CASE STUDY: EVALUATING THE FEASABILITY OF CO-TREATING BIOCHEMICAL REACTOR EFFLUENT AND MINING INFLUENCED WATER¹

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Abstract. Biochemical reactors (BCRs) are a passive treatment technology used to reduce metals concentrations and increase the pH of mining influenced water (MIW). The practice of mixing municipal wastewater with MIW is known to remove metals from the MIW, destroy pathogens, and lower the biochemical oxygen demand of the wastewater. (Strosnider et al. 2009). Characteristics of typical BCR effluent, including a near neutral pH and elevated concentrations of sulfide, alkalinity, biochemical oxygen demand, and residual nutrients (i.e., nitrogen and phosphorus) are similar to typical municipal wastewater water characteristics. Mixing MIW with BCR effluent may have several synergistic effects, including reducing the metals and acidity load associated with the MIW, reducing the biochemical oxygen demand and sulfide concentrations of the BCR effluent, and ultimately reducing the footprint requirements for a passive treatment system utilizing BCRs.

In July 2009, a field study was conducted to evaluate the treatment accomplished by mixing BCR effluent with MIW generated at the Standard Mine Superfund Site near Crested Butte, Colorado. The field demonstration included batch and continuous flow mixing tests. The study results suggest mixing MIW and BCR effluent can accomplish metals removal rates greater than 90% for cadmium, copper, lead, and zinc

Additional Keywords: metal removal, sulfate reducing bioreactor, acid mine drainage, passive co-treatment

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Introduction

The Standard Mine Superfund Site (Site) is an abandoned underground mine located about four miles west of Crested Butte, Colorado at an elevation of approximately 11,000 ft above sea level. Significant Site features include underground workings and an adit which discharges mining influenced water (MIW) to Elk Creek. Adit discharge is net acidic with elevated concentrations of Cd, Cu, Fe, Mn, Pb, and Zn (Golder 2009, PWT 2009). The concentrations of these constituents of concern (COCs) exceed the State of Colorado Department of Health and Environment (CDPHE) water quality standards for the receiving stream, Elk Creek (Segment 11, Upper Gunnison Basin) (CDPHE 2007) (Table 1). CDPHE water quality standards were used as reference criteria to compare biochemical reactor (BCR) effluent and mixed waters. These criteria are being used for comparison purposes only, they are not meant to represent potential Site discharge standards which have not yet been promulgated.

Parameter	Acute Standard ¹	Chronic Standard ¹
	0.0009	
Cadmium, dissolved (mg/L)	$(tr)^2$	0.00025
Copper, dissolved (mg/L)	0.007	0.005
Iron, total (mg/L)	NE	1.0 (Trec) ³
Lead, dissolved (mg/L)	0.03	0.0012
Manganese, dissolved (mg/L)	2.37	1.31
Zinc, dissolved (mg/L)	0.079	0.069

Table 1: Water Quality Standards For Elk Creek, Based On Protection Of Aquatic Life

Notes:

1 – Acute and chronic standards were calculated based on a hardness value of 50 mg/L

2 – tr = trout standard

3 – Trec = the indicated standard is a total recoverable

4 – the water supply standards are total metals mg/L = milligrams per liter

NE = not established. Indicated water quality standard does not exist for the target parameter.

In 2007, a pilot-scale BCR was constructed to treat MIW discharged from the adit. Pilot BCR design and construction activities were previously reported (Reisman et al., 2008). The BCR has operated with intermittent stoppages in flow since September 2007. Monitoring data from 2007 through 2008 indicate the BCR effluent has a negative oxidation-reduction potential (ORP), a pH of about 6.2, and elevated concentrations of alkalinity, sulfide, biochemical oxygen demand (BOD), and total coliforms (Golder, 2009). Metal removal rates from 2007 to 2008 for Cd, Cu, Pb, and Zn were greater than 98%, which is typical for the BCR treatment technology

(Gusek et al., 2008). The sulfide and alkalinity concentrations reported for the BCR effluent indicate the BCR effluent may contain residual treatment capacity, and may be able to reduce MIW acidity and metals concentrations via formation of alkalinity-induced metal hydroxides and metal sulfide precipitates.

