



2003 AFCEE Technology Transfer Workshop

San Antonio, Texas

Promoting Readiness through Environmental Stewardship

Differentiating In Situ Oxidation from In Situ Dilution or Displacement

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Outline

- **In situ oxidation applications**
- **In situ oxidation processes**
- **Case study**
- **Pilot testing recommendations**
- **Justifications for recommendations**



Injection and Reaction Processes

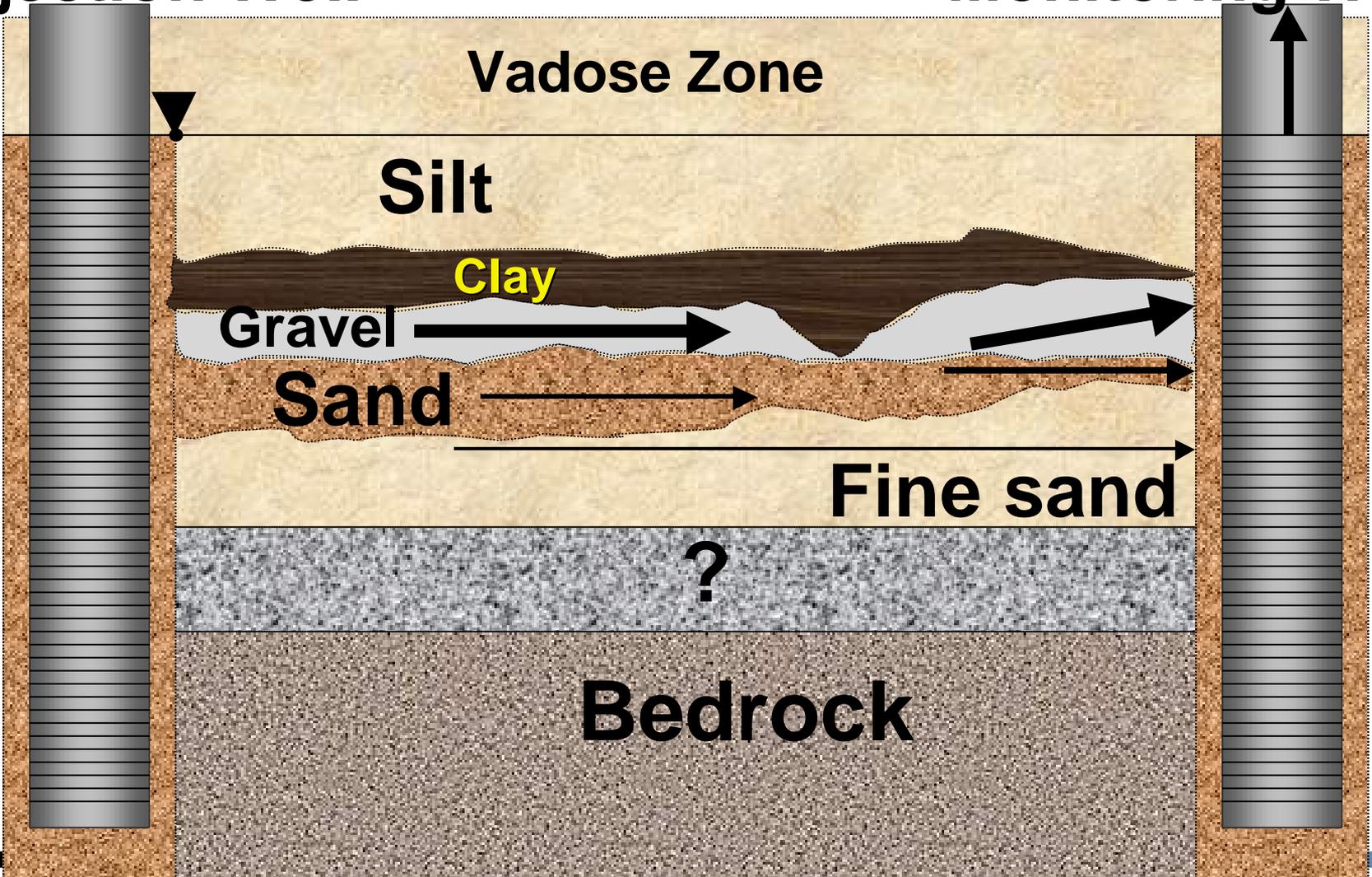
- **Injection = displacement**
- **Dissolved species will be displaced**
- **Sorbed species contacted – Treated?**
- **Organics will be retarded**
- **Dispersion = mixing (Significant?)**
- **Mixing of active oxidant and contaminant = Treatment**
 - **True for dissolved phase contaminants**
 - **Not always true for sorbed species**



