Sulfate Reducing Bioreactor for Sulfate, Metals and TDS Removal

THREE YEAR PERFORMANCE REVIEW

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Background

- Passive water treatment has become a common method of achieving water quality goals and decreasing costs associated with long-term mine water drainages
- It does, however require significant refinement especially regarding long-term performance and achievement of predictable performance year to year.

Outline

- Regulatory Background
- SRB Design
- Performance
- Residuals
- Conclusion

Regulatory Impacts

- Mining company entered into a Consent Order requiring development of a passive system rather than install an RO system.
- The system had to achieve the desired permitted levels for pH, sulfate and metals
- New permit requirements include TDS (1500 mg/L).

Background

- Mine discharges into the Monongahela River
- Historically discharge treated to adjust pH and reduce metals to comply with WQS
- Permit renewal process and Monongahela River listing for sulfate impairment 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
- Existing lime plant noit capbale of meeting new discharge requirements

Mine Water Characteristics

• Sulfate	3100 mg/L
• Iron	120 mg/L
• Mn	2 mg/L
• pH	7 - 8
• Alkalinity	400 mg/L

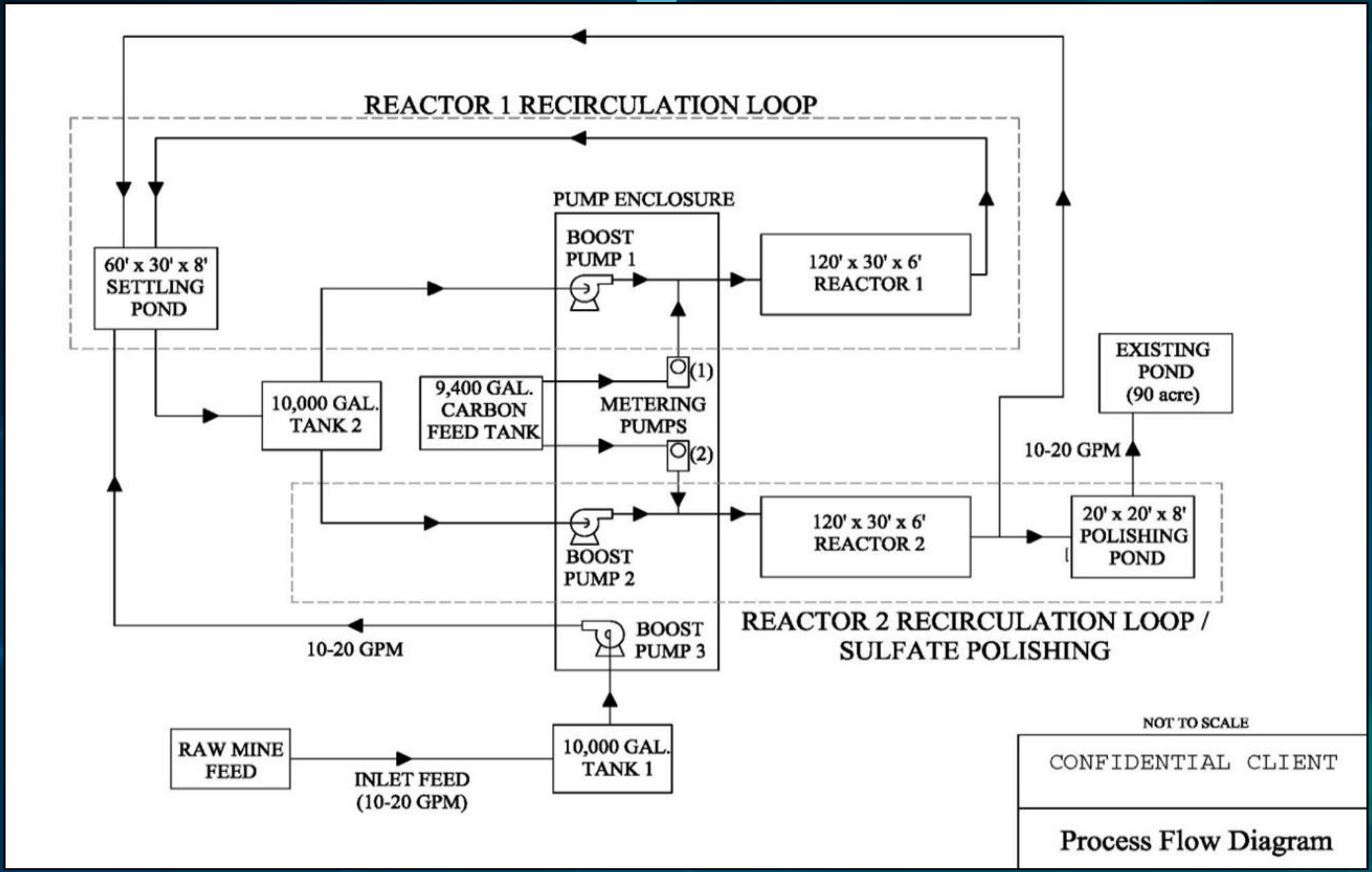
Design Considerations:

