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# **Combining Persulfate, *In Situ* Ferrate Generation and Sustained Bioremediation for Safer, More Effective Remedial Actions**

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# Presentation Outline

## 💧 ISCO fundamentals

- 💧 Chemical oxidations and oxidation potentials
- 💧 Partial oxidation = Known Limitation 1
- 💧 Contaminant rebound = Known Limitation 2

## 💧 Persulfate activation using ferric oxide, buffer and ferrate stabilizer

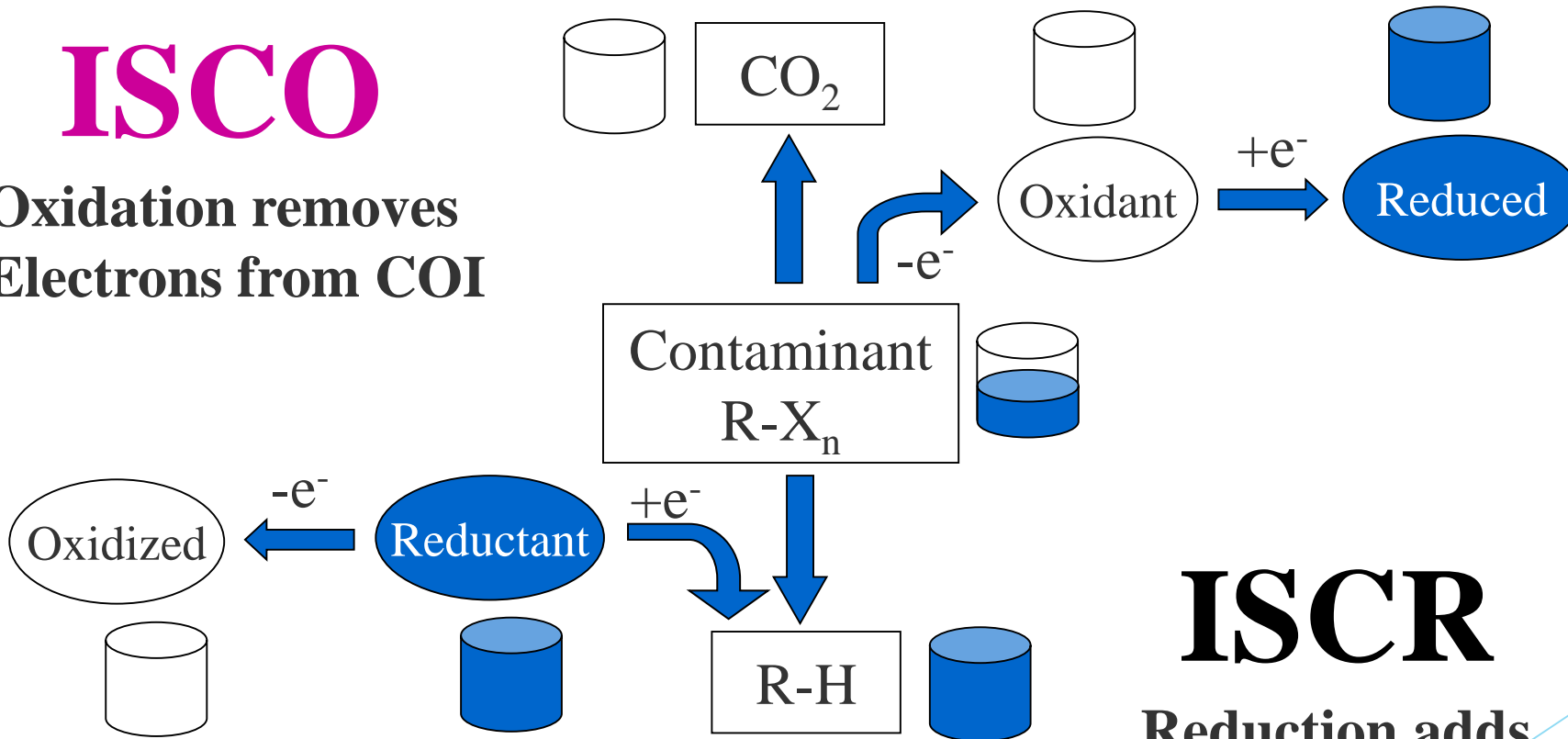
- 💧 Composition and modes of action
- 💧 In Situ ferrate production = more complete oxidation to address KL1
- 💧 Iron biogeochemistry = manages rebound to address KL2
- 💧 Iron reactions yield safer ISCO process ( $H_2S$  production)
- 💧 Case Studies

