Permeable Reactive Barriers for Treatment of Arsenic-Contaminated Groundwater

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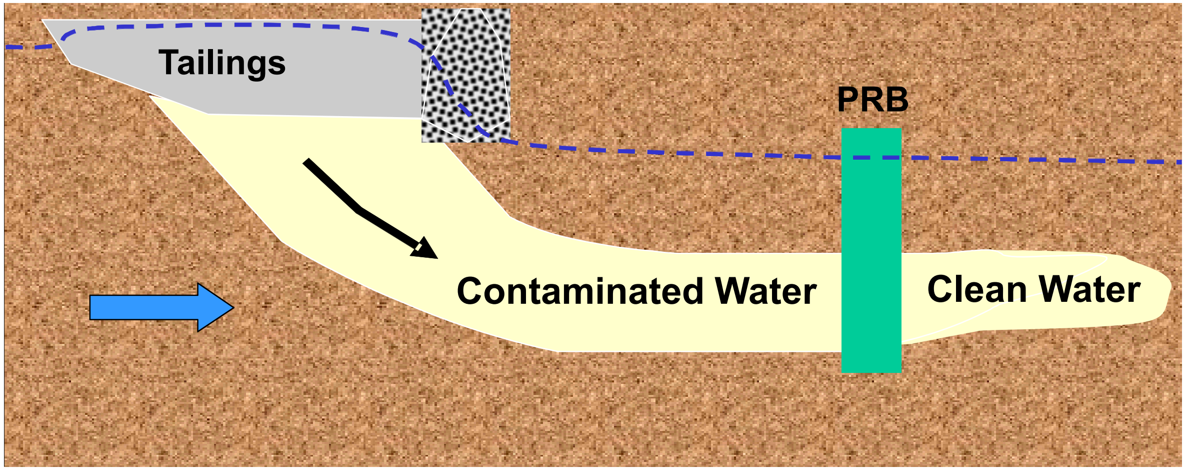


MEND

Background: Permeable reactive barriers

- A trench installed in the path of a contaminant plume and filled with reactive materials designed to remove contaminants

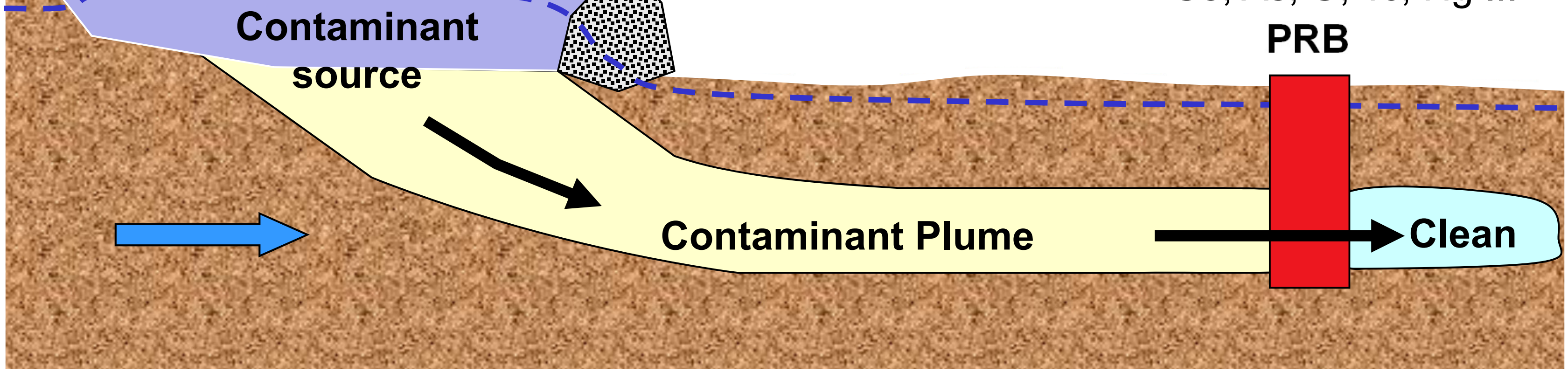
Reactive materials promote metal removal by

- Change redox state of groundwater environment in the PRB
- Precipitate metals as insoluble solids; adsorption and coprecipitation
- Installation costs similar to setup of P & T systems

Benefit:

- Passive operation – Have low energy and maintenance costs

Treatment of Fe, Cr, Se, As, U, Tc, Hg ...



Early PRBs for metals

Some early PRBs used for metal treatment include

Treatment of mine drainage Nickel Rim Mine Tailings, Sudbury Canada

Sulfate reduction barrier, 1995

Cr and TCE treatment, USCG Elizabeth City NC

Zero valent iron barrier, 1996

Of approximately 250 PRBs worldwide today; 30% treat inorganic contaminants, 10% are for treatment of mining related groundwater

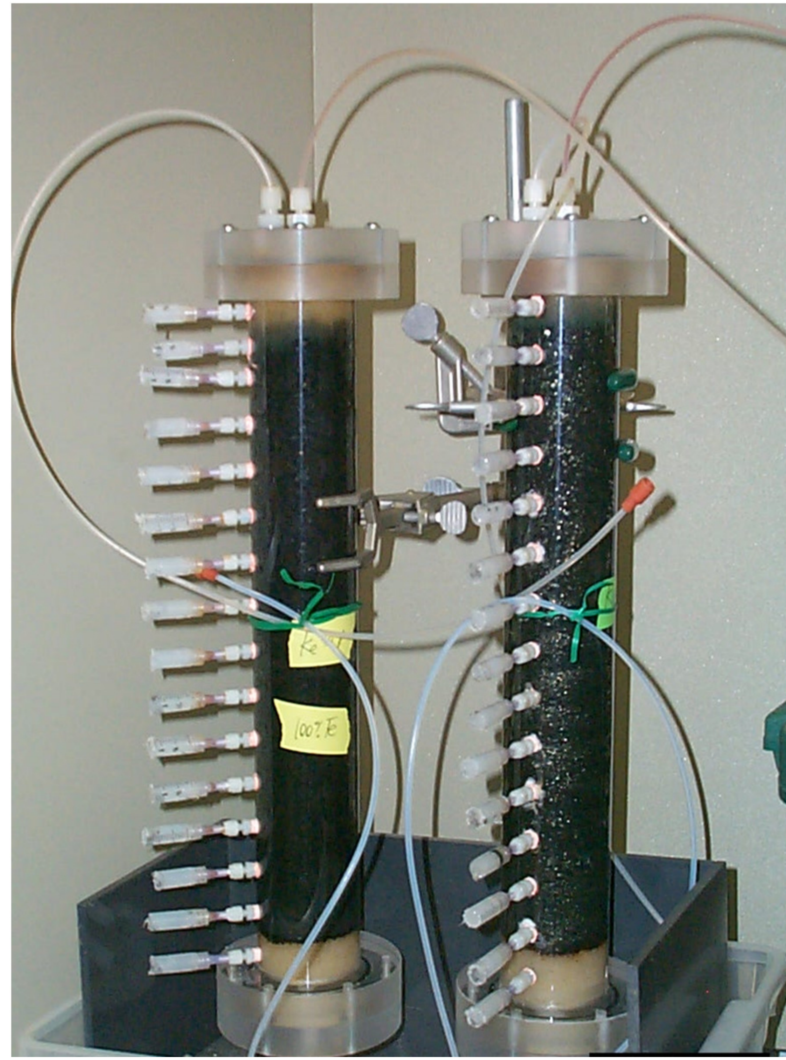
Arsenic in water

- Arsenic is a common contaminant in groundwater
  - Mining, pesticide use, chemical manufacturing, wood preservative, natural processes
- A carcinogen and suspected to cause birth defects
- Health Canada Guideline for As in Drinking Water is 0.01 mg/L
- Under reduced conditions, As(III) (arsenite) predominates
  - Exists as neutral complex or at higher pH as an oxyanion
- Under oxidized conditions, As(V) (arsenate) predominates
  - Exists as an oxyanion at most pH values
- As(III) is more toxic and more mobile than As(V)

Lab column tests

Several reactive materials found suitable for passive treatment of As

1. Mixtures containing zero valent iron (ZVI) filings and organic carbon
2. Mixtures containing basic oxygen furnace (BOF) slag, from steel manufacturing



Objective of the presentation

To review research done to evaluate the performance of these materials in field-scale PRB installations

• Materials used & proposed mechanisms of treatment

• Descriptions of the sites and the PRB installations

• Review field performance of these PRBs for As removal

Arsenic removal with organic carbon

- **Organic carbon** (electron donor) added in excess can stimulate naturally-occurring bacterially mediated sulfate reduction in subsurface

  $$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S$$

- Arsenic removal by precipitation of low-solubility metal sulfides

  $$2As^{3+} + 3H_2S \rightarrow As_2S_{3(s)} + 6H^+$$

  (orpiment)

