Chemical Oxidation Update: New Method for Activating Persulfate

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Vancouver, ON
February 11, 2016

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Outline

- Oxidant and Persulfate Review
- Activation Mechanism
  - Oxidative and Reductive Pathways
- New Activation Method
  - Oxidative Pathways
  - Reductive Pathways
- Summary and Conclusions

OXIDANT & PERSULFATE REVIEW

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Chemical Oxidation Principles

- Oxidants are introduced or mixed into the soil and groundwater to react with the organic contaminants
- Chemical oxidation treatments are commonly used in potable and wastewater applications
- Oxidants are non-specific and will react with the targeted contaminants AND with the soil organic and mineral content.
- Chemical oxidation reactions involve the transfer of electrons and the breaking of chemical bonds
- Water is the carrier for the oxidants used in chemical oxidation (except for ozone)

4

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Introduction to Sodium Persulfate

- 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)
  - Other Persulfate Salts are available (potassium and ammonium) for sodium sensitive aquifer
- 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 for sodium persulfate

5

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Other Persulfate salt (potassium or ammonium) comparative properties

Stability

Sodium persulfate is a safe to handle, stable crystal as with potassium and ammonium,

ALL Persulfate radicals have a significantly longer life *in situ* than peroxide radicals, allowing for greater penetration into the contamination zone.

Solubility

Ammonium persulfate 85 g / 100 g H_2O at 25 C
Potassium persulfate 6 g / 100 g H_2O at 25 C
Sodium persulfate 73 g / 100 g H_2O at 25 C

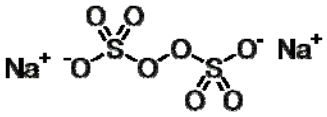
Targeted groundwater concentration above 5 g of persulfate per litre

Nitrogen content in ammonium persulfate could help Bioremedation processes after the oxidation phase

6

Fundamental Chemistry

- Activated Sodium Persulfate is based upon the persulfate anion:



- Persulfate is a peroxygen, and similar to hydrogen peroxide, it can be split at the O-O bond forming the sulfate radical:

$$^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^{-} \rightarrow {}^{-}O_3S\text{-}O\bullet \quad \bullet O\text{-}SO_3^{-}$$

7

Why Activate?

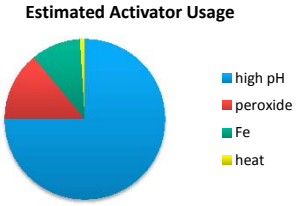
- Formation of radicals that are:
  - More powerful oxidants ($SO_4\bullet$ and $OH\bullet$) than persulfate itself
  - Reductants ($O_2\bullet^-$)
  - Nucleophiles ($O_2\bullet^-$ and HO_2^-)
  - Kinetically much faster reacting
- Two primary methods of activations:
  - Mechanism 1 - Donation of an electron
  - Mechanism 2 - Reactions with water

Oxidant	Standard Reduction Potential (V)	Reference
Hydroxyl radical ($OH\bullet$)	2.59	Siegrist et al.
Sulfate radical ($SO_4\bullet^-$)	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 ($O_2\bullet^-$)	-0.33	Siegrist et al.
ZVI	-0.45	CRC (76th Ed)

8

Persulfate Activation Chemistries for the Remediation of Soil and Groundwater

- **Heat**
- **Divalent metals and zero valent iron**
- **Chelated metals**
- **Hydrogen peroxide activation**
- **Alkaline activation**
- **Surface Activation (recent development)**
- **Novel Organic Activation**



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Purchase of Peroxychem's Persulfate includes rights to practice the inventions covered by the patents in the purchase price of the product.