- Set a performance based 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
- Devise a system for residual treatment (sulfide gas and S^0)
- Achieve TDS limits (as of 2016)
- Minimize O+M costs for partially "sustainable" and cost-effective system

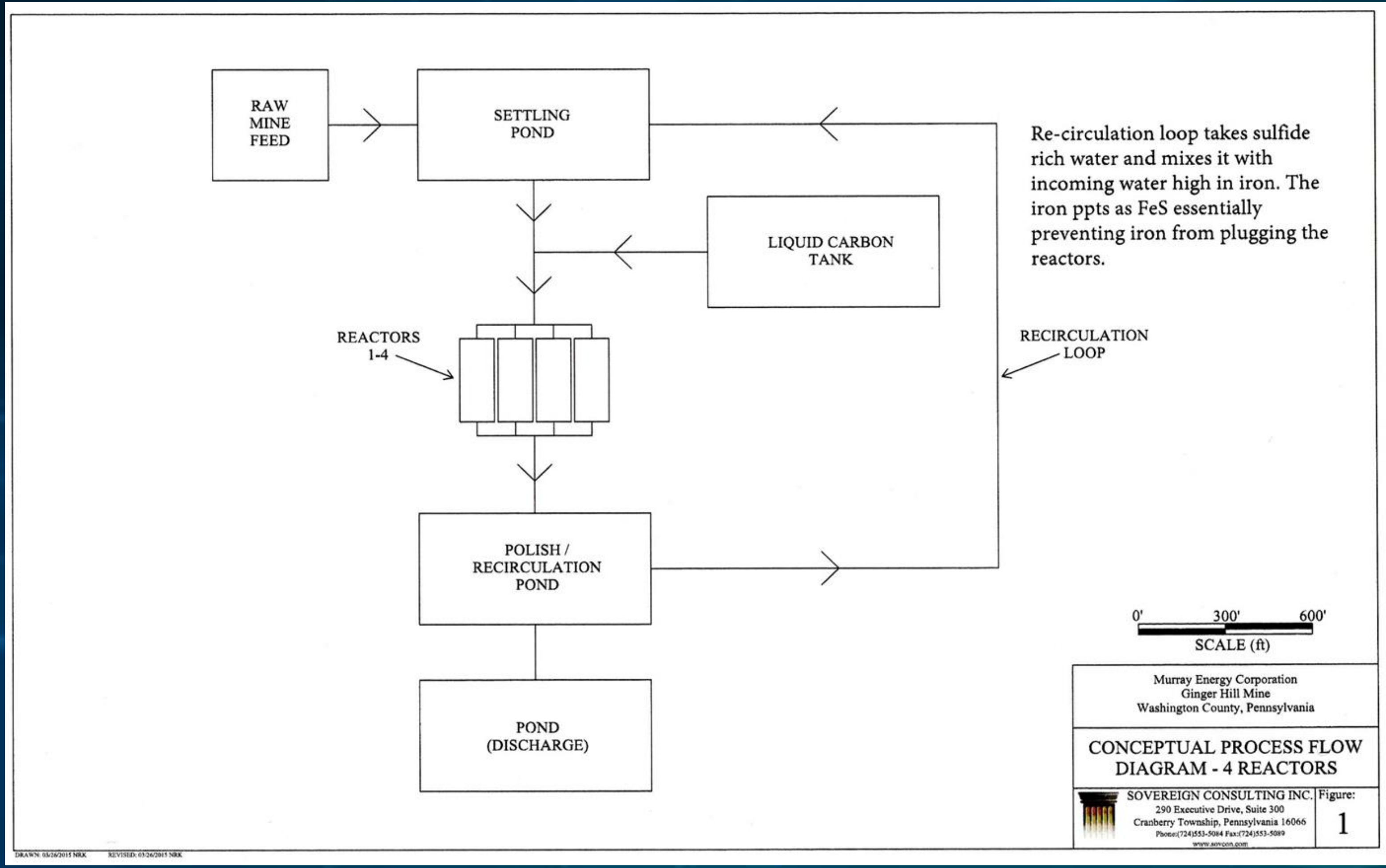
SRB Design Summary

- 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)

Process Flow Diagram



Process Flow (Simplified)



