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EXPANDING RESOURCES

Passive Bioremediation of Mining Influenced Water Treatment Using Sulfate Reducing Bioreactors

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Presentation Outline

- Introduction
  - Mining Impacted Water
  - Passive Sulfate Reducing Bioreactor
- Goal & Approaches
- Results
  - Bench-scale SRBR operation
  - Full-scale SRBR investigation
- Conclusion and Recommendation

Mining Influenced Water (MIW)

- **Acid Rock Drainage (ARD) and other waters related to mining and mineral processing**
- **Chemistry**
  - **Low pH with metals and sulfate**
    - Common metals: Al, Fe, Cd, Co, Cu, Cr, Ni, Pb, Zn
  - **Neutral pH with metal and/or sulfate**
    - No Al or Fe
    - Additional metals: As, Mo, Sb, Se, U
- **Seasonal fluctuation of flow rate and chemistry**

- **Pumping MIW back to active mining operation or water collection basin/evaporation**
- **Necessity of sustainable solutions to capture and treat MIW**

Comparison of Active and Passive Sulfate Reducing Bioreactor (SRBR)

- Biological MIW treatment
  - Cost effective and eco-friendly

	Active SRBR	Passive SRBR
Reactor type	Completely stirred tank reactor Membrane reactor Submerged packed bed reactor	Packed reactor
Microbial growth	Suspended growth Attached growth	Attached growth (media = substrate)
Electron donor	Liquid or gas phase	Solid phase Slowly degradable liquid

- Sulfate reduction rate
  - Active treatment >> Passive treatment

Passive SRBR

- Attractive for
  - Closed mine or mill sites
  - Remote sites lacking infrastructure
  - Long term MIW source with relatively low flow rate

- System attributes
  - Natural slow release organic substrates
  - Low sludge production & disposal: cost effective & eco-friendly
  - Low level of operation and maintenance

Metal Removal in Passive SRBR

- **Produces biogenic sulfide & alkalinity**
  - $SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow H_2S + 2H_2O + 2CO_2$
- **Cationic metal removal**
  - $M^{2+} + H_2S \rightarrow MS + 2H^+$

- **Requires low reduction potential (Eh) < -100 mV**
- **Electron acceptor is sulfate**
- **Electron donor is product of natural organic substrate (NOS) fermentation**

Design & Operation Factors of Passive SRBR

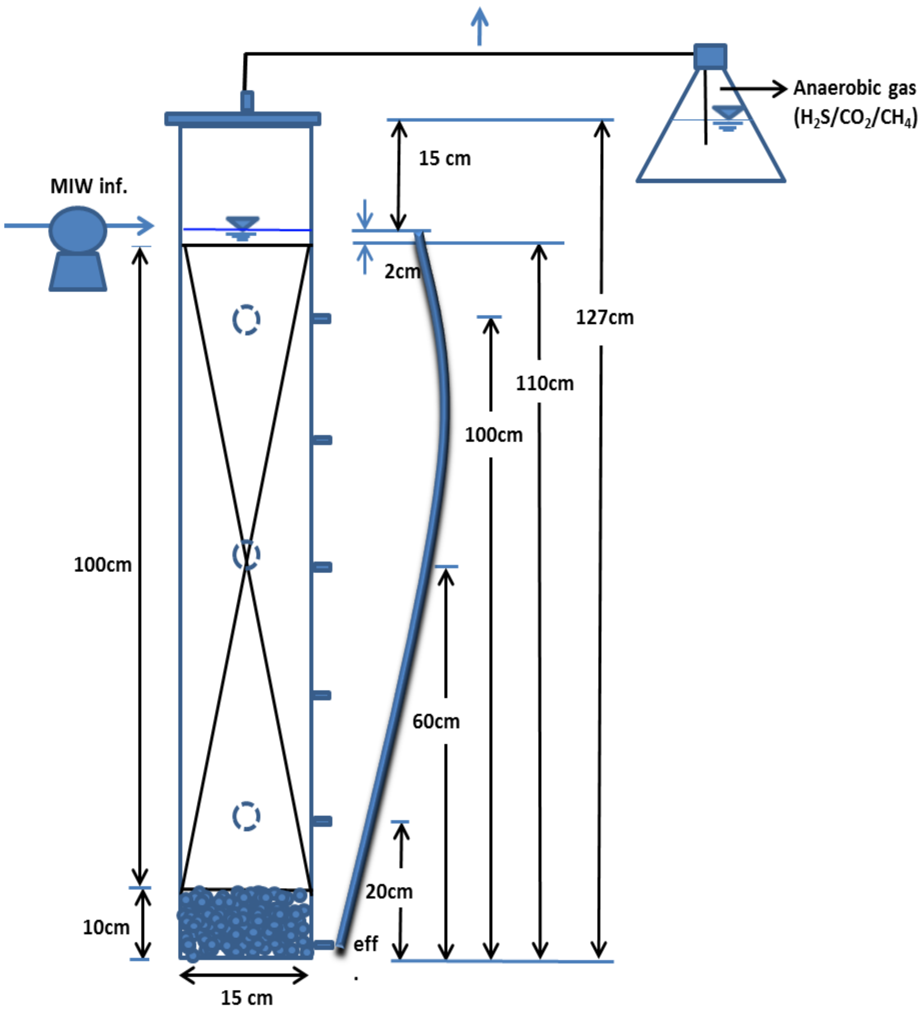
- **Optimal substrate composition for general & specific MIW treatment**
- **SRBR design & operation factors**
  - **Optimal metal loading rate: 0.3 mole/m^3-d of metal (or sulfate)?**
  - **Optimal depth of substrate zone: ~3-6 ft?**
  - **Metal and proton acidity of MIW vs. alkalinity produced from sulfate reduction and limestone**
  - **Hydraulic retention time (HRT)**
    - **Maximize sulfate reduction and metal removal rate**
    - **Minimize the surplus H_2S based on stoichiometric ratio between sulfate reduction rate and metal removal rate**
- **Pre-treatment and/or post-treatment**