- Many types of organic carbon are suitable, are widely available and are inexpensive – key factors for a suitable reactive material
  - e.g. wood chips, brewery waste, straw, municipal leaf compost

Arsenic removal with granular ZVI filings

- **ZVI** has been effective for treatment of a range of reducible metals and organic contaminants
- Adsorption of As onto ferric (oxy)hydroxide corrosion surfaces on ZVI
- Coprecipitation of secondary As-bearing ferric (oxy)hydroxides
- ZVI is expensive (~\$770/tonne or \$2300/m^3)

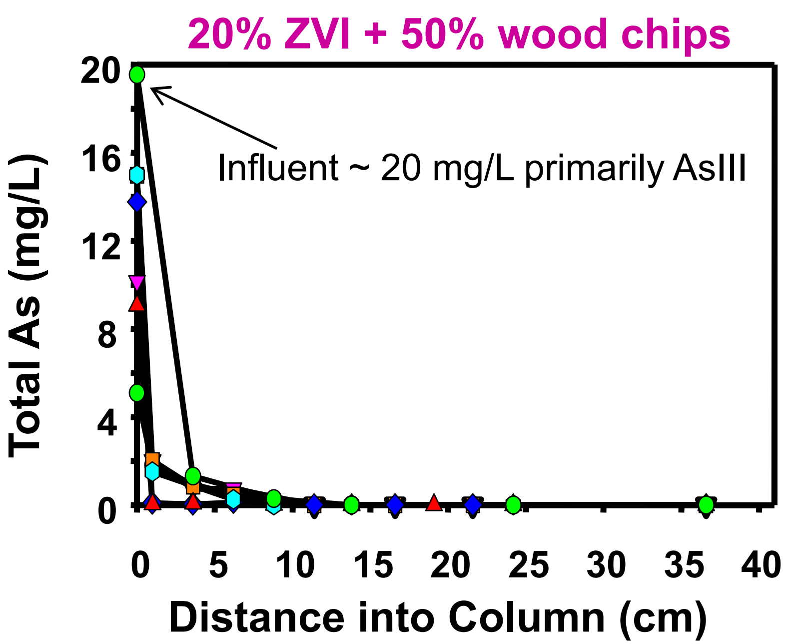
Arsenic removal with ZVI + organic carbon mixtures

- ZVI mixed with OC: greater success due to multiple pathways of treatment
- ZVI is a strong reductant: reduction of water

$$Fe^0 + 2H_2O \Rightarrow Fe^{2+} + H_{2(g)} + 2OH^-$$

- Hydrogen gas used by SRB in the PRB→ metal sulfide precipitation

Column trial with mine water:



Results

- ~20 mg/L As→ 0.01 mg/L
- 2.5 years, 242 PV of treatment of mine water
- Rapid removal of As
- No breakthrough of As >0.01 mg/L
- More recent investigations show similar treatment with lesser amounts ZVI

Basic Oxygen Furnace Slag (BOFS)

- Steel-making byproduct commonly used in cement and road aggregate
- About 55% is amorphous material (generally unreactive glasses)
- Balance is crystalline phases
  - Fe-Ca-Mg oxides and silicates (e.g. FeO, Fe_3O_4, Ca_2SiO_4 etc)
- Abundant lime & portlandite - dissolution drives pH alkaline
  - Lime $CaO + H^+ \Rightarrow Ca^{2+} + OH^-$ log K = 33
- Large surface area (> 5 m^2/g)
- Inexpensive, widely available: key factors for a suitable reactive material

As treatment with Basic Oxygen Furnace Slag (BOFS)

- Adsorption of oxyanions (As, Se) and heavy metals (e.g. Pb, Zn) onto BOFS surfaces
- Coprecipitation of As-bearing Fe oxides and oxyhydroxides
- Precipitation of low-solubility Ca-arsenate minerals
  - e.g. Arsenate apatite $Ca_5(AsO_4)_3OH$

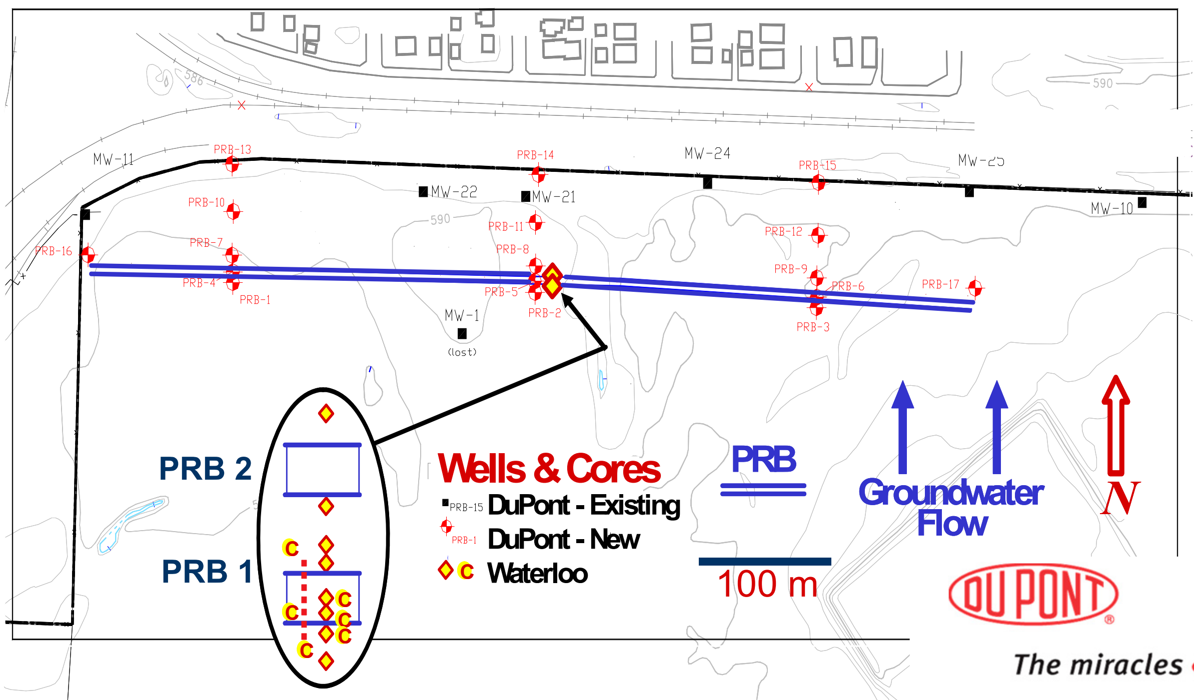
Arsenic PRB case studies

- **One full scale PRB:**
  - Chemical production facility (USA), BOFS
  - Water chemistry similar to typical mine drainage
- **Two pilot scale PRBs:**
  - Gold mine tailings area in Ontario (ZVI+OC)
  - Fertilizer production facility in South Carolina (ZVI+OC)

Full-scale BOFS PRB

Chemical manufacturing facility

- Installed spring 2002 by DuPont at a site in East Chicago, Indiana
- 100% granular BOF slag
- Two parallel, 550 m long, 11 m deep, 0.6 m wide barriers, separated 3 m
- 1-3 mg/L As plume with neutral pH, high SO_4, Fe, Pb, Zn



