

# CHEMICAL OXIDATION TECHNIQUES FOR THE *IN SITU* REMEDIATION OF HYDROCARBON IMPACTED SOILS

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# Introduction

- In-situ, cost effective remediation technique for reducing the mass, mobility and/or toxicity of contaminated soils and groundwater
- Involves the introduction of chemical oxidants into subsurface soil and groundwater to destroy organic contaminants – mineralisation to carbon dioxide & water or oxidation to a relatively less harmful form that may be suitable for subsequent treatment

# Introduction

- Selection of the appropriate oxidant is dependent upon the:
  - nature and type of contaminant
  - level of remediation required
  - viability of oxidant delivery
  - type of soil and hydrogeology of the site
- Three main oxidants utilized:
  - Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ )/Fenton's Reagent
  - Permanganates ( $\text{KMnO}_4$ ,  $\text{NaMnO}_4$ )
  - Ozone

# Reaction Chemistry

- Reaction chemistry is different for each oxidant (e.g. simplified stoichiometric reactions of TCE):
  - Hydrogen Peroxide:
$$3\text{H}_2\text{O}_2 + \text{C}_2\text{HCl}_3 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} + 3\text{HCl}$$
  - Fenton's Reagent:
$$[2\text{H}_2\text{O}_2 + \text{Fe}^{+2}] + \text{C}_2\text{HCl}_3 \rightarrow \text{Fe}^{+3} + 3\text{Cl}^- + 2\text{CO}_2 + \text{H}^+ + 2\text{H}_2\text{O}$$
  - Potassium Permanganate:
$$2\text{KMnO}_4 + \text{C}_2\text{HCl}_3 \rightarrow 2\text{CO}_2 + 2\text{MnO}_2 + 2\text{KCl} + \text{HCl}$$
  - Ozone:
$$\text{O}_3 + \text{H}_2\text{O} + \text{C}_2\text{HCl}_3 \rightarrow 2\text{CO}_2 + 3\text{HCl}$$
- Generally a multi-step process involving the production of intermediates, which may impact the performance of the oxidant
- Oxidants are generally non-selective
  - will also oxidize natural organic matter present in the soil → substantial increase in total oxidant demand

# Hydrogen Peroxide/Fenton's Reagent

- $\text{H}_2\text{O}_2$  has a relative oxidizing power of 1.31 ( $E^\circ=1.8\text{v}$ )
- When combined with iron (II) it undergoes a Fenton-like reaction yielding hydroxyl radicals ( $\text{OH}\cdot$ ) with relative oxidizing power of 2.06 ( $E^\circ=2.8\text{v}$ )



- $\text{OH}\cdot$  radicals are unstable
- Applicable in both vadose and saturated zones
- Contaminants oxidizable include:
  - Chlorinated solvents
  - Non-chlorinated solvents
  - PAH's
  - Esters
  - Pesticides
  - VOC's
  - SVOC's
  - phenols, and others

# Hydrogen Peroxide/Fenton's Reagent

- pH: acidic conditions (pH2-pH4) best; applicable up to near neutral
- Amendments:  $\text{Fe}^{2+}$  and acid (eg.  $\text{FeSO}_4$ )
- Dosage: 5-50wt%  $\text{H}_2\text{O}_2$ , multiple dosing common
- Stability: easily degrades in soil/groundwater
  - $\text{H}_2\text{O}_2$  readily decomposes to  $\text{H}_2\text{O}_{(v)}$  &  $\text{O}_2$
- Potential Detrimental Effects/Disadvantages:
  - $\text{Fe}^{2+}$  colloid genesis & substantial gas evolution
  - Temperature increase (exothermic reaction)
  - Subsurface pH lowered if inadequate buffering
  - Adverse impact of Fenton's reagent on microbial populations
- Advantages:
  - Low chemical cost
  - Relatively rapid reaction process
  - Breakdown of  $\text{H}_2\text{O}_2$  to oxygen → stimulate aerobic biological activity
  - Applicable over a wide range of VOC's & SVOC's
  - Range of reliable field application information available

