



In Situ Chemical Oxidation (ISCO) Overview

presentation for

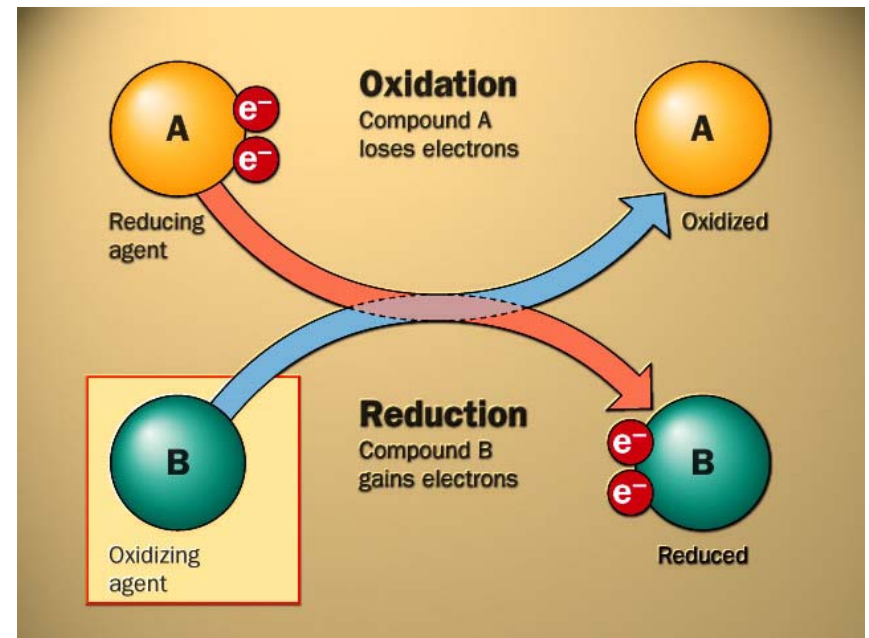
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by:

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What is ISCO?

- **Chemical Oxidation** is any chemical reaction in which a compound gives up electrons such as in combination with oxygen or oxidizing free radicals.
- **ISCO** is the process of degrading toxic organic contaminants "in place" to benign byproducts via injection of chemical oxidants.



Presentation

- Steps before ISCO
- Overview of Oxidants
- ISCO Design & Implementation
- Health and Safety



Steps Before ISCO

Site Characterization

- **Lithology.** Sandy soils are relatively straightforward; however, silts and clays can be tough?
- **Type of contamination.** Are the contaminants amenable to ISCO? Contaminants with double bonds easier than single bonds.
- **Nature of Contamination.** Is there NAPL? May need to combine ISCO with enhanced fluid recovery?
- **Where is it Present?** Unsaturated, Smear or Saturated Zone Contamination?
- **Mass of contamination.** Kg of organic compounds present? Adsorbed Mass?
- **Site constraints.** Effects of ISCO on existing infrastructure (i.e. buildings, utilities, etc.)? Can injection points be installed?

Managing Expectations

- **Set reasonable treatment goals.**
Achieving the most stringent drinking water cleanup criteria (e.g. 1.0 ppb for benzene) may turnout to be expensive.
- **Keep your treatment options open.**
ISCO may need to be combined with existing pump and treat, SVE or EFR systems for best results and costs.

