# Acidity Neutralization Cell (ANC) Pretreatment for BCR Influent

Crystal and Bullion Mines, Basin Mining Area Superfund Site, Montana

Field Pilot and Laboratory Column Treatability Studies

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$$Ch2m_{sm} \longrightarrow Ch1 + C_{sm} + C$$

### **Passive Treatment Overview**

- Most PTS targeting trace metal removal are multicomponent (staged) systems built around one or more main biochemical reactor (BCR) unit.
- The BCR media is designed to support high levels of anaerobic microbial activity over an extended timeframe (>10 years)
- Metal removal is through both biological and abiotic removal mechanisms; however, the media is prone to plugging by oxyhydroxides due to removal of hydrolysable metals (e.g., ferric iron and aluminum)
- Where mine drainage is highly acidic with a significant amount of hydrolyzable metals, an acid neutralization cell (ANC) containing media with high neutralization capacity may be used as pre-treatment in front of a main BCR unit.



### **Passive Treatment Overview**

- ANC is used as a pre-treatment step in passive treatment systems to lower the overall influent acidity, remove hydrolyzable metals, and raise the pH.
- Generally small vertical- or horizontal-flow basins filled with organic materials and a relatively high proportion of limestone.
- The organic substrate in this media mix is used primarily as a matrix support for even distribution of sand-sized limestone, rather than to create high reducing conditions.
- The main function of an ANC is abiotic limestone dissolution and acid neutralization.
- ANCs are not designed for an extended life cycle (for example, decades), and require periodic media replacement (for example, 2-5 years, depending on size and load).
- Consequently, they are best configured to allow easy media change-out.



### **Demonstration Site**



### Location

 The Crystal & Bullion Mine sites are abandoned mines located in Jefferson County, Montana near the town of Basin, between Helena and Butte.





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# **Key Features**

- Surface and underground mining (including gold, silver, copper, lead, and zinc) between 1885 and 1983.
- remote location, at high elevation (7,500 to 8,000 ft amsl); very difficult to access in winter (only by snow machine).
- not supplied with electrical power, water, or other utilities.
- The adit discharge is acidic
- COCs are Al, As (Bullion), Cd, Cu, Pb, and Zn; also contains elevated Fe and As (Crystal)
- Ecological risk associated with the adit discharge, but little or no human health risk
- Passive Treatment Systems are the EPA's preferred remedies for the adit discharges at the Crystal and Bullion Sites



### **Proof of Concept** Field Pilot "Barrel" and Laboratory Column Studies



# Experimental Design – Field Pilot Barrel Study



 Started June 26, 2014 and ran continuously for nearly 15 weeks; shut down and dismantled on October 7, 2014

- Conducted as "Proof of Concept" to demonstrate ANC – BCR design
- Three, two-stage, pilot-scale, treatment systems operated in parallel
- Gravity flow from mine portal to collection sump
- Peristaltic pump to deliver controlled-flow AMD to each array
- Flow by gravity once delivered to system
- Gravity discharge back to Uncle Sam Gulch Creek



### Experimental Design – Lab Column Study



- Conducted to refine from "proof of concept" to develop design parameters (i.e., optimize HRT)
- Two-stage column systems representing the first two stages of a PTS (i.e., ANC & BCR)
- Four continuous-flow column systems operated in parallel using synthetic Bullion and Crystal Mine water as influent.
- Operated over a range of HRTs.



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x - sampling point: I = influent; M = midpoint between Stages A and B (ANC effluent); E = BCR effluent; x = midpoint in Stage A = ANC: Sta

# Experimental Design – Lab Column Study

### **Column Testing Conditions**

		Influent	Trial A HRT			Trial B HRT				
			ANC			ANC				
System	Influent	Flow	ANC1	ANC2	total	BCR	ANC1	ANC2	total	BCR
ID	Water	[mL/min]	[hours]	[hours]	[hours]	[days]	[hours]	[hours]	[hours]	[days]
PTS-1	Bullion	3	3	3	6	5	1.5	1.5	3	2.5
PTS-2	Crystal	6	6	N/A	6	3	3	N/A	3	1.5
PTS-3	Crystal	6	6	N/A	6	5	3	N/A	3	2.5
PTS-4	Crystal	6	6	N/A	6	7		Discor	ntinued	

#### Notes:

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Trial A: March 9 - April 27; Trial B: May 1 - June 18 (approximately 7 weeks each)
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- PTS-1 ANC divided in half to allow evaluation of two different ANC HRTs simultaneously
- PTS-2 through -4 treated synthetic Crystal Mine water at different BCR HRTs.
- Trial A was conducted during the first half of the approximately 14-week study
- During Trial B, the influent flow rates were doubled, effectively halving the treatment unit HRTs
- PTS-4 system was not operated in Trial B.