Goal & Approach

- **Development of Full-scale SRBR design and operation factors**
- **Understanding metal removal mechanism**
  - **Bench-scale SRBR operation**
    - **Comparison of sulfate & metal removal rates and efficiencies of different Natural Organic Substrates (NOS)**
    - **Evaluation of effect of EBCT on bioreactor performance**
    - **Investigation of metal & mineral precipitates and microbial community on the surface of NOS**
  - **Full-scale SRBR investigation**
    - **Necessity of pre- and post-treatments**
    - **Flow rate and water chemistry**

Scheme of Bench-scale SRBR

- Height : ID = 50”: 6”
- NOS mixture depth: 39”(18 L Vol.)
- NOS: ~1” except sawdust & walnut shell
- Limestone: 0.2” particle
- 5 liquid sampling ports
- 3 solid sampling ports
- Down flow mode



Biochemical Reactor (BCR)

Compositions of NOSs Used for SRBRs

	limestone, wt.%	alfalfa hay wt.%	sawdust wt.%	woodchip wt.%	walnut shell wt.%	total, g	density, g/L
SRBR-1	**30**	**10**	**10**	**50**		3,890	216
SRBR-2	**30**	**35**	**35**			3,730	208
SRBR-3	**30**	**35**		**35**		3,630	196
SRBR-4	**30**		**35**	**35**		5,220	289
SRBR-5	**30**	**70**				3,510	189
SRBR-6	**30**		**70**			6,240	341
SRBR-7	**30**			**70**		3,940	220
SRBR-8	**30**				**70**	14,370	790

MIW and Operation

Analytes	pH	SO_4^{2-}	Al	Ca	Cu	Fe	Mn	Mg	Zn
Conc.(mg/L)	6.4	5,000	<8.0	560	<0.1	<1.0	4.0	770	170

- **Inoculation**
  - **Day 26: all SRBRs with sulfate reducing mixed culture enriched in Lab**
  - **Day 190: SRBRs-1, 3, 4, 6, and 7 with SRBR-2 effluent**
  - **Day 381: SRBRs-1, 4, 6, and 7 with cow and steer manure**

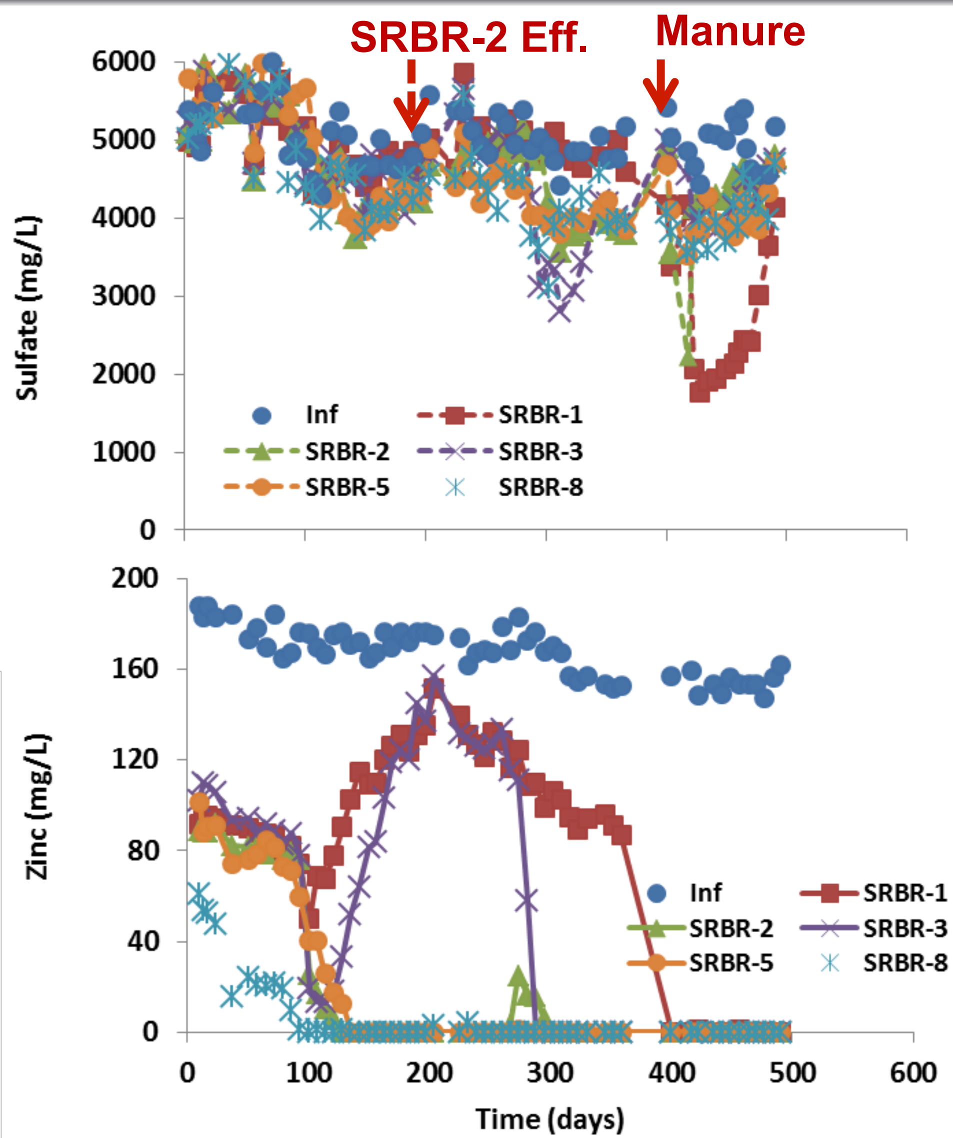
- **Flow rates**
  - **No flow up to day 70**
  - **Increased from 0.4 to 1.2 L/d based on reactor performance**