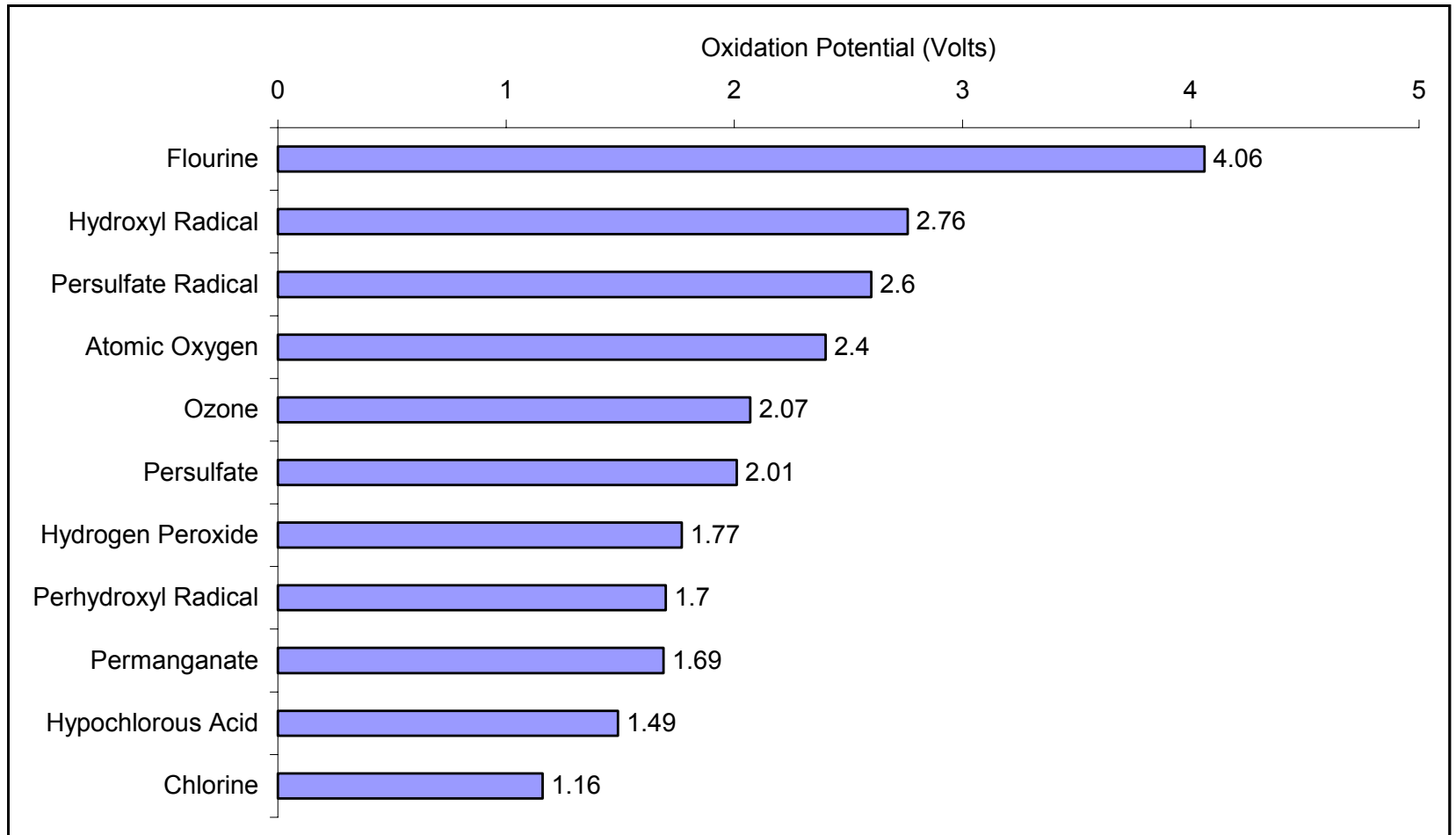


Commonly Used ISCO Technologies

Commonly Used ISCO Technologies & Reactive Species

<u>Oxidant</u>	<u>Reactive Species</u>
Sodium/ Potassium Permanganate	Permanganate (MnO_4^-) anion
Sodium Persulfate	Sulfate ($\text{SO}_4^{\bullet-}$) Radicals
Ozone	Ozone (O_3)
Peroxone (Ozone + H_2O_2)	Ozone (O_3) Hydroxyl ($\text{OH}\bullet$) Radicals
Classic Fenton's Reagent ($\text{pH} \leq 3$)	Hydroxyl ($\text{OH}\bullet$) Radicals
Modified Fenton's Reagent (MFR)	Hydroxyl ($\text{OH}\bullet$) Radicals, Perhydroxyl ($\text{HO}_2\bullet$) Radicals, Superoxide ($\text{O}_2^{\bullet-}$) Radicals, Hydroperoxide (HO_2^-) anions

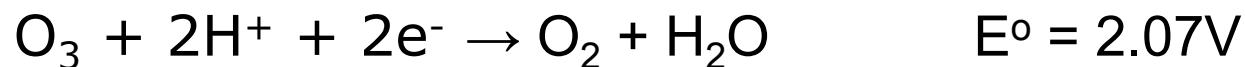
Oxidation Potential of Various Oxidizing Species



Ozone

- Ozone is a gas. It is typically produced on site via high voltage discharge in air or oxygen using ozone generators.

- Oxidation potential = 2.07 V.



- Amenable Contaminants:

Chlorinated ethenes (i.e. PCE), aromatics (i.e. BTEX), aliphatics and some PAHs in aqueous phase. Adsorbed contamination may be difficult to treat.

- Stoichiometry: e.g. 1.1 lbs O₃ per lb TCE
- Cost = \$3-\$4/lb (assumes 10 lb/day capacity)

Ozone/ Peroxone

- Peroxone: When combined with hydrogen peroxide, ozone can produce hydroxyl radicals $\text{OH}\cdot$.



- Two mechanisms:
 - Direct oxidation by aqueous ozone
 - Oxidation by hydroxyl radicals produced from ozone decomposition by peroxide.

Ozone

Advantages

- Can treat a wide range of contaminants.
- Gas can travel farther than liquid or solid oxidants.
- Oxygen produced as a byproduct; therefore, potential for biostimulation.
- Vapors if captured and treated can also physically remove VOCs.
- When combined with hydrogen peroxide, can produce powerful hydroxyl free radicals.
- No hazardous chemicals to store on site.

Disadvantages

- High capital cost
- High O&M cost.
- Not effective towards adsorbed soil mass.
- Highly unstable.
- Vapor production.

Sodium/Potassium Permanganate

- Potassium permanganate is a solid. Sodium permanganate is commercially sold as 40% liquid.
- Oxidation potential = 1.7 V.



