



CHEMCO inc.

SOLUTIONS AND ENVIRONMENTAL PRODUCTS
WATERS - SOILS - AIR



Tackling Chlorinated Solvents Contamination What are the options

October 2016

Banff, AB

Prepared by Jean Paré, P. Eng.

Chemco Inc.



CHEMCO inc.

SOLUTIONS AND ENVIRONMENTAL PRODUCTS
WATERS - SOILS - AIR

Presentation Agenda

- Who we are
- In situ / Ex situ Chemical Oxidation
Principle and Applicability
- In situ / Ex situ Chemical Reduction
Principle and Applicability
- Design and injection parameters
- Case Study

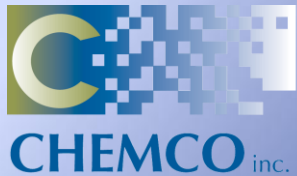
Who we are



CHEMCO inc.

SOLUTIONS AND ENVIRONMENTAL PRODUCTS
WATERS - SOILS - AIR

- Canadian Company founded in 1988
- Production and warehouse facilities in Quebec and throughout Canada vs Strategic Business Alliances
- Sectors of activity:
 - Industrial and Municipal Waste Water
 - Contaminated Soil and Groundwater
 - Air, Odours and Atmospheric Emissions (AC, filtering medias)
 - Process Water & Thermal Exchange Fluids (Glycols)
 - Drilling Fluids (Oil and Gas & Diamond exploration)
 - Aircraft Deicing Fluids
- Products (environmental): coagulants, flocculants, nutrients, bacterial preparations strains, oxidants, catalysts, oxygen and reductant, filtering media, odour control agents
- Services: technical support, product selection, product supply and sourcing, logistics, laboratories, design, and staff training.



SOLUTIONS AND ENVIRONMENTAL PRODUCTS
WATERS - SOILS - AIR

About our expertise, product and services

- **Training and Education:** technical transfer session, health and safety training;
- **Consulting and Technology Site Assessment:** technology support and selection (chemical oxidation, chemical reduction, co solvent-surfactant soil washing and enhanced bioremediation);
- **Products supply, logistic and storage:** nutrients, bacterial preparations strains, oxidants, reducing agent, catalysts, oxygen and hydrogen release compounds, co solvent-surfactant blends
- **Laboratory Services and Analysis:** Groundwater Parameter Analysis, Tracer Study, Soil and Groundwater Oxidant Demand Evaluation (SOD), Bench Scale Treatability testing.

Typical decontamination techniques

- Dig and Haul
- Pump and Treat
- Soil Vapour Extraction under vacuum with or without air/steam injection

→ Chemical Oxidation In-situ//Ex-situ

→ Chemical Reduction In-situ//Ex-situ

- Monitored Natural Attenuation

→ Enhanced Bioremediation

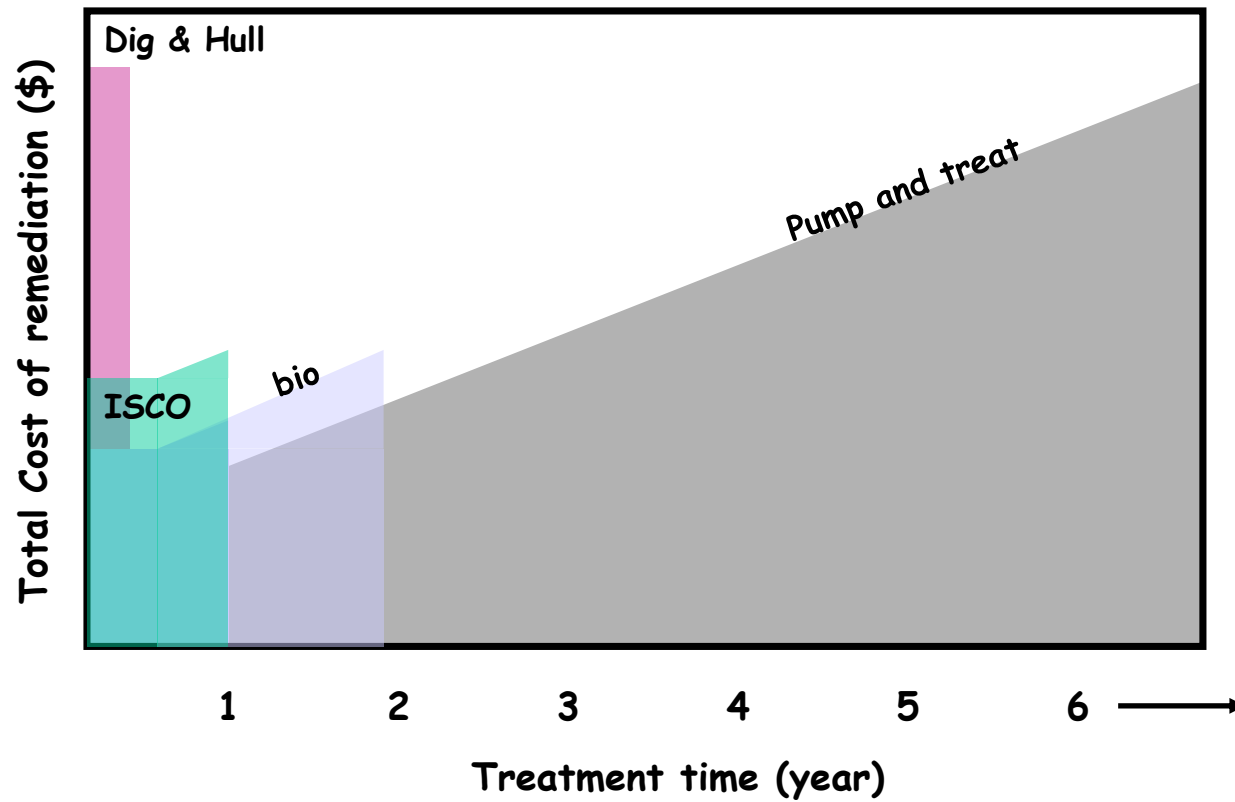
- Risk Analysis

→ Soil Washing

- Permeable Reactive Barriers

- Thermal degradation

Remediation time and cost



In Situ Chemical Oxidation / Ex Situ Chemical Oxidation Principle and Applicability

Chemical Oxidation Principles

In-situ // Ex-situ

- Oxidants are introduced or mixed into the soil and groundwater to attack the organic contaminants
- Chemical oxidation treatments are commonly used in potable and wastewater applications
- Oxidants are non-specific and will react with the targeted contaminants AND with the soil organic and mineral content.
- Chemical oxidation reactions involve the transfer of electrons and the breaking of chemical bonds
- Water is the carrier for the oxidants used in chemical oxidation (except for ozone)

Common Chemical Oxidants

- **Potassium or sodium permanganate**
- **Hydrogen Peroxide alone**
- **Catalyzed Hydrogen Peroxide**
 - Hydrogen Peroxide with iron (regular Fenton reagent reaction)
 - Need to establish acidic conditions (ideal pH between 4 and 6)
 - Modified Fenton Reagent with chelated species (neutral pH)
- **Ozone**
 - Ozone is a gas and must be produced on site
 - The gas must be injected into the soil
- **Persulfate**
 - Requires activation to generate free sulfate radicals.
 - Heat, chelated metal, alkaline, hydrogen peroxide, surface, organic can be used to activate the persulfate. Activation method can be adapted to site conditions.
- **Percarbonate**
 - Requires activation to generate free radicals
- **NOTES:**
 - 1. ALL THESE PRODUCTS REQUIRE ADEQUATE HANDLING PRACTICES AND SAFETY EQUIPMENT.**
 - 2. Chemical oxidation can slow down the biological activity but will NOT sterilize the soil completely (potential benefit because of lower toxicity after the Chemical Oxidation is completed)**

Oxidant	Potential (eV/mol)	Form	Persistence in soil
Fenton Reagent (OH*)	2.8	Liquid	Low to medium 2 to 5 days Retardants use can extend up to 20 days
Perozone (O ₃ + OH*)	2.8	gas/Liquid	Very Low 20 min to 2 days
Activated Persulfate (SO ₄ ⁻)	2.6	Liquid/suspension	Medium 10 to 30 days
Ozone (O ₃)	2.42 2.07	gas	Very Low 20 min to 2 days
Persulfate (S ₂ O ₈ ²⁻)	2.01	Liquid/suspension	Medium 10 to 30 days
Hydrogen Peroxide (H ₂ O ₂)	1.78	Liquid	Low 2 to 5 days
Permanganate (MnO ₄ ⁻)	1.68	Salt/Liquid	High More than 3 months

Compatibility oxidant/contaminant

Contaminant/Oxydant	MnO ₄	S ₂ O ₈	SO ₄ [*]	Fenton's	Ozone
Petroleum Hydrocarbon	L	G/E	E	E	E
Benzene	L	G	G/E	E	E
Phenols	G	L/G	G/E	E	E ¹
Polycyclic Aromatic Hydrocarbon (PAH)	L	G	E	E	E
MTBE	L	L/G	E	G	G
Chlorinated Ethenes (PCE, TCE, DCE, VC)	E	G	E	E	E
Carbon Tetrachloride	L	G	L/G	L/G	L/G
Chlorinated Ethanes (TCA, DCA)	L	G	G/E	G/E	G
Polychlorinated Biphenyls (PCB)	L	L	G	G/E	G ¹
Energetics (RDX, HMX)	E	G	E	E	E

L=Low G=Good E=Excellent 1=Perozone

Conditions for Selecting Chemical Oxidation

	Chemical Oxidation Applicability	Limitation / Disadvantages	Possible Alternative Options
Mobile NAPL	Probably not the best choice	High oxidant requirement (\$)	Liquid Extraction Thermal degradation
Residual NAPL (higher than 10,000's mg/kg)	Yes, but difficult	High oxidant requirement (\$)	Extraction with air/steam injection Thermal degradation
High conc. in soil/groudwater (10's – 10000's mg/kg)	Yes, good conditions	Normal considerations	Extraction with air/steam injection Bioremediation
Dissolved plume (< 1 mg/kg)	Yes, but could be costly	Higher cost due to SOD	Bioremediation, Reactive barriers

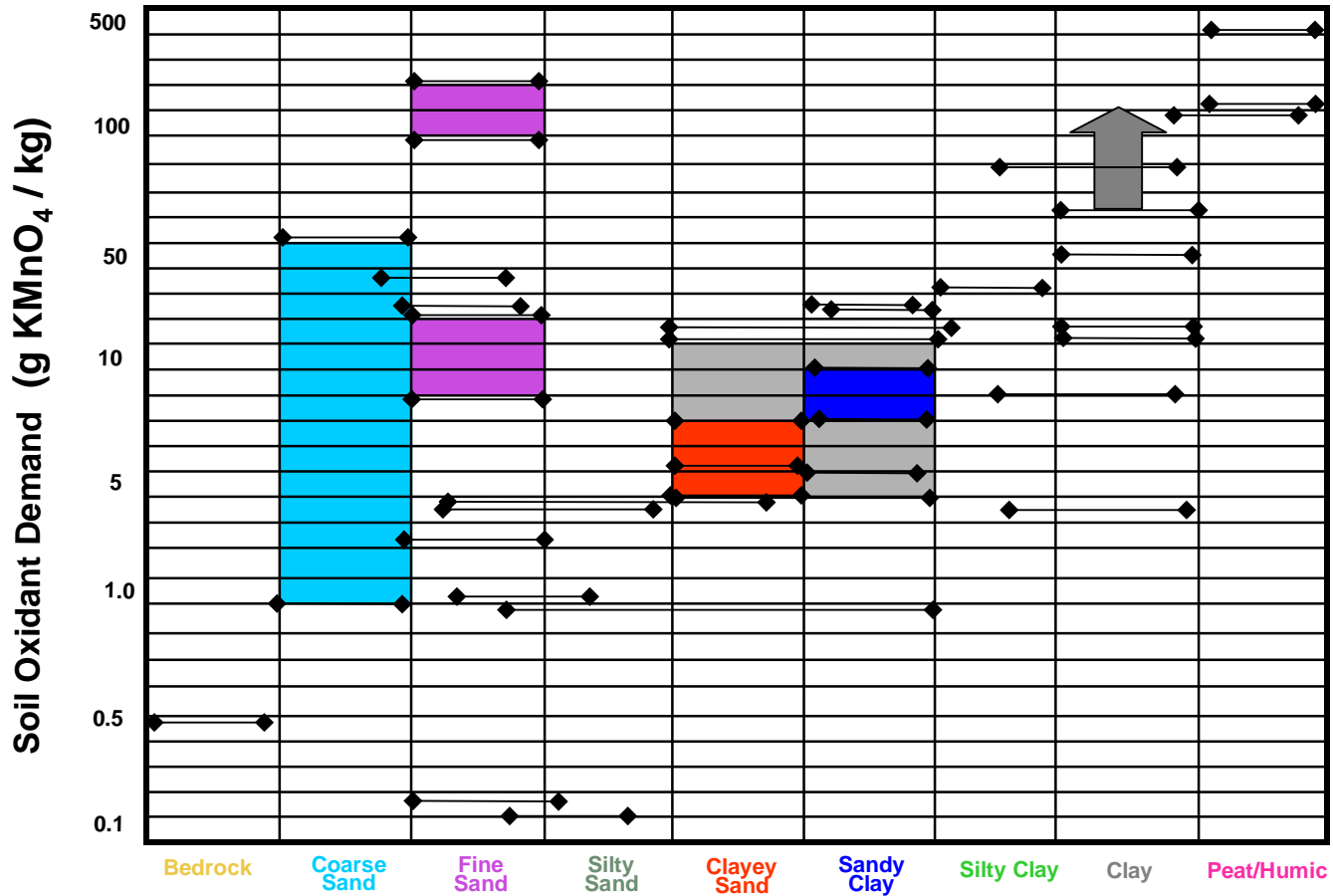
Soil Oxidant Demand (SOD)

