PASSIVE TREATMENT AND MONITORING AT THE STANDARD MINE SUPERFUND SITE, CRESTED BUTTE, CO[1]

David Reisman[2], Thomas Rutkowski, Pat Smart, James Gusek, and Michael Sieczkowski

Abstract. At the 2008 ASMR conference, data from the initial two months of operation of a U.S. EPA pilot biochemical reactor (BCR) was reported. The BCR was designed and constructed in August, 2007 to treat mining influenced water (MIW) emanating from an adit at a remote site in southern Colorado. The original objective of the study was to operate and monitor a BCR on a year-round basis in a harsh mountain environment. In the second year, a pilot chitin reactor was constructed for manganese removal. The treatment results from 13 months of BCR operation and 2 months of chitin reactor are presented. The treatment goal for the two pilot reactors was to determine compliance with the applicable surface water quality standards for the State of Colorado. Several attributes of the treatment and monitoring system were unique. It was constructed at an elevation of 11,000 feet a.m.s.l. (3,353 meters), was designed to operate year-round, and was totally passive, using solar energy for the monitoring system and pump power. Due to the site being inaccessible during winter months, this remote monitoring system was designed to collect samples and monitor field variables through the winter months. Field variables were measured and stored by Hydrolab™ sondes. Influent and effluent water quality samples were collected and stored in Teledyne™ ISCO™ 6712 samplers. For the first year of operation, the field variable data were transmitted via Stratolink™ satellite communicators. Due to operational issues, the Stratolink™ units were replaced with satellite phones in September 2008. The contaminants of concern (COCs) in the MIW are cadmium, copper, iron, lead, manganese, and zinc. BCR metal removal rates averaged approximately 98% over the first year of operation for cadmium, copper, lead, and zinc. Despite these high removal rates, the BCR effluent exceeded the applicable water quality standards for cadmium, lead, and zinc. Iron and manganese removal rates varied over the first year of BCR operation and were not sufficient to achieve the applicable water quality standards. The removal of manganese by the chitin reactor was inconsistent with an average percent removal rate of 23% over the first two months of operation. Since data are limited on biochemical and chitin reactors operating in elevated and harsh winter locations, the acquired data are unique for MIW remediation.

Additional Keywords: ARD, MIW, biochemical reactor, BCR, sulfate reducing bioreactor, SRB, chitorem® BCR , chitin, satellite data transmission, heavy metals remediation, passive treatment, Green Remediation

---

[1] Paper was presented at the 2009 National Meeting of the American Society of Mining and Reclamation, Billings, MT, ***Revitalizing the Environment: Proven Solutions and Innovative Approaches*** May 30 – June 5, 2009. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

[2] David Reisman ETSC, Office of Research and Development, US EPA, Cincinnati, OH 45268, Thomas Rutkowski Golder Associates Inc., 44 Union Blvd #300, Lakewood, CO 80228 Pat Smart and James Gusek Golder Associates Inc., 44 Union Blvd #300, Lakewood, CO 80228 Michael Sieczkowski, CHMM, Technical Sales Director, JRW Bioremediation, L.L.C., Lenexa, KS,

Proceedings America Society of Mining and Reclamation, 2009 pp 1107-1128
DOI: 10.21000/JASMR09011107
http://dx.doi.org/10.21000/JASMR09011107

Introduction

In 2007, the Engineering Technical Support Center (ETSC) of the Office of Research and Development of the U.S. Environmental Protection Agency (EPA) and Golder Associates Inc. designed and constructed a pilot scale treatment system (Pilot) to treat mining influenced water (MIW) from an adit at the Standard Mine Superfund Site (Site) near Crested Butte, Colorado. The project was conducted in cooperation with EPA Region 8. Mining activity began at the Standard Mine around 1874. However, the most significant operations began in 1931 with the mining of Pb, Zn, silver, and gold. Operations ceased in 1966, the mine was abandoned, but wastes at Standard Mine continued to impact surface water in the area. The adit chosen for the pilot project drains into Elk Creek, which is devoid of all aquatic life and feeds directly into Coal Creek. Crested Butte's drinking water supply is taken from Coal Creek four miles downstream from the former mine. The project presented several challenges since the mine adit was at an elevation of 11,000 feet above mean sea level (a.m.s.l.) (3353 meters), provided no available electric power, and had limited access for 6 or more months during the winter season because of snowfall and harsh weather.

The site climate is characterized by long cold winters and short summers. A Natural Resources Conservation Service (NRCS) weather station on Schofield Pass (Station No. CO07K115) is the closest weather station to the site (approximately 8 miles, or 12.9 km northeast of the site) and is located at a similar elevation (10,700 feet a.m.s.l.). Based on its location at a similar elevation, the weather station is the best available measuring surrogate for the Site. The Schofield Pass average annual temperature is -0.1 °C, the average winter (December through February) temperature is -9.2 °C, and the average summer (June through August) temperature is 9.6 °C. Snow cover usually exists from mid-November through May or June, with the annual snowfall typically ranging from 400 to 700 inches (7.62 to 17.8 meters).

Description of Treatment Technologies

To date, the Pilot consists of two treatment technologies: an anaerobic BCR and a chitin reactor. An aerobic polishing cell (APC) was also constructed. Descriptions of the two technologies follow.

Biochemical Reactors

A BCR is typically a gravity-flow bioreactor with a limestone-buffered organic treatment medium that requires minimal operation and maintenance (Gusek, 2002). Typical full-scale BCRs resemble bermed ponds and operate as vertical-flow reactors. The Pilot limestone-buffered organic substrate (LBOS) contained the following mixture, by weight: 10% hay, 50% wood chips, 30% limestone, 10% cow manure. Thomas (2002) summarized the following BCR treatment processes:

- biological reduction of sulfate to sulfide and subsequent precipitation of metal sulfides,

- alkalinity increase due to biological sulfate reduction and dissolution of limestone contained within the substrate,
- precipitation of metal hydroxides, and
- sorption of trace metals (e.g., Cd, Cu, Pb, Zn) to metal hydroxides and the organic medium.

More recent research has shown that the formation of bicarbonate may be a factor in metal removal in a BCR as the metals can precipitate as metal carbonates. Our research has also shown that in solid substrate reactors, some metals bound in the substrate may be discharged in the early start-up of the cell, and metals in the effluent in early stages exceed the influent concentrations. As stated in a previous paper, this BCR was fed with both manure and a drum of substrate-material that was inoculated with a complex consortium of bacteria from another site that treated MIW (Reisman et al., 2008). The BCR was also allowed a short-term adaptation period (Reisman et. al., 2008). The pilot BCR cell was completed in August 2007 and began treating water in September 2007. A photo of the completed BCR cell is provided in Fig. 1.

