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FREEPORT-MCMORAN

Mining Webinar Series: Successful Implementation of Biologically-Based Passive Remediation Systems

May 1, 2018

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Who is Freeport-McMoRan Inc.?

Freeport-McMoRan Inc. (FCX) is a premier U.S.-based natural resources company with an industry-leading global portfolio of mineral assets. FCX is the world's largest publicly traded copper producer. FCX's portfolio of assets includes the Grasberg minerals district in Indonesia, one of the world's largest copper and gold deposits; significant mining operations in the Americas, including the large-scale Morenci minerals district in North America and the Cerro Verde operation in South America.

Our global workforce, comprised of employees and contractors, includes approximately 53,000 members. FCX has a strong commitment to safety performance, environmental management and to the local communities where it operates. FCX is a founding member of the International Council on Mining and Metals (ICMM) and committed to implementation of the ICMM Sustainable Development Framework.

Environmental Technology and Life Cycle Transformation

Delivers value across the portfolio by:

A. Identifying, developing and deploying technology to more effectively and efficiently manage liabilities

B. Developing and deploying experience and expertise to:

   a. reduce reclamation and closure costs

   b. reduce closure risk

C. Developing residual resource projects and products to reduce holding costs and extend sustainability of facilities

D. Increasing project deployment velocity in accordance with market conditions and changing regulations

E. Providing data necessary for obtaining agency and public acceptance of innovative programs

Environmental Technology & Life Cycle Analysis Team

Water Treatment	Active water treatment Liability management
Source Control	Liability prevention
Migration Control	Liability management ***Passive Bioremediation***
Residual Resources	Monetizing residual assets Generating offset costs
Life Cycles Analysis	Implement advances in technology Minimize and manage future liabilities Develop sustainable practices

What is ahead?

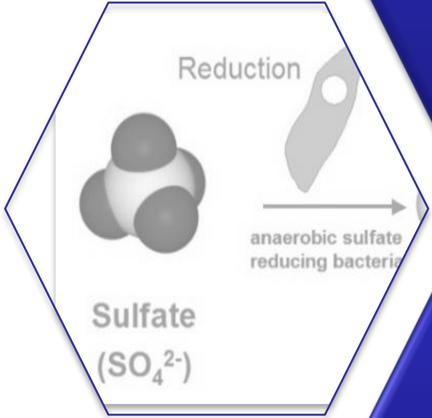
- What constitutes a biologically-based passive bioremediation system?
- Factors affecting successful implementation
- Design criteria (opportunity for success)
- Short break + questions
- Test cases
  - Laboratory treatability testing
  - On-site pilot-scale treatability testing
  - Successful implementation
- Questions / Discussion

What is a Biologically-Based Passive Bioremediation System?

Biologically-based passive water treatment strategies

Rock Reactors

Reactive “Barriers”

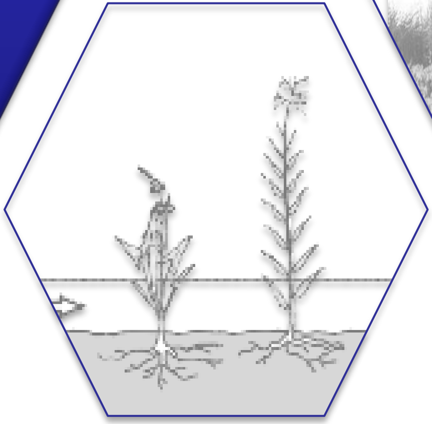


Sulfate-Reducing Bioreactors

Constructed Wetlands

Enhances natural processes

physical, chemical, and biological



Acronyms Used

- BCR – BioChemical Reactor
- BOD – Biochemical Oxygen Demand
- EBCT – Empty Bed Contact Time
- FWS – Free Water Surface Wetland
- SRBR – Sulfate-Reducing BioReactor
- HRT – Hydraulic Retention Time
- NOS – Natural Organic Substrate
- MeLR – Metal Loading Rate
- MeRR – Metal Removal Rate
- SLR – Sulfate Loading Rate
- SRB – Sulfate-Reducing Bacteria
- SRR – Sulfate Removal Rate
- VFW – Vertical Flow Wetland

Active vs. Passive Sulfate-Reducing Biochemical Reactors (SRBR)

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

Sulfate reduction rate (SRR) & Metal removal rate (MeRR)

Active treatment >> Passive treatment

Primary Components of Biologically-Based Passive Bioremediation System

- Pre-treatment alkalinity reactor
  - Alkalinity source (limestone)
  - Raise pH to precipitate Al and Fe decreasing acidity loading

- Sulfate-reducing biochemical reactor (SRBR)
  - Electron source (organic substrate)
    - Sulfate (electron acceptor) to Sulfide ions
    - Targets metal precipitation as metal sulfides
  - Alkalinity source (limestone and sulfate reduction)
    - Achieve circumneutral pH

Primary Components of Biologically-Based Passive Bioremediation System

- Constructed wetland or aqueous polishing cell (APC)
  - Sequestration (plant roots, stems, and leaves)
  - Precipitation (oxides, oxyhydroxides, carbonates)
  - Sorption (mineral and biological)
  - Sedimentation
  - Filtration
  - Increase alkalinity
  - Increase dissolved oxygen
  - Reduced BOD

Biologically-Based Passive Bioremediation System Design Criteria

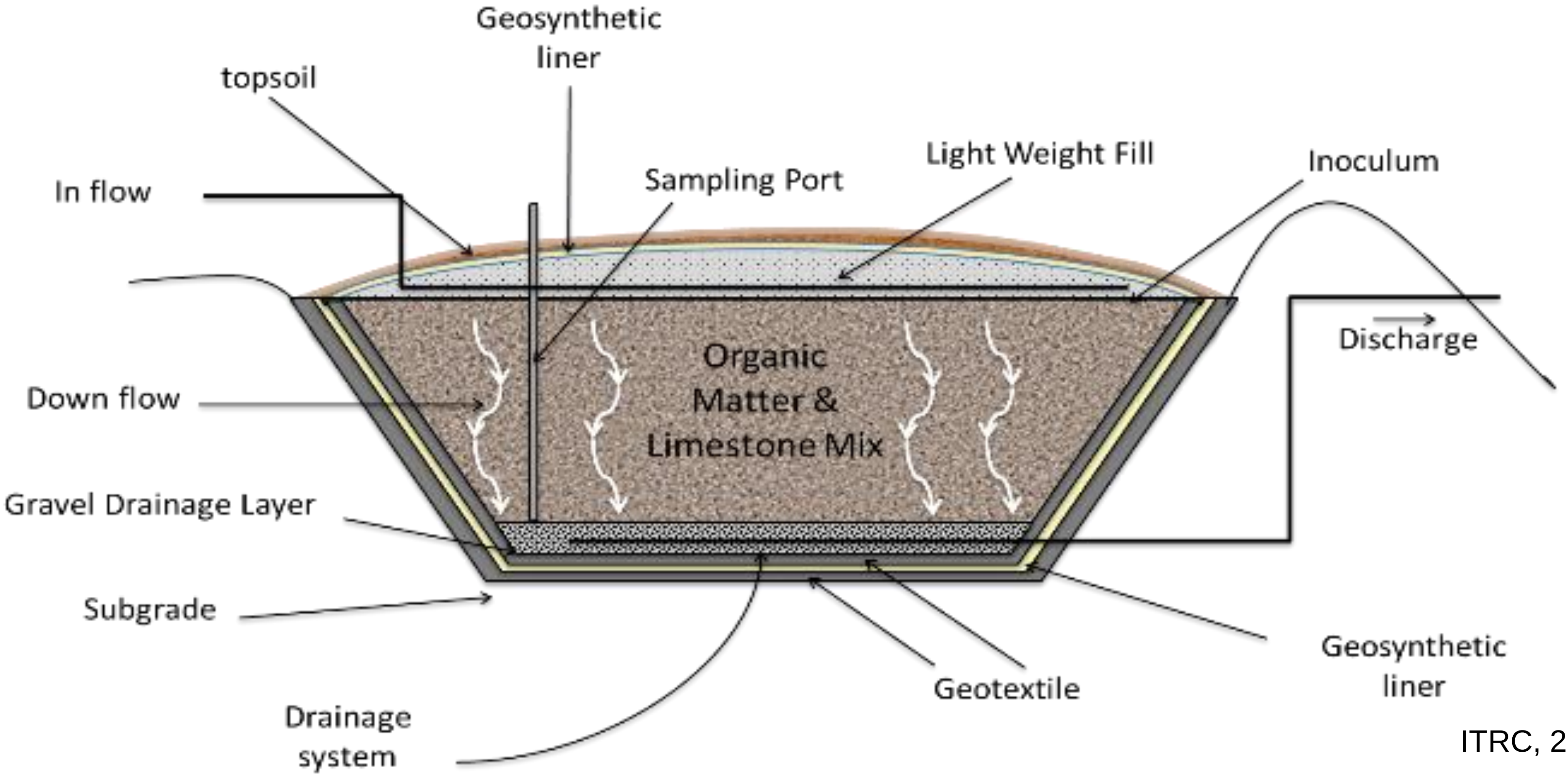
- Flow Rate
  - Low flow rates (1 to 50 gpm) most favorable
  - Hydraulic retention time (HRT)
    - Reaction rates
    - Treatment criteria
    - Longevity
- Mass Loading
  - Sulfate – critical to successful SRBR application
  - Metals – acidic metals (Al, Fe); metal sulfides (Zn, Cu, Cd, Pb, Ni, Co); oxidized metalloids (Mn)
  - Potential toxins (DO, H_2S, antibacterial materials)

