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24th Annual Florida Remediation Conference
Orlando, Florida
December 4 - 6, 2018

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

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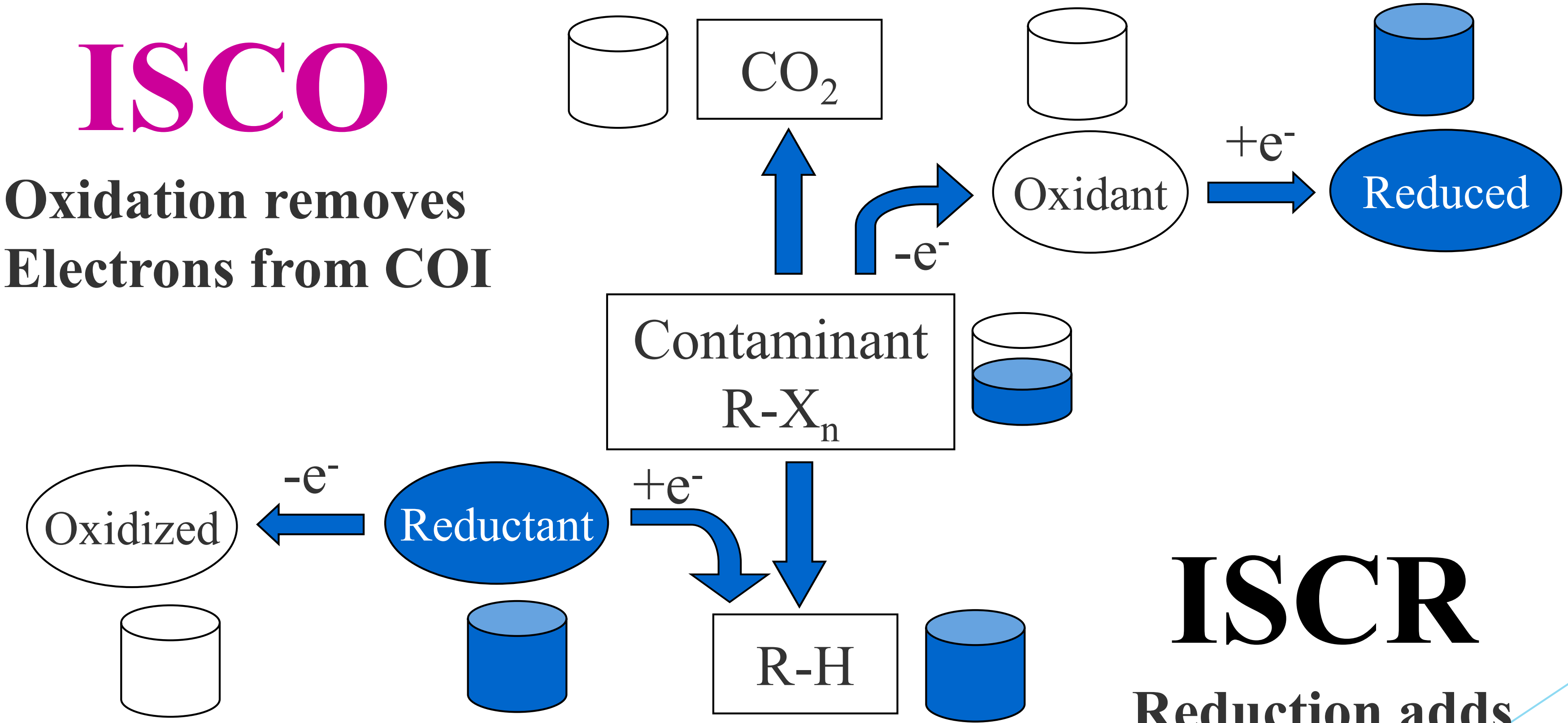
Presentation Outline

- ISCO fundamentals
  - Chemical oxidants and oxidation potentials
  - Partial oxidation = Known Limitation 1
  - Contaminant rebound = Know 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
- Developments and Summary

Electron Transfer Reactions

ISCO

Oxidation removes Electrons from COI



ISCR

Reduction adds Electrons to COI

ISCO = Breaking Bonds

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

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stronger oxidizer

Oxidation Potentials	Volts
Fluorine (F_2)	2.87
Hydroxyl radical ($OH\bullet$)	2.80
Sulfate radical ($SO_4\bullet$)	2.60
Ferrate (Fe^{+6})	2.20
Ozone (O_3)	2.08
Persulfate ($S_2O_8^{-2}$)	2.01
Hydrogen peroxide (H_2O_2)	1.78
Permanganate (MnO_4^-)	1.68
Chlorine (Cl_2)	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 (complex; Fe IV, V, VI possible)
- Treats wide range of contaminants
- Extended *in situ* lifetime w/ continual production
- Provides Fe as alternative e- acceptor, etc

