Optimization of In-Situ Chemical Oxidation Design Parameters

by

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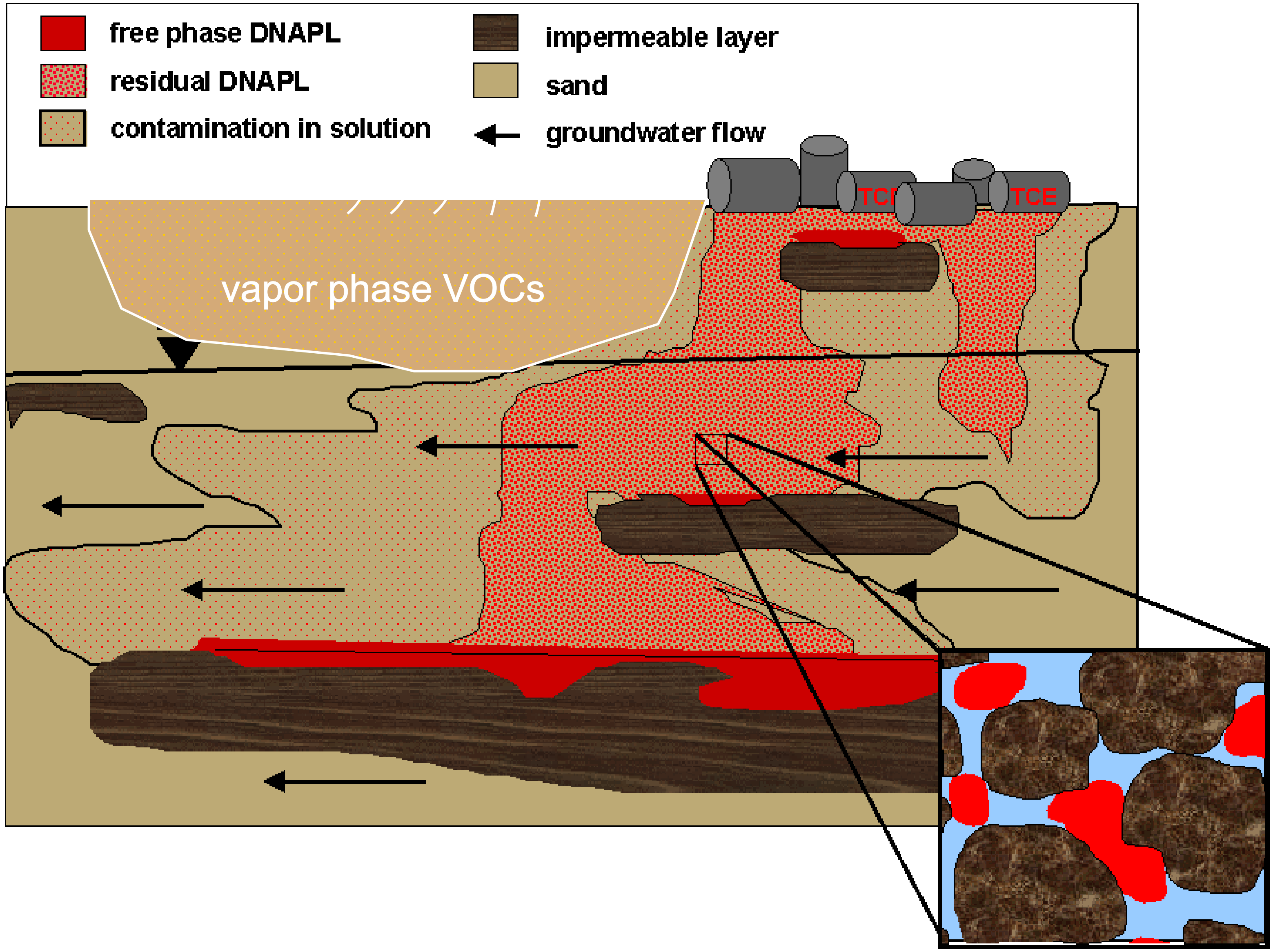
Target Contaminants

- Common solvents
  - Chloroethenes – PCE, TCE, DCEs, VC
  - Chloroethanes – TCAs, DCAs
  - Chlorobenzenes – TCBs, DCBs, CB
  - Chloromethanes – CT, MC
- BTEX, MTBE, 1,4-dioxane
- PCBs, PAHs

