provectus
ENVIRONMENTAL PRODUCTS™

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

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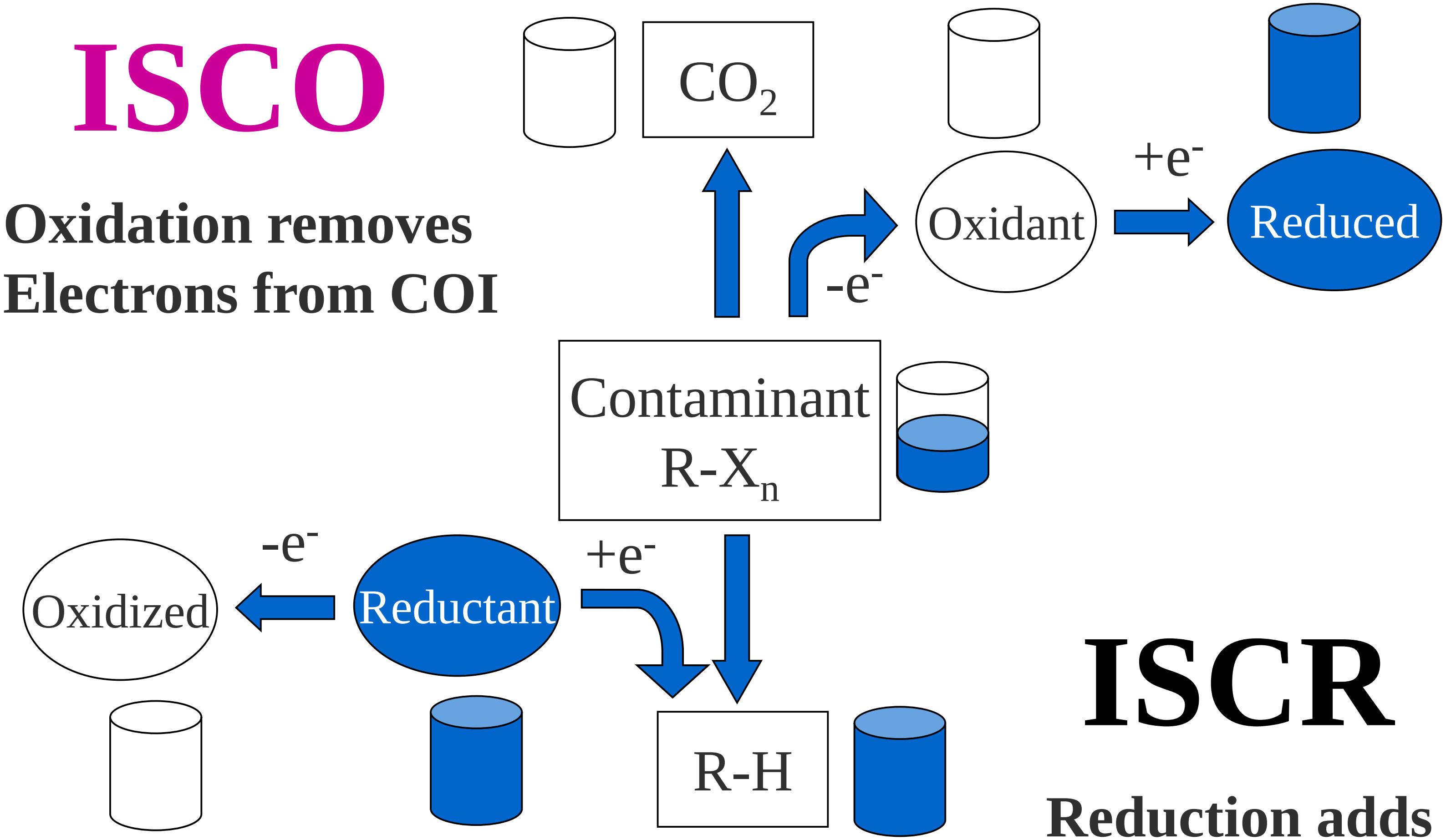
Presentation Outline

- ISCO fundamentals
  - Chemical oxidants and oxidation potentials
  - Partial Oxidation = Known Limitation 1
  - Rebound = Known Limitation 2
- Provect-OX®
  - Composition and Modes of Action
  - *In Situ* Ferrate Production = More Complete Oxidation (addresses KL1)
  - Iron Biogeochemistry = Manages Rebound (addressed KL2)
  - Integrated Fe Reactions yields safer ISCO process (H_2S production)
  - Case Studies
- Summary

Electron Transfer Reactions

ISCO

Oxidation removes Electrons from COI



CO_2

Oxidant

$+e^-$

Reduced

$-e^-$

Contaminant

$R\text{-}X_n$

$-e^-$

Oxidized

Reductant

$+e^-$

R-H

ISCR

Reduction adds Electrons to COI

ISCO = Breaking Chemical Bonds

- Oxidant must be able to accept electrons
  - Capacity = Equivalent weight (MW / No. electrons)
- Ultimate end point is mineralization
  - Partial oxidation is common

Bond Type	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**

Oxidation Potentials of Common ISCO

stronger oxidizer

Oxidation Potentials	Volts
Fluorine (F_2)	2.87
Hydroxyl radical (OH●)	2.80
Persulfate radical (SO_4●)	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

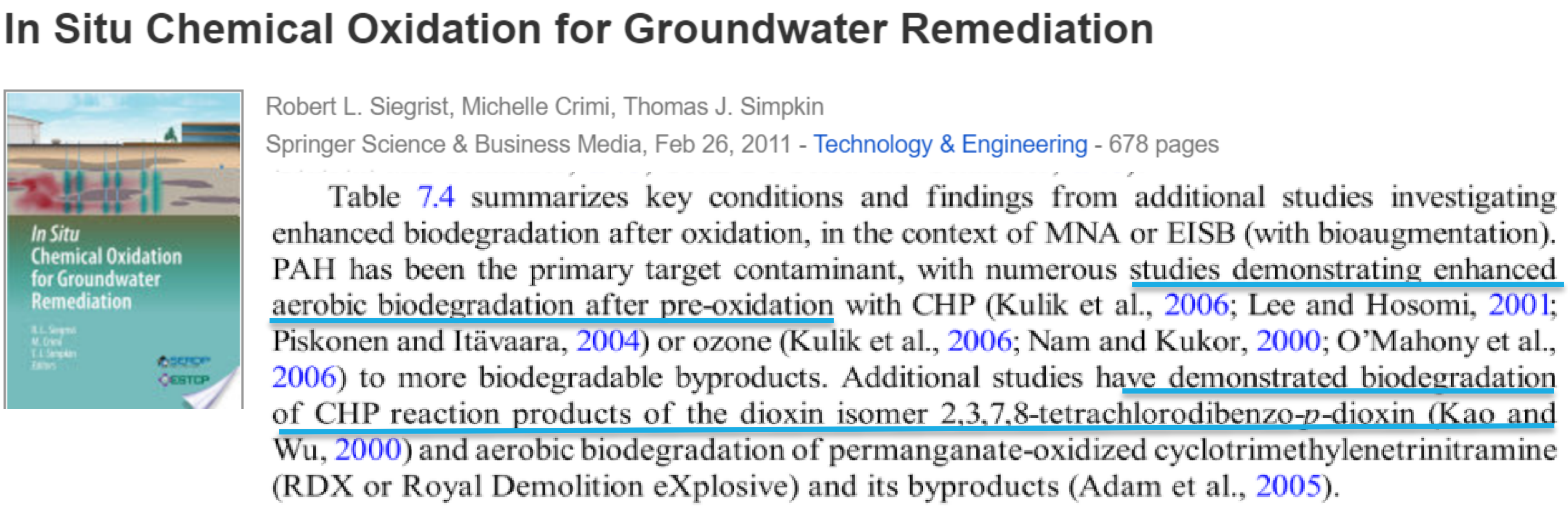
Provect-OX
- Generates Ferrate (Fe IV, V, VI possible)
- Treats wide range of contaminants
- Extended *in situ* lifetime w/ continual production
- Provides Fe as alternative e- acceptor, etc