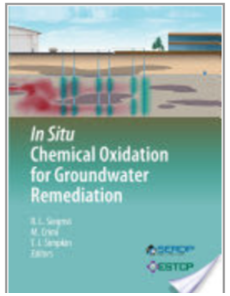
Ozone
- Treats wide range of contaminants
- Short subsurface lifetime
- Limited use in saturated zone

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 – 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

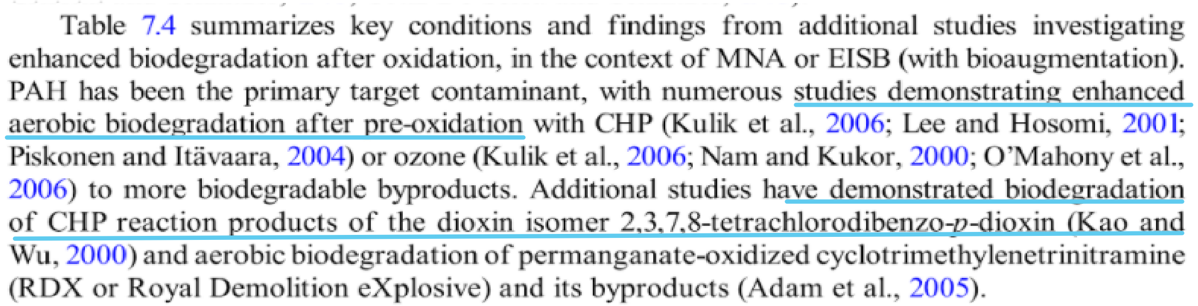
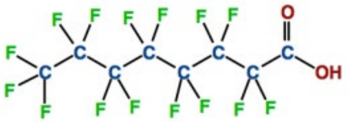
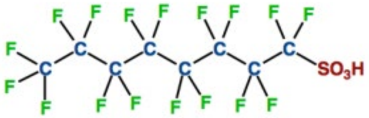


Table 7.4 summarizes key conditions and findings from additional studies investigating enhanced biodegradation after oxidation, in the context of MNA or EISB (with bioaugmentation). PAH has been the primary target contaminant, with numerous studies demonstrating enhanced aerobic biodegradation after 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).



PFOA - perfluorooctanoic acid



PFOS - perfluorooctanesulfonic acid

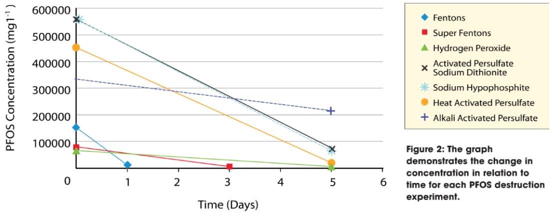


Figure 2: The graph demonstrates the change in concentration in relation to time for each PFOS destruction experiment.

I. Ross, 2012. PE News

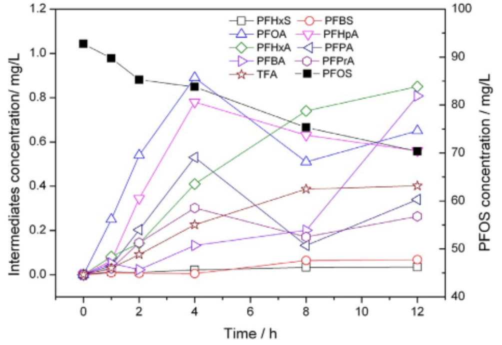


Figure 8. Changes in the concentration of PFOS and intermediates through the PFOS defluorination in UV/$K_2S_2O_8$ system.
doi:10.1371/journal.pone.0074877.g008

26 known +39 unknowns compounds
http://authors.library.caltech.edu/59251/1/jp801081y-file002.pdf

