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# IET

**Innovative Environmental Technologies, Inc.**

**“Safer, More Effective ISCO Remedial Actions Using Non-Extreme  
Persulfate Activation to Yield Sustained Secondary Treatment”**

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# Presentation Outline

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## Overview of ISCO Technologies

- Oxidizing agents
- Recognized effectiveness
- General chemistries of reactions

## Use of Persulfate for ISCO Treatment

- Mode of Action
- Limitations of convectional activation technologies

## Provect-OX™ Self-Activating ISCO/Enhanced Bioremediation

- ISCO Mode of Action
- Biological Mode of Action
- Potential advantages
- Case Studies

## Conclusions



## *In Situ* Chemical Oxidation (ISCO)

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- ISCO involves:
  - Injection of an oxidizing agent into the subsurface to destroy organic compounds.
  - The by-products for complete mineralization include carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O) and oxygen (O<sub>2</sub>).
- Goal is to mineralize or transform contaminants of concern (COCs)



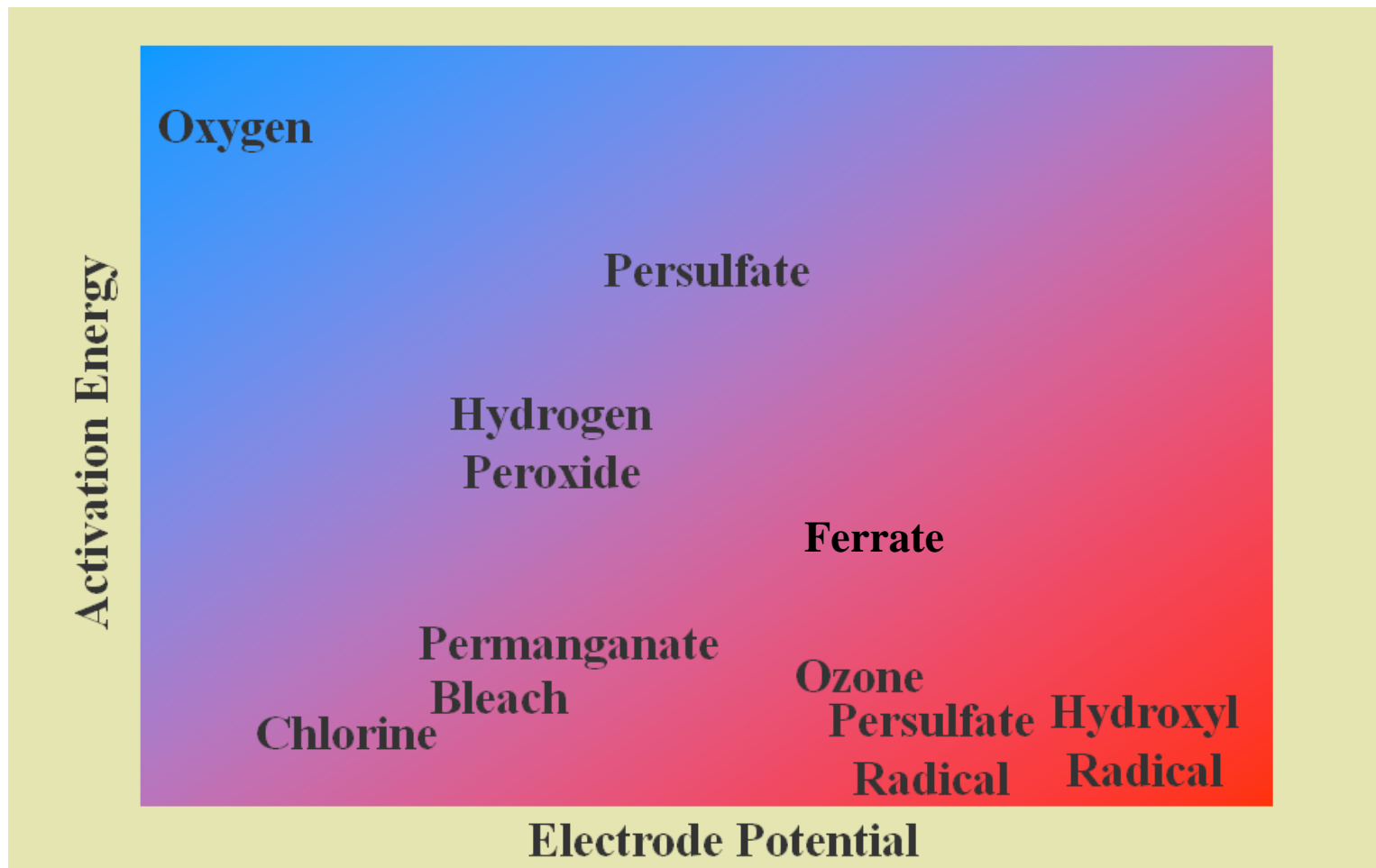
## Common Oxidizing Agents

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<b>Oxidant</b>	<b>Potential (V)</b>	<b>Form</b>
Fenton's Reagent ( $\text{OH}^\bullet$ )	2.80	Liquid
Activated Persulfate ( $\text{SO}_4^{\bullet-}$ )	2.60	Salt/Liquid
Ferrate ( $\text{Fe}^{6+}$ )	2.20	Gas
Ozone ( $\text{O}_3$ )	2.07	Gas
Persulfate ( $\text{S}_2\text{O}_8^{2-}$ )	2.01	Salt/Liquid
Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ )	1.78	Liquid
Permanganate ( $\text{MnO}_4^-$ )	1.68	Salt ( $\text{KMnO}_4$ ) Liquid ( $\text{NaMnO}_4$ )

# Reactivity of Oxidizing Agents





# Basic Oxidizing Agent Reactions

## Ozone (No Activator)

- $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$   $E_o=2.07\text{ V}$
- Hydroxyl Radical
