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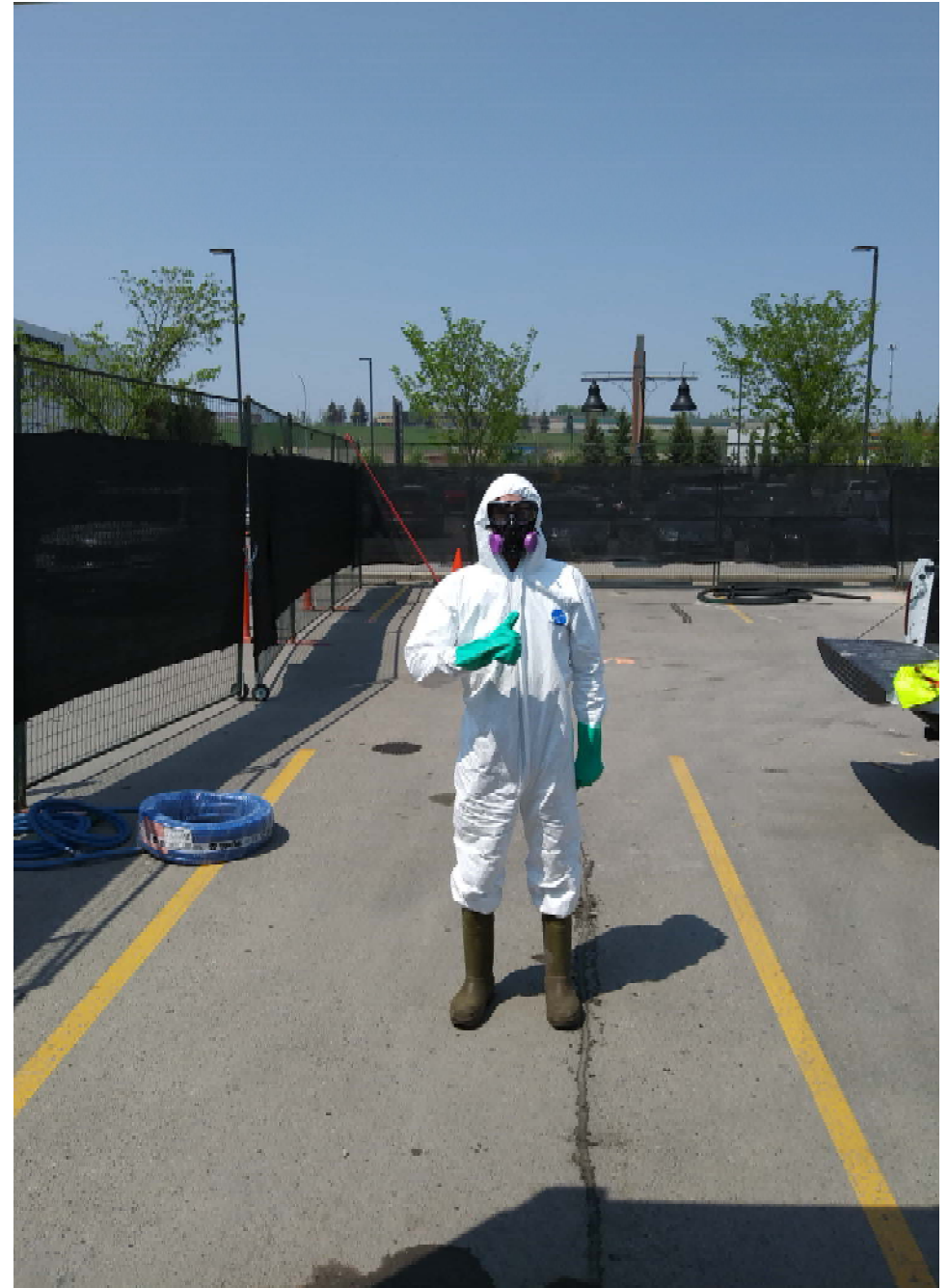
# Case Study: Pilot Scale In-Situ Remediation of Dissolved Metals Plume

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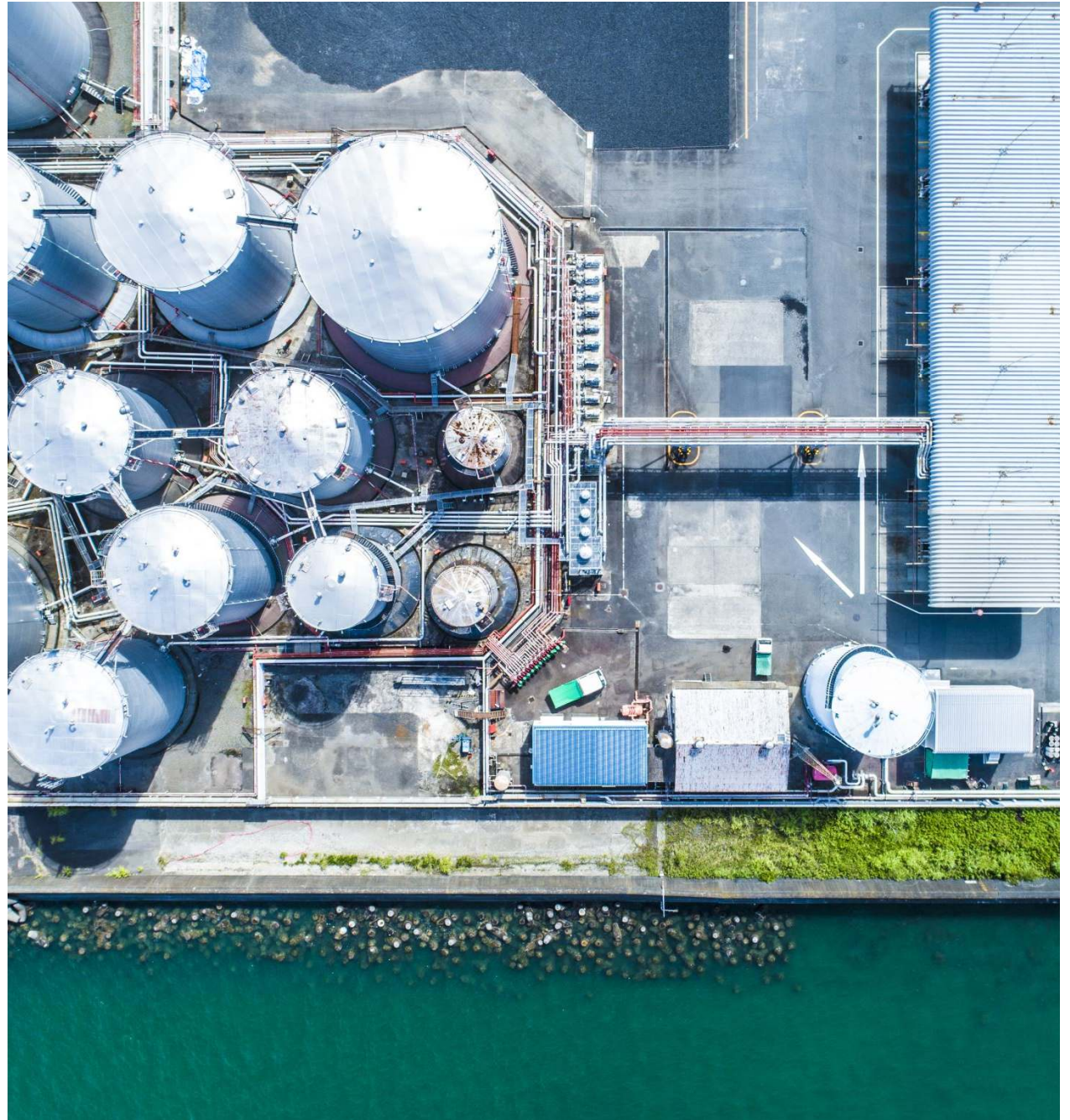
## Outline

