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

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

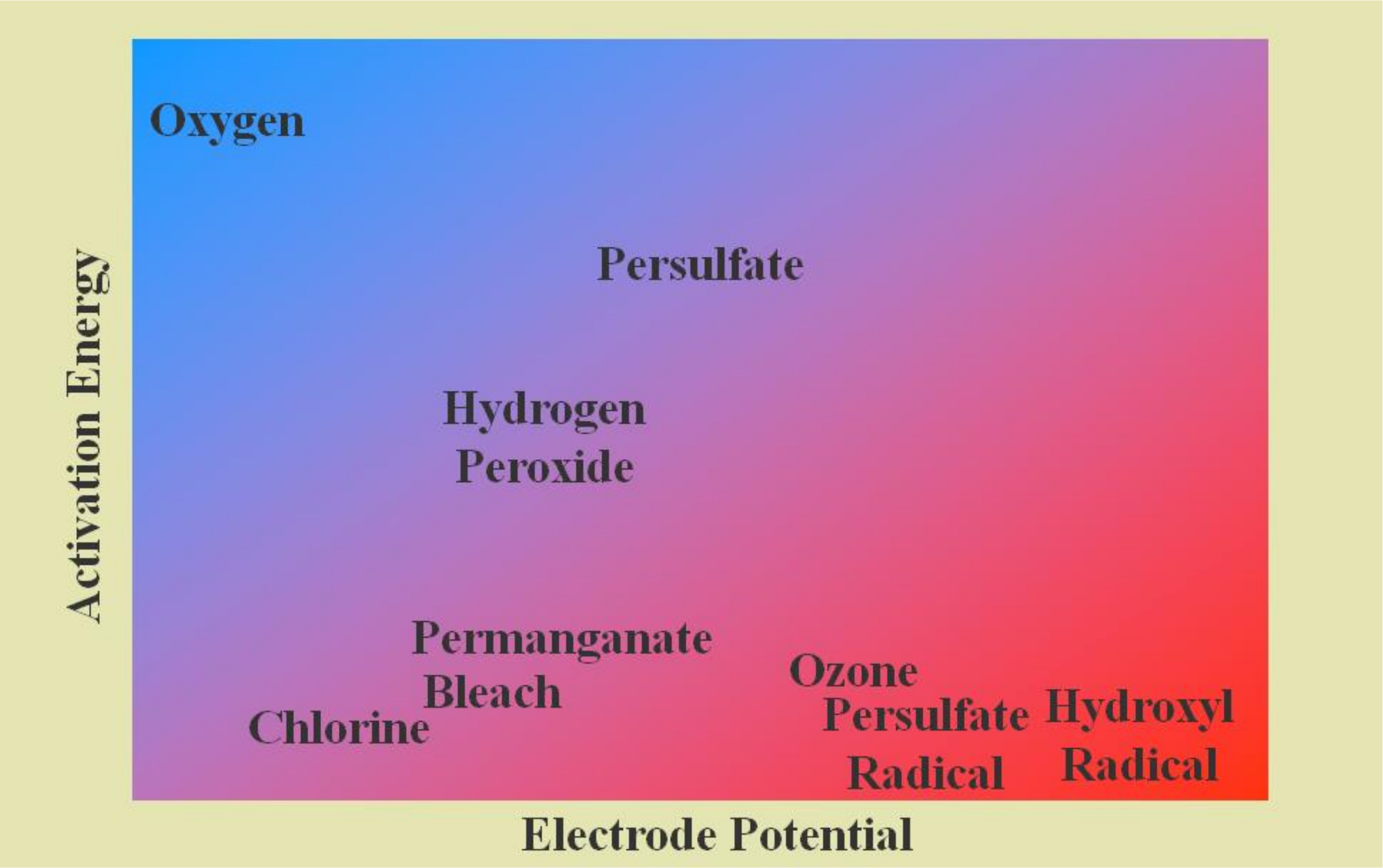
In Situ Chemical Oxidation (ISCO)