Full-scale SRBR

Design parameter	Design value
Flow rate	7 gpm (26.5 L/min)
Metal loading rate	0.3 mole/m^3-day
Depth of substrate	3 ft. (0.91 m)
EBCT/HRT	34.8 days/17.4 days assuming 50% porosity
pH/sulfate	3.28 / 2,640 mg/L
Metal (mg/L)	Fe (272), Cu (62), Zn (88), Al (22), Mn (27)
Substrate composition (wt.%)	Limestone (30), woodchip (49.5), hay (10), sawdust (10), manure (0.5)

Bench-scale SRBR Results

Substrate – Alfalfa Hay and Walnut Shell



SRBR-1: **alfalfa hay 10%**
sawdust 10%
woodchip 50%

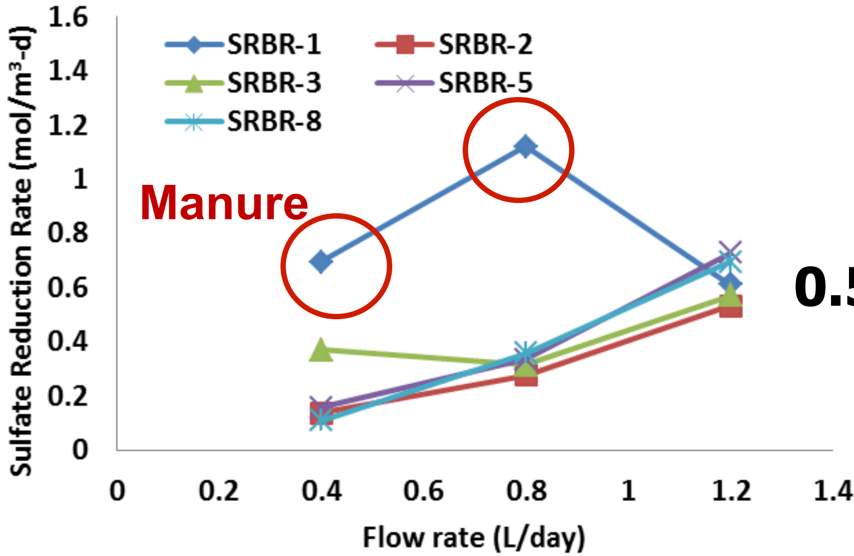
SRBR-2: **alfalfa hay 35%**
sawdust 35%

SRBR-3: **alfalfa hay 35%**
woodchip 35%

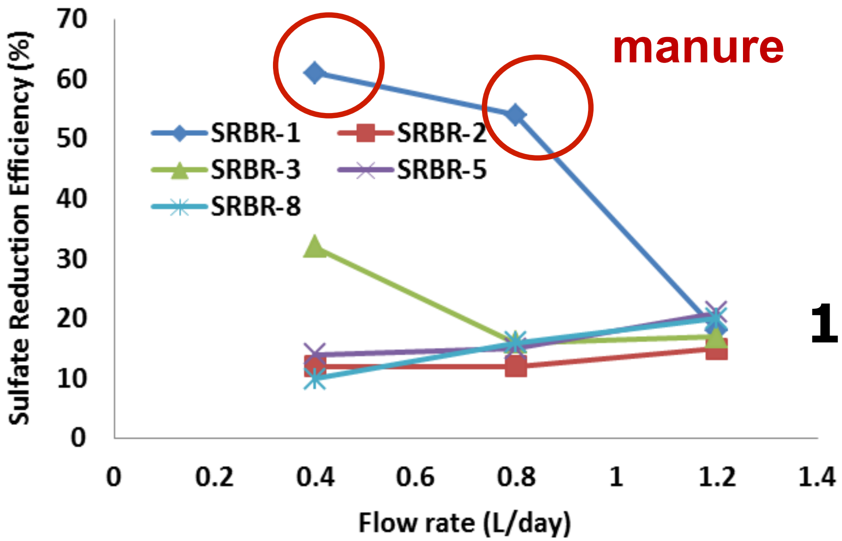
SRBR-5: **alfalfa hay 70%**

SRBR-8: **walnut shell 70%**

Sulfate Reduction Rate (SRR)