1. Site History & Investigations
2. Conceptual Site Model & Remedial Design
3. Bench Scale Testing
4. Pilot Scale Injections
5. Results & Interpretation/Lessons Learned
6. Next Steps
7. Questions



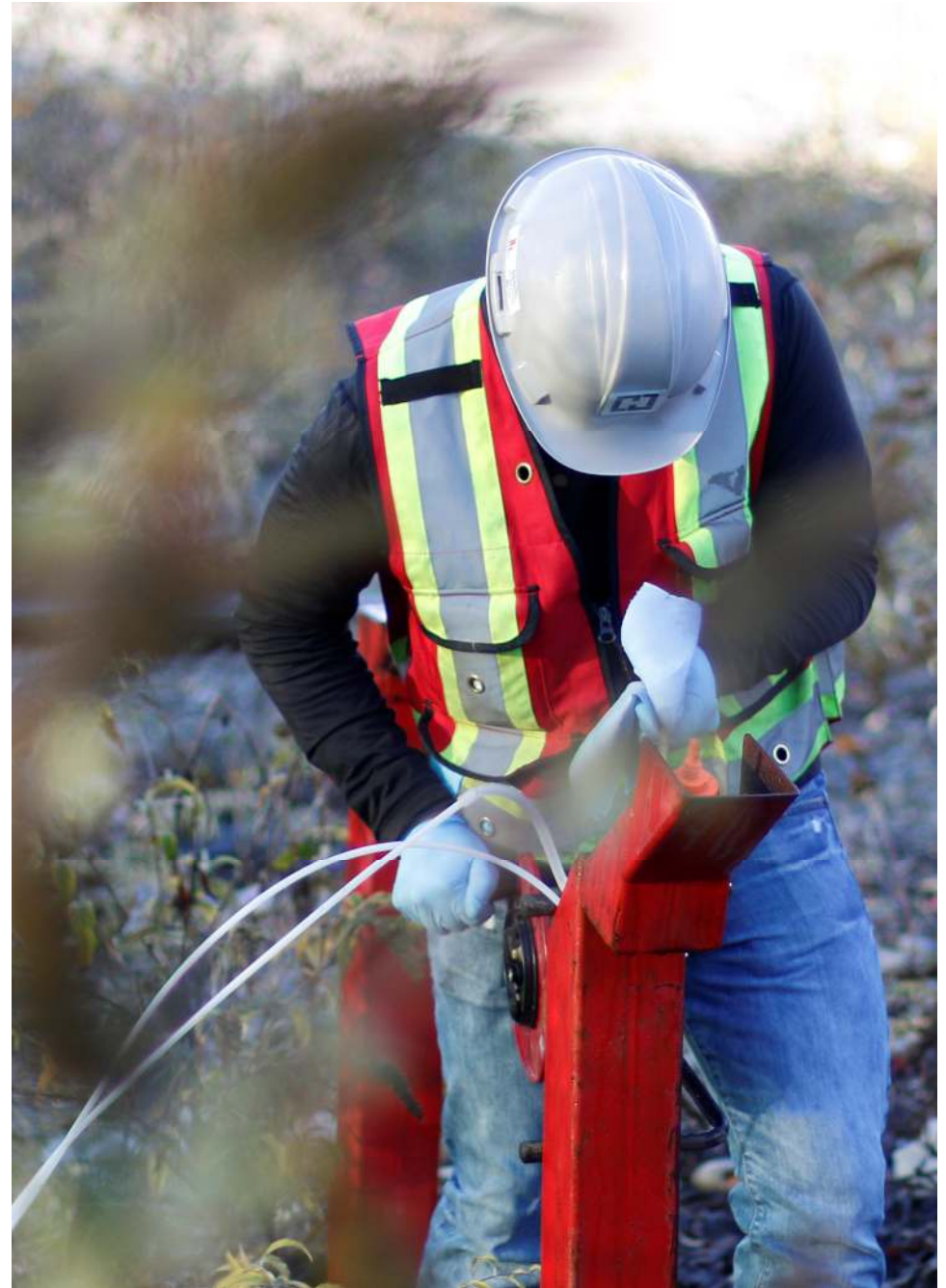
# 1

## Site History & Investigations



## Site History

- Former Industrial Site
- Copper used as a catalyst
- Spent catalyst dumped into the ground
- Decommissioned in late 1980's
- Investigation and remediation since early 1990's



# Site Investigations



Copper Plume ~700 m long defined by 4 wells



2015 Hemmera SSI

Identified new hot spot 3x higher concentration  
Soil mineralogy analysis (BCR 701/modified Tessier)  
500 mg-Fe/kg-soil; ~30% limestone



Porewater sampling

Copper reaching river at ~7x guideline



Toxicity Testing

Currently at effects threshold



Geochemical Model using PHREEQCI

Concentrations expected to increase ~10x



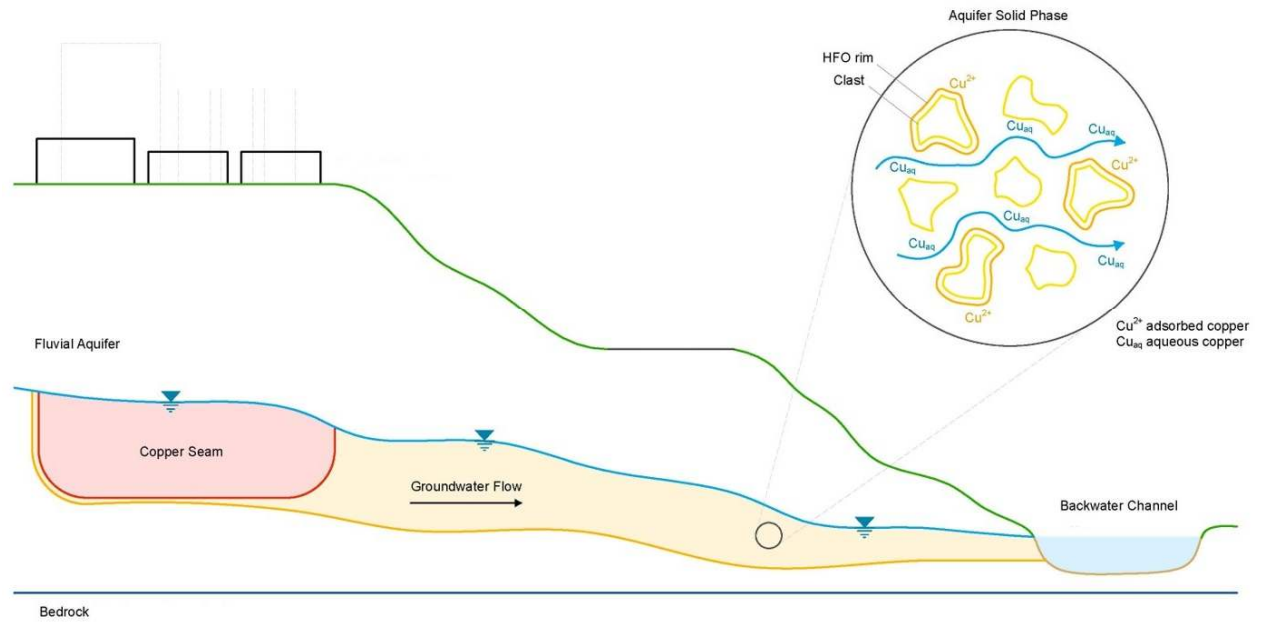
Remediation required



How to remediate dissolved metals?

