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EPA/ITRC/RTDF Permeable Reactive Barrier Short Course

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Section 1

Permeable Reactive Barriers: Application and Deployment

sect1

EPA/ITRC/RTDF
Permeable Reactive Barrier Short Course

Permeable Reactive Barriers: Application and Deployment

U.S. Environmental Protection Agency (EPA)
- Technology Innovation Office (TIO)
- National Risk Management Research Laboratory (NRMRL)

Interstate Technology & Regulatory Cooperation Work Group (ITRC)

Remediation Technologies Development Forum (RTDF)

Interstate Technology & Regulatory Cooperation Work Group

- The Interstate Technology & Regulatory Cooperation Work Group (ITRC) is a state-led, national coalition
- ITRC's mission: to create tools and strategies to reduce interstate barriers to the deployment of innovative hazardous waste management and remediation technologies

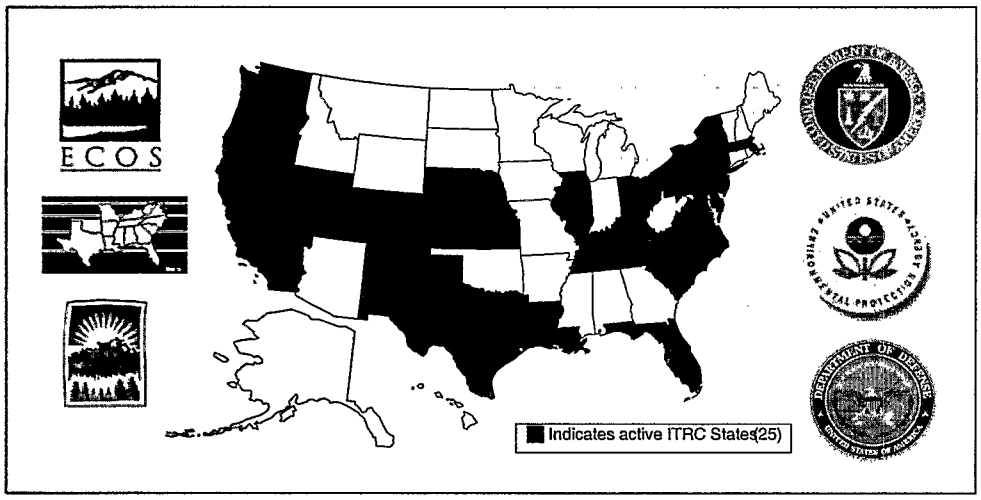
sect1

What is the ITRC?

Environmental regulators working with industry and stakeholders to:

- Support the nation's $200 billion environmental technology industry
- Improve state permitting processes
- Speed deployment of technologies through interstate and regulatory collaboration

Who is the ITRC?



What are the Products and Services Offered by the ITRC ?

- ITRC offers Trail Maps, called "Guidance Documents," to guide regulators and users in the deployment of innovative technologies.
- These "Guidance Documents" come in three forms
  - Technical / Regulatory Requirements
  - Technology Overview
  - Case Studies
- Over 20 ITRC Guidance Documents are available for seven different technology areas.
- More details about ITRC are available at http://www.itrcweb.org

Remediation Technologies Development Forum

- The Remediation Technologies Development Forum (RTDF), sponsored by U.S. EPA, fosters partnerships between the public and private sectors to undertake research, development, demonstration, and evaluation efforts to address mutual cleanup needs.
- The RTDF consists of seven Action Teams focusing on specific high-priority problems, such as chlorinated solvent contamination, and innovative technologies, such as permeable reactive barriers.
- More details about RTDF are available at <http://www.rtdf.org>.

sect1

Course Developers

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- Matt Turner—*New Jersey Department of Environmental Protection*
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- John Vogan—*EnviroMetal Technologies, Inc.*
- Scott D. Warner—*Geomatrix Consultants, Inc.*

Acknowledgments

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- Environmental Management Support, Inc. (EMS)
- Coleman Research Corporation
- RTDF and ITRC course reviewers
- EPA course reviewers
- EPA Forums
- EPA Regions

Goals for This Course

- Provide timely and accurate information about PRB design, construction, monitoring, and economics
- Provide practical tools for making regulatory decisions concerning PRB design and deployment

Course Topics

- Introduction
- Design Data—Site Characterization
- Zero-Valent Metals
- Design Data—Laboratory and Pilot-Scale Tests; Design Calculations
- Compliance Monitoring, Performance Monitoring, and Long-Term Maintenance

sect1

Course Topics (continued)

- Case Studies
- Design Exercise
- Emplacement Techniques
- Permitting and Implementation
- Non-Metallic Reactive Materials
- Economic Considerations

Why Provide This Course?

- Permeable reactive barriers may be appropriate for more than 500 sites in the next 10 years
- The potential cost savings for using PRBs instead of a conventional technology may collectively range from $500 million to greater than $1 billion

Schedule

- Day 1
  - 8:15-12:00 Welcome, Introduction, Site Characterization, Zero-Valent Iron: Laboratory and Pilot Scale Tests, Design Calculations, Compliance and Performance Monitoring, Long-Term Maintenance
  - 12:00-1:00 Lunch, Case Study Presentation
  - 1:00-5:15 Design Exercise, Emplacement, Permitting and Implementation, Questions and Open Discussion
- Day 2
  - 8:10-12:00 Treatment of Metals, Non-Metallic Reactive Materials, Economics, Questions and Open Discussion, Wrap Up

Resources

- Course manual contains overheads for all course topics
- Handouts
- Bibliography (primary references used in development of course materials)
- RTDF, ITRC, EPA (TIO, NRMRL) Web site addresses

  www.rtdf.org/barriers.htm

  www.itrcweb.org

  www.epa.gov/tio

  www.epa.gov/ada/kerrcenter.html

  clu-in.org

Section 2

Introduction to Permeable Reactive Barriers (PRBs) for Remediating and Managing Contaminated Groundwater In Situ

sect2

EPA/ITRC/RTDF
Permeable Reactive Barrier Short Course

Introduction

Permeable Reactive Barriers for Treating and Managing Contaminated Groundwater In Situ

RTDF Remediation Technologies Development Forum

INTERSTATE TECHNOLOGY COOPERATION REGULATORY ITRC

EPA

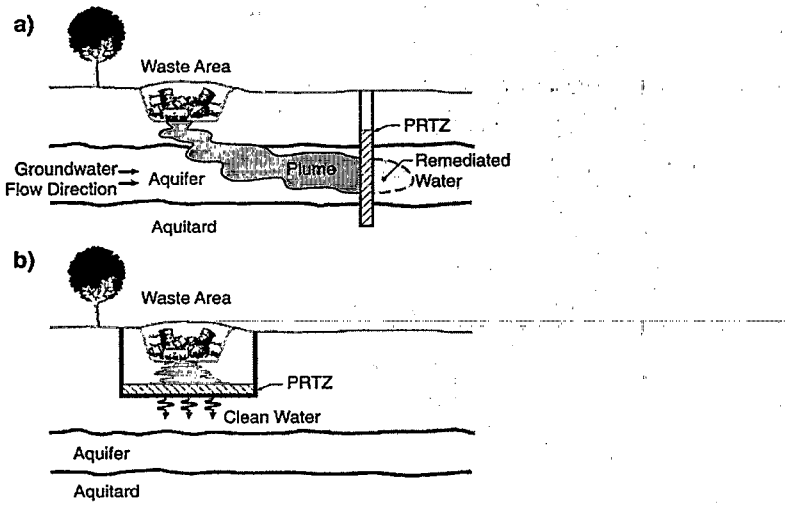
What?

A Permeable Reactive Barrier (PRB):

- A permeable zone containing or creating a reactive treatment area oriented to intercept and remediate a contaminant plume
- Removes contaminants from the groundwater flow system by physical, chemical, or biological processes

sect2

Concept



Why Use a PRB?

- Treatment occurs in the subsurface
- Typical treatment is passive
- Lower costs than conventional methods
- Allows full economic use of a property
- Robust
- Monitoring can be focused

sect2

Treatment Matrix

- Zone or material that promotes treatment
- Focus on zero-valent iron [Fe^0]

  to treat groundwater affected by

  - chlorinated ethenes
  - chlorinated ethanes
  - chlorinated methanes (some)
  - dissolved metals

Treatment Materials; Treatable Contaminants

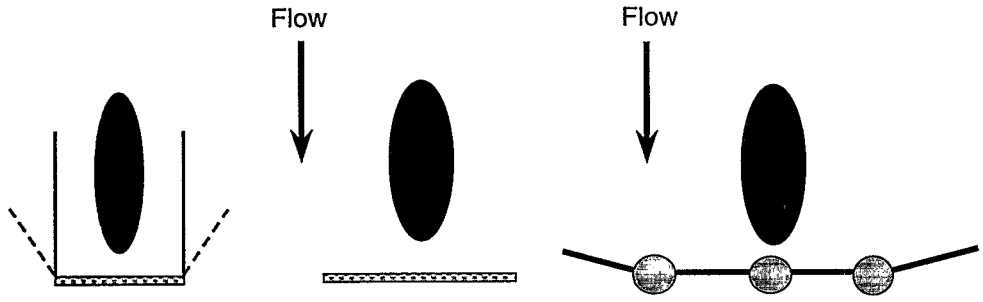
Treatment Material	Target Contaminants	Technology Status
Zero-valent iron	Halocarbons, reducible metals	In practice
Reduced metals	Halocarbons, reducible metals	Field demonstration
Metal couples	Halocarbons	Field demonstration
Limestone	Metals, acid water	In practice
Sorptive agents	Metals, organics	Field demonstration, in practice
Reducing agents	Reducible metals, organics	Field demonstration, in practice
Biologic electron acceptors	Petroleum hydrocarbons	In practice, field demonstration

sect2

Hydraulic Control Systems

- Controls velocity through the reactive media
- Routes affected groundwater through the treatment zone (horizontal and vertical)
- Prevents migration around treatment zone
  - funnel and gate, low permeability barriers
  - continuous wall

Hydraulic Control Systems



Low Permeability Barriers Funnel & Gate

Continuous Wall

Caissons/Multiple Gates

Map View

sect2

Current Applications

- Full-scale installations
  - >20
- Pilot-scale demonstrations
  - >40
- Laboratory-scale tests
  - >100
- Feasibility assessments
  - >1000 (likely)

Current and Future Research

- Expand list of treatable contaminants
- Faster reaction/treatment time
- Deeper (and more complex) emplacement
- Inexpensive reactive materials
- Less expensive emplacement
- Performance monitoring
- Longevity

sect2

Research Organizations

- Government
  - EPA, DOE, DOD
- Academia
  - Waterloo, Stanford, Oregon Graduate Institute, Rice
- Industry
  - DuPont, General Electric, Monsanto
- Private
  - users and designers

Section 3

Collection and Interpretation of Design Data I: Site Characterization for PRBs

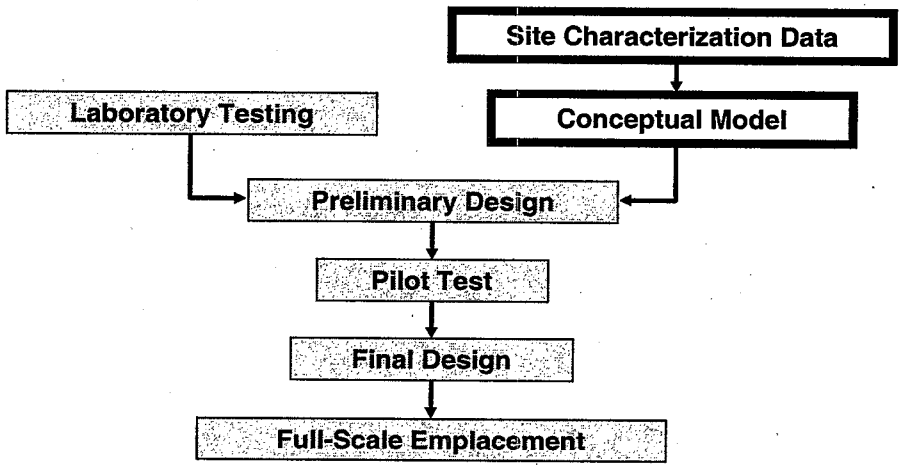
sect3

EPA/ITRC/RTDF
Permeable Reactive Barrier Short Course

Collection and Interpretation of Design Data I:

Site Characterization for Permeable Reactive Barriers

Path to PRB Design and Emplacement



sect3

Purpose

- To address the importance of characterizing a site before reactive barrier installation
- To identify the critical aspects of site characterization
- To discuss ways to get this information

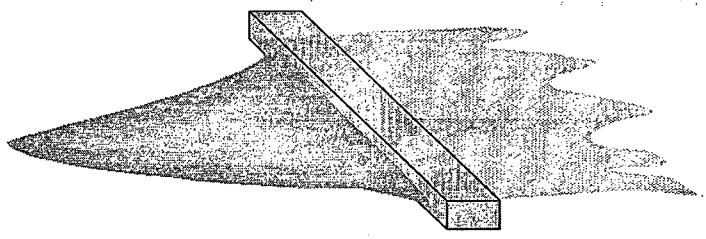
Topics

- Goals
- Potential problems
- Site characterization issues
- Site characterization methods and tools
- Monitoring methods and approaches

sect3

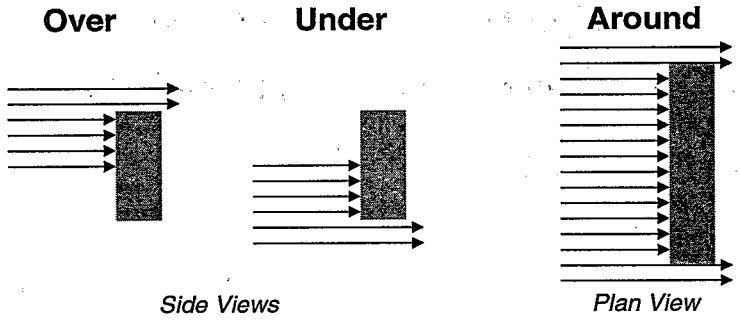
Goal = Passive Remediation System

- The plume enters under the natural gradient
- The entire plume is captured by the system
- Regulatory concentration goals are achieved at point of compliance



Potential Problems

- The plume could pass over, under, or around the barrier
- The groundwater flow direction or velocity might change
- Incomplete remediation as higher concentrations reach the barrier
- Loss of surface reactivity—precipitate coatings, etc.
- Barrier plugging, decreased permeability



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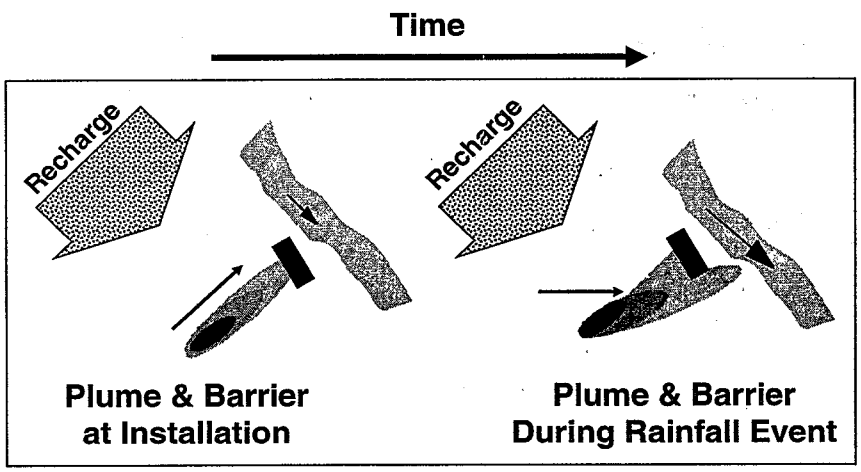
Site Characterization Issues to Address to Achieve Goal

- Hydrology
- Geology
- Contaminant distribution within the aquifer
- Geochemistry
- Microbiology

These parameters are not discrete, but highly interactive.

Hydrology

- Groundwater flow
  - direction (gradient)
  - velocity
  - flux
- Seasonal changes in groundwater flow velocity, direction (e.g. due to recharge events)
- Effects of nearby intermittent pumping
- Provide data for construction of groundwater flow model



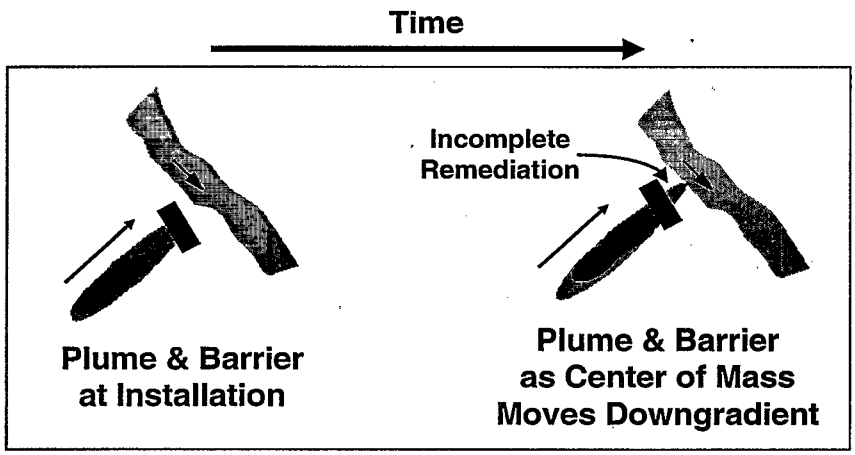
Geologic Setting

- Depositional environment
  - type, mineralogy, TOC
- Stratigraphy
  - depths and continuity of sand layers, clay layers, bedrock
    - keyed barrier or hanging wall
    - zones of water/contaminant movement
    - degree of fracturing

sect3

Contaminant Distribution

- Identify contaminants and degradation products
- Plume location in all dimensions
  - x, y, z, concentrations and time
  - Is natural attenuation occurring?
    - Has steady state been reached?
    - Are the high concentration zones moving?
    - What concentrations will reach the wall?



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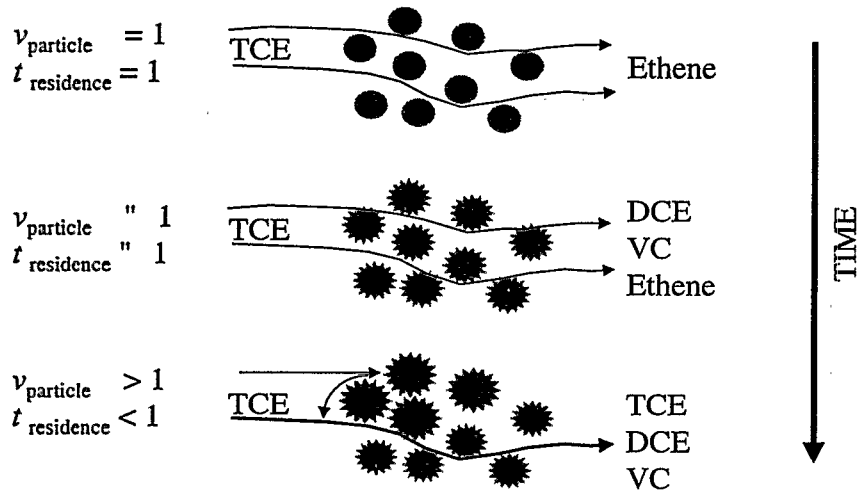
Hydraulic Conductivity Distribution

- Controls flux
- May vary by several orders of magnitude

Geochemistry Considerations

- Oxygen concentration
  - O_2 is preferred electron acceptor
  - high O_2, increased $Fe(OH)_3$ precipitation
- Carbonate alkalinity
  - precipitation of $Fe(CO)_3$ (siderite)
  - precipitation of $Ca(CO)_3$ (calcite)
- Sulfate concentration
  - possible sulfide formation



$$Fe^0 + 1.5O_2 + 6H^+ \rightarrow Fe(OH)_3 + 1.5H_2$$

Rust

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3 \text{ (siderite)}$$

Water Quality Parameters

- **Major ions (Na, Ca, Mg, K, SO_4, Cl, HCO_3)**
- **Dissolved oxygen distribution**
- **Redox potential (Eh)**
- **Needed input parameters for geochemical modeling**

sect3

Microbiology

- Beneficial effects, i.e., enhanced remediation
  - upgradient natural attenuation of plume?
  - degradation products?
- Detrimental effects
  - biofouling and loss of permeability

Data Collection Prior to Implementation of Site Characterization

- Existing monitoring well data
  - water table depths
  - water quality
- Historical records
  - aquifer tests, maps
  - statigraphy
  - recharge areas
  - drainage basins

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Characterization Methods—Conventional

- Soil borings
- Soil gas survey
- Shallow groundwater survey
- Groundwater monitoring wells

Characterization Methods—Innovative

- Use push tool technologies where appropriate
  - Geoprobe® and Hydropunch®
  - cone penetrometers
- Surface geophysical techniques
  - ground-penetrating radar
  - seismics
- Map and model the results
  - hydrologic
  - geochemical

Surface Geophysical Techniques

- Ground penetrating radar
  - buried objects
  - water table depth
  - bedrock depth
- Seismics
  - water table depth
  - bedrock depth
  - fractures
  - strata thickness

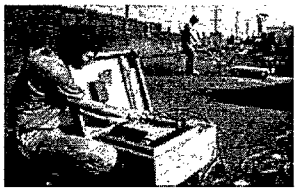
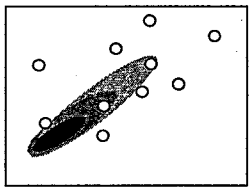
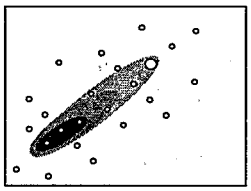


Photo courtesy of Spectrum Environmental Services,Inc.

Push Tool Technologies

- Driven rapidly and inexpensively
  - more samples can be collected, allowing:
    - denser coverage of the area
    - evaluation of a larger area
- Can collect water, soil, and soil-gas samples





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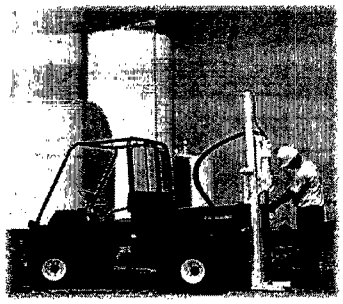
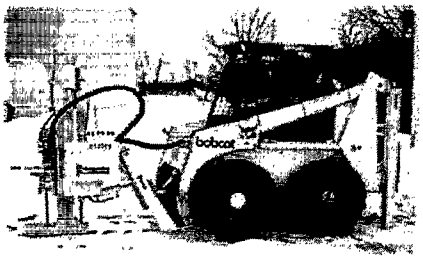
Push Tool Technologies

- **Discrete vertical delineation of aquifer**
  - **better data on stratigraphic continuity**
  - **depending on the tools, you can get:**
    - **soil resistance to penetration**
    - **soil saturation**
    - **hydraulic conductivity**
    - **electrical conductivity**
    - **NAPLs using laser-induced fluorescence, etc.**

Geoprobe® Model 5400



Geoprobe® Model 4220



Geoprobe® Model 540B

Photos courtesy of Geoprobe Systems

Hydrologic Characterization Tools

- Pumping tests
- Slug tests
- Lab permeameter tests
- Borehole flowmeters
- Borehole dilution tests
- Tracer tests
- Permeable flow velocity probes
- Potentiometric information

Map and Model the Results

- Will help to decide if data is sufficient
- Aid in determining the design and location of the reactive barrier(s)
- Development of monitoring network design

sect3

Groundwater Flow Model

- Predict flow velocities under different conditions
- Evaluate effectiveness of hanging wall
- Evaluate different funnel and gate designs
- A complex flow model may not always be necessary
- Decision depends on site-specific conditions and objectives

Conclusions

- A thorough site characterization is needed for the immediate and continued success of a reactive barrier installation
- The "passive" nature of the technology makes this critical
- Good hydrologic characterization essential to remedial effectiveness

Conclusions (continued)

- Current conditions must be known and future conditions predicted
- Push technologies and surface geophysics offer rapid, economical ways to get the needed data

Summary List of Field Design Data

- Groundwater flow, direction, velocity, temporal and spatial variability
- Aqueous geochemistry (pH, Eh, DO, alkalinity, sulfate, other cations-anions, TOC)
- Microbiology (natural attenuation?, biofouling)
- Stratigraphy (esp. confining layers)
- Contaminant distribution, flux (3D and time)

Section 4

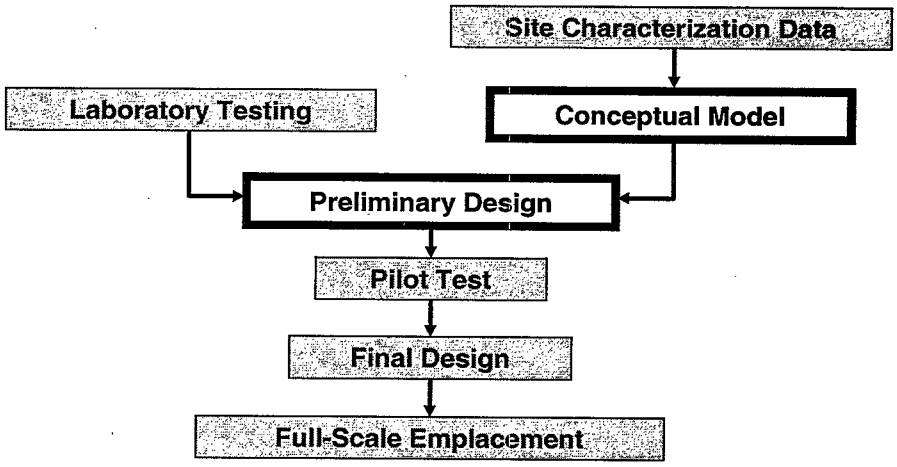
Reactive Materials: Zero-Valent Iron

EPA/ITRC/RTDF
Permeable Reactive Barrier Short Course

Reactive Materials:

Zero-Valent Metals

Path to PRB Design and Emplacement



sect4

Zero-Valent Metals

- Promote degradation of chlorinated organic compounds
- Promote precipitation of redox sensitive trace metals, radionuclides

Reactive Metal: Desirable Characteristics

- Effective in removing contaminants of concern
- Compatible with subsurface environment
- Persistent over long time periods
- No adverse geochemical reactions or byproducts
- Low operating and maintenance costs
- Readily available
- Low to moderate cost

History

- Research at the University of Waterloo into in situ VOC degradation, beginning in late 1980s
- Various metals could remove VOCs from contaminated groundwater
- Iron is reactive, readily available and relatively inexpensive
- Over 500 potential sites identified

Cooperative Technology Development

- Initial research at University of Waterloo
- U.S. EPA RTDF/ITRC
- U.S. DOD-sponsored programs (VOCs)
- U.S. DOE-sponsored programs (trace metals)
- RICE Consortium (U.S. DOD initiative)
- Industrial research groups (General Electric, Dupont, Monsanto)

sect4

Granular Iron

Typical Granular Iron Characteristics

Grain size range: 2.0 to 0.25 mm (-8 to +50 mesh)

Bulk density: 2.6 g/cm^3 (160 lb/ft^3)

Specific surface area: ~ 1.0 m^2/g

Hydraulic conductivity: 5 x 10^{-2} cm/sec (142 ft/day)

Cost: ~ $350 to $400 US/ton + shipping

sect4

Iron Specifications

- Low carbon content (typically less than 3%)
- Low level of trace metal impurities
- No surface films

Reaction Mechanism - VOCs

- Corrosion of iron drives reaction
- Iron provides electron source for reduction (dechlorination) of organics
- Pathway is not complete stepwise dechlorination
- More highly chlorinated compounds degrade faster (TCE degrades faster than vinyl chloride)

Thermodynamics of Iron as a Reductant

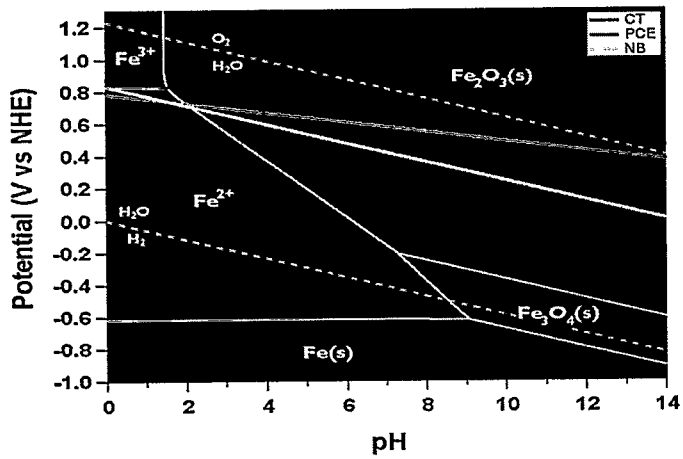


Figure Courtesy P. Tratnyek, Oregon Graduate Institute

Reaction Summary—VOCs

$$Fe^0 \longrightarrow Fe^{+2} + 2e^-$$

$$2H_2O \longrightarrow 2H^+ + 2OH^-$$

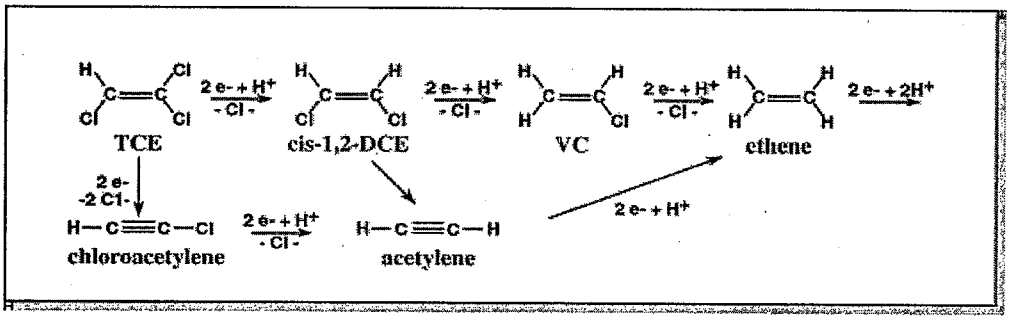
$$2H^+ + 2e^- \longrightarrow H_{2(g)}$$

$$X\text{-}Cl + H^+ + 2e^- \longrightarrow X\text{-}H + Cl^-$$

$$C_2HCl_3 + 3H^+ + 6e^- \longrightarrow C_2H_4 + 3Cl^-$$

sect4

Chemical Process - VOCs



Key Interfacial Processes

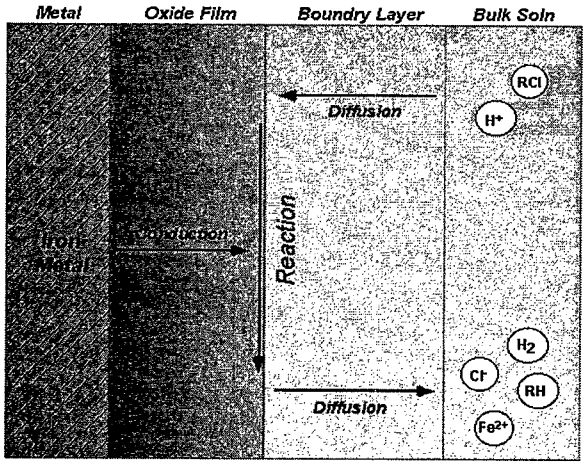
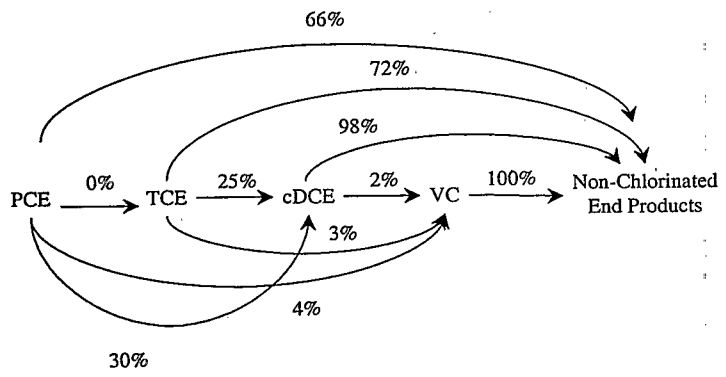
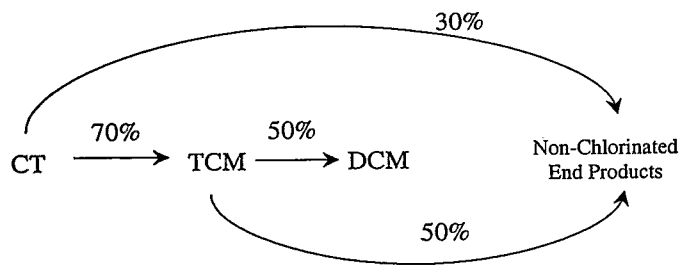


