SOVEREIGN CONSULTING INC.
AN ENVIRONMENTAL SERVICES FIRM

SULFATE REMOVAL FROM COAL MINE WATER IN WESTERN PENNSYLVANIA: REGULATORY REQUIREMENTS, DESIGN AND PERFORMANCE

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Outline

Part 1

- Regulatory background on sulfate in mine water discharge
- Analysis of existing technologies to treat sulfate
- Design considerations in Sulfate Bioreactors

Part 2

- Pilot Test System Design, Construction, and Startup
- Pilot Test System Performance
- Future Considerations in Large-Scale Design

Part 1. Regulatory Review

NPDES Permitting of Mine Discharges

- Historically required pH and metals to comply with WQS
  - Accomplished with a lime treatment plant
- Permit renewal process and Monongahela River listing for sulfate occurred almost simultaneously
- Listing of Monongahela for sulfate based on lack of assimilative capacity resulting in no additional sulfate
- The 250 mg/L target was the default discharge value

Mine Water Characteristics

• **Sulfate**	**3000 mg/L**
• **Iron**	**120 mg/L**
• **Mn**	**2 mg/L**
• **pH**	**7 - 8**
• **Alkalinity**	**600 mg/L**

Regulatory Impacts

- New regulatory discharge limits affect water treatment
- A review of available technology.
  - Chemical methods
  - Membrane methods
  - Biological methods
- Reverse Osmosis (RO) was recommended method for removing sulfate and other salt.
- Propose Sulfate Reducing Bioreactors (SBR) as an alternate, less expensive technology compared to RO and others

SRB Small Field Pilot

SRB Field Pilot Test

SRB Small Field Pilot

SRB Cost Analysis

Capital Costs	**$5,000,000**
O & M	**$200,000/yr**

- **-Full-time operator**
- **-Carbon source utilization**
- **-Power**

5 yr cost	**$6 MM**
RO 5 yr cost	***>$41 MM***

Technology Selection

- **Mining Co. negotiated a Consent Order that allowed the development of SRB technology for treating sulfate in mine water discharge**
  - Year long pilot - 2015
  - Full scale design and construction - 2016
  - Full scale operation by 2018
  - Transfer technology to State abandoned mines in 2018
  - Performance criteria – sulfate removal that results in equivalent mass removal as discharge limit per year
    - Additional mass “credits” from treating State mine water could be used
  - Plan B description – if preferred technology fails

SRB Design Considerations

- **Pilot tests demonstrated sulfate reduction was possible to the target levels. However, a number of issues needed resolution to complete a full-scale design.**
  - Identify a design sulfate reduction rate
  - Determine best carbon source for maintaining reduction rate and longevity
  - Assess media options to prevent flow changes and plugging from metal sludge loading
  - Examine systems for residual handling (metals, sulfide gas, and ^{0}S)
  - Minimize O+M costs for partially “sustainable” and cost-effective system

Sulfate Reduction Rate

- **What sulfate reduction rates are attainable?**
  - Literature based sulfate reduction rates 250-1000 mmol sulfate/m3 reactor-day
  - Variations in reduction rate with temperature
  - Consent order allows for mass reduction per year without meeting concentration based discharge limit (250 mg/L)
  - Pilot test would determine attainable rates
  - Sized pilot for 1000 mg/L reduction in sulfate assuming 500 mmol SO4/m3 reactor-day rate
    - Twin 6'x30'x120' reactors
    - Size can be a limiting factor

Carbon Utilization/Longevity

- **SRB Carbon Source**
- **Solid carbon media**
  - Wood chips, manure, compost
  - Cheap
  - No ongoing O+M
  - Media is utilized over time and may need to be dug out and replaced
  - Difficult to control utilization rate to achieve COD/sulfate ratio
  - Media can plug due to metals loading and degradation
- **Liquid carbon media**
  - Ethanol, molasses, lactate
  - Can be metered/dosed in at desired rate
  - Easy to refill a tank
  - Mitigates freezing issues
  - Media does not deteriorate and plug with cellulotic material
  - Can find cheap waste material to offset higher cost

Plugging/Metals Loading

- **Due to high metals loading reactors can plug over time**
  - Surface area vs. hydraulic properties
  - Utilize liquid carbon source
  - Take advantage or sulfide production to create a recirculation loop for removing metals in the mine water before it enters the reactors
    - Recirculation allows for iron removal
    - Recirculation allows for water movement to help regulate temperature
    - Requires dredging but consists only of metal sludge and not spent media
  - Utilize large, unreactive cobbles as reactor support