- Amenable Contaminants:
Chlorinated ethenes (i.e. PCE), aromatics (except benzene), aliphatics and some PAHs in aqueous phase. Adsorbed contamination may be difficult to treat.
- Stoichiometry: e.g. 2.4 lbs per lb TCE
- Cost: \$2.50-\$3.50 per lb KMnO_4 ; \$6-\$7 per lb NaMnO_4

Sodium/ Potassium Permanganate

Advantages

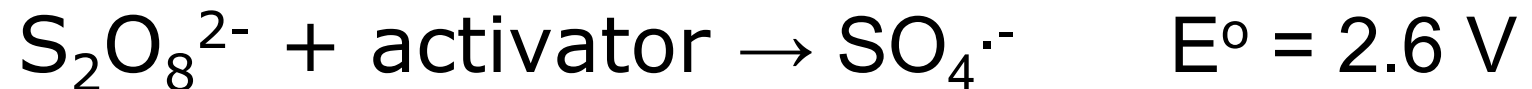
- Good longevity.
- Easy to apply.
- Potassium permanganate is relatively inexpensive i.e. \$2.50-\$3.50 per pound (however limited solubility).
- Large spacing of injection points possible due to high oxidant stability.
- Ideal for aqueous phase contaminants with no adsorbed mass present.

Disadvantages

- Sodium permanganate is expensive i.e. \$6.00-\$7.00 per pound.
- Large quantities needed for effective treatment.
- Not effective towards adsorbed soil mass.
- Ineffective towards benzene and chlorobenzene.
- Purple color.
- Black Manganese dioxide precipitate can potentially reduce subsurface permeability.

Sodium Persulfate

- Sodium persulfate is a solid.
- Oxidation potential = 2.6 V.



- Stoichiometry: e.g. 5.5 lbs per lb TCE
- Cost: \$1.50-\$2 per lb + Activator Cost

Sodium Persulfate

- **Heat Activation** = Heat(>40°C) + Na₂S₂O₈
- **Catalyst Activation** = Chelated Iron + Na₂S₂O₈
- **Alkali Activation** = Alkali (pH>10.5-11) + Na₂S₂O₈
- **Peroxide Activation** = H₂O₂+ Na₂S₂O₈
- **Modified Fenton's Reagent (MFR) Activation**
= Chelated Iron + H₂O₂ + Na₂S₂O₈

Sodium Persulfate

- Activation Methods Treatment Effectiveness
 - Heat Activation – chlorinated alkenes, **chlorinated alkanes**, aromatics, aliphatics and PAHs.
 - Hydrogen Peroxide Activation - chlorinated alkenes, **chlorinated alkanes**, aromatics, aliphatics and PAHs.
 - Chelated Iron Activation – chlorinated alkenes, aromatics, aliphatics and some PAHs.
 - Alkali Activation - chlorinated alkenes, aromatics, aliphatics and some PAHs.
 - MFR Actiation – chlorinated alkenes, **chlorinated alkanes**, aromatics, aliphatics and PAHs.

Sodium Persulfate Activation Methods

VOCs Treatment Effectiveness

	Chlorinated Alkanes	Chlorinated Alkenes	Ethers	Carbon Tet.	Aromatics	Misc. VOCs
Catalyst Activation		Best (87%)	2 nd Best (8%)		Best (96%)	2 nd Best (61%)
Alkali Activation (pH 9-10)						
Peroxide Activation	2 nd Best (16%)			2 nd Best (27%)		
MFR Activation	Best (23%)	2 nd Best (44%)	Best (17%)	Best (38%)	2 nd Best (57%)	Best (70%)

Sodium Persulfate Activation Methods

SVOCs Treatment Effectiveness

	Phenols	PAHs	Amines	Phthalates	Substituted & Chlorinated Benzenes	Heterocyclic Aromatics	PCBs
Catalyst Activation	2nd Best (99%)	2nd Best (49%)	2nd Best (74%)	2nd Best (28%)	2nd Best (66%)	2nd Best (87%)	2nd Best (48%)
Alkali Activation (pH 9-10)							
Peroxide Activation							Best (50%)
MFR Activation	Best (>99%)	Best (59%)	Best (96%)	Best (75%)	Best (83%)	Best (>99%)	

Sodium Persulfate

Advantages

- Good longevity.
- Easy to apply.
- High solubility.
- Large spacing of injection points possible due to high oxidant stability; however activator delivery at large spacing can be difficult.
- No vapor production if used with chelated iron or alkali activation.

Disadvantages

- Large quantities needed for effective treatment.
- Not effective towards adsorbed soil mass (except hydrogen peroxide activation).
- Sulfate production could be a regulatory nightmare.
- Low pH (i.e. <2-3) conditions can mobilize metals.