- Any oxidant will react and be consumed by the organic material contained in the soil and by some minerals.
- Bench scale testing and/or pilot testing are recommended for better and more exact SOD evaluation



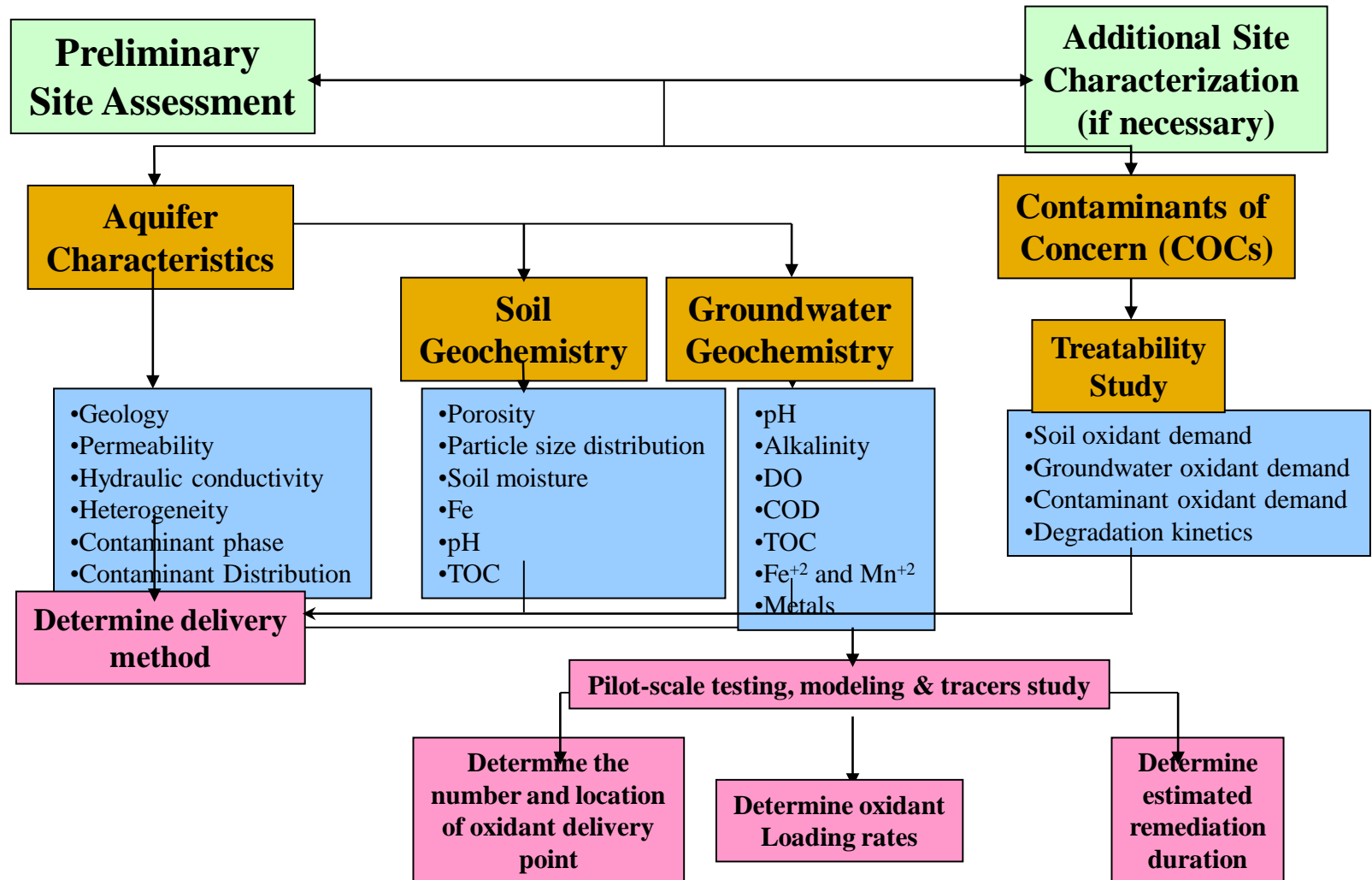
Soil Oxidant Demand (SOD)

(adapted from Shaw E & I presentation - 2003)





Carus Haz Rem Assessment Process



Geological Considerations

Geological Considerations	MnO ₄	S ₂ O ₈	SO ₄ [*]	Fenton's	Ozone
Non-consolidated material					
• Sand and gravel	E	E	E	E	E
• Silty sand	G/E	G	G	L	L
• Mixed	G/E	G/E	G	L	L
Consolidated material					
• High flow	E	E	L/G	L/G	L/G
• Low Flow	G	G	G	L	L

L=Low G=Good E=Excellent

Source: Carus Chemical Company

Hydrogeological considerations

Hydrogeological considerations	MnO ₄	S ₂ O ₈	SO ₄ [*]	Fenton's	Ozone
Saturated Zone	E	E	G	G	G
Non-saturated Zone	G *	L/G	L/G	L/G	G
with groundwater flux:					
• slow	G	G	G	L	L
• fast	G	G	G	G	G

L=Low G=Good E=Excellent * If temporarily flooded.

Source: Carus Chemical Company

Geochemical Considerations

Geochemical Considerations	MnO ₄	S ₂ O ₈	SO ₄ [*]	Fenton	Ozone
Presence of carbonates	E	E	G	L	L
High dissolved metal content	L	G	E	E	L
High organic matter content	L	G	G	L	L

L=Low G=Good E=Excellent

Source: Carus Chemical Company

Additional Considerations

Criteria	MnO ₄	S ₂ O ₈	SO ₄ *	Fenton	Ozone
Gas Production	Low	Low	Low	High	High
Heat Production	Low	Low	Low	High	Low
Fugitive Emissions	Low	Low	Low	High	High
Availability	E	E	E	E	G
Ease of handling	G/E *	E	E	G	G
Impact on water quality	Mod.	Mod.	Mod.	Mod.	Low
Patent Restrictions	Low	High	High	High	High
Technological Development	E	L	G	E	G
Information availability	G	L	G	G	G
Field trial	G	L	G	G	G

L=Low G=Good E=Excellent Mod. = Moderate

* Sodium

Additional considerations (2)

- **All oxidants can change the oxidation state of metals and thus increase their solubility and mobility**
- **Metals of particular concern are: chrome, lead, uranium, selenium, vanadium**
- **In most of these cases, the metals will come back in their reduced state once all of the oxidant has been consumed by the environment**
- **Impurities contained in the oxidant must be evaluated**
- **In the case of arsenic, oxidation will help immobilizing the metal by reducing its solubility**

Compatibility oxidant/contaminant

Contaminant/Oxydant	MnO ₄	S ₂ O ₈	SO ₄ [*]	Fenton's	Ozone
Petroleum Hydrocarbon	L	G/E	E	E	E
Benzene	L	G	G/E	E	E
Phenols	G	L/G	G/E	E	E ¹
Polycyclic Aromatic Hydrocarbon (PAH)	L	G	E	E	E
MTBE	L	L/G	E	G	G
Chlorinated Ethenes (PCE, TCE, DCE, VC)	E	G	E	E	E
Carbon Tetrachloride	L	G	L/G	L/G	L/G
Chlorinated Ethanes (TCA, DCA)	L	G	G/E	G/E	G
Polychlorinated Biphenyls (PCB)	L	L	G	G/E	G ¹
Energetics (RDX, HMX)	E	G	E	E	E

L=Low G=Good E=Excellent 1=Perozone

Sodium and potassium permanganate

- **Sodium Permanganate**

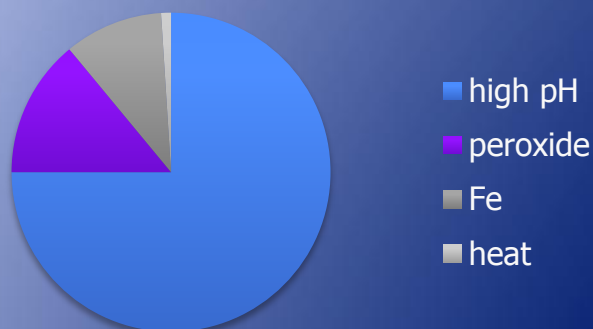
- Liquid
- Available up to 40 %
- Less complex injection equipment
- Smaller injection volumes
- Lower injection time
- Higher cost than potassium

- **Potassium Permanganate**

- Powder (dust issue)
- Soluble to 3 % (field)
- More complex injection equipment
- Higher injection volume
- Longer injection time
- Less expensive than sodium