Figure Courtesy P. Tratnyek, Oregon Graduate Institute

Observed Percent Molar Conversions - Chlorinated Ethenes



Observed Percent Molar Conversions - Chlorinated Methanes



Note: Chlormethane (CM) may appear as an additional intermediate. DCM and CM are not degraded by Fe(0).

sect4

Common Compounds - Concentration Ranges Treated

Compound	*Concentration Range (ppb)*	*Compound*	*Concentration Range (ppb)*
PCE	10 - 50,000	CT	100 - 25,000
TCE	25 - 400,000	TCM	50 - 20,000
cis 1,2-DCE	200 - 200,000	1,1,1-TCA	45 - 600,000
VC	40 - 25,000		

Contaminants Treatable by Fe^0 in PRBs

Organic Compounds			
Methanes	• tetrachloromethane • trichloromethane	Propanes	• 1,2,3-trichloropropane • 1,2-dichloropropane
Ethanes	• hexachloroethane • 1,1,1-trichloroethane • 1,1,2-trichloroethane • 1,1-dichloroethane	Other	• hexachlorobutadiene • 1,2-dibromoethane (EDB) • freon 113 • freon 11 • lindane • N-nitrosodimethylamine • nitrobenzene
Ethenes	• tetrachloroethene • trichloroethene • cis-1,2-dichloroethene • trans-1,2-dichloroethene • 1,1-dichloroethene • vinyl chloride		

sec14

Contaminants With Unknown Treatability

Organic Compounds

- chlorobenzenes
- chlorophenols
- certain pesticides
- PCBs

Common Contaminants Presently Not Treatable by Fe^0

Organic Compounds

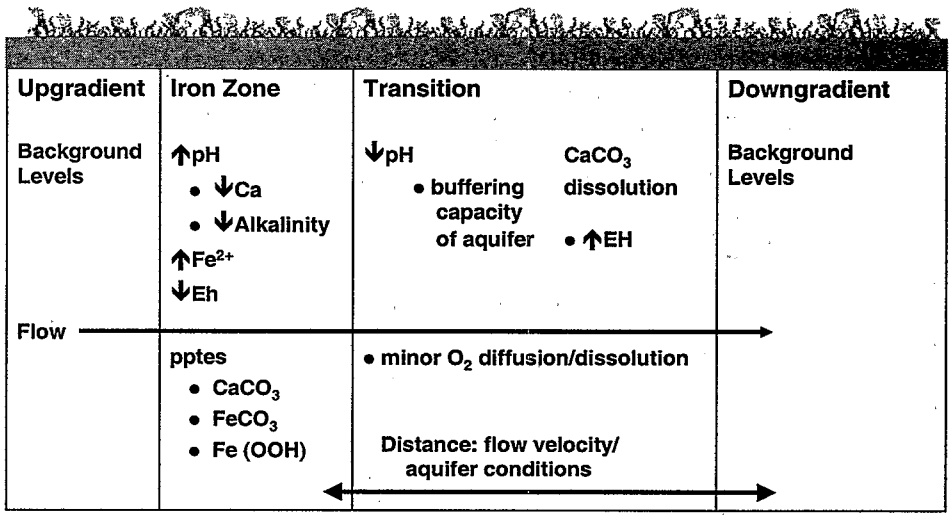
- dichloromethane (methylene chloride)
- 1,2-dichloroethane
- BTEX compounds
- petroleum hydrocarbons

sect4

Changes in Inorganic Groundwater Chemistry

- Introduction of Fe^{2+} → ferrous hydroxide precipitates
- pH increase
- Carbonate equilibrium affected → carbonate precipitates
- Sulfate reduction → sulfide precipitates
- Implications for long-term performance

Inorganic Chemistry

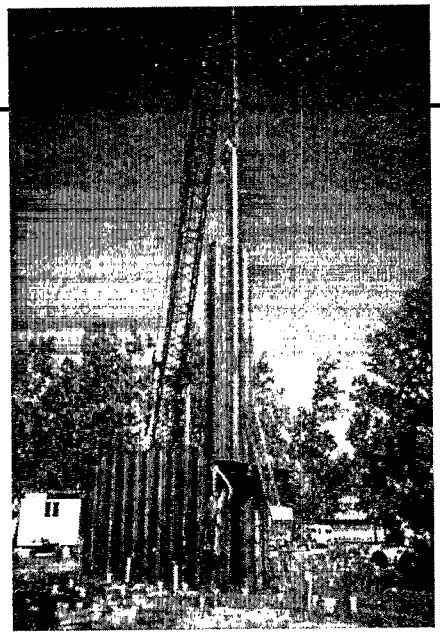


sec4

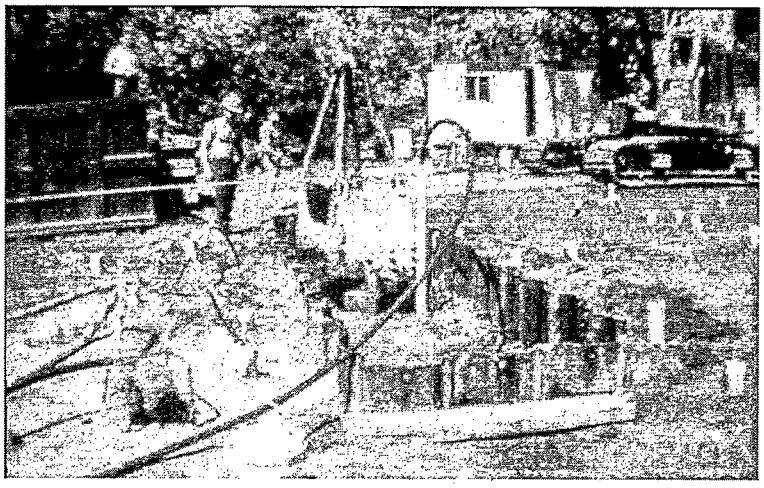
Waterloo Permeable Reactive Wall Field Trial 1991

- CFB Borden, Ontario, Canada
- Unconfined sand aquifer
- Groundwater flow velocity: 9 cm/day
- Water table: 2.5 m bgs
- Groundwater contaminants
  - TCE 253 mg/L
  - PCE 43 mg/L
- Reactive wall (20 m^3)
  - 22% granular iron and 78% coarse sand

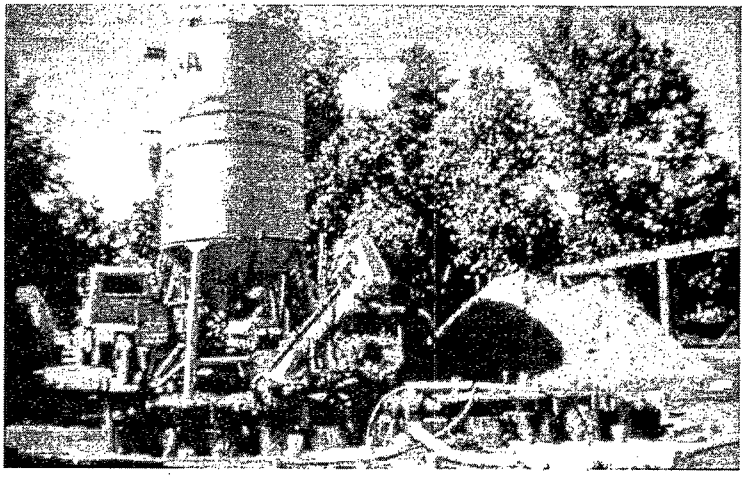
Waterloo Field Trial



Waterloo Field Trial

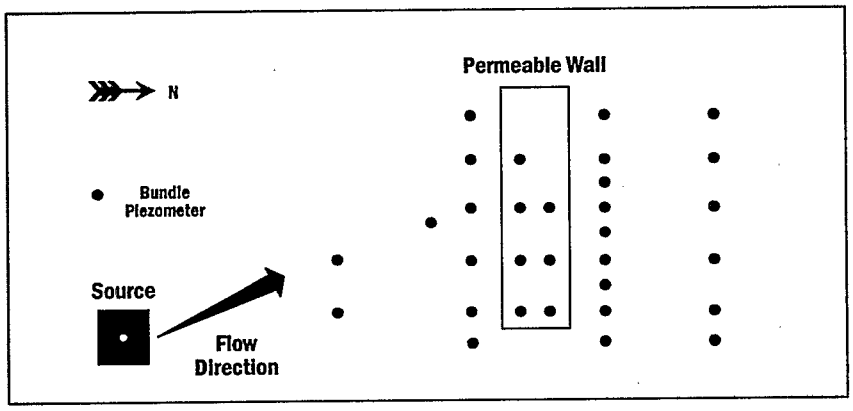


Waterloo Field Trial

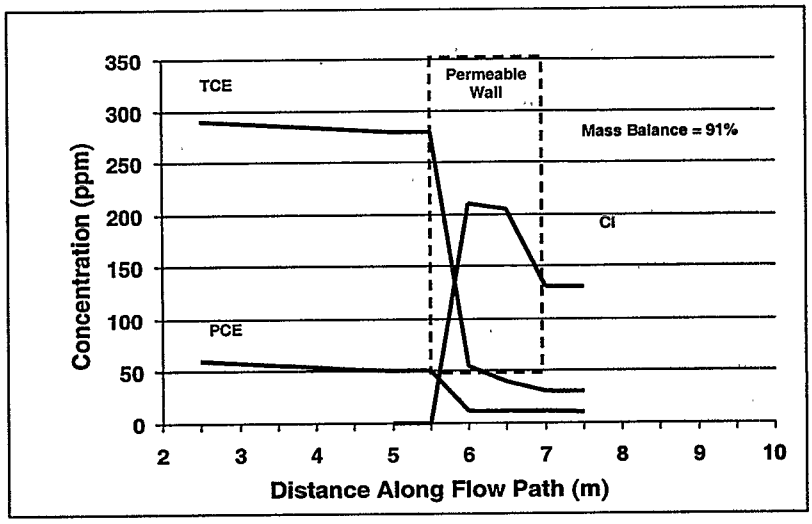


sect4

Waterloo Permeable Reactive Wall Field Trial 1991



Waterloo Permeable Reactive Wall Field Trial 1991



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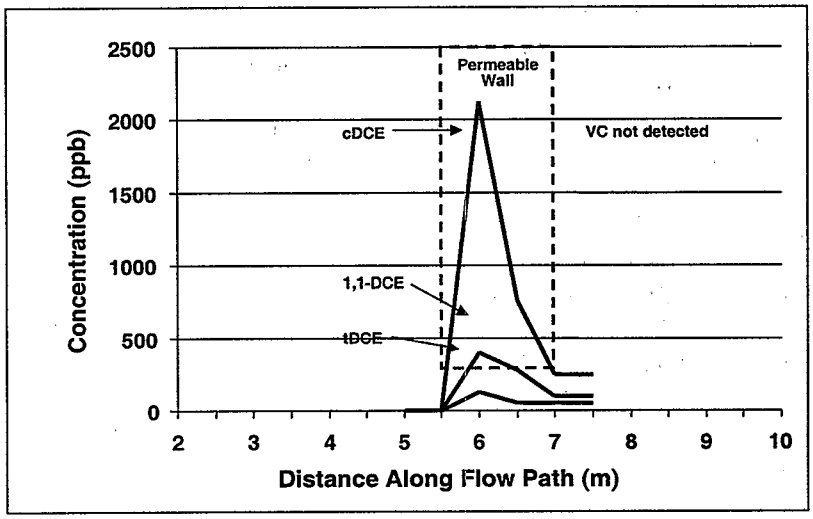
Waterloo Permeable Reactive Wall Field Trial 1991



Waterloo Permeable Reactive Wall Field Trial Results

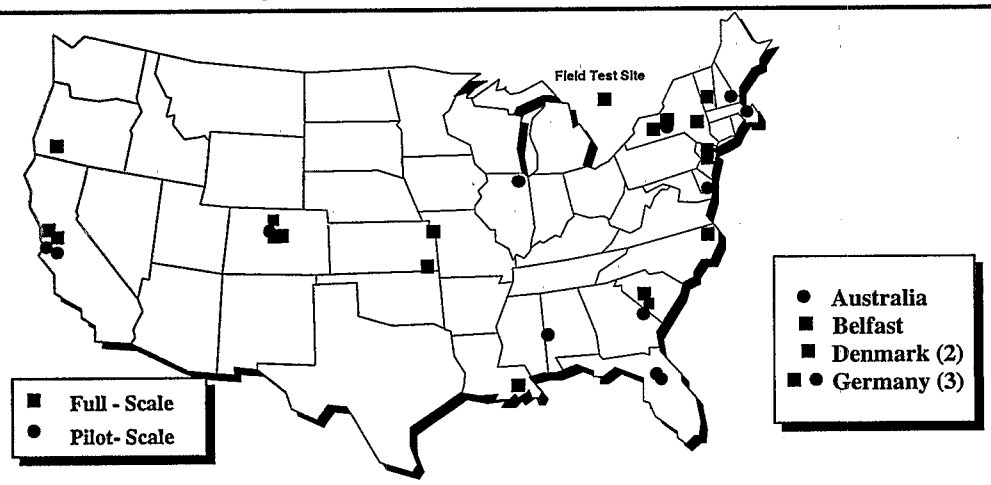
- Almost 5 years of consistent operation
- 90% TCE and 86% PCE removal
- Breakdown products (e.g., vinyl chloride) degraded
- Insignificant amounts of precipitates

sect4

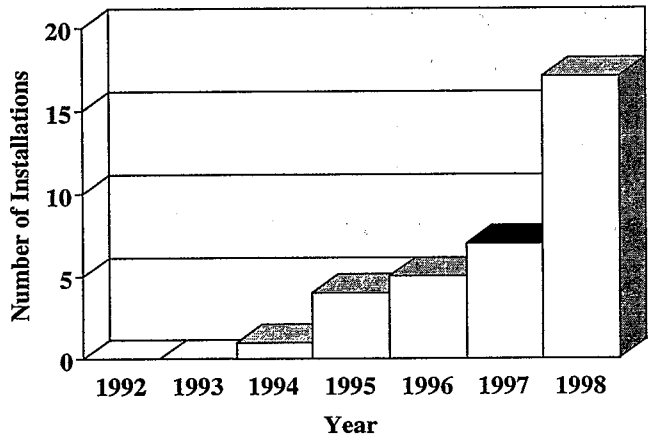
Current Status (early 1999)— PRBs for VOC Removal

- 22 full-scale systems
  - 14 private facilities
  - 3 U.S. DOD facilities
  - 2 U.S. DOE facilities
  - 3 other government facilities

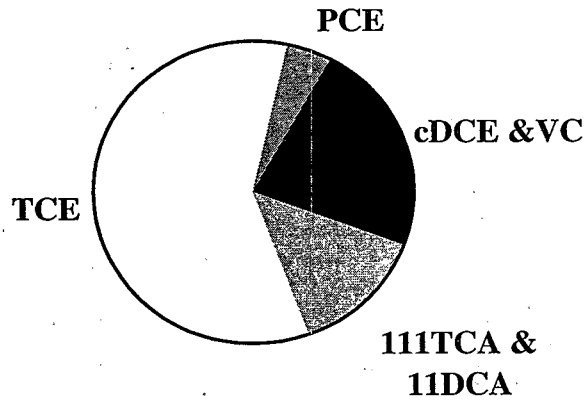
Field Projects



Technology Acceptance



Primary Contaminants Treated



sect4

Long-Term Performance Data

Organic

- Consistent VOC degradation over several years
- No evidence of microbial fouling
- No site has yet required "retrofitting" or iron replacement

Long-Term Performance Data

Inorganic

- Most carbonate precipitates occur at upgradient interface (coring evidence) or in upgradient mixed iron/gravel zones
- Accumulation of precipitates over time *may* cause porosity/permeability loss
- No evidence of hydraulic plugging due to precipitates

sect4

Trends in Field Applications

- Database degradation rates in design
- Decrease in granular iron costs
- Sand-iron mixtures to accommodate construction constraints
- Increase focus on plume characterization to minimize installation costs
- Combined PRB/natural attenuation remedies
- Sequenced PRB remedies

Technology Advancements

- Degradation/removal of other contaminants
- Enhancements to increase degradation rates
- Long-term O&M procedures
- Innovative installation techniques
- Sequenced treatment (metal/biological)
- Source zone remediation

sect4

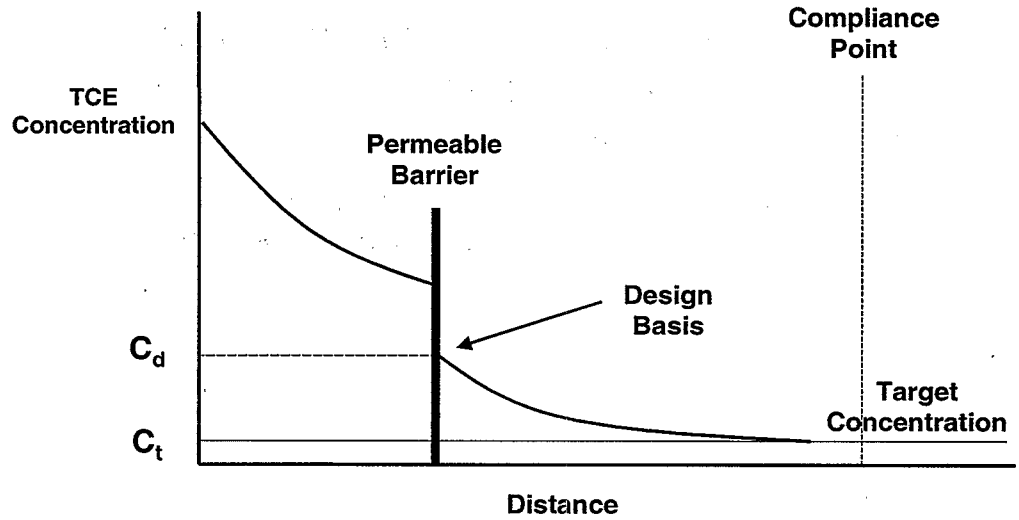
Sequenced Treatment Zones

- Combine granular iron with other in situ treatment technologies
- Key design parameter
  - the ability of the treatment technologies to accommodate geochemical changes from one treatment zone to another

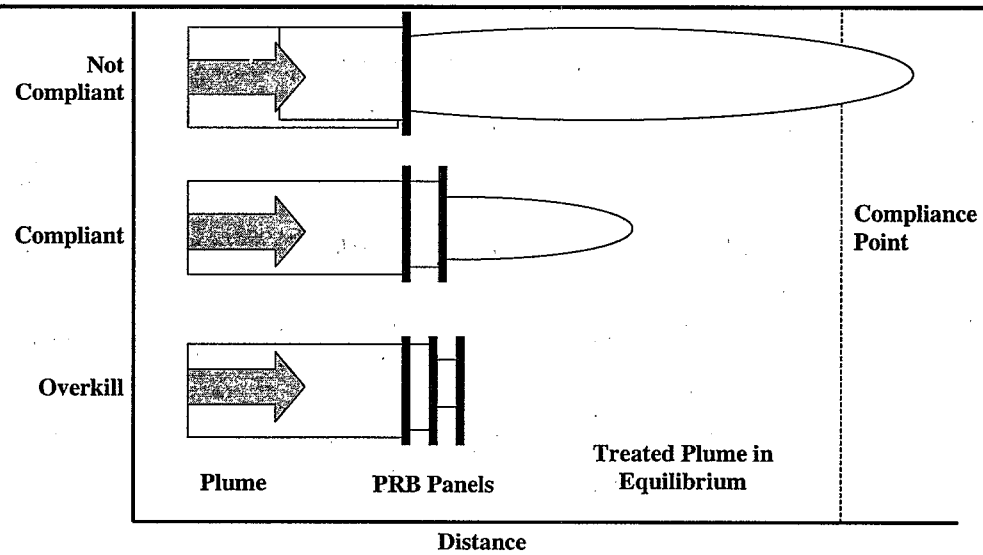
Synergy with Natural Biodegradation Processes

- Both are reductive processes
- PRB enhances reducing environment
- Understand processes and incorporate into design
- Barrier location relative to source and compliance point
- Relative reaction rates of parent and daughter products
- Take advantage of available space and residence time for natural biodegradation

Natural Biodegradation



Cost Effective Construction Scenarios



Section 5

Collection and Interpretation of Design Data II: Laboratory and Pilot Scale Tests; Design Calculations

sect5

EPA/ITRC/RTDF
Permeable Reactive Barrier Short Course

Collection and Interpretation of Design Data II:

Laboratory and Pilot-Scale Tests

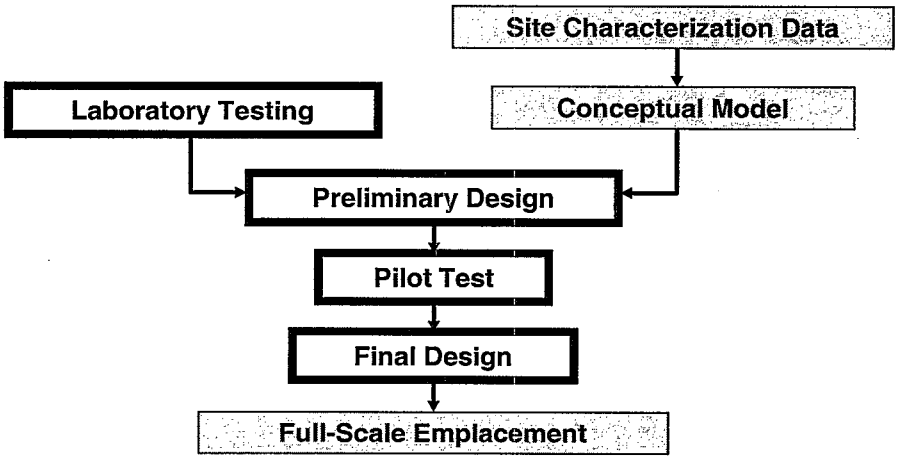
Design Calculations

RTDF Remediation Technologies Development Forum

INTERSTATE TECHNOLOGY & REGULATORY COOPERATION ITRC

EPA

Path to PRB Design and Emplacement



sect5

Why Perform Laboratory Testing?

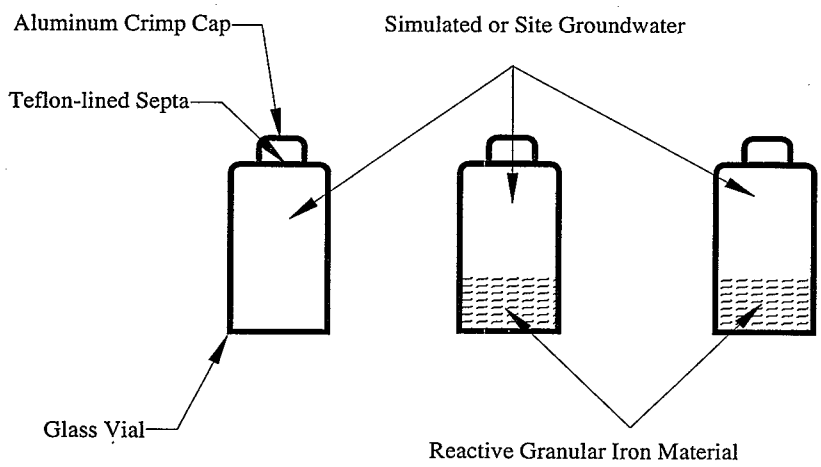
- Complex ambient water chemistry
- Atypical contaminants
  - additives
  - complex organic compounds
- Laboratory tests can be designed to confirm assumptions (i.e., inexpensive)
- Comprehensive laboratory testing can be reserved for most complex cases

Types of Laboratory Tests

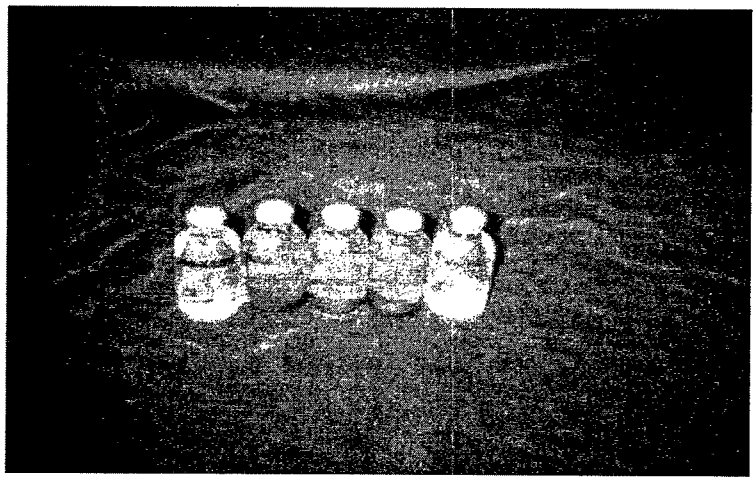
Batch Tests	Column Tests
Contaminants of unknown treatability	Contaminants known to degrade
Static conditions	Flowing conditions
Relative reactivity of different materials	Treatment rate in candidate material

sect5

Schematic of Set-Up for Batch Tests



Batch Reactivity Tests



sect5

Interpretation of Batch Test Data - VOCs

- Plot VOC concentration vs. time
- Apply first-order rate equation to calculate half-life

First Order Kinetics

$$C/C_o = e^{-kt}$$

$$\ln (C/C_o) = e^{-kt}$$

C = measured or desired concentration

C_o = initial concentration

k = first order rate constant (t^{-1})

t = time

Half-Life ($t_{1/2}$)

$$t_{1/2} = \ln(2) / k = 0.693 / k$$

- Usually expressed in units of minutes, hrs, days
- Literature values may show "normalized" k, $t_{1/2}$ (unit surface area of reactive metal/ml of water)

Bench-Scale Design Studies

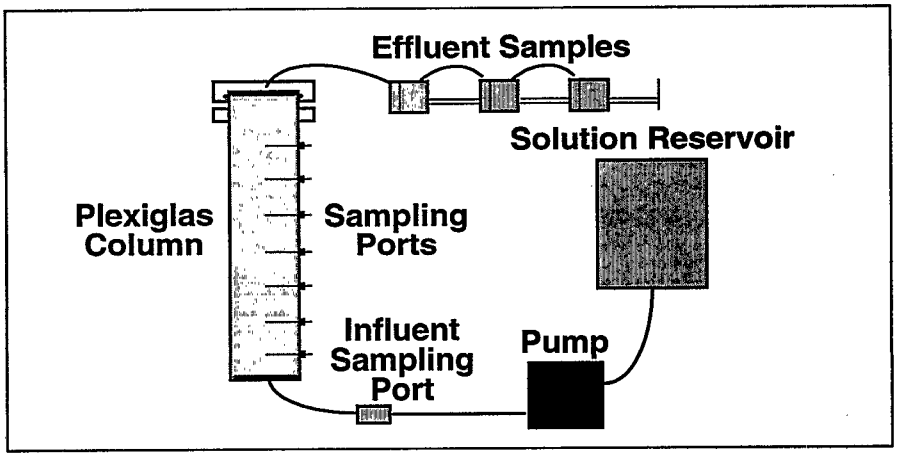
- Column tests using site groundwater
- Simulate site conditions
- Determine removal/degradation rates
- Changes in inorganic chemistry

sec15

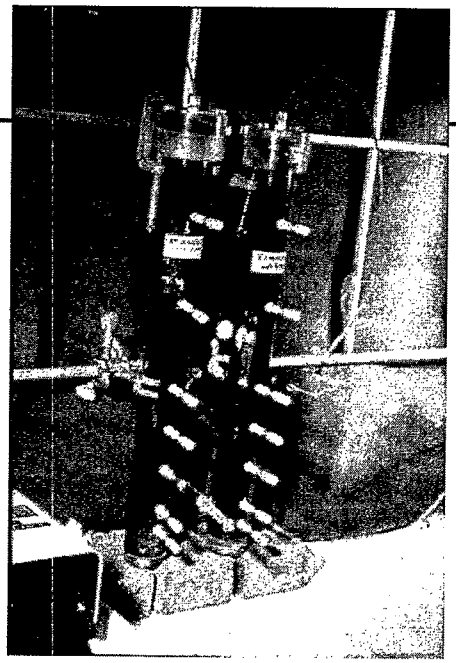
Possible Triggers For Column Studies

- Nitrate levels
- Non-chlorinated organic carbon content
- Dissolved oxygen
- DCA/DCM production
- Guar-based installation methods
- High (100s mg/L) total VOC concentrations

