This is the second training on Permeable Reactive Barrier Walls from the ITRC. It responds to student requests to provide additional detail and describe advancements in the science and engineering to design, install, maintain and monitor reactive barrier systems. This curriculum will train students using case studies to describe long-term performance of iron-based systems and design them according to the heterogeneities of the subsurface. New construction techniques for excavation and wall emplacement have improved dramatically and the attention of barrier construction is as critical as is performance monitoring. This training is designed for State and Federal regulators and the practicing consultants. Site owners and community stakeholders will find this new information interesting as well. The training does not focus on the basic science and engineering of barrier systems but does present information from industry and State regulators using up to date case studies to document the data.

This training also describes non-iron barrier systems, the material most commonly used and the mechanisms encouraging a reduction in contaminant concentrations with in the systems.

This presentation can be accessed at: http://www.clu-in.org/conf/itrc/advprb

Three ITRC PRB documents are available as supportive materials for this course at www.itrcweb.org and at: http://www.clu-in.org/conf/itrc/advprb/resource.htm

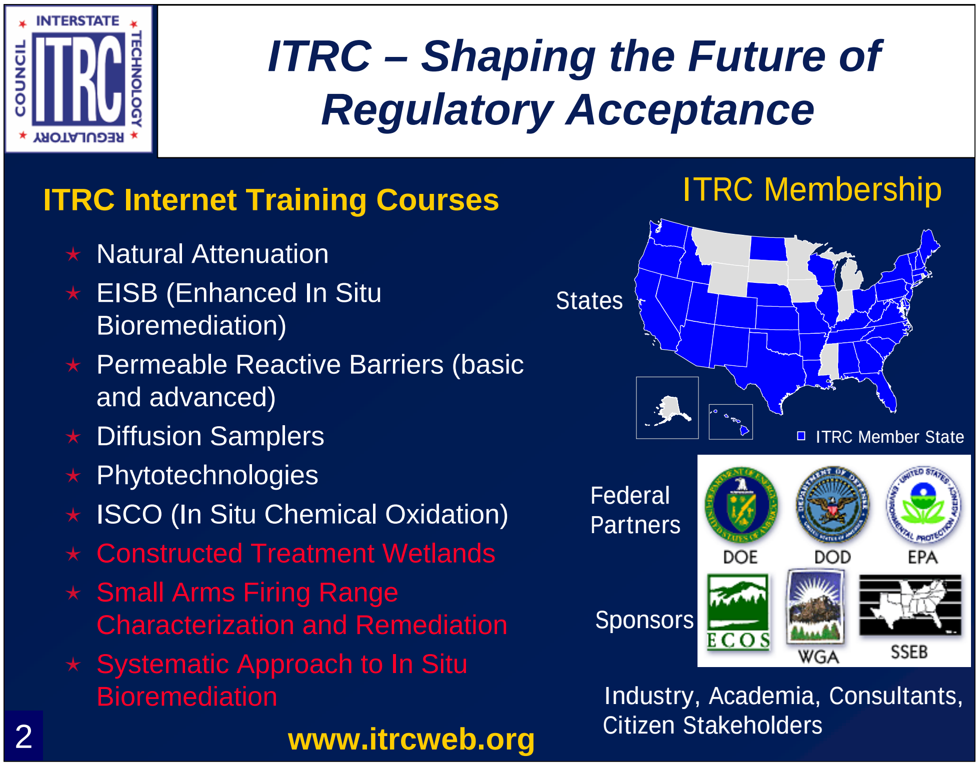
****

ITRC – Interstate Technology and Regulatory Council (www.itrcweb.org)

EPA-TIO – Environmental Protection Agency – Technology Innovation Office (www.clu-in.org)

ITRC Course Moderator:

Mary Yelken (Western Governors' Association/ITRC – myelken@westgov.org)

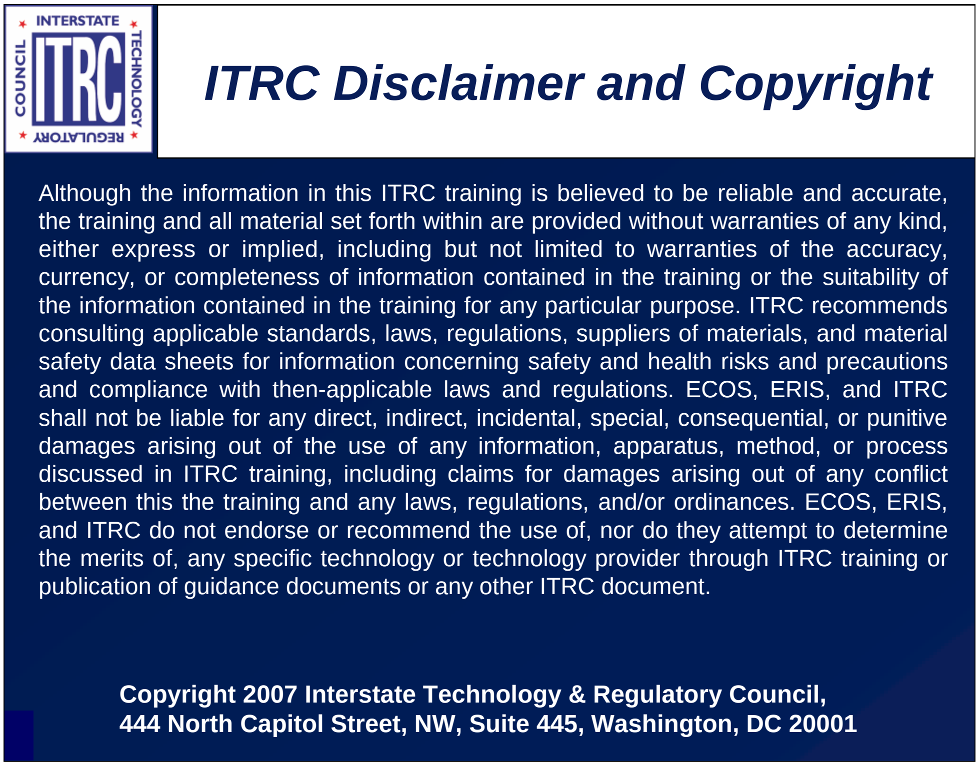


The bulleted items are a list of ITRC Internet Training topics – go to www.itrcweb.org and click on "internet training" for details.

The **Interstate Technology and Regulatory Council (ITRC)** is a state-led coalition of regulators, industry experts, citizen stakeholders, academia, and federal partners that work to achieve regulatory acceptance of environmental technologies. ITRC consists of 40 states (and the District of Columbia) that work to break down barriers and reduce compliance costs, making it easier to use new technologies and helping states maximize resources. ITRC brings together a diverse mix of environmental experts and stakeholders from both the public and private sectors to broaden and deepen technical knowledge and streamline the regulation of environmental technologies. Together, we're building the environmental community's ability to expedite quality decision-making while protecting human health and the environment. With our network approaching 6,000 people from all aspects of the environmental community, ITRC is a unique catalyst for dialogue between regulators and the regulated community.

ITRC originated in 1995 from a previous initiative by the Western Governors' Association (WGA). In January 1999, it affiliated with the Environmental Research Institute of the States, ERIS is a 501(c)3 nonprofit educational subsidiary of the Environmental Council of States (ECOS). ITRC receives regional support from WGA and the Southern States Energy Board (SSEB) and financial support from the U.S. Department of Energy, the U.S. Department of Defense, and the U.S. Environmental Protection Agency.

To access a list of ITRC State Point of Contacts (POCs) and general ITRC information go to www.itrcweb.org.



Here's the lawyer's fine print. I'll let you read it yourself, but what it says briefly is:

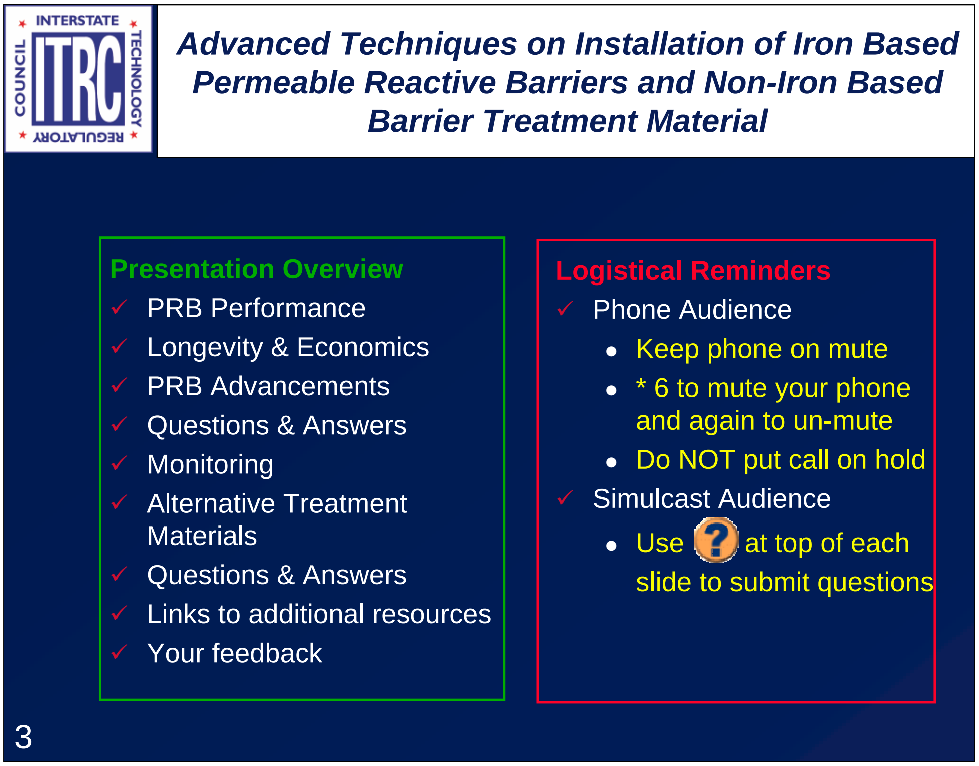
•We try to be as accurate and reliable as possible, but we do not warrantee this material.

•How you use it is your responsibility, not ours.

•We recommend you check with the local and state laws and experts.

•Although we discuss various technologies, processes, and vendor's products, we are not endorsing any of them.

•Finally, if you want to use ITRC information, you should ask our permission.