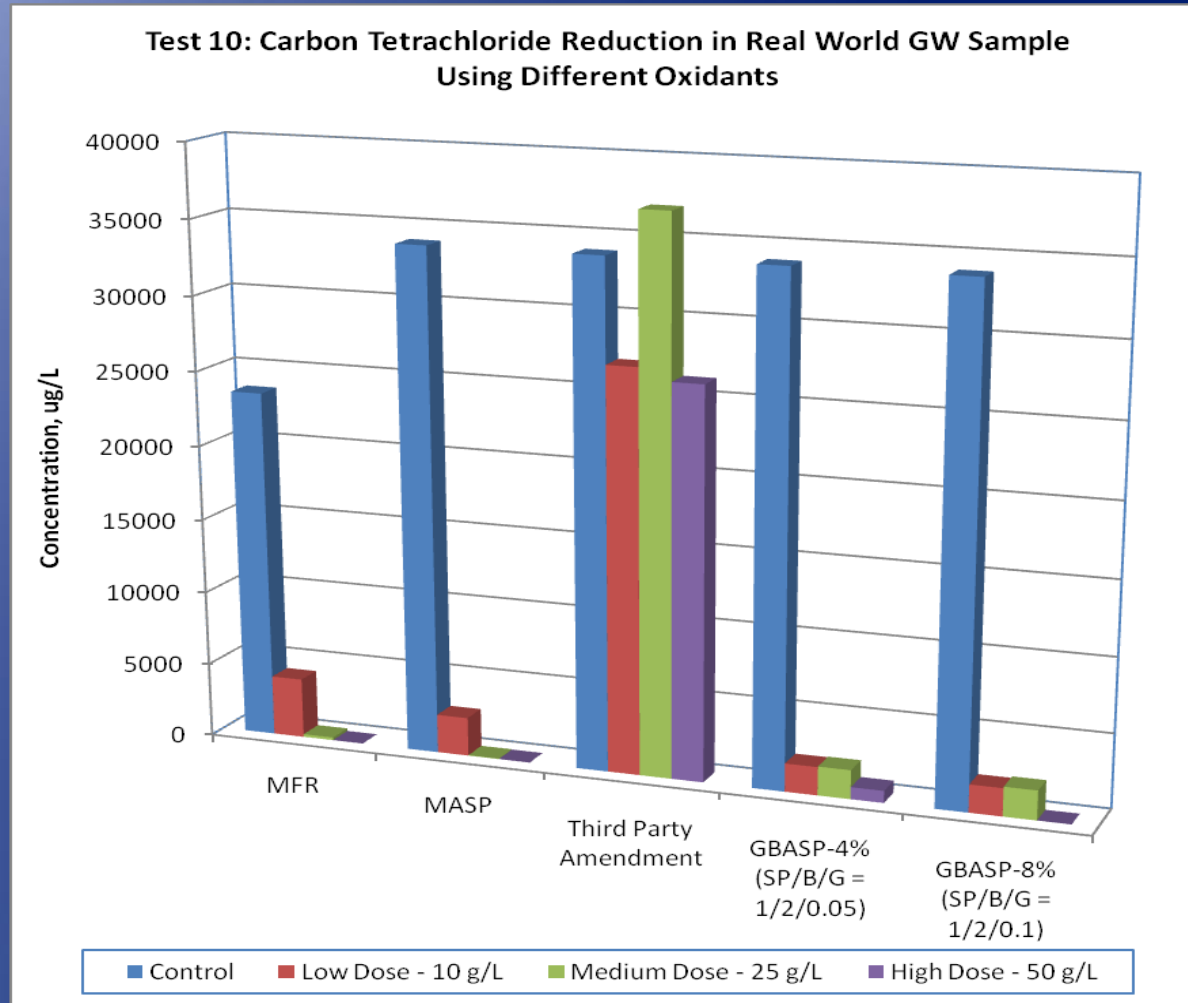
Current Persulfate Activation Mechanism

Estimated Activator Usage



- Alkaline Activated Persulfate
 - High pH
 - Well suited for suited for most applications
 - Reductants, oxidants and nucleophiles
- Iron-Chelate Activated Persulfate
 - Chlorinated ethenes and hydrocarbons
 - Less contaminant mass
- Heat
 - Complex sites
 - Polishing step after thermal treatment
- Hydrogen Peroxide
 - Sites that benefit from vigorous reaction with both hydrogen peroxide and sodium persulfate
- Surface Activation
 - Solid activator – all in – one product

Third Party Bench Test Looking at Treating Carbon Tetrachloride Site



In Situ Chemical Reduction / Ex Situ Chemical Reduction Principle and Applicability

Chemical Reduction Principles

In situ // Ex situ

- In Situ Chemical Reduction (ISCR) is defined as “a process that combines biotic and abiotic reactions to treat contaminants by creating reducing conditions”
- ISCR can be **enhanced by anaerobic bioremediation**
- ISCR also provides abiotic/chemical degradation component if a metal (zero valent iron or other) is present

Common Chemical Reducing Agents

- **Sugars**

- Molasses
- high fructose corn syrup
- whey

- **Fatty acids**

- Lactate
- Butyrate
- propionate

- **Emulsified Vegetable Oils**

- Soybean Oil

- **Complex Fermentable Carbon complex**

- lecithine
- polylactate

- **Zero Valent Iron (ZVI)**

- **Soluble Iron Compounds**

Selection Factors

- ORP of the aquifer
- Hydrogen vs. Acidity produced
- Biodegradation rate / longevity
- Ease of injection and distribution

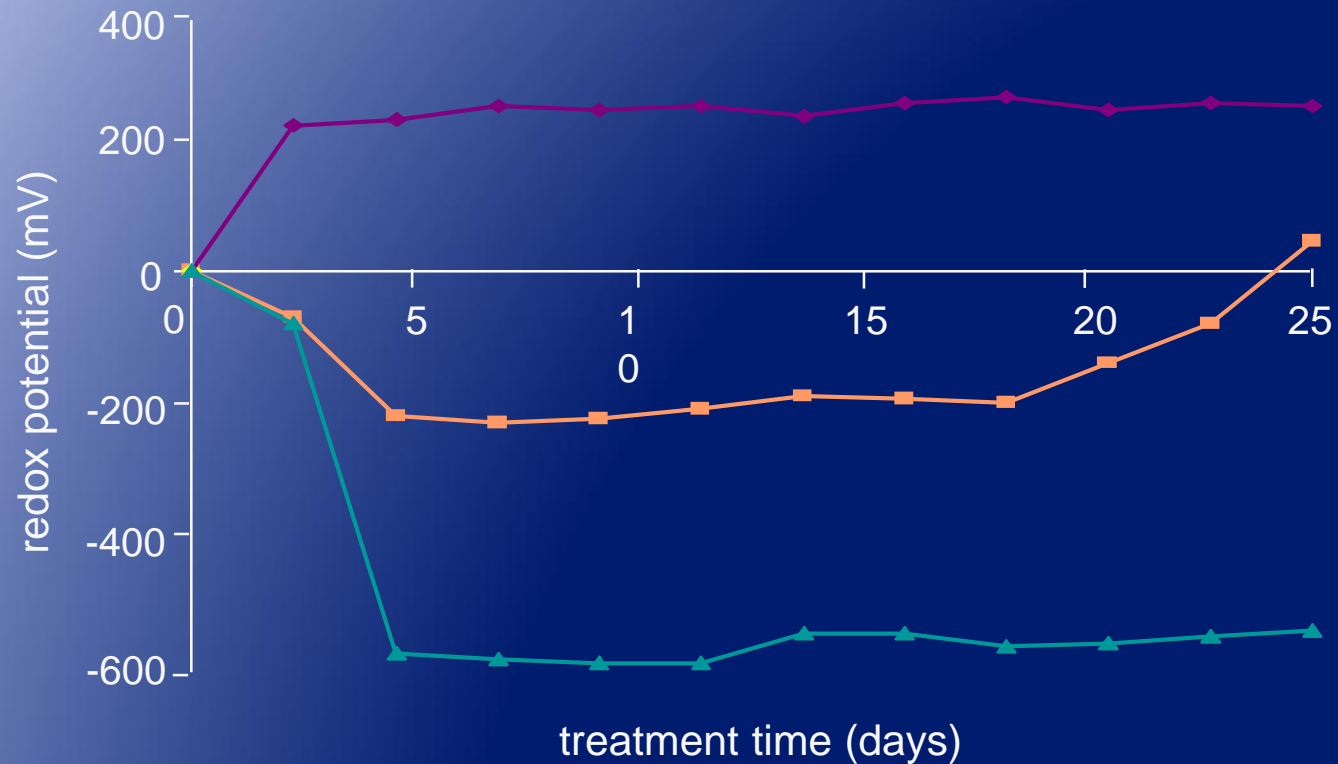


Selection: Hydrogen Factor

Substrate	Formula	MW	H ₂ O	H ₂ per mole	H ⁺ per mole	H ⁺ /H ₂	H ₂ / Kg
Lactic Acid	C ₃ H ₆ O ₃	90	12%	6	3	0.50	59
Na Lactate	C ₃ H ₆ O ₃	112	40%	6	3	0.33	32
Glycerol	C ₃ H ₈ O ₃	92	0	7	3	0.43	76
Ethyl Lactate	C ₅ H ₁₀ O ₃	118	2%	7	5	0.71	58
Sucrose (molasses)	C ₁₂ H ₂₂ O ₁₁	342	65%	24	12	0.50	25
Soybean Oil	C ₅₆ H ₁₀₀ O ₆	873	0	157	56	0.36	180
Lecithin	C ₄₂ H ₈₂ NO 8P	758	100%	122	39	0.321	124
ZVI	Fe ⁰	56	0	1	Consumes acidity		18

Source: EOS Remediation

Redox Potential in Soil during Reductive Phase

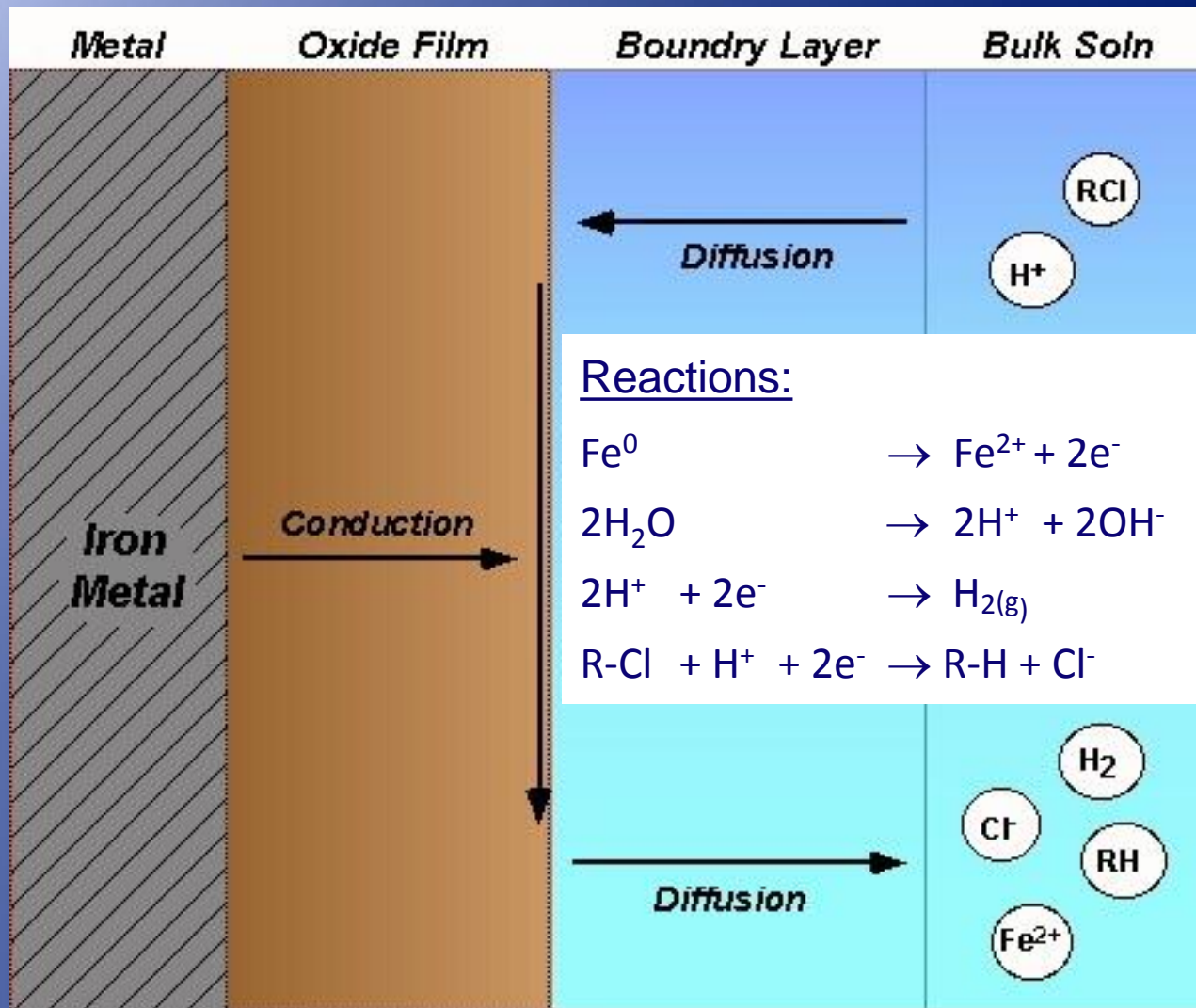


◆ Control ■ Fermentable Carbon ▲ ZVI + Carbon technology

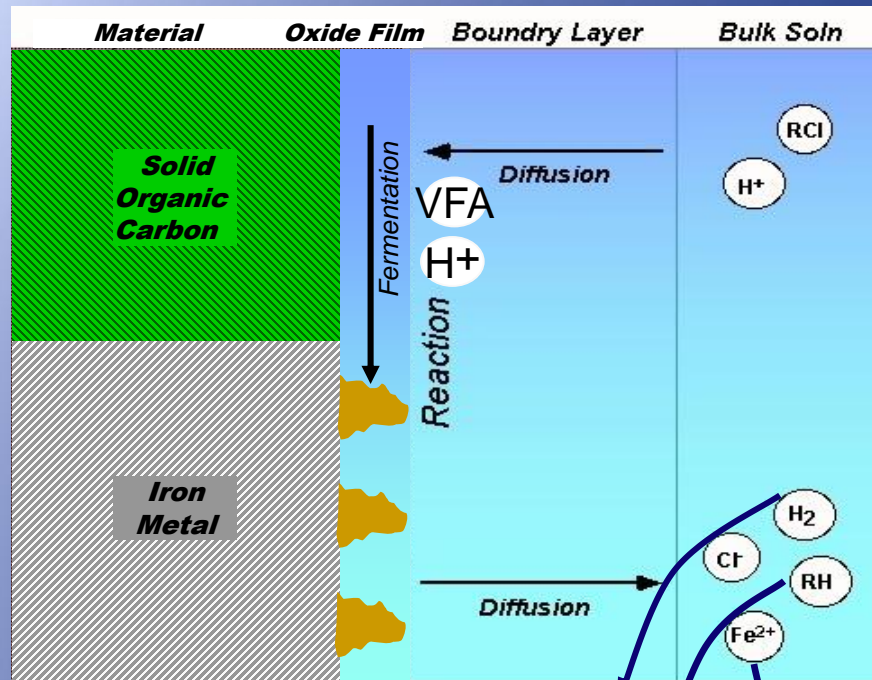
ISCR: Multiple Dechlorination Mechanisms