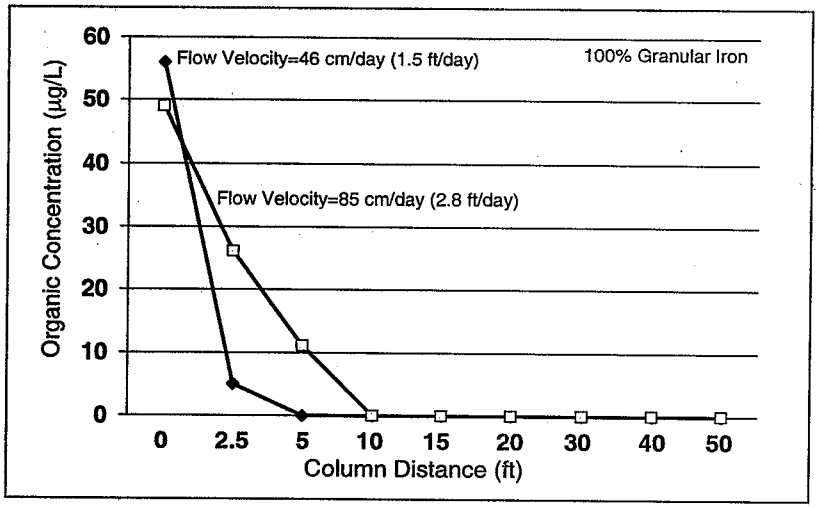
Column Treatability Study



Laboratory Column Apparatus



TCE



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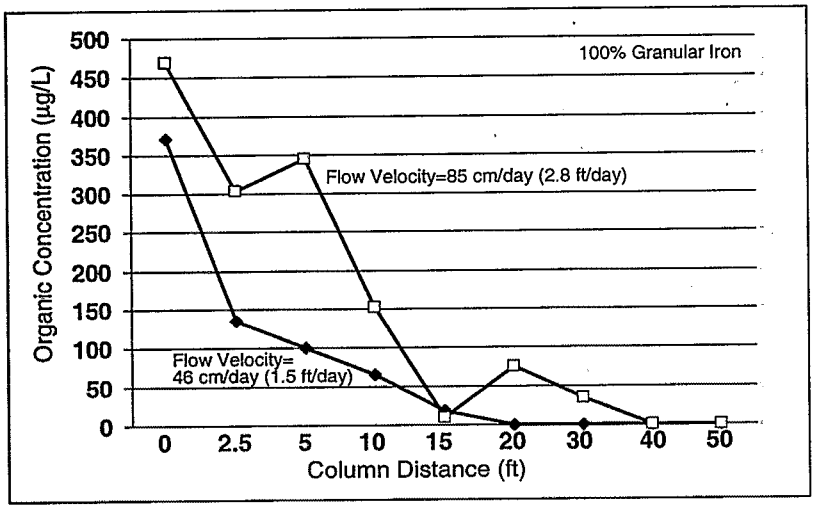
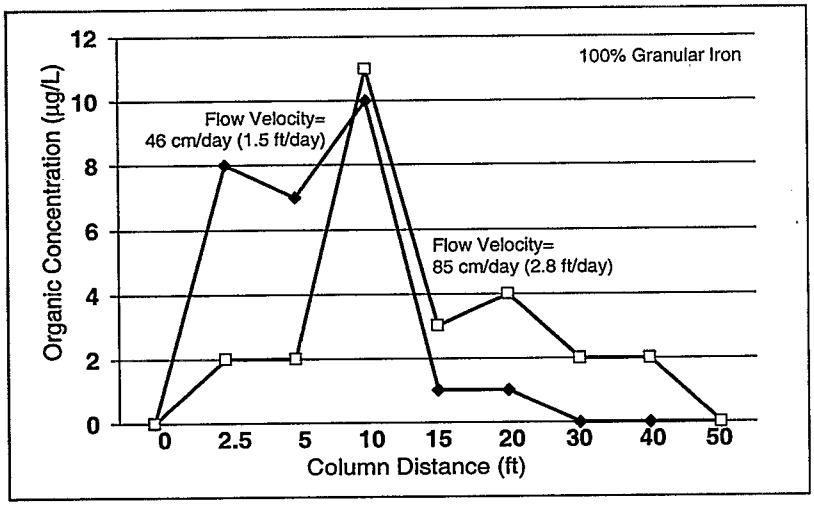
cDCE



VC



Interpretation of Column Data—VOCs

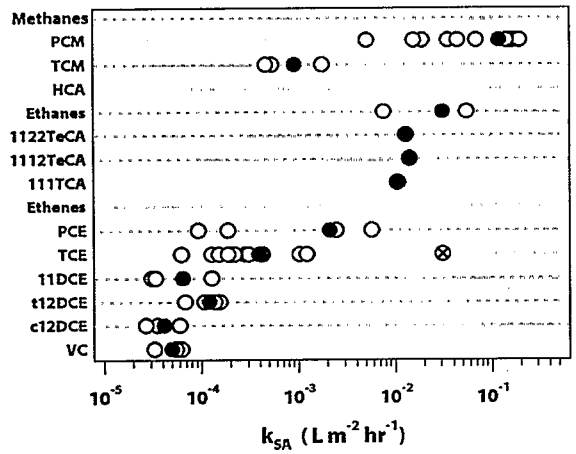
- Plot VOC concentration vs. distance along column
- Convert to concentration vs. time profiles using flow rate
- Apply first-order rate equation to calculate half-life

Column Treatability Test Results

Compound	*Typical Half-Life (hours)*	*Compound*	*Typical Half-Life (hours)*
PCE	0.5-2	CT	0.5-1
TCE	0.5-2	TCM	1-3
cis 1,2-DCE	2-6	1,1,1-TCA	0.5-2
VC	2-6		

sect5

Rate Constants for Degradation by Iron



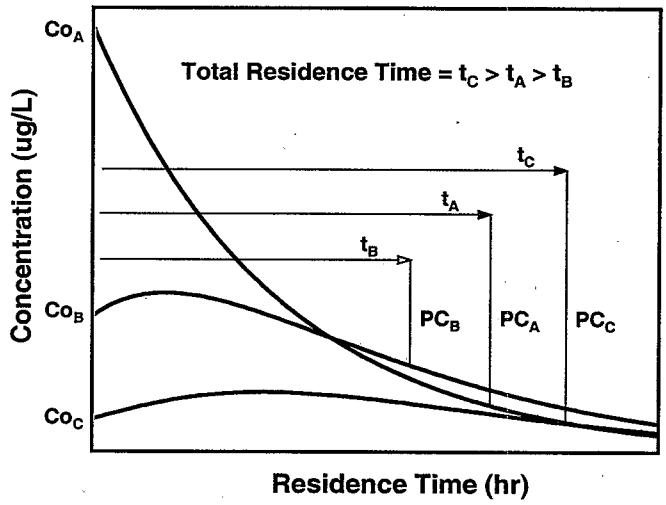
Reference: Johnson, et al., 1996, EST 30(8), 2634-2640

Residence Time Calculation—VOCs

- Assume concurrent production and degradation of each VOC in solution
- Express this concurrent production and degradation using first-order kinetic model
- Determine total residence time required
- Adjust residence times to account for lower field groundwater temperatures

sect5

Residence Time Calculation—VOCs



Co Initial Concentration
PC Performance Criteria
t Residence Time

Geochemical Modeling of Inorganic Column Data

- Assess mechanism of trace metal removal
- Examine potential precipitation/stability of various mineral phases using saturation indices
- Decline in carbonate species can be used to make (very) preliminary estimate of porosity loss over time due to carbonate precipitation

sec15

Groundwater Flow Modeling Studies

- Determine design velocity through treatment zone
- Determine length of system required to capture plume
- Assess potential for bypass/underflow

Groundwater Flow Modeling Studies

- Combine aquifer characteristics and reactive material properties
- Effects of reactive material variability
- Effects of changing material properties over time
- Permeable barrier configuration
- Identification of monitoring well locations

Groundwater Velocity through a PRB

- For a continuous wall, groundwater velocity can be approximated using the aquifer velocity:

$$V = Ki / n$$

V = groundwater flow velocity
K = hydraulic conductivity
i = hydraulic gradient
n = porosity

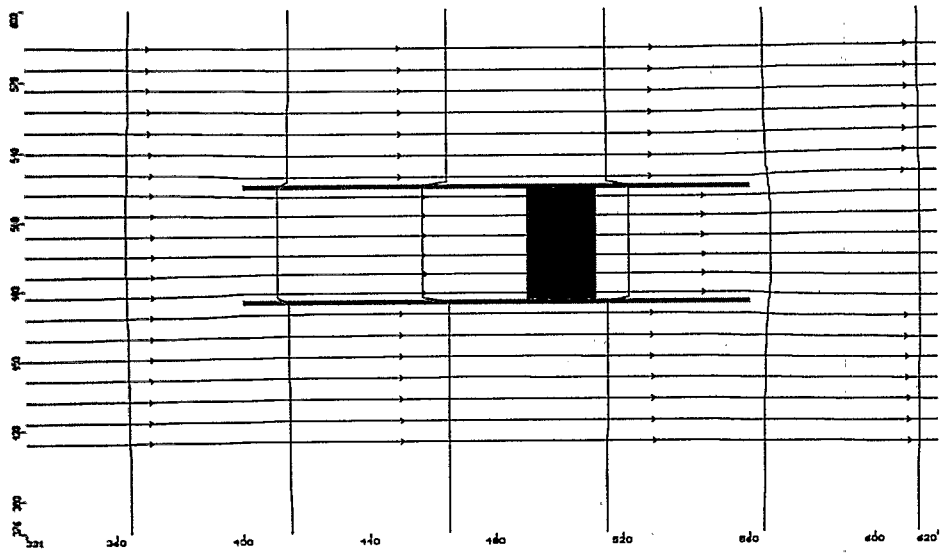
- Model simulations are likely necessary for a funnel and gate configuration

Example PRB Flow Model—Assumptions

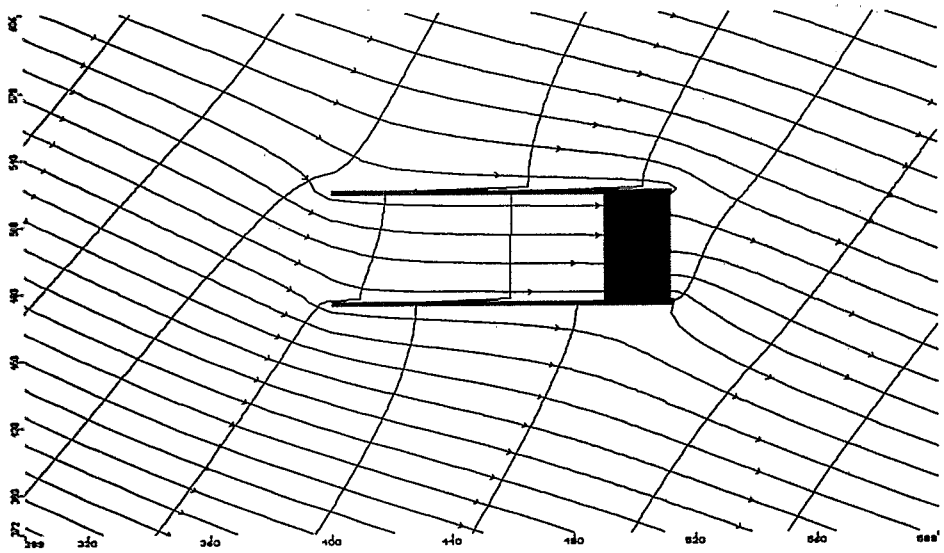
Hydraulic conductivity:

Homogeneous Aquifer:	10ft/d
Pea gravel:	500 ft/d
Iron:	50 ft/d
Hydraulic Gradient:	0.01 ft/ft
Pathline tick mark interval:	200 days
Head contour:	0.5 ft

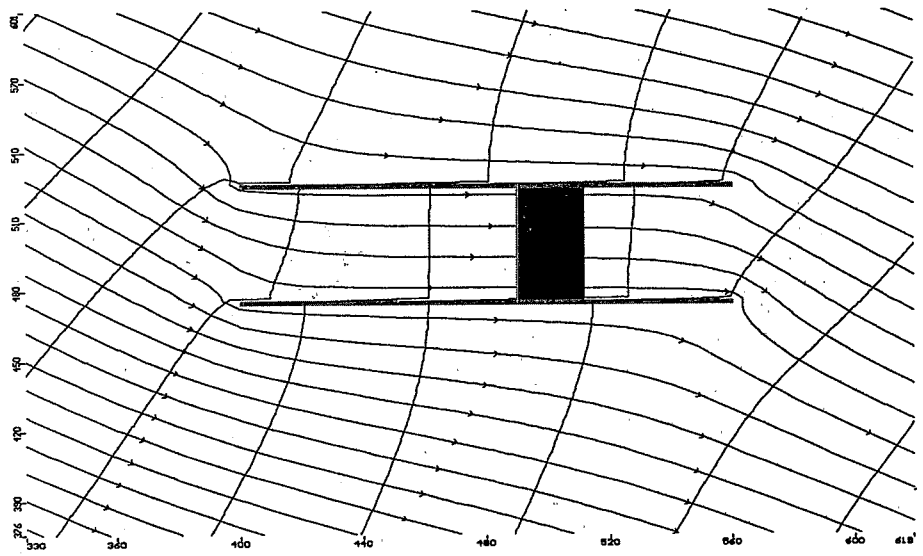
Model Results—Uniform Flow Field



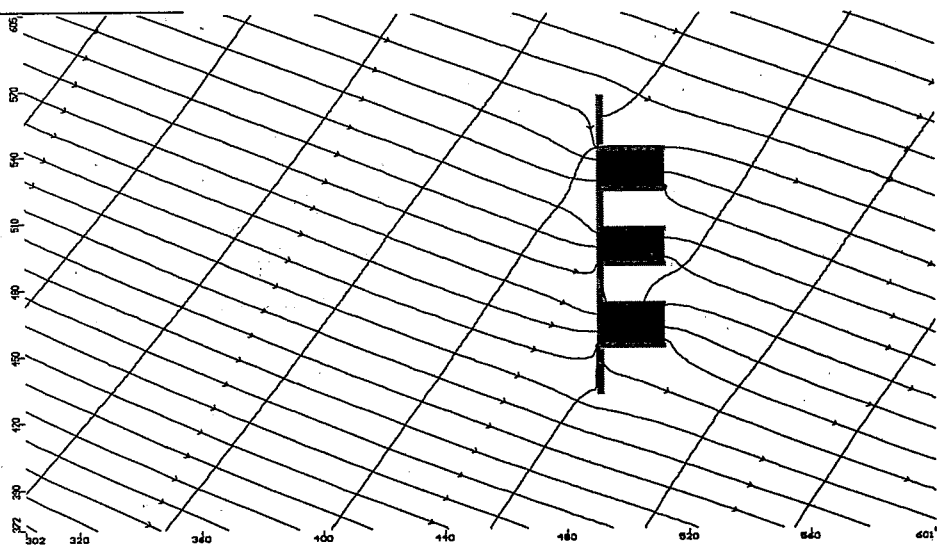
Model Results—Non-Uniform Residence Time in Gate



Model Results—Modified Gate Design

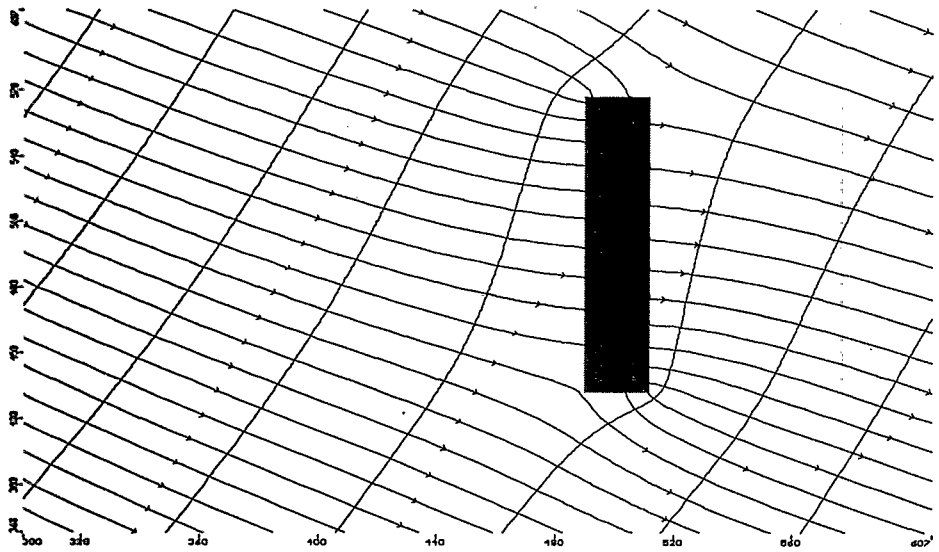


Model Results—Funnel and Multiple Gates



sect5

Model Results—Continuous Wall



Dimensions of PRB

- Residence time requirement (bench scale studies/database)
- Treatment zone flow velocity (model results)
- Thickness = residence time x groundwater velocity
- Determine length and depth of system required to capture plume, prevent underflow

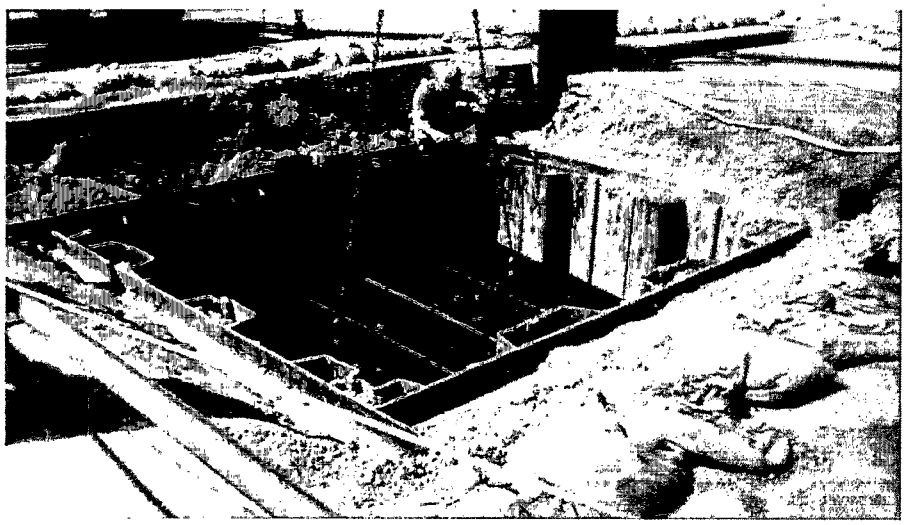
Field Applications

- Pilot-scale testing
  - at field site
  - above-ground reactor
  - small in situ system
- Full-scale implementation

Pilots Demonstrating "Proof of Concept"

- Data collection, velocity measurements, coring
- New York, 1995
- Lowry AFB, 1995
- Moffett Federal Airfield CA, 1996
- Dover AFB, DE, 1997

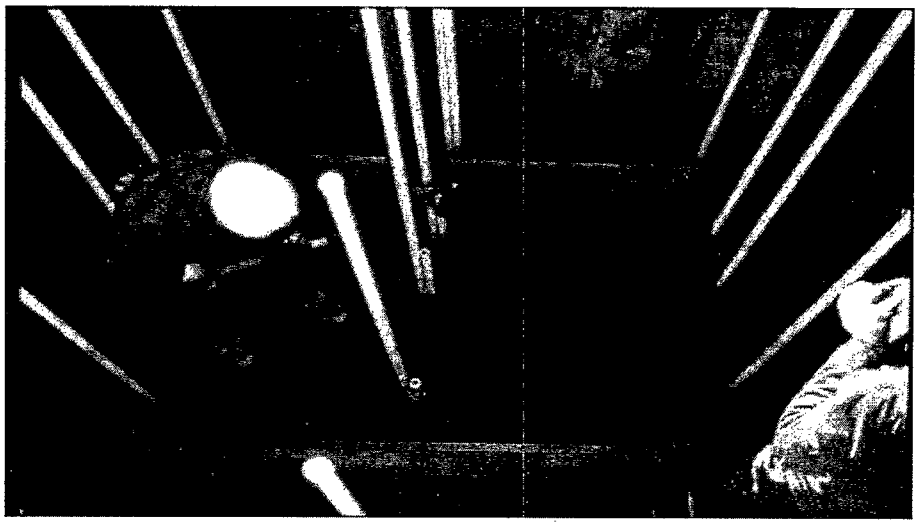
Pilot Installation—Moffett Field



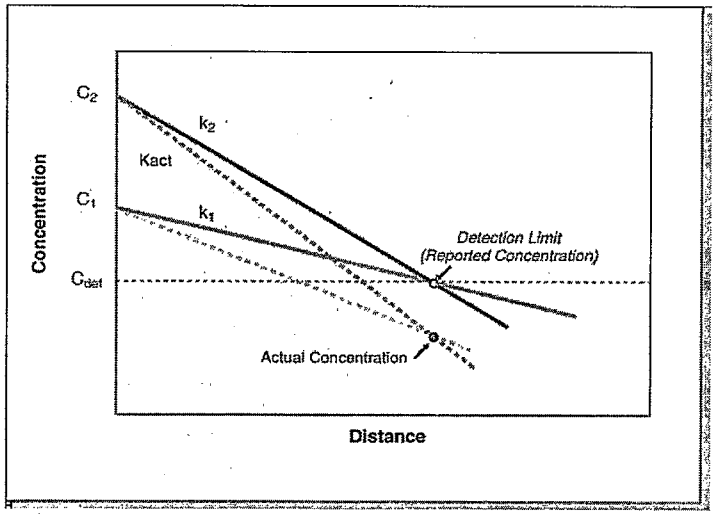
Pilot Installation—Moffett Field

sect5

Pilot Installation— Lowry Air Force Base



Uncertainty in Measured Pilot-Scale Degradation Rates



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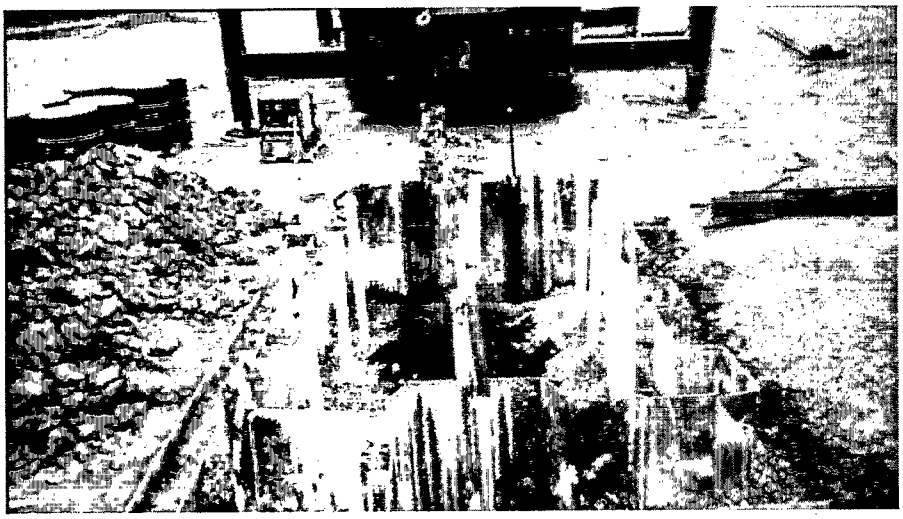
Pilot Installation—New York



Success in Meeting Regulatory Criteria

In Situ Installation, New York (May 1995)

Compound	Influent Conc. (ppb)	Downgradient Conc. (ppb)
TCE	32 - 330	< 1 - 1.6
cDCE	98 - 550	< 1 - 7.6
VC	8.1 - 79	< .5 - 1.2

sect5

Pilot-Scale Degradation Rates

In Situ Installation, New York (May 1995)

Compound	Predicted Half Life[a] (hr)	Observed Half Life[b] (hr)
TCE	0.4 to 1.1	< 4.0
cDCE	1.5 to 4.0	3.0 to 5.0
VC	2.0 to 6.0	5.0 to 10.0

[a] from laboratory studies

[b] two point curves using detection limit as second point and measured field velocity

Full-Scale Design and Implementation

- Is a pilot needed?
- Is model refinement needed?
- Hydraulic and geochemical characterization along line of installation
- Choice of construction method vs PRB dimensions

Section 6

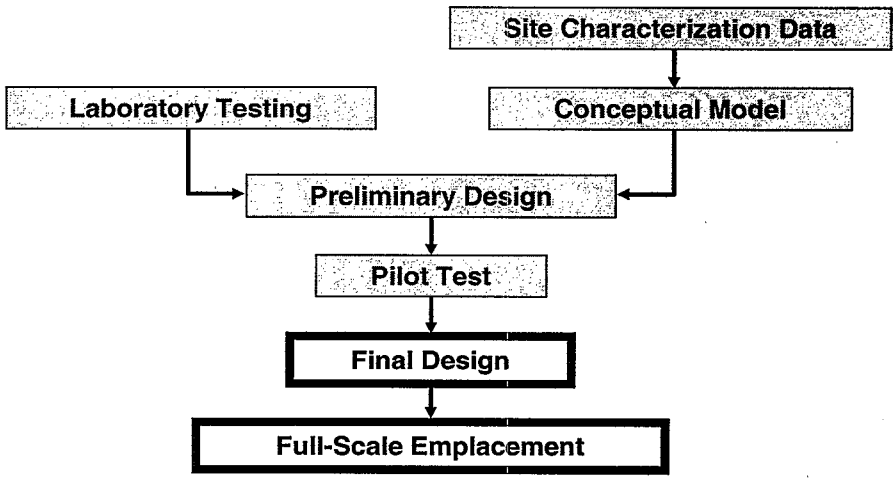
Compliance Monitoring, Performance Monitoring, and Long-Term Maintenance for PRBs

sect6

EPA/ITRC/RTDF
Permeable Reactive Barrier Short Course

Compliance Monitoring, Performance Monitoring and Long-Term Maintenance for Permeable Reactive Barriers

Path to PRB Design and Emplacement



sect6

Compliance Monitoring

- Objective
  - determine compliance with the applicable groundwater standard or criteria
- Regulatory requirements for monitoring
- Focus is on the site and compliance point

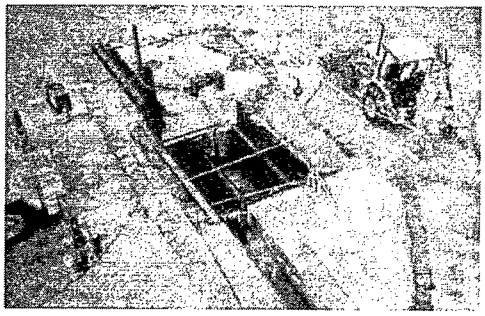
Procedure

- Identify groundwater standard/criteria
- Develop monitoring network based on groundwater modeling
- Determine compliance points/wells
- Prepare monitoring plan/QAPP
- Monitor for compliance with standard

Monitoring Well Construction Methods

- Aquifer wells
  - follow state-specific requirements for installation
- Wells within or near the PRB
  - small-diameter wells (1-2" wells)
  - typically no sand pack or grout required
  - installation
    - suspended in reactive media prior to backfilling
    - pushed or drilled into the reactive media

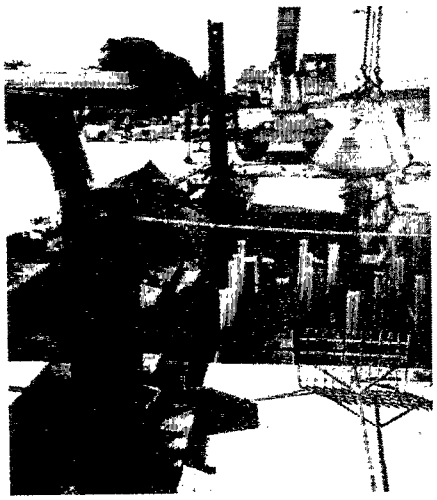
Installation of Monitoring Wells



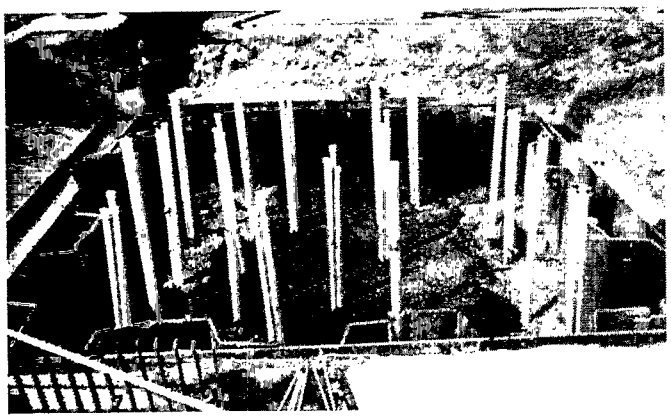
Pilot Permeable Reactive Barrier
Moffett Federal Airfield

sect6

Monitoring Well Placement at Moffett Field



Monitoring Well Placement at Moffett Field



Sampling

- Representative samples require special procedures
- Retention time within PRB cannot be compromised
- For all wells—low-flow sampling procedure recommended
- For wells within or near the PRB—low-flow sampling and collection of smaller sample volumes is necessary

Low-Flow Sampling

- Benefits for PRB
  - lower purge volume, slower rate
  - representative samples of mobile fraction within groundwater
  - retention time within PRB unaffected
  - more "passive" sampling method

sect5

Low-Flow Sampling Procedure

- Use of peristaltic, low-speed submersible or bladder pumps
- Continuous monitoring of water quality parameters
  - dissolved oxygen
  - specific conductance
  - redox potential
  - turbidity
  - pH
  - temperature
- Sample collected upon equilibration of parameters
  - ±10 percent for DO and turbidity
  - ±3 percent for conductance
  - <0.3 feet groundwater drawdown
- Typical purge rate 100-500 mL/min

Monitoring Frequency Considerations

- Groundwater flow velocity
- Reactive media residence time
- Contaminants of concern
- Fluctuation in contaminant concentration
- Location and placement of PRB
- Seasonal fluctuations in groundwater elevation

Monitoring Frequency

- First quarter after installation
  - monthly monitoring—analytical and field parameters
  - weekly monitoring—groundwater levels
- Initial monitoring program (1-2 years)
  - quarterly monitoring—analytical and field parameters
  - monthly monitoring—groundwater levels
- Long-term monitoring
  - Frequency of monitoring can be reduced based on operational stability
- Post-closure monitoring
  - monitoring for leachable constituents of reactive media or contaminants of concern

Monitoring Frequency

- Dependent on groundwater velocity and groundwater modeling
- After installation an equilibrium period may occur during which data may not represent the steady state monitoring conditions of the PRB
- Periodic evaluation and adjustment of monitoring program should be conducted

Monitoring Frequency

Suggested Permeable Reactive Barrier Monitoring Frequency For Inorganics and Radionuclide Contamination