### Results



### Adit Discharge Characteristics and Treatment Targets

		Βι	Illion Mine	Crystal Mine		Treatment Target	
Parameter	<u>Units</u>	Average	Range	<u>Average</u>	Range	<u>Acute</u>	<u>Chronic</u>
Flow	gpm	4.9	1.80 - 14.4	25.1	4.49 - 49.4		
Temperature	°C	5.2	0-9.7	5	2.5 - 7.0		
pH (field)	SU	2.9	2.5 - 3.7	4.1	3.5 - 5.8		
Conductivity	µS/cm	1,840	1,130 - 3,100	747	478 – 1,270		
Sulfate (SO <sub>4</sub> )	mg/L	995	718 – 1,302	406	240 - 528		
<b>Dissolved Metals</b>	/Elements					-	
Aluminum (Al)	µg/L	14,850	8,900 - 21,120	3,170	564 – 7,310	750	87
Arsenic (As)	µg/L	2,480	160 - 10,100	122	37.0 – 315	340	150
Cadmium (Cd)	µg/L	435	251 – 1,070	559	331 – 737	8.73	0.76
Copper (Cu)	µg/L	8,120	2,060 - 23,600	5,770	2,610 - 9,330	51.7	30.5
Iron (Fe)	µg/L	160,000	127,000 - 206,000	39,300	19,500 – 55,100		1,000
Lead (Pb)	µg/L	402	196 – 801	37.3	7.00 – 73.7	477	18.6
Manganese (Mn)	µg/L	21,700	16,200 - 29,700	11,100	6,390 - 15,100		
Nickel (Ni)	µg/L	83.9	59.7 – 109	34.8	24.2 - 41.9	1,516	169
Silver (Ag)	µg/L	<1		<0.5		44	
Zinc (Zn)	µg/L	47,800	23,400 - 141,000	43,300	24,500 – 55,900	388	388

# Field Pilot – Results

- ANC in all three arrays raised pH, lower acidity, and increased alkalinity
- BCR-3 best performance complete acidity removal, higher pH

Parameter	Influer Units Averag		nt ge	Midpoint Average		Effluent Average	
BCR-1	•						•
pH	s.u.	3.67		6.15		6.36	
Acidity	mg/L as CaCO3	197		26.5	<	24.8	<,a
Alkalinity	mg/L as CaCO3	5.00	U	81.8		125	
BCR-2							
pH	s.u.	3.67		6.35		6.15	
Acidity	mg/L as CaCO₃	197		10.7	<,a	14.0	<,a
Alkalinity	mg/L as CaCO₃	5.00	U	167		214	
BCR-3							
pH	s.u.	3.67		6.56		6.50	
Acidity	mg/L as CaCO₃	197		10.0	U	10.0	U
Alkalinity	mg/L as CaCO3	5.00	U	171		221	

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# Field Pilot – Results (ORP)

- While the ANC performed well, the BCR never obtained highly reducing conditions expected
- BCR-2 and -3 achieved negative ORP in final effluent
- BCR-1 had positive effluent ORP, but still achieved sulfate reduction
- BCR-3 reached negative ORP after ANC, but the BCR did not become highly reducing and the rate of sulfate reduction was well below normal
- BCR-2 had the highest rate of sulfate reduction