# 2

## Conceptual Site Model



# Hydrogeological Site Conceptual Model

- Glacial Outwash (Gravel and Cobble)
- High K ( $>10^{-3}$  m/s)
- Underlain by low K bedrock
- Entire thickness impacted
- No impacts in bedrock



# Geochemical Behaviour of Copper

- Dominant species is cupric i.e. Cu(II)
- Adsorbs onto hydrous ferric oxide/iron oxyhydroxides
  - HFO for short
- Competition for adsorption sites

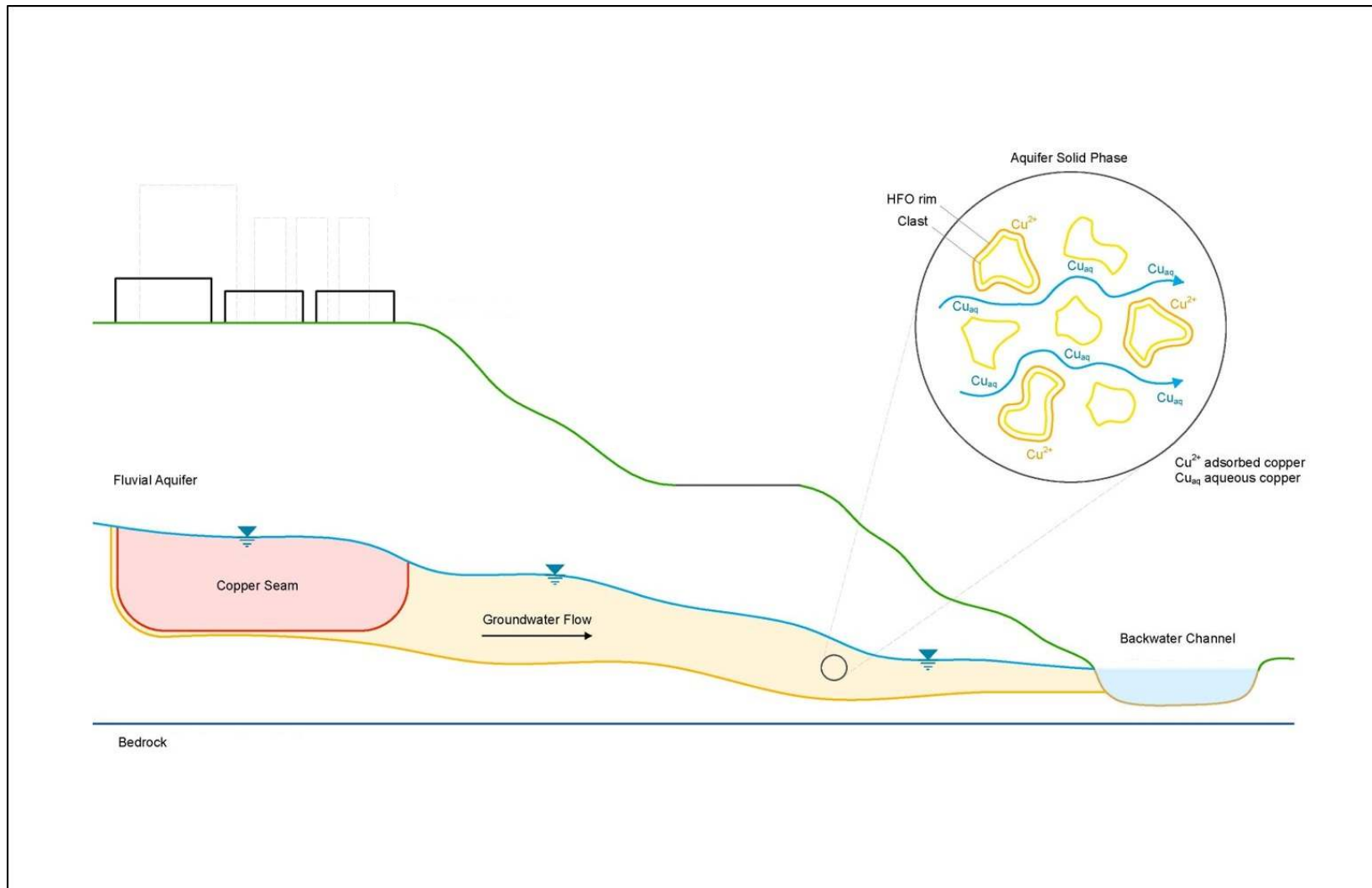
## General Affinity of Dissolved Species for Fe(OH)<sub>3</sub>



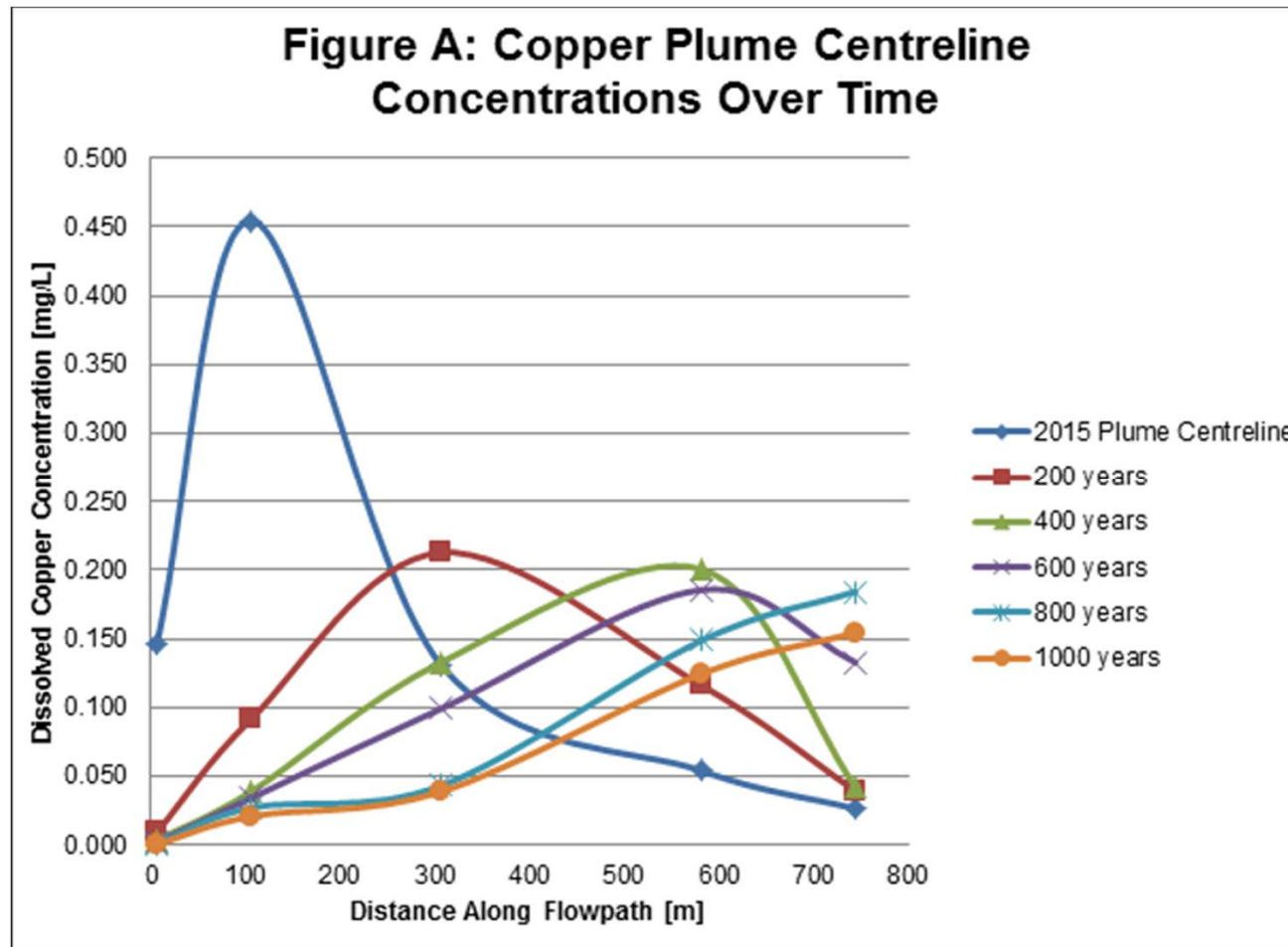
Arsenate (As<sup>5+</sup>) most strongly adsorbed, boron least strongly adsorbed