System Photos

System Photos

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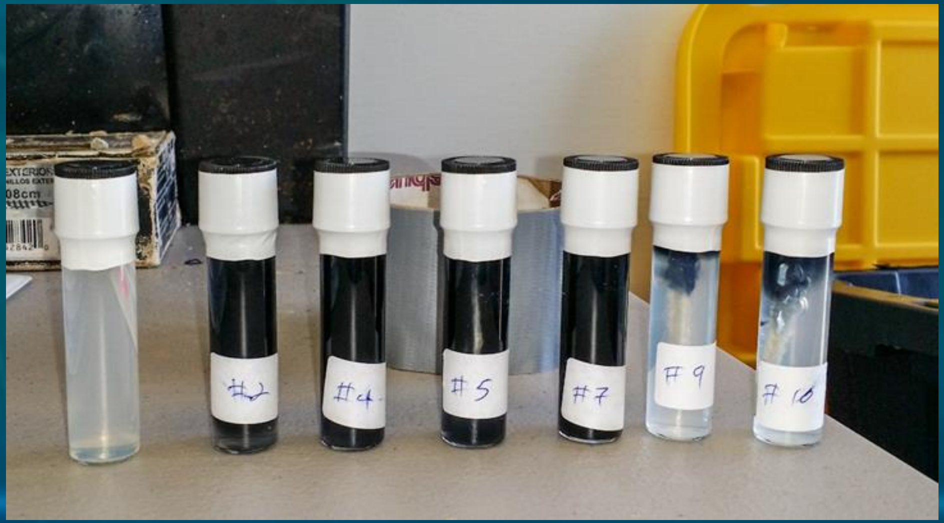
SRB System Startup

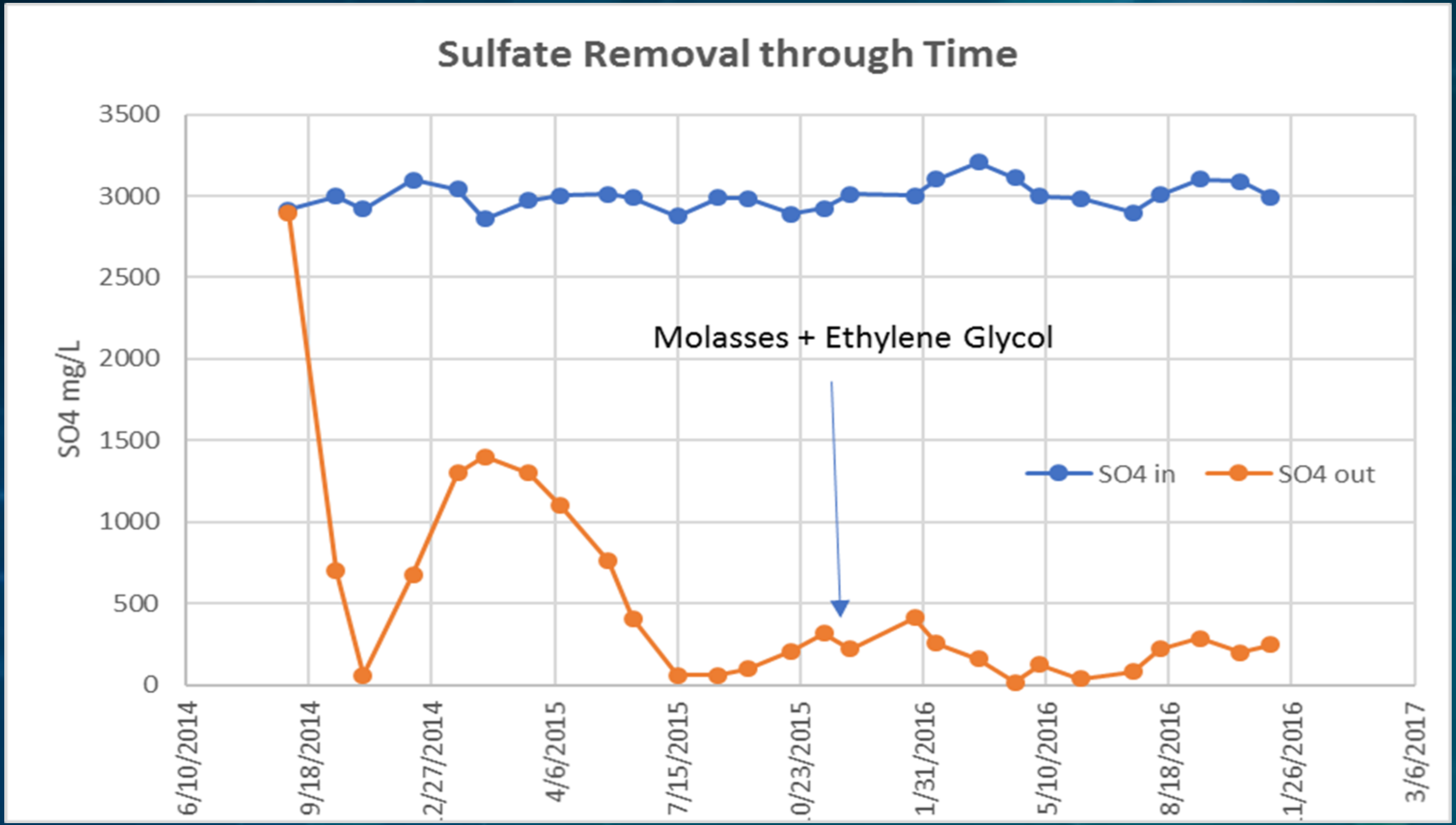
- Monitoring in bioreactors using 10 sample points to ensure conditions for sulfate reduction created
  - ORP, dissolved oxygen monitored for anaerobic environment
  - SRB monitored using field test kit to see if population viable



