Chemical Oxidation Technologies:
Lessons Learned & Best Practices from Expert Perspectives

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Today's Agenda

Chemical Oxidation Technologies:

- Overview: Chemistries, HSE Issues, CoC Applications
- Site Characterization
- Bench-Scale Testing
- Pilot-Scale Testing
- Full-Scale Systems
- Monitoring Chemox Remediation
- Regulatory Concerns and Issues
- Case Histories: Bench-, Pilot-, and Full-Scale
- Additional References
- Your Questions and Discussion

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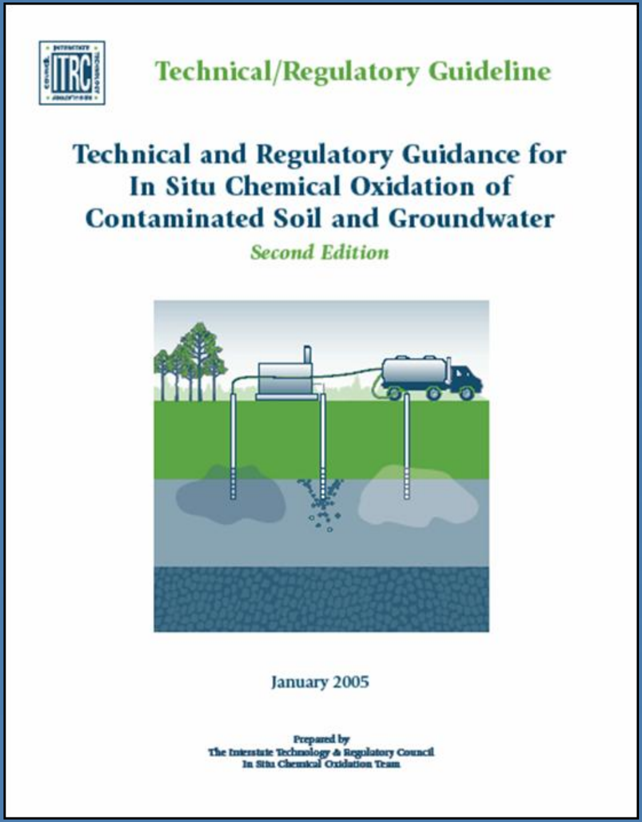
ITRC's ISCO-2 Document

- Regulatory permits
- Health and safety issues
- Oxidant application
- Conceptual site model
- System strategies
- Dosage considerations
- Performance monitoring
- Cost considerations
- Emerging ISCO technologies
- Acronyms, glossary, case studies
- ITRC ISCO team contacts


Technical/Regulatory Guideline

Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater

Second Edition

January 2005

Prepared by
The Interstate Technology & Regulatory Council
In Situ Chemical Oxidation Team

Source: The ISCO-2 document provides a detailed ready reference for consideration of an ISCO proposal/project. ISCO guidance document is available on www.itrcweb.org under "Guidance Documents" and "In Situ Chemical Oxidation"

Chemical Oxidation Overview

Chemical Oxidation = *Chemox*

Applicability to Petroleum Hydrocarbon Contaminant Concentrations

– ***Potentially can be applied to site-specific conditions:***

- **Ground water & soil at lower ppm concentrations**
  - May be effective, but other technologies may be more cost-effective
- **Ground water & soil at higher ppm concentrations**
  - "Sweet spot" for application where the relatively short duration of Chemox can outperform other longer-term & costly O&M technologies
- **Soil-sorbed residual LNAPL**
  - May be effective with a correspondingly high oxidant dosage
- **Mobile LNAPL (free-phase petroleum product)**
  - An aggressive application for Chemox with the highest oxidant dosages
  - Mandates better than average site characterization
  - **Flawless Chemox process controls are critical to control reactions**

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Chemical Oxidation Overview

- *Ex-situ:* Above ground treatment of contaminants
  - *Ex-situ* treatment examples for soil and groundwater
    - Backhoe / Soil Tilling / Heads: mixing soil with oxidants
    - Frac tanks: mixing groundwater with oxidants

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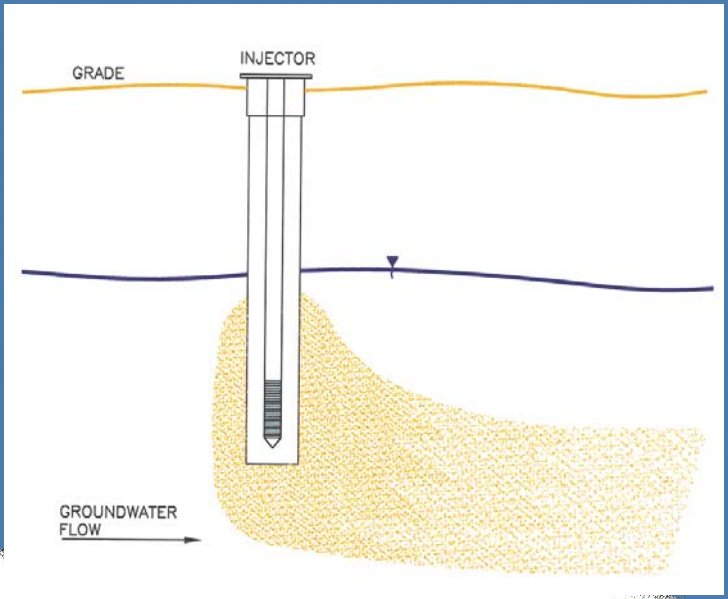
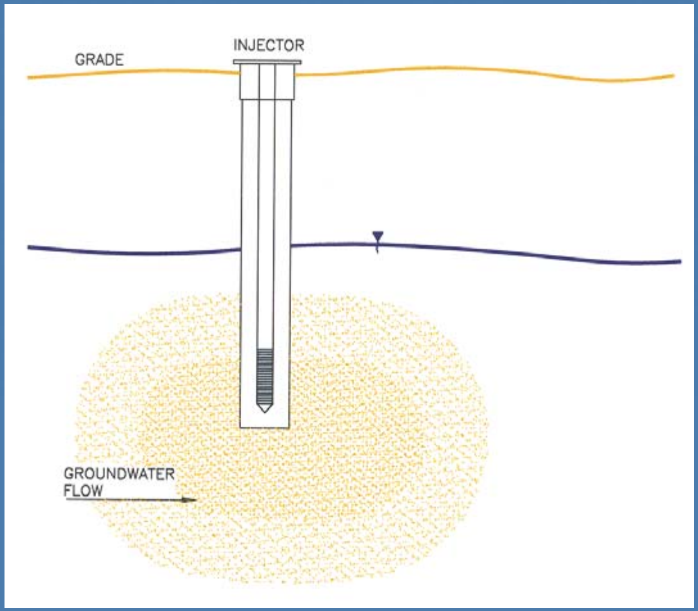
Chemical Oxidation Overview

- *In-situ:* In place treatment of contaminants
  - "*In-Situ* Chemical Oxidation", or ISCO

- **Diffusion Method**



- **Dispersion Method**



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Best Lithologies for Injection Technologies

- **Homogeneous well-sorted, medium- to coarse-grained sand is the best lithology**
  - high permeability and low hydrostatic pressure
- **Fractured bedrock can be injected into through temporary, drilled points**
  - However, flow rate, volume and treatment effectiveness need to be monitored closely to ensure that the micro-fractures within the bedrock don't become clogged or congested
- **Overlying clay layers increase the probability of success**
  - Because they form a seal, or cap, that prevents treatment chemistry from exuding through the surface and improves horizontal dispersion
- **Any lithology can be injected into…**
  - However, the more heterogeneous the formation is and the more clayey the site is, the harder it is to predict and direct exactly where the reagents are delivered

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Oxidizing Chemistries: Health, Safety & Environment (HSE) Concerns

- **Read & understand material safety datasheets (MSDS)** prior to materials handling (reference MSDS websites as needed)
- **Potential hazard risks to mitigate and avoid:**
  - extreme contact risk, especially to eyes
    - Personal protective equipment (PPE) is a must
    - Readily available eyewash / shower
  - inhalation and dermal contact
- **Ensure oxidants compatibility with equipment and materials**
- **Store and protect oxidants** (heat/cold & sun/rain, as appropriate)
- **Develop site-specific Health and Safety Plans (HASPs)** in accordance with 29 CFR 1910.120 guidance
- <u>**Enforce HASP requirements for everyone on-site!**</u>

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Oxidizing Chemistries: HSE Concerns

Investigate, characterize and understand your site and surrounding area!

- **Complete a competent receptor survey**
- **Evaluate potential migration pathways**
  - Utility corridors, particularly underground
  - Potential conduits for vapors & liquids transport
  - Geologic/Hydrogeologic fractures
- **Consider surface runoff discharge points & ultimate discharge**
  - Weather patterns
  - Precipitation collection basins & run-off routes
- **Infrastructure concerns**
  - Buildings, roadways, underground piping, sewers, wells
  - UST systems and underground piping/pumps
  - Overhead hazards
  - Evaluate current infrastructure elements' integrity
    - Assess whether infrastructure can withstand possible geological and physical stresses due to Chemox remediation

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Oxidizing Chemistries: HSE Concerns

- **Available on-site space**
  - Working space for remediation equipment
- **Traffic patterns**
  - People
  - Vehicles
- **Site accessibility**
  - On-site personnel, public, visitors
  - Emergency vehicles
  - Ingress/Egress routes, primary and alternates
- **Hospital options & routes**
  - All on-site personal should have up-to-date OSHA, First Aid, and First-Responder training
  - On-site HASP read, communicated, and signed by all on-site personnel and visitors

Example: Additional HSE Considerations for a Specific Pilot-Scale Site

HSE Considerations:

- No history of vapor migration via underground pathways

- Deep groundwater to maintain at least a 20-foot separation (vertical & horizontal) between injection points and any active UST system, utilities, basements, etc.

Case Study Site Selection Criteria:

- Little natural organic material (NOM, e.g., peat)
  - Minimize non-selectivety of OH• to organics

- Relatively high permeability soils to sustain gravity flow of oxidant reagents

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Candidate Chemox Chemistries

Available oxidants

Oxidant	Potential (v)
Fenton's Reagent ($OH^{\bullet}$)	2.8
Activated Persulfate ($SO_4^{-\bullet}$)	2.6
Ozone (O_3)	2.07
Persulfate (S_2O_8)	2.01
Hydrogen Peroxide (H_2O_2)	1.78
Permanganate (MnO_4^-)	1.68

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Candidate Chemox Chemistries

- **Ozone**
  - O_3 (gas) - may react with soil or groundwater constituents to proc produce radicals such as $OH^{\bullet}$ + $O_2^{\bullet -}$
  - Sometimes injected with peroxide - O_3+H_2O_2 generates hydroxyl radicals
- **Fenton's Reagent / Catalyzed Hydrogen Peroxide**
  - Classical: acidified ferrous iron (Fe^{2+}) catalyzes H_2O_2 to produce $OH^{\bullet}$ radicals
  - Modified (*aka* catalyzed hydrogen peroxide): chelated iron catalyzes H_2O_2 to produce various radicals, used at ambient pH
  - Best known Chemox reagent, but potentially the most dangerous if the chemistry is not managed properly

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Candidate Chemox Chemistries

Persulfate

- Sodium & Potassium Persulfates
  - Persulfate anions ($S_2O_8^{2-}$) dissociate in water
  - Activators such as heat, ferrous iron, chelated iron, high pH, and peroxide increase oxidative strength through formation of sulfate radicals ($SO_4^{-\bullet}$)

Oxygen-supplying peroxides (solids)

- Calcium peroxide (CaO_2)
- Magnesium peroxide (MgO_2)
- Sodium percarbonate ($Na_2CO_3 \bullet 3H_2O_2$)

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Considerations for ISCO Treatment

	Peroxide	Ozone	Permanganate	Persulfate
Vadose zone treatment	**Successful (need adequate soil moisture)**			
Potential detrimental effects	Gas evolution, heat, **By-products, resolubilization of metals**	Gas evolution, **By-products, resolubilization of metals**	**By-products, resolubilization of metals**	**By-products, resolubilization of metals**
pH/alkalinity	**Effective over a wide pH range**, but carbonate alkalinity must be taken into consideration		**Effective over a wide pH range**	**Effective over a wide pH range**, but carbonate alkalinity must be taken into consideration
Persistence	**Easily degraded in contact with soil/groundwater unless inhibitors are used**	**Easily degraded in contact with soil/ groundwater**	**The oxidant is very stable**	
Oxidant demand	**Soil oxidant demand varies with soil type and oxidant and contaminant oxidant demand is based on total mass and mass distribution (sorbed, dissolved and free phase)**			
Soil permeability and heterogeneity	**Low-permeable soils and subsurface heterogeneity offer a challenge for the distribution of injected or extracted fluids**			

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Source: Table 1–7 in ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

Geochemical Considerations

- Understand the background natural conditions that influence and are influenced by Chemox chemistries
  - Plume and background oxidation-reduction (redox) conditions
  - Naturally occurring concentrations of Iron as Ferrous (Fe^{2+}) and Ferric (Fe^{3+})
  - Metals mobilization (e.g., Cr(VI) formation)
  - Precipitation of Manganese Dioxide (MnO_2(s))
  - Carbonate and other scavenger reactions
- Need a good geochemical characterization of the site!

