Introduction to In-Situ Chemical Oxidation

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Introduction

- Oxidation Chemistry
- Oxidant Selection
- Applicable Contaminants and Site Conditions
- Remediation Timeframes
- Safety Considerations

Technology Basis

- Addition of an oxidant to promote direct oxidative destruction of organic contaminants to acceptable end products (e.g., CO_2, H_2O, chloride)
- Various oxidants are in common use:
    - Catalyzed hydrogen peroxide
    - Ozone
    - Permanganates
    - Persulfate
    - Solid phase peroxygens

Potassium Permanganate
Delivery System

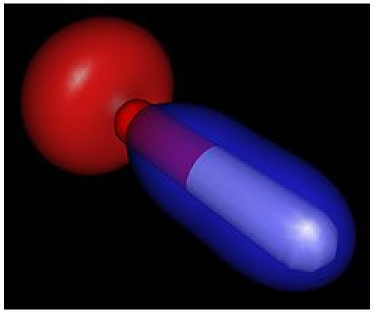
Technology Basis

- Oxidation is accomplished by the direct contact of a reactive chemical species with the contaminant(s) of concern
- Example: Hydrogen peroxide mixed with ferrous iron at low pH results in formation of a hydroxyl radical which acts as the reactive species:

1. $Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + \boxed{OH\cdot} + OH^-$
2. $Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + OOH\cdot + H^+$

Hydroxyl Radical

- The radical then reacts with the contaminant, resulting in non-regulated by-products and CO_2
- Direct oxidation also occurs
  - Ozone, permanganate, peroxide and persulfate anion


Hydroxyl Radical

ISCO History

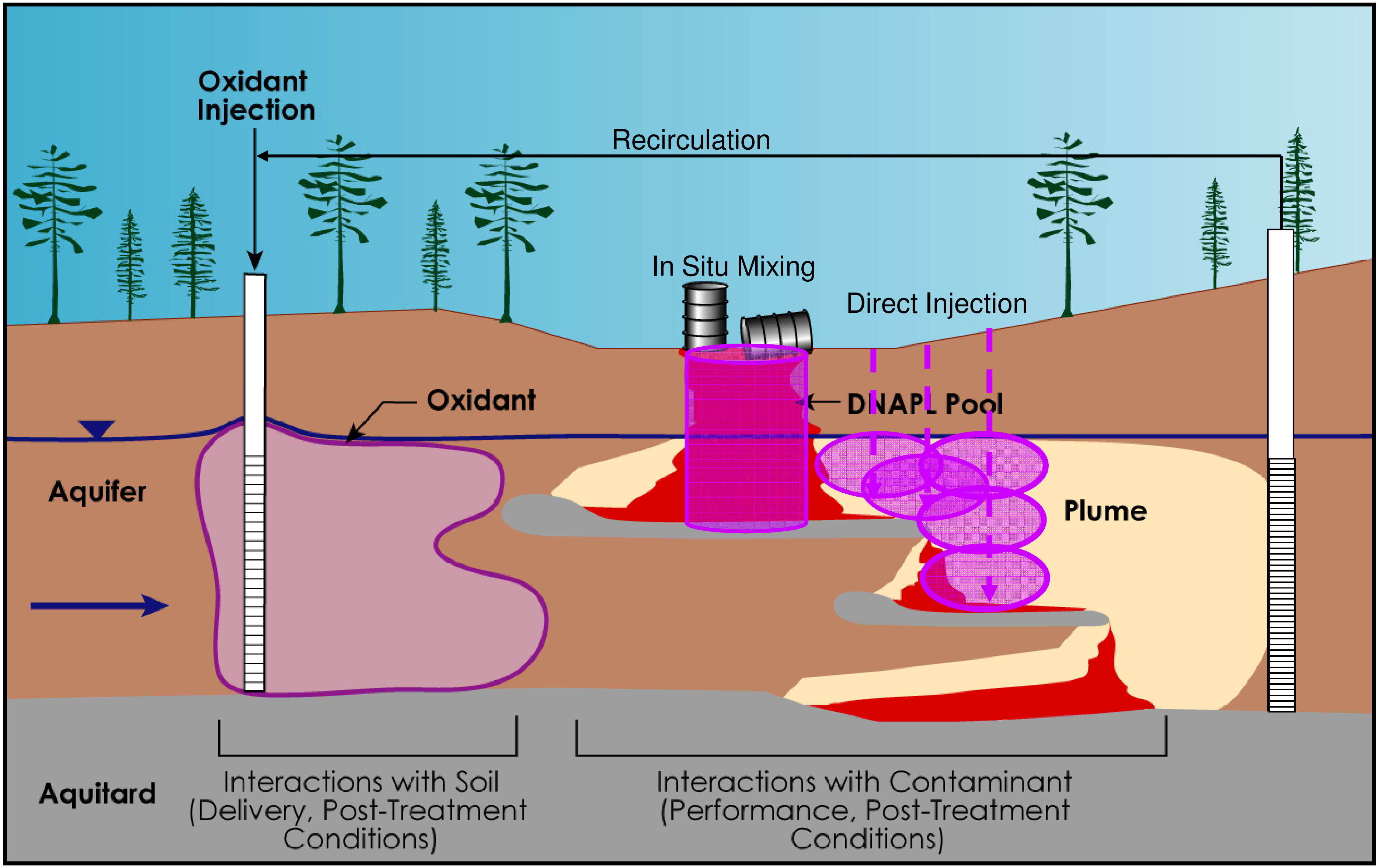
- Permanganate discovered to be a strong oxidizer in 1659; used for water treatment since early 1900s
- Fenton’s chemistry discovered in late 1800s
- Environmental applications of Fenton’s reagent began in early to mid 1990s
- Permanganate for chlorinated ethenes began in 1989; well-established by late 1990s
- Ozone sparging for semi-volatiles began in late 1980s; continued development to date
- Interest in persulfate in mid to late 1990s; commercial applications began in early 2000s
- In situ trials with other oxidants since the early 1990s; catalyzed hydrogen peroxide (CHP), permanganate, and persulfate are most widely used for in situ applications.

Johann Rudolf Glauber – Discovered $KMnO_4$ in 1659

Evolution of Oxidant Use

- Hydrogen peroxide - 1980s
  - Fenton’s chemistry was violent, vigorous at best
  - *21st Century* – Catalyzed hydrogen peroxide (CHP)
- Ozone - early 1990s
- Permanganate - late 1990s
- Persulfate - 2002+
- Solid Phase Peroxygens - 2004+
- Delivery Enhancements - 2007+
  - Surfactant-enhanced ISCO

Conceptual Design



ISCO - Pros and Cons

Pros

- Rapid treatment with mass destruction, in-situ
- Selection of proper oxidant allows of treatment of wide spectrum of chemicals
- Applicable in overburden and bedrock
- Appropriate for source zones or "hot spots"
- Generally innocuous end products
- Accepted by most regulatory agencies

Cons

- Natural oxidant demand (NOD) consumes oxidant
- Delivery limited by heterogeneity or low permeability
- Post-treatment rebound
- Can mobilize certain metals
- Health and safety concerns
- Often not cost effective for dispersed or dilute plumes
- Injection and storage permit requirements

Oxidant Selection

Oxidant	Oxidation Potential (V)	Target Compounds
Permanganate	1.77	Chloroethenes, cresols, chlorophenols, some nitro-aromatics
Catalyzed Hydrogen Peroxide (i.e., Fenton-like)	2.7	TPH, most organic contaminants (inc. PCBs)
Ozone (O_3 gas)	2.07	Chlorinated solvents, phenols, MTBE, PAHs, fuels and most organics
Persulfate	2.1	BTEX, MTBE, 1,4-dioxane, chlorinated solvents, phenols, TCP, PCBs, etc.
Activated Persulfate	2.6	