  - $O_3 + H_2O \rightarrow O_2 + 2OH\cdot$
  - $2O_3 + 3H_2O_2 \rightarrow 4O_2 + 2OH\cdot + 2H_2O$
  - $2OH\cdot + 2H^+ + 2e^- \rightarrow 2H_2O$   $E_o=2.76\text{ V}$

## Persulfate (Requires Activation)

- $S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$   $E_o=2.01\text{ V}$
- $S_2O_8^{2-} \rightarrow 2(SO_4^-)\cdot$   $E_o=2.50\text{ V}$

## Hydrogen Peroxide (Requires Activation)

- $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$   $E_o=1.77\text{ V}$
- $H_2O_2 \rightarrow 2OH\cdot$ ;  $2OH\cdot + 2H^+ + 2e^- \rightarrow 2H_2O$   $E_o=2.76\text{ V}$

## Permanganate (No Activator)

- $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$   $E_o=1.70\text{ V}$ 
  - $K^+$ ,  $Na^+$



# Accepted Oxidizing Techniques for Specific COCs

Oxidant	Amenable VOC's	Reluctant VOCs	Recalcitrant VOCs	Limitations
Peroxide, Old Fenton's	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA	DCA, CH <sub>2</sub> Cl <sub>2</sub>	TCA, CT, CHCl <sub>3</sub>	Stability (25-95% decomp/hr), low pH
Peroxide, New Fenton's	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA	DCA, CH <sub>2</sub> Cl <sub>2</sub> , TCA, CT, CHCl <sub>3</sub>		Stability (10-50% decomp/hr)
Potassium Permanganate	PCE, TCE, DCE, VC, TEX, PAH	MTBE, TBA	TCA, CT, B, CHCl <sub>3</sub> , DCA, CB, CH <sub>2</sub> Cl <sub>2</sub>	Soil oxidant demand
Sodium Permanganate	PCE, TCE, DCE, VC, TEX, PAH	MTBE, TBA	TCA, CT, B, CHCl <sub>3</sub> , DCA, CB, CH <sub>2</sub> Cl <sub>2</sub>	Soil oxidant demand
Sodium Persulfate, Fe	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA	DCA, CH <sub>2</sub> Cl <sub>2</sub> , CHCl <sub>3</sub>	TCA, CT	Stability (10-25% decomp/wk), low pH
Sodium Persulfate, Base	All VOCs			Stability (10-25% decomp/wk), NaOH costs
Sodium Persulfate, Heat	All VOCs			Stability (10-50% decomp/day), low pH, heating costs
Ozone	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA		DCA, CH <sub>2</sub> Cl <sub>2</sub> , CHCl <sub>3</sub> , TCA, CT	Mass Delivery, Volatilization



