Optimizing remediation approaches at mine sites: how understanding biogeochemical processes and modeling can guide mine treatment

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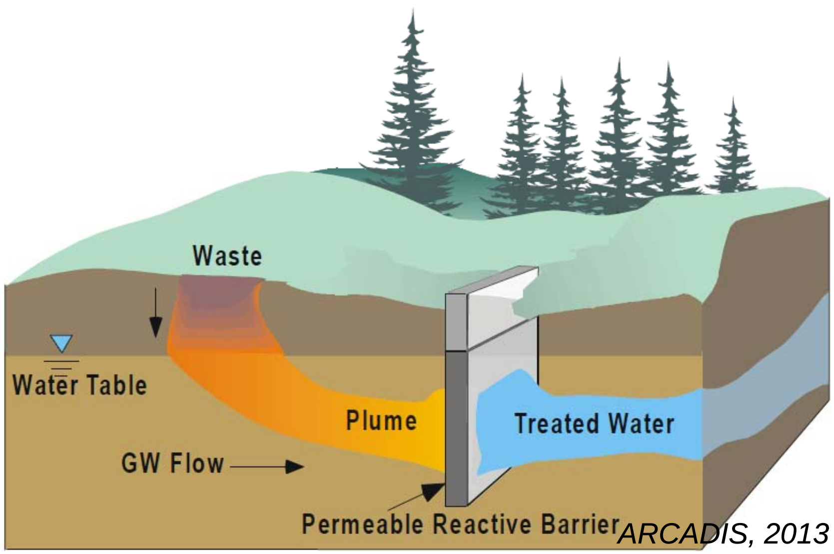
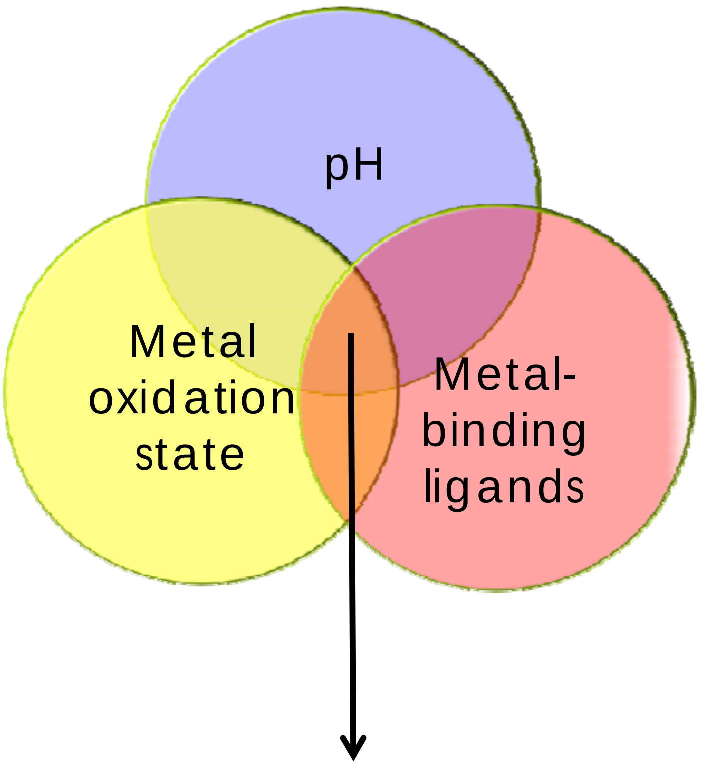
Metal treatment strategies



- Pump and Treat/ Conventional water treatment facilities
  - Groundwater and/or surface water treatment
  - Ion exchange, reverse osmosis, lime addition, etc.
- Constructed wetlands, covers
  - Surface water
  - Mine wastes
- *In Situ* approaches - groundwater
  - Reduction [U(VI) → U(IV)]
    - ✓ Biological: Organic carbon injection
    - ✓ Chemical: Sulfide injection
  - Mineral Precipitation
    - ✓ Soluble phosphate injection
- *In Situ*: Reactive Barriers

Metal mobility: importance of redox



Mineral precipitation/dissolution and adsorption

Mining and remediation often perturbs redox state of system

Effect of pH – redox– ligands on metal mobility

1. Equilibrium

2. Disequilibrium
   Opportunity for biotic processes
   Kinetics of reactions important

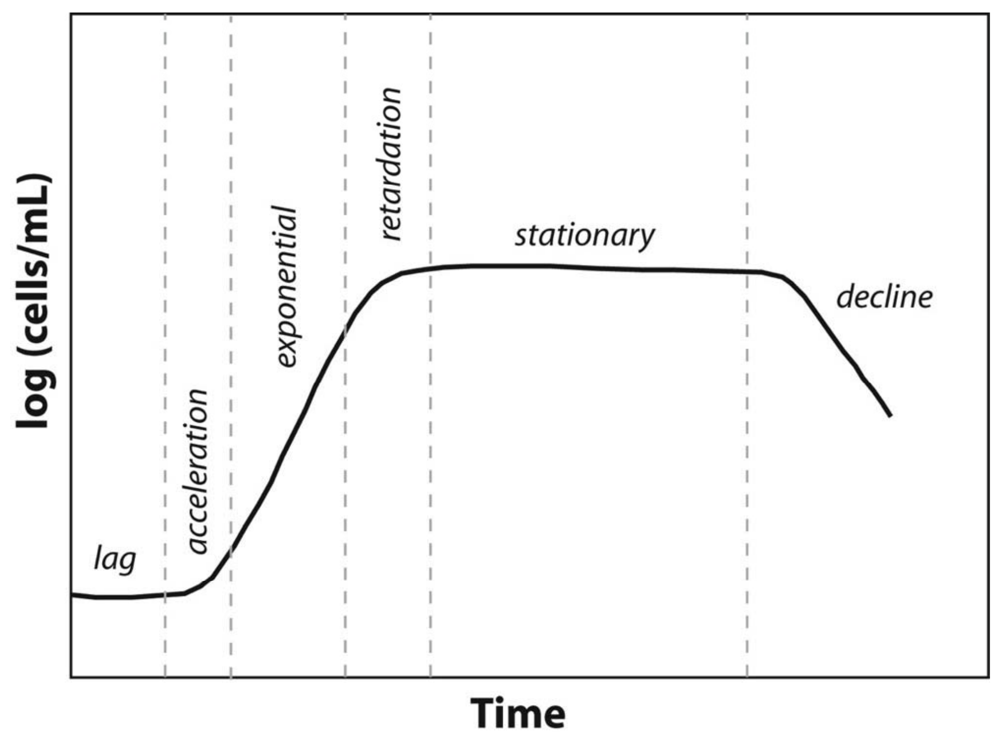
$$4Fe^{2+} + O_2 + 4H^+ \longrightarrow 4Fe^{3+} + 2H_2O$$

$$3Fe^{3+} + 6H_2O + K^+ + 2SO_4^{-2} \longrightarrow K(Fe)_3(SO_4)_2(OH)_6 + 6H^+$$

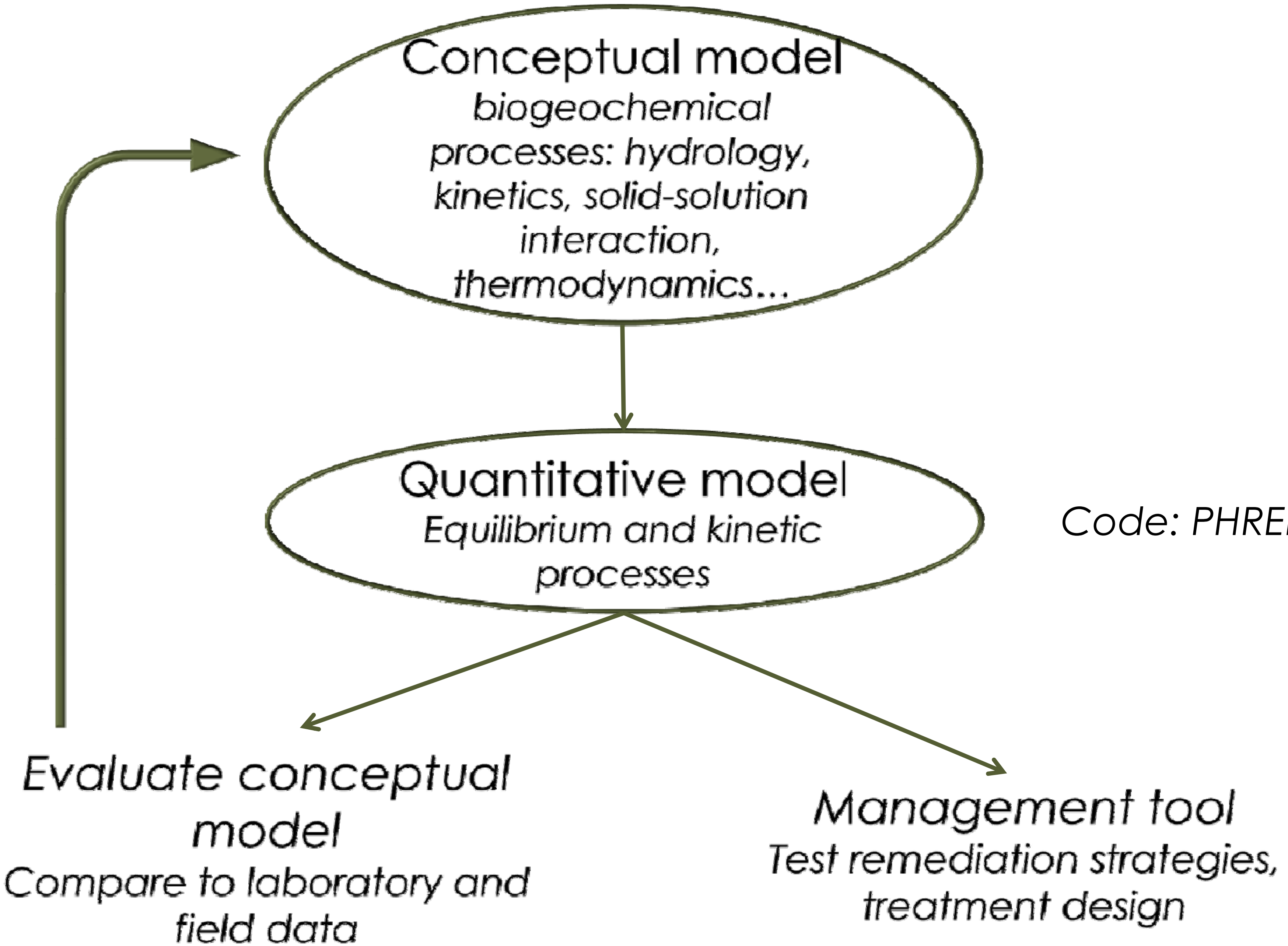
$$8Fe^{3+} + 14H_2O + SO_4^{-2} \longrightarrow Fe_8O_8(OH)_6(SO_4) + 22H^+$$