The concept of mixing sulfide-laden water with MIW to form metal sulfide precipitates has been identified as an effective method for treating MIW (Alvarez et al., 2007). Off-line sulfate reducing bioreactors are an active biological treatment process which employs mixing to selectively precipitate metal sulfides (Johnson and Hallberg, 2005). In the active treatment system, operating conditions are closely monitored and controlled to optimize biological sulfide generation; this process is operator intensive. While the concept of off-line sulfate reduction has been proven in water treatment applications, it has received only limited study in passive or semi-passive treatment applications. A semi-passive bioreactor system constructed at the Leviathan Mine Superfund Site in California used off-line sulfide generation to treat the water. However, this system is considered semi-passive because it used a liquid carbon nutrient, pHadjustment chemicals, and chemical addition pumps. Passive co-treatment of organic rich, nutrient laden reducing waters with untreated MIW has been documented in two separate studies (Gusek et al., 2008, Strosnider et al., 2009). These studies found co-treatment of MIW and BCR effluent to be effective in treating metals in the MIW and pathogens and nuisance parameters (e.g., sulfide, BOD) in the BCR effluent.

The term co-treatment implies that each water treats the other in a mutually beneficial process: The BCR effluent treats the MIW by removing metals via metal sulfide precipitation and sorption to organic matter while the MIW treats the BCR effluent by removing sulfides, diluting nuisance parameters such as BOD, N, and P, and destroying bacteria (e.g., total coliforms) with acidity. From a full-scale design perspective, co-treatment of MIW and BCR effluent could decrease the footprint required for a passive treatment system both by reducing the area necessary to remove metals and acidity from the MIW and by reducing the area necessary for aerobic treatment of nuisance parameters present in BCR effluent.

In 2009, a field study was performed at the Site to characterize co-treatment of BCR effluent and MIW. The study was performed to determine a recommended mixing ratio, hydraulic retention time, and sludge generation rate that would be used to size a mixing pond or similar system component. The mixing study took place over the course of a three-day period and consisted of several field tests designed to evaluate the effects of mixing BCR effluent with MIW.

Materials and Methods

The mixing study included 1-liter batch and continuous flow tests. To conduct these tests, bulk samples of BCR effluent and MIW were collected in dedicated 5-gallon plastic buckets using the BCR influent and effluent ISCO[™] samplers installed in the BCR monitoring shed (Reisman et al, 2008). Bulk samples were stirred thoroughly before collecting aliquots of test sample water. Summaries of the field activities conducted and measurements observed and recorded during this study are presented below.

Batch tests were performed using ratios of BCR effluent to MIW ranging from 3BCR:1MIW to 1BCR:4MIW, by volume. These tests were performed to identify two mixing ratios for adoption in the continuous flow tests. Batch tests were conducted by mixing one-liter samples of mixtures of BCR effluent and MIW. BCR effluent and MIW volumes were measured using a 1,000 mL graduated cylinder, mixed together manually in a dedicated plastic beaker for approximately 30 seconds, and allowed to settle for at least 20 minutes, after which samples were collected for laboratory analysis of dissolved target metals and alkalinity/acidity. Temperature, pH, conductivity, Zn concentrations, and alkalinity were field-measured after collecting analytical laboratory samples from the mixed volumes. The volume of BCR effluent and MIW added to each batch test, mixing ratios, and field measurements are provided in Table 2. Additionally, two batch tests were performed with samples of acidified MIW intended to simulate MIW characteristics observed in the spring of 2007 and 2008 (Golder, 2009). For these tests, aliquots of MIW were acidified to target pH values of 4.0 and 3.0 using concentrated HNO₃ acid. The acidified aliquots were then mixed with BCR effluent as described above.

Two continuous flow studies were performed using mixing ratios of 1BCR:3MIW and 1BCR:1.5MIW, by volume. These ratios were selected based on the field results of the batch tests, which indicated these ratios resulted in mixed alkalinities greater than 100 mg/L as CaCO₃. The apparatus used for each continuous test included two peristaltic pumps, one of which metered BCR effluent and the other of which metered MIW into the bottom of a common 5-gallon bucket. The MIW and BCR effluent mixed in the bucket and flowed by gravity out a

bulkhead at approximately ³/₄-height into the bottom of a second 5-gallon bucket. The water further mixed in the second 5-gallon bucket before discharging to the ground surface via a bulkhead installed in the bucket sidewall (Fig. 1A and 1B).



Figure 1A: Field Laboratory used during mixing study



Figure 1B: Apparatus used for continuous flow tests

Figure 1A and 1B: Field Apparatus used to during mixing study tests.

