SOVEREIGN CONSULTING INC.
AN ENVIRONMENTAL SERVICES FIRM

Sulfate Removal in Biochemical Reactors and Scrubbers Treating Neutral Low-Metal Concentration MIW

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ASMR NATIONAL MEETING – MORGANTOWN, WV

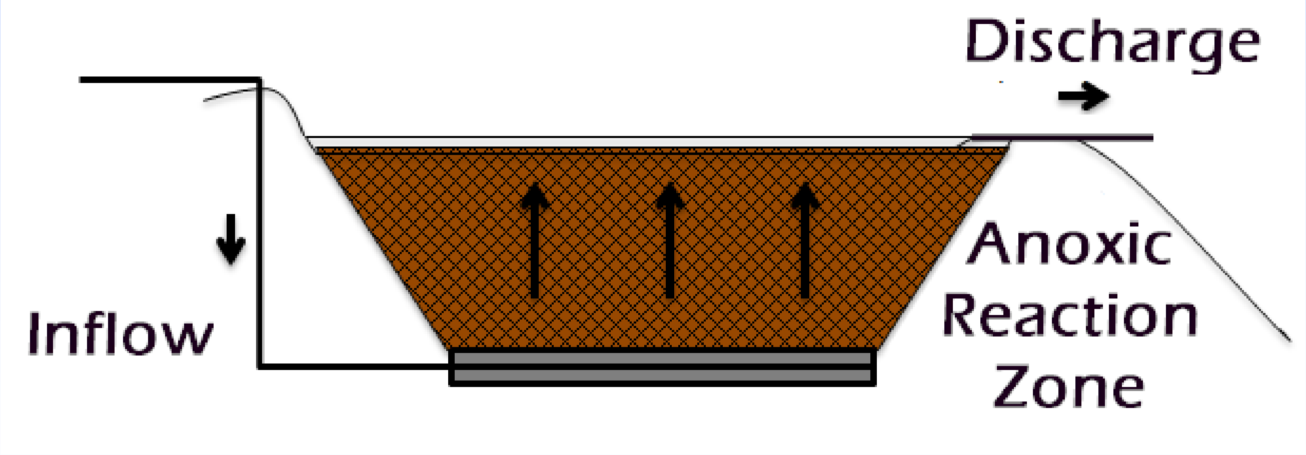
Background

- Active mine site
- mining influenced surface water
- circumneutral pH.
- 3000 mg/L sulfate,
- low metal concentrations
- Sulfate limit 250 mg/L

Background

- ❑Biochemical Reactors (BCRs)
- ❑Treat water via sulfate reduction

Upflow Biochemical Reactor



Passive Treatment Chemistry 101

- Sulfate reduction:

$$SO_4^{2-} + 2\ CH_2O \longrightarrow HS^- + 2\ HCO_3^- + H^+$$

- Metal sulfide precipitation:

$$Me^{2+} + HS^- \longrightarrow MeS + H^+$$

If there is not enough M^{+2} H_2S will be lost as a gas

Background

- Sulfate Polishing Units (SPUs) proposed to remove residual hydrogen sulfide/sulfide.

Objectives

Primary Goals

- Test Passive Treatment concept at bench scale using MIW from the site to remove sulfate and meet a 250 mg/L standard
- Test which organic media mixtures in the BCRs were more efficient in removing sulfate.
- Evaluate sulfate removal under varying MIW flow/loading rates

Objectives

Secondary Goals

- ❑ Determine if one of the three solids as inorganic media in the SPUs remove hydrogen sulfide/sulfide.

