- The webinar will start promptly at 12:00 EST There will be a Q&A session during the last 10 - 15 minutes of the webinar
- All participants will be on mute
- One day after the webinar has been concluded an email will be sent that will allow you to download a copy of the webinar

- The webinar is being recorded and will also be made available via email
- Please use the "Chat" (see the icon to ask questions for the presenters. Questions will be answered at the end of the webinar. If any questions are missed due to a lack of time, we will follow-up via email after the webinar.

# ISCO
# State of the Art vs. State of the Practice

Michael Marley & Dennis Keane
XDD Environmental

September 2, 2021

# Pre-Design Considerations

## Proper Preparation Prevents Poor Performance
**– Charlie Batch**

**You Needed This:**

**But What You Got Was….**

# Pre-Design Engineering Components

- Step 1: Solid Conceptual Model
  - Contaminant type
  - Contaminant phase
  - Location of contaminant
  - Media properties
- Step 2: Oxidant selection
- Step 3: Oxidant dosage and performance
- Step 4: Pilot testing

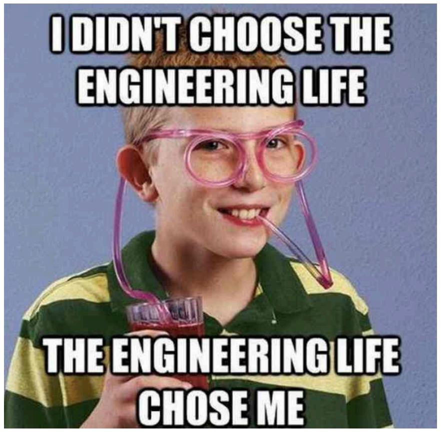
- Setting expectations based upon the above information

# Step 2:  Oxidant Selection

- Step 1 feeds into Step 2
  - Nearby Structures?  Off gassing may preclude peroxide-based chemistries.
  - Lower permeability materials?  Longer residence time required of oxidant.
  - Chlorinated ethanes?  Higher energy oxidant like alkaline activated persulfate.
    - Contaminant type limits oxidant selection.
  - Impacts primarily in the vadose zone?  Ozone or mixing or permeability is low enough to retard oxidant migration.
  - Significant quantities of DNAPL?  Excavation, thermal, or “other” followed by ISCO polishing?

# Step 3: Oxidant Performance
# Simple as a Call to Tech. Support?

- Remedial design using dosing spreadsheets
- Usually a minimum dosing/application recommended
  - Good start…provides “cost-effective” starting point
- Must account for highly variable/sensitive design parameters:
  - TOD, SOD, etc.
  - Interferences/scavengers, distribution
- Very site-specific
  - Additional evaluation often recommended
  - by the vendors
  - ….but often ignored….



# Oxygen Release Compound Mass Loading

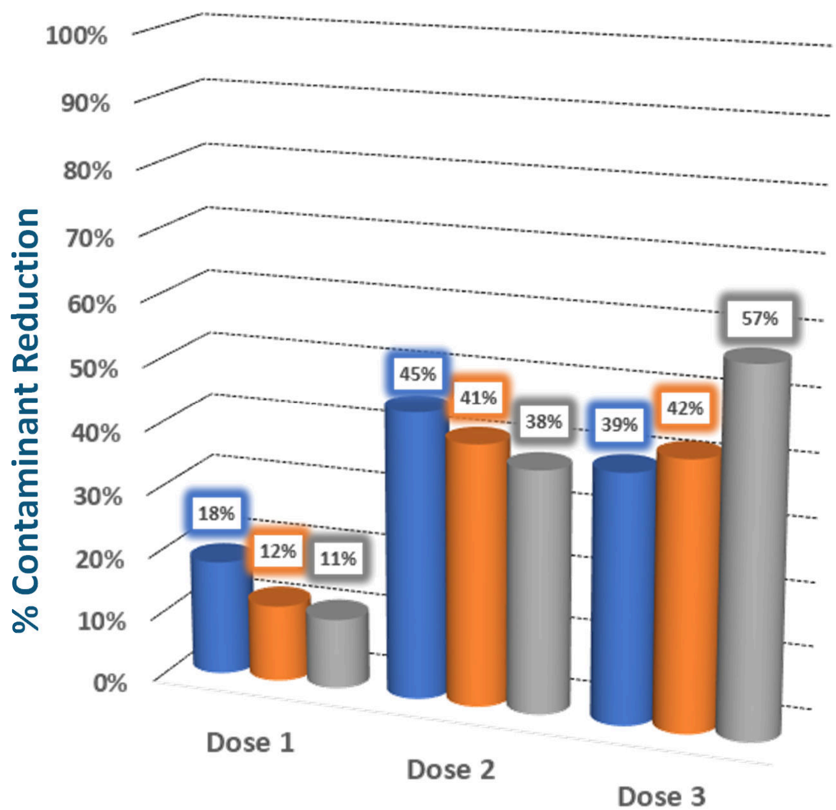
- Superfund site:
  - Multiple source/plume with chlorinated solvents and petroleum hydrocarbons

- Comparison of oxygen release products for petroleum plume
  - Evaluated three oxygen release compounds plus controls
  - Requested dosing recommendations from each product vendor to hit goals
  - Tested three products at the highest recommended dosage of any product*

* Some of above vendors recommended treatability testing to validate dosage assumptions

# Vendor Design Estimates

(objective >90% Reduction with Single Dose)

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**All Recommended Dosing Levels Failed,**

**Even After 3 Applications at the Maximum Dose Recommendation**

# Bench Testing Objectives

- Calculate the total oxidant demand (TOD)
  - Can vary by orders of magnitude
  - Has a significant impact on effectiveness and cost
- Determine the effectiveness (ability and kinetics) of an oxidant
- Determine catalyst requirements
- Evaluate by-product formation
- Analyze potential for metals mobilization
- Run treatability for scale-up to field implementation (see next example)