Figure 1. The constructed BCR with exposed substrate

The BCR technology has been shown to be effective at low temperatures (Gusek, 2000). Sulfate-reducing bacteria have been well-researched and are known to be active at temperatures as low as -40 °C (Postgate, 1979), but the Standard Mine BCR did not reach this temperature. Hence, the engineering challenge of BCR treatment in cold climates is to deliver a constant flow rate to the treatment medium and to monitor site-specific metal loading rates to appropriately design future BCR cells for the site.

Unlike typical BCRs, the Standard Mine pilot BCR design included a solar-powered pump to ensure to the extent practicable that the unattended BCR received the design flow of one gallon per minute (gpm)

(3.8 liters per minute) during the winter. Precisely metering flow at this low rate is difficult using a weir, flume, or throttling valve due to likelihood of iron hydroxide fouling. Indeed, the infiltration gallery (comprised of a perforated pipe surrounded by pea gravel) suffered from this phenomenon in May 2008, and flow to the BCR ceased as a result.

Figure 2. The BCR cell with insulating cover and sampling shed in background

Chitin Reactor

The chitin reactor treatment medium is ChitoRem™, a commercially-available remediation product available from JRW Bioremediation (Lenexa, KS), and the material was mixed with sand in the reactor. The ChitoRem™ used in the testing was SC-20, which is largely composed of crab-shell chitin. ChitoRem™ has been used for the bioremediation of a broad range of constituents including chlorinated solvents, metals, and mining influenced waters (Korte et al., 2008). ChitoRem™ contains about 20% chitin (general formula $C_9H_{15}O_5N$), 40% limestone ($CaCO_3$), 30% protein (Ruiz et al. 2008), and 10 % other materials. Similar to the BCR technology, ChitoRem™ can be placed in a flow-through reactor and create anaerobic conditions that likely precipitate metals as sulfides. ChitoRem™ has also been shown to be effective at Mn removal (Venot et al., 2008). The chitin reactor is an emerging technology whose chemical reactions and Mn removal mechanisms are not completely understood. Unlike the BCR technology, the use of ChitoRem™ to treat MIW has only begun to receive attention over the past several years, and long-term treatment performance has not been documented.

To further evaluate the technology, a pilot chitin reactor was designed and constructed for polishing and to remove Mn from the pilot BCR effluent. The chitin reactor was constructed and began treatment in July 2008. The chitin reactor was housed in a 1,500 gallon plastic septic tank. A network of perforated collection pipes was installed in the bottom of the tank and overlain with ¾” pea gravel to facilitate effluent collection. Coarse sand (10,000 lbs.) was mixed with chitin (2,500 lbs.) at a ratio of about 1:1 by volume and placed in the tank above the pea gravel layer. The in-place medium volume was approximately 1,400 gallons. No winter sampling system was added to the chitin BCR. A photo of the chitin reactor is provided in Fig. 3.

Figure 3. The chitin reactor, housed in a septic tank, prior to burial

Aerobic Polishing Cell

In the summer of 2008, a 4-cell aerobic polishing cell (APC) was constructed to receive one-half of the BCR effluent. The last cell of the 4-cell structure will be developed into a Mn removal bed using an alkaline rock substrate. Each cell is approximately 10 feet by 25 feet (3 meters by 7.6 meters). The APC treatment goals are to decrease the BCR effluent biochemical oxygen demand and lower effluent Mn and Fe concentrations. No winter sampling system was added to the APC. The APC was installed late in the 2008 season, so data from that system was not collected for this paper.

Methods

The BCR monitoring system was equipped with TeledyneISCO 6712 autosamplers, Hydrolab™ sondes, and data transmission hardware. The chitin reactor was monitored manually by field personnel only. An approved EPA sampling and Quality Assurance Project Plan was developed and updated for 2008 (Reisman et al., 2008).

Sampling

Sampling procedure differed between months when the site was accessible (July through October) and months when the site was inaccessible due to winter weather (November through June). These two periods will be termed summer and winter for the purposes of this paper. Winter access to the site was typically limited and was only possible on snowshoes and skis when weather and avalanche conditions persisted. Personnel visited the site three times during the 2007-2008 winter for pilot maintenance and sample collection.

Summer Sampling. During summer months when the site was accessible, BCR and chitin reactor pH, temperature, oxidation reduction potential (ORP), dissolved oxygen, and conductivity were measured using a field-calibrated YSI™ 556 multimeter. Influent and effluent BCR field variables (pH, temperature, ORP) were also measured at 15 minute intervals on a year-round basis by Hydrolab™ sondes. Both the YSI and Hydrolab™ ORP probes contain a silver chloride reference electrode (Ag/AgCl) in a potassium chloride solution. The probes were calibrated with Zobell's solution, which measures +225 mV.

Summer water quality samples were collected for laboratory analysis of dissolved metals, total metals, alkalinity, and sulfate. Samples were stored on-ice and submitted to the EPA ORD laboratory in Cincinnati, OH under chain-of-custody protocols.

Winter Sampling. Winter BCR influent and effluent water quality samples were collected by ISCO™ 6712 autosamplers. The autosampler bottles were pre-filled with nitric acid in order to preserve the samples. The ISCO™ samples were periodically collected on site visits and submitted to the EPA ORD laboratory under chain-of-custody protocols for analysis of total metals and sulfate. The ISCO™ samples were never frozen during site visits because the autosamplers were housed in an insulated and partially-heated shed (Reisman et al., 2008). Water samples were collected in 2007. A control was analyzed using EPA Method 6010B, and additional water was frozen for 30 days, defrosted and the same type of metal analyses was completed. EPA found no significant differences between the control and the frozen samples. Since the chitin reactor was installed in July 2008, the reactor has yet to be sampled during winter months.

Flow Monitoring

The BCR influent flow rate was monitored using a TRACOM™ 60^o trapezoidal flume and an ISCO™ 700 bubbler module installed on the influent ISCO™ 6712 autosampler. The bubbler module enabled the ISCO™ sampler to measure the water level in the flume and calculate the flow rate**.**

Remote Monitoring.

To monitor the BCR performance remotely during the winter, the pilot was equipped with Stratolink™ satellite transmitters that transmitted field measurements (pH, temperature, ORP) and flow data. The data were typically viewable within several hours of collection on ISCO™'s Sampler Station Access™ webpage. Field variables and flow data were downloaded from the webpage on a monthly basis. The data collected by the sondes were also downloaded during site visits.

