THIRD-YEAR PERFORMANCE OF 55-GALLON BIOREACTORS TREATING MINING INFLUENCED WATER FROM THE NATIONAL TUNNEL IN BLACK HAWK, COLORADO[1]

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Abstract. Mining influenced water (MIW) from the National Tunnel drains into the North Fork of Clear Creek in Black Hawk, Colorado. Fifty-five gallon bioreactors were set up in June 2006 to investigate the performance of two different solid phase substrate mixtures and an ethanol fed system with limestone support. The MIW from the National Tunnel in 2009 was near neutral and contained major average dissolved metals of Fe = 40 mg/L, Zn = 6, and Mn = 19. The overall goal was to develop design guidance for a full-scale bioreactor system.   All bioreactors were effective in removing at least 95% of influent zinc. Average 2009 iron and manganese removals for the solid phase bioreactors were 80% and 45%, respectively. In contrast, the ethanol fed reactors released iron and manganese at 50 to 300% above influent values. The solid phase bioreactors have consistently been effective at removing zinc and a large fraction of iron since startup. The manganese removal capability began to develop after one year of operation and became relatively consistent after two years of operation. The bioreactors constructed with solid phase substrate have effectively removed a significant fraction of the influent metals in the National Tunnel over the three-year operating period.

Additional Key Words: passive treatment, acid mine drainage, heavy metals, sulfate reducing bioreactor

Introduction

The National Tunnel drains mining influenced water (MIW) to the north fork of Clear Creek in Black Hawk, Colorado. The National Tunnel is within the Clear Creek/Central City Superfund Site. The National Tunnel MIW exhibits average pH values just below neutral and a range of dissolved metal concentrations as shown in Table 1. Copper, Mn and Zn are in excess of Clear Creek Operable Unit 4 Record of Decision (OU4 ROD) remediation goals (Table 1, US EPA 2004). Concern about the water quality in Clear Creek has spurred research on passive treatment methods using sulfate-reducing biochemical reactors (BCRs). In 2006 the pilot-scale passive treatment system in Black Hawk designed with a target hydraulic residence time of 3 days was installed through a joint effort between Colorado School of Mines (CSM), the U.S. Environmental Protection Agency (EPA), the Office of Research and Development's Engineering Technical Support Center (ETSC) and Golder Associates (Venot et al., 2008a). Passive treatment was chosen because it is a potentially cost effective alternative to active treatment. Passive treatment involves biologically mediated remediation, it uses microbiological interactions with limited or no chemical or energy input, requiring much less cost for operation and maintenance (Hiibel et al., 2008, Neculita et al., 2007, Johnson and Hallberg 2005). Additionally, it does not create as much hazardous waste as active treatment (Johnson and Hallberg 2005). Sulfate-reducing BCRs are used to remove metals and increase pH (Prieto et al., 2008). BCRs are typically downward or horizontal flow systems that utilize gravity flow for transport of MIW through the substrate (Neculita et al., 2007, Johnson and Hallberg 2005). The goal was to assess the effectiveness of different BCR substrates to provide effective, long-term treatment of National Tunnel MIW.

Sulfate-reducing BCRs demonstrated significant removal of metals including iron, copper zinc, and manganese from National Tunnel MIW over the course of six months in 2006 (Buccambuso et al., 2007). The initial BCRs were installed in three pairs, each pair containing variations of substrate mixtures providing a carbon source for the sulfate-reducing bacteria. All three configurations; one liquid-phase ethanol-fed and two solid-phase, organic substrate mixtures successfully removed Zn to below 0.1 mg/L, but were relatively ineffective at Mn removal.

Table 1- Previously measured influent parameter ranges and remediation goals

Criteria	2006-2007 measured range (mg/L)	2007-2008 measured range (mg/L)	Remediation Goal (mg/L)[1]
Copper	0.00-0.09	0.03-1.09	0.015
Iron	38-48	41-65	NCC[2]
Manganese	16-20	20-25	2.021
Zinc	5.1-6.8	19.3-31.5	0.675
Sulfate as S	260-296	268-457	NCC[2]
pH	6.0-6.6	4.8-6.4	NCC[2]
Temperature	6.2-17.1	4.6-9.2	NCC[2]

[1] North Fork of Clear Creek surface water remediation goals
[2] Not a contaminant of concern (USEPA 2004)

Several improvements were made to the BCR systems in 2007 to address hydraulic and winterization issues present in the previous system. Piping and layout were optimized to provide regular influent flow to the BCRs and reduce clogging by iron-hydroxide precipitates. Heating systems were also installed to ensure that BCRs and their influents and effluents did not freeze during cold months, to provide year-round treatment. With the modifications there were not as many freezing events or flow changes from power outages, but there were still isolated instances of fluctuating flow and temperature. Reactor contents were not modified or removed during the series of improvements (Venot et al., 2008).