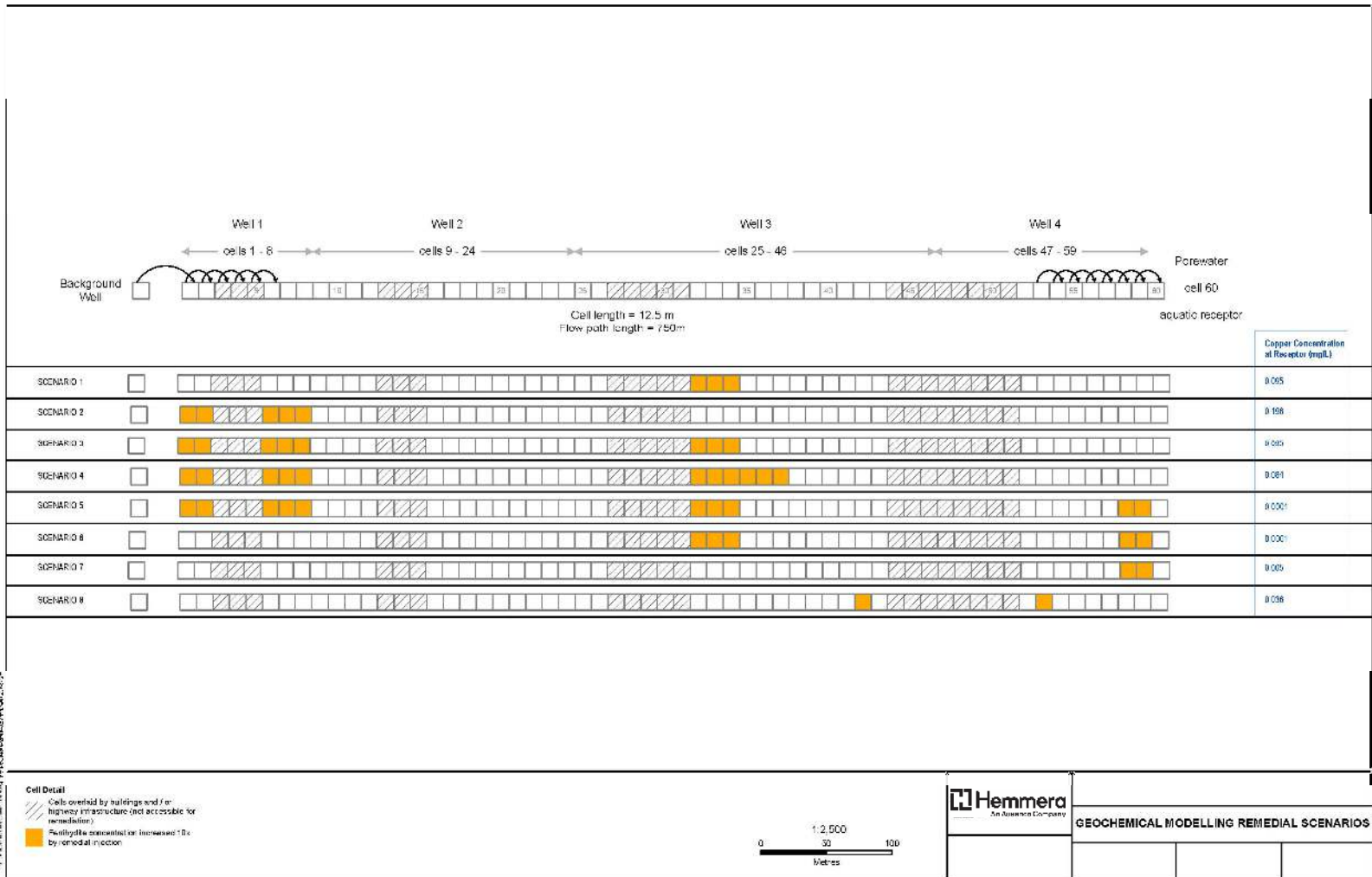
# Conceptual Site Model – Copper Plume



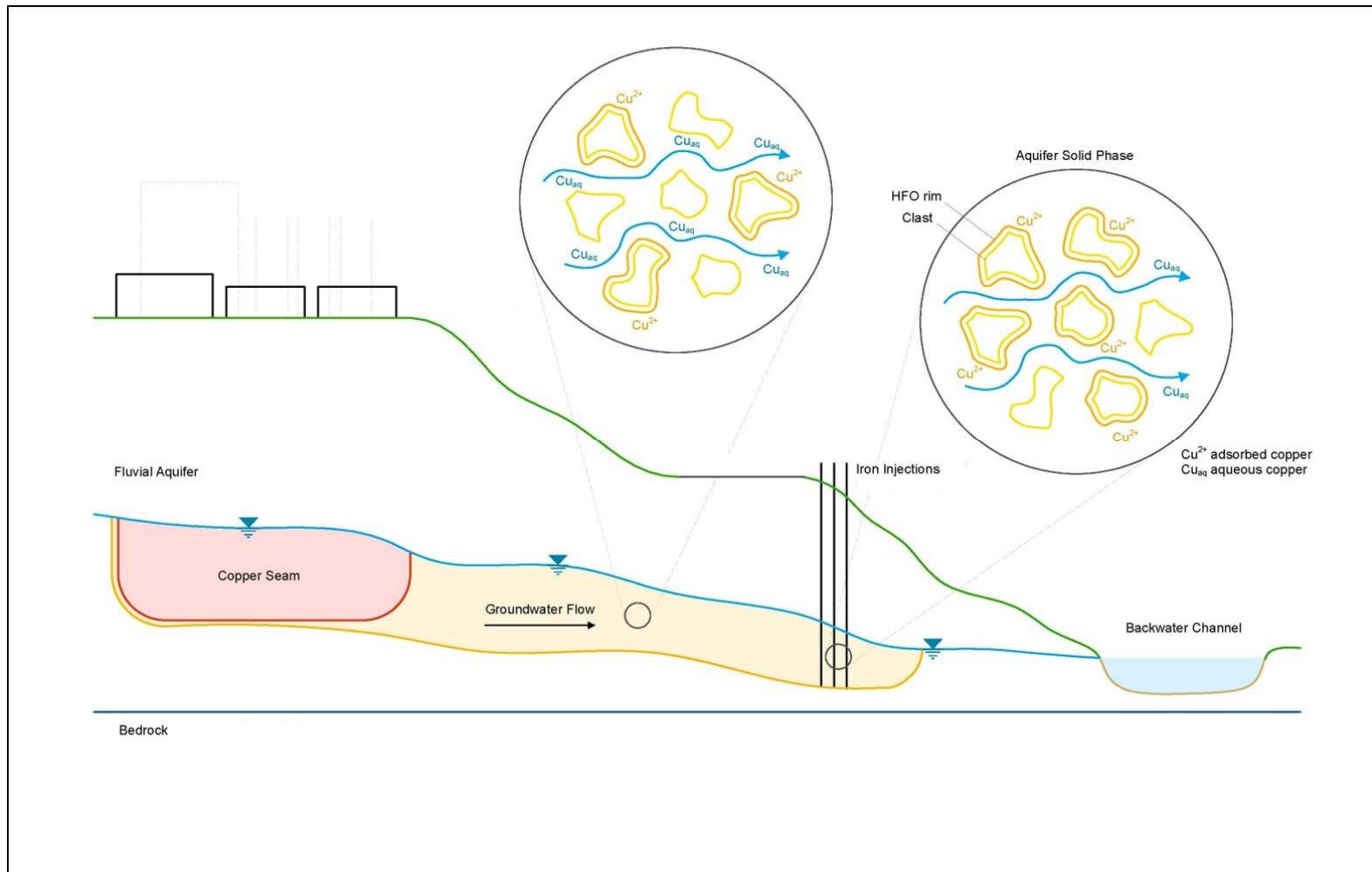
# Conceptual Site Model – Copper Desorption/Adsorption