Conventional Fenton's Chemistry



H_2O_2 = Hydrogen Peroxide

Fe = Dissolved Iron

$\text{OH}\bullet$ = Hydroxyl Radicals

$\text{pH} \leq 3$ = Aquifer Acidification

Fenton, H.J.H. (1894). *J. Chem. Society*, 65, 899

Haber, F., and Weiss, J.J. (1934). *Proc. Roy. Soc. London, Ser. A*, 147, 332

Conventional Fenton's Chemistry

Concerns

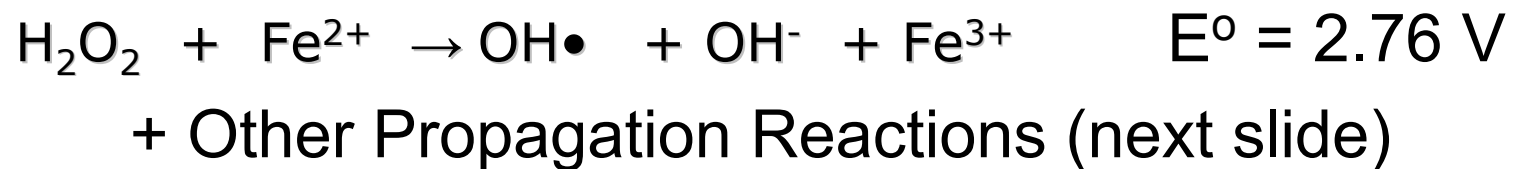
- Highly acidic pH (2-4)
- Desorption
- Highly exothermic reaction
- Precipitation

Why

- Destruction of microbial activity & leaching of metals
- Contaminant migration
- PVC Melting, Organic Vapors
- Increase in iron & soil fouling

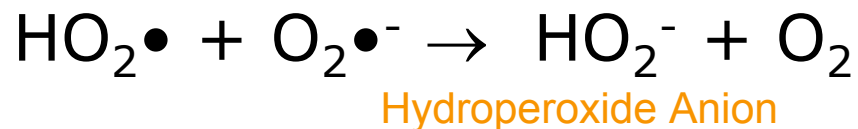
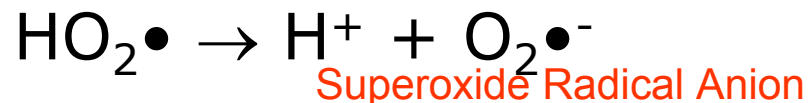
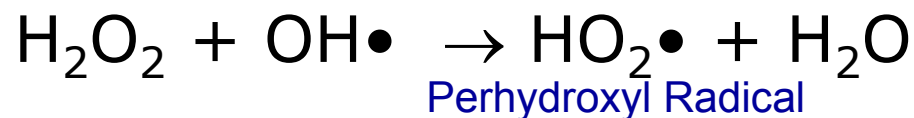
Modified Fenton's Reagent (MFR)

- MFR consists of liquid stabilized hydrogen peroxide and chelated iron catalyst.
- Oxidation potential = 2.76 V.



- Stoichiometry: e.g. 1.2 lbs peroxide per lb TCE + catalyst
- Cost: \$0.35-\$0.75 per lb + catalyst cost