Parameter	Frequency
A - First Quarter After Installation	
Field Parameters	Monthly
Inorganic Analytes***	
Inorganic Contaminants	
Radionuclides	
Groundwater Levels	Weekly (until equilibrium is reached)
B - Initial Monitoring Program (1 - 2 years)	
Field Parameters	Quarterly
Inorganic Analytes***	
Inorganic Contaminants	
Radionuclides	
Groundwater Levels	Monthly, then to be determined
C - Long Term Monitoring	
Field Parameters	Quarterly (may be modified based on performance)
Inorganic Analytes***	
Inorganic Contaminants	
Radionuclides	
Groundwater Levels	
D - Post-Closure Monitoring	
Inorganic Contaminants of Concern	To be determined based upon the closure method and data collected during operation of the PRB
Leachable Constituents from Reactive Media	
Radionuclides of Concern	

Suggested PRB Monitoring Frequency For Chlorinated Solvent Contamination

Parameter	Frequency
A - First Quarter After Installation	
Field Parameters	Monthly
Organic Analytes	Monthly
Inorganic Analytes	Monthly
Groundwater Levels	Weekly (until equilibrium is reached)
B - Initial Monitoring Program (1 - 2 years)	
Field Parameters	Quarterly
Organic Analytes	Quarterly
Inorganic Analytes	Quarterly
Groundwater Levels	Monthly, then to be determined
C - Long Term Monitoring	
Field Parameters	Quarterly (may be reduced based upon operational stability)
Organic Analytes	
Inorganic Analytes	
Groundwater Levels	
D - Post-Closure Monitoring	
Inorganic Parameters (Fe & other leachable constituents)	To be determined based upon data collected during operation

Monitoring Parameters

Field and Laboratory Parameters

Analyte or Parameter	Analytical Method	Sample Volume [b]	Sample Container	Preservation	Sample Holding Time
Field Parameters					
Water Level	In-hole Probe	None	None	None	None
pH	In-hole Probe or Flow-thru Cell	None	None	None	None
Groundwater temperature	In-hole Probe	None	None	None	None
Redox Potential	Flow-thru Cell	None	None	None	None
Dissolved Oxygen	Flow-thru Cell [a]	None	None	None	None
Specific Conductance	Field Instrument	None	None	None	None
Turbidity	Field Instrument	None	None	None	None
Salinity	Field Instrument	None	None	None	None
Organic Analytes					
Volatile Organic Compounds (VOCs) [c]	USEPA SW846, Method 8240	40 mL	Glass VOA vial	4°C, pH<2	14 Days
				No pH adjustment	7 Days
	USEPA SW846, Method 8260a or b	40 mL	Glass VOA vial	4°C, pH<2	14 Days
				No pH adjustment	7 Days
	40 CFR, Part 136, Method 624	40 mL	Glass VOA vial	4°C, pH<2	14 Days
				No pH adjustment	7 Days
Inorganic Analytes					
Metals [d]: K, Na, Ca, Mg, Fe, Al, Mn, Ba, V, Cr^{+3}, Ni	40 CFR, Part 136, Method 200.7	100mL	Polyethylene	4°C, pH<2, (HNO_3)	180 days
Metals: Cr^{+6}	40 CFR, Part 136, or HACH method	200ml	Glass, Plastic	4°C	24 hours
Anions: SO_4, Cl, Br, F	40 CFR, Part 136, Method 300.0	100mL	Polyethylene	4°C	28 days
NO_3	40 CFR, Part 136, Method 300.0	100mL	Polyethylene	4°C	48 hours
Alkalinity	40 CFR. Part 136, Method 310.1	100mL	Polyethylene	4°C	14 days
Other					
TDS	40 CFR, Part 136, Method 160.2	100 mL	Glass, Plastic	4°C	7 days
TSS	40 CFR, Part 136, Method 160.1	100 mL	Glass, Plastic	4°C	7 days
TOC	40 CFR, Part 136, Method 415.1	40 mL	Glass	4°C, pH <2 (H_2SO_4)	28 days
DOC	40 CFR, Part 136, Method 415.1	40 mL	Glass	4°C, pH <2 (H_2SO_4)	28 days
Radionuclides					
Field Screening	HPGe gamma spectroscopy	None	None	None	None
	FIDLER				
Gross α / Gross β activities (screening)	Gas Proportional Counting	[e] 125 ml	[e] polyethylene	[e] pH<2, (HNO_3)	[e] N/A
Specific Isotopes (Am, Cs, Pu, Tc, U)	Alpha Spectroscopy	[e] 4 L	[e] polyethylene	[e] pH<2, (HNO_3)	[e] 6 months
	Gamma Spectroscopy				

[a] - If <1.0 mg/L use photometric field kit for analysis.
[b] - See Section 7.4 (Sampling) of this report for variances in sample volumes.
[c] - GC methods may be substituted once identity of compounds and breakdown products are verified.
[d] - Other metals analytes which are characteristic of the media should be included.
[e] - General guidelines, the parameter is a laboratory specific parameter.

sect6

Compliance Monitoring Parameters

- Field parameters—pH, temperature, redox potential, dissolved oxygen, conductance, turbidity, salinity, groundwater level
- Organic analytes (as necessary)
- Inorganic analytes (as necessary)
- Radionuclides (as necessary)

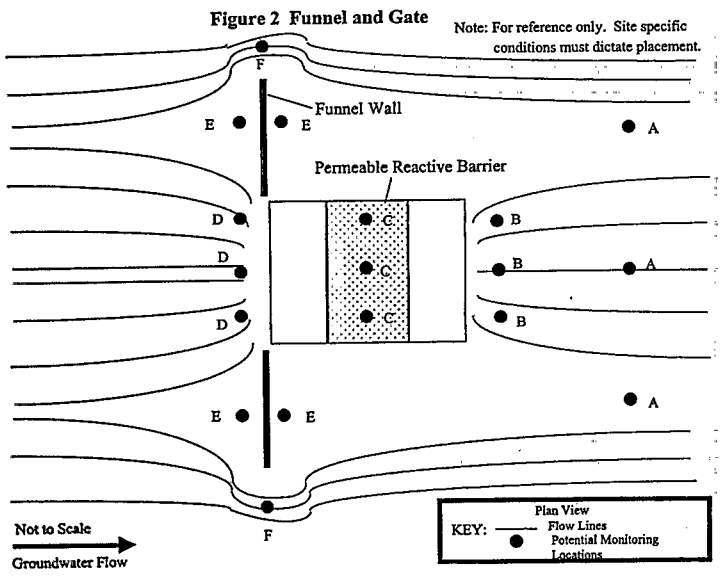
Monitoring Well Placement

- Groundwater modeling will determine the placement and the number of monitoring wells required
- Wells may need to be installed in different water-bearing units or at multiple levels within the same water-bearing zone
- Dependent on configuration of PRB (i.e., funnel and gate vs. continuous wall)
- Negotiations between involved parties

General Guidelines for Well Placement

- Upgradient of PRB
- Downgradient of PRB
- Sidegradient of PRB
- Possible within PRB (if PRB installed within a plume)

Hypothetical Example of Monitoring Well Placement



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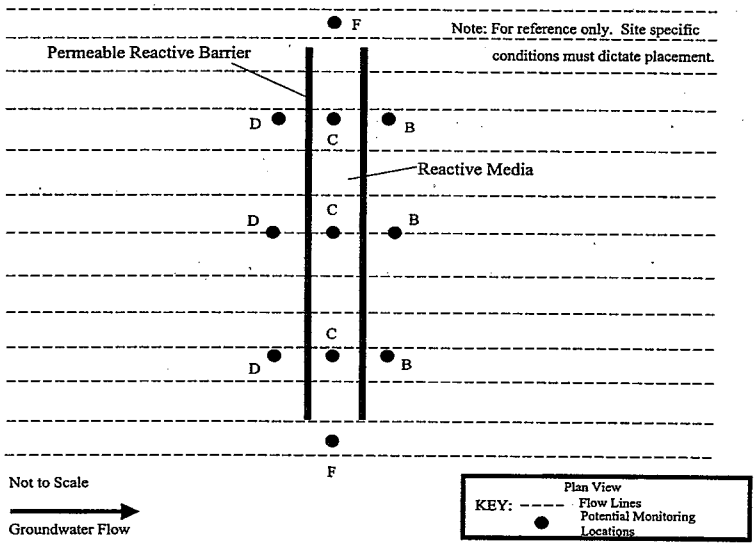
Hypothetical Example of Monitoring Well Placement (cont.)

Figure 3 Continuous Wall



Performance Monitoring

- Verification of performance of wall as designed
  - also an element of QA for installation/emplacement
  - verification of achievement of intended hydrogeochemistry
- Focus is on the wall itself, not the site or compliance points or boundaries
  - early warning for decrease in wall performance
- Not typically considered regulatory monitoring requirements

sect6

Performance Monitoring—Extent/Scope

- Duration and extent of monitoring determined by:
  - site-specific hydrogeochemistry
  - performance sampling objectives
  - negotiations among involved parties
  - current status of specific barrier technology development, maturity

Performance Monitoring—What

- Changes in system reactivity
- Changes in site and reactive wall hydraulics over time
- Changes in contaminant residence time
- Short circuiting

Performance Monitoring

- Reactivity
  - collection of core samples of the reactive media
  - analysis of emplaced iron over time
    - surface precipitates

SEM Photo–Iron Surface

Precipitation of Oxides on Iron

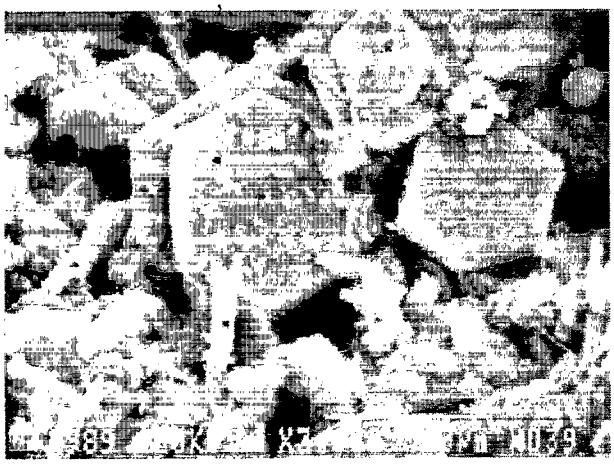


Figure Courtesy P. Tratnyek, Oregon Graduate Institute

Performance Monitoring

- **Hydraulics**
  - **head measurements**
  - **tracer tests (research)**
  - **in situ flow meters**

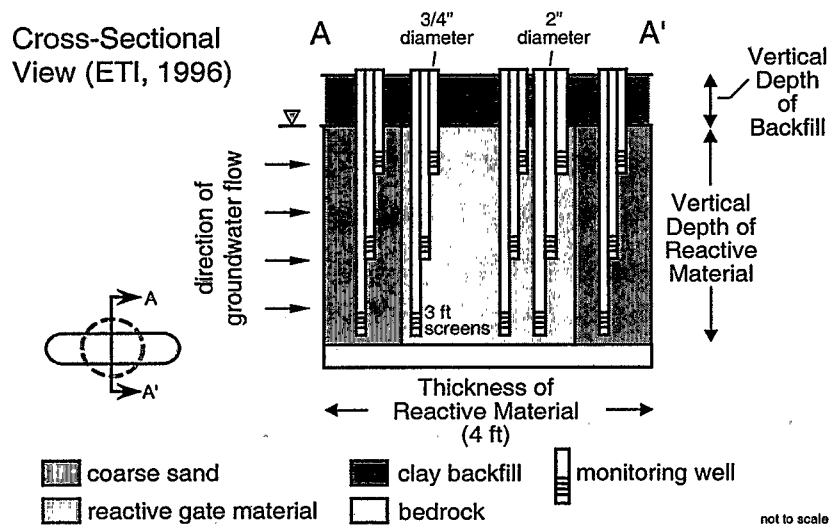
Performance Monitoring

- Contaminant degradation/transformation
  - contaminants of concern and by-products
- Geochemical indicator parameters
  - pH, redox potential, DO, ferrous iron, sulfide, alkalinity
  - cheap, inexpensive field tests

Multi-level Sampling

- High resolution of vertical distribution of contaminants and other water quality data
- "Passive" sampling of groundwater necessary
- Identify short circuiting or changes in residence time affecting contaminant removal
- Effective for tracer testing

Design Plan for the Permeable Barrier Installed at the Somersworth Sanitary Landfill, NH



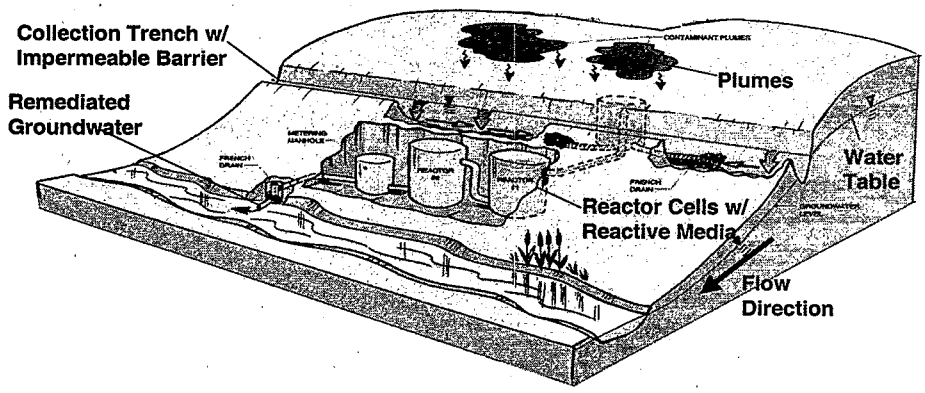
Long-Term Maintenance

- Development of operation and maintenance plan as well as a closure plan is essential
- Contingency sampling plan necessary in the event the PRB fails to meet performance or compliance criteria
- Reactive media restoration or replacement

Long-Term Maintenance— Hydraulic Considerations

- Accumulation of precipitates over time may cause porosity/permeability reduction
- Carbonate precipitates occur at upgradient interface (coring evidence)
- Iron (oxy) hydroxides form on iron surface
- Microbial fouling
- To date, no evidence of hydraulic plugging due to precipitates or fouling

Passive Collection with Reactor Cells



USDOE Rocky Flats Mound Site Plume, Tetra Tech EM, Inc. 1998

sect6

Operations and Maintenance

- Rejuvenation technology is in development stage
- May consist of mechanical restoration or replacement of affected section
- Ultrasound techniques
- A lump sum cost could be budgeted into O&M once every 5–10 years

Considerations in PRB Maintenance and Closure

- Loss of permeability through the reactive media
- Contaminant desorption from reactive media
- Potential for spent reactive material to provide a future contaminant source
- Concentrations of contaminants (metals or radionuclides) in reactive media affect disposal options
- Reaching capacity of the reactive media

Considerations in PRB Maintenance and Closure (continued)

- Future use of property
- Cost of removal vs. long-term operation and maintenance
- Regulatory requirements for closure
- Non-contaminant changes in downgradient water quality
- The potential need for institutional controls

Performance Monitoring/ Long-Term Maintenance

- Scope and extent of performance monitoring expected to decrease with increasing acceptance of technologies
- Long-term maintenance requirements current subject of intensive research

Section 7

PRB Emplacement Techniques

EPA/ITRC/RTDF
Permeable Reactive Barrier Short Course

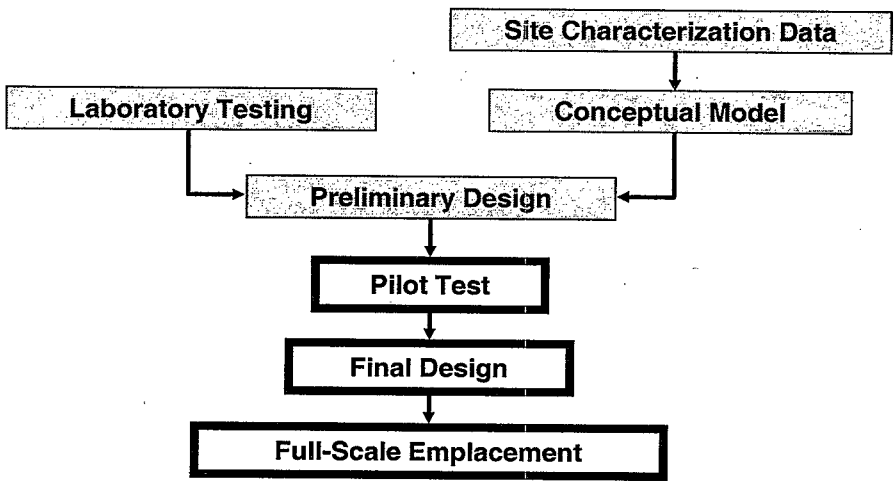
PRB Emplacement Techniques

RTDF
Remediation Technologies Development Forum

INTERSTATE TECHNOLOGY REGULATORY COOPERATION ITRC

EPA

Path to PRB Design and Emplacement



sect7

Overview

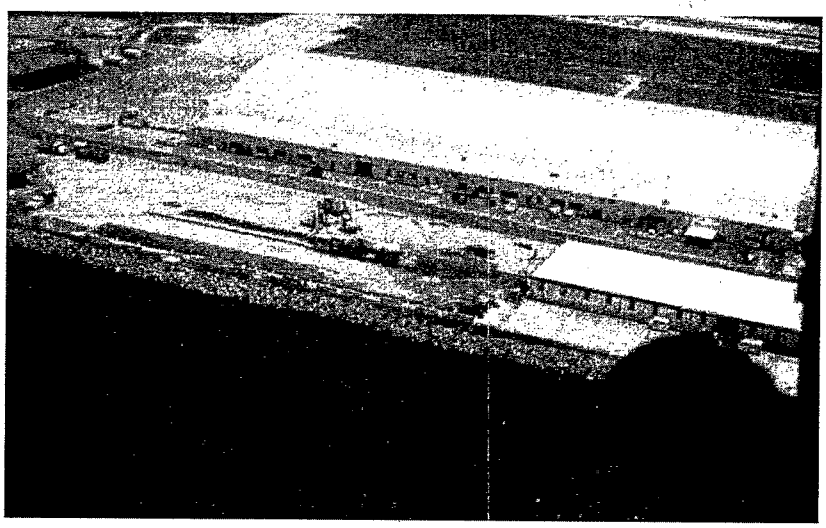
- Current emplacement methods
- Recent emplacement advances

Permeable Barrier Configurations

- Continuous reactive wall
- Funnel and gate
- Alternative designs
  - in situ reactor
  - GeoSiphon cell (WSRC)

Continuous Reactive Walls

- Wall of reactive material extends across entire plume
  - continuous zone of reactive material
  - no impermeable sections
  - little disturbance of groundwater flow

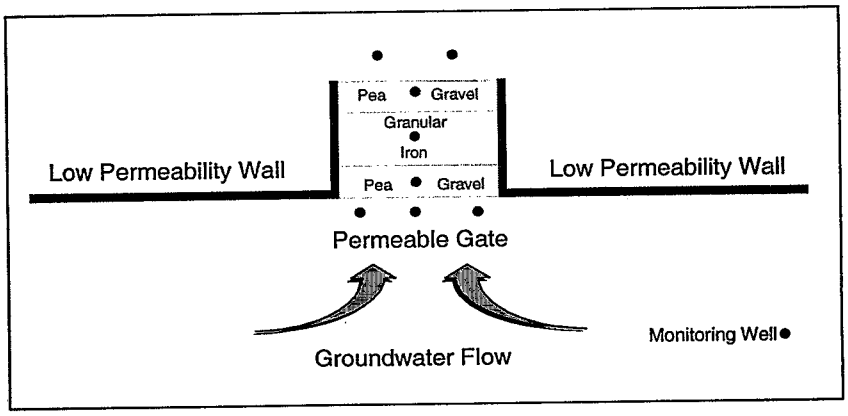


sect7

Funnel and Gate

- Low permeability funnel
  - potential for flow around and beneath system
- Permeable treatment gate
  - higher velocity created in treatment zones
  - well-defined treatment zone facilitates monitoring

Conceptual Funnel and Gate



sect7

Comparison of Treatment Systems

	Continuous Wall	Funnel and Gate
Volume reactive material	Large	Limited
Residence time	Greater	Less
Flow system disturbance	Small	Large
Monitoring zone	Large	Small

Full-Scale Systems

- 15 continuous reactive walls
  - cofferdam (6)
  - trenching machine (8)
  - hydrofracturing (1)
- 5 funnel and gate systems
  - slurry wall (3)
  - sheet piling (1)
  - HDPE (1)
- 2 in situ reaction vessel systems

Full-Scale Treatment Systems

Continuous Wall

- Sunnyvale, CA
- Sunnyvale, CA
- Elizabeth City, NC
- South Carolina
- New York
- Superfund Site, NJ
- Kansas City, MO
- Denmark (2)
- Fairfield, NJ
- Watervliet, NY
- Sumter, SC
- Louisiana
- Seneca, NY
- Germany

Funnel & Gate

- Coffeyville, KS
- Lakewood, CO
- Colorado
- Oregon
- Vermont

Other

- Northern Ireland
- RFETS, CO

Example Site

100 ft. long, 30 ft. deep, 1.8 ft.flow-through thickness

Construction Method (unit cost)	Mobilization	Construction	Iron	Total
1993 Funnel and Gate (sheet pile funnels)	$50,000	$175,000	$312,000	$537,000
Continuous Trencher ($500/linear feet)	$75,000	$50,000	$189,000	$314,000
Vibrated Beam/Mandrel ($10/sq ft)	$75,000	$120,000	$189,000	$384,000
Jetting ($40 /sat sq ft)	$50,000	$110,000	$189,000	$349,000
Bioslurry Trench ($10/sq ft)	$50,000	$30,000	$189,000	$269,000

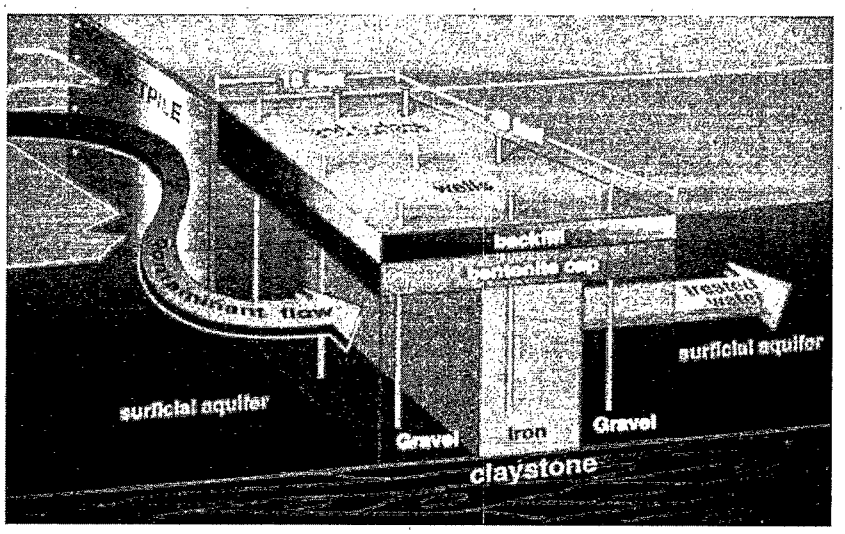
Notes: Unit costs are based on discussions with contractors (trencher, mandrel) or reported literature values (letting Bioslurry trench)

sect7

Case Studies Illustrating Design/Emplacement Issues

1) Funnel and gate, sheetpiling
2) Continuous wall, trencher
3) Continuous wall, hydrofracturing
4) Continuous wall, jetting

Denver Fed Center



Site Design Summary
In-situ System, FHA Facility, CO (Oct/96)

Impermeable Zone
- 1,040 ft total length

Treatment Zone:
- 4 treatment zones
- 40 ft wide (each), 20 ft depth
- 5 to 10 ft saturated thickness

Influent Groundwater
- TCE and DCE isomers
- (≤ 700 ppb), VC (≤ 15 ppb)

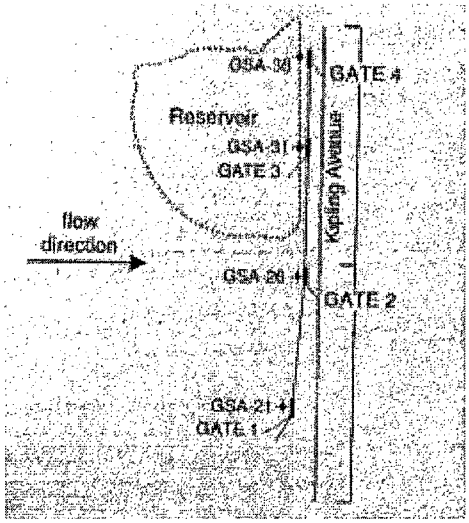
Cost	
Construction	*$675,000*
Granular Iron	*$225,000*
Total	*$900,000*

Site Design Summary
In-situ System, FHA Facility, Co (Oct/96)

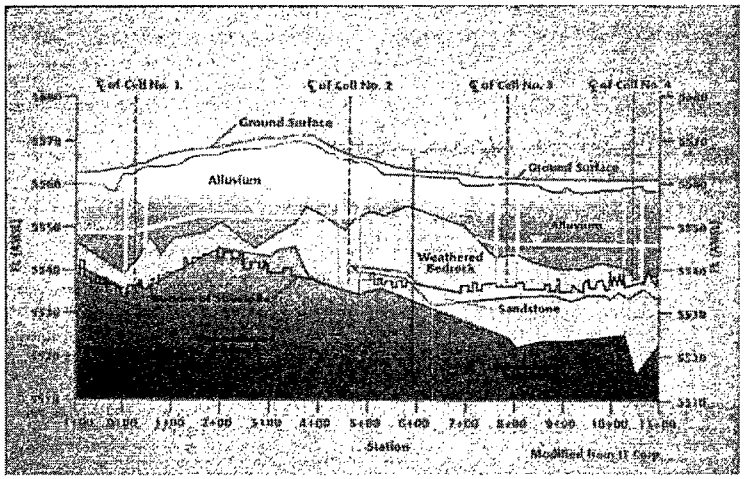
Construction
- Lateral variation in concentration and velocity used to minimize iron costs
- Sheet pile "funnel" installation difficult due to lithology
- "Fast track" implementation schedule

sect7

Permeable Reactive Barrier Configuration
FHA Facility, Colorado



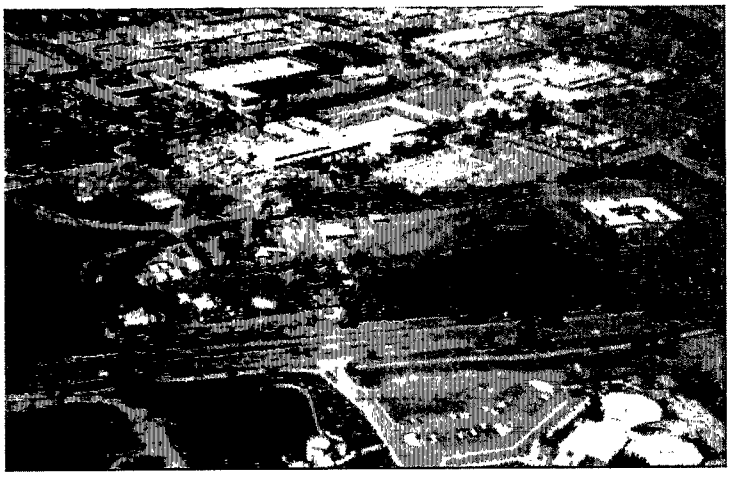
South-North X-Section



Primary Groundwater Contaminants at PRB

1,1,1-TCA	200 μg/L
1,1-DCE	230 μg/L
TCE	600 μg/L
cis-DCE	170 μg/L
vinyl chloride	16 μg/L

Boundary of DFC
Looking to the West



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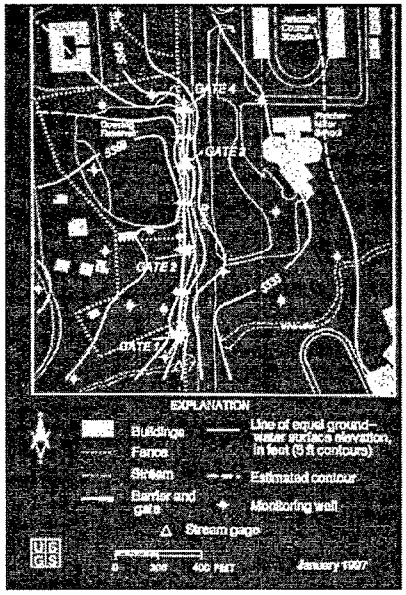
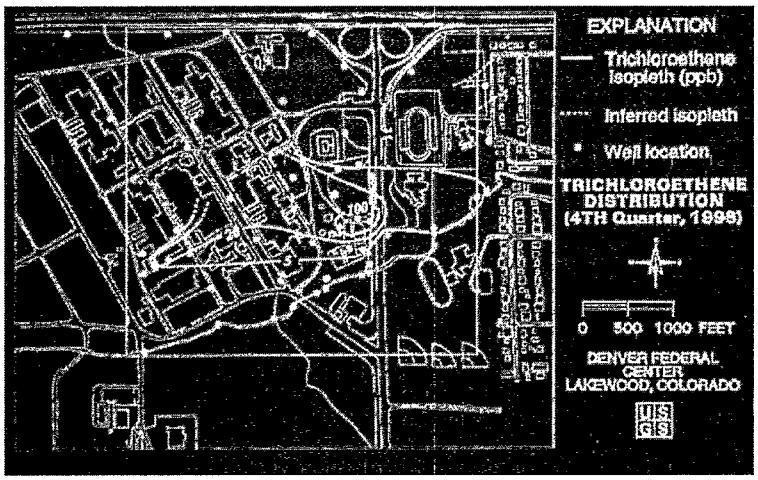
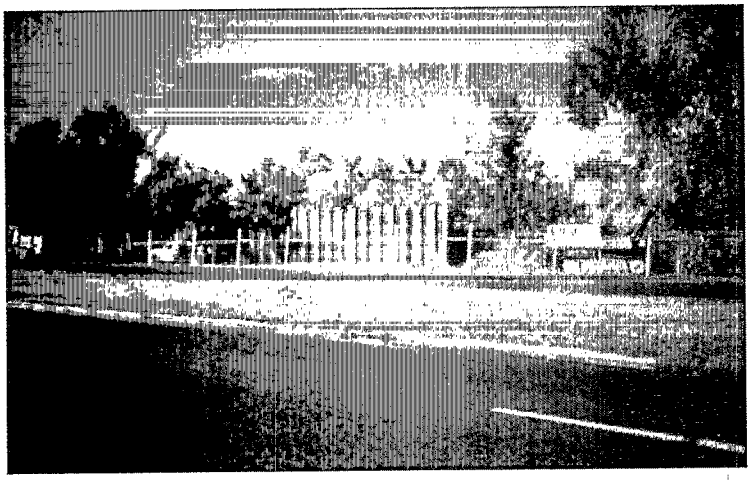
Denver Federal Center–Ground Water Contours