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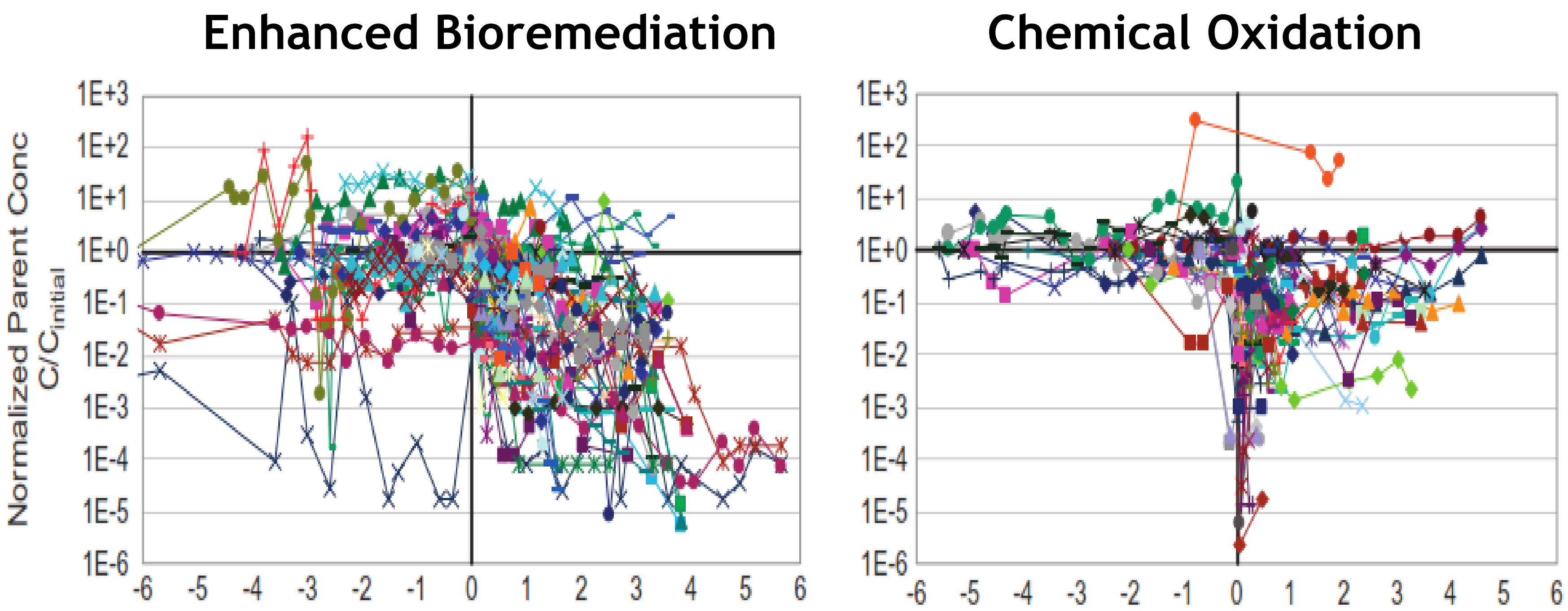
Contaminant Rebound – Known Limitation with ISCO



X-axis showing sampling time (years) relative to initial treatment (Time 0)

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.

T.M. McGuire et al./ Ground Water Monitoring & Remediation 26, no. 1: 73–84 77

Provect-OX® ISCO Technology

- Sodium Persulfate + Ferric Oxide ISCO Reagent
  - Chemical Oxidation via Sulfate (SO4•) Radical
  - Chemical Oxidation via Ferrate (Fe6+)
- 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:

$$2\,Fe^{+3} + 3\,OCl^{-} + 4\,OH^{-} \rightarrow 2\,FeO_4^{-2} + 3\,Cl^{-} + 2\,H_2O$$

$$S_2O_8^{-2} + Fe^{+3} \rightarrow SO_4\bullet^{-} + SO_4^{-2} + Fe^{(+4\text{ to }+6)}$$

Oxidation Potentials	Volts
Fluorine (F_2)	2.87
Hydroxyl radical (OH●)	2.80
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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	$<1\times10^{-5}$	<1
2a	80:20:0 in buffer (Na_2HPO_4)	<0.4	$<1\times10^{-5}$	<1
1b	80:16:4 Terr-OR in DI water	0.330	2.87×10^{-4}	>3,000
2b	80:16:4 Terr-OR in buffer (Na_2HPO_4)	0.306	2.66×10^{-4}	>3,000

$C_{Fe(VI)} =$ Fe(VI) concentration (M)
$A_{515} =$ Absorbance at 515 nm (-)
$\varepsilon_{515} = 1150\ M^{-1}cm^{-1}$
$l =$ Path length (1.0 cm)