- ❑ Estimate the longevity of the different organic mixtures in the BCRs

Substrate Selection

- Want reactive substrate
  - Need large reduction in sulfate
  - Need larger systems
- Locally available
- Inexpensive

Treatment Train Mixtures and Materials

Biochemical Reactors (BCRs)

Material	BCR 1	BCR 2	BCR 3
Biochar	0%	0%	10%
Wood Pellets	0%	20%	40%
Limestone	10%	10%	10%
Oat Straw	85%	65%	35%
Animal Manure	5%	5%	5%
Total	100%	100%	100%

Materials Used in BCRs

Straw

Wood Pellets

Deer Manure

Biochar

Treatment Train Mixtures and Materials

Sulfide Polishing Units (SPUs) or Scrubbers

Material	SPU	Quantity
Soil/Rock	SPU 1	1.9 kg
Scrap Metal (Steel cans)	SPU 2	6.1 kg
Magnetite (granular)	SPU 3	4.1 kg

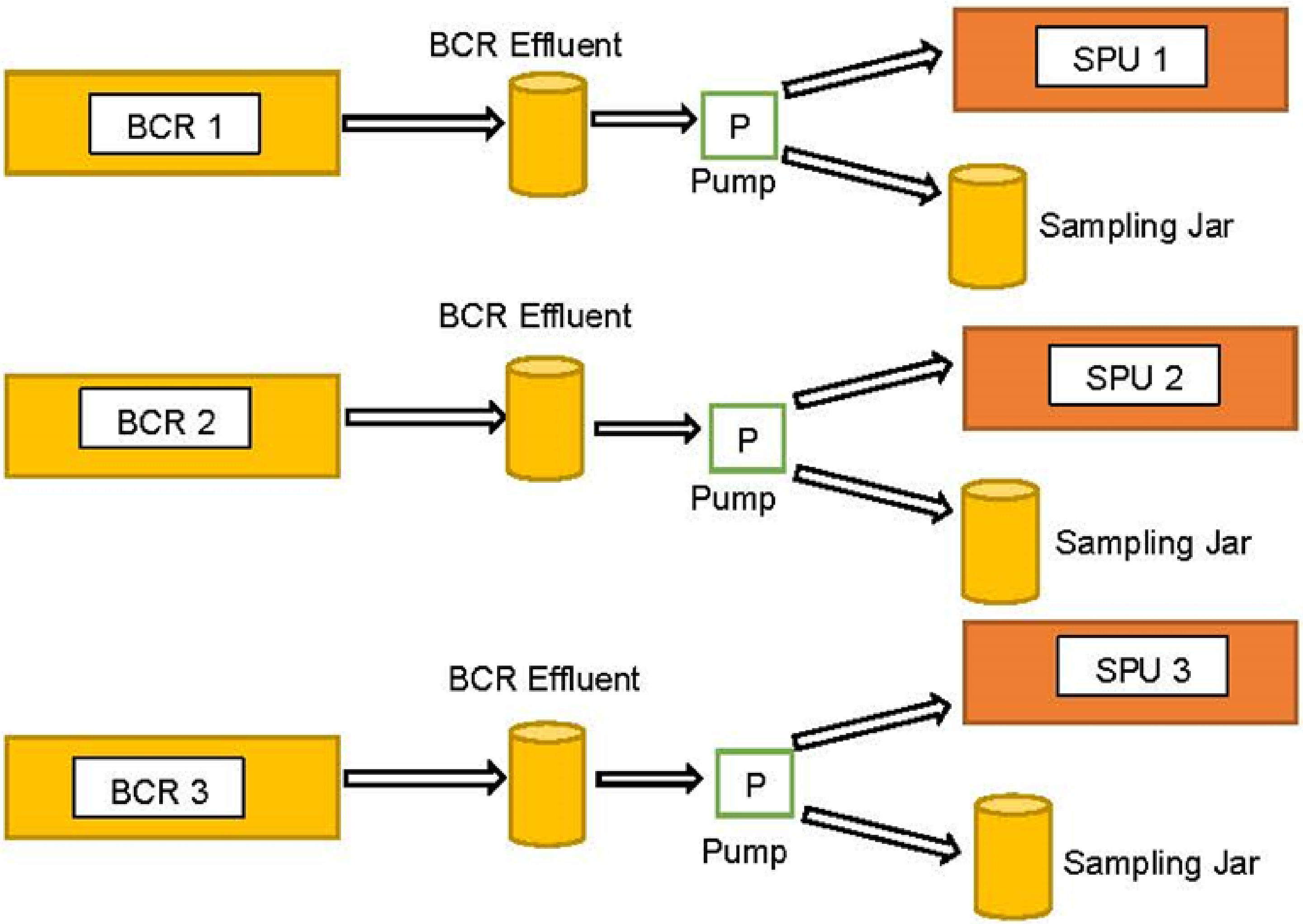
Materials Used in SPUs

Site Soil

Scrap Metal

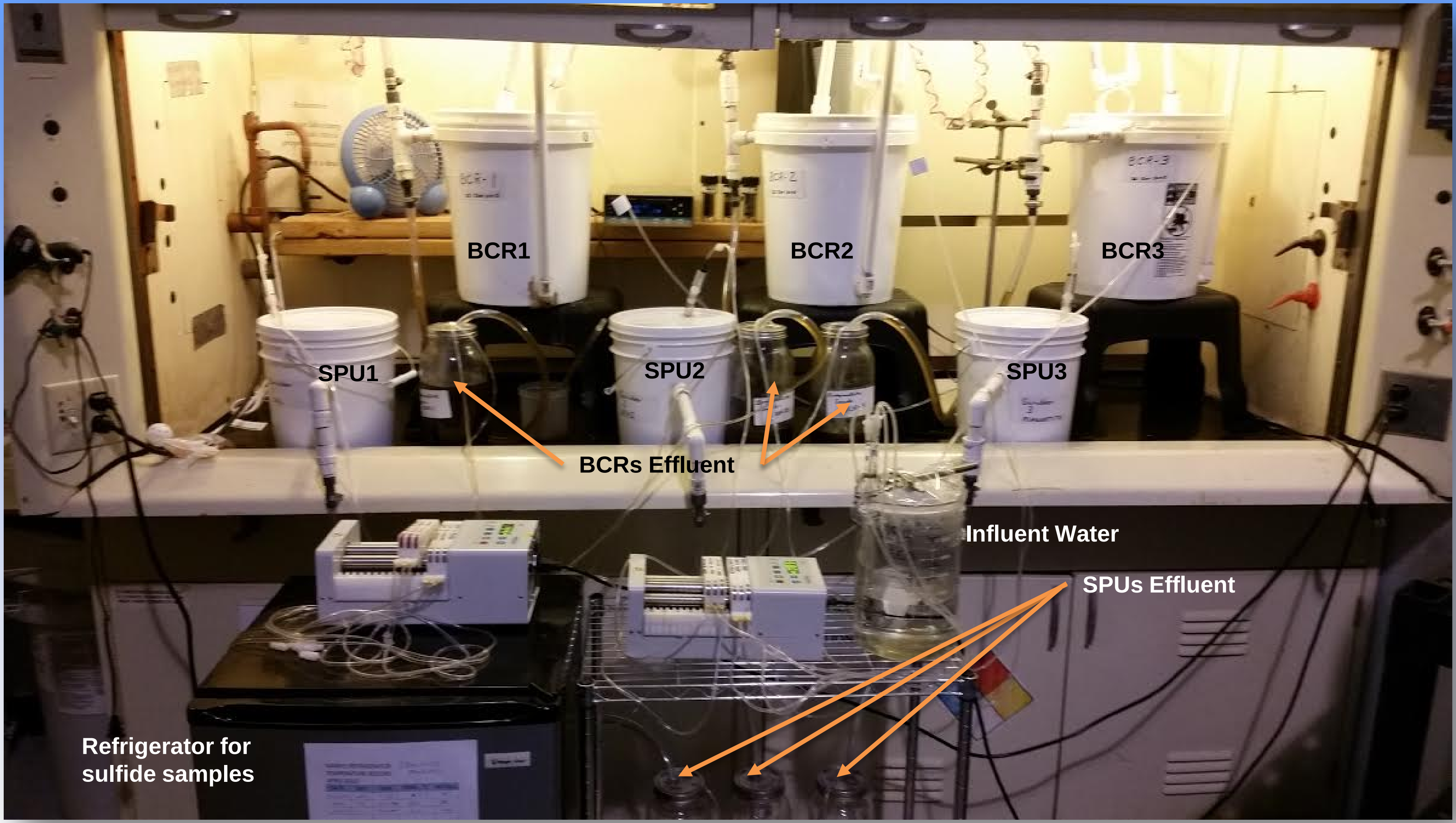
Magnetite

Bench Scale Process



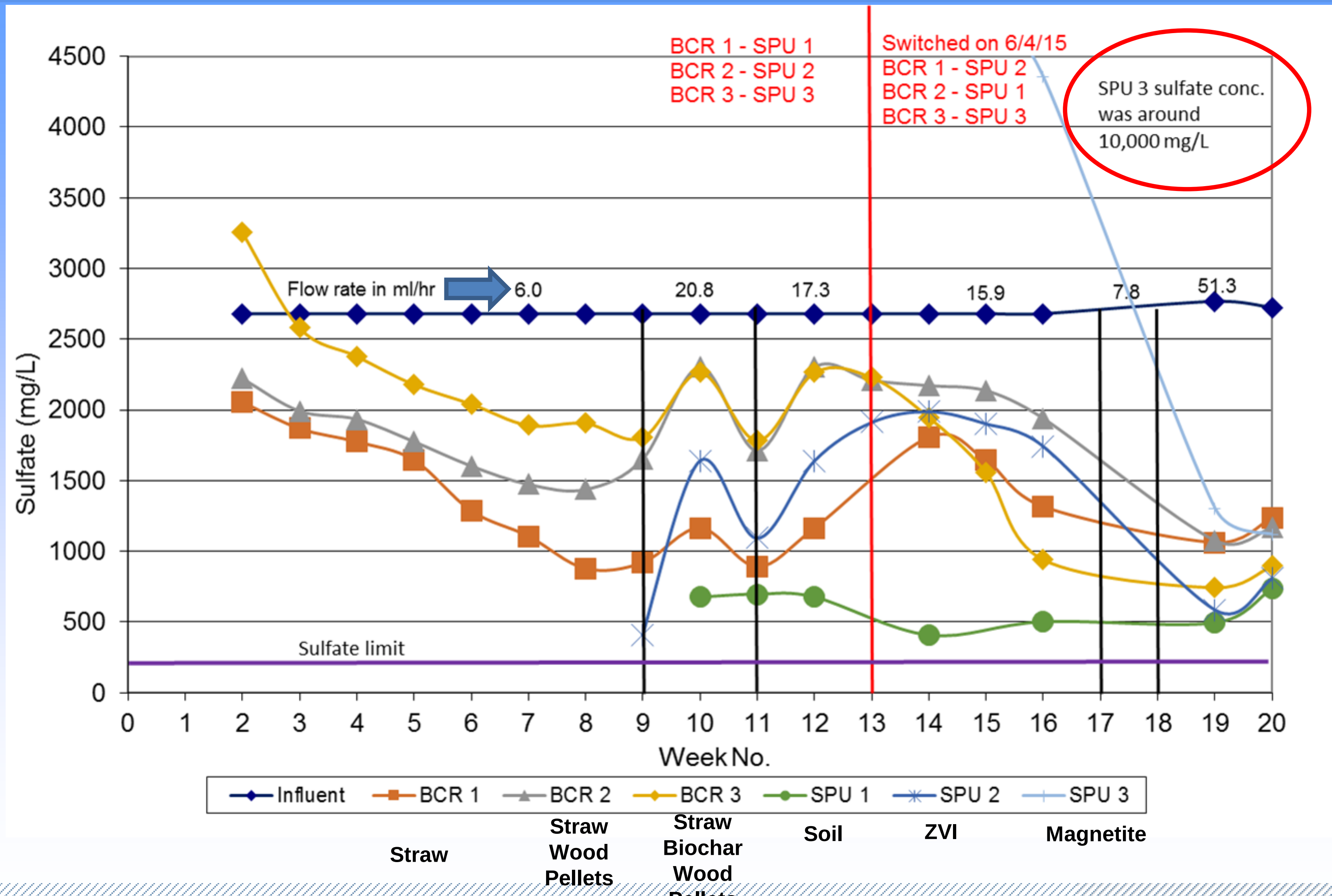
BCR: Biochemical Reactor
SPU: Sulfide Polishing Unit or Scrubber