Injection Flow Paths

Injection Well

Monitoring Well

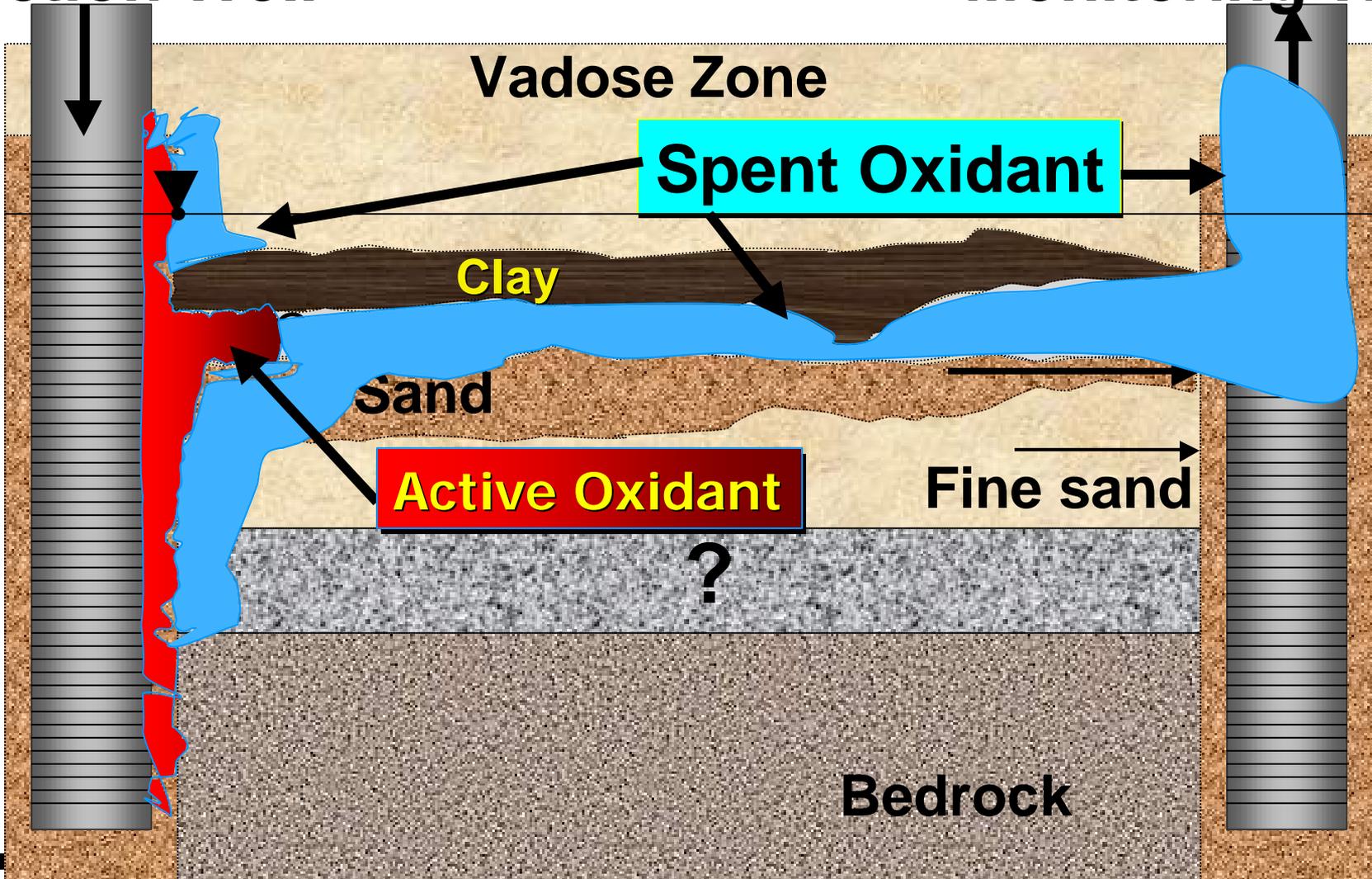




Early Injection

Injection Well

Monitoring Well