Validation of Ferrate Production

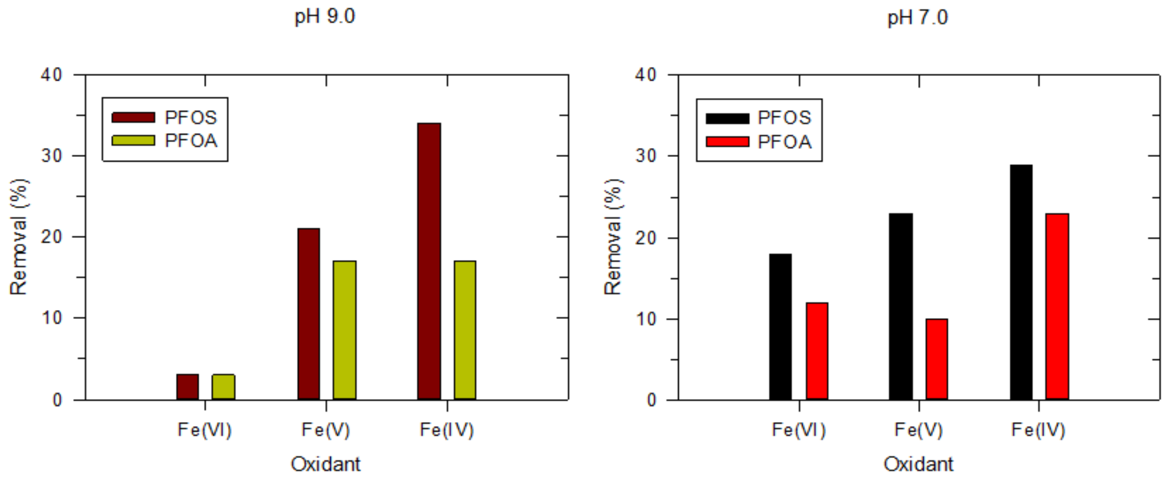
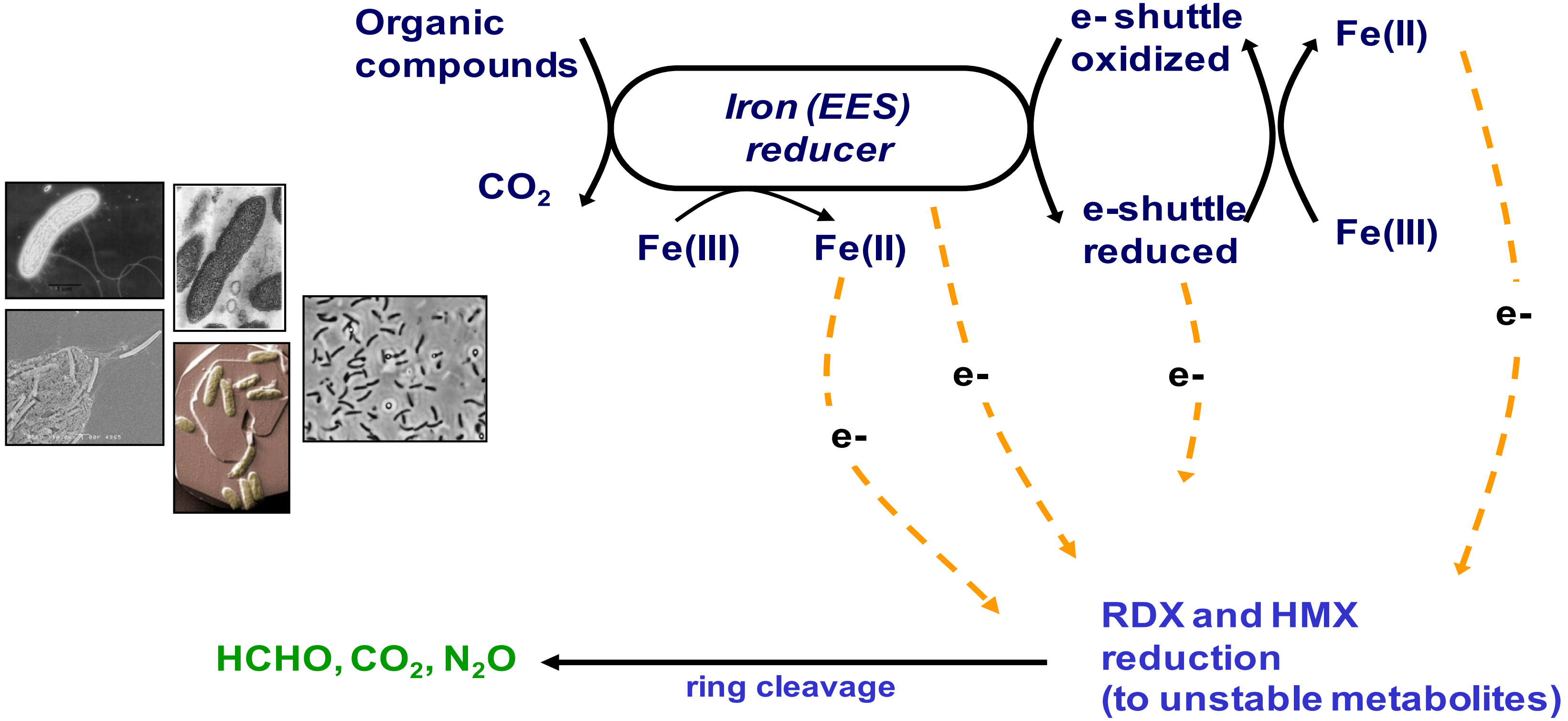