Trends in ISCO Field Deployment

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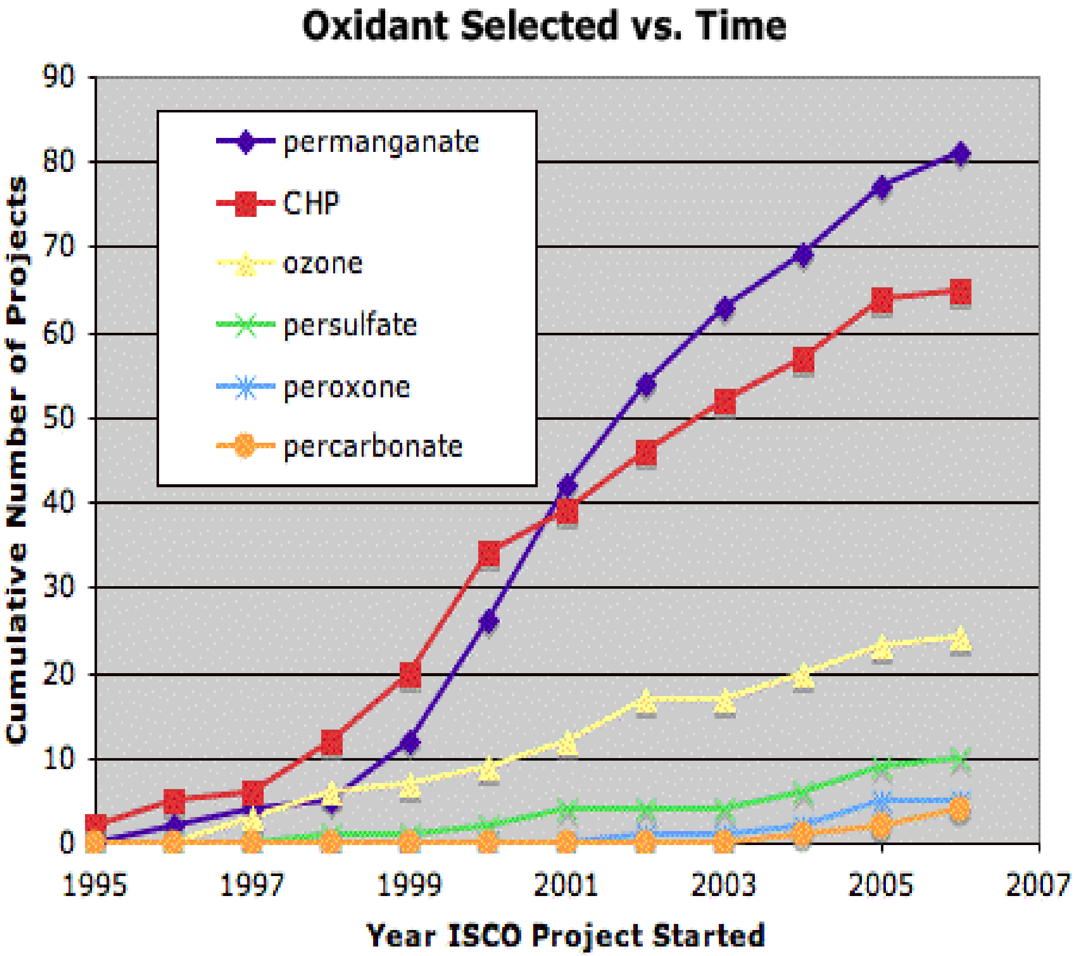


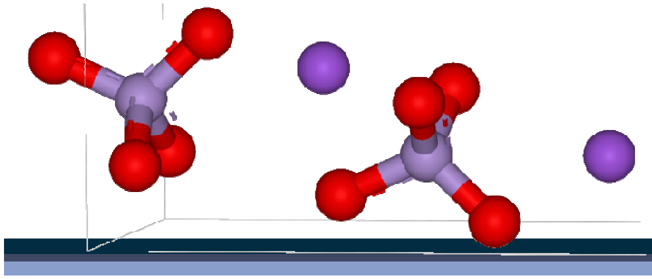
Project ER-0623 *DISCO Beta Nov. 17, 2008 *

ESTCP

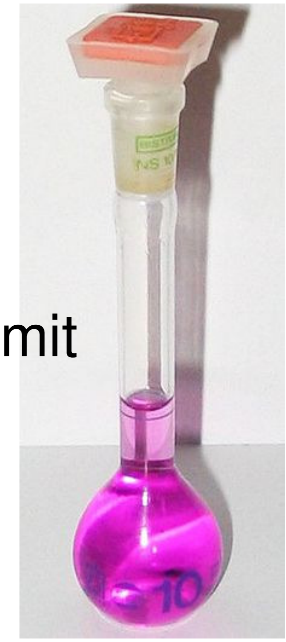
Permanganate - $NaMnO_4$ and $KMnO_4$

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2(s) + 4OH^-$$

- Treats specific COCs (PCE, TCE, DCE, VC, some others)
- Direct oxidation at ambient pH
  - Lower power oxidant, cleaves double bonds
- Reaction rates – minutes to days
  - Can persist for weeks to months, reduces rebound
- Residual manganese dioxide – MnO_2
  - Formation of rinds that can encapsulate solvents, can limit treatment



Manganese Dioxide



Permanganate Reactions

Solubility (g/L)

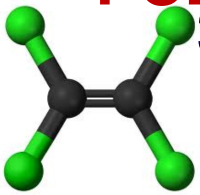
$KMnO_4 \rightarrow MnO_4^- + K^+$ **42**

Potassium
Permanganate
Crystals

$\mathrm{NaMnO_4 \rightarrow MnO_4^- + Na^+}$ **900**

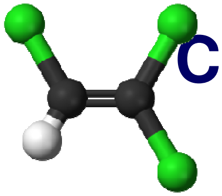
Sodium
Permanganate

PCE Oxidation:



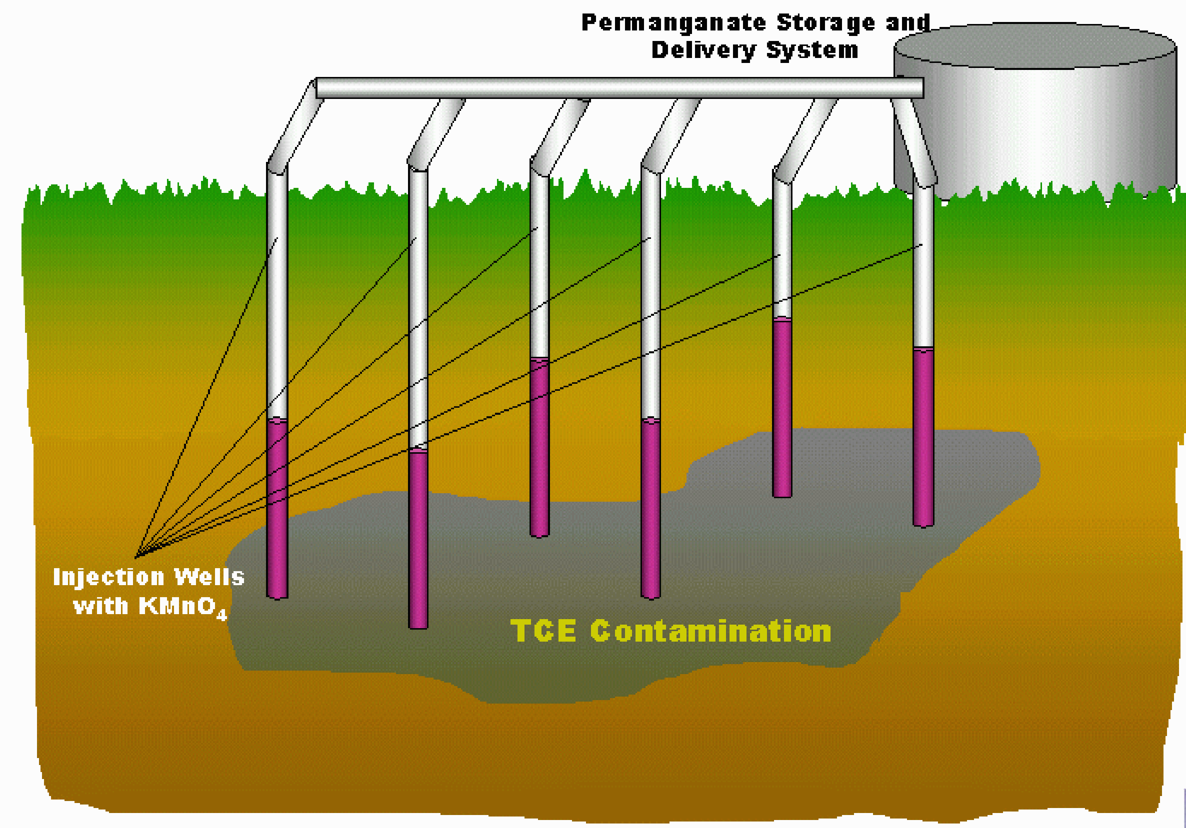
$3C_2Cl_4 + 4MnO^-_4 + 4H_2O \longrightarrow 6CO_2 + 12Cl^- + 4MnO_2(s) + 8H^+$

TCE Oxidation:



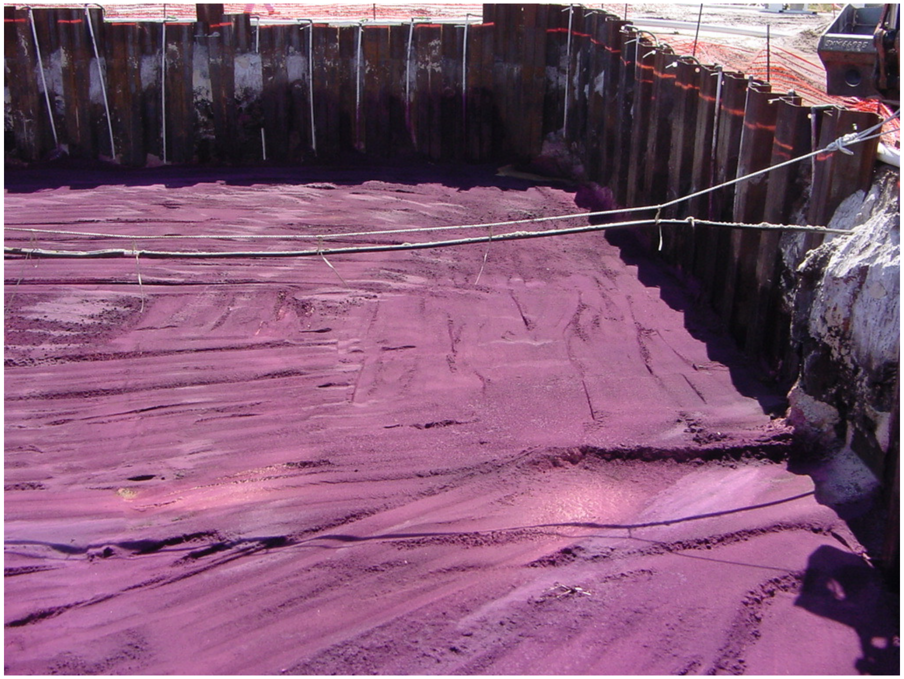
$C_2Cl_3H + 2MnO^-_4 \longrightarrow 2CO_2 + 3Cl^- + 2MnO_2(s) + H^+$

Permanganate Application



Permanganate in Groundwater

Permanganate Application



Solid-Phase
Permanganate Delivery

Permanganate – Target Compounds

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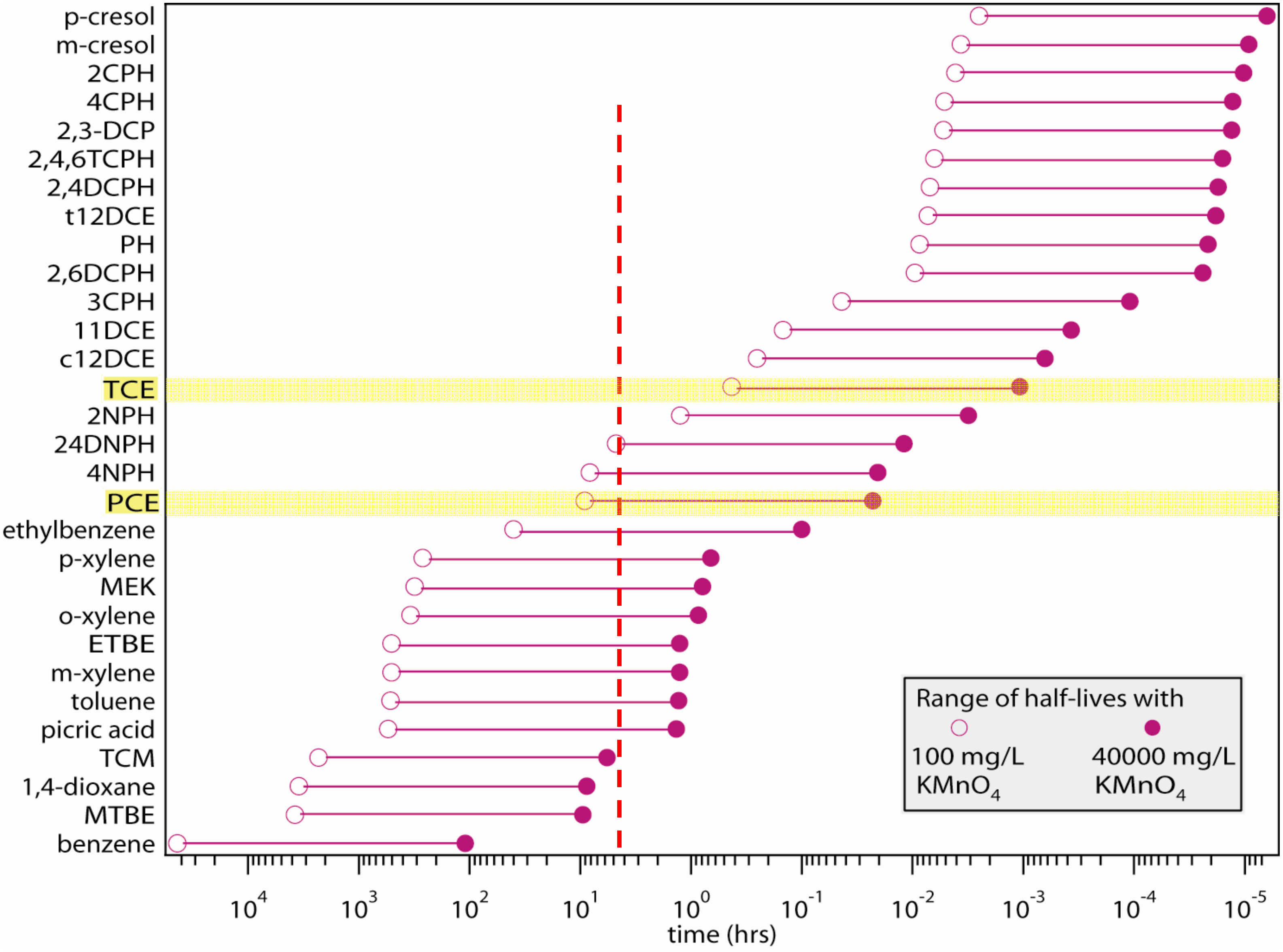


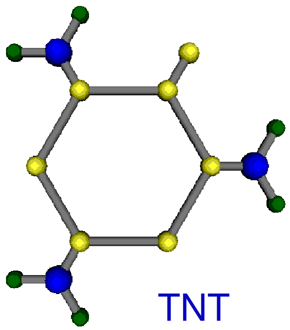
Permanganate – A Selective Oxidant

Works well for

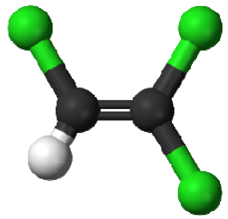
- Chlorinated ethenes
- Probably chlorophenols & cresols
- Possibly alkynes, alcohols, explosives, sulfides, and others?

Does not work well for

- Chlorinated ethanes or methanes
- Most hydrocarbons (incl. BTEX, fuels, creosote)
- Most pesticides
- PCBs
- Dioxins
- Oxygenates (MTBE, 1,4-Dioxane)



TNT

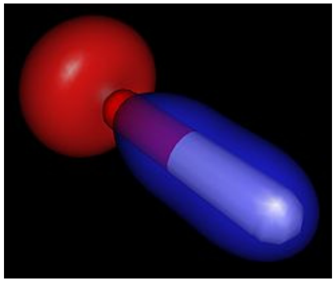


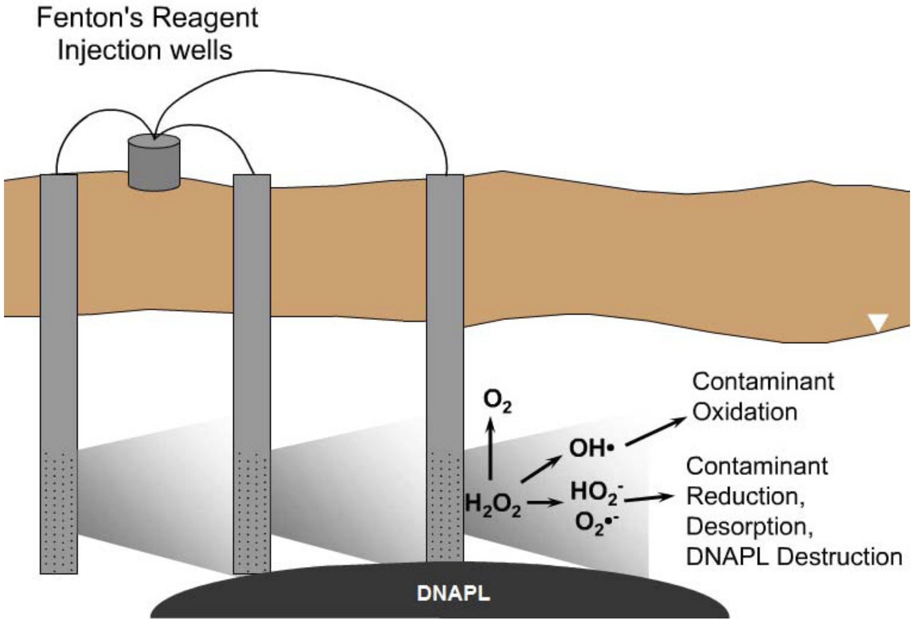
TCE

Catalyzed Hydrogen Peroxide

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

(pH <3 to maintain iron solubility)





- $OH^{\cdot}$ is highly reactive;
  fast reactions, short half-life, exothermic
- H_2O_2 ends up as oxygen off-gas
- Modified Fenton's recipes work at neutral pH
- Inject 5 to 25% peroxide (depending on vendor)
- Strongest oxidizer typically used for enviro. applications

