

THE POWER OF RUST!

Leveraging the Adsorptive Properties of Iron Oxyhydroxides to **Remediate Dissolved Metals**

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LL Hennera An Ausenco Company

Outline

- Background
- CSM for metal release and attenuation
- Geochemical Modeling to Support ROE
- Remedial CSM
- Bench Scale Testing
- Results, Discussion
- Next Steps



Definitions and Acronyms

• Iron Oxyhydroxides = Hydrous Ferric Oxides

• Example – ferrihydrite Fe(OH)₃

HFO used as acronym throughout presentation

• CSM = Conceptual Site Model



Background

- Former Industrial Facility adjacent to river
 - Freshwater aquatic habitat fish rearing
- Industrial Processes involved use of Copper as a catalyst
- Spent catalyst poured into the ground "the Copper Pit"
- Remedial Excavation in 1990s to water table
- ~113,000 m³ estimated in 1990s
- ~400,000 m³ estimated in 2018 based on Hemmera data
 - Changing guidelines values; Plume dispersion



Background

- Dissolved metals plume (primarily copper)
- Porewater samples indicate currently discharging at 7x guideline concentration
- Risk Assessment indicated unacceptable risk to freshwater aquatic life (tox testing)
- Will conditions improve or worsen over time?



Background





Background - CSM





Field Program

- Collected samples for BCR analysis along flow path
 - HFO and calcite molar concentrations!
- Prepared reactive transport model using PHREEQC
 - HFO and calcite set as equilibrium phases
- Predict long-term behavior of plume and concentration at receptor
 - [Cu] to increase by >5x!



Geochemical Modeling





Geochemical Modeling – Spatial Profiles



- Proposing to inject ferrous sulphate heptahydrate
- Precipitate HFO
 - $2FeSO_4 + 1/2O_7 + 5H_2O \rightarrow 2Fe(OH)_3 + 2H_2SO_4$
 - Reaction needs pH neutralization sufficient limestone present?
 - O₂ required to oxidize ferrous iron to ferric iron natural oxidant present?
- Adsorb metals = decrease dissolved concentration
 - $\equiv FeOH^+ + Cu^{2+} \rightarrow \equiv FeOCu^{2+} + H^+$



- Geochemical modeling indicates increasing HFO from 500 mg/kg to 5000 mg/kg =
- Dissolved Copper from 0.2 mg/L \rightarrow <0.007 mg/L
- Collect Soil for Columns
- Increase HFO using FeSO₄·7H₂O
- Oxidize (if needed) with CaO₂ to estimate O₂ required







Copper Concentration It Receptor (mg/L)	
1.095	
). 196	
0.095	
0.084	
1.0001	
0.0001	
0.005	
1.036	
DIAL SCENAR	los





Bench Scale Testing of Remedial Approach

 600L of groundwater from MW18-17 with [Cu] ~ 0.3 mg/L – field filtered

10 pails of soil from proposed remedial injection area

- Soil placed in coolers
- Saturated with contaminated groundwater
- Placed in oxygen free glove box (argon)
- Ferrous sulphate added
- Periodic measurement of Fe²⁺ using HACH
- Oxidize with CaO₂ if necessary

Bench Scale Testing of Remedial Approach



Columns 6.5" x 3' 16.5 cm x 91.44 cm















- Insufficient natural oxidant in aquifer material to oxidize ferrous to ferric iron (Column 1)
- Added CaO₂ as oxidant
- Column 2 and Column 3 mixed with ferrous sulphate and calcium peroxide simultaneously, left overnight
- Added more calcium peroxide following morning due to detectable Fe^{2+}











- GW velocity estimated at 0.4-0.7 m/day
- For columns 0.9144 m = ~1.5 2 day residence time
- To evaluate kinetics flow rate set to ~4 mL/min
- ~= to 1 day residence time
- Program proceeded for 35 days



- 5 ports on side of columns
 - 0.1 m
 - 0.3m
 - 0.4572 m
 - 0.6 m
 - 0.8144m
- Plus 1 outlet on the top
- If [Cu] >0.007 mg/L, sample from next port until <0.007 mg/L