# Example – ISCO Peer Review – Diagnosis of Failure by Others

- SOP Treatability Design using CHP Flawed
  - Was "considered a success" as TCE was ND in test reactor
  - Half-life (HL) < 5hrs
    - XDD data analysis of CHP concentration and gas generated – HL not reported
    - Gas generation outside well location, oxygenating the aquifer and diluting / stripping TCE
  - Loss of TCE in treatability:
    - TCE vapor concentration measured in off-gas, and
    - Theoretical gas volume generated
- 21 pore volumes of reagent solution used in treatability tests
  - Common SOP issue
  - Not representative of field applications
  - XDD uses 1 to 2 PVs in treatability studies

# Example – ISCO Peer Review - Diagnosis of Failure, by Others

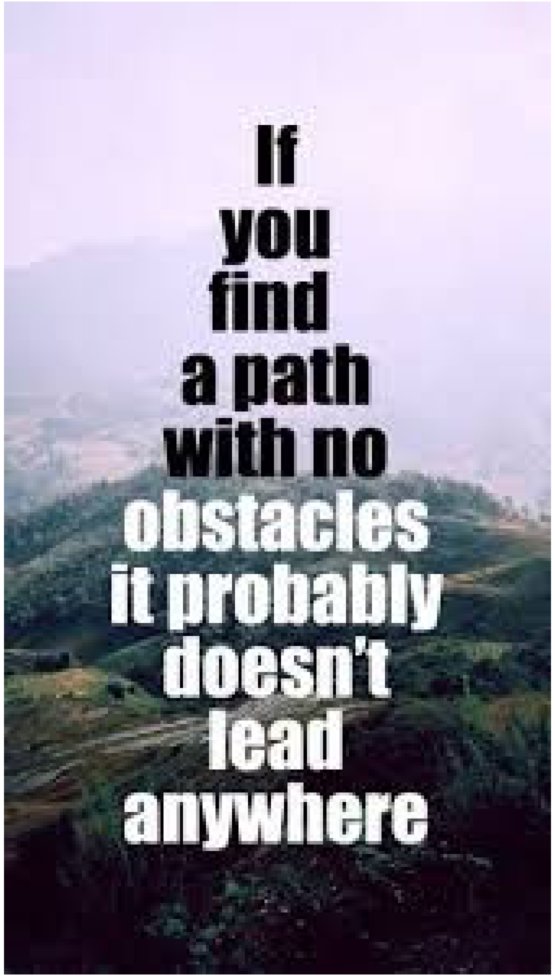
- Full-scale CHP Injection was performed 2016
  - Injected ~12k gallons CHP
  - Off-gassing / daylighting – not highlighted in treatability reporting
  - Concentrations of TCE in source area doubled
  - Degradation ratios:
    - Treatability: 1136 grams of CHP / gram of TCE (very high)
    - Field: 248 – approx. 5 times lower ratio
    - Treatability lab ratio, only 4 Kg of TCE would be removed
- Key Issues
  - Wrong Oxidant
  - Wrong Dosing
  - Expertise would have avoided failures


*Eastern Surplus Superfund Site*

# Pilot Study Design

# Why Pilot Test? Chemical vs. Physical

- Real World vs. Treatability Testing
  - Lab cannot fully emulate field conditions
- Evaluate injection methods
  - Engineering aspects (pumping rates/pressures, etc.)
- Reduce risk and increase certainty
  - High-cost sites
  - Elevated public scrutiny



# Pilot Test Objectives – What Data Do We Need?

- Radius of influence (ROI)
- Flowrate and pressure
  - Delivery rate > reaction rate = oxidant stability
- Confirm oxidant/activator loading
- Confirm mass reduction
- Assess matrix diffusion/penetration

- Identify other issues:
  - Daylighting
  - Preferential Pathways
  - Unexpected reactions/interferences
  - Rebound