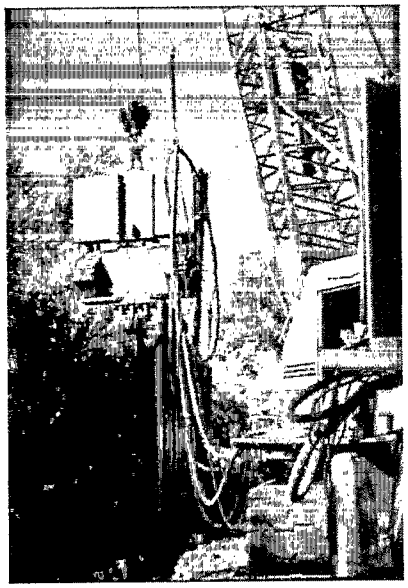
Denver Federal Center–TCE Contours



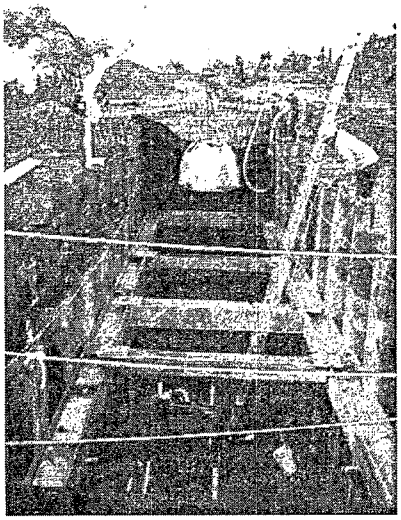
Denver Federal Center–Sheet Pile Installation



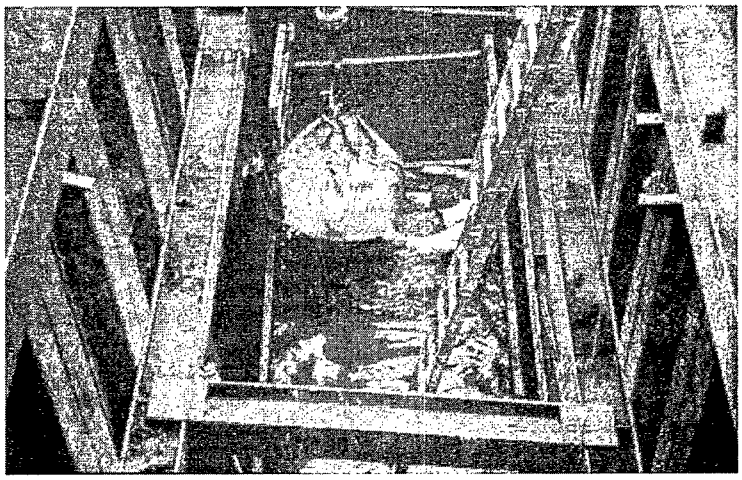
Vibratory Hammer Driving Sheet Pile



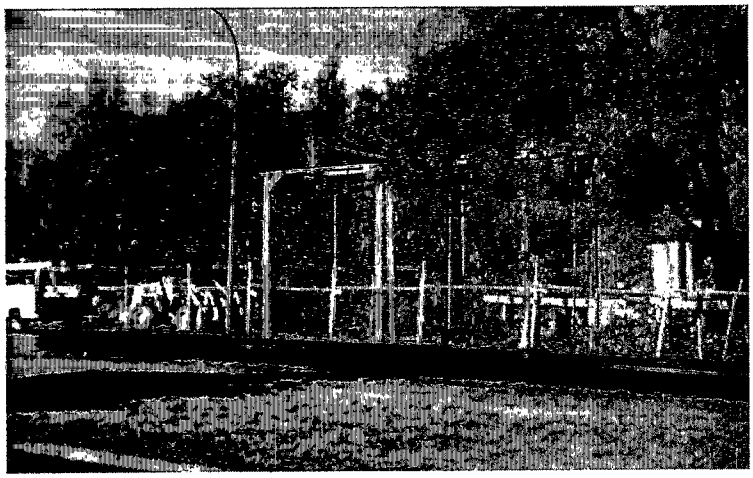
Denver Federal Center–Gate Construction



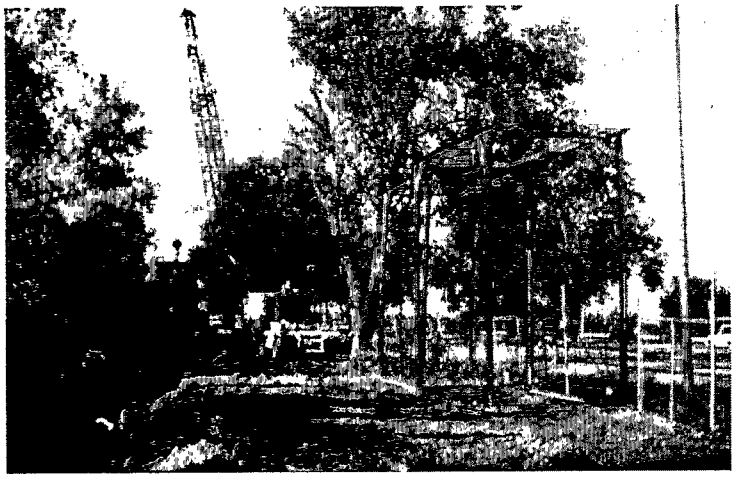
Denver Federal Center–Placing Fe^0 in Cell One



Template for Reaction cell



Denver Federal Center–Wall Construction



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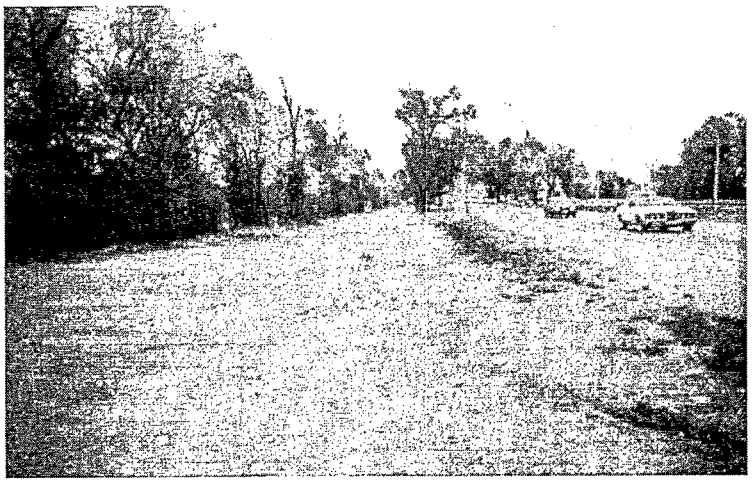
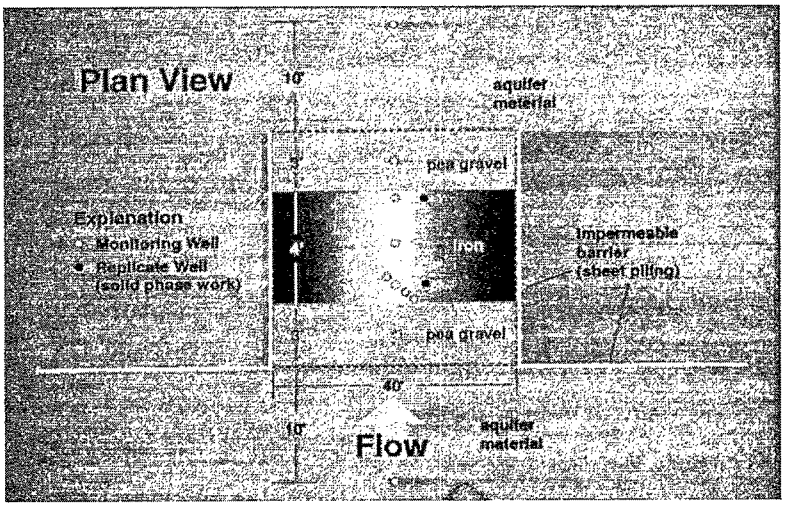
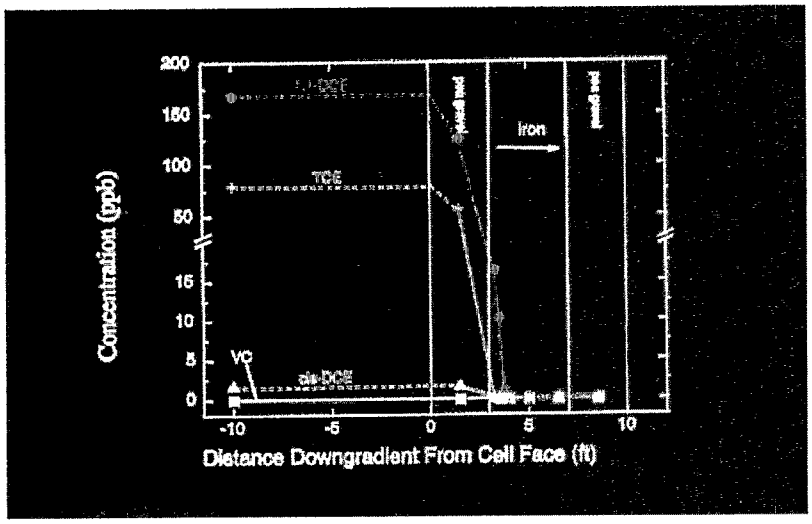
Denver Federal Center–Wall Completion



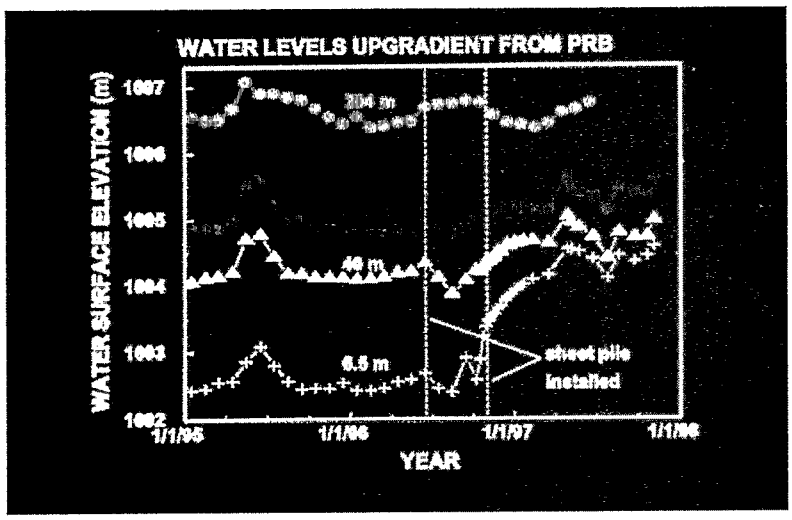
Multi-Level Piezometers, Cell Z



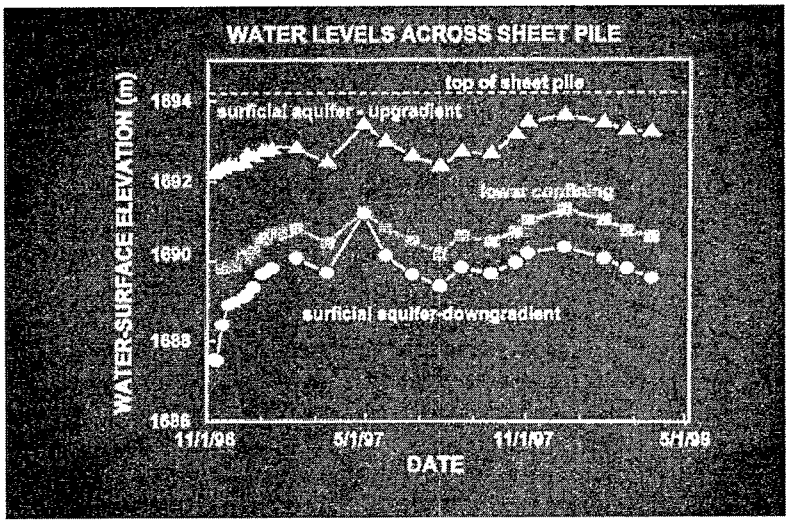
Denver Federal Center–Gate Z



Denver Federal Center–Water Levels



Denver Federal Center–Water Levels



cssstd1

PRB Emplacement Case Study

Continuous Wall

Case Study—New York Site

- Site located in Syracuse area
- 100s of ppb TCE, cDCE, TCA requiring treatment
- Water table at 3 ft bgl, clay zone at 15 to 17 ft bgl

casstd1

Rationale For PRB Implementation—New York Site

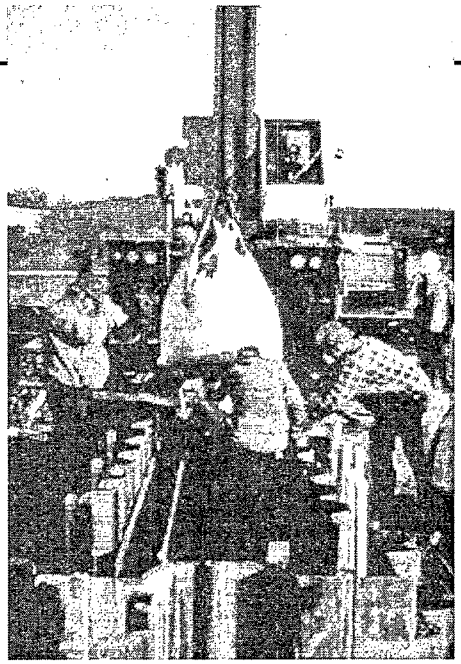
- PRP no longer active at site
- Savings of at least $0.6M relative to pump and treat
- Shallow plume
- Contaminants amenable to treatment

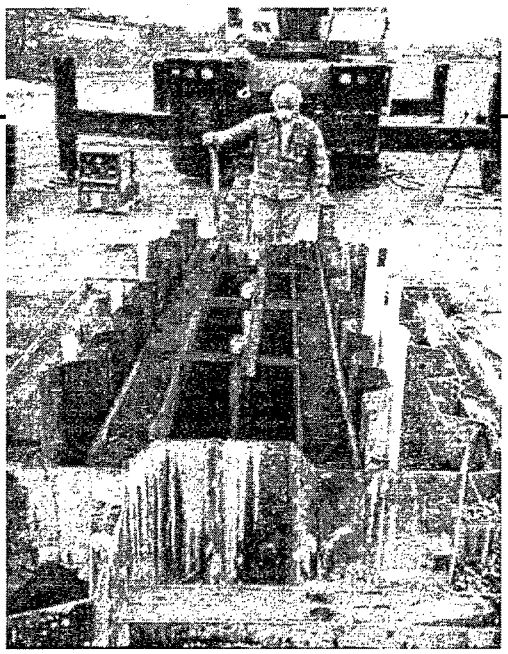
Site Design Summary

Pilot-Scale In Situ System, New York (May 1995)

- Impermeable zone:
  - 15 ft of sealable joint sheet pile on either side of treatment zone
  - 15 ft depth
- Treatment zone:
  - 10 ft length
  - 3½ ft flow-through thickness
- Influent groundwater:
  - 100s of ppb TCE, cisDCE, TCA

csstd1





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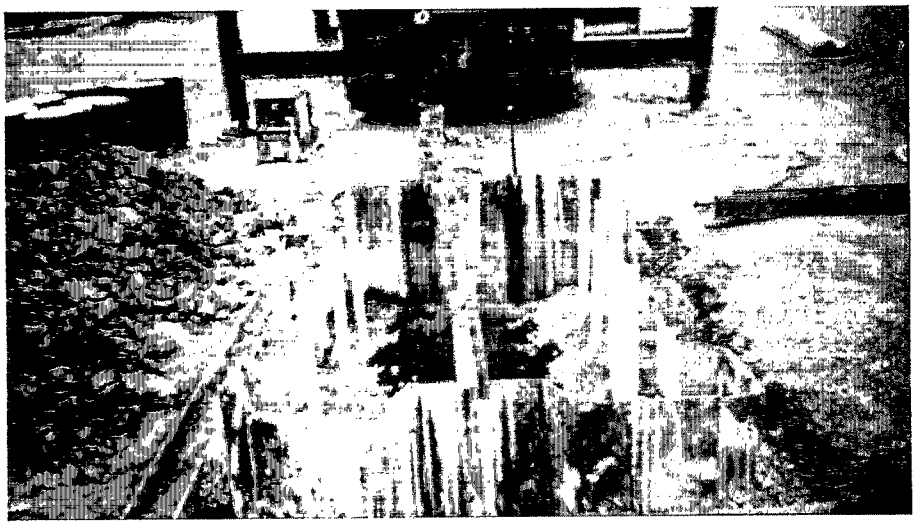
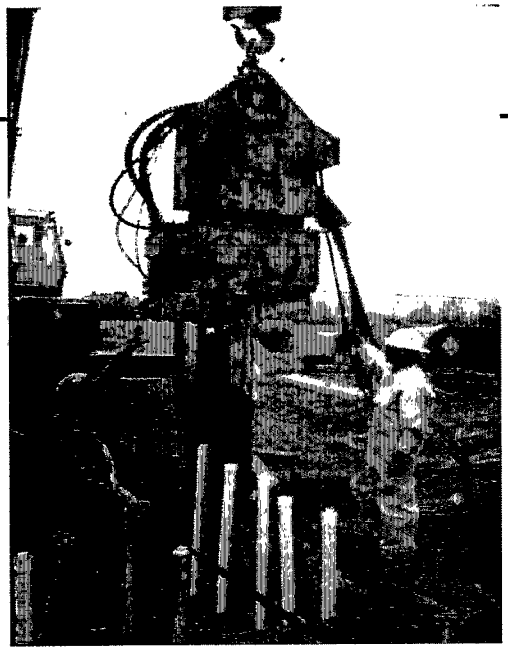
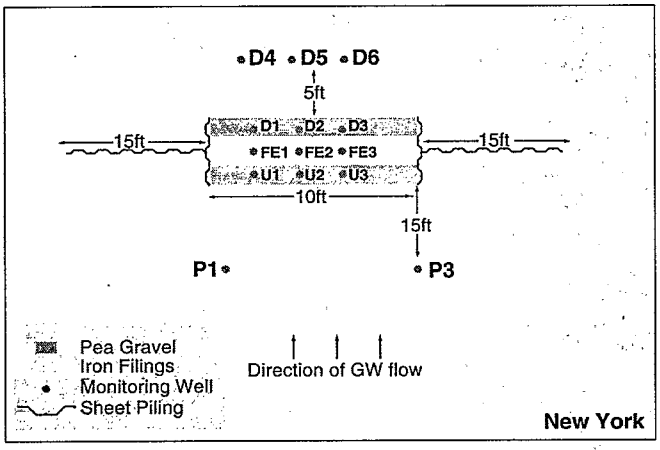


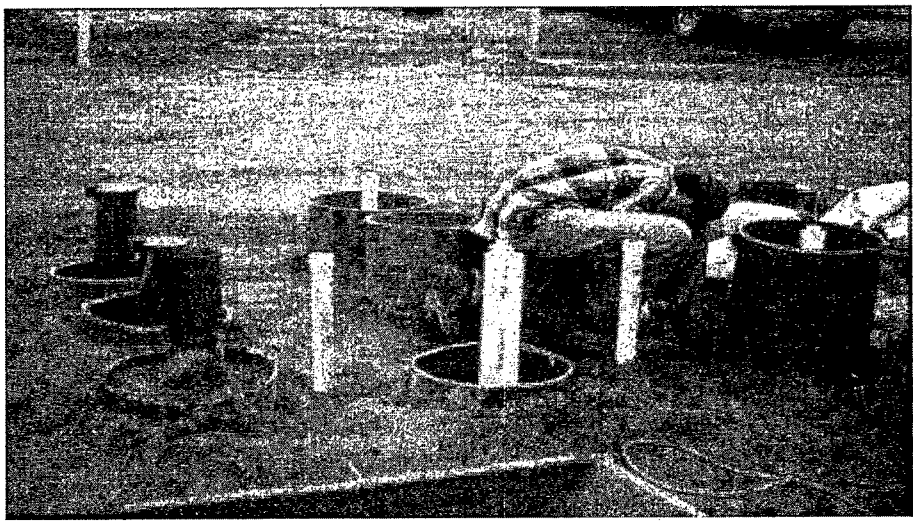


csstd1

Permeable Reactive Barrier Configuration

New York, Pilot-Scale





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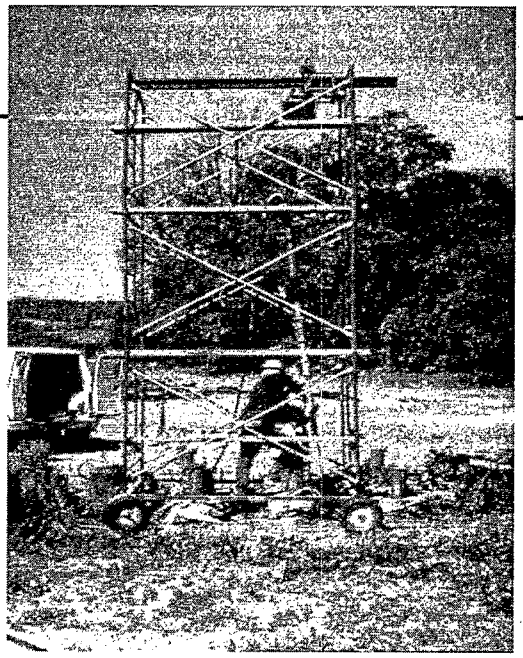
Observed VOC Concentrations Along the Center Transect—New York

Well Location	Concentration Along Center Transect (mg/L)					
	TCE		cDCE		VC	
	Oct. 1995	June 1997	Oct. 1995	June 1997	Oct. 1995	June 1997
Upgradient Pea Gravel	160	189	450	98	79	53
Midpoint of Iron Zone	<1.0	2.0	2.0	<7.8	<1.0	<0.7
Downgradient Pea Gravel	1.5	<1.7	7.5	15	1.2	<0.7

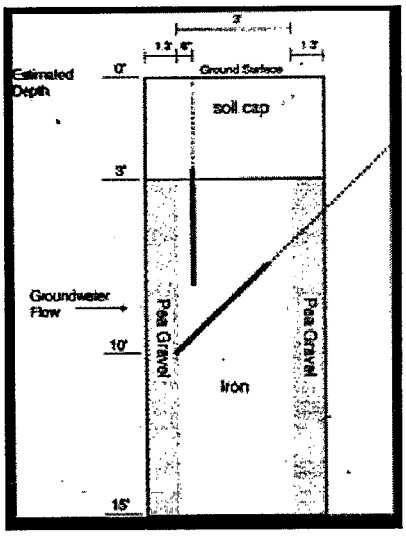
Changes in Inorganic Chemistry Along Center Transect—New York

	Monitoring Well Location			
Chemical Parameter (unit)	U2	FE2	D2	D5
Ca (mg/L)	90.6	9.6	15.4	33.6
Fe (mg/L)	<0.1	0.158	<0.1	0.159
Mg (mg/L)	12.7	7.33	4.23	5.95
HCO_3 (mg/L)	291	47.8	56.5	Na
Cl (mg/L)	47.4	49.2	42.8	Na
SO_4 (mg/L)	17.2	<5.0	<5.0	--
pH	7.39	9.46	8.56	7.06
Eh (mV)	261	-459	-156	-16.5

csstd1



Cross Section of Core Sample Locations, NY



Core Results

- Coring 2 years after installation
- Carbonate precipitates predominate and occur only within a few inches of the upgradient interface
- Reactivity maintained after 2 years
- No evidence of microbial fouling

csstd1

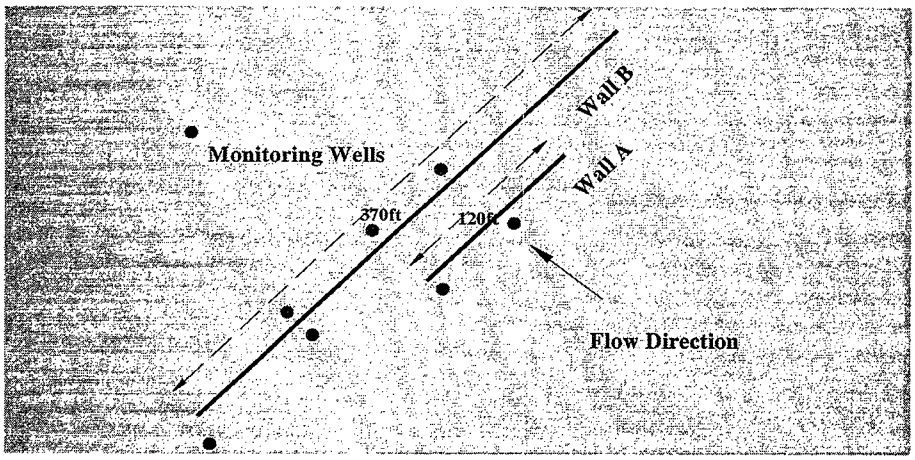
Site Design Summary

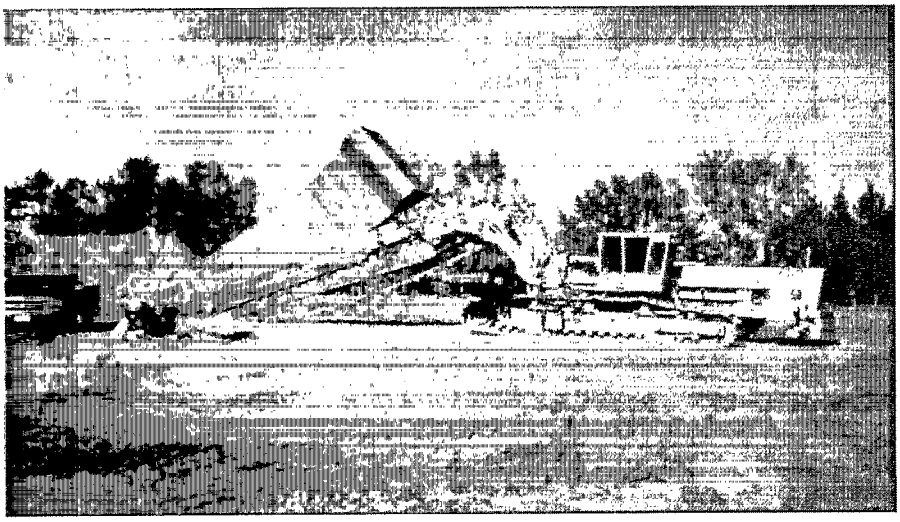
Full-Scale System, New York (1997)

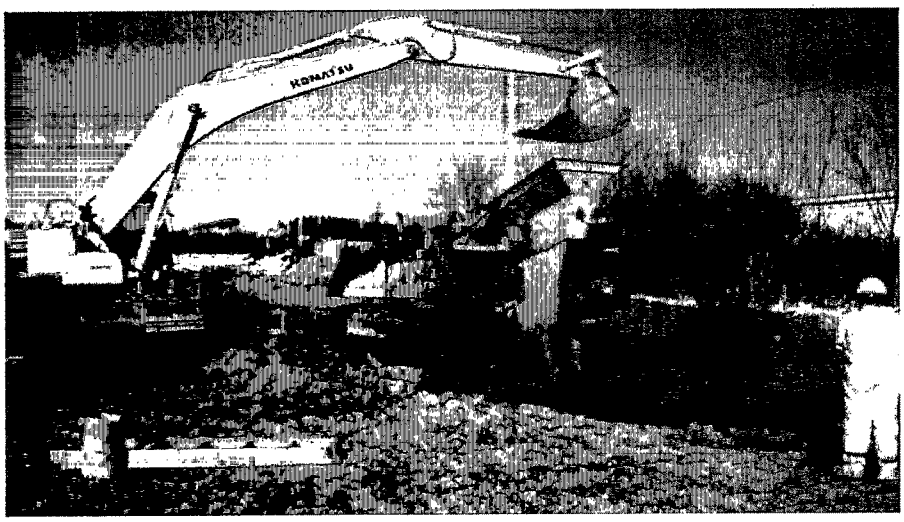
- Two parallel continuous treatment walls (100% iron):
  - 120 ft length Wall A
  - 370 ft length Wall B
  - 1 ft flow-through thickness
  - 18 ft depth (▼ 3')
- Cost (including design, materials, site preparation/restoration) = $797,000

Conceptual Continuous Wall

Industrial Facility, New York






KOMATSU

csstd1

Full-Scale Monitoring—New York

- Quarterly monitoring program
- Consistent flow through system observed
- Location of monitoring wells, VOCs in aquifer downgradient of wall make treatment efficiency difficult to determine
- Wells in iron show VOCs below detection limits

prb5b

Recent Advancements in PRB Emplacement

- Alternatives to Excavation and Trenching

Incentives for Emplacement Advancement

- PRB Depth
  - Need to go deeper
  - Emplacement across selected depth intervals
- Construction issues
  - Obstructions (overhead and underground)
  - Unstable soils
  - Worker exposure

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Incentives for Emplacement Advancement

- PRB Thickness
  - Many applications require only a few inches of iron
- Cost
  - Construction costs
  - Disposal of spoils
  - Reduce excessive iron usage

Recent Emplacement Advancements

- Vertically Oriented Hydraulic Fracturing
- Jetting
- Tremie Tube

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Caldwell Trucking Superfund Site

- Permeable Reactive Barrier Emplacement Using Hydraulic Fracturing

Project Highlights

- Permeable barrier installed as an alternative to pump and treat
- Vertical hydraulic fracturing technology used for emplacement
- Goal was primarily to protect a surface water receptor
- PRPs agreed to install PRB at risk
- Stakeholders discussing ROD change after 12 months of performance monitoring

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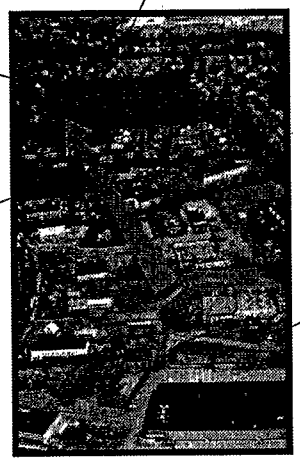
Site Background

- 11 acre waste disposal site in northern New Jersey
- No potable use of impacted groundwater
- Significant discharge of groundwater to surface water through downgradient "seep"
- Only identified risk is direct contact with impacted seep / surface water