Fundamental processes and modeling

- Improve modeling by increasing fundamental biogeochemical processes
- Identify key reactions
- Reaction Kinetics vs. equilibrium
  - Microbial processes
  - Precipitation



Biogeochemical modeling



Code: PHREEQC

Complexity: laboratory → field

Laboratory

Field

Batch reactors
Pure cultures (bacteria)
Synthetic water
Pure mineral phases

Column experiments
Microbial community
Site-specific solids

In situ experiments

Pilot and full-scale treatment/remediation

Key processes

Rates

Heterogeneity and complexity

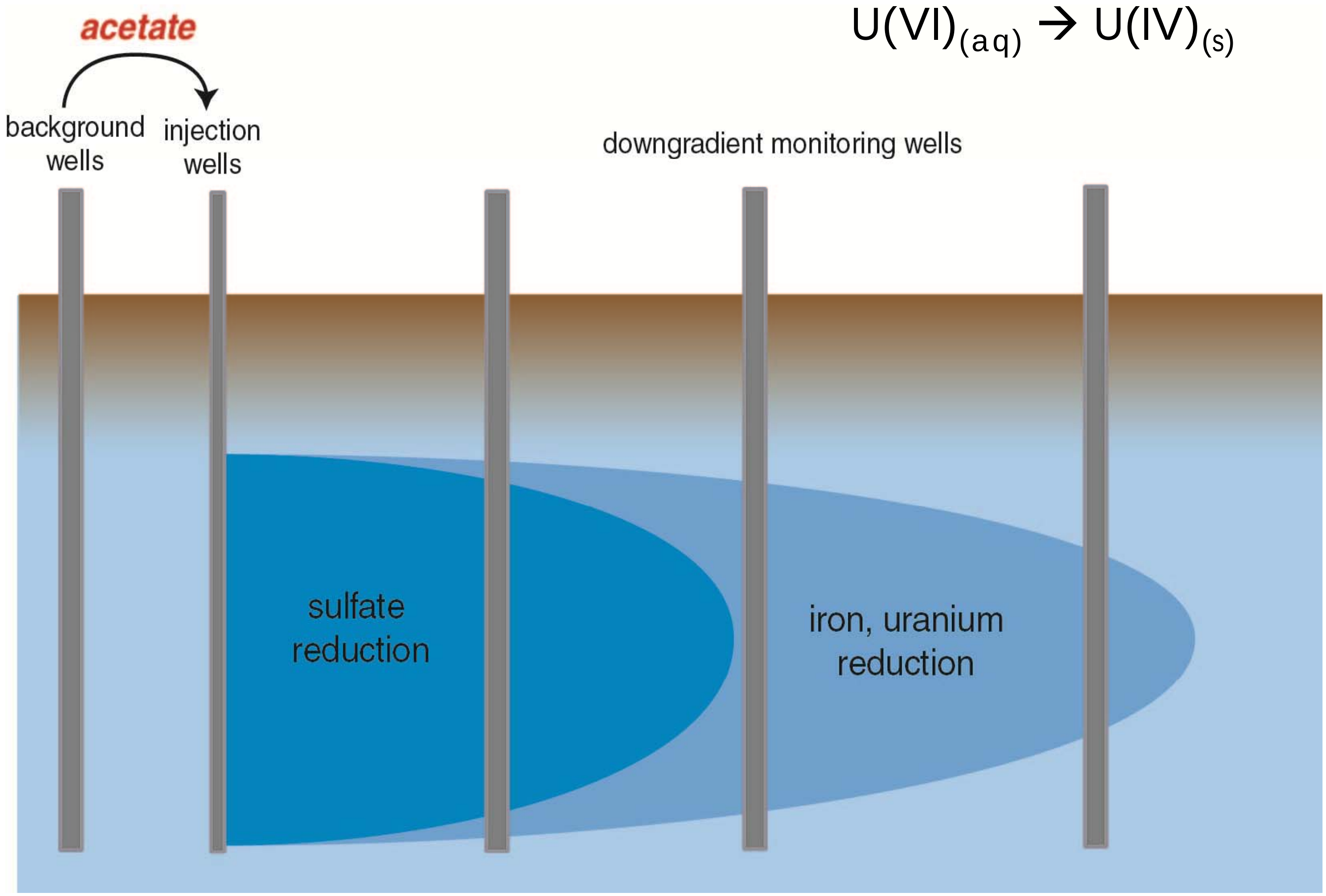
Case studies

- Case study 1: Bioremediation of a uranium-contaminated aquifer
- Case study 2: Removal of dissolved uranium and surface passivation of ore by phosphate amendment
- Case study 3: Acid mine drainage (AMD) pipeline scaling

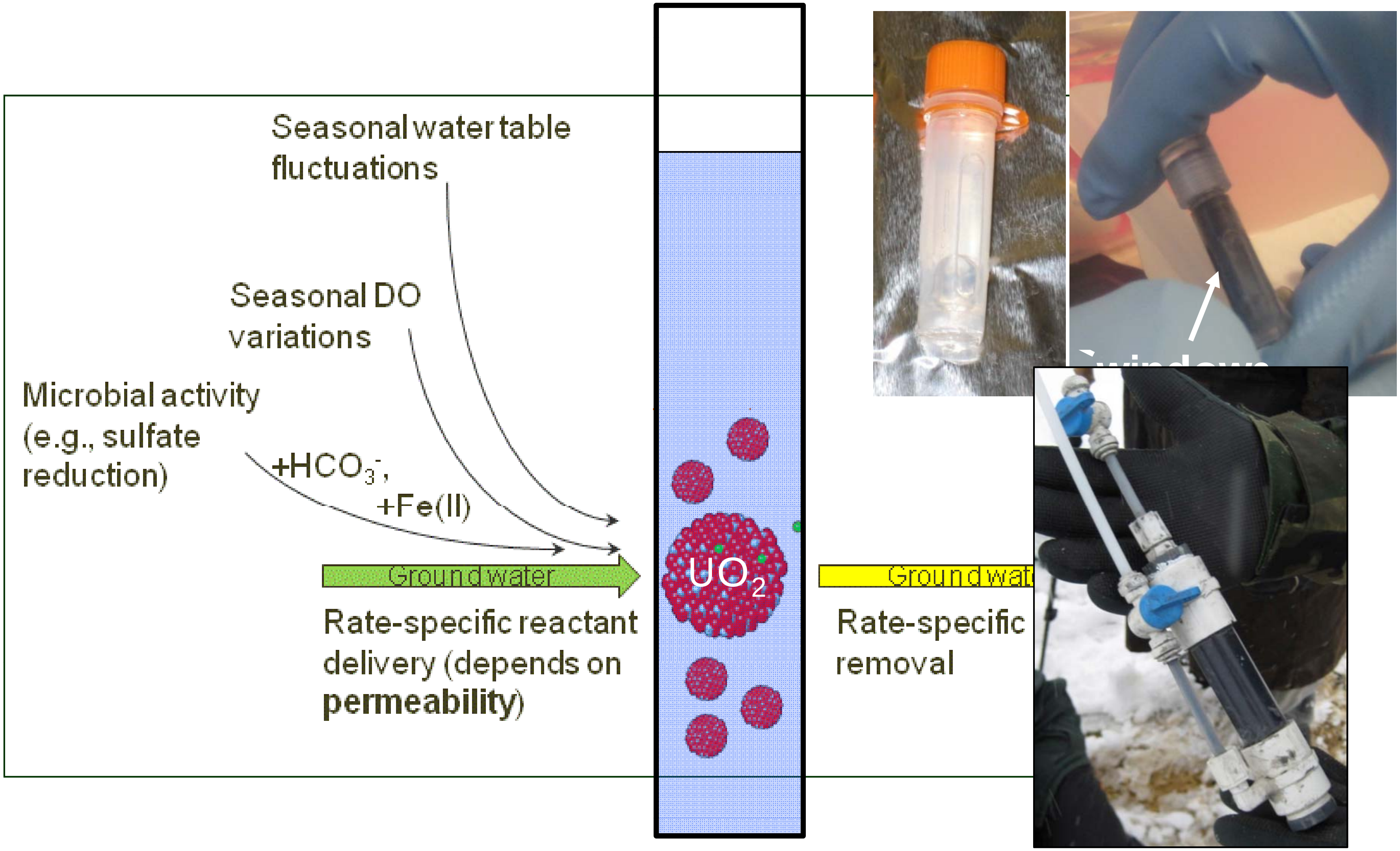
Case study 1: Bioremediation at Rifle, CO

