Characterization and Remediation of Iron(III) Oxide-rich Scale in a Pipeline Carrying Acid Mine Drainage at Iron Mountain Mine, California, USA

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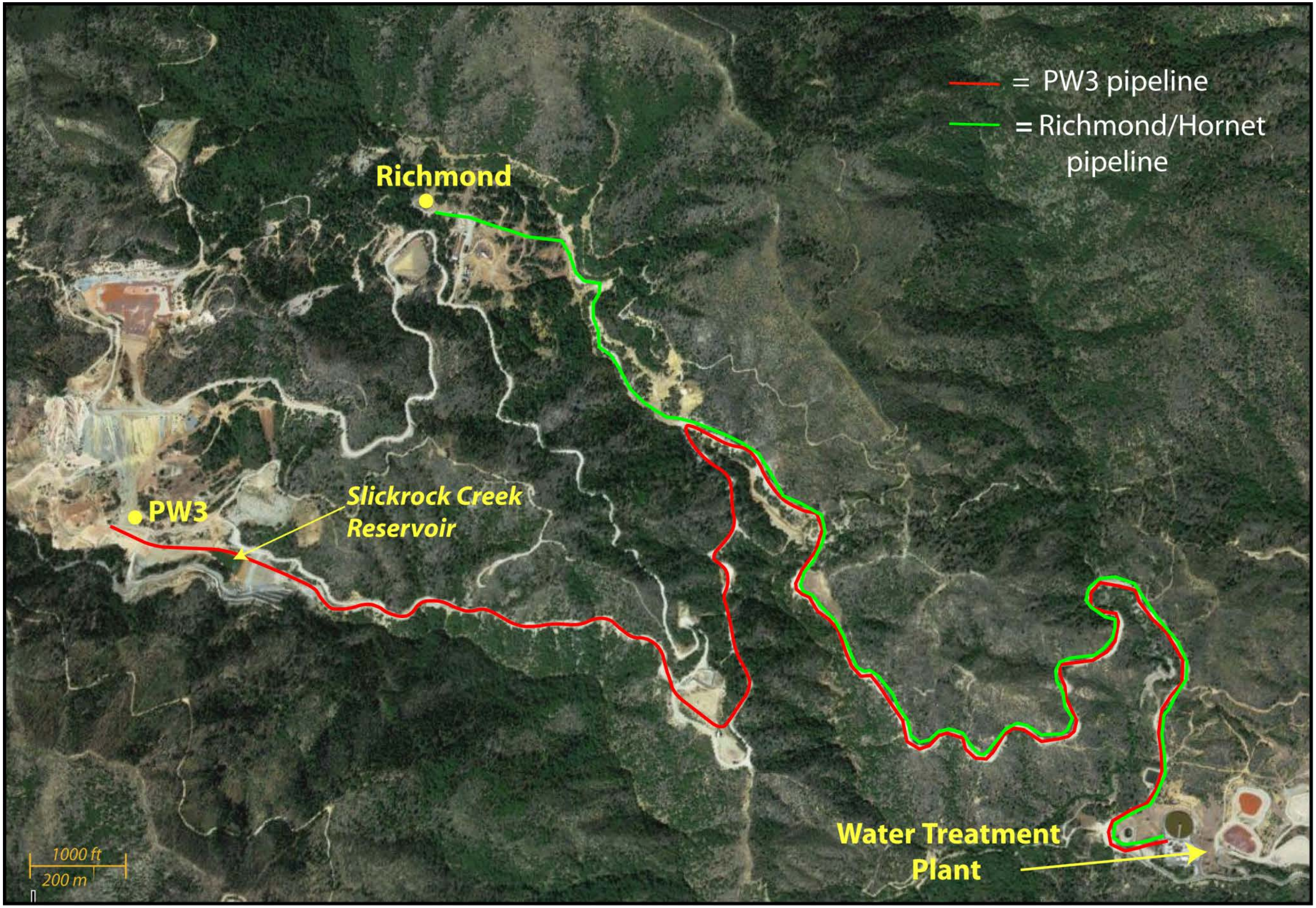
August 13, 2014