Biologically-Based Passive Bioremediation System Design and Operational Considerations

- Water quality objectives
- Site conditions and topography
- Available infrastructure
- Higher flow rates provide less contact time for the same sized sulfate-reducing bioreactor
  - Incomplete reactions
  - Wash out (bacteria; fine sulfide precipitates)
- Potential toxins (dissolved oxygen, excess H_2S, antibacterial materials used in substrate)

Sulfate-Reducing Biochemical Reactor

- SRBR reduces sulfate to aqueous hydrogen sulfide
- Metal (Fe, Cd, Co, Cu, Ni, Zn) sulfides precipitate and are removed from the aqueous phase
- Adds alkalinity and increases pH (circumneutral)



ITRC, 2013

SRBR Design Criteria the Basics
Sulfate Loading / Removal

- Sulfate loading rate (SLR)

$$SLR_m\left[\frac{mmol}{day}\right] = \mathrm{Q}\ [\frac{L}{day}] \times \mathrm{Sulfate}[\frac{\mathrm{mg}}{\mathrm{L}}] \times \frac{mmol\ Sulfate}{96\ mg\ Sulfate}$$

- Sulfate removal
  - Sulfate reduction to sulfide

$SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow H_2S + 2H_2O + 2CO_2$

e- acceptor e- donor (natural organic substrate) reactive sulfide product

  - Sulfate removal rate (SRR) is calculated using

$$SRR_m\left[\frac{mmol}{Kg{\cdot}day}\right] = \frac{\mathrm{Q}\ [\frac{L}{day}]}{M_s[Kg]} \times \Delta\, Sulfate\ [sulfate_{in} - sulfate_{out}\ mmol]$$

mass of bioreactor substrate

Size of SRBR required is determined based on the SLR and SRR

SRBR Design Criteria the Basics
Metal Loading / Removal

- Metal loading rate (MeLR)

$$MeLR_m\left[\frac{mmol}{day}\right] = \mathrm{Q}\,[\frac{L}{day}] \times \sum Metals\,[\frac{mmol}{L}]$$

- Cationic metal removal
  - Metal sulfide precipitation

$$\mathrm{M^{2+} + H_2S \longrightarrow MS + 2H^+}$$ (reactive sulfide)

  - Metal removal rate (MeRR) is calculated using

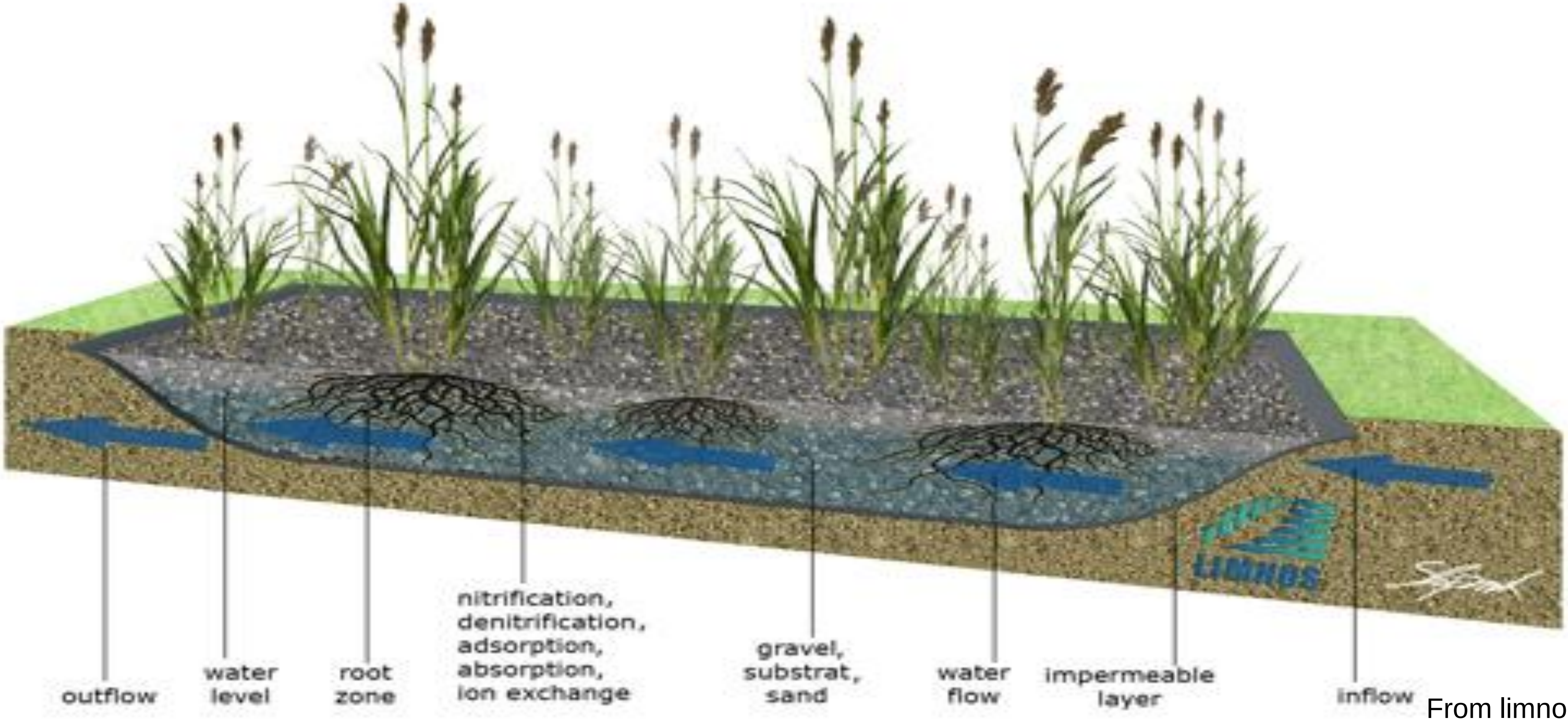
$$MeRR_m\left[\frac{mmol}{Kg \cdot day}\right] = \frac{\mathrm{Q}\left[\frac{L}{day}\right] \times \Delta\, Metal\,[Metal_{\mathrm{in}} - Metal_{out}\, mmol]}{M_s[Kg]}$$