Operational History

BCR Operational History

Upon completion of BCR construction, the cell was filled with adit MIW on 08/9/07 and allowed to incubate for two weeks. Beginning on 08/22/07, BCR effluent water was pumped back into the BCR for four weeks to re-circulate the high organic matter in the effluent water and thus stimulate biological activity. The volume of the re-circulation water was equivalent to three BCR pore volumes (Reisman et al., 2008).

On 09/19/07, after two weeks of incubation and four weeks of recirculation, the BCR began receiving an average daily flow of 1 gpm (3.8 liters per minute) of adit water, delivered by the previously described pump. The BCR effluent was routed directly to Elk Creek, as the APC had not been completed. Between 09/19/07 and 10/15/08, flow to the BCR ceased or was increased above the design flow rate of 1 gpm during the following periods:

- 01/04/08 - 01/25/08 - This flow stoppage was likely due to persistent cloudy weather that prevented the solar panel recharging of the batteries powering the influent pump.
- 02/28/08 – 04/02/08 - This flow stoppage was due to influent pump failure. The pump was replaced during a site visit on 4/2/08.
- 04/02/08 – 04/28/08 - Flow to the system ceased most likely due to clogging of the infiltration gallery.
- 06/ 27/08 – 7/23/08 - Flow to the BCR stopped due to clogged delivery pipes, most likely due to debris and Fe hydroxide fouling.
- 07/23/08 – 10/8/08 - The BCR flow rate was increased to 2 gpm from July 23 through October 8, 2008 to test BCR performance at a higher flow rate.

In summary, flow to the BCR was halted for about 15 weeks during the first year of operation due to pump failure, infiltration gallery and delivery pipe clogging. In July, changes were made inside the adit tunnel by creating several sediment traps to attempt to minimize sediment and iron hydroxide precipitants from entering the delivery system. Note that although influent water was prevented from entering the BCR, treatment of MIW inside the BCR continued.

Chitin Reactor Operational History

The chitin reactor received gravity flow of BCR effluent. The chitin reactor began treating water on 07/30/08 and continued to receive flow through 10/02/08 without apparent interruption. BCR effluent flowed into a gravity distribution box, which controlled the amount of flow to the chitin reactor. The design flow of the chitin reactor was 0.5 gpm; it received half of the BCR effluent flow. During a period immediately following construction, the chitin BCR received all of the effluent flow as the APC was being constructed. This influent period lasted for approximately 6 weeks. The BCR and chitin flow rates are shown in Fig. 4.

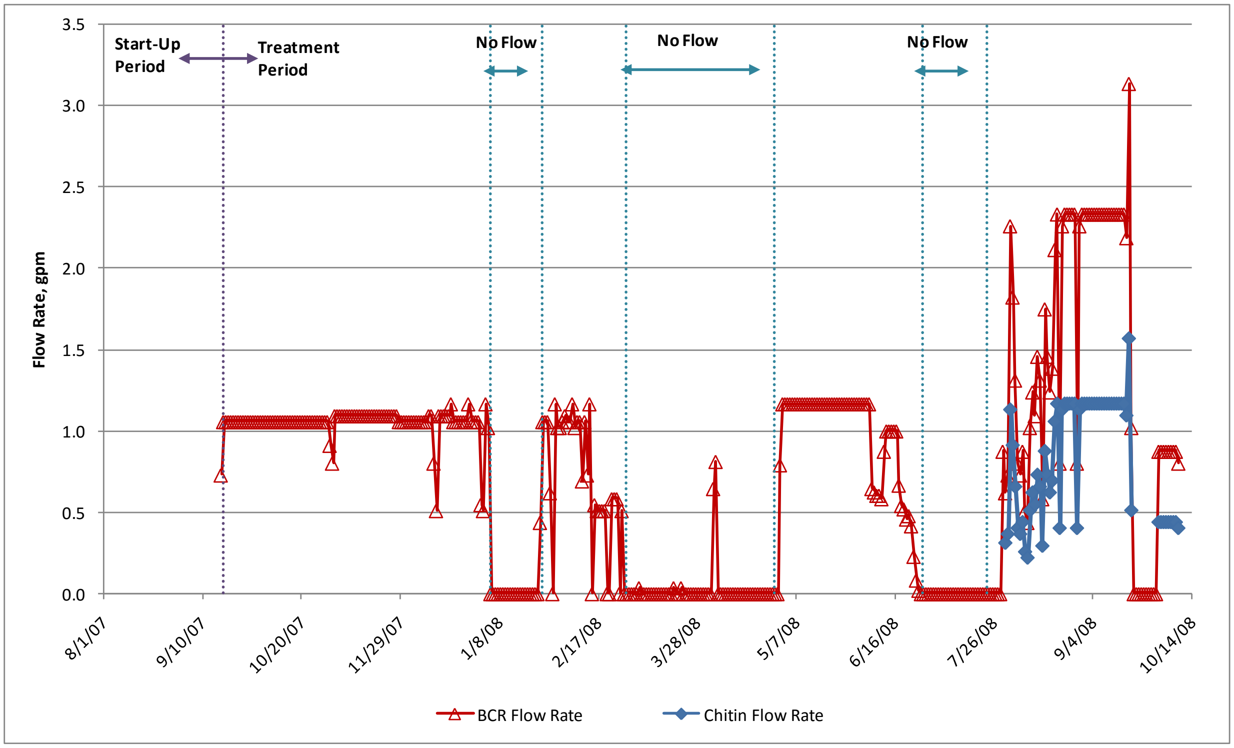


Figure 4. BCR and Chitin Reactor Flow Rates

BCR Results

The BCR treatment results are divided into field variables and metals analyses. The results are limited to the operating period (09/19/07 -10/15/08) and do not include the samples collected during the startup period (incubation or re-circulation period 08/09/07 -09/19/07) or periods of flow stoppage. However, the data presented on the Fig. 5 – 12 include all results from the startup period, treatment period, and periods of flow stoppage. The graphs include the State of Colorado Department of Health and Environment (CDPHE) water quality table value standards for metals for the receiving stream, Elk Creek (Segment 11, Upper Gunnison Basin) (CDPHE, 2007).