- ISCO involves:
  - Injection of an oxidizing agent into the subsurface to destroy organic compounds.
  - The by-products for complete mineralization include carbon dioxide (CO_2), water (H_2O) and oxygen (O_2).
- Goal is to mineralize or transform contaminants of concern (COCs)

Common Oxidizing Agents

Oxidant	Potential (V)	Form
Fenton’s Reagent ($OH^{\bullet}$)	2.80	Liquid
Activated Persulfate ($SO_4^{-\bullet}$)	2.60	Salt/Liquid
Ferrate (Fe^{6+})	2.20	
Ozone (O_3)	2.07	Gas
Persulfate ($S_2O_8^{2-}$)	2.01	Salt/Liquid
Hydrogen Peroxide (H_2O_2)	1.78	Liquid
Permanganate (MnO_4^-)	1.68	Salt ($KMnO_4$) Liquid ($NaMnO_4$)

Reactivity of Oxidizing Agents



Basic Oxidizing Agent Reactions

Ozone (No Activator)

- $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$ E_o=2.07 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 V

Persulfate (Requires Activation)

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

Hydrogen Peroxide (Requires Activation)

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

Permanganate (No Activator)

- $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ E_o=1.70 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_2Cl_2	TCA, CT, $CHCl_3$	Stability (25-95% decomp/hr), low pH
Peroxide, New Fenton's	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA	DCA, CH_2Cl_2,TCA, CT, CHCl3		Stability (10-50% decomp/hr)
Potassium Permanganate	PCE, TCE, DCE, VC, TEX, PAH	MTBE, TBA	TCA, CT, B, $CHCl_3$, DCA, CB, CH_2Cl_2	Soil oxidant demand
Sodium Permanganate	PCE, TCE, DCE, VC, TEX, PAH	MTBE, TBA	TCA, CT, B, $CHCl_3$, DCA, CB, CH_2Cl_2	Soil oxidant demand
Sodium Persulfate, Fe	PCE, TCE, DCE, VC, CB, BTEX, PAHs, MTBE, TBA	DCA, CH_2Cl_2, $CHCl_3$	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_2Cl_2, $CHCl_3$, TCA, CT	Mass Delivery, Volatilization