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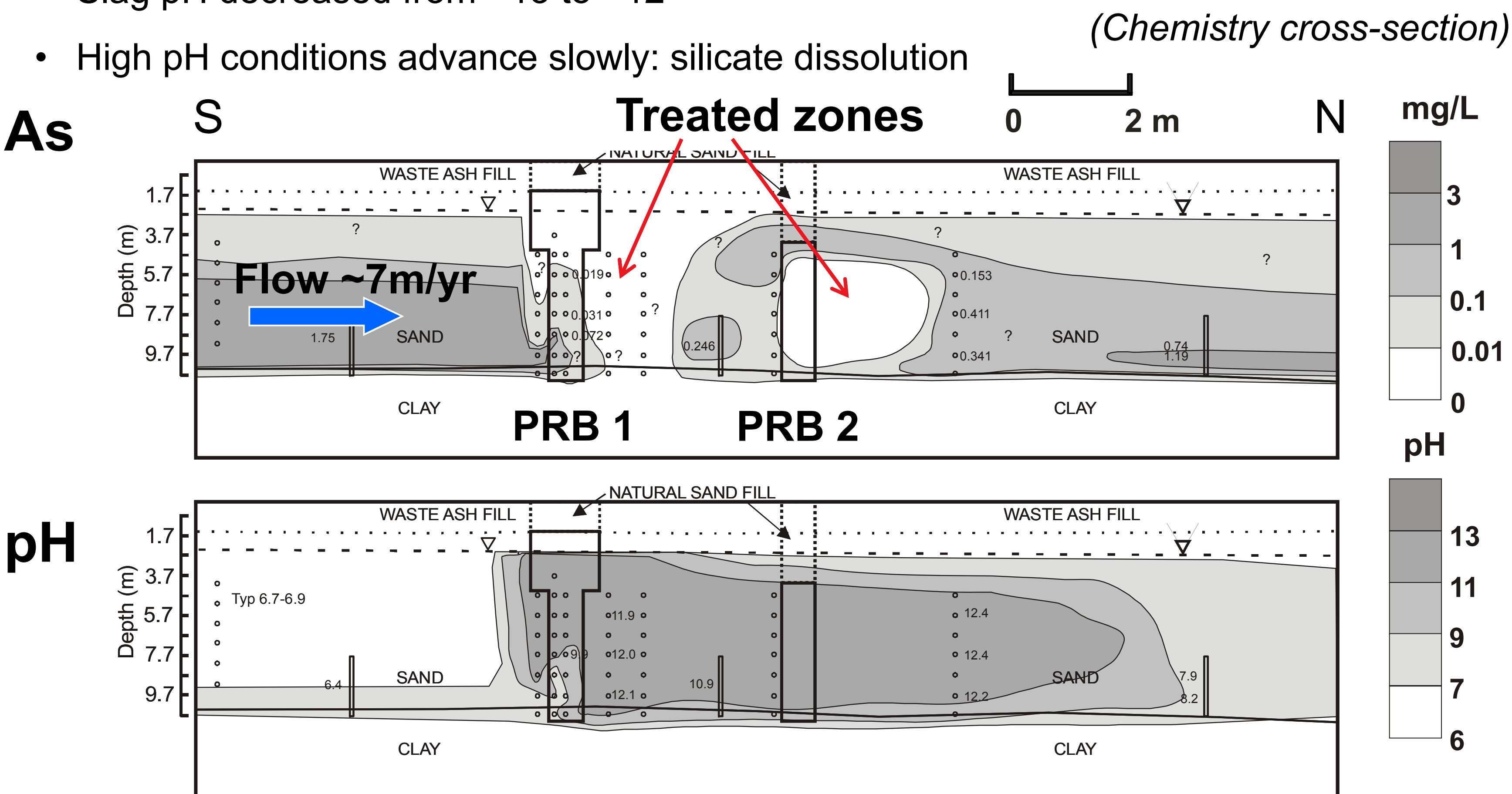
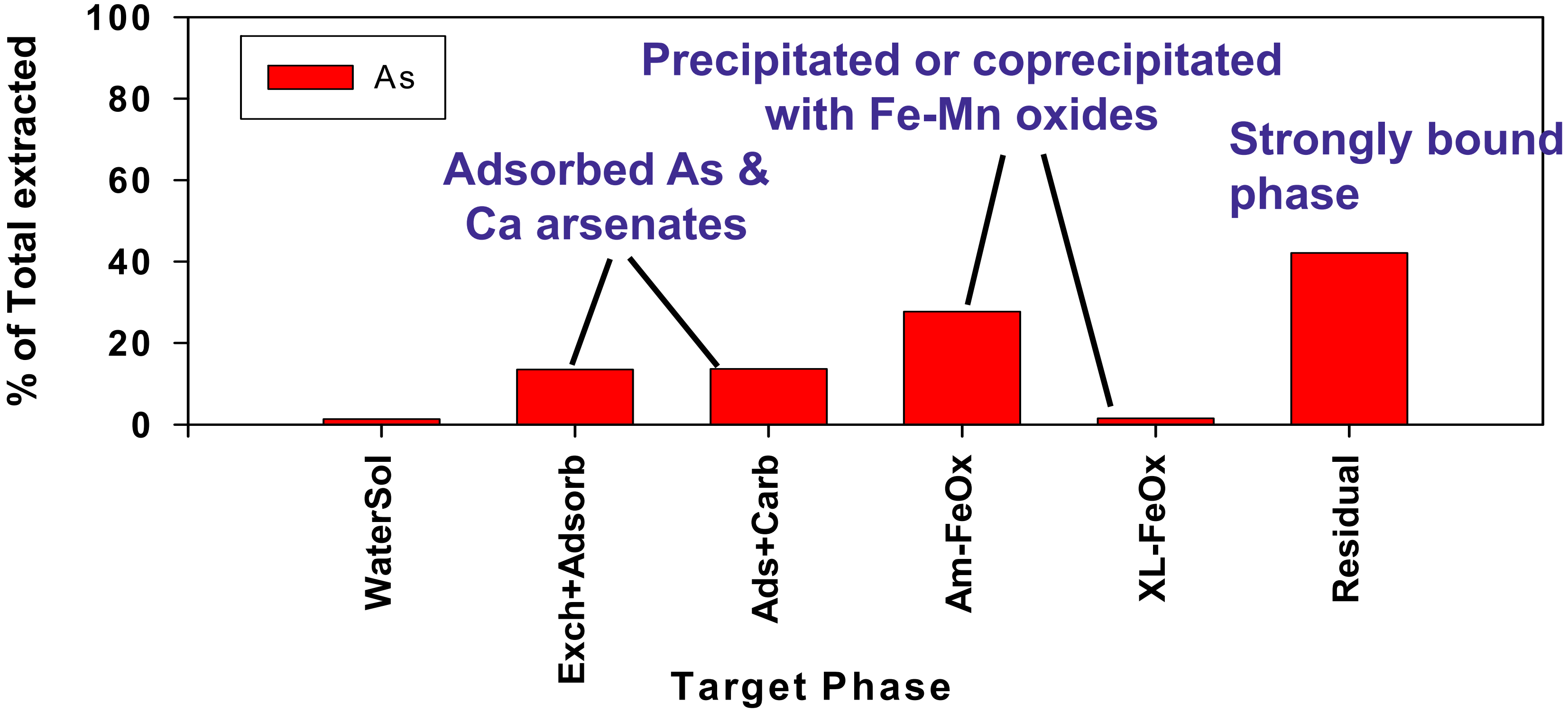
BOFS PRB Chemistry @ 5 years, 2007

- Inflow 1-3 mg/L As (mainly AsIII) removed to <0.01 mg/L; clean zone developing downgradient at 4 m/yr
- Second PRB intercepts As that breaks through first PRB
- Slag pH decreased from >13 to <12
- High pH conditions advance slowly: silicate dissolution



Selective sequential extractions: Mode of As removal

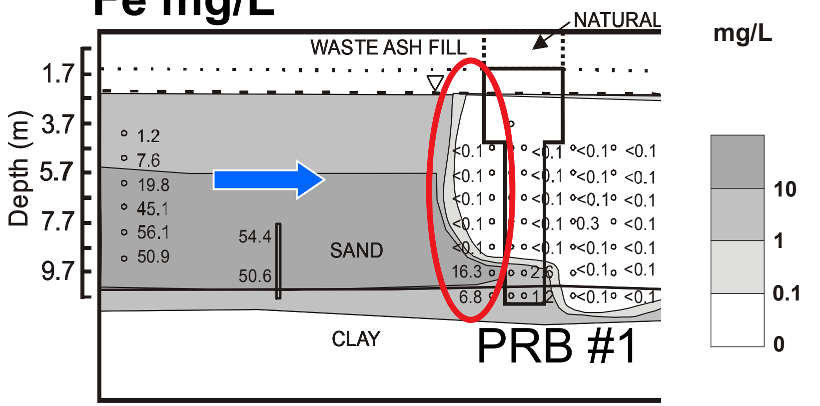
- Arsenic accumulating in a variety of phases
- Probable removal by adsorption, calcium arsenate precipitation and coprecipitation with Fe and Mn oxyhydroxides



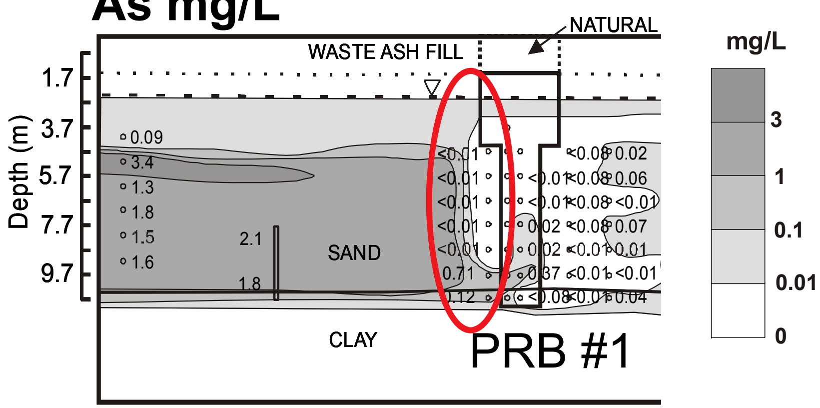
Arsenic Removal

- 20-60 mg/L influent Fe precipitates from water due to high pH near PRB
- Coprecipitation of As with Fe (oxy)hydroxides