Mechanism	Material	Description
1. Direct Chemical Reduction	ZVI alone and Carbon	<ul style="list-style-type: none">• Redox reaction at iron surface where solvent gains electrons and iron donates electrons• Abiotic reaction <i>via</i> beta-elimination
2. Indirect Chemical Reduction	ZVI alone and Carbon	Surface dechlorination reactions mediated by magnetite and green rust precipitates formed from iron corrosion products
3. Stimulated Biological Reduction	Carbon alone	Anaerobic reductive dechlorination involving fastidious microorganisms Strongly influenced by nutritional status and pH of aqueous phase
4. Enhanced Thermodynamic Decomposition	ZVI alone and Carbon	Energetics of dechlorination more favorable under lower redox conditions generated by combined ZVI corrosion + carbon fermentation (ΔG , Nernst equation, pH, Eh, T, P)

Direct Dechlorination Reactions with ZVI



Carbon + ZVI Synergies Generate Multiple Dechlorination Mechanisms: ISCR



1. Direct Iron Effects:

Hydrocarbon generation:

2. Indirect Iron Effects: Dissolved iron precipitates to reactive minerals

3. Biostimulation:

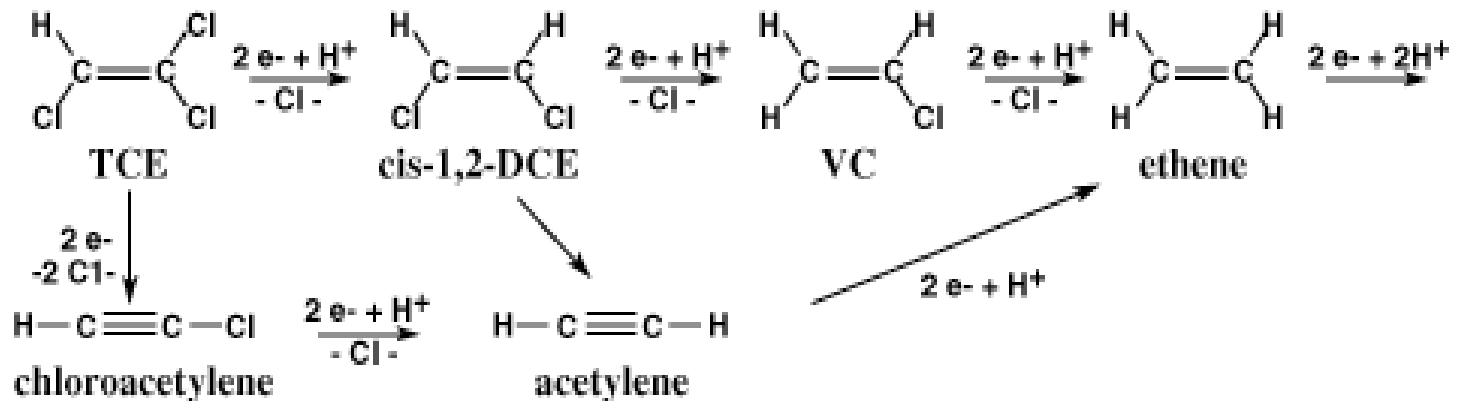
- Serve as electron donor and nutrient source for microbial activity
- VFAs reduce precipitate formation on ZVI surfaces to increase reactivity
- Facilitate consumption of competing electron acceptors such as O₂, NO₃, SO₄
- Increase rate of iron corrosion/H₂ generation

4. Enhanced Thermodynamics:

- Very low redox reached by addition of fermentable carbon and ZVI (-500 mV)
- Two processes simultaneously reduce Eh
- Enhances kinetics of dechlorination reactions via higher electron/H⁺ pressure

Contaminant Reduction Pathways with Iron and Carbon as Drivers

Biological Pathway Driven by Hydrogen from both Fermenting Carbon and Iron

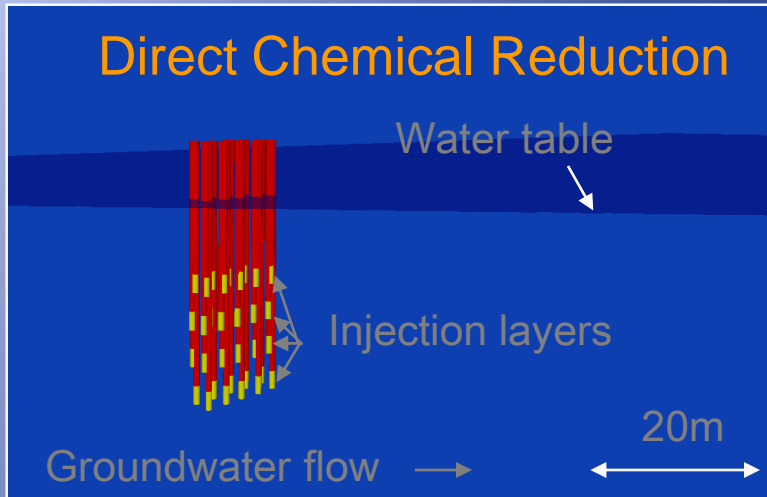


Abiotic Pathway (β -Elimination): Direct Iron-mediated Chemical Reduction

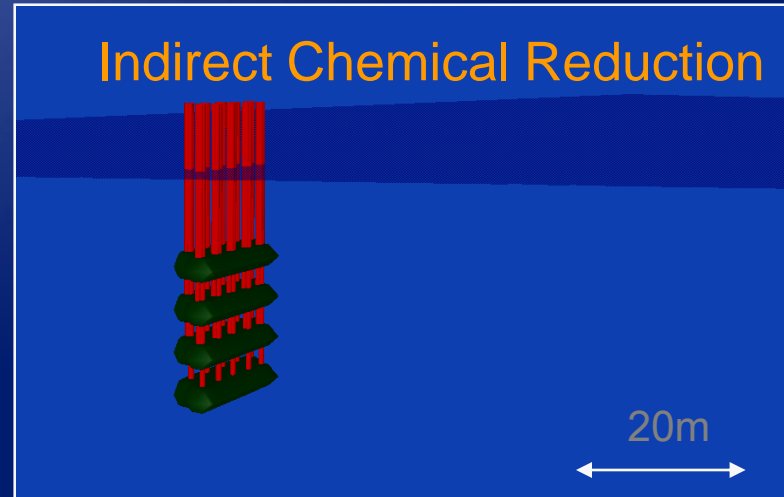
- Abiotic reactions minimize/eliminate DCE/VC.
- Secondary iron mineral by-products like pyrite (FeS) generate persistent reactive zones supported by modest amounts of background carbon.
- Biological reactions have advantages in physical distribution and longevity.
- Synergy between iron and carbon facilitates more efficient destruction.

ISCR ZVI + Carbon Treatment Mechanisms

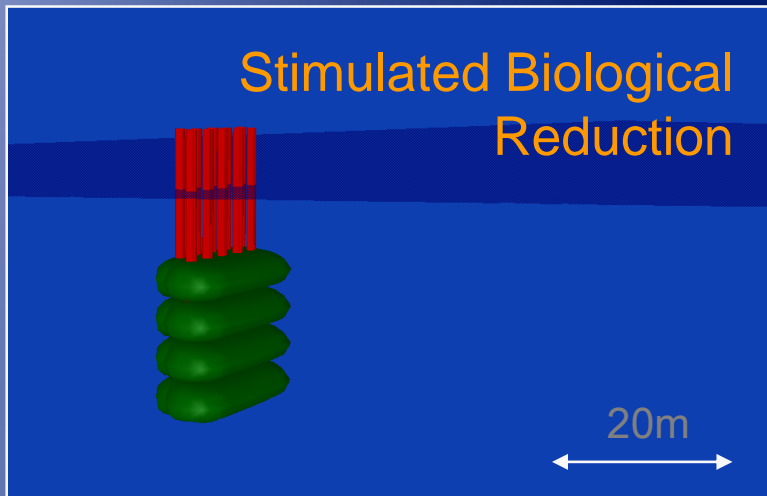
Direct Chemical Reduction



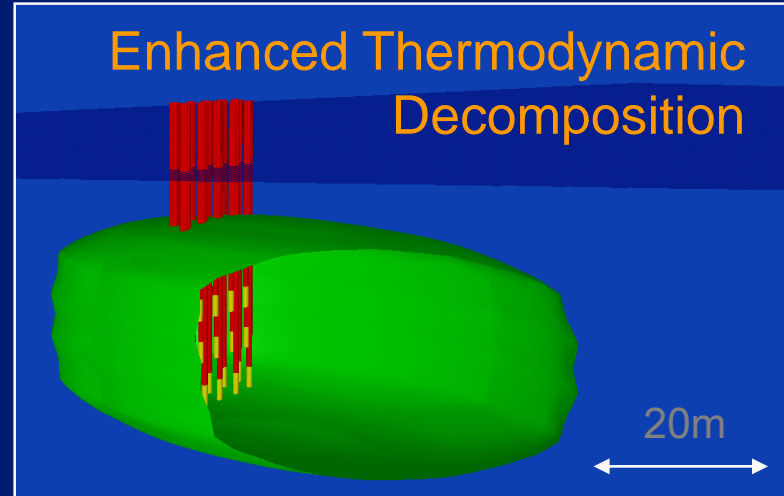
Indirect Chemical Reduction



Stimulated Biological Reduction



Enhanced Thermodynamic Decomposition



Defining *In Situ* Bioremediation

- Natural Attenuation – biotransformation occurs naturally: indigenous microbes & nutrients present (Monitored Natural Attenuation - MNA)
- Biostimulation / bioenhancement - indigenous microbes present, but substrates &/or nutrients must be added to foster bioactivity
 1. Aerobic bioremediation; needs oxygen
 2. Anaerobic bioremediation; no oxygen
- Bioaugmentation – indigenous microbes not present, so organisms are added