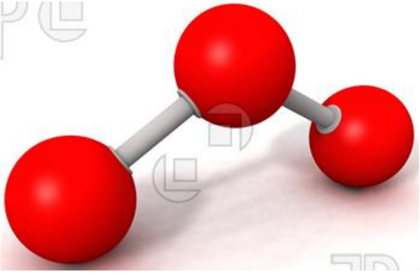
Catalyzed Hydrogen Peroxide

- Much more complex chemistry than permanganate
  - Primary reactive species is hydroxyl radical (OH•)
  - Other transient oxygen species including superoxide anion ($O_2•^-$) and hydroperoxide (HO_2^-), both of which are reductants
- CHP is transport limited
  - Highly reactive hydroxyl radicals can react with H_2O_2, carbonate, & any transition metals (mineral forms of Fe & Mn)
  - Unlikely to persist longer than a few days in groundwater
- Strong oxidation can treat most organics
  - Heating and off-gas formation can be leveraged for treatment

Ozone - O_3

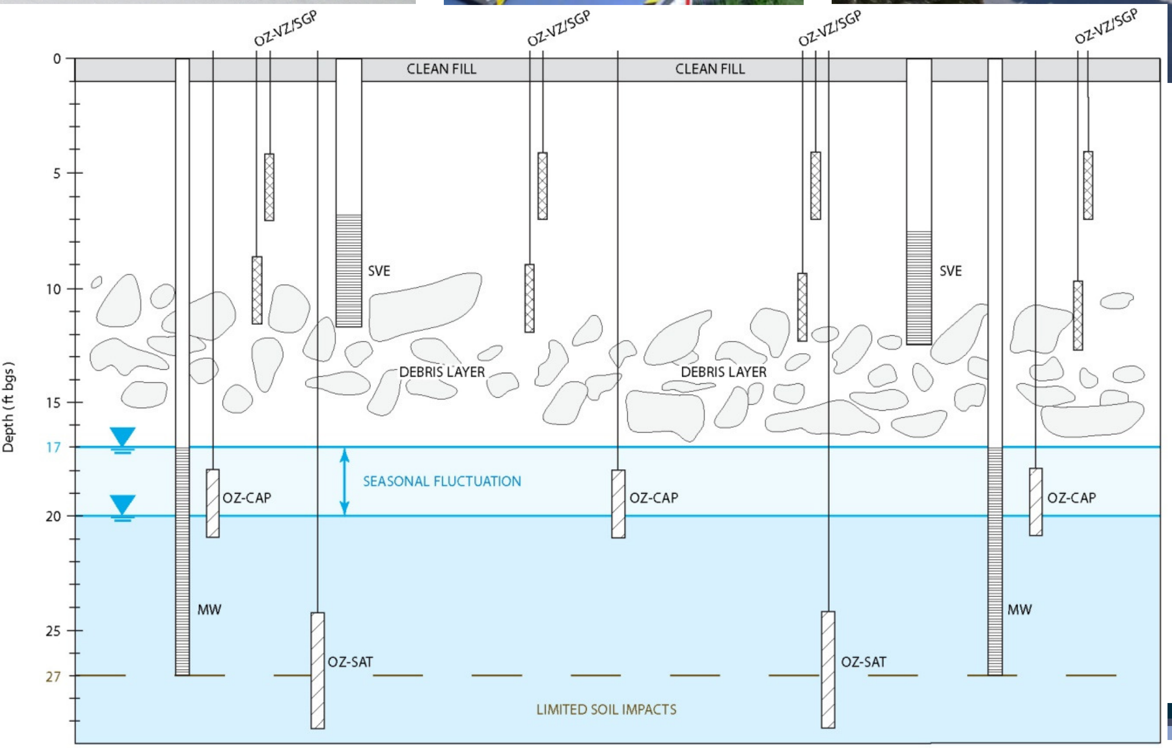
$$O_3 + HO_2^{-} \rightarrow OH^{\bullet} + O_2^{\bullet -} + O_2$$

- Non-specific COC treatment (chlorinated solvents, PAHs, fuels and most organics)
- Fast reaction rate – seconds to minutes
  - Transport limited – affects well spacing and injection rate
- Pulsed injection better than continuous sparging
  - Enhances aerobic microbial processes and desorption
- Can be effective for vadose zone treatment (but need moisture)
- Typically successful with lowest g/kg dosage



Ozone
Molecule

Ozone Sparging System

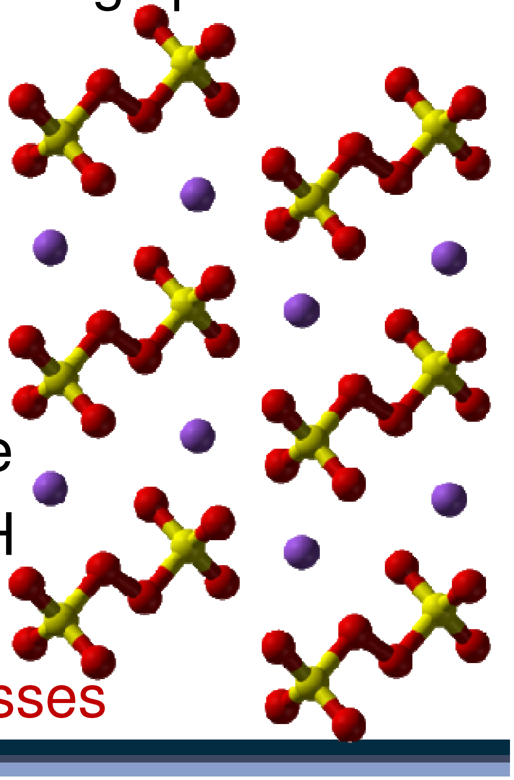


Persulfate - $Na_2S_2O_8$

$$Me^{n+} + S_2O_8^{\ 2-} \rightarrow SO_4^{-\bullet} + Me^{(n+1)+} + SO_4^{2-}$$

$$SO_4^{-\bullet} + RH \rightarrow R^{\bullet} + HSO_4^{-}$$

- Can treat a wide range of COCs (solvents, etc.)
  - Can produce a broad range of oxidizing and reducing species
- Direct decomposition rate is slow
  - Promise of a low SOD oxidant
- Requires activation by:
  - Ferric iron/EDTA - Lower power and slower rate
  - Heat - Activation rate proportional to temperature
  - Base/Alkaline - Activation rate increases with pH
- By-products are sulfate and salts
- Used by consultants & vendors - proprietary processes



Surfactant-Enhanced ISCO

- Typically coupled with base-activated persulfate
- Designed to overcome dissolution rate limitations - oxidation occurs across the liquid-solid/NAPL interface
- Improve sweep efficiency via viscosity reduction
- *Achilles Heel*
  - NAPL mobilization - both surfactant and elevated pH reduce interfacial tensions
  - Surfactants exert an oxidant demand and increase cost
- Applied by consultants, in tandem with vendors / academics

Solid Phase Peroxygens

- Calcium peroxide - CaO_2
  - *BiOx®, Cool-Ox™, RegenOx™*
- Calcium peroxide and sodium persulfate
  - *Klozur® CR*
- Designed to improve ease of handling and have slow release characteristics
- Typically injected on a closely spaced grid
  - Transport limitations inherent
- In situ performance has been variable
  - Soil mixing can be cost competitive (depends on site conditions

Integration with Other Technologies

Bioremediation (following ISCO)

- Short-term: oxidants disinfect microbial communities in the treatment zone & inhibit biodegradation
- Long-term: oxidant products (MnO_2, O_2, or SO_4) create electron donor demand that must be overcome prior to dechlorination

Groundwater/Vapor Extraction/MPE (with CHP)

- Generation of heat/vapor may be used to mobilize VOC mass

Cosolvent/Surfactants (concurrent with ISCO)

- To enhance dissolution from DNAPL during ISCO
- Delivery is still the limiting factor

Thermal (before ISCO)

- Residual heat used to activate persulfate for post-thermal polishing

In Situ Thermal Treatment

Design & Implementation

1. Oxidant Selection
   - Each class of oxidants has unique characteristics
     - Contaminants that can be treated
     - Reaction rates & activation chemistry
     - Ability to distribute, persistence
     - Impurities or by-products
   - Bench testing develops a site-specific basis for oxidant/activator consumption rates and demands
   - Bench testing can assess treatability of complex mixtures

Samples for
Bench Testing

Design & Implementation

2. Oxidant Demand

- In addition to the target contaminants, various factors place demand on (use up) the oxidant
    - Natural oxidant demand (NOD)
    - GW oxidant demand (GWOD)
- Each contribute to required oxidant volume & cost
- Site-specific oxidant demand can be tested in the laboratory

Oxidant Demand Test Kit

Natural Oxidant Demand (NOD)

- The consumption of oxidant due to reactions with the background soil
- Usually attributed to oxidation of organic carbon and reduced mineral species (esp. divalent Fe and Mn, sulfides)
- Units: grams of oxidant per kg of soil
- Excludes demand exerted by contaminants

Measuring NOD

1. Theoretical NOD
    - Similar to ThBOD for wastewater (calculated based on the chemical composition of the soil)
2. Batch reactors (i.e., BOD bottles)
    - Current protocol: ASTM D7262-07
    - Protocols similar for permanganate and persulfate
3. Modified COD
    - Standard wastewater analysis method (novel method)
    - High temperature digestion with permanganate
    - Correlates closely with 12 month batch reactor studies