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

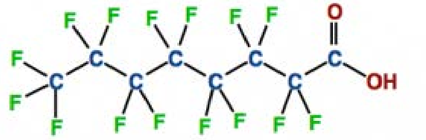


In Situ Chemical Oxidation for Groundwater Remediation

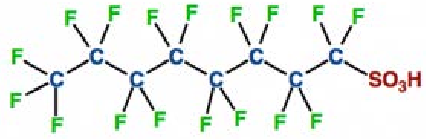
Robert L. Siegrist, Michelle Crimi, Thomas J. Simpkin

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).



PFOA - perfluorooctanoic acid



PFOS - perfluorooctanesulfonic acid

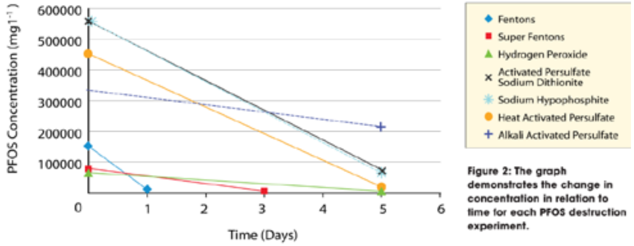


Figure 2: The graph demonstrates the change in concentration in relation to time for each PFOS destruction experiment.

I. Ross, 2012. PE News

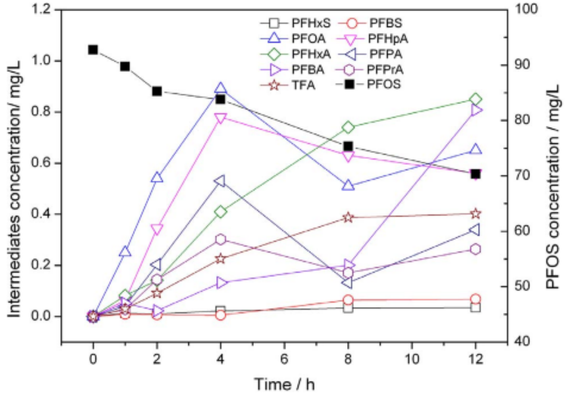


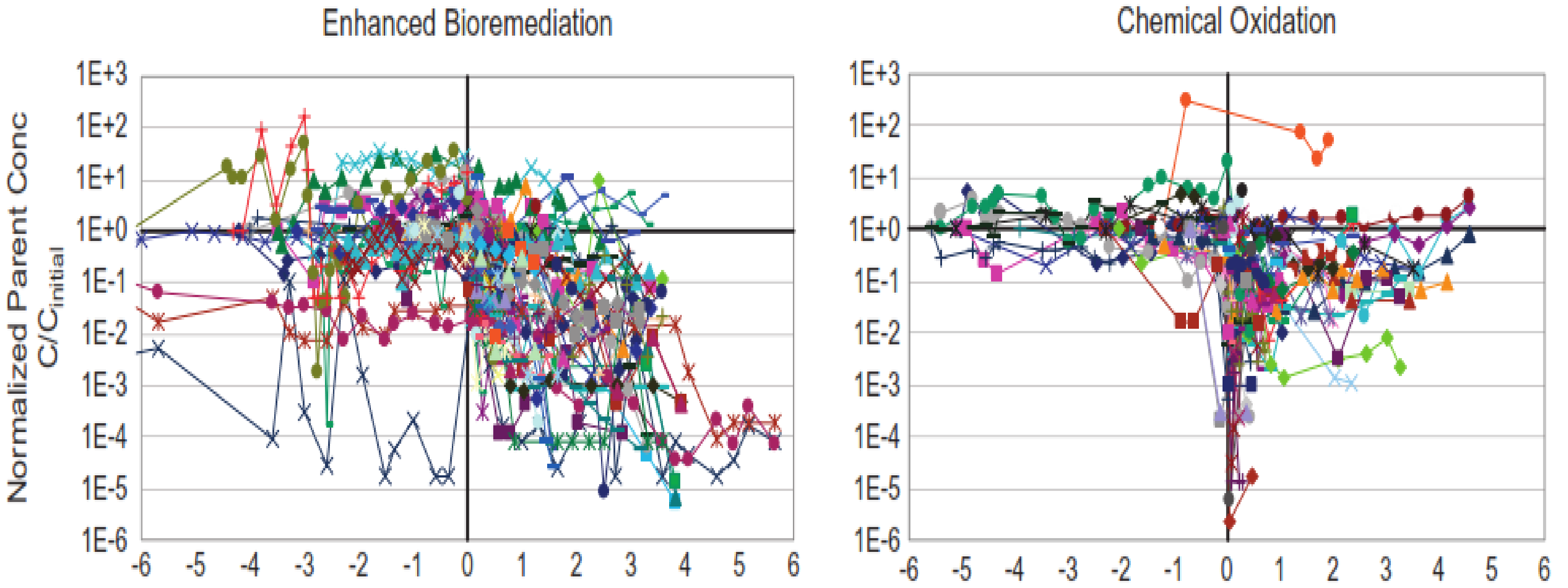
Figure 8. Changes in the concentration of PFOS and intermediates through the PFOS defluorination in UV/$K_2S_2O_8$ system.
doi:10.1371/journal.pone.0074877.g008

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

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.

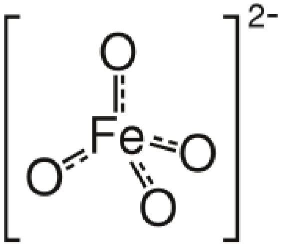
T.M. McGuire et al./ Ground Water Monitoring & Remediation 26, no. 1: 73–84 77

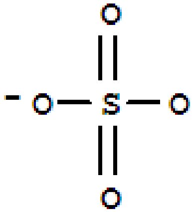


X-axis showing sampling time (years) relative to initial treatment (Time 0)

What is Provect-OX®?