Short Circuiting

- **Reactor sizing and configuration**
  - Long and narrow which uses reactor horizontally
  - Down-flow barriers can easily create flow paths to use full depth of reactor
  - Max retention rate in each reactor of 24 hours
- **Water flow**
  - Need enough water flow to prevent freezing
  - Design and rock support prevents turbulence which would add dissolved oxygen
  - Recirculation can help regulate flow rates

SRB Design Summary

- **Sulfate Reducing Bioreactors constructed to test viability of semi-passive system**
  - Two ethanol fed bioreactors filled with large cobbles
  - Recirculation loop blends with system influent for metals removal through metal sulfide precipitation
  - Polishing pond placement after reactors and before discharge
  - Design should:
    - Provide constant flow
    - Deliver constant carbon source at desired COD/sulfate ratio
    - Prevent reactor plugging
    - Prevent freezing
    - Allow for simple system changes (e.g. dose rate and flow rate)

END OF PART 1

PART 2

- System final design, construction and startup
- System performance
- Future considerations in large-scale design

SRB Pilot Test System Overview

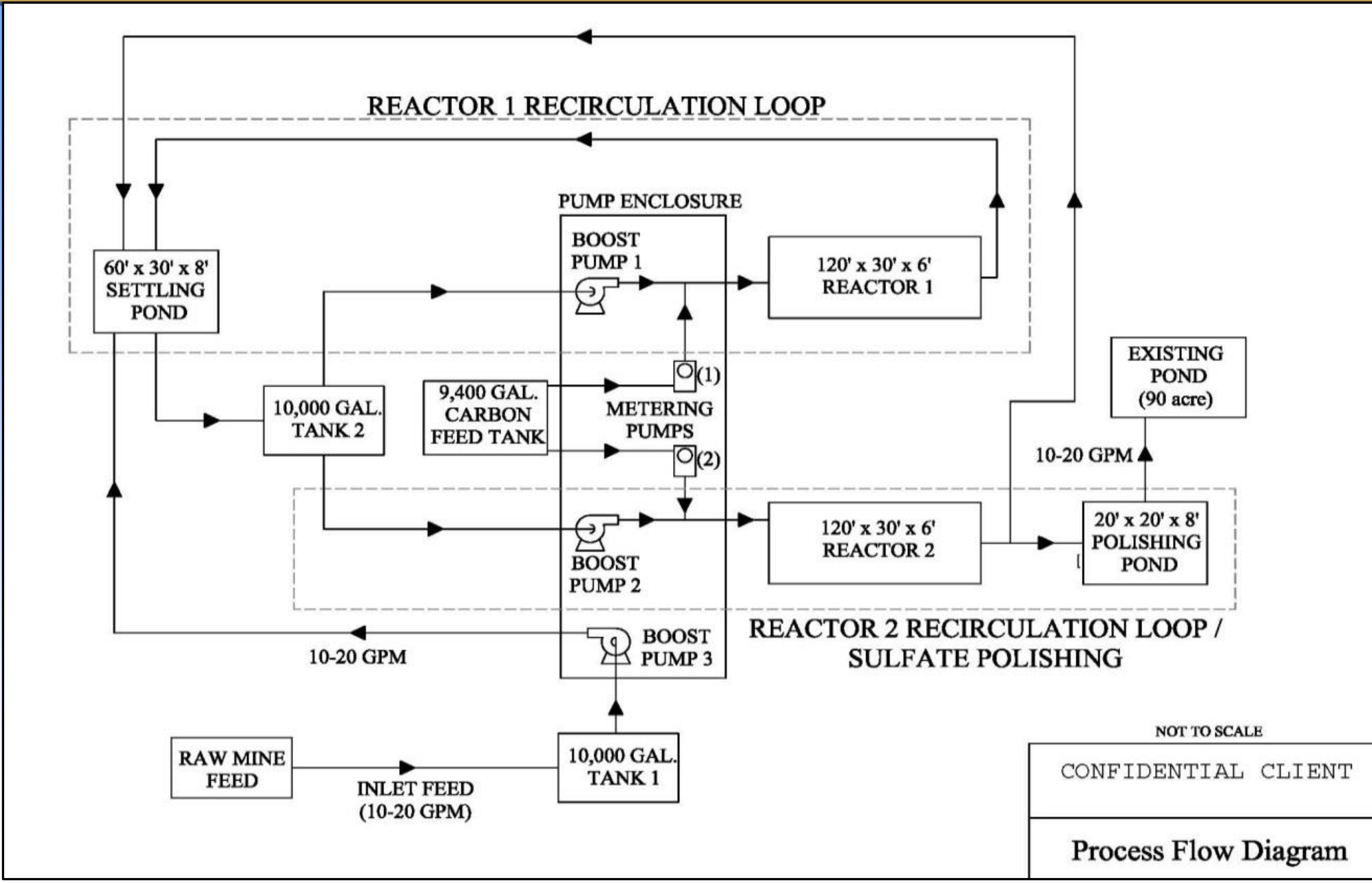
- Mine water at 500 gpm to be treated characterized by:
  - Sulfate 3000 mg/L
  - Iron 120 mg/L
  - Mn 2 mg/L
  - pH 7 - 8
  - Alkalinity 600 mg/L