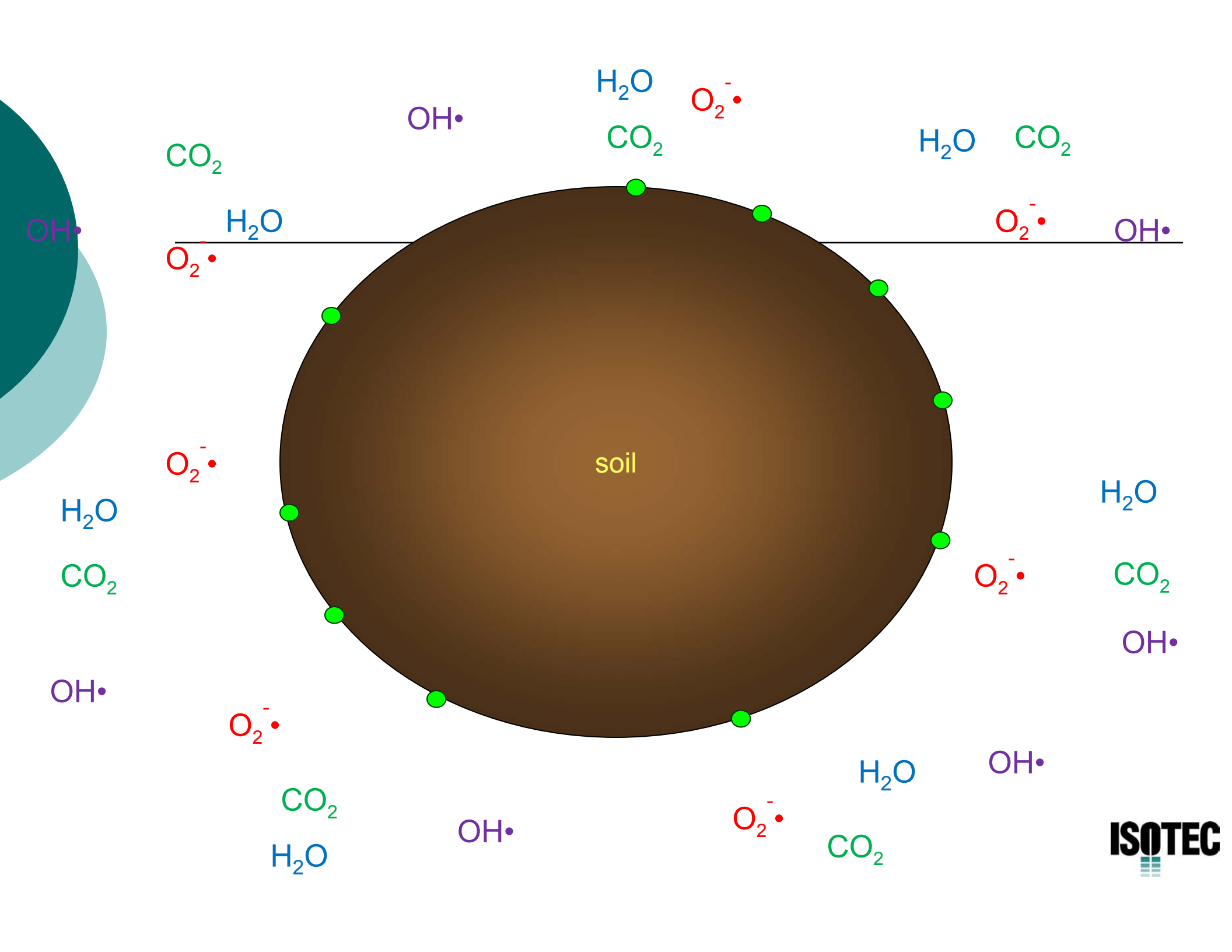
Modified Fenton's Reagent



Aquifer Acidification Not Needed

DESORPTION

- Critical because free radicals are aqueous species.
- Desorption needs to occur for thorough treatment of soil-bound contaminant sources.
- If soil-bound contaminants are not desorbed, rebound is likely months after ISCO has been implemented.



Modified Fenton's Reagent

Amenable Contaminants

- Hard to treat recalcitrant compounds, chlorinated alkenes(PCE), chlorinated alkanes (TCA), pesticides, wood preservatives, oxygenates (MTBE/TBA), aromatics (BTEX), fuel oil
- OH• will oxidize nearly all carbon-carbon double bonds, and most extractable hydrogen atoms
- Problem compounds: free product layers >1/2 inch - may not be cost effective

Modified Fenton's Reagent

Advantages

- Effective for both adsorbed soils and NAPLs.
- No acids are utilized
- High catalyst mobility
- Gravity feed or low pressure injection systems
- Low reagent concentrations
- Controlled reaction

Disadvantages

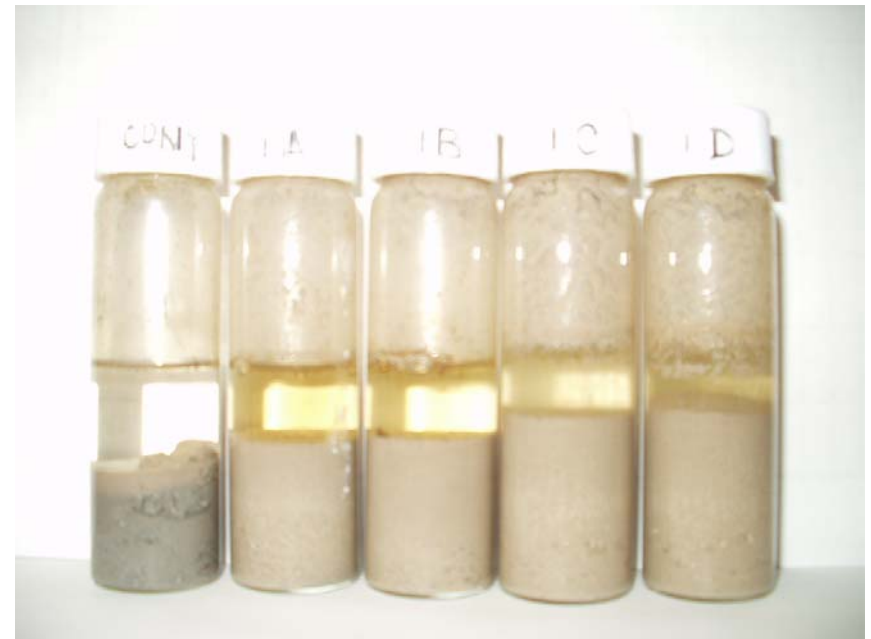
- Hydrogen peroxide is unstable.
- Vapor production



ISCO Design & Implementation

Bench Scale Study

- Bench scale studies are critical.
- Determine oxidant demand (i.e. NOD) and whether your contaminants can be treated.
- Soil slurries better than groundwater experiments. Never put too much water in the soil slurry.
- Oxidant doses should be similar to those that can be applied safely and at a reasonable cost in the field.



Pilot Study

- Lab studies can never replicate “real world” conditions.
- Select a representative test cell (not necessarily the worst).
- Prepare to do multiple applications.
- Need to collect lots of data. Collect both soil and groundwater data.