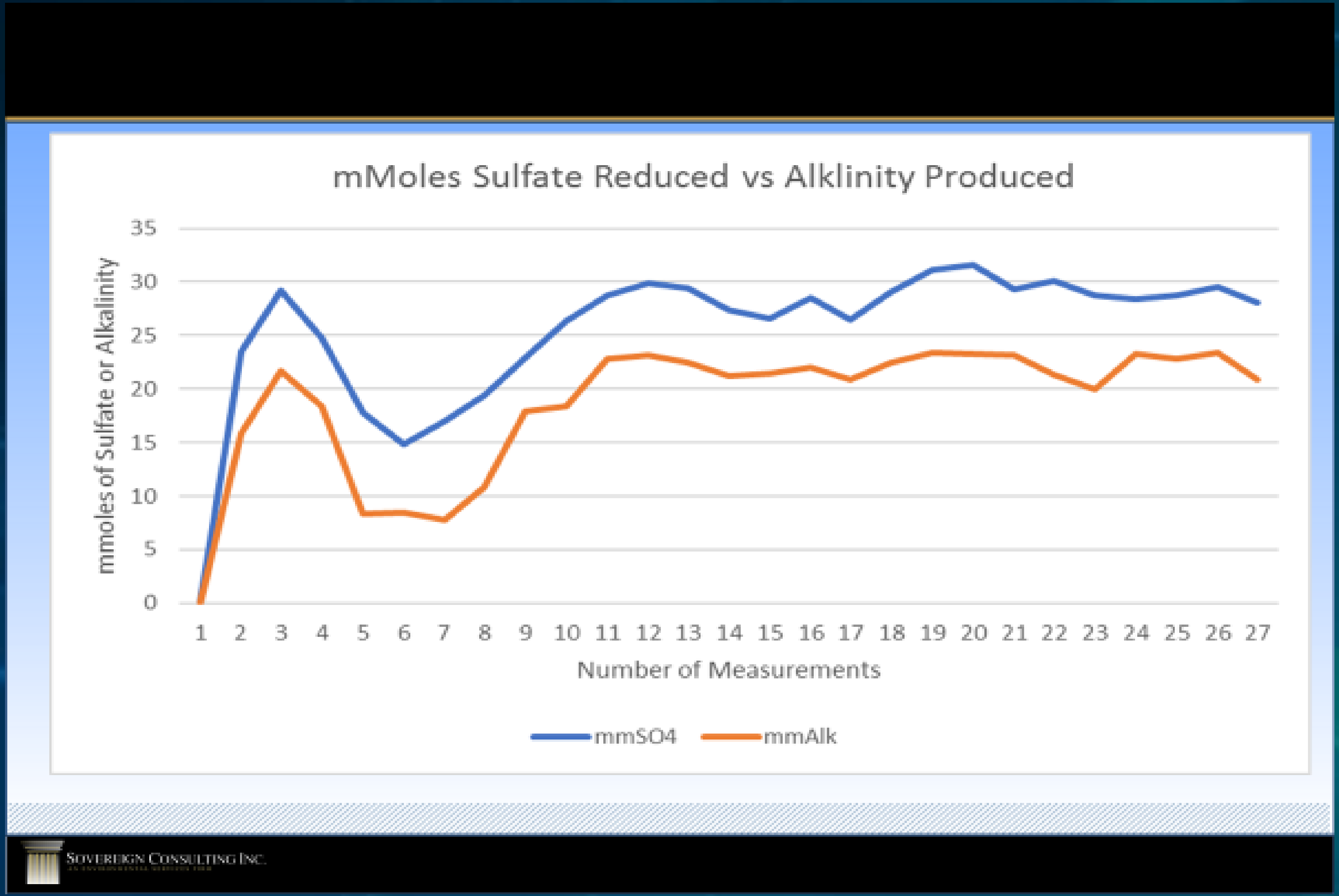
System Performance (8/2014 – 12/2016)