Fe(III) + sulfate → Fe(II)-sulfides

$U(VI)_{(aq)} \rightarrow U(IV)_{(s)}$



In situ experiment: U(IV) re-oxidation rates

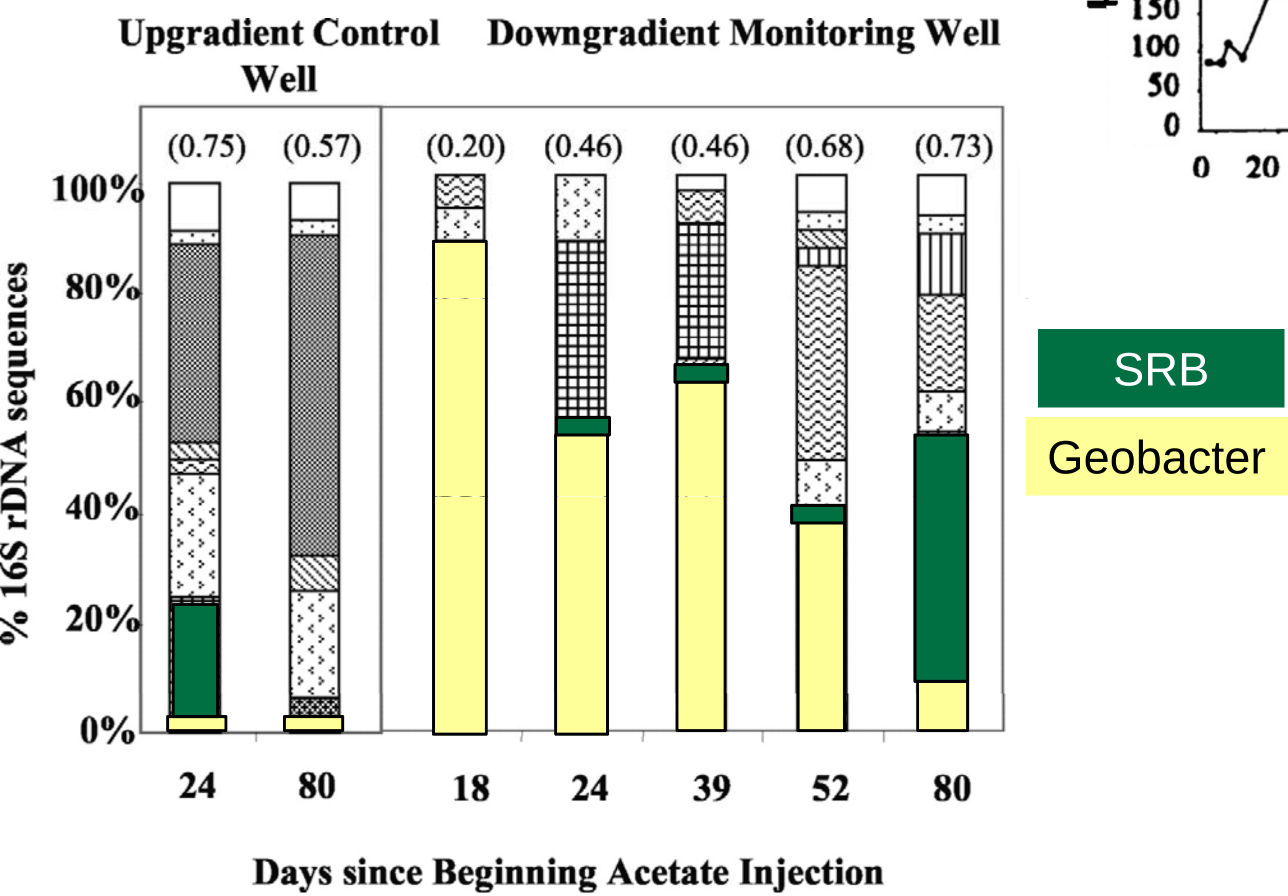


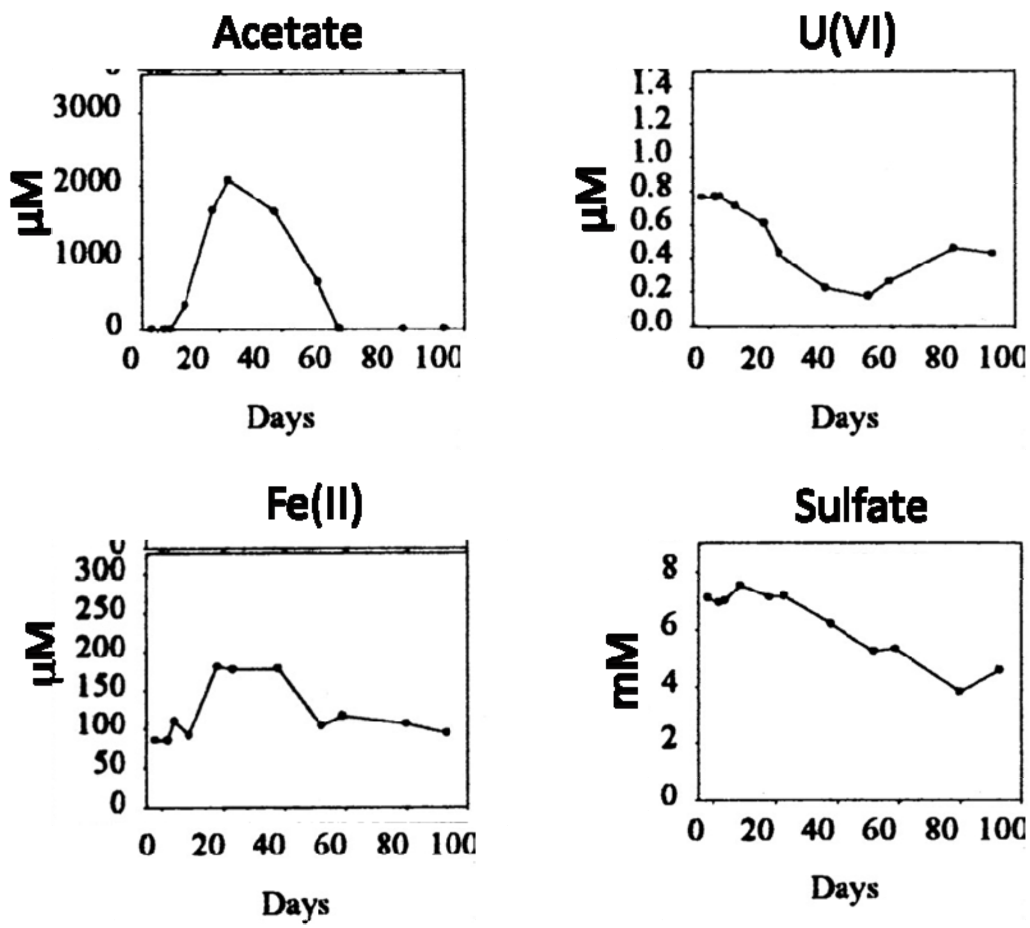
Biomass, other surface reactions retard oxidative dissolution

Campbell, KM, et al., ES&T 2011, Bargar et al., PNAS 2013

Field-scale Bioremediation

Microbial U(VI), Fe(III), sulfate reduction
Removal: U, V, Se
Increase: As





Geobacter species were dominant during Fe(III) and U(VI) reduction

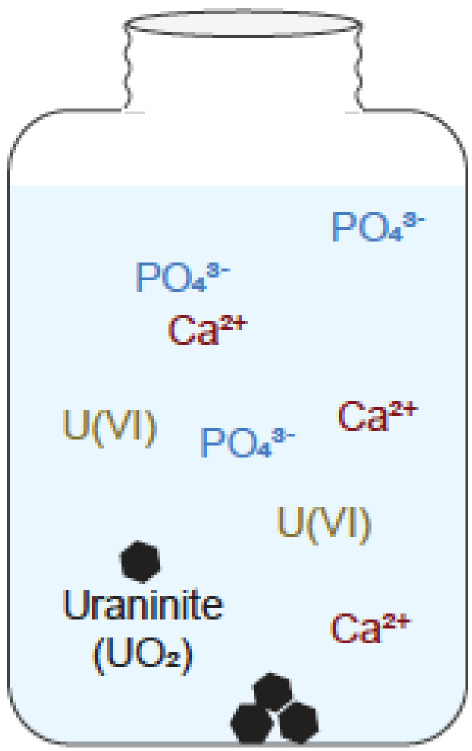
Population shifted to sulfate reducers

Anderson et al., AEM 2003

Case study 2: Phosphate amendment

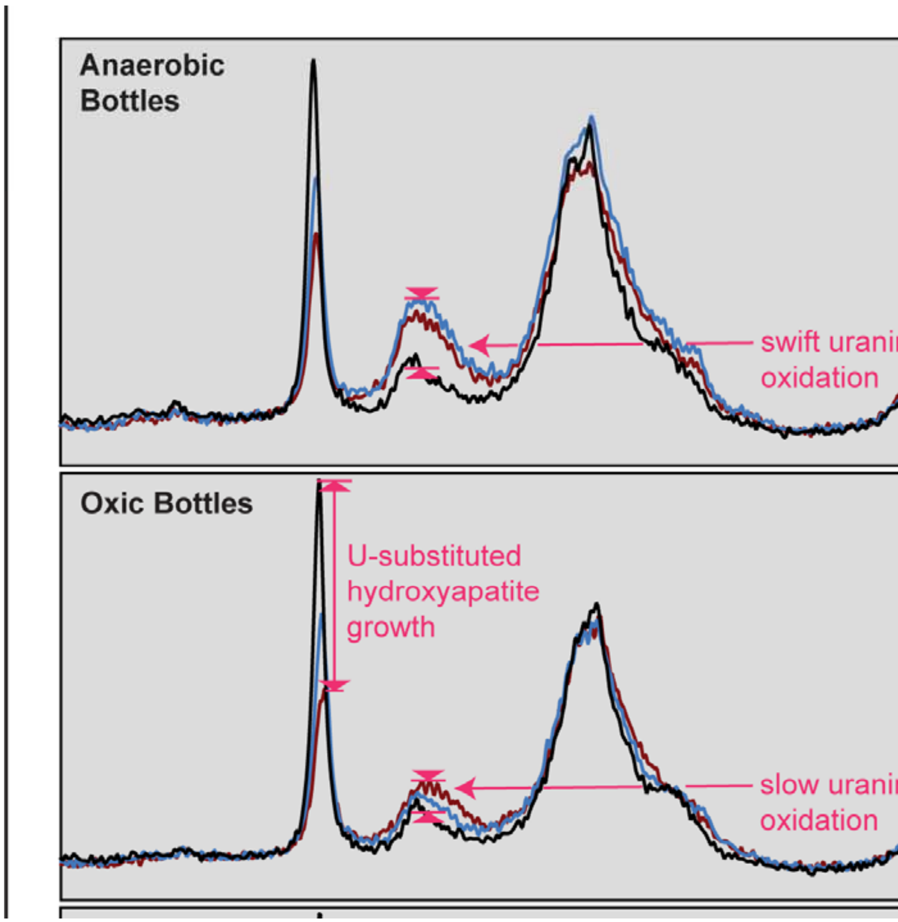
$5Ca^{+2} + 3HPO_4^{-2} + H_2O \rightarrow Ca_5(PO_4)_3OH + 4H^+$ ***Hydroxylapatite***