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Oxidant Effectiveness

Oxidant	Amenable contaminants of concern	Reluctant contaminants of concern	Recalcitrant contaminants of concern
Peroxide/Fe	TCA, PCE, TCE, DCE, VC, BTEX, chlorobenzene, phenols, 1,4-dioxane, MTBE, *tert*-butyl alcohol (TBA), high explosives	DCA, CH_2Cl_2, PAHs, carbon tetrachloride, PCBs	$CHCl_3$, pesticides
Ozone	PCE, TCE, DCE, VC, BTEX, chlorobenzene, phenols, MTBE, TBA, high explosives	DCA, CH_2Cl_2, PAHs	TCA, carbon tetrachloride, $CHCl_3$, PCBs, pesticides
Ozone/ Peroxide	TCA, PCE, TCE, DCE, VC, BTEX, chlorobenzene, phenols, 1,4-dioxane, MTBE, TBA, high explosives	DCA, CH_2Cl_2, PAHs, carbon tetrachloride, PCBs	$CHCl_3$, pesticides
Permanganate (K/Na)	PCE, TCE, DCE, VC, [BTEX], PAHs, phenols, high explosives	Pesticides, BTEX	Benzene, TCA, carbon tetrachloride, $CHCl_3$, PCBs
Activated Sodium	PCE, TCE, DCE, VC, BTEX, chlorobenzene, phenols, 1,4-dioxane, MTBE, TBA	PAHs, explosives, pesticides	PCBs

Source: Table 1–6 (amended) in ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

Site Characterization

Typical Site Management Problems

- Site complexities
  - Complicated hydrogeology
  - Multiple contaminants of concern (CoCs)
  - Multiple receptors/pathways
- Multiple phases of investigation and remediation
- Deliverables that are not stand-alone documents
- Changes in consultants
- Changes in regulatory oversight
- Case load

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Common Outcome

- An abundance of data
- Lack of clarity concerning the major site issues and how to move the site toward closure

Suggestion

- Direct the Responsible Party (RP) to complete a Site Conceptual Model

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Site Conceptual Model (SCM)

- EPA: A representation of site conditions developed using readily available (existing) data that illustrates the relationship between contaminants, retention/transport media, and receptors.
  - EPA. November 2000. *Using the Conceptual Site Model to Select Performance Standards and Develop Data Quality Objectives in the CAS.*

- SCM's Purpose:
  - Organize information already known about the site
  - Help identify additional information that must be obtained
  - Suggest when site characterization is complete
    - If the SCM is not likely to significantly change upon collection of additional information, the existing data are adequate

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Developing the Site Conceptual Model

- Subsurface geology
- Site topography
- Aquifer geochemistry (particularly important to Chemox)
  - Soil and groundwater data
    - such as pH, temperature, conductivity, dissolved oxygen, ORP
  - Monitored natural attenuation terminal electron acceptor / donor parameters
    - Fe^{+3}, Fe^{+2}, Mn^{+2}, NO_3, SO_4, sulfide, chloride, alkalinity, TOC, CO_2, CH_4, dissolved-H_2
- Identification of major migration pathways for CoCs
- Direction / gradient / velocity of groundwater flow
- Surface and subsurface structures
- Underground utilities
- Surface water features / uses, and potential receptors in the area

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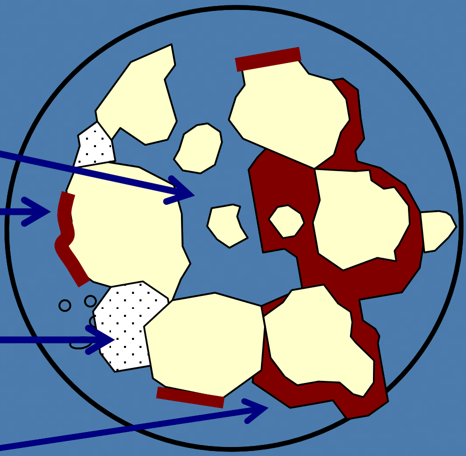
Developing the Site Conceptual Model

- Characterize the distribution and mass of contaminants present in the four phases in the contaminated zone
  - **Soil gas-phase**
  - **Sorbed-phase**
  - **Dissolved-phase**
  - **Non-aqueous phase liquid (NAPL) or free-phase**



Graphic source:
Suthersan, 1996
in ITRC's,
ISCO-2, 2005

- Sorbed- and free-phase typically constitute the majority (>50% to over 75%) of the petroleum hydrocarbon mass
- Saturated zone distribution and partitioning governed by site-specific geochemical conditions and partitioning coefficients (K_{ow})

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SCM Features

The SCM is generally documented by written descriptions and supported by maps, geological cross-sections, tables, diagrams and other illustrations.

- EPA. November 2000. *Using the Conceptual Site Model to Select Performance Standards and Develop Data Quality Objectives in the CAS.*

1. **Local and regional plan view maps showing location of sources, extent of contamination, direction and rate of groundwater flow, and locations of receptors**
   - An interpretive drawing is suggested; not a plot of laboratory results
   - "Receptors" include, but are not limited to, all supply wells within a given distance of the source area

2. **Cross-section maps showing subsurface geologic features, depth to groundwater, man-made conduits, monitoring well construction, and an interpretive drawing of the vertical extent of soil contamination**
   - An interpretive drawing is suggested; not a plot of laboratory results
     - Arulanantham, R. December 2000. *Assessment and Management of MtBE Impacted Sites*

✓ ***Vapor Intrusion Survey evaluation can be important to:***
- ***Establish baseline prior to Chemox injection***
- ***Monitor Chemox remediation and vapors mobilization***
- ***Protect receptors by monitoring on-site & off-site conditions***

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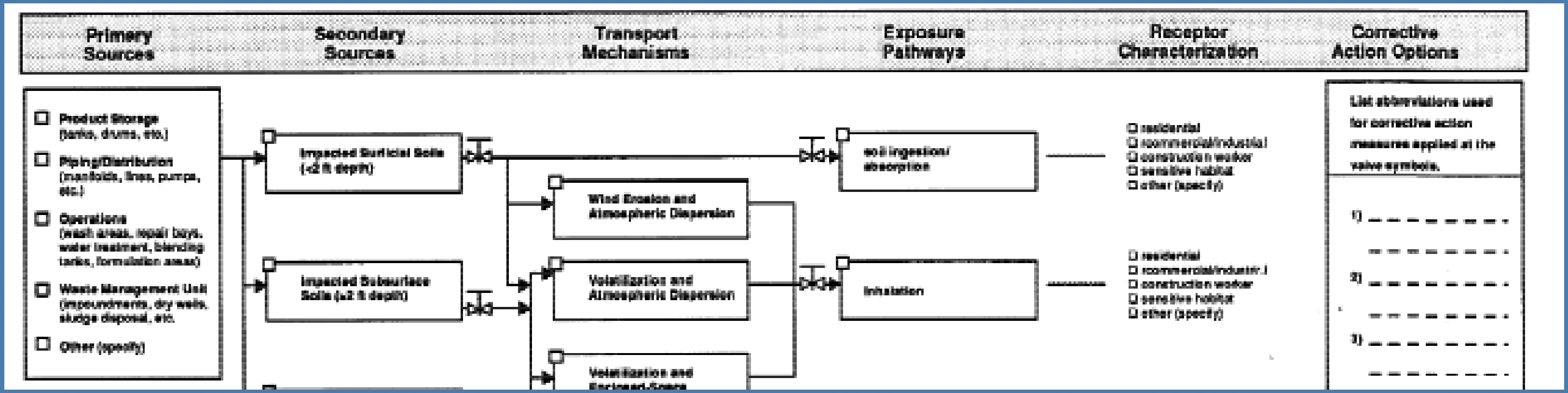
SCM Features

3. **Exposure evaluation flowchart**
   - Similar to Figure 2 in the **ASTM *E 1739 Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites***



4. **Plots of chemical concentrations vs. time**
   - For example, if groundwater monitoring is being conducted, plots should be prepared for each monitoring well which has had detectable levels of CoCs
5. **Plots of chemical concentrations vs. distance from the source**
6. **Summary tables of chemical concentrations in different media**
7. **Boring and well logs (including construction/screening)**

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Chemox's Specific Project Needs

- Remediation objectives and CoC's clean-up goals
- Mass & distribution of free-phase
- Length, width and vertical extent of contamination
  - Soil and groundwater data
  - Depth to groundwater and flow velocity and direction
- Type of lithology and associated density and porosity
- Boring logs and site maps
- Site use: past, present and future
- Location of site utilities and source of water for Chemox use

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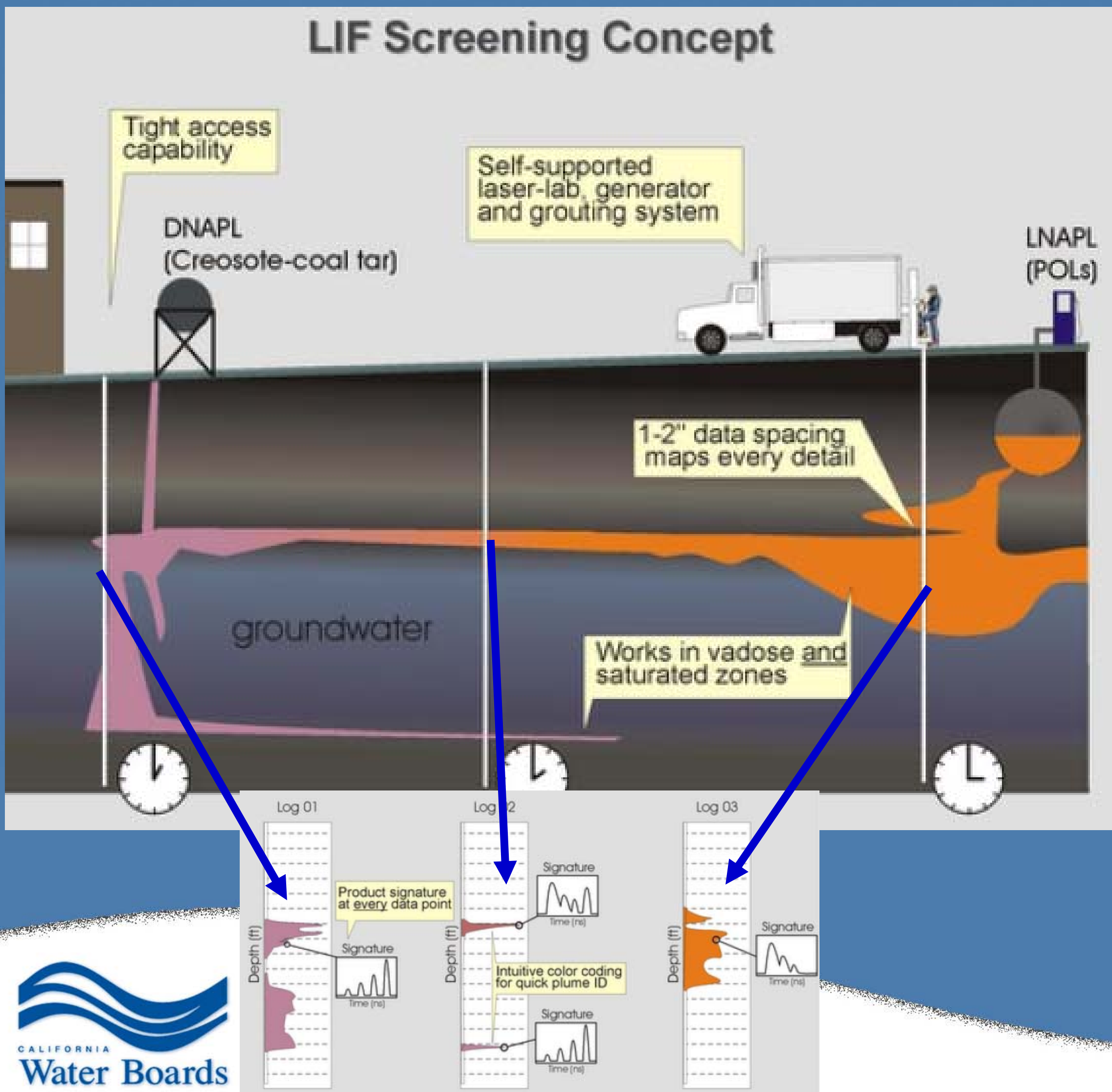
Recent Developments in Site Investigation Tools