Soil Type vs. Oxidant Demand

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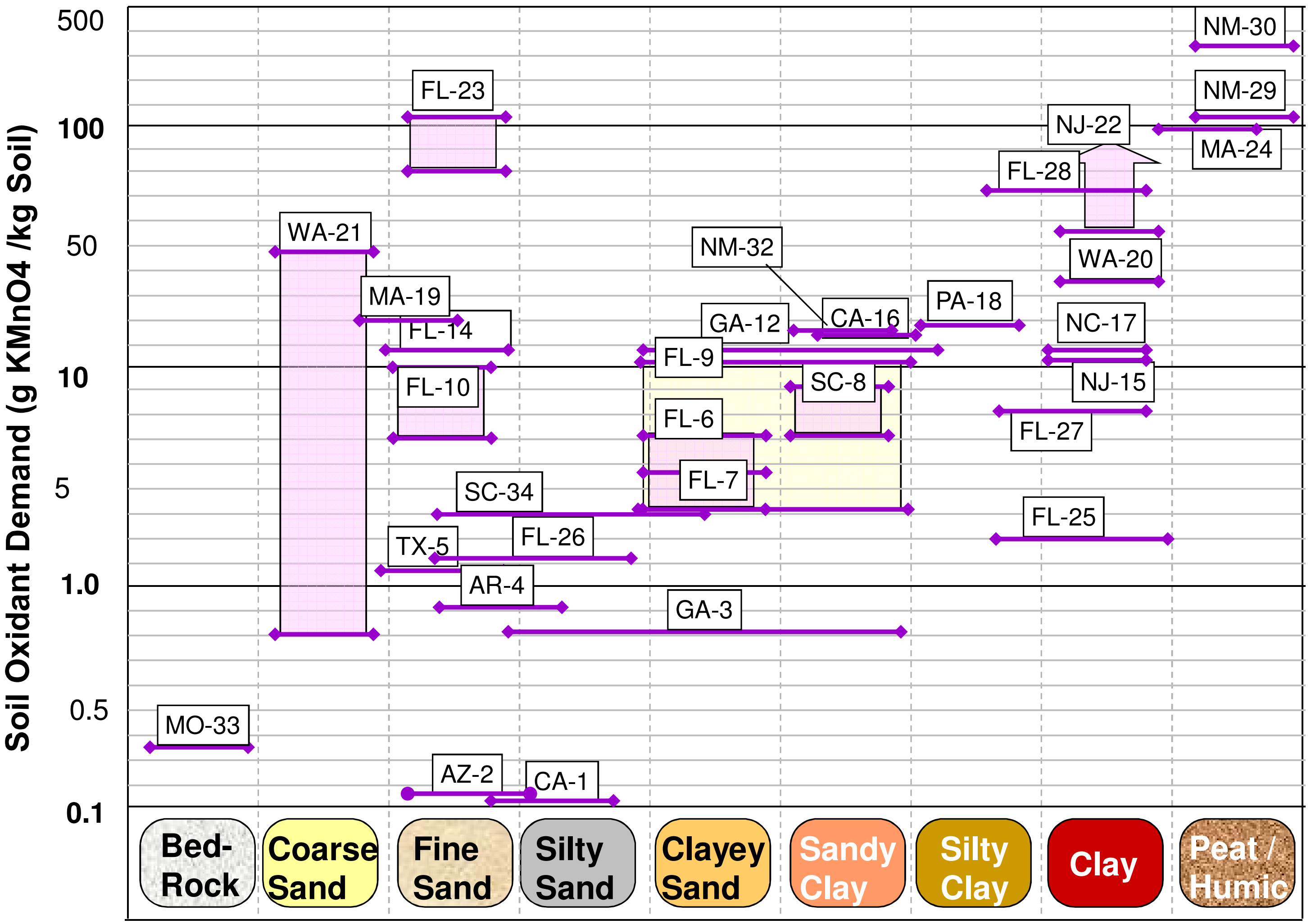
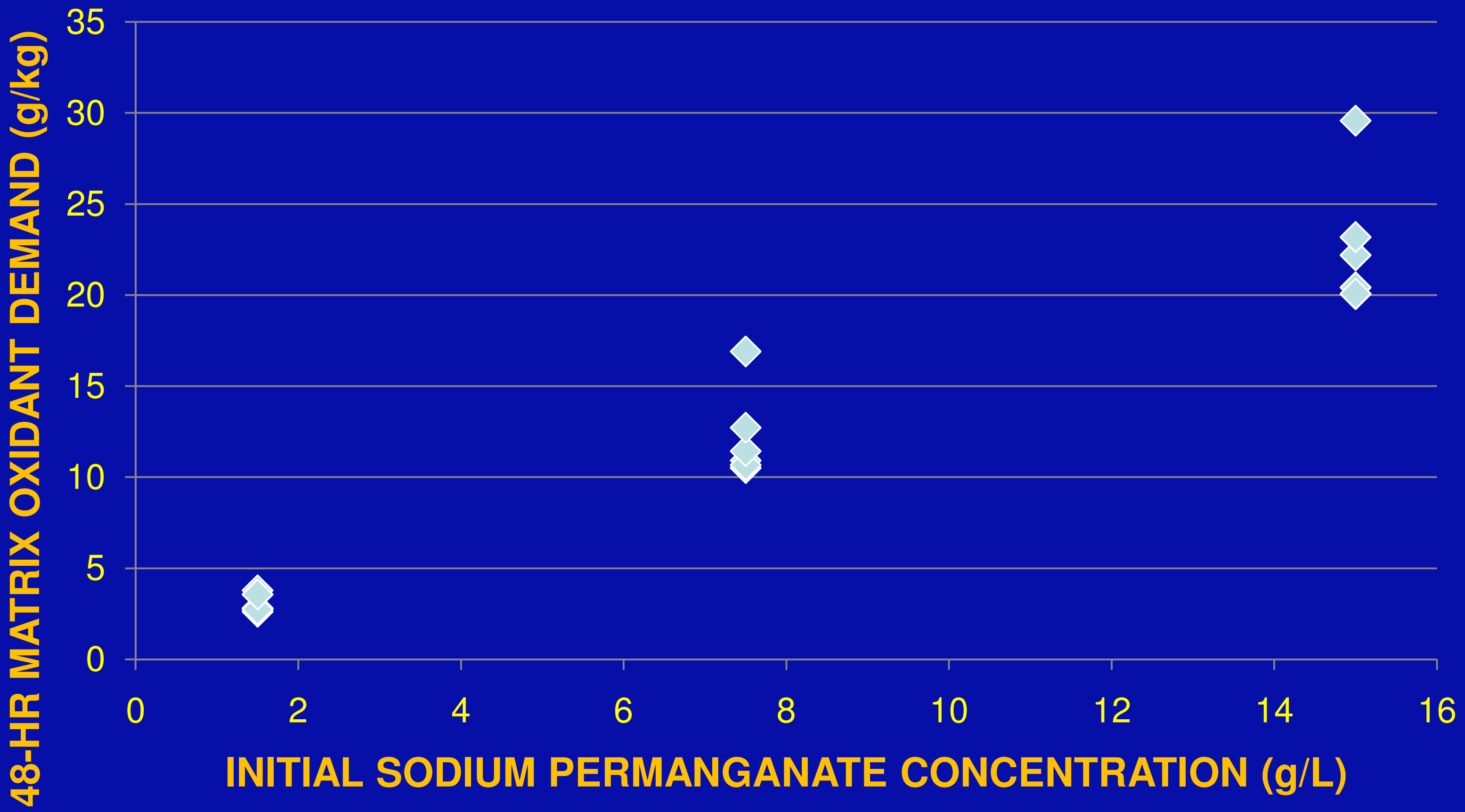


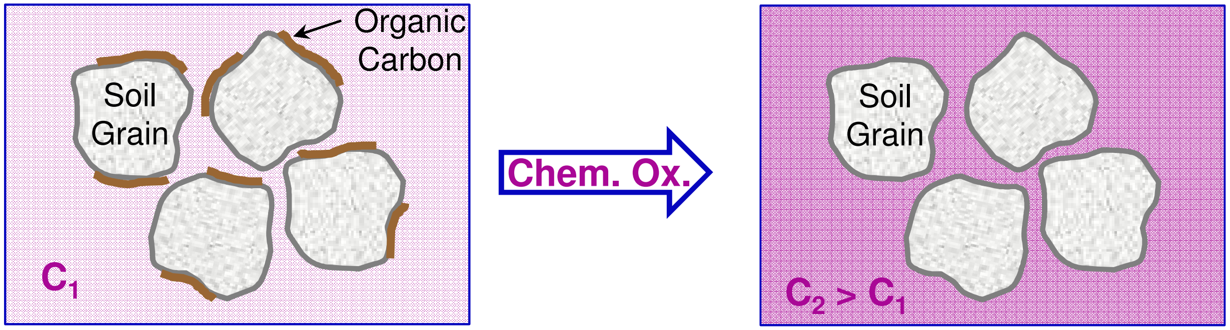
Initial Oxidant Concentration Affects Observed Oxidant Demand