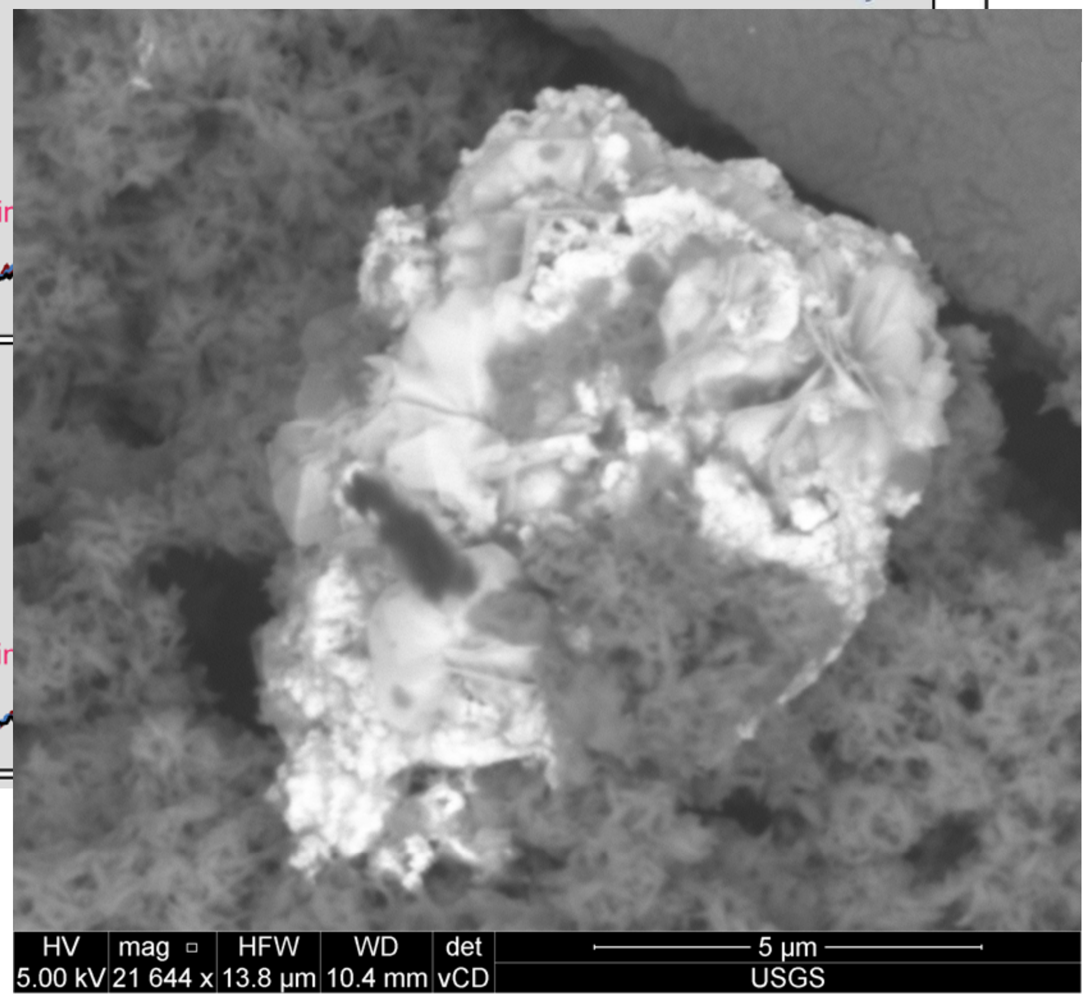
$2H^+ + 2UO_2^{+2} + 2PO_4^{-3} \rightarrow H_2(UO_2)_2(PO_4)_2$ ***Autinite***



- Phosphate amendment effective as U(VI) treatment
- Can Ca-PO4 precipitation passivate surface of U(IV) ores?

Rates of precipitation and oxidation





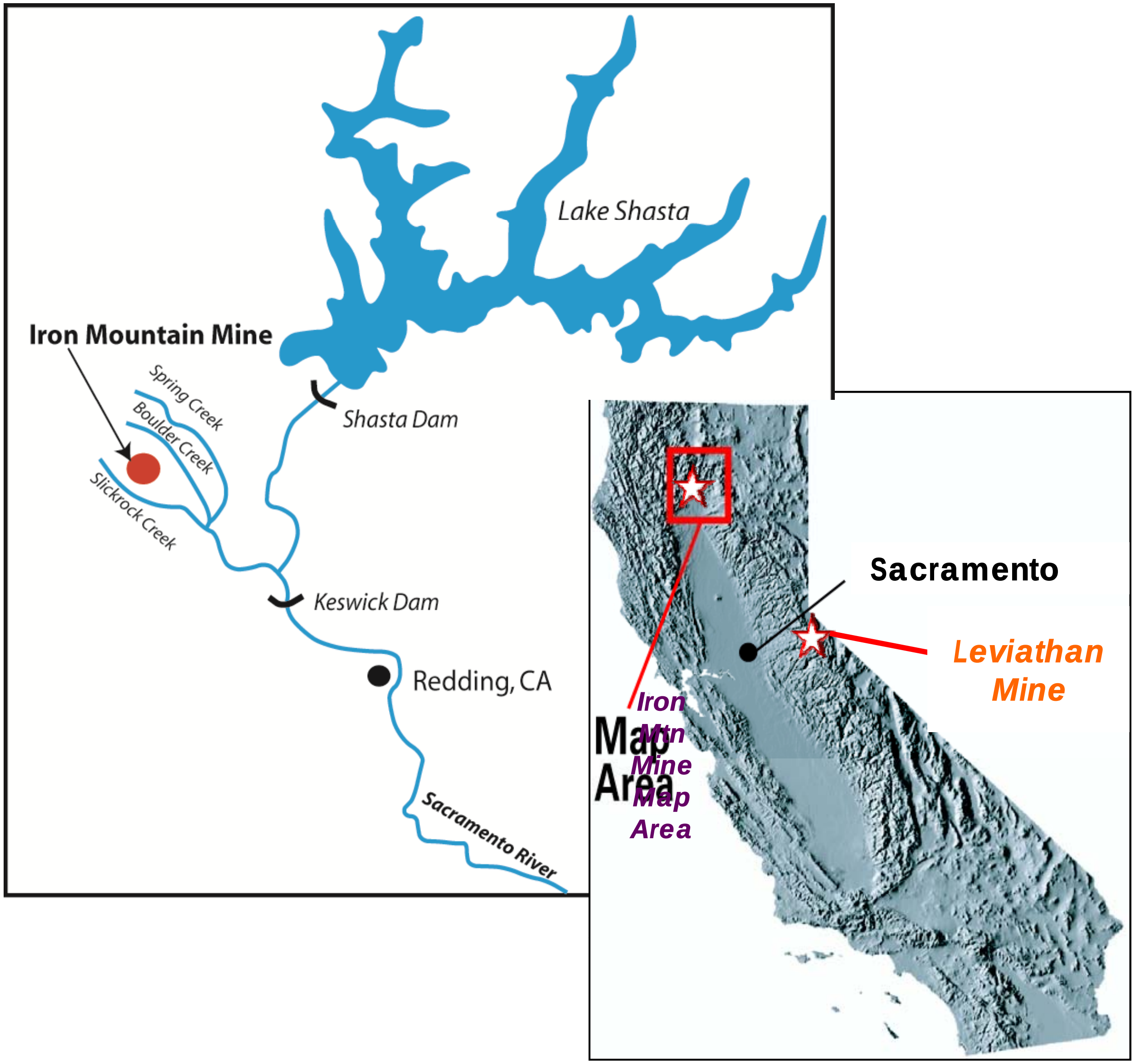
Next step: U ore column studies

Uranium remediation: case study 1&2

- Bioremediation – reducing conditions
  - Challenging to control microbial community
- Phosphate amendment – oxidizing or reducing conditions
  - Passivation of U(IV) surfaces may prevent continued oxidation
- Combined bioremediation/phosphate amendment

- Application:
  - In situ recovery (ISR mines)
  - Conventional mining
  - Legacy sites