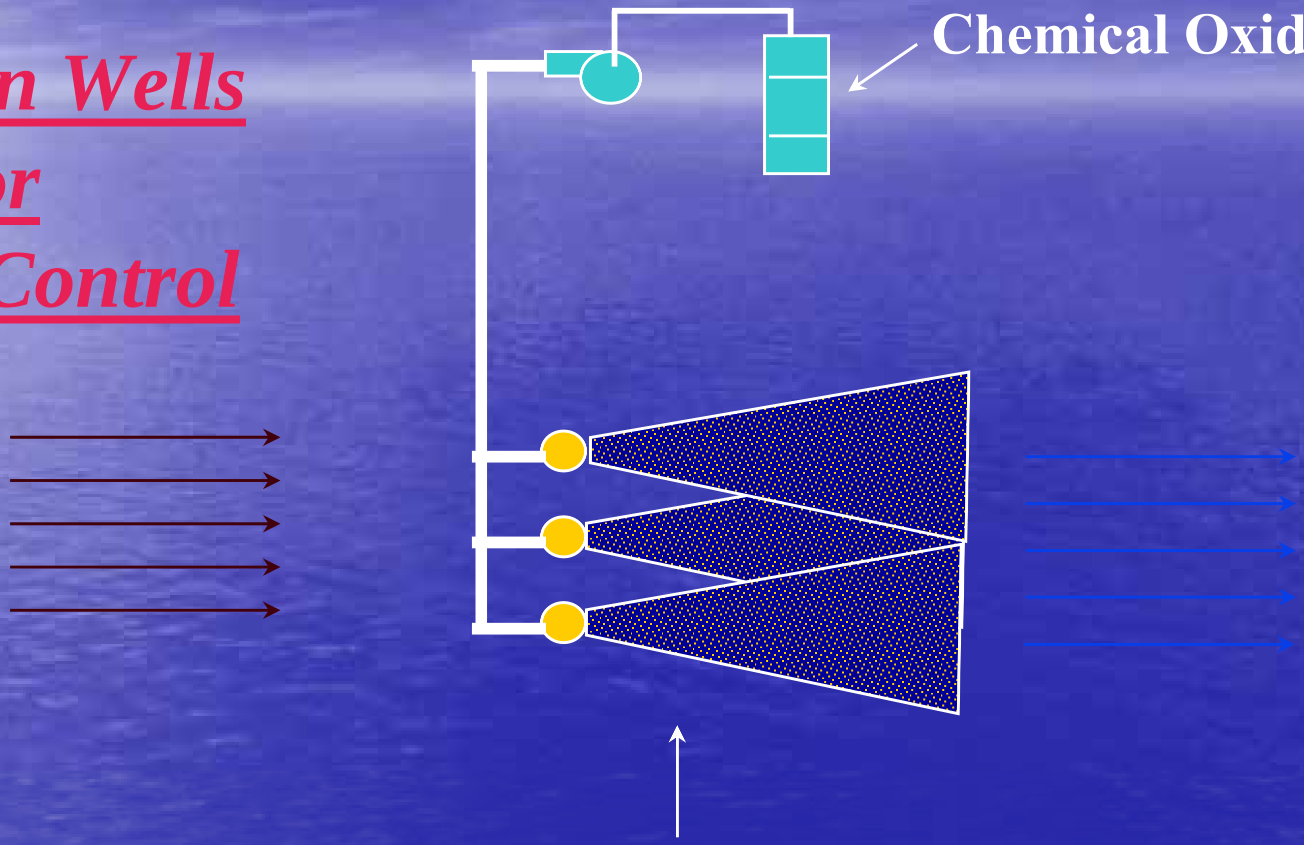
Dense Non Aqueous Phase Liquids (DNAPLs)



Reference: J. Schaerlaekens, 2002

Possible In-Situ Applications of Chemical Oxidants in the Subsurface - Source Control