Figure 3. Oxidation of perfluorooctylsulfonate and perfluorooctanoic acid by one application of ferrates at pH 9.0 and 7.0 after five days.

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

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



Organic compounds

CO_2

Iron (EES) reducer

Fe(III)

Fe(II)

e- shuttle oxidized

e-shuttle reduced

Fe(II)

Fe(III)

e-

e-

e-

e-

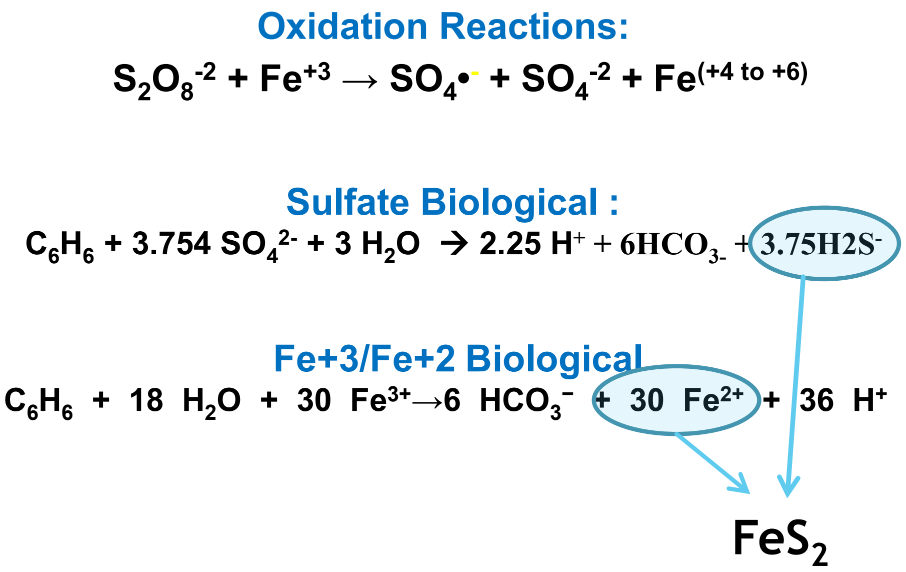
RDX and HMX reduction (to unstable metabolites)

ring cleavage

$HCHO, CO_2, N_2O$

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

Managing Rebound



Oxidation Reactions:

$S_2O_8^{-2} + Fe^{+3} \rightarrow SO_4^{\bullet -} + SO_4^{-2} + Fe^{(+4\ to\ +6)}$

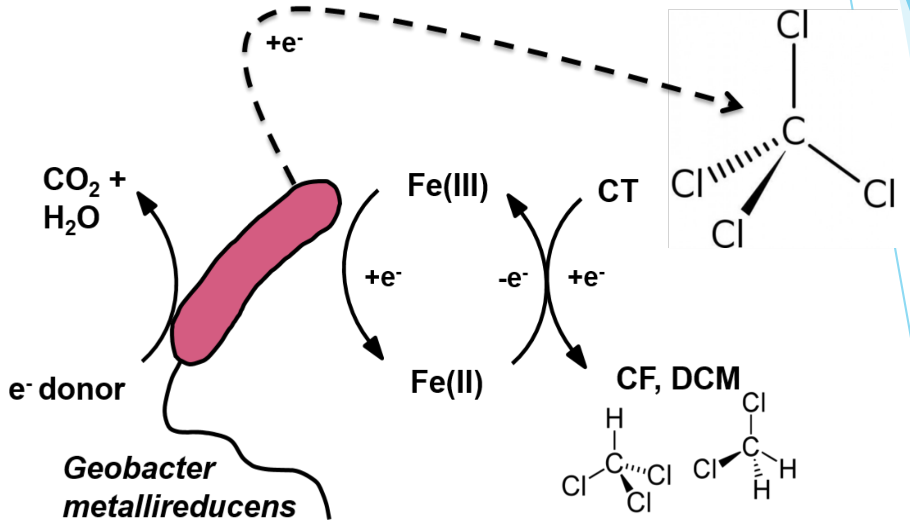
Sulfate Biological :