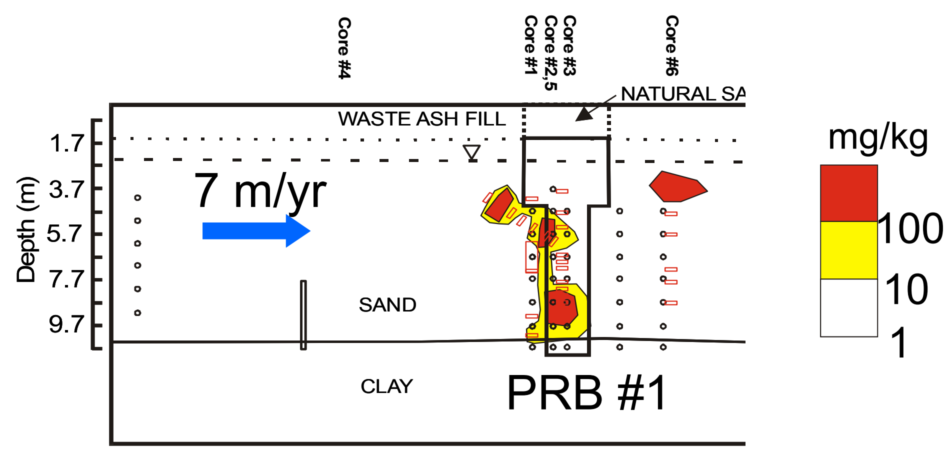
Fe mg/L



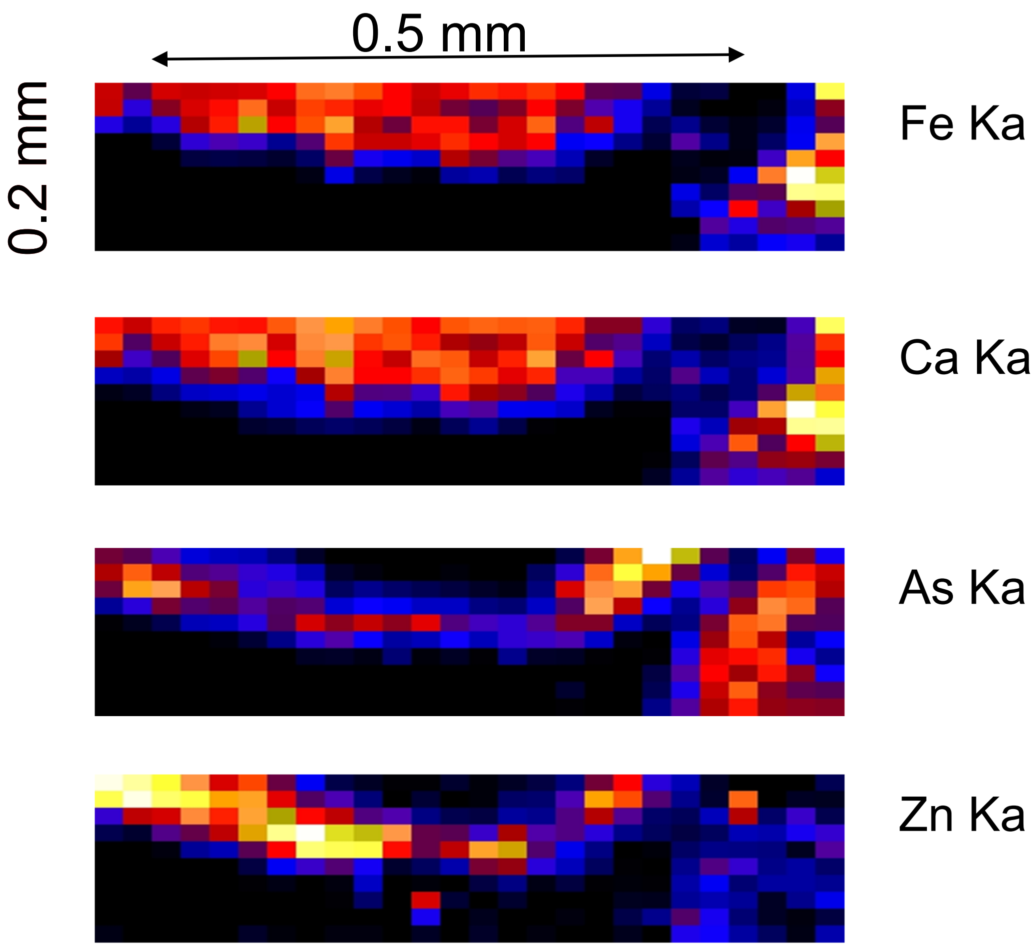
As mg/L



As mg/kg on solids



Synchrotron XRF map of BOFS grain thin section



- Rim of Ca-Fe rich BOFS grain is enriched with As and Zn
- Adsorption onto Fe-oxide in the BOFS
- Coprecipitation of As-bearing Fe (oxy)hydroxides
- Precipitation of Ca-arsenates and arsenites
- $Zn(OH)_2$ and Zn-silicates

UW5P from PRB, map2
NSLS, BNL, Beamline X27

Other observations

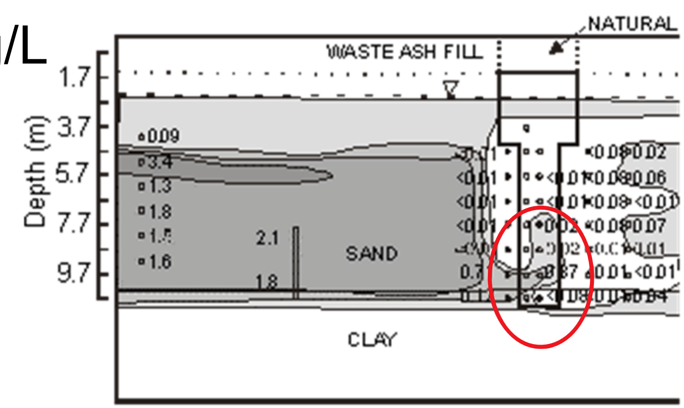
- Decreases in permeability and reactivity observed near bottom of PRB
- Attributed to secondary mineral formation: gypsum, calcite
- High SO_4 concentrations and carbonate alkalinity in groundwater at the base of the aquifer

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \qquad \textit{Gypsum}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \qquad \textit{Calcite}$$

- Better reconnaissance → improved design

As mg/L



Pilot scale ZVI + OC PRB

Pilot scale ZVI + OC PRB

PRB mixture

- 30% wood chips (locally available)
- 30% gravel (for permeability)
- 40% zero valent iron filings