The continuous tests were performed using total flow rates of 150 mL min⁻¹, with a hydraulic retention times of approximately 2 hours. Field measurements, including temperature, ORP, dissolved oxygen, pH, and specific conductivity were measured about every ten minutes in the second mixing container. After operating the continuous test for four hours, samples were collected for laboratory analysis. Samples collected for analysis of total concentrations were collected by placing the sample container in the effluent stream of each mixing apparatus. Sample volumes for dissolved metals were collected by pumping water from the surface of the second bucket and filtering with a 0.45 micron filter.

Water quality parameter measurements were performed using Oakton pH 110 Series meter for pH, ORP, and temperature, an Oakton DO 300 series for dissolved oxygen, and an Oakton CON 400 series for specific conductance. The water quality meters were calibrated daily before testing. Dissolved Zn concentrations were measured in the field using a Hach[™] Zinc Colorimeter II Test Kit. Field measurements of Zn were performed by field filtering samples with a 0.45 µ filter and following the protocol included in the test kit instructions. Alkalinity was also measured in the field with a Hach[™] Alkalinity Test Kit. During the continuous flow test, flow rates of BCR effluent and MIW were measured using a stopwatch and a graduated cylinder.

Sludge volume generation was measured during the continuous flow test (Table 3). One-liter samples of mixed test waters were placed in Imhoff cones and allowed to settle for 4 hours. Periodically, the sludge volume in each Imhoff cone was measured.

Aqueous samples collected during the mixing study were submitted to Microbac Laboratories Inc of Marietta, OH (Microbac) for metals analysis (ICP-MS), BOD, total coliforms, and ACZ Laboratories Inc. of Steamboat Springs, Colorado (ACZ) for sulfide analysis. Samples were placed on ice immediately after collection, and were transported to the analytical laboratories under chain of custody protocols. Laboratory reported concentrations were used to evaluate the co-treatment resulting from different mixtures of BCR effluent and MIW. Some inherent dilution of the influent MIW was expected as a result of dilution of MIW with BCR effluent water. To account for this dilution effect, dilution calculations were performed to determine expected mixed water concentrations resulting from a conservative mass balance mixture. The dilution calculations employed a conservative mass balance approach to calculate the expected concentrations resulting from mixing BCR effluent with MIW, assuming no treatment occurred. The expected mixed concentrations were calculated according to equation 1:

$$C_{3} = (V_{1} \times C_{1} + V_{2} \times C_{2}) / V_{3}$$
(1)

Where V_1 and C_1 are the volume and concentration of BCR effluent, V_2 and C_2 are the volume and concentration of MIW, V_3 is the volume of the BCR / MIW mixture ($V_3 = V_1+V_2$), and C_3 is the expected concentration of the target constituent.

The expected concentrations for Cd, Cu, Fe, Pb, Mn Zn, Ba, Ca, Mg, and Mn were calculated. Barium, Ca, Mg, and Mn concentrations were selected because these are conservative constituents that should not be affected by the mixing process.

Results and Discussion

Field measurements recorded during sample collection activities are provided in Tables 2 and 3 for the batch and continuous flow tests, respectively.

A comparison of the expected concentrations based on the dilution calculation and actual concentrations observed for Ba, Ca, Mg, and Mn is provided in Fig. 2. Laboratory concentrations were generally similar to the expected concentrations for these constituents, indicating these metals behaved conservatively in the mixing process, and that field-measured volumetric mixing ratios were accurate.

A comparison of expected and actual concentrations for cadmium, copper, lead and zinc are shown on Fig. 3. Laboratory results were consistently less than the expected concentrations indicating these metals were being removed (i.e., precipitated) by the mixing process.

Percent removals were calculated with the difference between the expected concentration (i.e., based on dilution) and the actual concentrations. The removal rates are specific to the mixing pond and should not be confused with BCR metal removal rates. Percent removals for batch and continuous tests appear to vary as a function of the metal and the mixing ratio (Fig. 4).

With the exception of the 1BCR:4MIW and 3BCR:1MIW percent removals, the batch test percent removal rates increase as the mixing ratio increases (i.e., more BCR effluent and less MIW). The 1BCR:4MIW and 3BCR:1MIW removal rates are anomalously high and low, respectively, and do not fit the trend suggested by the other mixtures. The 1.5BCR:1MIW and 2BCR:1MIW batch tests achieved removal rates for cadmium, copper, lead, and zinc greater than 95%. As the mixing ratio decreased (i.e., less BCR and more MIW) the removal rates also generally decreased. In the 1BCR:1.5MIW batch sample, the metal removal rates decreased to less than 90% for Cd, Cu, and Pb. As such, there appears to be an inflection point at the 1.5 BCR:1MIW ratio; removal rates decrease substantially at lower mixing ratios. The continuous flow results, also shown in Fig. 4, have some significant discrepancies with the batch results.