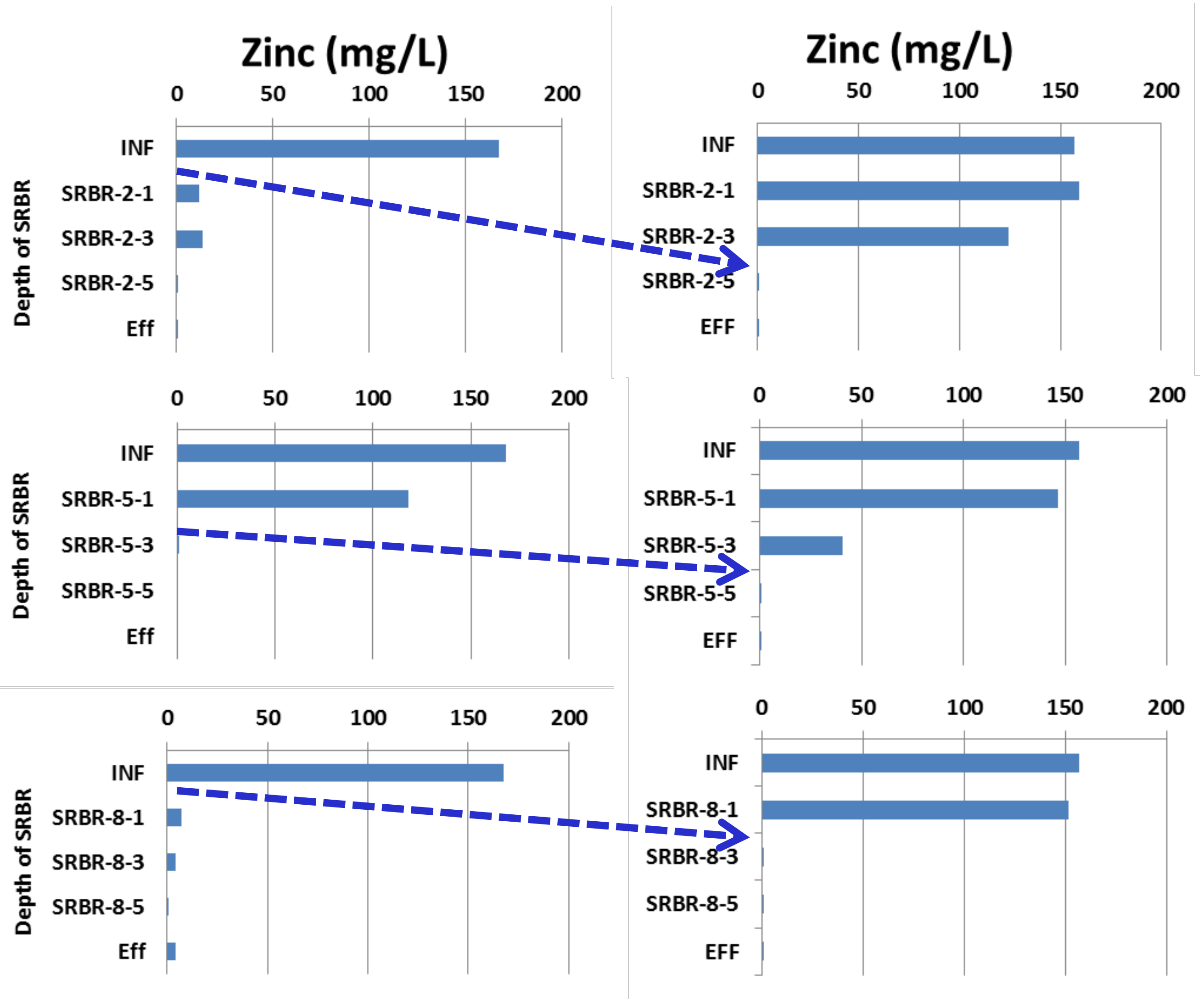
0.5-0.7 mole/m^3-day



15-20%