- **Laser-induced fluorescence (LIF)** delineates petroleum, oil, & lubricant in vadose & saturated zones
- LIF signal is directly proportional to the petroleum concentration
- LIF, in conjunction with direct push deployment, yields a detailed three-dimensional map of the contaminant distribution

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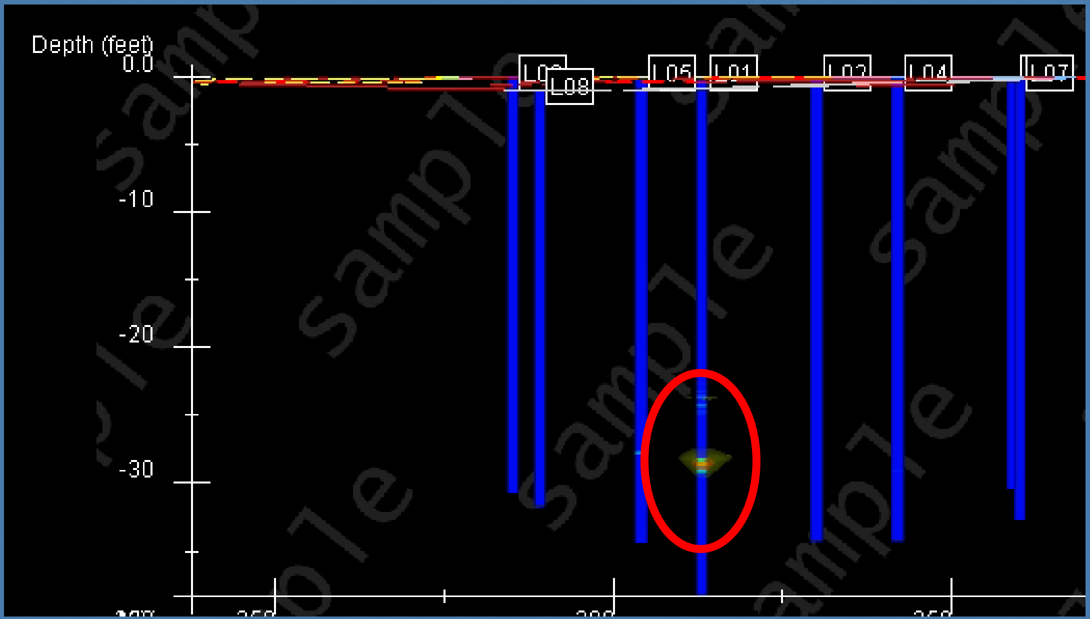
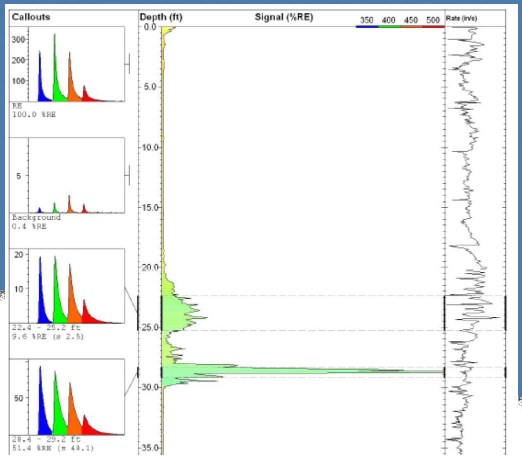
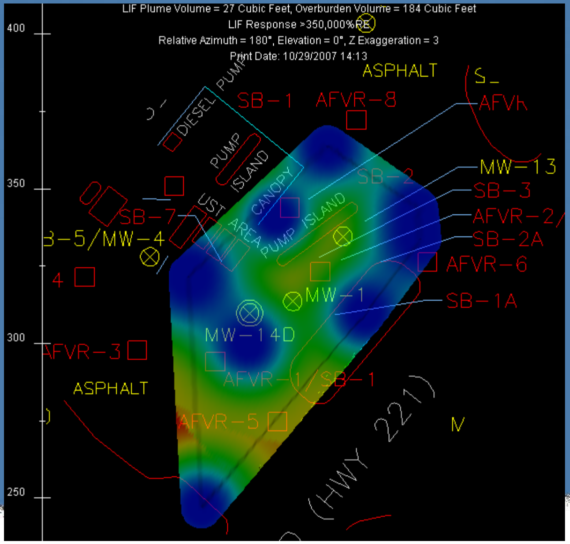
Recent Developments in Site Investigation Tools



- **LIF used to confirm localized distribution of free-phase**
- Chemox now can reliably target free-phase LNAPL
- Injection points locations match residual LNAPL for effective treatment





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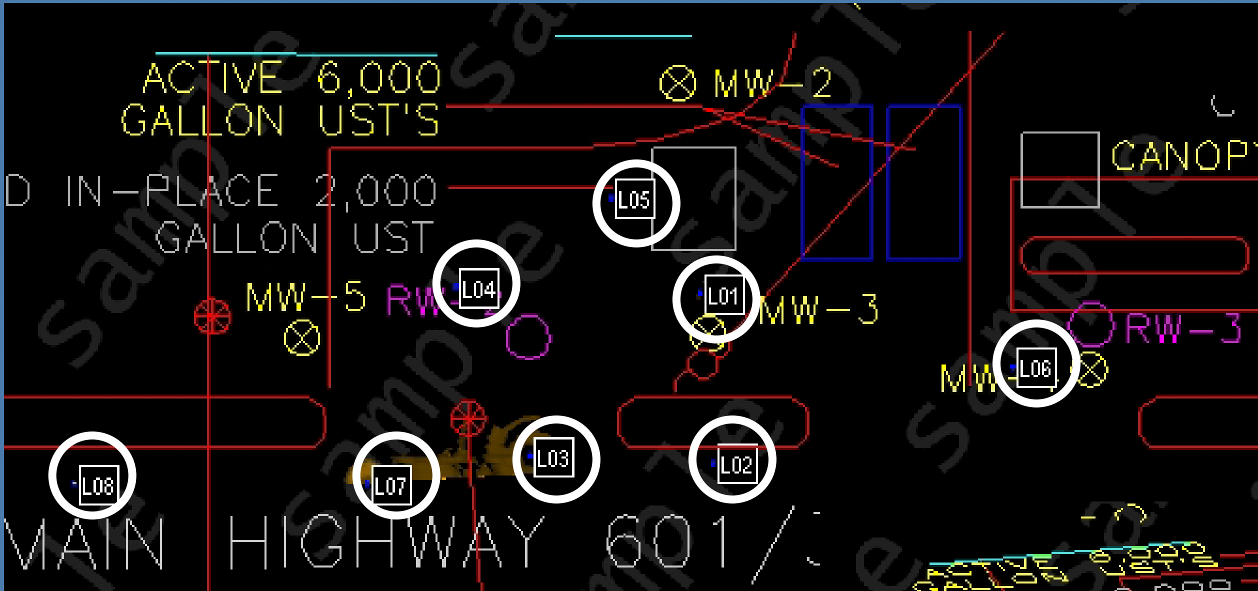
Recent Developments in Site Investigation Tools



- Southeastern U.S. site with periodic LNAPL in MWs
- LIF established distribution of free-phase LNAPL

- One-day, $10K event to delineate remaining mass
- Site strategy: Chemox plus enhanced fluid recovery designed for focused treatment of residual LNAPL and free-phase LNAPL

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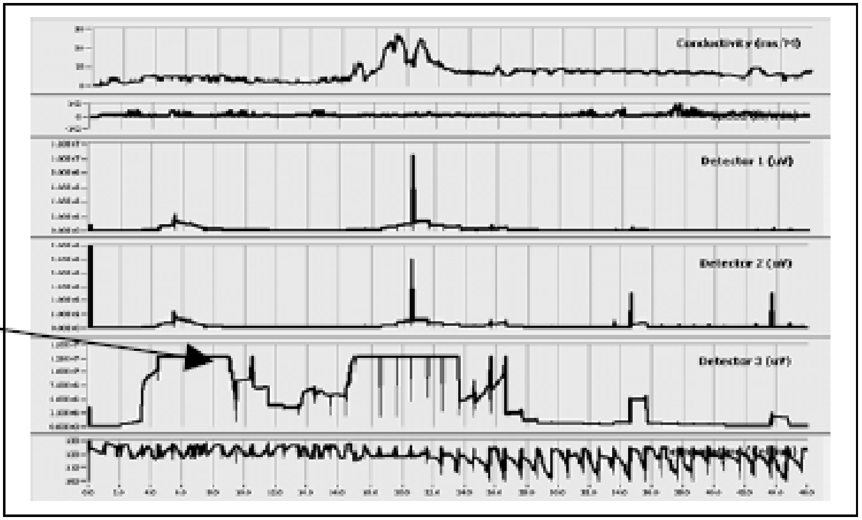
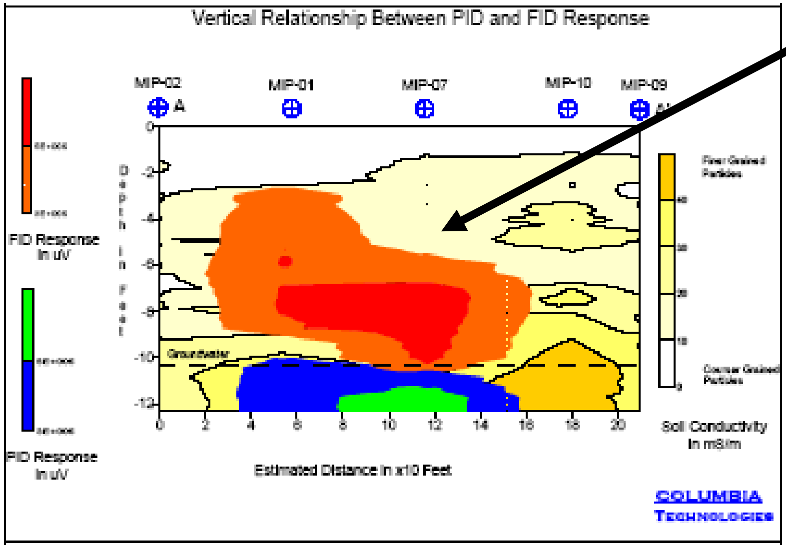
Recent Developments in Site Investigation Tools

Membrane Interface Profiles show:

- Electrical Conductivity
- Penetration Rate
- PID Response
- FID Response
- ECD Response
- Probe Temperature

This data can be observed in real time as the probe is pushed into the ground. Hard copy and EDD are available upon hole completion.





This **Vertical Transect** through 5 MIP locations shows a fining downward sequence of sands to clays, the groundwater table at 10 ft and the extent of both PID and FID anomalies.

Note that the PID response indicates a petroleum smear zone at the top of the water table. The FID response indicates a methane vapor cloud in the vadose zone above the petroleum occurrence suggesting methanogenic degradation is occurring.

Summary

- **SCMs can assist in completing a sound site characterization and working through common site management problems and issues**

- **Chemox remediation feasibility testing and remedial action selection utilizes most, if not all, of the information developed for the SCM**

- **<u>Chemox requires clearly defined site remediation objectives and clean-up goals</u>**

And particularly for Chemox applications…

- **Delineation! Delineation! Delineation!**
  - Leads to the Right Chemistry
  - Leads to the Proper Implementation
  - Gives the Best Possible Chemox Results

Bench-Scale Testing

Treatability testing is laboratory testing performed on soil and/or water to provide information *beyond* "what is the concentration of the contaminant?"