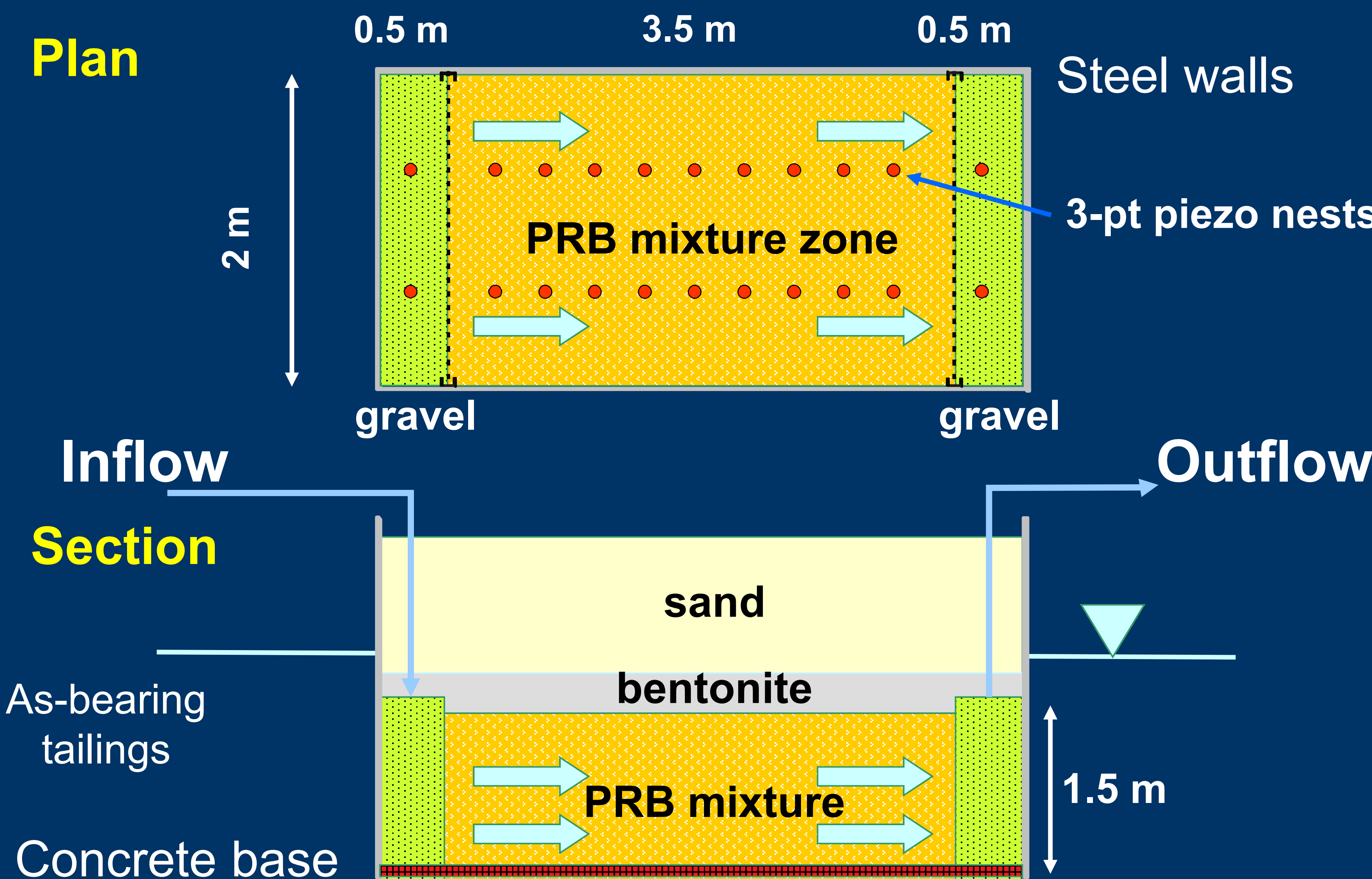
Sheet piling walls

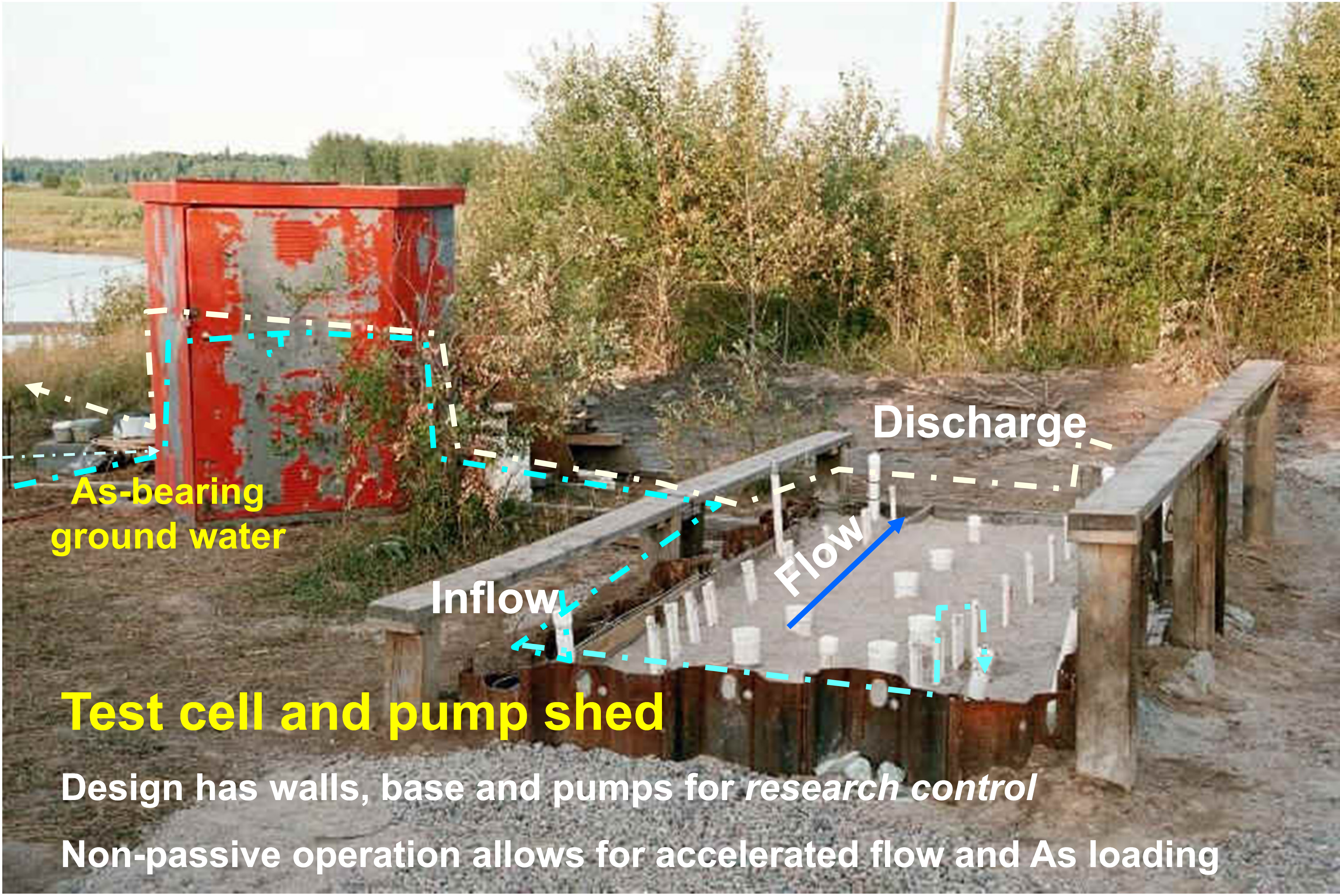
4.5m x 2m x 3.5m (L,W,D)

Groundwater

- Site groundwater: 1-3 mg/L As, neutral pH, 500 mg/L SO_4, low metals, reduced
- Test condition: 15-30 mg/L As

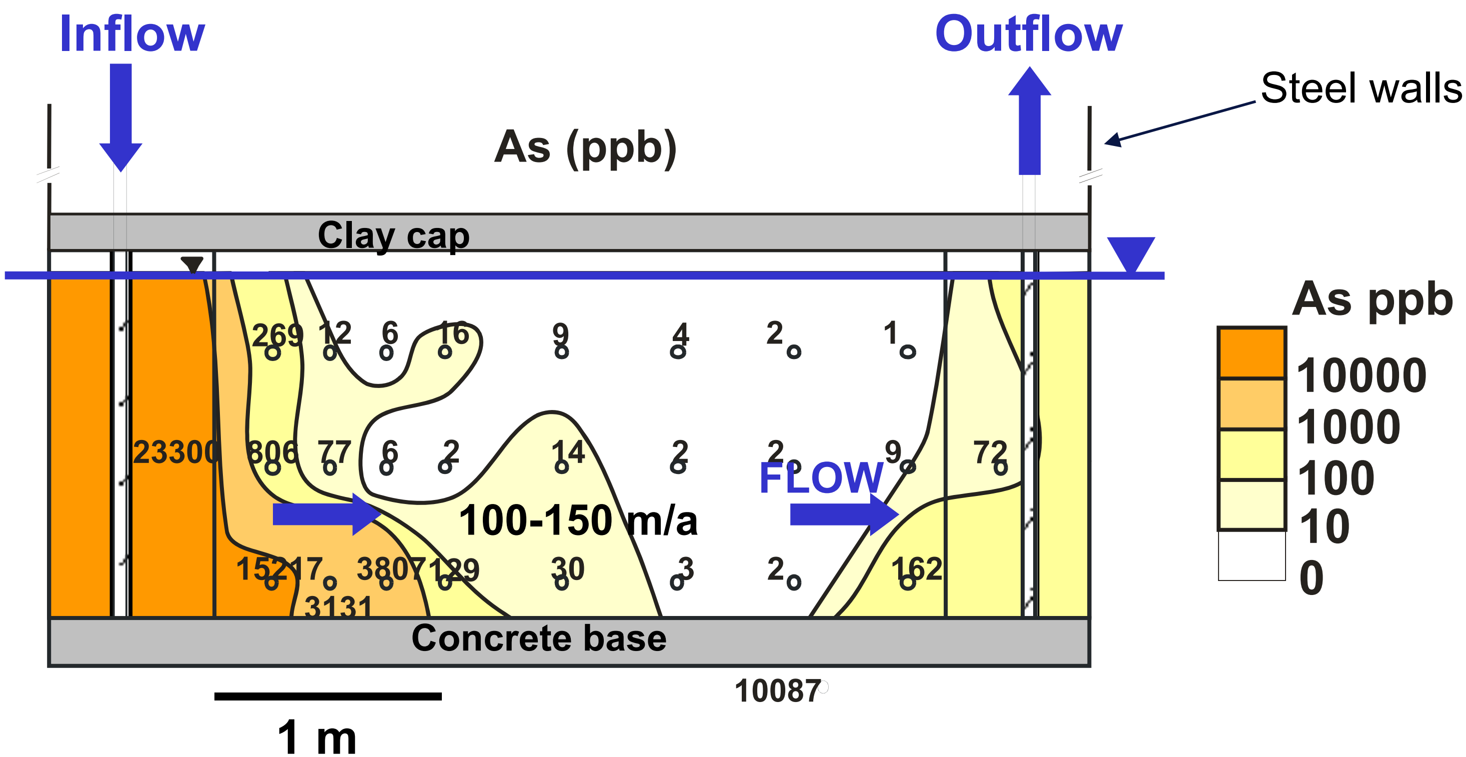
Pilot scale ZVI+OC PRB




Discharge
As-bearing ground water
Flow
Inflow
Test cell and pump shed
Design has walls, base and pumps for *research control*
Non-passive operation allows for accelerated flow and As loading