Table 2: Field measurements conducted during batch mixing tests

	Total	BCR effluent	MIW			Oxidation- reduction				
Sample ID	Volume	Volume	volume	pН	Temperature	potential	Conductivity	DO	Alkalinity	Zinc
-									mg/L as	
	L	mL	mL	Su	°C	mv	us/cm	mg/L	CaCO ₃	mg/L
BCR -Influent	1.0	0	1000	5.97	12.6	167	523	NM	10	NM
1:4 BCR:MIW	1.0	200	800	6.28	18.8	NM	628	3.5	120	0.66
1:3 BCR:MIW	1.0	250	750	6.22	16.6	NM	636	NM	140	0
1:2 BCR:MIW	1.0	333	667	6.24	16.8	NM	686	NM	160	0
1:1.5 BCR:MIW	1.0	400	600	6.22	16.9	NM	730	NM	200	0
1:1 BCR:MIW	1.0	500	500	6.23	17.4	9.5	774	NM	220	0.01
1.5:1 BCR:MIW	1.0	600	400	6.25	17.4	-162	848	NM	260	0.02
2:1 BCR:MIW	1.0	667	333	6.24	17.9	-181	908	NM	260	0.02
3:1 BCR:MIW	1.0	750	250	6.12	19.5	-141	963	NM	320	0
BCR Eff 7/23	1.0	1000	0	6.19	16.2	-265	1151	0.11	NM	0.2
Acidified MIW,										
pH3.7	1.0	305	695	6.18	NM	116	754	3.92	115	0.11
Acidified MIW,										
pH3.0	1.0	345	655	6.06	NM	220	781	4.38	110	0.03

Notes:

L = liter

mL = milliliter

mg/L = milligrams per liter

NM = not measured

oC = degrees Celsius

us/cm = microsiemens per centimeter

Parameter	units	1:3 BCR: MIW Test	1:1.5 BCR:MIW Test
BCR Flow Rate	mL/min	36	62
MIW flow Rate	mL/min	110	86
pH	s.u.	6.25	6.27
ORP	Mv	100	89
Temperature	оС	15	14.3
Specific Conductivity	us/cm	733	781
Dissolved Oxygen	mg/L	4.54	4.04
Zinc	mg/L	0	0
Alkalinity	mg/L as CaCO₃	120	160
Sludge Volume	mL sludge / 1000 mL water	0.5	0.3
Notes:			

Table 3: Field measurements collected during continuous flow tests

L = litermL = milliliter

mg/L = milligrams per liter NM = not measured

1 M = 10t measured

oC = degrees Celsius

us/cm = microsiemens per centimeterwater quality measurements shown in this table reflect measurements recorded prior to sample collection.



Figure 2: Comparison of laboratory reported concentrations (blue) vs. calculated concentrations based on a conservative mass balance (red).



Figure 3: Comparison of laboratory reported concentrations (blue) vs. calculated concentrations based on a conservative mass balance (red). "Actual Concentrations" were concentrations reported by Microbac.



Figure 4: Calculated percent removal calculations for batch samples. Samples shown in the above graph were batch test sample results, with the exception of 1:3 continuous and 1:1.5 continuous test samples.

Aside from dilution, metal removal processes associated with mixing include metal sulfide precipitation and sorption to organic matter. Hydroxide precipitation is unlikely for Cd, Cu, Pb, and Zn at the pH values measured in the mixed samples which were typically less than 7 standard units (s.u.). Mixing study results for the COCs are summarized on Table 5. Discussions of COC concentrations observed during the mixing study follow.