National Conference on Mining-Influenced Waters

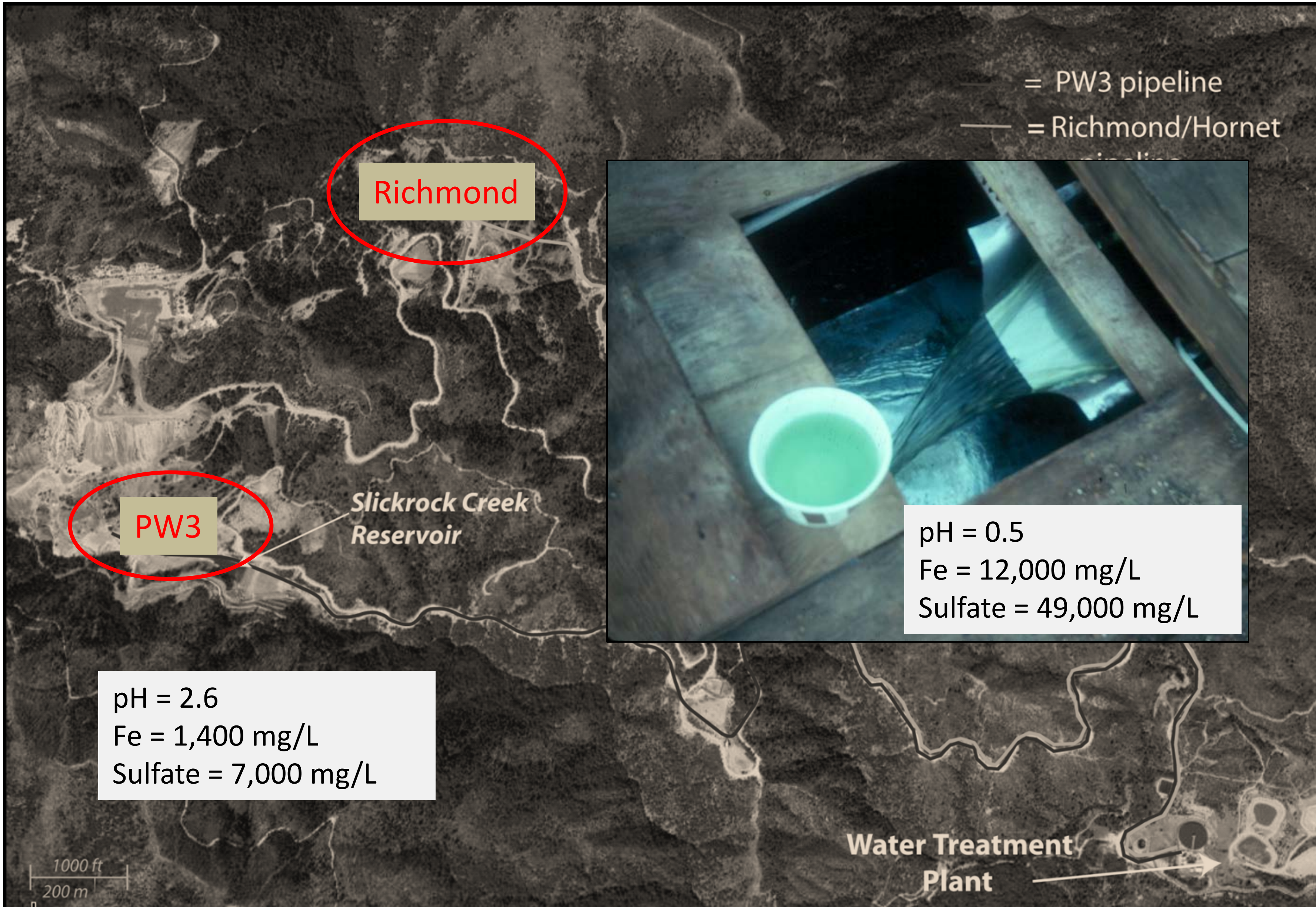
Pipe scale in AMD pipeline

Pipe scale causes clogging and requires costly clean-out every 2-4 years

Pipelines and water treatment at IMM



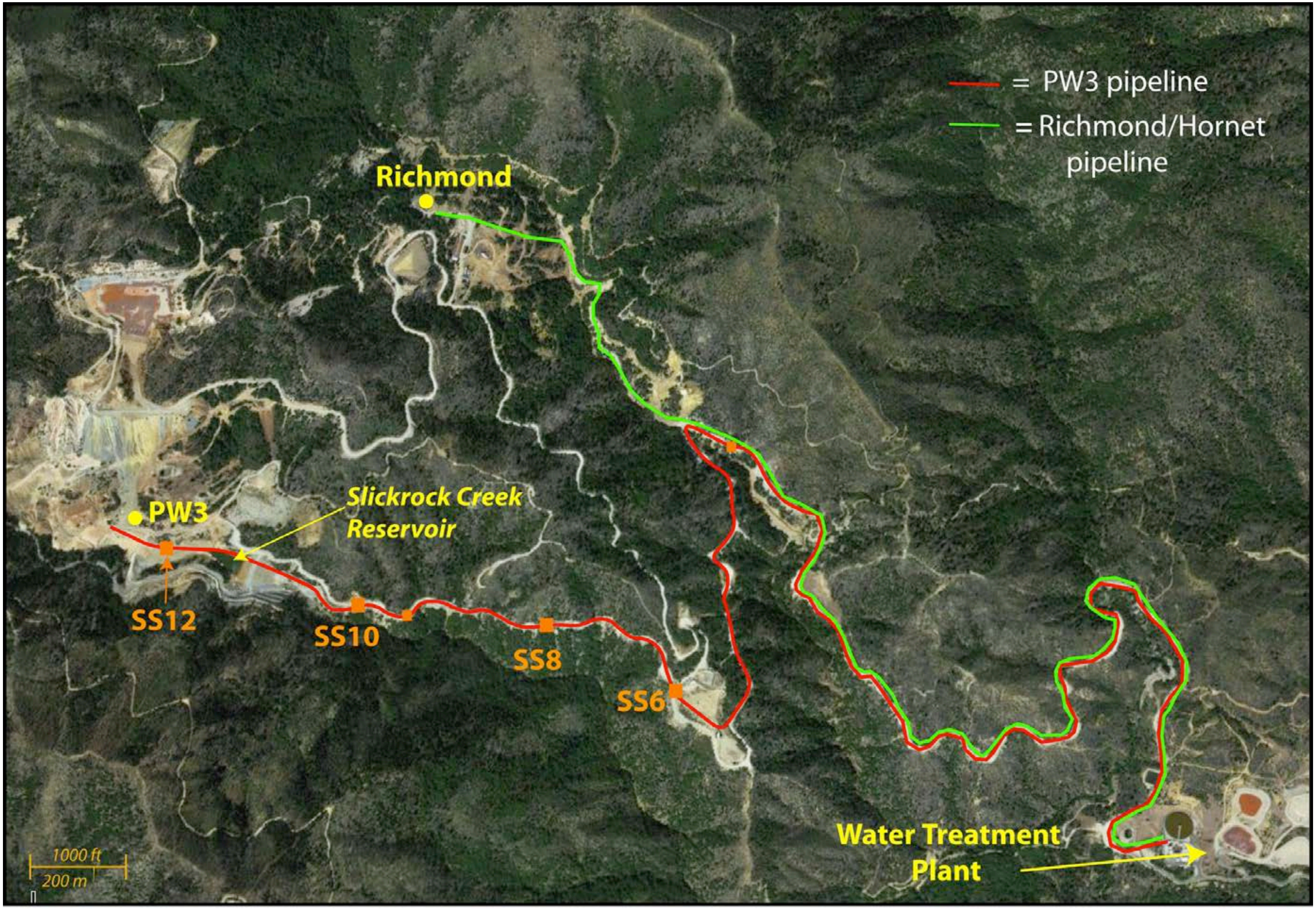
Influent water to pipelines



pH = 0.5
Fe = 12,000 mg/L
Sulfate = 49,000 mg/L

pH = 2.6
Fe = 1,400 mg/L
Sulfate = 7,000 mg/L

Water and Scale Sample Collection



Research Objectives

1. Characterize water chemistry and pipe scale composition

2. Identify biogeochemical processes leading to scale formation

3. Identify strategies to prevent or retard scale formation in the pipeline

Pipeline Water Chemistry

Portal → downstream

Site name	*pH*	*Fe(T)* mg/L	*Fe(II)* mg/L	*Fe(III)* mg/L	*Sulfate* mg/L
PW3	2.62	1460	1440	<40	6890
SS12	2.63	1400	1400	<40	6690
SS10	2.71	1390	1320	70	6480
SS8	2.73	1360	1040	320	6820
SS6	2.74	1360	1060	300	6770

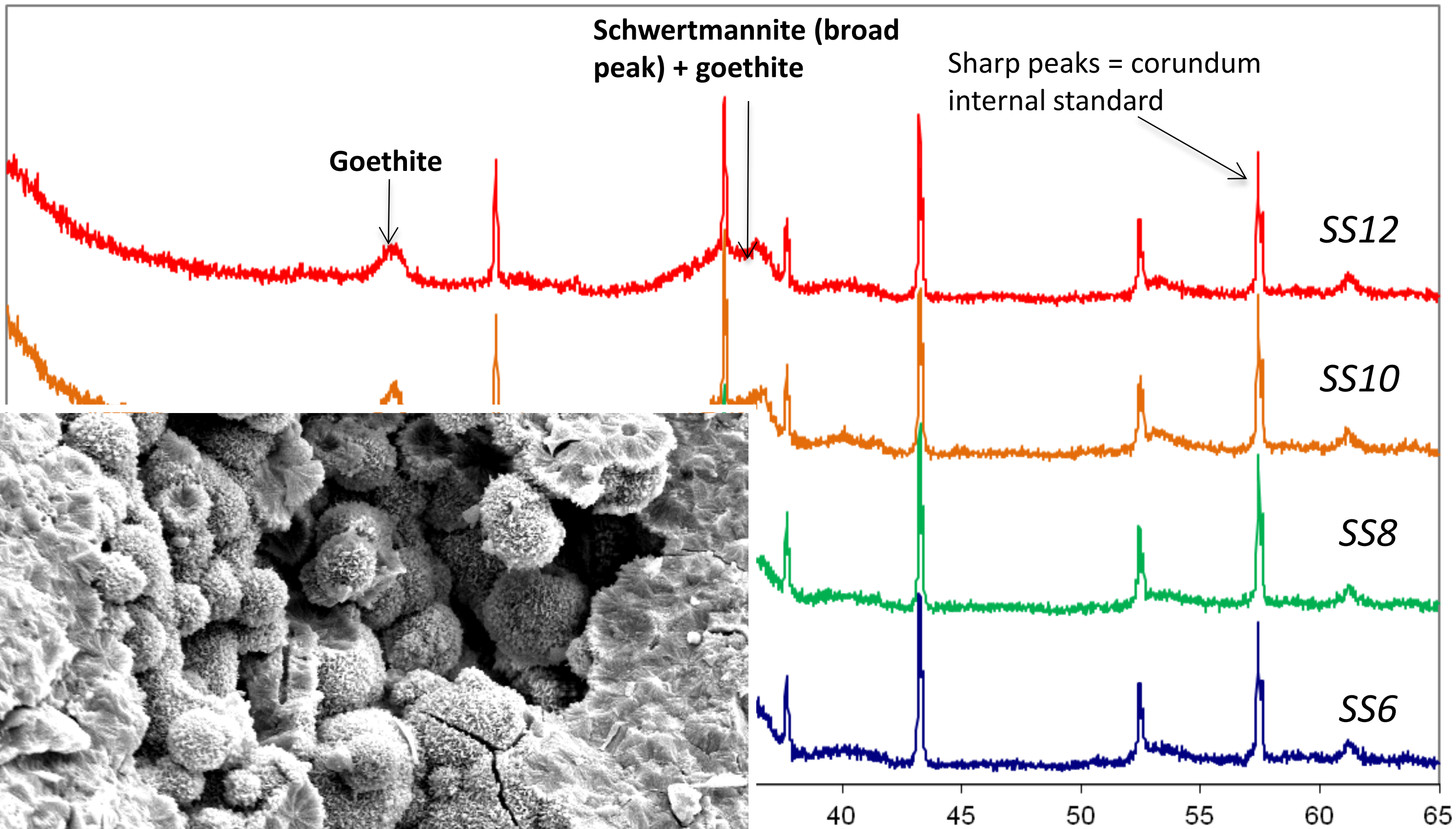
Fe(II) oxidation and Fe(III) precipitation