Performance @ 4 years

- Groundwater mixed to contain 15-35 mg/L As was injected into the PRB
- Velocity 2-3 times greater than site conditions
- Residence time controlled at 5-10 days
- Effective (>99.9%) removal of As for more than 80 PV of flow (4 yrs)



Geochemical conditions in the PRB

- Moderate population of SRB detected
- Sulfate reducing conditions established

$$2CH_2O + SO_4^{2-} \dashrightarrow 2HCO_3^- + H_2S$$

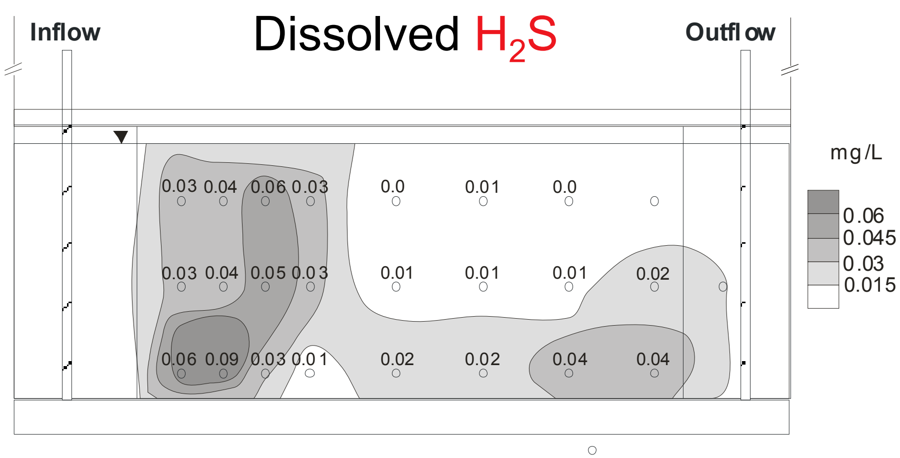
- Enrichment of $\delta^{34}S$ in residual porewater SO_4

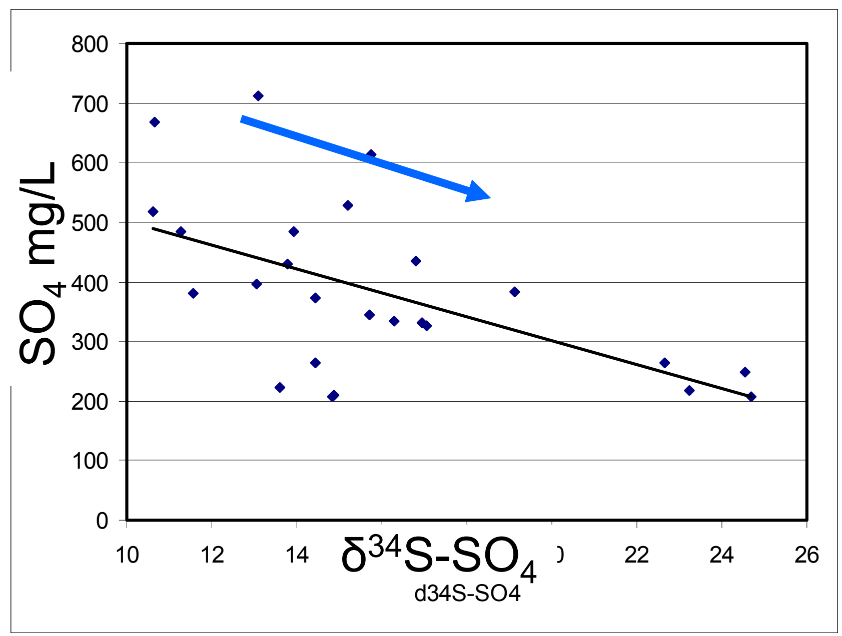
$2As^{3+} + 3H_2S \rightarrow As_2S_{3(s)} + 6H^+$