# Permanganates: $\text{KMnO}_4$ , $\text{NaMnO}_4$

- The permanganate ion has relative oxidizing power of 1.24 ( $E^\circ=1.7$ )
- Reaction with organic compounds:  
$$\text{R} + \text{MnO}_4^- \rightarrow \text{MnO}_2 + \text{CO}_2 \text{ or } \text{R}_{\text{ox}} + \text{others}$$
where, R = organic contaminant of concern  
Rox = oxidized intermediate organic compound
- Due to its multiple valence states, Mn can participate in numerous reactions and is applicable in saturated zone over wide pH range
- Contaminants oxidizable include:
  - Chlorinated solvents
  - Alkenes
  - PAH's
  - Phenols
  - Sulfides
  - Pesticides
  - MTBE
  - BTEX

# Permanganates: $\text{KMnO}_4$ , $\text{NaMnO}_4$

- Amendments: none
- Dosage: 0.02-4.0wt%, single & multiple dosing
- Stability: very stable/persistent in subsurface
- Potential Detrimental Effects/Disadvantages:
  - $\text{MnO}_2$  colloid genesis
  - Regulatory concerns regarding unreacted permanganate in GW
  - Subsurface pH lowered if inadequate buffering
- Advantages:
  - Oxidation reactions are not exothermic
  - Readily soluble in water
  - Easy of delivery to contaminated zone
  - Applicable over a wide pH range
  - Oxidant not toxic to local microbial population

# Ozone (O<sub>3</sub>)

- Gas phase oxidizer with relative oxidizing power of 1.77 (E°=2.1)
- Generated artificially on site by electric generators
$$\text{O}_2 + \text{Electric Current} \rightarrow \text{O}_3$$
- Applicable in:
  - Typically in vadose zone
  - treatment of LNAPL accumulations in the capillary fringe
  - Injected with air sparging in saturated zone
- Contaminants oxidizable include:
  - Chlorinated solvents
  - Aliphatic hydrocarbons
  - PAH's
  - Aromatics
  - Chlorinated alkenes
  - Phenols
  - Pesticides
  - BTEX

# Ozone (O<sub>3</sub>)

- pH: natural soil pH; best at acidic conditions
- Dosage: 5wt% (from O<sub>2</sub>) or 1wt% (from air), multiple dosing
- Stability: limited in soil; short half-life
- Potential Detrimental Effects/Disadvantages:
  - High reactive rate, instable with short half-life (produced on site)
  - Will escape through surface if site geology does not provide means of natural containment
  - Colloid genesis and minimal gas evolution
  - Minor to high temperature increase (exothermic reaction)
  - Subsurface pH lowered if inadequate buffering
- Advantages:
  - Greater ease of delivery of gaseous than aqueous oxidant
  - Minimal degradation during injection
  - Provides beneficial oxidation and biostimulation

# GEOLOGY & HYDROGEOLOGICAL EFFECT ON OXIDANT PERFORMANCE

- Data required prior to remediation design & implementation:

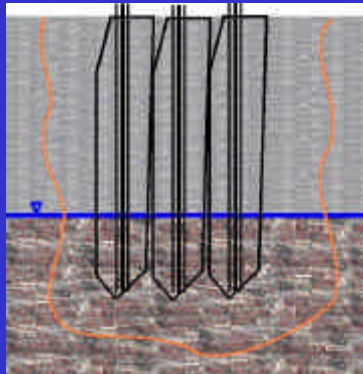
All In-Situ Chemical Oxidation Technologies	Contaminant delineation, VOCs, COD, soil and/or GW pH, hydraulic conductivity, soil classification, GW gradient, vadose zone permeability, oxidation reduction potential, DO, GW depth and conductivity
Hydrogen Peroxide/ Fenton's Reagent	Soil and/or GW iron content Soil and/or GW alkalinity
Potassium Permanganate	Soil and/or GW Manganese concentration Permanganate impurities
Ozone	Vadose zone moisture content

- Additional data required:
  - Geologic & hydrogeological characteristics of the site
  - Depth & thickness of the contaminated region
  - Permeability
  - Physical & chemical heterogeneities

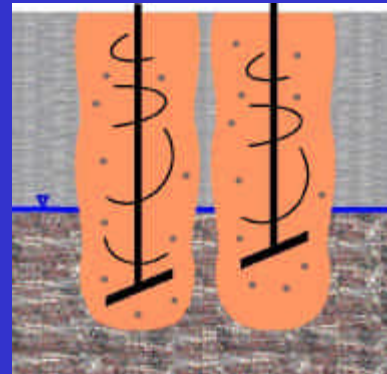
# GEOLOGY & HYDROGEOLOGICAL EFFECT ON OXIDANT PERFORMANCE