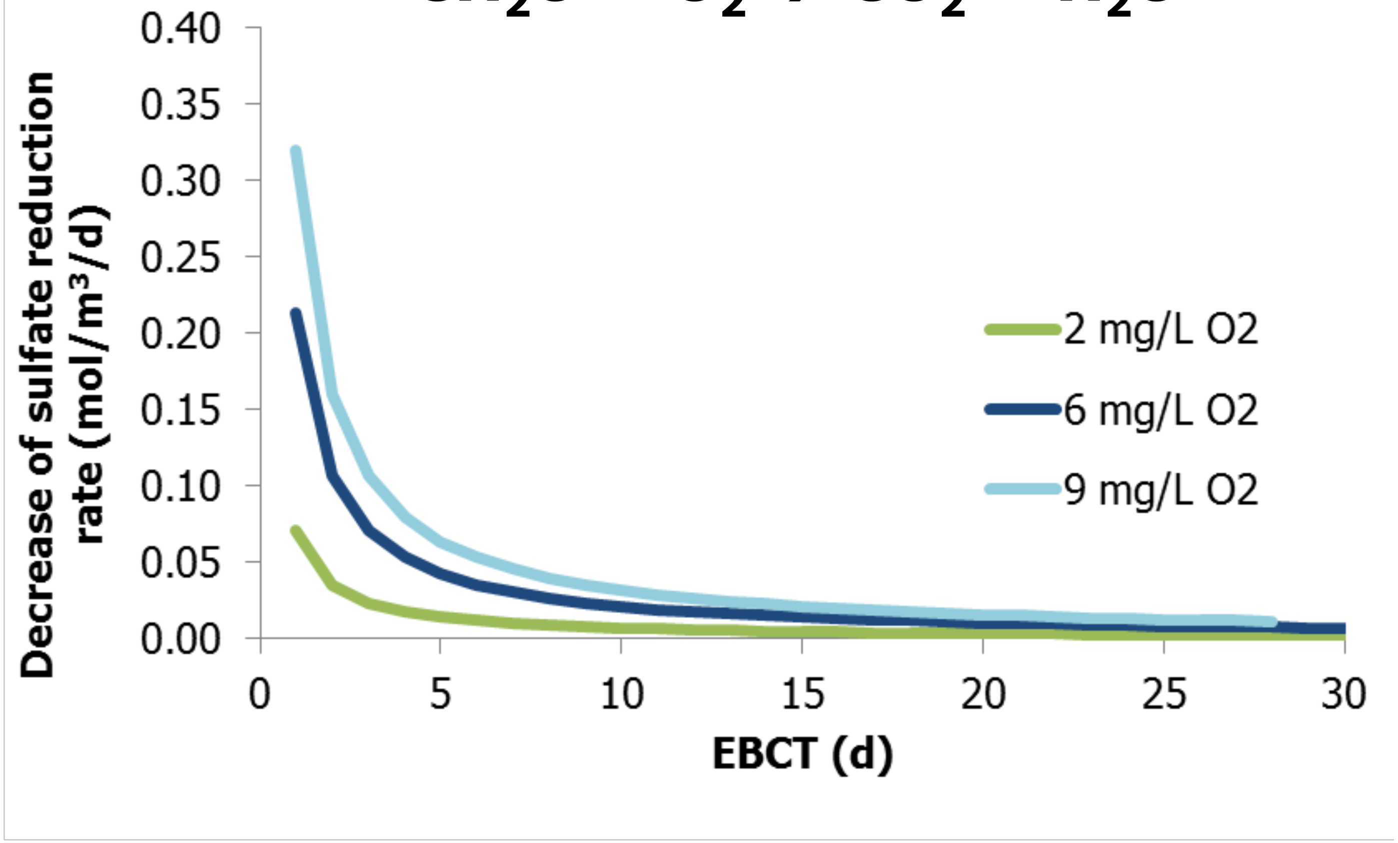
Influence of Flow Rate on Zn Removal Depth