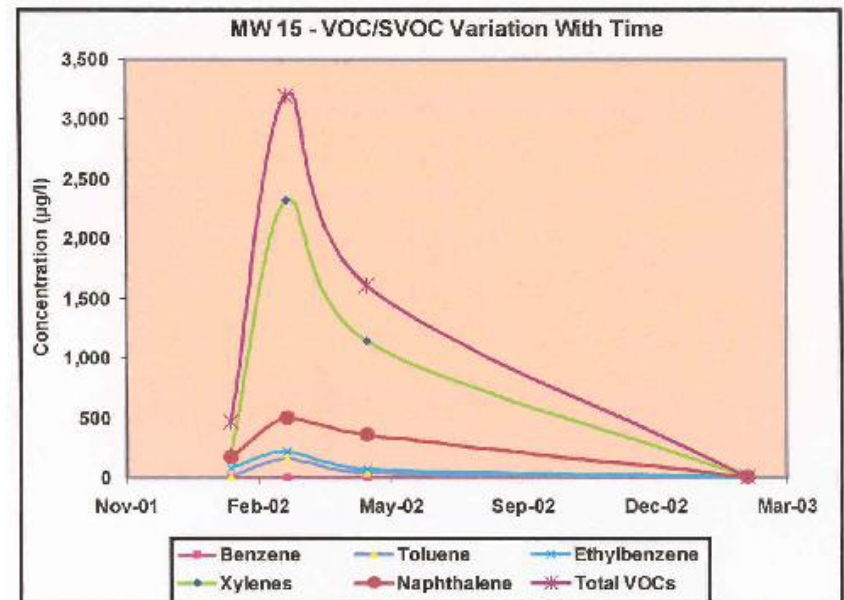


Data Collection

- Pilot studies can generate confusing data.
- Do not rely on groundwater concentrations alone as >80-90% contaminant mass is typically present in soils.
- Collect both soil and groundwater data.
- Allow sufficient time gap before you collect post-treatment samples e.g. if the groundwater is still purple, the data will show ND results when permanganate is used.

Data Interpretation

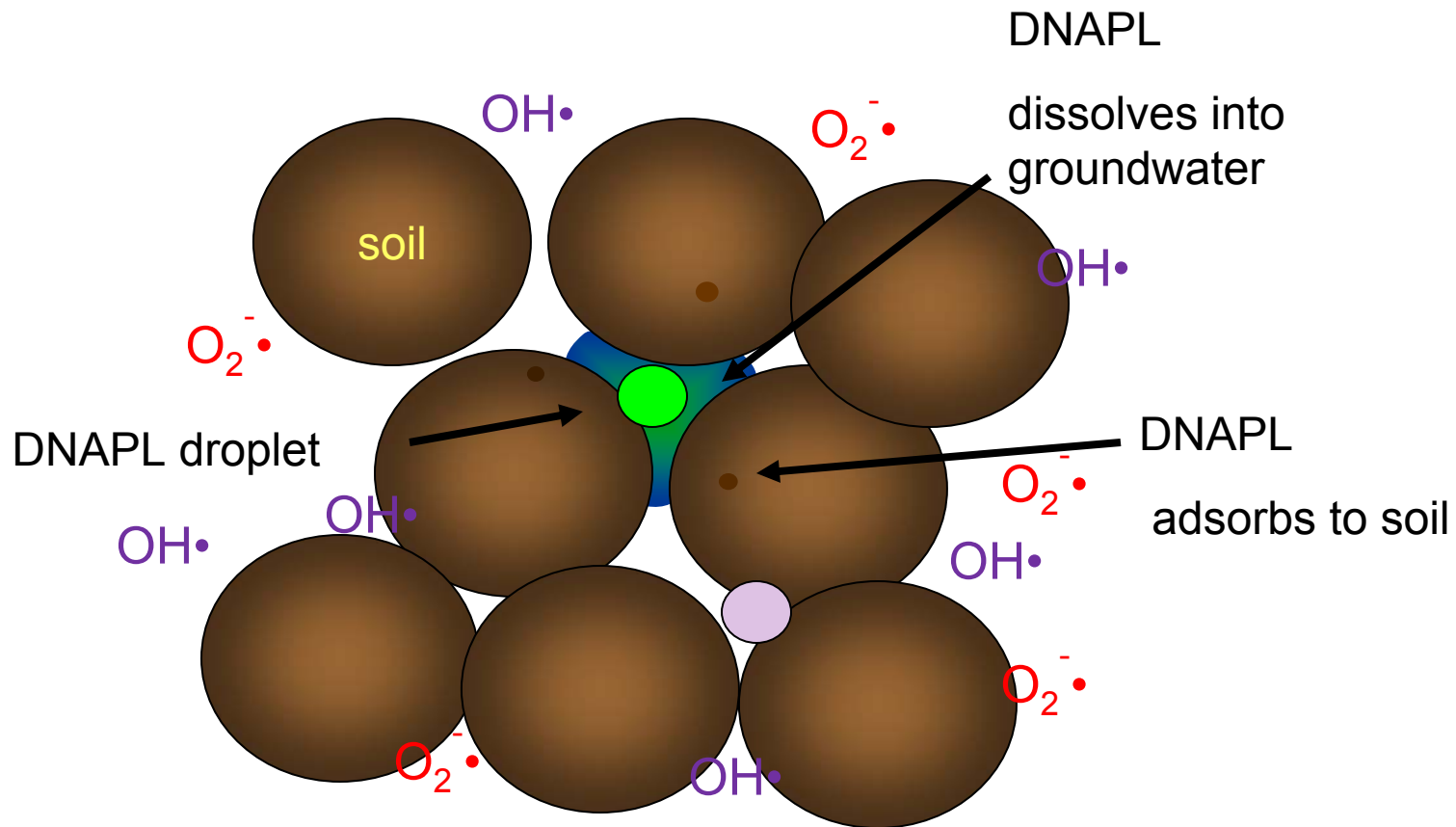
- Expect desorption to be significant during initial events.
- Increased groundwater VOC concentrations means the technology is working (for MFR).