- Physical Heterogeneities:
  - Variations in geological formations, layering, existing high permeable pathways
  - Natural or caused by human intervention (underground pipes)
- Chemical Heterogeneities:
  - Presence of reduced minerals & organic matter in GW
  - Generated reaction products (e.g.  $\text{CO}_2$ ,  $\text{MnO}_{2(s)}$ )
  - pH
  - Presence of carbonates & bicarbonates
  - Variability in NOM

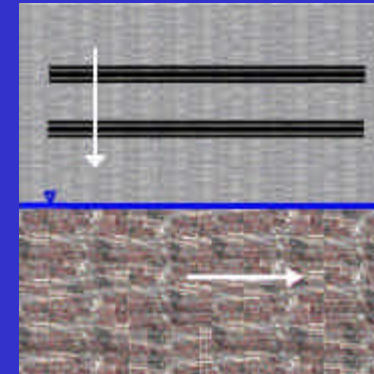
# OXIDANT DELIVERY METHODS



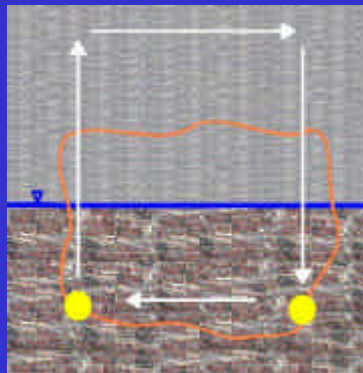
Lance Permeation



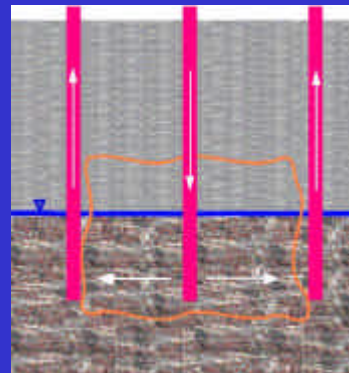
Deep Soil Mixing



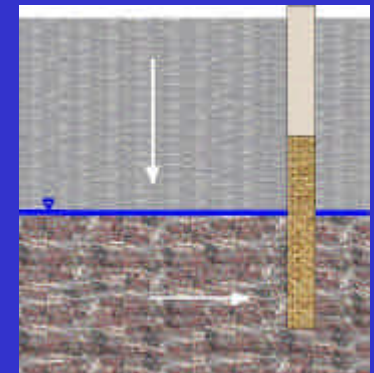
Soil Fracturing



Horizontal Well Flushing

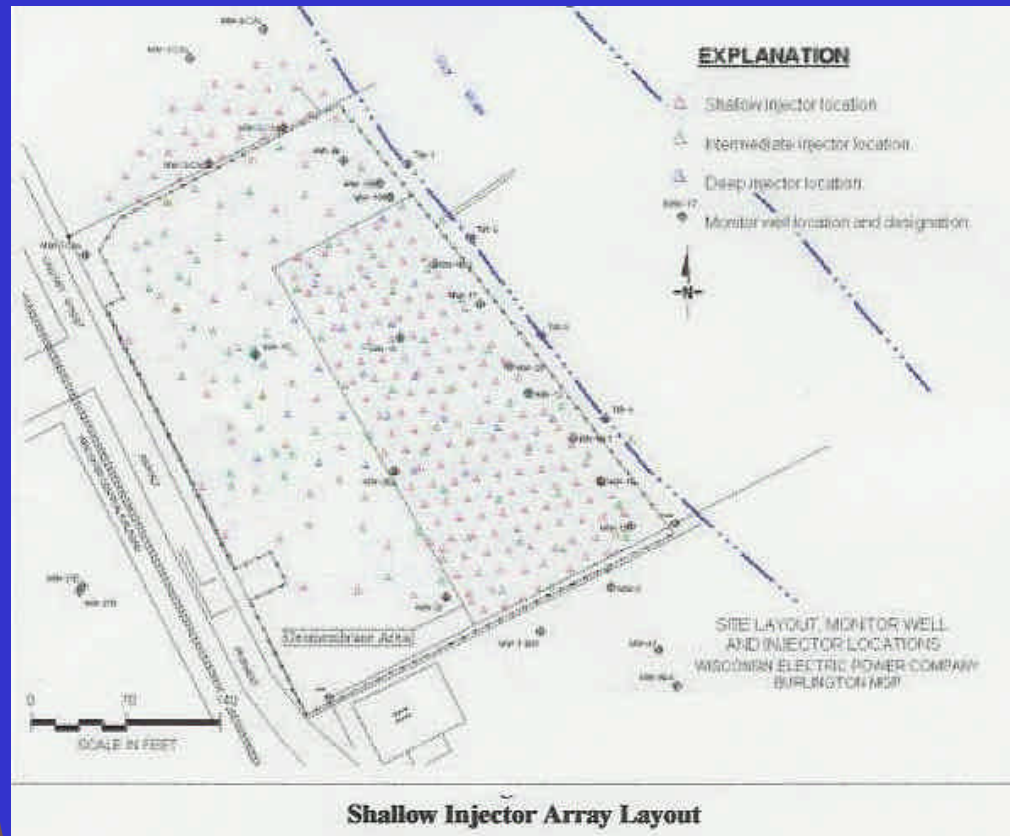


Vertical Well Flushing

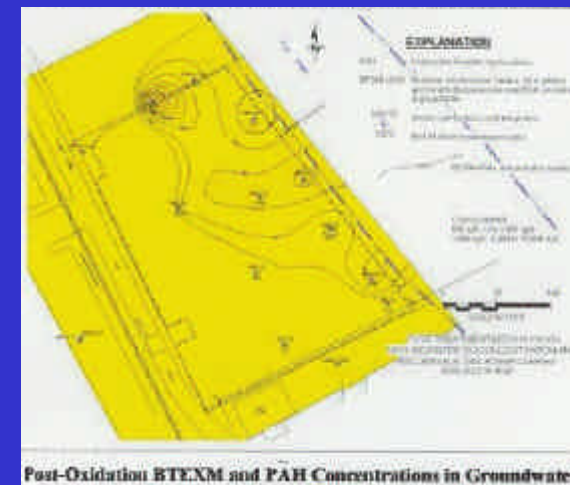
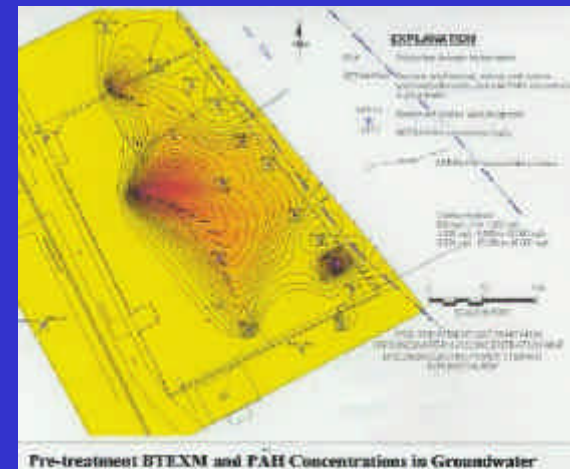