## 💧 Summary

# Electron Transfer Reactions

## ISCO

**Oxidation removes  
Electrons from COI**



## ISCR

**Reduction adds  
Electrons to COI**

## ISCO = Breaking Bonds

<b>Bond Type</b>	<b>Oxidation Potential Volts (eV)</b>
<b>Carbon-Carbon (single) Long chain hydrocarbons PAHs, DRO, GRO</b>	<b>2.5</b>
<b>Carbon-Carbon (one and a half) Aromatic Type - BTEX and PCP</b>	<b>2.0</b>
<b>Carbon-Carbon (double) HVOCs, PCE, TCE, DCE, VC</b>	<b>1.5</b>
<b>Carbon-Hydrogen (Alkanes)</b>	<b>1.0</b>

stronger oxidizer ↑

Oxidation Potentials	Volts
Fluorine (F <sub>2</sub> )	2.87
Hydroxyl radical (OH●)	2.80
Sulfate 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>

#### Fenton's

- Treats wide range of contaminants
- Short subsurface lifetime
- Difficult to apply in reactive soils

#### Persulfate

- Treats wide range of contaminants
- Sulfate radical forms slower than the hydroxyl radical, allowing a larger radius of influence

#### Provect-OX

- Generates Ferrate (Fe IV, V, VI possible)
- Treats wide range of contaminants
- Extended *in situ* lifetime w/ continual production
- Provides Fe as alternative e- acceptor, etc

#### Ozone

- Treats wide range of contaminants
- Short subsurface lifetime
- Limited use in saturated zone

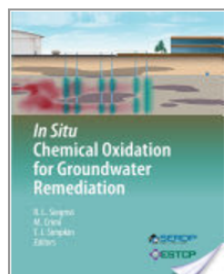
#### Permanganate –

- Treats limited range of contaminants
- Partial oxidation of TPHs, etc
- Long subsurface lifetime
- Potential effects on hydrogeology

Higher oxidation potential (V) = stronger oxidizer

# Partial COI Oxidation – A Known Limitation with ISCO

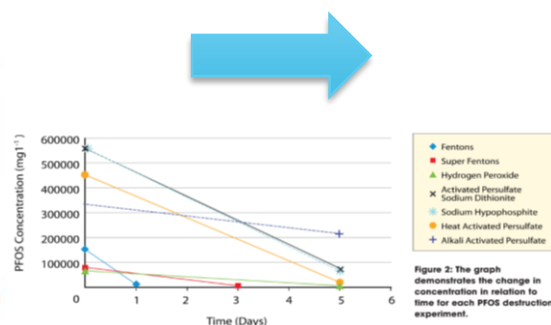
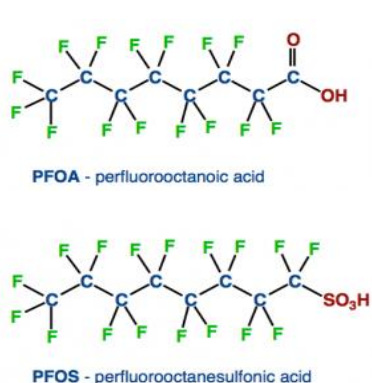
## In Situ Chemical Oxidation for Groundwater Remediation



Robert L. Siegrist, Michelle Crimi, Thomas J. Simpkin

Springer Science & Business Media, Feb 26, 2011 - [Technology & Engineering](#) - 678 pages

Table 7.4 summarizes key conditions and findings from additional studies investigating enhanced biodegradation after oxidation, in the context of MNA or EISB (with bioaugmentation). PAH has been the primary target contaminant, with numerous studies demonstrating enhanced aerobic biodegradation after pre-oxidation with CHP (Kulik et al., 2006; Lee and Hosomi, 2001; Piskonen and Itävaara, 2004) or ozone (Kulik et al., 2006; Nam and Kukor, 2000; O'Mahony et al., 2006) to more biodegradable byproducts. Additional studies have demonstrated biodegradation of CHP reaction products of the dioxin isomer 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (Kao and Wu, 2000) and aerobic biodegradation of permanganate-oxidized cyclotrimethylenetrinitramine (RDX or Royal Demolition eXplosive) and its byproducts (Adam et al., 2005).