mass of bioreactor substrate

Size of SRBR required is determined based on the MeLR and MeRR

Constructed Wetlands for MIW Remediation

- Emphasize specific wetland qualities for improved treatment
- Used in conjunction with other treatment technologies
- Free water surface and vertical flow wetlands preferred
- Targets biochemical oxygen demand (BOD) and manganese



From limnos.si

Constructed Wetland Design Criteria Basics

- Loading Rates
- Flow Rates
    - Hydrology and hydraulics are critical
    - Low to moderate flow rates are most favorable
- Metal Removal

(physical, biological, and chemical removal processes)

- Sedimentation
- Sorption (mineral and biological)
- Precipitation (oxidation, reduction)
- Filtration
- Sequestration by plants (roots, stems, and leaves)

Constructed Wetland Design – Sizing based on BOD

- Biochemical oxygen demand (BOD)
  - BOD removal must be accounted for when sizing wetlands that emphasize oxidation
  - Daily Mass Loading Sizing Method
    - Loading rate method

Daily mass loading $$DML_{BOD}\left[\frac{mg}{day}\right] = \mathrm{Q}\left[\frac{\mathrm{L}}{day}\right] \times C_{BOD}\left[\frac{mg}{L}\right]$$

Size of wetland $$Area_{BOD}[ha] = DML_{BOD}\left[\frac{Kg}{day}\right] / DLR_{BOD}\left[\frac{Kg}{ha*day}\right]$$

where the daily loading rate (DLR) for BOD = 60 - 100 Kg/ha/day

EPA (1998) recommends loading rate = 54 lbs BOD/acre/day, which results in discharge typically <30 mg/L (Iowa DNR 2007)

Constructed Wetland Design – Sizing based on BOD

- BOD first-order rate (kinetic) removal method:

$$\frac{C_e - C^*}{C_i - C^*} = e^{-K_T t}$$

C_e, C_i, and C^* = effluent, influent, and background BOD (mg/L)

K_T = reaction rate constant (day^{-1}) for BOD

t = hydraulic residence time (day)

$$\text{where } t = \frac{Area\ (m^2)x\ depth(m)}{flow\ rate\ (\frac{m^3}{day})}$$

Q = flow rate (L/day)

C_t = target concentration

Constructed Wetland Design – Sizing based on Mn

Once BOD has been removed then one can account for biologically-mediated oxidation of Mn when sizing wetlands

Daily mass loading sizing method

Loading rate method

Daily mass loading $DML_{Mn}\left[\frac{mg}{day}\right] = \mathrm{Q}\left[\frac{\mathrm{L}}{day}\right] \times C_{Mn}\left[\frac{mg}{L}\right]$

Size of wetland $Area_{Mn}[ha] = DML_{Mn}\left[\frac{mg}{day}\right] / DLR_{Mn}\left[\frac{mg}{ha*day}\right]$

where the daily loading rate (DLR) for Mn = 1,000 – 2,000 mg/m^2*/day*

Constructed Wetland Design – Sizing based on Mn

First-order removal rate (kinetic) method:

$$\frac{C_e}{C_i} = \mathrm{e}^{\left(-\frac{kA}{Q}\right)}$$

A = area (m^2)

k = areal constant (m/d)

Q = flow rate (m^3/d)

C_i , C_e, C^*, C_t = influent, effluent, background, and target concentrations

Biologically-Based Passive Bioremediation System Design Criteria

- Data requirements
  - Flow rates (variability, seasonality)
  - Water chemistry (sulfate & metal loading; anions)
  - Site attributes (topography, available area, etc.)
  - Substrate / plant availability
  - Discharge requirements
  - Financial and infrastructure constraints
- Initial design criteria calculations
  - Sulfate loading/removal rates
  - Metal loading/removal rates
  - Oxygen loading rate (low metal loadings)

Break (Questions and Answers)

Selected Case Studies – Treatability Testing

Laboratory / Bench-Scale

Montana, Little Belt Mountains, USA

- Historical MIW
- Seepage water management

Montana Treatability Study (US EPA)

- Limestone reactor
  - 42” tall x 8” diameter
- SRBRs
  - 12 columns (46” tall)
  - With limestone pre-treatment (4”diameter)
  - Without limestone pre-treatment (4” or 8”diameter)
- VFWs
  - 4 tanks (24” x 24” and substrate 16” deep)

Montana Treatability Study (US EPA) Initial Flow Rate Calculations

Method	Optimal Flow Rate	Criteria
Metal Reduction (1)	**1.5 L/day**	**remove target metals, except Mn**
Sulfate reduction (2)	**0.9 L/day**	**neutralize metal acidity**
Oxygen loading (3)	**4.0 L/day**	**maintain anaerobic condition**

$$(1)\ Q = \frac{MeRR_m\left[\frac{mmol}{Kg\cdot day}\right]\times M_s[Kg]}{\sum Metals\ [\frac{mmol}{L}]}$$

$$(2)\ Q = \frac{SRR_m[\frac{mmol}{Kg\cdot day}]\times M_s[Kg]}{\sum Acidity[\frac{mmol}{L}]} \times \frac{2\ mmol\ Alkalnity}{mmol\ Sulfate\ Reduction}$$

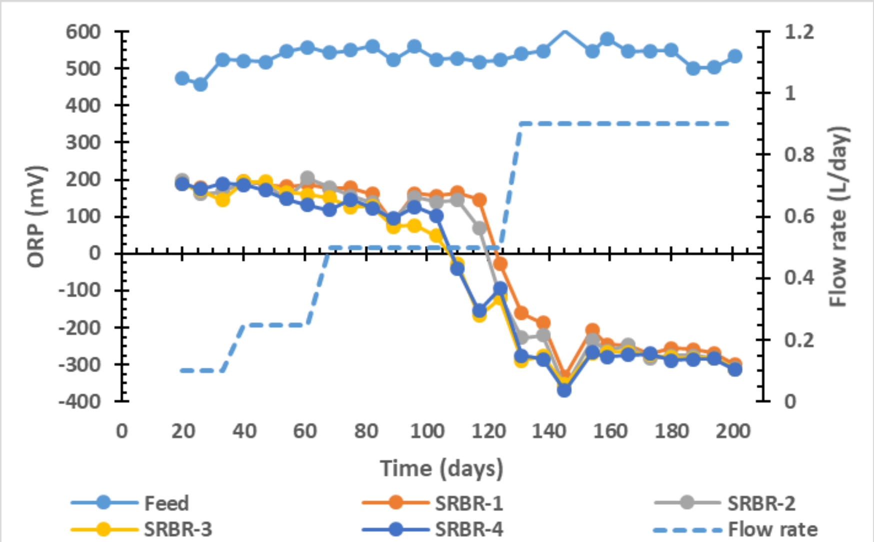
$$(3)\ Q = 0.1\times\ e_{SR}\times\frac{32\ mg\ O_2}{mmol\ O_2}\times\frac{1}{O_2[\frac{mg}{L}]}\times\frac{mmol\ O_2}{4\ me^-}$$