Flow rate = 0.8 L/d | **Flow rate = 1.2 L/d**

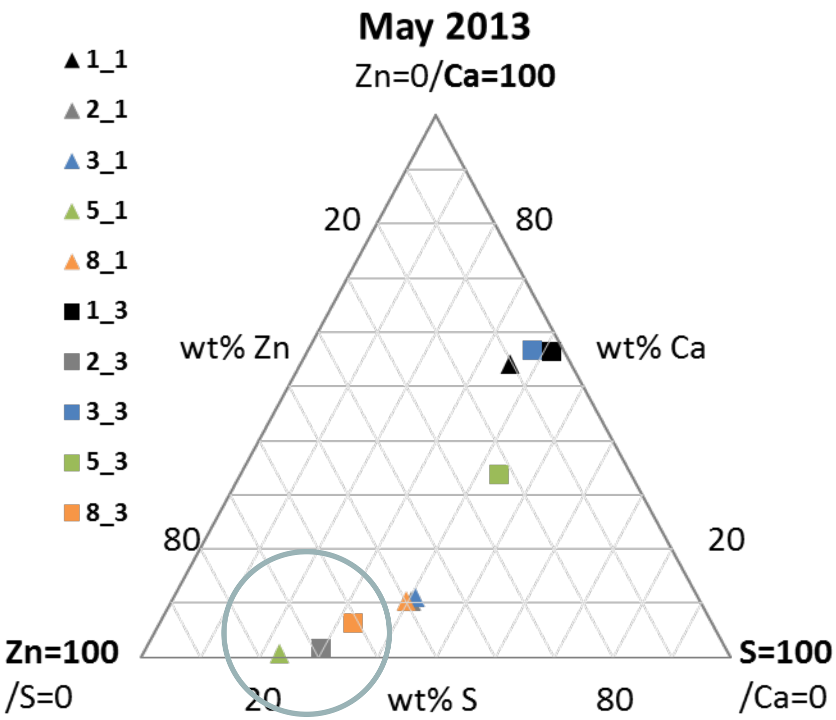


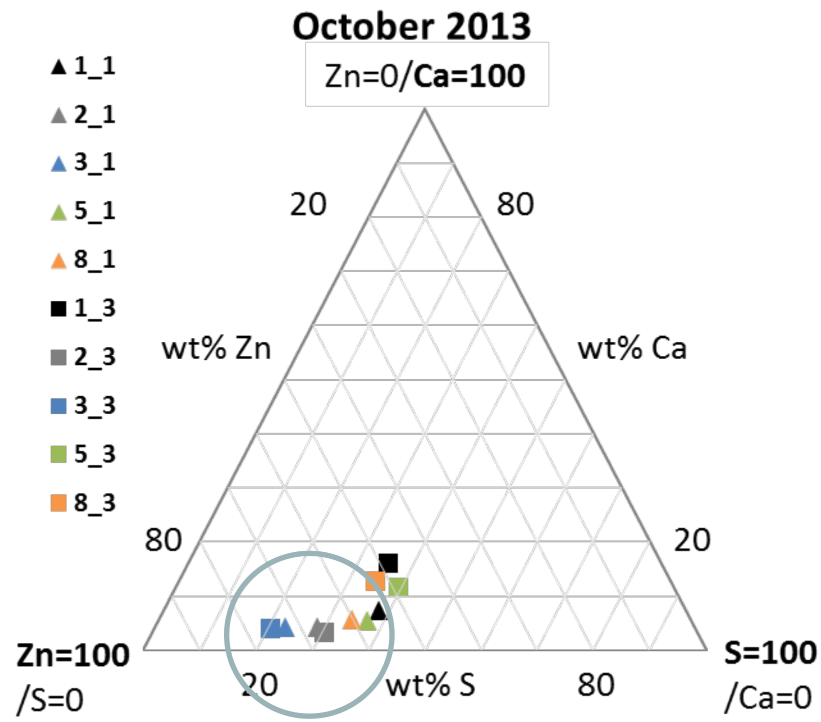
Effect of O_2 Loading and EBCT on SRR

- $CH_2O + O_2 \rightarrow CO_2 + H_2O$



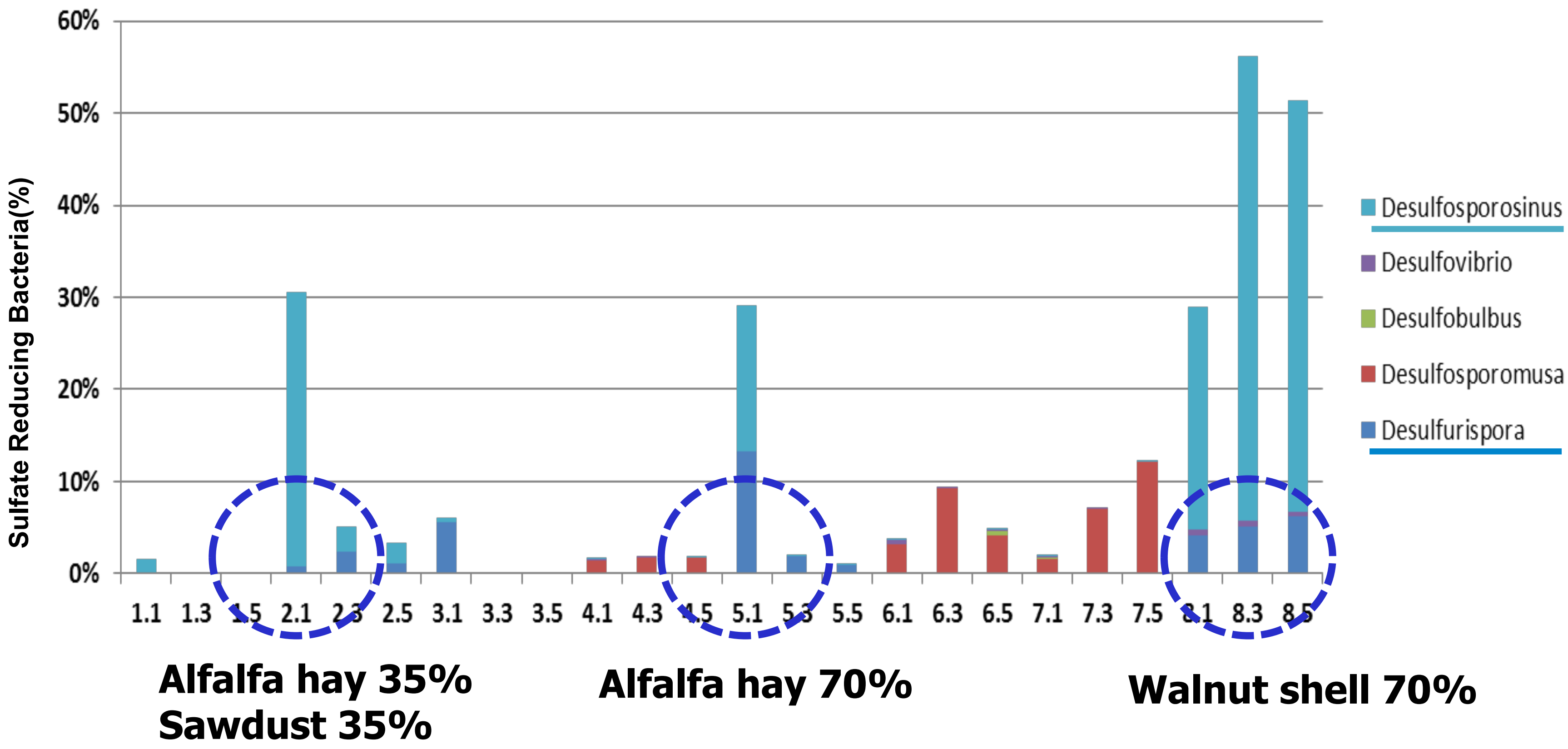
Relative Weight Ratio of Zn, Ca, and S





- $Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4$
- $Ca^{3+} + CO_3^{2-} \rightarrow CaCO_3$
- $Zn + S^{2-} \rightarrow ZnS$
- $Zn + CO_3^{2-} \rightarrow ZnCO_3$

