Biochemical Reactors for Hard Rock Mining-Influenced Water: Overview of Treatability Studies and Lessons Learned for Implementation

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Outline

- Introduction
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  - Water Chemistries
- Study Questions and Goals
- Study Test Setup
- Pre-Treatment
- Evaluating Metal Removal Mechanisms
  - Key Parameters and Examples
- BCR System Stresses
- Operations and Maintenance
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BCR Treatment

- Biochemical Reactor (BCR) Treatment: (ITRC 2012)
  - An engineered treatment system that uses an organic substrate (electron donor) to drive microbial and chemical reactions to reduce concentrations of metals, acidity, and sulfate in mining-influenced water.

$$SO_4^{-2} + 2\ CH_2O = H_2S + 2\ HCO^{-}_3 \qquad H_2S + Me^{+2} = MeS\ (solid) + 2H^{+}$$

- Requires sulfate and carbon electron donor for sulfate-reducing bacteria (SRB) to metabolize
- Electron donors:
  - Solid plant- based materials – wood chips, sawdust, compost, straw, brewers waste, etc.
  - Aquatic-based: crab shell (chitin), oyster shells, fish bones, etc.
  - Liquid-based: ethanol, methanol, molasses, propylene glycol, volatile fatty acids (acetic, propionic, lactic)
- Inoculum for SRB and other necessary bacteria needed – Dairy cow or other manures
- Often limestone mixed with substrate to increase buffering capacity

MIW Chemistry

Site		Barker-Hughesville		Blue Ledge		Formosa	Bunker Hill		Tenmile
MIW		Danny T Adit		DR0-01 Drainage		Formosa Adit	Rex Adit	Success Adit	National Extension Adit
Analyte	Units	Year 1 AVG	Year 2 AVG	Year 1 AVG	Year 2 AVG	Year 1 AVG	April 2014	Historic AVG	November 2014
		T	T	T	T	T	T	T	T
Aluminum	ug/L	15,750	13,390	20,046	17,960	13,560	32	114	80
Arsenic	ug/L	237	188	5	2	50	3	0.4	202
Cadmium	ug/L	222	255	120	127	165	32	211	19
Copper	ug/L	1,610	1,023	14,613	13,780	4,536	4	13	61
Iron	ug/L	154,000	154,900	4,604	4,111	158,400	25	151	4,480
Lead	ug/L	257	185	9	4	28	430	58	180
Nickel	ug/L	34	35	260	244	38	3	16	<6
Zinc	ug/L	58,350	57,180	21,378	22,950	65,120	6,500	45,594	3,080
Acidity	mg/L	637	667	226	217	NM	<2	NM	12
Alkalinity	mg/L	<1	<10	<10	<10	<5	15	89.0	29
Sulfate	mg/L	1,983	1,116	462	524	1,936	36	255.5	40
pH	su	2.8	2.6	3.1	3.2	3	5.4	6.6	6.2

Study Questions and Goals

Goal is implement passive or semi-passive treatment systems with low maintenance at remote high elevation abandoned mine sites

1. What is the metal removal efficiency?
2. What is the extent of sulfate reduction?
3. What is the necessary BCR hydraulic retention time?
4. What pre-treatment methods are needed for different MIW types?
5. What is the minimum sulfate required for adequate metal sulfide formation?
6. What sulfate addition methods can be used to increase influent sulfate?
7. How do lower temperatures effect BCR performance?
8. What post-treatment methods can be used to reduce nutrients and increase dissolved oxygen?