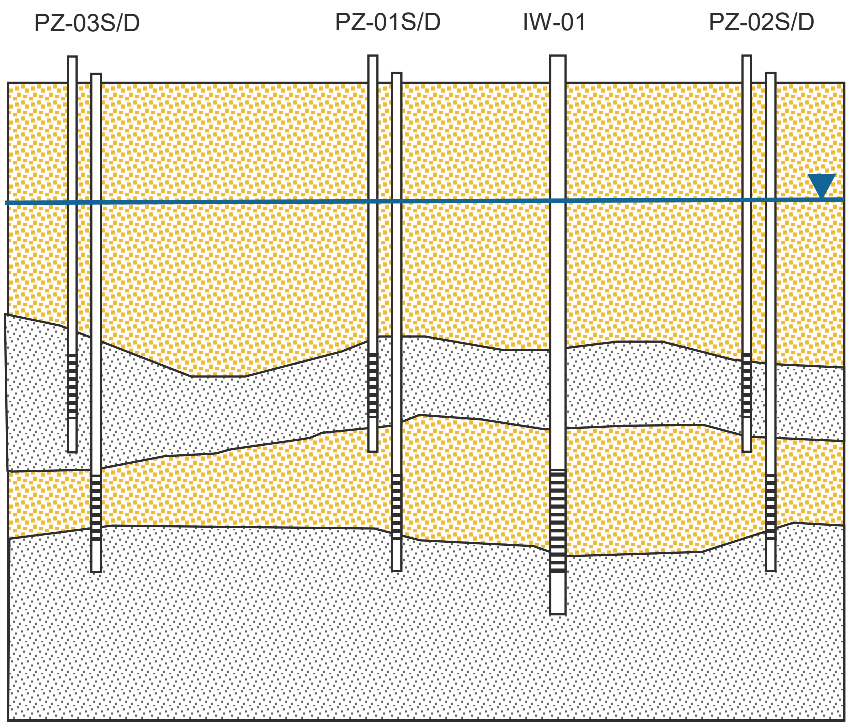
**Need Robust Monitoring Plan**

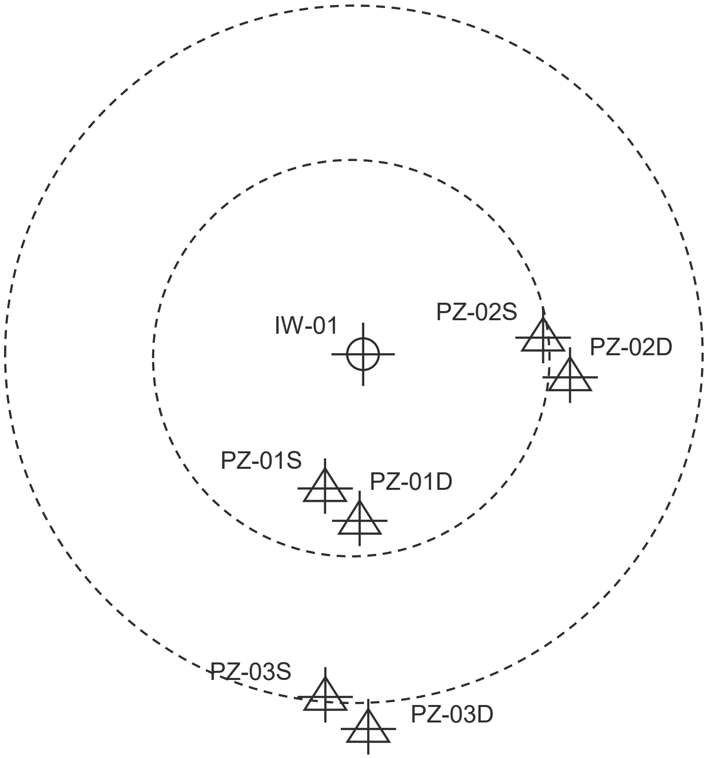
**Confirm Oxidant Contact and Effectiveness**

**Estimate How Many Applications**

**Confirm Delivery Methods/Rates**

# Pilot Test Design:  Traditional Direct Injection Tests

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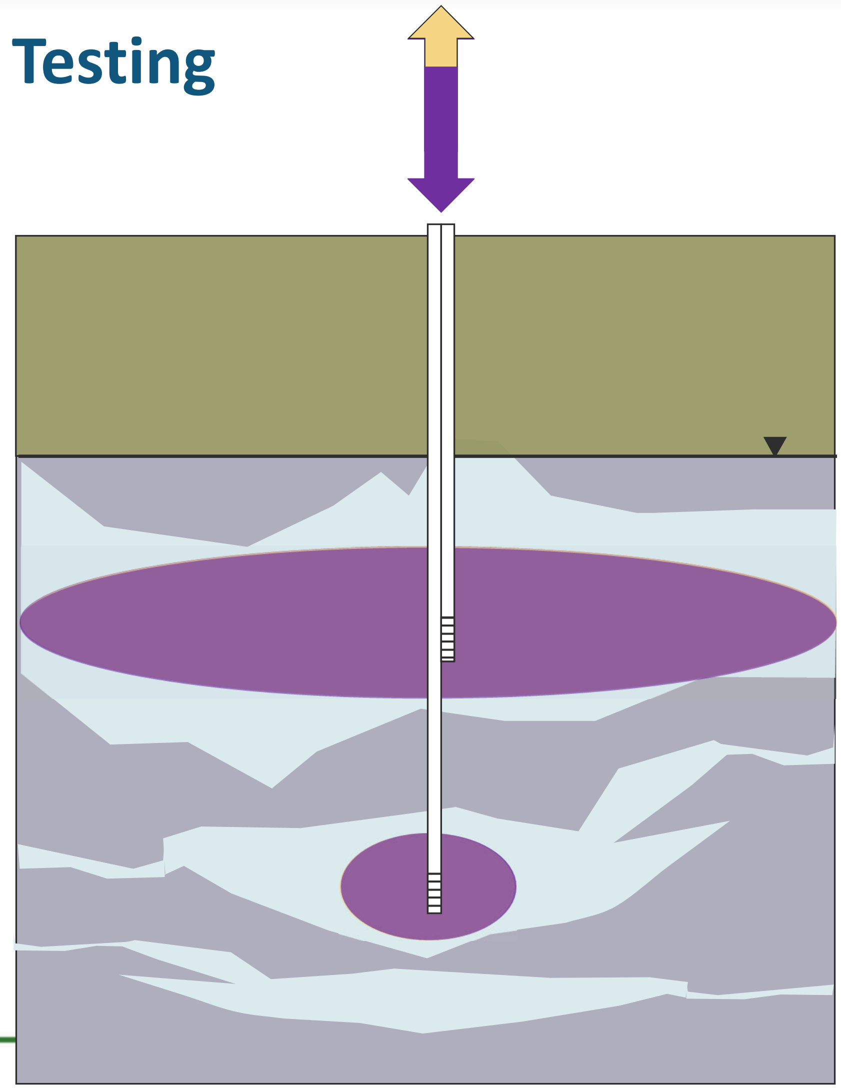
# Pilot Test Design:  Push-Pull & Pull-Push Testing

- Inject known volume of oxidant and “conservative” tracer
- Extract and analyze change



## Advantages

- Short duration
- Use existing well
- Estimate of TOD
- Estimate of COC destruction