Relative Abundance of Sulfate Reducing Bacteria

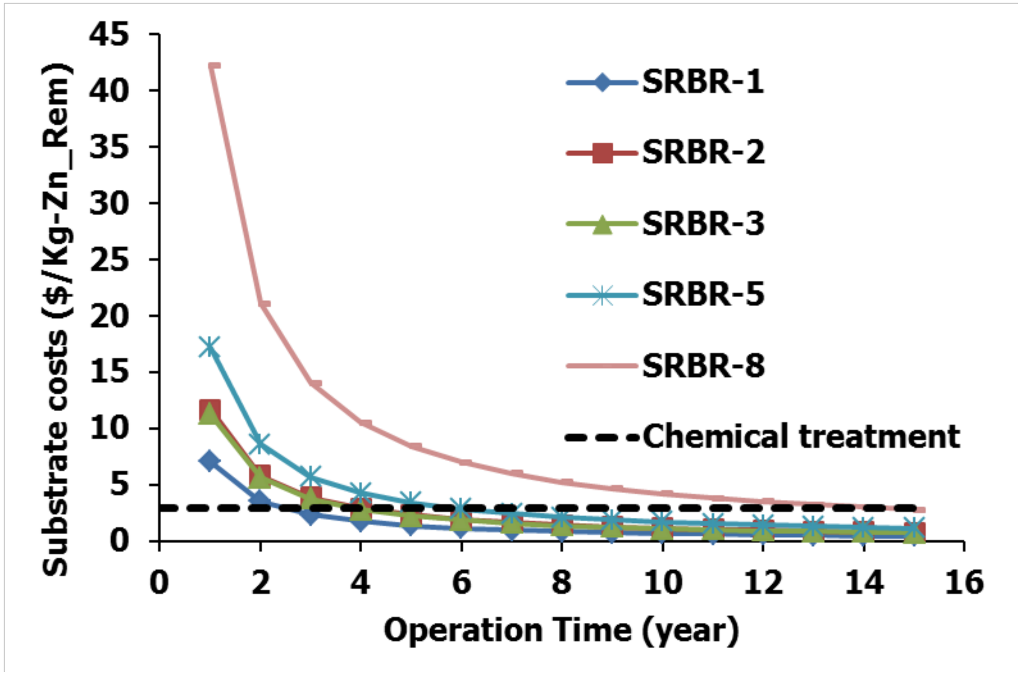


Cost Analysis

- **Substrate costs for 18 L of bed volume**

SRBRs	SRBR-1	SRBR-2	SRBR-3	SRBR-4	SRBR-5	SRBR-6	SRBR-7	SRBR-8
Costs ($)	0.525	0.869	0.840	0.488	1.281	0.581	0.375	3.146

***Unit costs ($/lb): Limestone (0.0172); Alfalfa hay (0.23); Sawdust (0.053); Woodchip (0.054); Walnut shell (0.14)**



- **EBCT=15 days (1.2 L/d)**
- **Zinc=170 mg/L**
- **Chemical treatment costs : ~$3/kg Zn removal**