Design & Implementation

3. Dosing/Injection Strategy

- Most common delivery method is batch injection using direct push techniques (DPT – Geoprobe)
- Tendency toward low volume and high oxidant concentration (to deliver oxidant dose quickly)
- This approach often fails – longer (or repeat) injections at lower concentration may be better

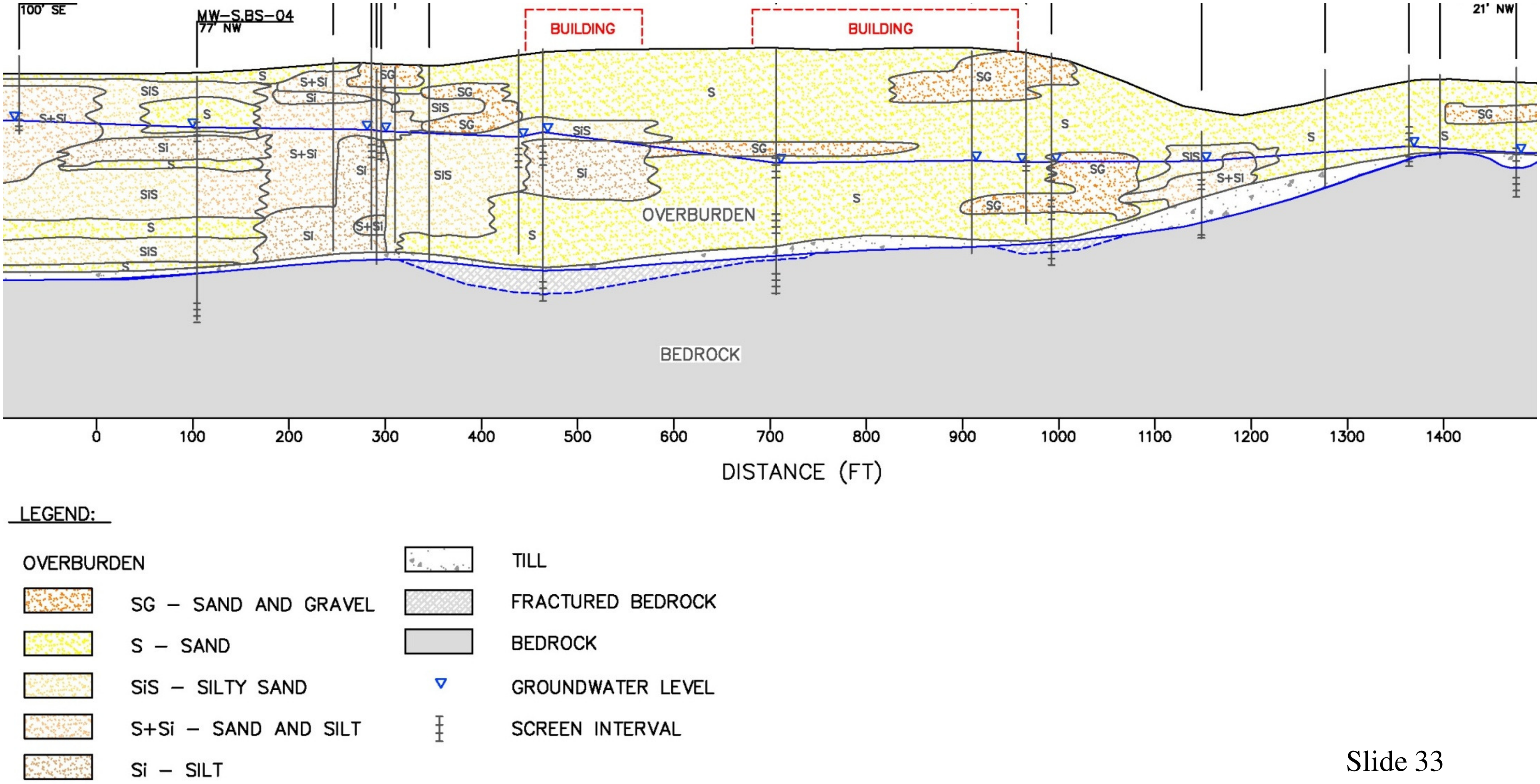


Design & Implementation

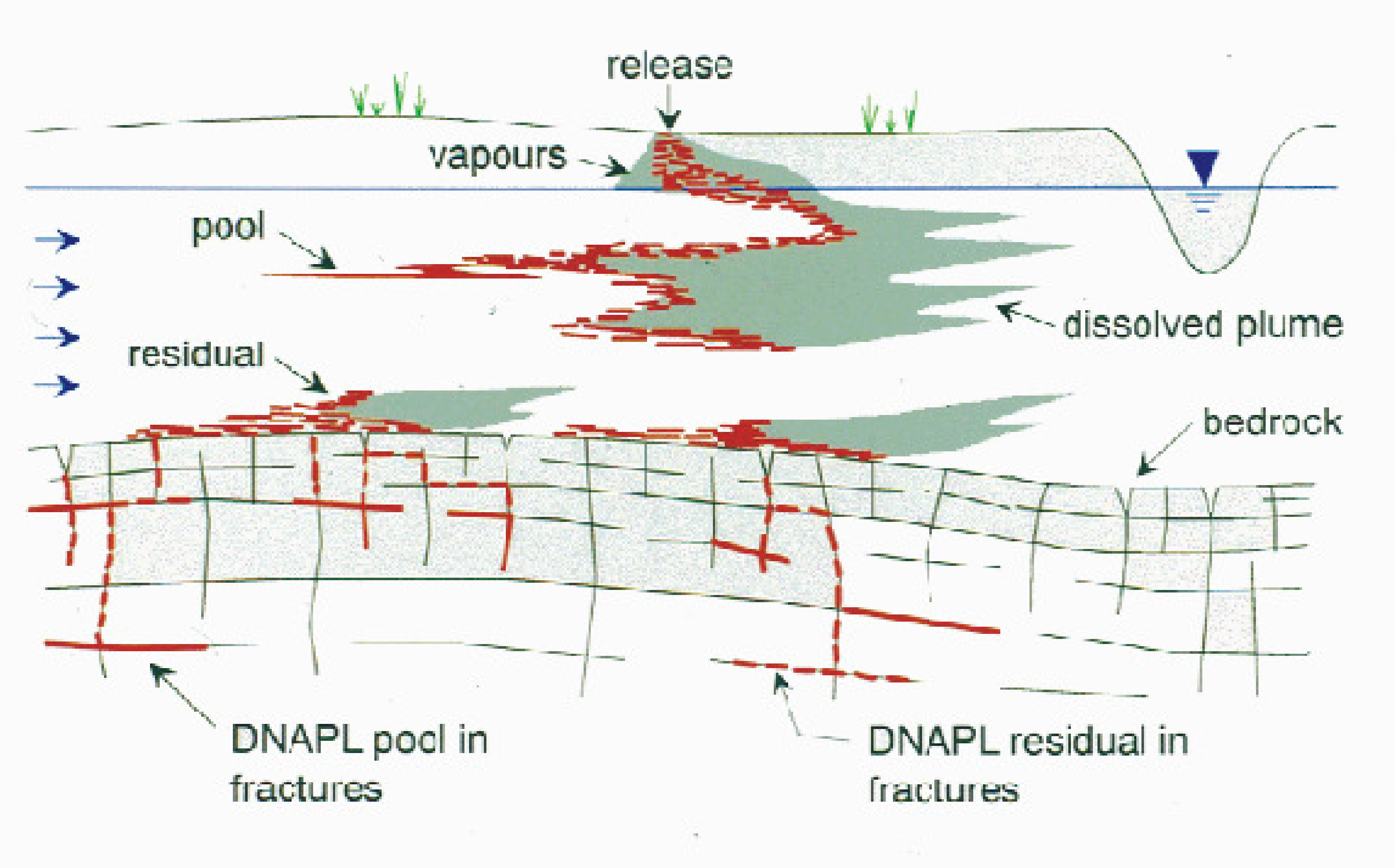
4. Achieving Oxidant Distribution

- Direct injection can result in uneven distribution
- Recirculation (even temporary) can improve distribution
- Creative combinations work – pulsing, semi-constant head, recirculation, pull-push
- High-energy methods – larger diameter auger and fracturing

