Permeable Reactive Barriers as a tool for remediation of contaminated groundwater, Hyderabad, India

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Collaborative Research Program with NGRI and NGI*

Collaboration between NGRI and NGI in environmental studies of urban and industrially developed areas related to soil and ground water contamination

*(NGRI=National Geophysical Research Institute)
(NGI=Norwegian Geotechnical Institute)
Areas of Co-operation

Long-term co-operation in the field of environmental geochemistry/geotechnology

Definition and application of suitable methods and tools to perform detailed environmental studies in India
Methodology for Co-operation

Environmental site assessments and training using

- field methods
- modeling
- risk assessment
- remediation techniques
Site selection

Katedan Industrial Development Area (KIDA)

- Geological mapping
- Topography, hydrology, drainage, land use maps
- Well inventory (location and specifications)
- VS (resistivity) - profiling
- Exploratory borings / monitoring well
- Field testing (slug test, etc.)
- Field sampling of sediments, soil and groundwater
KIDA

- 300 large and small industries
- Producing/processing
  - Paints/pigments
  - Batteries
  - Metal treatment
  - Steel rolling
  - Cotton
  - Synthetic yearns
  - Engineering goods

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Topographically irregular tors of granites, the granitic hills and mounds can be observed in the area.

The granites are highly weathered. Pegmatite veins, quartz reefs and dolerite dykes are also observed.

The thickness of the weathered layer varies from few feet depth to 70-80 ft. The water bearing horizons are weathered granite and fractured portion of the rock.

The southern portion is higher than northern portion and gently slopes down towards the north.
Sediment Location Map

Pre-Monsoon

Ura Cheruvu

Chilan Lake

Narsabaigunta

Noor Mohammad Lake

Devullama Cheruvu

Post-Monsoon

Ura Cheruvu

Chilan Lake

Narsabaigunta

Noor Mohammad Lake

Devullama Cheruvu
Distribution of Zinc (ppb) in Surfacewater

Pre- Monsoon

Post- Monsoon

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Distribution of Arsenic (ppm) in Sediments

Pre-Monsoon

Post-Monsoon

- 7 - 50
- 51 - 100
- 101 - 200
- 201 - 400
- > 400
Distribution of Chromium (ppm) in Sediments

Pre- Monsoon

Post- Monsoon

- 11 - 50
- 51 - 100
- 101 - 200
- 201 - 300
- 301 - 502
- 31 - 50
- 51 - 100
- 101 - 200
- 201 - 232
- 630,704

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Distribution of Nickel (ppm) in Sediments

Pre- Monsoon

Post- Monsoon

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Distribution of Lead (ppm) in Sediments

Pre- Monsoon

Post- Monsoon

- 26 - 50
- 51 - 100
- 101 - 200
- 201 - 500
- 501 - 1603
Distribution of Zinc (ppm) in Sediments

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Distribution of Arsenic (ppb) in Surfacewater

Pre-Monsoon

Post-Monsoon

Green dots: 3 - 10
Red dots: 11 - 20
Plus signs: 21 - 48

Green dots: 5 - 10
Red dots: 11 - 17

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Distribution of Chromium (ppb) in Surfacewater

Pre-Monsoon

Post-Monsoon

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Distribution of Lead (ppb) in Surfacewater

Pre- Monsoon

Post- Monsoon

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PERMEABLE REACTIVE BARRIER (PRB) TECHNOLOGY

Permeable Reactive Barriers (PRBs) is an emplacement of reactive material through which contaminated plume flows and gets treated by combination of various physical, chemical, and biological reactions occurring within a reactive zone.

**Advantages of PRB**
- Low maintenance and operation cost
- More durability
- Low installation cost
- High removal efficiency
- Non toxic end products

**Targeted contaminants treatable in PRBs**
- Metals, Inorganics and Nutrients
- Chlorinated solvents and Pesticides
- Fuel hydrocarbons and Radio nuclides
IMPORTANT PRB INSTALLATION FACTORS

- Hydrogeological characteristics of site
- Characterization of contaminant
- Reactant residence time
- Suitability of reactive media
- Geometry of reactive media

REACTIVE MATERIALS IN USE

Reactive media ranges from
- zero-valent iron
- activated alumina
- zeolites, limestone
- activated carbons
- coal
- mineral oxides
- organic composts
- many more.
REACTIONS INVOLVED IN TREATMENT PROCESS

- Adsorption/sorption
- Precipitation
- Oxidation/reduction
- Biodegradation

DESIRABLE CHARACTERISTICS

- Availability and cost
- Porosity and surface area
- Hydraulic performance
- Environmental compatibility and stability
Geochemical PRBs for Inorganics

- Zero-valent iron: reductive precipitation of electroactive metals and metalloids