- Sulfate
- Alkalinity
- Metals
- Residuals
- Sulfide (aq)
- Sulfide (g)
- TDS

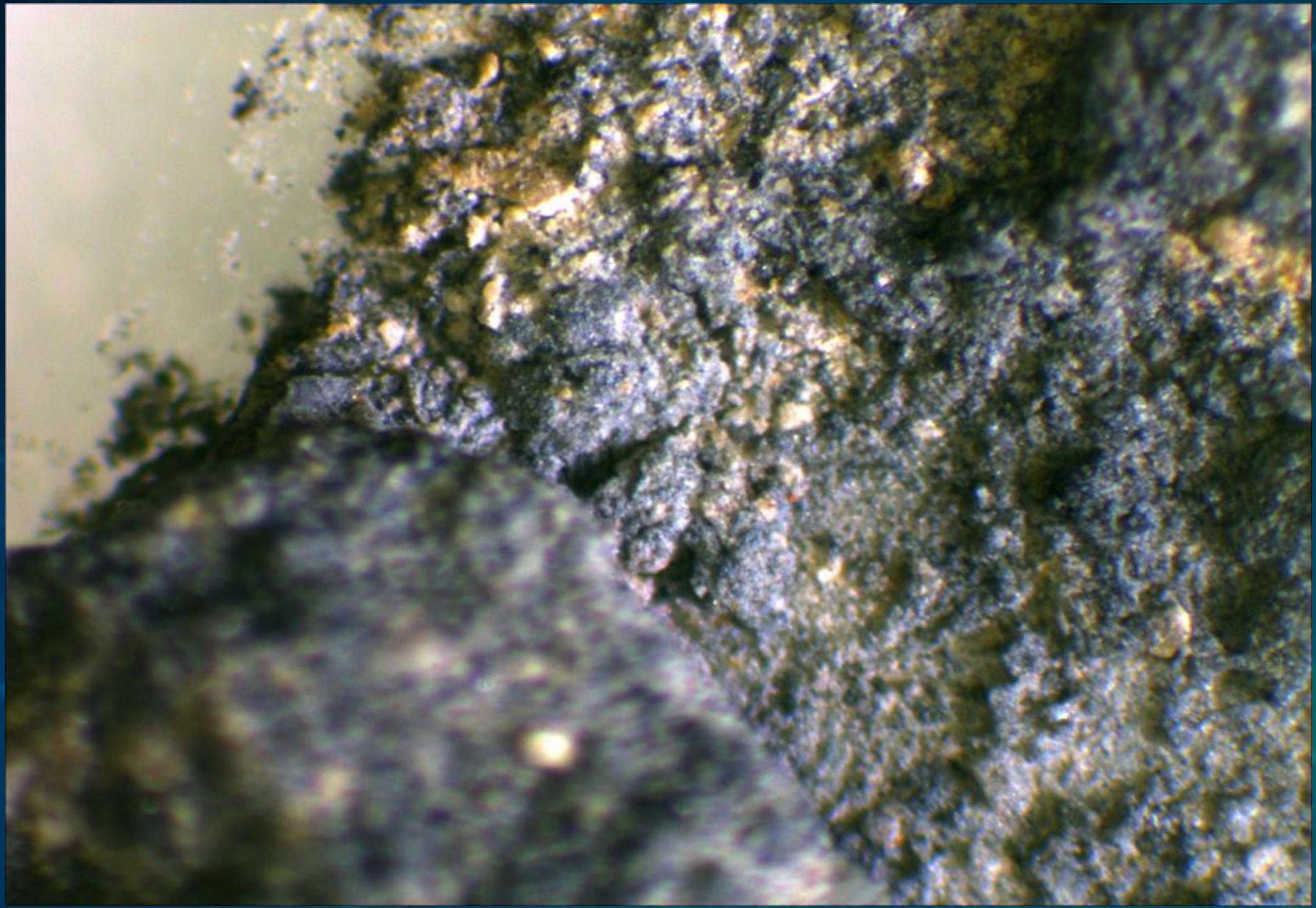
Sulfate Concentrations vs. Time



Sulfate and Alkalinity



System Performance Metals



Metals Removal Loop