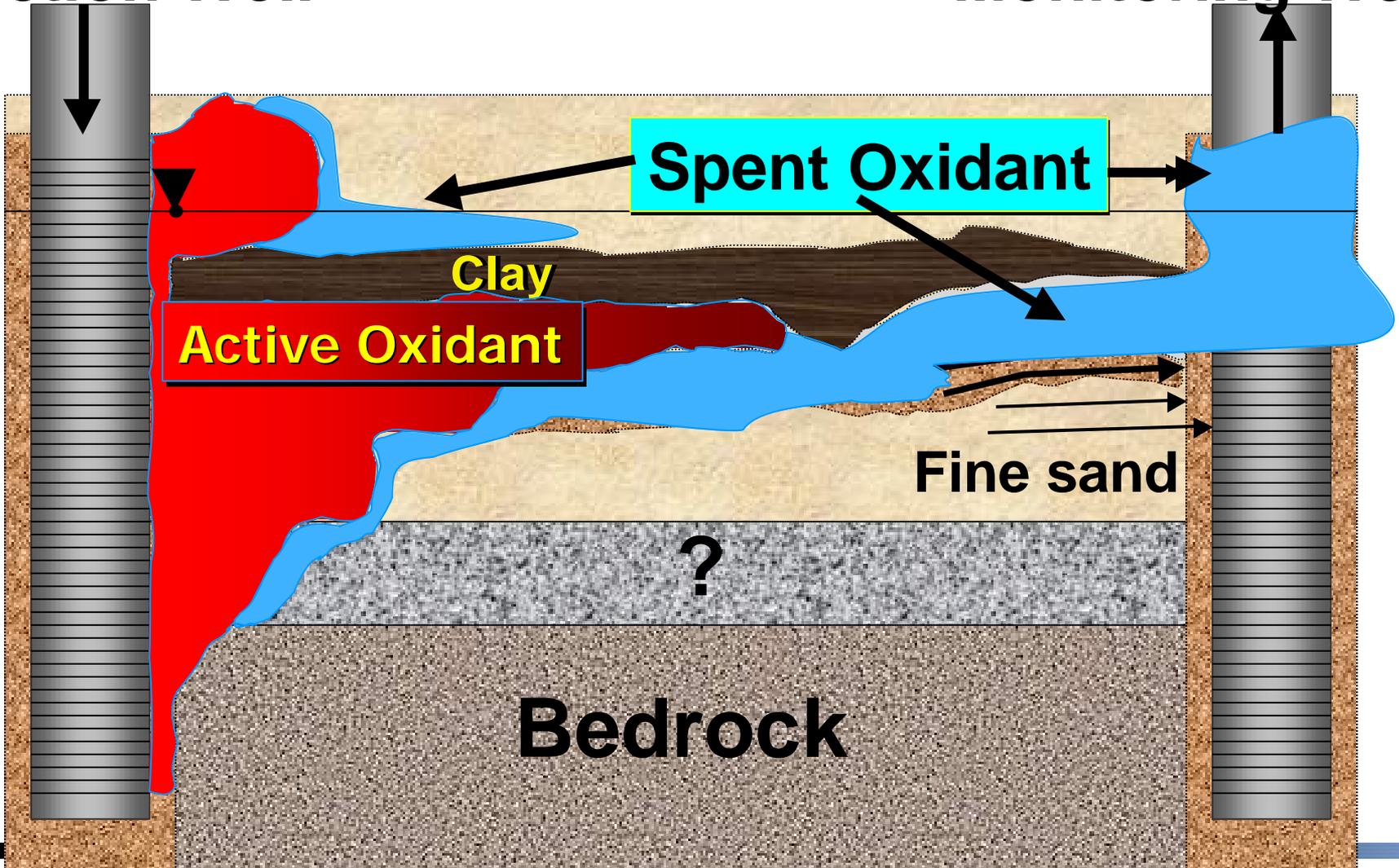




Mid Injection

Injection Well

Monitoring Well

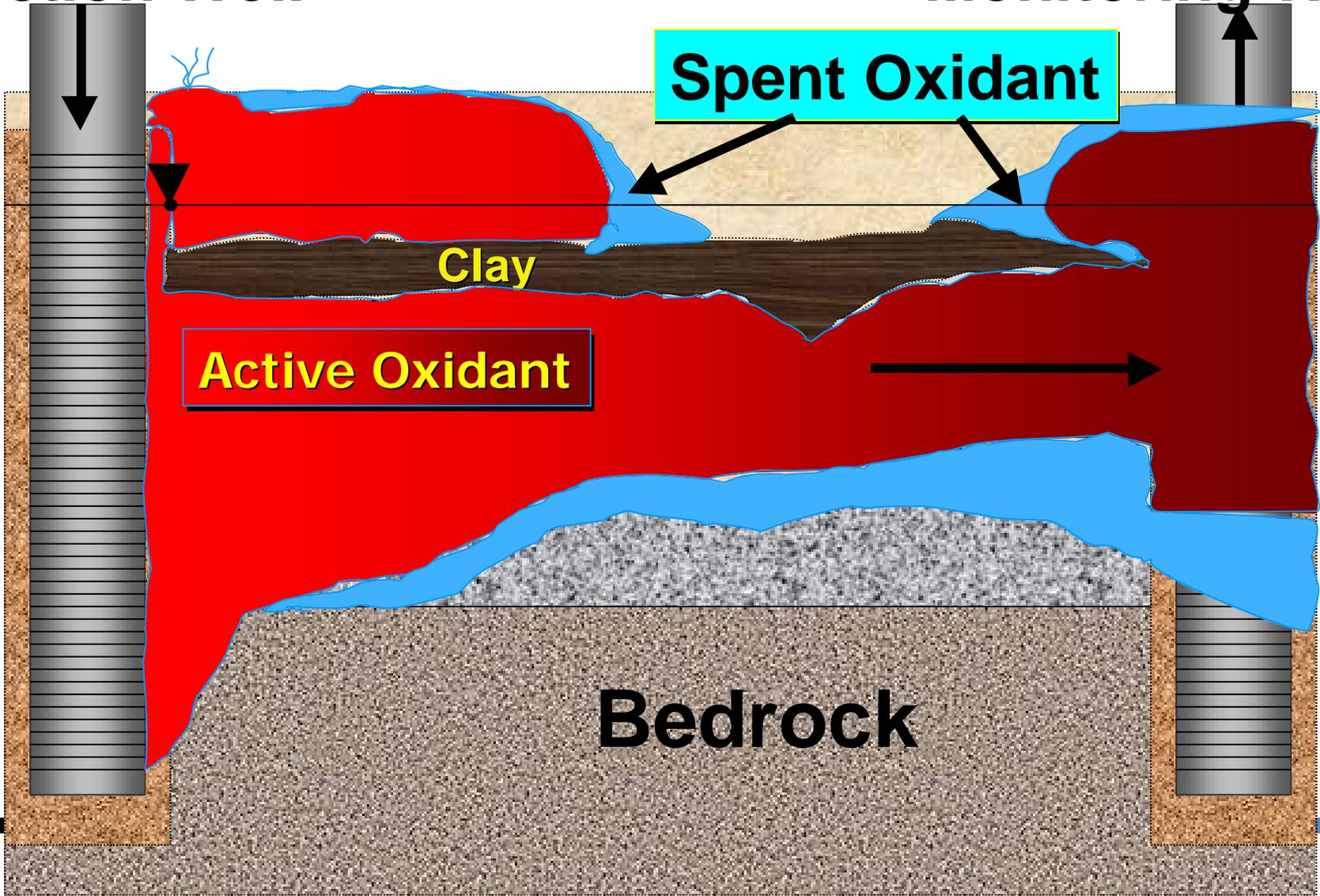




“Oxidant Sweep”