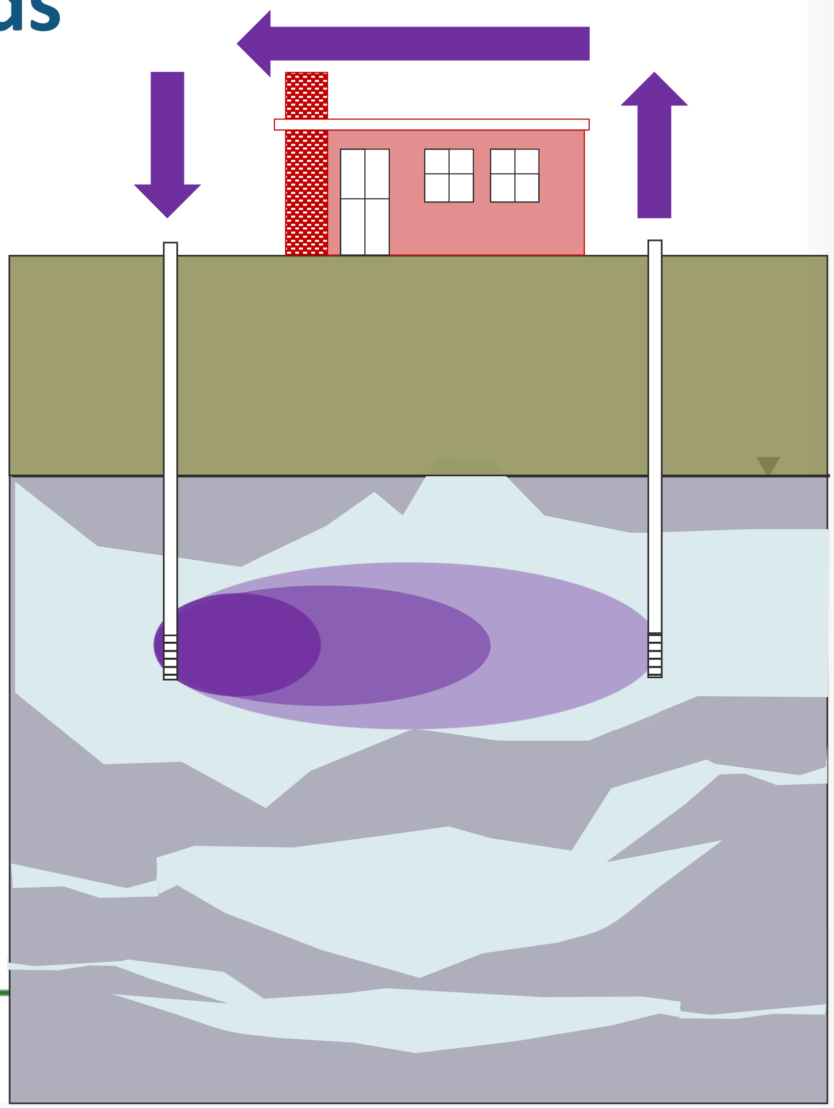
## Disadvantages

- Provides limited information on full-scale delivery method
- Generates groundwater that may require disposal or treatment

# Recirculation Methods

## Closed Loop Recirculation

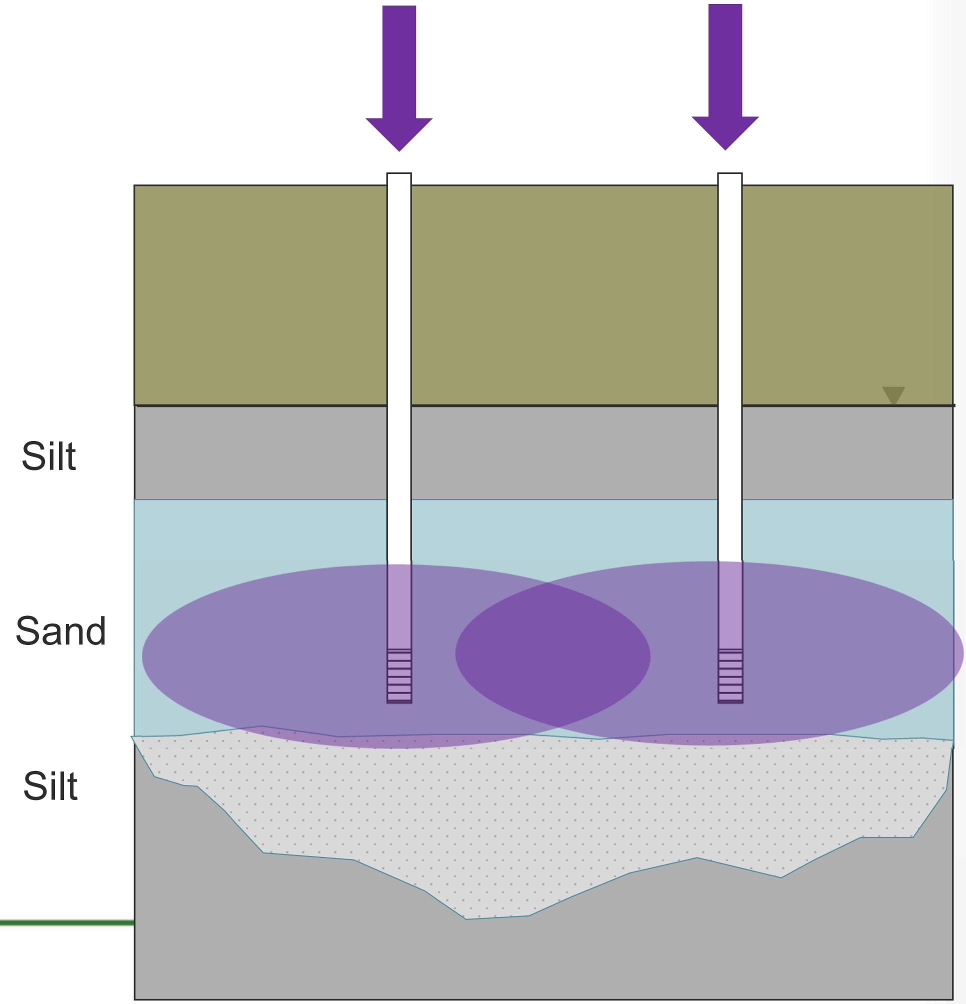
- What it does:
  - Minimizes displacement of aqueous plume
  - Allows transport of solution below obstructions
  - Potentially enhance ROI/distribution within injection grid
- Typical Applications:
  - Sites where mass of contamination in the aqueous phase is a concern
  - Enhanced contact time
  - Sites with limited access
  - Overcome injection issues related to gas evolution or other hydrogeological issues



# If You Need Longer Contact

**Can Do Multiple Doses or extend contact:**

- Oxidant (or other amendments) will eventually penetrate
- Concentrations of amendments decrease over time until next dose
- Use recirculation to maintain higher concentrations over time



# Pilot Test Design - Summary

- Focus planning on “physical” parameters
  - Robust monitoring to assess contact/distribution
- Evaluate delivery mechanism
  - Sustainable flow / pressures
  - Daylighting
- Answer Critical Questions:
  - Is mass of oxidant enough for mass of contaminant?
  - Can I deliver adequate solution volume?
  - Groundwater velocity/density driven transport affecting distribution?