Typical ISCO Bench Test Objectives

- Verify contaminant removal
- Estimate oxidant requirement
- Assess effect of treatment on secondary water quality (e.g., **bromate, Cr(VI),** pH, dissolved iron, mobilization of metals)
- Assess attenuation of secondary parameters

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COC Removal/Mechanism

- Ozone, Fenton's reagent
  - TPH, BTEX, fuel oxygenates generally removed
  - Removal mostly due to destruction, but some volatilization, especially for Fenton's
  - Acetone typical by-product; occasionally TBA from MTBE
- Activated persulfate
  - Removal of TPH, BTEX, fuel oxys more variable in PRIMA's experience
  - Effectiveness may depend upon activator used (heat is most effective, but not always practical)
  - By-products not common with TPH; occasionally halogenated intermediates

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Oxidant Requirements

- Calculated – ozone, persulfate
  - Chemical equations can be written for specific compounds (eg benzene, MTBE), but not mixtures such as TPH
  - Chemical equations assume conversion to CO_2
  - Calculated values do not account for natural organic matter and non-target compounds
  - Calculated values do not account for rapid decomposition of oxidant (ozone, Fenton's reagent) decompose relatively quickly
- Empirical
  - Ozone, activated persulfate—measure soil and groundwater demand
  - Fenton's reagent—can't measure oxidant demand, so measure longevity of Fenton's reagent instead

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Potential Secondary Effects

- Bromate
  - Formed by ozonation of naturally occurring bromide
  - Amount formed depends upon amount of ozone applied, but formation is site-specific
- Cr(VI)
  - Formed from oxidation of soil chromium
  - Most common with permanganate, ozone; rare with activated persulfate or Fenton's reagent
  - Amt. formed site-specific depends upon amt. of oxidant applied
- Metals mobilization
  - Mobilization highly site-specific
  - Mobilization may occur due to change in pH or presence of chelating agent associated with oxidant

Cr(VI) Attenuation

- Most soils have some ability to attenuate Cr(VI)
  - Organic matter reduces Cr(VI) to Cr(III)
  - Reduced mineral species can convert Cr(VI) to Cr(III)
  - Microbial activity can generate reducing conditions [i.e., from sulfide, nitrite, or other species capable of supplying electrons to Cr(VI)]
- ISCO may affect ability of soil to attenuation Cr(VI)
  - ISCO destroys many compounds that could attenuate Cr(VI)
  - Downgradient soil may still readily attenuate Cr(VI)

Test Procedures

- Test design depends upon test goals
- Sources of tests include
  - PRIMA Environmental
  - Clients/regulators/other stakeholders
  - Scientific literature
- Common protocols (PRIMA)
  - Batch tests (column tests usually not practical)
  - Use soil (composited) and groundwater (composited)
  - 1:5 soil to liquid ratio (necessary in order to have enough water for post-treatment analyses)
  - Room temperature (18-25°C)

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Ozone Apparatus-Batch

Ozone Apparatus-Columns

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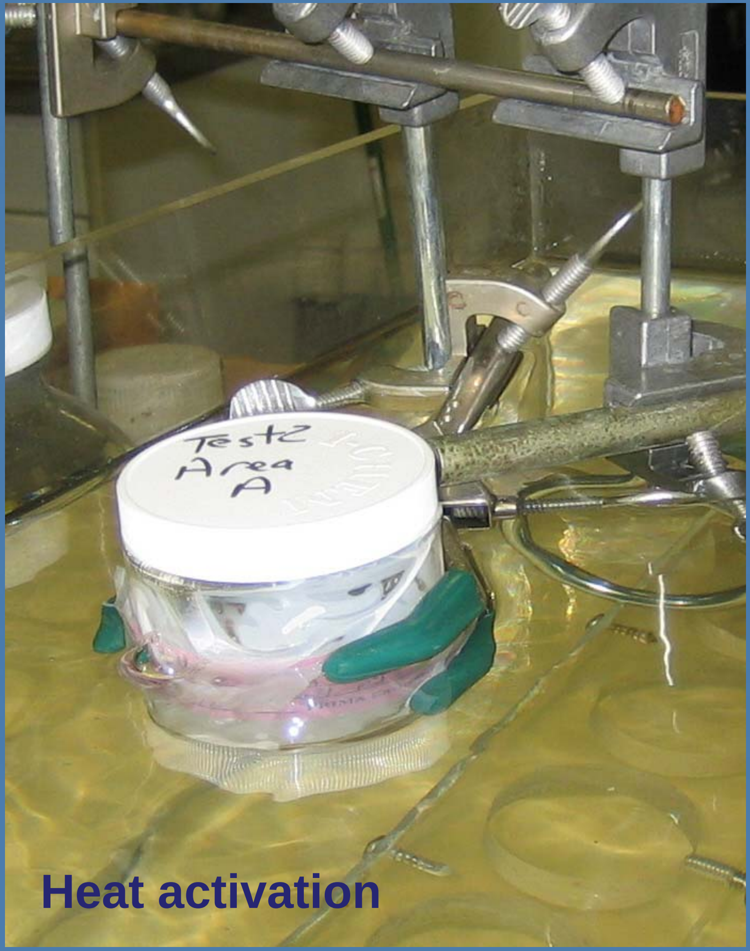
Fenton's Apparatus

Activated Persulfate



What Lab Testing Can Do

- Determine whether a specific oxidant can destroy site CoCs
- Estimate the amount of reagent required
- Identify which secondary effects may potentially be an issue during field application
- Determine whether secondary effects are likely to be transient (e.g., can Cr(VI) attenuate?)

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What Lab Testing Can Do—cont'd

- Help troubleshoot field results (e.g., if good removal occurs in lab, poor removal in field may be due to difficulty delivering reagent)
- Provide a better understanding of the site
- Raise the comfort level of stakeholders

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What Lab Testing Cannot Do

- Perfectly simulate field conditions
  - Can’t determine *exact* amount of reagent needed
  - Can’t predict the *exact* degree of change in a secondary parameter
  - Predict *exactly* how long secondary effects will last
- Promise perfect results in the field
  - Applicability of bench test results depends upon how well test soil / groundwater represents the site
  - Success of ISCO depends upon skill and experience of field remediation team

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Pilot-Scale Testing and Full Scale Implementation

Current *In-Situ* Methodologies

Diffusion method

Dispersion method

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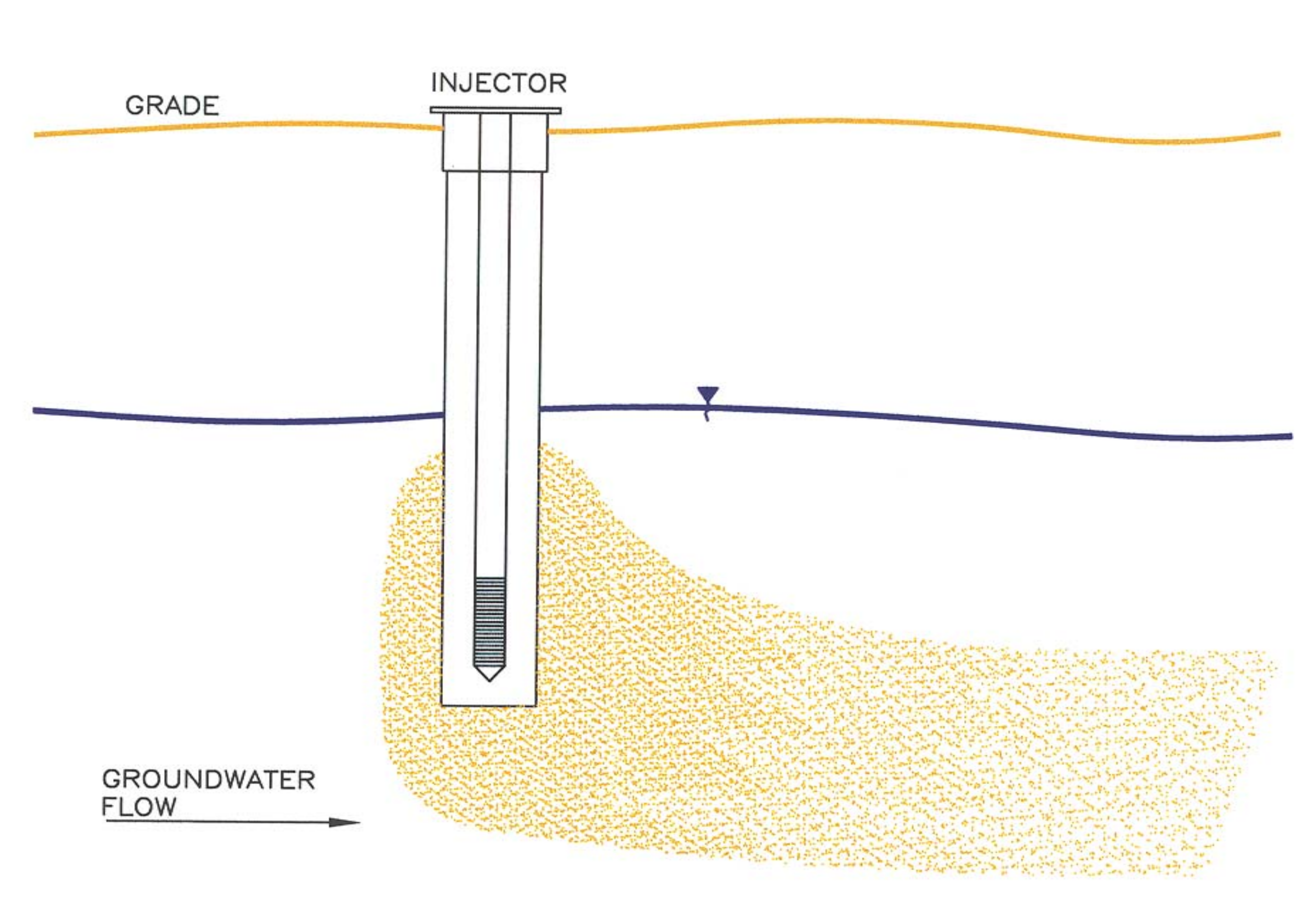
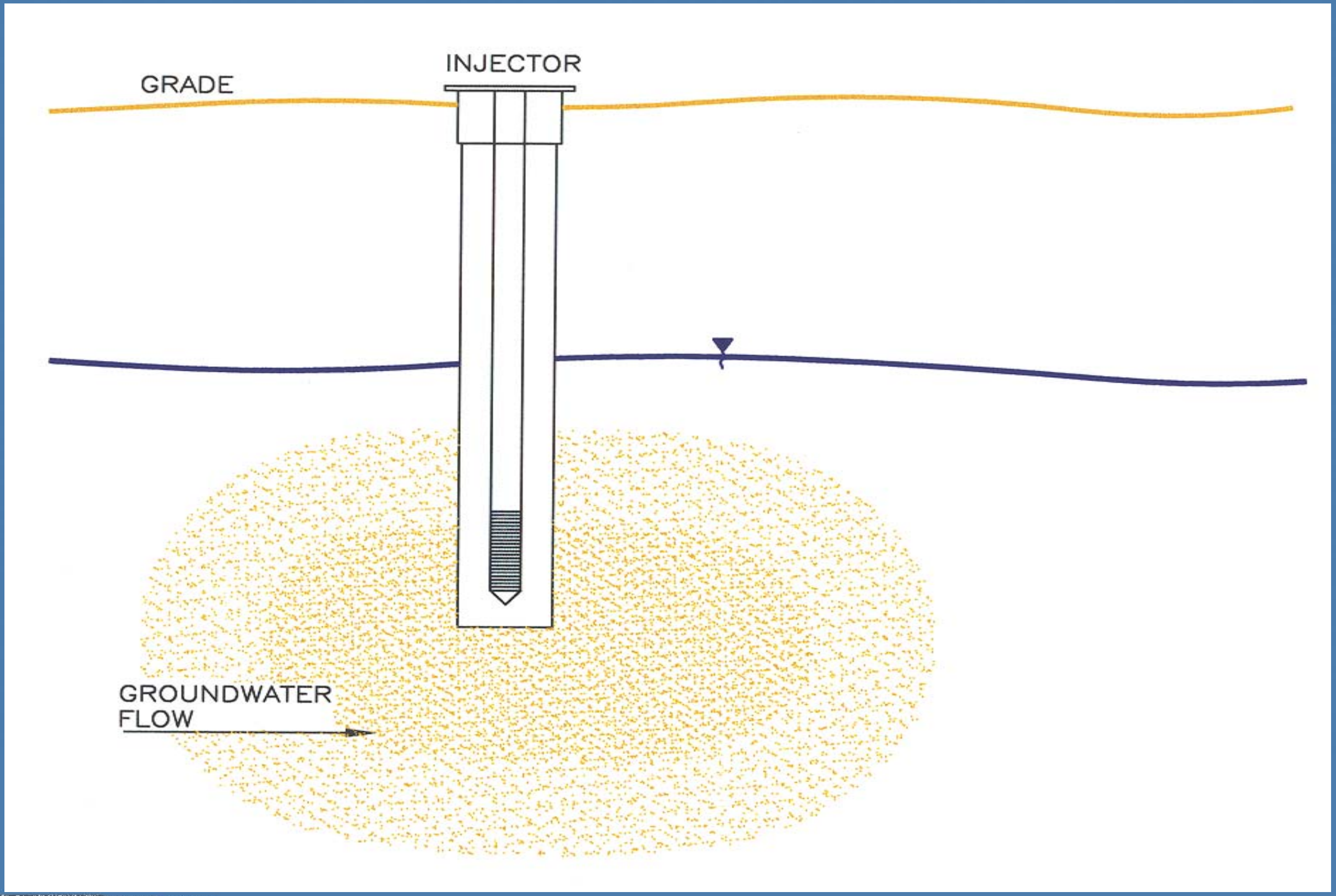
Diffusion



Dispersion



Types subsurface mixing techniques

- Grouted injection points
- Backhoe mixing
- Auger / Grinder mixing
- Direct Push
- Horizontal injection

Injection Rod With Disposable Point

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Example Injection Site

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Specialized Injection Trailer

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Specialized Injection Trailer