I. Ross, 2012. PE News

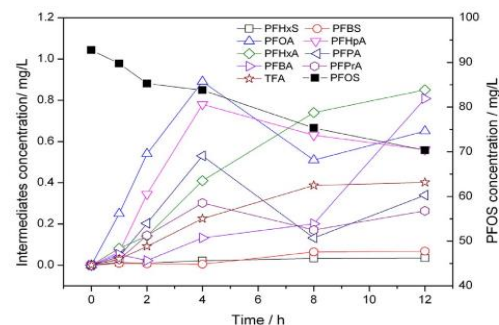


Figure 8. Changes in the concentration of PFOS and intermediates through the PFOS defluorination in UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system. doi:10.1371/journal.pone.0074877.g008

26 known +39 unknowns compounds

<http://authors.library.caltech.edu/59251/1/jp801081y-file002.pdf>

# Contaminant Rebound – A Known Limitation with ISCO

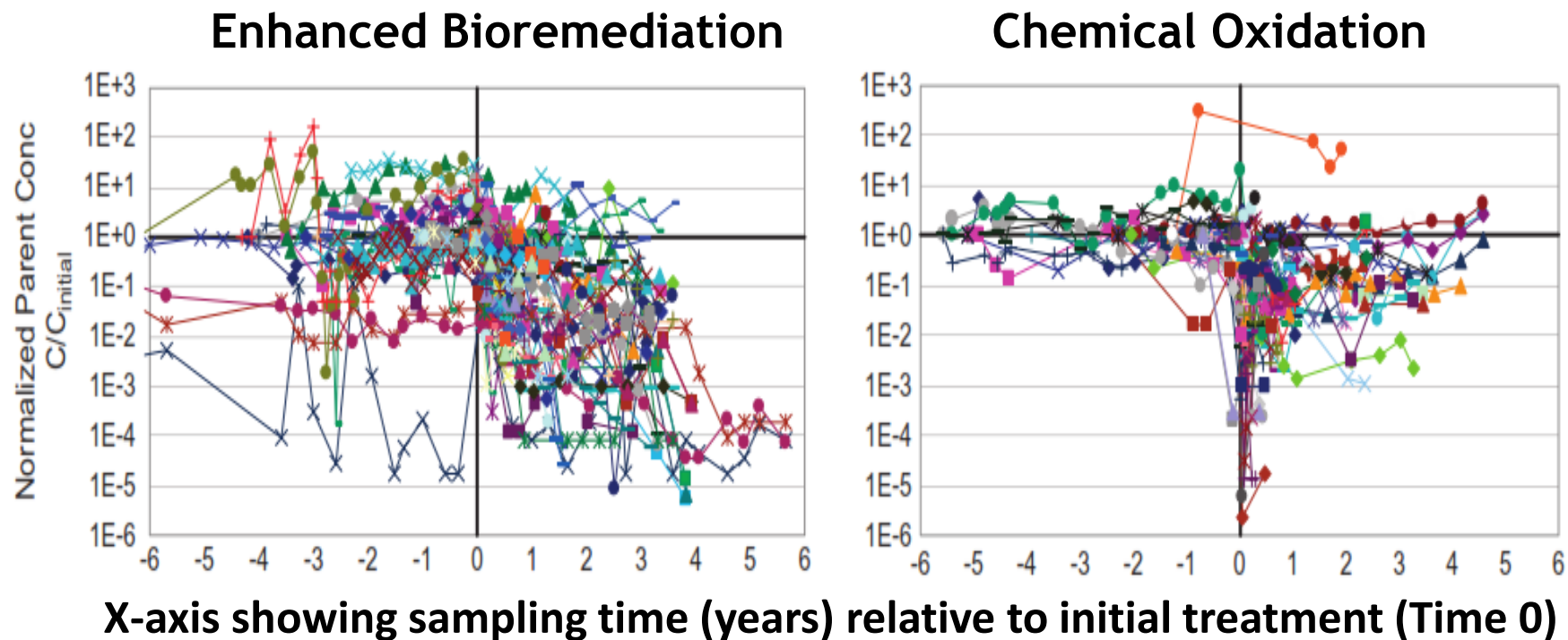


Figure 1. Temporal concentration records for wells at source depletion sites. Concentration is normalized by the initial measured concentration. Sampling time is normalized by the time of the initial source depletion treatment.