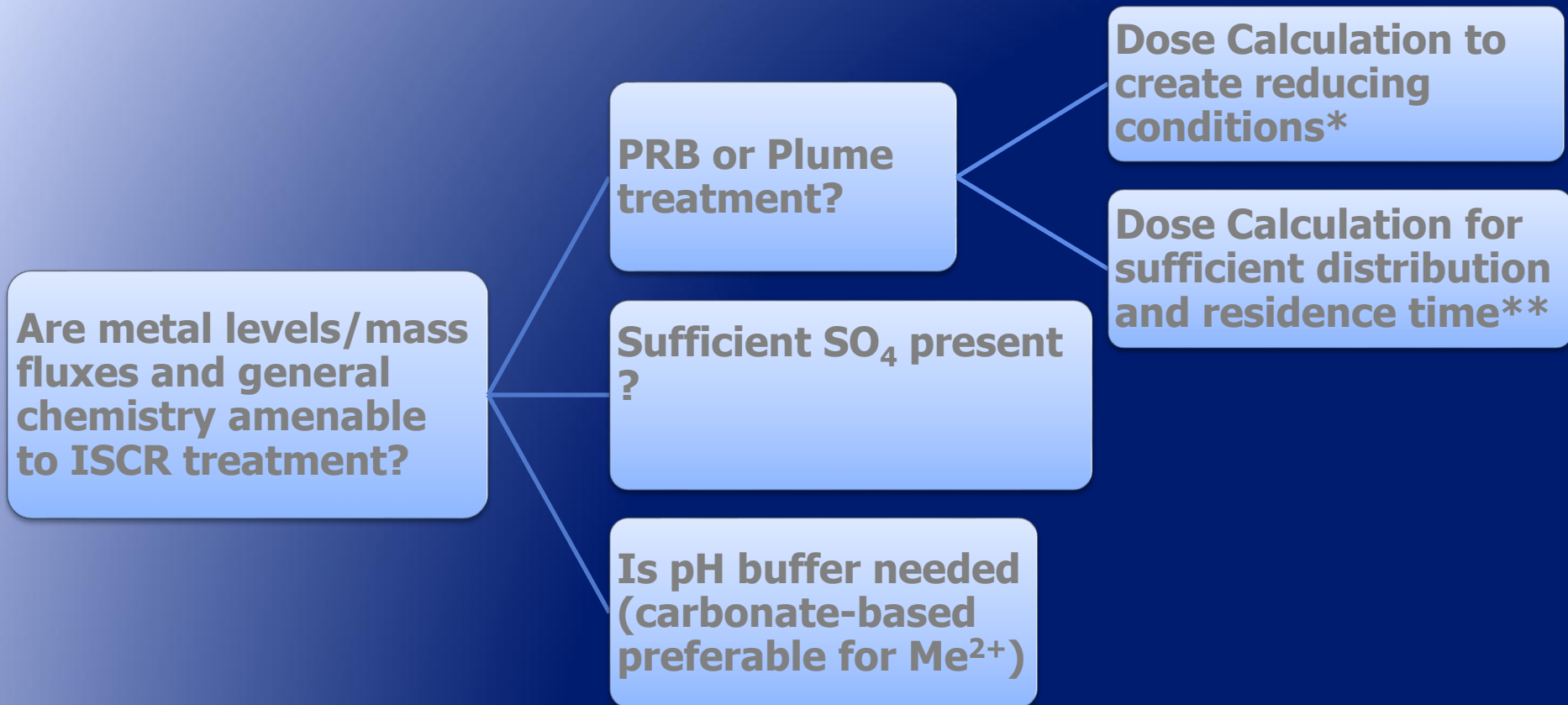
Design & Injection

Design and Field Measurements Requirement

- Total concentration in soil and groundwater of targeted metals
- Dissolved (field filtered) metals concentrations
- pH, Redox Potential (Eh), Dissolved Oxygen
- Cation scan (calcium, sodium, magnesium, silicon)
- Anion Scan (chloride, sulfate, nitrate)
- Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC)
- Alkalinity

These parameters are used to assess the applicability of an ISCR approach and for optimizing the application rate. The same parameters are also recommended monitoring parameters.

Design Considerations ZVI + CS



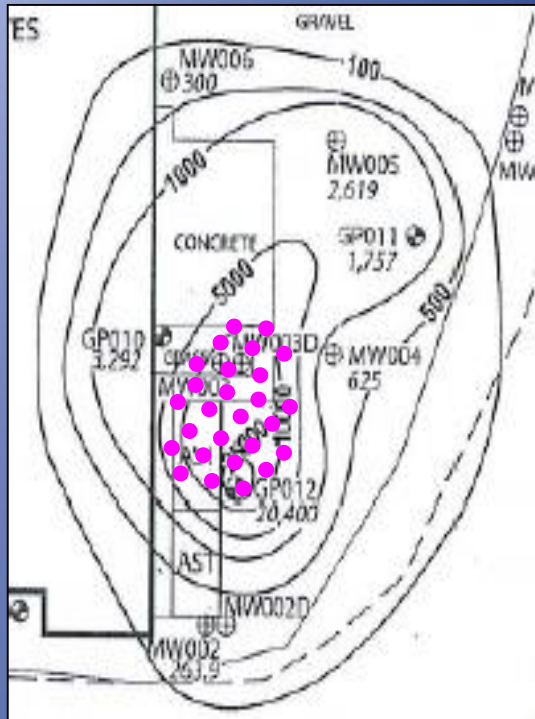
Parameters to consider for a successful enhanced bioremediation

- Temperature, pH
- Nutrients Balance (C:N:P ratio)
- Site geology and hydrogeology consideration
- Proper micro-organisms presence
- Aerobic or anaerobic conditions to support bioremediation in soil and groundwater.



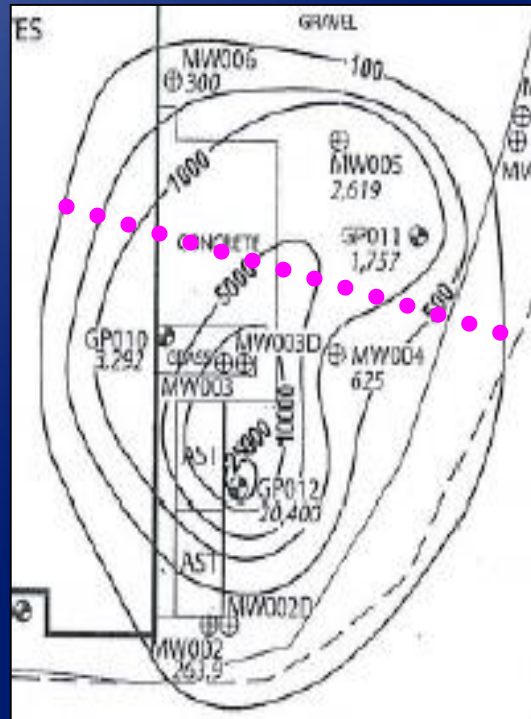
ISCR Conceptual Remedial Design Strategies

Source Area/
Hotspot Treatment



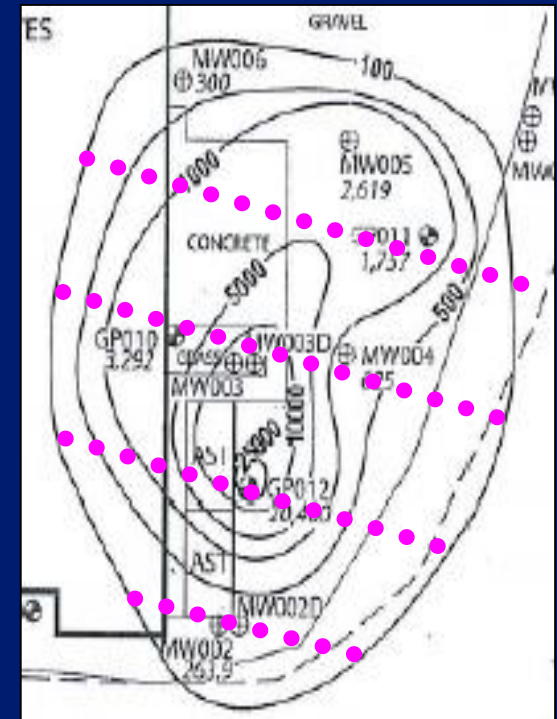
Dosing: 0.15 to 1% wt/wt
Spacing: 5 to 15 ft (DPT)

Injection PRB for
Plume Control



Dosing: 0.4 to 1% wt/wt
Spacing: 5 to 10 ft (DPT)

Plume
Treatment



Dosing: 0.05 to 0.2% wt/wt
Line Spacing: based on 1 year
g.w. travel distance

Bench Scale Laboratory testing

- Site groundwater and aquifer material needs to be used.
- Proper sampling and sample handling is essential to avoid sample alteration (aeration) that may result in testing artifacts.
- Flow through column tests are preferable to batch test.
- Field pilot-scale test are strongly recommended as a feasibility step, either following the lab evaluation or stand alone, for As treatment especially.



ISCR Installation Methods

- Direct Placement:
 - Trenching
 - Excavations
 - Direct soil mixing
- Injection Methods:
 - Direct injection
 - Well injections
 - Hydraulic fracturing
 - Pneumatic fracturing
 - Jetting
 - Electrokinetic



In Resume

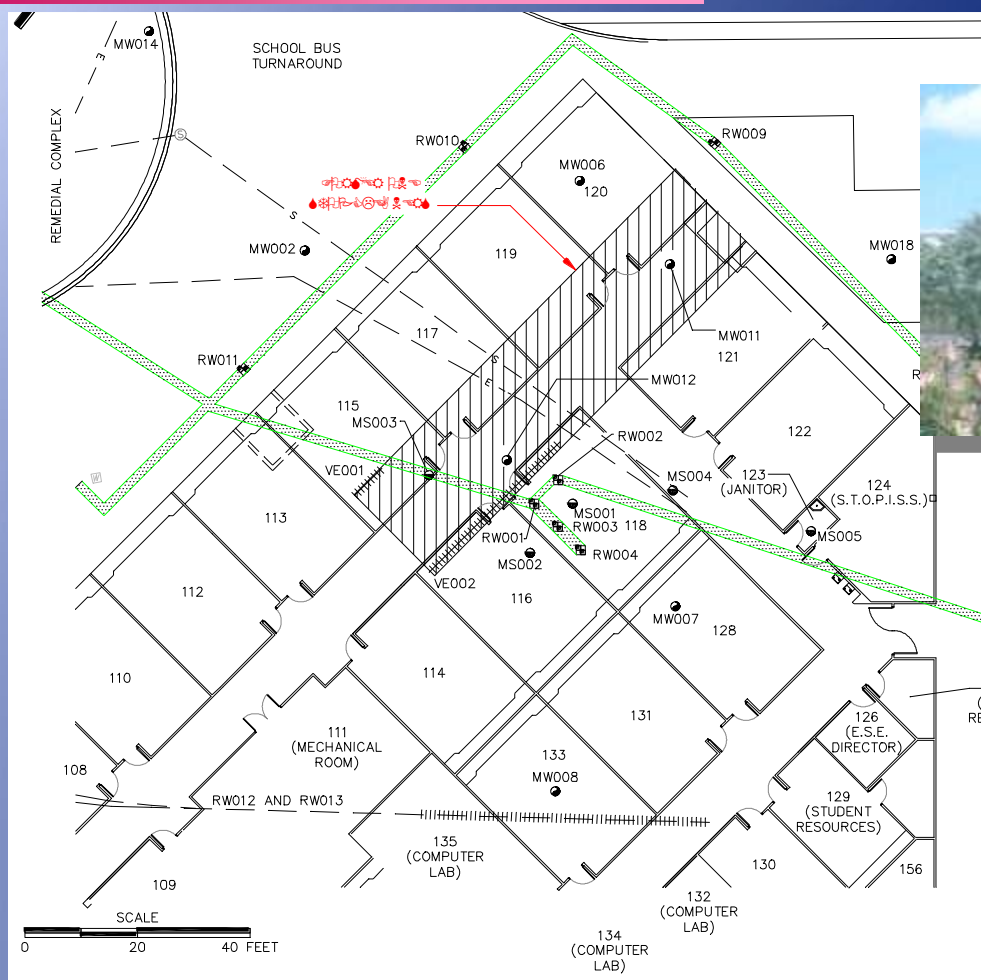
Principle and Applicability

Enhanced Bioremediation Advantages

- Enhances natural in-situ processes already at play (typically uses natural groundwater gradient, naturally occurring biodegradation).
- Low energy and cost effective
- Relatively easy to manage and handle.
- Can be used in tandem with other remedial technologies that address small amounts of residual soil and groundwater contamination