Field Results

pH. Sonde measurements were consistent with field measurements recorded during sample collection activities. Influent field and sonde pH readings ranged from 3.8 to 7.1 s.u.; effluent field and sonde pH ranged from 5.7 to 7.8 s.u. The stream standard for pH is 6.5 to 9.5 s.u. The BCR effluent pH was less than 6.5 s.u. at the beginning of the operating period and again during late July and August 2008. The low effluent pH values during the startup period are typical and are likely due to biological fermentation, which produces acidity. BCR effluent typically ranges from 6.0 to 8.0 s.u. (ref?); values between 6.0 and 6.5 are not uncommon (Reisman 2008).

Temperature. In general, the rate of biological treatment correlated positively with temperature. Influent field and sonde temperature measurements varied from 1.2 to 13 ^{o}C, and effluent field and sonde temperature ranged from 1.6 to 11.9 ^{o}C. The average influent and effluent sonde measurements were 3.2 and 3.9 ^{o}C for the operating period. As expected at a high altitude site, the sonde data revealed significant seasonal variation in both the influent and effluent BCR water temperatures. Notable differences were observed between field and sonde temperature measurements (Fig. 4). These differences were likely due to ambient air temperature influencing the field measurements during sample collection activities, as well as the sensitivity of the different measuring equipment. Daily minimum ambient temperature, as measured at the Schofield Pass weather station, has been included on Fig. 4. The lowest daily ambient minimum temperature was -28 ^{o}C on 12/29/07, 01/17/08, and 01/18/08.

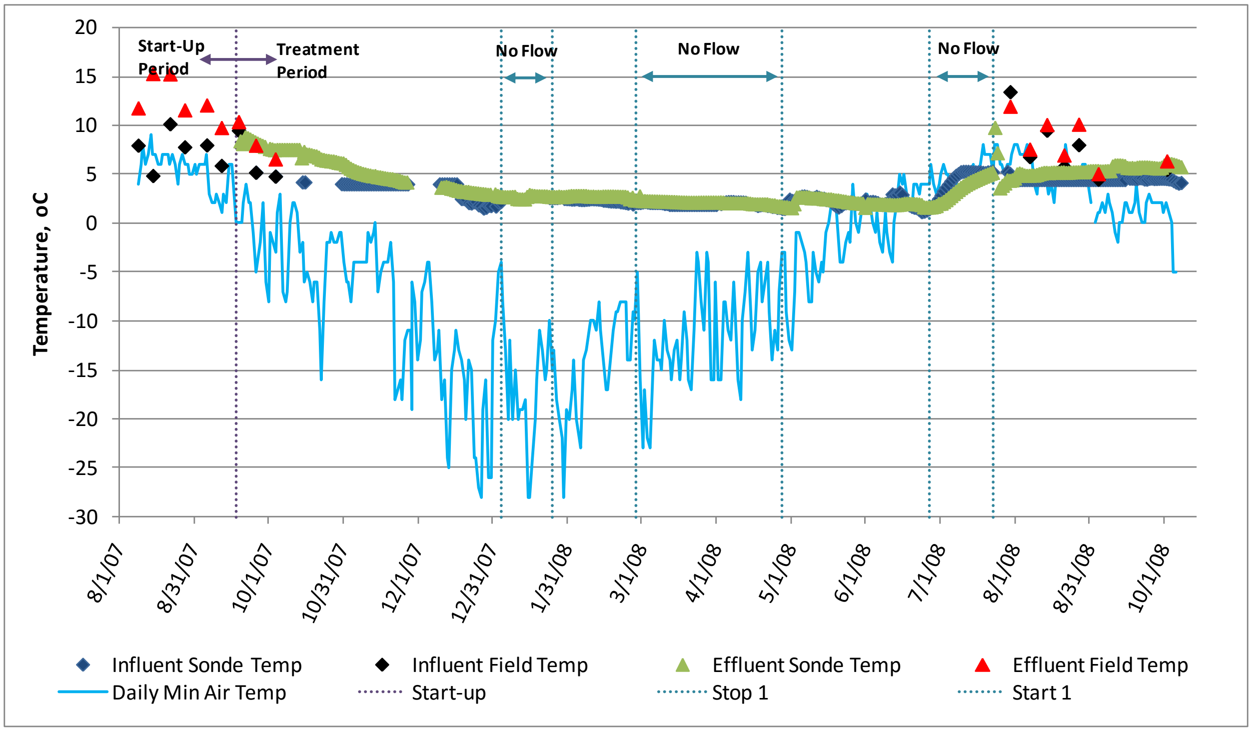


Figure 5. BCR Temperature Data including Daily Minimum Temperature (Daily Low) recorded at the Schofield Pass Weather Station

Oxidation Reduction Potential (ORP). Influent ORP field and sonde measurements ranged from 19 to 748 millivolts rmv), and effluent sonde readings ranged from -62 to –543 mv as shown on Figure 6. Negative ORP values indicated anaerobic conditions conducive to sulfate reduction. Significant differences were observed between the sonde and the field equipment because the sonde ORP probes did not maintain calibration. The sondes were calibrated infrequently during the winter due to limited site access, and the ORP calibration appeared to read correctly for a few days, and then needed re-calibration. The sonde ORP data were considered qualitative only, indicative of generalized reducing or oxidizing conditions. Both the field measurements and sonde data indicated that the BCR effluent was consistently anaerobic. All ORP measurements were taken with a silver chloride reference electrode and have not been corrected to the standard hydrogen electrode potential (i.e., Eh).