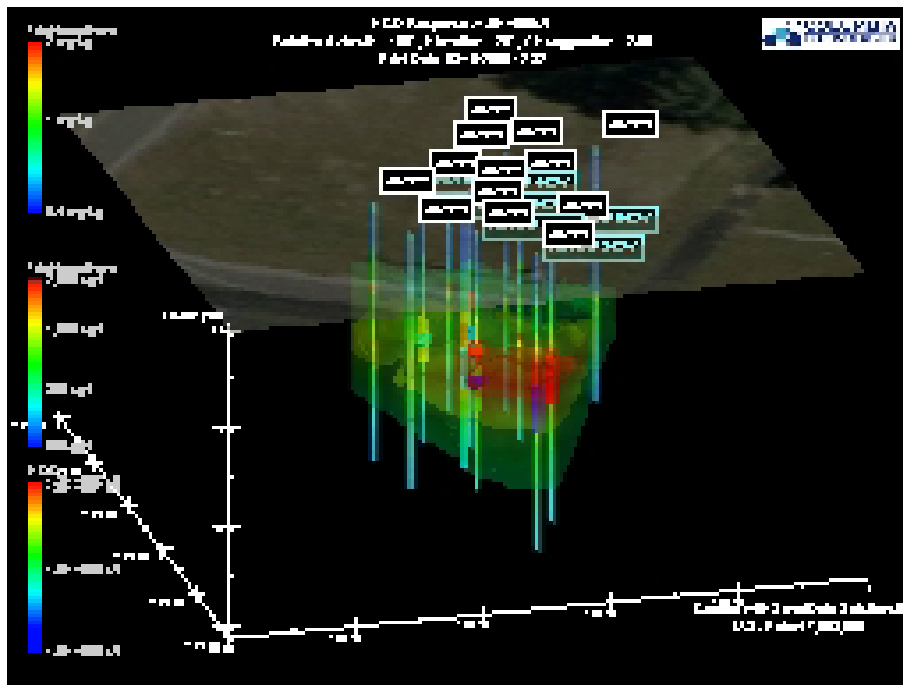
Effects of DNAPL

- DNAPLs can lead to confusing data as there is no easy way to measure how much is present.
- Larger DNAPL globules break up into smaller globules.
- Groundwater concentrations will increase due to DNAPL solubilization.
- Soil concentrations can also increase due to DNAPL globule breakup and redistribution.
- Need to look for other parameters to measure treatment effectiveness e.g. chloride increases.

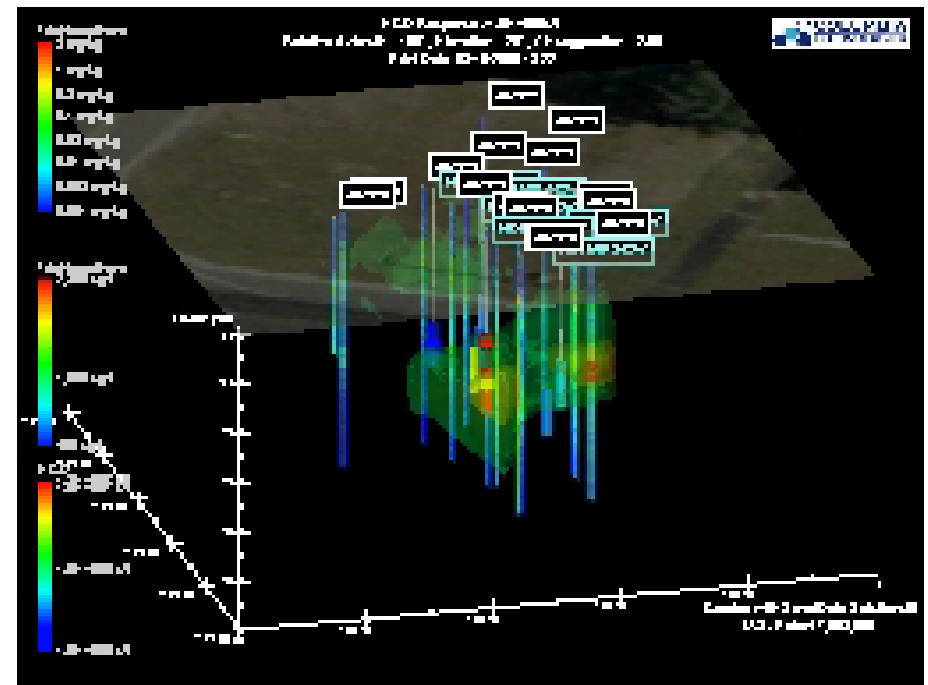
Modified Fenton's Reagent – DNAPL Treatment