Case Study

One Stop Dry Cleaner

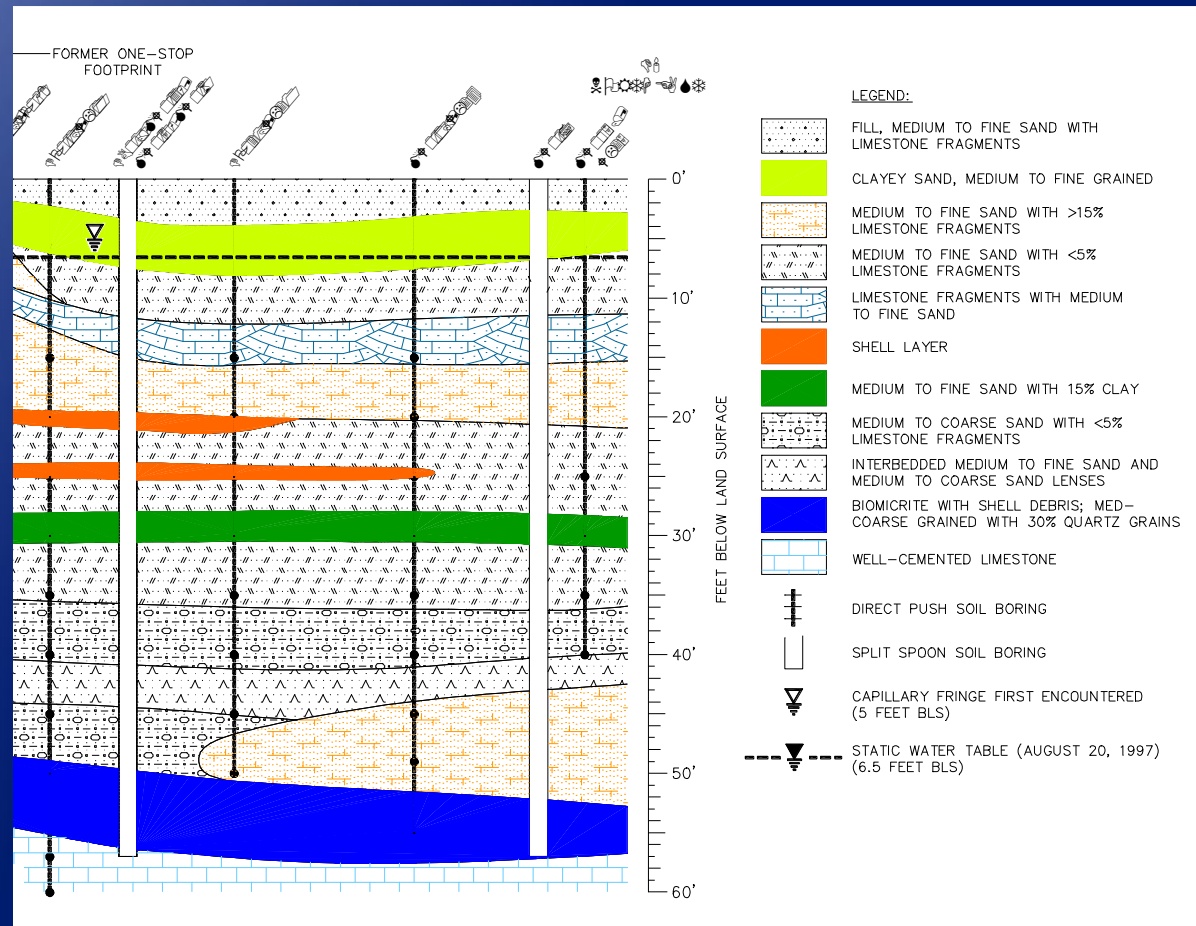


- Former mall converted to charter school
- Drycleaning operations stopped in 1996

One Stop Dry Cleaner

Assessment Summary

- Presumptive residual DNAPL
- Hydraulic conductivity: 38 to 993 ft/day
- Depth to water: 6 to 7 ft. bls
- City wellfield is impacting plume (up to 3 ft/day)
- 45 soil samples (up to 486 mg/kg)
- Dissolved PCE > 99,000 ug/L



One Stop Dry Cleaner

Remedial Strategy

AOC 1:

Unsaturated Source : SVE

(0 – 8 ft bls)

- Source reduction to minimize leachate
- Aggressive remediation of unsaturated soils

AOC 2:

Saturated Source: ISCO

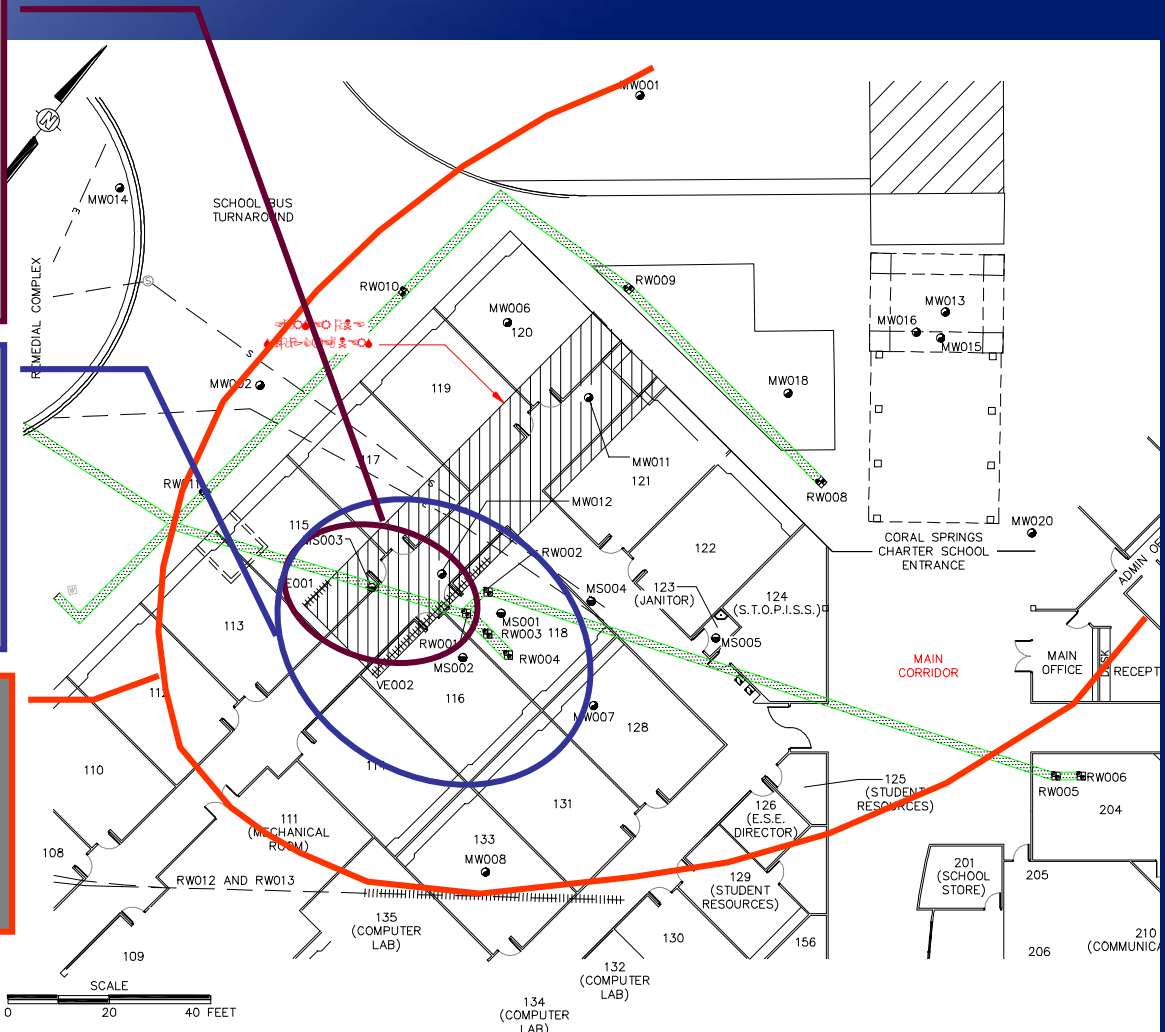
(8 -70 ft bls)

- Saturated soil treatment
- Groundwater remediation
- Residual DNAPL treatment

AOC 3: Extended Dissolved Plume; P&T

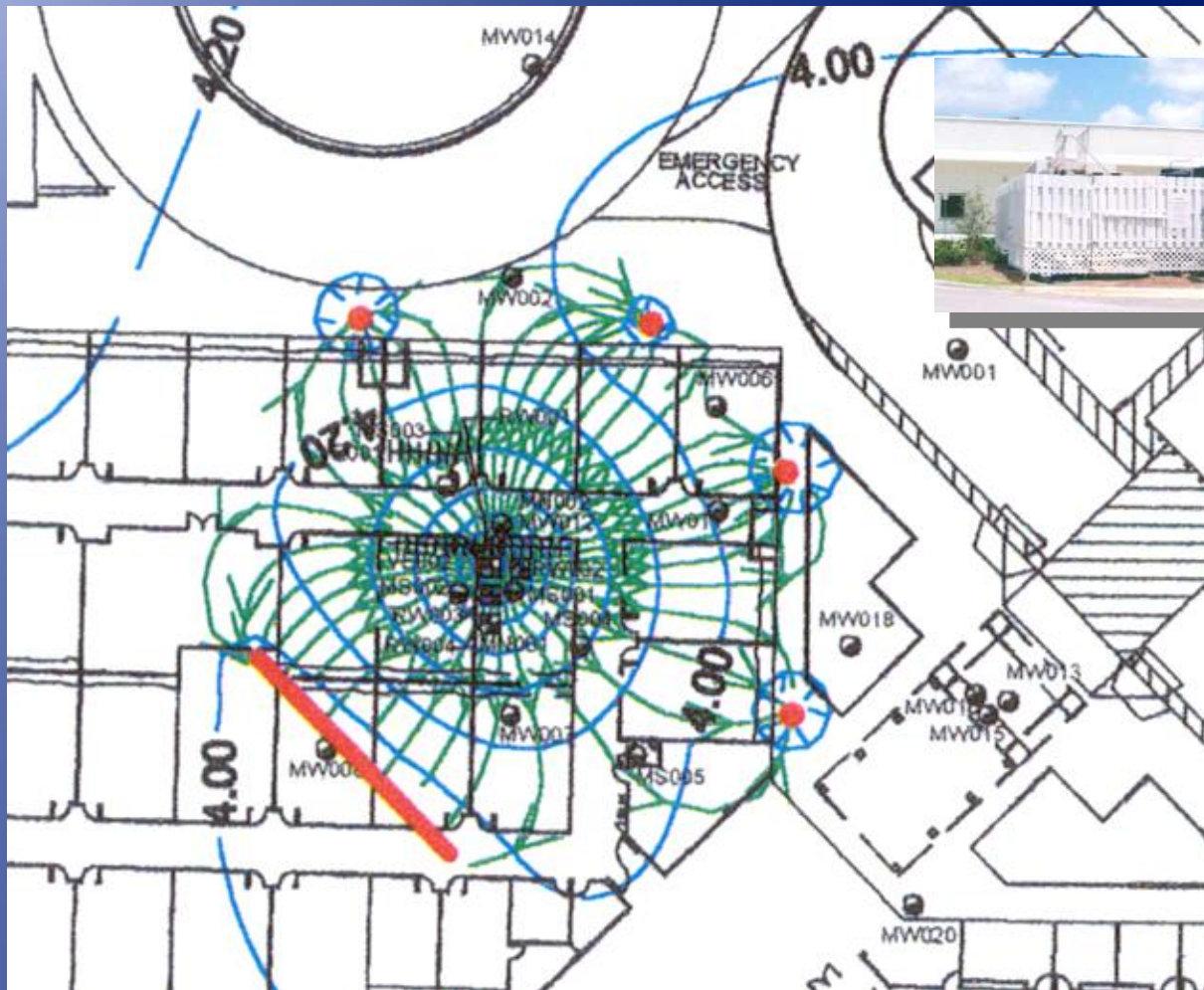
(8 – 60 ft bls)