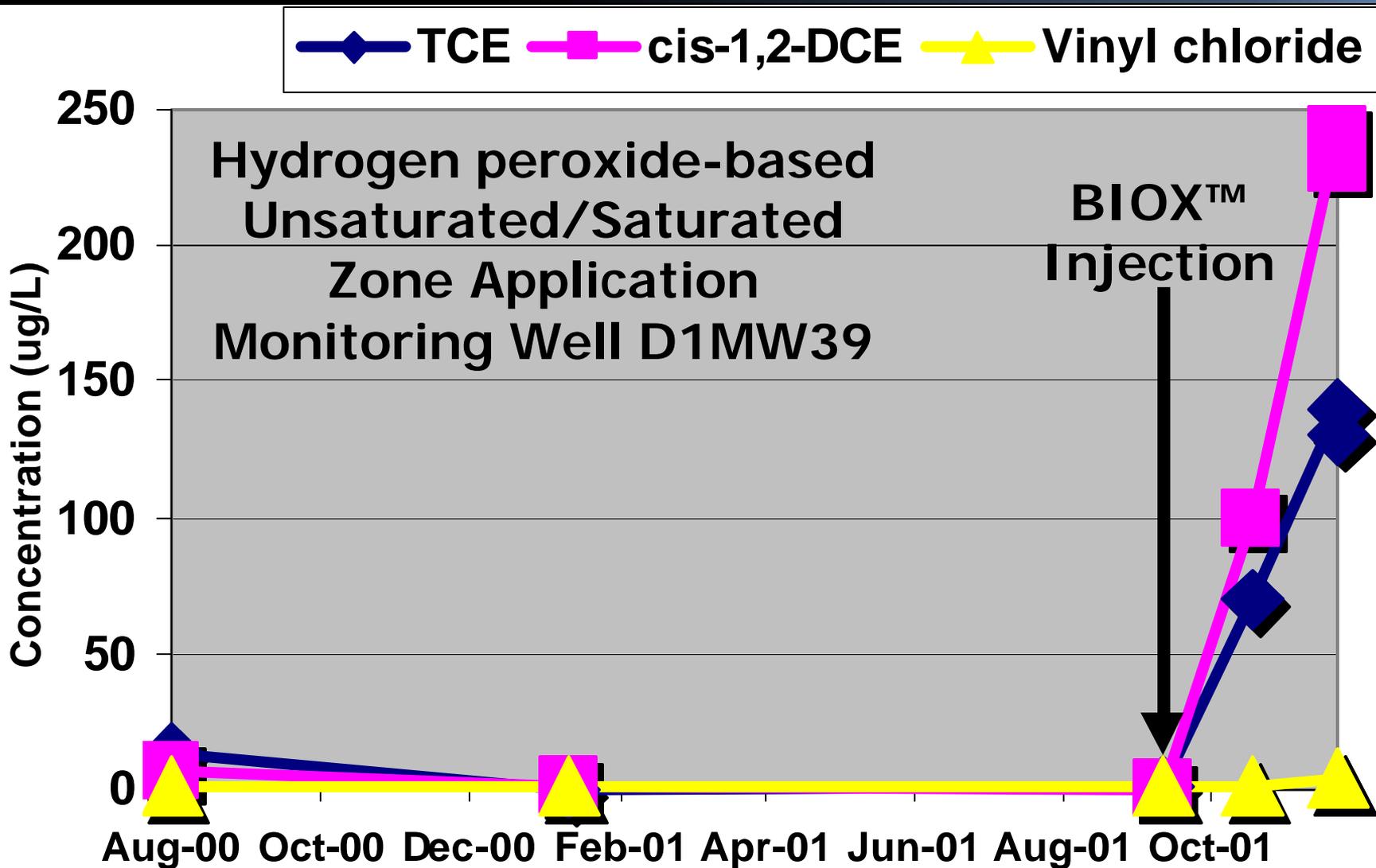
Injection Well

Monitoring Well





Autopsy: Gentile AFS, OH



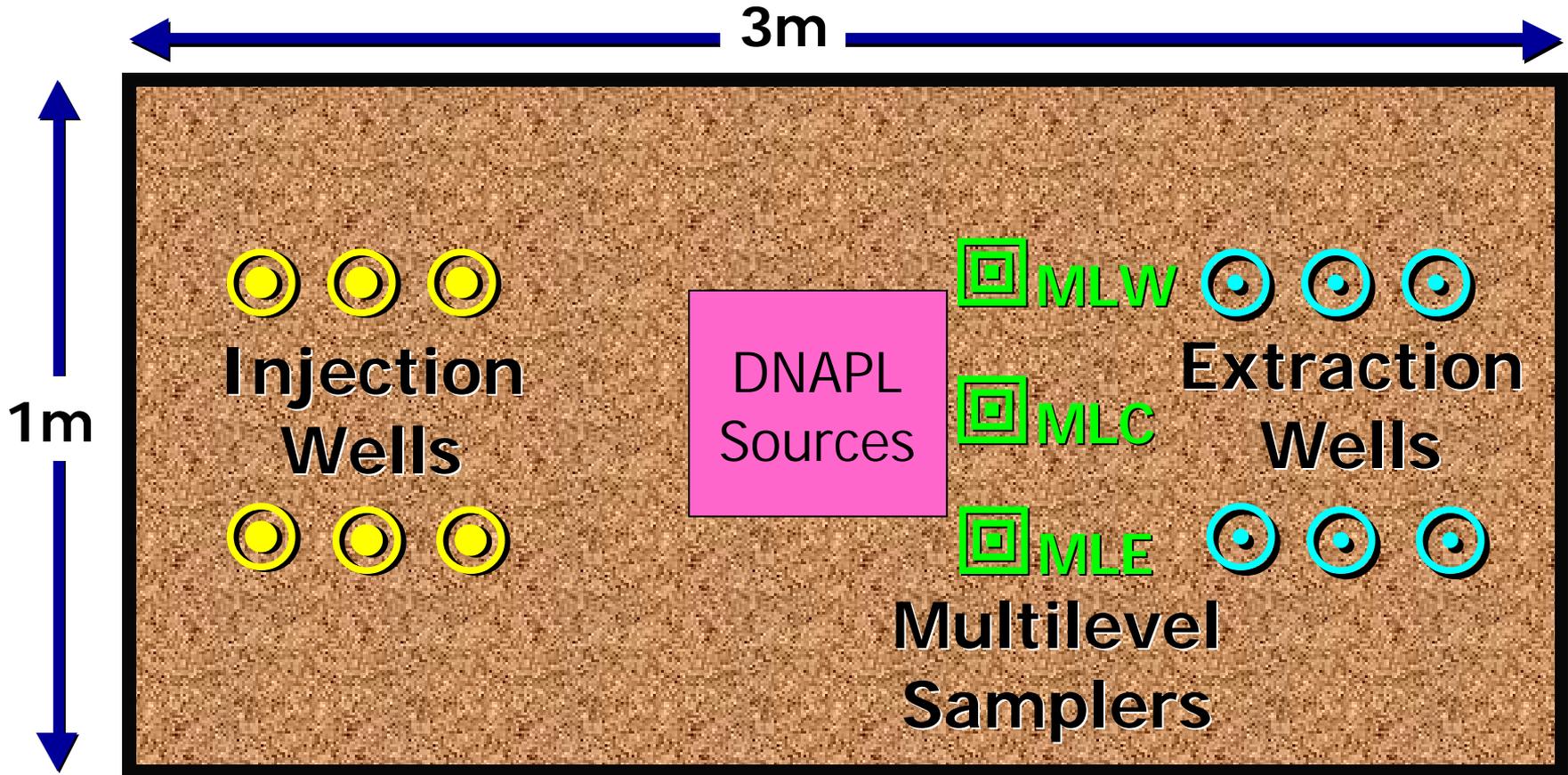


Autopsy: Canadian Forces Borden

- **Site: Canadian Forces Borden (CFB) (Schnarr, 1998)**
 - **3m (L) x 1m (W) x 2.5m (D) sheet piled cell**
 - **10^{-3} cm/sec sand; horizontally bedded; mm to cm features**
 - **Porosity = 0.33; Foc = 0.02%**
 - **Pore volume = 2.48 m³ (2500 L)**
 - **6 extraction wells; 6 injection wells**
 - ◆ **Upper, Intermediate, and Lower levels**
 - **3 sampling clusters, 5 vertical levels**
 - **Test 1 – Single 1L DNAPL Source**
 - **Test 2 – 6 localized sources, 8L DNAPL**