					Un-Mixed Samples				
Analyte	Units	Laboratory Reporting Limit	Laboratory Method Detection Limit	Acute Water Quality Criteria ¹	Chronic Water Quality Criteria ¹	BCR Influent ²	BCR Effluent		
Cadmium	mg/L	0.000500	0.000125	0.00090	0.00025	0.18	<0.000125	_	
Copper	mg/L	0.0020	0.00050	0.007	0.005	0.0050	0.00135		
Iron	mg/L	0.100	NA	NS	1.0	0.26	0.542		
Manganese	mg/L	0.00200	0.000500	2.37	1.31	11	15.4		
Lead	mg/L	0.00100	0.000250	0.030	0.0012	0.21	0.00190		
Zinc	mg/L	0.00250	0.00500	0.0079	0.069	28	0.0150		
рН ²	s.u.	NA	NA	6 to 9	6 to 9	5.8	6.3	_	
					Batch Mixing	Tests			
Analyte	Unite	1:4		1:2	Batch Mixing 1:1.5	Tests 1:1	1.5:1	2:1	3:1
Analyte	Units	1:4 BCR:MIW ³	1:3 BCR:MIW ³	1:2 BCR:MIW ³	Batch Mixing 1:1.5 BCR:MIW ³	Tests 1:1 BCR:MIW ³	1.5:1 BCR:MIW ³	2:1 BCR:MIW ³	3:1 BCR:MIW ³
Analyte Cadmium	Units mg/L	1:4 BCR:MIW ³ 0.00776	1:3 BCR:MIW ³ 0.0353	1:2 BCR:MIW ³ 0.0266	Batch Mixing 1:1.5 BCR:MIW ³ 0.0175	Tests 1:1 BCR:MIW ³ 0.00110	1.5:1 BCR:MIW ³ 0.000545	2:1 BCR:MIW ³ 0.00141	3:1 BCR:MIW ³ 0.0173
Analyte Cadmium Copper	Units mg/L mg/L	1:4 BCR:MIW ³ 0.00776 0.00703	1:3 BCR:MIW ³ 0.0353 0.0967	1:2 BCR:MIW ³ 0.0266 0.0754	Batch Mixing 1:1.5 BCR:MIW ³ 0.0175 0.0494	Tests 1:1 BCR:MIW ³ 0.00110 0.00415	1.5:1 BCR:MIW ³ 0.000545 0.00268	2:1 BCR:MIW ³ 0.00141 0.00498	3:1 BCR:MIW ³ 0.0173 0.0495
Analyte Cadmium Copper Iron	Units mg/L mg/L mg/L	1:4 BCR:MIW ³ 0.00776 0.00703 2.22	1:3 BCR:MIW ³ 0.0353 0.0967 0.471	1:2 BCR:MIW ³ 0.0266 0.0754 0.454	Batch Mixing 1:1.5 BCR:MIW ³ 0.0175 0.0494 0.383	Tests 1:1 BCR:MIW ³ 0.00110 0.00415 0.22200	1.5:1 BCR:MIW ³ 0.000545 0.00268 0.390	2:1 BCR:MIW ³ 0.00141 0.00498 0.456	3:1 BCR:MIW ³ 0.0173 0.0495 0.573
Analyte Cadmium Copper Iron Manganese	Units mg/L mg/L mg/L mg/L	1:4 BCR:MIW ³ 0.00776 0.00703 2.22 12.1	1:3 BCR:MIW ³ 0.0353 0.0967 0.471 11.8	1:2 BCR:MIW ³ 0.0266 0.0754 0.454 13.1	Batch Mixing 1:1.5 BCR:MIW ³ 0.0175 0.0494 0.383 12.9	Tests 1:1 BCR:MIW ³ 0.00110 0.00415 0.22200 14.1	1.5:1 BCR:MIW ³ 0.000545 0.00268 0.390 14.3	2:1 BCR:MIW ³ 0.00141 0.00498 0.456 14.6	3:1 BCR:MIW ³ 0.0173 0.0495 0.573 14.9
Analyte Cadmium Copper Iron Manganese Lead	Units mg/L mg/L mg/L mg/L mg/L	1:4 BCR:MIW ³ 0.00776 0.00703 2.22 12.1 0.0190	1:3 BCR:MIW ³ 0.0353 0.0967 0.471 11.8 0.114	1:2 BCR:MIW ³ 0.0266 0.0754 0.454 13.1 0.0919	Batch Mixing 1:1.5 BCR:MIW ³ 0.0175 0.0494 0.383 12.9 0.0588	Tests 1:1 BCR:MIW ³ 0.00110 0.00415 0.22200 14.1 0.00410	1.5:1 BCR:MIW ³ 0.000545 0.00268 0.390 14.3 0.00302	2:1 BCR:MIW ³ 0.00141 0.00498 0.456 14.6 0.0053	3:1 BCR:MIW ³ 0.0173 0.0495 0.573 14.9 0.0574
Analyte Cadmium Copper Iron Manganese Lead Zinc	Units mg/L mg/L mg/L mg/L mg/L mg/L	1:4 BCR:MIW ³ 0.00776 0.00703 2.22 12.1 0.0190 17.1	1:3 BCR:MIW ³ 0.0353 0.0967 0.471 11.8 0.114 13.7	1:2 BCR:MIW ³ 0.0266 0.0754 0.454 13.1 0.0919 10.1	Batch Mixing 1:1.5 BCR:MIW ³ 0.0175 0.0494 0.383 12.9 0.0588 5.16	Tests 1:1 BCR:MIW ³ 0.00415 0.22200 14.1 0.00410 1.38	1.5:1 BCR:MIW ³ 0.000545 0.00268 0.390 14.3 0.00302 0.103	2:1 BCR:MIW ³ 0.00141 0.00498 0.456 14.6 0.0053 0.350	3:1 BCR:MIW ³ 0.0173 0.0495 0.573 14.9 0.0574 2.64