# Conceptual Site Model – Remedial Simulations



# Conceptual Site Model – Copper Remediation

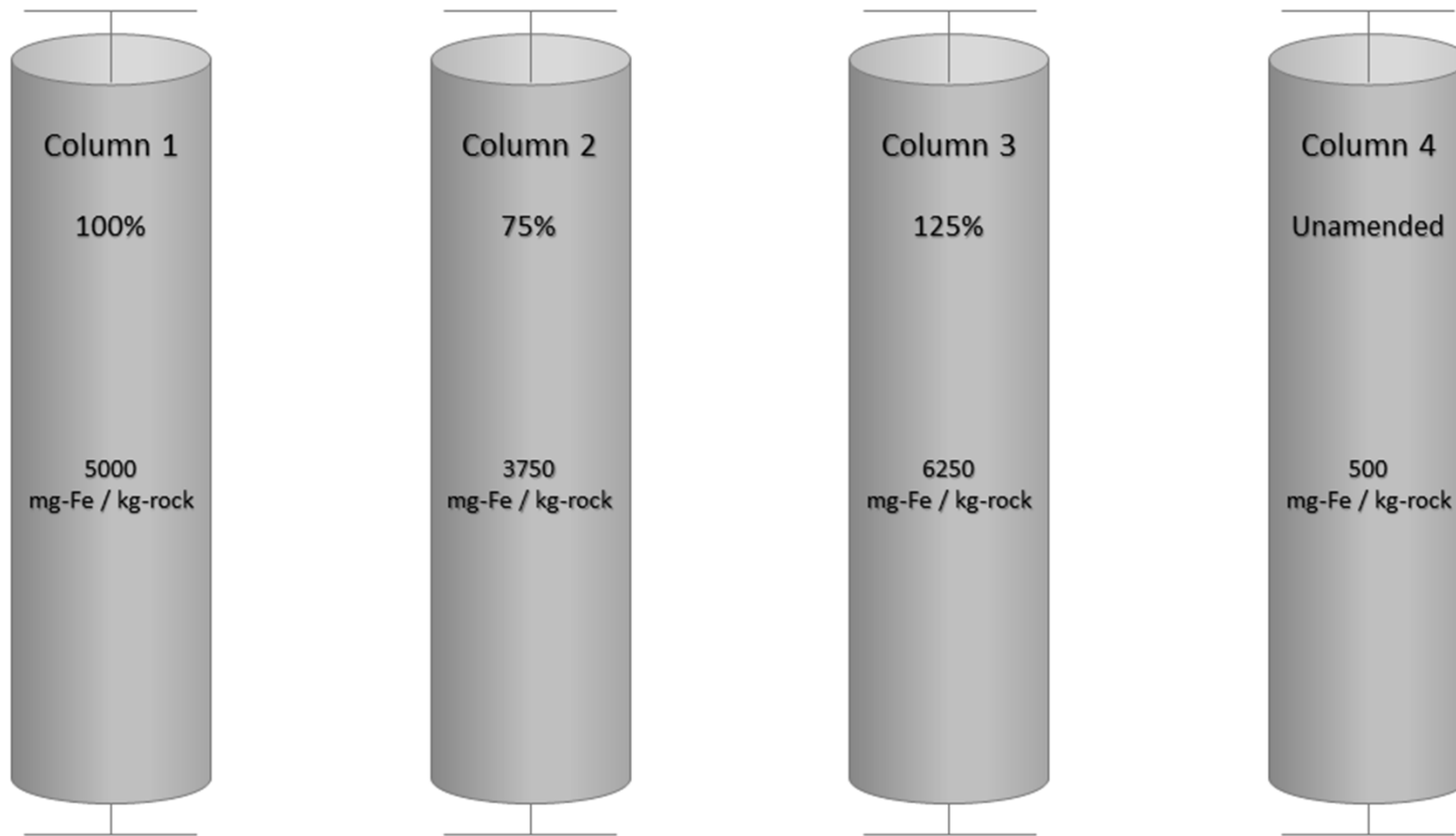


# 3

## Bench Scale Testing



# Bench Scale Testing - Columns

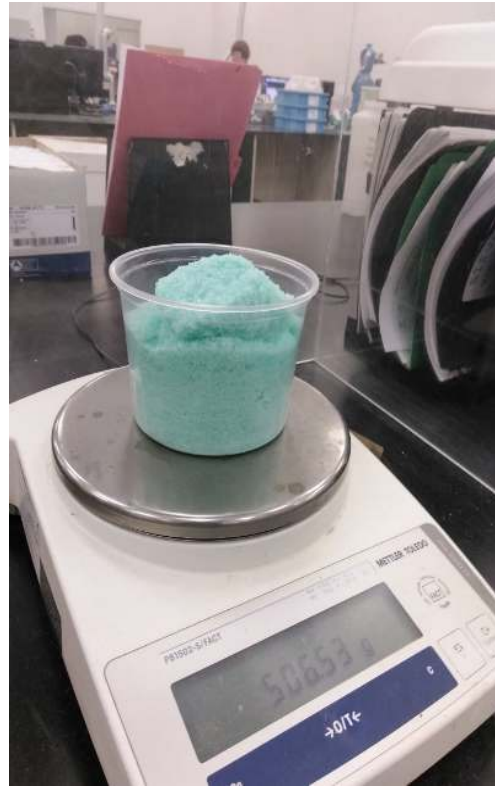


Columns 6.5" x 3'  
16.5 cm x 91.44 cm

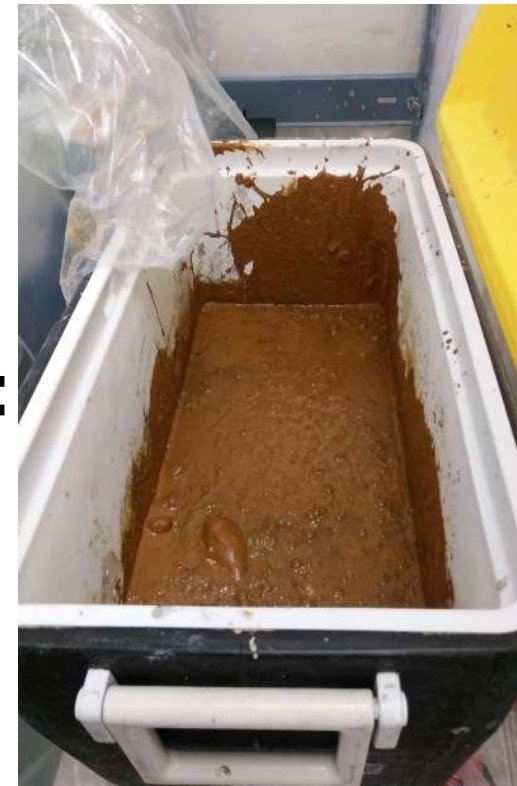
# Bench Scale Testing – Iron Recipe



+