- Organic carbon: sulfate reduction, metal sulfide precipitation
  - Patents U.S. 5,362,394 5,514,279; Europe EP 0 502 460 B 1

- BOF* Slag: sorption and co-precipitation removal of phosphate and arsenic
  - Patents U.S 5,876,606.; Europe GB 962338-7
  *BOF=Basic Oxygen Furnace

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Zero-Valent Iron for Electro active Metals: Field installations

- Corrosion of metallic iron by groundwater creates strongly reducing and elevated pH conditions
- Reductive precipitation of electro active metals and metalloids
- Chromium (VI): Elizabeth City, NC; Industrial site, Wisconsin; Hard Krom - Denmark
- Radio nuclides: US DoE Facilities (Oak Ridge, Durango, Monticello, Fry Canyon, Rocky Flats); Industrial site, Colorado
- Arsenic: Red Lake, ON; Generating Station, N ON; Charleston, SC
- Selenium: Generating Station, N ON; Monticello, UT
Chromium (VI) and Chlorinated Solvents

- US Coast Guard Support Center, Elizabeth City, NC
- Cr(VI) concentrations as high as 10 mg/L
- TCE as high as 5.65 mg/L
- Alkalinity 40-140 mg/L as CaCO₃; SO₄ < 100 mg/L
- Groundwater velocity ~ 15 cm per day
- Installation in 1996; 45 m wide, 0.6 m thick, 7.3 m deep; 100 % granular iron (porosity ~0.5)
- Installation and monitoring of performance (Blowes et al. (EPA/600/R-99/095abc) and Wilkin et al. (EPA/600/S-02/001))
USCG Wall Installation
Continuous Trencher

PRB
Source Zone

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Long-term Performance

- Field investigations and numerical modelling
- Reductive precipitation and co-precipitation
  - $\text{Cr(III)}$ and iron oxyhydroxides
- Excellent Cr removal; < 0.01 mg/L in multi-level monitors 0.1 m into PRB in 2001
- Secondary precipitates (iron oxyhydroxides, carbonates, sulfides; decreasing concentrations of Ca, Mg, Mn); estimates for porosity of 0.3 to 0.36 after 20 years
- Microbial activity (eg. sulfate reduction)
- Reactivity for contaminant treatment maintained
Arsenic Removal by Zero-Valent Iron and ZVI/ Organic Carbon Mixtures

- Applications include field-scale PRB trials for mine-tailing porewater (Ontario, Canada) (Bain et al., 2002); leachate from coal-combustion wastes (Ontario) (McGregor et al., 2002); and former phosphate-fertilizer site (Charleston, SC)

- Organic carbon materials have included plant-based compost and wood-production wastes

- Decreased per unit volume costs
Arsenic Removal from Groundwater
Derived from Mine Tailings

• Laboratory and field-scale trial (Bain et al., 2002)
• Northern Ontario mine site
• Two reactive mixtures in laboratory:
  – 100 % zero-valent iron
  – 20 % zero-valent iron with organic carbon mixture
• Columns operated for two years
• Field trial: zero-valent iron mixture
• Field trial initiated in 2002
Laboratory Column Setup

Influent Tailings
Water Characteristics:
• pH 7.2
• Alkalinity ~100 mg/L as CaCO₃
• Sulfate ~560 mg/L
• Fe ~0.4 mg/L
• As ᵗₒᵗ ~10 mg/L

Column test operated for approximately two years
- Outflow consistently higher pH than inflow
- Higher outflow pH values in 100Fe column
As Treatment

- 8-20 mg/L As$_{\text{total}}$ input
- < 0.005 mg/L As$_{\text{total}}$ outflow for both columns
Arsenic Concentration Profiles
100% Iron Column

• Removal of As within 10 cm travel in reactive media
Arsenic Concentration Profiles
20% Iron Column

- Removal of As within 10 cm travel in reactive media

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Arsenic Treatment

- Stable profiles of dissolved arsenic in treatment media
  - ~110 PV; non-detectable beyond 11 cm in 100 % ZVI
  - ~210 PV; non-detectable beyond 11 cm in 20 % ZVI mixture

- Reductive precipitation
PRB Installation

• Two PRB zones
  – PRB 1: ZVI (15 Vol %) and wood chips (40 Vol %)
  – PRB 2: ZVI (Vol 55 %)

• Installation using excavation and fill with trench box; some cobbles and sediments remained at bedrock surface

• Each zone 6.5 m x 2.0 m thick x ~3.0m deep
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Distance Along Flow path (m)

Arsenic (mg/L)

E (mV)

PRB 1

September
November

0.0
0.2
0.4
0.6

-300
0
300
600

0 1 2 3 4 5 6 7

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Summary of field PRB Performance