Table 5: Summary of constituent of concern analytical results obtained during the mixing study

		Continuous Flow Mixing Test		
Analyte	Units	1:1.5 BCR:M 1:3	BCR:MIW ³	
Cadmium	mg/L	0.0453	0.0108	
Copper	mg/L	0.114	0.0297	
Iron	mg/L	0.665	0.443	
Manganese	mg/L	11.8	12.6	
Lead	mg/L	0.141	0.0361	
Zinc	mg/L	11.2	4.58	
рН ²	s.u.	6.4	6.5	

Notes

1 Water quality criteria are used for a comparative basis only, see Table 1.

2 BCR influent Sample analyses and reported pH analyses were performed by EPA ORD Laboratory in Cincinnati, Ohio

3 BCR:MIW = Volumetric ratio of BCR effluent mixed with MIW (BCR Influent)

"<" = concentration was less than the laboratory method detection limit.

mg/L = milligrams per liter

s.u. = standard units

Bold values indicate reported concentration is greater than the acute water quality criterion

Italicized values indicate reported concentration is greater than the chronic criterion, but less than the acute criterion

<u>Cadmium</u>

The acute and chronic water quality criteria for Cd are 0.0009 mg/L and 0.00025 mg/L, respectively. Reported Cd concentrations ranged from below the Microbac detection limit of 0.000125 mg/L (BCR effluent) to 0.18 mg/L (MIW sample). Cadmium concentrations were below the acute and chronic criteria in the BCR effluent only. The 1.5BCR:1MIW batch sample had the next lowest Cd concentration (0.0005 mg/L) which is greater than the chronic standard but less than the acute standard.

The Cd concentration (0.0173 mg/L) reported for the 3BCR:1MIW batch sample was higher than the concentrations reported for the 2BCR:1MIW, 1.5BCR:1MIW, and 1BCR: 1MIW samples.

The Cd concentration in the continuous flow sample 1BCR:3MIW was lower than Cd concentrations in the batch sample 1BCR:3MIW (i.e., 0.011 mg/L continuous, 0.035 mg/L batch). Conversely, the 1BCR:1.5MIW continuous flow test yielded higher reported Cd concentrations than those observed in batch sample 1BCR:1.5MIW. Although the Microbac practical quantitation limits (i.e., method reporting limit) for Cd are greater than the chronic water quality limit of 0.00025 mg/L, the Microbac detection limit (0.000125) was less than the chronic water quality standard.

Copper

The acute and chronic water quality criteria for Cu are 0.007 mg/L and 0.005 mg/L, respectively. Batch mixing ratios of 4BCR:1MIW, 1BCR:1.5MIW, 1BCR:1MIW, 1.5BCR:1MIW, and 2BCR:1MIW yielded Cu concentrations less than the acute and chronic standards. Batch samples 3BCR:1MIW, 1BCR:3MIW, pH 3.0, and pH 3.7 contained Cu concentrations greater than the acute and chronic standards. Copper concentrations for continuous flow tests were 0.015 mg/L for the 1BCR:3MIW sample and 0.042 mg/L for the 1BCR:1.5MIW sample.

Iron

The chronic water quality standard for Fe is 1.0 mg/L. All iron concentrations, including those for MIW and BCR effluent, were below the standard. The reported MIW and BCR effluent Fe concentrations were 0.26 and 0.28 mg/L, respectively.