Case study 3: acid mine drainage



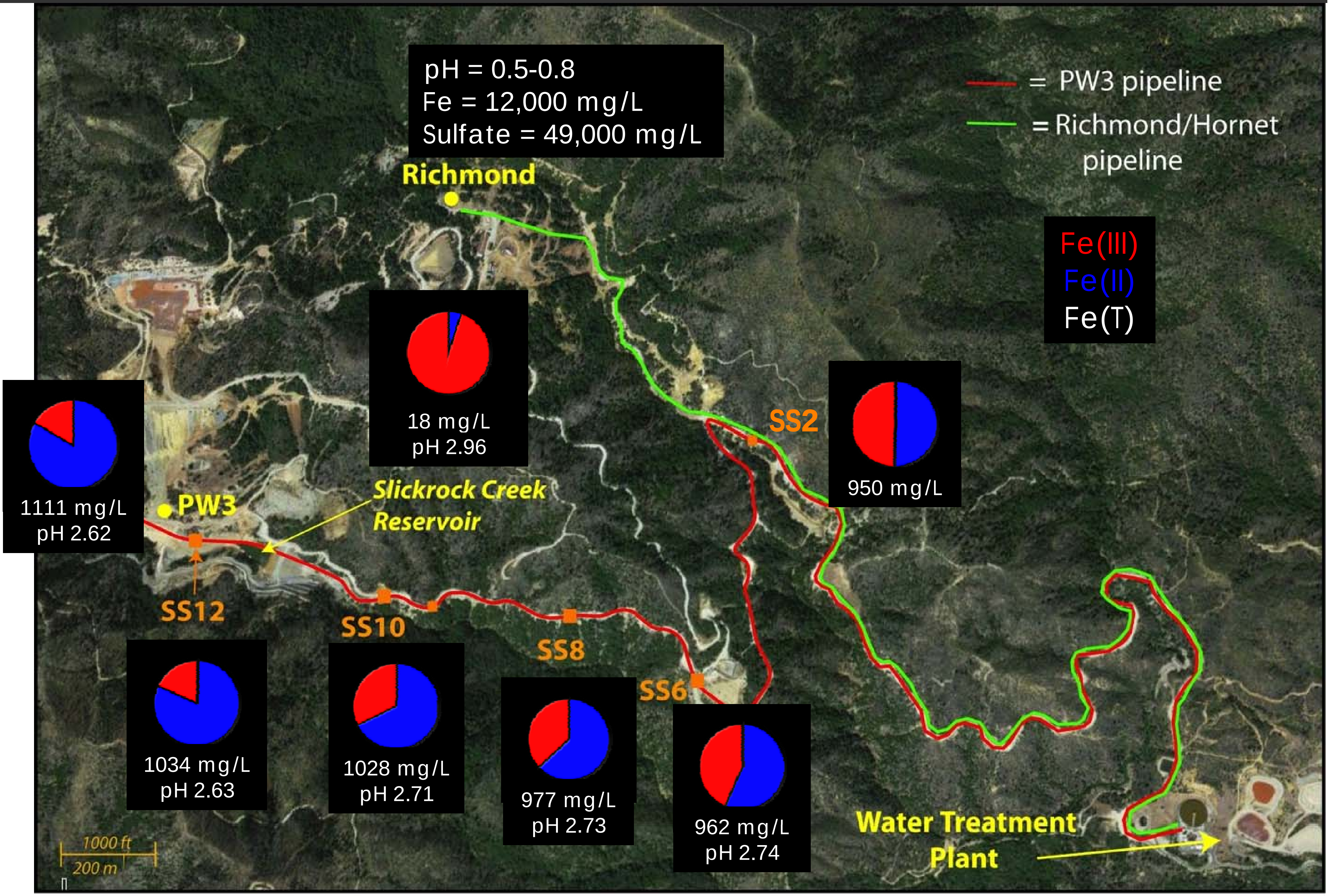
Precipitation in AMD pipelines – “scale”

Iron Mountain Mine

Leviathan Mine

Pipe scale requires costly clean-out at IMM every 2-4 years, and complete replacement of pipes at LM every year – ***common problem in AMD pipelines***

Water chemistry at Iron Mountain Mine



Mechanism of scale formation

Unfiltered water

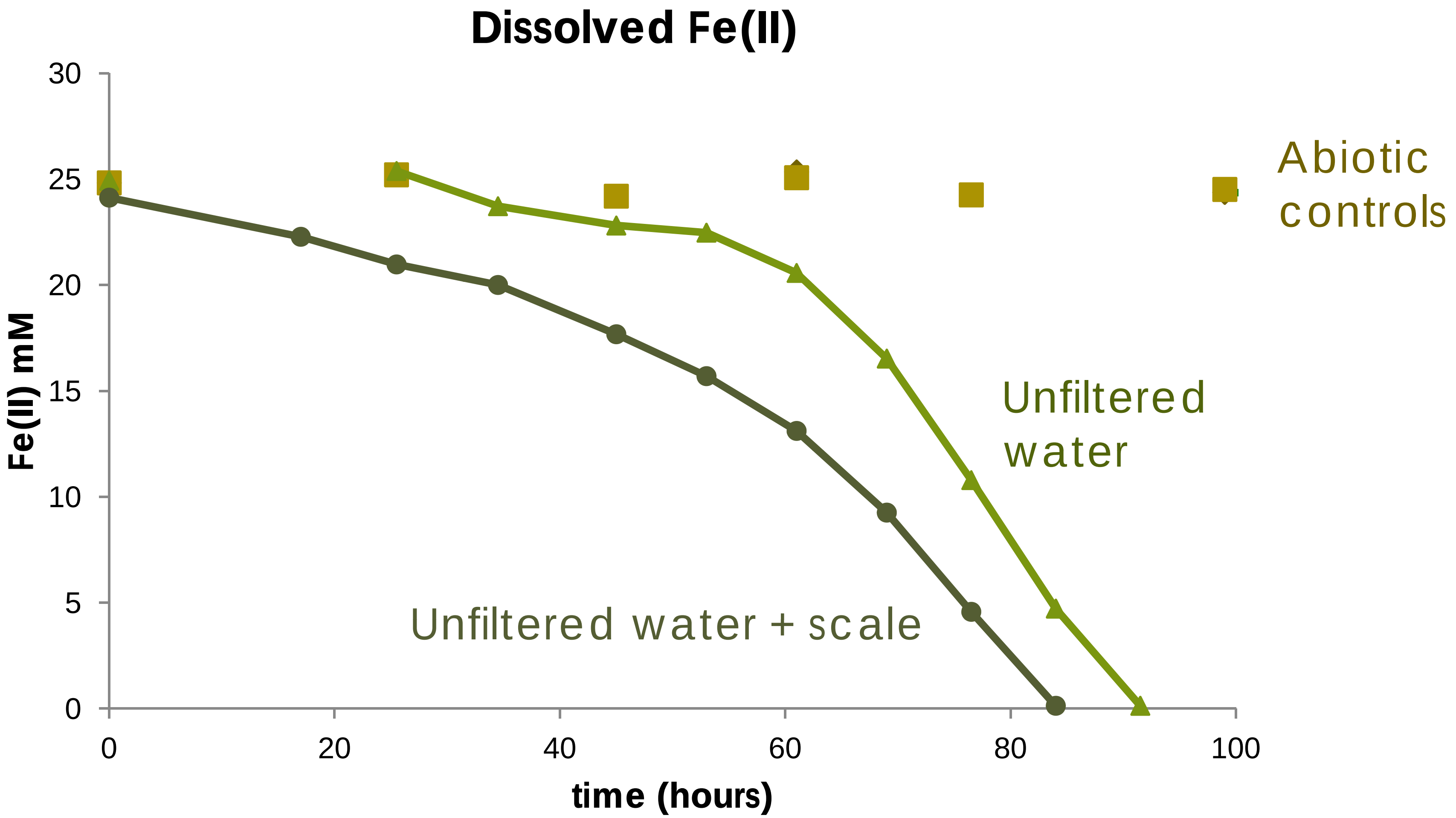
→ **Water only** = Biotic Fe(II) oxidation