Bench Scale Set-up

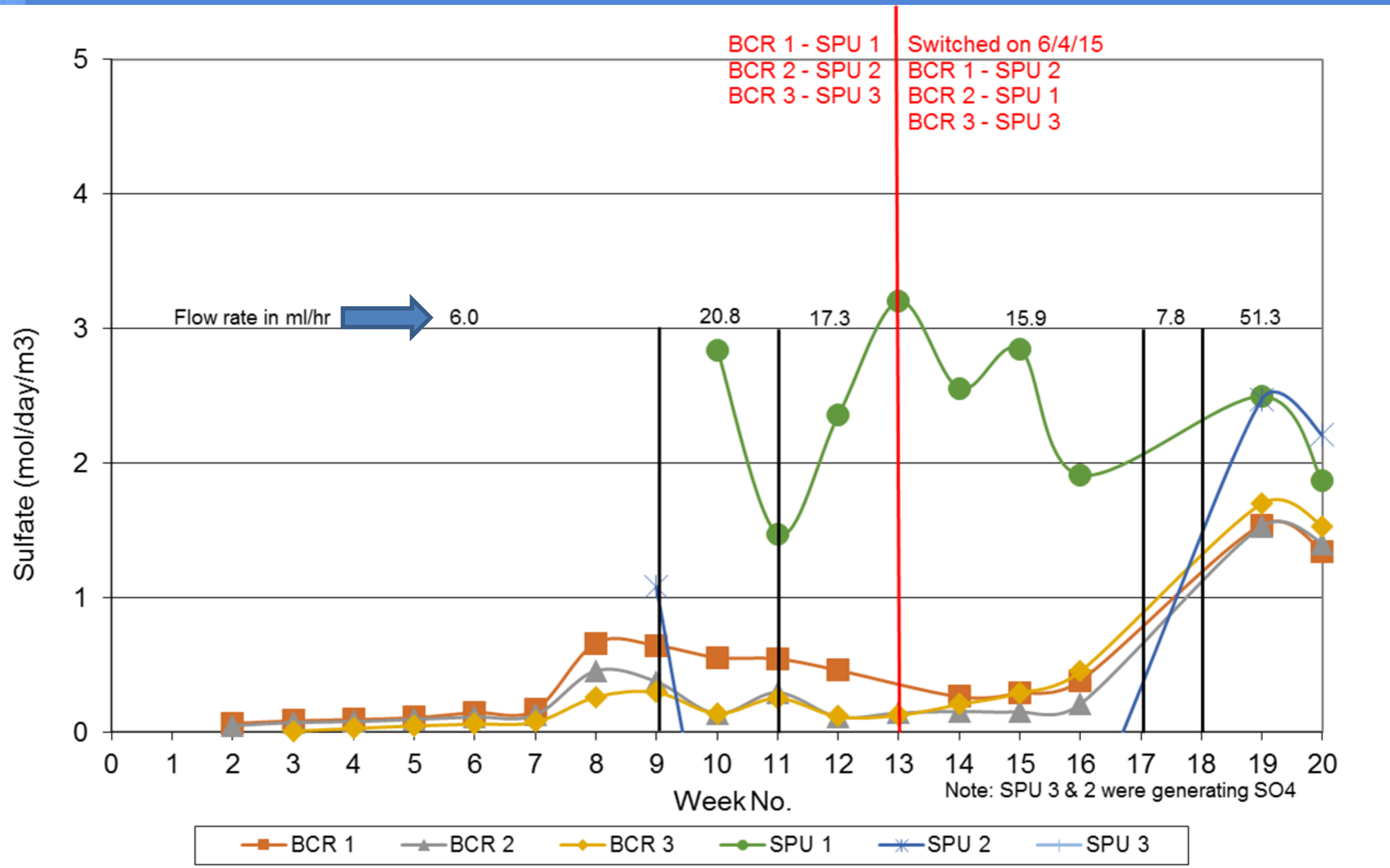


Solfatara Laboratories LLC

Sulfate Removal



Sulfate Removal



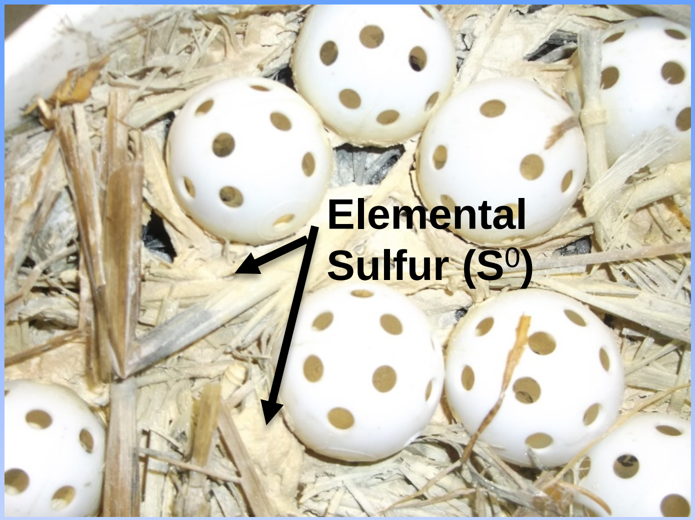
Straw **Straw Wood Pellets** **Straw Biochar Wood Pellets** **Soil** **ZVI** **Magnetite**

BCRs Longevity

BCR Cells Substrate Longevity

BCR	Carbon (kg)	Average Carbon Consumption (g/day)	Bench Longevity (years)	Projected Full Scale Longevity (years)
1	0.4	0.16	3.0	18
2	0.6	0.11	5.2	31
3	1.2	0.13	9.1	54

BCRs & SPUs Autopsies



S^0 on top of all BCRs

No S^0 in SPU1

No S^0 in SPU2

Top of BCR

BCR1 Cross Section

What Did We Learn?

- All BCRs were able to achieve sulfate removal rates of 1.3 to 1.5 mol SO_4^{-2} /m^3-day.
  - Much higher than the "typical" design rate of 0.3 mol SO_4^{-2} /m^3-day

- Higher sulfate removal rates were achieved in the SPU1 and 2, 1.9 and 2.2 mol SO_4^{-2} /m^3-day, respectively.

- None of the BCR mixtures provided sufficient microbial activity to meet the 250 mg/L sulfate standard

What Did We Learn?

- Sulfate was removed as elemental sulfur in all BCRs. Likely the result of HS^- under microaerophilic conditions.
- Only low to non detect levels of H_2S & S^{-2} were measured in effluent
- No S^0 on top of SPU 1 & 2. However, within the pH range in the SPUs, HS^- oxidation possibly to thiosulfate, a soluble S compound (Hughes et al. 2009).