- Sodium Persulfate + Ferric Oxide ISCO Reagent
    - Chemical Oxidation via Sulfate (SO4•) Radical
    - Chemical Oxidation via Ferrate (Fe6+•) Radical
- Enhances Biological Attenuation via Sulfate and Iron Reduction Processes
- Terminating Reaction Results in Pyrite: An Abiotic Reactive Particle with similar Kinetics to ZVI (BiRD / Pseudo-ISCR)
- Easily Transitions from Oxidation to Biological Attenuation to Abiotic Mineralization
- Safely Handled Catalyzed Process without the Hazards of Extreme Activators Caustics





Provect-OX Oxidation Potentials

Ferrate salts can easily be prepared from iron salts, hypochlorite and a base:

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

$$S_2O_8^{-2} + \text{ACTIVATOR}\ [Fe^{+3}] \rightarrow SO_4\bullet^{-} + e^{-} \rightarrow SO_4\bullet^{-2}$$

Oxidation Potentials	Volts
Fluorine (F_2)	2.87
Hydroxyl radical ($OH\bullet$)	2.80
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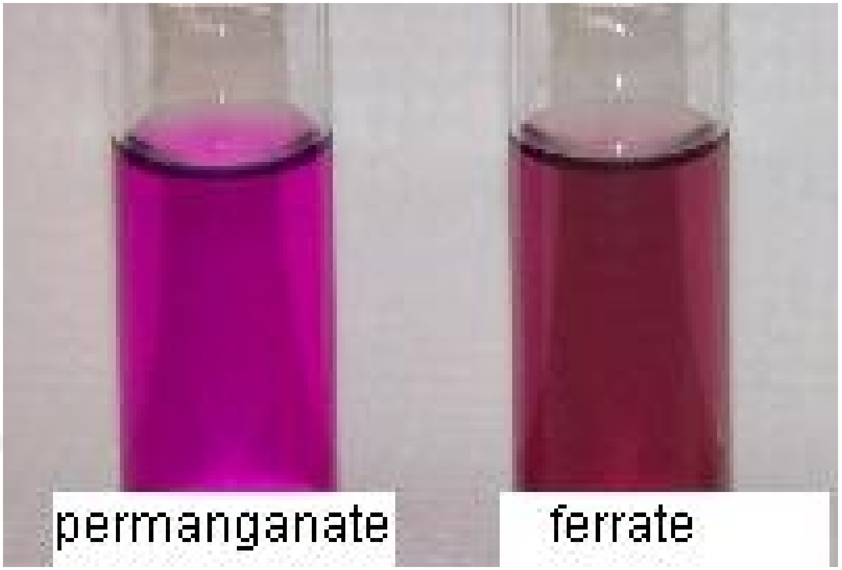
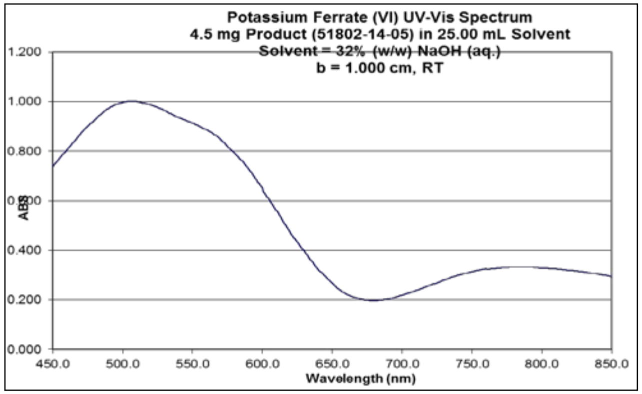
https://sites.google.com/site/ecpreparation/ferrate-vi



Validation of Ferrate Generation

Rx	Provect-OX Composition Persulfate:Fe2O3:ferrate stabilizer (4 hrs)	Abs 515 nM	Ferrate VI [M]
1a	80:20:0 in DI water	<0.4	$<1x10^{-5}$
2a	80:20:0 in buffer (Na_2HPO_4)	<0.4	$<1x10^{-5}$
1b	80:16:4 in DI water	0.330	$2.87x10^{-4}$
2b	80:16:4 in buffer (Na_2HPO_4)	0.306	$2.66x10^{-4}$


Potassium Ferrate (VI) UV-Vis Spectrum
4.5 mg Product (51802-14-05) in 25.00 mL Solvent
Solvent = 32% (w/w) NaOH (aq.)
b = 1.000 cm, RT

$$C_{Fe(VI)} = \frac{A_{515}}{\varepsilon_{515} * l}$$

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

Ferrate Improves ISCO Performance

- Ferrates (Fe^{+6}, Fe^{+5} and Fe^{+4}) are very powerful oxidants that can expand the applications of ISCO to more persistent COIs (*e.g.*, PFOS/PFOA)

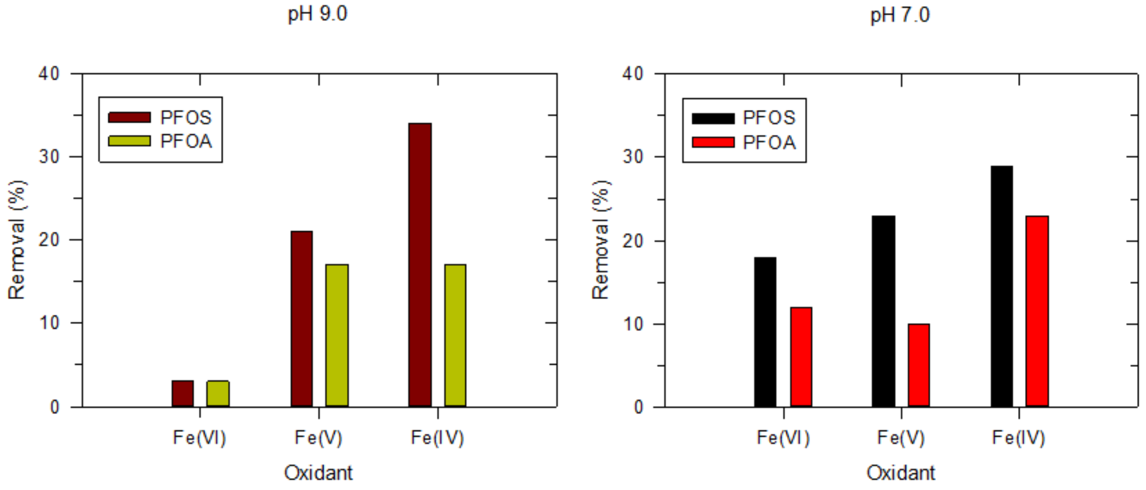
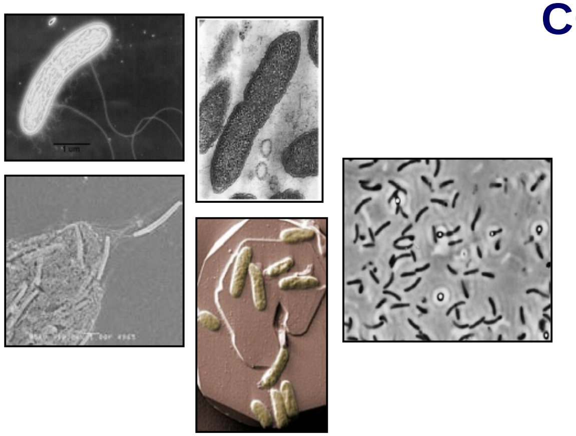