# Provect-OX<sup>®</sup> ISCO Technology

- 💧 **Sodium Persulfate + Ferric Oxide ISCO Reagent**
  - Chemical Oxidation via Sulfate ( $\text{SO}_4^\bullet$ ) Radical
  - Chemical Oxidation via Ferrate ( $\text{Fe}^{6+}$ )
- 💧 Enhances Biological Attenuation via Sulfate and Iron Reduction Processes
- 💧 Terminating Reaction Results in Pyrite: An Abiotic Reactive Particle with similar Kinetics to ZVI
- 💧 Easily Transitions from Oxidation to Biological Attenuation to Abiotic Mineralization
- 💧 Safely Handled Catalyzed Process without the Hazards of Extreme Activators Caustics

## Managing ISCO Limitations





# Multiple Oxidation Reactions

Ferrate (IV, V VI) salts can be prepared from iron salts, hypochlorite and a base:



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

## Managing Partial Oxidation

# Validation of Ferrate Production

Rx	Provect-OX Composition Persulfate:Fe2O3:buffer/ferrate stabilizer (4 hrs)	Abs 515 nM	Ferrate VI [M]	Ferrate VI (ppm)
1a	80:20:0 in DI water	<0.4	$<1 \times 10^{-5}$	<1
2a	80:20:0 in buffer (Na <sub>2</sub> HPO <sub>4</sub> )	<0.4	$<1 \times 10^{-5}$	<1
1b	80:16:4 Terr-OR in DI water	0.330	$2.87 \times 10^{-4}$	>3,000
2b	80:16:4 Terr-OR in buffer (Na <sub>2</sub> HPO <sub>4</sub> )	0.306	$2.66 \times 10^{-4}$	>3,000



$C_{\text{Fe(VI)}}$  = Fe(VI) concentration (M)

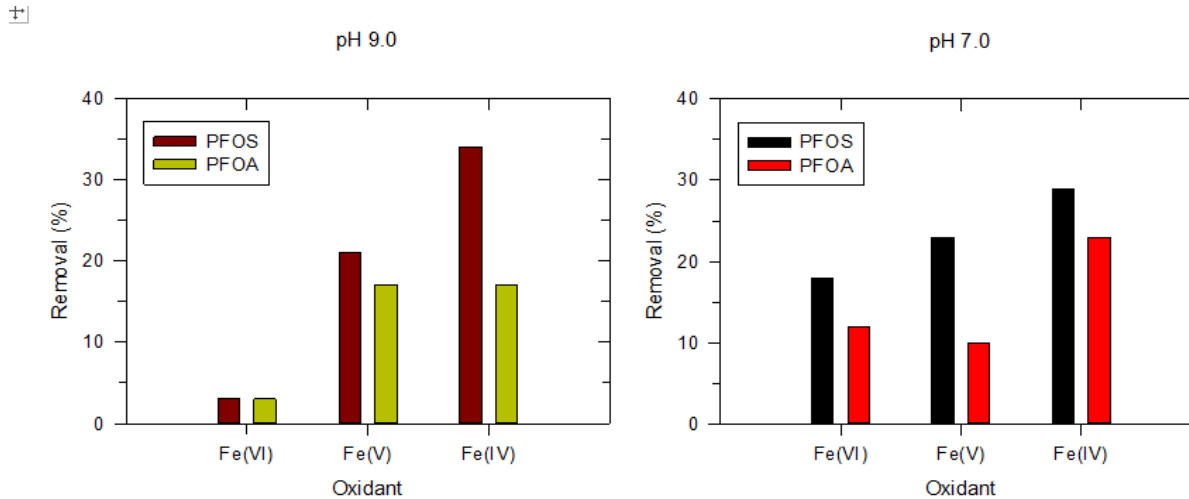
$A_{515}$  = Absorbance at 515 nm (-)