Treatment Walls

# H<sub>2</sub>O<sub>2</sub>/Fenton's Reagent Application

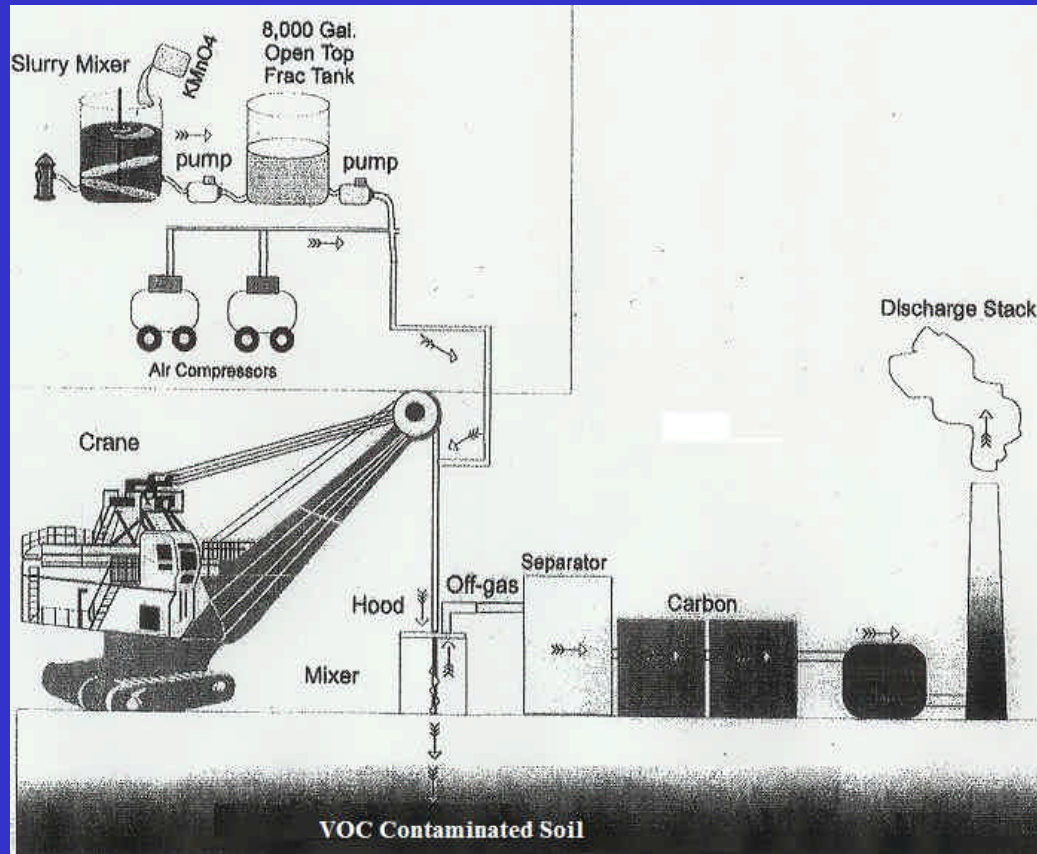


**Shallow Injector Array Layout**



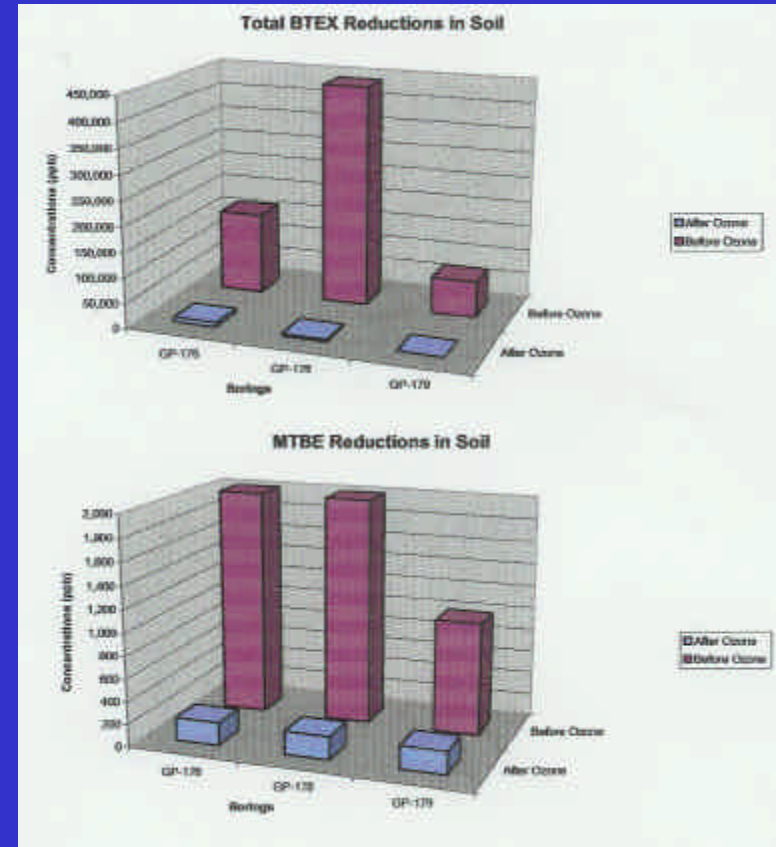