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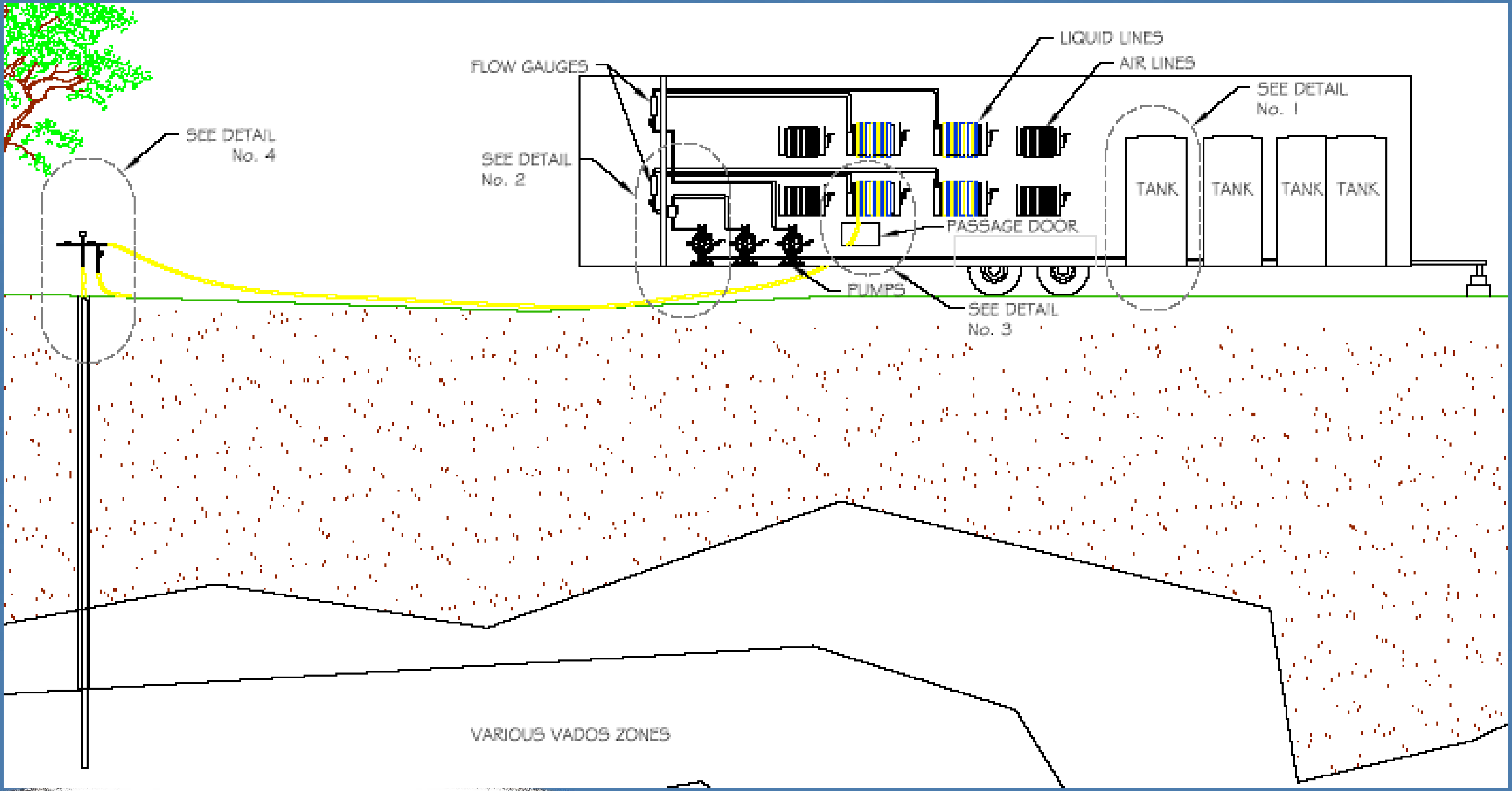
Trailer Flow Diagram & Details



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Hydro-Fracturing Pump

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Evaluate Site-Specific Lithology for Injection Efficiency & Effectiveness

- **Homogeneous well-sorted, medium- to coarse-grained sand is the best lithology**
  - high permeability and low hydrostatic pressure
- **Fractured bedrock can be injected into through temporary, drilled points**
  - However, flow rate, volume and treatment effectiveness need to be monitored closely to ensure that the micro-fractures within the bedrock don't become clogged or congested
- **Overlying clay layers increase the probability of success**
  - Because they form a seal, or cap, that prevents treatment chemistry from exuding through the surface and improves horizontal dispersion
- **Most lithologies can be injected into…**
  - However, the more heterogeneous the formation is and the more clayey the site is, the harder it is to predict and direct exactly where the reagents are going

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Design Criteria for Implementation

Pilot study should be conducted before full scale operations

- Pilot study will ensure that:
  - Results of the TOD and bench scale treatability study are effective in their design
  - Design criteria are modified as needed before full-scale implementation & operations

- Pilot study should be conducted within and adjacent to the most contaminated zone on site
  - Utilizing at least one monitoring well or compliance point
  - Should be a representative location of the site

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Design Criteria for Pilot Testing (cont.)

Pilot tests are performed on a representative portion of the field site to evaluate & determine critical design factors:

- Radius of influence, rate of application, and bulk mass transport effectiveness
- Maintenance of subsurface temperature and pressure in a safe and efficient manner
- Efficiency and effectiveness of the chemical reactions
- Field oxidant mass/volume delivery & dose estimates
- Sustained delivery rates can be achieved
- Cost estimates for full-scale implementation

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Design Criteria for Full-Scale Implementation

- Full scale design is based on observations from the pilot test along with bench test and NOD results
- Final field oxidant mass/volume delivery & dose estimates
- Determination of final Cost estimates for full-scale implementation

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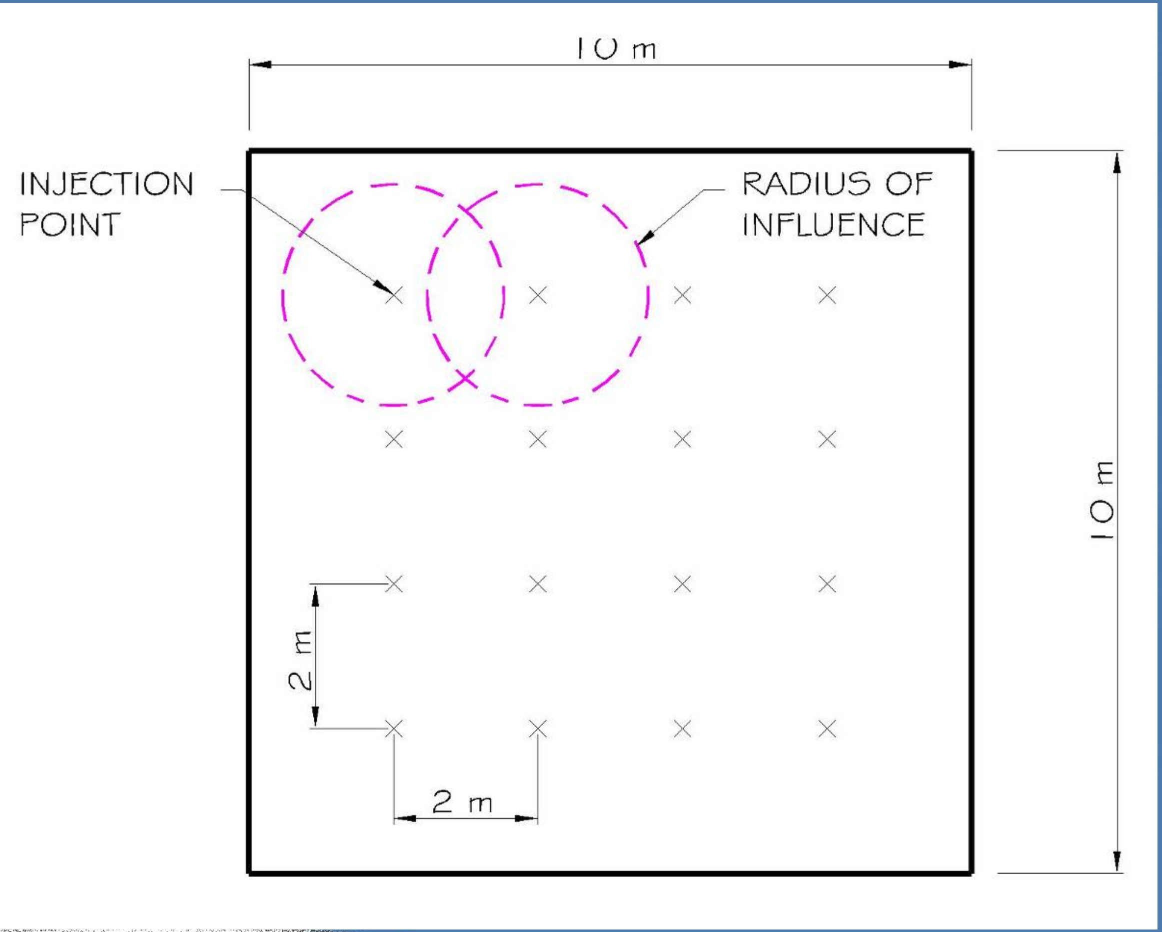
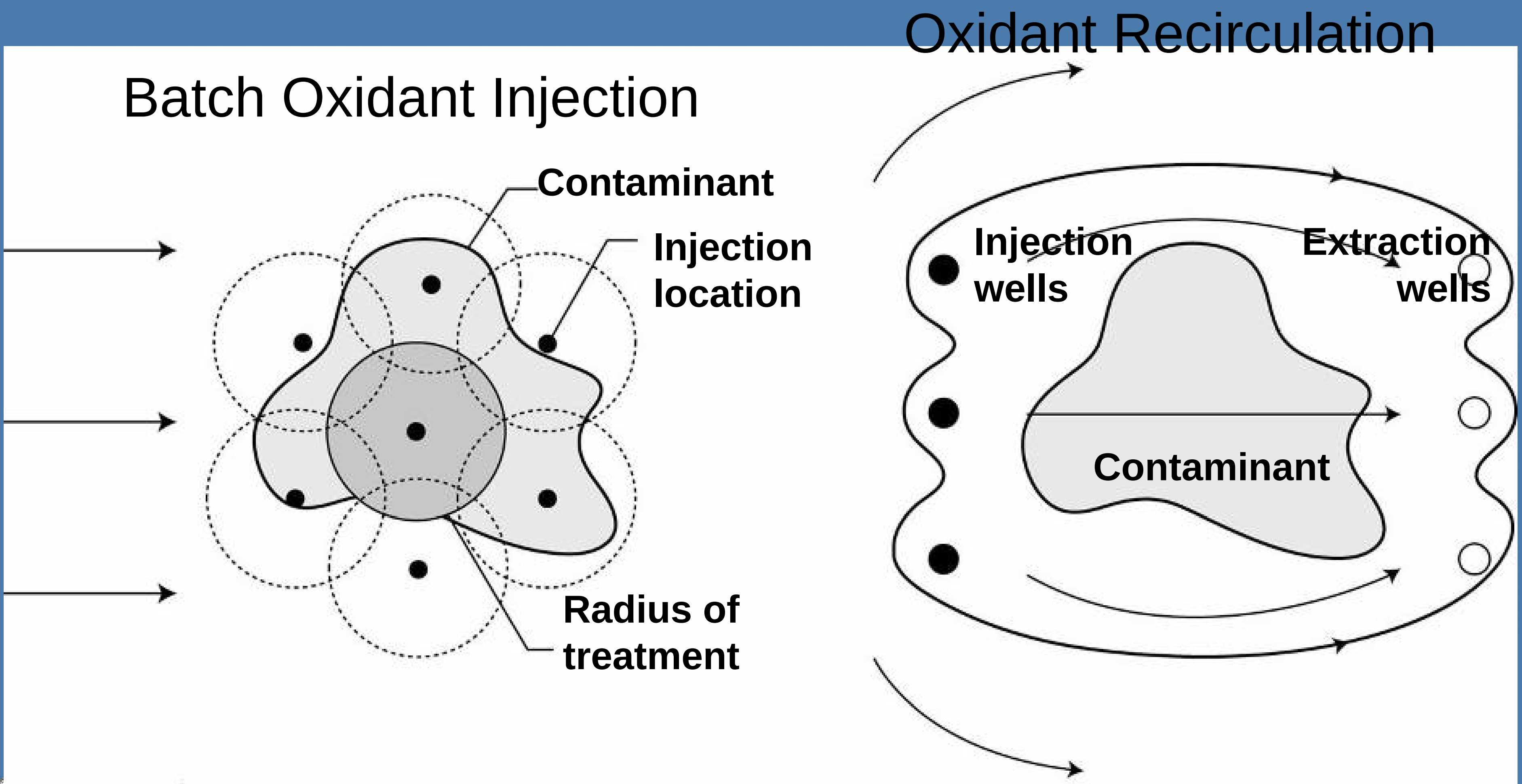
Typical Injection Point Layout