$C_6H_6 + 3.754\ SO_4^{2-} + 3\ H_2O \rightarrow 2.25\ H^+ + 6HCO_{3-} + 3.75H2S^-$

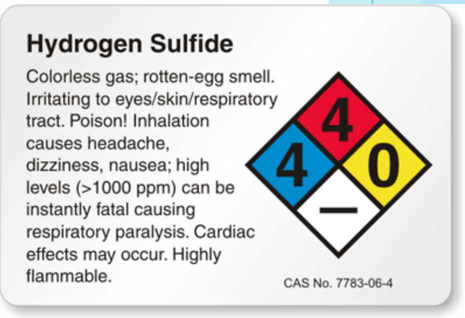
Fe+3/Fe+2 Biological

$C_6H_6 + 18\ H_2O + 30\ Fe^{3+} \rightarrow 6\ HCO_3^- + 30\ Fe^{2+} + 36\ H^+$

FeS_2



- **100 lbs Sodium Persulfate → 80 lbs sulfate – what happens to that??**
- **If used as an electron acceptor, then SRB → 80 lbs H_2S-**
- **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 H2S Removal

Provect-OX® with Terr-OR™

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

- When Chelated Fe^{+2} used as activator EDTA Consumes the Oxidant
- When Caustic is used as activator
  - Short lived reaction
  - H2S 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

$S_2O_8^{-2} + Fe^{+3} \rightarrow SO_4\bullet^{-} + SO_4^{-2} + Fe^{(+4\text{ to }+6)}$

Phase #2 – Iron Reduction

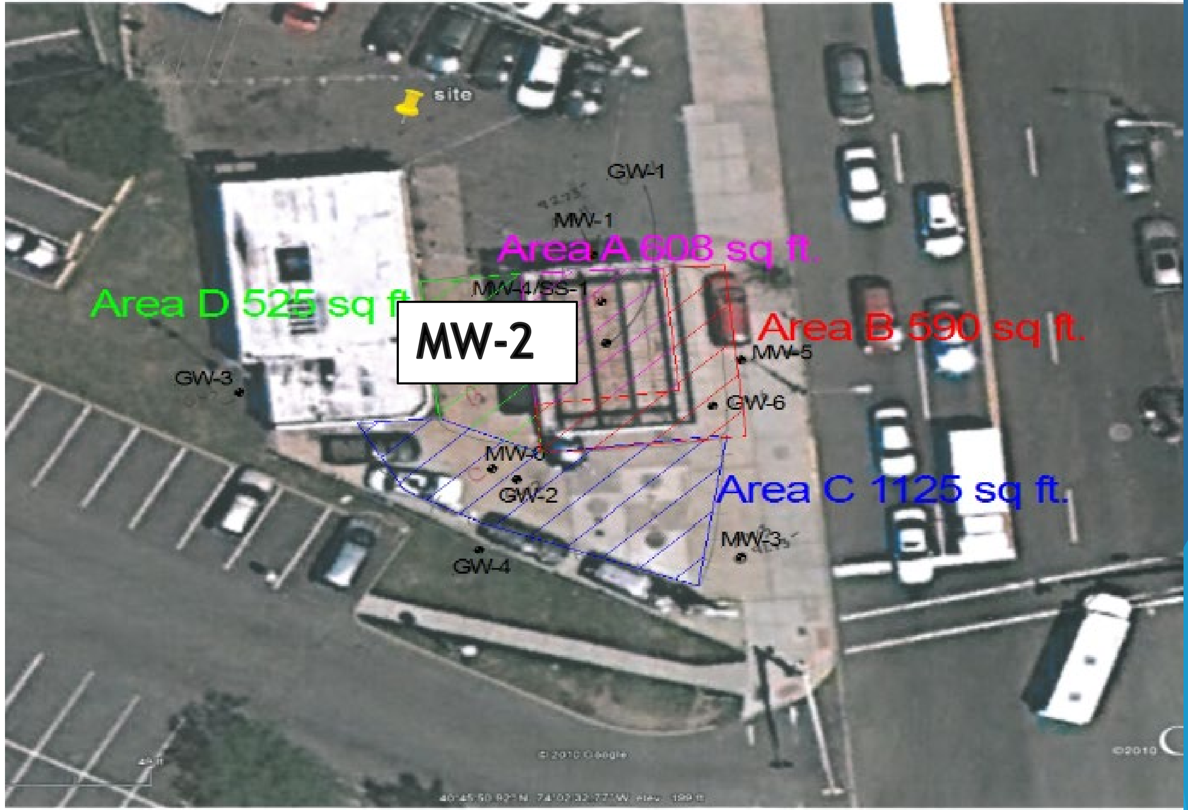
$Fe^{+3}(OH)_3^{-} + C_6H_6 \text{--->} CO_2 + H_2O + Fe_2+$