All BCRs demonstrated the ability to consistently remove zinc through September 2009 to below the remediation goal. Partial Mn removal was observed in 2009 in contrast to the lack of Mn removal in 2006. In addition, the solid phase substrate BCRs also removed a significant amount of Fe. However, the ethanol fed system released iron and manganese above the influent values in 2009. This paper will discuss the treatment performance for the third year of BCR operation.

Methods

BCR System Configuration

The discharge point for the National Tunnel adit is located adjacent to the Mill Street Bridge in Blackhawk, Colorado, under which the pilot-scale BCRs are located. Initial installation of the treatment system occurred in June 2006. National Tunnel drainage was fed to the reactors composed of 208 L plastic drums, designated ETOH 1, ETOH 2, HYWD 3, HYWD 4, CSWD 5,

and CSWD 6. These names are based on the substrate of interest in each reactor pair (Buccambuso et al, 2007). See discussion below and Table 2 for an elaboration on the separate BCRs.

The National Tunnel water was continuously fed down a section of pipe along which "T" junctions lead to valves (timer-controlled) which feed individual reactors (Fig. 1). The flow to each reactor was set by adjusting the open time period of the valve. The flow from a hose connected to each timer was measured with a graduated bucket and stop-watch to determine the time period required to deliver 5.7 L per cycle. The valves for the series of reactors open one at a time such that no two valves are open at the same time, ensuring equal flow to each. Raychem™ heat trace tape (purchased from Grainger Industrial Supply, www.grainger.com) was used to prevent freezing issues. The heat trace tape was run along the entire length of the main influent pipe with "T" splices allowing a length of heat tape to run down the piping to each reactor, around each reactors three times, and up each effluent hose. All exposed heat trace along PVC pipes and hoses was covered with standard foam pipe insulation whereas 7 cm thick fiberglass water heater insulation sheets were wrapped around timers and reactors (Venot et al. 2008a). The reactors are downward flow reactors with a gravel base to equalize flow through the reactor. Once flow exited the substrate it collected at the gravel base and exited through effluent overflow hose.
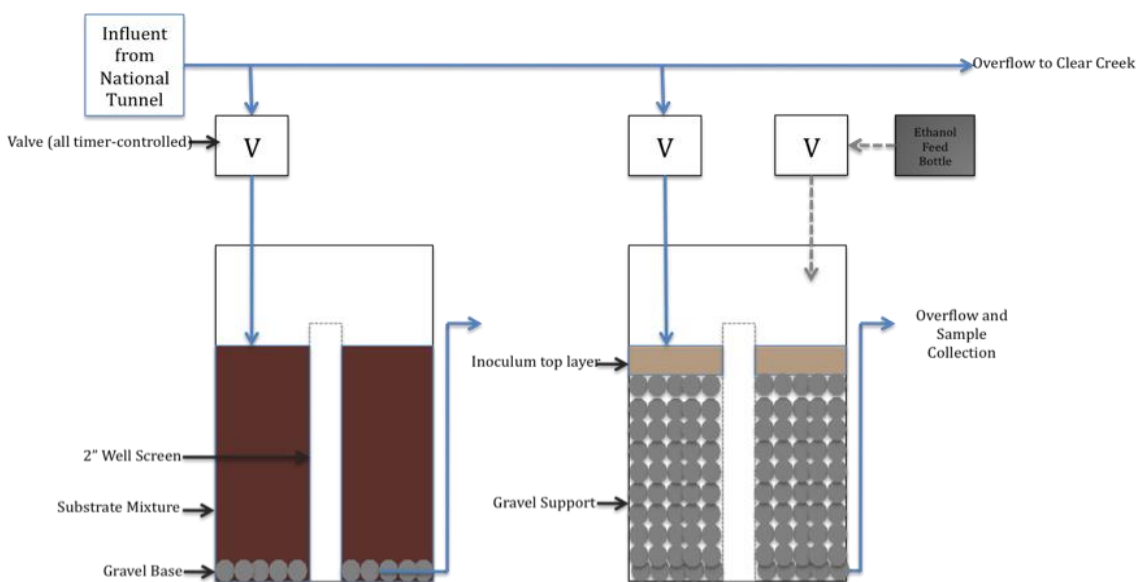

Figure 1. Biochemical reactor test configuration for solid phase substrate (left) and ethanol-fed, liquid phase substrate (right).