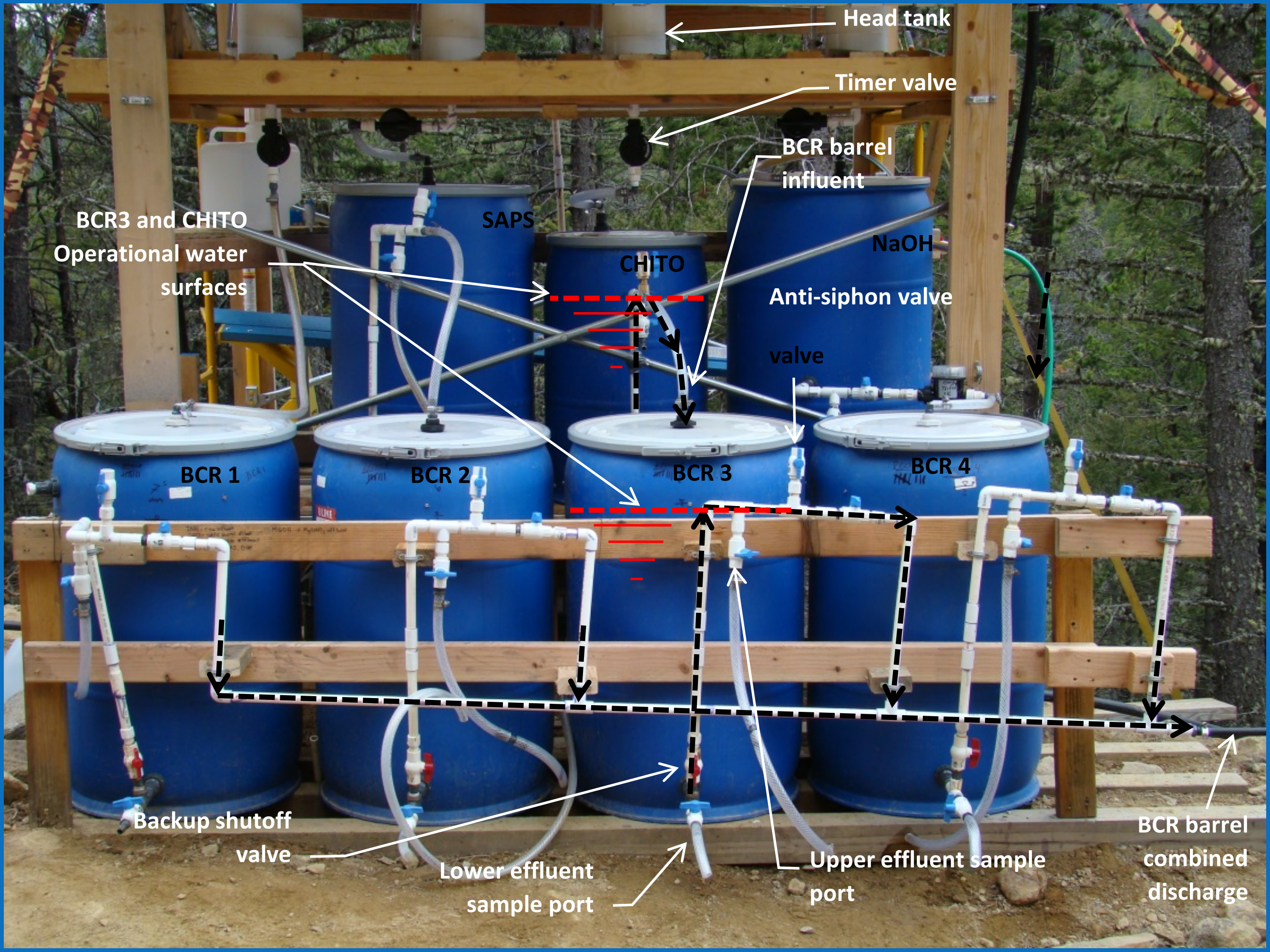
Study Test Setup

Site	Blue Ledge (2012-2013)	Barker-Hughesville (2013 - 2014)	Formosa (2013)	Bunker Hill (2014)	Tenmile (2015)
MIW	DR-01 Drainage	Danny T Adit	Formosa Adit	Rex and Success Adits	National Extension Adit
Acidic MIW?	X	X	X		
Laboratory BCR Batch	X	X			
Laboratory BCR Column			X	X	X
Field Pilot (Barrel-Scale)	X	X	X		
Liquid BCR Substrate	X			X	
Pre-Treatment	X	X	X		X
Low-Sulfate				X	X
Low-Temperature	X	X			X
Post-Treatment	X	X			

- Studies completed between 2012 and 2015
- Various phases of testing based on project status, funding, and goals
- Earlier studies provided lessons learned for later studies
  - Similar MIW types, substrates, flow rates, pre-treatments, etc.

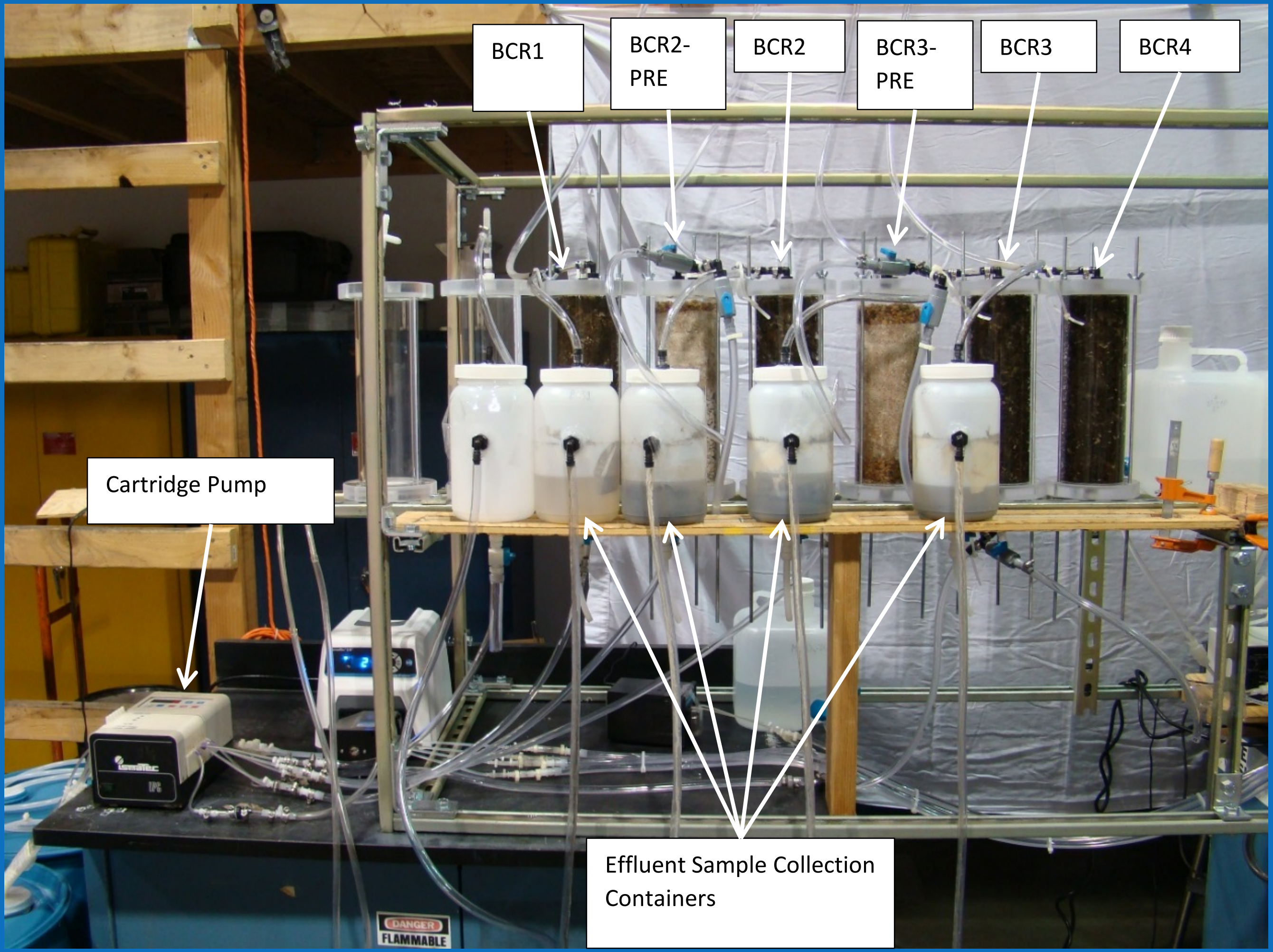
Barker Hughesville, Danny T Year 2 – Barrel Test Setup