Limitations of Traditional Persulfate Activation Techniques

- **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

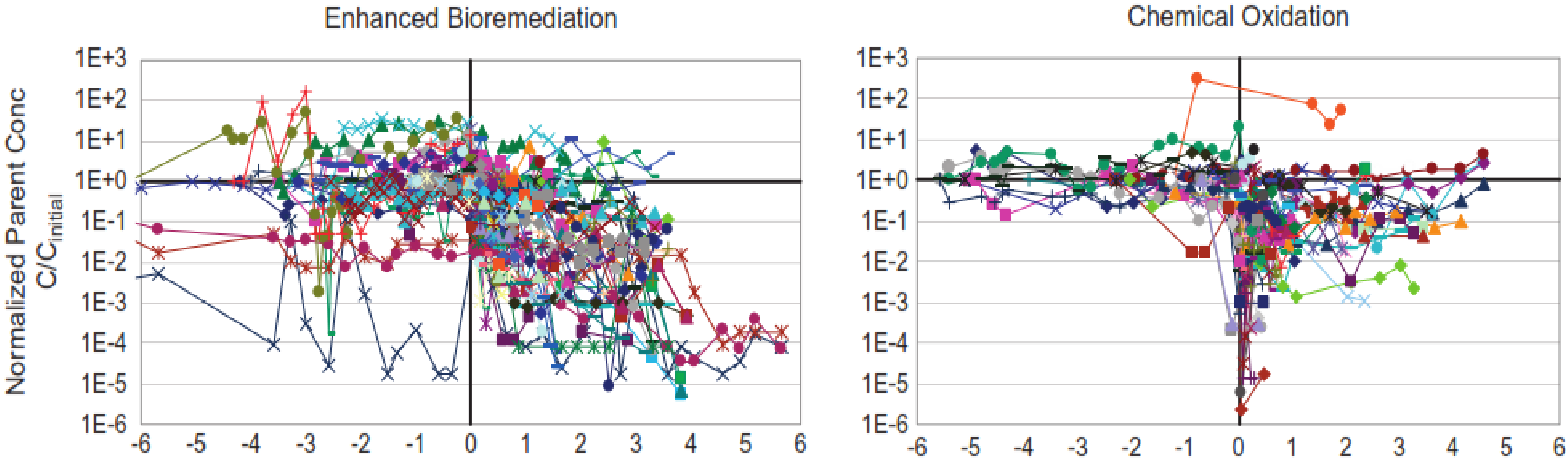


Figure 1. Temporal concentration records for wells at source depletion sites. Concentration is normalized by the initial measured concentration. Sampling time is normalized by the time of the initial source depletion treatment.

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

Self-Activating ISCO / Enhanced Bioremediation Reagent

Provect-OX™ = Sodium Persulfate + Ferric Oxide (Fe_2O_3)

- Chemical Oxidation via Sulfate ($SO_4^{\bullet}$) Radical
- Chemical Oxidation via Ferrate ($Fe^{6+\bullet}$) Radical

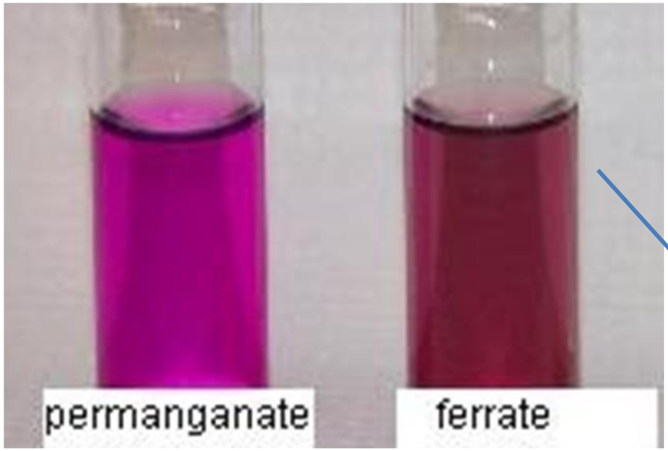
$$2\ Fe^{3+} + 3\ OCl^{-} + 4\ OH^{-} \rightarrow 2\ \mathbf{FeO_4^{2-}} + 3\ Cl^{-} + 2\ H_2O$$

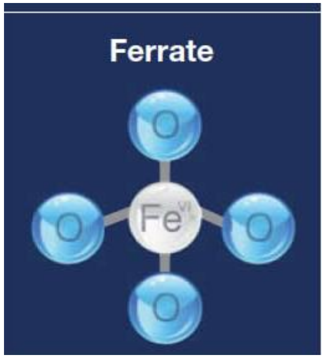
$$S_2O_8^{2-} + \text{ACTIVATOR } [Fe^{3+}] \rightarrow SO_4^{-}\bullet + e^{-} \rightarrow SO_4^{2-}\bullet$$

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

Oxidation Potentials	Volts
Fluorine (F_2)	2.87
Hydroxyl radical ($OH\bullet$)	2.80
Persulfate 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





Provect-OX™ ISCO Processes

- 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

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:

$$C_6H_6 + 3.75\ SO_4^{2-} + 3\ H_2O \text{ --> } 0.37\ H^+ + 6\ HCO_3^- + 1.87\ HS^- + 1.88\ H_2S^-$$

$$C_7H_8 + 4.5\ SO_4^{2-} + 3\ H_2O \text{ --> } 0.25\ H^+ + 7\ HCO_3^- + 2.25\ HS^- + 2.25\ H_2S^-$$

Provect-OX™ Biological Attenuation Processes

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

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

$$C_7H_8 + 21\ H_2O + 36\ Fe^{3+} \text{------->} 7\ HCO_3^- + 36\ Fe^{2+} + 43\ H^+$$

$$C_8H_{10} + 24\ H_2O + 42\ Fe^{3+} \text{------->} 8\ HCO_3^- + 42\ Fe^{2+} + 50\ H^+$$