→ **Water + scale** = Biotic Fe(II) oxidation, effect of scale

→ *0.1µm filtration* → **Control** = Abiotic Fe(II) oxidation

Iron Mountain Mine and Leviathan Mine samples

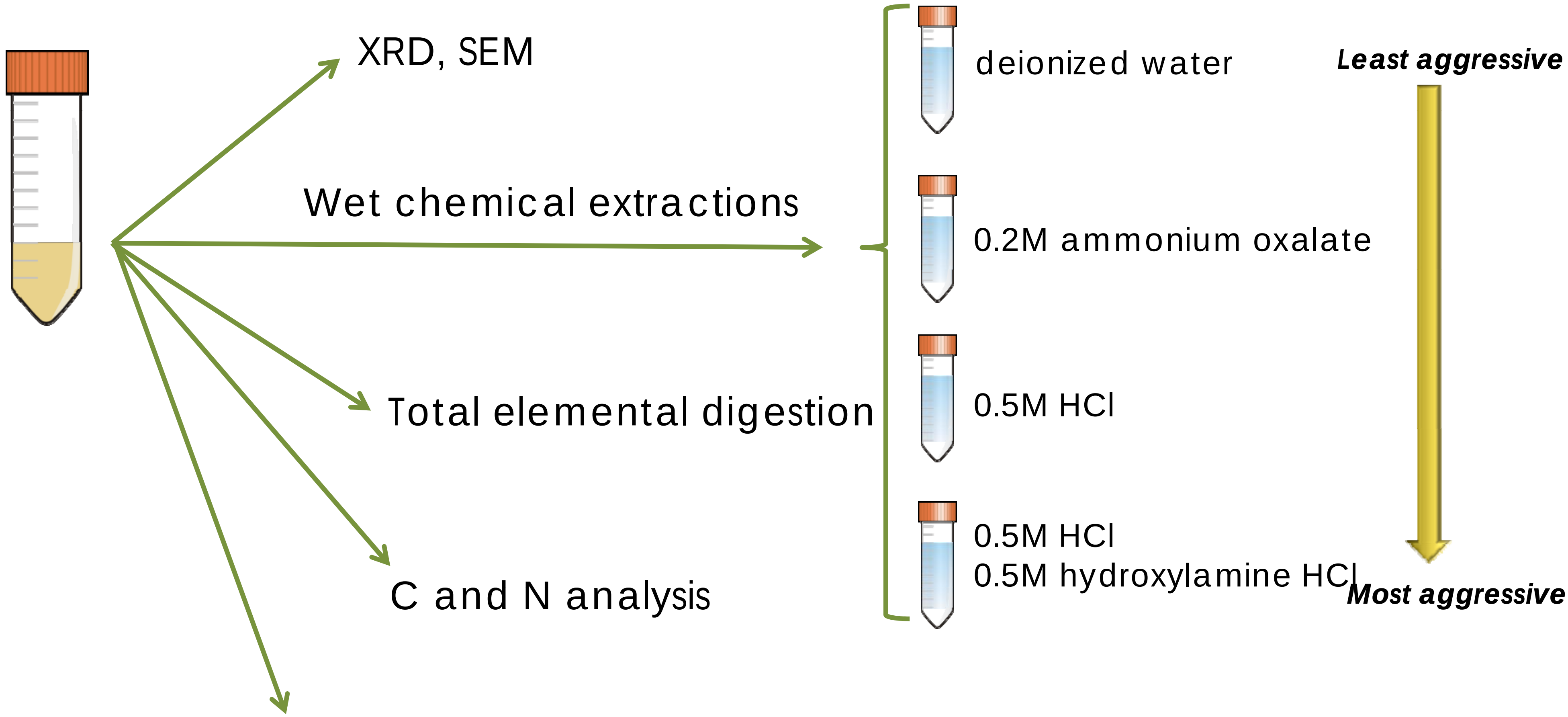
Mechanism of scale formation



Fe(II) oxidation pH< 5 is a biotic process

$$4Fe^{2+} + O_2 + 4H^+ \longrightarrow 4Fe^{3+} + 2H_2O$$

Scale characterization

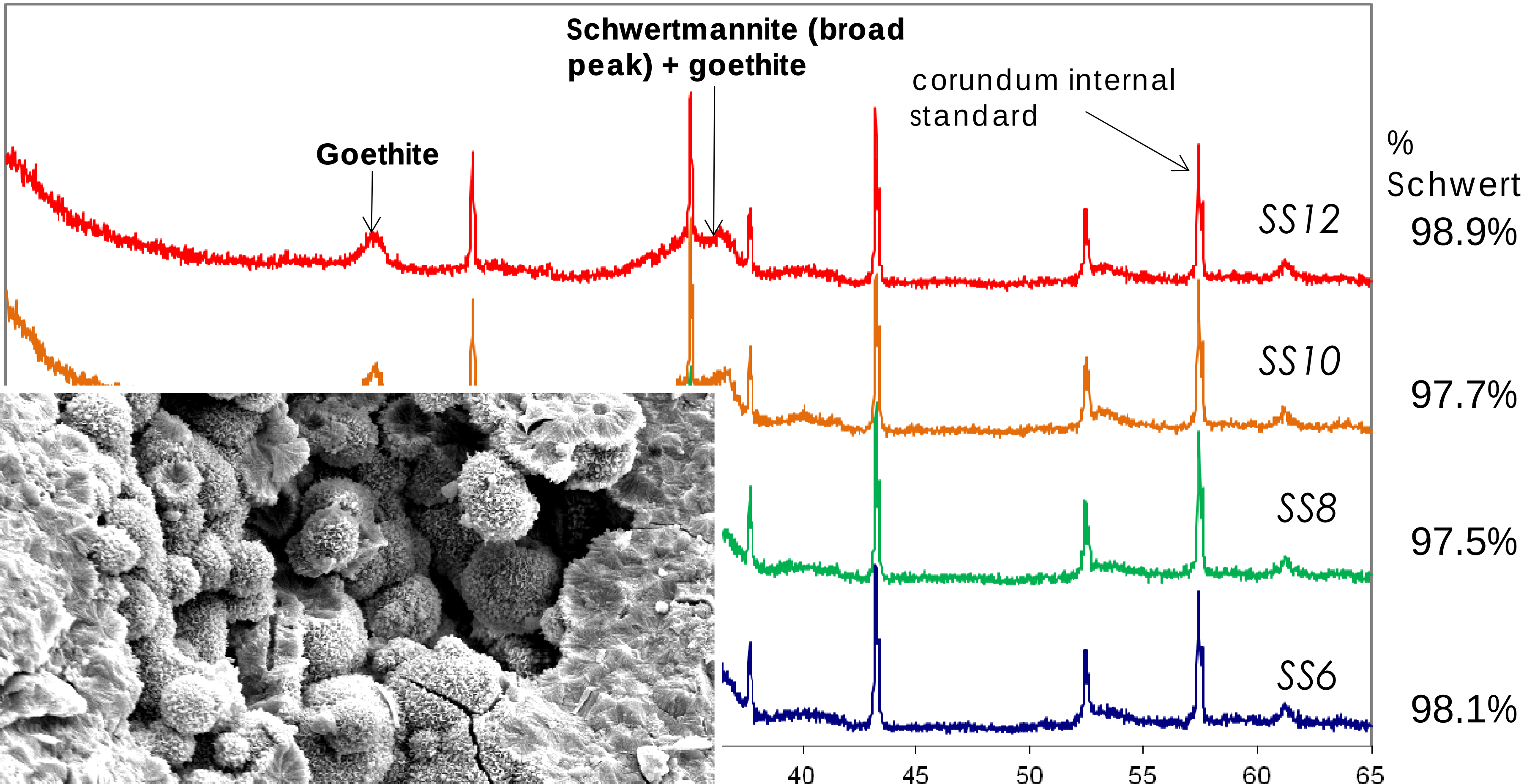


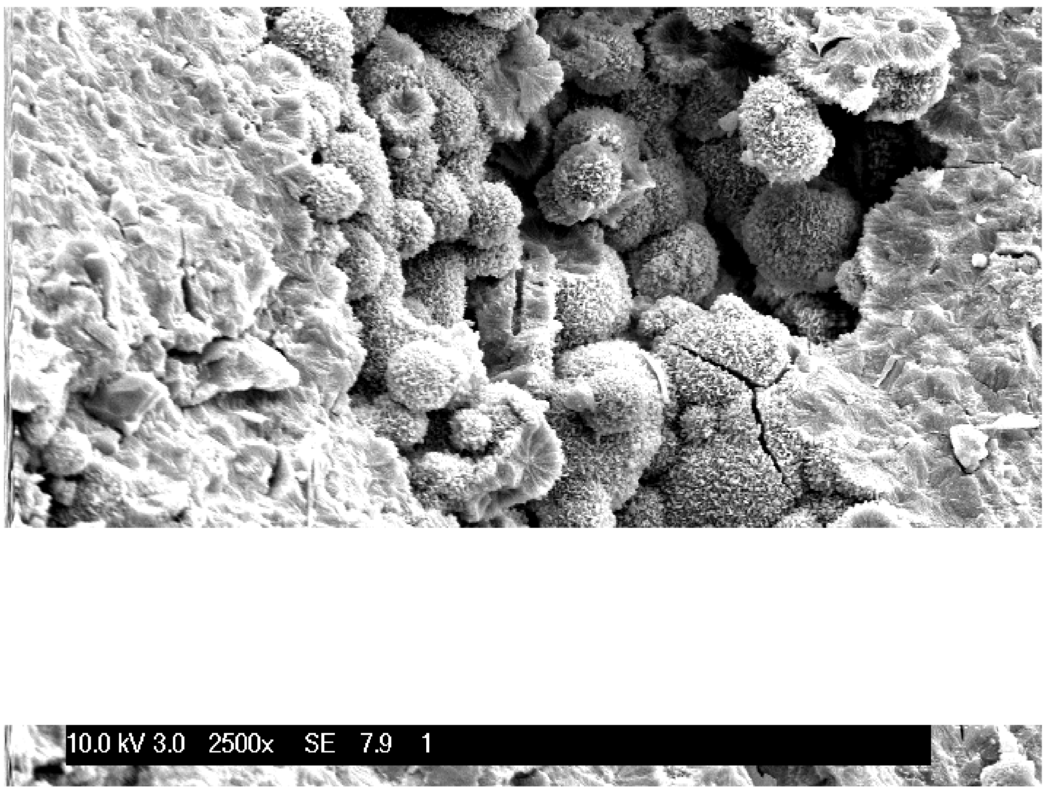
Microbial community:

- 16S rDNA by 454-pyrosequencing
- Fe-oxidizing bacteria (MPNs)

Schwertmannite* (*$Fe_8O_8(OH)_6SO_4$*)** *and* ***Goethite (FeOOH) *reference compounds*