$\epsilon_{515}$  =  $1150 \text{ M}^{-1}\text{cm}^{-1}$

$l$  = Path length (1.0 cm)

## Managing Partial Oxidation

# Validation of Ferrate Production

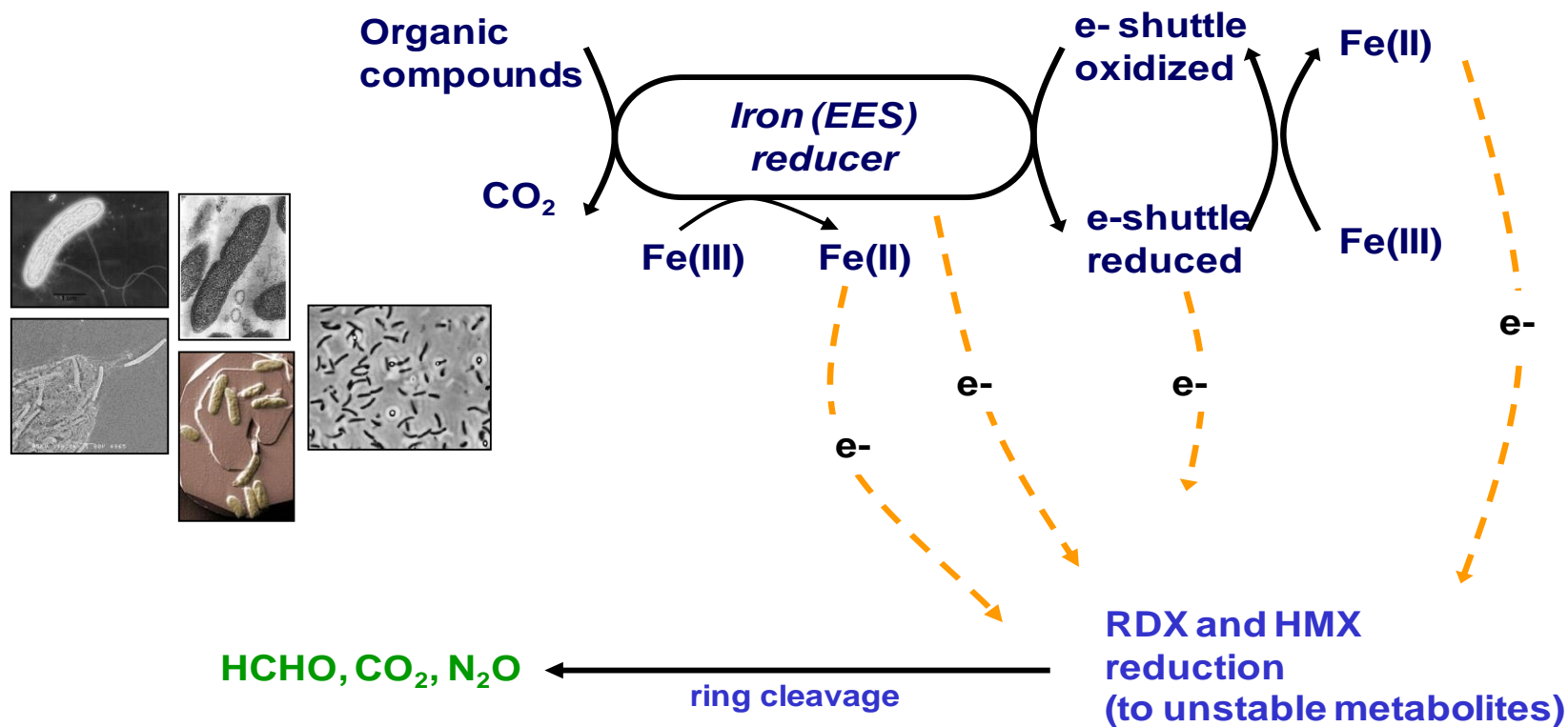


- $\text{Fe}^{+6}$  longer lived (>10 hr), less reactive
- $\text{Fe}^{+4}$  shorter lived (<1 hr), more reactive
- Longevity pH dependent

Figure 3. Oxidation of perfluorooctylsulfonate and perfluorooctanoic acid by one application of ferrates at pH 9.0 and 7.0 after five days.