Phase #3 – Sulfate Reduction

$C_6H_6 + SO_4^{2-} + H_2O \rightarrow H^{+} + HCO^{3-} + HS^{-}$

Phase #4 – Ferrous Sulfide Formation

$HS^{-} + Fe^{+2} \rightarrow FeS_2$



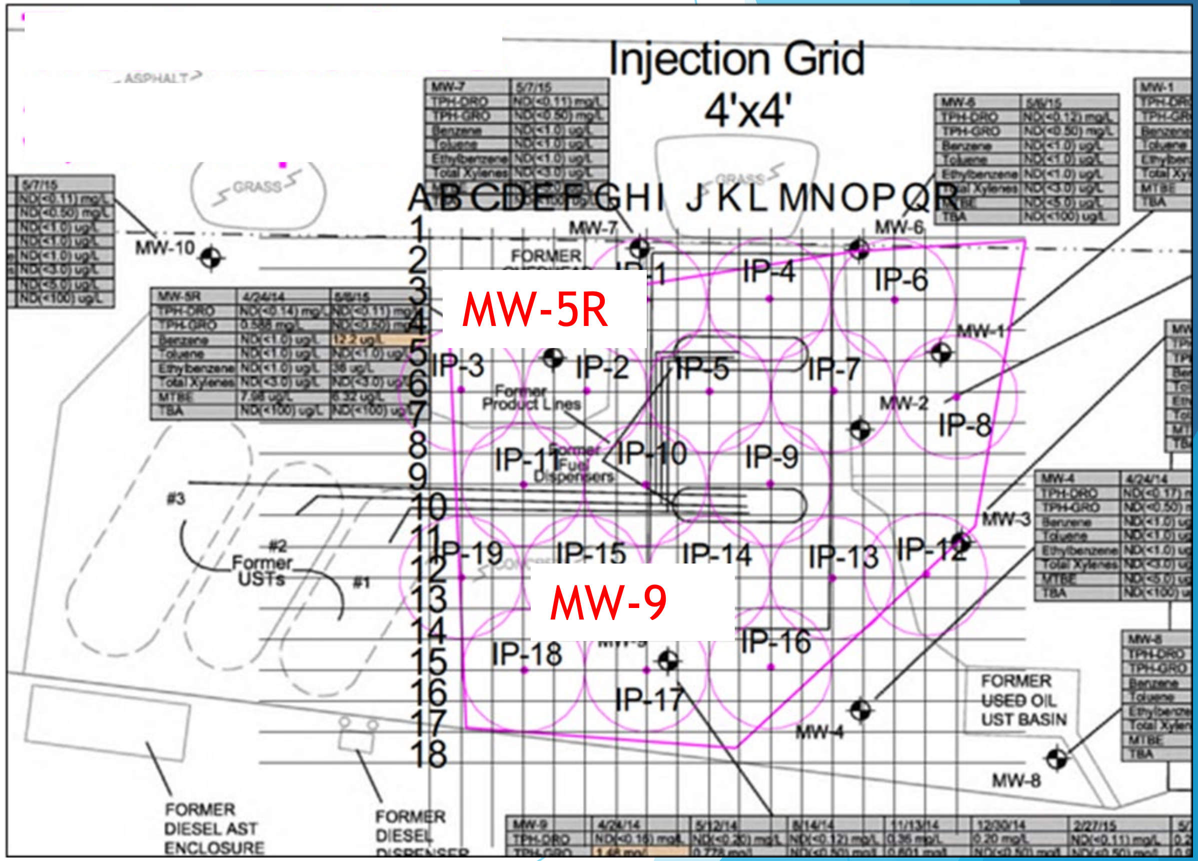
Courtesy Innovative Environmental Technologies, Inc.
Design and Implementation

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

$$Fe^{+3}(OH)_3^{-} + C_6H_6 \text{--->} CO_2 + H_2O + Fe_2+$$

Phase #3 – Sulfate Reduction

$$C_6H_6 + SO_4^{2-} + H_2O \rightarrow H^{+} + HCO^{3-} + HS^{-}$$

Phase #4 – Ferrous Sulfide Formation

$$HS^{-} + Fe^{+2} \rightarrow FeS_2$$

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

Case Study – Mendota

- 12,100 lbs Provect-OX
- 15 g / kg soil
- 5 day application period
- Goals reached
  - PCE 38,000 mg/kg to <900 mg/kg
  - Toluene 4,000 to <100 mg/kg

