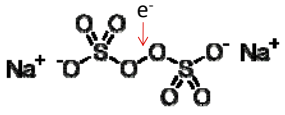
Persulfate Activation: Electron Donation

- Similar to Fenton's Reagent:

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

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



- Activation methods based on one electron transfer:
  - Reduced metals: Fe (II), Fe (0), etc
  - Organics
  - Hydrogen peroxide

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Persulfate Activation: Reactions with Water

- Sodium persulfate is activated when the solution is raised to pH > 10.5
- Alkaline Activation (Furman et al., 2010):

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

(note: $H_2O_2 \leftrightarrow HO_2^- + H^+$ $pK_a = 11.7$)

- Forms:
  - Oxidative radical: $SO_4^{\bullet-}$, and $OH^{\bullet}$
  - Reductive radical: $O_2^{\bullet-}$
  - Nucelophiles: $O_2^{\bullet-}$ and HO_2^-
- Analogous to the chemistry that has been studied with catalyzed hydrogen peroxide (CHP)

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ORGANIC ACTIVATION

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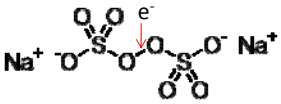
Organic Activation

- 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: US 2014/0116960 (WSU) and US 2013/0248458 (PeroxyChem)

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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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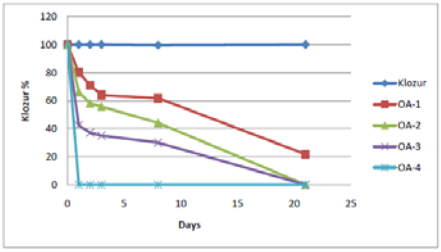
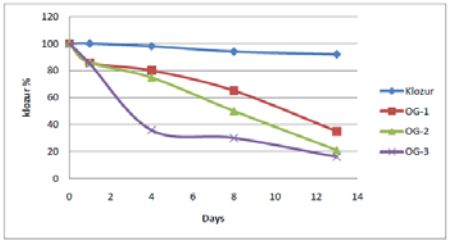
Rate of Reaction with Persulfate





- Residual persulfate concentrations over time at room temperature (~25˚C)
  - OA 1 = 0.1:1
  - OA 2 = 0.25:1
  - OA 3 = 0.5:1
  - OA 4 = 1:1

  - OG -1= 0.1:1
  - OG-2 = 0.25:1
  - OG-3 = 0.5:1

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ORGANIC ACTIVATION:
OXIDATIVE PATHWAY

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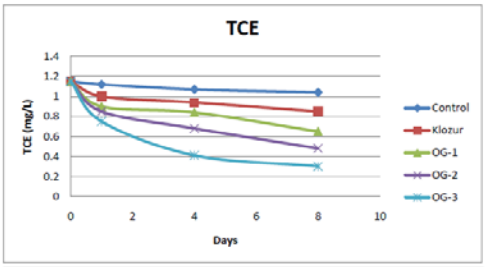
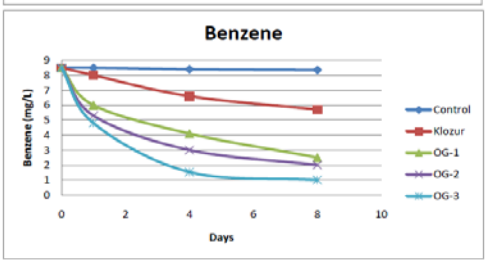
Contaminant Treatment





- Contaminant concentrations at 2◦C
  - OG- 1 = 0.1:1
  - OG- 2 = 0.25:1
  - OG- 3 = 0.5:1