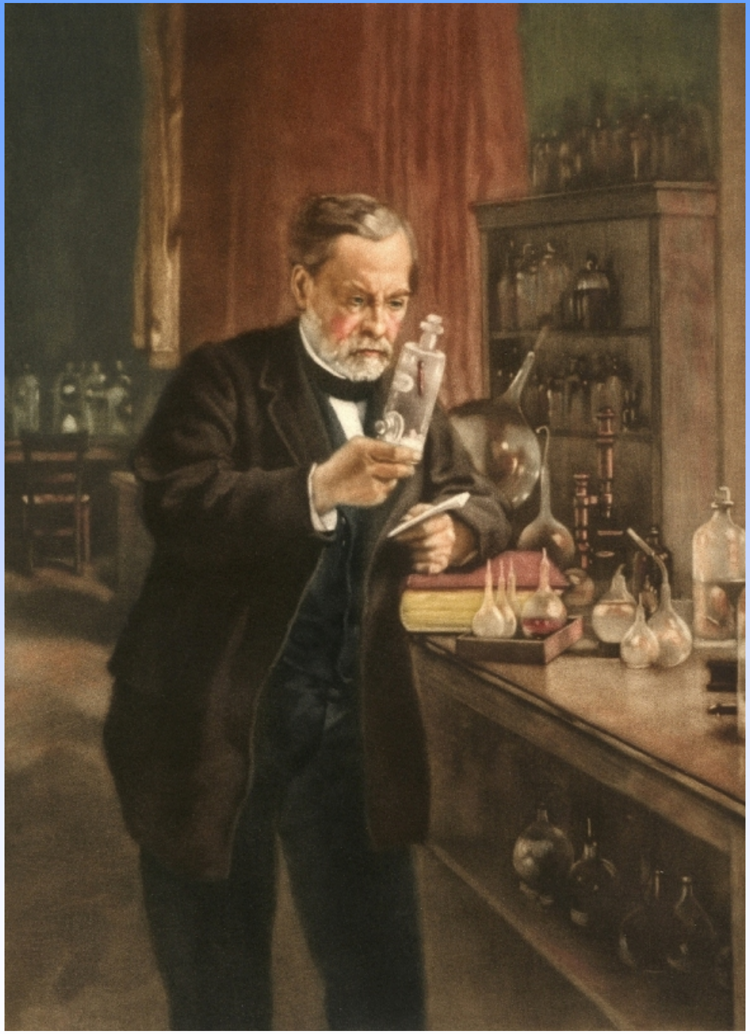
BCR Longevity Findings

- BCR1 (straw-dominated) longevity may be too short to be worth considering for full scale design.
- Projected BCR2 (straw & wood pellets) longevity for a full scale plant is consistent with the longevity estimates at other mining sites.
  - Chosen for full scale
  - Pellets replaced by wood chips
- Biochar did not appear to substantially increase reduction rate

SPUs Findings

- SPU3- released high levels of sulfate suggesting contamination of magnetite
  - Results not included
- SPUs were operated to remove residual hydrogen sulfide/sulfide but they also removed more sulfate.
- SPU1 (site soil) removed sulfate at a higher rate than other media throughout the test.
  - Used for final design

Thank You



“In the fields of observation, *chance favors* only *the prepared mind*.”

L. Pasteur

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Chemistry 101

- Sulfate reacts with organic carbon
  - Produce hydrogen sulfide and bicarbonate
  - Hydrogen sulfide reacts with metals
  - Produce metal sulfide and hydrogen

$$SO_4^{-2} + 2\ CH_2O \ = \ H_2S + 2\ HCO^-_3$$

$$H_2S + M^{+2} \ = \ MS\ (solid) + 2H^+$$

- Limestone is often necessary
  - Increase the alkalinity
  - Consume hydrogen
  - Thus raise the pH

$$2H^+ + 2HCO_3^{-1} \ = \ 2\ H_2CO_3$$

$$2H^+ + CaCO_3(solid) \ = \ Ca^{+2} + 2HCO_3^{-1}$$

- If there is not enough M^{+2}
  - H_2S will be lost as a gas

Background

Sulfate reduction

$$SO_4^{-2} + 2\ CH_2O\ =\ H_2S + 2\ HCO_3^-$$

$$H_2S + M^{+2}\ =\ MS\ (solid) + 2H^+$$

If there is not enough M^{+2}

H_2S will be lost as a gas

SPUs Findings

- SPU1 & 2 were like mini-BCRs in series with the BCRs, using discharged organic C to promote microbial activity and the organic material provided support.
- No S^0 on top of SPU 1 & 2. However, within the pH range in the SPUs, HS^- oxidation possibly to thiosulfate, a soluble S compound (Hughes et al. 2009).

Conclusions

- The magnetite we used appeared to be contaminated and was not an effective media for sulfate removal.
- Sulfate percent removal in the SPUs was: 35% (SPU1 paired with BCR2) and 37% (SPU2 with BCR3).
- BCR2 and 3 substrate mixtures appear to provide reasonable longevity values.