- Sulfate Reducing Bioreactors constructed to test viability of semi-passive system
  - Built for metals removal and to maximize sulfate reduction
    - Determine and minimize ongoing O+M costs
  - Alternative to typical RO system

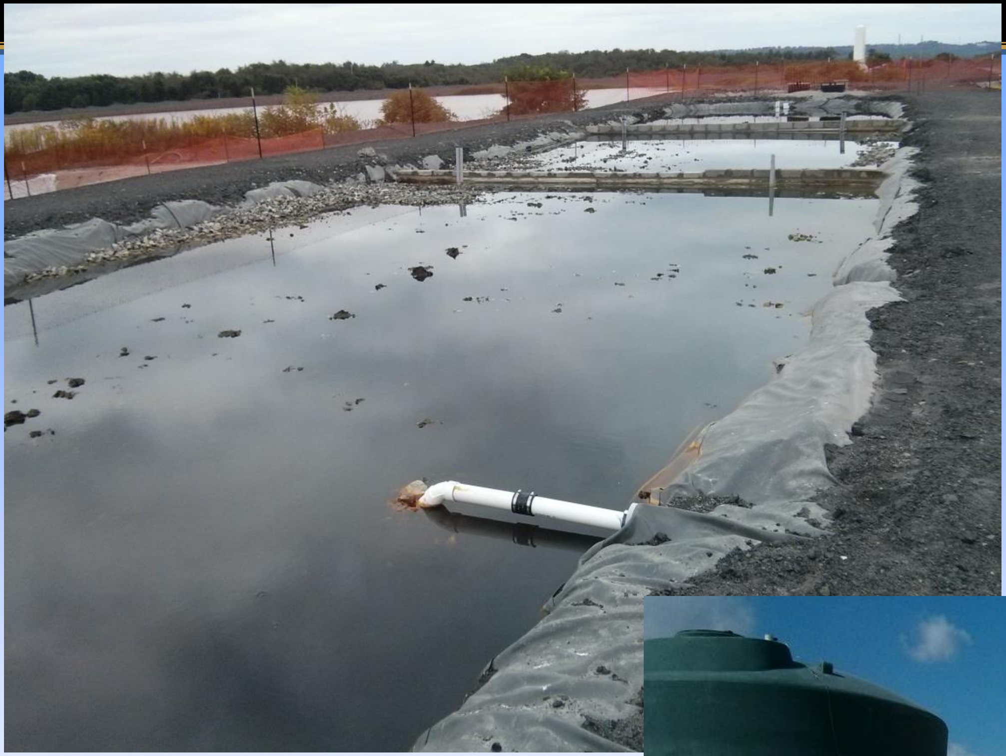
SRB Pilot Test System Overview

- Dual bioreactors
  - Filled with large, unreactive cobbles
  - Barriers to create snake-like flow to contact media
  - Five nested monitoring points in each reactor to monitor conditions in reactor
  - Approximate 24 hour residence time in each reactor
    - 72 hours to cycle through entire system
- Additional System Elements
  - Recirculation Loop with Settling Pond for metals removal
  - Polishing pond after second reactor prior to discharge
  - COD provided by liquid ethanol fed by metering pumps
  - Initial flow rate 10 gpm for scalability