Supporting ITRC documents (available at www.itrcweb.org or http://www.clu-in.org/conf/itrc/advprb/resource.htm)

***** "Design Guidance for Application of Permeable Barriers to Remediate Dissolved Chlorinated Solvents"**

***** "Regulatory Guidance for Permeable Barrier Walls Designed to Remediate Chlorinated Solvents"**

***** "Regulatory Guidance For Permeable Reactive Barriers Designed to Remediate Inorganic and Radionuclide Contamination"**

Today's Instructors

★ **Matthew Turner**
- NJ Dept. of Environmental Protection
- 401 E. State St.
- Trenton, NJ, 08625
- T 609-984-1742
- F 609-633-1454
- mturner@dep.state.nj.us

★ **Arun Gavaskar**
- Battelle
- 505 King Ave.
- Columbus Ohio 43201
- T 614-424-3403
- F 614-424-3667
- gavaskar@battelle.org

★ **Mike Duchene**
- EnviroMetal Technologies, Inc
- 745 Bridge St W, Suite 7
- Waterloo, Ontario N2V 2G6
- T 519-746-2204
- F 519-746-2209
- mduchene@eti.ca

★ **Scott Warner**
- Geomatrix Consultants, Inc.
- 2101 Webster St, 12th Fl
- Oakland, Ca 94612
- T 510-663-4269
- F510-663-4141
- swarner@geomatrix.com

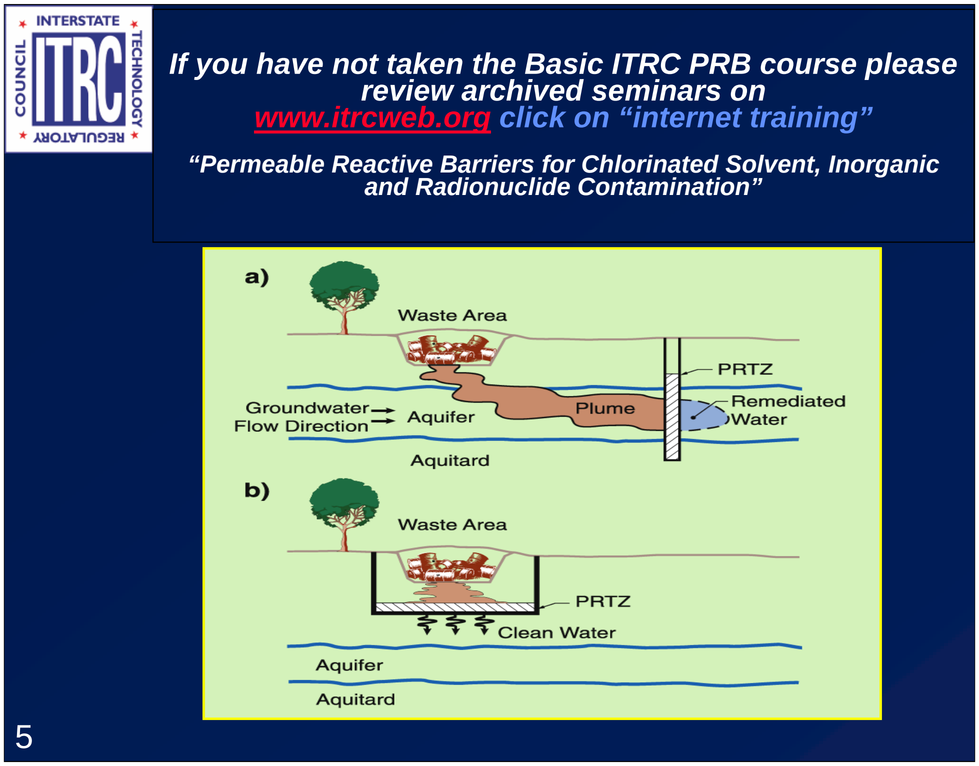
4

Matthew Turner has a B.S. in Biology and a M.S. in Environmental Science. With 15 years experience in the environmental field, he is currently employed by the New Jersey Department of Environmental Protection as a Case Manager in the Site Remediation Program. He is a member of the Interstate Technology and Regulatory Cooperation Workgroup where he has served as the leader of the Permeable Barrier Wall Subgroup since 1997. He is also a participant in the Remediation Technology Development Forum's Action Team on Permeable Reactive Barriers.

Arun Gavaskar is a Research Leader/Group Leader in the Environmental Restoration Department at Battelle, Columbus, Ohio. He has a background in chemical engineering and environmental technology, and has worked for thirteen years in the remediation and industrial pollution prevention areas. His current research interests include the remediation of a variety of groundwater, soil, and sediment contaminants, namely, DNAPL and dissolved-phase chlorinated solvents, heavy metals, and PCBs/dioxins. He also co-chaired the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds at Monterey, California in May 2000.

Scott Warner is a Principal Hydrogeologist at Geomatrix Consultants, Inc. with 14 years experience and expertise in hydrogeology, geochemistry, and innovative soil and groundwater treatment technologies. He has B.S. in engineering geology from U.C.L.A. and M.S. in geology from Indiana University, Bloomington. Mr. Warner has provided consultation to the U.S. Department of Energy, the U.S. Department of Defense, the U.S. Environmental Protection Agency, and many private companies on innovative remediation technologies, including the use of bioremediation, permeable reactive barriers, and related technologies. He has also provided expert witness work with respect to litigation involving environmental remediation and geochemistry. He also leads Geomatrix focus groups on VOC/DNAPL remediation, and arsenic in groundwater. Mr. Warner is a steering committee member of the Remediation Technologies Development Forum, Permeable Barriers Subgroup, and is a lead developer and instructor for the USEPA-sponsored permeable reactive barriers short course.

Mike Duchene is a senior engineer at EnviroMetal Technologies Inc. (ETI) with more than 10 years consulting engineering experience in the environmental field. He received both his Bachelors of Applied Science and Masters of Applied Science in Civil Engineering from the University of Waterloo. He joined ETI in October 1999. Prior to joining ETI, Mike worked primarily as a design engineer and designed and operated several groundwater remediation systems. At ETI, his responsibilities include managing various engineering aspects of the design and installation of PRBs. Mike is primarily involved in assisting clients in the detailed design of PRBs including detailed assessments of groundwater hydraulics, assessment and specification of potential construction techniques, and construction QA/QC protocols. He is also involved in the development and evaluation of innovative construction methods and the interpretation of chemical and hydrogeological performance data for completed PRBs.



It is important that you know that this is a follow-on course to the first ITRC Permeable Reactive Barrier course.

We pointed out in the introduction to this course that you could and should access and review the archived version of the 1st course before taking this course. We hope to limit our questions to those relative to this advanced training.

Hydraulic Performance of Field PRBs
"Lessons learned for future applications"

- Groundwater capture zone
  - **Ensuring that the barrier captures sufficient water**
  - **Ensuring that the barrier captures the targeted water**
- Residence time
  - **Ensuring that groundwater flowing through the barrier gets sufficient residence time for contaminant removal to target levels**

6

Variety of Hydrogeologic Characteristics of PRB Sites

Site	NAS Alameda	Dover AFB	Lowry AFB	Moffett Field	Seneca Army D
Aquifer Type	Unconfined	Unconfined	Unconfined	Semi-confined	Unconfined
Aquifer Material	Artificial Fill	Silty Sand	Silty Sand, Sand, Gravel	Sand Channel	Glacial Till
Aquitard Depth (ft)	20	40	17	25	10
Aquifer Conductivity (ft/d)	221	7.4	6.0	30	25
Aquifer Gradient (ft/ft)	0.007	0.0018	0.035	0.0007	0.01
Groundwater Velocity (ft/d)	4.4	0.04	0.7	0.7	1.4

7

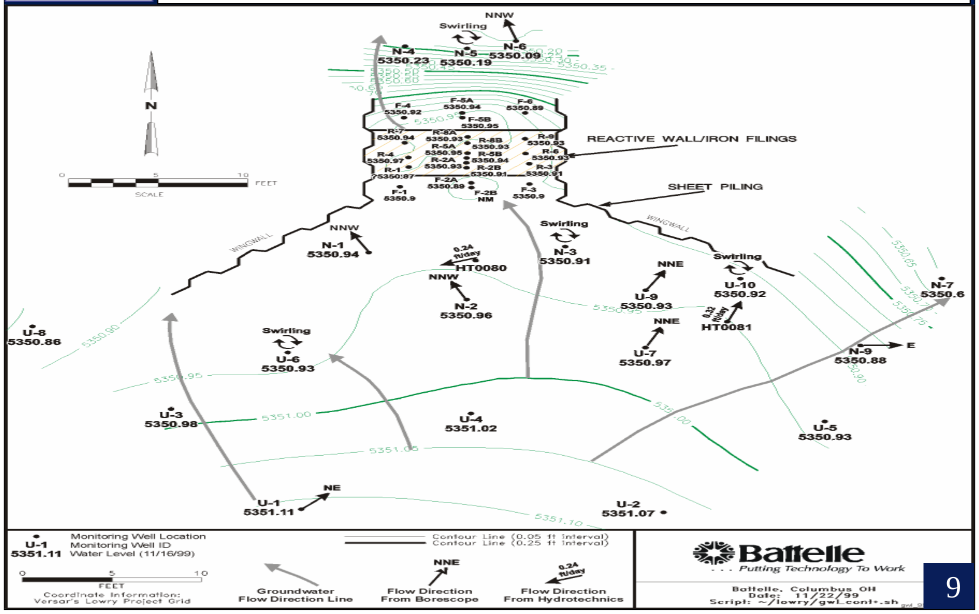
PRB at Lowry AFB (Denver, CO)
"Determining groundwater capture zone"

- Funnel & gate design pilot-scale system
- Constructed in Nov. 1995
- Master Builders iron (45 tons)
- Funnel walls keyed into bedrock at 17 ft bgs
- Stream flowing on east side of barrier

8

INTERSTATE TECHNOLOGY REGULATORY COUNCIL ITRC

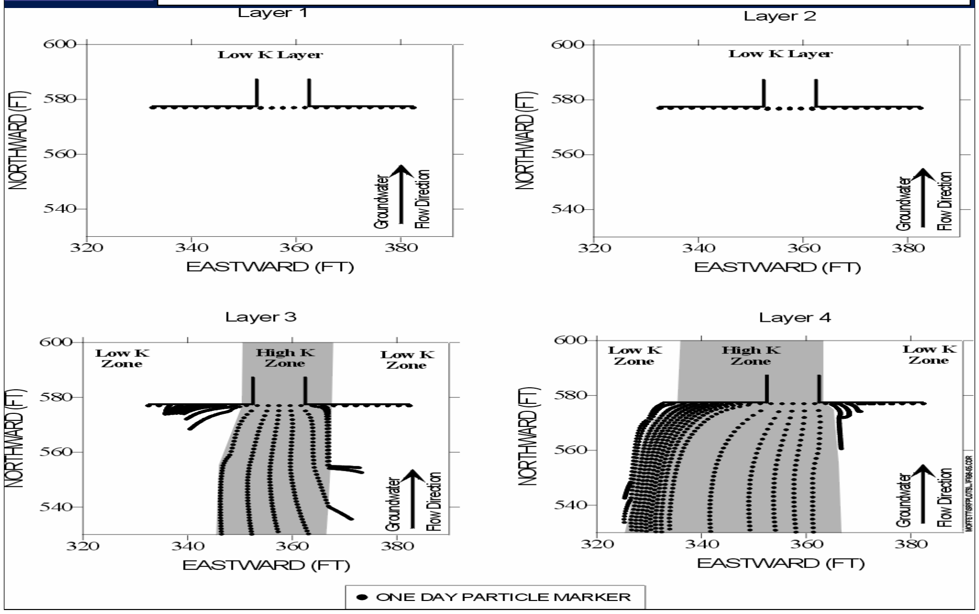
Lowry AFB: *Asymmetric Capture Zone Caused by Stream Flowing on East Side*