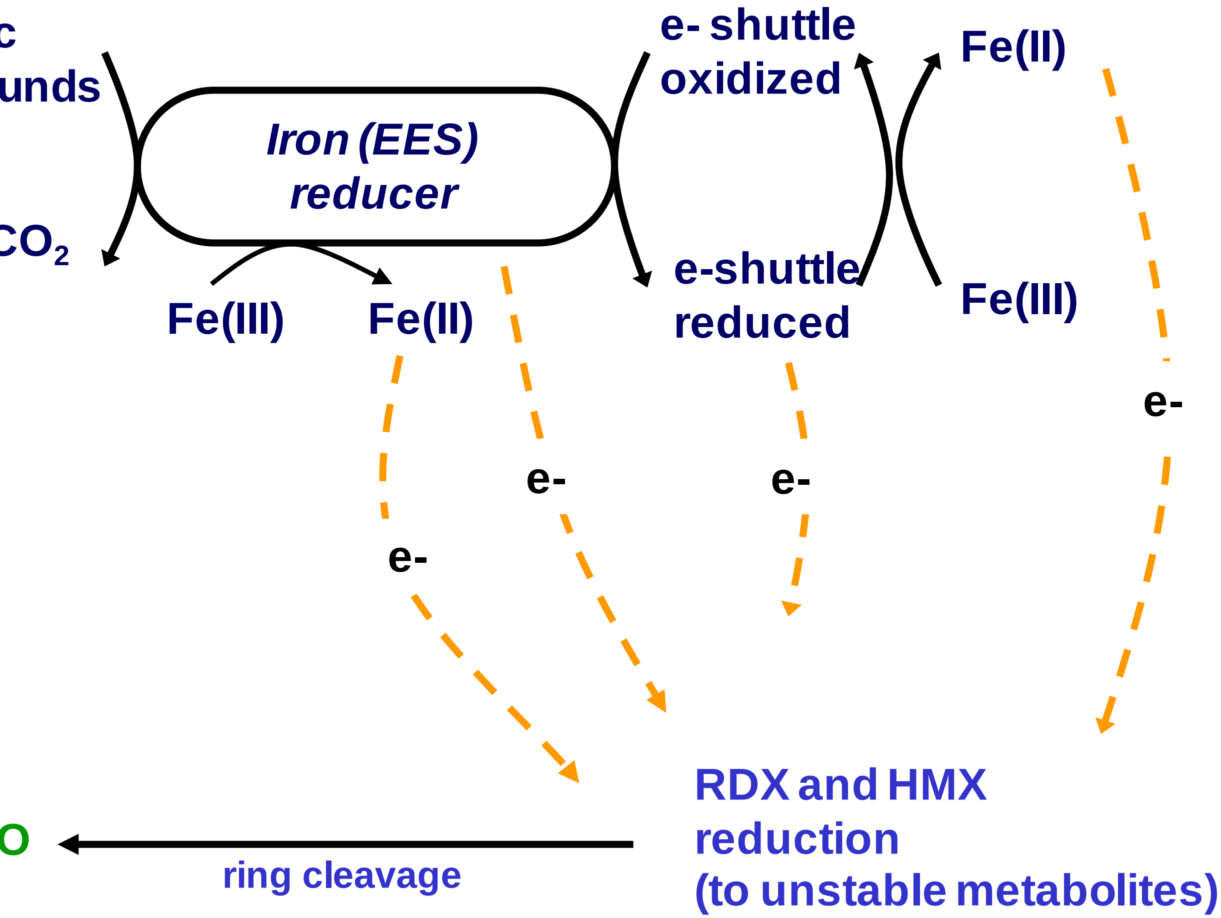
Figure 3. Oxidation of perfluorooctylsulfonate and perfluorooctanoic acid by one application of ferrates at pH 9.0 and 7.0 after five days.

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

- “Continuous” ferrate generation *in situ* w/ buffered conditions
  - proprietary ferrate stabilizer
  - requires active oxidant
  - Fe present in excess, persistent [years] and relatively immobile

Fe-Reducing Bacteria aid COI Removal





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

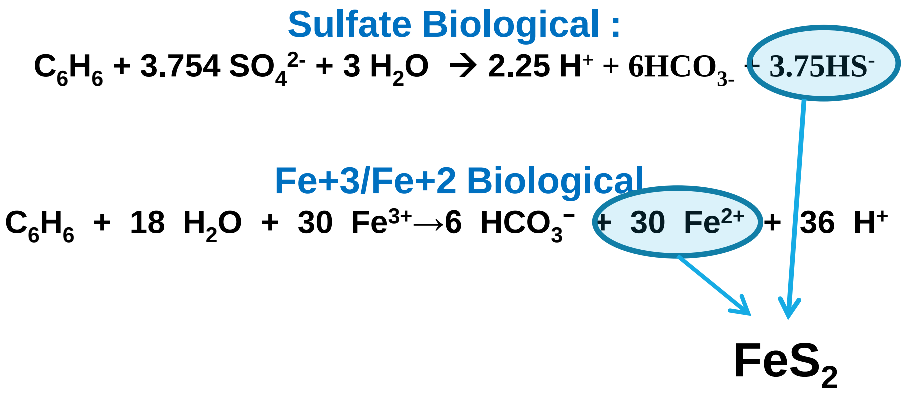
$HCHO, CO_2, N_2O$

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

Fe-Reducing Bacteria aid H_2S Removal

Oxidation Reactions:

S2O8- + Fe0 → Fe+3 + SO4- + SO4-2.
S2O8- + Fe(III) → Fe(IV) → Fe(V) → Fe(VI)



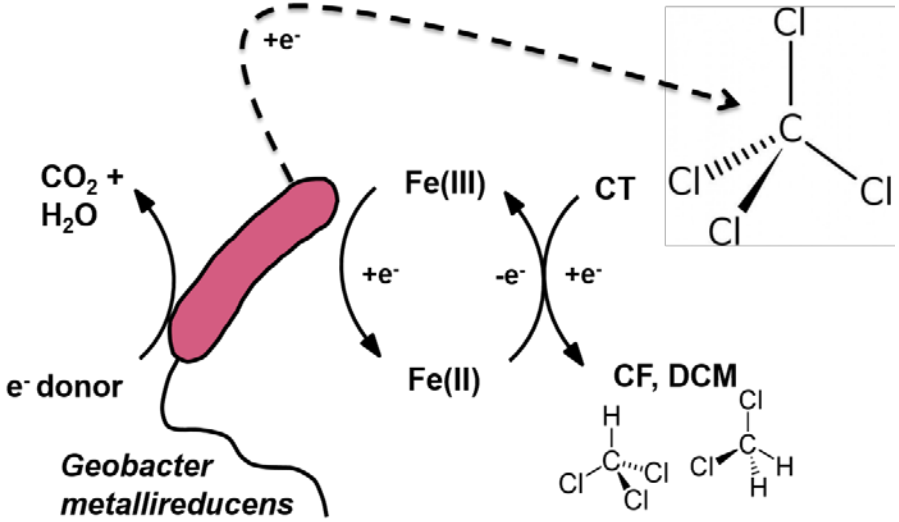
Sulfate Biological :