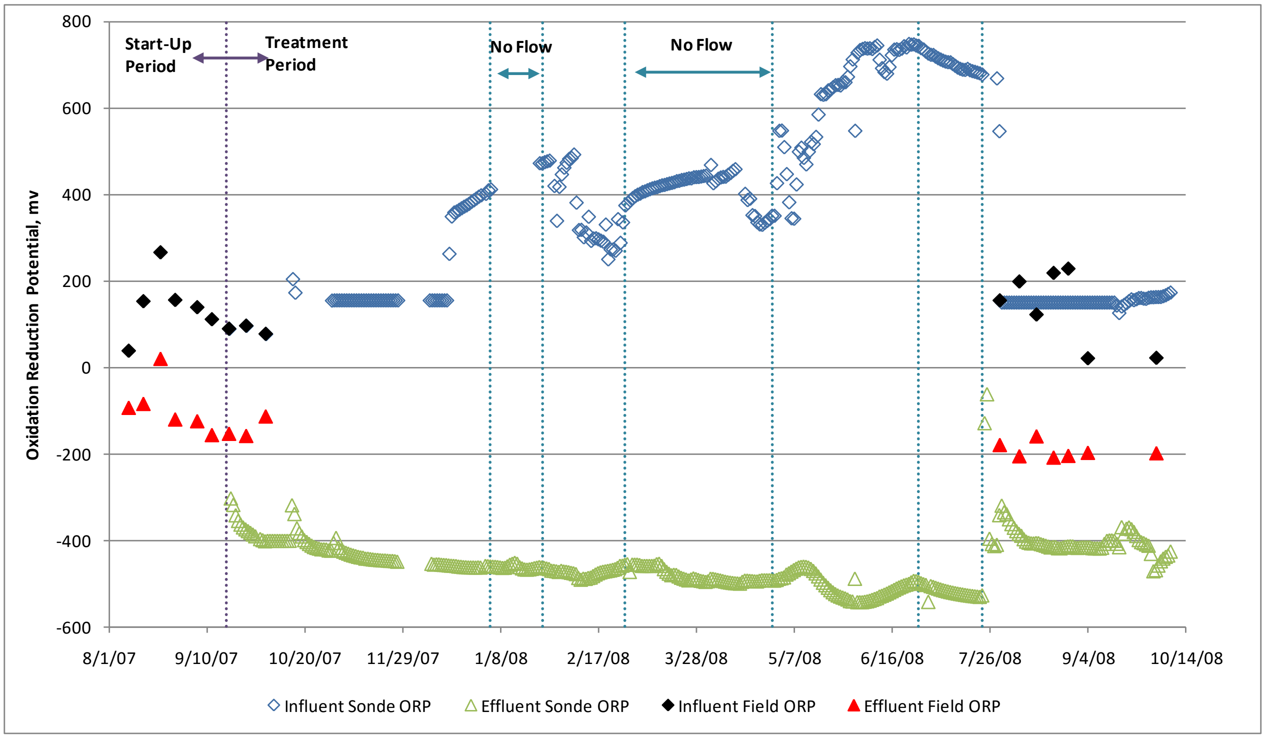


Figure 6. BCR ORP Data

Contaminants of Concern

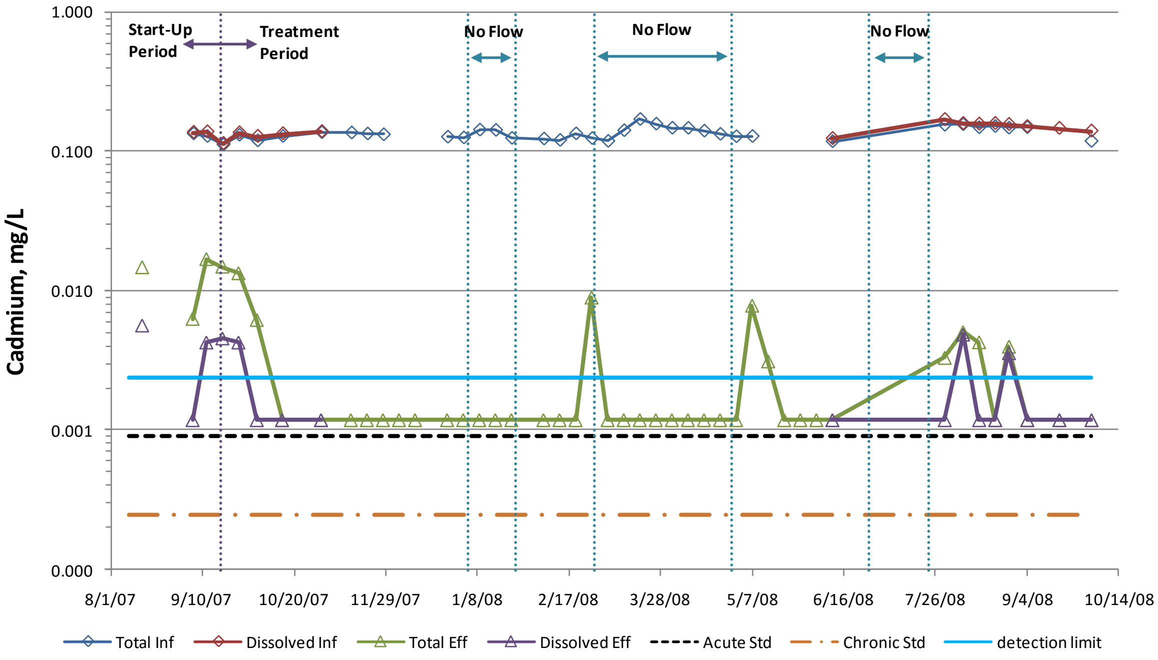
The CDPHE water quality standards for five of the six COCs (Cd, Cu, Pb, Mn, and Zn) are for the dissolved fraction (Table 1). The water quality standard for Fe was for total recoverable Fe, and "Total" and "total recoverable" analyses are considered identical and the terms are used interchangeably in this paper. From 2007 to 2008, 48 samples were analyzed for total Fe concentrations, and 21 additional dissolved analyses were performed. From November 2007 to June 2008 (i.e., winter sampling), sampling for metals was limited to total concentration samples because they were collected by the ISCO autosampler. The ISCO sample bottles were preserved with nitric acid, which precluded the collection of total and dissolved samples. The laboratory results are presented in Table 1. Laboratory results below the detection limit were assumed to be equal to half the laboratory detection limit.

Table 1. BCR Summary Results for Contaminants of Concern (all units are in mg/L)

Variable	Acute[1,2]	Chronic[1,2]	Influent			Effluent		
			Avg.[3]	Min	Max	Avg.[3]	Min	Max
Cadmium	0.0009 (tr)[4]	0.00025	0.14	0.11	0.17	0.00	0.00	0.00
Copper	0.007	0.005	0.26	0.04	1.06	0.00	0.00	0.01
Iron (total)	NA	1.0 (trec)[5]	5.23	0.16	21.22	2.01	0.01	16.48
Lead	0.03	0.0012	0.54	0.02	2.23	0.01	0.00	0.03
Manganese	2.37	1.31	10.99	5.34	12.71	10.53	7.44	14.67
Zinc	0.079	0.069	26.46	20.98	30.87	0.55	0.01	1.50

1 – Metal table value standards based on a hardness of 50 mg/L.
2 – Metal standards are dissolved unless otherwise stated.
3 – Percent removal was calculated from average influent and effluent concentrations..
4 – tr – Trout standard.
5 – Trec – the standard is total recoverable. The summary data for Fe are all total concentrations.
Shaded values exceed the Chronic water quality standard.