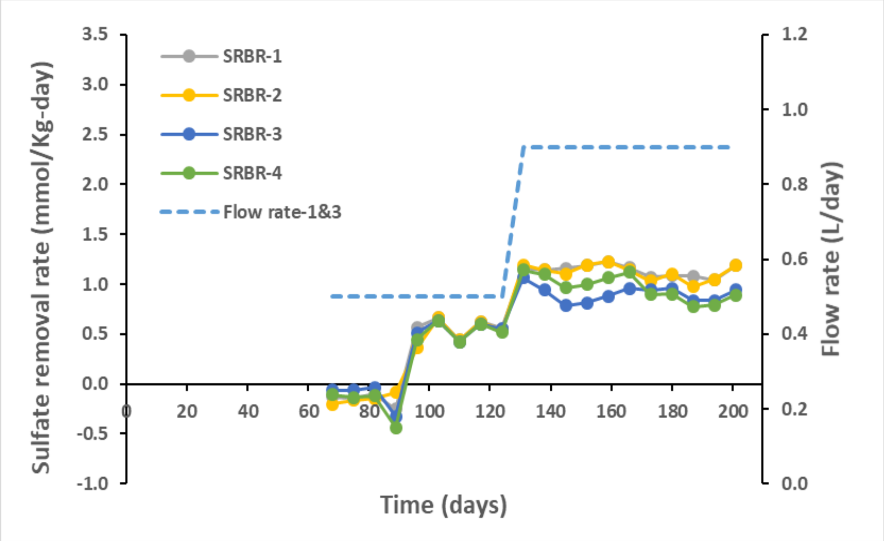
where $MeRR_m$ = SRRm = 0.6 mmol/Kg-day; M_s=10 Kg

$$e_{SR} = SRR_m \times M_s \times \frac{8\ me^-}{mmol\ of\ Sulfate\ Reduction}$$

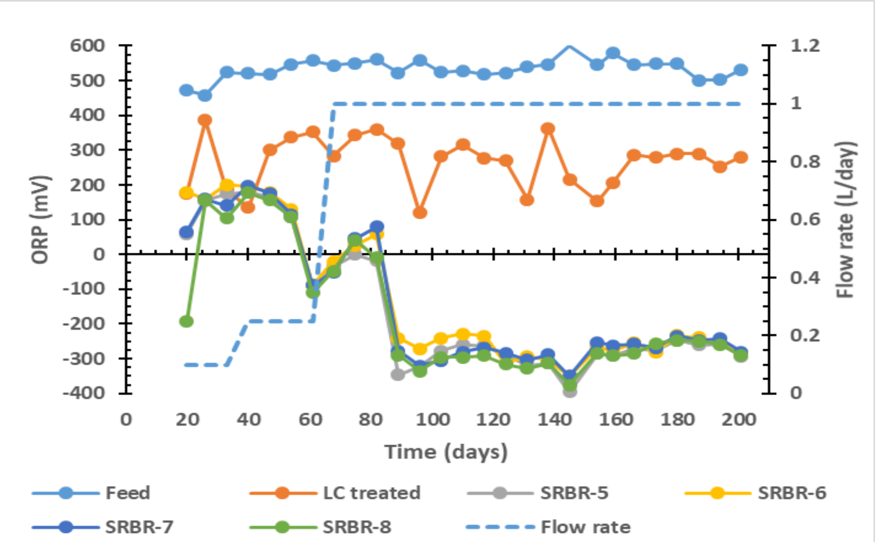
Montana Treatability Study (US EPA) Laboratory SRBR Data