- 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

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

$$\mathbf{Fe^{2+} + 2S^{2-} \text{ -------> } FeS_2 + 2e}$$

Provect-OX™ Potential Advantages

- 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

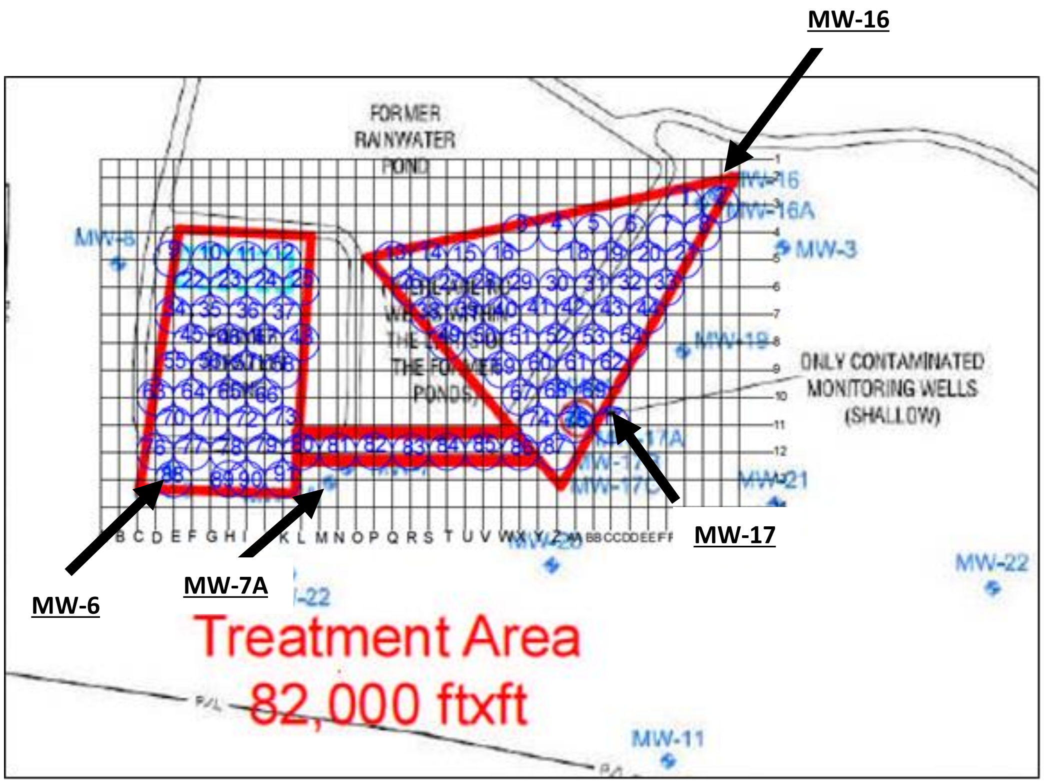
- Uses Fe^{3+} as activator (no persulfate "Master Supplier")
- Conserves Oxidant – Unlike other Persulfate Activators
- Multiple ISCO processes via formation of reactive ferrate species = better ISCO
- Enhances bio attenuation utilizing both iron and sulfate reduction

- Encourages the formation of pyrite / Prevents H_2S formation
- Long-lived reactions – sustained treatment manages rebound
- Cost-effective – reduces need for multiple injection events

Provect-Ox™ Case Study 1

- Single injection event at a wood treating facility in Midwestern United States in July 2013 to remediate soils and groundwater impacted by the historical release of heavy ended petroleum compounds.
- Total treatment area of approximately 82,000 square feet, treating between 13 and 22 feet below ground surface.

  - ➢ 91 injection points
  - ➢ Spaced 34 ft apart
  - ➢ 22,022 lbs of Provect-OX



Injection Equipment

IET 20' MOBILE INJECTION SYSTEM

Injection Feed Tank – Configuration

Feed Systems, Safety Systems, Compressed Gas Systems
All piping Welded Stainless Steel
Floors Coated in Chemical Resistant RinoLining

Case Study 1 - Groundwater SVOC Analytical Data

Table 1. VOC Data for MW-6 (µg/L).