9

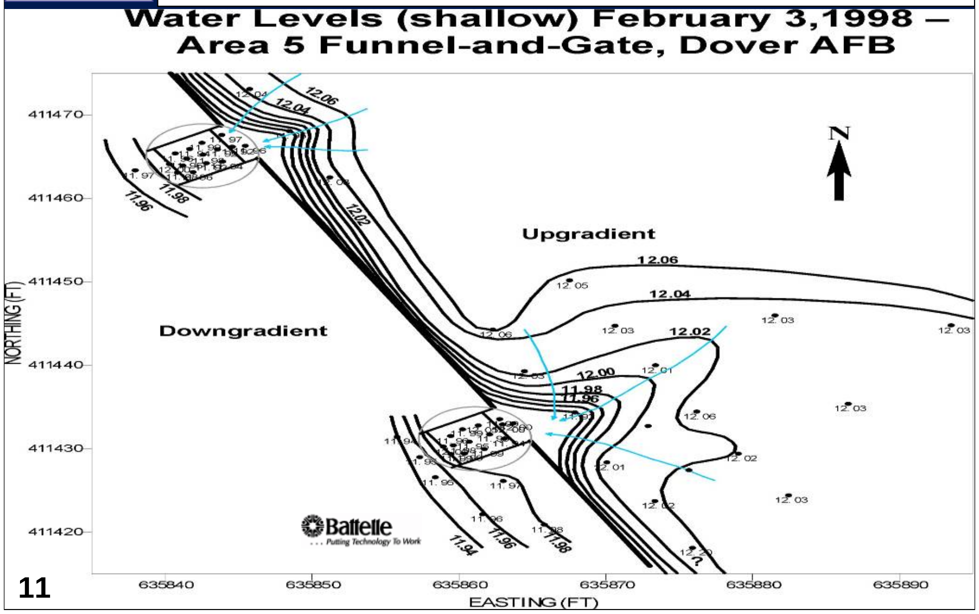
NAS Moffett Field

"Effect of aquifer heterogeneity on capture"



Asymmetric Capture Zone

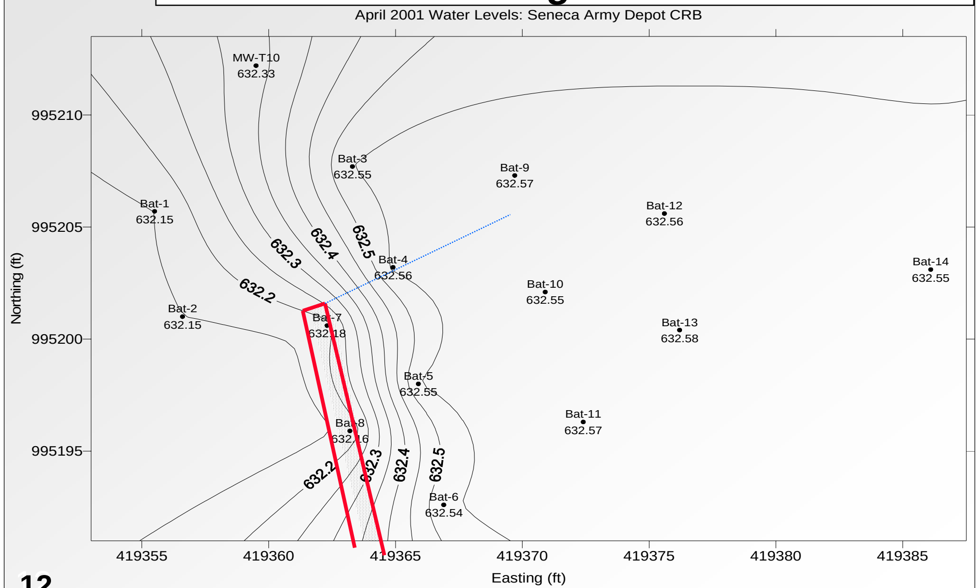
"Aquifer with very low gradients"



11

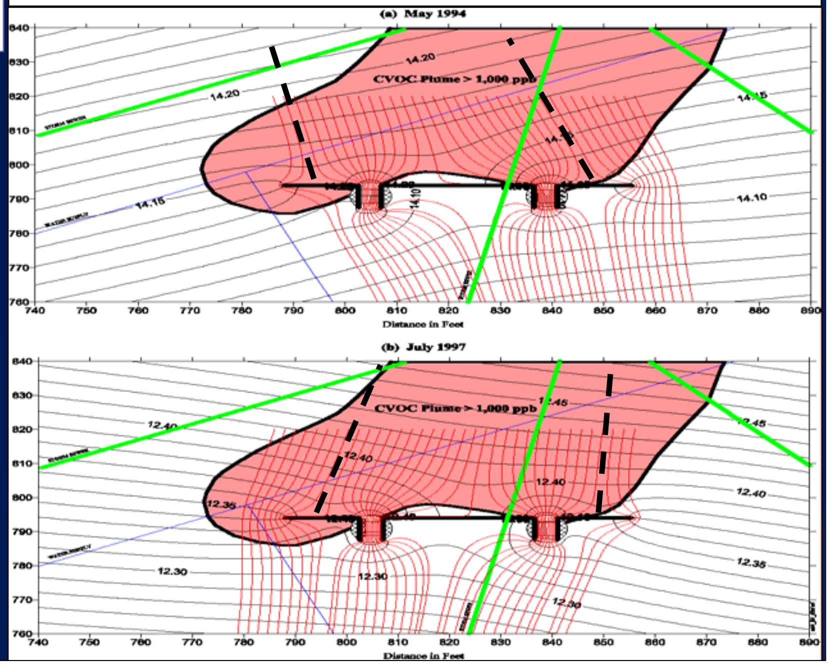
Continuous Reactive Barrier at Seneca Army Depot

"Determining flow divide"

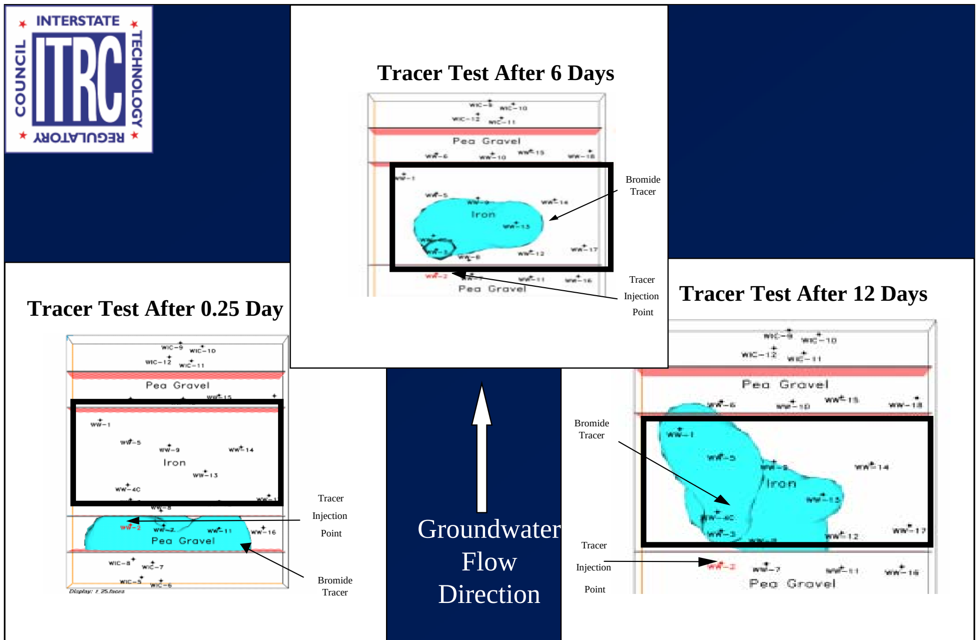


12

Dover AFB "Accounting for Seasonal Fluctuations in Groundwater Flow Direction"