Injection Wells
for
Plume Control



Chemical Oxidant Solution

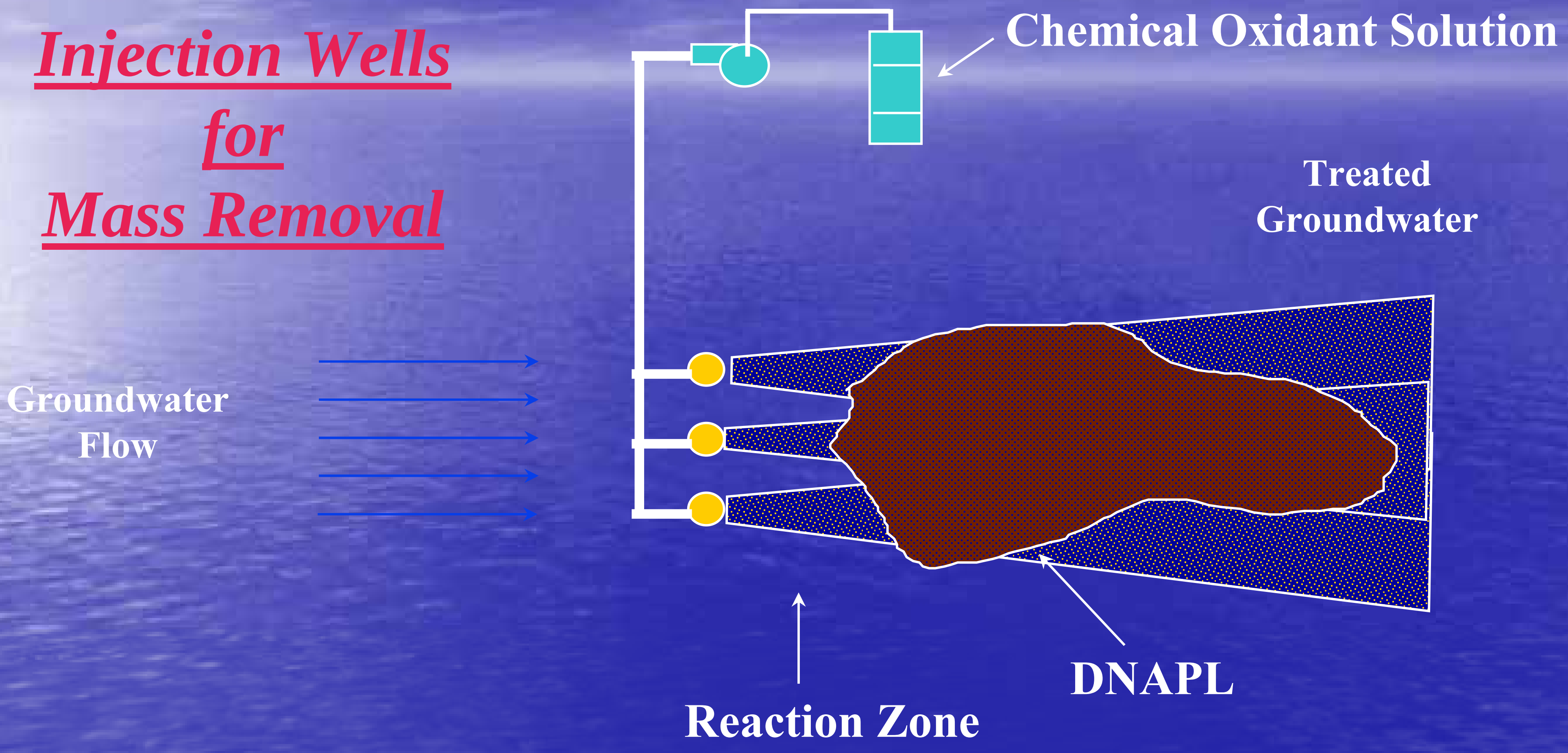
Contaminated Groundwater

Treated Groundwater

Reaction Zone

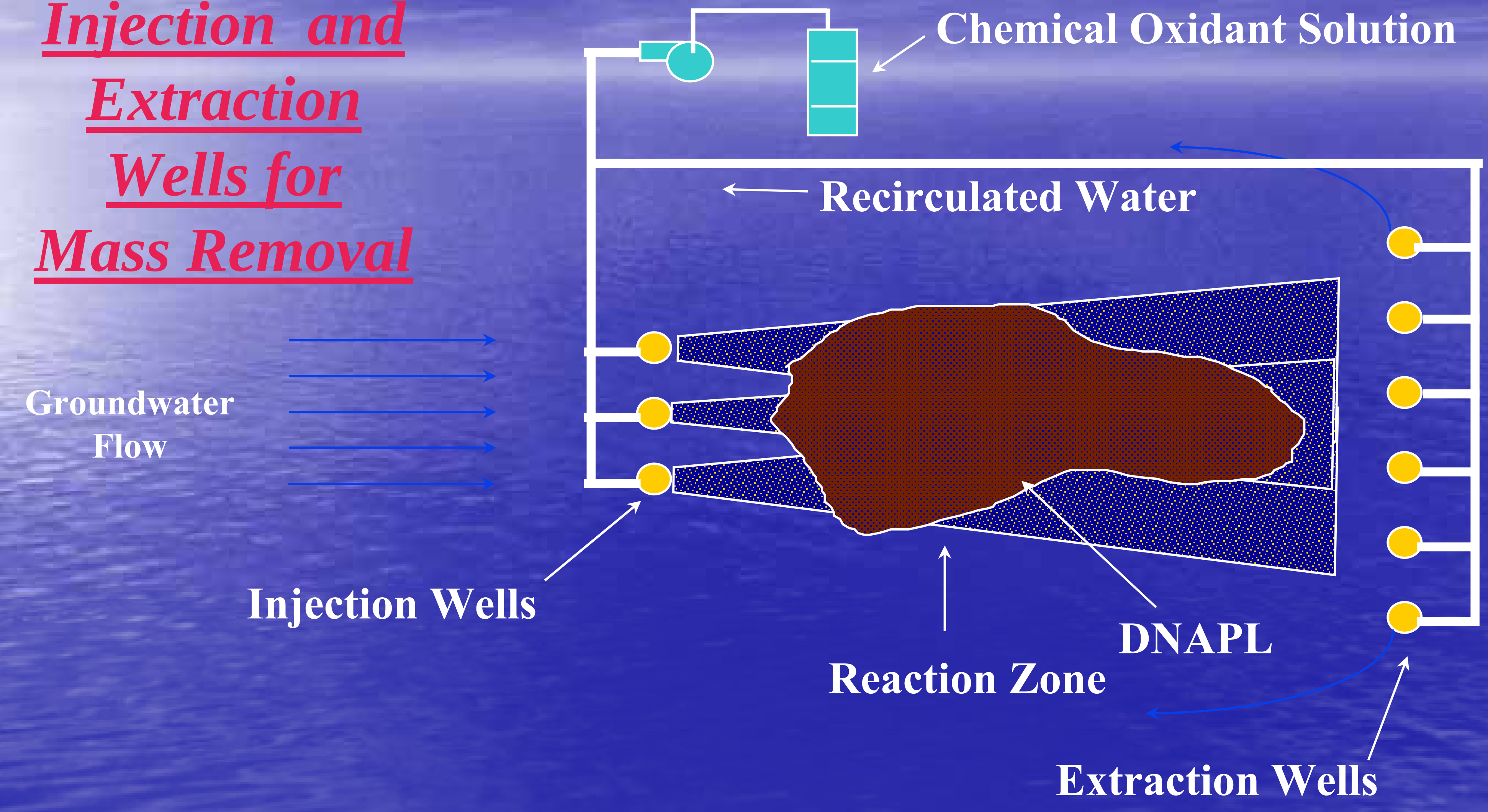
Possible In-Situ Applications of Chemical Oxidants in the Subsurface - Mass Removal

