Spatial and Temporal Trends in Groundwater Chemistry and Precipitate Formation at the Elizabeth City Permeable Reactive Barrier

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Long-Term Performance Monitoring of Zero-valent Iron PRBs

- U.S. Coast Guard Support Center, Elizabeth City, NC
  (June 96; Peerless iron, Continuous Wall; Cr+VOCs)
- Denver Federal Center, Lakewood, CO
  (Nov 96; Peerless iron, Funnel-and-Gate; VOCs)

Evaluate:
- Contaminant behavior
- Groundwater geochemistry
- Mineral precipitates
- Microbial community characterization
- Hydraulic performance
Performance Summary

• Consistent degradation of contaminants over 6+ y

• Cr completely removed, never above MCL in any downgradient sampling points

• The PRB has achieved containment of chrome plating shop plume (source area now being addressed)

• Organic compounds removed to less than MCL in most sampling points most of the time

• Multiple sources of chlorinated organic compounds at the site
Soil core sampling

Groundwater sampling
Total Dissolved Solids
TDS, mg/L

Moffett Field (820)
Lowry AFB (2900)
Elizabeth City (250-350)
Denver Fed Ctr (900-1200)
Y-12 (470-3225)
Monticello (1300)

Data source: Tri-Agency PRB Initiative, Combined report
Elizabeth City – Spec. Cond.

Zero-valent iron zone

Depth, m

Distance, m

(µS/cm)

[transect 2]
Anionic composition

- Sulfate
- Iron sulfides; Sulfate GR
- Calcite/aragonite; Carbonate GR; Iron hydroxy carbonate

Diagram:
- Chloride
- Bicarbonate
- DFC
- E. City
Sulfate

[transect 2]
Core Analysis Methods

Tools

- SEM-EDS
- Reflected-light microscopy
- Transmission Electron microscopy (TEM)
- XPS (x-ray photoelectron spectroscopy)
- XRD (x-ray diffraction)
- Inorganic carbon analysis/Sulfur analysis/δ^{34}S
- Microbial assays
Inorganic Carbon Analysis

N\textsubscript{2} gas flow 5\% perchloric acid 5\% silver nitrate

Heated

CO\textsubscript{2} gas

Carbon Coulometer

Acid-volatile carbon (calcite, aragonite, siderite, GR CO\textsubscript{3}, rhodochrosite, magnesite)

Peerless Iron (unreacted)
15 ppm AVC
Sulfur Analysis

**Combustion**
- (sulfate S, elemental S, sulfide S)
- **Peerless Iron (unreacted)**
  - 5 ppm S

**Sequential Extraction**
- (AVS=FeS; CRS=FeS2)
Mineral/Biomass Accumulation – E. City

Sulfur

Inorganic Carbon

PLFA

Flow

Aquifer

Iron

Aquifer

Depth, m

2680 ppm

Position, m

2614 pmoles/g

Depth, m

4816 ppm

Position, m
Impact of Mineral and Biomass Accumulation: Hydrology and Contaminant Residence Time

\[ \rho_e \downarrow, K \downarrow, \text{Gradient} \uparrow \]
Seepage velocity \( \downarrow \)

PRB

Zone of increased buildup, increased \( \tau \)

Decreased \( \tau \)
Elizabeth City – pH

[transect 2]
Total S vs AVS

Acid-volatile Sulfide, mg/kg vs Total Sulfur, mg/kg

- Denver Federal Center
- Elizabeth City
X-Ray Diffraction

FeS weak
Aragonite weak
Magnetite strong
Siderite absent
Fe-OH-CO3 strong
GRCO3 present
SEM/TEM

Furukawa and Wilkin (2002) ES&T, in press
Inorganic C with time

Inorganic C, mg/kg

Distance, cm

aquifer

iron

- 2001
- 2000
- 1999
- 1998a
- 1998b
Mass Accumulation – E. City

- Inorganic Carbon: 8 kg/y (19 ppm)
- Sulfur: 32 kg/y (77 ppm)

Integrated accumulation
4600 cm x 530 cm x 60 cm

Accumulation, kg

Time

- 1996
- 1997
- 1998
- 1999
- 2000
- 2001
- 2002

Graph showing the accumulation over time with linear trends for Inorganic Carbon and Sulfur.
Porosity loss – Elizabeth City
Assume all ppt in front 10 cm, initial porosity = 50%
Porosity loss - DFC

Assume all ppt in front 10 cm, initial porosity = 50%
Pore loss estimations

- Flow rate (flux in)
- Sulfate concentration/removal efficiency
- Bicarbonate concentration/removal efficiency
- Initial PRB porosity
- Iron corrosion (pore volume gain), oxidation (loss)
- Mineral molar volumes
Microbial Biomass – PLFA Dist.

From Gavaskar et al., 2002
Long-term performance: Overview

• Consistent degradation of contaminants over 6 y

• Spatial heterogeneity of mineral and biomass accumulation

• Buildup correlated to GW chemistry (TDS) and flow rate

• Fe$^0$ is long-term sink for C, S, Ca, Si, N, Mg, +/- Mn (mass balance on C & S)

• Porosity loss rate from 1 to 4% per y of original available V
Long-term performance: Overview - cont

- Reactive transport codes – data gaps
- Vertically resolved hydro/geochem data needed during site characterization
- Correlation between declining performance and changing geochemical parameters not evident after 6 y