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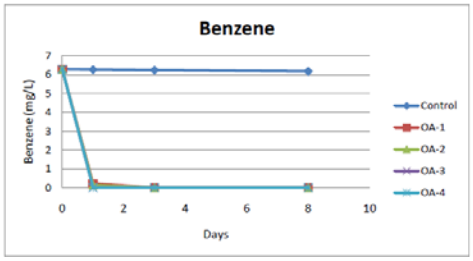
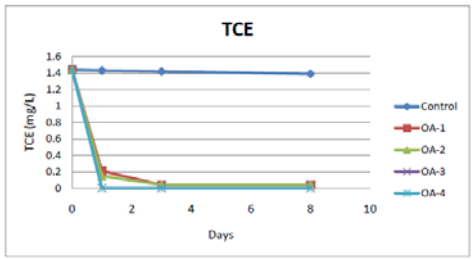
Contaminant Treatment

- Contaminant concentrations over time at ~2◦C
  - OA- 1 = 0.1:1
  - OA-2 = 0.25:1
  - OA- 3 = 0.5:1
  - OA- 4 = 1:1





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ORGANIC ACTIVATION: *REDUCTIVE PATHWAY*

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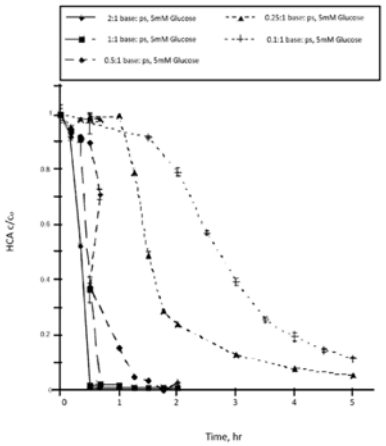
Enhanced Reductive Ability with Increasing pH

- Treatment of reductant probe (Hexachloroethane) with increasing concentrations of sodium hydroxide



Courtesy of Washington State University

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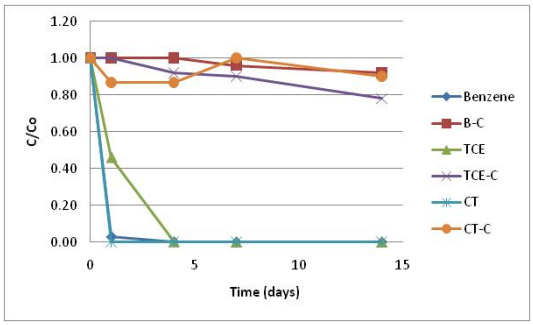
Alkaline with Organic



- Rapid treatment with oxidative and reductive pathway
- Under similar test conditions, more rapid than AAP alone for benzene and CT

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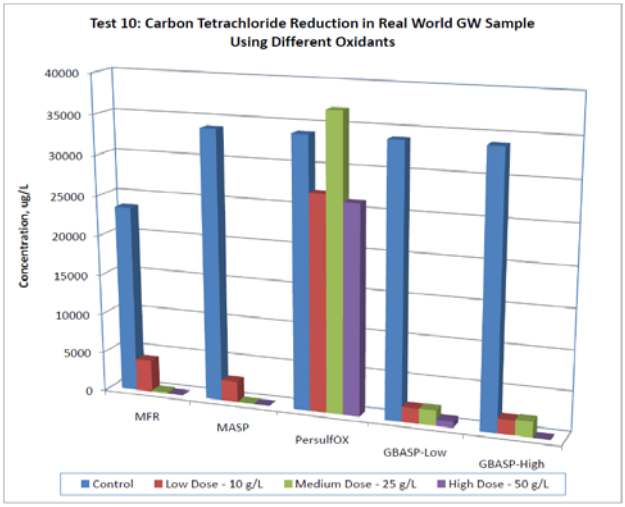
Third Party Bench Test Looking at Treating Carbon Tetrachloride Site



Courtesy of ISOTEC

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Conclusions

- New method of activation that will provide ease of use and treatment benefits
- Certain organics can be used to activate persulfate forming oxidative and reductive treatment pathways
  - Oxidative with activation by organic
  - Oxidative and reductive under alkaline conditions
- Potential to add organic with persulfate to be delivered to site as an activator/persulfate blend

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Questions

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