Injection Wells for Mass Removal



Possible In-Situ Applications of Chemical Oxidants in the Subsurface - Mass Removal

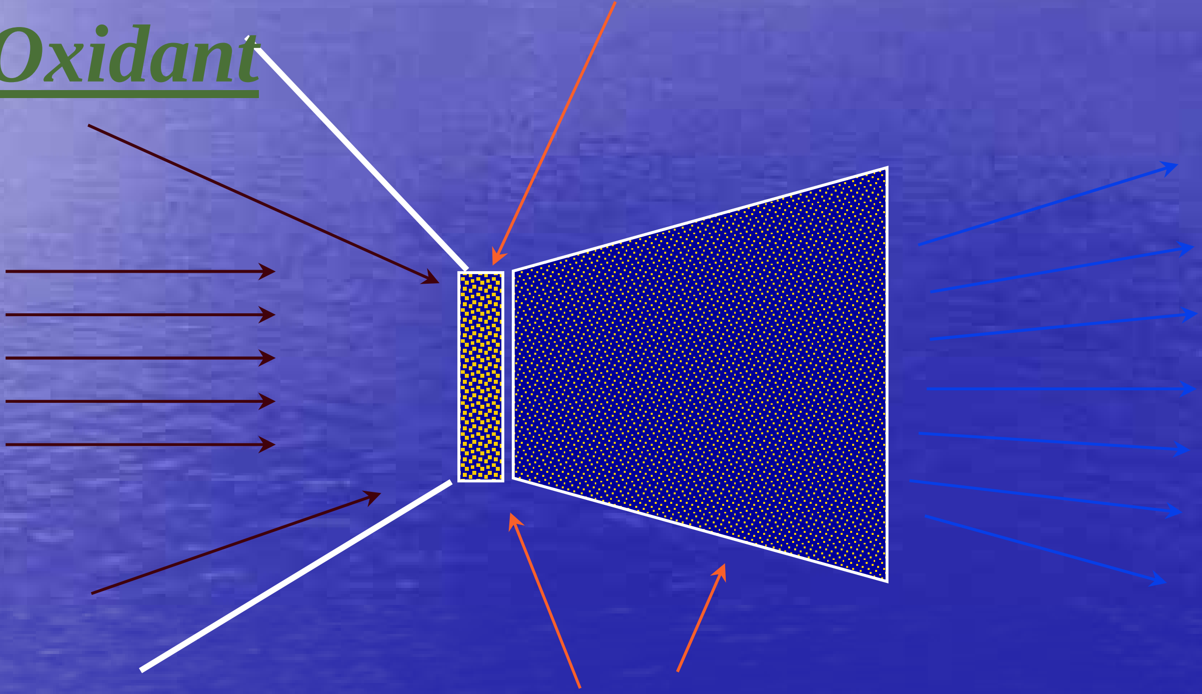
Injection and Extraction Wells for Mass Removal



Possible In-Situ Applications of Chemical Oxidants in the Subsurface - Source Control

Funnel and Gate

Passive Oxidant Release



Removable Chemically Loaded Cassette Or Periodically Dosed Cell

Contaminated Groundwater

Treated Groundwater

Reaction Zones

Potential Oxidants & Oxidant Potentials!!