Parameter	Units	Influent Average	Midpoint Average	Effluent Average	
BCR-1					
ORP	mV	298	60.6	28.5	
Sulfate	mg/L	380	368	336	
Sulfate reduction <sup>a</sup>	mg/L		12	44	
Sulfide	mg/L		0.13	0.14	
COD	mg/L			134	
BCR-2					
ORP	mV	298	42.2	-25.5	
Sulfate	mg/L	380	361	259	b
Sulfate reduction <sup>a</sup>	mg/L		19	121	
Sulfide	mg/L		0.12	3.3	
COD	mg/L			287	
BCR-3					
ORP	mV	298	-15.6	-31.5	
Sulfate	mg/L	380	377	b 331	b
Sulfate reduction <sup>a</sup>	mg/L		3	49	
Sulfide	mg/L		0.89	1.5	
COD	mg/L			218	

#### **Redox Conditions Indicator Data**

# Field Pilot – Trace Metal Results (Zn)

- All three systems achieved effluent dissolved concentrations of Al, As, Cu, and Pb that were lower than the respective treatment targets (Montana WQS)
- Cd & Zn were the most challenging metals for effective treatment
- In general, BCR-2 exhibited the best removal rates for Cd & Zn
- After re-inoculation, BCR-2 trended towards water quality standard
- BCR-1 and -3 removed zinc, but not below the target water quality standard



# Field Pilot – Autopsy

- After decommissioning the pilot, the barrels were drained and substrate investigated
- The limestone-amended ANC's exhibited a sharp boundary of ferric and aluminum oxyhydroxides overlying relatively "fresh" substrate
- Purple S-bacteria were observed colonizing the substrate between the barrel wall and the substrate; may have impacted ORP values
- Elemental S at top of BCR indicate sulfate reduction and sulfide generation





BCR

- The column testing exhibited similar results for pH, acidity, and alkalinity compared with the field study.
- pH was effectively neutralized in the ANC for both waters and at HRTs of 3 and 6 hours, and pH was neutralized nearly as well even at an ANC HRT of 1.5 hours
- Influent acidity was reasonably well neutralized (e.g., alkalinity ≥ acidity in ANC effluent) for both waters at HRTs of 3 and 6 hours, although there was some evidence of slightly incomplete acidity neutralization for Bullion Water in Trial B (total HRT = 3 h)



- ORP was sufficiently low (-200 to -300 mV) in BCR Effluent, for both the Bullion and Crystal systems, to indicate strongly reducing redox conditions conducive to sulfate reduction
- A considerable excess of sulfate reduction (compared to the amount needed for sulfide precipitation of metals) occurred in all systems during Trial A
- In Trial B, the amounts of sulfate reduction exhibited were similar to the theoretical stoichiometric requirements for metals removal. No adverse effect on removal of Cd, Zn, or Fe was observed.



6-Apr

26-Apr

- Sulfate Reduction

17-Mar

25-Feb

Sulfate-Influent Sulfate-BCR Effluent

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25-Jun

5-Jun

Sulfide-BCR Effluent

16-May

---- Sulfate-ANC Midpoint — Sulfate-ANC Effluent

- Typically 97 99+% removal efficiencies for all dissolved metals/elements of concern (Al, As, Cd, Cu, Fe, Pb, Zn) – both ARD sources
- Dissolved metals concentrations in virtually all BCR effluent samples met compliance with their respective treatment targets
- Similar removal for all HRTs tested, including the shortest HRTs evaluated for each treatment unit type: ANC – 3 hours; BCR – 1.5 days for Crystal (PTS-2B) and 2.5 days for Bullion (PTS-1B



- Elements largely removed in the ANC: AI, As, Cu, and Pb – plus Fe in Crystal systems but only roughly one-half of the Fe in Bullion systems (due to the markedly higher influent concentration).
- Elements largely removed in the BCR: Cd and Zn, plus approximately one-half of Fe in the Bullion system.



Zn, µg/L



### **Considerations for Design and Construction**



# **Residence Time and Unit Sizing**

- HRT for sizing of ANC and BCR units in full-scale design of mine water passive treatment systems for the Bullion and Crystal Mine sites:
  - Bullion and Crystal ANC: 6 hours
  - Bullion BCR: 4 to 4.5 days (suggest 4 days at the design maximum flow)
  - Crystal BCR: at least 3 days (suggest 4 days at the design average flow)







### **Conceptual Design for Crystal Mine Adit**



Preliminary PFD Crystal Mine PTS

### Thank You