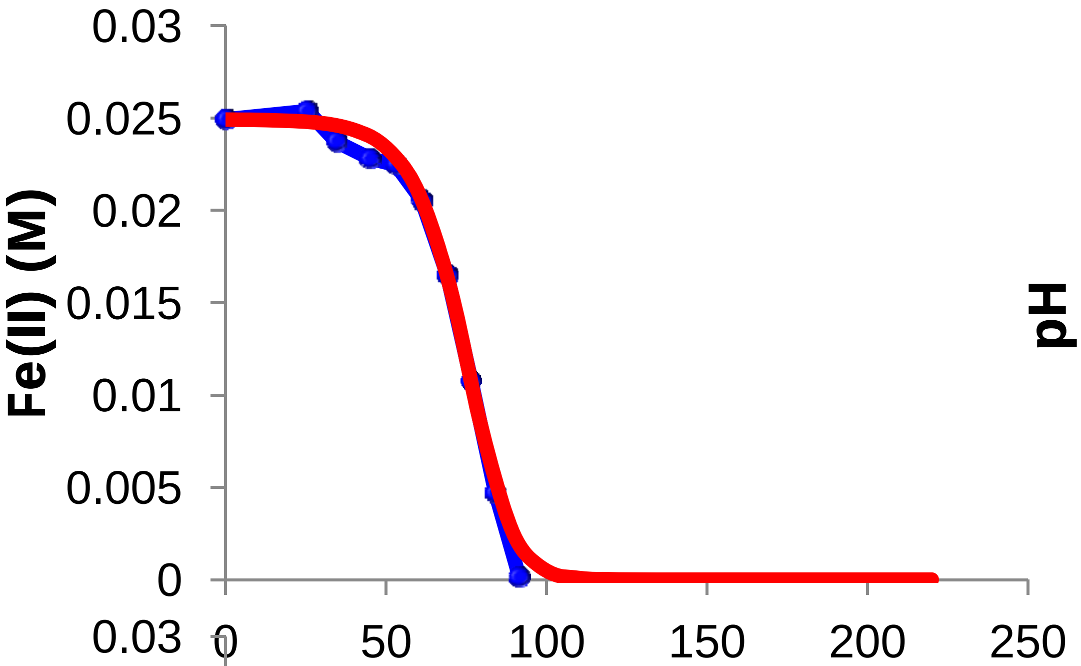
Scale characterization

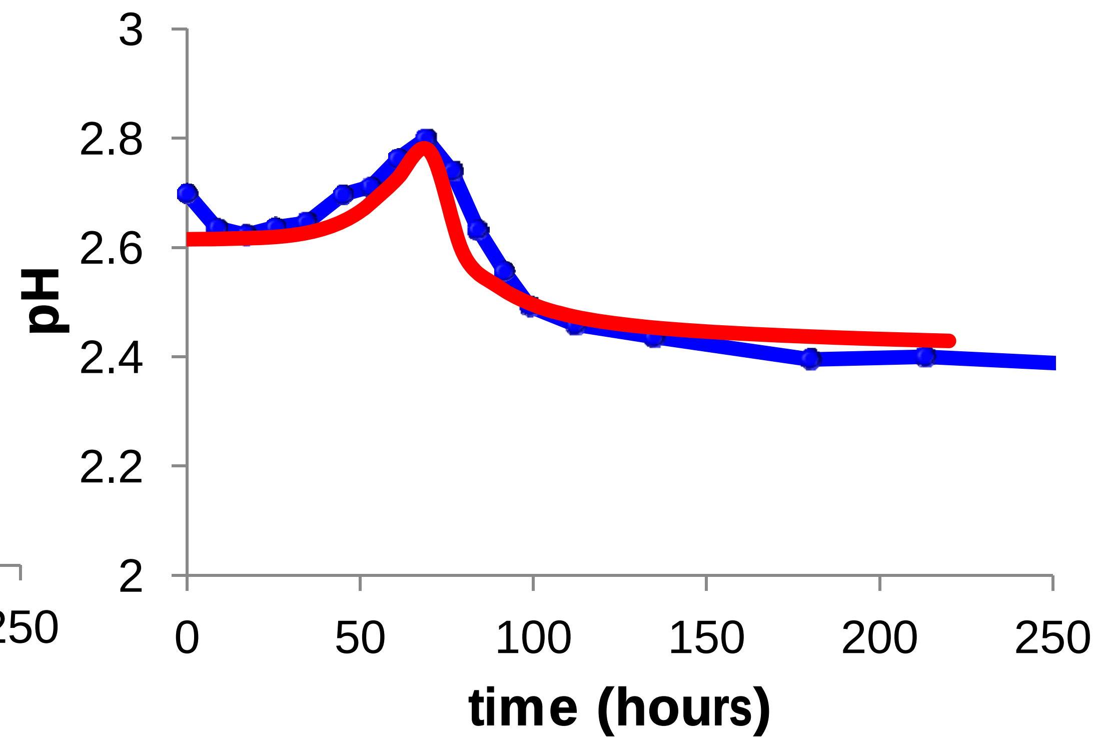


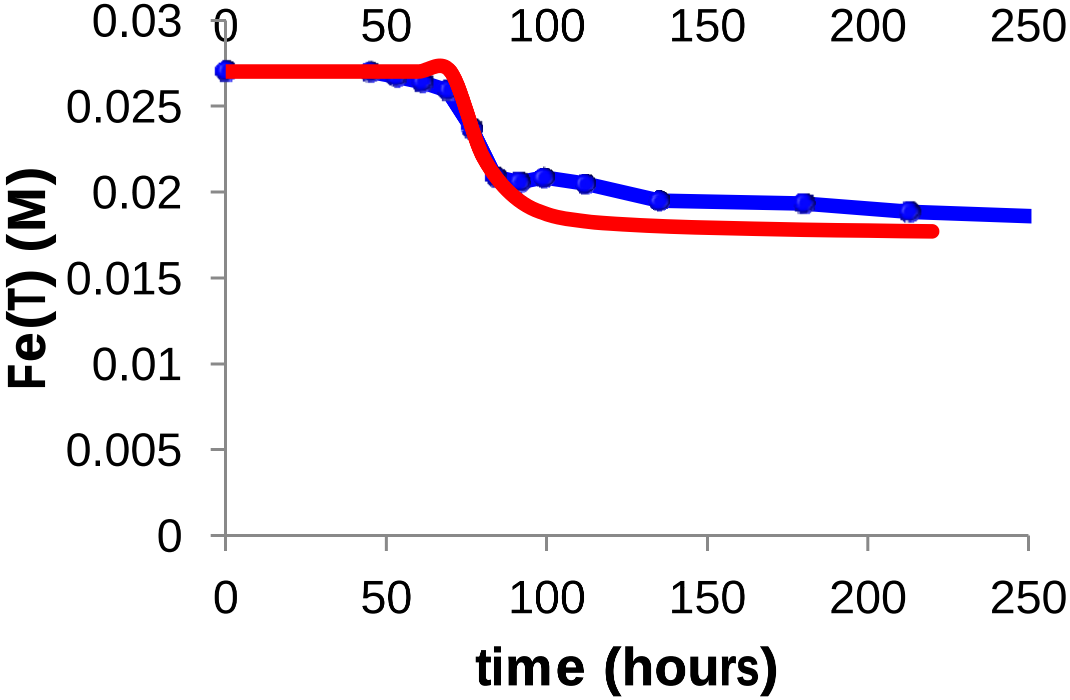


Primarily ***Schwertmannite*** [ideal composition: $Fe_8O_8(OH)_6SO_4$] *with minor* ***Goethite*** [FeOOH]

Geochemical model – batch experiments





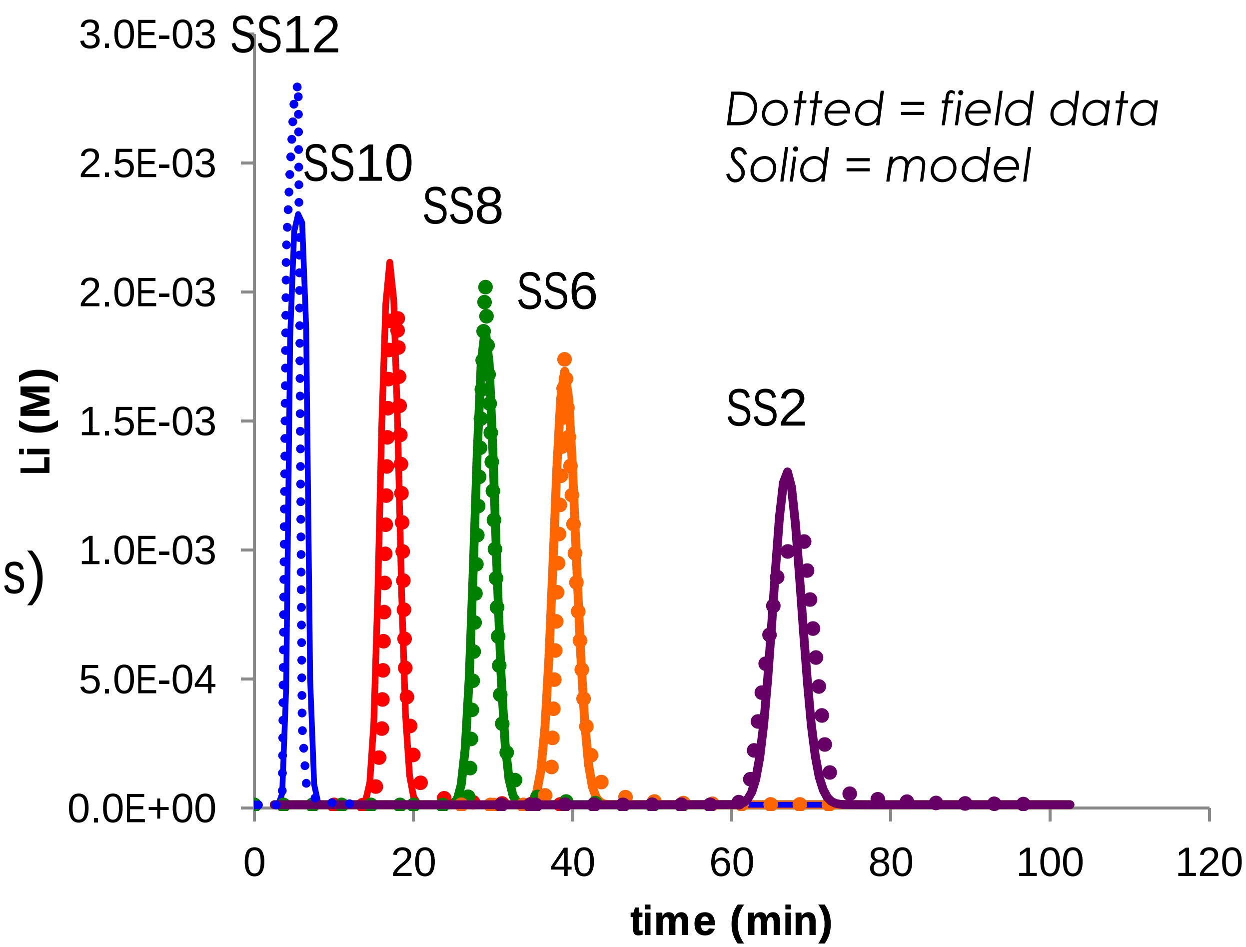


- ***Kinetics for microbial Fe(II) oxidation***
  - Based on Michaelis-Menten enzyme kinetics
  - Kinetics depends on substrate (Fe(II)) and cell concentration
- ***Kinetically controlled schwertmannite precipitation***