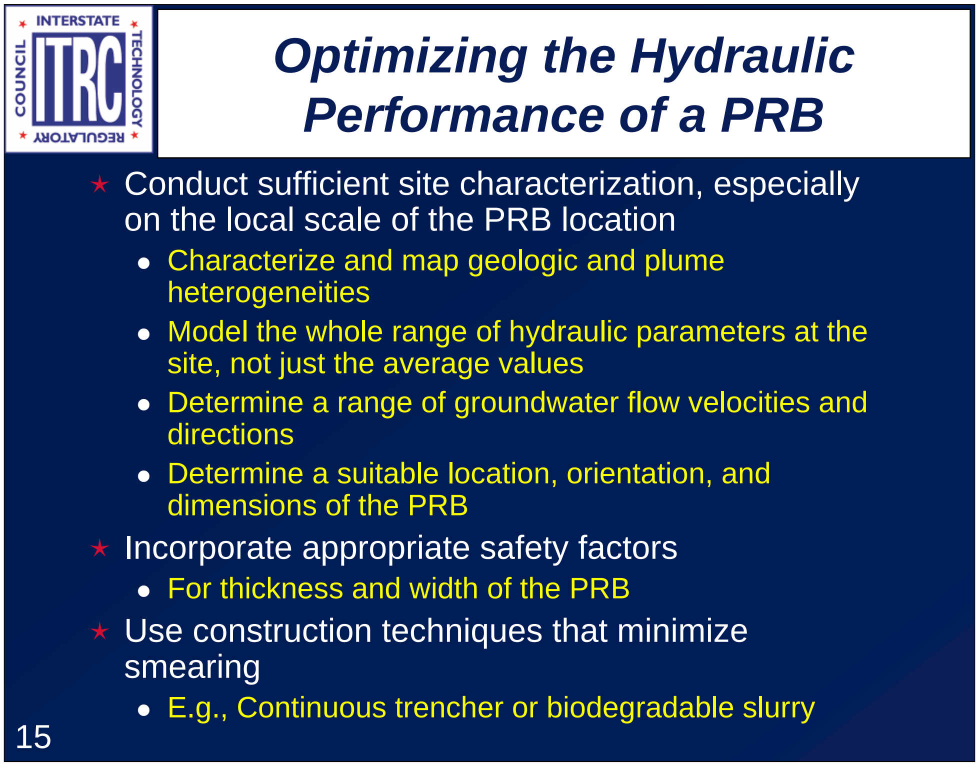
13



14

PRB at NAS Moffett Field – Tracer Test

Residence time distribution and preferential pathways in the barrier medium



Water levels

Still the best method

Look at seasonal and historical water level maps

Selectively use groundwater probes, if unusually heterogeneous flow system

In-situ Hydrotechnics™ sensor

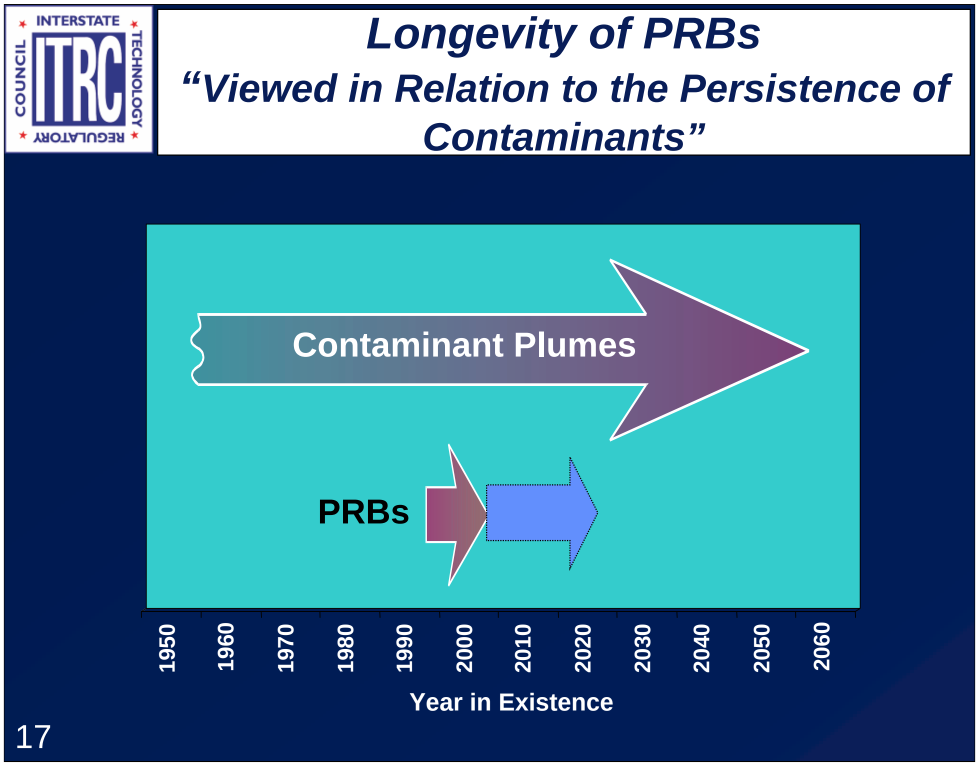
Down-hole heat pulse sensor

Colloidal borescope

Hydraulic Assessment Tools for Site Characterization and Design

- Water levels
  - Still the best method
  - Look at seasonal and historical water level maps
- Selectively use groundwater probes, if unusually heterogeneous flow system
  - In-situ Hydrotechnics™ sensor
  - Down-hole heat pulse sensor
  - Colloidal borescope
- Tracer Tests (good tool, but may be more expensive)

16



Field Investigation

Groundwater analysis (influent and effluent)

Geochemical modeling

Iron core analysis

Hydraulic monitoring (tracer test, flow sensors, hydraulic modeling)

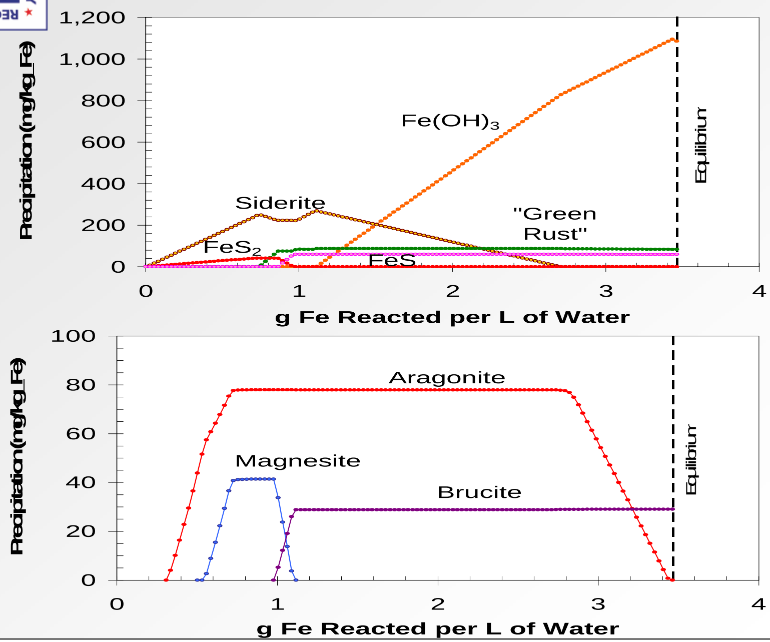
Laboratory Investigation

Long-term field performance simulation in columns

Monitor change in degradation rates as iron ages

Detailed analysis of corrosion compounds

Geochemical Modeling
"Moffett Field



18

Change in Groundwater Species Concentrations within Moffett Field Barrier (mg/L)

	Na	K	Mg	Ca	HCO_3	Cl	NO_3	SO_4
Influent	35.5	2.1	66.9	165	412	42.2	2.0	333
Effluent	29.1	1.4	1.0	10.4	62	39.1	0.0	18.0
Change	6.4	0.7	65.9	155	350	3.1	2.0	315
% Change	18%	34%	98%	94%	85%	7%	100%	95%

19

Iron Core Sampling from NAS Moffett Field Barrier (looking for long-term changes that may affect iron performance)

20

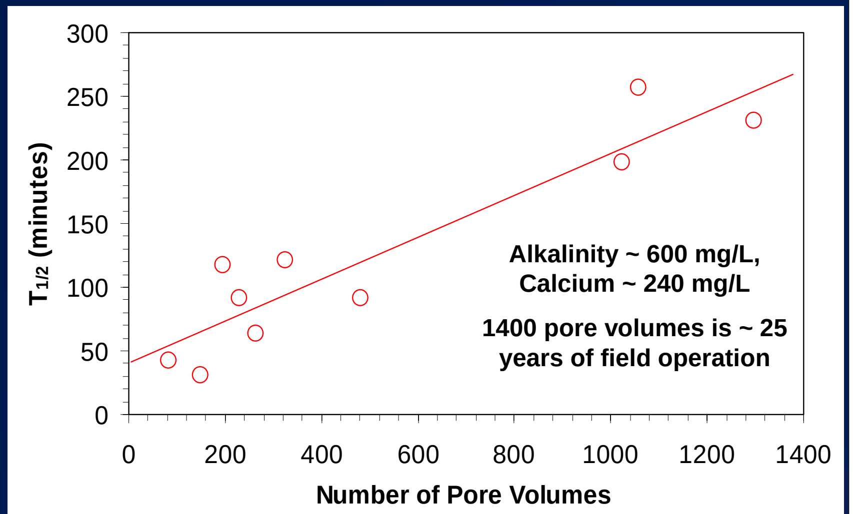
SEM Image of Silt from Monitoring Wells in the Iron at Moffett Field (illustrates the types of precipitates that deposit in the barrier)

EDS Analysis

Element	Atom %
Ca	23.3
Mg	3.5
Al	1.9
Si	15.3
Fe	18.7
Ti	0.5
Mn	1.7
S	2.1
O	32.0

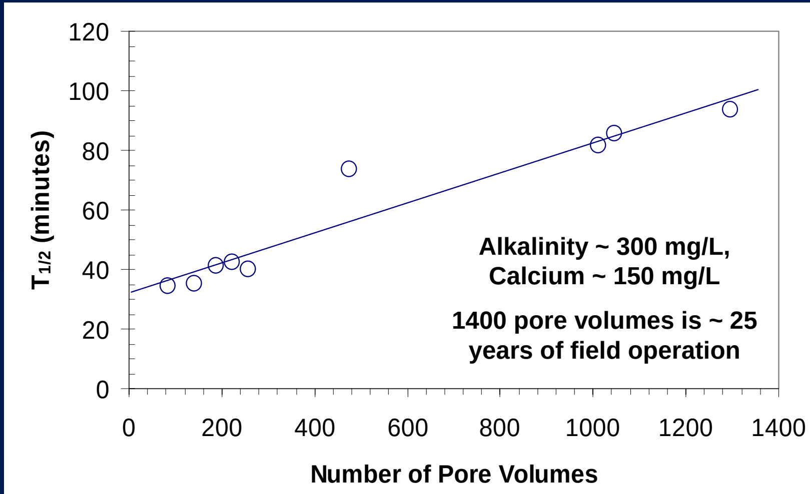
21

TCE Half-Life Changes over Time for Iron Barrier at Lowry AFB -- Long-Term Column Test



22

TCE Half-Life Changes for Iron Barrier at NAS Moffett Field -- Long-Term Column Test



23

Geochemistry of a PRB
- Implications for Longevity and Economics

- PRBs have a finite reactive life. The iron may become dormant sometime in the future, unless rejuvenated or replaced in some way
- Predicting the longevity of a PRB depends partly on the accuracy of flow estimates (hydraulics)
- Colloidal flow and deposition in monitoring wells may be factors that mitigate precipitate buildup in reactive medium.
- Economic issue – will payback on the capital invested in the PRB occur before its reactivity is exhausted
  - Indications from several sites are that it will

24

Economic Analysis of PRB versus P&T System - Present Value (PV) is a method of discounting future costs to the present

Fairfield, NJ Site (See links @ end of seminar)		Dover AFB Site (Analysis done by Battelle)	
Discount Rate = 7%	PV (30 yrs)	Discount Rate = 3%	PV (30 yrs)
P&T System	$1.6 M	P&T System	$4.9 M
7 year PRB life	$1.3 M	5 year PRB life	$5.5 M
10 year PRB life	$1.2 M	10 year PRB life	$4.6 M
30 year PRB life	$1.1 M	20 year PRB life	$4.1 M
		30 year PRB life	$4.1 M

25

Advancements in PRB Construction: "Construction Methods and Factors"

- GENERAL METHODS
  - Excavation
  - Injection
  - Other
- FACTORS
  - Geology
  - Depth of PRB
  - Target zone
  - Flow-through thickness of PRB
  - Variation of thickness along length and depth
  - Surface and subsurface obstructions
  - Site access and working area
  - QA/QC requirements

26

Excavation refers to methods where aquifer material is removed and replaced with the reactive material.