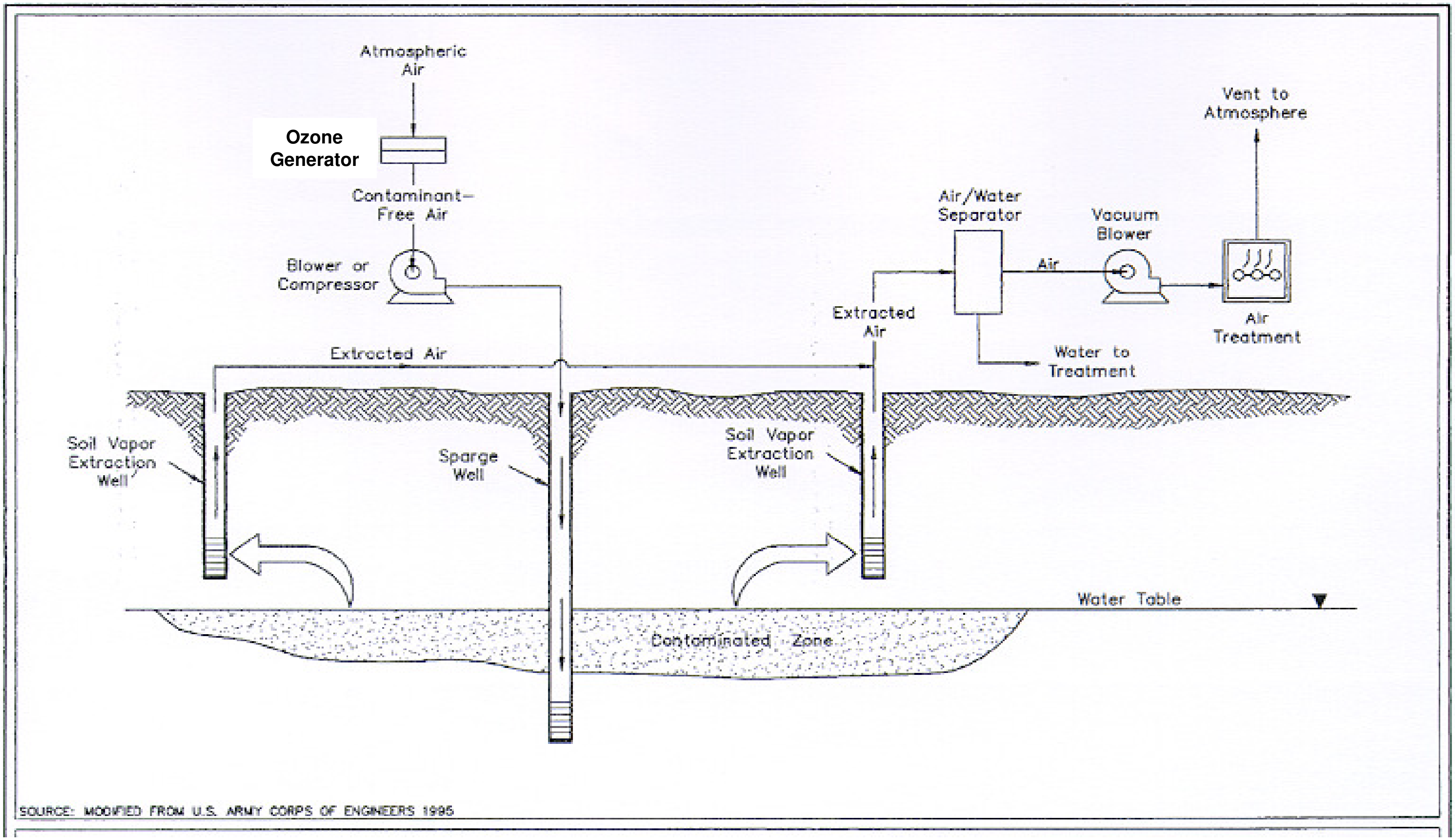
Heterogeneity



Impacts of Stratigraphy



Gas-Phase Delivery (Ozone)



SOURCE: MODIFIED FROM U.S. ARMY CORPS OF ENGINEERS 1995

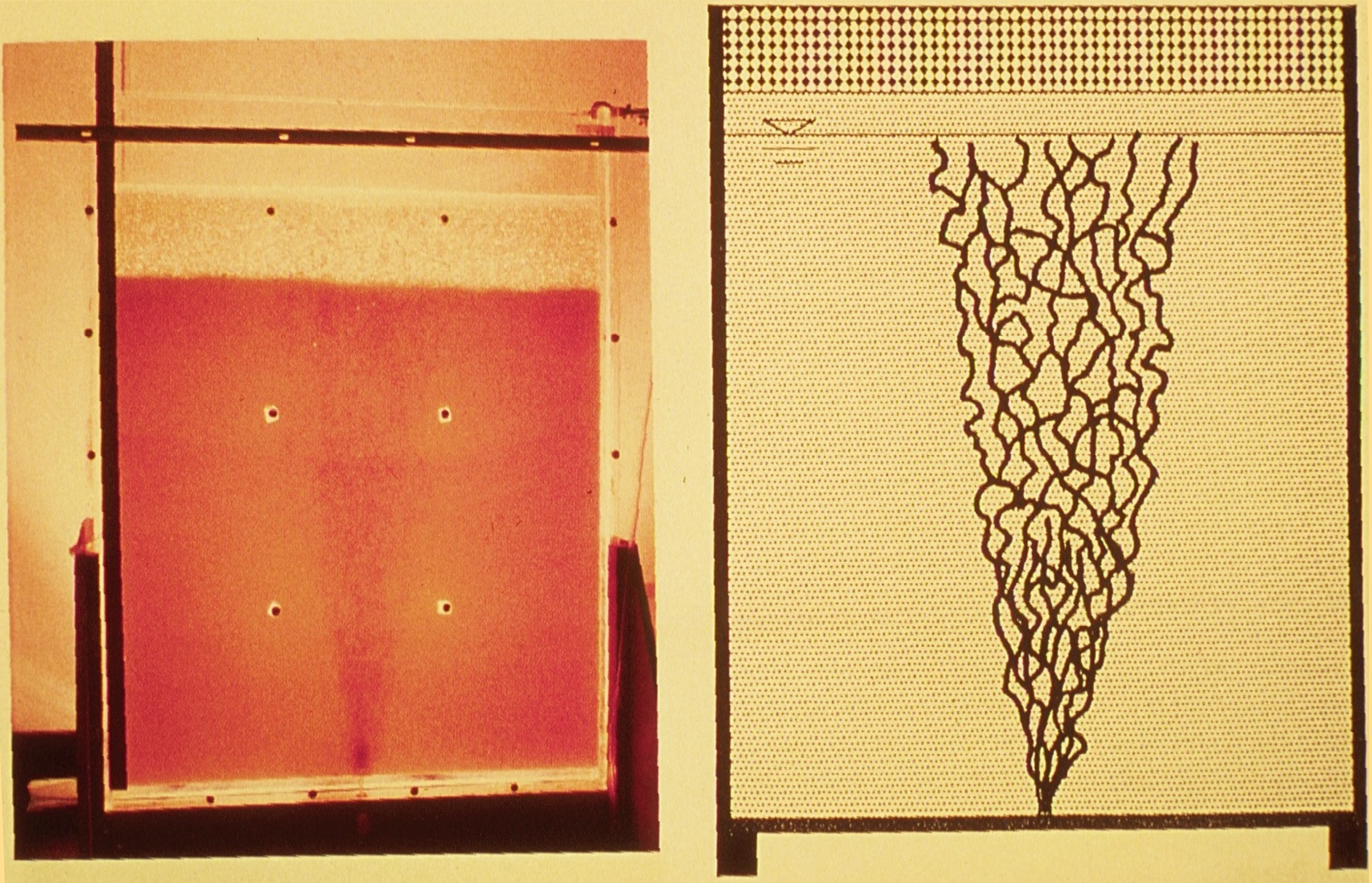


Figure 7. Air channel pattern at moderate air injection rate in 0.75 mm uniform bead medium: (a) photograph; (b) drawing.