Geochemical model – field observations

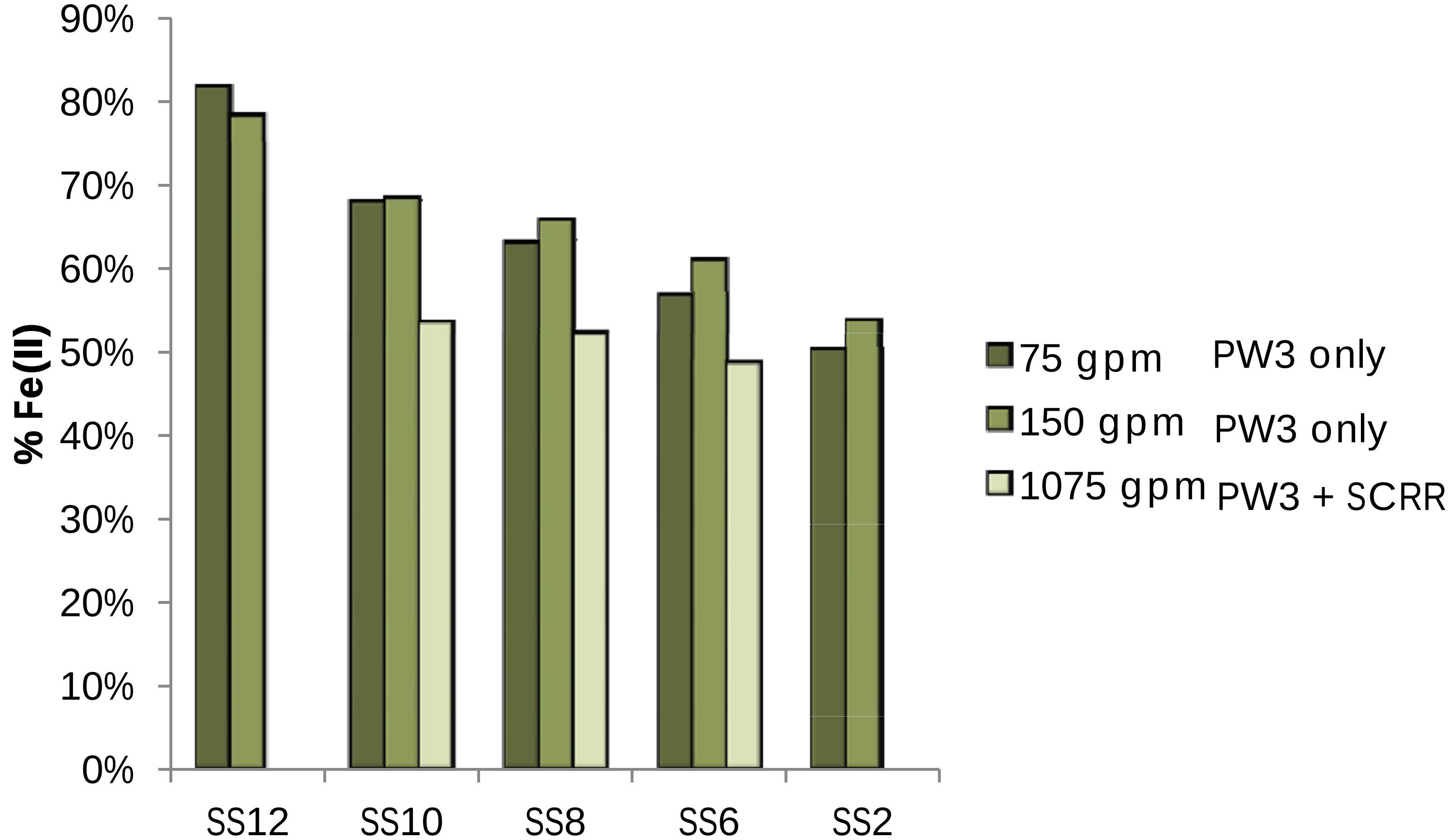
"Slug"-style injection of conservative tracer Li

- Travel times
- Dispersivity
- 3 flow regimes:
  - 75 gpm (4.7 L/s)
  - 150 gpm (9.5 L/s)
  - 1075 gpm (67.8 L/s)



> Variable velocity in each section of pipeline

Remediation test 1: increased flow



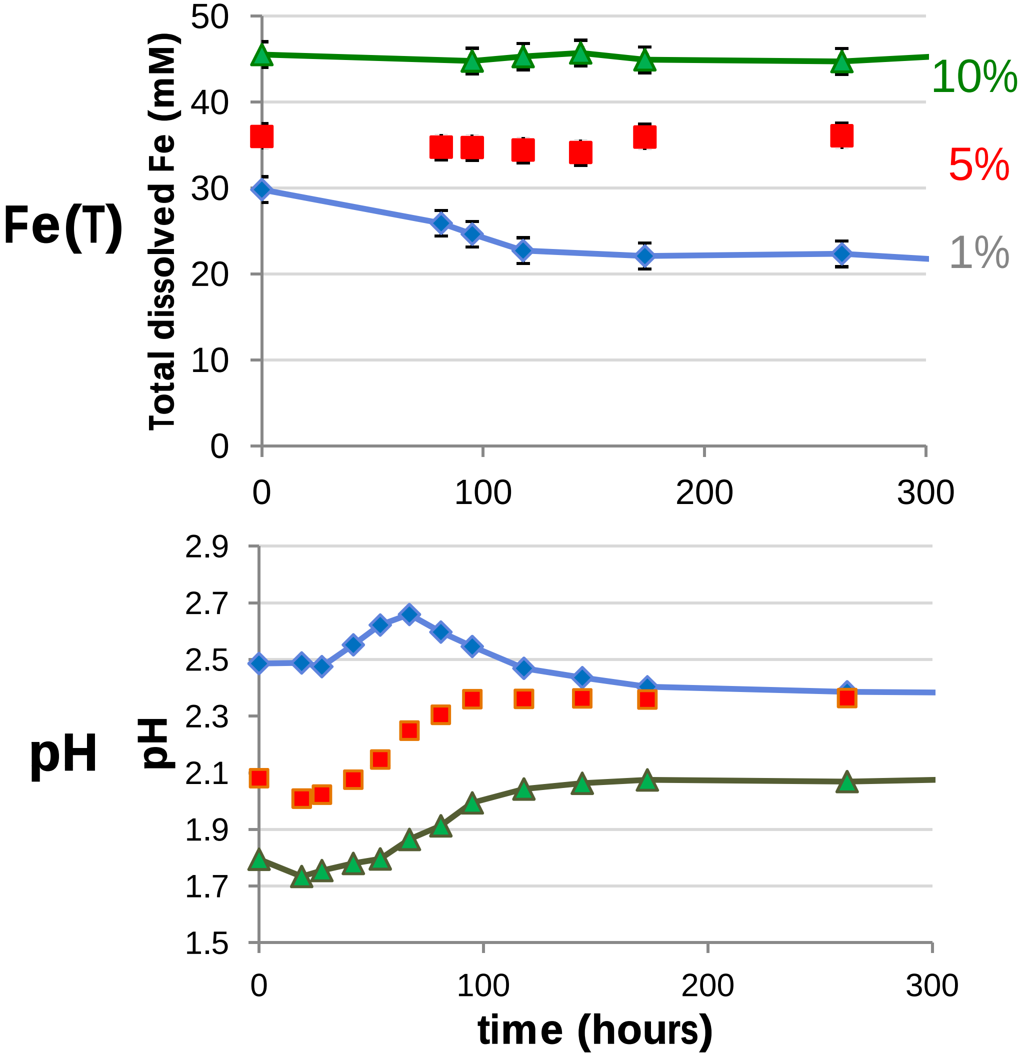
- Doubling flow from 75 to 150 gpm slightly decreased amount oxidized
- Highest flow rate (1075 gpm) slowed Fe(II) oxidation

→ **Model can be used to simulate effect of running pipeline at higher flow rates**

→ **Effect on treatment plant operations**

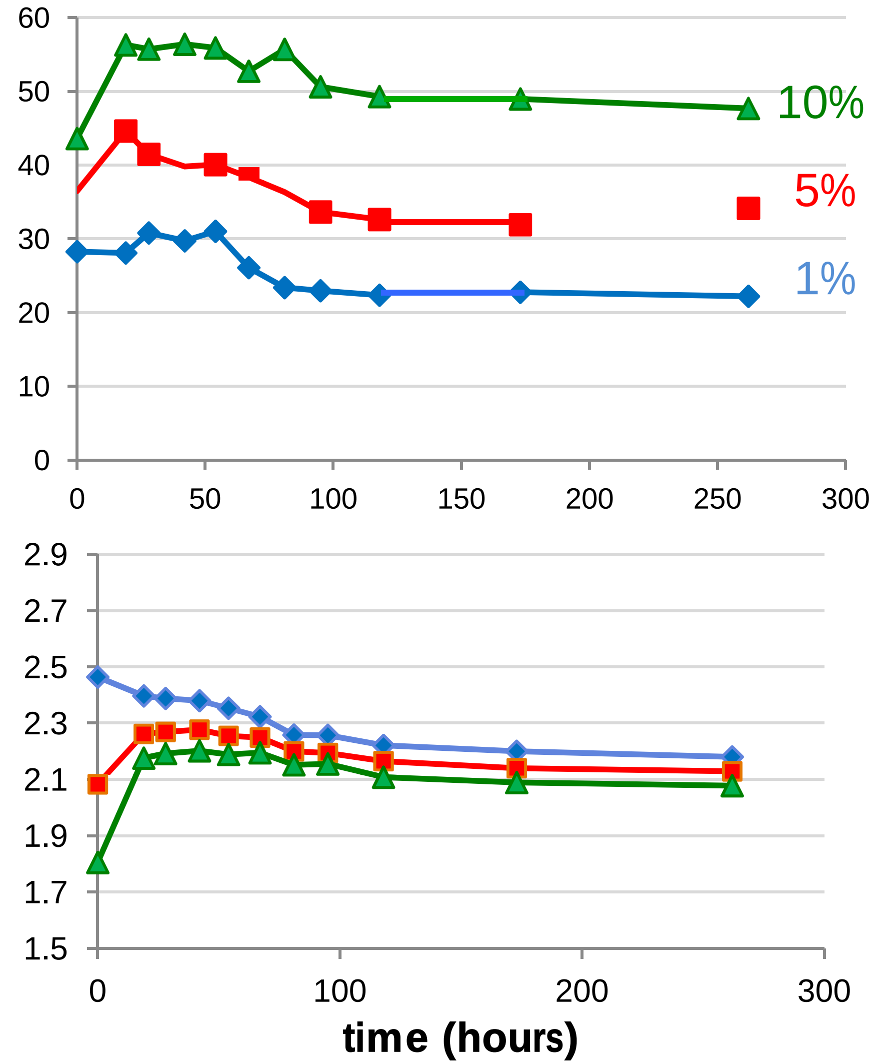
Remediation test 2: mixing with low pH water

no scale



Precipitation in 1% Richmond – none in 5%, 10%

with scale



Scale buffers pH to 2.1-2.2

Decreasing pH effective in preventing scale formation

Conclusions

- Understanding fundamental biogeochemical processes improves conceptual and numerical models
  - Balance complexity and broad applicability
- Strong links between microbiology, mineralogy, hydrology, and water chemistry crucial
  - Model development
  - Site management
- Case studies illustrate treatment approaches
  - Surface AMD
  - Aquifer bioremediation and phosphate amendment
  - Bridge laboratory to field scale

Thank you for your attention!

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