- Groundwater remediation
- Plume containment



One Stop Dry Cleaner

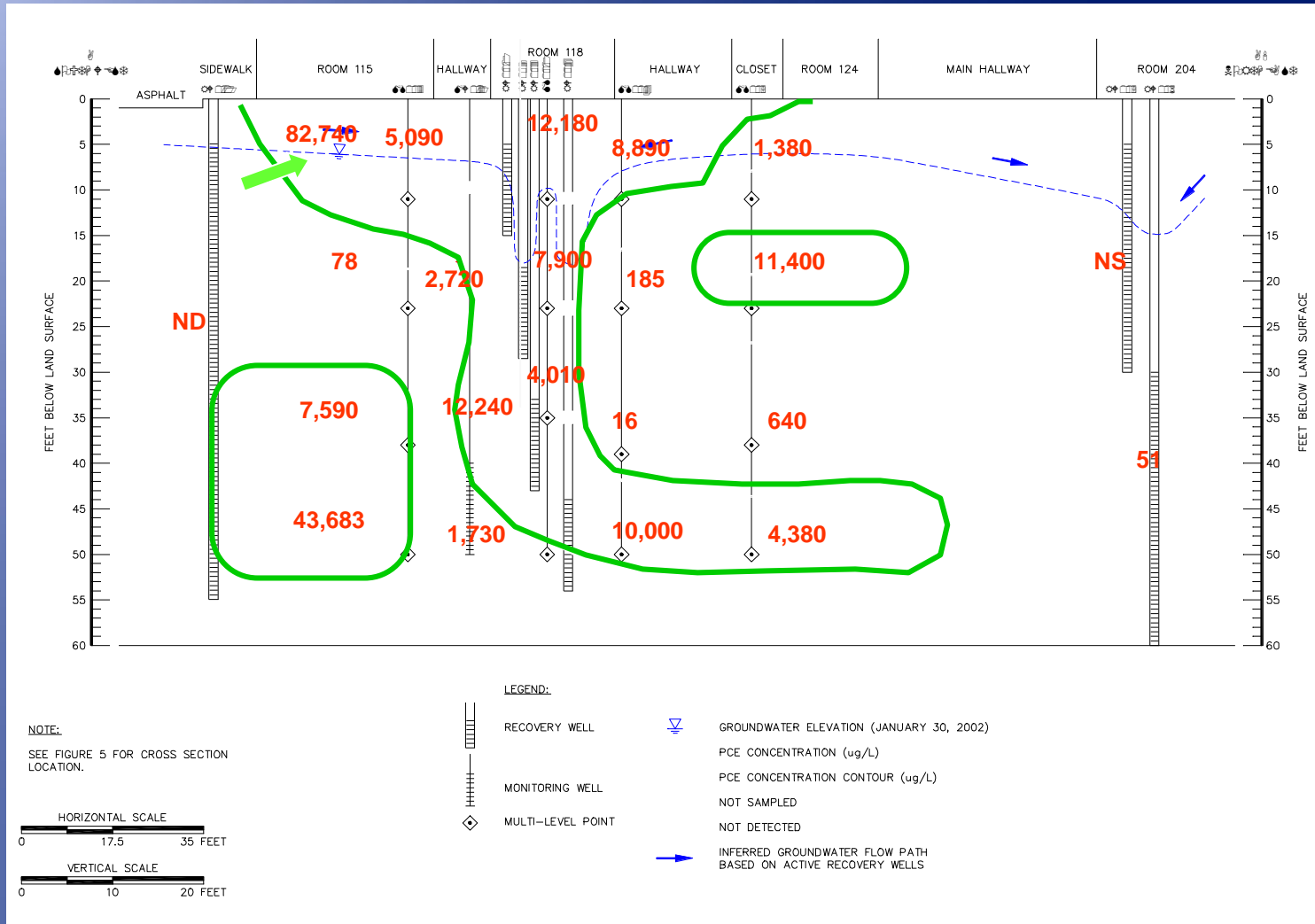
Groundwater Injection/Recovery



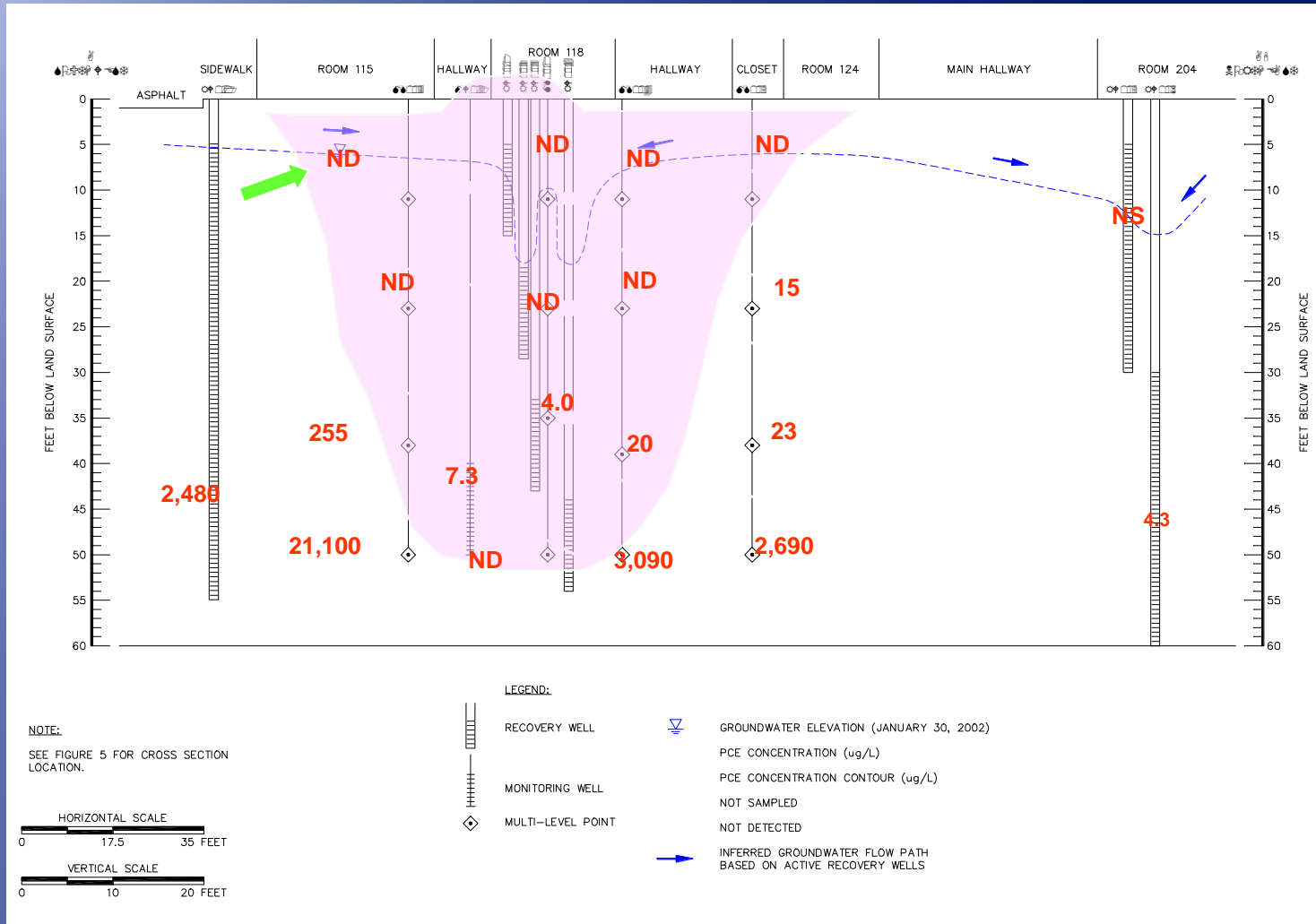
Equipment compound

- 3.6M Gallons of groundwater recovered, treated, and reinjected
- 822,300 Gallons of 0.6% KMnO_4 were injected
- 42,440 Pounds of KMnO_4 was placed (13 cycle bins)
- Injection flows were typically 2 to 14 gpm at 5 psig (initial)

Pre-Injection Dissolved VOHs - Jan 2002

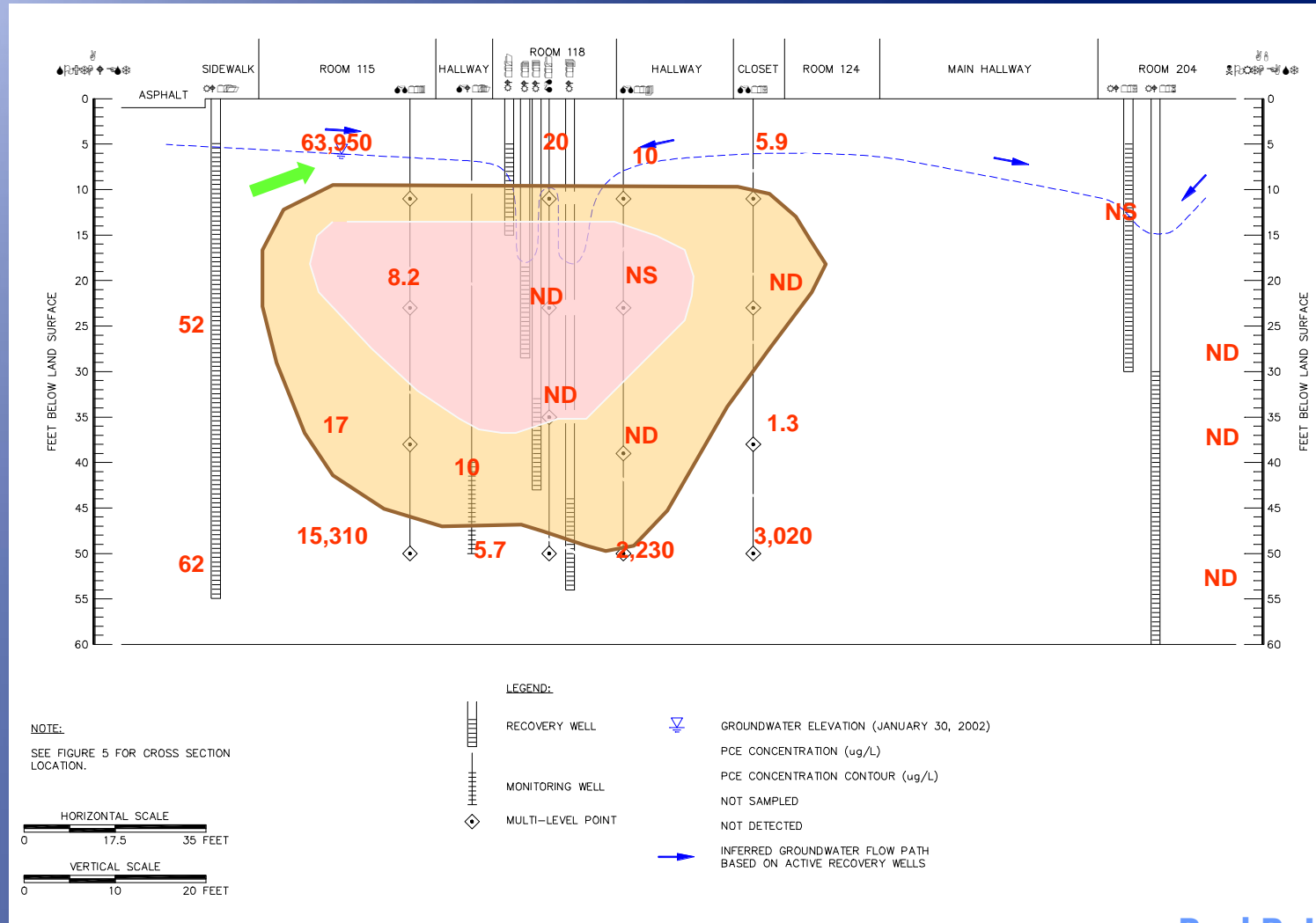


Post-Injection Dissolved VOHs - May 2002



Paul R. Lear, Ph.D.

Post-Injection Dissolved VOHs – Oct. 2002



Paul R. Lear, Ph.D.

One Stop Dry Cleaner

Phase I Dissolved Mass Reduction Estimates

Zone	Depth (ft. bls)	Pre-Injection		Post Injection Rebound		%
		Average Concentration (ug/L)	Dissolved Mass Estimate (lbs.)	Average Concentration (ug/L)	Dissolved Mass Estimate (lbs.)	
A	5 – 15	5,922	43.6	37?	-15?
B	15 – 30	2,068	22.9	423	3.12	-89
C	30 – 45	2,896	32.0	361	3.99	-88
D	45 - 55	5,944	44.1	2,794	20.6	-53
Total:			143		64.7?	-55?

- The ISCO system has been very effecting at mass reduction in the center of the dissolved plume.
- Rebound sampling has shown that 21 wells were reduced from starting PCE concentrations ranging from 180 ug/L to 63,950 ug/L to non-detect levels.
- The strong rebound or (recharging due to leachate) at MS003 and the deeper contamination represent the areas of significant mass still remaining on site.

Paul R. Lear, Ph.D.

Acknowledgements

- Carus Chemical
- ERM Corporation
- EOS Remediation
- Peroxychem Corporation
- Regeneration
- Progressive Engineering & Construction
- Recover

Thank you for your attention !
Have a good day !!!