Groundwater Flow from Source to Seep Area



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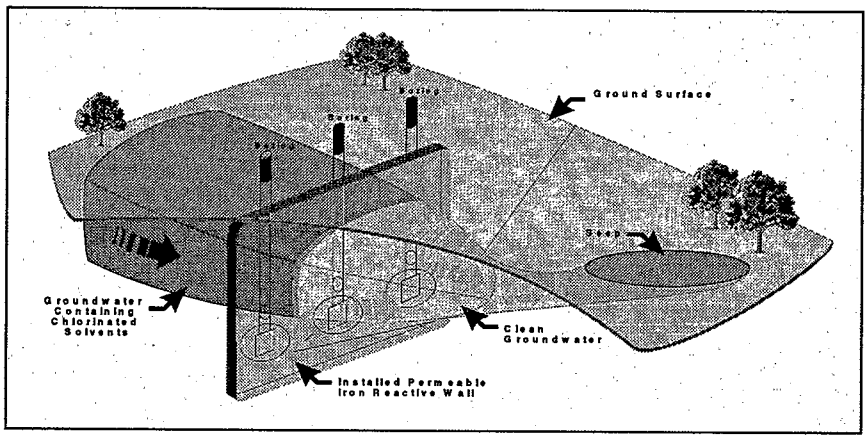
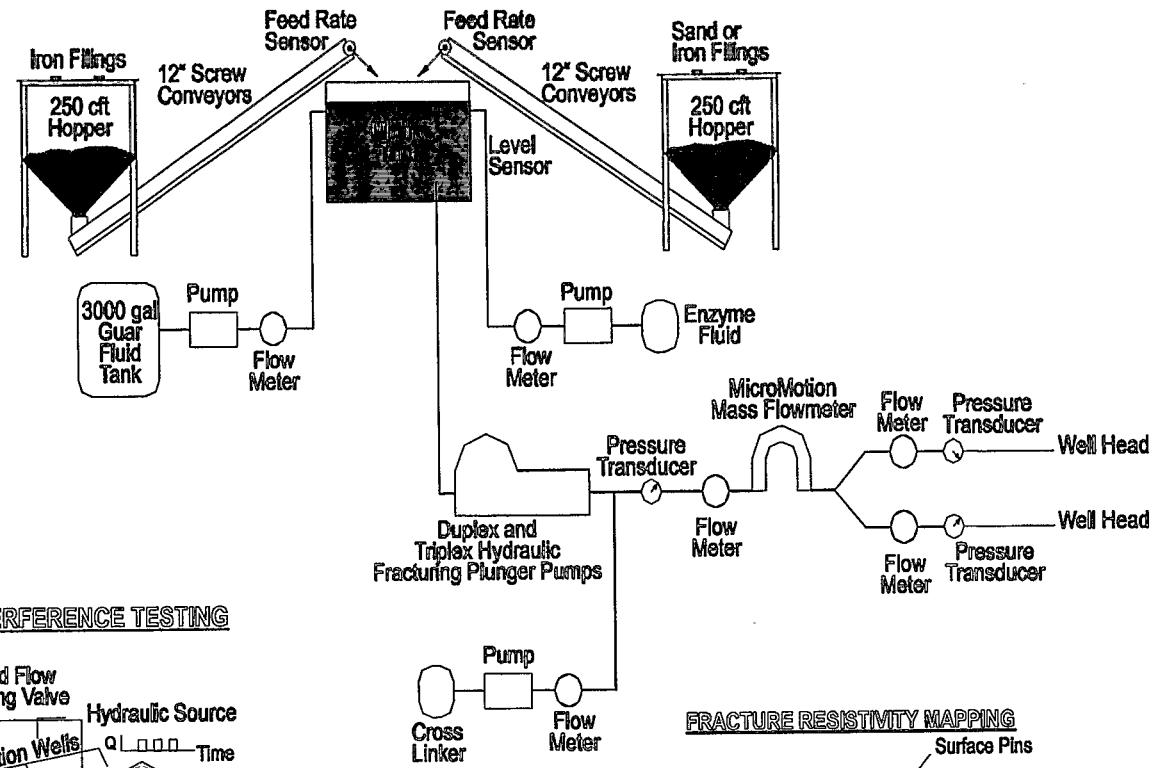
Subsurface Iron Reactive Barrier

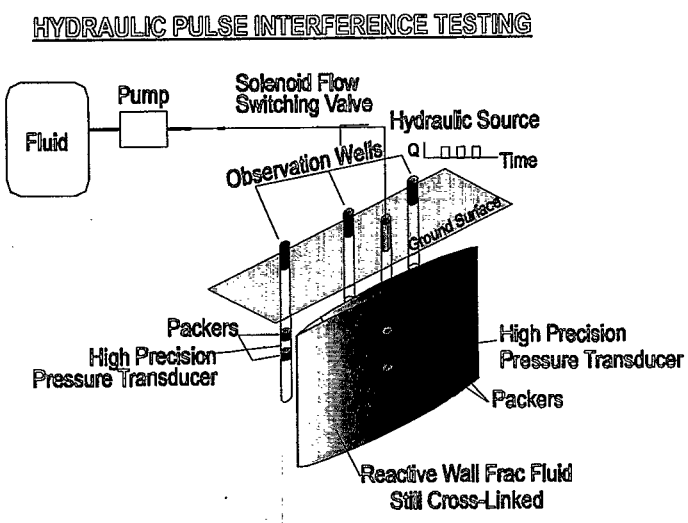


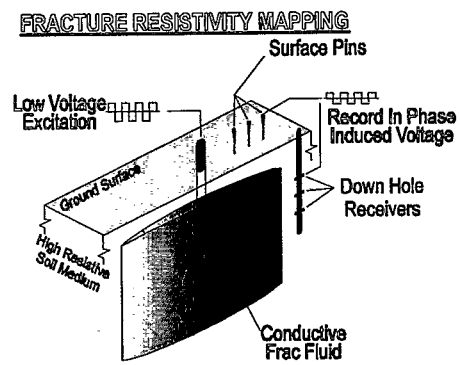
Overview of Hydraulic Fracturing Technology

- Iron suspended in guar-based gel
- Fractures initiated using proprietary down-hole tool
- Iron-bearing gel injected at high pressure/low velocity
- Fractures propagate along vertical orientation
- Adjacent fractures coalesce to form continuous wall
- Gel breaks down leaving permeable iron barrier

Hydraulic Fracturing System Equipment and Instrumentation







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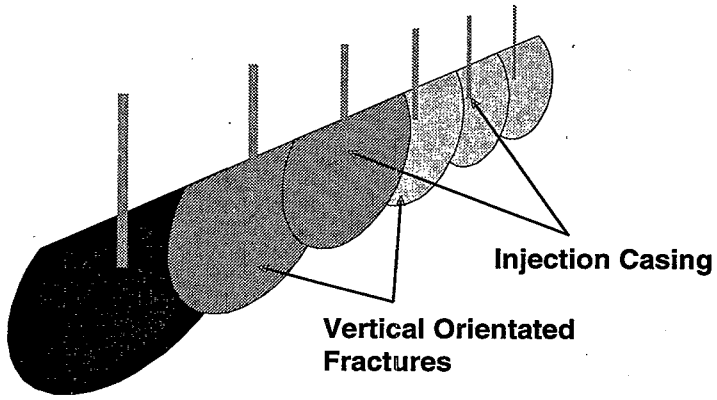
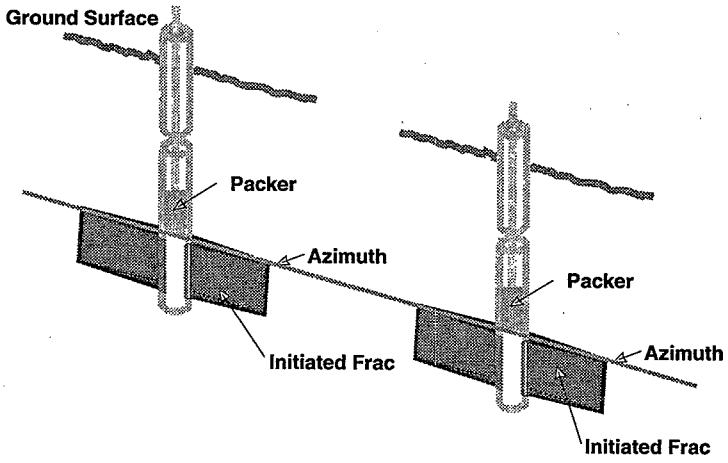
Overlapping Fractures



Initiation Of Fracture



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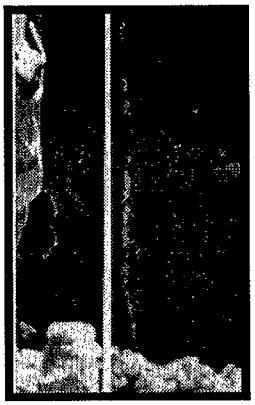
Azimuth Control of Fracture Orientation

Frac coalescence beneath surface



Frac orientated along required azimuth

Vertical Fracture Thickness

Thin continuous frac

Thick continuous frac

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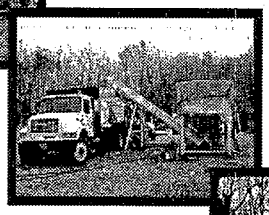
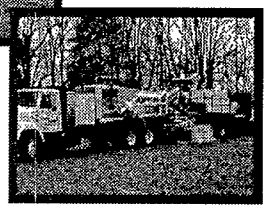
Mixing and Pumping System

Mixing equipment

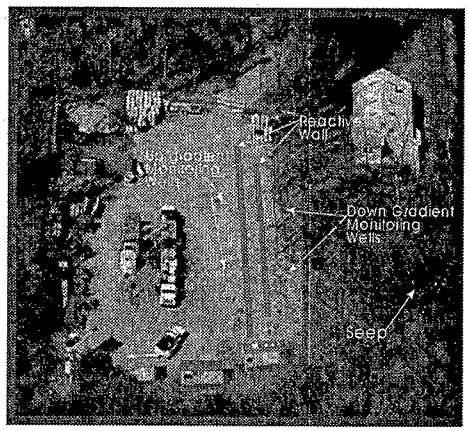


Hoppers loading iron into equipment



Control/pumping unit

Iron Reactive Barrier at Caldwell Superfund Site



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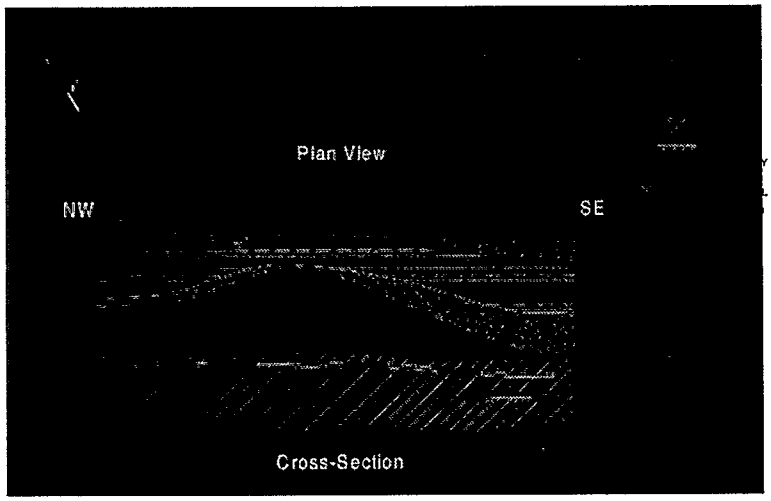
Geological Cross-Section Along Reactive Wall



Why We Chose Fracturing for Iron Emplacement

- Depth to 65 feet
- Desire to maintain integrity of clay layer
- Small iron thickness required (7 inches)
- Complex upper bedrock zone
- Minimize site disruption
- Ability to "tweak" after installation

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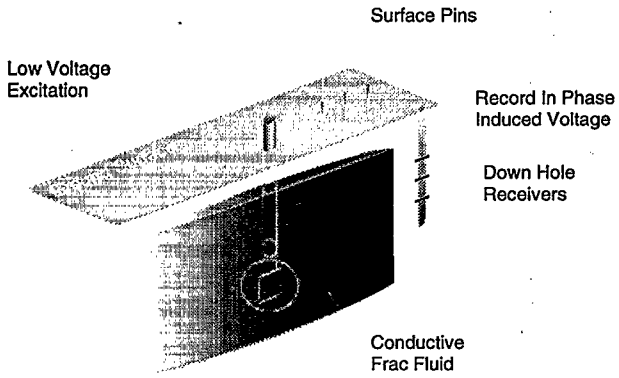
Design Overview

- Designed to achieve 12 half-lives for TCE
- Spans 40-foot depth interval from 25 to 65 feet below ground
- Lab studies indicate 4-inch fracture thickness achievable in B-zone
- Two walls in series: 150-foot and 100-foot lengths
- Hydrofrac wells at 15-foot spacing

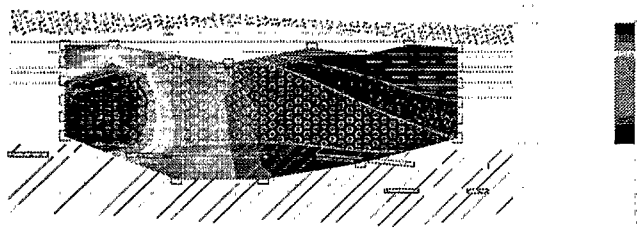
Construction

- Hydraulic fracturing of unconsolidated zone
- Permeation infilling of upper bedrock zone
- Construction QA
  - electrical resistivity
  - hydraulic pulse testing
- 10,000 square feet of barrier installed
- Construction completed March 1998

Active Resistivity



HydroFrac Injection in B1 & B2



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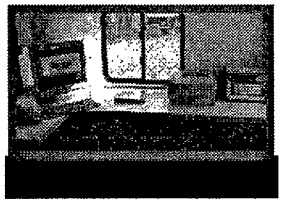
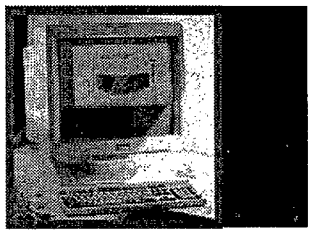
Real Time Instrumentation Display



Real Time Data Acquisition & Recording

Display of Resistivity & Injection Time Histories



Display of Frac Geometry

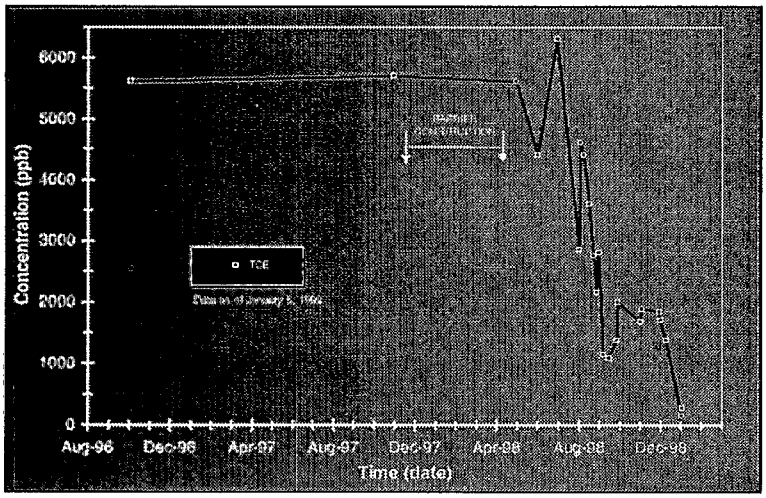
Current Status of Project

- Seep concentrations reduced from 6,000 ppb to 200 ppb to date
- Barrier extension and upgrade underway to enhance performance
- Total project cost $ 2 M
- Project seen as success by all stakeholders
- Final site-wide remedy under discussion

Monitoring

- Performance monitoring: 12 month shakedown and performance monitoring period using up- and down-gradient monitoring wells
  - Basis for contractor's warranty
- Compliance monitoring: surface water in the seep and creek (quarterly - VOCs only)
  - Basis for regulatory acceptance

Seep TCE Concentrations Caldwell Trucking Site



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Key learnings

- Hydraulic fracturing is a viable and cost effective emplacement technology for PRBs
- Importance of understanding stratigraphy and groundwater flow
- 12 month performance and shakedown period a good idea
- PRB technology is robust and flexible

An Active Plant Site

- Permeable Reactive Barrier Emplacement Using Jetting

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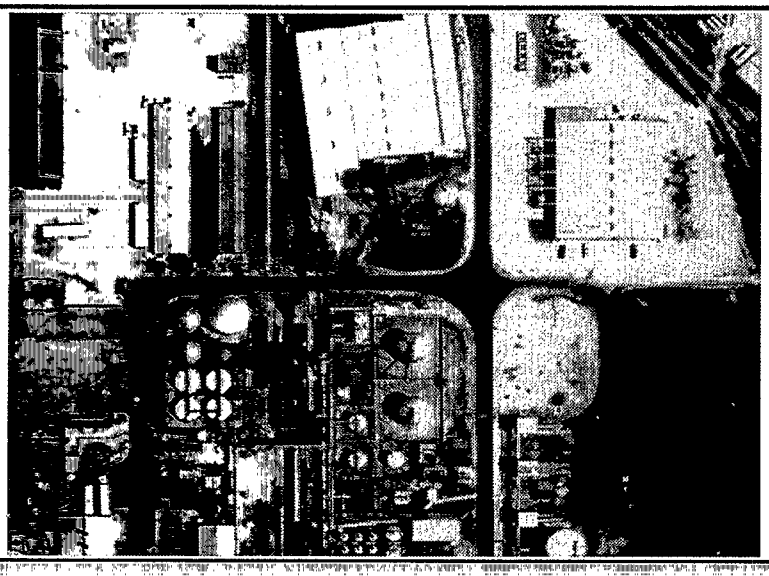
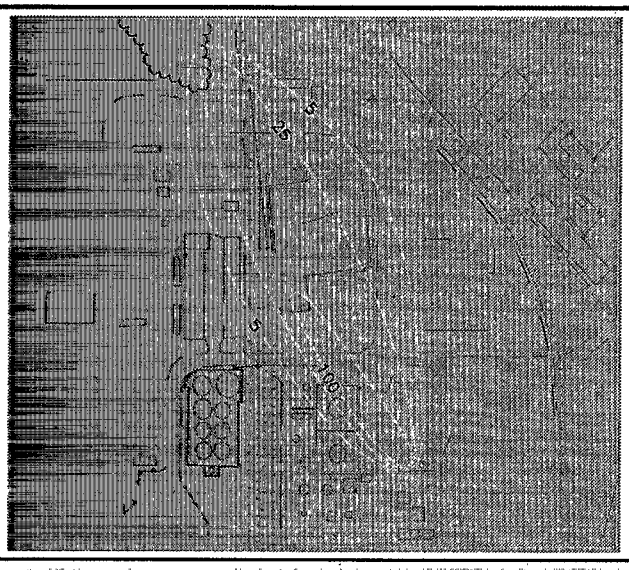
Area Of Concern



TCE Plume



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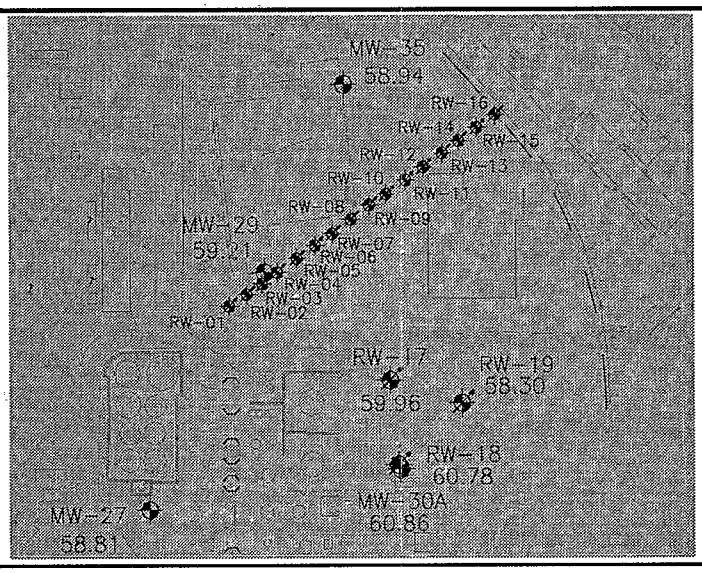
Existing P&T System



Project Highlights

- A PRB of 2 to 4 inches is required
- PRB will be 485 feet long by 15 feet deep and be emplaced by jetting
- -30/+70 mesh iron will be jetted
- Iron will be suspended in a guar gum slurry
- Twelve utility & 2 road crossings
- Working near or underneath a water tower

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Site Characteristics

- Groundwater velocity of 0.09 feet / day
- $k = 3.4 \times 10^{-4}$ cm/sec to 1.2×10^{-3} cm/sec
- Depth to groundwater is roughly 5 feet
- Mudstone confining unit at roughly 15 feet
- No known use of TCE on the facility
  - Limited contractor pipe cleaning is suspected

PRB Design

- One 2-inch wall for most of the plume width
- Two 2-inch walls in series for the 100 ppb portion of the plume
- Wall depth is roughly 15 feet
- Numerous utilities and obstructions within wall alignment

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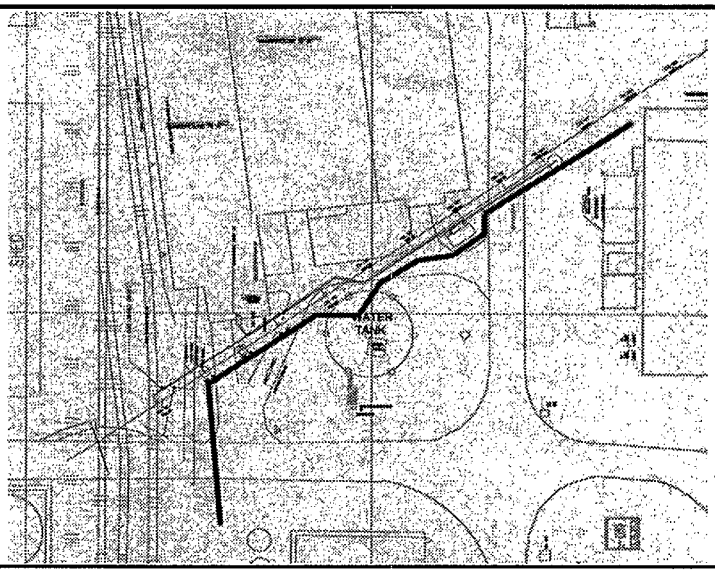
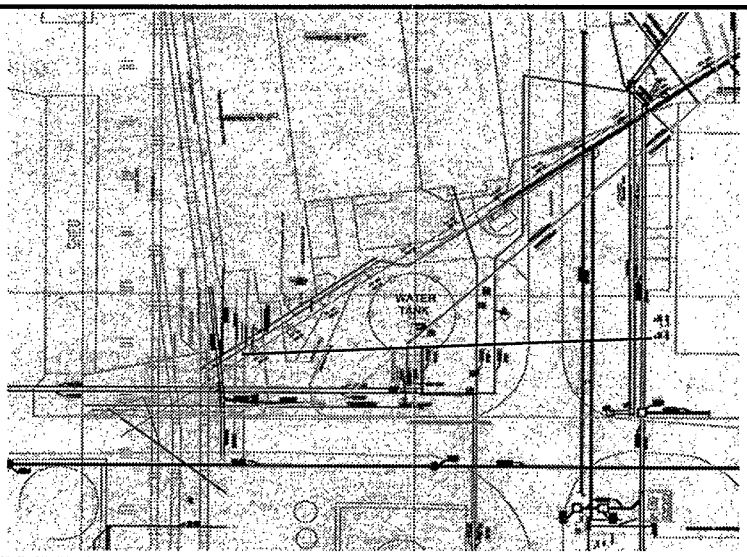
PRB Emplacement Challenge



What Utilities?



What is Jetting?

- A high velocity stream of fluid erodes a cavity in the soil matrix.
- A portion of the soil matrix is mixed with the reactive media (iron filings).
- Jetting creates either columnar or panel type structures in the sub-surface.

Jetting Energy

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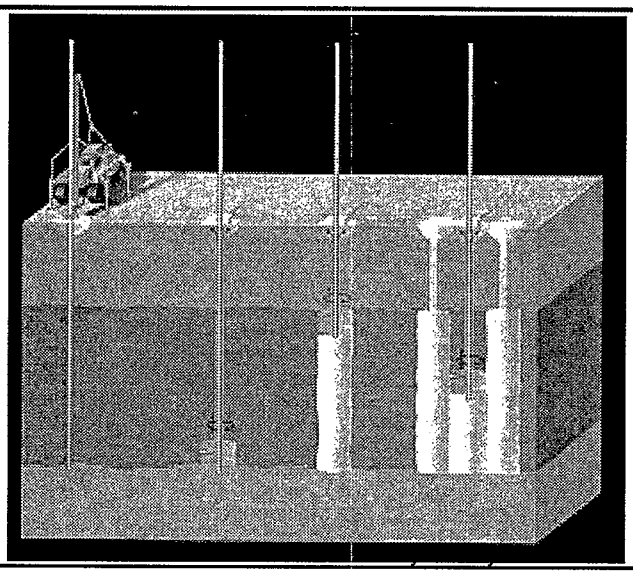
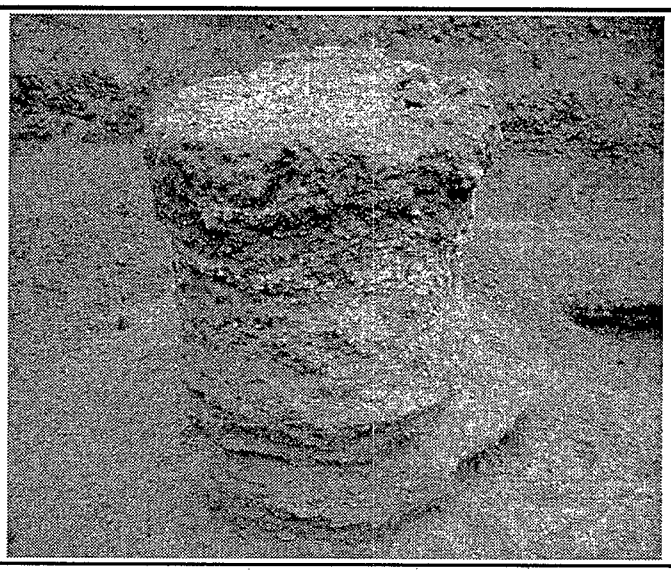
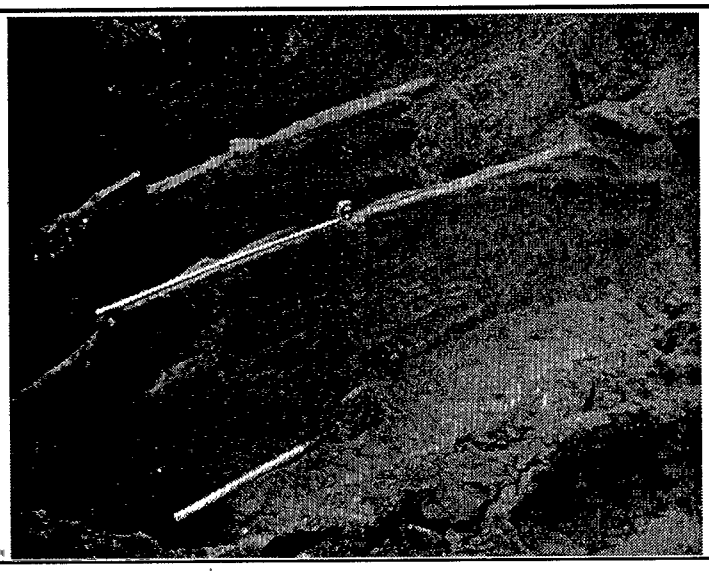
Jetting Process



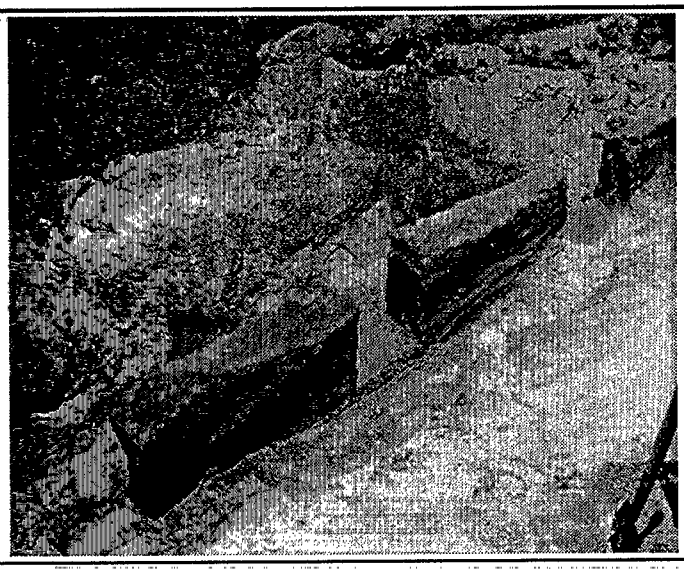
Columnar Emplacement



Panel Emplacement



Panel Emplacement



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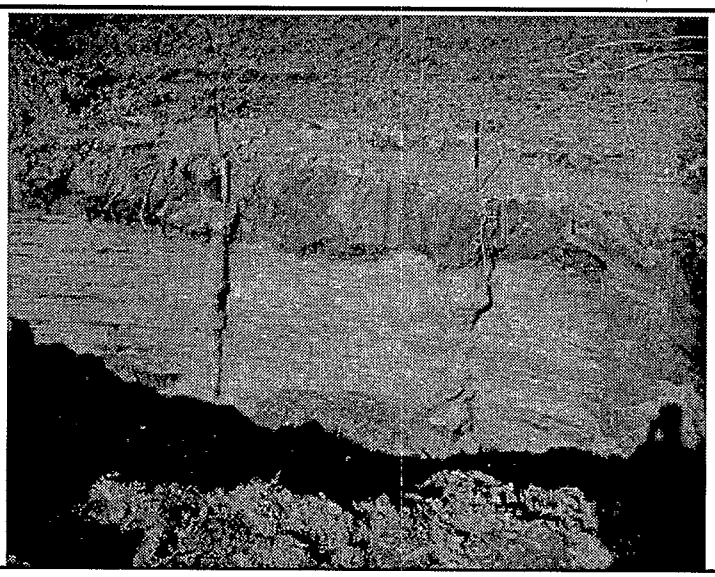
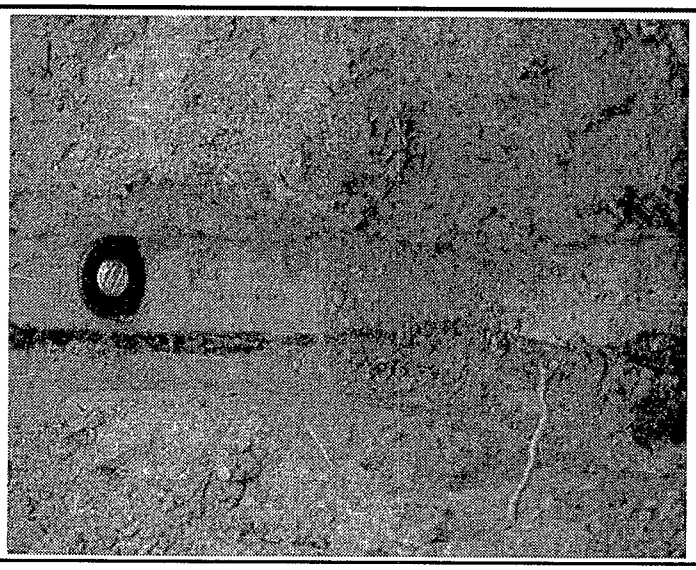
Interconnecting Panels