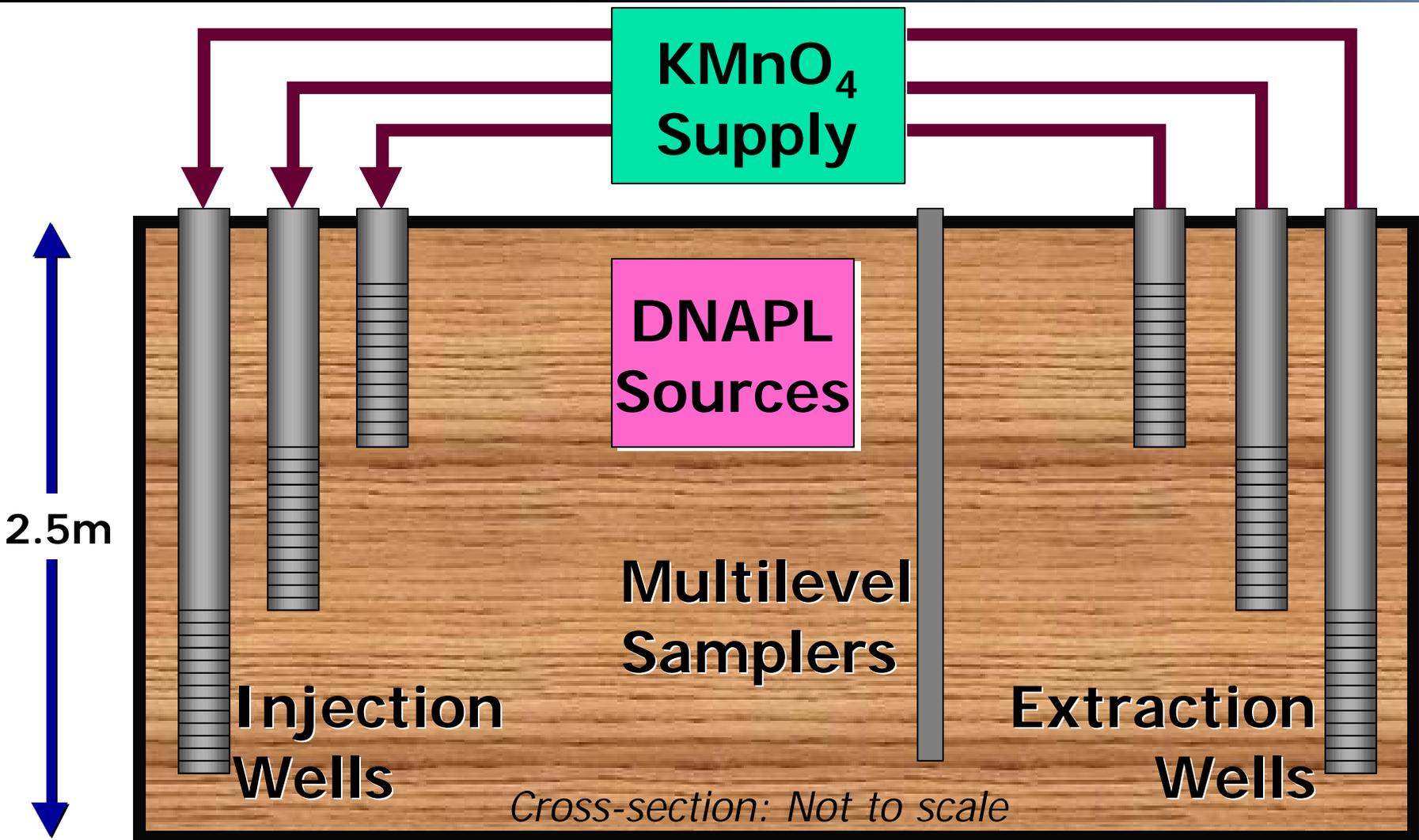
CFB Field Pilot Test Cell



Plan View
Not to scale



CFB Field Pilot Test Cell





Test 1: Uniform DNAPL Source

- 1 L PCE in middle, upper one-third of cell
- 10,000 mg/L KMnO_4 circulated
- 3 pore volume exchanges across upper two-thirds of cell in 50 days
- 7 pore volume exchanges across upper one-third of cell (i.e. source) in 120 days
- 4 pore volume exchanges of water across upper one-third of cell in 60 days
- After 13 days Chloride increased in MLC1
- >90% Destruction, 110 kg KMnO_4



Test 2:

Heterogeneous DNAPL Sources

- 4 L PCE, 4 L TCE in six 2.5cm x 1m long soil cylinders in middle, upper one-third of cell
- 64,000 mg/L (saturated) KMnO_4 circulated
- MnO_2 removed in sand filter
- 48 L/day recirculation rate across cell; 5.6 pore volumes in 290 days
- After 83 – 104 days, PCE effluent = 10 – 50 mg/L; TCE higher; KMnO_4 effluent = nondetect (colorless) = No oxidant breakthrough
- After 250 days, PCE and TCE effluent < 0.010 mg/L; KMnO_4 effluent = influent
- After 290 days, 62% of original source oxidized



Summary: CFB Site

- Multiple pore volumes exchanges occurred before oxidant breakthrough
- Relatively uniform sandy site requires > 6 pore volume exchanges of oxidant to achieve 60 – 90% source reduction
- Uniform source treated 90+% source reduction
- Heterogeneous sources ~62% source reduction
- Recirculation and continuous oxidant dosing required for source treatment
- Single event injections only likely to partially treat more permeable zones



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Pilot Testing Recommendations



Evaluate Site-specific Applicability

Examples:

- Fenton's Chemistry requires active iron (i.e. pH 2-3)
- "It can be seen that the Fenton's Reaction is extremely sensitive to anions, and phosphate ions in particular will seriously suppress the Fenton system's ability to oxidize dichlorvos (i.e. target contaminant)." (Lu, M. C. et. al. 1997)
- "When applied to low permeability media (e.g. silts and clays) hydrogen peroxide can modify the pore size and pore continuity within the media and significantly reduce permeability." (Hargett et. al., 1985). This reduction in matrix and bulk deposit permeability may inhibit the subsequent delivery of treatment agents to contaminated zones. Fenton's reagent injection can also cause land surface subsidence.