**Many Designs Are Focused on the Chemical Process With Little Consideration For the Physical Delivery Process**

# Field Design

# Considerations for a Successful ISCO Application

- Detailed Characterization of Extent and Distribution of Contaminant
  - Surgical targeting – use today's tools to define
- Adequate Oxidant Loading (Treatability Testing)
  - Loading for target demand
  - Account for non-target demand
  - Critical design step, cannot skip this, but it often is....
- Establish contact with sufficient oxidant (pilot testing)
- Monitoring Progress / Real-Time Field Adjustments

**5 g/Kg SOD vs.**

**10 g/Kg SOD?**

**Doesn't Sound Like Much**

**But We Just Doubled**

**The Oxidant Cost**

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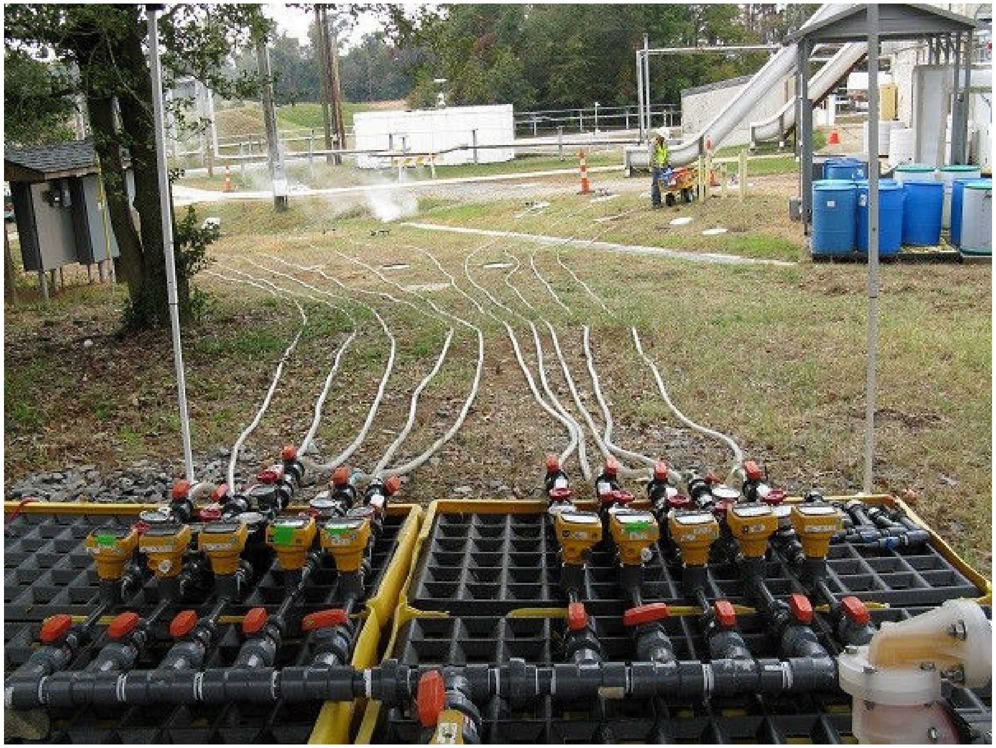
# Establishing Contact:
# Injection Strategies

## Common Strategies*

- Direct Injection
- Advective Transport
- Recirculation
- Pull-Push
- Density Driven Transport
- Fracturing/High Pressure and Specialized Tools

## Solid Oxidants

- Slurry Emplacements / Slow Release
- Mixing



# #1 Issue: Low Injection Volumes

- Poor distribution / limited ROI
- More likely to follow preferential pathways
- Rely on advection/diffusion
- Higher total oxidant demand (TOD)

Less Volume → Less Oxidant → Less Cost

Potentially - Less Success

# #2 Issue: Limited Contact – Space and Time

## Contact with Contaminants

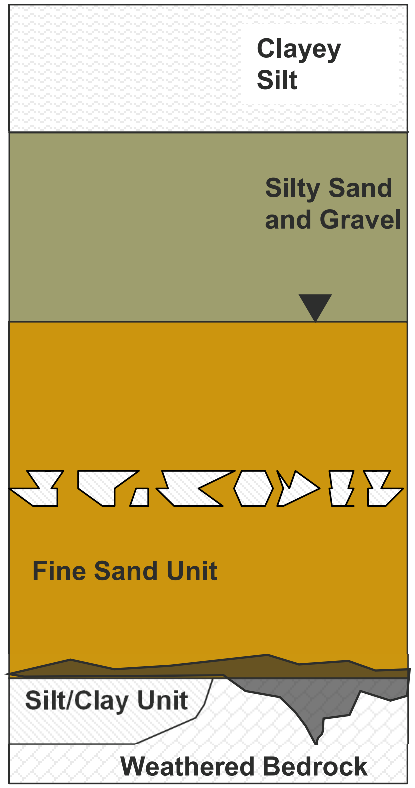
- Need to understand hydrogeology and contaminant distribution
- Tailor injection strategy to geology (recirculation/diffusion-based contact, etc.)
- Groundwater velocity – not often considered