Starting COI Concentration (ppm)	Ending COI Concentration (ppm)	Treatment Time
38,000 PCE 4,000 Toluene	< 900 PCE < 100 Toluene	1 week

Building on Provect-OX Technology

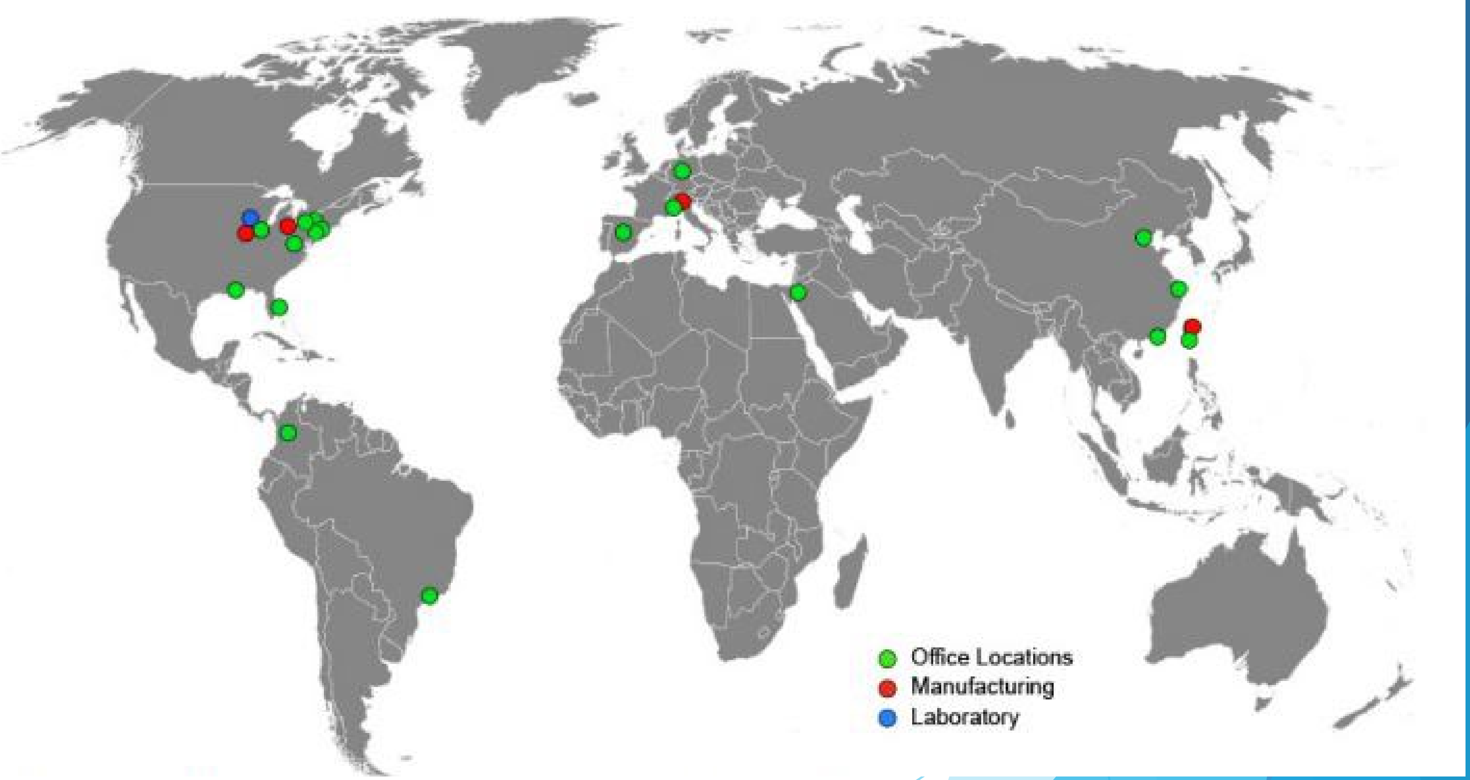
- Provect-OX contains sodium persulfate with a solubility of 55.6 g/100 mL at 20C
- Provect-OX2 combines sodium persulfate + potassium persulfate (solubility of 5 g/100 mL at 20C)
- The potassium persulfate provides an extended release of oxidant for many months versus weeks
- Allows permeable reactive 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!

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