Estimate Oxidant Demand

- **Major oxidant sinks:**
 - Naturally occurring organic carbon
 - Reduced minerals
 - Non-specific reactions – e.g. catalase (H_2O_2)
 - Contaminants
- **Bench-scale tests are useful if multiple oxidant doses are used**
- **Permanganate – 2 – 15 g/kg clean soil; 3 – 22 kg/m³ clean soil; \$12 - \$88/m³ clean soil**



Estimate Injection Volume Requirements

Assumed Radius of Influence (ft)	Porosity	Target or Injection Well Screened Interval (ft)	Required Volume of Injectant to Achieve Assumed Radius of Influence (gal)	Time to inject at 10 gpm (Hours)	Number of Injection Wells to Cover 1 Acre
2.50	0.30	10.00	441	0.7	2,218
5.00	0.30	10.00	1,762	3	555
10.00	0.30	10.00	7,050	12	139

For recirculation systems –
Estimate pore volume exchange rates



Time Considerations

- Four commercially available 35% hydrogen peroxide solutions were tested for rates of decomposition by Fenton's reagent.
- No significant differences in decomposition rates of these aqueous commercial products.
- Near complete decomposition of 3 and 10% hydrogen peroxide Fenton's reagent mixtures occurred with 60 – 80 minutes and 25 – 30 minutes respectively. (Aldershof, B. K. et. al. 1997).
- The rate of hydrogen peroxide reduction by solid samples from two Illinois aquifers; they report half-lives between 1 and 4.5 hours (Barcelona, 1991)
- Hydrogen peroxide decomposition is catalyzed by the mineral birnessite [γ -MnO₂ (s)] with a half-life of 9.35 minutes at 21.1°C and pH 7.6 (Barcelona, 1991)
- Hydrogen peroxide was completely decomposed within a 1 foot zone surrounding the injection well (Lawes, 1991)



Consider Injection Rates Versus Oxidant Decomposition Rates

- Complete decomposition of 10% hydrogen peroxide Fenton's reagent mixtures occurred within 25 – 30 minutes
- It would take 45 minutes to inject oxidant at 10 gpm across a 2.5 foot radius of influence, 10 foot thick zone.
- Effective radius of influence
 - Well screen clean
 - Diminishing oxidant delivery versus distance
 - Diminishing oxidant delivery versus soil F_{oc}



Evaluate Ground Water Velocity versus Oxidant Longevity

- Short-term performance sampling should be conducted after oxidant is expended
- Effective use of conservative tracers requires consideration of ground water velocities
- Estimate time for upgradient contaminated ground water to flow into pilot test area, if applicable
- Ground water advection and solute dispersion may facilitate mixing of longer-lasting oxidants (e.g. MnO_4^-)
- Rebound in “slow” aquifers may take > 1 year = Long-term performance monitoring



Indicators of Spent Oxidant at Monitoring Wells

Fenton's Reagent

- Lower contaminant concentrations
- Nondetect H_2O_2
- High dissolved oxygen
- High redox readings
- Lower pH
- Higher iron
- Higher chloride

Permanganate

- Lower contaminant concentrations
- Nondetect MnO_4
- No color = MnO_2
- Brown color
- High redox readings
- $\text{Mn} > \text{MCL}$
- Higher Na or K
- Higher chloride



Indicators of Active Oxidant at Monitoring Wells

Fenton's Reagent

- Lower contaminant concentrations
- High H_2O_2
- High dissolved oxygen
- High redox readings
- Lower pH
- Higher iron
- Higher chloride

Permanganate

- Lower contaminant concentrations
- High MnO_4
- No color = MnO_2
- Brown color
- High redox readings
- $Mn > MCL$
- High Na or K
- Higher chloride



Directly Monitor Oxidant: H₂O₂

- **Difficulty:** Significant dilution required - 35% H₂O₂ = 350,000 mg/L
- **Hydrogen peroxide**
References: Thiocyanate Colorimetric Determination of Nonmetals, 2nd ed., Vol. 8, p. 304 (1978) Chemetrics.
- The thiocyanate method consists of ammonium thiocyanate and ferrous iron in acid solution. Hydrogen peroxide oxidizes ferrous iron to the ferric state, resulting in the formation of a red thiocyanate complex. Chlorine will not interfere with this method. Ferric iron will interfere. Results are expressed as ppm (mg/L) H₂O₂.
- The DPD method is derived from the DPD method. It offers greater sensitivity and fewer interferences than the thiocyanate method. Hydrogen peroxide reacts with DPD in the presence of potassium iodide to form a blue reaction product. Results are expressed as ppm (mg/L) H₂O₂.
- The Titrimetric Method. The titrimetric method using ceric sulfate as the titrant and ferroin is the end point indicator. A color change from green to orange signals the end of the titration.