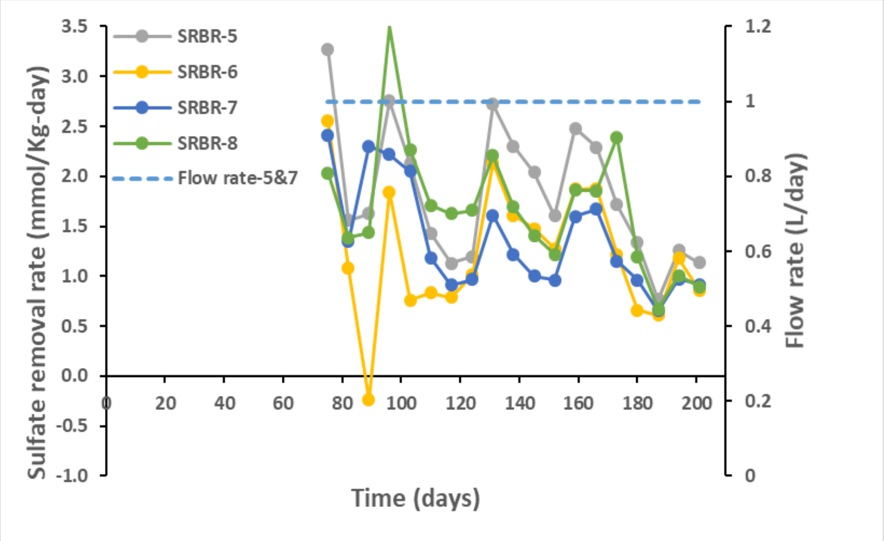
Without Limestone Pre-Treatment





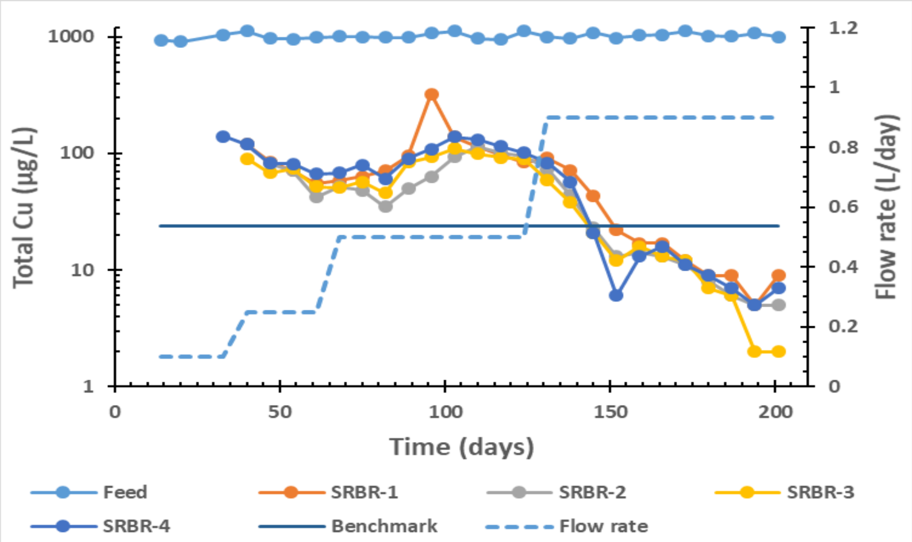
With Limestone Pre-Treatment

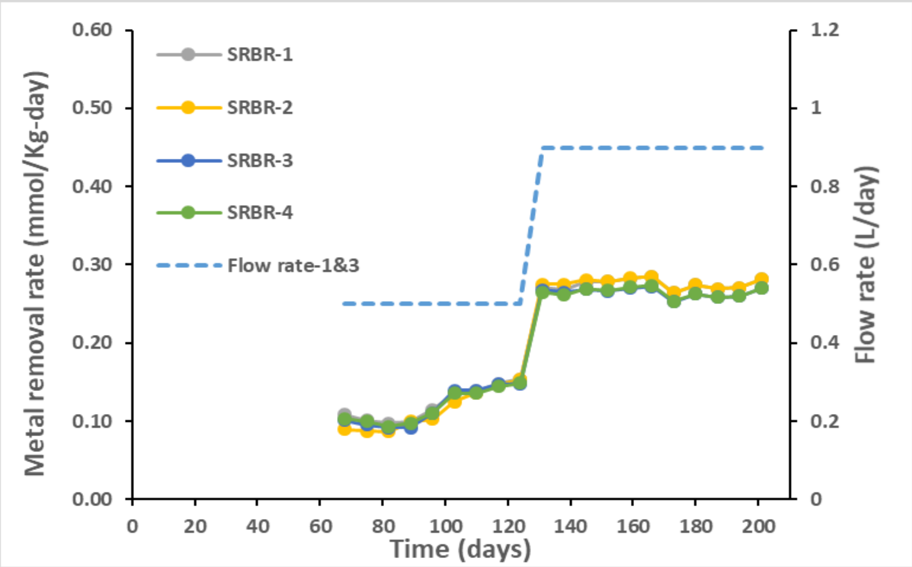




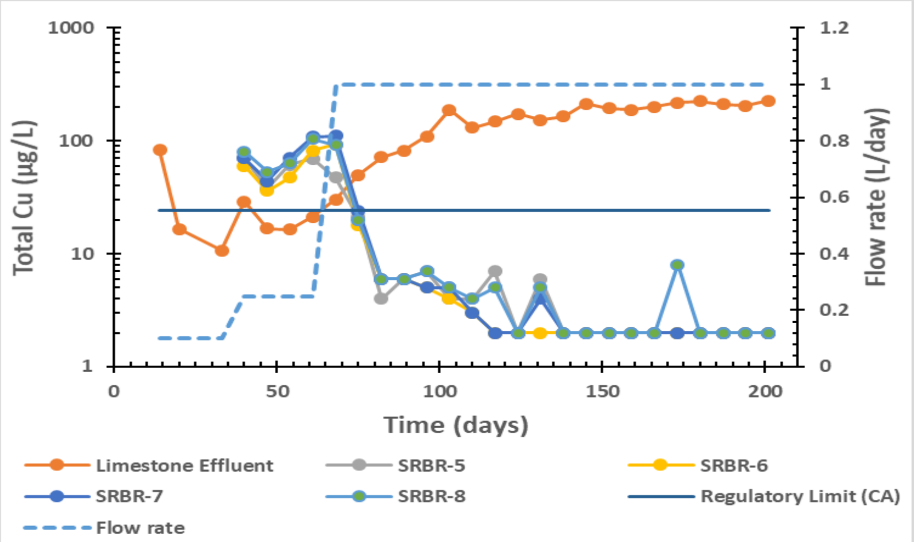
Montana Treatability Study (US EPA) Laboratory SRBR Data

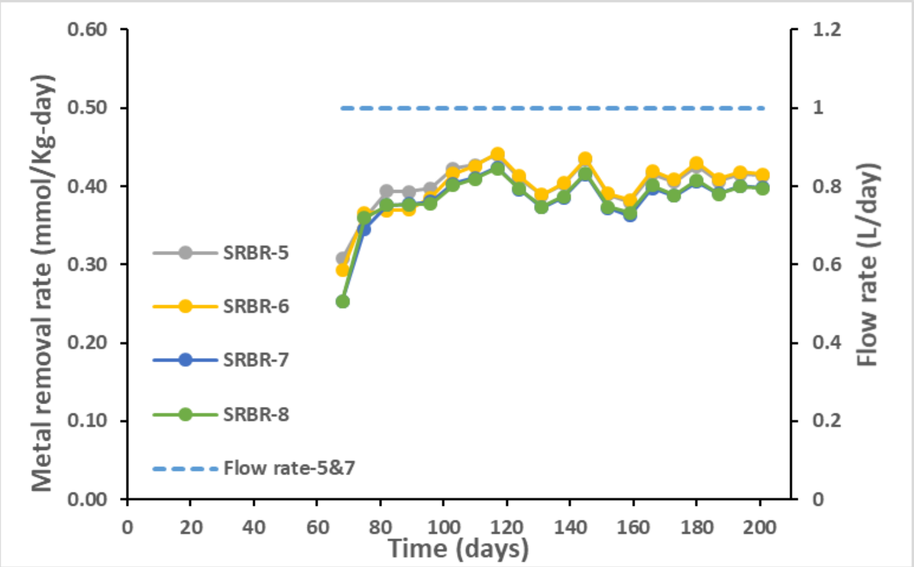
Without Limestone Pre-Treatment





With Limestone Pre-Treatment





Montana Treatability Study (US EPA) Observations

- Collaborative planning is key to success
- Flushing of organics during initial low flow test phase led to analytical challenges
- Initial inoculation phase of SRBR may not have been required – recommend beginning with low flow
- SRR achieved thus far = 0.5 mmol/Kg-day
- MeRR achieved thus far = 0.5 to 0.8 mmol/Kg-day

Selected Case Studies – Treatability Testing

On-site pilot-scale treatability testing for full-scale design

Tyrone, NM, USA

- Operational mine
- Reclaimed leaching facility
- Pre-closure MIW treatability

MIW – high TDS waters (18,000 mg/L) with
MIW metals
(Al 850, Fe 67, Cu 970, Zn 340, and Mn 500 mg/L)
and sulfate (16,000 mg/L)