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

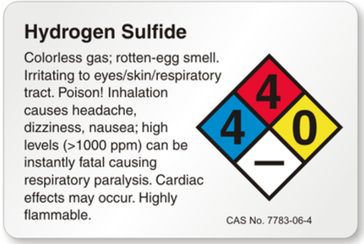
Fe+3/Fe+2 Biological

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

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 poisonous 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

Buffered Provect-OX®
Coupled Oxidation w/ Sustained Bioremediation

US Patent 9,126,245;

patents pending

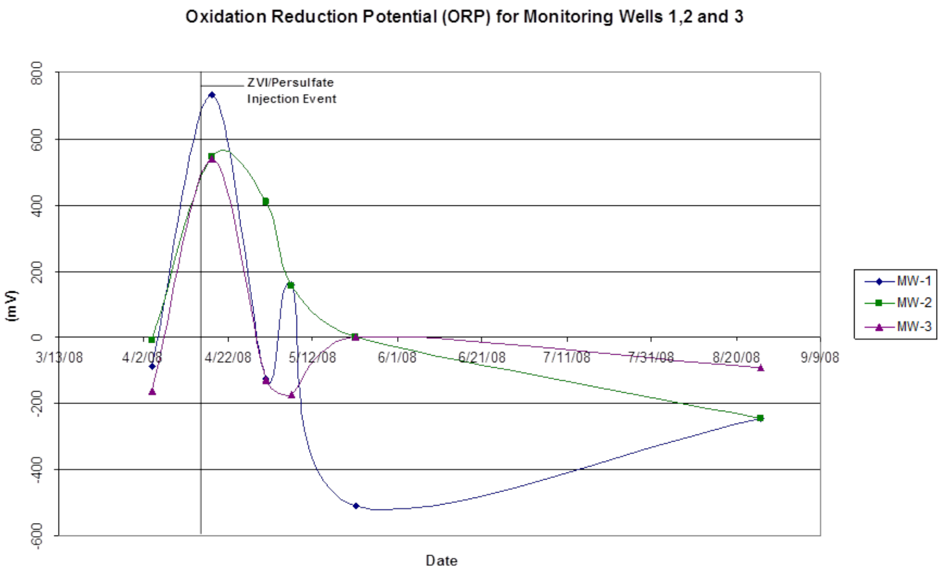
- **Safely Handled; All in one bag**
- **Uses Fe^{+3} as activator**
  - **No Heat generated = safer**
  - **Conserves Oxidant**
  - **Enhances Bioattenuation Fe + SO_4**
  - **Encourages the Formation of Pyrite**
  - **Minimizes release of H_2S**
  - **Minimizes heavy metal mobilization**
- **Formation of Reactive Ferrate Species**
- **Proprietary reactive ferrate stabilizer**

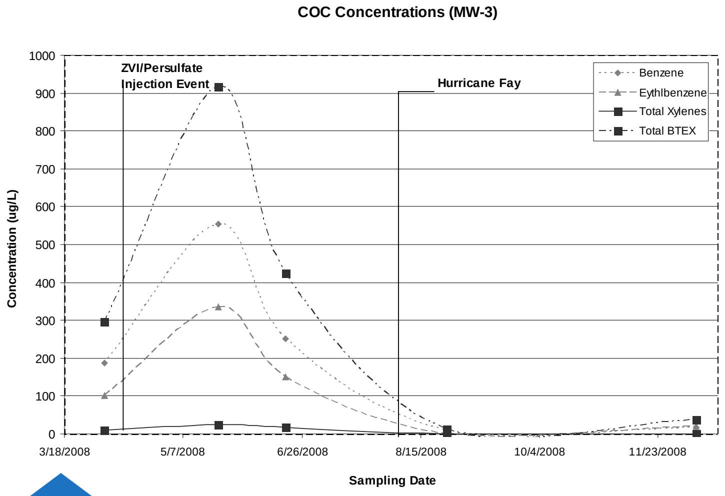
- **When Chelated Fe^{+2} used as activator EDTA Consumes the Oxidant**
- **When Caustic is used as activator**
  - **Short Lived Reaction**
  - **H_2S Formed**
  - **Secondary plumes / metals (Cr)**
  - **Can generate extreme heat**
  - **Handling and Safety issues**

pH 10+ Does Not Promote Bio

Does Not Manage Rebound

Treatment of BTEX and TMB using Provect-OX


Oxidation Reduction Potential (ORP) for Monitoring Wells 1,2 and 3


COC Concentrations (MW-3)

Phase #1 - Oxidation

S2O8- + Fe0 → Fe+3 + SO4- + SO4-2.
S2O8- + Fe(III) → Fe(IV) → Fe(V) → Fe(VI)