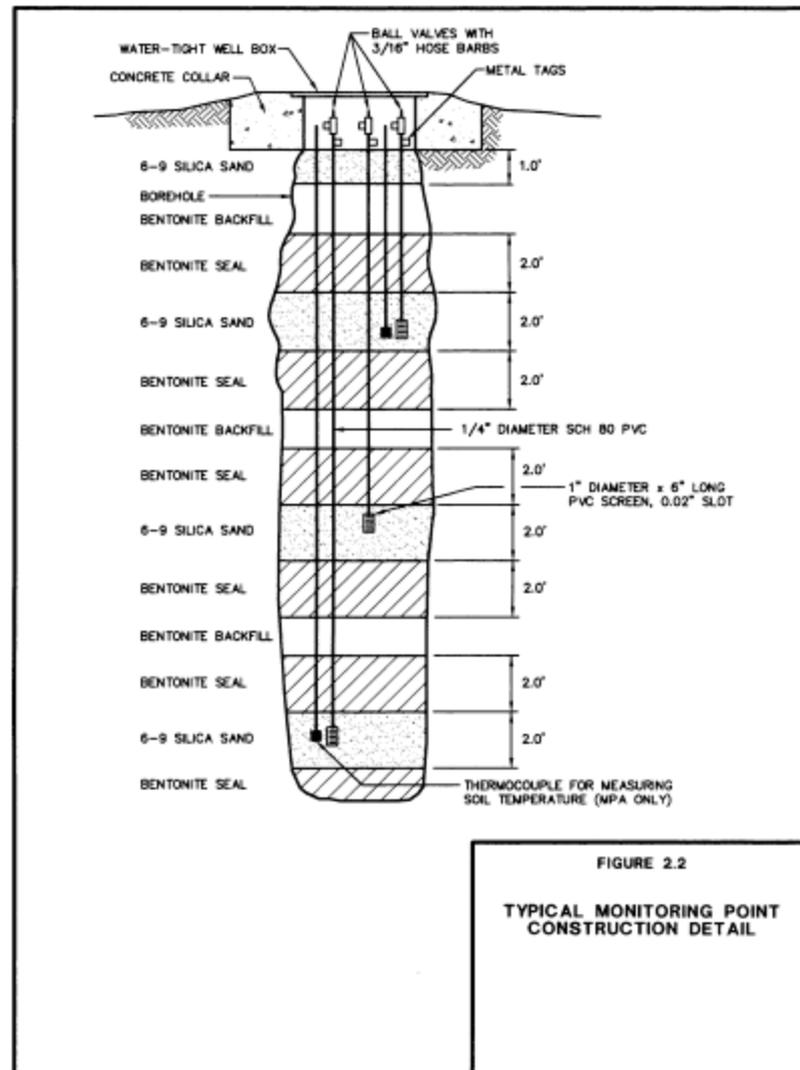
Directly Measure Oxidant: MnO_4^-

- KMnO_4 is measured by titration by thiosulfate or spectrophotometrically
- Fresh reagent – Deep purple
- Spent reagent – Brown
- MnO_2 precipitate - Black



Monitor Soil Gas for Displaced Gases and Contaminants

- Significant volumes of gas are produced
 - Fenton's >> Permanganate
- Significant temperature increases
 - Fenton's >> Permanganate
- Consider nearby buildings, ignition sources, utilities



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Use Conservative Tracers

- Consider Bromide, iodide, etc.
- Contaminant concentration and geochemical indicator data can/will be ambiguous
- Tracers can be measured in the field to more immediately ascertain injection flow paths and oxidant delivery efficiencies
- Permanganate includes:
 - K or Na tracer – beware of background concentrations
 - Color or Mn “tracers” – MnO_2 precipitation



Directly Test for Displacement and Dilution

- **Inject water and tracer in one area of the site**
- **Compare contaminant concentrations over time to oxidant injection areas**
- **Consider temperature and gas generation effects in oxidation treatment areas**
 - **Exothermic and gas producing oxidation reactions**



Consider Recirculation

- Oxidants demonstrated effective on dissolved contaminants, not sorbed
- Oxidant will be preferentially delivered to more permeable zones
- CFB tests demonstrated need for multiple pore volume exchanges
- Provides control, improves mass balance capabilities, and easy restart
- May be the only effective method



Summary

- Oxidants “work” because they are “highly reactive”
- “Highly reactive” with porous media and then contaminants
- Higher reactivity requires higher pore volume exchange rates, dosing, and duration of oxidant resupply
- Methods of addressing preferential flow paths, oxidant demand, and contaminant distribution define success or failure



Summary (cont)

- **Homogeneous, low organic carbon, distilled water sites with low concentrations of dissolved chlorinated ethenes are excellent candidates for in situ oxidation**
- **“Otherwise, you get what you put into it.”**
- **Aggressive well-designed delivery is essential to success**



Purpose of this Presentation Revisited

- **Regardless of method of application in situ oxidation includes contaminant dilution, displacement, and treatment**
- **Understanding in situ contaminant dilution, displacement, and treatment is very challenging**
- **A poorly designed pilot test often provides nothing more than a false positive**



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