Cadmium. Influent dissolved Cd concentrations were fairly consistent, ranging from 0.11 to 0.17 mg/L (Fig. 7). Total and dissolved concentrations were generally equal, indicating the influent Cd was predominantly in the dissolved (particle size less than 45 μm) form. BCR effluent dissolved Cd concentrations ranged from below the detection limit of 0.0024 mg/L to 0.0049 mg/L. Of the 17 dissolved analyses performed, 6 resulted in dissolved concentrations greater than the detection limit (36%). The average percent removal for Cd was 98.5%.



All values below the laboratory detection limit are graphed as one-half the detection limit.

Figure 7. BCR Cadmium Concentrations

The chronic Cd stream water quality standard (0.00025 mg/L) was less than the EPA ORD laboratory equipment detection limit for Cd (0.002 mg/L). Again, for graphing and data analysis purposes, concentrations below the laboratory detection limit were entered as half the detection limit. As seen on Fig. 7, it appears that the effluent Cd concentrations were consistently above the chronic standard. However, given the relatively high detection limit, it is possible that the effluent concentrations were below the chronic standard.

Copper. Influent dissolved Cu concentrations ranged from 0.04 to 1.06 mg/L (Figure 5). Dissolved concentrations were generally similar to total concentrations. Of the 17 dissolved Cu analyses performed on BCR effluent water, only one sample (6% of analyses) exceeded the chronic standard. These results indicate the BCR is capable of treating dissolved Cu to levels below this target water quality chronic standard. The average Cu percent removal was 98.6%.

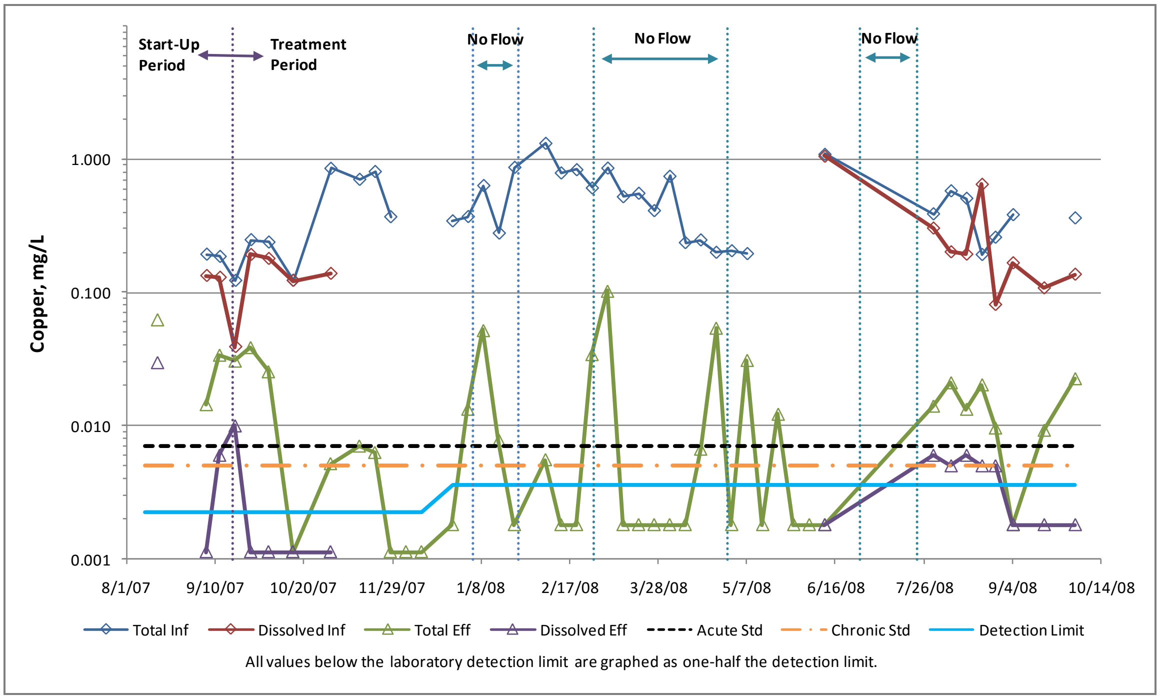
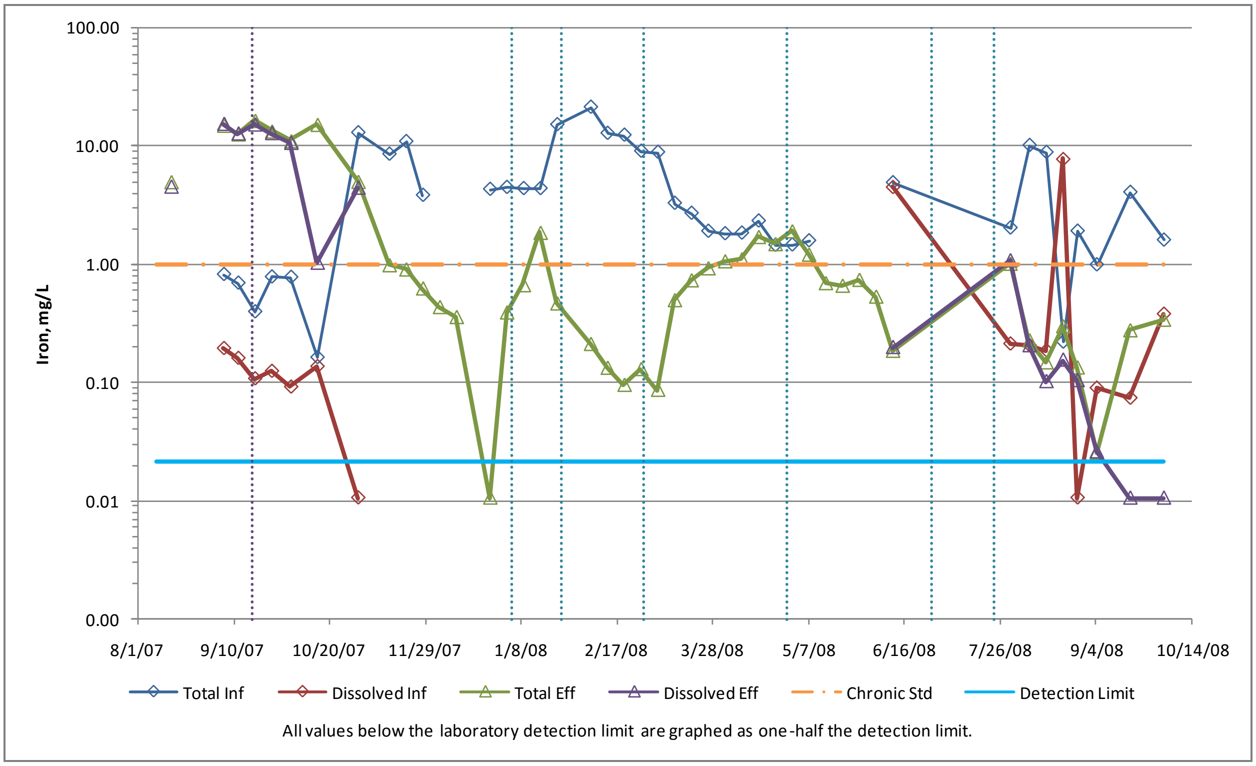