- Permanganate: 1.68 V
- Persulfate: 2.01 V
- Activated Persulfate: 2.6 V
- Hydrogen Peroxide: 1.78 V
- Fenton’s Reagent: 2.8 V
- Ozone: 2.07 V

Fenton's Reagent

$$H_2O_2 + Fe^{2+} \rightarrow OH \bullet + OH^- + Fe^{3+}$$

Optimum pH range: 2 - 4

Typical dose of Fe^{2+} = 5 - 100 mg/L

Typical dose of H_2O_2 = 50 – 20,000 mg/L

Surface Catalyzed Decomposition of H_20_2

$$2H_2O_2 \rightarrow 2H_2O + O_2(g)$$

Summary of Fenton's Reagent for In Situ Subsurface Remediation

Benefits/Limitations

- Complete oxidation and rapid destruction in water - ·OH in Aqueous Systems
- H_20_2 decomposes fast in soil (surface catalysis)
- Chelating Fe(II) helps sustain the Fenton's Reagent process
- ·OH production requires low pH = 3 to 4
- Heat generated
- Sparging due to O_2 gas generation
- May help biodegradation

O_3 (Ozone) Chemistry

Direct oxidation under acidic conditions

$$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + 2H_2O$$

Free radical formation

$$O_3 + OH- \longrightarrow O_2- + HO_2 \cdot$$

Summary of Ozone for In Situ Subsurface Remediation

Benefits/Limitations

- Highly unstable; quickly breaks down to oxygen
- Easy to apply in vadose zone
- Can oxidize wide range of organics
- Difficult to apply in saturated zone (sparging)
- Possible formation of bromate (a carcinogen)
- May require soil vapor extraction system for off-gas control
- Can be costly (ozone generators, confined space air monitoring, stainless steel or Teflon equipment, oil-free environment)

$KMnO_4$ Chemistry

Reduction (pH < 7)

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

Oxidation

$$C_2HCl_3 + 4H_2O \longrightarrow 3Cl^- + 2CO_2 + 9H^+ + 6e^-$$

Overall Reaction

$$5C_2HCl_3 + 6MnO_4^- + 3H^+ \longrightarrow 15Cl^- + 10CO_2 + 6Mn^{2+} + 4H_2O$$

$KMnO_4$ Chemistry

Oxidation of Mn^{2+}

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2(s) + 4H^+$$

Complete Mineralization Reaction

$$C_2HCl_3 + 2MnO_4^- \longrightarrow 3Cl^- + 2CO_2 + 2MnO_2(s) + H^+$$

MnO_2 catalyzed decomposition of $KMnO_4$

$$2MnO_4^- + H_2O \xrightarrow{MnO2(s)} 4MnO_{2(s)} + 3O_{2(g)} + 4OH^-_{(aq)}$$

Note: Above reaction typical of soil oxidation

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By-Products of PCE Oxidation by $KMnO_4$