- Example of complex barrel test setup with pre-treatment



Bunker Hill, Rex Adit – Column Test Setup

- Example of column test setup with sulfate addition pre-treatments



Pre-Treatment Methods

SAPS	
Material	Substrate Mix (v/v %)
Inert Gravel	7.5%
Compost	12.5%
Manure	12.5%
Limestone	67.5%

- Oxidation/Settling
  - Crucially important for high Al/Fe/Pb waters to maximize metal oxyhydroxide formation and settling
- Successive Alkalinity Producing System (SAPS)
  - Limestone layer overlain by organic substrate
  - Recommend adding inert gravel and/or wood chips to upper organic layer for structure
- Chitorem+Sand+Gravel
  - Construct and operate similar to SAPS
- Alkaline Addition
  - Magnesium hydroxide, sodium hydroxide, lime
  - Requires semi-passive system (e.g., solar, wind, water power) and greater O&M
- Sulfate Addition
  - For low-sulfate type MIWs – e.g., less than ~100 mg/L
  - Gypsum cell
  - Magnesium sulfate solution dosing

Evaluating Metal Removal Mechanisms

How do we know metals are removed through sulfate reduction and metal sulfide formation vs. sorption or other precipitation reactions?

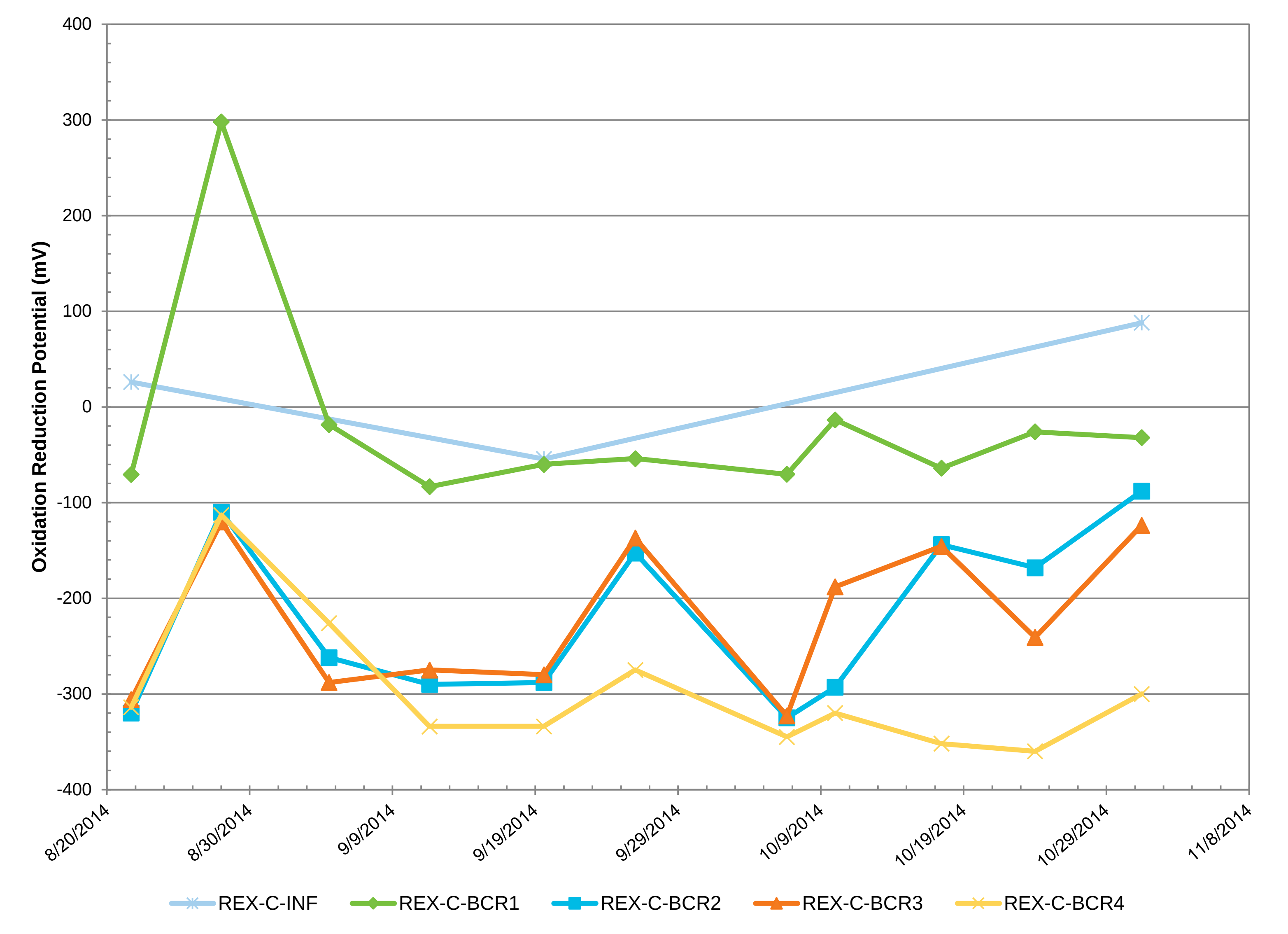
- Correlate field and analytical laboratory results with metal removal efficiency (MRE)
- Oxidation-reduction potential (ORP), dissolved oxygen (DO), pH, and temperature
- Sulfide, sulfate, and sulfate reduction rate (SRR)
- Acidity and alkalinity
- Microbiology analysis DNA/RNA
- Organic acids
- Electron microprobe of substrate or precipitate
- Sulfide smell!