- Typical injection is from the outside moving in

Delivery Systems
Batch vs. Recirculation



Source: ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

Conditions that Require Special Consideration

- Low permeable soils
- Deep aquifers and very shallow aquifers
- LNAPL / DNAPL
- Confined formations
- High organic soils
- Old landfills and dumps
- River embankments
- Under buildings

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Source: ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

Delivery Systems Application

Approaches to increase effectiveness:

- Recirculation
- Pneumatic fracturing
- Hydraulic fracturing
- Unsaturated zone delivery

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Source: ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

Dosage Considerations

- Natural Organic Demand (NOD) and Reduced Inorganic Matter (RIM) **contribute heavily to the oxidant demand**

- Nutrients and electron acceptors/donors important to bacterial recovery if post-ISCO remediation desirable

Non-Radical Chemistry: Permanganate Dosing:

- Sodium permanganate: Up to 20% - batch / recirculation

- Potassium permanganate: Up to 4% - batch / recirculation

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Source: ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

Dosage Considerations - Radical Chemistry

- **Peroxide** Generally 4% to 20%
  - Options: Low pH / iron addition
Neutral pH / chelating agents / iron < 15%
High pH
  - Excess peroxide and iron affects the reaction chemistry negatively
- **Ozone** < 10% in oxygen; < 1% in air
- **Persulfate** < 20%; buffer acidity e.g., sodium carbonate (Na_2CO_3)
  - Excess catalyst and chelating agents affects reaction chemistry negatively; very corrosive

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Source: ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

Chemical Oxidant Loading

Is based on the four main points

- Average contaminant loading in the groundwater
- Average soil concentrations: this will take into account sorbed-phase material
- Natural organic demand (NOD)
- Area of the plume Width*Length*Depth

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Monitoring Chemox Remediation

Oxidant Specific Monitoring Parameters

- **Permanganate**
  - Monitor well - color, oxidation / reduction potential (ORP), conductivity, chloride, manganese dioxide
- **Persulfate**
  - pH, dissolved oxygen (DO), ORP, conductivity, and/or persulfate in monitor wells
- **Ozone**
  - Continuous monitoring of ozone gas, carbon dioxide (CO_2), volatile organic compounds (VOCs), and oxygen (O_2)
- **Peroxide (Fenton's)**
  - Injection well - pH, temperature, pressure
  - Monitor well - pH, temperature, color, ORP, DO, conductivity, VOCs

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Source: ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

Monitoring (cont.)

- As the remedial effort progresses, you should see a trend towards:
  - High O_2
  - Low CO_2 and PID readings,

….meaning the remediation treatment reaction is almost complete

- The Chemox treatment process is completed:
  - When the desired amount of treatment chemistry has been applied
  - When the reagents are spent; the chemistry will continue to react in the subsurface
    - either by self-destruction (e.g., Fenton's)
    - or by contacting contaminants or other organic matter

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Remedial Degradation Products from Chemox of Petroleum Hydrocarbons

- **Fenton's Reagent will yield carboxylic acids**
  - Carboxylic acids are fatty acids that occur naturally in soil before eventually turning into carbon dioxide, oxygen and water
  - Some metals may be released from native soils during Fenton's applications
- **Persulfate** reaction with target species **subsequently breaks down into sulfate ions**

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Remedial Degradation Products from Chemox of Petroleum Hydrocarbons

- **Catalysts for the treatment chemistries may persist**
  - Fenton's is catalyzed with ferrous sulfate and iron levels may increase in the soil and groundwater
  - Persulfate may be catalyzed with either ferrous iron (Fe^{+2}), sodium hydroxide (NaOH), lime, calcium peroxide (CaO_2), or hydrogen peroxide (H_2O_2).
    - A high pH, only temporary, may be seen within the aquifer if NaOH, lime or CaO_2 are utilized to catalyze sodium persulfate
    - CaO_2 will also release oxygen slowly over time to stimulate aerobic biodegradation of petroleum hydrocarbons
    - H_2O_2 will also release oxygen, but most oxygen will be released immediately
    - The use of Fe-EDTA for catalyzing sodium persulfate may release low levels of metals that buffer back to baseline concentrations within a month or two, depending on the site's soil characteristics

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Vapor Observations

- No observed lag-time - vertically or horizontally
- Field measurement of vapors closely correlated to the quantity of oxidant being injected
- Vapor generation appears mobile and widespread in the subsurface
  - Can be a HSE concern
- Indications that vapor can exist several hours after ceasing oxidant injection
  - Can be a HSE concern

✓ **With subsurface vapor/pressure generation (e.g., Fenton's Reagent), Chemox should not to be implemented without full-focus and evaluation of HSE concerns**
  - ✓ **vapor migration pathways, receptors, etc.**

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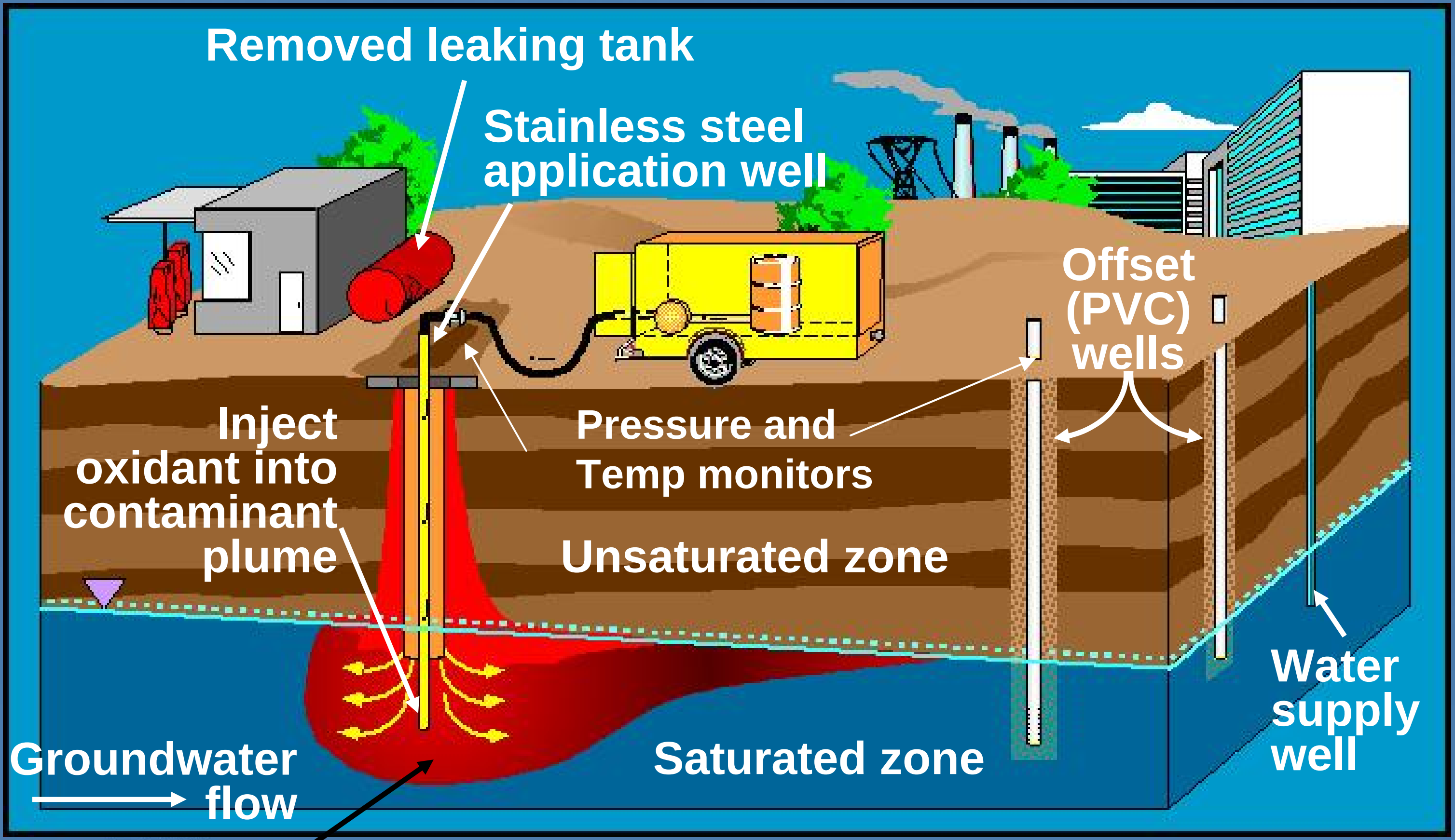
Monitoring Locations



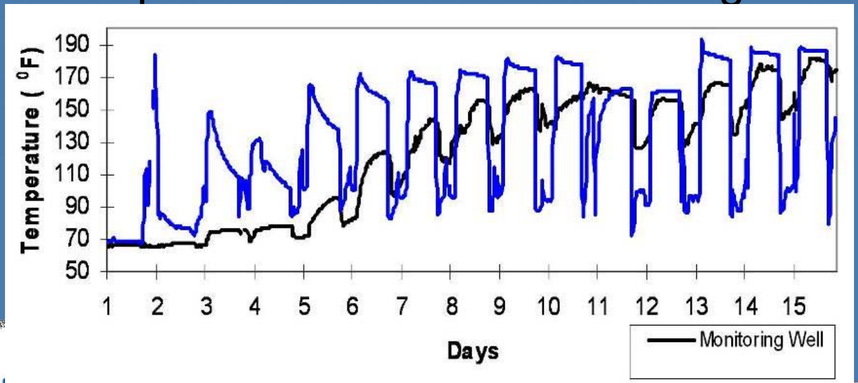
Plume of dissolved contaminants

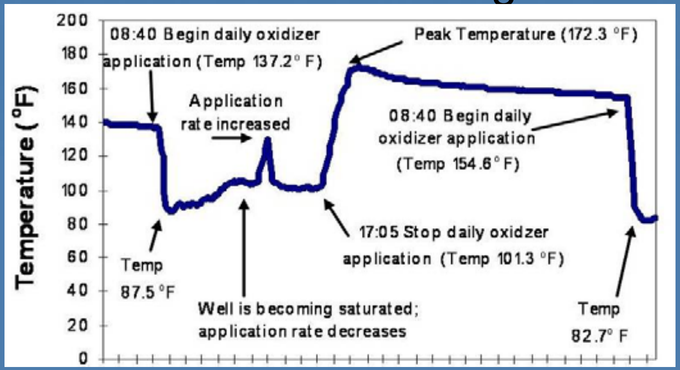
Source: ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

Pressure and Flow Monitoring

Temperature and Pressure Gauges

Flow Metering





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Source: ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

Case Histories:
Bench-, Pilot- and Full-Scale

Case Studies - Background

- The case studies presented here represent both petroleum hydrocarbons and chlorinated solvents.
- In general, clients tend to go directly to Pilot-scale Chemox applications for petroleum hydrocarbons without bench-scale.
- While this trend for Chemox of petroleum hydrocarbons exists, these following case studies offer reasons why scale-up testing can be valuable and should be considered as a useful, cost-effective step in scaling up the design of Chemox systems targeting petroleum.

Case Study #1

Property Redevelopment Pilot-Scale

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General Information

- Successful bench and pilot scale project
  - Bench-scale soil tested for TOD
  - Pilot-scale testing parameters, based upon TOD, was implemented:
- Old dumping area
- Soil: Sand with trace silts
- Depth of contamination: 20 to 55 feet
- Contaminants: Creosote, BTEX, and Naphthalene
- Oxidant injected 25% Klozur® Sodium Persulfate
- Number of injection points: 8
- Number of days of injecting: 2