Process Flow Diagram



System Photos

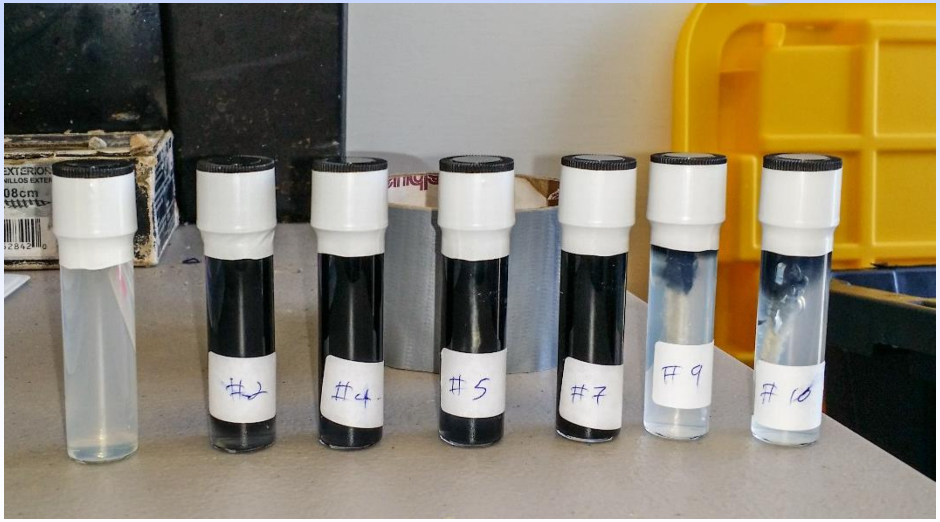


SRB System Startup

- Reactors and ponds filled with mine water
- 55-gallon drums (2) used to inoculate SRB
  - Filled with mine water
  - 5lbs of fresh manure added
  - Drums monitored periodically for H_2S odors
- SRB solution spread throughout reactors after 2 weeks
- Water circulated without discharge
  - Some ethanol added to jumpstart

SRB System Startup

- Monitoring in bioreactors using 10 sample points to ensure conditions for sulfate reduction created
  - ORP, dissolved oxygen monitored for anaerobic environment
  - SRB monitored using field test kit to see if population viable



SRB System Performance

Sampling Date	Sulfate (mg/L)	Temp (°C)	ORP (mV)	Sulfide (mg/L)	Iron (mg/L)	Mn (mg/L	Alkalinity (mg/L)
9/25/2014	2900	16.1	-116	0	103	1.45	620
10/1/2014	1950	14.4	-299	12	0.49	0.139	na
10/9/2014	1600	13.9	-393	85.6	2.75	0.08	1610
10/16/2014	700	12.6	-379	82	0.3	0.03	na
10/23/2014	58	10.5	-366	61.2	0.3	0.01	1910
10/30/2014	101	8.9	-391	76.8	0.78	0.027	1980
11/6/2014	493	2.8	-390	107.4	2.7	0.25	1720
11/13/2014	808	1.8	-401	94	1.7	0.14	1670
11/20/2014	997	3	-374	69.2	1.5	0.11	na
12/11/2014	1488	2.5	-389	na	na	na	na
12/19/2014	1450	2.6	-381	na	na	0.05	na
1/29/2015	1510	2.1	-377	56	1.26	0.89	1200
2/5/2015	1500	2.5	-397	66	1.27	0.94	1010
3/12/2015	1870	4.1	-399	2.8	28.1	1.04	642
4/20/2015	976	5.5	-393	100	26.6	0.59	1490