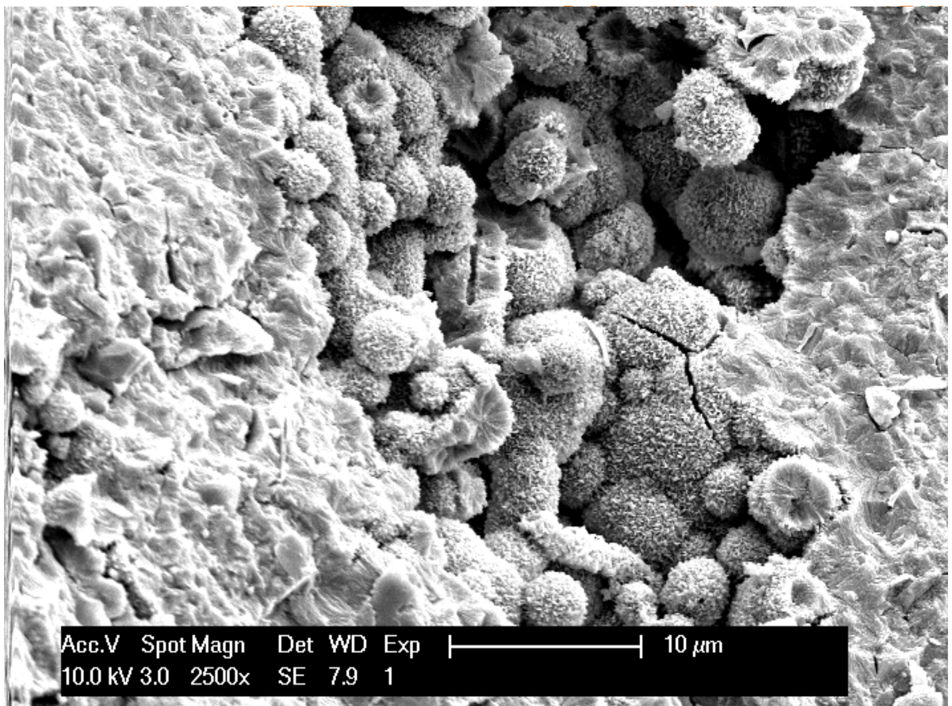
Characterization of Pipe Scale

- XRD, SEM
- Wet chemical extractions
  - deionized water
  - 0.2M ammonium oxalate
  - 0.5M HCl
  - 0.5M HCl
    0.5M hydroxylamine HCl
  - ***Least aggressive*** → ***Most aggressive***
- Total elemental digestion
- C and N analysis (biomass)
- Microbial community
  (16S rRNA by 454-pyrosequencing)
  Fe oxidizing bacteria (MPNs)

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

Characterization of Pipe Scale

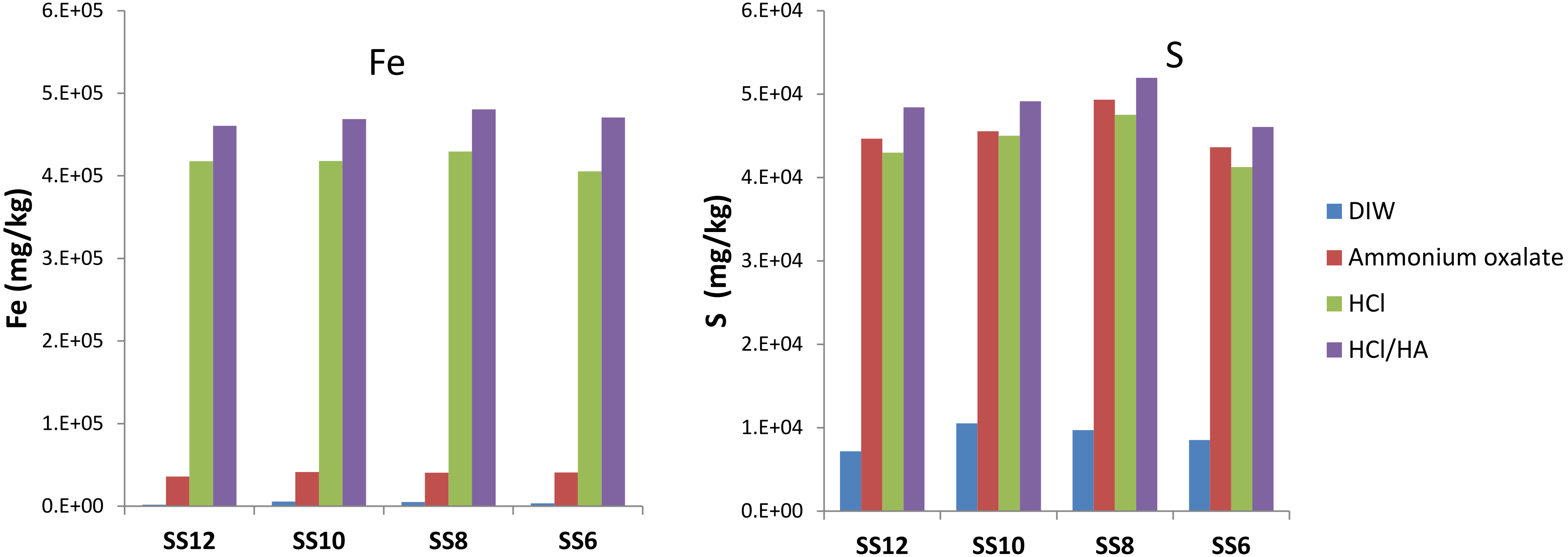




SEM courtesy of Amy Williams

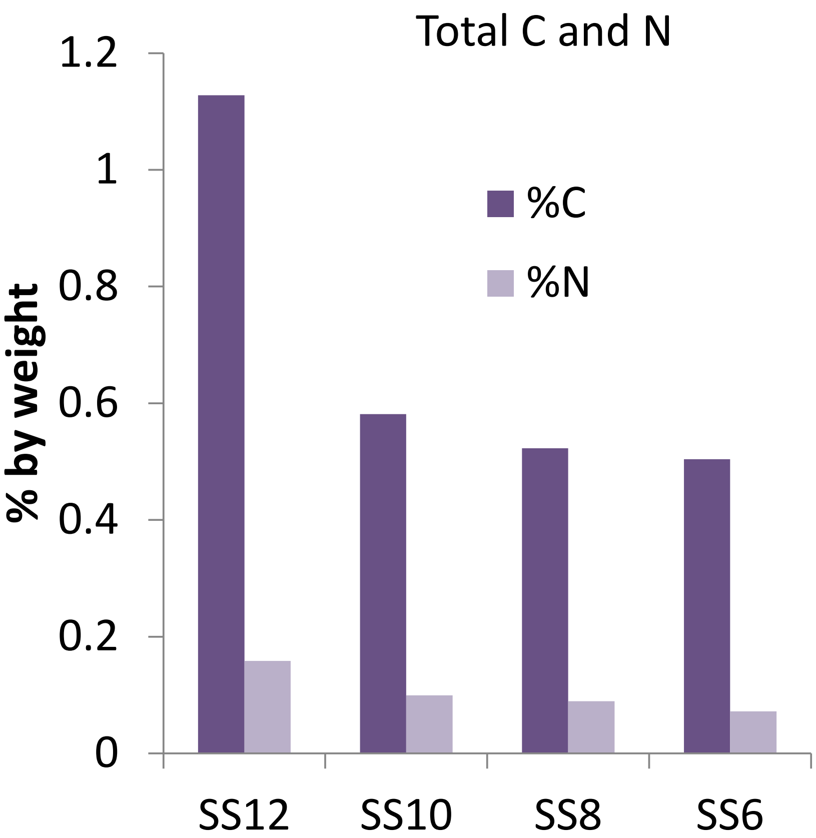
Bulk mineralogy is similar in all scale: Primarily ***Schwertmannite*** [ideal composition: $Fe_8O_8(OH)_6SO_4$] *with minor* ***Goethite*** [FeOOH]