- “Continuous” ferrate generation *in situ* with buffered conditions and proprietary ferrate stabilizer

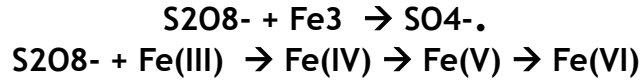
## Managing Partial Oxidation



Adapted from Kwon and Finneran , Biodegradation, 2008 , V19(5), Page 705

## Managing Rebound

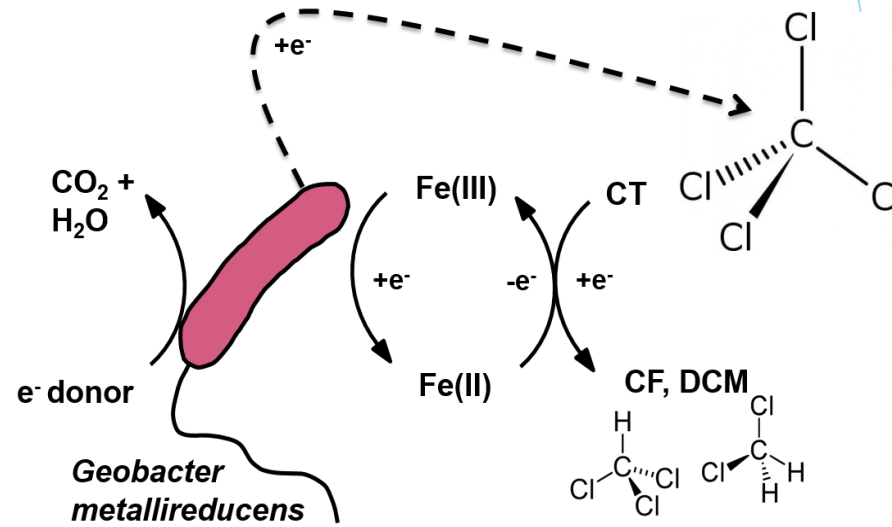
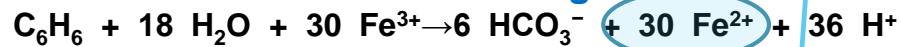
### Oxidation Reactions:



### Sulfate Biological :



### Fe+3/Fe+2 Biological



- 100 lbs Sodium Persulfate → 80 lbs sulfate – **what happens to that??**
- If used as an electron acceptor, then SRB → 80 lbs H<sub>2</sub>S-
- Biological Attenuation via Sulfate + Iron Reduction Processes essential to manage this gas *in situ*

### Hydrogen Sulfide

Colorless gas; rotten-egg smell. Irritating to eyes/skin/respiratory tract. Poison! Inhalation causes headache, dizziness, nausea; high levels (>1000 ppm) can be instantly fatal causing respiratory paralysis. Cardiac effects may occur. Highly flammable.



CAS No. 7783-06-4

# Fe-Reducers Aid H<sub>2</sub>S Removal

# Provect-OX® with Terr-OR™

- Forms reactive ferrate + sulfate reactions
- Safely Handled; all in one bag
- Uses  $\text{Fe}^{+3}$  as activator
  - No heat generated = safer
  - Conserves oxidant
  - Enhances bioattenuation  $\text{Fe} + \text{SO}_4$
  - Encourages the formation of pyrite
  - Minimizes release of  $\text{H}_2\text{S}$
  - Minimizes heavy metal mobilization
- Terr-OR buffer / reactive ferrate stabilizer

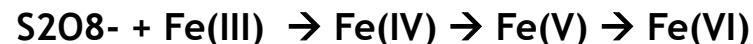


- When Chelated  $\text{Fe}^{+2}$  used as activator EDTA Consumes the Oxidant
- When Caustic is used as activator
  - Short lived reaction
  - $\text{H}_2\text{S}$  formed
  - Secondary plumes / metals (Cr)
  - Can generate heat
  - Handling and safety issues (50% sodium hydroxide)
- pH 10+ Does Not Support Biological reactions
- Does Not Manage Rebound