Figure 8. BCR Copper Concentrations

Iron. Unlike the other COCs, the water quality standard for Fe is for the total recoverable fraction. Influent total Fe concentrations ranged from 0.16 to 21 mg/L. BCR effluent Fe concentrations varied considerably. From August 2007 through November 14, 2007, BCR effluent total and dissolved Fe concentrations were consistently greater than both the influent concentrations and the chronic standard of 1 mg/L. The reducing conditions in the BCR cells had the potential to result in mobilization of redox-sensitive metals, such as Fe and Mn. This condition has been observed previously during startup of new

BCRs from the release of Fe from the BCR substrate material (Reisman 2008). Once the Fe present in the substrate (exact source material unknown) has been depleted, the BCR effluent Fe concentrations decreased. Of the 36 total Fe analyses performed on BCR effluent after November 14, 2007, 8 (22%) resulted in Fe concentrations above the chronic standard. Total and dissolved concentrations were below 1 mg/L since August 1, 2008. The average percent removal for total Fe was only 65% due to the high Fe concentrations in the influent water.



All values below the laboratory detection limit are graphed as one-half the detection limit.

Figure 9. BCR Iron Concentrations

Lead Influent dissolved Pb concentrations ranged from below the detection limit of 0.008 mg/L to 2.23 mg/L. Dissolved influent concentrations were generally slightly lower than the total concentrations as shown on Fig. 10. The BCR effluent Pb concentrations varied from below the detection limit of 0.008 mg/L to 0.034 mg/L. The highest effluent Pb concentrations were observed during startup of the cell. Dissolved Pb concentrations were below the laboratory detection limit in all samples collected in 2008. The average percent removal for Pb was 98.1%.

The chronic water quality standard for Pb (0.0012 mg/L) was less than the EPA laboratory water detection limit for Pb (0.008 mg/L). For graphing and data analysis purposes, concentrations below the laboratory detection limit were entered as half the detection limit.

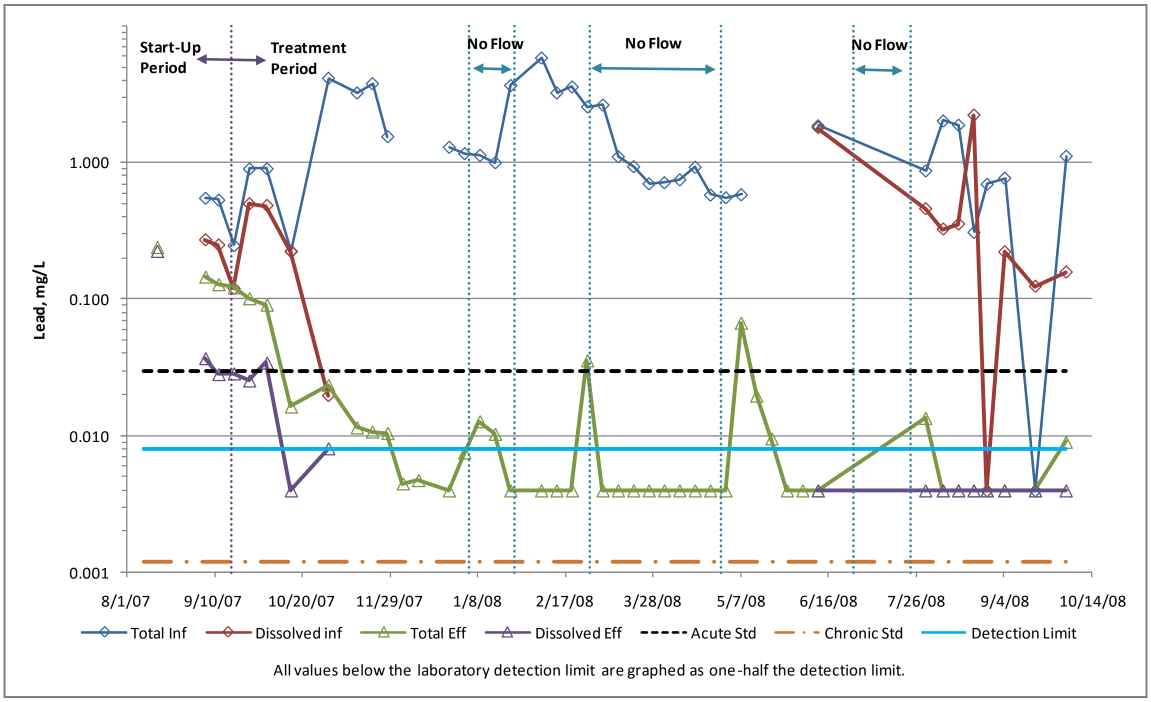


Figure 10. BCR Lead Concentrations

Manganese. Dissolved influent Mn concentrations ranged from 5.3 to 12.7 mg/L. Dissolved influent concentrations were comparable to total concentrations; practically all of the Mn present in the BCR influent was present in the dissolved form (Fig. 11). BCR effluent Mn concentrations varied considerably throughout the monitoring period. Initially, BCR effluent Mn concentrations were greater than influent concentrations, indicating Mn was being released by the substrate. Similar to Fe concentrations, the effluent Mn concentrations decreased to less than influent concentrations around mid-November 2007. However, during the 2007-2008 winter period, effluent total Mn concentrations increased considerably, reaching a maximum concentration of 21 mg/L on May 7, 2008. From August 2, 2008 through October 2, 2008, BCR effluent Mn concentrations were consistently lower than influent concentrations. Influent and effluent dissolved Mn concentrations were above the water quality standards in all samples. The BCR technology does not remove Mn in high percentages; the chitin reactor and APC were installed to test removal of Mn from BCR effluent.