Oxidation-Reduction Potential and Dissolved Oxygen

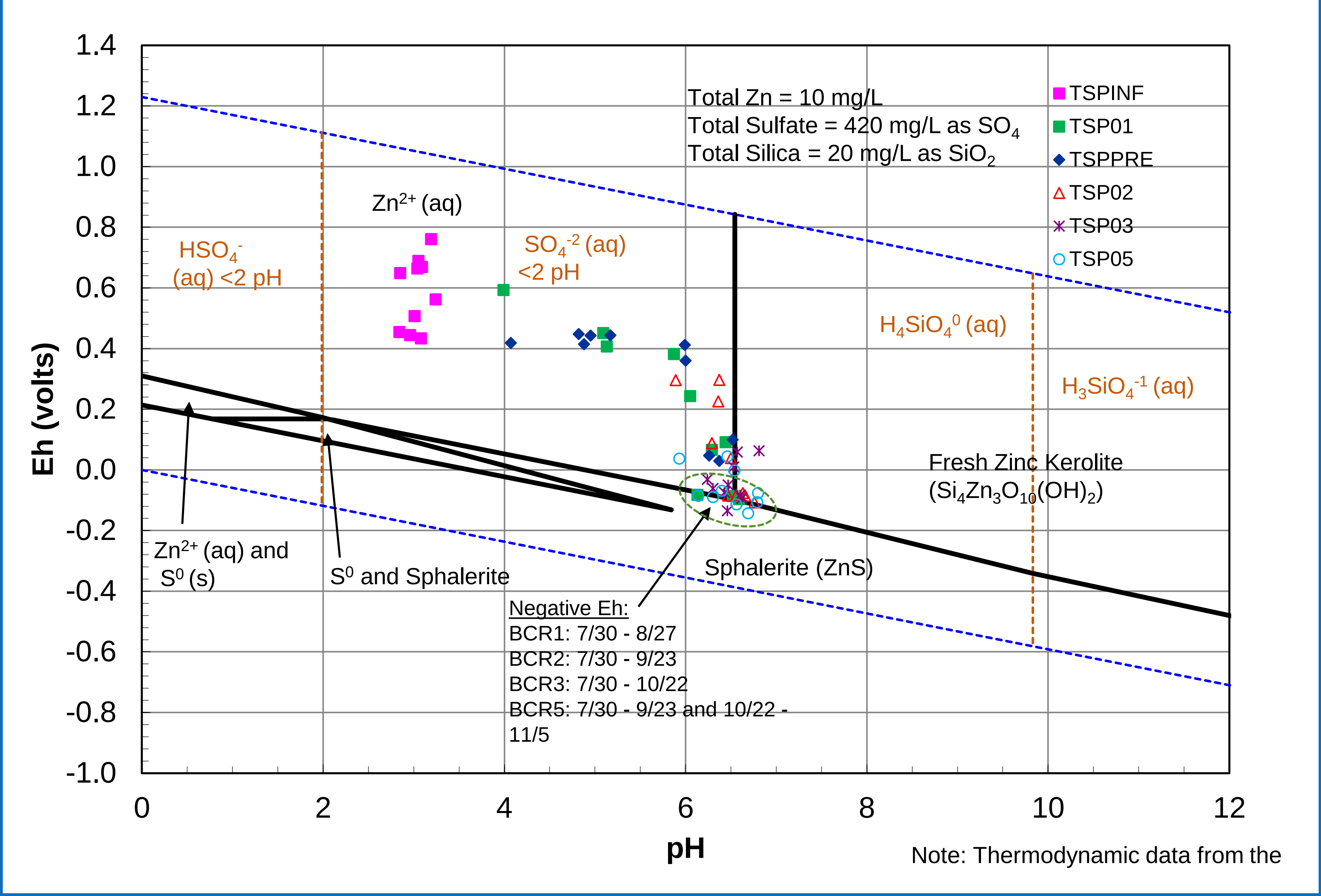
Increased DO and ORP could are stress triggers that effect system performance