# Case Study – Gas Station, NJ

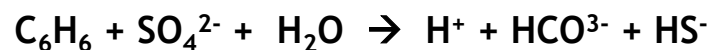
## Phase #1 - Oxidation



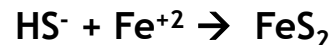
## Phase #2 - Iron Reduction



## Phase #3 - Sulfate Reduction



## Phase #4 - Ferrous Sulfide Formation



Courtesy Innovative Environmental Technologies, Inc.  
*Design and Implementation*

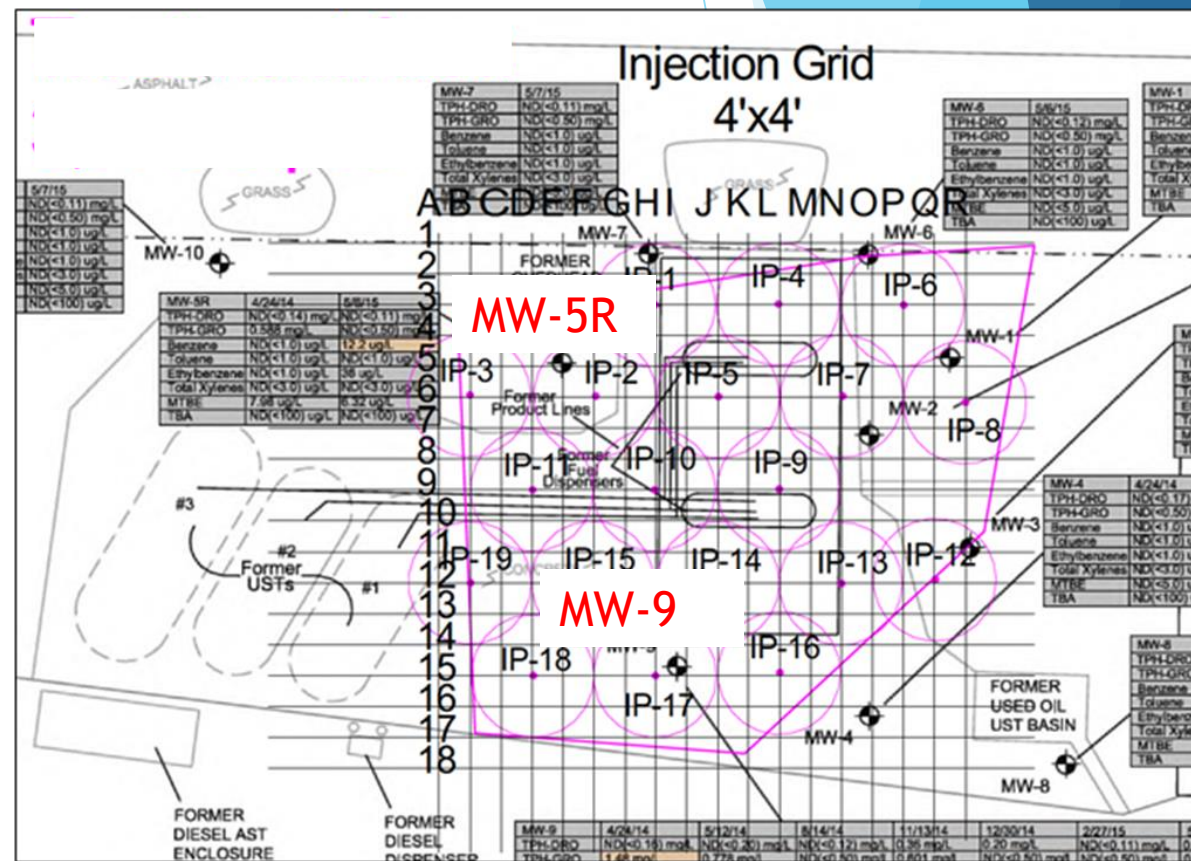
## Case Study – Gas Station, NJ

- 💧 2,850 sq ft with 4 to 14 ft bgs
- 💧 Primarily fill
- 💧 Total of approximately 4,400 lbs of Provect-OX injected
- 💧 MW-2
  - 💧 Total BTEX 35 ug/L to ND after 8 months
  - 💧 Maximum iron concentration after injection 2.01 mg/L (7x baseline)
  - 💧 Sulfate 56.6 mg/L to 1,510 mg/L (injection) to 332 mg/L after 8 months
  - 💧 ORP from -14 to +220 (injection) to -40 after 8 months
  - 💧 pH range from 6.86 to 7.43