SRB System Performance Summary

SULFATE REDUCTION

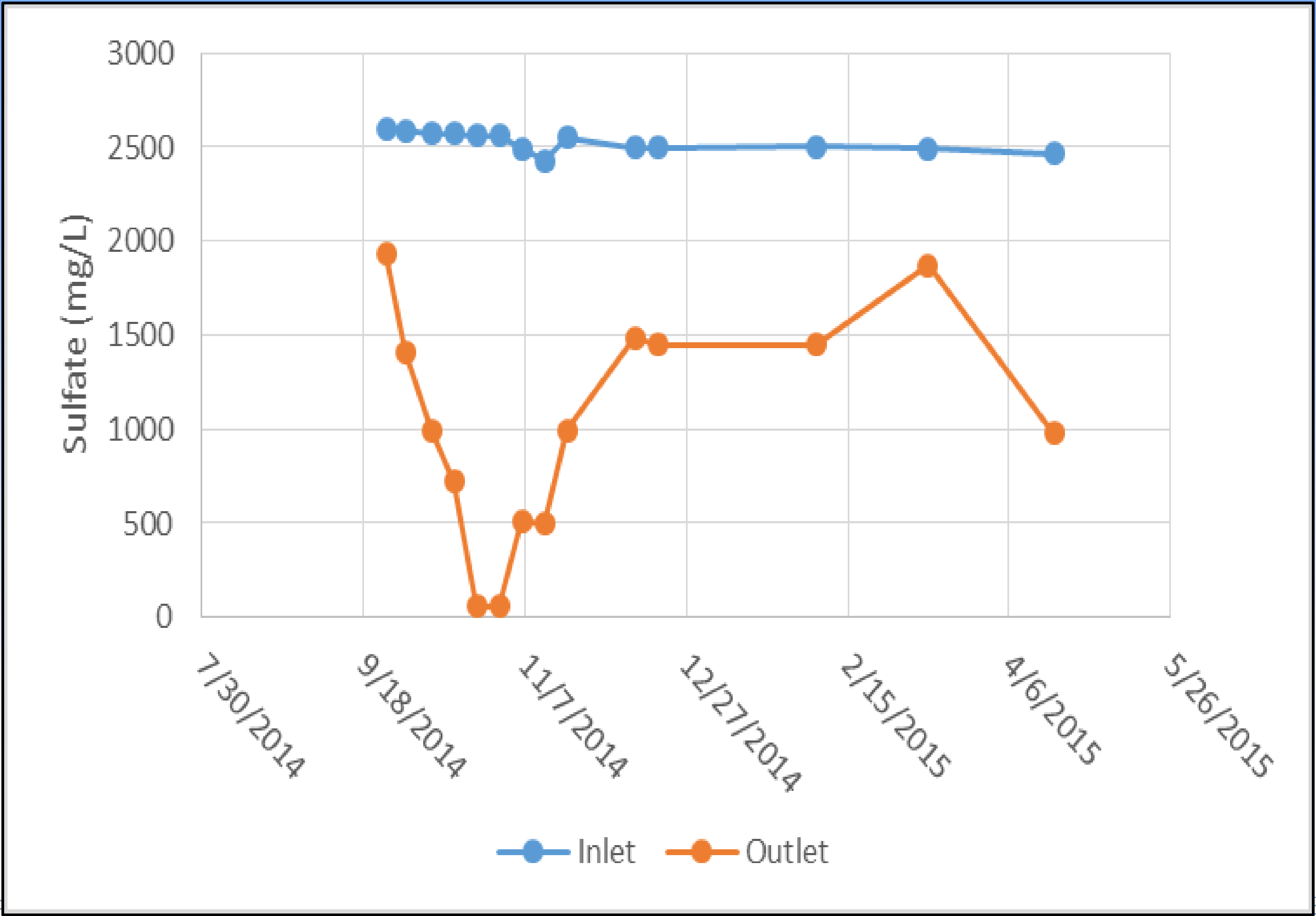
- System able to reduce sulfate to achieve discharge standards in warmer weather
  - Sulfate reduction rates seen up to 1500 mmol SO_4/m^3 reactor-day
  - 500 mmol SO_4/m^3 reactor-day in colder weather
- COD/SO_4 ratio of 1 targeted for optimal sulfate reduction
- Sulfate reduction rates temperature dependent

METALS

- 90% of metals removed in Settling Pond due to recirculation
- 99% of metals removed prior to discharge at the outfall