MW-6				
Sampling Date	**07/2013**	**10/2013**	**01/2014**	**04/2014**
Benzo(a)pyrene	17,000	ND	ND	ND

ND: Not Detected

Table 2. VOC Data for MW-7A (µg/L).

MW-7A				
Sampling Date	**07/2013**	**10/2013**	**01/2014**	**04/2014**
Benzo(a)pyrene	18,000	ND	ND	ND

ND: Not Detected

Table 3. VOC Data for MW-16 (µg/L).

MW-16				
Sampling Date	**07/2013**	**10/2013**	**01/2014**	**04/2014**
Benzo(a)pyrene	20,000	ND	ND	ND

ND: Not Detected

Table 4. VOC Data for MW-17 (µg/L).

MW-17				
Sampling Date	**07/2013**	**10/2013**	**01/2014**	**04/2014**
Benzo(a)pyrene	19,000	ND	ND	ND

ND: Not Detected

Provect-OX™ Case Study 2

- Single injection event implemented at a former gas station in Northern New Jersey in August 2013 to remediate soils and groundwater impacted by the historical release of BTEX compounds.
- Total treatment area of approximately 3,100 square feet, treating between 4 and 14 feet below ground surface.

- ➢ 26 injection points
- ➢ Spaced 8-10 ft apart
- ➢ 4,392 lbs of Provect OX

Case Study 2 – Field Parameters & VOC Analytical Data

	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 (^{o}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

	MW-2				
Sampling Date	06/20/2013	10/02/2013	11/26/2013	02/28/2014	05/28/2014
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

Case Study 2 – Field Parameters & VOC Analytical Data

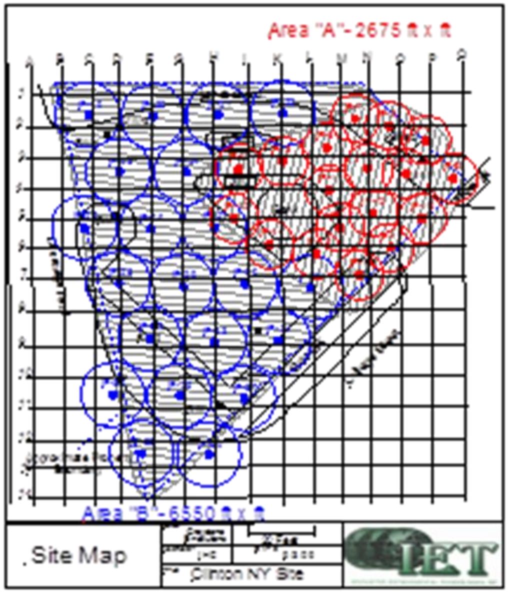
	MW-5						
Sampling Date	06/2013	10/2013	11/2013	02/2014	05/2014	09/2014	12/2014
pH	6.78	6.71	6.68	6.71	6.49	6.95	6.68
ORP (mV)	-23	+230	+180	+95	-68	-78	+118
D.O. (mg/L)	0.32	1.08	0.56	4.32	0.99	0.96	3.13
Conductivity (mS/cm)	1.05	1.24	2.00	4.61	2.57	1.89	2.01
Temperature (^{o}C)	17.7	21.7	16.8	8.8	14.3	22.8	14.2
Groundwater Elevation (ft)	93.35	90.43	89.14	92.56	93.20	91.27	92.25
Sulfate (mg/L)	70.9	123.0	247.0	339.0	279.0	343.0	314
Total Iron (mg/L)	4.85	5.44	4.64	5.84	14.3	5.16	2.04
Dissolved Iron (mg/L)	3.53	3.24	3.22	3.91	12.0	4.26	0.35