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

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

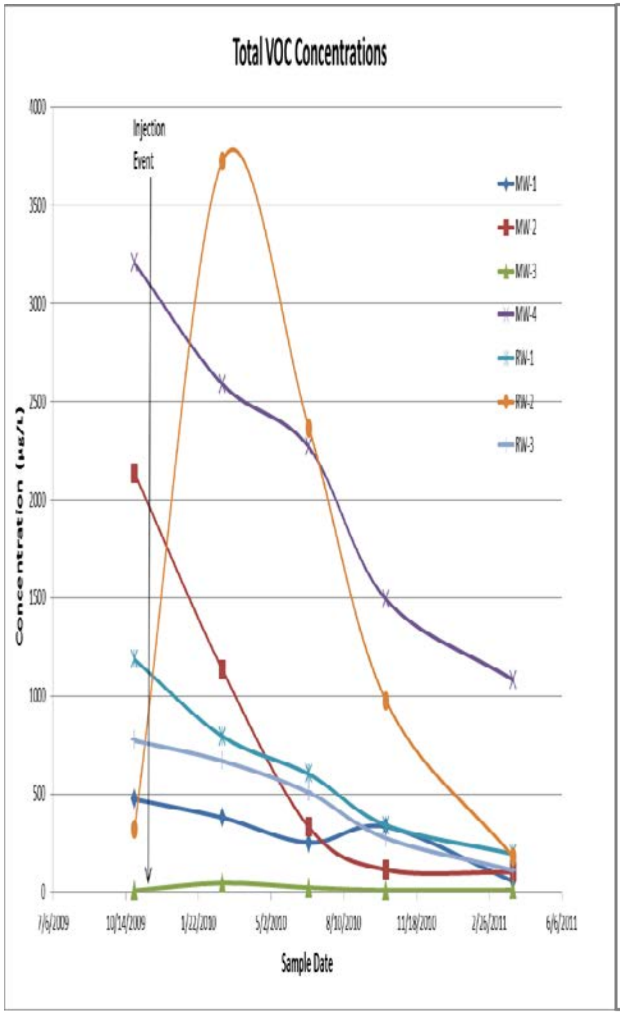
Provect-OX Field Case Study – NJ Site

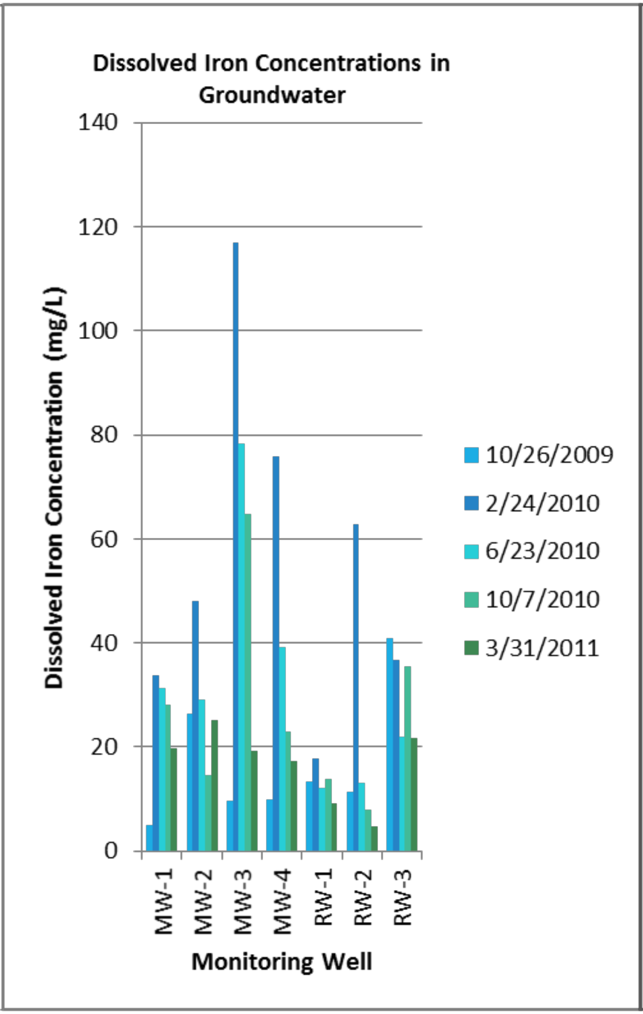
- 4,392 lbs injected
- 75 usg / 35 dpt

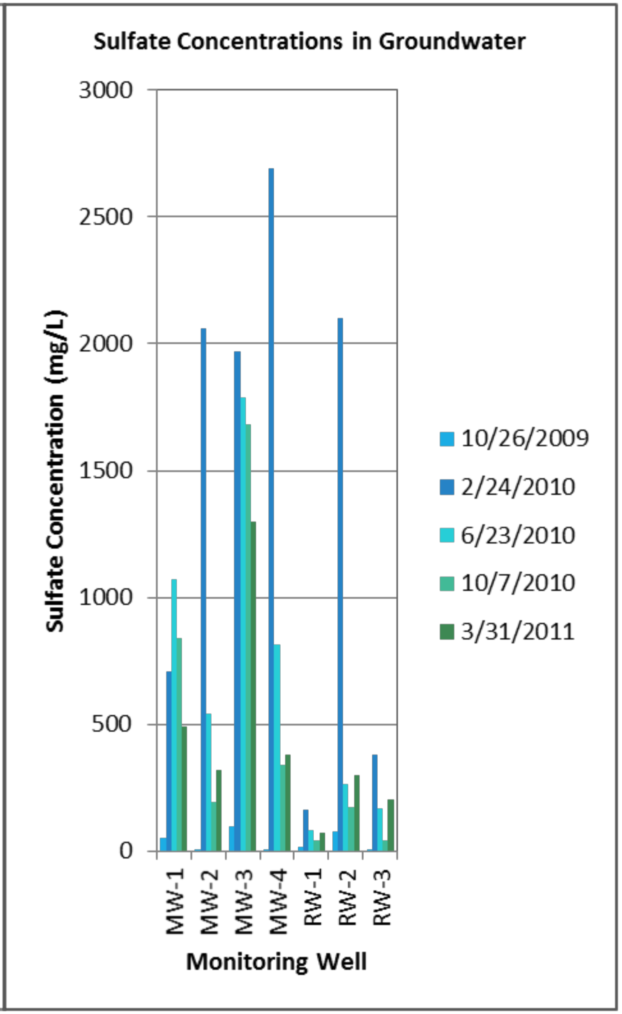
	MW-2				
Sampling Date	06/20/2013	10/02/2013	11/26/2013	02/28/2014	05/28/2014
pH	7.27	6.88	6.89	6.86	7.43
ORP (mV)	-14	+220	+86	+55	-40
D.O. (mg/L)	2.17	0.76	0.90	0.85	0.83
Conductivity (mS/cm)	0.97	3.44	1.52	2.38	1.55
Temperature (°C)	17.7	20.4	17.0	12.2	14.3
Groundwater Elevation (ft)	94.05	90.43	88.86	92.93	93.70
Sulfate (mg/L)	56.6	1,510	266	980	332
Total Iron (mg/L)	0.377	2.01	0.149	0.089	0.160
Dissolved Iron (mg/L)	0.249	1.83	0.0097	ND	ND
Benzene (ppb)	ND	7.20	43.4	ND	ND
Toluene (ppb)	ND	2.33	0.38	ND	ND
Ethylbenzene (ppb)	ND	4.08	ND	ND	ND
Total Xylenes (ppb)	ND	21.04	3.16	ND	ND

Provect-OX *In Situ* Field Case Study

Demonstrated Sulfate and Iron Utilization as Terminal Electron Acceptors







Upstate New York Site

Provect-OX Field Case Study - Posters

- **12,100 lbs Provect-OX**
- **15 g /kg soil**
- **5 day application period**
- **RAO <Target Csat Soil**

PCE < 2,420 (above 1m)
PCE <1,254 (below 1m)
Toluene < 1,654

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

Summary

- **Provect-OX contains persulfate + ferric oxide + proprietary ferrate stabilizer (ratios can vary based on site conditions)**
- **Combination of chemistries + *in situ* ferrate generation expands the range and improves the effectiveness of ISCO projects**
- **Excess Fe sustains secondary bioremediation processes that help manage COI rebound**
- **Safer ISCO chemistry (all components in one bag, minimizes generation of H_2S explosive / poisonous gas, minimizes heavy metal mobilization to avoid secondary plumes)**
- **Other benefits relate to safety, regulatory compliance, and sustainability**

Provectus Environmental Products

OUR TECHNOLOGIES

Provect-IR® Solid, Antimethanogenic ISCR Reagent
As the prime developer of the original EHC® ISCR reagent, staff now at Provectus know that Provect-IR is a genuine improvement on the ISCR process and its older product formulations. Provect-IR uses carbon substrate more efficiently and therefore is more cost effective. Remedial designs can use less amendment and get expected results without excessive methane generation.