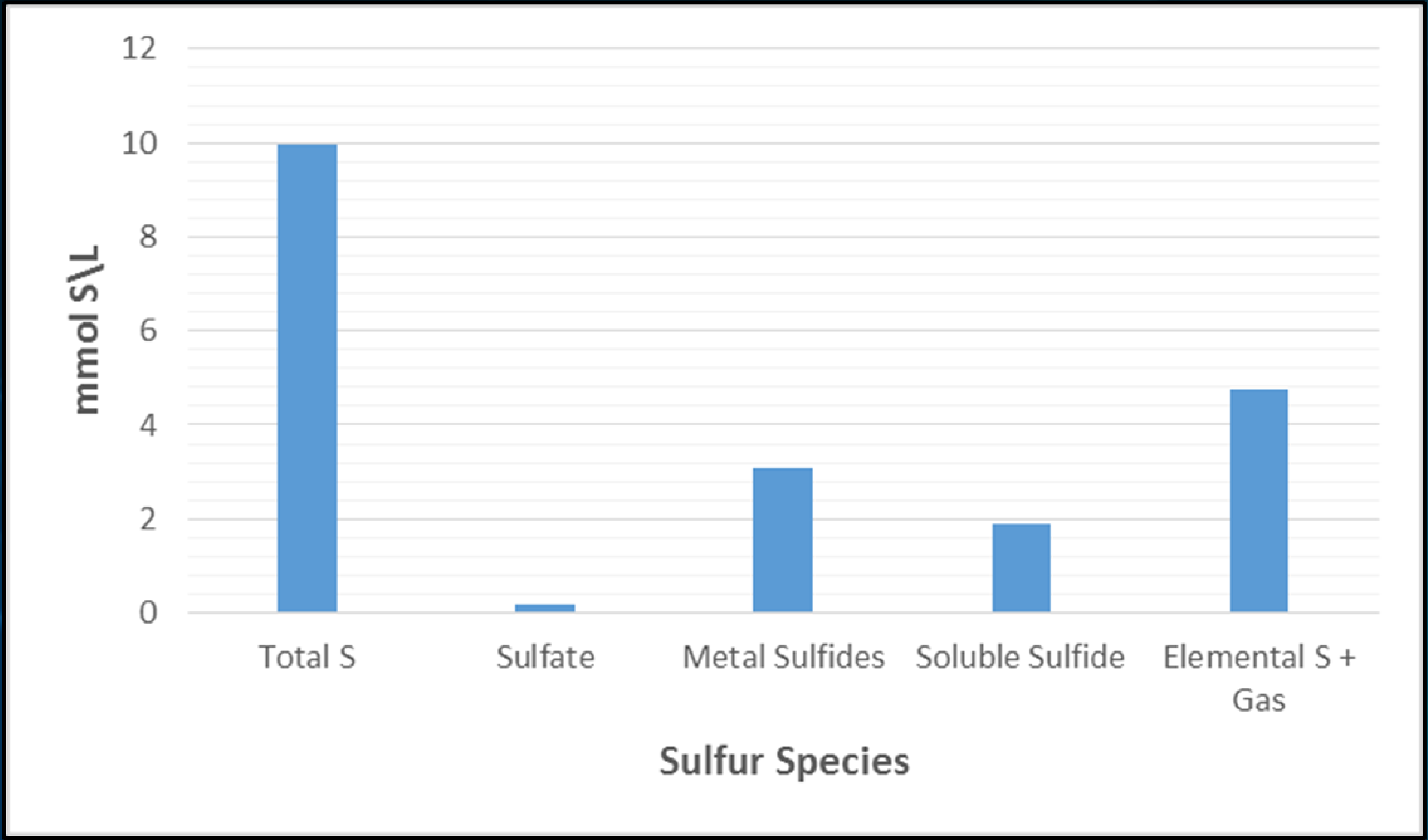
- Removed in Influent pond
- Fe and Zn via sulfide ppt
- Mn as carbonate

Metal	Influent	Effluent
Fe	100 to 130 mg/L	<0.4 mg/L
Zn	4 to 11 mg/L	<0.02 mg/L
Mn	14 to 23 mg/L	< 0.3 mg/L