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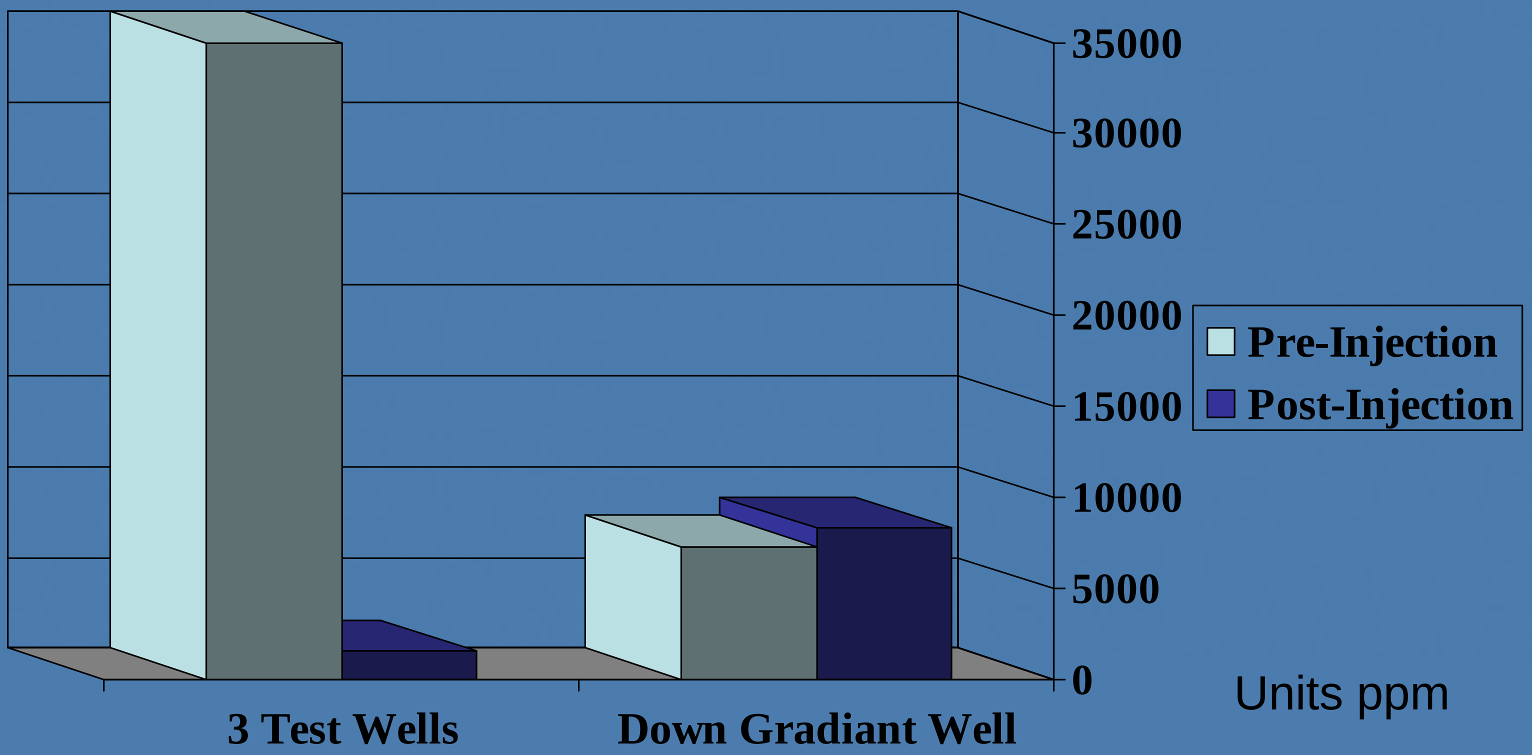
Groundwater Results



Units ppm

Case Study # 2

Site Redevelopment

General Information

- Unsuccessful pilot-scale testing
  - Bench-scale testing of soil for TOD successfully completed, and design criteria established for pilot-scale test
- Abandon Manufacturing Facility
- Soil: Clay
- Depth of contamination: 20 to 35 feet
- Contaminants: PCE and TCE
- Chemical injected :Hydrogen Peroxide and Soduim Persulfate
- Number of injection points: 16

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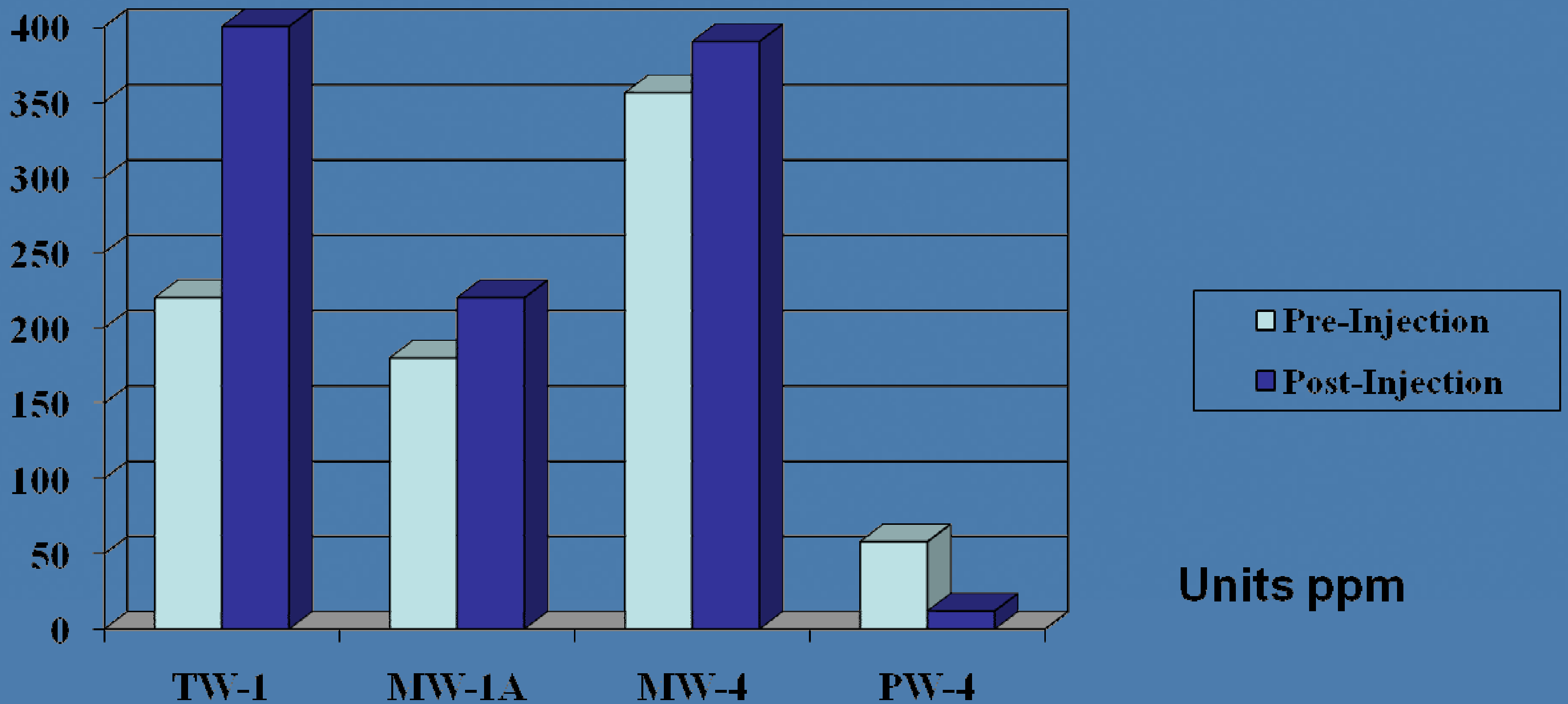
Groundwater Results



Units ppm

Case Study # 3

Property Transaction Site

General Information

- Successful field implementation
  - Bench test successfully completed
- Oil Refinery (pipeline leak)
- Soil: silty clay
- Depth of contamination: 4 to 13 feet
- Contaminants: BTEX
- PermeOx® Plus and Sodium Persulfate injected 15% to 40% (Klozur® ENA)
- Number of injection points: 35
- Number of days on injecting: 3

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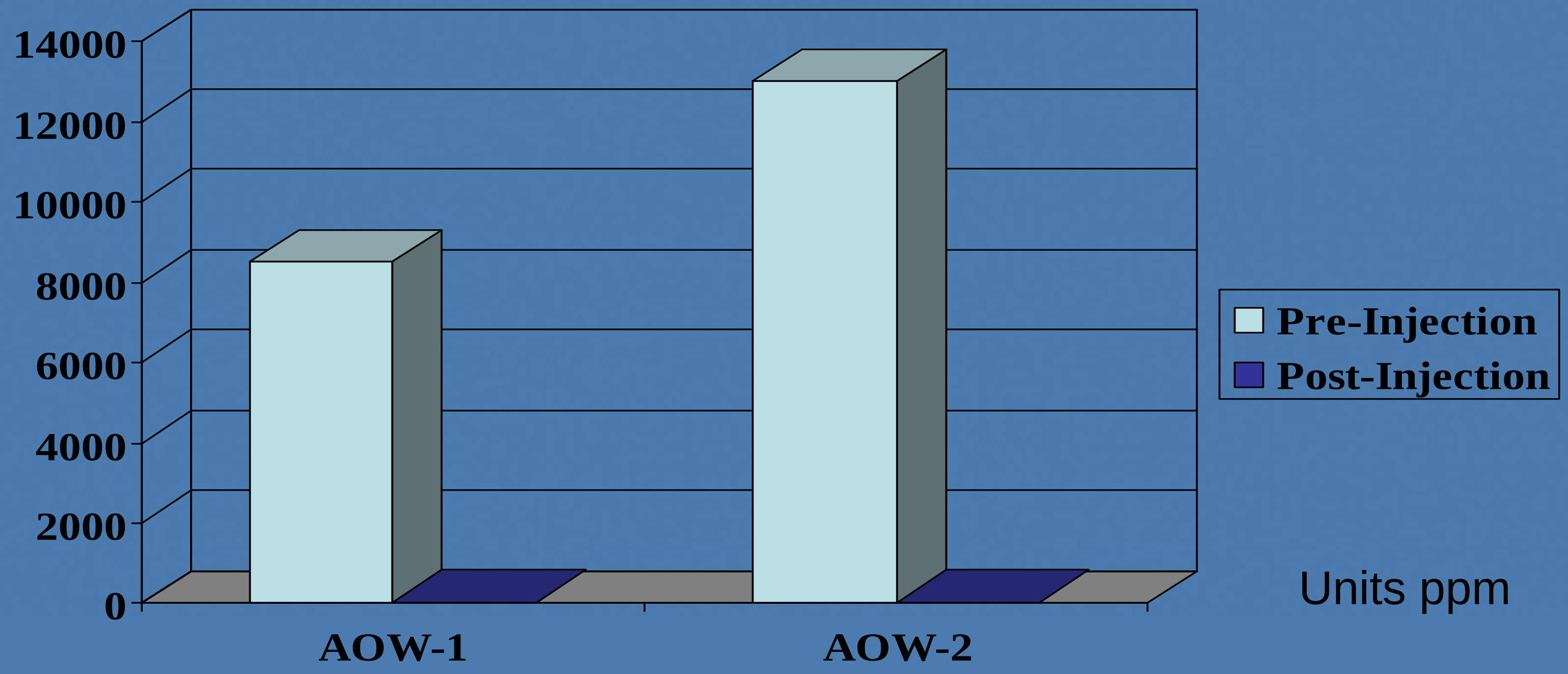
Groundwater Results



Units ppm

Case Study # 4

- Successful bench-scale testing of soil containing petroleum hydrocarbons and lead
  - Soil sample was tested for TOD
  - Successful treatment of lead noted, but natural oxidant demand was high, resulting in the need for multiple oxidant injections to overcome the oxidant demand and to achieve satisfactory petroleum hydrocarbon reductions
- The site area proved to be too small for a pilot-scale test
- Due to background oxidant demand needing to be overcome in order to reduce CoC levels, Chemox at this site was not a costs-effective option
  - Dig & haul was a more cost-effective option offering assurance that all CoC contamination was removed from the site

Case Study # 5

Property Transaction Site

In-Situ Enhanced Vacuum Truck Recovery

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In-Situ Solubilization & Recovery

- One of the techniques used to overcome the problem of the slow release of immobilized NAPLs is to solubilize them with surfactants (Edwards, D. A. et al).