Provect-IRM® Solid Antimethanogenic ISCR / Metal Stabilization Reagent
More effective means of metal immobilization/ISCR that minimizes production of methylmetal(loids) for safer, more effective, long-term immobilization.

Provect-OX™ Self-Activating ISCO/ Enhanced Bioremediation Reagent
Persulfate-based ISCO reagent that is unique in terms of its safety (no extreme activators; no heat generated) and effectiveness, as it actively integrates ferrate chemistry and enhanced bioremediation as part of the overall treatment process – only ISCO reagent designed to manage rebound.

Provect-CH4® Methanogen Inhibitor and ERD/ISCR Supplement
Water-soluble amendment to effectively control methane production when combined with various ERD amendments (*e.g.*, [emulsified] oils, lecithin, lactates, molasses, sugars, etc.) or conventional ISCR reagents.

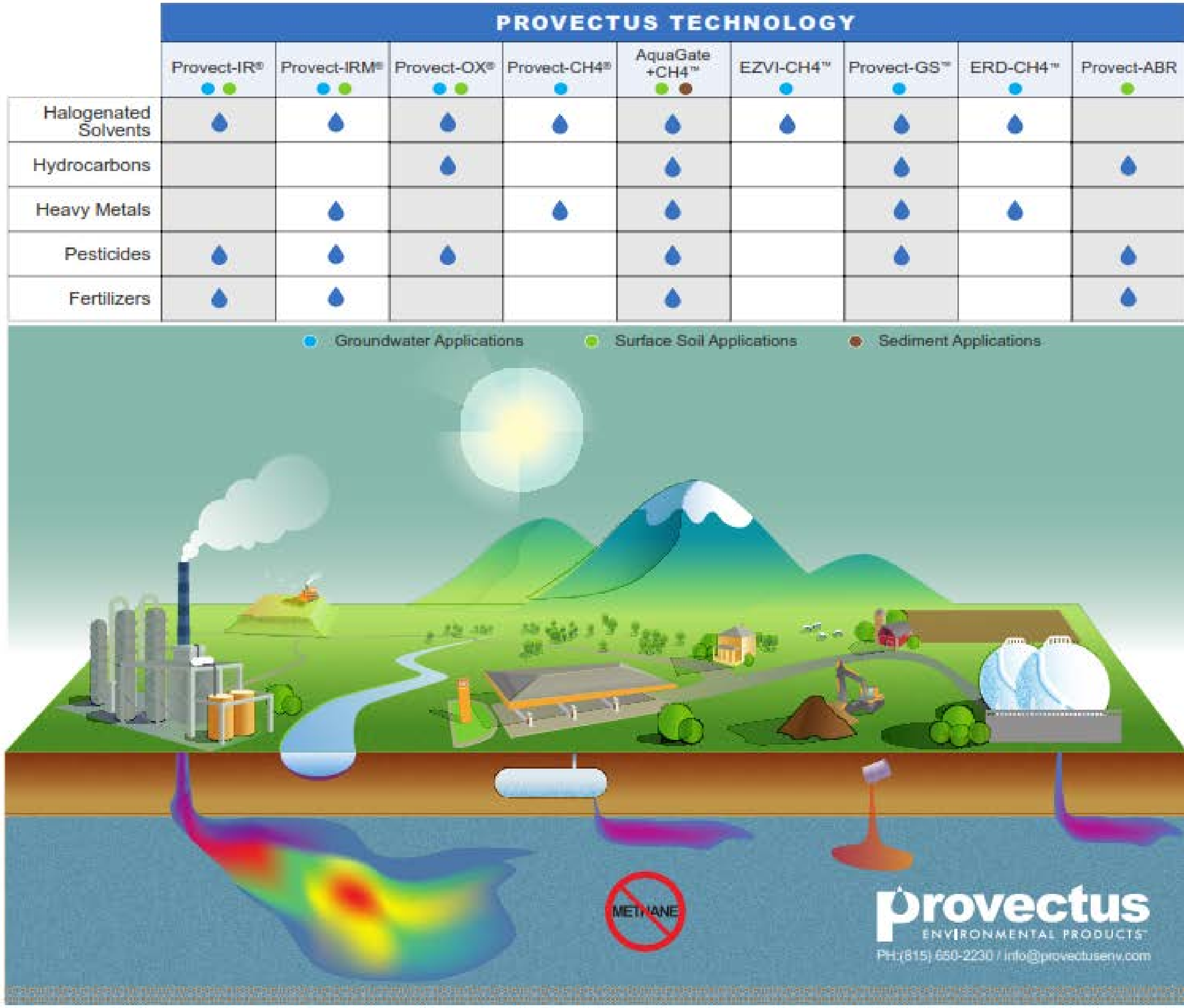
AquaGate+CH4™ Antimethanogenic Reactive Capping Technology
Developed in collaboration with AquaBlok, LTD subaqueous caps can be constructed more effectively by minimizing gas ebullition and contaminant methylation.

EZVI-CH4™ Antimethanogenic DNAPL Treatment
Unique reagent can be used for safe and effective treatment of chlorinated solvent DNAPL sources.

Provect-GS™ NAPL Immobilization Technology
A liquid reagent developed in collaboration with Beazer East, Inc. for *in situ* geophysicochemical immobilization (ISGI) of DNAPL sources.

ERD-CH4™ Liquid Antimethanogenic ISCR Reagent
Liquid, antimethanogenic ERD amendment that can be applied via screened systems. By inhibiting methanogenesis, this is a more efficient, longer-lived and safer ERD approach.

Provect-ABR Aerobic Bioremediation Reagent
Soil amendment for accelerated aerobic biodegradation of organic compounds.