- General rule of thumb: < -150 mV ORP conditions amenable to sulfate reduction
- Typical ORP from -200 to -400 mV correlates very well with:
  - Detectable sulfide in the effluent (e.g., >1 mg/L)
  - Positive sulfate reduction rate (e.g., >100 mmol SO_4/m^3-day)
  - Alkalinity generation (e.g., >200-300 mg/L)
  - High and consistent metal removal efficiency (e.g., >90%)
- General rule of thumb: DO less than 2-3 mg/L
- Some DO probes can produce unreliable results
- Utilize optical DO meter if possible

Rex Mine – ORP Results



Blue Ledge Year 2 – Eh/pH Diagram for Zinc Species



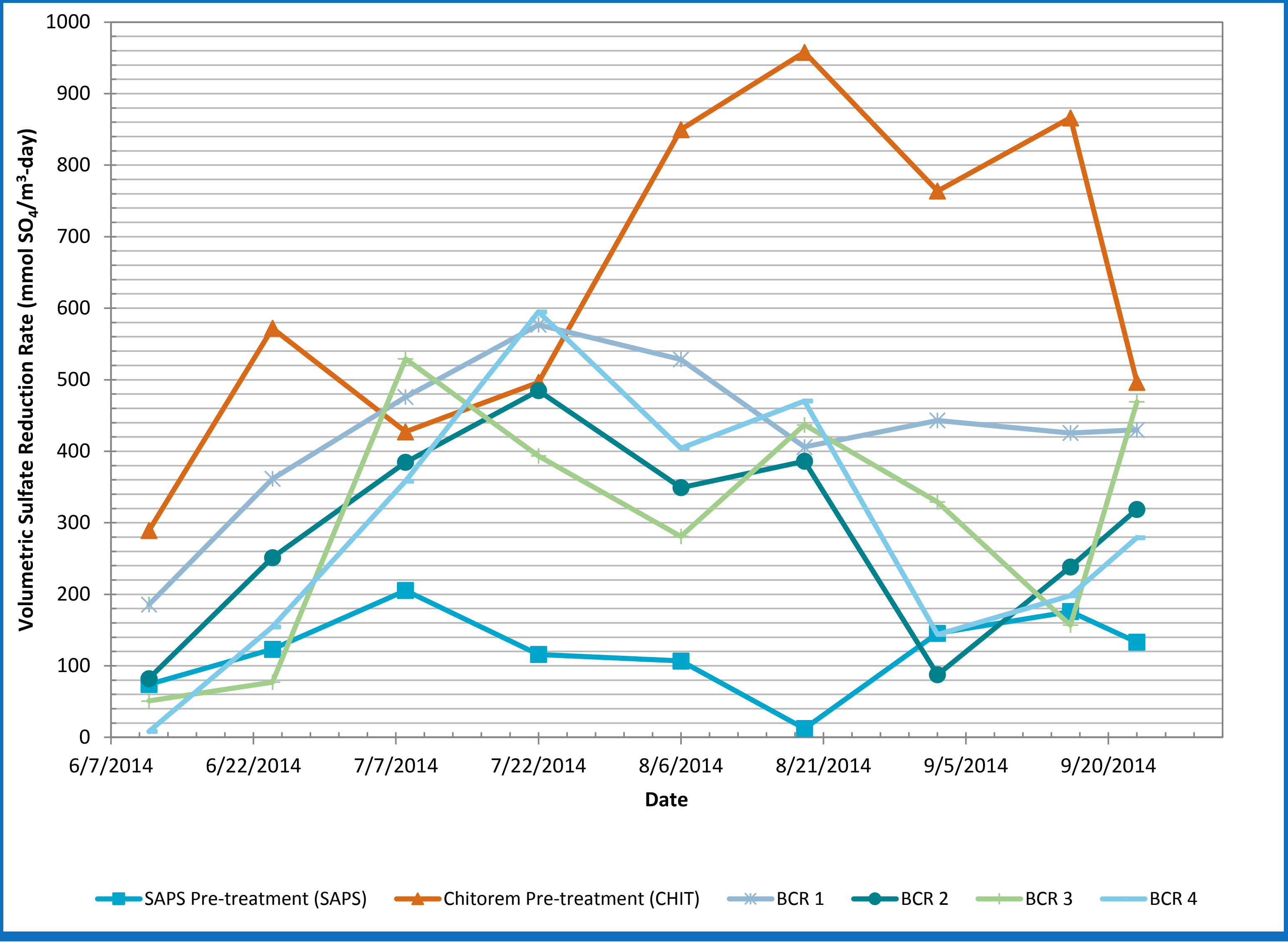
Sulfate Reduction Rate (SRR) and Sulfide

- Use sulfate reduction rate for design sizing – still a good approach after 30 years!
  - Numerous studies have calculated SRR within range of 100 to 1000 mmol SO_4/m^3-day
  - ~300 mmol SO_4/m^3-day good starting design parameter
  - Calculate BCR reactive substrate volume based on metal load and SRR