System Photos

Sulfate Concentrations vs. Time

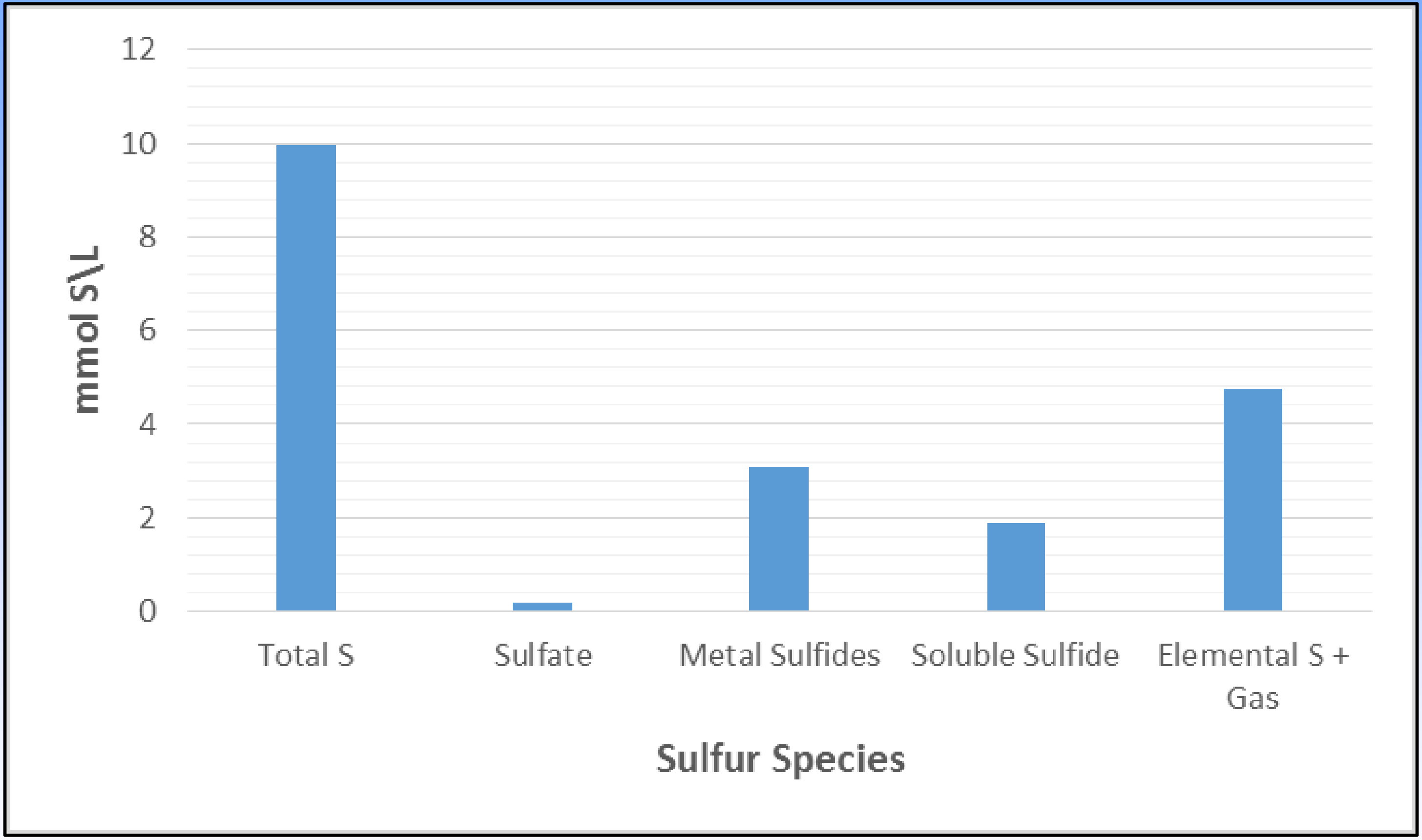


SRB System Performance Summary

<u>OTHER BY-PRODUCTS</u>

- Anaerobic conditions maintained
- Alkalinity produced in proportion to sulfate reduction (ratio of approximately 0.5)
- Dissolved sulfide <100 mg/L at outfall
- H_2S gas in treatment area but below all health and safety thresholds in breathing zone
  - Operators had meters on them at all times
- Elemental sulfur generated