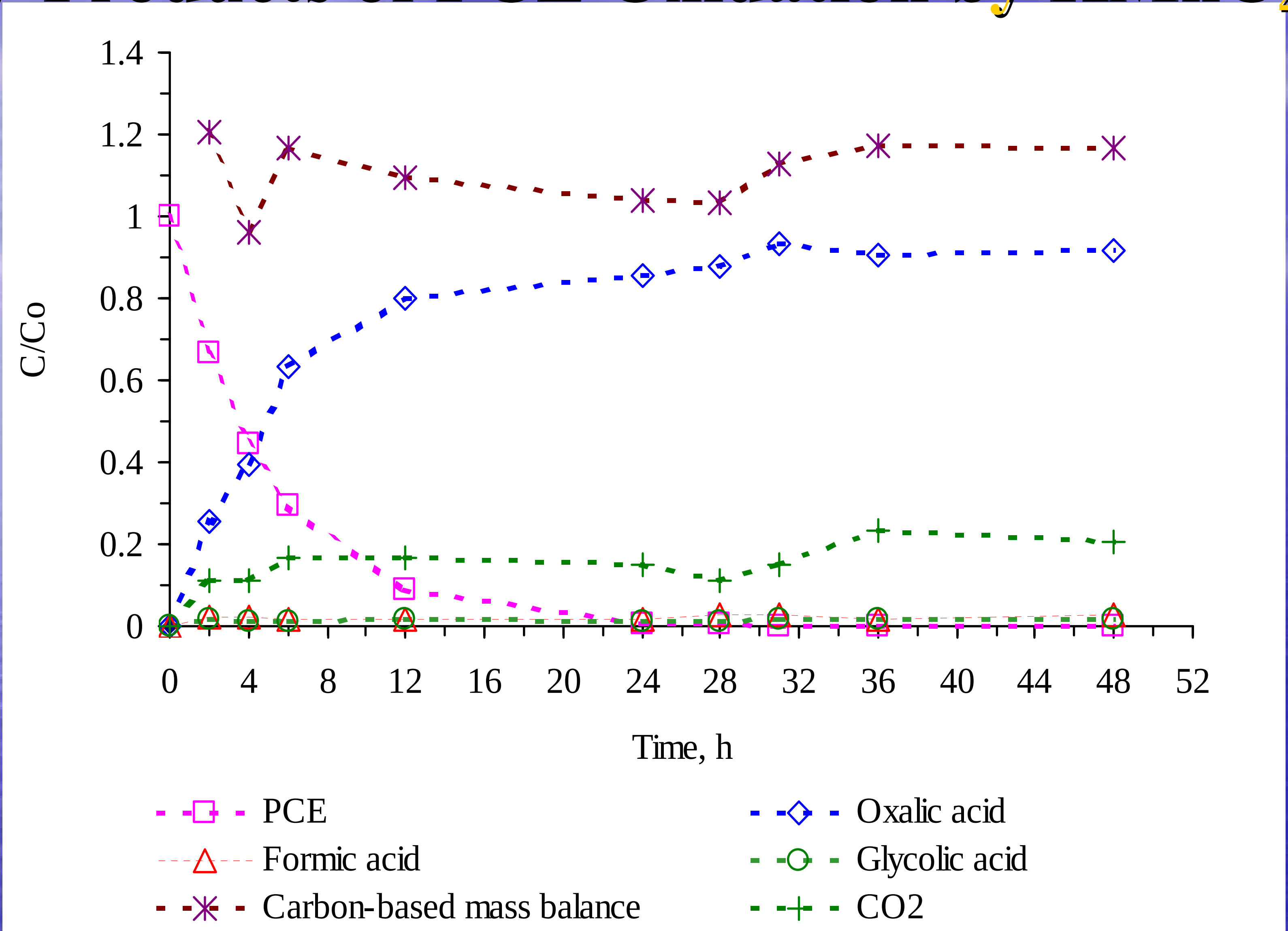

Figure 4.2 Distribution of products (in C/C_0 based on carbon in $[PCE]_0$) vs time in $KMnO_4$ oxidation of PCE at pH 7.0

Summary of Permanganate for In Situ Subsurface Remediation

Benefits/Limitations

- Effective on chlorinated ethenes
- Effective over a wide range of pH (3 to 12)
- Forms MnO_2 (s) Precipitate
- Soils with High SOD a problem
- Mass Transfer Limitation with DNAPL
- Soil Heterogeneity a Problem
- Materials Handling Issues
- Metals impurities; some pore clogging
- Intermediates may enhance anaerobic biodegradation

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Sodium Persulfate ($Na_2S_2O_8$) Chemistry

1. Two Electron Acceptor 1/2 Reaction

$S_2O_8^{--} + 2H^+ + 2e^- \Rightarrow 2HSO_4^-$ $E_o = 2.12$ v

2. Thermally Catalyzed Reduction - free radical pathway

$S_2O_8^{--} + \text{Heat} \Rightarrow 2 \cdot SO_4^-$ $E_o = 2.6$ v (kinetically fast)

3. Fe2+ Catalyzed Reduction - free radical pathway

$S_2O_8^{--} + Fe^{++} \Rightarrow Fe^{+++} + SO_4^{--} + \cdot SO_4^-$ (kinetically fast)