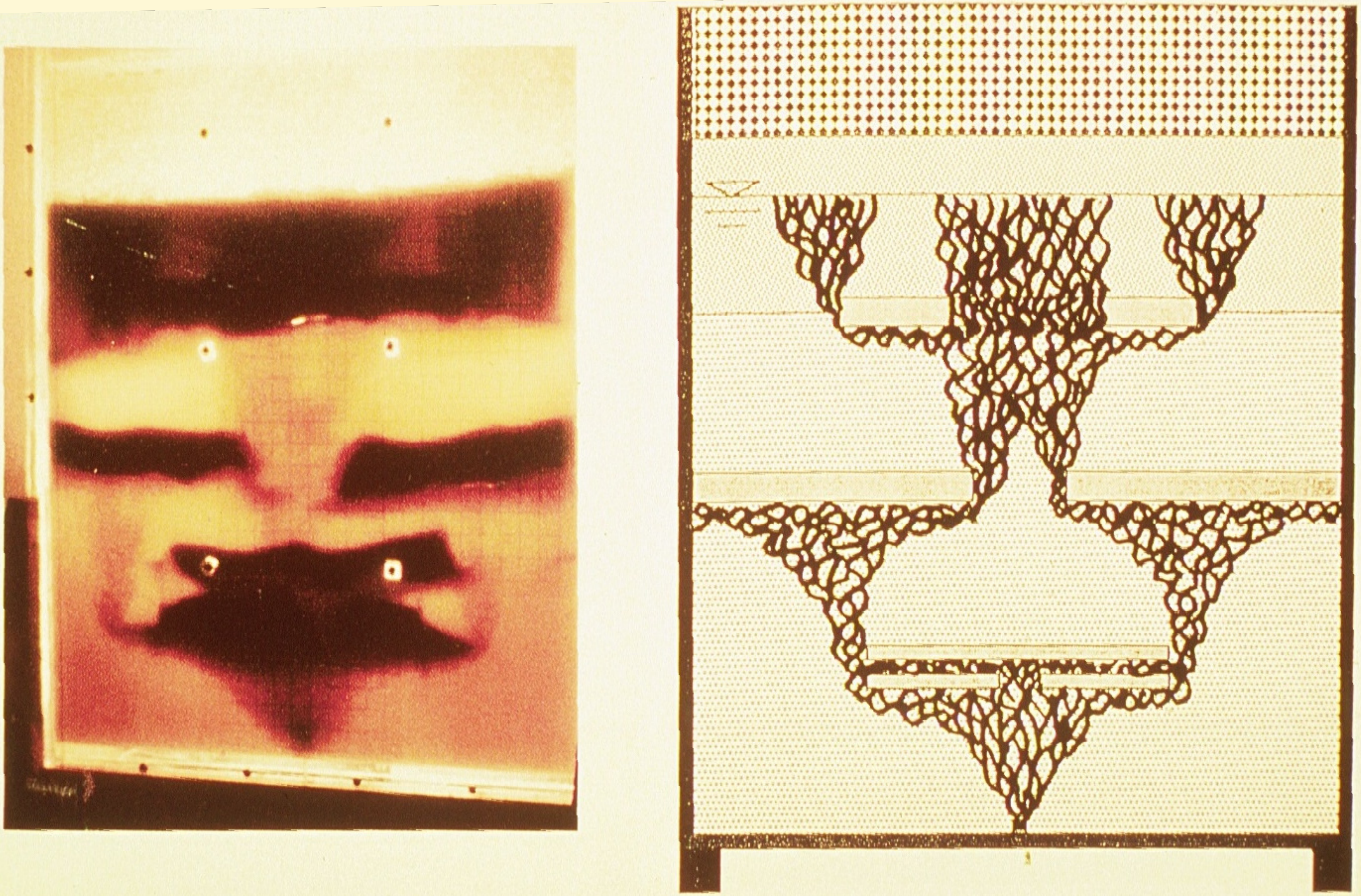
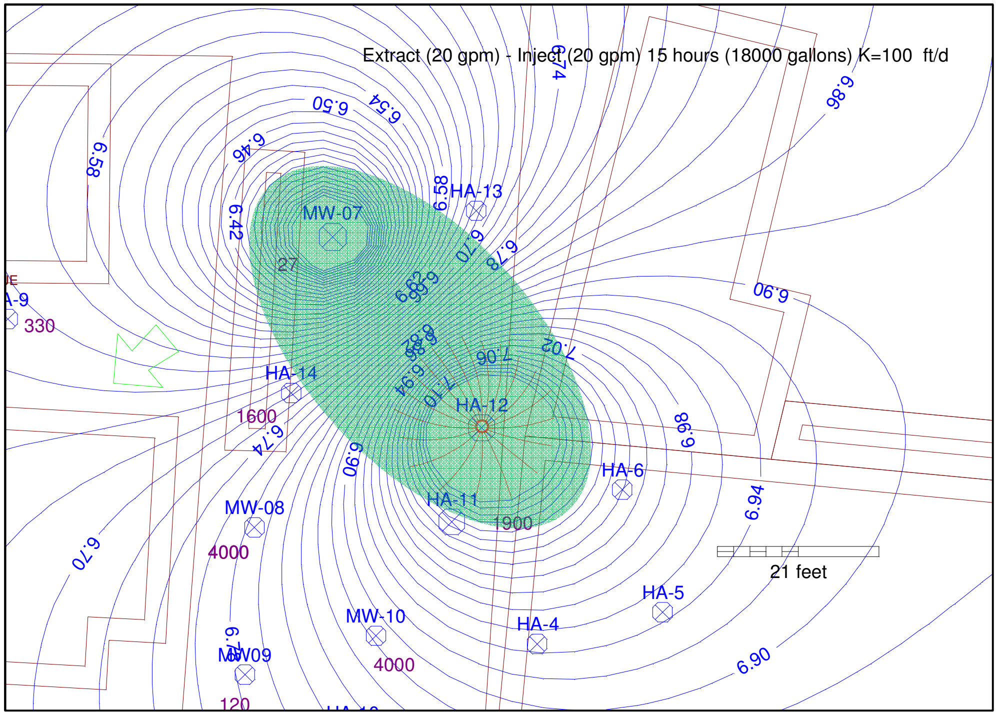


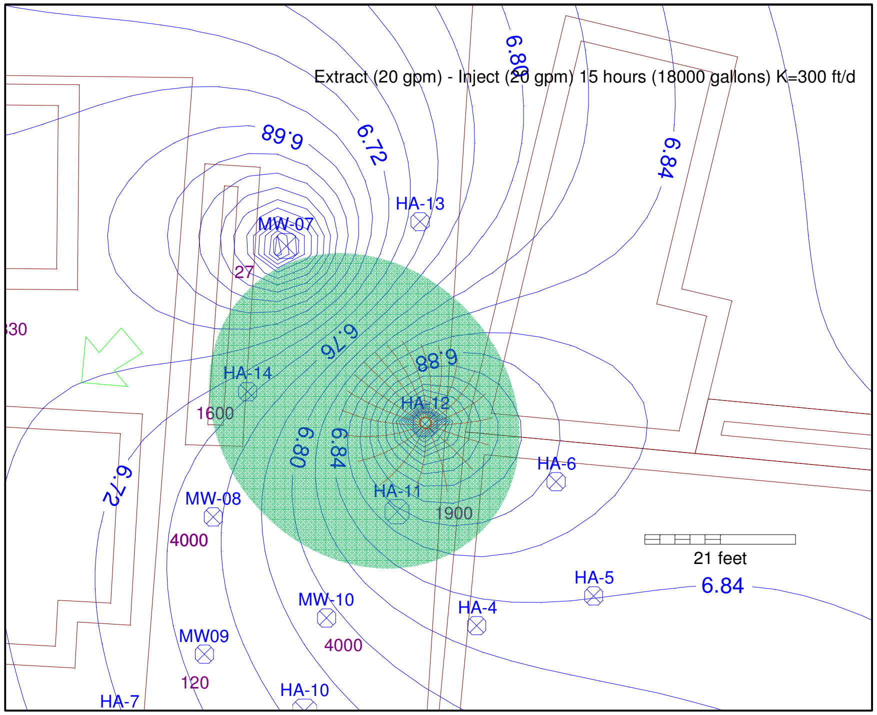
Figure 15. Air channel pattern in a stratified medium at lower air injection rates: (a) photograph; (b) drawing.

Hydraulic Conductivity

Both Scenarios: Extract and Reinject @ 20 gpm for 15 hours

Contour interval on both maps = 0.2 ft.





K = 100 ft/d

K = 300 ft/d

Factors Affecting Remediation Time

- Oxidant selection
- Oxidant dose
- Contaminant distribution
- Soil organic carbon content and oxidant demand
- Site hydrogeology
- Remedial Action Objectives
- Stakeholder considerations

Safety Considerations

- Mixing with incompatible materials may cause explosive decomposition
- Spills onto combustible materials can cause fires
- Health hazards are acute, not chronic
- Peroxide decomposes into water and oxygen which can promote flammable conditions

Reaction of permanganate with glycerol

Skin immediately after 30% H_2O_2 exposure

Safety Considerations

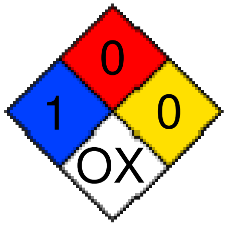
Some EH&S scenarios to plan for:

- Surfacing of amendment
- Identification of preferential pathways
- Splash and pressurized line hazards
- Decontamination and container management

Permanganate
Surfacing in a Bay

Permitting

- National Fire Protection Association (NFPA 430)
  - Storage and handling of liquid or solid oxidizers - notify authority having jurisdiction
  - Emergency Response training program required
  - Signage required



- Underground Injection Control (UIC) permitting
- Other state requirements (e.g., Remedial Additive Requirements per MCP in MA)

Homeland Security Requirements

- Chemical Facilities Anti-Terrorism Standards (CFATS)
- H_2O_2 and $KMnO_4$ are listed chemicals of interest if:
  - $H_2O_2 \geq 35\%$ concentration
  - Either > 400 lbs
- Storage facility required to submit a Chemical Security Assessment Tool (CSAT) Top-Screen.
- Permanganates also regulated by DEA

Questions?

- Oxidation Chemistry
- Oxidant Selection
- Applicable Contaminants and Site Conditions
- Remediation Timeframes
- Safety Considerations

Contact Information

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