## Anisotropic conditions

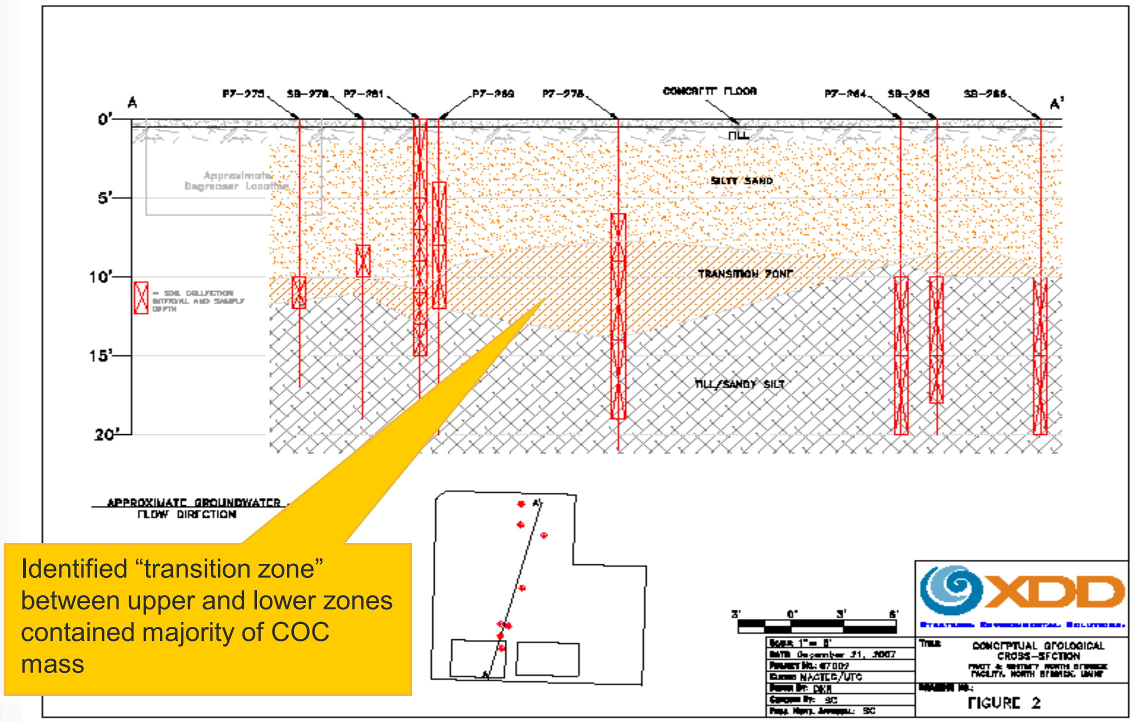
- Permeability differences
- Utility conduits/short circuiting
- Density driven transport

## Oxidant Stability

- TOD differences
- Gas Evolution



# Failure Mechanisms – Oxidant Stability - Example




## Highly Unstable (Short Half-Life)

- Poor distribution of active oxidant at required radius of influence
- Gas generation
- Heat generation

## Highly Stable – Good (Most of the time)

- Inefficient contact due to high groundwater velocities
- Oxidant is "washed out" of treatment area prior to reacting
- Potential migration to sensitive receptor

# #3 Issue:  Everything Else That Can Go Wrong…

- Geology can drive selection of oxidant
- Vapor intrusion concerns
- Stratigraphy/trapped gas - daylighting
- Oxidant interaction with infrastructure
- Impact to sensitive receptors
- Perception issues

# Injection Tools For More Difficult Conditions

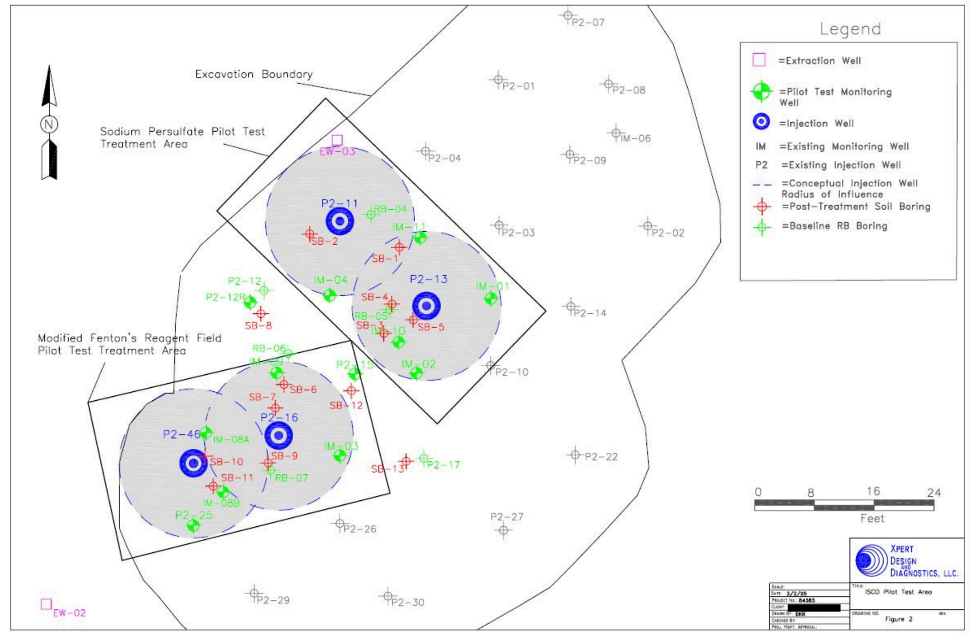
- Pressure Pulse Technology
  - Adapted from Oil and Gas Industry
  - Wavefront Technology Solutions - Sidewinder Tool
  - Badger Injection Solutions
- Fracturing
  - FRx Hydraulic
  - Pneumatic (GeoSierra/Cascade, ARS/NJIT)
- Water Jet/Controlled Fracturing
  - BioJet (EOS Remediation)
  - Controlled Jet Injection (FRx)
- Pressure Grouting/Mixing – Jet Mixing – 2 to 5 feet diameter