4. Production of Hydroxyl Free Radicals

$\cdot SO_4^- + H_2O \Rightarrow \cdot OH + HSO_4^-$ Eo= 2.7 v

5. Also photolytic or acid catalyzed

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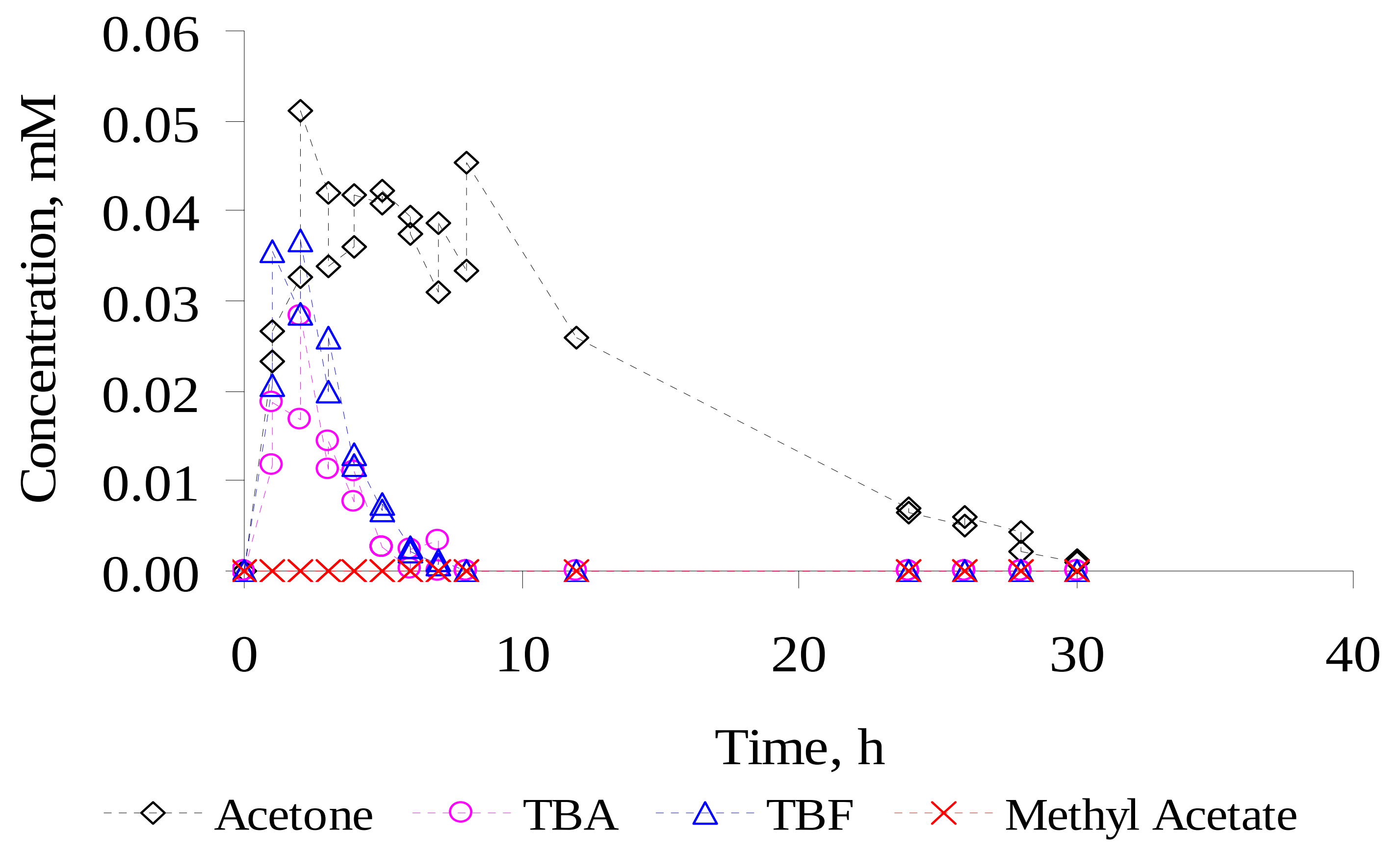
Volatile organic intermediates found in MtBE-persulfate reactions



$[MTBE]_0$~0.06 mM; $[Na_2S_2O_8]_0$~31.5 mM; pH ~ 7; Temp. = 40 ^{o}C.

Summary of Persulfate for In Situ Subsurface Remediation

Benefits/Limitations

- Direct oxidation and free radical oxidation
- Heat and transitional metals catalysis
- Can treat most contaminants when catalyzed
- Stable in the subsurface environment (months)
- Less affinity for natural soil organics than permanganate
- Sulfate radical more stable than the hydroxyl radical (↑ transport)
- Mass transfer limitations with DNAPL
- Soil heterogeneity a problem
- Materials handling issues
- Intermediates and sulfate may enhance anaerobic biodegradation

The Ideal Oxidant!

- Complete and rapid oxidation of target compounds
- Non-reactive with soil organics and inorganics
- No intermediates or solid phase products
- Non-toxic in groundwater and soil (reactants and products)
- No oxidant residual remaining long-term
- Low cost, easy materials handling

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Reactions of Oxidants…in the Subsurface

Reactants

$\text{Cl}^{-}\text{VOC}_{\text{degradable}}$ + $\text{VOC}_{\text{non-degradable}}$ + Oxidant +
Org. Carbon + Reduced Inorganics (water and soil)

Intermediates

(e.g., Partially Oxidized Soil Surface + Reduced Oxidant
(cations and anions + Precipitated Metals
+ Organic Carbon)

End Products

$CO_2 + Cl^{-} + H_2O + \text{VOC}_{\text{non-degradable}}$ +
H^{+} + Stable Intermediates + Oxidized
Inorganics [e.g., $MnO_2(s)$, $Fe(OH)_3(s)$] +
Oxidized Soil Surface

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Parameters that Impact Oxidation

- pH
- Temperature
- Concentration of reactants
- Transitional metals
- Competing organic compounds
- Solution composition/chemistry
- Availability of contaminants (in solution)

Got Treatability Study??