400 day pilot-scale on-site treatability study

Tyrone Mine Treatability Study

- Evaluated 2 pre-treatment strategies
- plus 2 SRBR substrate compositions

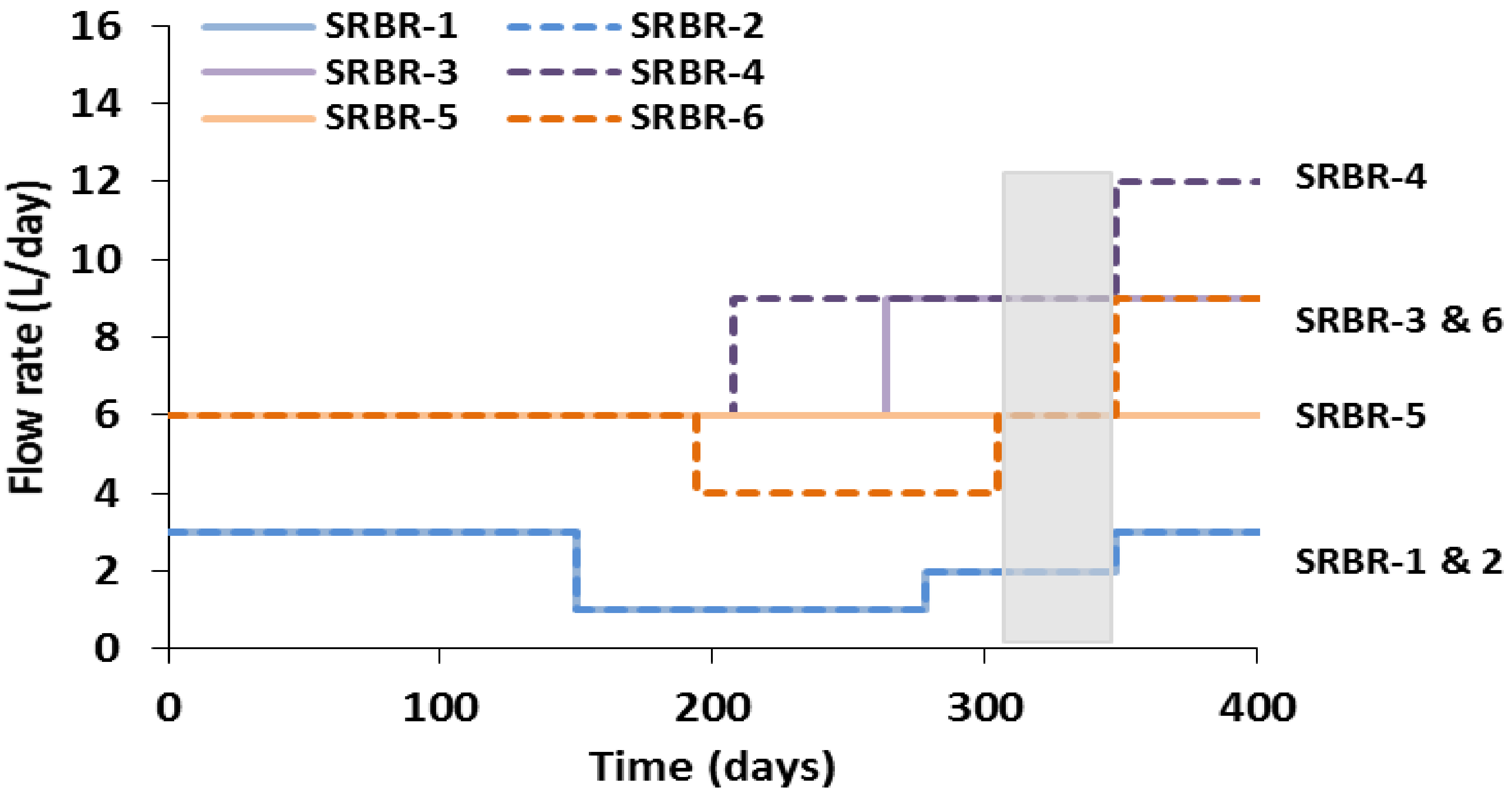
- 6 paired - 90 gallon SRBRs operated in down flow configuration

- Evaluated treatment effectiveness for paired vertical flow wetlands (VFW) to reduce Mn and BOD following the primary treatment SRBRs.

- Area of VFW = 0.62 m^2 with 40 cm deep substrate

- 3 native species: *Schoenoplectus olneyi*, *S. acutus*, *Typha domingensis*

Tyrone Mine Treatability Study - SRBR



Operational flowrates for each of the SRBRs. Shaded area represents the time period of operations at optimal metal removal rate.

Tyrone Mine Treatability Study – SRBR

Metals and sulfate %removal at optimal flowrate for each treatment strategy. Sulfate-16,000, Al-850, Fe-67, Cu-970, Zn-340, and Mn-500 mg/L.

	Flow rate	HRT	Al (%)	Fe (%)	Cu (%)	Mn (%)	Zn (%)	Sulfate (%)
SRBR-1[1]	2 L/d	80 d	99.3	100	100	68	100	72
SRBR-2[1]	2 L/d	80 d	98.8	96	100	19	100	68
SRBR-3[2]	9 L/d	16 d	80.0	–	100	26	100	18
SRBR-4[2]	9 L/d	17 d	79.3	–	100	34	100	30
SRBR-5[3]	6 L/d	24 d	73.2	–	100	10	99	27
SRBR-6[3]	6 L/d	26 d	54.7	–	100	0	100	28

Percent Removal = ((Concentration In – Concentration Out) / Concentration In) x 100

1) *Primary treatment SRBR without pre-treatment*
2) *Calcium hydroxide pre-treatment followed by the primary treatment*
3) *Limestone pre-treatment followed by the primary treatment*

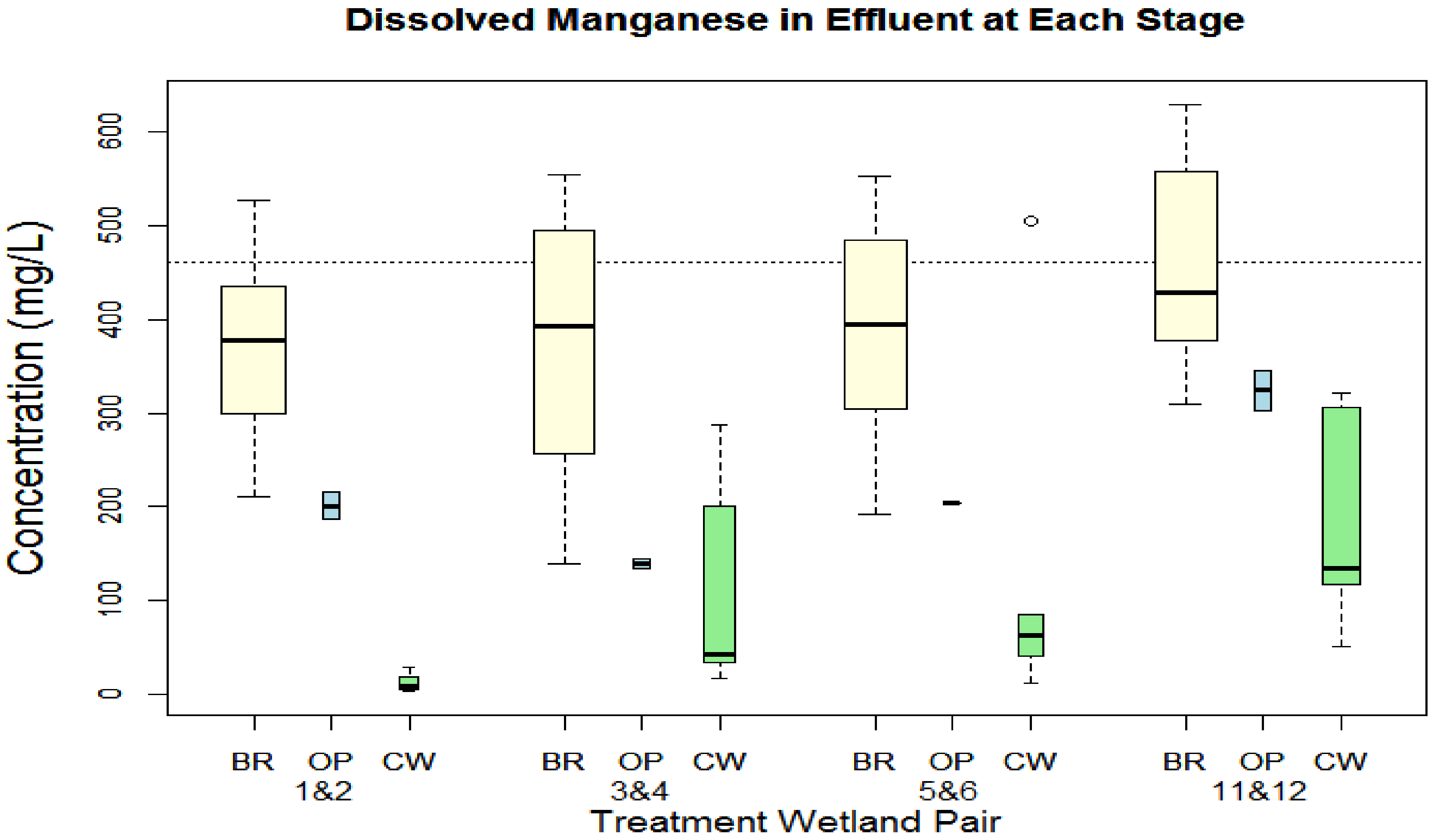
Tyrone Mine Treatability Study – SRBR

Metal loading and removal rates for each SRBR at optimal flow rates for each treatment strategy.