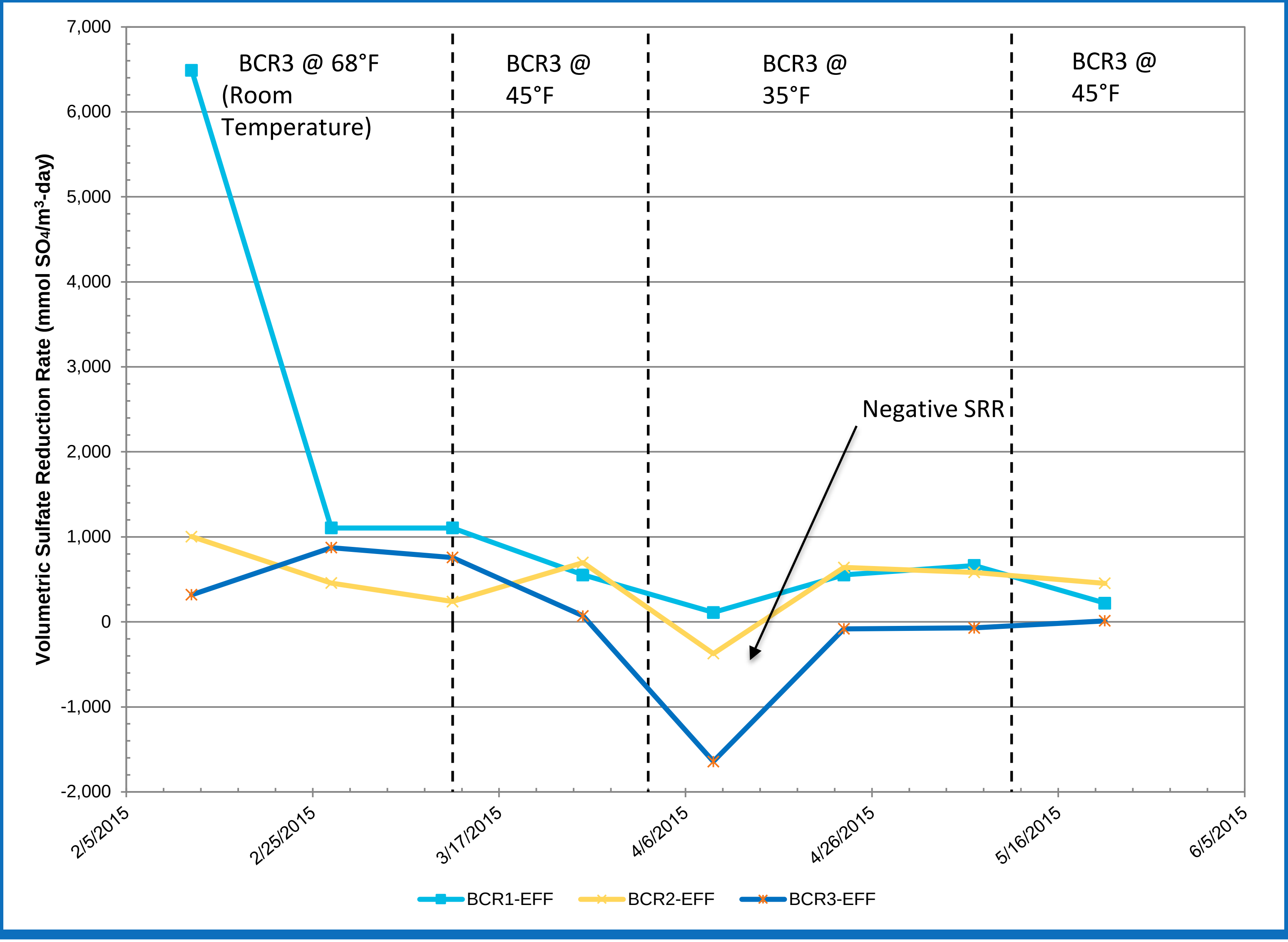
$$R_{SO4} = \frac{C_{SO4\ IN} - C_{SO4\ OUT}}{M_{SO4} \times V_s} \times Q_d$$

- Usually always excess sulfide not bound with metals in the effluent – quickly converts to hydrogen sulfide gas when exposed to atmosphere