Sulfur Speciation

Elemental Sulfur in Reactors

Sulfur Mass Balance



Sulfide Residuals Management

Method 1

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

$S^{=}$ to H_2S rapid

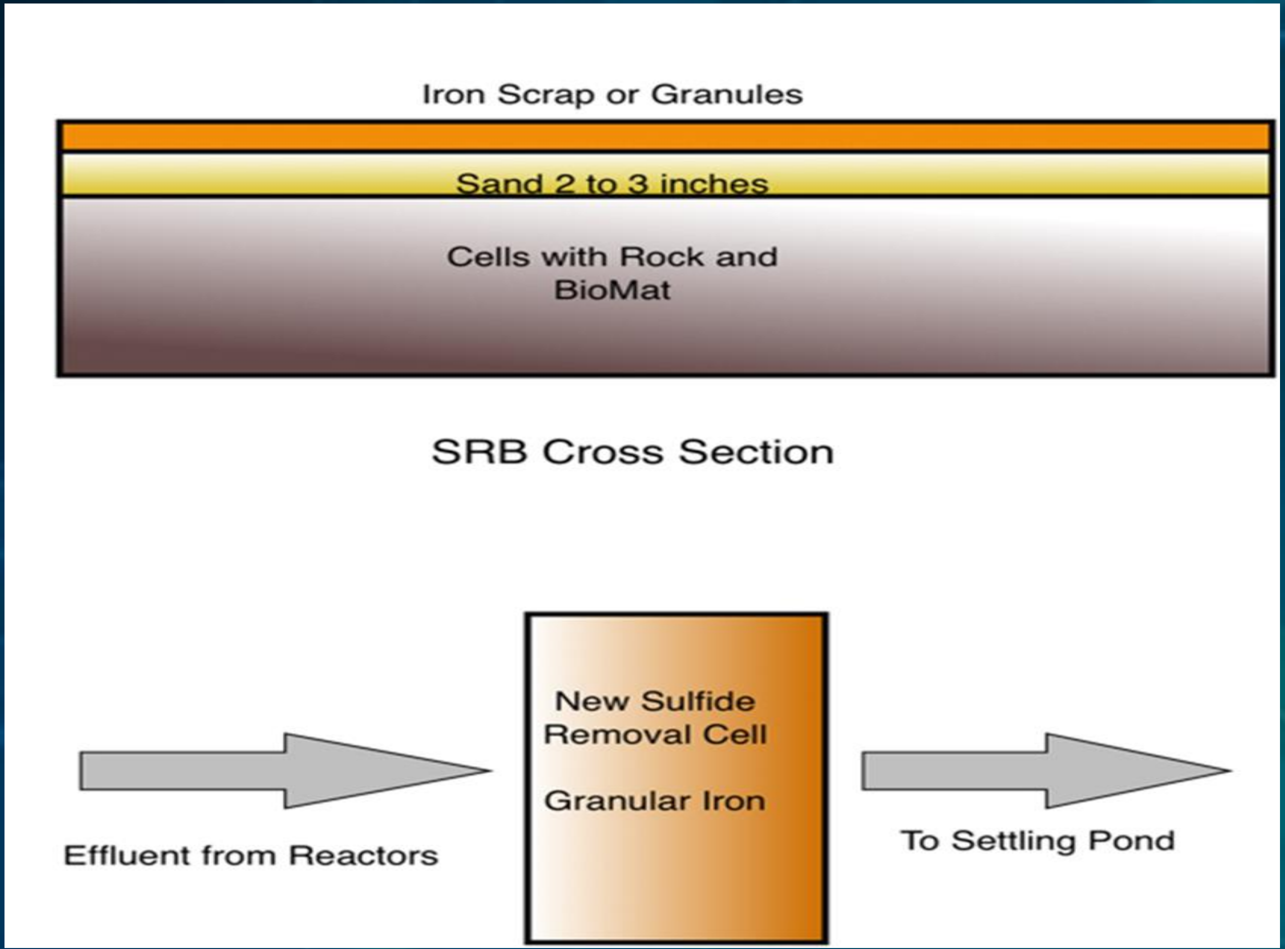
$S^{=}$ to $SO_4^{=}$ slow

Forcing conversion to ^{0}S eliminates odors/toxicity (H_2S) and conversion back to SO_4

Method 2

Percolation through granular iron

Granular Iron for Sulfide Removal



Total Dissolved Solids

- The Mon River was de-listed in 2015, while the system was performing well for the agreed upon standards, could the system be adapted to meet TDS requirements?
- TDS generally is composed of anions and cations that are normally removed via IX or membrane/filtration methods
- These are the same systems we sought to avoid in the passive system developed for sulfate removal.

TDS (cont)

- **Breaking down the problem:**

Analyte	Mine Effluent Lime Plant	Mine Effluent SRB
Na	1350 mg/L	1350 mg/L
HCO3	400 mg/L	1630 mg/L
SO4	3100 mg/L	<300 mg/L
Cl	450 mg/L	450 mg/L
TDS	4800 mg/L	2800 mg/L