# Case Studies

# Case Study 1: Where Have You Been All My (Half) Life?

## Superfund Site in Maine

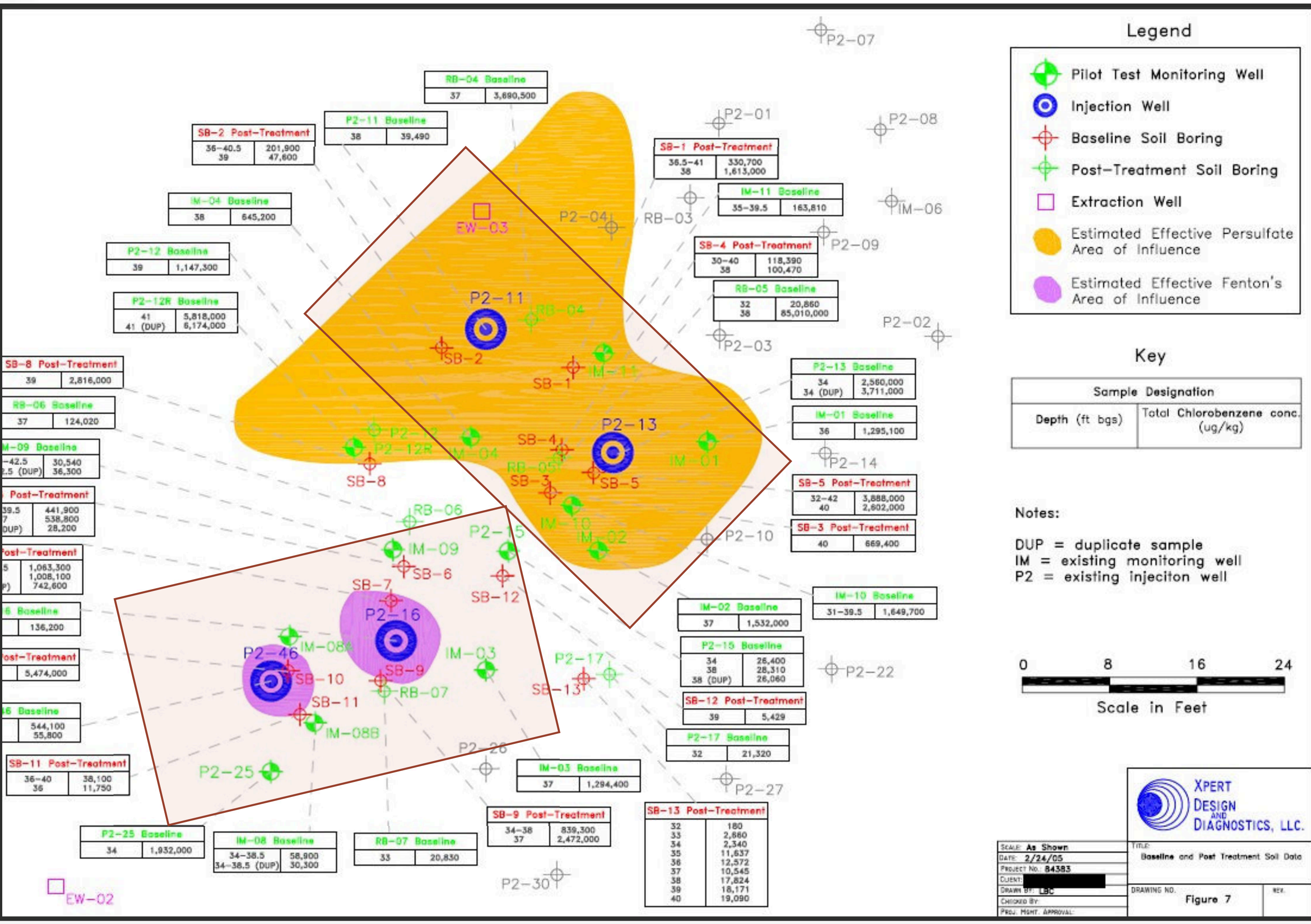
- Chlorobenzene impacted overburden/weathered bedrock interface
- Catalyzed hydrogen peroxide (CHP) originally tested and selected by Army Corp (>90% mass reduction in tests looked good!)




## XDD conducted peer review of prior test

- Identified potential failure mechanisms (peroxide instability)
- Conducted additional bench tests using stabilized CHP and activated persulfate

# Case Study 1: Effective Oxidant Distribution




- Peroxide Performance:
  - Um….yeah how bout them Red Sox!
- Persulfate Performance:
  - Est. 3,600 lbs chlorobenzene degraded
  - 83% conc. reduction on soil

# Case Study 2: New York, NY
# Petroleum Hydrocarbons In Situ Treatment with ISCO

- Limited Time Offer! During 32 story building construction

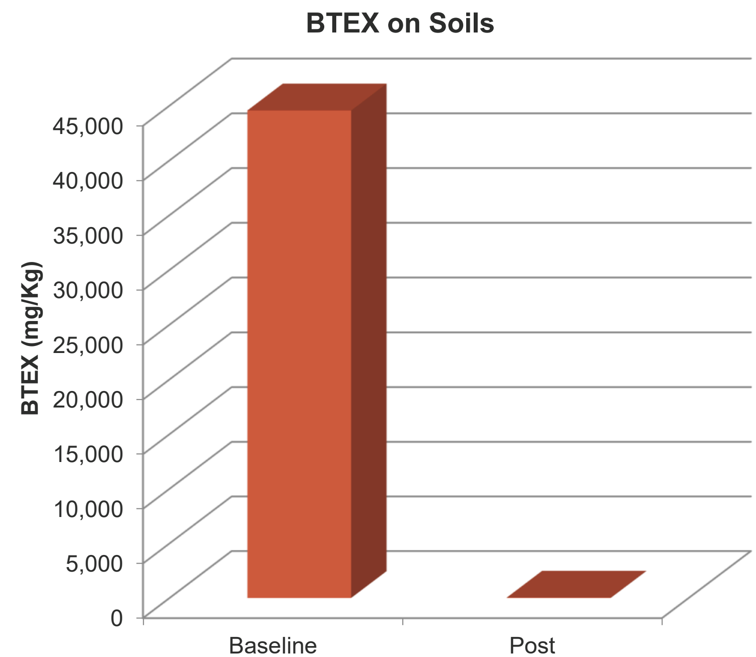
- RUSH TAT Treatability Study
  - Tested multiple oxidants
  - Alkaline activated persulfate selected
  - Oxidant loading determined