=



# Bench Scale Testing Program Results

Graph C: Column 3 (75%) Results





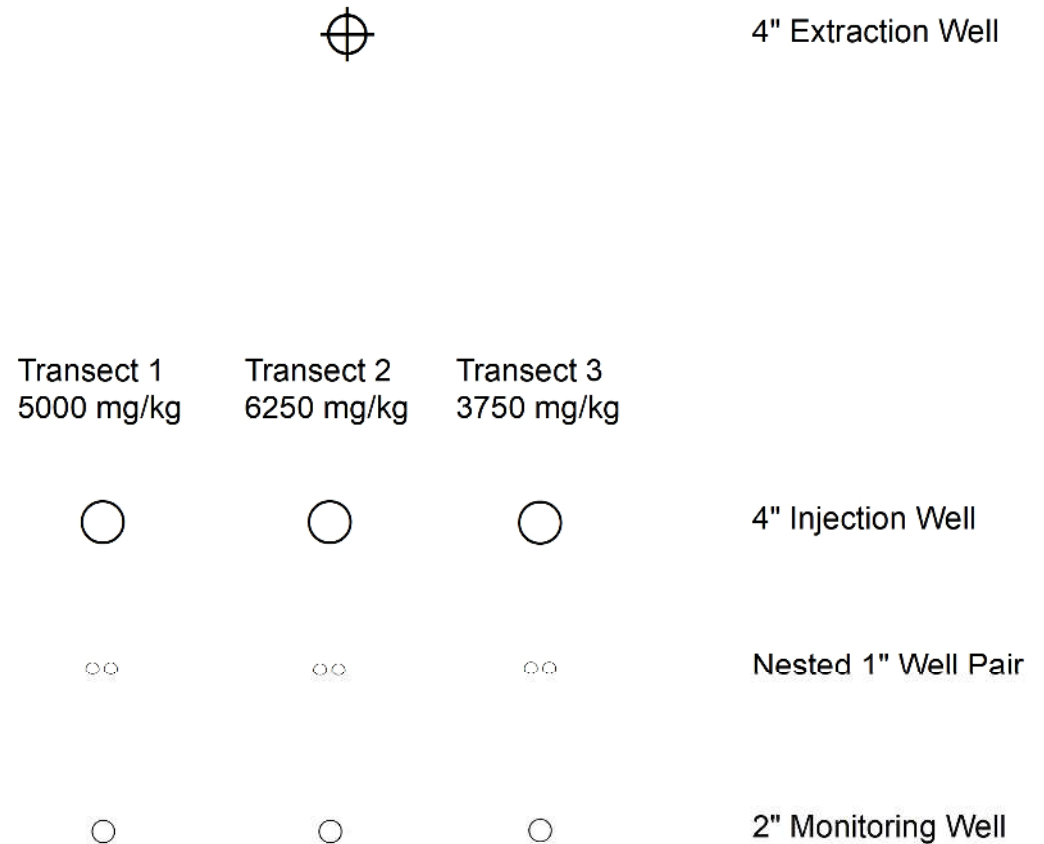
# 4

## Pilot Scale Injections

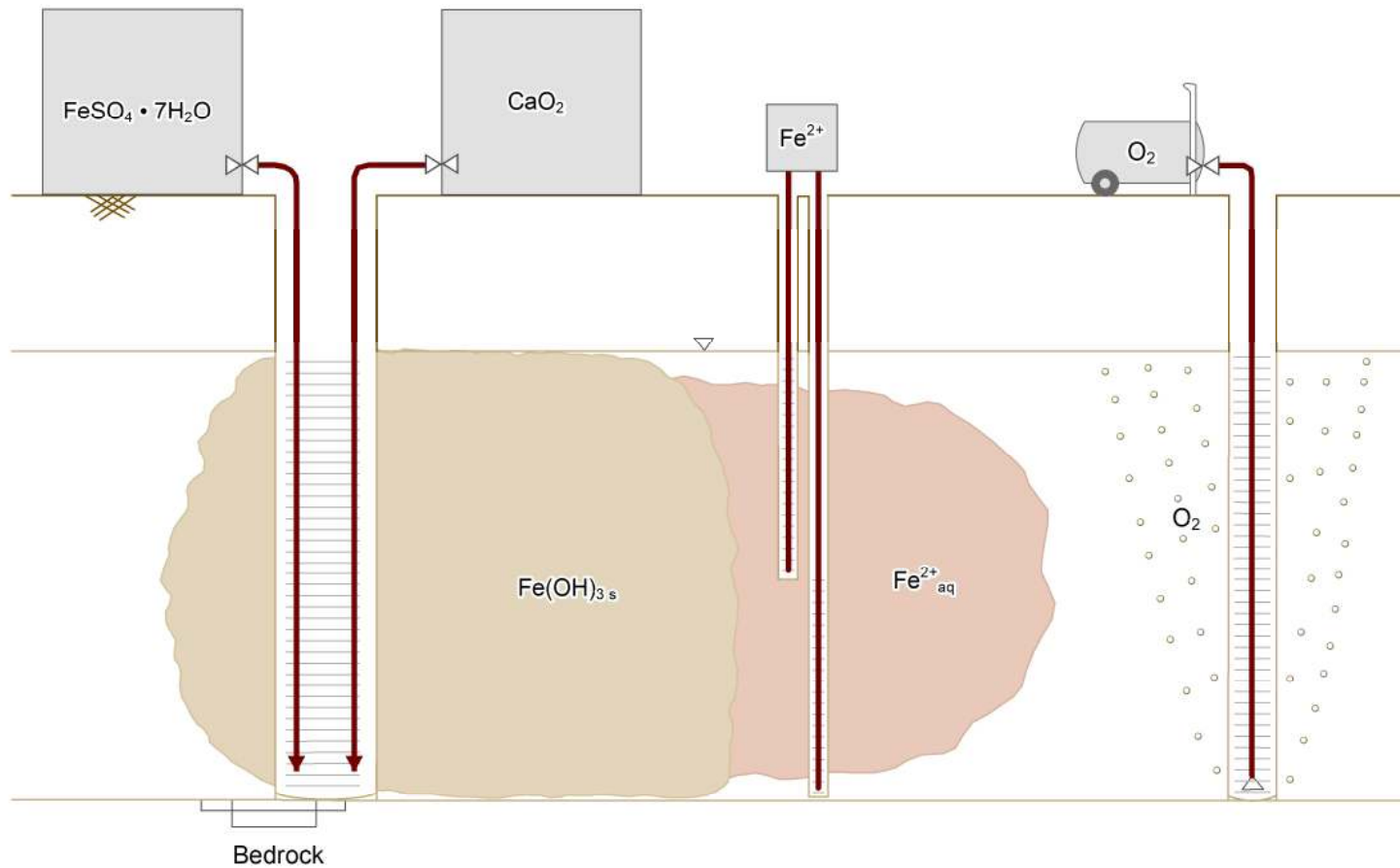


# Pilot Scale Injections

- 1 m3 calcium peroxide
- 0.5 m3 groundwater
- 1 m3 ferrous sulphate
- 0.5 m3 groundwater
- HACH monitoring for ferrous iron