Panel Type PRB



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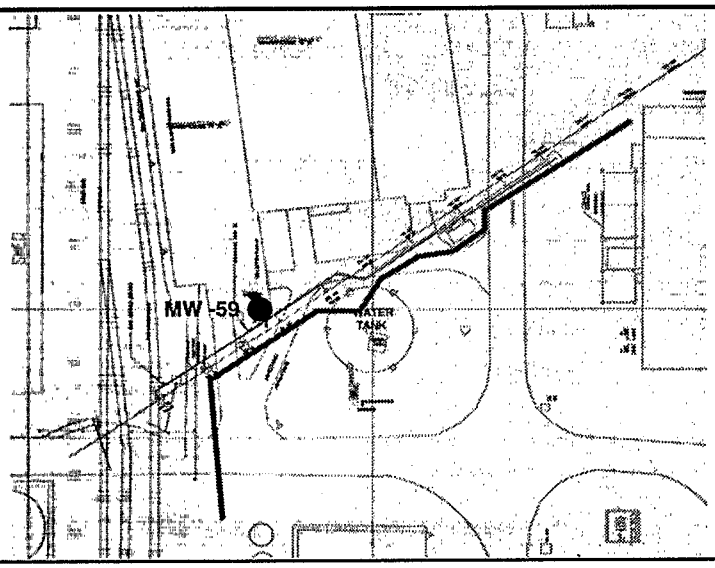
Columnar Type PRB

Monitoring System



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Why Jetting Was Selected

- PRB thickness of 2 to 4 inches
- Over 12 utility & 2 road crossings
- Working near or underneath a water tower
- Reduction of emplacement costs
- Reduction in worker exposure

Current Status of Project

- Project is slated to be in the field in August 1999

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Key Learnings To Date

- Jetting appears to be a viable emplacement technology for PRBs
- Thin and thick PRBs can be emplaced
- Depths in excess of 50 feet are possible
- Understanding geo-technical aspects of stratigraphy are important
- Worker exposure and spoils can be minimized

DOE's Paducah Gaseous Diffusion Plant

- Permeable Reactive Barrier Emplacement Using Tremie Tube

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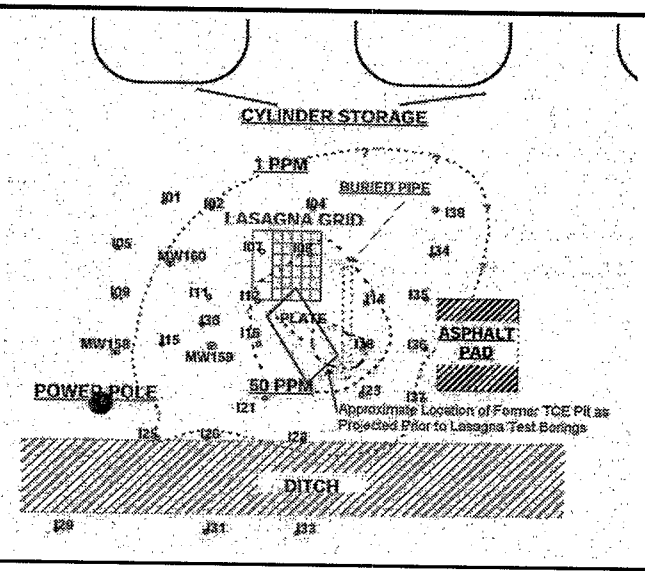
Project Highlights

- Thin (2-inch) reactive zones were emplaced as part of Lasagna technology demonstration project at a DOE site.
- Emplaced 100 linear feet to a depth of 45 feet
- Spoils generation were minimal
- Tremie tube emplacement proved to be cost-effective

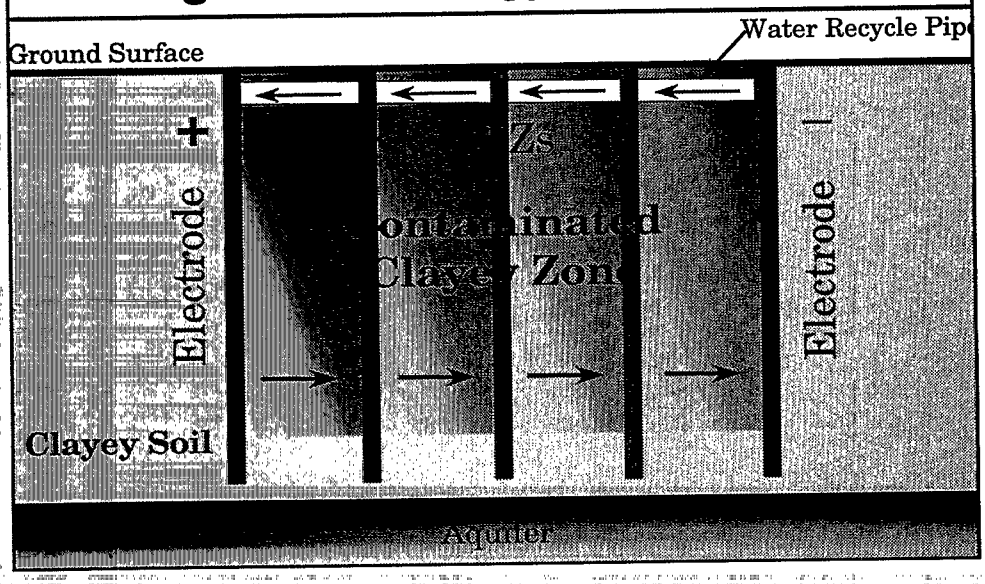
PGDP's TCE Plume



Site Characteristics

- TCE plume in tight clayey soil
- Very low hydraulic conductivity
- Depth to groundwater is roughly 10 feet
- Thickness of clayey zone is roughly 50 feet

What is Lasagna Lasagna Technology?



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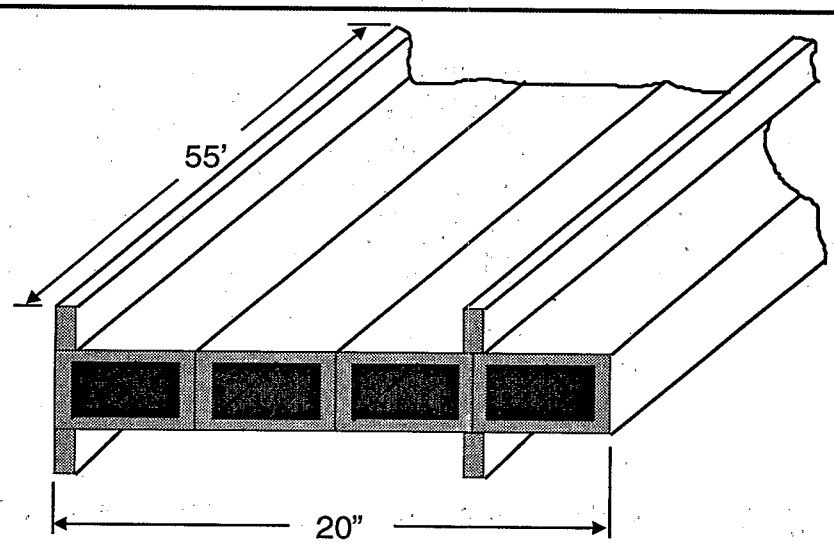
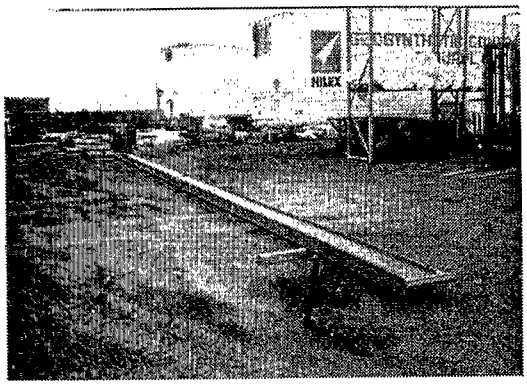
What is Tremie Tube Technology?

- Tremie tube technology is the use of a tubural structure through which material is transferred into the ground without the material mixing with the soil.

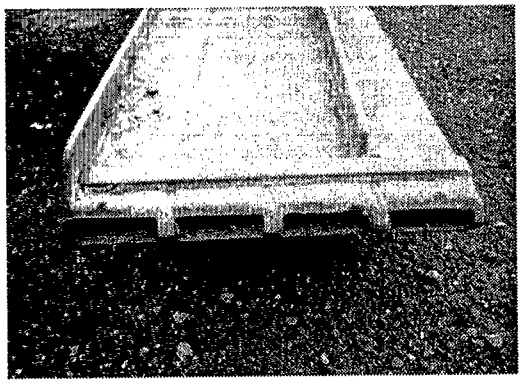
PGDP's Tremie Tube



Overall View



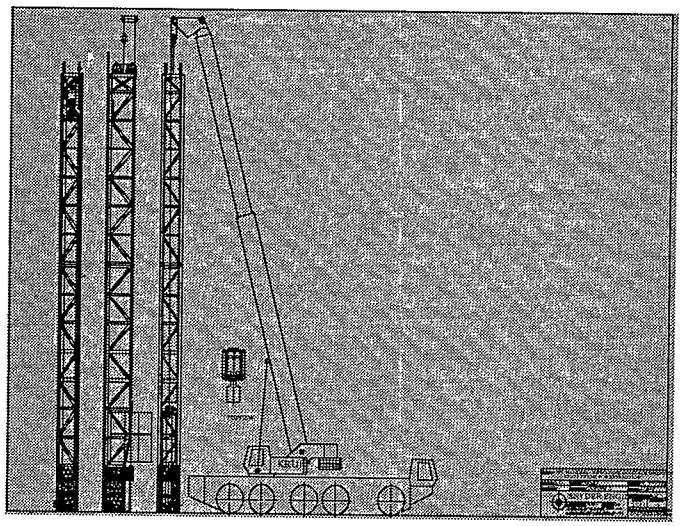
Bottom Edge



prb5b

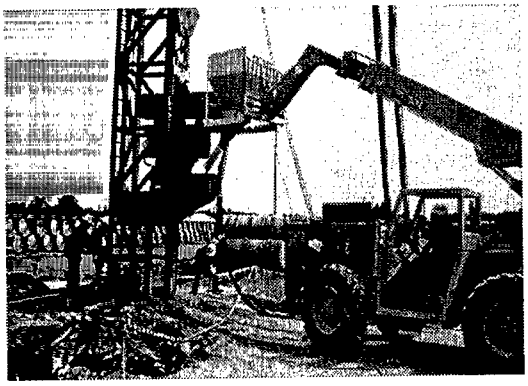
Driveshoe

Emplacement System



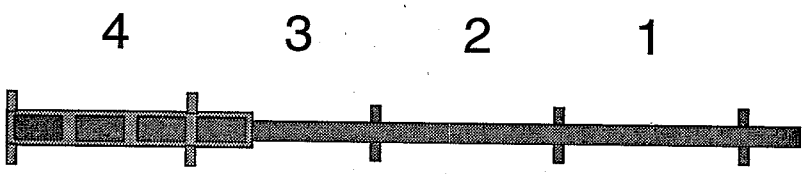
Tremie Tube at Depth

Placement of Materials



prb5b

Emplacement Sequence



Forming a continuous wall using the tremie tube method with sequential emplacements

Case Study Summary

- Why was tremie tube technology selected?
  - Emplace thin (2") treatment zones
  - Reduce emplacement costs
  - Reduce spoils generation & disposal costs
  - Reduce worker exposure

Key learnings

- Tremie tube technology is a viable emplacement alternative for PRBs
- Worker exposure can be significantly reduced
- Spoils generation can be minimized

Conclusions

- PRBs can be placed cost-effectively to depths > 100 ft.
- PRBs can be emplaced across selected depth intervals
- Thin panels can be emplaced without excess iron usage
- Recent advancements allow PRB emplacement where trenching and excavation would be problematic

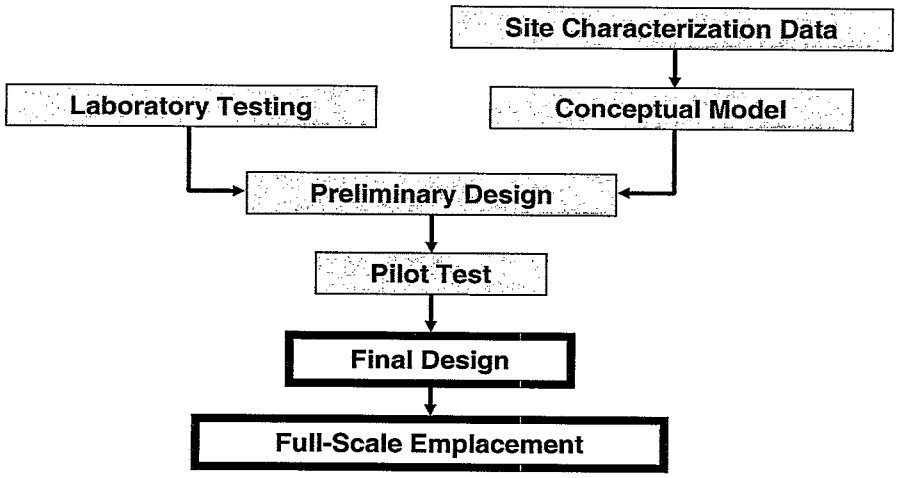
Section 8

PRB Permitting and Implementation

EPA/ITRC/RTDF
Permeable Reactive Barrier Short Course

PRB Permitting and Implementation

Path to PRB Design and Emplacement



Considerations

- Permitting
- Legal
- Planning
  - scheduling, access, health and safety
  - spoils management
- Construction QA/QC
- Verification
- Post-construction

Regulatory Oversight Framework

- CERCLA program
  - permit equivalency
- RCRA program
- State regulatory programs

Permitting Issues

- National Pollution Discharge Elimination System (NPDES)
- Underground Injection Control (UIC)
- Air Quality
- Local permits
- Site-specific permits (i.e., wetlands)
- *PRB technology-specific permit does not exist*

NPDES

- Triggered for the disposal of excess water generated during installation
  - installation method-dependent
  - may require permit for discharge to groundwater, surface water, or POTW

UIC

- Triggered by reactive media placement
  - not typically required for the placement of solid media by excavation, caisson, mandrel, or continuous trencher, etc.
  - may be required for the placement in liquid form by jet-grouting, hydrofracturing, etc. State-specific requirement.

Air Quality

- Triggered by emissions generated during installation of PRB
  - should be evaluated on a site-specific basis
  - not typically required where PRB is placed downgradient of the source area

Other Regulatory Issues

- Waste disposal - classification
- Public involvement / comment periods
- Deed restrictions - notifications
- Health and safety issues

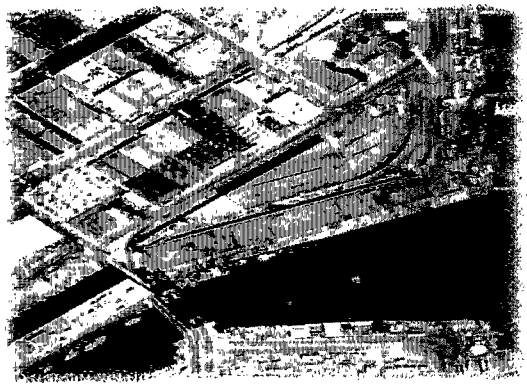
Legal Considerations

- Landowner issues
- Long-term maintenance agreements
- Access agreements
  - during installation
  - for ongoing monitoring
- Disruption

sect8

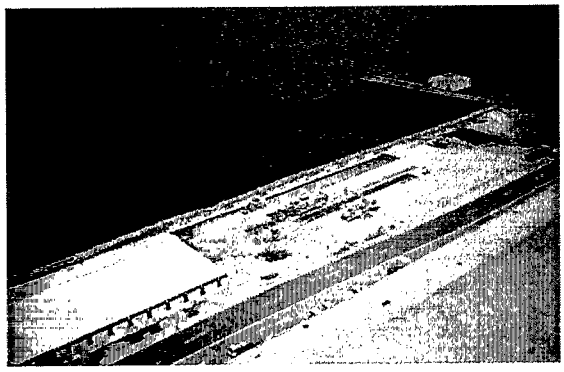
Constructability

- Site photograph—San Francisco Bay Area
  - dense commercial area



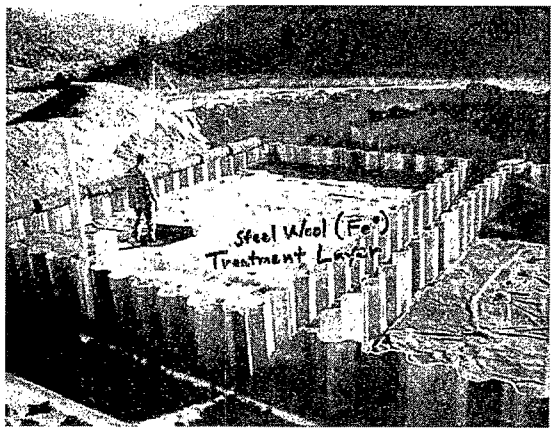
Constructability

- Site photograph—Elizabeth City, NC
  - moderate commercial area



Constructability

- **Site photograph—Durango, Colorado**
  - **remote area**



Courtesy DOE-Grand Junction, CO

Constructability

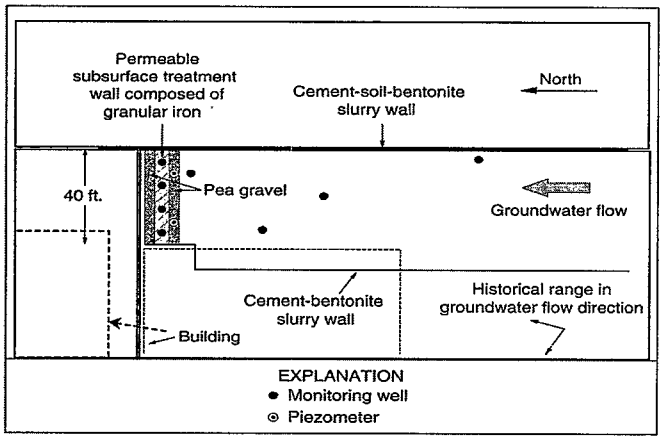
Building, legal, nearby remediation, utilities

Adjacent site remediation

Construction under building

Deed restriction

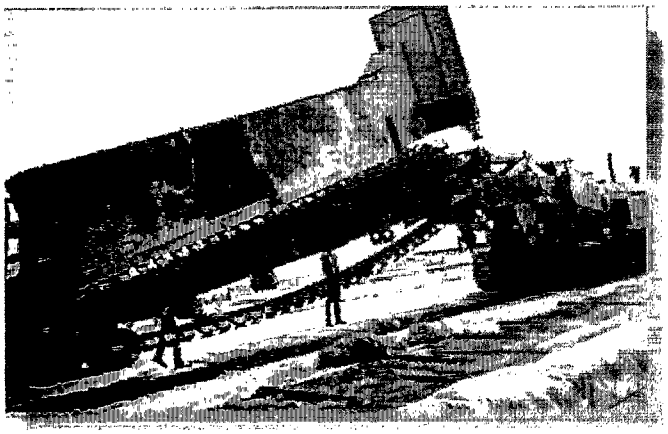
Future construction



sect8

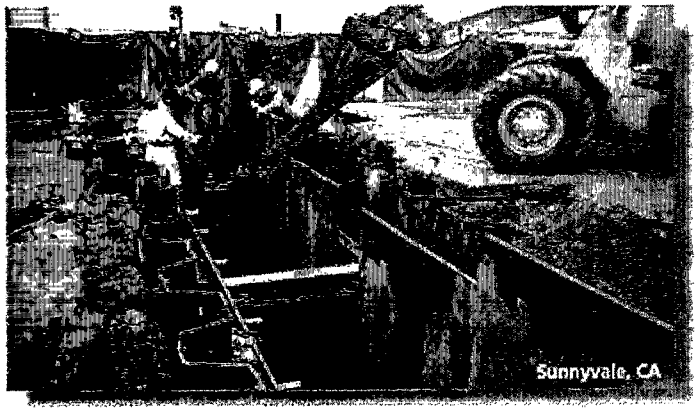
Constructability

- Heavy equipment



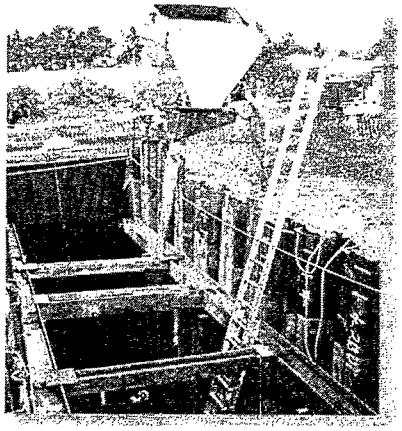
Constructability

- Access



Constructability

- Equipment mobility



Constructability

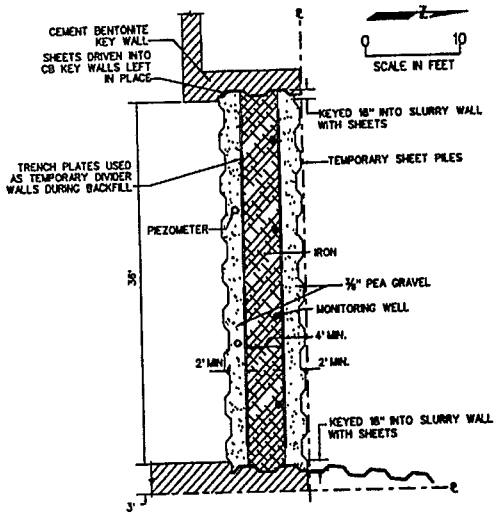
- Building Constraints

Constructability—Geotechnical and Structural

- Cone penetrometer soundings
- Soil property testing
- Geotechnical assessment
- Pre-/post-construction building survey
- Dewatering design
- Designing for the unknown

Geotechnical Design

- Geotechnical plan - example



Section 9

Treatment of Metals; Non-Metallic Reactive Materials

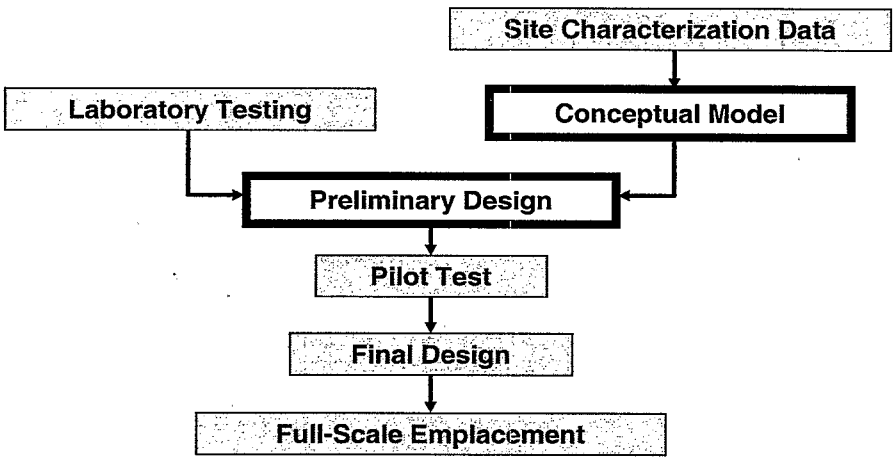
sect9

EPA/ITRC/RTDF
Permeable Reactive Barrier Short Course

A. Treatment of Metals by Fe^0 PRB Systems

B. Non-Metallic Reactive Materials for Promoting PRB-Based Treatment

Path to PRB Design and Emplacement



Treatment Mechanisms

- pH control (acid neutralization)
- Chemical precipitation (oxidation and reduction)
- Coprecipitation on mineral surfaces
- Sorption reactions
- Biological enhancement
- Sequential treatment

Treatment Materials; Treatable Contaminants

Treatment Material	Target Contaminants	Technology Status
Zero-valent iron	Halocarbons, reducible metals	In practice
Reduced metals	Halocarbons, reducible metals	Field demonstration
Metal couples	Halocarbons	Field demonstration
Limestone	Metals, acid water	In practice
Sorptive agents	Metals, organics	Field demonstration, in practice
Reducing agents	Reducible metals, organics	Field demonstration, in practice
Biologic electron acceptors	Petroleum hydrocarbons	In practice, field demonstration

Non-Metallic Treatment Materials

- Limestone
- Precipitation agents
  - gypsum, hydroxyapatite, organic compost
- Sorptive agents
  - granular activated carbon, bone char, phosphatics, zeolites, coal, peat, synthetic resins

Non-Metallic Treatment Materials

- Reducing agents
  - organic compost, dithionite, hydrogen sulfide, bacteria, acetate, corn syrup, molasses, organic compost
- Biological enhancements
  - oxygen source, hydrogen source, carbon source nitrate

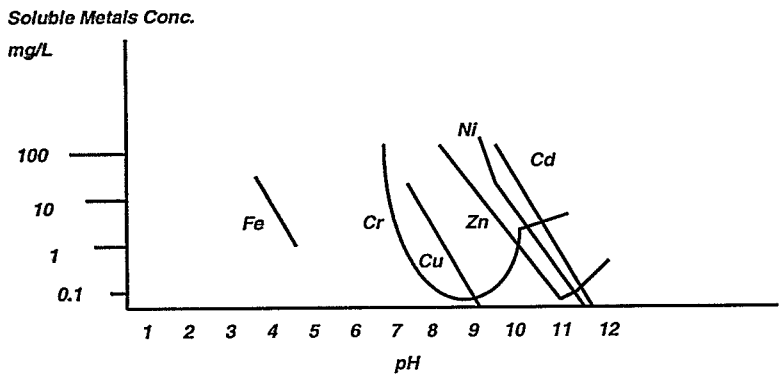
Chemical Precipitation

- The creation of an insoluble phase from combining the target contaminant with a slightly soluble anionic material
- Example materials:
  - limestone, hydrated lime, hydroxyapatite

Pb^{-water} + hydroxyapatite ($CaPO_4$)= > Pb-phosphate$_{(s)}$

Chemical Precipitation—pH Control

- Metal solubility as a function of pH



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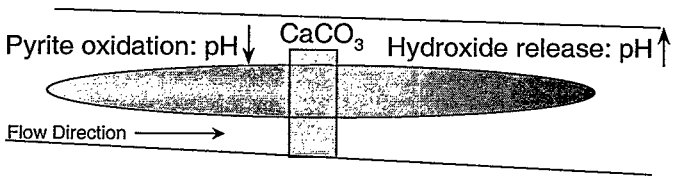
pH Control

- The use of a PRB to either raise or lower the aqueous system pH
- Indirect pH control through biological activity
- Example materials include:
  - lime, crushed limestone, organic compost
  - pyrite, carbonic acid

pH Control—Example

- PRB composed of crushed limestone to treat acid water conditions

$$FeS_2 + 3.5\ O_2 + H_2O = 2\ SO_4^{2-} + Fe^{2+} + 2\ H^+$$
$$Fe^{2+} + 0.25\ O_2 + 2.5\ H_2O = Fe\ (OH)_3 + 2\ H^+$$

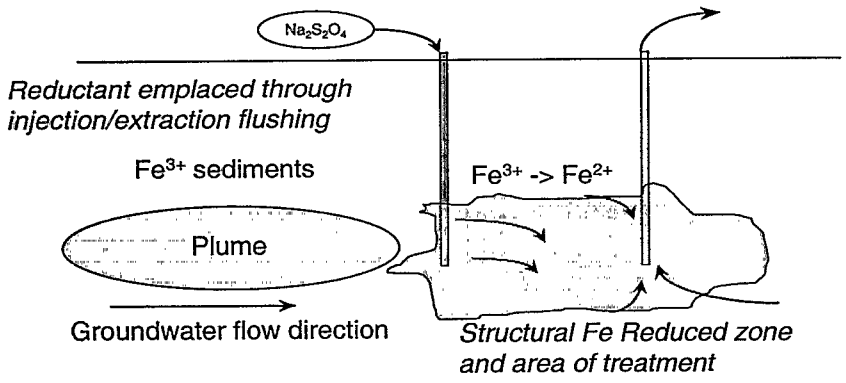


Oxidation-Reduction

- Geochemical modification of the aqueous environment through manipulation of oxidation-reduction potential
- Example materials:
  - sodium dithionite ($Na_2S_2O_4$) to reduce Fe(III) to Fe(II)
  - organic compost to reduce sulfate, generate HS, and indirectly form metal precipitates

Oxidation-Reduction Example

- Geochemically manipulated PRB from injection of sodium dithionite (Fruchter, et al.)