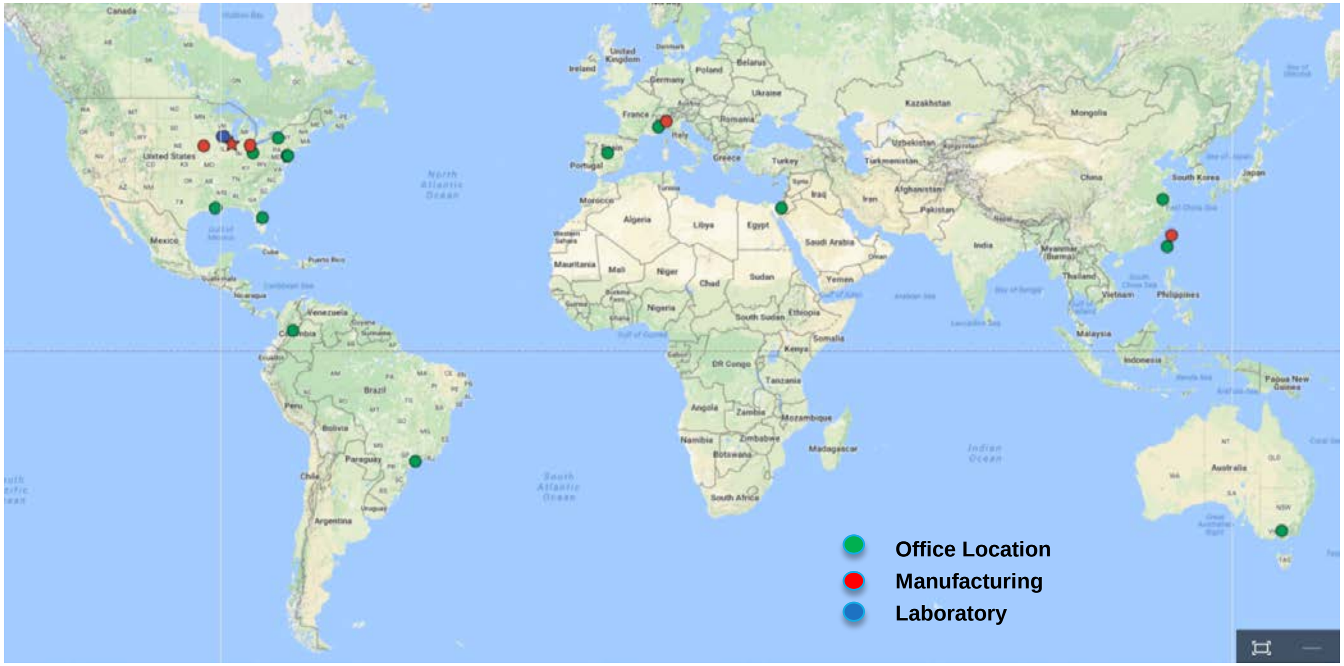
PROVECTUS TECHNOLOGY

	Provect-IR® 🔵 🟢	Provect-IRM® 🔵 🟢	Provect-OX® 🔵 🟢	Provect-CH4® 🔵	AquaGate +CH4™ 🟢 🟤	EZVI-CH4™ 🔵	Provect-GS™ 🔵	ERD-CH4™ 🔵	Provect-ABR 🟢
Halogenated Solvents	💧	💧	💧	💧	💧	💧	💧	💧	
Hydrocarbons			💧		💧		💧		💧
Heavy Metals		💧		💧	💧		💧	💧	
Pesticides	💧	💧	💧		💧		💧		💧
Fertilizers	💧	💧			💧				💧

🔵 Groundwater Applications 🟢 Surface Soil Applications 🟤 Sediment Applications

Provectus Environmental Products

- Complimentary Site Evaluation
- Complimentary review of quarterly field performance data for 1 year with every project
- Laboratory Treatability Studies
- Turn-Key, Pay-for-Performance Contracting Options
- Project Specific Guarantees and Warranties



- USA (Illinois, New York, Ohio, Pennsylvania, Louisiana)
- Australia, Brazil, China, Colombia, Israel, Italy, Spain and Taiwan

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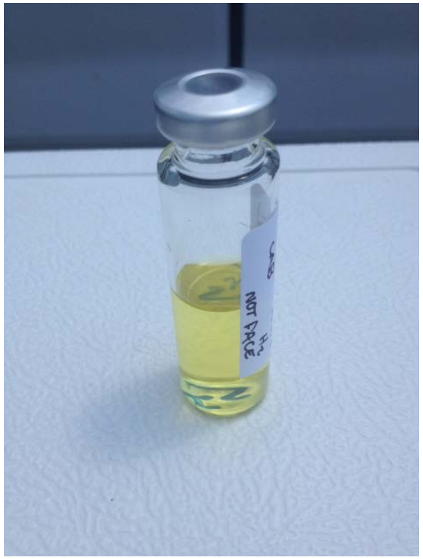

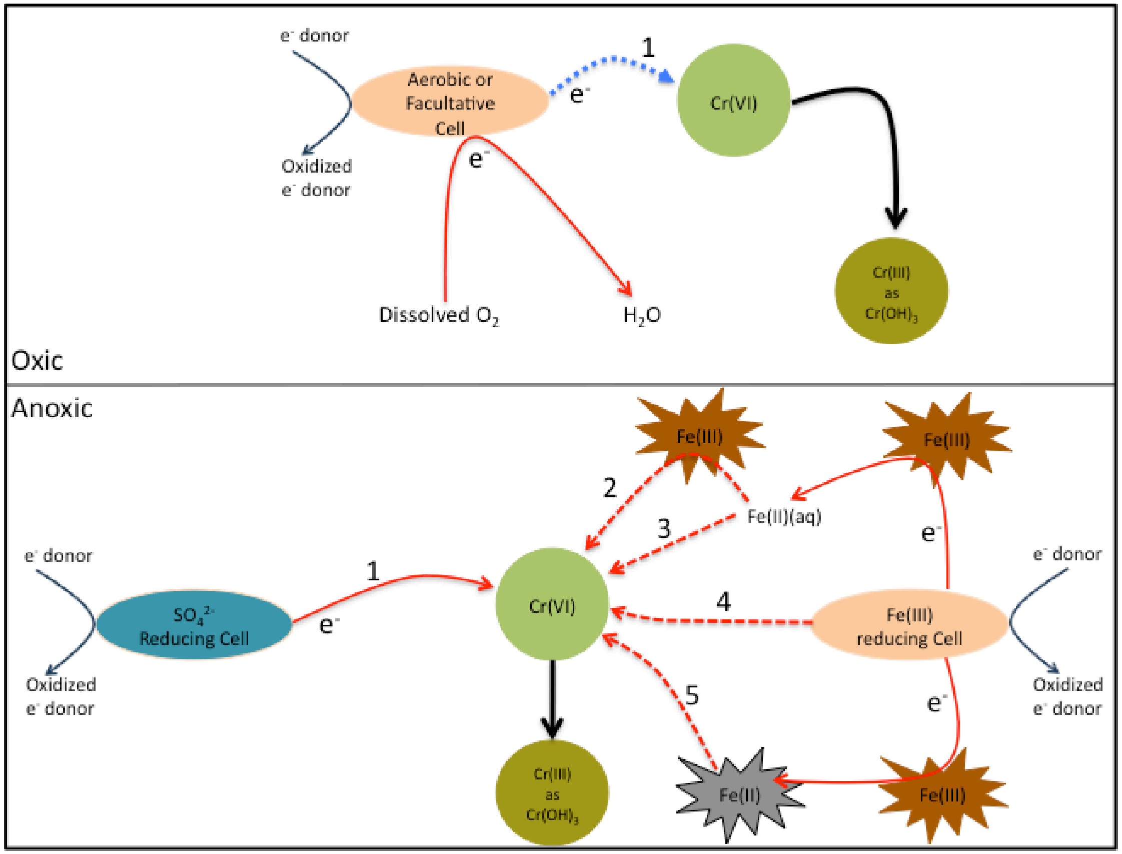

Conceptual model of combined biotic-abiotic Cr(VI) reduction