Sulfur Mass Balance



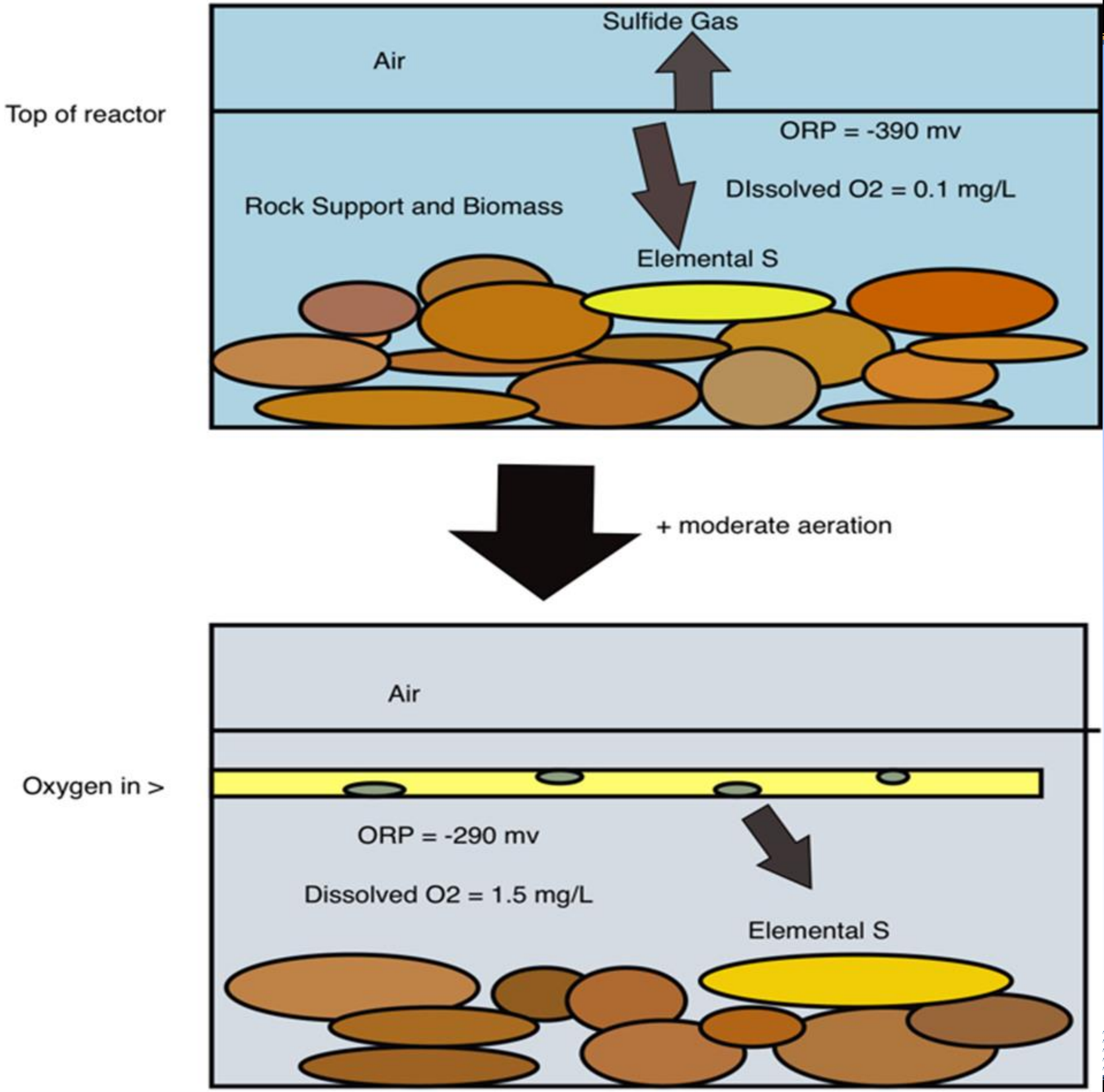
Manipulating Sulfur Speciation

$S^{=}$ to ^{0}S (rapid)

HS^{-} and H_2S to ^{0}S (rapid)