TDS Reduction

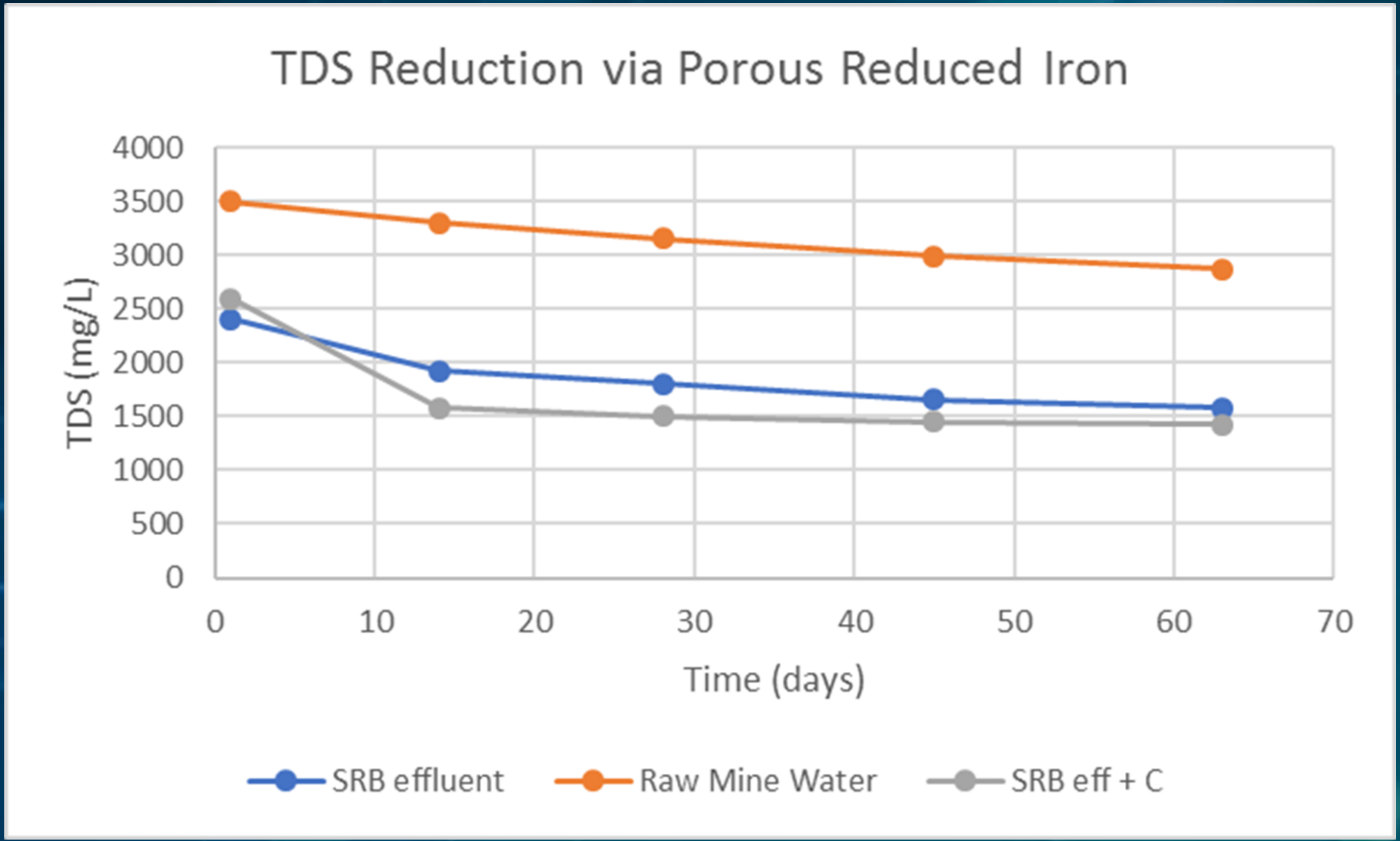
- Modeling the effect of adding different reagents to remove bicarbonate or sulfate indicated chemical methods could be effective for sulfate and bicarbonate mine waters:
  - $Ca(OH)_2$ plus CO_2
  - $Ba(OH)_2$ to polish
  - Effective if TDS is 2400 mg/L or less
- PRB papers showed:
  - Lower conductivity on effluent side of PRB
  - Nitrate could not be reduced in presence of high chloride
- Removal of Na and Cl was targeted.

TDS Reduction with Solid Media

- Previous project work and literature reviews indicated that a porous iron media could provide the necessary characteristics to at least partially remove “salt” to achieve TDS standards (eg 2400 mg/L to 1500 mg/L)

- A zero valent iron like material can be used as a the raw material for creating an activated, porous material features amenable to capture of sodium and chloride (low charge density and single hydration spheres)

Desalination



SRB System Performance Summary

- Anaerobic conditions maintained with high sulfate reduction rates even in winter
- Alkalinity produced in proportion to sulfate reduction (ratio of approximately 0.6 to 0.7)
- Dissolved and gaseous sulfide largely solved
- O&M to date has included carbon replacement ($35,000/yr), pump and valve replacements ($6000 overall)

Treatment Flow Chart

Sulfate Reduction

- Metal Precip as Sulfides
- Sulfate Reduction and Alkalinity Production

Residuals Treatment

- Sulfide (g and aq) Removal w/ Fe
- TDS (Na and Cl) Removal

Discharge

- Low Sulfate, metals
- Alkaline (near neutral pH)
- TDS < 1500 mg/L

SRB System Performance Summary

- Media clogging occurred twice so far and only in the first 2 cells. Backhoe was used to loosen the clogs which were due to biomass buildup.
- TDS reduction will occur but over an extended time-frame and only in mine effluents with Na and Cl.
- Requires increased reaction rate for salt removal.

Questions/Discussion

- **For more information contact:**
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