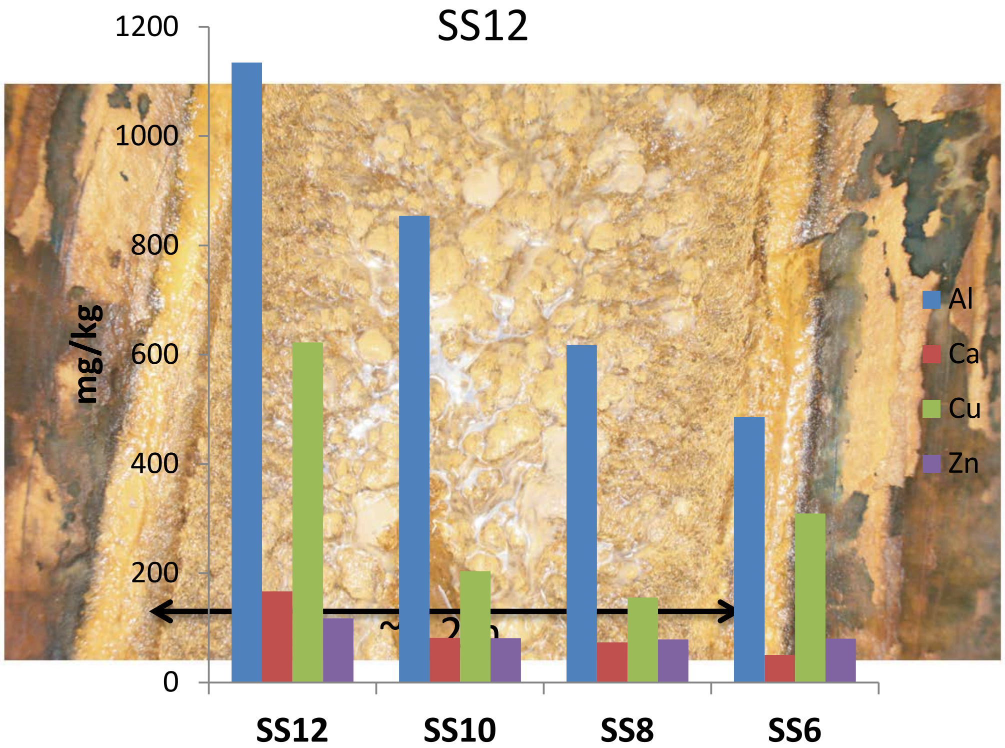
Characterization of Pipe Scale



Fe and S were dominant elements in extractions –
Schwertmannite as primary phase
Similar amounts of Fe and S extracted in all 4 scale samples –
Bulk mineralogy is similar along the pipeline

Characterization of Pipe Scale





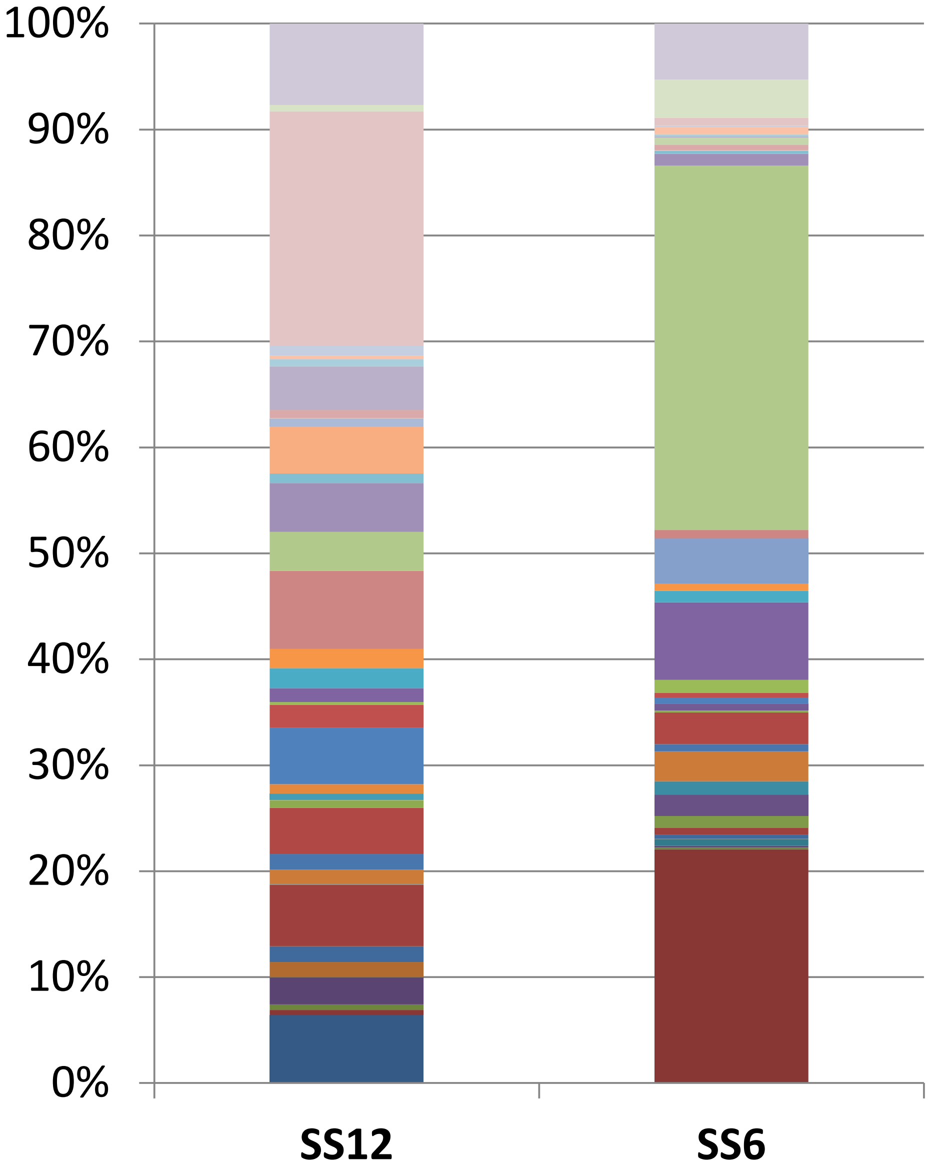
Phosphate-extractable cells also highest in SS12

Most Probable Number (MPNs) for iron oxidizing organisms

Biomass decreases along pipeline

Certain trace elements decrease along pipeline

Scale Microbial Community (16S)



Dominant classifications:

- Spirochaetales
- Xanthomonadales
- Burkholdariales
- Acidithiobacillales
- Nitrosprales
- Holophagales
- Chloroflexi
- Propionobacteriales
- Acidibacteriales
- Thermoplasma

- ➢ Diverse microbial community
- ➢ Different community up-and down-stream
- ➢ Many groups with known Fe oxidizers and other C,N metabolisms

Research Objective 1

- Fe(II) is oxidized to Fe(III) in the pipeline, resulting in scale precipitation
- Scale mineralogy: schwertmannite with trace amounts of goethite, jarosite
- Biomass and trace elements in scale decrease along the length of the pipeline
- Microbial community is diverse and is different between upstream and downstream scale

Research Objective 2: biogeochemical mechanisms

Iron(II) oxidation at pH <3:

Abiotic oxidation is ***slow***…

… but microbially-mediated Fe(II) oxidation has been well-documented

Acidithiobacillus, Leptosprillium, Ferroplasma, Sulfobacillus, Acidimicrobium…

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

Research Objective 2: biogeochemical mechanisms

Batch experiments:

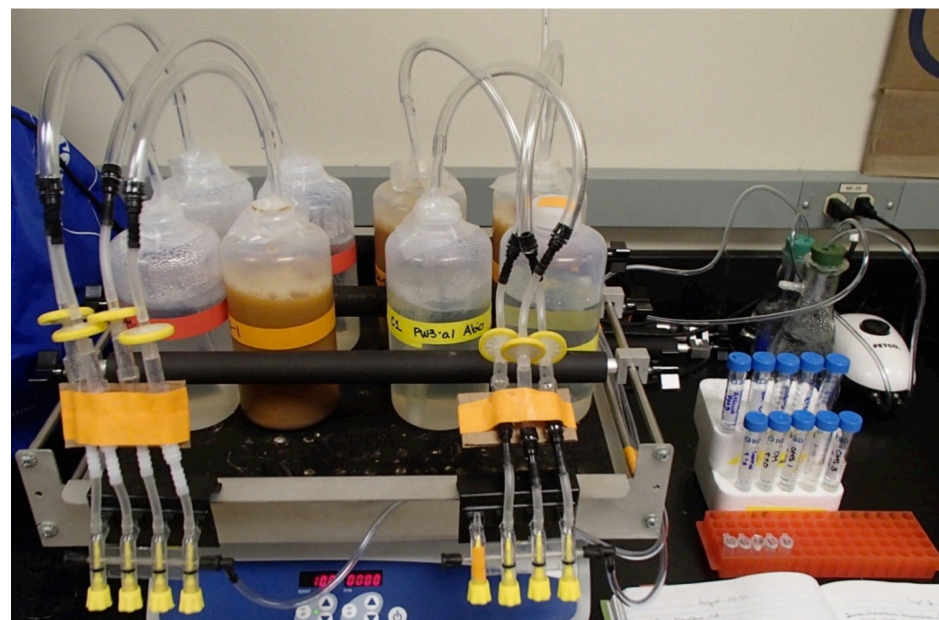
Unfiltered PW3 water

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

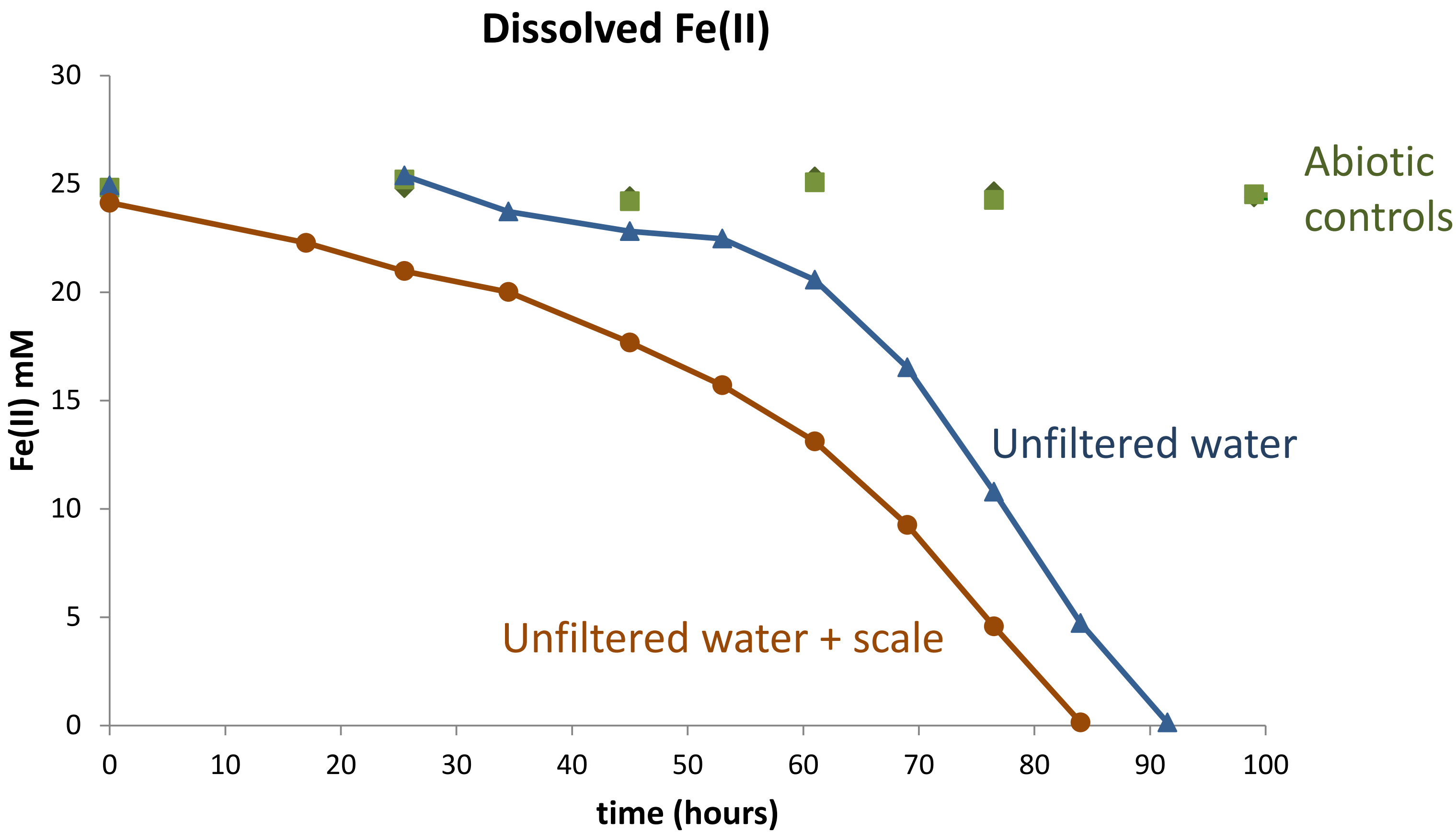
→ **Water + scale** = Biotic Fe(II) oxidation, effect of scale