One key to success: Proper activation for your contaminant and site lithology and hydrogeology

9

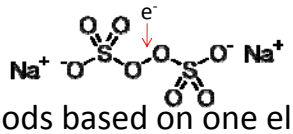
ACTIVATION MECHANISM

Mechanism 1 - 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
  - Surface Activation

Mechanism 2 - 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)

NEW ACTIVATION METHODS

ORGANIC ACTIVATION AND OXIDATIVE PATWAYS

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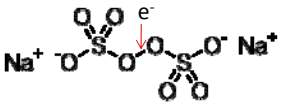
Organic Activation

- 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

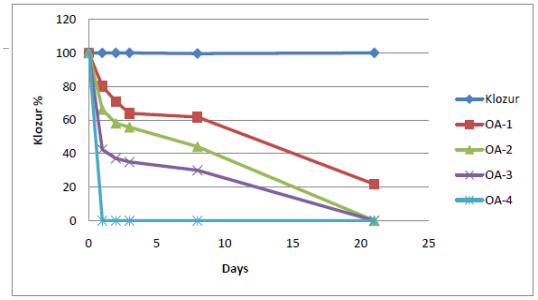
Patent Pending Technology: US 2014/0116960 (WSU) and US 2013/0248458 (PeroxyChem)

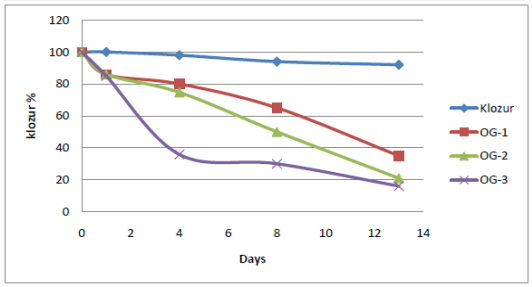
14

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

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**

Klozur = sodium persulfate 100 %

NOVEL ACTIVATION METHODS

ORGANIC ACTIVATION:

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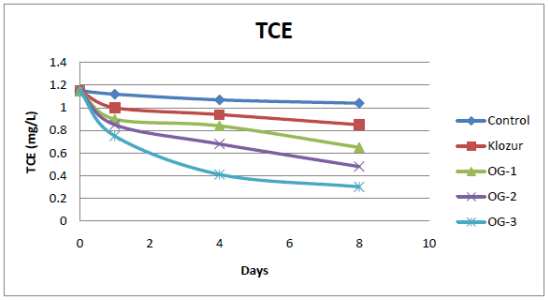
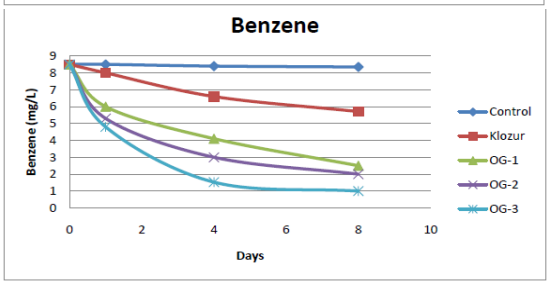
Contaminant Treatment





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

18

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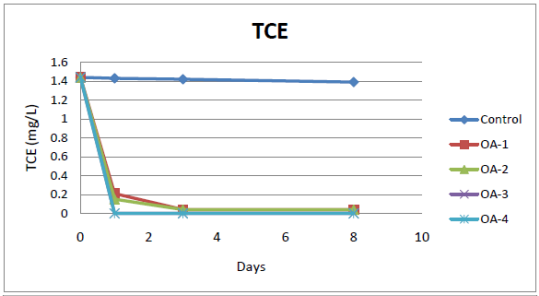
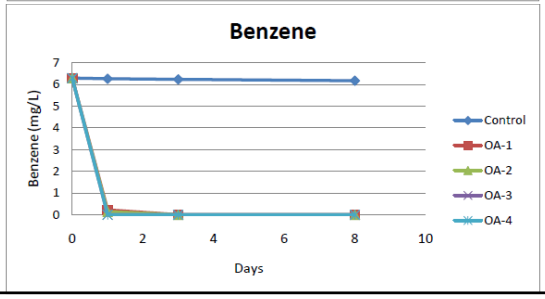
Contaminant Treatment