Full-scale SRBR Investigation Results

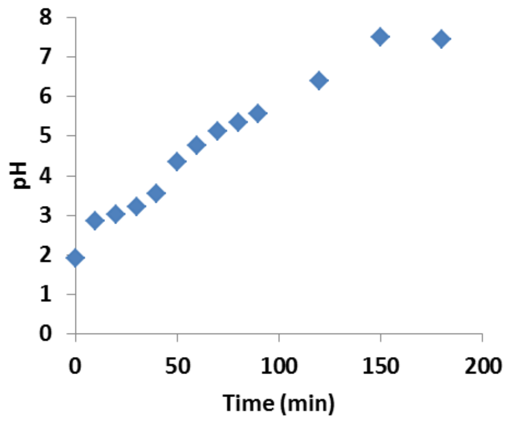
Field Investigation

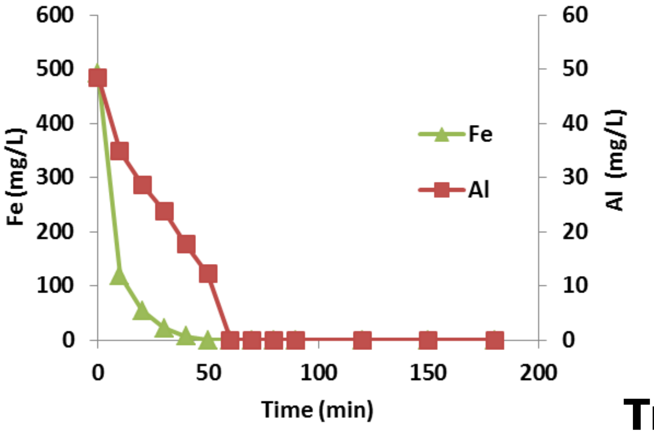
- **Al and Fe precipitates can clog SRBR inlet piping and zone**

SEM-EDS analysis

Al	54%
Zn	16%
Cu	13%
Fe	10%
Ca	6%

✓ **Pre-treatment to increase pH and remove Al and Fe**





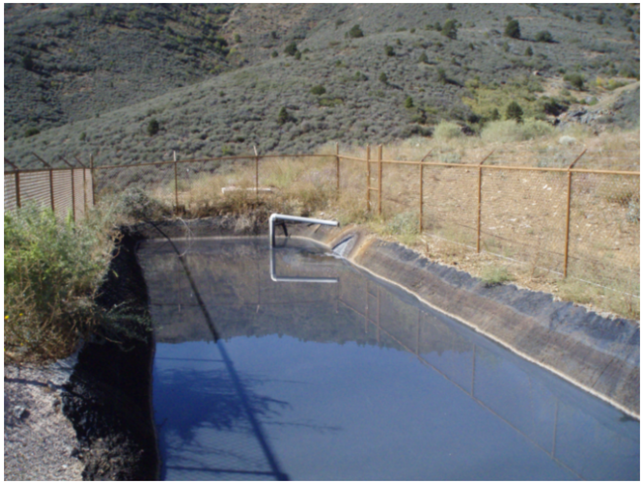
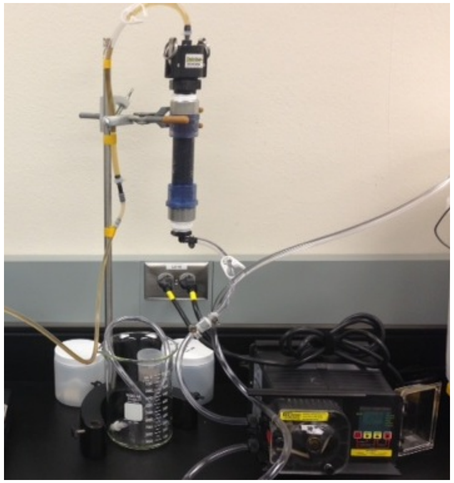
Treatment using Limestone

Field Investigation (cont'd)

- **Overestimation of MIW quantity and quality for projected treatment duration**
  - **Average flow rate decreased to 1.82 gpm after 2 year operation, then ~ 1 gpm (design 7 gpm)**
  - **EBCT ~134 days/265 days (design 34 days)**
  - **Sulfate reduction rate 0.04-0.08 mole/m^3-d**
  - **Metal loading rate 0.0016-0.05 mole/m^3-d**

Field Investigation (cont'd)

- Mn and metal sulfide particles not effectively removed in SRBR
  - Mn: 8.2 mg/L in influent to 5.2 mg/L in effluent
  - Total Fe in effluent > influent, occasionally
  - ✓ Post-treatment required
    - Oxidation, adsorption, ion exchange for Mn
    - Settling, sorption, or filtration for metal sulfide particles

Conclusions & Recommendations

Bench-scale SRBR operation

- **Alfalfa hay and walnut shell are efficient electron donors**
- **Deeper substrate depth to treat higher flow rate MIW**
- **Suggested design factors for the specific MIW:**
  - **Empty bed contact time: 15 days**
  - **Minimum substrate depth: 3 ft.**
  - **Sulfate reduction rate: 0.5-0.7 mole/m^3-day (associated Zn removal > 0.17 mole Zn removal/m^3-day)**

Full-scale SRBR investigation

- **Pre-treatment to increase pH and remove Al and Fe prior to SRBR**
- **Post-treatments to remove Mn and metal sulfide particles from SRBR**

Current Research

- Operating pilot-scale SRBRs on a site
- Limestone pretreatment to pH 5.5 using pH < 3.5 MIW containing high Al and Fe
- Comparison of sulfate and metal removal between walnut shell and pecan shell packed SRBR

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