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

All bottles aerated and placed on shaker table



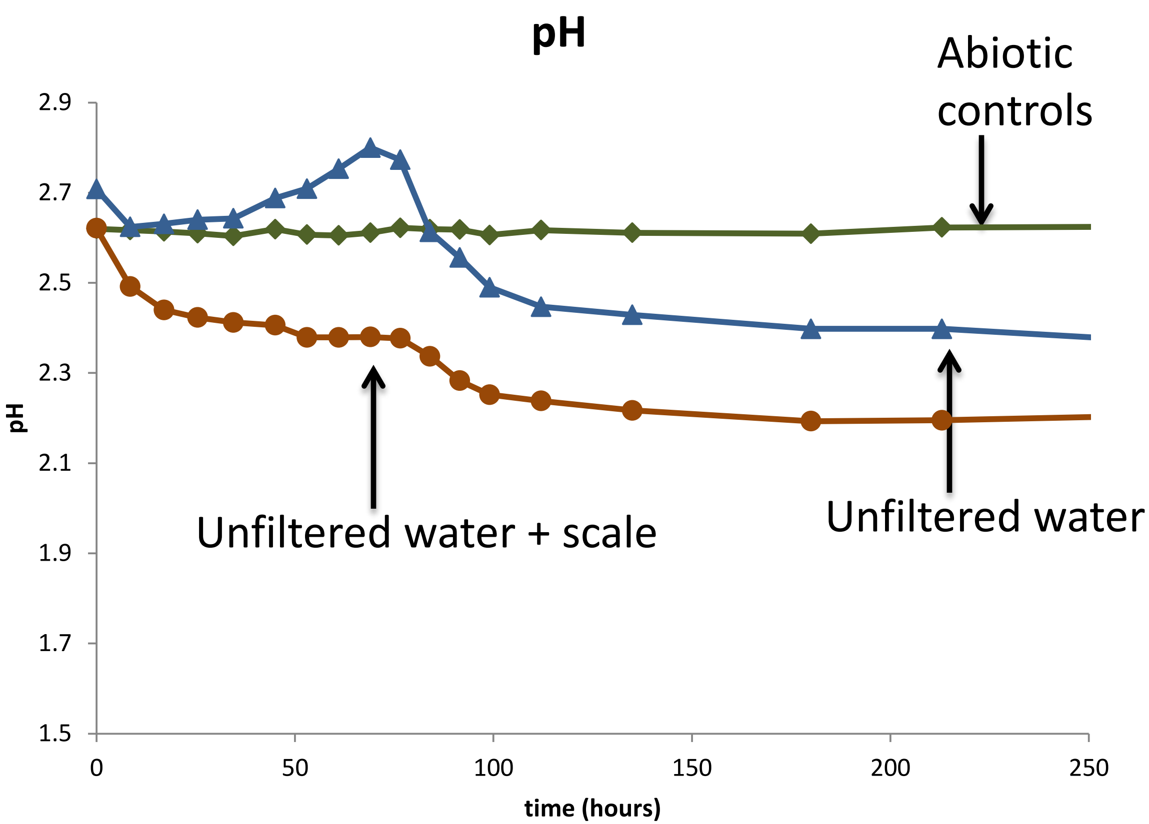
Microbial Iron(II) Oxidation



Fe(II) oxidation is a biotic process

Presence of scale impacts iron oxidation rates

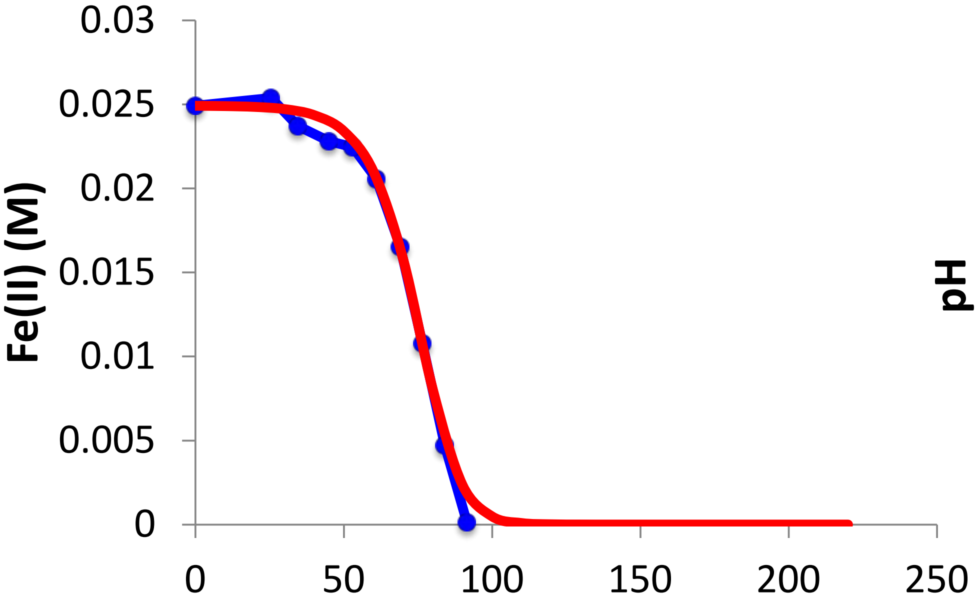
Microbial Iron(II) Oxidation

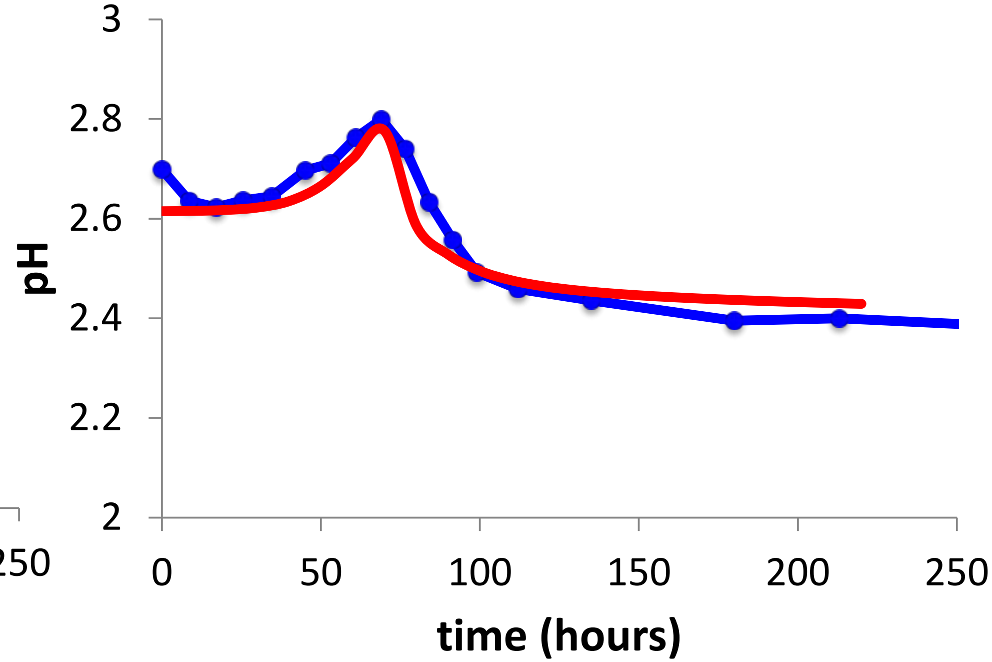


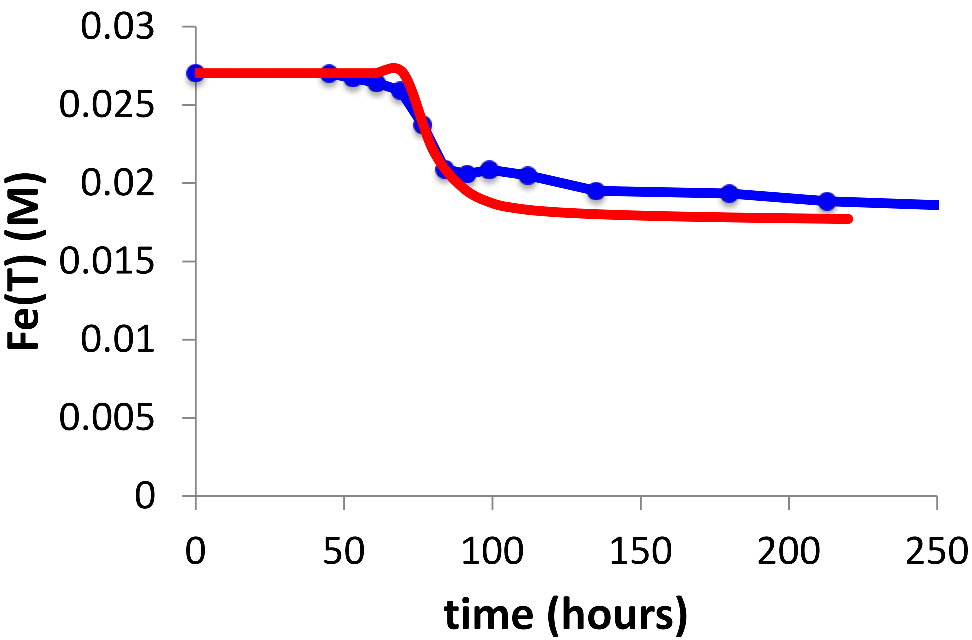
- Iron oxidation = increase pH
- Iron precipitation = decrease pH
- Iron precipitation is "seeded" by scale
- Precipitate formed in water only condition is Schwertmannite

Microbial Fe(II) oxidation	$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$
Fe(III) hydrolysis/polymerization	$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+$
Schwertmannite precipitation	$8Fe^{3+} + SO_4^{2-} + 14H_2O \rightarrow Fe_8O_8(OH)_6(SO_4) + 22H^+$