orpiment

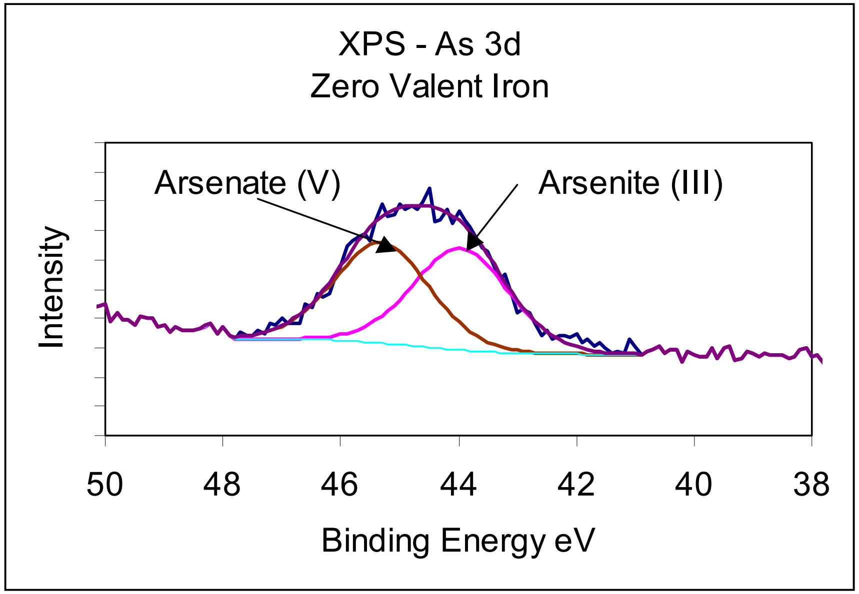
Isotopic Evidence of SO_4 reduction

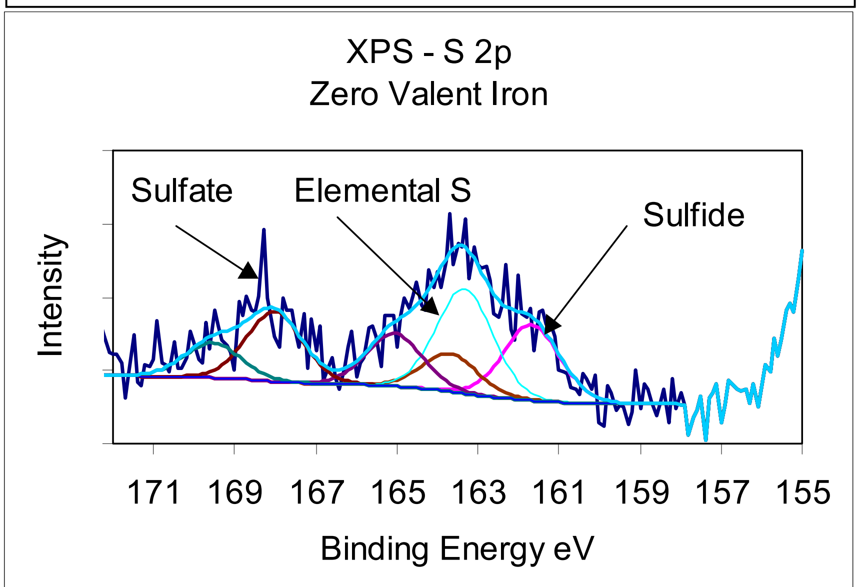
^{34}S enrichment of SO_4 in PRB water





XPS surface analysis – ZVI+OC PRB solids



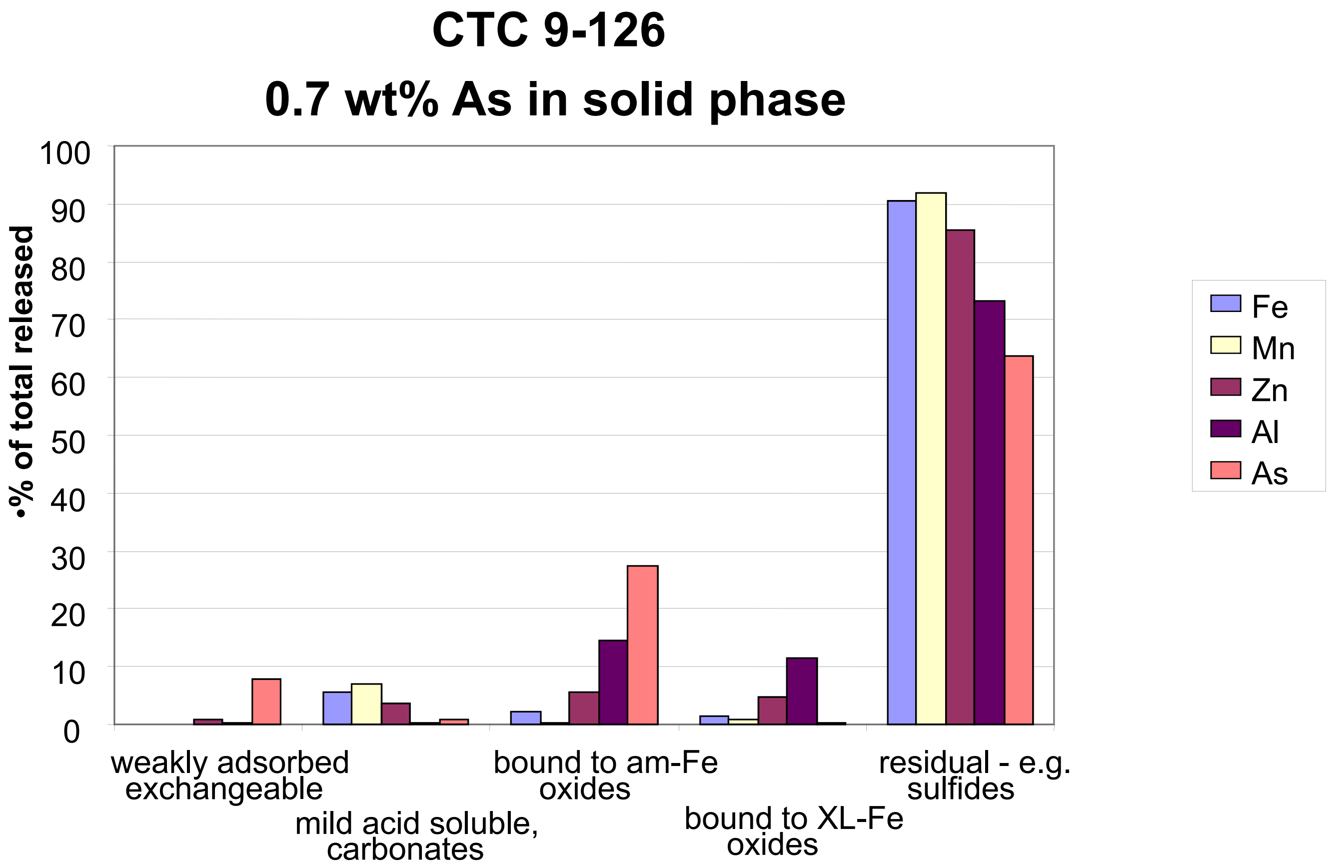


AsIII and AsV present on solids

- Adsorption onto and coprecipitation with Fe oxyhydroxides on ZVI and where OC is replace by Fe (oxy)hydroxides
- Adsorbed on iron sulfides
- Confirmed with mineralogy, SEM-EDX, sequential extractions

- Probable precipitation of As-bearing sulfides
- Not detected by optical mineralogy or SEM-EDX

Selective sequential extractions: Mode of As removal

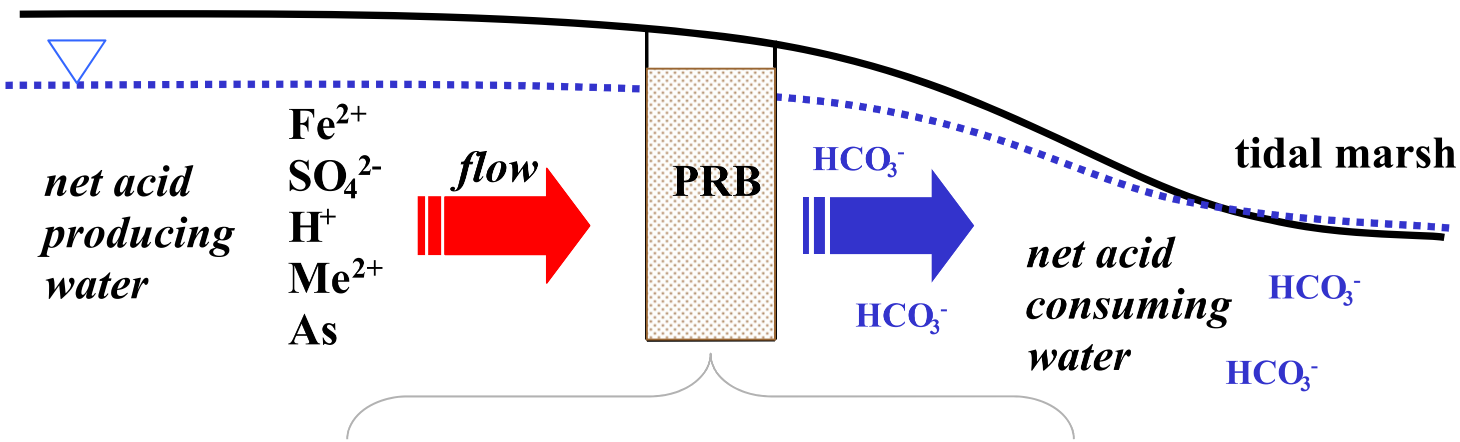


- Chemical attack of selected target phases that may attenuate As
- Arsenic detected mostly in residual phase but As sulfide not detected by mineralogy as a discreet phase

Fertilizer production facility

- Production and storage of sulfuric acid; oxidation of sulfide minerals distributed in surface wastes
- GW contamination by As, Cd, Pb, low pH
- Pilot scale PRB installed in 2002:

20% ZVI, 30% compost, 5% limestone, 45% gravel



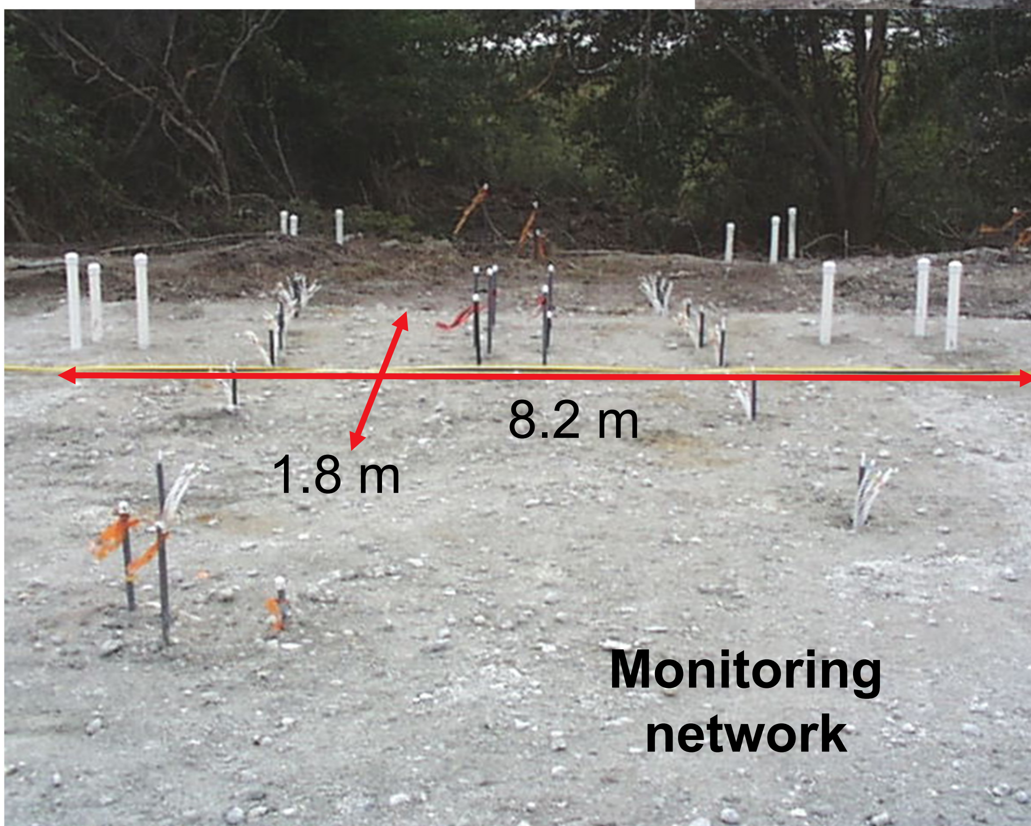
$$SO_4^{2-} + 2CH_2O \longrightarrow H_2S + 2HCO_3^-$$

$$Me^{2+} + HS^- \longrightarrow MeS + H^+$$

$$Fe^{2+} + HS^- \longrightarrow FeS + H^+$$

R. Ludwig, EPA

PRB Emplacement (biopolymer trench)