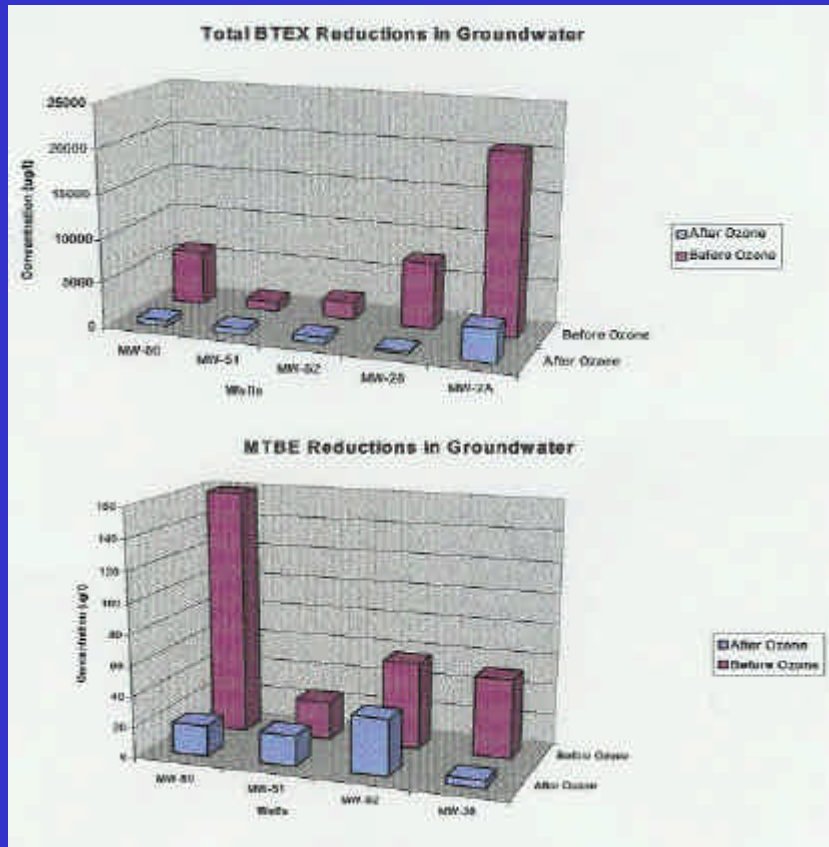
- Reference: Lingle, Jim, Elizabeth Hellman, Mike Noel and Jim Wilson. (2001) Full Scale Chemical Oxidation of Manufactured Gas Plant Hydrocarbons in Soil and Groundwater Using Fenton's Reagent.