# Case Study – Gas Station, WV

## St. Albans, WV Site

- Former Gas Station
- Approx. 3,800 sq ft area
- Impacted with BTEX, MTBE, TBA
- Primarily clay with depth to water ca. 5 ft bgs
- Treatment interval from 6 to 12 ft bgs
- Two monitoring wells impacted
- Goal was significant reductions



Courtesy Innovative Environmental Technologies, Inc.  
*Design and Implementation*

## Case Study – Gas Station, WV

### 💧 MW-9 Highest Concs. – 1 Year

- 💧 Benzene 77 ug/L to ND
- 💧 Ethylbenzene 66 ug/L to ND
- 💧 MTBE 72 ug/L to ND
- 💧 TBA 1,480 ug/L to ND

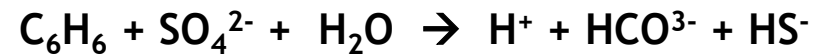
### 💧 MW-5R – 2 Year

- 💧 Benzene 12.2 ug/L to 2.01
- 💧 Ethylbenzene 36 ug/L to ND
- 💧 Sulfate 1,350 mg/L
- 💧 Iron 38.1 mg/L

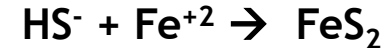
### Phase #2 - Iron Reduction



### Phase #3 - Sulfate Reduction



### Phase #4 - Ferrous Sulfide Formation





# Case Study – Mendota

## 💧 Mendota Site

- 💧 Active facility with desire for one-time application
- 💧 500 tons of contaminated, vadose zone soil
- 💧 PCE >35,000 mg/kg and Toluene >4,000 mg/kg
- 💧 Goal was to reduce below site-specific soil saturation limits
- 💧 PCE goal ca. 2,000 mg/kg and
- 💧 Toluene goal ca. 1,000 mg/kg



# Building on Provect-OX Technology

- Provect-OX contains sodium persulfate with a solubility of 55.6 g/100 mL at 20C
- Provect-OX2 combines sodium persulfate + potassium persulfate (solubility of 5 g/100 mL at 20C)
- The potassium persulfate provides an extended release of oxidant for many months versus weeks
- Allows permeable reactive barrier (PRB) approaches to target petroleum hydrocarbons
- Introduction to excavations that include access limitations (e.g., buildings, roads, etc.)
- Similar to Provect-OX, we can manufacture on a site-specific basis



# Summary

- ◆ Combination of Provect-OX and Provect-OX2 contain persulfate + ferric oxide + proprietary ferrate stabilizer (ratios can vary based on site conditions)
- ◆ Traditional oxidation chemistries + *in situ* ferrate generation expands the range and improves the effectiveness of ISCO
- ◆ Provect-OX2 can be used for PRBs, limited access areas of concern, etc.
- ◆ Excess Fe sustains secondary bioremediation processes that help manage COI rebound
- ◆ Safer ISCO chemistry - all components in one bag, minimizes generation of  $H_2S$ , minimizes heavy metal mobilization to avoid secondary plumes
- ◆ No extreme activation chemistries employed (pH 11 aquifers?)
- ◆ Other benefits relate to safety, regulatory compliance, and sustainability

# Our Services

- 💧 Complimentary Site Evaluation
- 💧 Complimentary Review of Field Data
- 💧 Laboratory Treatability Studies
- 💧 Turn-Key, Pay-for-Performance & Shared-Risk Contracting Options
- 💧 USA
  - 💧 Illinois
  - 💧 New Jersey
  - 💧 Louisiana
  - 💧 Pennsylvania
  - 💧 Ohio
- 💧 Australia, Brazil, China, Colombia, Israel, Italy, Spain and Taiwan



# Thank You!

***[www.provectusenvironmental.com](http://www.provectusenvironmental.com)***

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