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Case Study (treatability)

Site background:

- Geological Features
  - a fractured bedrock aquifer
  - primarily consisting of interbedded units of graywacke sandstone and shale
  - open fractures occur both vertically and spatially across the area

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- Hydrogeology:
  - ➢ Groundwater has both near horizontal and downward gradients.
  - ➢Hydraulic conductivity of weathered and visibly fractured rock: 2.8E-5 to 6.7E-4 cm/sec
  - ➢Mean fracture porosity: 8%
- Site Impacts – Contamination with Chlorinated VOCs:

  Water has:
  - – 1,1,1-TCA 477 mg/L
  - – 1,1-DCA 19 mg/L
  - – 1,1-DCE 120 mg/L

Evaluated Remediation Technologies

- Feasibility Studies
  - ➢ Enhanced Anaerobic Bioremediation
  - ➢ Bimetallic Nanoscale Particle Treatment
  - ➢*In Situ* Chemical Oxidation (**subject of this talk**):
    - ✓Fenton-Type (CFR and MFR)
    - ✓Permanganate
    - ✓Persulfate

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Objectives of ChemOx FS Study

- Selected Oxidants: CFR, MFR, Permanganate and Persulfate
  - Assess capability of degrading targeted CVOCs
  - Determine the impact of pH, iron catalyst dose and reactant concentrations
  - Determine the most effective reaction conditions

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Evaluation Factors
for Selected ChemOx Processes

- Oxidation strength (treatment efficiency)
- Subsurface stability (chemical consumption)
- Gas production
- Heat generation
- Precipitation
- Water quality impacts

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Analytical Facilities

GC-MSD Used for CVOCs Analyses

Ion Chromatography Used for Analysis of Chloride

pH Meter for pH Measurement

Spectrometer Used for H_2O_2, KMnO4 and Na2S2O8 Analyses

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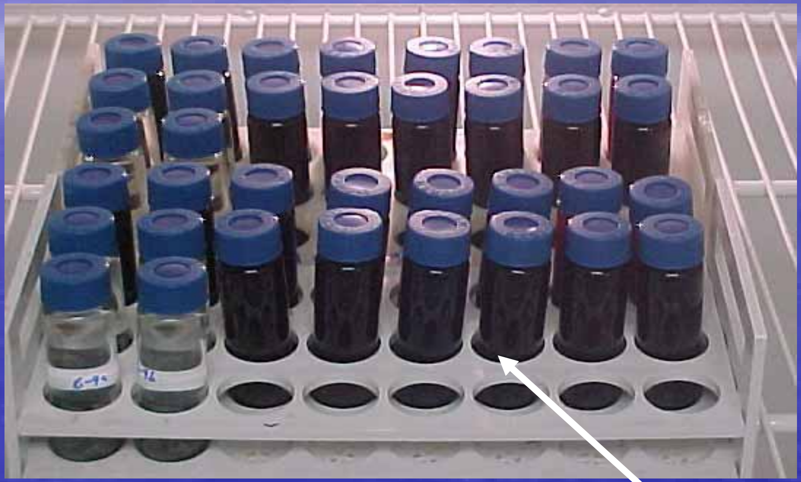
Typical Experimental Systems Used for the Study (degradation of CVOCs in rock-groundwater media)

CFR and MFR tests



Permanganate and persulfate tests

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Findings (CFR and MFR)

- Processes effective in degrading the target CVOCs (TCA, DCE and DCA).
- Extent of degradation of target CVOCs increased with increasing concentrations of H_2O_2. 4% H_2O_2 completely degraded the target CVOCs in 48 hrs.
- Heat released was insignificant (less than 1°C).
- Precipitation increased at higher catalyst concentrations but decreased at lower pH levels.
- Gas generation was directly proportional to the concentrations of H_2O_2 and Fe(II) catalysts.

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Findings (CFR and MFR)

- Gas stripping effect was significant (35%-44% for TCA).
- Higher residual oxidant concentration for the MFR process (chelating the Fe(II) with DTPA or EDTA enhances the effectiveness of the FR process when pH is not adjusted).
- The optimum Fe(II) dose was 75 mg/L (high residual oxidant concentration, excellent degradation capability, low gas generation and low precipitation).

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Findings (permanganate, persulfate)

- Permanganate Oxidation Process
  - ✓highly effective in degrading 1,1-DCE
  - ✓little reactions with TCA and DCA
  - ✓generation of heat and gas → not observed
  - ✓produced precipitates
- Fe(II)-EDTA Catalyzed Persulfate Oxidation Process
  - ✓ high degradation of TCA and DCE
  - ✓produced precipitates
  - ✓generation of heat and gas → not observed

Comparison of ChemOx Processes for Destruction of CVOCs

Evaluation Factors	CFR	MFR	Iron-catalyzed Persulfate	Permanganate
Oxidation strength	high	high	high	high for DCE low for TCA
Subsurface stability	low	low	high	high
Gas production	high	high	not observed	not observed
Heat generation	high	high	low	low
Precipitation	moderate	high	moderate	high
Water quality impacts	low	moderate	moderate	moderate

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Conclusions

- Chemical oxidation processes are affected by site-specific conditions. Lab treatability tests can:

1. determine the most appropriate chemical oxidation technology to apply using batch and column tests.
2. Optimize the design parameters such as oxidant and catalyst concentrations.
3. Assess the impact of chemical oxidation on groundwater pH, temperature, gas presence, and water quality.

- Got treatability, Got optimum help!!

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