Injection methods involve the placement of the reactive media directly into the subsurface with no or minimal removal of aquifer material.

All construction methods have advantages and disadvantages. These are the primary factors to consider when evaluating the technical feasibility of the available construction methods.

Target zone refers to the depth interval where the PRB is to be installed (e.g. 50 to 80 ft bgs).

Excavation Methods for PRB Installation

Method	Depth	Installation Thickness	Number of Installations*
Unsupported Excavation	< 25 ft	> 1 ft	3
Supported Excavation	< 25 ft	> 2 ft	4
Biopolymer Slurry Excavation	<120 ft	> 1.5 ft	8
Continuous Trenching	<25 ft	1 - 2 ft	9
Cofferdam (Sheet pile)	<30 ft	> 3 ft	14

* Iron PRB for VOC treatment only

27

Unsupported excavation can be used where formation will remain open without collapsing for long enough to place reactive media (e.g. dense tills, highly weathered bedrock). Unsupported excavation is the least expensive method.

Supported excavation uses some type of shoring system such as trench boxes or hydraulic shores to temporarily support the trench until the reactive material is placed.

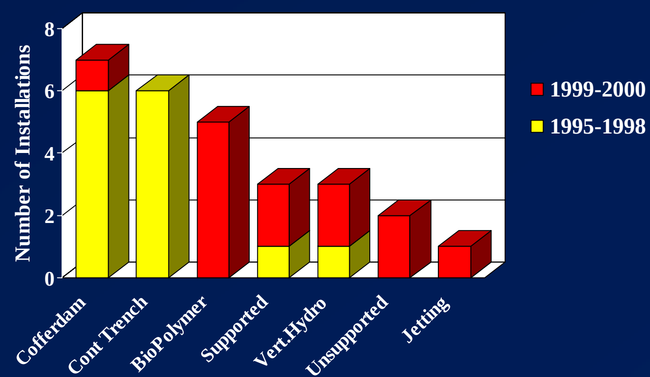
Biopolymer slurry is used to temporarily support the excavation until the reactive material is placed.

Continuous trenching simultaneously excavates the soil and places the reactive material in one pass.

Cofferdam or sheet pile involves driving sheet pile around the perimeter of the PRB and excavating the material from within.

Biodegradable Slurry Construction

- *Historically used as a drilling fluid and to support excavations for collection drains since 1980’s*
- *Most recent full-scale installations of iron for VOC treatment have involved the use of a biodegradable slurry*



28

Biopolymer uses biodegradable slurry for excavation support

Vertical hydrofracturing and jetting use biodegradable slurry to suspend the iron to allow it to be pumped.

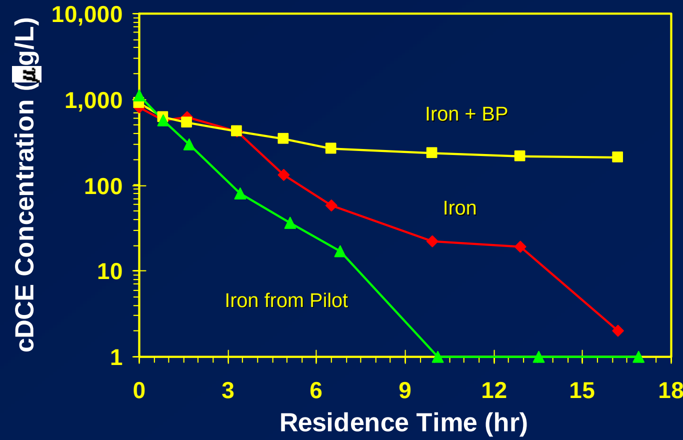
“Supported” is excavation using either a trench box or hydraulic shoring for support.

Biodegradable Slurry For Excavation Support

- Guar Gum (Galactomannan)
  - Most commonly used biodegradable slurry
  - Powder milled from specially grown beans
  - Long chain carbohydrate
  - Forms a viscous solution in water
- Biodegradable Slurry Preparation for Excavation Support
  - Guar gum powder
  - Biostat preservative
  - pH Adjustment (soda ash)
- Procedure
  - Slurry is pumped into trench as excavation proceeds
  - Granular iron placed through slurry
  - Enzyme breaker added after backfill

29

Bench-Scale Tests with Biodegradable Slurry



Source: Focht et al., 2001

30

Results from column tests. Residence time is residence time in bench-scale column. “Iron and BP” is an iron column that was saturated with biodegradable slurry then broken with enzyme breaker. “Iron” is an iron column without biodegradable slurry. “Iron from pilot” is iron collected in cores from a pilot installation completed with biodegradable slurry and packed into a laboratory column. All tests were completed at 10 deg. C.

Conclusion: Short-term negative effects of biodegradable slurry on VOC degradation rates observed in original laboratory test were not observed in the column test of material from the field core.

See: Focht. R.M., Vogan, J.L. and Krug, T.A. “Biopolymer Construction Techniques for Installation of Permeable Reactive Barriers Containing Granular Iron for Groundwater Remediation” presented at the Division of Environmental Chemistry, American Chemical Society, San Diego, CA April 1-5, 2001

Somersworth Pilot Test Monitoring Results - 3 Months

Parameter	Upgradient	Distance into Iron-Sand Zone		Downgradient
		25 cm	50 cm	
PCE (µg/L)	130	<5	<5	7
TCE (µg/L)	220	<5	<5	44
cDCE (µg/L)	120	<5	<5	170
VC (µg/L)	27	<5	<2	<2
ORP (mV)	-143	-457	-522	-185
pH	6.4	9.0	9.7	6.5
TOC (mg/L)	7	59	63	12
PLFA (cells/mL)	$10^{4.8}$	$10^{5.7}$	$10^{5.1}$	$10^{4.9}$

Source: GeoSyntec Consultants

31

Complete degradation of VOCs in PRB

Increase in pH and decrease in ORP as expected

Increase in TOC attributed to broken down guar gum remaining within PRB

Biodegradable Slurry Use for Excavation Support

Date	Site	Contaminant	Media
May 1997	Vancouver, BC (pilot)	Heavy Metals	Compost
Nov 1997	Y12 Plant, Oak Ridge, TN (pilot)	Metals	Granular Iron
Aug 1999	Pease AFB, NH	VOCs	Granular Iron
Oct 1999	Industrial Site, Seattle, WA	VOCs	Granular Iron
Nov 1999	Somersworth Landfill, NH (pilot)	VOCs	Granular Iron
Jun 2000	Pease AFB, NH	VOCs	Granular Iron
Jul 2000	Somersworth Landfill, NH	VOCs	Granular Iron
Aug 2000	Lake City Army Ammunition Plant, MO	VOCs	Granular Iron
Dec 2000	Industrial Facility, Los Angeles, CA	VOCs	Granular Iron
Mar 2001	Vancouver, BC	Heavy Metals	Compost and Granular Iron
Jun 2001	Needham, MA	VOCs	Granular Iron

32

Biodegradable Slurry Mixing and Placement


Placement in Trench

33

Guar gum in powered form is mixed with water in a slurry mixer.

Soda ash is added to adjust pH to between 9 and 10 and a biostat is added to slow the natural biodegradation of the guar gum.

Viscosity of the guar gum is measured with a Marsh Funnel.

Guar gum is pumped into the trench as excavation proceeds to maintain a hydraulic head on the trench.

Excavation with Biodegradable Slurry Support

Excavation

Modified Tremie

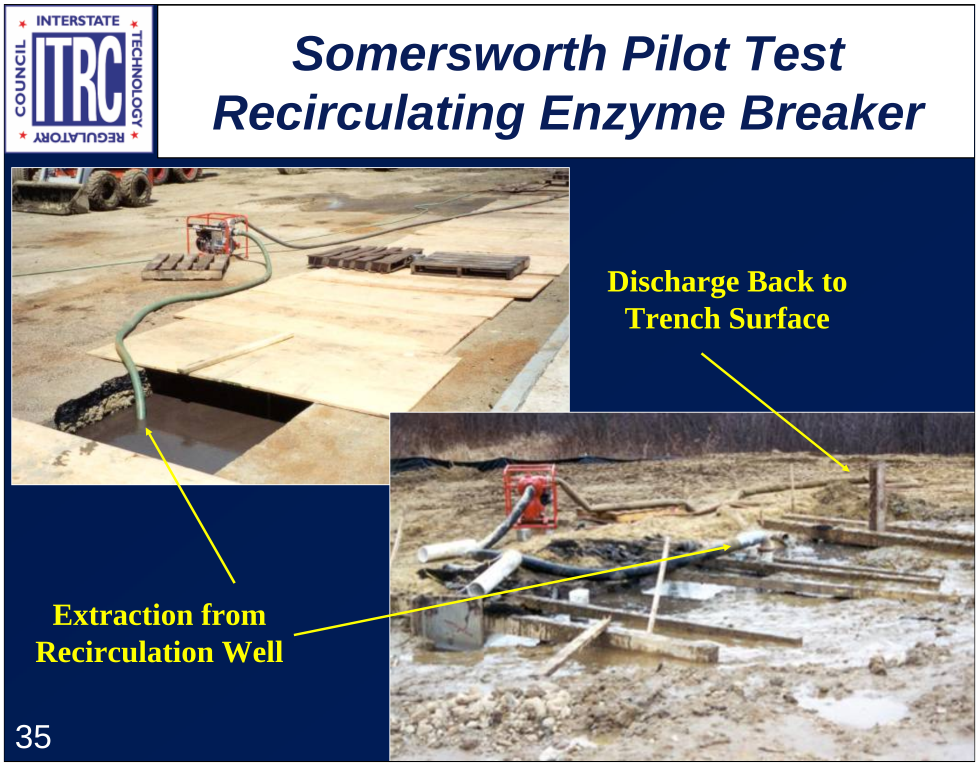
34

Biodegradable slurry level is maintained above groundwater table to provide hydraulic head on trench.

Biodegradable slurry in trench spoils is allowed to drain back into excavation.

Granular iron or iron sand mixture will not "flow" through tremie into backfill.

Tremie pipe is maintained a short distance above the backfilled material to minimize drop through biodegradable slurry.



Enzyme breaker is added to trench surface, into extraction wells, and/or through injection points or other wells.

Water is extracted and discharged to trench surface or re-injected through wells.

