Can PHC-Impacted Fractured Limestone Be Remediated Using ISCO?

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Background

- Remediation of groundwater in fractured rock has proved problematic
  - Mackay & Cherry 1989
  - Parker et al., 2010
- Fractured Rock
  - Small fracture porosity (0.1 to 0.001%)
  - Large matrix porosity (2 to 25%)

Modified after Parker, 2013
Background

• Requires integrated approaches

Modified after Parker, 2013
Background

Modified after Kueper and Davies, 2009
Background

- Remediation of groundwater in fractured rock is governed by diffusion out of rock matrix (i.e. back diffusion)
- Rate of diffusion governed by:
  - Concentration
  - Time
  - Porosity
  - Organic carbon
  - Biological reactions
  - Redox species, etc.
Background

- How do we attempt to address remediation in fractured rock
- Integrated approach:
  - Combination of technologies
  - Reduction of mass
  - Increase biomass
Background

- How do we attempt to address remediation in fractured rock
- Integrated approach:
  - Combination of technologies
  - Reduction of mass
  - Increase biomass
  - Create a diffusion “reactive front”
Background

$T = \text{Spill}$

Groundwater Flow
Background

T = Spill

T = Injection

Groundwater Flow

C/Co
Background

T = Spill

T = Injection

T = Post - Injection

Groundwater Flow
Background

Persulphate Anion

\[ S_{2}O_{8}^{2-} + 2H^{+} + 2e^{-} \rightarrow 2HSO_{4}^{-1} \]

Activation

\[ SO_{4}^{\cdot-} + e^{-} \rightarrow SO_{4}^{2-} \]

Initiation

\[ S_{2}O_{8}^{2-} \rightarrow SO_{4}^{\cdot-} + (SO_{4}^{\cdot-} \text{ or } SO_{4}^{2-}) \]

Propagation

\[ SO_{4}^{\cdot-} + H_{2}O \rightarrow OH^{\cdot-} + HSO_{4}^{-} \]

Termination

\[ SO_{4}^{\cdot-} + RH \text{ or } M \rightarrow SO_{4}^{2-} \]
Background

Persulphate Anion

$$S_2O_8^- + 2H^+ + 2e^- \rightarrow 2HSO_4^{-1}$$

Activation

$$SO_4^{\cdot-} + e^- \rightarrow SO_4^{-2}$$

Initiation

$$S_2O_8^{2-} \rightarrow SO_4^{\cdot-} + (SO_4^{\cdot-} \text{ or } SO_4^{-2})$$

Propagation

$$SO_4^{\cdot-} + H_2O \rightarrow OH^{\cdot-} + HSO_4^-$$

Termination

$$SO_4^{\cdot-} + RH \text{ or } M \rightarrow SO_4^{-2}$$
Study Site

- Remedial program
  - Excavation of overburden to limestone surface
  - Pumping of NAPL
  - ISCO of dissolved phase
  - EAB of residue
Site

• Residential site, Central Ontario
• Fuel oil spill
  • ~600 L
• Geology
  • Glacial overburden (~1 m thick)
  • Fractured limestone
• Hydrogeology
  • Water table within limestone
  • ~0.5 m/year fluctuation
  • Packer testing
• Geochemistry
  • Iron/sulphate reducing
PHC Plume

Source

Plume

Groundwater Flow
PHC Plume

Background Well
Source
Plume
Impacted Well
Groundwater Flow
Injection Program

- Oxidant
  - Sodium persulphate activated sodium hydroxide
  - Supplemented with 100 mg/L NaBr tracer

- Injection program
  - Four injections over 6 months
  - 2 locations
    - Background & Impacted
  - Injections completed using packers
    - 15 wt.% $S_2O_8$
    - 20 psi
    - 650 L/well per injection
Monitoring Program

• Cores of rock collected
  • Pre injection
  • 1, 6 & 12 months after last injection event
  • Frozen on site
  • Sampled in lab at 5 cm intervals
• Analysis
  • Persulphate,
  • Bromide and
  • pH
Non-Impacted Fracture Profiles

Persulfate $C/C^0$

Bromide $C/C^0$

Depth (cm)

28 Days
182 Days
358 Days
PHC-Impacted Fracture Profiles

Persulfate C/C₀

Bromide C/C₀

Depth (cm)

28 Days
182 Days
358 Days
Bromide Profiles

Bromide C/Co

Depth (cm)

0 0.2 0.4 0.6 0.8 1.0

Non-Impacted

28 Days
182 Days
358 Days

Bromide C/Co

Depth (cm)

0 0.2 0.4 0.6 0.8 1.0

Impacted

28 Days
182 Days
358 Days

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Persulphate Profiles

Persulfate C/Co

Depth (cm)

Non-Impacted

Impacted

28 Days

182 Days

358 Days
pH Profiles

pH: Non Impacted

pH: Impacted
Model

- BioRedox-MT3DMS
  - Van Genuchten analytical solution
  - 3 D
  - 1 D simulations
  - Calibration based on Merkel (2010)
    - ESTCP diffusion column
    - Compared with Sra (2010)
  - Bromide degradation negligible
  - Persulphate half lives between 25 & 50 days
Bromide Calibration

Data for $t=182$ days suggests that a downward velocity continued after injection.
Persulphate Simulation

Non Impacted Fracture

Model versus Observed
(t=28d)

Model versus Observed
(t=182d)

Model versus Observed
(t=352d)

Half life is 25 days
Persulphate Simulation

PHC-Impacted Fracture

Model versus Observed (t=28d)

Model versus Observed (t=182d)

Model versus Observed (t=352d)

Observed: Impacted Area  Model

Half life is 15 days
Persulphate Simulation

PHC-Impacted Fracture Sensitivity Analysis

Model versus Observed (t=28d)

Model versus Observed (t=182d)

Model versus Observed (t=352d)
Treatment

Total PHCs (µg/L)

Days

$S_2O_8$ Injections

ORM Injections

Days

0 200 400 600 800 1000 1200
Observations

- Fractured rock remediation provides a special challenge due to diffusion-controlled processes
- Limited tools available to address diffusion
- Chemical oxidation tools include:
  - High concentrations
  - Persistence
  - Long term oxidant source
- Diffusion of persulphate
  - ~20 cm impacted matrix vs ~30 cm vs non-impacted matrix
- Persulphate degrades in absence of PHCS:
  - ~ 25 day half live vs 15 days in presence of PHCs
- pH activation may be issue
  - Evaluated pH (>10) observed at 10 cm for less than 3 months in both impacted and non-impacted matrices, suggesting buffering reactions are occurring
Questions