	Flow Rate (L/d)	HRT (d)	Metal Removal Rate (MeRR, mmol metal/Kg·d)			Sulfate Removal Rate (SRR, mmol SO_4^{2-}/Kg·d)
			All metals	All metals except Mn	All metals except Mn, Al, Fe	
SRBR-1[1]	2	80	0.99	0.91	0.33	1.87
SRBR-2[1]	2	80	1.02	0.99	0.36	1.95
SRBR-3[2]	9	16	0.86	0.57	0.50	1.55
SRBR-4[2]	9	17	0.85	0.58	0.51	1.65
SRBR-5[3]	6	24	0.59	0.49	0.37	1.03
SRBR-6[3]	6	26	0.51	0.51	0.39	1.11

1) *Primary treatment SRBR without pre-treatment*
2) *Calcium hydroxide pre-treatment followed by the primary treatment*
3) *Limestone pre-treatment followed by the primary treatment*

Tyrone Mine Treatability Study – Constructed Wetland



Boxplots summarizing dissolved Mn concentrations in effluent at each stage of the treatment system (excluding pre-treatment)

Tyrone Mine Treatability Study – Constructed Wetland

Summary statistics for treatment efficiency, area-adjusted removal, and first-order removal rate of dissolved Mn among constructed wetland pairs.

Wetland Pair	Mn treatment efficiency (%) $\left(\frac{C_{in} - C_{out}}{C_{in}}\right) x\ 100$	Area-adjusted removal (g/m²·d) $(C_{in} - C_{out})\frac{Q}{A}$	First-order removal (m/d) $\frac{Q}{A} ln\left(\frac{C_{in}}{C_{out}}\right)$
1 & 2	96%	0.62	0.010
3 & 4	70%	0.63	0.008
5 & 6	69%	0.91	0.008
11 & 12	59%	1.23	0.006
Median:	69%	0.63	0.008

Tyrone Mine Treatability Study - Observations

- Active chemical treatment is more efficient than passive limestone treatment considering chemical costs and maintenance. But requires active system and adds to sludge disposal generation and costs.
- Direct MIW treatment is technically feasible, however, an amorphous sludge forms on top layer of SRBR that may decrease efficiency.
- Pre-treatment can reduce SRBR size by a factor of 4
- High TDS MIW is treatable but treatment objectives critical

  550 mg Mn/L, 980 mg Cu/L, and 380 mg Zn/L

  with 160 mg Fe/L and 940 mg Al/L
- Metal removal rates for Cu and Zn were calculated to be

  0.14 - 0.21 mol/m^3-d or 0.33 - 0.51 mol/ton-d
- Constructed wetland augments SRBR to effectively remove Mn, treat BOD, and remove particulate precipitates following SRBR.

Selected Case Studies – Success

Iron King, AZ, USA

- Historical mine seep
- Voluntary Remediation Project (VRP)
- MIW management

- Glory hole remediated to shed clean water and limit infiltration into mine workings
- Biologically-based passive bioremediation system constructed 2009
- MIW seepage to SRBR decreased from 10 gpm in 2009 to <2 gpm by 2017

Iron King – Construction and 2012

Adit 2009 – MIW from a glory hole located above the adit.

MIW is collected in the adit and directed to connex then to the SRBR

SRBR & APC overview

Iron King – The Magic Mix

Substrate composition (wt%):

Wood Chips (aged)	(49.5)
Sawdust	(10)
Alfalfa Hay	(10)
Limestone	(30)
Manure	(0.5)

Iron King – Construction and 2012

Settling Pond

Receives water from SRBR, allows settling of particulates and directs effluent to the APC

Aerobic Polishing Cell (APC)

Iron King – Design and Operational Parameters

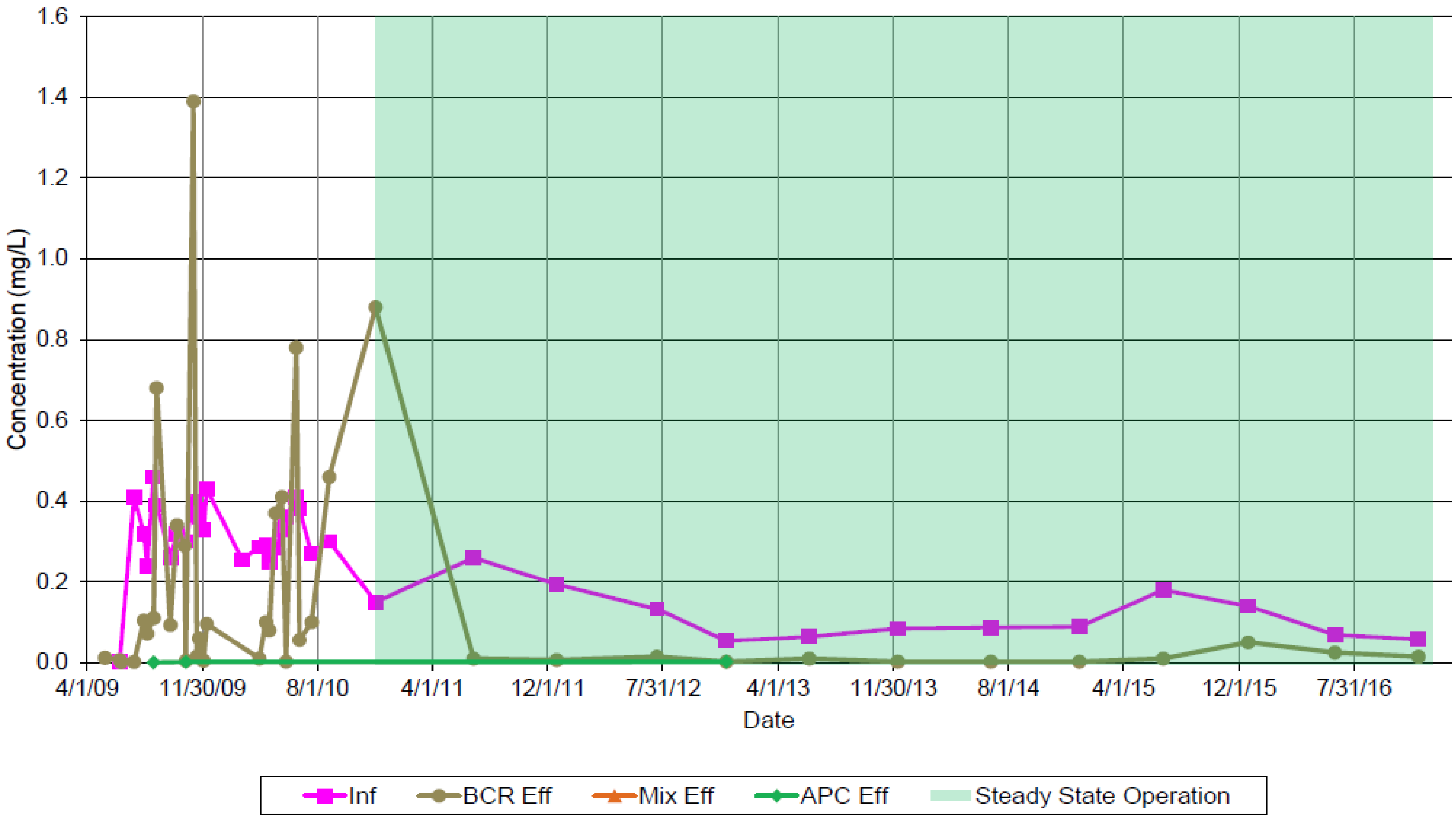
- Target analytes Zn and Cd
- Design flow rate = 7 gpm based on