Manganese

Laboratory manganese concentrations ranged from 11.3 mg/L (MIW sample) to 15.9 mg/L (BCR effluent sample). The Mn concentrations for mixed samples were relatively unchanged; significant Mn removal did not occur in the mixing process. Manganese is typically not removed in anaerobic passive treatment systems (Golder, 2009).

Lead

The acute and chronic water quality criteria for Pb are 0.03 mg/L and 0.0012 mg/L, respectively. Lead concentrations ranged from 0.0019 mg/L (BCR effluent) to 0.21 mg/L (MIW

sample). During the batch tests, Pb concentrations from samples 1BCR:4MIW, 1BCR:1MIW, 1.5BCR:1MIW and 2BCR:1MIW were less than the acute standard of 0.03 mg/L but greater than the chronic standard of 0.0012 mg/L. The remaining batch tests were all above the acute standard. During the continuous flow test, the lead concentrations for both mixing ratios exceeded the chronic standard. Also, the 1BCR:1.5MIW continuous flow sample concentration (0.14 mg/L) was inconsistent with the 1BCR:1.5MIW batch sample (0.059 mg/L).

<u>Zinc</u>

The acute and chronic water quality criteria for zinc are 0.079 mg/L and 0.069 mg/L, respectively. Zinc concentrations ranged from 27.8 mg/L (MIW sample) to 0.33 mg/L (BCR effluent). All reported zinc concentrations were greater than the acute (0.079 mg/L) and chronic (0.069 mg/L) standards. Batch test concentrations indicate Zn concentrations generally decreased as the mixing ratio of BCR effluent to MIW increased. Samples from mixing ratios of 1BCR:1.5MIW, 1.5BCR: 1MIW, and 2BCR:1MIW had similar Zn concentrations of approximately 0.5 mg/L. The sample collected from the 1BCR:3MIW ratio during the continuous flow test had a similar Zn concentration to the 1BCR:3MIW batch sample. However, the Zn concentration (6.0 mg/L) in the continuous sample 1BCR:1.5MIW was an order of magnitude greater than the Zn concentration reported for the same mixing ratio during the batch test.

During the continuous flow mixing tests, samples were submitted for analysis of sulfide, biochemical oxygen demand, and total coliforms. These parameters are typical nuisance parameters which affect the aesthetics of the BCR effluent water. Discussion of laboratory reported concentrations for these parameters is presented below.

Sulfide

Continuous flow samples collected from the 1BCR:3MIW and 1BCR:1.5MIW tests were analyzed for sulfide concentrations by ACZ. The BCR effluent sulfide concentration was 34 mg/L. The continuous flow 1BCR:3MIW and 1BCR:1.5MIW samples contained sulfide concentrations of 1.8 and 2.3 mg/L, respectively.

Biochemical Oxygen Demand

The BCR effluent BOD concentration was 403 mg/L. The continuous flow 1BCR:3MIW and 1BCR:1.5MIW samples contained BOD concentrations of 99 and 153 mg/L, respectively.

Total Coliform -

BCR effluent and continuous flow samples were below the detection limit for total coliform. BCR effluent concentrations of total coliform have steadily decreased since pilot operation began in August 2007 as the cow manure has been flushed from the pilot BCR substrate (Golder 2009).

Sludge Generation

The sludge generation rate was measured during the continuous flow tests (Table 3). The generation rates for the continuous flow 1BCR:3MIW and 1BCR:1.5MIW tests were 0.5 mL of sludge per 1,000 mL of water treated and 0.3 mL of sludge per 1,000 mL of water treated, respectively. The settled sludge volume was measured after six hours of settling time. The observed sludge generation rates and sludge volumes present in the Imhoff cones were too small to facilitate measurement of sludge settling characteristics.

The recommended detention time for the mixing process needs to be sufficient for the mixing reactions and physical clarification to occur. Based on the field parameter data and laboratory results, the chemical reaction time required for the mixing process appears to be relatively short. Field parameters did not fluctuate substantially after the initial mixing occurred and laboratory samples collected less than an hour after mixing (batch tests) showed high dissolved metal removal rates. Furthermore, the removal rates did not improve during the continuous tests which were sampled after approximately four hours. In terms of settling, the sludge generation testing was suspended after six hours. Given the low amount of sludge generated, it was not possible to ascertain a sludge settling rate. Given the uncertainty regarding the settling rate, a conservative minimum detention time of 12 hours is recommended. Future testing to determine the detention time is recommended and should include measurement of total as well as dissolved metal concentrations at various depths in mixed samples and further examination of the settling rate.