Contact information:

E-mail: jean.pare@chemco-inc.com

Tel: 418-953-3480

Web site: www.chemco-inc.com

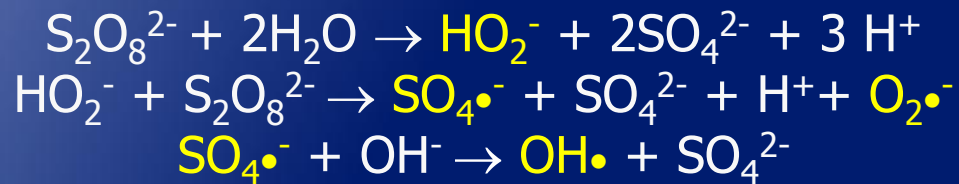
Oxydation Détails

Permanganate (sodium or potassium) Implementation

- Effective from pH (3 to 12, optimum 7) for desired chemical interaction
- Low contaminants residual value obtainable
- High density (around 1.3) helps distribution and penetration
- Long reaction times allow higher distribution distance and better desorption processes
- Applicable in many soil types
- Manganese dioxide can be kept in solution using a polyphosphate mix

Persulfate Activation: Reactions with Water

- Sodium persulfate is activated when the solution is raised to $\text{pH} > 10.5$
- Alkaline Activation (Furman et al., 2010):

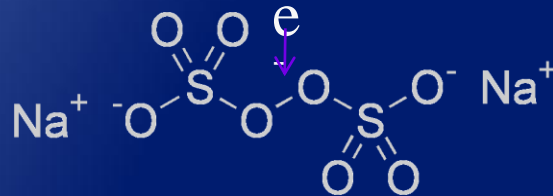


(note: $\text{H}_2\text{O}_2 \leftrightarrow \text{HO}_2^- + \text{H}^+$ $\text{pK}_a = 11.7$)

- Forms:
 - Oxidative radical: $\text{SO}_4^{\bullet-}$, and $\text{OH}\bullet$
 - Reductive radical: $\text{O}_2^{\bullet-}$
 - Nucleophiles: $\text{O}_2^{\bullet-}$ and HO_2^-
- Analogous to the chemistry that has been studied with catalyzed hydrogen peroxide (CHP)

Persulfate Activation: Electron Donation

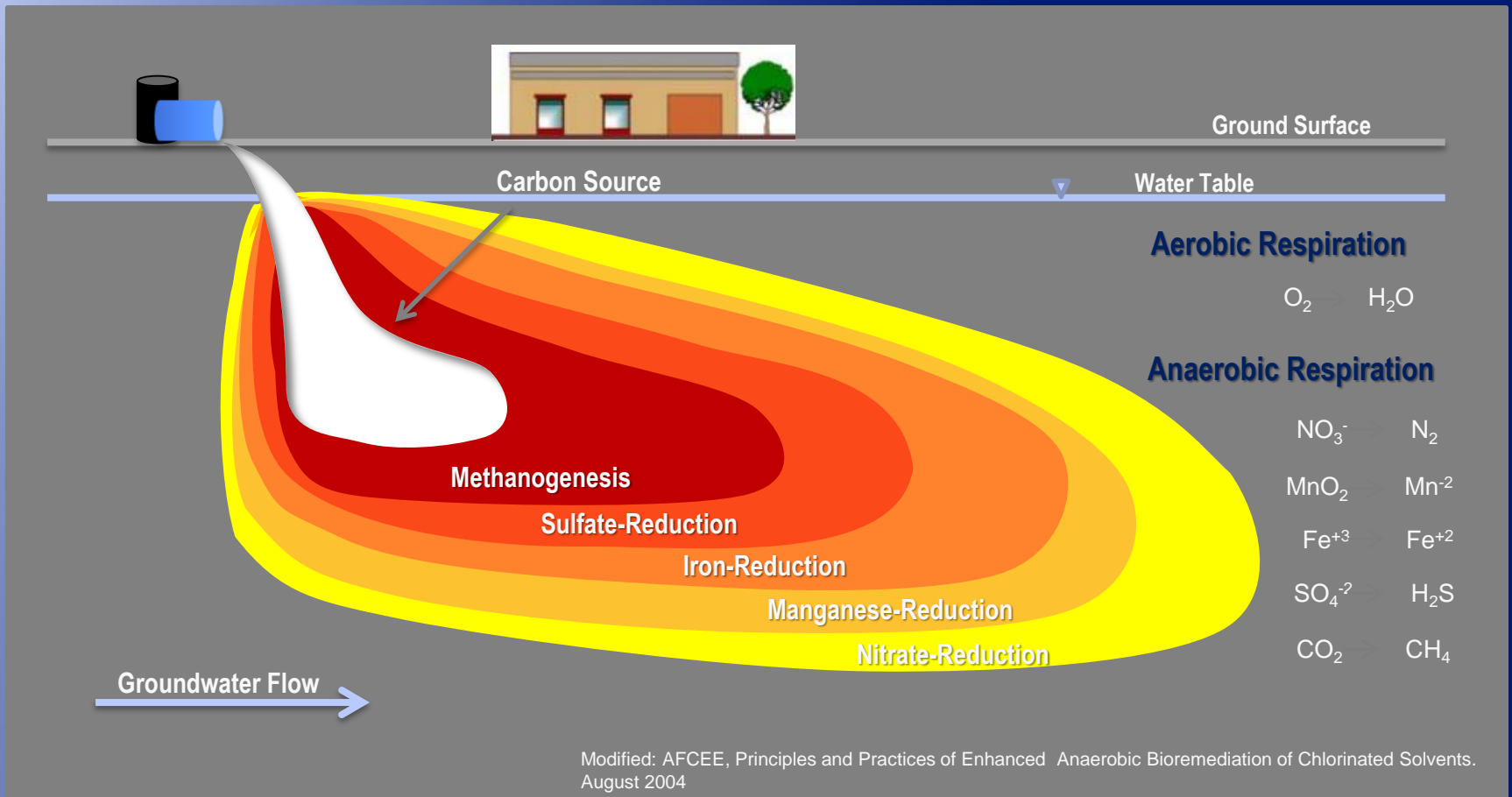
- Similar to Fenton's Reagent:



- Activation methods based on one electron transfer:
 - Reduced metals: Fe (II), Fe (0), etc
 - Organics
 - Hydrogen peroxide

Reduction Détails

Selection: ORP Factor



What is Bioremediation?

"bio-remediate" means to use biological organisms to solve an environmental problem such as contaminated soil or groundwater.

Fermentation

Electron Donor

- Natural DOC
- Sodium Lactate
- Molasses
- Vegetable Oil (EOS)
- Non-Chlorinated hydrocarbon

+

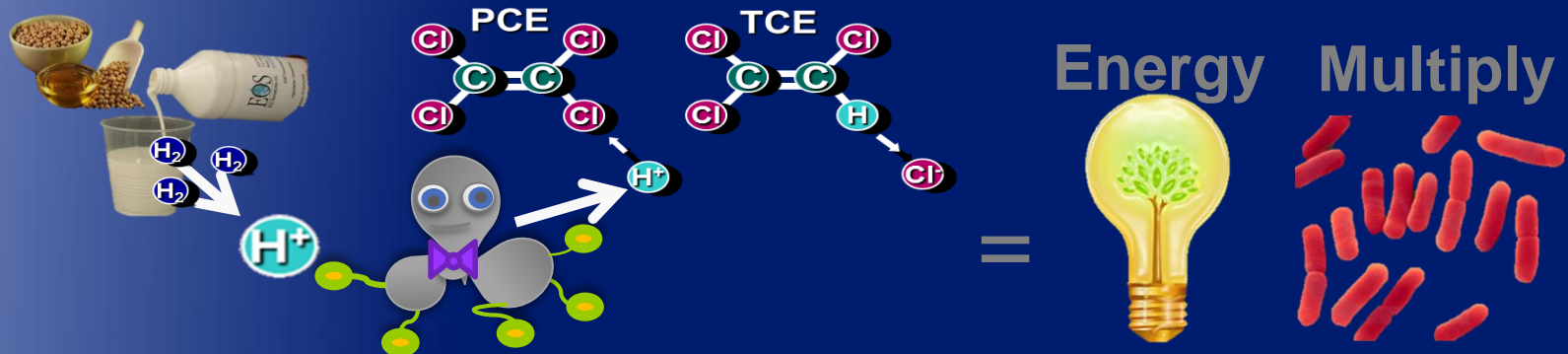
Respiration

Electron Acceptor

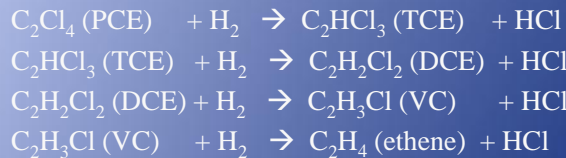
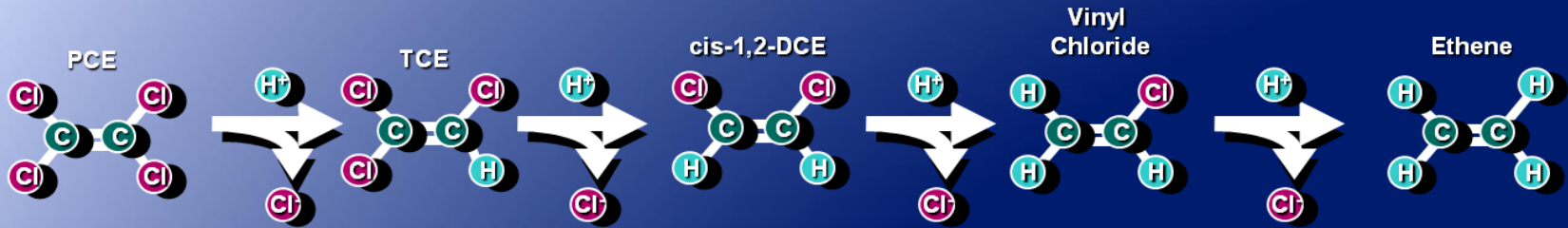
- Oxygen
- Nitrate
- Iron
- Sulfate
- CVOC (PCE & TCE)

- Cornell University

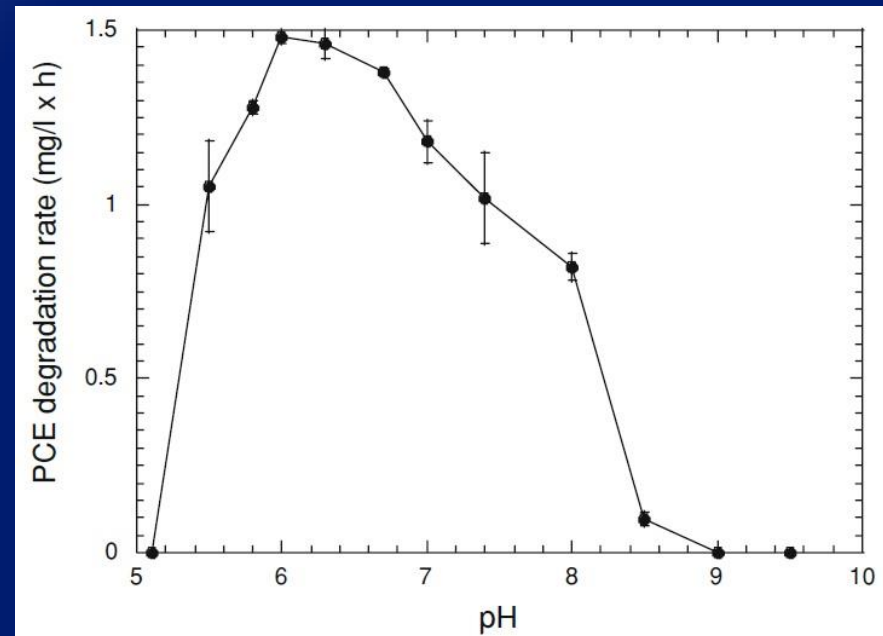
<http://ei.cornell.edu/biodeg/bioremed/>



Managing Aquifer pH



**Optimum pH for PCE
reduction appears to be
6.0 – 7.0**



Vainberg, S., R.J. Steffan, R. Rogers, T. Ladaa, D. Pohlmann and D. Leigh, 2006. Production and Application of Large-Scale Cultures for Bioaugmentation, The Fifth International Remediation of Chlorinated and Recalcitrant Compounds Conference, Monterey, CA.