  5,000 mg/L Sulfate, 130 mg/L Cu, 0.4 mg/L Cd, 150 mg/L Zn
- Current operating flow rate ~ 1.8 gpm with

  1,500 mg/L Sulfate, 4.2 mg/L Cu, 0.06 mg/L Cd, 17 mg/L Zn
- Current SRBR Effluent Concentrations

  <500 mg/L Sulfate, <0.01 mg/L Cu, <0.03 mg/L Cd, <0.01 mg/L Zn
- Zero discharge from APC

Iron King – Successful Implementation – Total Cd



Golder Associates

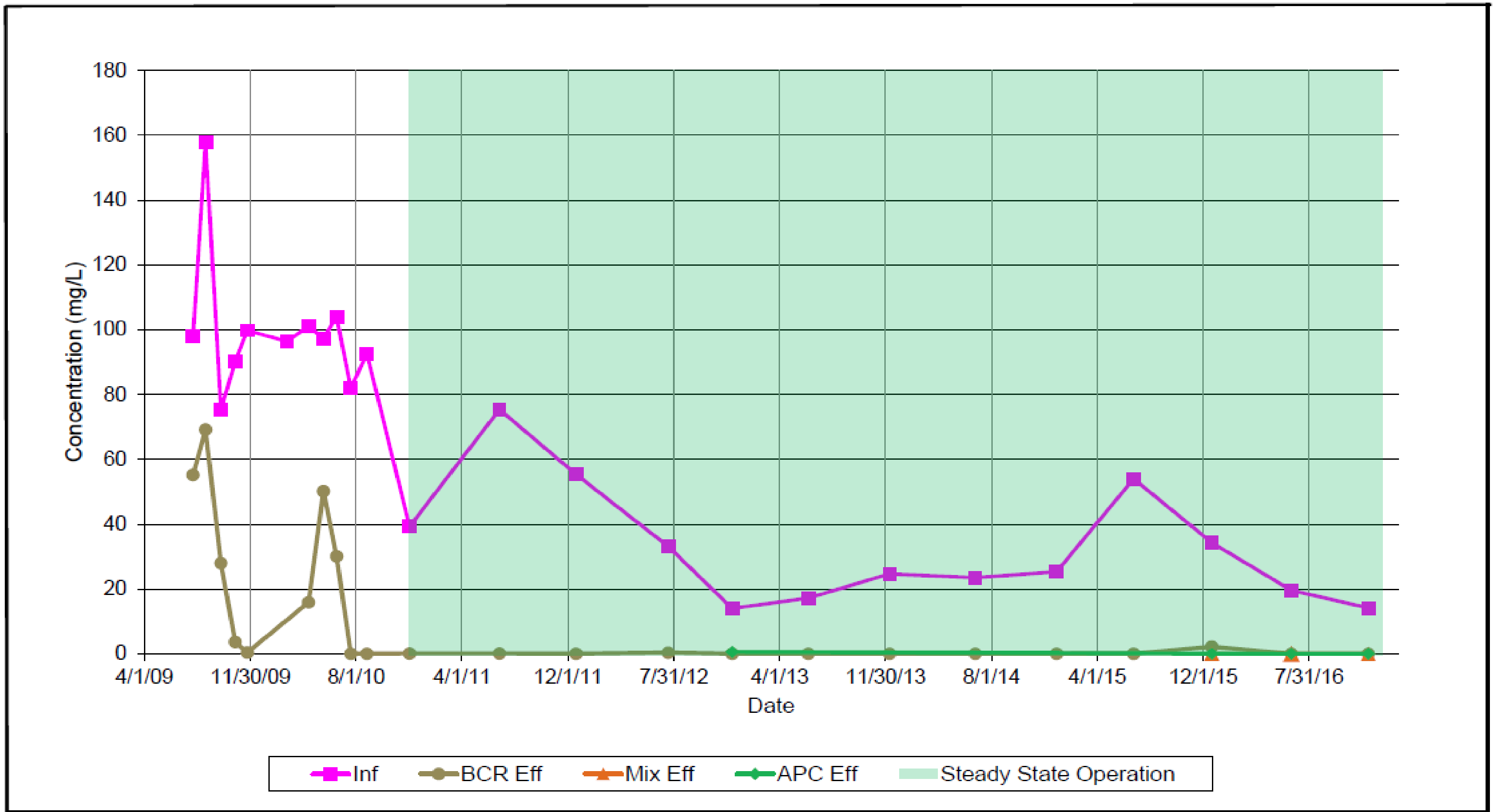
Denver, Colorado

Total Cadmium (mg/L)

IRON KING VOLUNTARY REMEDIATION MONITORING

DRAWN	AMM	DATE	February-17	JOB NO	1402463
CHECK	RJS	SCALE	NA	DWG REV NO NO	
REVIEWED	PEP	FILE NAME		FIGURE NO	15

Iron King – Successful Implementation – Total Zn



Golder Associates

Denver, Colorado

Dissolved Zinc (mg/L)

IRON KING VOLUNTARY REMEDIATION MONITORING

DRAWN	AMM	DATE	February-17	JOB NO	1402463
CHECK	RJS	SCALE	NA	DWG REV NO NO	
REVIEWED	PEP	FILE NAME		FIGURE NO	14

Iron King – Achieved VRP Objectives and Project Goals

- Source control key to longevity of bioremediation system
- No pre-treatment required for flow rate and water chemistry
- Removal efficiency 99.3% for dissolved Fe, Al, Zn, Cu, and Cd
- Dissolved Ni, Se, As, and Be all less than the laboratory detection
- SRBR SRR = 0.27 mol/ton-d; 0.12 mol/m^3-d
- SRBR MeRR = 0.10 mol/ton-d; up to 0.05 mol/m^3-d
- Settling pond removes suspended particulates leaving the SRBR prior to distribution through APC
- APC provides final polishing of water quality and transpiration
- 7.6 million gallons of seepage treated
- Treatment system created a zero-discharge facility

Biologically-Based Passive Bioremediation System Observations

- Collaboration and planning key to success.
- Ability to treat a wide range of MIW flows and chemistry.
- Lab and pilot-scale testing important.
- Optimum sulfate removal rate and metal removal rates may be higher than published rates – value of bench and pilot-scale testing.
- Water quality objectives for any given project drives the size of the treatment system.
- Biologically-based passive bioremediation systems are an effective treatment system for MIW, especially for lower flow applications.

Biologically-Based Passive Bioremediation System Design Criteria

- Data Requirements
  - Flow Rates (variability, seasonal)
  - Water Chemistry (sulfate & metal loading; anions)
  - Site Attributes (topography, available area, etc.)
  - Substrate / Plant availability
  - Discharge Requirements
  - Financial and Infrastructure Constraints
- Initial Design Criteria Calculations
  - Sulfate Loading/Removal Rates
  - Metal Loading/Removal Rates
  - Oxygen Loading Rate (low metal loadings)

Final Questions and Answers
Webinar Wrap-up