QA/QC for Excavated PRBs

- Construction
  - **Depth, length, flow-through thickness**
  - **Backfill composition**
  - **Amount of backfill placed**
- Development/Breaking
  - **Viscosity of recirc water**
  - **TOC in PRB**
- Long-Term
  - **Gradient across PRB**
  - **Permeability**

36

•depth measured with weighted tape

•Confining unit confirmed with borehole information, excavator effort, samples from unit and/or geophysical methods

•Minimum width set by width of excavator bucket

•Bulk weight of sand and iron mixed in a batch used to determine percent iron. Magnetic separation test used to confirm uniform mixture.

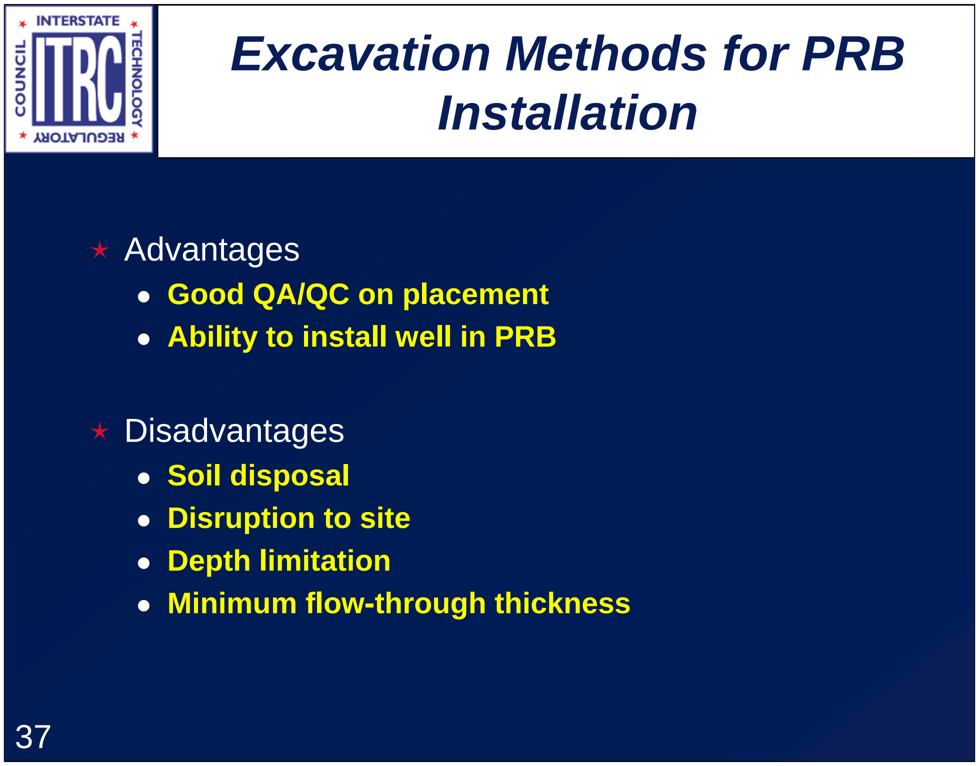
•Samples collected in situ tested with magnetic separation test

•Viscosity of water extracted during bioslurry breaking decreases as guar gum breaks

•TOC indicates presence of guar gum but not how much it has broken

•Hydraulic gradient will indicate if the permeability of the PRB is reduced

•Permeability of backfill can be assessed with slug tests.



Good QA/QC on placement location (e.g. depth, length, width)

Able to QA/QC backfill (reactive media)

Able to monitor groundwater in PRB due to flow-through thickness of PRB

Disadvantages

Excavated soil requires disposal

Disruption to site activities

Depth limitation

Large flow-through thickness may not be required at some sites

Example of Construction Costs

	Construction	Iron	Total
Backhoe Construction, OH 1999 • 8 ppm TCE • 20 ft deep, 200 ft long • v = 0.01 ft/day	$36,000	$28,000	$64,000
BioPolymer Trench, NH 1999 • 10 ppm cDCE; 5 ppm TCE; 1 ppm VC • 33 ft deep, 150 ft long • v = 0.3 ft/day	$200,000	$130,000	$330,000
Trench Box, WY 1999 • 21 ppm TCE; <1 ppm cDCE, < 1 ppm VC • 23 ft deep, 565 ft long • v = 1.3 ft/day	$1,400,000	$600,000	$2,000,000

38

Injection Methods for PRB Installation

Method	Depth	Installation Thickness	Number of Installations
Vertical Hydrofracturing	30 – 200 ft	< 0.5 ft	5
Jetting – Columnar	< 200 ft	< 0.5 ft	2
Jetting – Panels, Diaphragms	< 200 ft	< 0.25 ft	1
Pneumatic Fracturing	< 200 ft	Variable	4

Installations of Iron PRBs for VOC treatment only

39

Biodegradable Slurry for Jetting Applications

Biodegradable Slurry for Jetting

- Guar Gum
- Enzyme Breaker
- Granular Iron (typically finer grained)

Slurry for jetting (prior to adding iron)

Biodegradable Slurry for Vertical Hydrofracturing

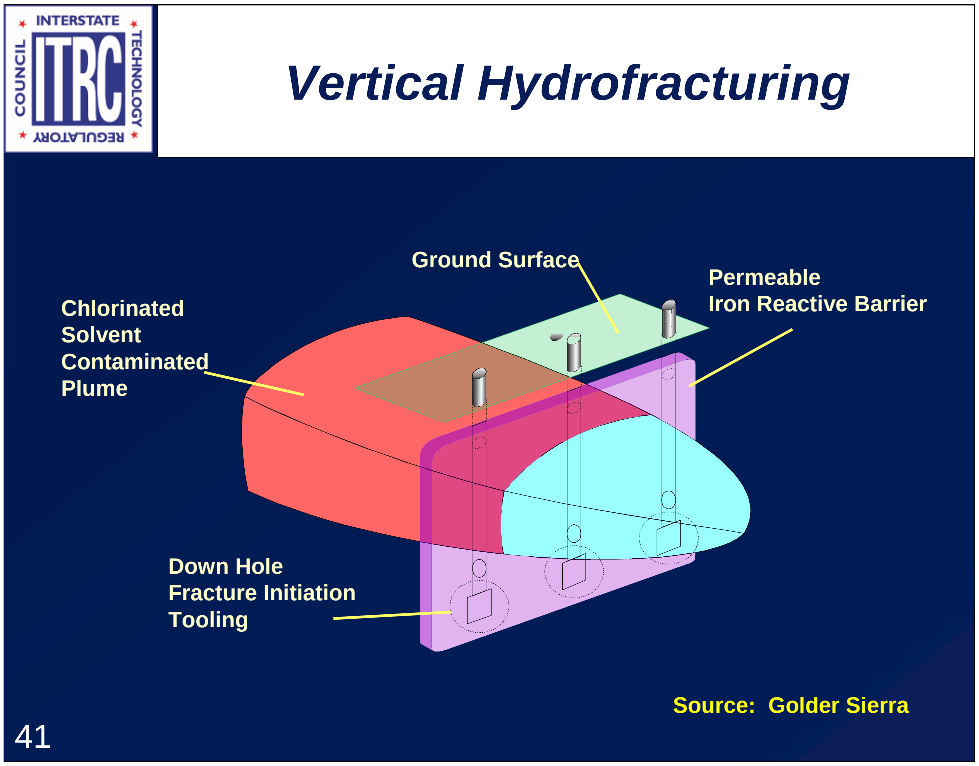
- Proprietary Mixture
  (Guar Gum, Cross-Linker,
  Enzyme Breaker,
  Fine grained granular iron)

Cross linked guar with iron

40

For jetting applications, the biodegradable slurry is used to suspend the granular iron to allow it to be pumped. The enzyme breaker is added prior to injection as the slurry only needs to be viscous for a short time until the granular iron is jetted into place.

For vertical hydrofracturing, the guar gum is cross-linked to form a very viscous gel which allows the fracture to propagate.



-boreholes installed along PRB alignment

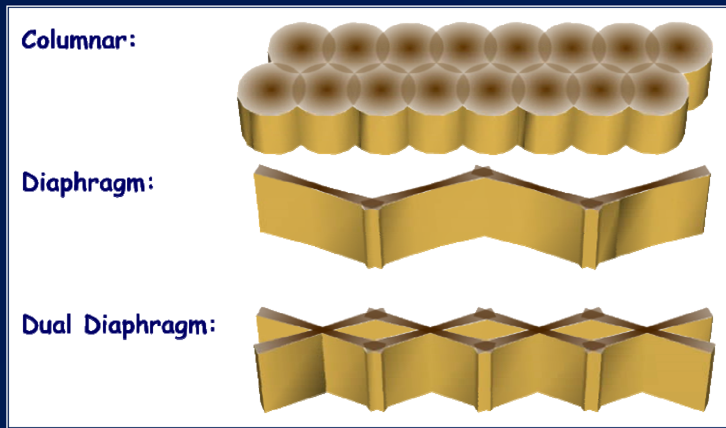
-Specialized frac casing is grouted into borehole

-Controlled vertical fracture is initiated at the required azimuth orientation and depth

-Iron is blended with hydroxypropylguar (HPG)

-Injection at multiple well heads to form continuous PRB

Jetting Configurations



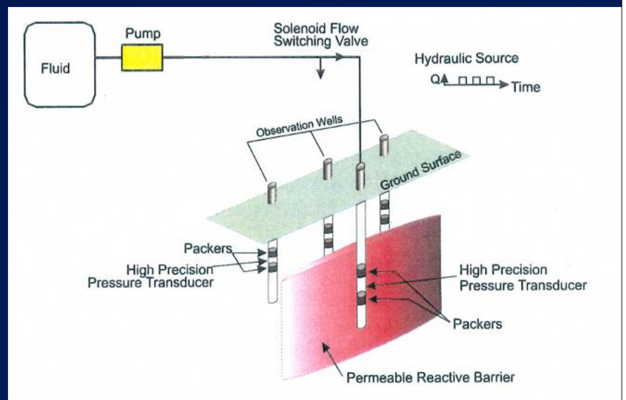
42

Jetting uses high pressures (about 5,000 to 6,000 psi) to jet a finer grained iron into the natural aquifer formation. The jetting tool is advanced into the formation to the desired depth. The iron is suspended in biodegradable slurry and is injected from nozzles as the tool is withdrawn. If the tool is rotated a columnar iron zone is created. The diameter of injection will depend on several factors, but distances of 2 to 7 ft are expected. If the tool is not rotated, and has only one or two opposing nozzles, a thin diaphragm treatment wall can be created. Diaphragm walls may be 2 to 3 inches of 100 percent thick near the point of injection, but may be several inches of a mix of iron and aquifer material further away.