Barker Danny T Year 2 – Sulfate Reduction Rate



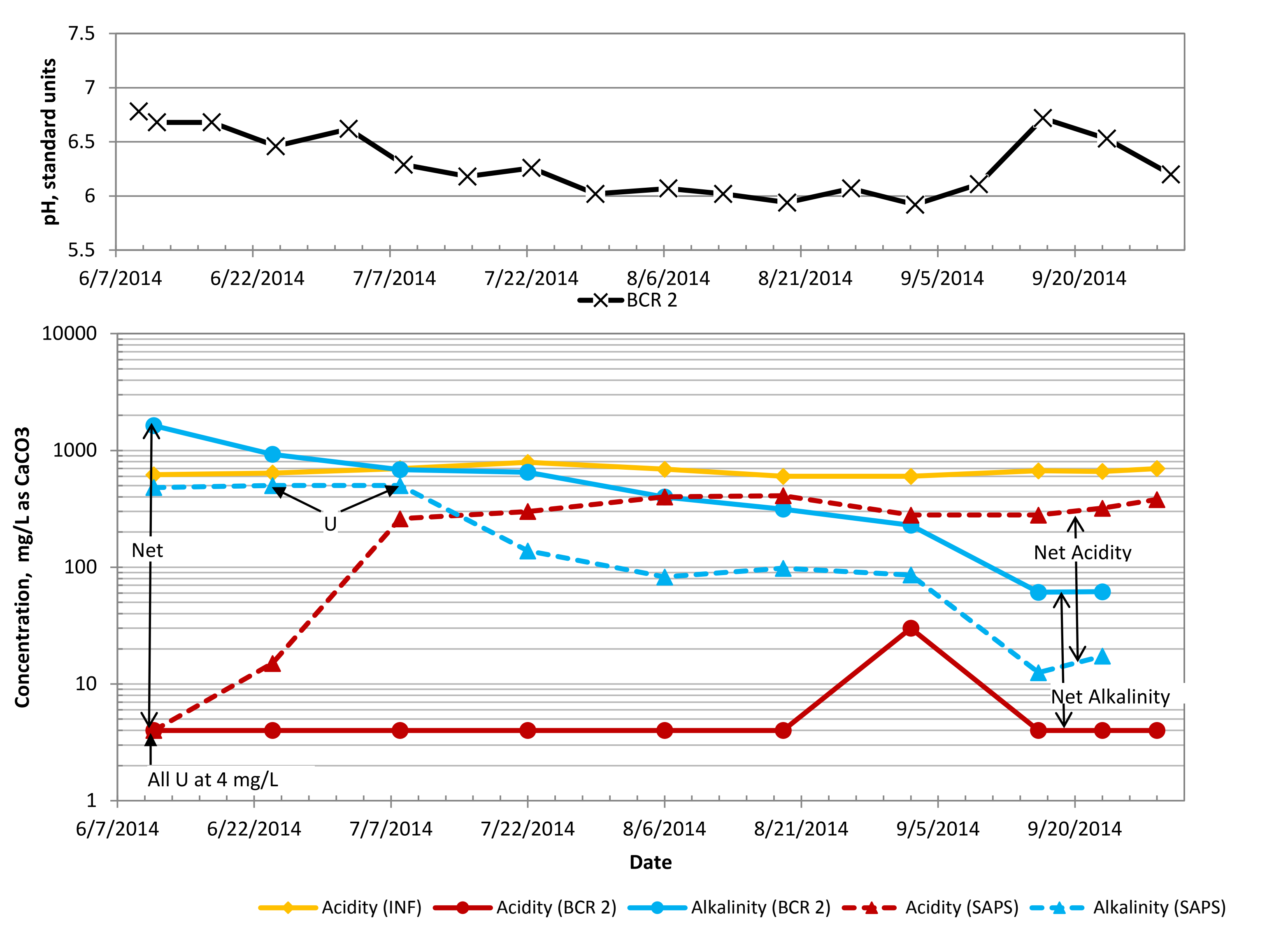
National Extension – Sulfate Reduction Rate



pH, Acidity, and Alkalinity

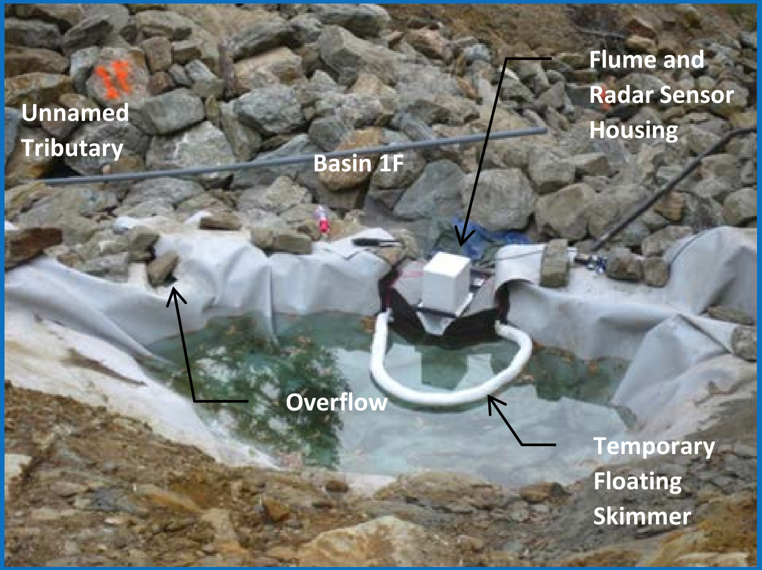
- System should be generating enough alkalinity through sulfate reduction to buffer acidic pH, in addition to limestone dissolution
- Acidity in acidic MIW should go to non-detect (typically >4 mg/L)
- Treated effluent pH should be above 6.0 for an acidic MIW (i.e., less than 4 su)
- Difficult to discern how much alkalinity is being generated by sulfate reduction or limestone dissolution
- Acidity can be generated through anaerobic fermentation of carbon sources - VFAs
- Evaluate acidity/alkalinity balance for performance