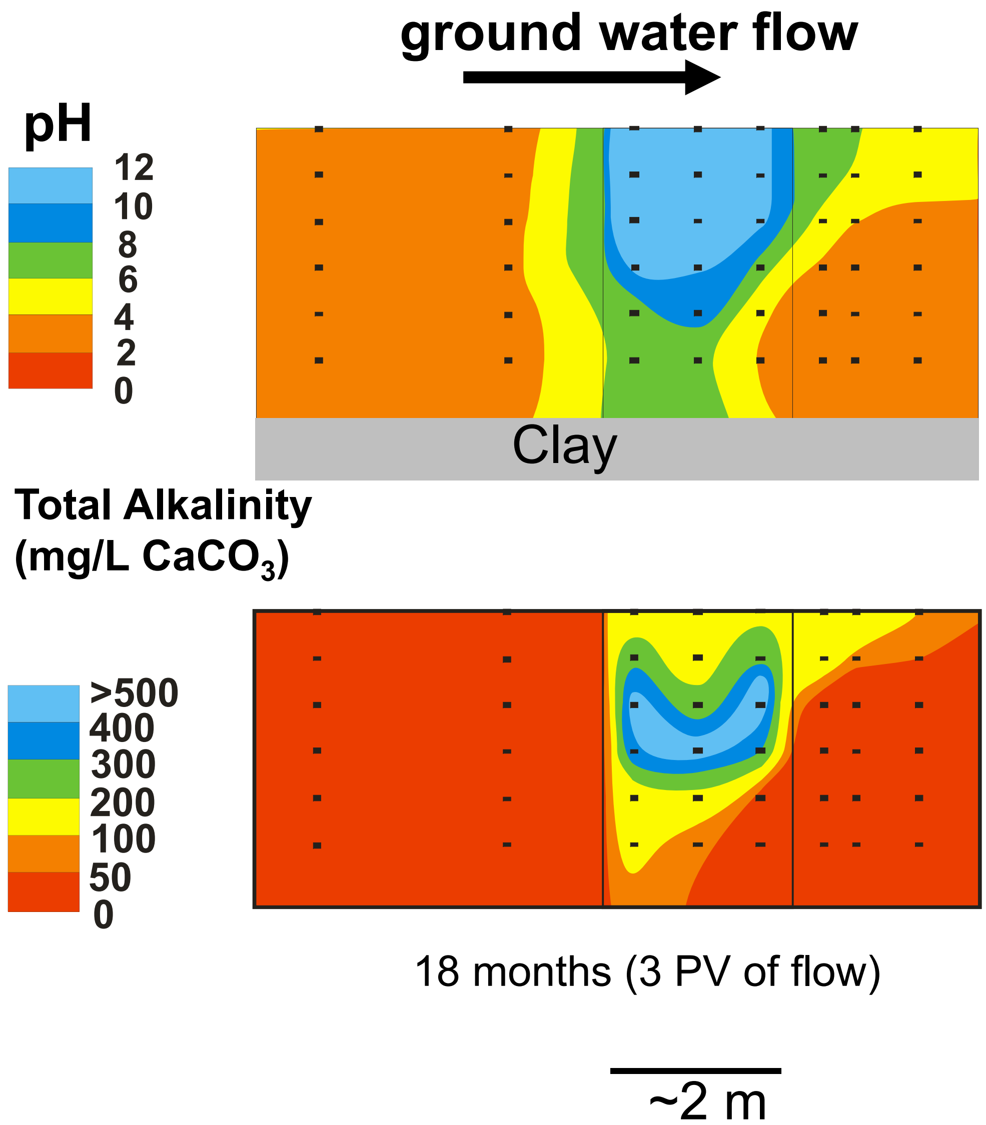


Approx 8.2 x 1.8 m L,W x 2.3 m depth below WT

R. Ludwig, EPA

Chemistry

- Neutralization of acidic (pH 2-3) water
- Generation of alkalinity
  - Dissolution of limestone
  - Sulfate reduction
  - Corrosion of iron/reduction of water
  - Long residence time due to slow groundwater velocity (3-5 m/yr)



18 months (3 PV of flow)

Chemistry

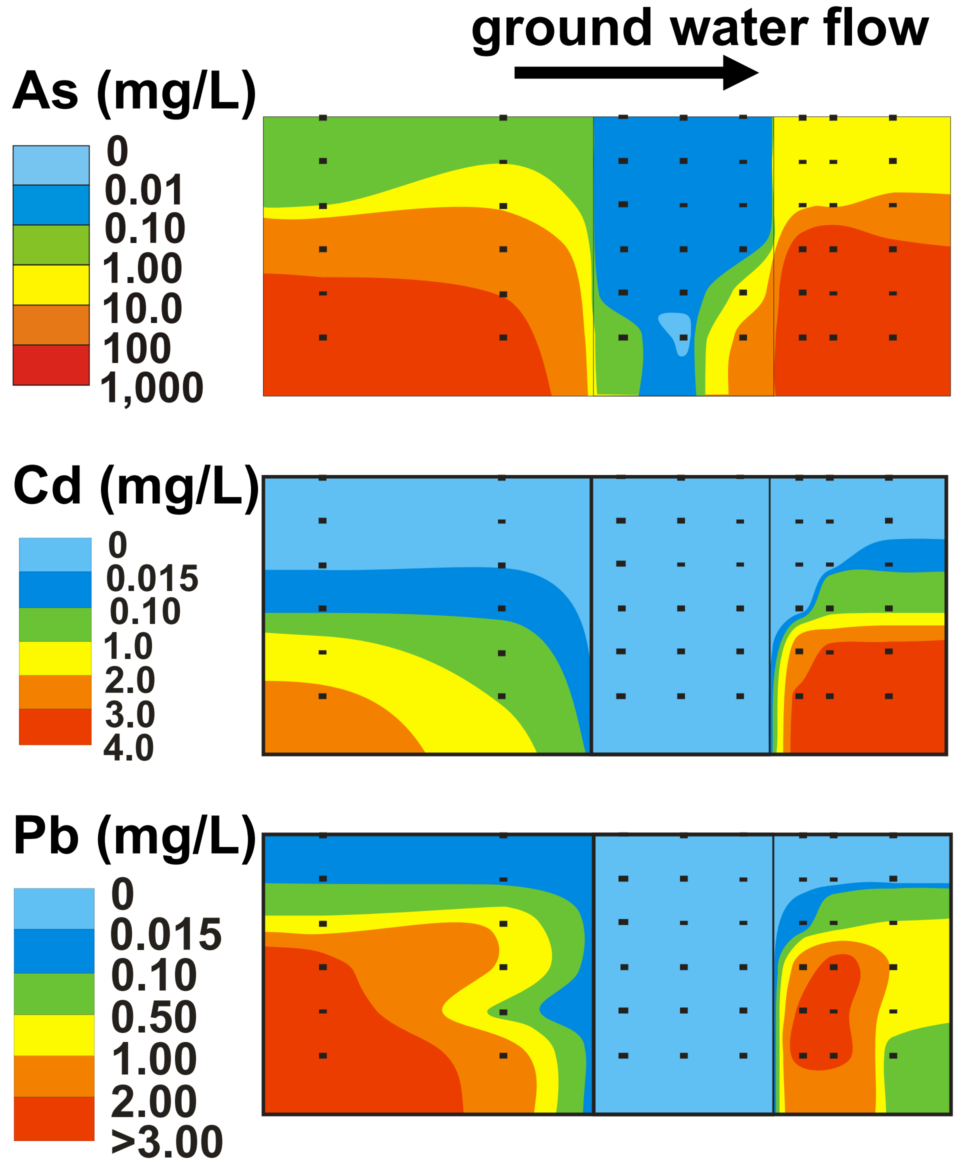
• Distinct removal of high concentrations of SO_4, As and heavy metals

• Significant population of SRB have developed (10^4 > PRB)

• Enrichment of ^{34}S in SO_4

• As-sulfide precipitation and coprecipitation with Fe oxyhydroxides

$Me^{2+} + HS^{-} \rightarrow MeS + H^{+}$



18 months (~3 PV)

Summary

- BOF slag and mixtures of ZVI filings with organic carbon were both effective in field PRBs for As treatment
- Effective in a variety of groundwater environments (industrial, mining, northern, warm)
- BOFS – low cost media, widely available, probable earlier replacement
- ZVI + OC mixtures – higher cost per ton but greater longevity
- PRBs are a potential alternative to conventional means of treatment (P&T)

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Acknowledgements

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