# KMnO<sub>4</sub> Application:



- Reference: Gardner, F.G., N.E. Korte, J. Strong-Gunderson, R.L. Siegrist, O.R. West, S.R. Cline and J. Baker (1998). Implementation of Deep Soil Mixing at the Kansas City Plant. Final project report by Oak Ridge National Laboratory for the Environmental Restoration Program at the DOE Kansas City Plant. ORNL/TM-13532. .

# OZONE Application:



Reference: Resource Control Corporation (2000). In-Situ Oxidation of Petroleum Hydrocarbons Utilizing Ozone: Case Histories.

# TECHNOLOGY STATE OF THE ART

- Performance of in-situ chemical oxidation technologies has indicated promise
- It is a developing technology
- Successful application of in-situ oxidation treatments has been achieved and reported
- In Alberta, oxidation technology has been used even for oxidation of hydrocarbon impacted soils in areas with restricted access, such as underneath buildings

# TECHNOLOGY STATE OF THE ART

- A better understanding of different aspects of the technology is still necessary:
  - Conclusive identification of the mechanisms of reaction, intermediate and final products generated
  - Impact of CO<sub>2</sub> generation on soil conductivity and volumetric changes
  - Effects of uneven distribution of oxidant
  - Understand/develop the relationship between required oxidant and soil organic matter with contaminant content
  - Need to develop it more as a science than as an art
  - Effects of contaminant weathering
  - Kinetics of adsorption-desorption

# CONCLUDING REMARKS

- *In-situ* chemical oxidation is an **evolving** technology
- Success of selecting and implementing *in-situ* oxidation technology is dependent upon:
  - contaminant properties
  - oxidant selection
  - site conditions
  - method of delivery
- Field applications have demonstrated extremely high reduction in contaminants can be achieved with proper oxidant

# CONCLUDING REMARKS:

- Factors supporting its viability for the mass reduction of contaminants in soil and groundwater:
  - Efficiency
  - Speed of reaction
  - Relatively low cost
  - Reliability
  - Simplicity
  - Rapid
  - Aggressive
  - Non-selective
  - Treat/Reduce mass contaminant with minimum surface disturbance
  - Work alone or with companion remediation technologies

# QUESTIONS