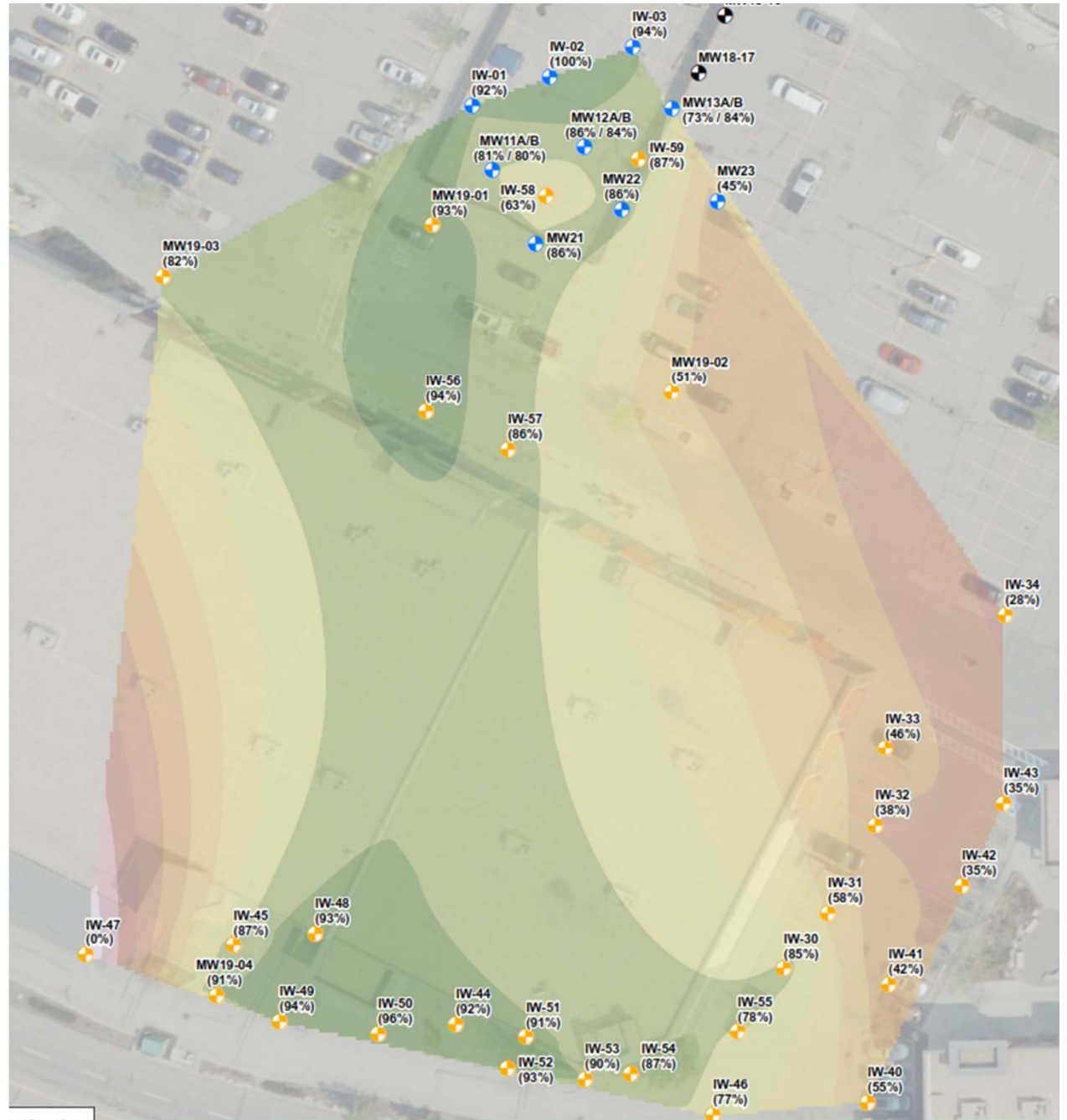
# Pilot Scale Injections



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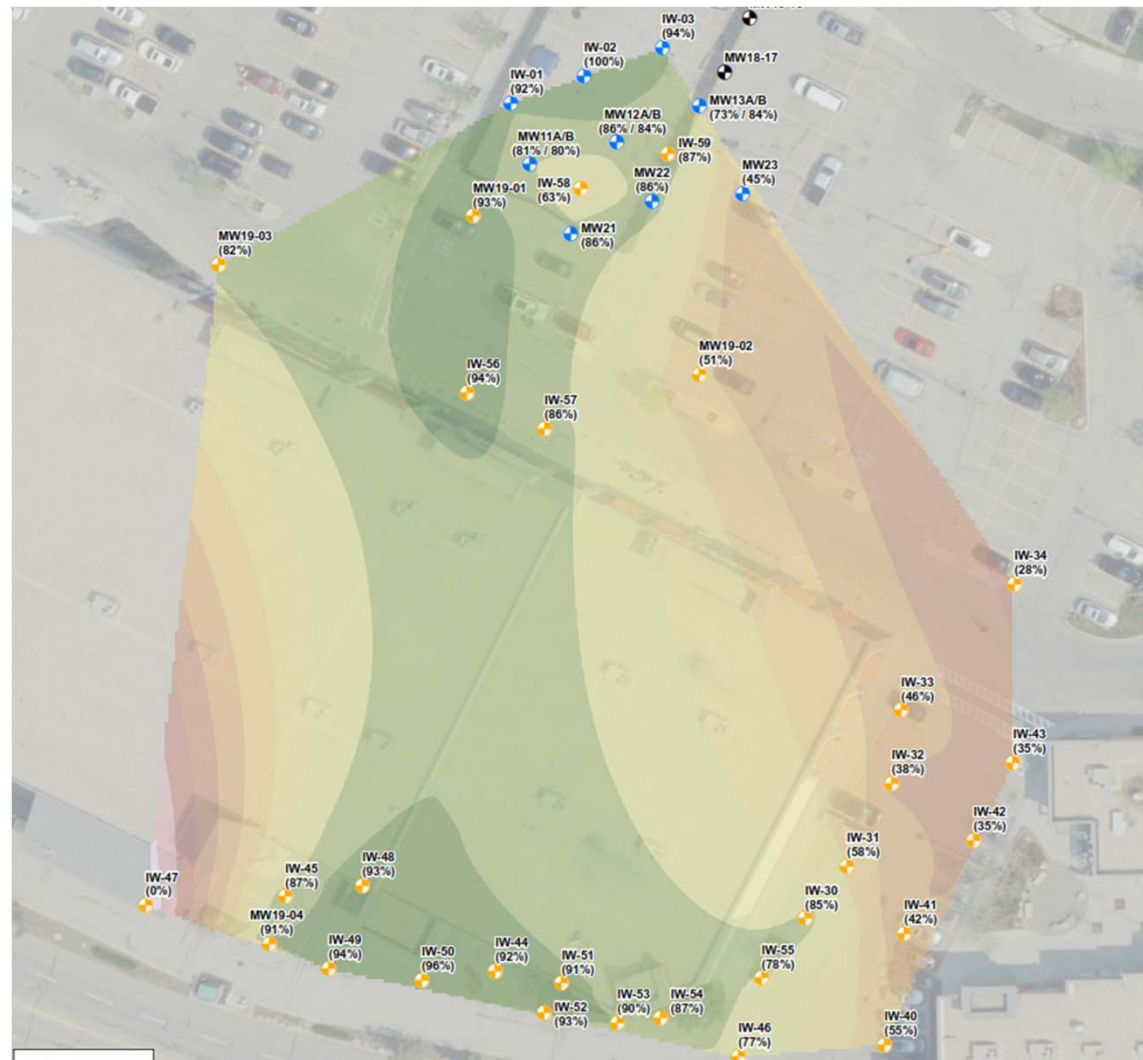
# 5

## Results & Interpretation



# Results and Interpretation

- Digital data collection
- Dashboard
- Percent Removal



# Results and Interpretation

- Confirmatory Tessier analysis
- Target HFO not reached (Fraction 3)
  - Max 3,040 mg-Fe/kg-soil
- Target dissolved Cu reached
  - Min dissolved Cu <0.006 mg/L
- Dissolved Cu did not rebound – stays adsorbed (Fraction 1)
  - Consistent with Tessier results
- Results suggest more stable iron-oxides precipitated (Fraction 4)

**Fraction 1. Exchangeable.** Numerous studies (15–23) performed on sediments or on their major constituents (clays, hydrated oxides of iron and manganese, humic acids) have demonstrated the adsorption of trace metals; changes in water ionic composition (e.g., in estuarine waters) are likely to affect sorption–desorption processes.

**Fraction 2. Bound to Carbonates.** Several workers (9, 11, 24, 25) have shown that significant trace metal concentrations can be associated with sediment carbonates; this fraction would be susceptible to changes of pH.

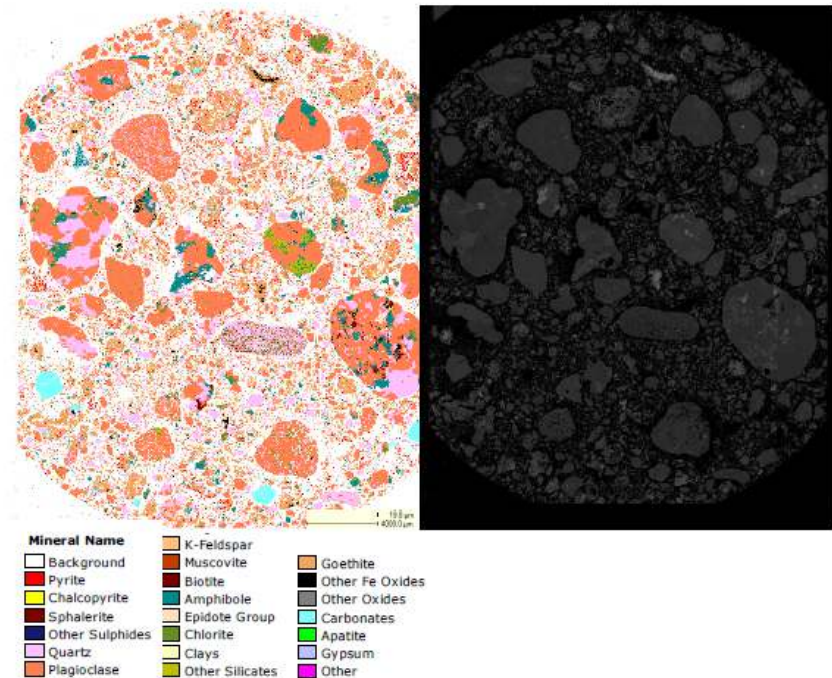
**Fraction 3. Bound to Iron and Manganese Oxides.** It is well established (26) that iron and manganese oxides exist as nodules, concretions, cement between particles, or simply as a coating on particles; these oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions (i.e., low Eh).