- Logistical Issues
  - Tight schedule: MUST complete in 2 weeks, before slab construction
  - Chemical compatibility with construction materials
  - Working around construction activities/space limitations
  - Maintain traffic accessibility

# Case Study 2: New York, NY
# Petroleum Hydrocarbons In Situ Treatment with ISCO

## Six days of chemical injection

- 6,500 SF Area – 35,000 Gallons Injected
- 73,000 pounds persulfate / 33,500 pounds NaOH
- Sand & Silty Sand (k range = 10-5 cm/s to 10-3 cm/s)
- Wavefront Technology Solutions USA "Sidewinder" enhanced injection tool
- Design anticipated 90% reduction




## Site closed by NYSDEC

- 92 to 95 % groundwater concentration reduction
- > 99 % reduction of BTEX, DRO + GRO on soils
- No rebound after 2 years

## Take Away:

- Critical up-front bench and design work for success, even when in a rush

# Conclusions

# Conclusions

- Poor performance often due to skipping the pre-design engineering:
  - Oxidant mass too low for mass of contaminant present
  - Volume of oxidant too low
  - Not understanding COC mass distribution and target stratigraphy
  - “Contact Limitations” – distribution and oxidant longevity
  - Not performing Site-specific treatability
- The consequences.....
  - No apparent effect
  - Rebound, and cost....

# Additional Technical Information

# Oxidation Chemistry

## Permanganate ($MnO_4^-$)

Direct Oxidation: $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_{2(s)} + 2H_2O$

## Persulfate ($S_2O_8^{2-}$)

Direct Oxidation: $S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$

Free Radical: $S_2O_8^{2-} + 2Fe^{+2}$ (or Heat) $\rightarrow 2SO_4^{-\bullet} + 2Fe^{3+}$

## Hydrogen Peroxide ($H_2O_2$)

Direct Oxidation: $H_2O_2 + H^+ + e^- \rightarrow OH^- + H_2O$

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

## Ozone ($O_3$)

Direct Oxidation Under Acidic pH's: $O_3 + 2H^+ + 2e^- \rightarrow O_2 + 2H_2O$

Free Radical Formation: $O_3 + OH^- \rightarrow O_2^- + HO_2^\bullet$

# Common Oxidants

| Oxidant | Potential (V) | Form | Cost/ equiv |
|---|---|---|---|
| Fenton's Reagent (OH•) | 2.8 | Liquid | ____ |
| Perozone ($O_3$ + Peroxide) | 2.8 | Gas/Liquid | ____ |
| Activated Persulfate ($SO_4^{-}$•) | 2.6 | Salt<br>Liquid | ____ |
| Ozone ($O_3$) | 2.42<br>2.07 | Gas | 0.020<br>0.053 |
| Persulfate ($S_2O_8^{2-}$) | 2.01 | Salt<br>Liquid | 0.030 |
| Hydrogen Peroxide ($H_2O_2$) | 1.78 | Liquid | 0.026 |
| Permanganate ($MnO_4^{-}$) | 1.68 | Salt<br>Liquid | 0.017 - K<br>0.031 - Na |



**Costs adapted from Siegrist et al., 2001**

DK1

# Chemical Background

**Slide 39**

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**DK1** Remove slide 3 and 4 - too technical for group.  Masters level chemistry.
Dennis Keane, 5/1/2018

DK2

# Contaminant Type

| Contaminant | $MnO_4$ | $S_2O_8$ | $SO_4\bullet$ | Fenton's | Ozone |
|---|---|---|---|---|---|
| Petroleum Hydrocarbon | G/E | G/E | G/E | E | E |
| Benzene | P | G | G/E | E | E |
| Phenols | G | P/G | G/E | E | E[1] |
| Polycyclic Aromatic Hydrocarbons (PAHs) | G | G | E | E | E |
| MTBE | G | P/G | G/E | G | G |
| Chlorinated Ethenes (PCE, TCE, DCE, VC) | E | G | E | E | E |
| Carbon Tetrachloride | P | P | P/G | P/G | P/G |
| Chlorinated Ethanes (TCA, DCA) | P | P | G/E | G/E | G |
| Polychlorinated Biphenyl's (PCBs) | P | P | P | P | G[1] |
| Energetics (RDX, HMX) | E | ? | E | ? | ? |

**P = poor G = good E = excellent 1=perozone**

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**Slide 40**

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**DK2** Add dioxane, PFAS into this slide?
Dennis Keane, 7/25/2018

# Permanganate – $MnO_4^-$

## Advantages

- High stability in subsurface
- Provides better overall efficiency
- Allows for diffusion into tight soils & porous rock
- No gas/heat production - less health & safety issues
- Applicable over wide pH range
- Many successful in-situ field applications

## Disadvantages

- Lower oxidation potential
  - Narrower range of contaminant applicability
- Metal impurities in product
- Potential pore clogging due to precipitates

# Persulfate – $S_2O_8$

## Advantages

- Can be catalyzed by reduced metals or heat to promotes Sulfate Free Radical (SFR) formation
- High oxidation potential
  - applicable to wide range of organics

## Disadvantages

- Reaction kinetics heavily dependent on activation technique
- May have high non-target demand
- Possible localized low pH

# Hydrogen Peroxide – $H_2O_2$

Advantages

- High oxidation potential
  - applicable to wide range of organics
- The most studied of the oxidizing compounds for remediation
- Can be combined with ozone (perozone)

Disadvantages

- Reaction's gas/heat production – health & safety hazard
- Short half-life
  - limited travel distances, requires closely spaced injection points
- Optimal pH between 3–5
- Ineffective in alkaline environments

# Ozone – $O_3$

## Advantages

- High oxidation potential
  - applicable to wide range of organics
- Extraction/Oxidation process
- Easier to apply than liquid oxidants in vadose zone
- Generated on-site, allows for continual application
- Decomposes to oxygen which can stimulate aerobic bioremediation

## Disadvantages

- Less stable than liquid oxidants resulting in shorter half-life
- Effective distribution in saturated zone requires array of injection points
- Confined aquifer usage requires pressure (gas) relief