Batch model: water only condition

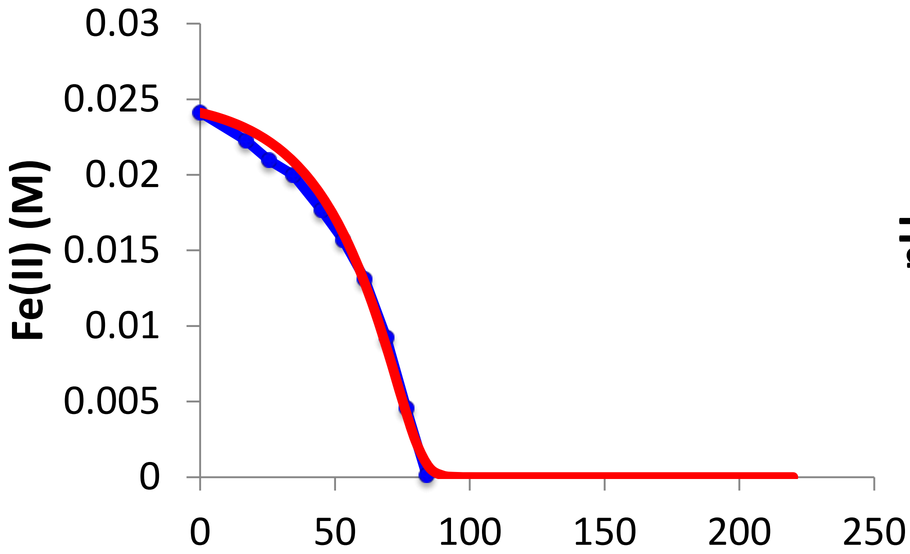


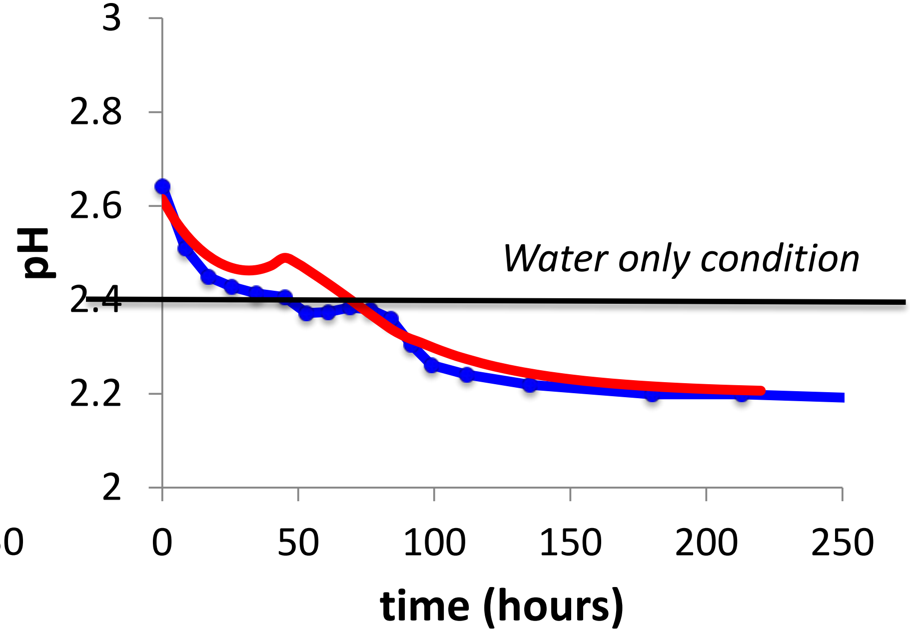


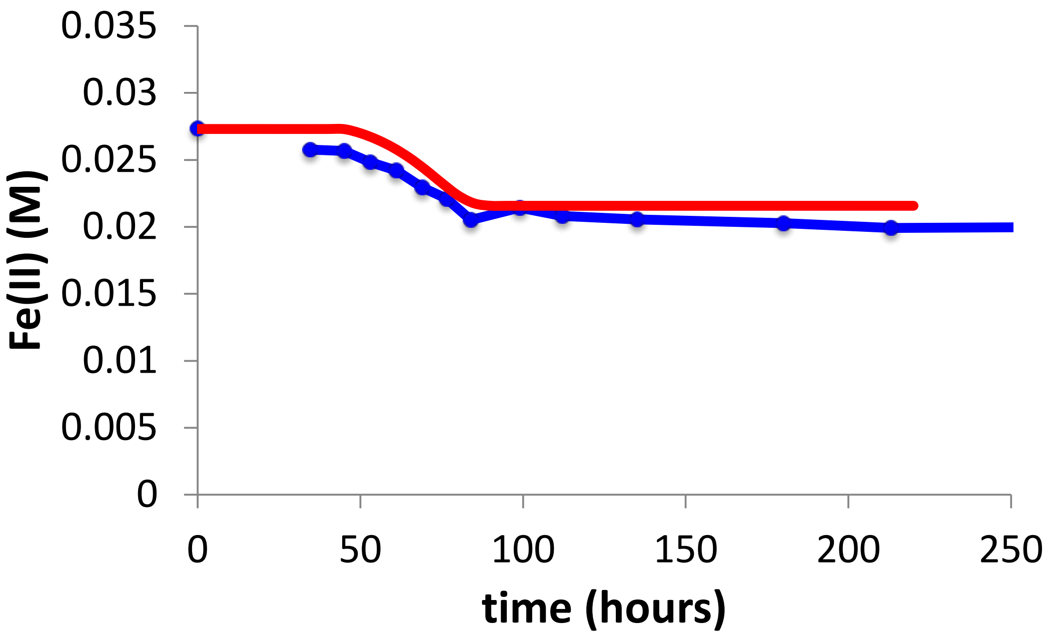


- PHREEQC geochemical code
- Microbial Fe(II) oxidation kinetics
- Kinetic schwertmannite precipitation
- Dissolved Fe(III) polymer included

Batch model: water + scale condition

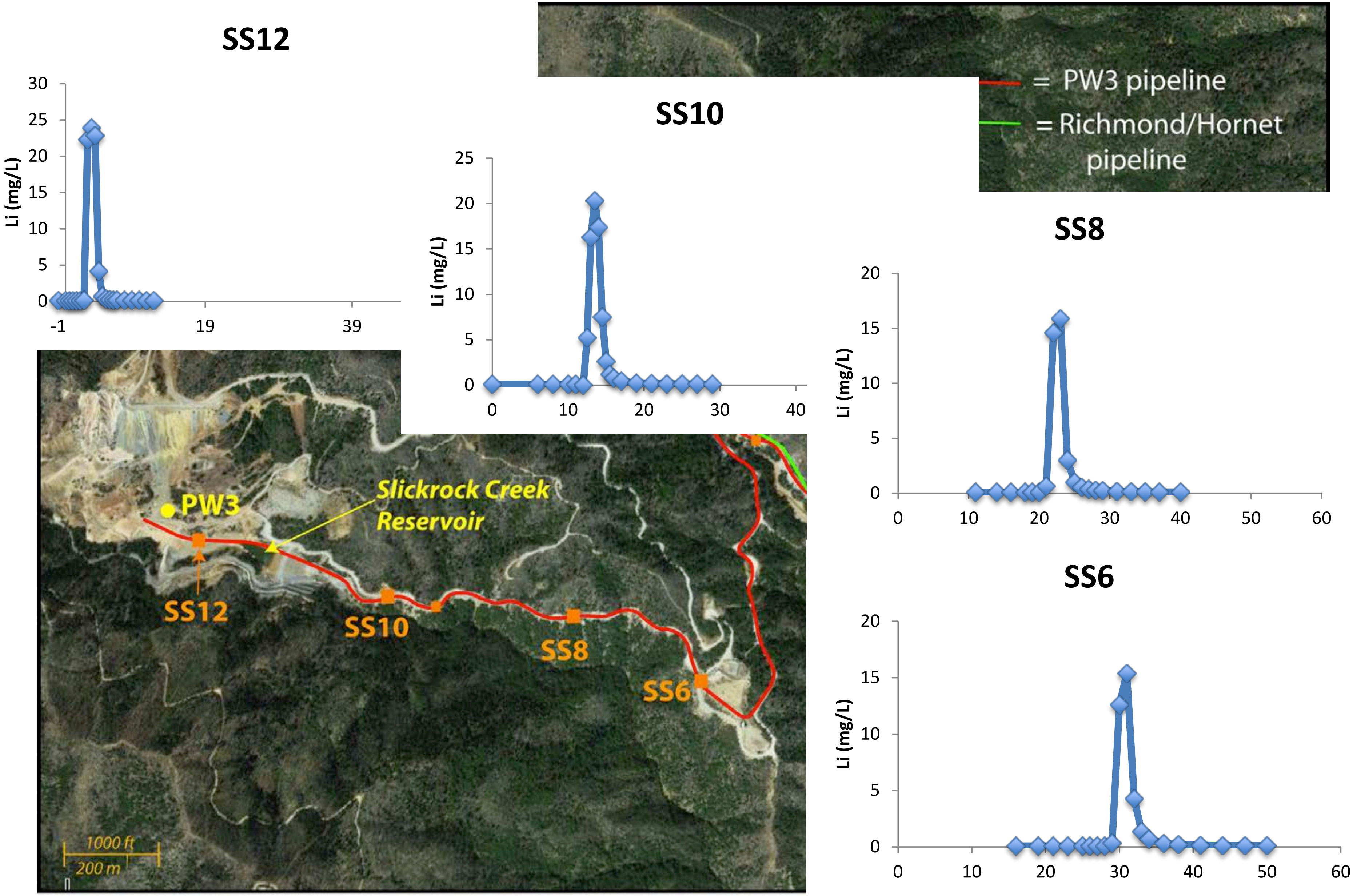






- Microbial Fe(II) oxidation kinetics
- Schwertmannite precipitation kinetics
- Kinetic surface pH buffering reaction