Conclusions

BCR effluent can be used beneficially to treat MIW, thereby significantly increasing the treatment capacity of a passive treatment system at little additional cost and footprint. Additionally, the mixing process provides polishing treatment of BCR effluent by removing sulfides, diluting nuisance parameters such as BOD, N, and P, and destroying bacteria (e.g., total coliform).

Study results indicated mixing BCR effluent with MIW can accomplish mutually beneficial passive co-treatment of both waters. The observed sulfide and metals removal and dilution of nuisance parameters such as BOD and Mn indicates that mixing provides a significant improvement in water quality. While an ideal mixing basin hydraulic retention time could not be designed as a result of this study a retention time of 12 hours was predicted to be adequately conservative for ensuring mixing basin performance. During the batch tests, mixing ratios of 1.5:1, and 2:1 BCR:MIW accomplished greater than 95% removal of Pb, Cd, and Zn. Based on these results, a full scale mixing basin system based on mixing BCR effluent with MIW at a ratio of 1:1 could decrease the BCR size by as much as 33%, and still remove 90% of the influent metals load. This estimated footprint reduction is a based on a conceptual passive treatment design, assuming the BCR would be designed with the same characteristics as the existing pilot BCR and that the mixing basin would be provide a 12 hour hydraulic retention time. Comparing the footprint of this mixing basin – BCR passive treatment system to the footprint required to treat the same MIW flow rate using only a BCR indicates the mixing basin – BCR system would require approximately 33% less space. These conceptual calculations don't consider the footprints required for aerobic polishing treatment of BCR effluent. The mixed water will contain lower BOD and TSS concentrations than BCR effluent, which will decrease the polishing treatment requirements.

References

- Alvarez, M.T. Crespo, C. Mattiasson, B. (2007) Precipitation of Zn(II), Cu(II) and Pb(II) at bench-scale using biogenic hydrogen sulfide from the utilization of volatile fatty acids Chemosphere 66 1677-1683. <u>http://dx.doi.org/10.1016/j.chemosphere.2006.07.065</u>.
- Colorado Department of Public Health and Environment (CDPHE). 2007. Regulation 35 -Classifications and Numeric Standards for Gunnison and Lower Dolores River Basins (amended 2/12/07, effective 7/1/07).
- Environmental Protection Agency (EPA). 2008. Laboratory Data Validation, Functional Guidelines for Evaluating Inorganic Analyses. Draft 11/08.
- Golder Associates Inc. (Golder) 2009. *Report on Standard Mine Pilot Passive Treatment System Operations and Results for 2007 and 2008.* Lakewood, CO. August, 2009.

- Gusek, J., T. Rutkowski, E. Blumenstein, B. Shipley. 2008. Two-year Sulfate Reducing Bioreactor Pilot Test at the Golinsky Mine, California. Proceeding of the 2008 American Society of Mining and Reclamation Conference. Richmond, Virginia. https://doi.org/10.21000/JASMR08010424
 - Johnson, D.B. Hallberg, K.B. (2005) Acid Mine Drainage remediation options: a review. Science of the Total Environment 338 3-14. <u>http://dx.doi.org/10.1016/j.scitotenv.2004.09.002</u>.
 - Pacific Western Technologies, Ltd. (PWT), 2009. Mixing Study Work Plan Standard Mine Superfund Site Gunnison County, Colorado. July 2009.
 - Reisman, D., T. Rutkowski, P. Smart, J.J. Gusek. 2008. The Construction and Instrumentation of a Pilot Treatment System at Standard Mine Superfund Site, Crested Butte, CO. Proceedings of 2008 National Meeting of the American Society of Mining and Reclamation, Richmond, VA, June 14-19, 2008. <u>http://dx.doi.org/10.21000/jasmr08010892</u>.
 - Reisman, D., T. Rutkowski, P. Smart, J.J. Gusek. 2009, Passive Treatment and Monitoring at Standard Mine Superfund Site, Crested Butte, CO, Proceedings America Society of Mining and Reclamation, 2009 pp 1107-1128. <u>http://dx.doi.org/10.21000/JASMR09011107</u>.
 - Strosnider, W.H., B.K. Winfrey, R.W. Nairn, 2009. Performance of an Ecologically-Engineered Multi-Stage Acid Mine Drainage and Municipal Wastewater Passive Co-Treatment System, Proceedings America Society of Mining and Reclamation, 2009 pp 1412-1432. <u>http://dx.doi.org/10.21000/JASMR09011412</u>.