# Limitations of Traditional Persulfate Activation Techniques

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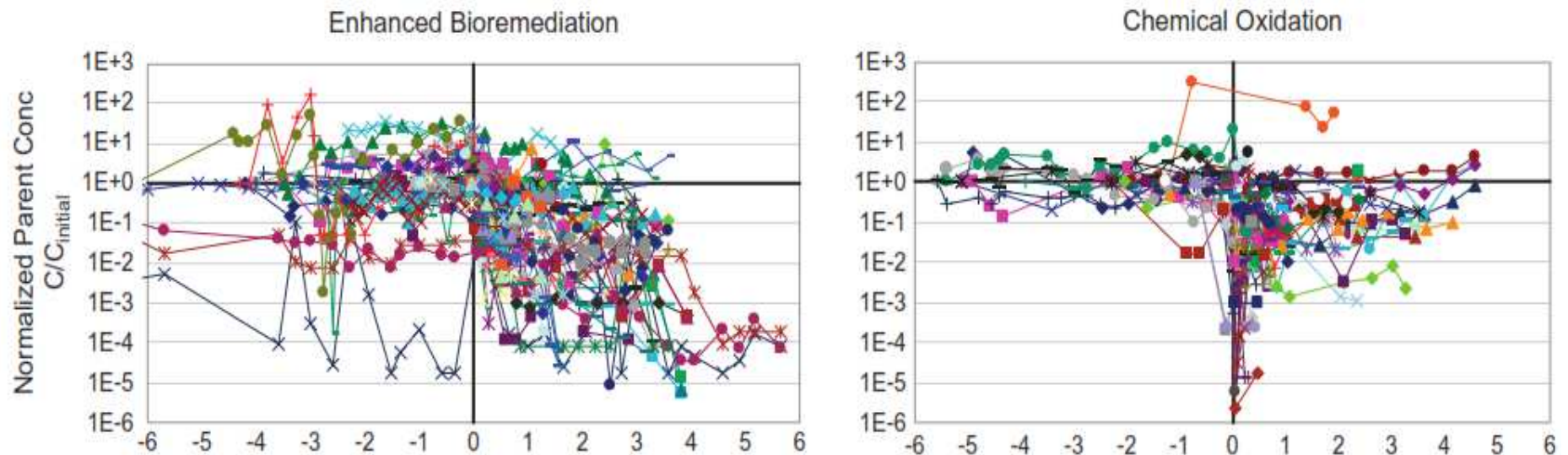
- **Divalent Metal Activation**
  - Oxidant consumption during conversion of ferrous iron to ferric iron
  - Inhibition of biological utilization of the generated ferric species (EDTA)
  - High oxidant consumption due to overdosing of the ferrous chelated iron
- **Caustic Activation**
  - Significant health and safety issues
  - Unsuitably high (extreme) pH environment for biological attenuation
  - Self-limiting biological attenuation process due to hydrogen sulfide generation
- **Heat Activation**
  - Difficult Implementation
  - High Cost
  - Elevated hydrogen sulfide production
- **Hydrogen Peroxide Activation**
  - Limited efficacy on many targeted compounds
  - Elevated hydrogen sulfide production
  - Produces heat and (excessive) gassing which can lead to surfacing issues



# General Limitation of Persulfate / ISCO = Rebound

## The ISCO reactions are short lived

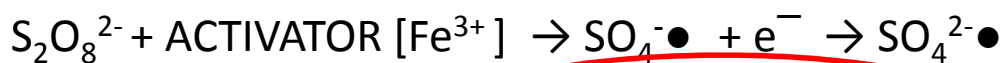
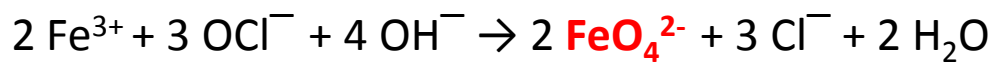
- Ozone (minutes to hours) Fenton's (hours to days) Persulfate (days to weeks) Permanganate (months).
- The ISCO process can enhance COC desorption
- Lack of secondary treatment mechanism mandates subsequent treatments



**Figure 1. Temporal concentration records for wells at source depletion sites. Concentration is normalized by the initial measured concentration. Sampling time is normalized by the time of the initial source depletion treatment.**

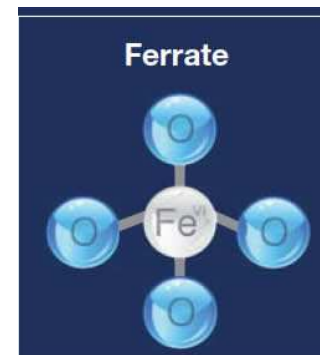
**Provect-OX™** = Sodium Persulfate + Ferric Oxide (Fe<sub>2</sub>O<sub>3</sub>)

- Chemical Oxidation via Sulfate (SO<sub>4</sub>•) Radical
- Chemical Oxidation via Ferrate (Fe<sup>6+</sup>•) Radical