- 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





19

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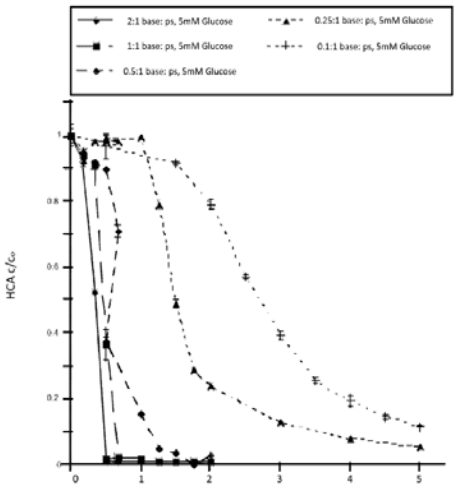
Enhanced Reductive Ability with Increasing pH

- Treatment of reductant prob (Hexachloroethane) with increasing concentrations of sodium hydroxide
- With 50 % less caustic than the regular alkaline activation



Courtesy of Washington State University

20

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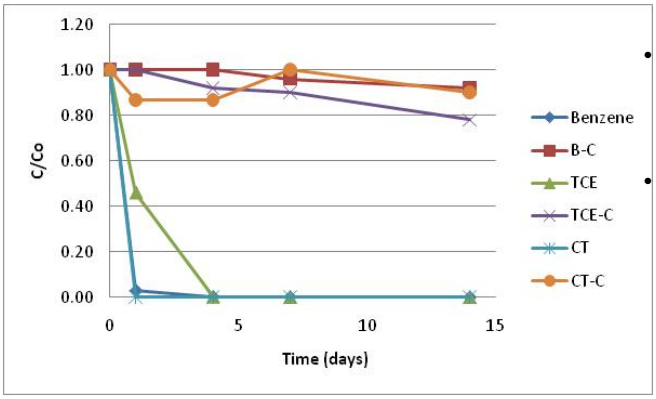
Alkaline with Organic Activation



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

21

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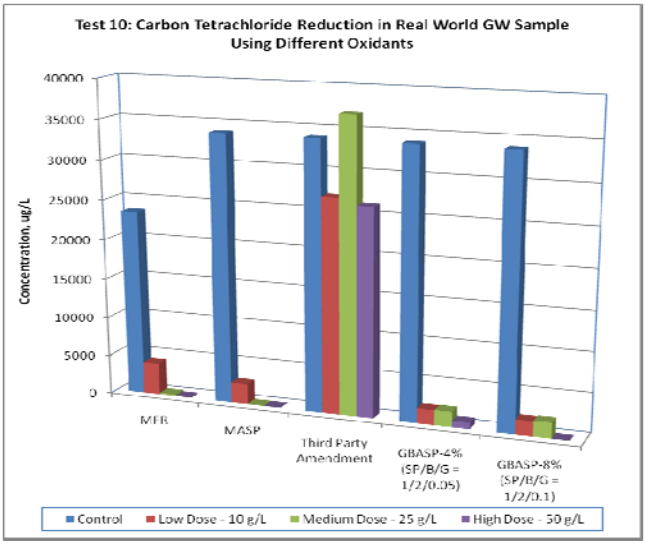
Third Party Bench Test Looking at Treating Carbon Tetrachloride Site



Courtesy of ISOTEC

22

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Conclusions

- Existing activation methods proven to be highly effective
- New method of activation:
  - Ease of use and treatment benefits
  - 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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- **Training and Education:** technical transfer session, health and safety training;
- **Consulting and Technology Site Assessment:** technology support and selection (chemical oxidation and reduction, co solvent-surfactant soil washing and enhanced bioremediation);
- **Laboratory Services and Analysis**: Groundwater Parameter Analysis, Tracer Study, Soil and Groundwater Oxidant Demand Evaluation (SOD), Bench Scale Treatability testing in saturated and unsaturated conditions.
- **Products supply, logistic and storage**: nutrients, bacterial preparations strains, oxidants, reducing agents, catalysts, oxygen and hydrogen release compounds, co solvent-surfactant blends;

TECHNOLOGY, INNOVATION & EXPERTISE

Questions

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