- Zero-valent iron and zero-valent iron combined with organic carbon materials provide removal of more than 95% of arsenic
- Two week residence time for groundwater in PRB
- Similar removal exhibited for Se and Cr
- Reductive precipitation
- Treatment in some parts of PRB affected by cobbles and sediments at PRB/bedrock interface
NGRI batch studies

Batch adsorption studies: Evaluation Procedure

- Synthetic solution containing As, Cd, Cu, Pb, Zn, Ni, Cr in different proportions ranging from 100 - 1000 ppbs was used.
- Synthetic solution was prepared from respective salts of elements.
- Reactive material used for batch test was pre-treated before use.
- Sample to reactive media ratio 1:10
- Shaking machine with horizontal top was used.
- Agitation of sample with reactive media at room temperature
- Filteration of eluate and its analysis
## Reactive materials used in NGRI batch studies and its removal process

<table>
<thead>
<tr>
<th>Reactive material used (particle size)</th>
<th>Removal process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron filings (4-6mm)</td>
<td>Reduction and co-precipitation</td>
</tr>
<tr>
<td>Limestone (4-5mm)</td>
<td>Precipitation</td>
</tr>
<tr>
<td>Charcoal (3-4mm)</td>
<td>Sorption</td>
</tr>
<tr>
<td>Concrete (4-6)</td>
<td>Sorption and co-precipitation</td>
</tr>
<tr>
<td>Lime (2-3mm)</td>
<td>Precipitation</td>
</tr>
<tr>
<td>Brick (4-5mm)</td>
<td>Sorption</td>
</tr>
<tr>
<td>Flyash (2-3mm)</td>
<td>Sorption</td>
</tr>
<tr>
<td>Activated alumina (2-4mm)</td>
<td>Sorption</td>
</tr>
</tbody>
</table>
# Screening batch NGRI test results with different reactive material and % removal

<table>
<thead>
<tr>
<th>S.No</th>
<th>Reactive materials</th>
<th>Cd(ppb)</th>
<th>As(ppb)</th>
<th>Cr(ppb)</th>
<th>Mo(ppb)</th>
<th>Ni(ppb)</th>
<th>Pb(ppb)</th>
<th>Se(ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>BLANK</td>
<td>1734</td>
<td>1315</td>
<td>9600</td>
<td>540</td>
<td>1964</td>
<td>9400</td>
<td>515</td>
</tr>
<tr>
<td>2.</td>
<td>IRON FILINGS</td>
<td>99.8%</td>
<td>68 %</td>
<td>BDL</td>
<td>99.7 %</td>
<td>BDL</td>
<td>87.5 %</td>
<td>BDL</td>
</tr>
<tr>
<td>3.</td>
<td>ACTIVATED ALUMINA</td>
<td>42 %</td>
<td>58 %</td>
<td>36 %</td>
<td>90 %</td>
<td>40 %</td>
<td>45 %</td>
<td>99.3 %</td>
</tr>
<tr>
<td>4.</td>
<td>LIMESTONE</td>
<td>49 %</td>
<td>66 %</td>
<td>99.8 %</td>
<td>22 %</td>
<td>30 %</td>
<td>BDL</td>
<td>5 %</td>
</tr>
<tr>
<td>5.</td>
<td>CHARCOAL</td>
<td>14 %</td>
<td>63 %</td>
<td>28 %</td>
<td>80 %</td>
<td>28 %</td>
<td>73 %</td>
<td>29 %</td>
</tr>
<tr>
<td>6.</td>
<td>LIME</td>
<td>BDL</td>
<td>89 %</td>
<td>99 %</td>
<td>12 %</td>
<td>BDL</td>
<td>BDL</td>
<td>93 %</td>
</tr>
<tr>
<td>7.</td>
<td>BRICK</td>
<td>29 %</td>
<td>19 %</td>
<td>89 %</td>
<td>93 %</td>
<td>25 %</td>
<td>BDL</td>
<td>99 %</td>
</tr>
</tbody>
</table>
Reduction of chromium and cadmium in batch tests (Iron fillings)
Reduction of arsenic and nickel in batch tests (Iron fillings)

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Results from NGRI batch tests

- Iron, lime is really very good whereas other materials are specific towards removal of some particular contaminants.

- The combination of reactive materials instead of single can achieve overall cleanup of contaminants.

- Further studies include the detailed investigation of cost effective reactive materials and its properties, batch test under different conditions, column flow studies, reactive mechanism with contaminants and design for PRB installation.
Drainage treatment system at transformer station (Southern Ontario, Canada)

- chamber; residence time of approximately one day
- influent arsenic <0.5 mg/L; effluent <0.002 mg/L
Give to the world the best you have, and the best will come back to you.
Thank you