- Surfactants are capable of emulsifying NAPLs to facilitate increased mobility and recovery efficiency (Chevalier *et al.*, 1997; Abdul *et al.*, 1990)

- In many cases this technique can then enhance bioremediation if the surfactant is not toxic to the NAPL degrading microorganisms

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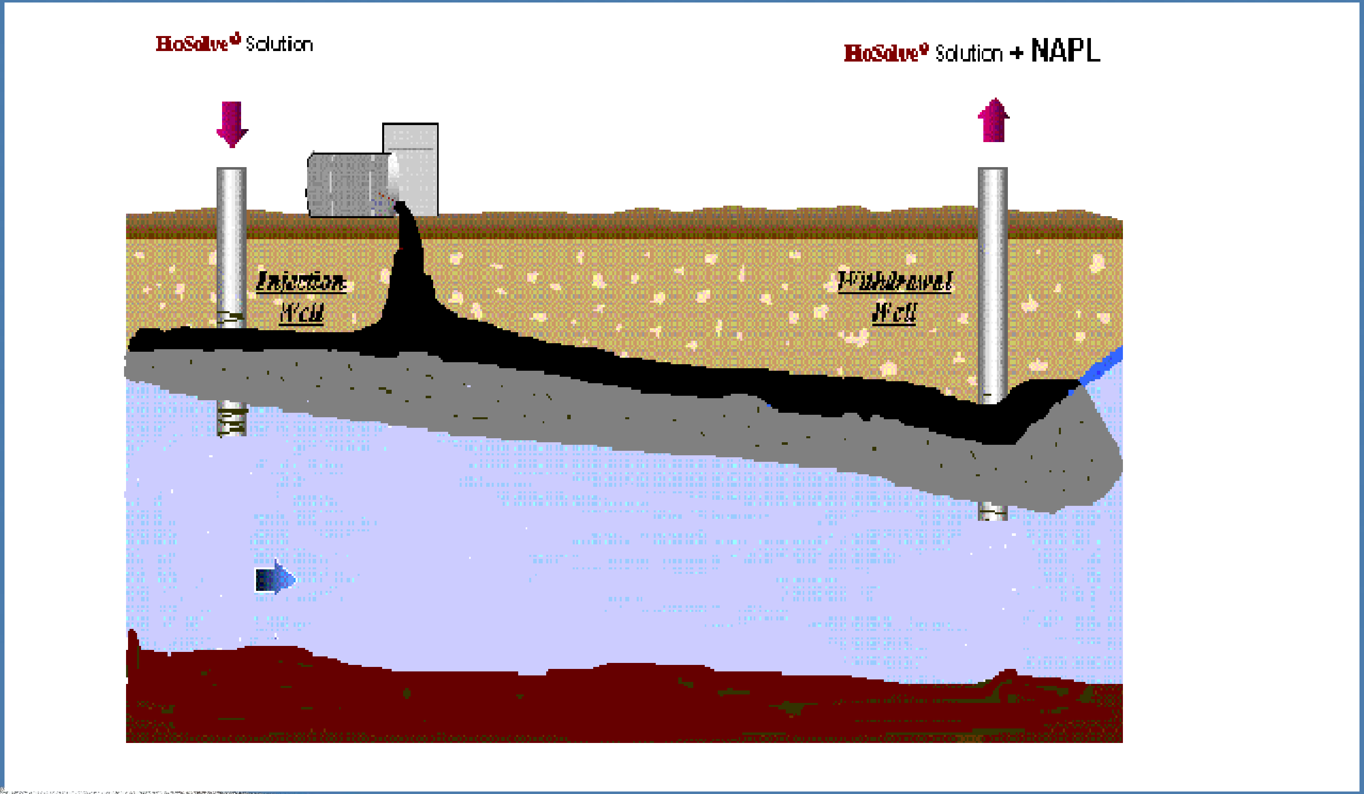
In-Situ Solubilization & Recovery

WHAT IS IT? WHAT DOES IT LOOK LIKE?



General Information

- Diesel release (re-filler and tank leak)
- Soil: silty sand and gravel
- Depth of contamination: 10 to 17 feet
- Contaminants: Free Product Diesel
- Catalyzed Sodium Persulfate injected 25%
- Number of injection & recovery points: 8
- Number of days on injecting: 1

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Vacuum Truck Recovery

- Before injection without enhancement only 4.5 to 6 gallons were recovered
- During the chemical injection along with enhanced recovery a total of 60 gallons were collected

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Variable Project Costs

- Volume of contaminant
- Size of the plume
- Type of lithology
- Days on site

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Keys to Success

- Delineation
- Right chemistry
- Proper implementation

Question and Answers Relating to Chemical Treatment

Regulatory Concerns & Issues

Performance monitoring

Performance expectations

Total mass evaluation

Regulatory perspective

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Performance Monitoring

- Establish baseline conditions and sampling locations before treatment
- Determine contaminant mass / concentration reduction
- Monitor contaminant release and/or mobilization
- Includes post-treatment and possibly closure monitoring

● Application Wells
● Monitor Wells

Source: ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

Performance Expectations

Risk, Mass, and Toxicity Reductions

- ISCO reduces contaminant mass through the oxidation process
- Mass reduction = reduction in risk
- Rapid reduction of source area concentrations to acceptable levels for biological polishing and plume control

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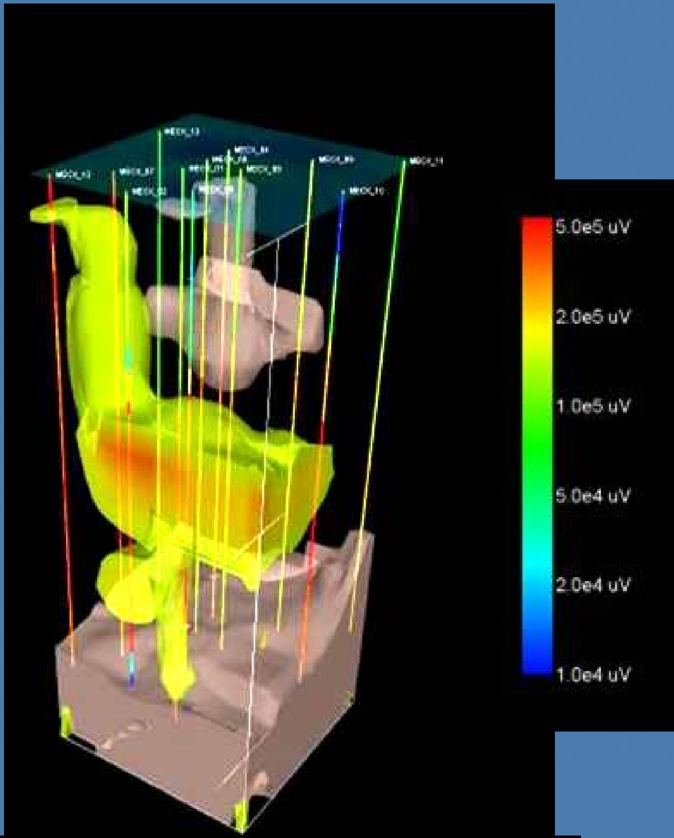
Source: ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

Total Mass Evaluation
Importance of Mass Calculations

- Evaluate pre- and post- total contaminant mass
- Sorbed- and non-aqueous phase mass converts to dissolved during treatment and until site reaches post treatment final equilibrium
- Possible "rebound" causes
  - Dissolution of sorbed- or non-aqueous phase
  - Inadequate site characterization
  - Change in groundwater flow direction
- Decrease in total mass may not be reflected in short-term dissolved concentrations



Electroconductivity Diagram

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Source: ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

Regulatory Perspective Summary

Life of a regulator

- Too many cases/many deadlines
- Needs to make sound technical decisions in a timely manner

The ISCO-2 document and other technical references…

- Detailed background information included
- Allows a regulator to feel much more confident in reviewing an ISCO proposal
- Provides a list of contacts

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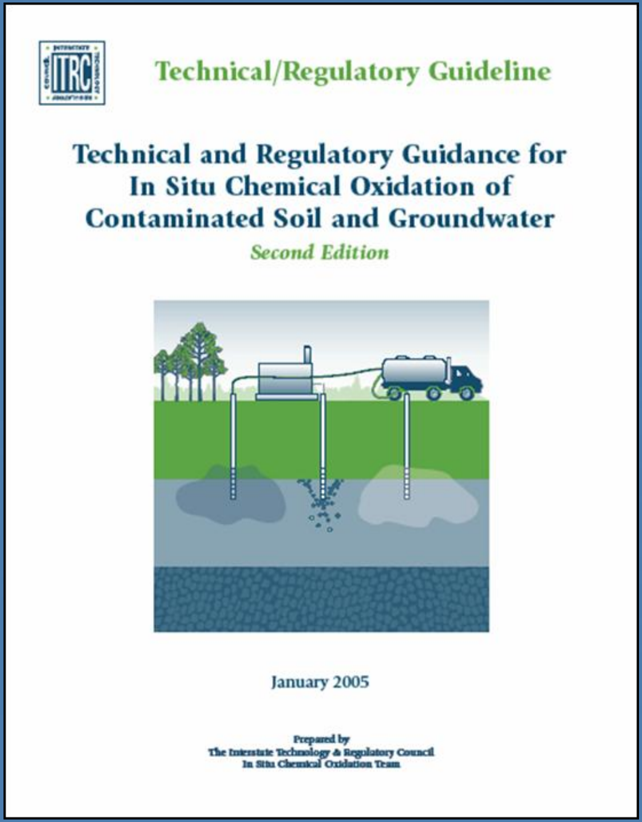
Source: ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

Additional References

Topics Included in ISCO-2 Document

- Regulatory permits
- Health and safety issues
- Oxidant application
- Conceptual site model
- System strategies
- Dosage considerations
- Performance monitoring
- Cost considerations
- Emerging ISCO technologies
- Acronyms, glossary, case studies
- ITRC ISCO team contacts


Technical/Regulatory Guideline

Technical and Regulatory Guidance for
In Situ Chemical Oxidation of
Contaminated Soil and Groundwater
Second Edition

January 2005

Prepared by
The Interstate Technology & Regulatory Council
In Situ Chemical Oxidation Team

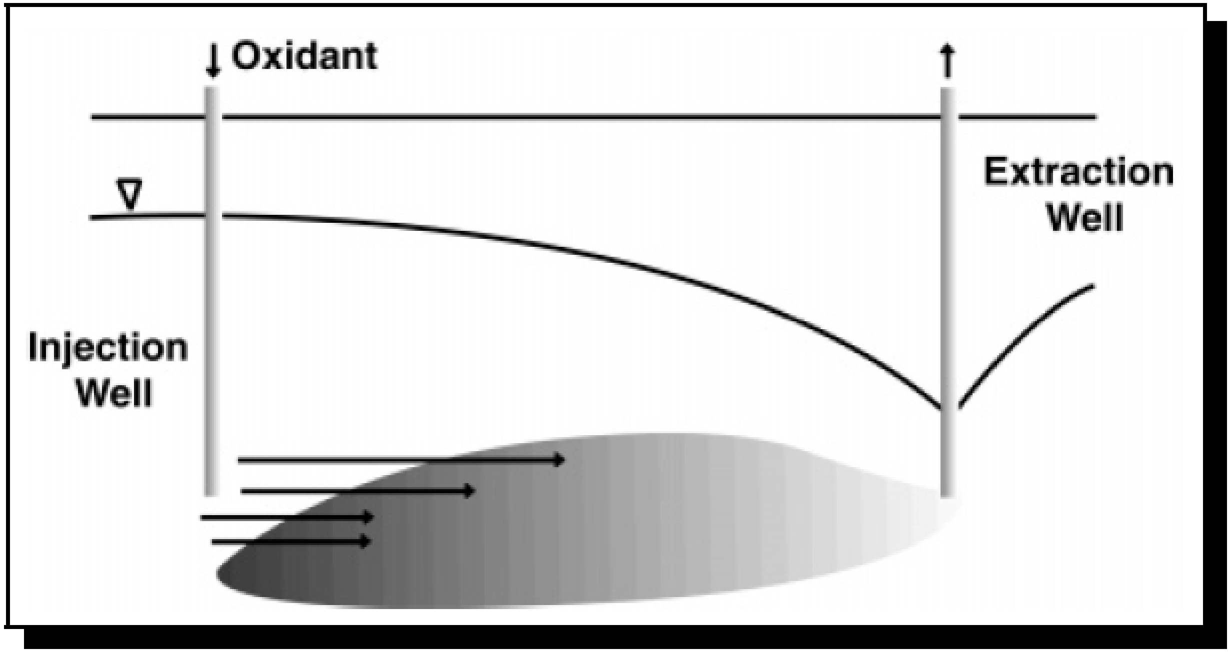
Source: ITRC's In Situ Chemical Oxidation of Contaminated Soil and Groundwater Second Edition (ISCO-2, 2005) available from www.itrcweb.org

United States Environmental Protection Agency
Solid Waste and Emergency Response (5102G)
EPA 542-R-98-008
September 1998
http://www.epa.gov/swertio1
http://clu-in.org

EPA

Field Applications of *In Situ* Remediation Technologies:

Chemical Oxidation



Water Boards

Peer-Reviewed Journals & Publications

ground water

Concentration Rebound Following In Situ Chemical Oxidation in Fractured Clay

by Keely Mundle[1], David A. Reynolds[2], Michael R. West[1], and Bernard H. Kueper[1,3]

Abstract

A two-dimensional, transient-flow, and transport numerical model was developed to simulate in situ chemical oxidation (ISCO) of trichloroethylene and tetrachloroethylene by potassium permanganate in fractured clay. This computer model incorporates dense, nonaqueous phase liquid dissolution, reactive aquifer material, multispecies matrix diffusion, and kinetic formulations for the oxidation reactions. A sensitivity analysis for two types of parameters, hydrogeological and engineering, including matrix porosity, matrix organic carbon, fracture aperture, potassium permanganate dosage, and hydraulic gradient, was conducted. Remediation metrics investigated were the relative rebound concentrations arising from back diffusion and percent mass destroyed. No well-defined correlation was found between the magnitude of rebound concentrations during postremedy monitoring and the amount of contaminant mass destroyed during the application. Results indicate that all investigated parameters affect ISCO remediation in some form. Results indicate that when advective transport through the fracture is dominant relative to diffusive transport into the clay matrix (large System Peclet Number), permanganate is more likely to be flushed out of the system and treatment is not optimal. If the System Peclet Number is too small, indicating that diffusion into the matrix is dominant relative to advection through the fracture, permanganate does not traverse the entire fracture, leading to postremediation concentration rebound. Optimal application of ISCO requires balancing advective transport through the fracture with diffusive transport into the clay matrix.

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