Composition of Solid and Liquid Phase Reactor Substrates

The composition of the substrates in the initial BCRs was not altered during modification of the treatment system in 2007. The composition of these original reactors is displayed in Table 2. Substrates were packed into the reactors on-site. A 7-10 cm layer of 3/4-inch (2cm) aggregate limestone base was first added to the solid-phase substrate reactors followed by the addition of substrates and a top layer of inoculum to a total volume of 170 L. Ethanol-fed reactors were packed solely with limestone then horse-manure inoculum to a total volume of 190 L. The percent composition of the packing in each reactor is presented in Table 2 (Buccambuso et al, 2007).

Table 2. Solid and liquid-phase reactor substrate composition by weight percent

Component	*ETOH1&2*	*HYWD3&4*	*CSWD5&6*
Wood chips	0 %	50 %	35 %
Corn stover	0 %	0 %	30 %
Hay	0 %	10 %	0 %
Horse manure	1 %	10 %	15 %
Limestone	99 %	30 %	20 %

Sampling Strategy and Methods

The sampling strategy is presented in Table 3. The analysis methods are described in Table 4. All samples were collected from the overflow hose (see Fig. 1) except for temperature which was taken from submerging a probe into the body of the reactor. The samples collected from the overflow hose were taken back to the lab in 250 mL acid washed plastic NALGENE® containers.

Table 3. Sampling frequency and analytes monitored

Analyte or Analyte group	Frequency of Sampling or Measurements	Sample Collection or Measurement Method	Sample container type/size	Measure-ment Location[1]	Preservation Method
Cu, Fe , Zn, Ca, Mg, Mn, S	Monthly	Grab, filtered	15 ml plastic vial (CSM)	L	Nitric acid, no ice CSM
pH	Weekly	Grab, unfiltered	NA	F	NA
Temperature	Weekly	Direct, reactor and ambient[2]	NA	F	NA

[1] Where measurement/analysis were be performed, field (F) or lab (L).
[2] Temperature was measured directly from the reactor and ambient air rather than a grab-type sample.

Table 4. Analytical methods

Analyte or Analyte group	Measurement Method	Equipment	Reporting Units	Detection Limit
Cu, Fe , Zinc, Ca, Mg, Mn	EPA 6010B ICP-AES (total metals)	Perkin Elmer Model 3000	mg/L	0.01 mg/L (lower limit) and $\pm$ 0.01 mg/L
pH	EPA 150.1	pH/mV meter with pH probe	s.u. units	$\pm$ 0.1 s.u. units
Temperature	--	Temperature meter with probe	Celsius	$\pm$ 0.1 $_o$C

Results and discussion

Influent characteristics in 2009 are presented in Table 5.

Table 5. National Tunnel MIW Characteristics in 2009

Criteria	Average	Min	Max
Copper (mg/L)	0.011	0.005	0.027
Iron (mg/L)	39.2	36.6	46.7
Manganese (mg/L)	17.9	17.6	21.8
Zinc (mg/L)	6.1	5.9	7.6
Sulfate as S (mg/L)	846	877	1054
pH	6.2	4.2	7.0
Temperature (°C)	10.3	8.0	12.2

Treatment performance

The average effluent pH from all BCRs from January to December 2009 was 6.9 with a standard deviation of 0.3 s.u. Although, there is no specific pH requirement stated in the surface water remediation goals, the EPA secondary treatment standard for instantaneous pH is 6.0 to 9.0 s.u. The effluent pH from the BCRs consistently met this standard.

Effluent iron from the BCRs was variable, as shown in Table 6. While no remediation goal for Fe is explicitly stated in the record of decision, removal of Fe is important to reduce mineral acidity. The HYWD and CSWD BCRs removed greater than 80% of the influent Fe. Effluent iron in the ETOH BCRs was consistently above the influent value.

Table 6. National Tunnel MIW influent and effluent iron
from January to December 2009

Iron	Average (mg/L)	Removal rates (%)
HYWD 3	2.6	92.9
HYWD 4	27.3	60.2
CSWD 5	0.2	99.5
CSWD 6	9.7	74.0
ETOH 1	159.7	-200.4
ETOH 2	101.8	-101.5

The range of effluent Zn from all BCRs in 2009 was 0.01 to 0.40 mg/L with an overall average of 0.04 mg/L. The effluent Zn from the HYWD and CSWD BCRs averaged 0.02 mg/L while the ETOH BCRs averaged 0.09 mg/L. All BCRs produced effluent Zn concentrations below the sulfate water remediation goal for the North Fork of Clear Creek of 0.675 mg/L.