INTERSTATE ITRC TECHNOLOGY REGULATORY COUNCIL

QA/QC for Injected PRBs

- Depths, length
- Mass of media injected
- Spoils volume and composition
- Induced earth tilts
- Geophysics
- Hydraulic gradient
- Hydraulic pulse interference test
- Cores from angle drilling



Hydraulic Pulse Interference Test
Source: Golder Sierra

43

•Confining unit confirmed with borehole information (before or during placement), injection tool advancement, and/or geophysical methods

•Density of injection mixture and flow rate are used to determine mass of granular iron injected.

•Alternatively the reactive material is injected in batches to track quantity injected.

•Columnar jetting results in some spoils at the ground surface. These spoils will contain some fraction of granular iron.

•Geophysical methods include active resistively monitoring

•Hydraulic gradient will indicate if the permeability of the PRB is reduced

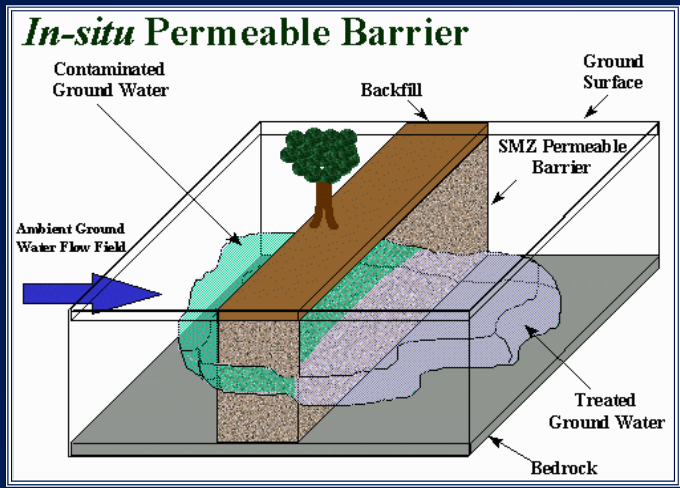
•Permeability of PRB can be assessed with hydraulic pulse interference testing

Injection Methods for PRB Installation

- Advantages
  - **Depth**
  - **Target Vertical Zones**
  - **Thinner PRBs**
  - **No or minimal soil disposal**
  - **Smaller equipment**
- Disadvantages
  - **Difficult to QA/QC on placement**
  - **Potential for mixing reactive material**

44

Question & Answers



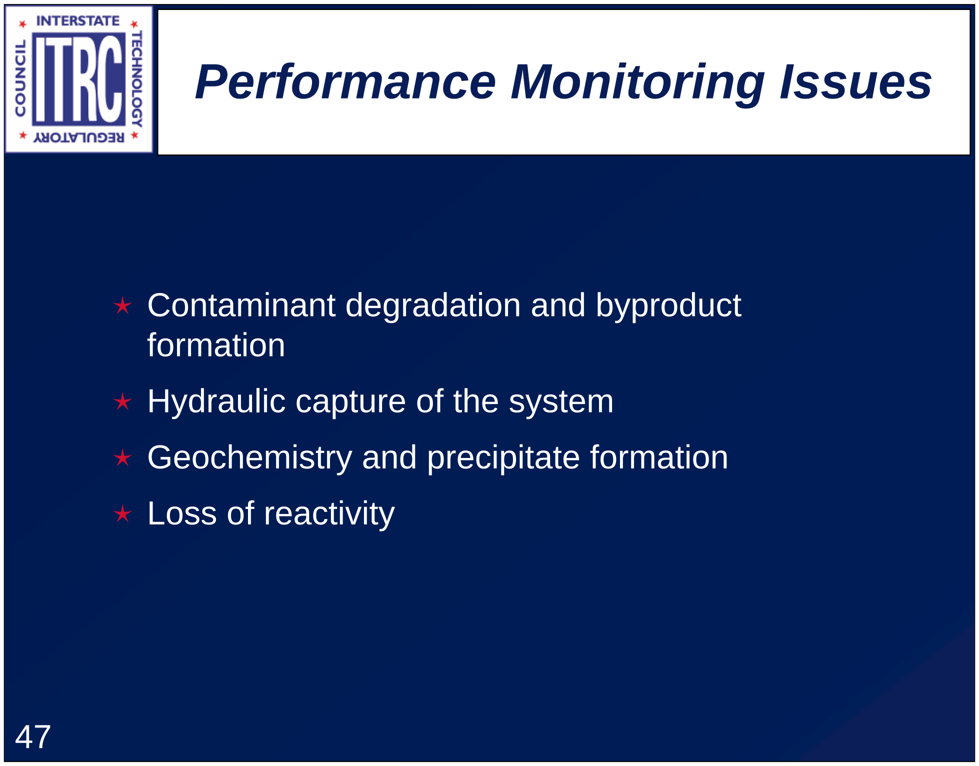
Oregon Graduate Institute and New Mexico Tech

45

Performance Monitoring

- Focus on the PRB system rather than the entire site
- Ensure operation of wall as designed
- Detect changes in performance
- Evaluation of physical, chemical and geochemical parameters over time
- Sampling frequency typically quarterly for the routine parameters
- Contingency sampling program necessary for unexpected conditions

46



Sampling Procedures

Passive sampling method for collection of groundwater samples

Collection of representative samples where the retention time within the reactive media is not altered

Smaller diameter wells are preferred (3/4 in.) with short screens

Passive Sampling Methods

Low Flow Sampling

Diffusion Sampler (ITRCweb.org)

In-situ Probes

Performance Indicator Parameters

- Can provide some measure of system performance
  - pH
  - DO
  - Eh/Redox
  - Alkalinity
  - Ferrous iron
  - Hydrogen

48

Inorganic Analysis

- Parameters which decrease through PRB indicating mineral precipitation
  - Alkalinity
  - Ca
  - Mg
  - Si
  - SO_4
  - NO_3
- Relatively Conservative Parameters
  - Na
  - K
  - Cl

49

Typical Inorganic Geochemistry
"New Jersey Site Data"

Source: Rockwell Automation/TRC Vectre, 2000 Diagram

Parameter (mg/L)	Upgradient	Iron PRB
Iron	32	0.8
Calcium	61	10
Magnesium	18	13
Sulphate	23	5
Alkalinity	197	77
TDS	336	184
pH	7.4	9.2
Eh (mV)	-205	-377

enviro**metal** technologies inc.

50

Hydraulic Evaluation

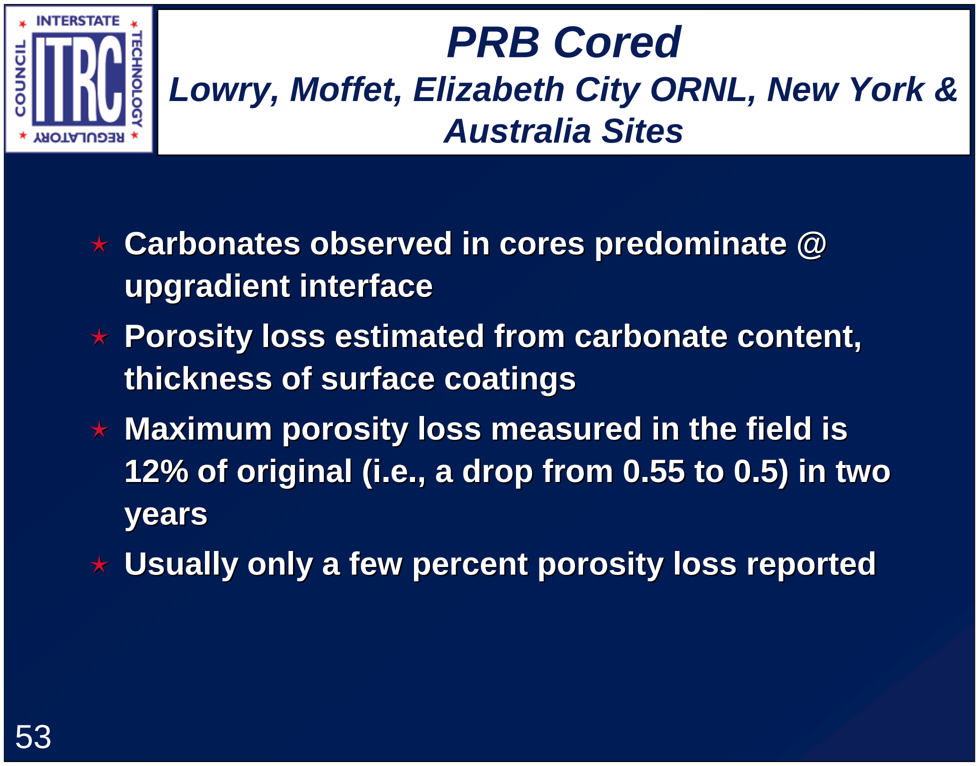
- Head Measurements
- Velocity Probes
- Tracer Tests
- Pump Tests

51

Velocity Probes

- HydroTechniques
  - Thermal perturbation technique
  - Measures the 3-D groundwater flow
- Colloidal Borescope
  - Visual means of observing colloids

52



Since recent data suggests this carbonate precipitation will move as a front through the iron as opposed to the initial concept that the carbonate precipitates will continue to form on the upgradient face until the PRB was plugged

ORNL has abundant Fe Oxide at the interface (High Nitrate & dissolved oxygen in the groundwater,

Analysis Methods for Cores

Scanning Electron Microscope

FTIR Spectroscopy

X-ray Photoelectron Spectroscopy

Raman Spectroscopy

Optical Microscope

Wet Chemistry Extractions

Total Carbon Analysis

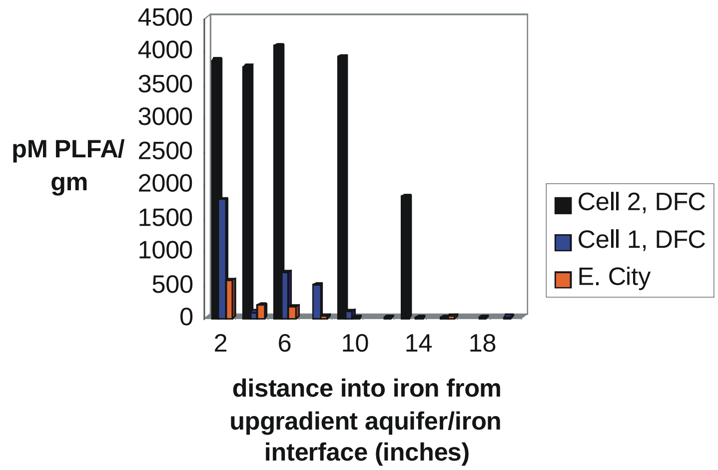
Long Term Performance Data

- Organic
  - **consistent performance with respect to VOC degradation rates**
  - **no evidence of microbial fouling under flowing conditions**
- Inorganic
  - **carbonate precipitation initially occurs at upgradient interface**
  - **accumulation of precipitates over time may cause loss of porosity / permeability losses**
  - **no evidence of hydraulic fouling due to precipitates**