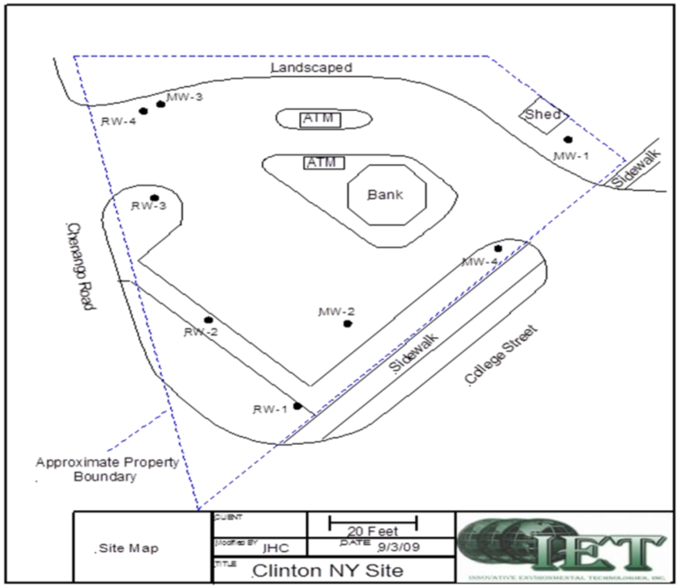
	MW-5						
Sampling Date	06/2013	10/2013	11/2013	02/2014	05/2014	09/2014	12/2014
Benzene (ppb)	3.38	1.91	0.52	ND	1.27	ND	ND
Toluene (ppb)	1.71	0.21 J	0.16	ND	0.57	ND	ND
Ethylbenzene (ppb)	15.6	0.4 J	ND	ND	14.2	ND	ND
Total Xylenes (ppb)	25.94	1.98 J	0.37	ND	7.85	ND	ND

Provect-OX™ Case Study 2

- Single injection event at a former gas station upstate New York to address soil and groundwater contamination due to the historical release of BTEX compounds.
- Total treatment area of 9,225 square foot area, treating between 9 and 15 feet below ground surface.

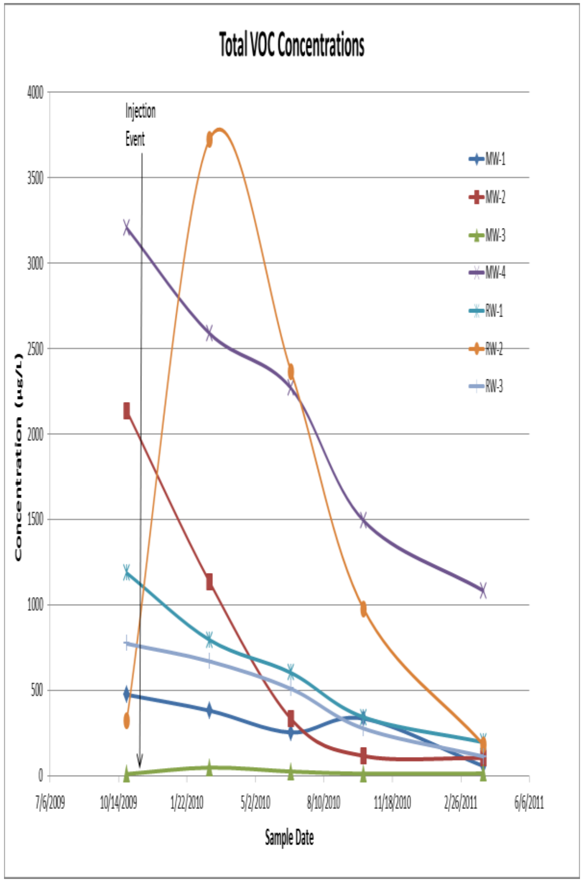
- ➢ 39 injection points
- ➢ Spaced 12-20 ft apart
- ➢ 8,006 lbs of Provect OX