In 2009, effluent Mn averaged 15 and 10 mg/L for the HYWD and CSWD BCRs, respectively. The BCRs were not designed for Mn removal. The ETOH BCRs consistently released Mn, average effluent Mn was 36 mg/L. The environment in many sulfate-reducing BCRs is supersaturated with respect to manganese carbonate, however, Mn removal is not typically observed (Halberg and Johnson 2007).

In 2009, the National Tunnel MIW average Cu concentration was below the surface water remediation goal for the North Fork of Clear Creek. Thus, copper removal efficiency is not presented for 2009.

Conclusion

Overall, the reactors have demonstrated metal removal and pH neutralization of the MIW from the National Tunnel drainage into the reactors third year of operation. In general, these abilities have persisted through periods of flow and temperature fluctuations caused by freezing temperatures and power outages.

ETOH BCRs were able to consistently remove zinc below the remediation goal of 0.675 mg/L. The continued release of iron and manganese during the third year of operation suggests that a more effective solids capture mechanism is required rather than just relying on solids retention in the bioreactor.

HYWD and CSWD BCRs were effective at maintaining Zn well below the remediation goal. The BCRs also removed 81% of influent Fe. The BCRs were effective at removing Mn to about half of the influent Mn.

The results from this investigation to date support the use of either the hay-wood or corn stover-wood substrate mixtures to meet the Zn remediation goal. In addition, hay-wood or corn stover-wood substrate mixtures greatly reduce Fe and Mn and thus the footprint of the required aerobic polishing systems because initial removal does not require as much polishing for subsequent steps. The hay-wood and corn stover-wood substrate mixtures possibly have better metal removal rates than the ethanol reactors because there is more surface area and smaller pore sizes and this can lead to better precipitate retention.

Literature Cited

Buccambuso, A. Ruhs, L. Figueroa, J.J. Gusek, T. Wildeman, M. Holmes, and D. Reisman. 2007. Ethanol-fed or solid-phase organic sulfate reducing bioreactors for the National Tunnel drainage, Clear Creek/Central City Superfund Site? Proceedings America Society of Mining and Reclamation, 2007 pp 95-105. http://dx.doi.org/10.21000/JASMR07010095.

Halberg, K.B. and D.B. Johnson. (2007). Biological manganese removal from acid mine drainage in constructed wetlands and prototype bioreactors. Sci. Total Environ. 338:115-124. http://dx.doi.org/10.1016/j.scitotenv.2004.09.011

Hiibel, S.R., L.P. Pereyra, L.Y. Inman, A. Tischer, D.J. Reisman, K.F. Reardon and A. Pruden. 2008. Microbial Community analysis of two field-scale sulfate-reducing bioreactors treating mine drainage. Environ Microbiol 10(8), 2087-2097. http://dx.doi.org/10.1111/j.1462-2920.2008.01630.x.

U.S. EPA (U. S. Environmental Protection Agency). 2004. Clear Creek Operable Unit 4 Record of Decision.

Johnson, D.B. and K.B. Hallberg. 2005. Acid mine drainage remediation options: a review. Sci Total Environ 338: 3-14. http://dx.doi.org/10.1016/j.scitotenv.2004.09.002.

Neculita, C.M., G.J. Zagury, and B. Brussière. 2007. Passive treatment of acid mine drainage in bioreactors using sulfate-reducing bacteria: critical review and research needs. J. Environ. Qual. 36:1-16. http://dx.doi.org/10.2134/jeq2006.0066.

Venot, C., L. Figueroa, T.R. Wildeman, D. Reisman, and M. Holmes (2008a) Pilot-Scale Evaluation of Solid and Liquid Phase Organic substrates used in Biochemical Reactors for the Treatment of Mining Influenced Water, Proceedings America Society of Mining and Reclamation, 2008 pp 1332-1351. http://dx.doi.org/10.21000/JASMR08011332Water, Proceedings America Society of Mining and Reclamation, 2008 pp 1332-1351.

Venot, C., L. Figueroa, R.A. Brennan, T.R. Wildeman, D. Reisman, and M. Sieczkowski (2008b) Comparing Chitin and Organic Substrates on the National Tunnel Waters in Blackhawk, Colorado for Manganese Removal, Proceedings America Society of Mining and Reclamation, 2008 pp 1352-1366. http://dx.doi.org/10.21000/JASMR08011352.