  Longevity issues must be evaluated on a site specific basis

54

Biomass Accumulation at the Elizabeth City and Denver Federal Center PRBs



From Wilkin, Puls, and Sewell (2001)

55

Monitoring Program - Commercial Site

- Sunnyvale PRB - Installed Nov. 1994
  - 1995-1997 Quarterly Monitoring - WL and Analytes
    - Low-flow sampling, flow-cell for DO, Redox, pH
    - 1997 - Inorganic analyses, gases, cell counts
  - 1998-2001 - Quarterly WL, Semi-annual Analytes
    - 1999 Inorganic analyses, down-hole probe (pH, redox)
  - 2000 - 5 Year Performance Evaluation
    - Hydrogen sampling, Passive Bag sampling pilot test
  - 2001 - Passive Bag sampling approved for full-time use

56

Alternative Treatment Materials for PRBs:
"Treatment Mechanisms"

- Chemical dehalogenation
- pH control
- Reduction-oxidation reactions (Redox)
- Sorption reactions (including ion exchange)
- Biological enhancement
- Sequential treatment

57

Reactive Media Selection Guidance

Treatment Material and Treatable Contaminants		
Treatment Material	**Target Contaminants**	**Status**
Zero-Valent Iron	Halocarbons, Reducible metals	In Practice
Reduced Metals	Halocarbons, Reducible Metals	Field Demonstration
Metals Couples	Halocarbons	Field Demonstration
Limestone	Metals, Acid Water	In Practice
Soptive Agents	Metals, Organics	Field Demonstration, In Practice
Reducing Agents	Reducible Metals, Organics	Field Demonstration, In Practice
Biological Electron Acceptors	Petroleum Hydrocarbons	In Practice, Field Demo

58

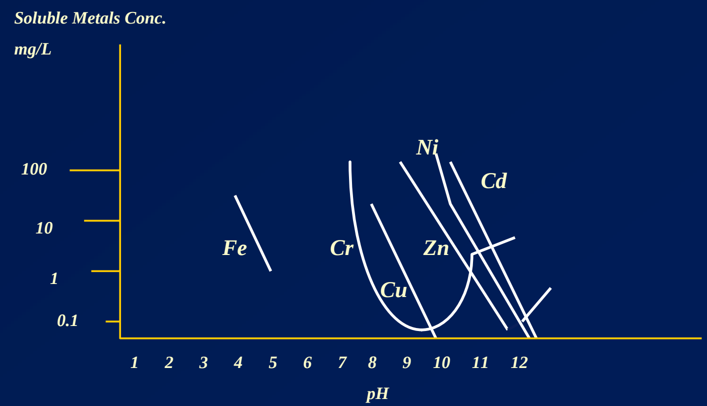
Non-metallic Treatment Materials

- pH control
  - **limestone, compost, organic material**
- Precipitation Agents
  - **gypsum, hydroxyapatite, organic compost, limestone**
- Sorptive agents
  - **GAC, bone char, phosphatics, zeolites, coal, peat, synthetic resins, organic compost**
- Reducing agents
  - **organic compost, sodium dithionite, hydrogen sulfide, bacterial agents, acetate, carbohydrates, molasses**
- Biological enhancements
  - **oxygen source, hydrogen source, carbon source, nitrate**

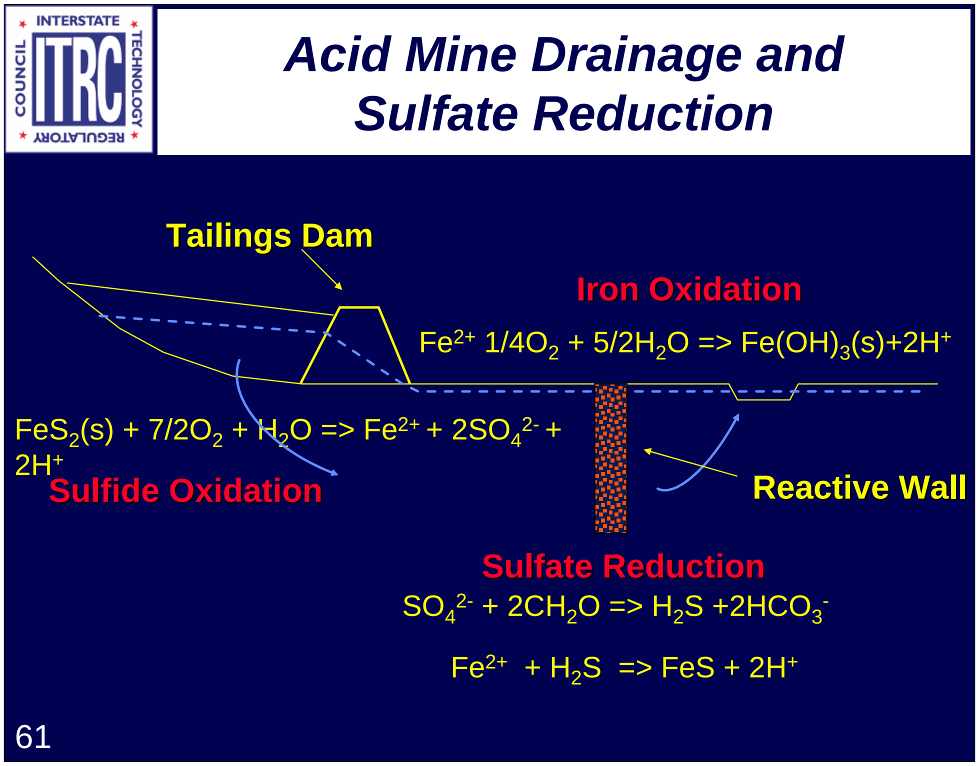
59

Chemical Precipitation—pH Control

- Metal solubility as a function of pH



60


INTERSTATE TECHNOLOGY REGULATORY COUNCIL ITRC
Acid Mine Drainage and Sulfate Reduction
Tailings Dam
Iron Oxidation
Fe^{2+} $1/4O_2$ + $5/2H_2O$ => $Fe(OH)_3$(s)+$2H^+$
FeS_2(s) + $7/2O_2$ + H_2O => Fe^{2+} + $2SO_4^{2-}$ + $2H^+$
Sulfide Oxidation
Reactive Wall
Sulfate Reduction
SO_4^{2-} + $2CH_2O$ => H_2S +$2HCO_3^-$
Fe^{2+} + H_2S => FeS + $2H^+$
61

Sorption Reactions

- Three types of reactions
  - **Hydrophobic**
  - **Hydrophilic**
  - **Ion Exchange**
- Chemicals sorb by:
  - **diffusion, adhesion, electrical attraction**
- Chemicals desorb by:
  - **diffusion, displacement by molecular affinity**

62

Sorption Reactions

- Sorption of Organics - good for:
  - **low water solubility compounds**
  - **hydrophobic compounds**
  - **not readily biodegraded compounds**
- Example materials
  - **GAC, peat, coal, organic-shale, zeolites**

63

Sorption Reactions

- Sorption of Inorganics - good for:
  - **metals**
    - **affinity on carbon Pb>Cu>Ni>Zn=Mn=Cd=Co**
  - **hydrophilic and ion exchange reactions**
- Example materials
  - **organic carbon, zeolites, clays, oxyhydroxides**

64

Biological PRB Media

- Added Terminal Electron Acceptor
  - **Aerobic - reduced contaminants (BTEX-MtBE)**
    - **O_2 most common e- acceptor**
    - **MgO_2, CaO_2**
  - **Anaerobic – oxidized contaminants (PCE)**
    - **nitrate, ferric iron, sulfate, e- acceptor**
- Added Co-substrate
  - **Vanilla – PCP**
- Bioaugmentation
  - **Add bacteria (MtBE)**

65

Sequential Treatment Design

- Use of two or more processes in sequence
  - treat a mixed plume
  - to increase effectiveness of principal treatment
  - polish treatment train
  - increase longevity of principal treatment

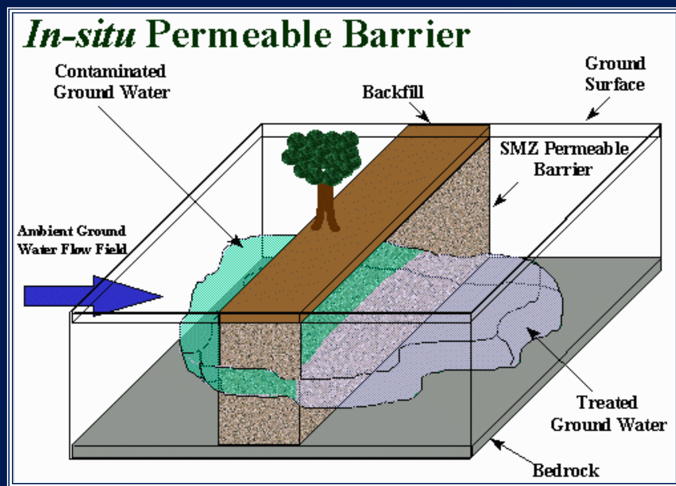
66

Sequential Treatment Design Issues

- Considerations
  - competing processes e.g. oxidizing v. reducing
    - sulfate competition
  - pH influences
  - interfering mineralization / biofouling
- Hydraulics
- Implementation

67

Question & Answers



Oregon Graduate Institute and New Mexico Tech

68

Links to additional resources: http://www.clu-in.org/conf/itrc/advprb/resource.htm

Your feedback is important – please fill out the form at: http://www.clu-in.org/conf/itrc/advprb/feedback.cfm

The benefits that ITRC offers to state regulators and technology developers, vendors, and consultants include:

•helping regulators build their knowledge base and raise their confidence about new environmental technologies

•helping regulators save time and money when evaluating environmental technologies

•guiding technology developers in the collection of performance data to satisfy the requirements of multiple states

•helping technology vendors avoid the time and expense of conducting duplicative and costly demonstrations

•providing a reliable network among members of the environmental community to focus on innovative environmental technologies

•**How you can get involved in ITRC:**

•Join a team – with just 10% of your time you can have a positive impact on the regulatory process

•Sponsor ITRC's technical teams and other activities

•Be an official state member by appointing a POC (Point of Contact) to the State Engagement Team

•Use our products and attend our training courses

•Submit proposals for new technical teams and projects

•Be part of our annual conference where you can learn the most up-to-date information about regulatory issues surrounding innovative technologies