Membrane Interface Probe (MIP) TCE Plume Site MFR Pilot Study Looking North

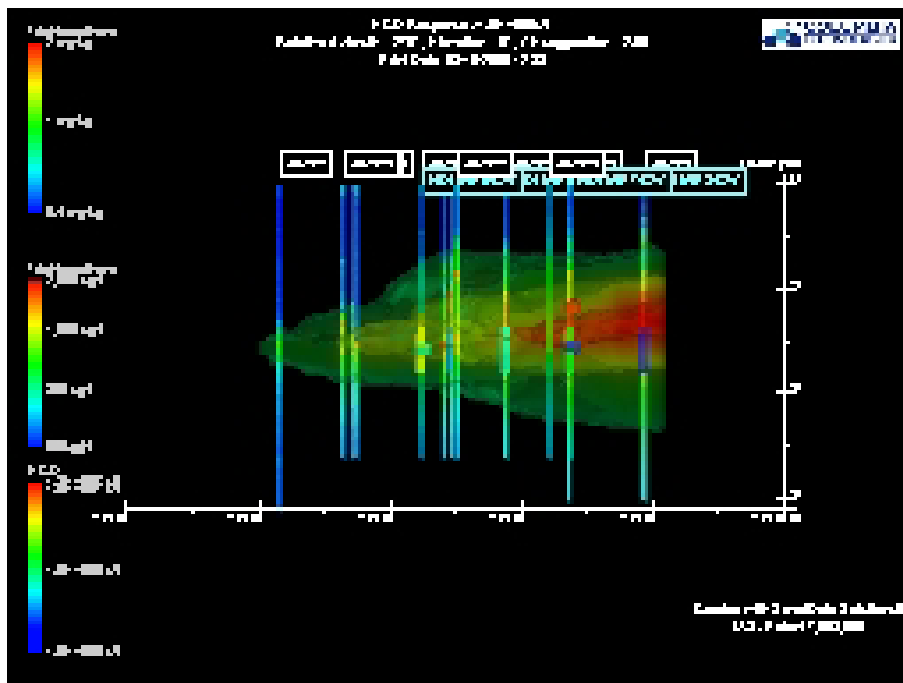


Baseline
Oct-2008

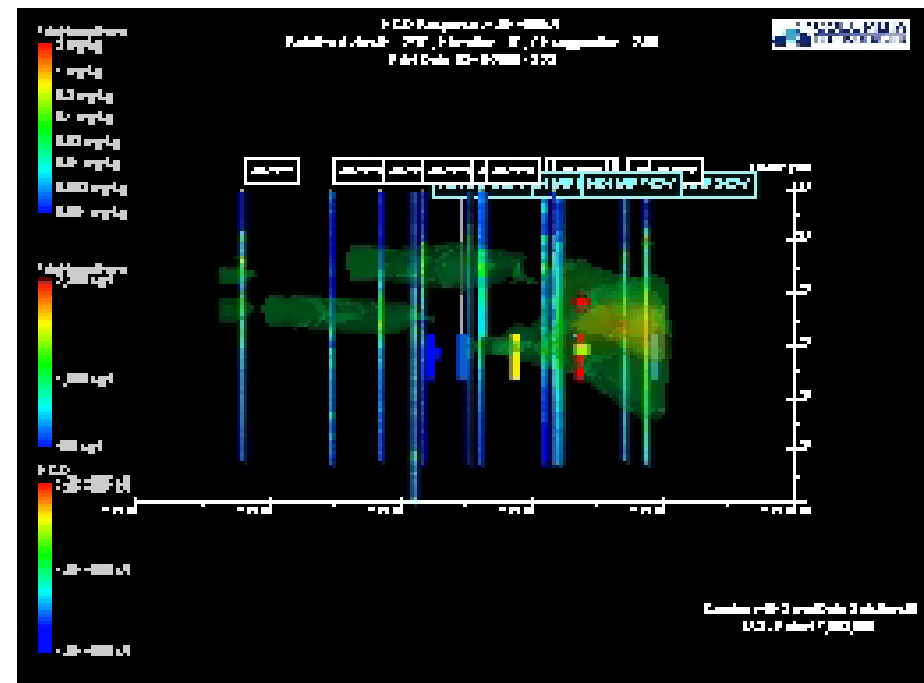


Post-Pilot
Feb-2009

Membrane Interface Probe (MIP) TCE Plume Site MFR Pilot Study Looking East



Baseline
Oct-2008



Post-Pilot
Feb-2009



Health and Safety

Health and Safety

- Oxidants are hazardous.
- High pressure = High temperature
- Always add concentrated material to dilute material and not vice versa.
- Splash and Eye protection is critical during oxidant transfer.

Health and Safety

- A space suit is not needed for doing ISCO. Have to be practical. Protection is important but it should not hamper communication or dexterity.
- In most cases, modified Level D PPE is adequate [i.e. gloves, steel toe boots, eye protection and splash protection (during transfers)].

Health and Safety

Loss Prevention System (LPS)

- First adopted by Exxon Mobil but gaining widespread popularity.
- Prepare activity hazard analysis (AHA or JHA) before you set foot on site.
- Train employees on Self Performance Self Assessment (SPSA) when you set foot on the site.
- Perform Loss Prevention Observation (LPOs) routinely.
- Prevent incidents before they happen.
- Use root cause analysis (RCA) for any near misses or incidents so they don't happen again.
- LPS is mostly common sense...but human errors are responsible for >90% of all accidents.

Thank You

Questions?

ISOTECSM
In-Situ Oxidative Technologies, Inc.
www.insituoxidation.com