**Fraction 4. Bound to Organic Matter.** Trace metals may be bound to various forms of organic matter: living organisms, detritus, coatings on mineral particles, etc. The complexation and peptization properties of natural organic matter (notably humic and fulvic acids) are well recognized, as is the phenomenon of bioaccumulation in certain living organisms. Under oxidizing conditions in natural waters, organic matter can be degraded, leading to a release of soluble trace metals.

Run at pH 2

# Geochemical Conclusions

- Initially colloidal, crystalline overtime
- Coprecipitation
- Copper concentrations stable
- HFO insoluble at prevailing pH/ORP
- No acidic/reducing sources up-gradient
- Sustainable



# Lessons Learned



**MOBILE  
COLLOIDS/SHEAR**



**3750 MG/KG TARGET**



# Lessons Learned



**MORE AGGRESSIVE  
OXIDANT**

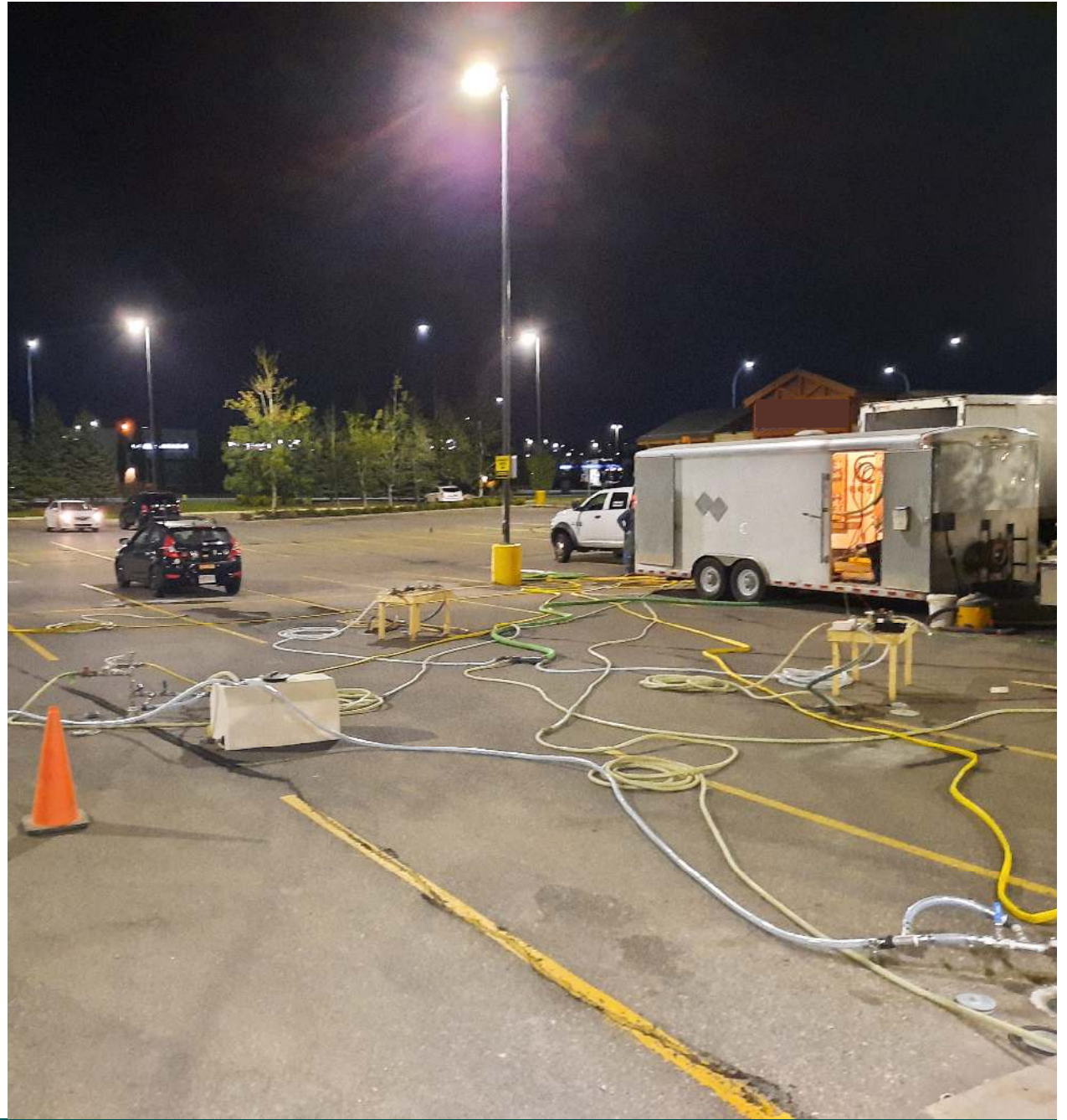


**HIGHER DOSING**

# 6

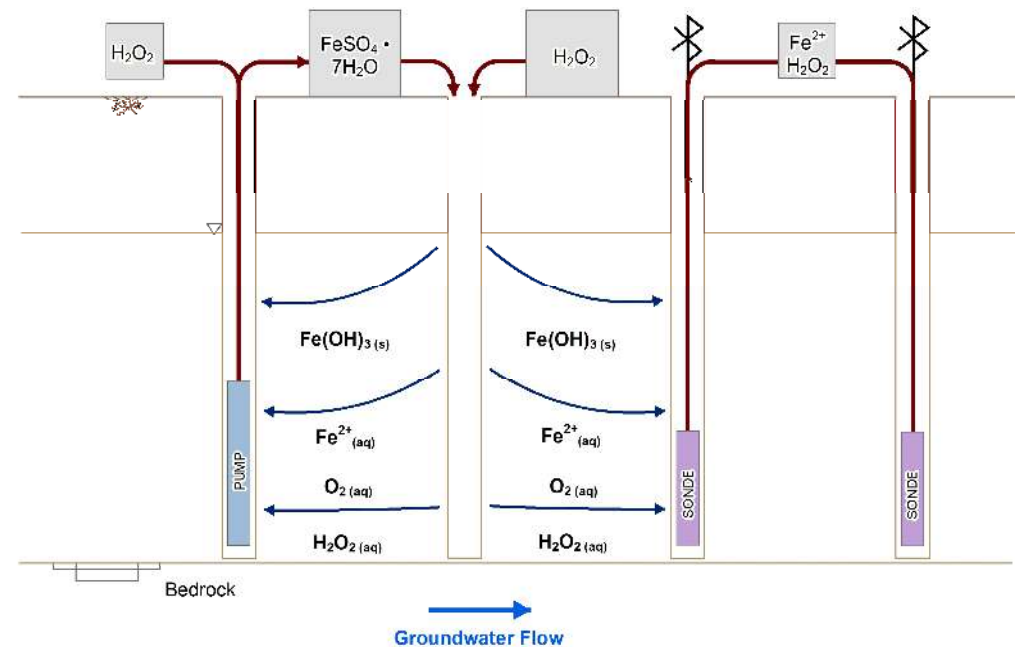
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## Next Steps



# Next Steps

- Full scale injections ongoing
- Performance verification to follow
  - HFO concentration
  - Percent Cu removal
  - Porewater sampling
- RemTech 2021?



*Questions?*

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