Oxidation Potentials	Volts
Fluorine (F <sub>2</sub> )	2.87
Hydroxyl radical (OH•)	2.80
Persulfate radical (SO <sub>4</sub> •)	2.60
Ferrate (Fe <sup>+6</sup> )	2.20
Ozone (O <sub>3</sub> )	2.08
Persulfate (S <sub>2</sub> O <sub>8</sub> <sup>-2</sup> )	2.01
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	1.78
Permanganate (MnO <sub>4</sub> <sup>-</sup> )	1.68
Chlorine (Cl <sub>2</sub> )	1.49

<https://sites.google.com/site/ecpreparation/ferrate-vi>





## Provect-OX™ ISCO Processes

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- Persulfate is activated by Fe(III) requiring lower activation energy than alternative mechanisms
- No consumption of persulfate oxidant
- Elevation of iron oxidation state to a supercharged iron ion (ferrate species) which can itself acts as an oxidant
- The supercharged iron cation consumption results into ferric species that act as a terminal electron acceptor for biological attenuation
- The generated sulfate ion from the decomposition of the persulfate acts as a terminal electron acceptor for sulfate reducers

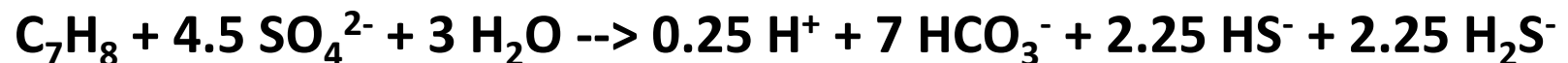


# Provect-OX™ Biological Attenuation Processes

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## Sulfate Reduction

- After dissolved oxygen depletion sulfate is used as an electron acceptor for anaerobic biodegradation by indigenous microbes (sulfidogenesis)
- Stoichiometrically, 1.0 mg/L of sulfate consumed by microbes results in the destruction of approximately 0.21 mg/L of BTEX compounds
- Sulfate acts as an electron acceptor in co-metabolic processes during bioremediation of petroleum products
- Basic reactions for the mineralization of benzene and toluene under sulfate reducing conditions:



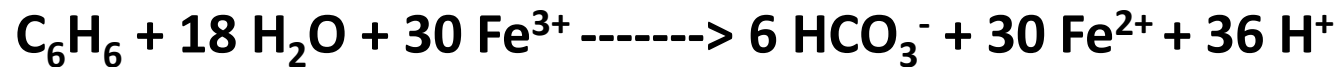


# Provect-OX™ Biological Attenuation Processes

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## Ferric Iron Reactions

- Ferric iron used as electron acceptor during anaerobic biodegradation of contaminants
- Stoichiometrically, the degradation of 1.0 mg/L of BTEX results in the average consumption of approximately 22 mg/L of ferric iron



- Ferric iron is reduced to Ferrous iron, which is soluble in water
- Ferrous iron is oxidized to Ferric iron and the iron cycling provides sustained secondary bioremediation via one electron transfer reactions (Weber *et al*, 2006)



# Provect-OX™ Biological Attenuation Processes

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## Pyrite Formation

- Sulfate residual is utilized as terminal electron acceptor by facultative organisms thereby generating sulfide
- The ferrous iron and the sulfide promote the formation of pyrite as a remedial byproduct
- This reaction combats the toxic effects of sulfide and hydrogen sulfide accumulation on the facultative bacteria
- Provides a means of removing targeted organic and inorganic COIs via precipitation reactions
- Pyrite possesses a high number of reactive sites that are directly proportional to both its reductive capacity and the rate of decay for the target organics





## Provect-OX™ Potential Advantages

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- Safely catalyzed process without the Hazards of Extreme Activators Caustics
- Can be provided pre-mixed in one bag
- Safely distributed in the field
- No Heat Generated – minimizes gassing and surfacing issues
- Uses  $\text{Fe}^{3+}$  as activator (no persulfate “Master Supplier”)
- Conserves Oxidant – Unlike other Persulfate Activators
- Multiple ISCO processes via formation of reactive ferrate species = better ISCO
- Enhances bio attenuation utilizing both iron and sulfate reduction
- Encourages the formation of pyrite / Prevents  $\text{H}_2\text{S}$  formation
- Long-lived reactions – sustained treatment manages rebound
- Cost-effective – reduces need for multiple injection events

# “Safer, More Effective ISCO Remedial Actions Using Non-Extreme Persulfate Activation to Yield Sustained Secondary Treatment”



## Questions