Barker Danny T Year 2 – SAPS/BCR2 pH, Alkalinity, and Acidity



BCR System Stresses

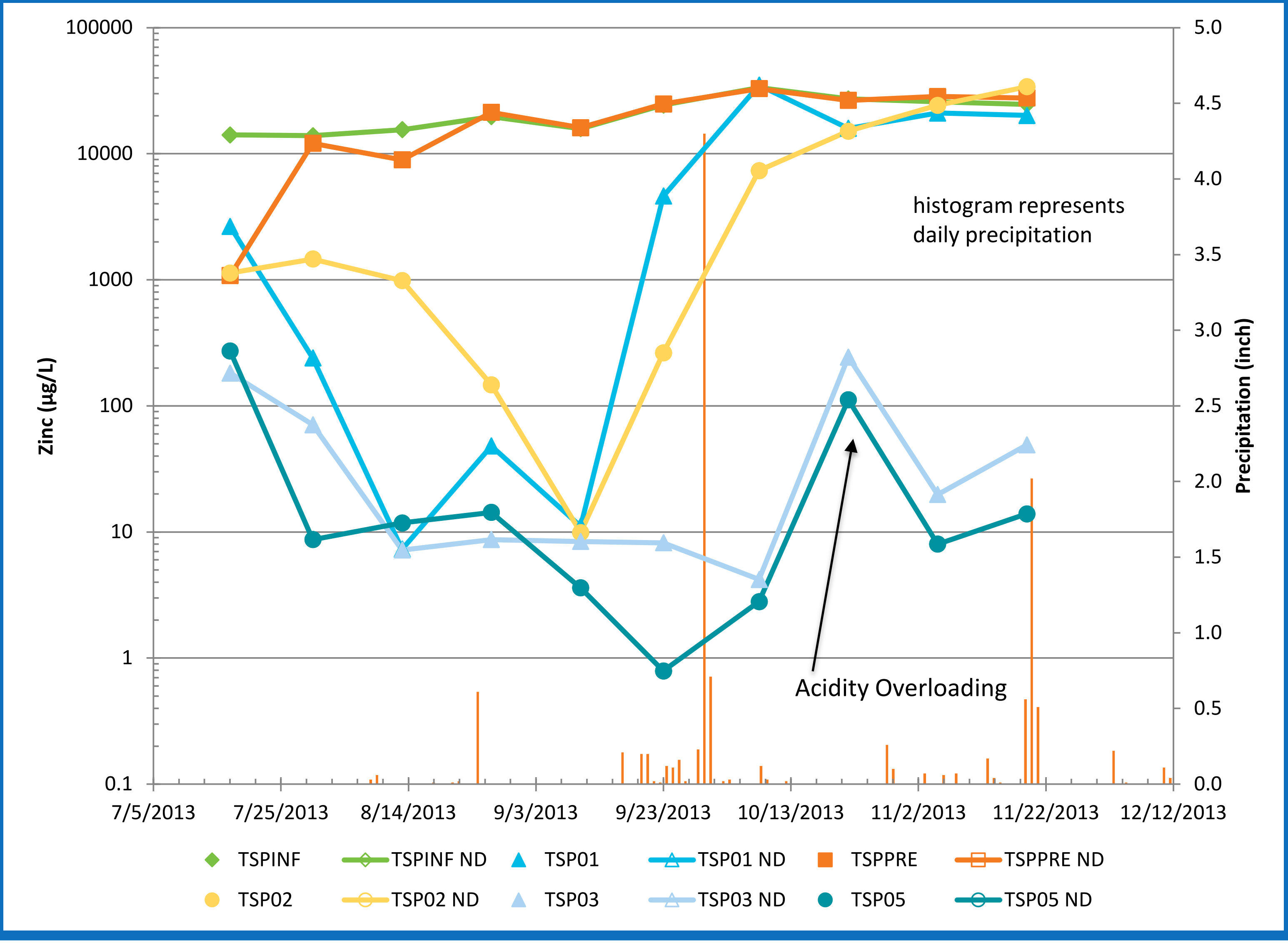
- Oxygen and Acidity (pH, Al, Fe)
  - Increased seasonal acidity and oxygen loads can shock BCR system
  - Acidity loading leads to plugging
  - Use pre-treatment for acidic/low-pH MIWs to reduce acidity and protect BCR
  - Design system based on sulfate reduction rate and metal loading
- Temperature
  - Sulfate reduction slows at lower temperatures
  - Decreased sulfate reduction and metal removal during winter likely – plan for in design



Operations and Maintenance

- Lab Column Limitations
  - MIW chemistry changes during storage
- Acidic MIW – issues with plugging of valves and plumbing
- Weekly inspection and sampling highly recommended
- Startup
  - Incubation and startup during warmer weather
  - Manual recycle of MIW helps spread inoculum and saturate pores
  - Provide incubation with no flow (1-2 weeks)
  - Allow at least week or more after flow through startup before first analytical sample
- Study Period
  - Sufficient time to establish sulfate reducing condition reactions
  - At least 3 months recommended

Blue Ledge Year 2 – Dissolved Zinc Concentrations



Substrates

- Plant-Based Materials
  - Variable mix recommended for structure and short-and-long term carbon sources
- Manure
  - Need to optimize inoculum needed while limiting excess BOD and nutrients in effluent (1-10%)
- Limestone
  - Higher limestone needed for acidic MIWs (20-30%)
  - Some limestone still needed for neutral MIWs due to acidity from organic acids
- Chitorem
  - Effective neutralizing capacity and organic substrate for maintaining sulfate reduction
  - No inoculum needed – has it's own SRB
  - Many potential uses as pre-treatment to BCR or mixed with other BCR substrates
  - Hydraulic limitations with fine-grained product (97% < 2mm) – recommend larger sized material
  - Locality and cost limitations
- Ethanol
  - Enhanced sulfate reduction rate and smaller footprint
  - Potentially less diverse microbial community leads to inability to adapt
  - Cost and need for semi-passive dosing system
  - Difficult to optimize minimum dose, while minimizing excess BOD in effluent

Questions?

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