Graph A: Column 1 (100%) Results







Graph C: Column 3 (75%) Results





Graph D: Column 4 (Control) Results







Graph E: Dissolved Oxygen Measurements









Column 1 Column 2 Column 3 Column 4

Parameter	Column 1 [mg/L]	Column 2 [mg/L]	Column 3 [mg/L]
Chloride	125	129	<u>129</u>
Sulfate	365	257	<u>1180</u>
Fluoride	0.11	0.12	0.04
Bromide	0.10	0.10	0.10
Dissolved Aluminum	0.005	<0.004	<0.004
Dissolved Antimony	<0.001	<0.001	<0.001
Dissolved Arsenic	<0.001	<0.001	<0.001
Dissolved Barium	<0.05	<0.05	<0.05
Dissolved Beryllium	<0.001	<0.001	<0.001
Dissolved Boron	0.08	0.02	0.04
Dissolved Cadmium	<0.000016	<0.000016	<0.00016
Dissolved Chromium	<0.001	0.033	0.009
Dissolved Cobalt	<0.0009	<0.0009	<0.0009
Dissolved Copper	<0.0008	0.0010	<0.0008
Dissolved Iron	<0.1	<0.1	<0.1
Dissolved Lead	<0.0005	<0.0005	<0.0005
Dissolved Manganese	0.020	<0.005	<0.005
Dissolved Molybdenum	<0.001	0.001	0.001
Dissolved Nickel	<0.003	<0.003	<0.003
Dissolved Selenium	0.0008	<u>0.0016</u>	<0.0005
Dissolved Silver	0.00011	0.00006	<0.00005
Dissolved Sodium	67.6	70.1	69.3
Dissolved Thallium	<0.0001	<0.0001	<0.0001
Dissolved Titanium	<0.001	0.001	<0.001
Dissolved Uranium	<0.001	<0.001	<0.001
Dissolved Zinc	<0.005	<0.005	<0.005



Column 4 [mg/L]
<u>126</u>
87.9
0.21
0.11
0.005
<0.001
<0.001
0.11
<0.001
0.07
<0.000016
<0.001
<0.0009
<u>0.0705</u>
<0.1
<0.0005
0.086
0.002
<0.003
<0.0005
<0.00005
67.8
<0.0001
<0.001
0.001
<0.005

- For all Columns
 - Decrease in concentration greater than predicted by PHREEQC
 - ~0.35 mg/L to <0.002 mg/L
 - Concentrations had not reached port 1 (10cm from base) at end of testing program
 - Column 2 (75%) top performer



- Column 2 and 3 exhibited high pH
 - Attributed to calcium peroxide
 - $CaO_2 + 2H_2O \rightarrow Ca(OH)_2 + H_2O_2$
 - $2H_2O_2 \rightarrow 2H_2O + O_2$
- pH in Column 2 did not decrease to background even after 35 pore volumes
- Adsorption not negatively effected by elevated pH



- Column 2 and 3 exhibited high DO
 - Attributed to calcium peroxide
 - $CaO_2 + 2H_2O \rightarrow Ca(OH)_2 + H_2O_2$
 - $2H_2O_2 \rightarrow 2H_2O + O_2$
- DO did not decrease to background even after 35 pore volumes
- Potential slow release of O₂ for pilot scale?



- Residence time for columns was less than in-situ
 - As little as <1/2 typical residence time
- Adsorption not kinetically inhibited for range of residence times/flow velocities



General Affinity of Dissolved Species for Fe(OH)₃

$$As^{5+} = Cu^{2+} = Be^{2+} = Pb^{2+} = PO_4^{3-}$$

> $Zn^{2+} > Cd^{2+} > As^{3+} > Ni^{2+} > SO_4^{2-}$
>> $Ba^{2+} >> Ca^{2+} >> B^{3+}$

Arsenate (As⁵⁺) most strongly adsorbed, boron least strongly adsorbed

Challenges

- Large % of cobbles difficult to mix
- Maintaining anoxic conditions while mixing
- Little available literature
 - Some sites in US, none identified in Canada
 - Direct push not possible
- Drilling in developed brown field site
- Homogeneous distribution during pilot scale
 - Well fouling



Uncertainties

- pH correction for HACH samples early Cu results representative?
- Extrapolation proposed injection area 10-20m wide, Columns 0.9144 m
- Column 3 (75%) top performer
- Verifying HFO concentrations using BCR on very coarsegrained soils
 - How to subsample representative 1kg in gravel and cobble substrate?



Next Steps

- Pilot Scale Injections Pending
 - Pending AEP approval injection near source; iron injection has not been tried in AB
- Packers and injection? Nested pairs?
- Oxidant to be used:
 - Air sparge to avoid pH increase?
 - CaO_2 slow release option to create oxidizing barrier d/g?



Thank you. Questions?

Contact Us

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