LiCl Tracer test for 1D reactive transport model



Research Objective 2

- Iron oxidation is biotic
- Iron precipitation is “seeded” by scale
- Precipitate formed in batch experiments is similar to scale
- Batch geochemical model
  - Kinetics: Microbial Fe oxidation, precipitation, surface buffering
- Field scale processes
  - In situ rates of Fe oxidation
  - 1D reactive transport model

    test remediation strategies

    application to other sites with pipe scaling

Research Objective 3 - mitigation

Mixing PW3 and Richmond waters:

- Fe(II) oxidation may be hard to control
- Precipitation can be prevented by decreasing pH

PHREEQC calculations of saturation index of schwertmannite

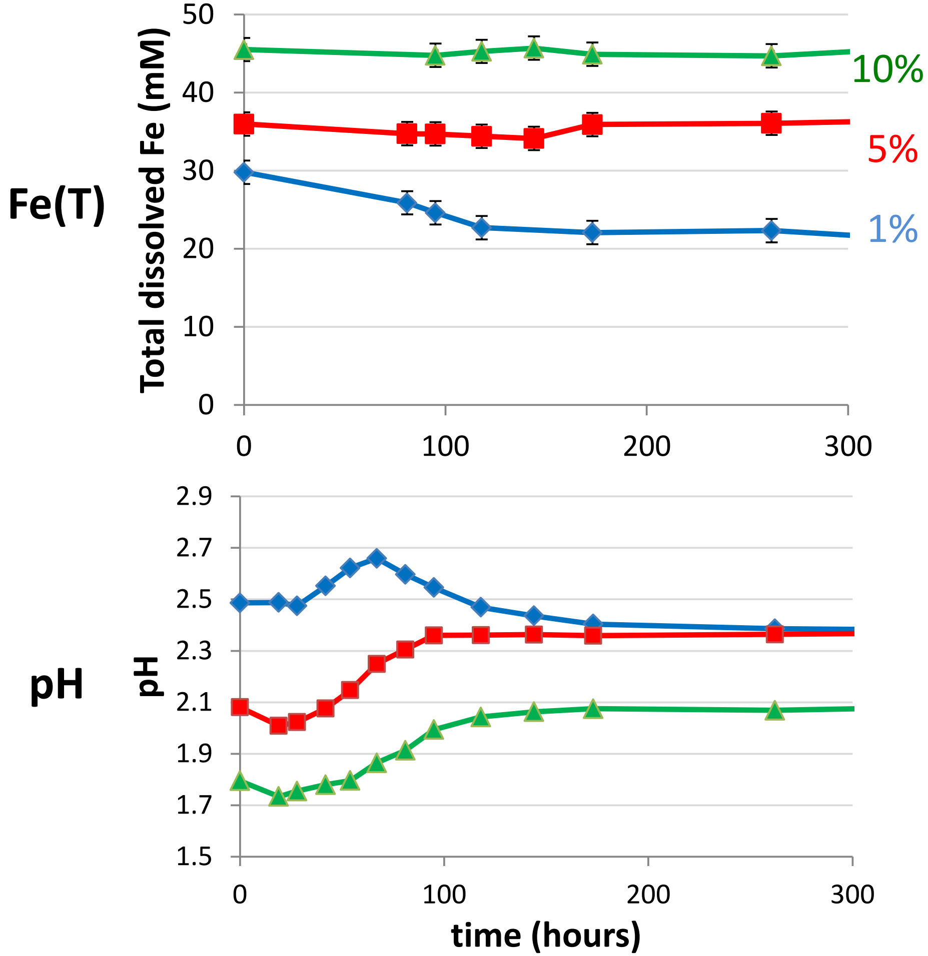
- Variable Fe(III) concentrations, mixing ratios (pH)
- ~5% Richmond + 95% PW3

Batch experiments:

- 1%, 5%, 10% Richmond water, balance PW3
- With and without scale (effect of pre-existing scale)
- Range of Fe(III) conditions by inoculating with a microbial culture

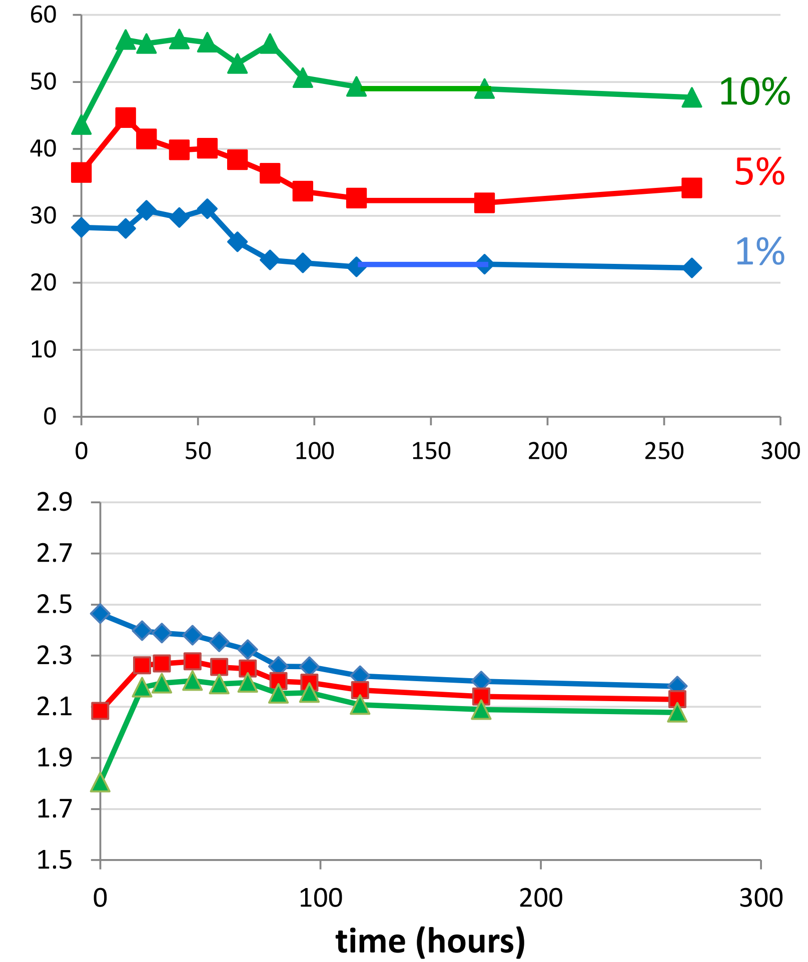
Pipe Scale Mitigation

no scale



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

with scale



Scale buffers pH to 2.1-2.2

Decreasing pH by mixing with Richmond effective in preventing scale formation

Conclusions

- Fe(II) is oxidized to Fe(III) in pipeline, resulting in precipitation
- Fe(II) oxidation is microbially mediated
- Scale is composed of schwertmannite, with minor goethite
- Presence of scale "seeds" precipitation

- Mixing of Richmond and PW3 as potential mitigation strategy
  - *Confirm with field tests, over range of chemistry*
- Presence of scale strongly buffers pH
  - Buffering capacity of scale and rate of scale dissolution are important considerations for other mitigation strategies

- 1D reactive transport model for testing biogeochemical processes, remediation strategies
  - *Field-scale modeling as guidance for effective planning*

Thank you for your attention!

Acknowledgements:

- Amy Williams (UC Davis)
- James Sickles (US EPA)
- Lily Tavassoli (US EPA)
- Rudy Carver (Iron Mountain Operations)
- Theron Elbe (Iron Mountain Operations)
- Don Odean (Iron Mountain Operations)
- Gary Campbell (USGS)
- JoAnna Barrell (Colorado School of Mines)
- David Metge (USGS)
- Deb Repert (USGS