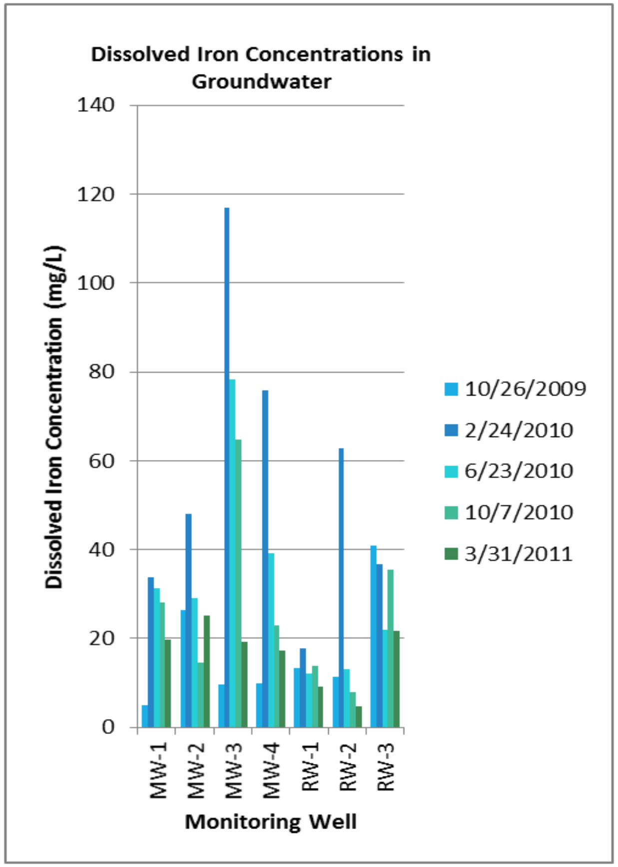


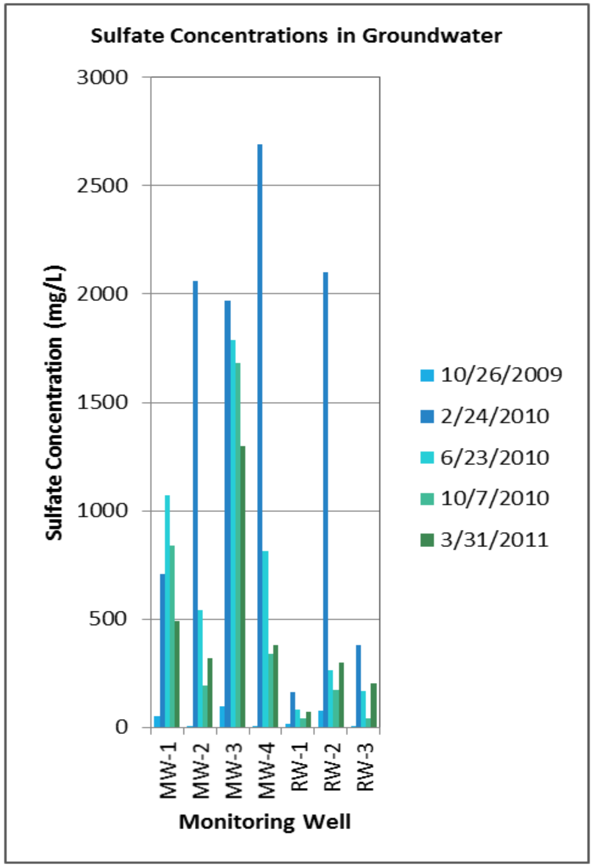


Case Study 3 – Geochemical and VOC Data

Sulfate and Iron Utilized as Terminal Electron Acceptors to Sustain Bioremediation and Minimize Rebound







CONCLUSIONS

- Provect-OX™ combines multiple ISCO and enhanced biological processes

- Safely catalyzed process without the Hazards of Extreme Activation
- No Heat Generated – minimizes gassing and surfacing issues

- Uses Fe^{3+} as activator (no persulfate “Mandated Supplier”)

- Long-lived reactions – sustained treatment manages rebound

- Demonstrated effectiveness under field conditions

- Cost-effective – reduces need for multiple injection events

Questions