Coprecipitation on Mineral Surfaces

- Definition: removing a soluble metal from solution through precipitation of another (carrier) component
- Allows metals to be removed beyond the limits predicted by equilibrium values
- Used often in wastewater treatment
- Example: removal of zinc from a flow system

  $FeCl_3 + 3H_2O \Longrightarrow Fe(OH)_3 + 3H^+ + Cl^-$

  Zn is trapped within and adsorbed to $Fe(OH)_3$

Sorption Reactions

- A general term to define processes of how chemicals sorb (attach) to and desorb (detach) from solid particles
- Divided into three types of reactions:
  - hydrophobic
  - hydrophilic
  - ion exchange

Sorption Reactions

- Chemicals sorb by:
  - diffusing into soil matrix
  - adhering onto organic matter on soil
  - attracted by electrical charge
- Chemicals desorb by:
  - diffusion along a concentration gradient
  - displacement by a molecule with higher affinity for the site

Sorption of Organics

- Good for compounds with
  - low water solubility
  - hydrophobic character
  - not easily biodegraded
- Example materials include:
  - GAC, peat, coal, organic-rich shale, zeolite

sect9

Sorption of Inorganics

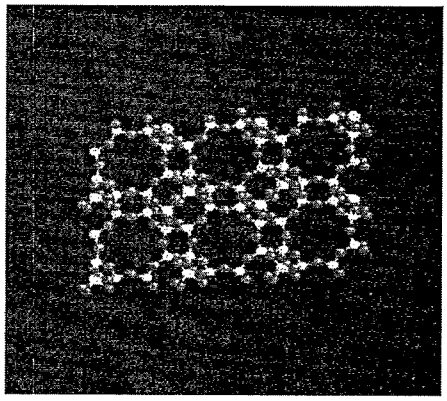
- Good for compounds such as metals
  - affinity on carbon: Pb>Cu>Ni>Zn=Mn=Cd=Co
- Well-suited to hydrophilic and ion exchange sorption reactions
- Examples include:
  - organic carbon, zeolites, clays, oxyhydroxides

Sorption Materials - Zeolites

Example:

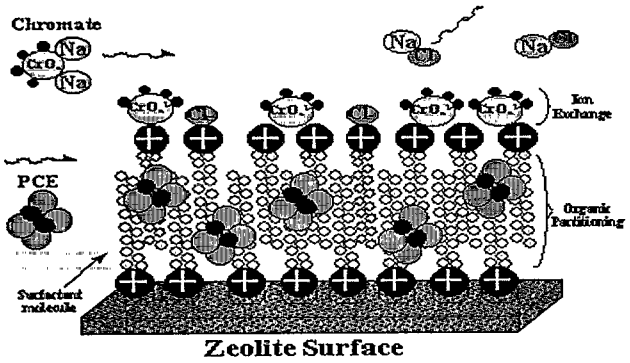
Clinoptilolite

$(Na, K, Ca)_{2\text{-}3}Al_3(Al, Si)_2Si_{13}O_{36}\text{-}12H_2O$



Enhanced Sorption

- Surface modified zeolite PRB to sorb metals (e.g., Cr, U, Sr, As)



Source: New Mexico Tech and Oregon Graduate Institute

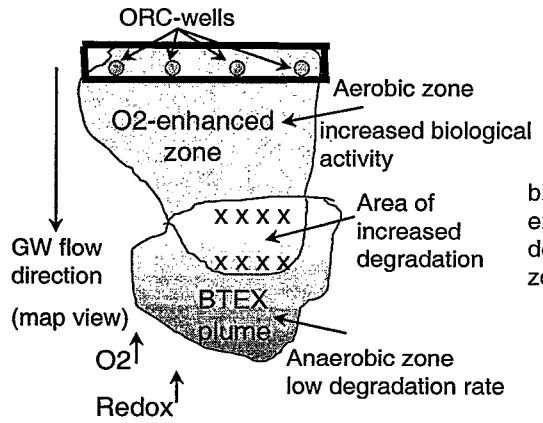
Biological Enhancement

- Addition of nutrients to stimulate microbial activity necessary for chemical degradation
- Example materials
  - oxygen-releasing compound or oxygen source to stimulate aerobic microbes (treat BTEX)
  - nitrate to stimulate anaerobic microbes
  - sugar (carbon source) to stimulate anaerobic microbes (treat chlorinated VOCs)
  - sulfate-reducing bacteria

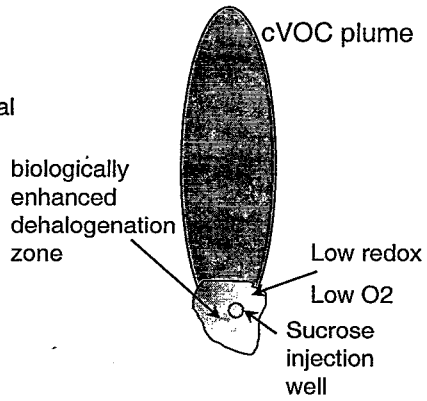
sect9

PRB as Biologically Enhanced Area

Oxygen release



Sucrose addition



ORC and HRC Barriers

- **Oxygen Release Compound**
  - **$MgO_2 + H_20 \rightarrow 1/2\ O_2 + Mg\ (OH)_2$**
- **Hydrogen Release Compound**
  - **Polyactate ester that releases lactic acid when hydrated**
  - **Lactic acid is metabolized anaerobically releasing H**

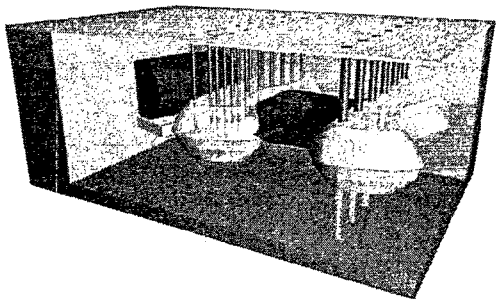


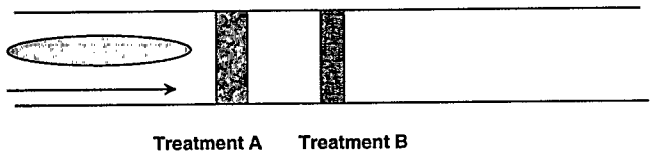
Diagram Courtesy Regenesis Bioremediation Products

Considerations for Using Reactants

- Understanding ambient hydro/geochemistry
  - hydrochemical type (major inorganics)
  - redox
  - organic content
- Understanding physical flow system
  - dispersion, heterogeneity, groundwater velocity
- Longevity of treatment
  - active life, need to re-apply

Sequential Treatment Design

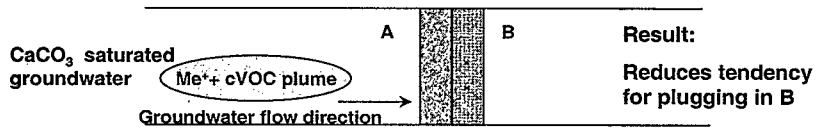
- Use of two or more processes in series to treat a mixed plume - advantages:
  - increase effectiveness of principal treatment
  - polish treatment
  - increase the longevity of the remedy



sect9

Sequential Design System (continued)

Example: Sorption - Dehalogenation



Treatment A - Zeolite for sorption of metals and carbonate - high porosity

Treatment B - Zero-valent metal to dehalogenate cVOC

Sequential Treatment—Issues

- Treatment process considerations
  - oxidizing vs. reducing conditions
  - pH affects
  - interfering mineralization/blinding
  - electron consumption
- Implementation
- Hydraulics

Case Studies

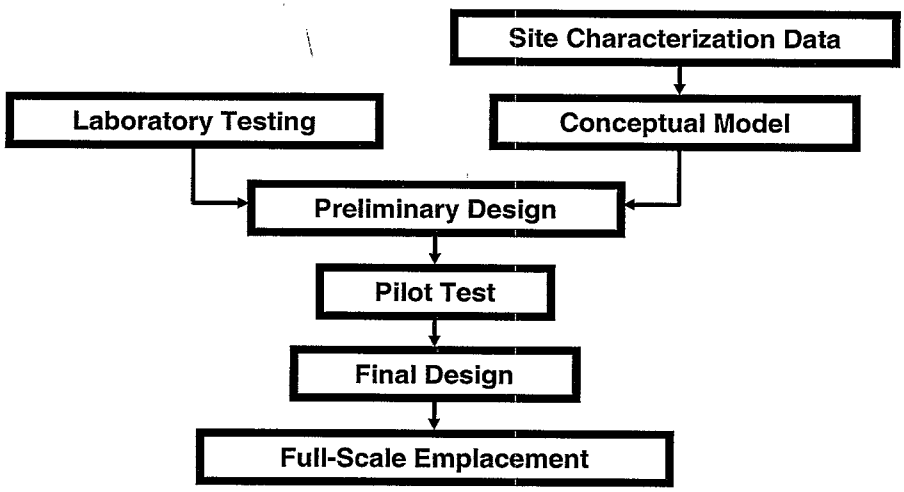
Section 10

Economic Considerations for PRB Deployment

EPA/ITRC/RTDF
Permeable Reactive Barrier Short Course

Economic Considerations for PRB Deployment

Path to PRB Design and Emplacement



sect10

Cost Considerations

- Site characterization
- Design (includes laboratory and field pilot, if necessary)
- Construction
  - reactive material
  - hydraulic barriers (if necessary)
  - disposal of excess soil and materials
- Monitoring
- Operation and maintenance
- Legal issues

Factors Affecting Treatment Cost

- Influent VOC concentrations and MCLs
- Groundwater velocity
- VOC degradation rates
- Depth, width, saturated thickness of plume
- Reactive material
- Installation method
- Licensing fees, if applicable

Cost Analysis Approach

- Present value
- Uniform template site methodology

Present Cost Definition

$$PV = \sum_{i=0}^{n} \frac{Y_i}{(1 + r)^i}$$

Where:

i = 0	Capital investment year
i = 1-->n	Operation and maintenance years
r =	Discount rate
Y =	Dollars expended in year 'i'
n =	Number of years

sect10

General Economic Assumptions

- Inflation is constant at 4%
- Cost of capital is constant at 12% for industry
- Analysis is done on a before-tax basis
- Remedial time frame is 30 years
- Monitoring cost per well per year is $2500
- Monitoring wells cost $2400 each

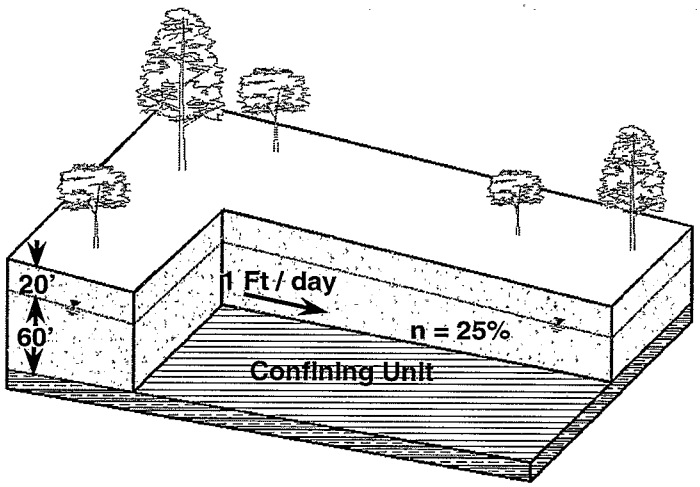
Template Methodology

- Establishes a consistent method to evaluate and compare groundwater cleanup technologies utilizing financially sound metrics
- Defines a generic template site
- Allows costs of alternatives to be compared on a uniform basis

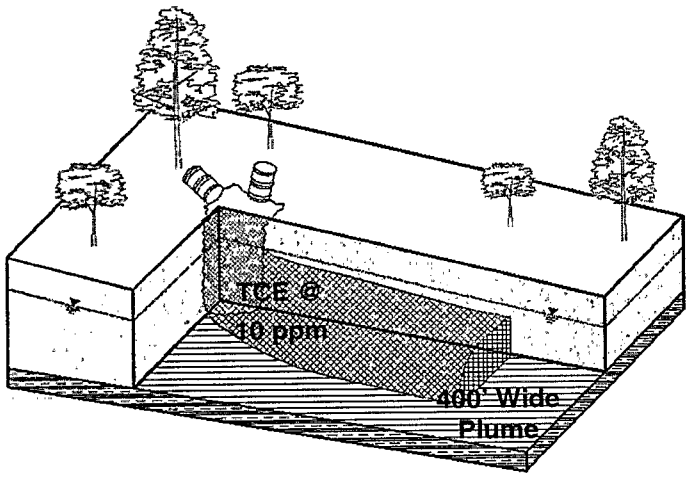
Template: Definition

- The template serves as a fixed model of the remediation site conditions for establishing:
  - physical site parameters
  - contaminant and concentration
  - remedial goals

Template Site



Plume Description



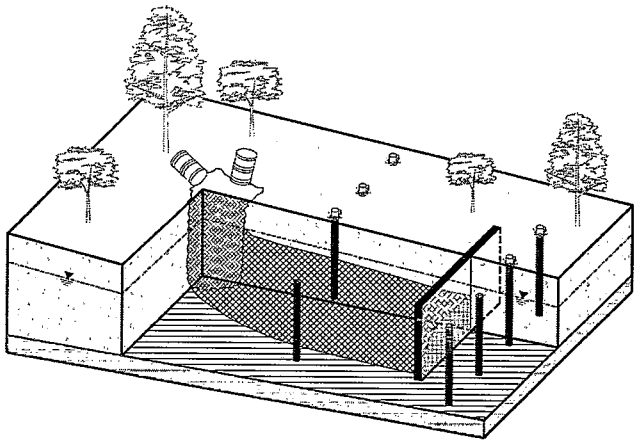
Other Contaminant Assumptions

- Remedial goals at compliance point
  - TCE = 5 ppb
  - cDCE = 70 ppb
  - VC = 2 ppb

Cost Analysis of PRBs

- Cost analysis of barriers
  - continuous
  - funnel and gate
- Comparison to pump and treat
- Comparison to intrinsic bioremediation

Continuous Reactive Wall



sect10

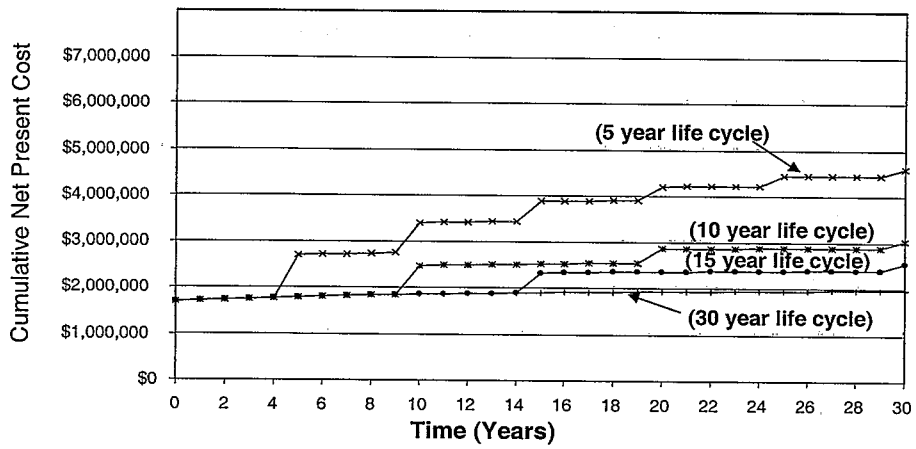
Continuous PRB Assumptions

- PRB emplacement cost: $20/ft^2
- Granular cast iron: $400/ton and 165 lbs/ft^3
- Barrier thickness: 1 foot (48 hr residence time)
- Licensing fee: 15% of capital
- Up front engineering cost: $200,000
- Number of monitoring wells: 10

Continuous PRB Summary

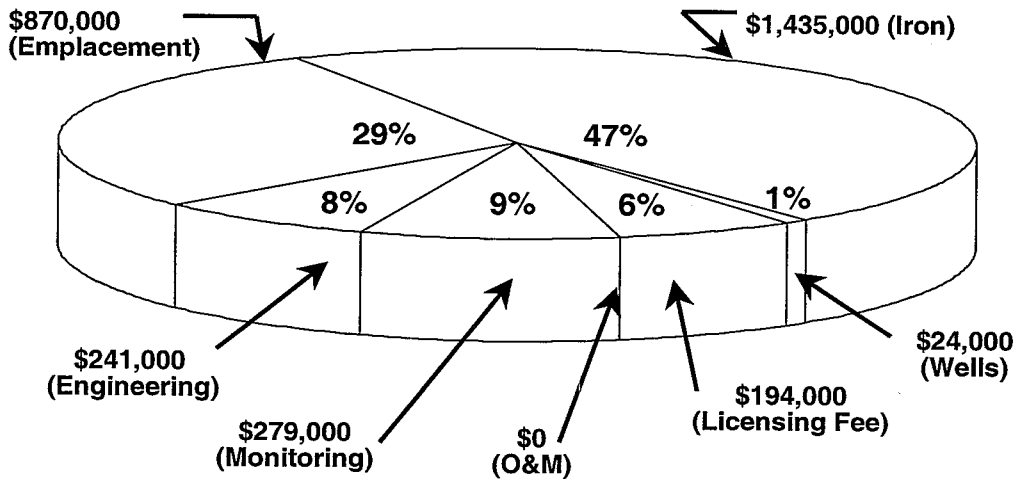
	Replacement Cycle			
Cost Item	5 Year	10 Year	15 Year	30 Year
Engineering	$299K	$240K	$222K	$200K
Emplacement	$1,434K	$870K	$690K	$480K
Iron	$2,367K	$1,435K	$1,138K	$792K
Wells	$24K	$24K	$24K	$24K
Licensing Fee	$194K	$194K	$194K	$194K
O&M	$0	$0	$0	$0
Monitoring	$279K	$279K	$279K	$279K
Total	$4,597K	$3,042K	$2,547K	$1,969K

Continuous Reactive Wall



Continuous Wall

(10–Year Replacement Cycle - $3,042K)



sect10

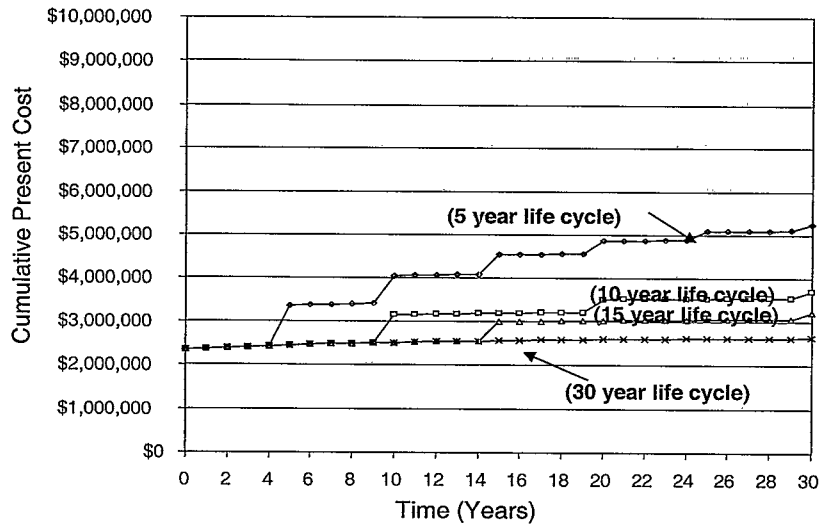
Funnel and Gate Assumptions

- Funnel emplacement cost: $25/ft^2
- Gate emplacement cost: $100/ft^2
- Granular cast iron: $400/ton and 165 lbs/ft^3
- Gate: 20 feet by 20 feet (48 hr residence time)
- Licensing fee: 15% of capital
- Up front engineering cost: $200,000
- Number of monitoring wells: 10

Funnel and Gate Summary

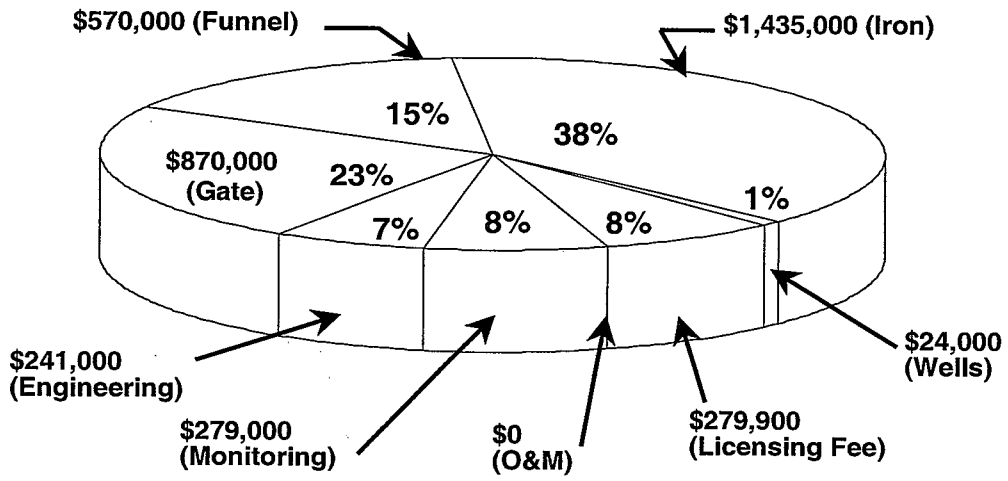
	Replacement Cycle			
Cost Item	5 Year	10 Year	15 Year	30 Year
Engineering	$299K	$240K	$222K	$200K
Gate	$1,434K	$870K	$690K	$480K
Funnel	$570K	$570K	$570K	$570K
Iron	$2,367K	$1,435K	$1,138K	$792K
Wells	$24K	$24K	$24K	$24K
Licensing Fee	$279K	$279K	$279K	$279K
O&M	$0	$0	$0	$0
Monitoring	$279K	$279K	$279K	$279K
Total	$5,523K	$3,698K	$3,203K	$2,625K

Funnel and Gate PV Summary



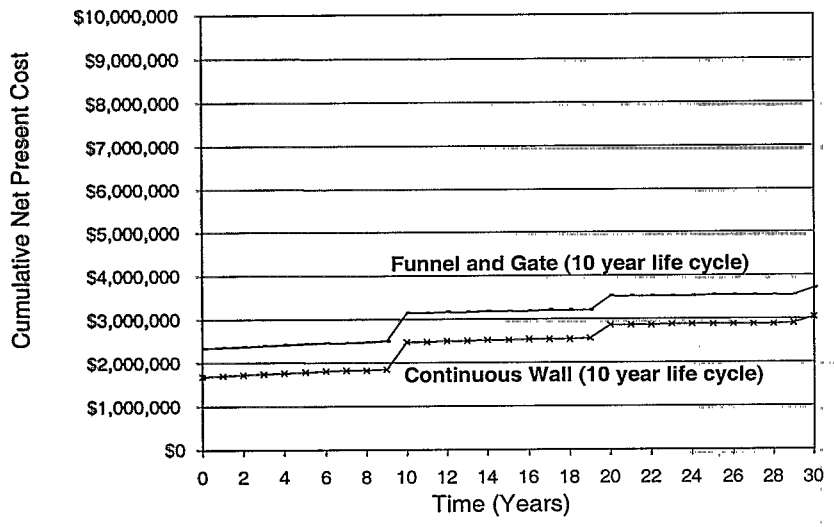
Funnel and Gate

(10 Year Replacement Cycle - $3,698K)

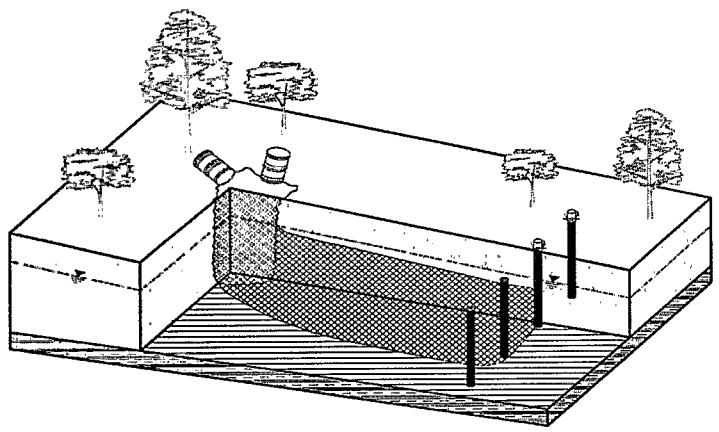


sec110

Continuous vs. F&G Summary



Pump and Treat



Pump and Treat Assumptions

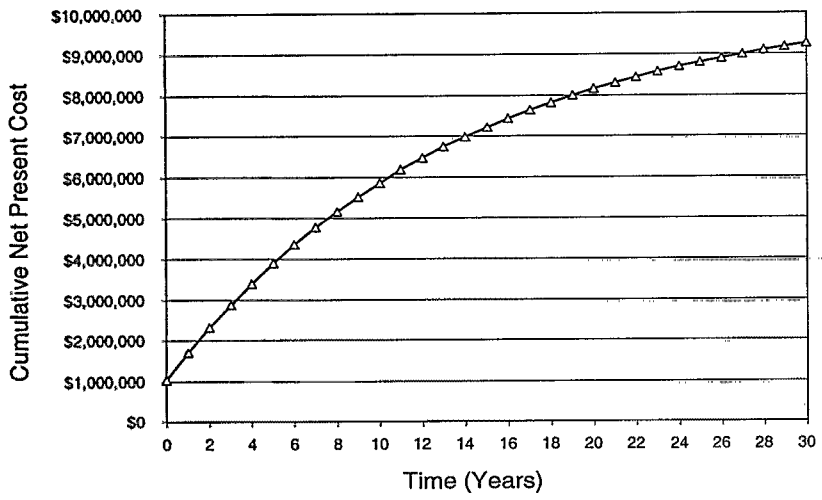
- In situ flux = 47 gpm
- P&T rate = 70 gpm
- Capital investment: $15K per installed gpm
- O&M cost: $20 per 1000 gallons treated

Pump and Treat Summary

	Year 1	NPV
Capital	$1,050K	$1,050K
O&M	$736K	$8,202K
Total	$1,786K	$9,252K

sect10

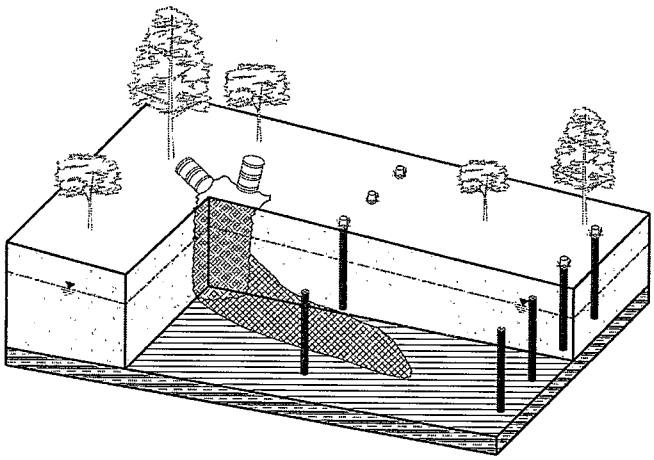
Pump and Treat



Intrinsic Bioremediation Assumptions

- Number of monitoring wells: 20
- Up front engineering: $250,000

Intrinsic Bioremediation

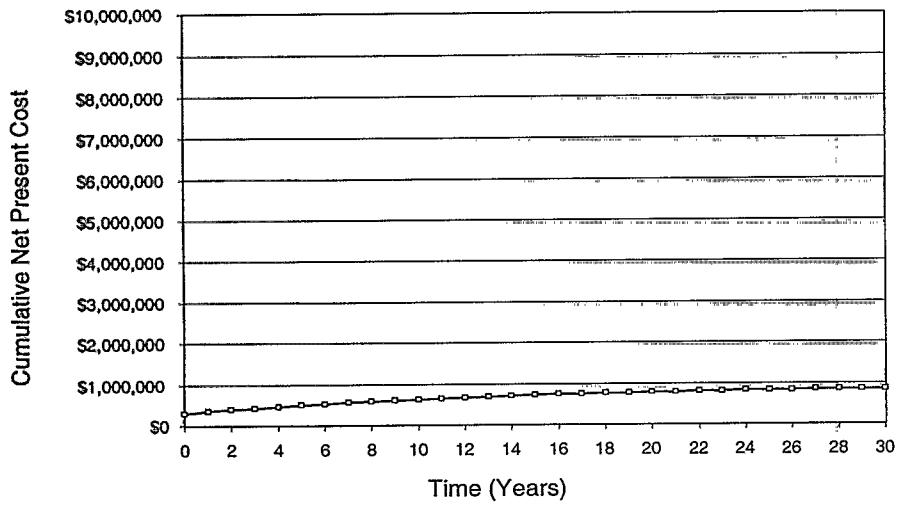


Intrinsic Bioremediation Summary

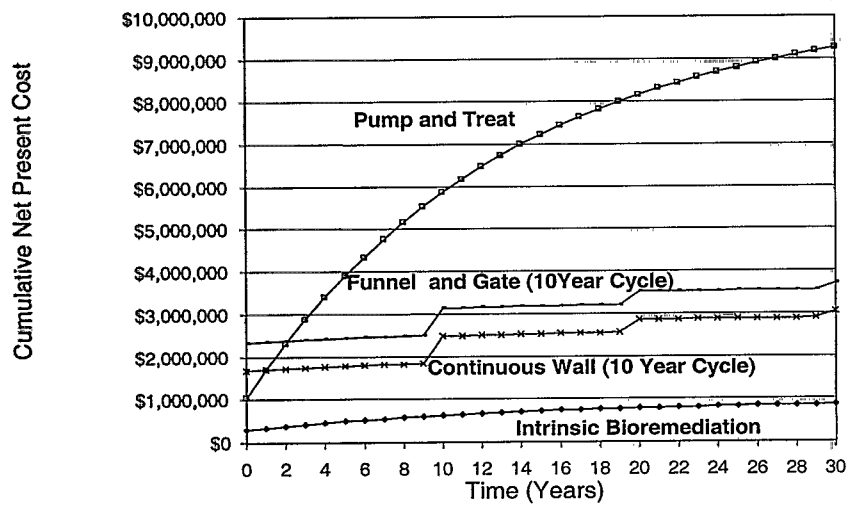
	Year 1	NPV
Engineering	$250K	$250K
Wells	$48M	$48K
O&M	$0K	$0K
Monitoring	$50K	$557K
Total	$348K	$855K

sect10

Intrinsic Bioremediation



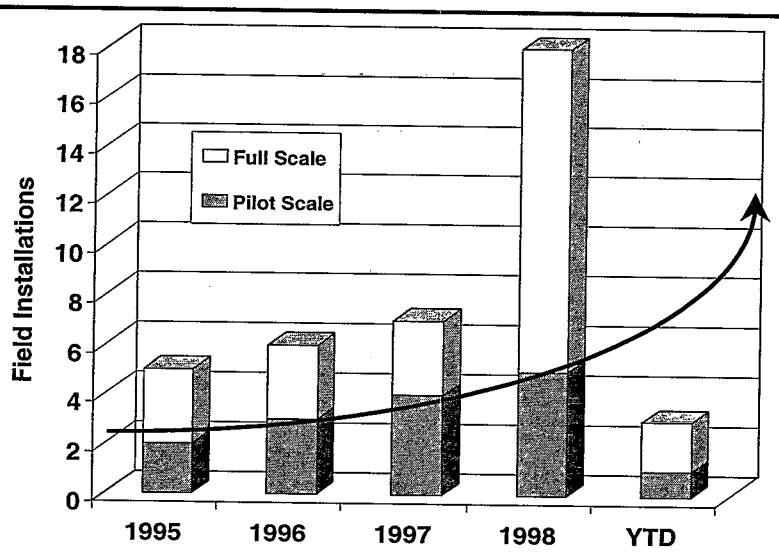
Overall NPV Summary



Conclusions

- Comparing remedial alternatives using the template site methodology is effective
- Permeable reactive barriers are cost-effective compared to pump and treat
- Synergy with natural biodegradation processes should be considered during the design stage

Conclusions



Section 11

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