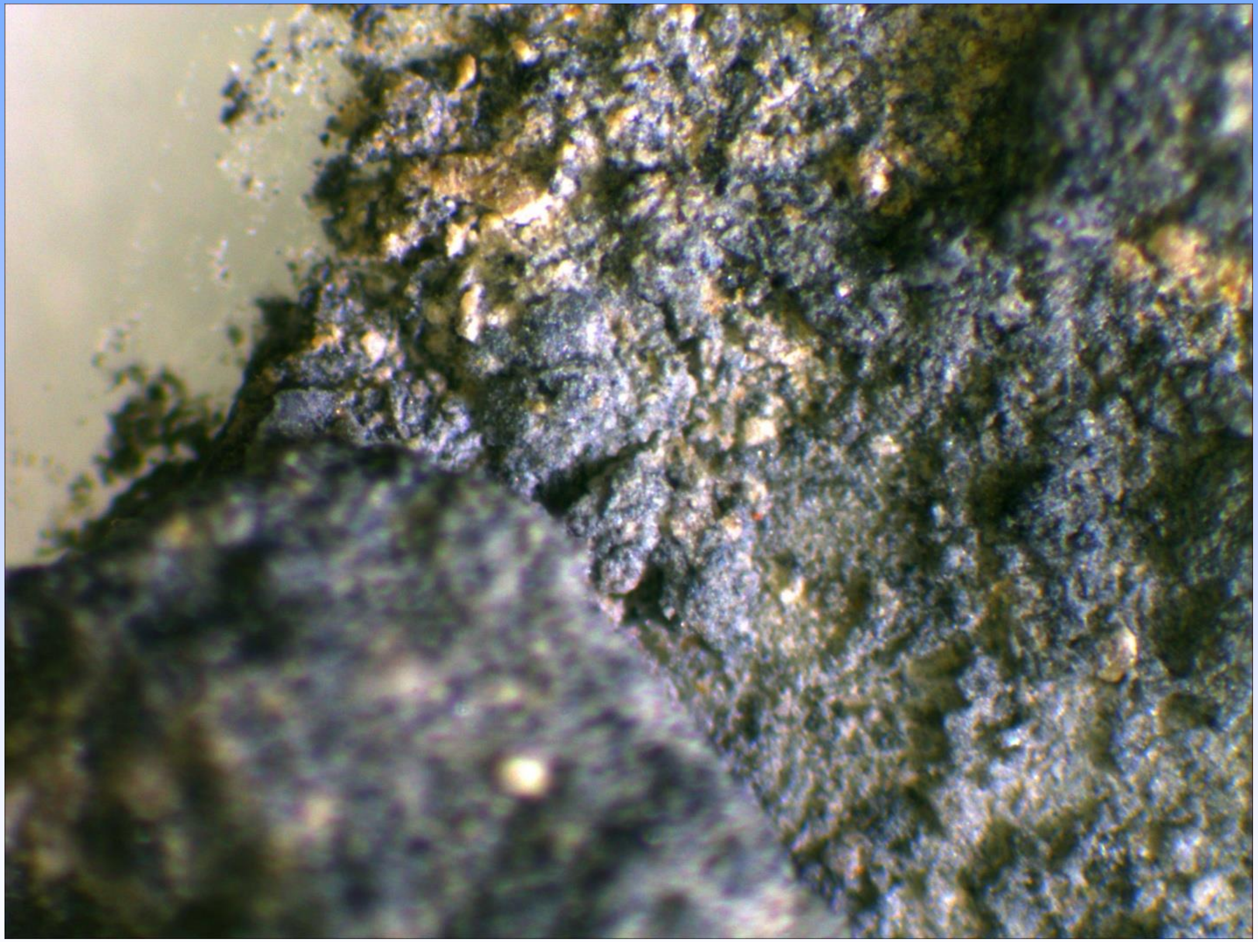
$S^{=}$ to $SO_4^{=}$ (slow)

- Forcing conversion to ^{0}S could minimize odors/toxicity (H_2S) and conversion of $S^{=}$ back to SO_4
- Methods?


Sulfide Gas
Air
Top of reactor
ORP = -390 mv
DIssolved O2 = 0.1 mg/L
Rock Support and Biomass
Elemental S
+ moderate aeration
Air
Oxygen in >
ORP = -290 mv
Dissolved O2 = 1.5 mg/L
Elemental S

Elemental Sulfur in Reactors

Iron Sulfide Formation



Potential Final Design Scenarios

- Final sizing and design of an SRB system based on
  - Influent loading – constant and known
  - Flow rate – can manipulate based on mine pool
  - Sulfate removal rate – varies over time
  - Discharge limits – because mass based consent order is some flexibility
- Can use different design criteria
  - Static flow→ Sulfate removal and discharge concentrations vary
  - Varying flow→ Can keep discharge concentrations constant
  - Different discharge limits→ Higher discharge at this site, smaller system
    - Utilize mass removal at other sites
- Cost-benefit analysis and negotiations with Regulators
- Current conceptual design scenarios with 5 acre footprint

Future Design Considerations

- Carbon source – ethanol vs molasses vs other liquid waste
- Performance over time/temperature
- Sulfur residuals
  - $H_2S(g)$
  - Elemental sulfur ^0S
- Metals residuals
- Other regulated analytes – e.g. osmotic pressure
- True O&M

Questions/Discussion

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Sulfate Concentrations vs. Temperature