Zinc. Influent dissolved Zn concentrations ranged from 21.0 to 30.9 mg/L (Fig. 11). Total and dissolved concentrations were almost identical during the monitoring period. Compared to other COCs, influent Zn concentrations were relatively stable during the monitoring period. Dissolved BCR effluent Zn concentrations ranged from below 0.009 mg/L to 1.5 mg/L. The average dissolved effluent concentration, 0.55 mg/L, exceeded the chronic standard, 0.069 mg/L. The average removal rate for Zn was 97.9%.

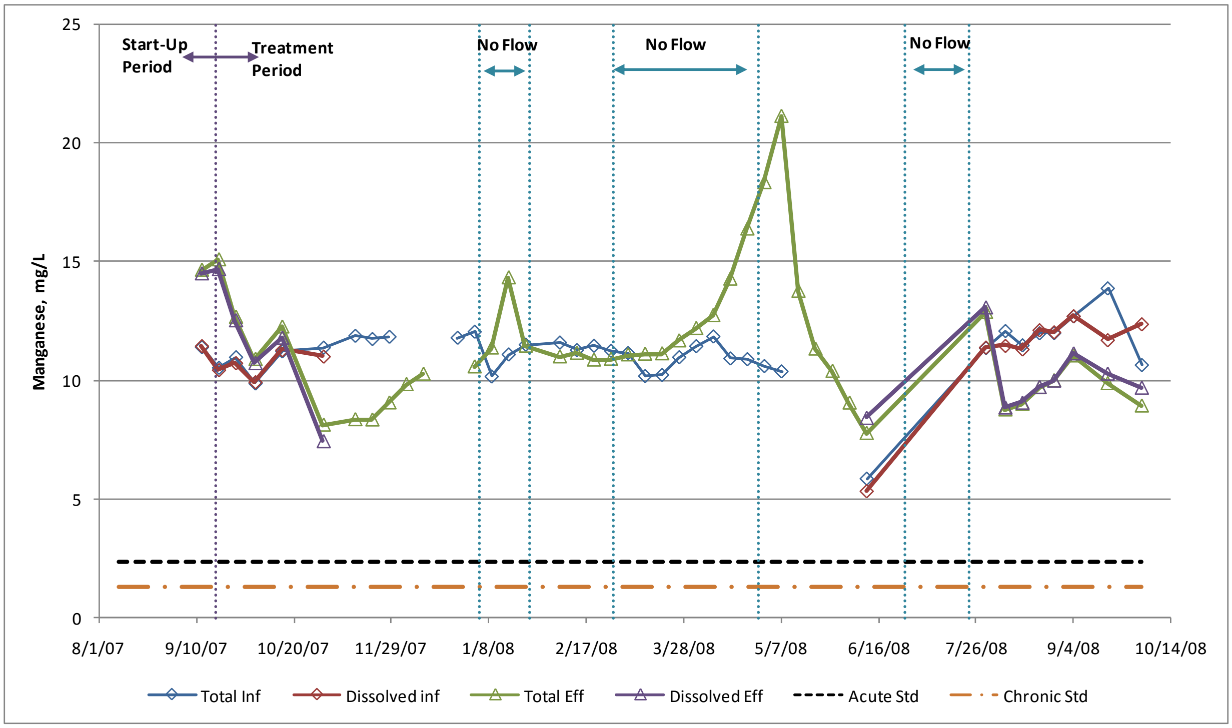
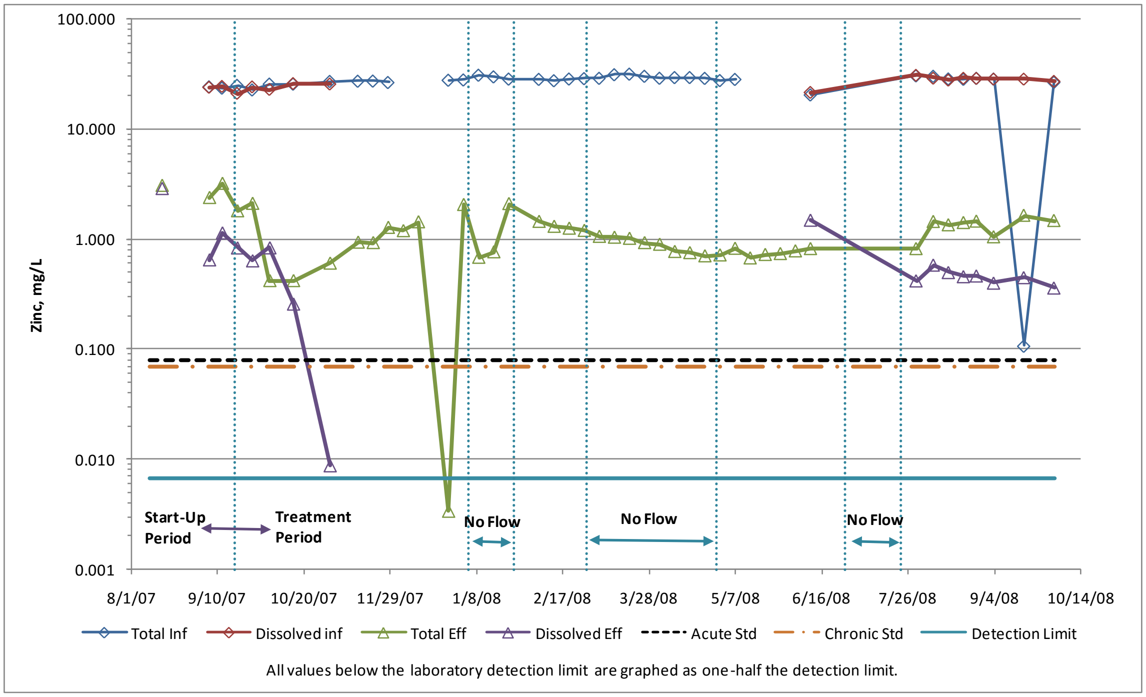


Figure 11. BCR Manganese Concentrations



All values below the laboratory detection limit are graphed as one-half the detection limit.

Figure 12. BCR Zinc Concentrations

Sulfate and Sulfide. BCR effluent sulfate concentrations were consistently less than influent sulfate concentrations indicating that sulfate reduction was occurring in the BCR. The average influent and effluent sulfate concentrations were 281 and 119 mg/L, respectively. Influent and effluent sulfide concentrations were measured 12 times during the 2007 and 2008 sampling seasons. Sulfide was not detected in the influent samples at concentrations above the laboratory detection limit of 0.8 mg/L. Effluent sulfide concentrations ranged from 0.9 to 27.5 mg/L. During 2008, the average effluent sulfide concentration was 21 mg/L. The presence of sulfide is a direct indicator of sulfate reduction.

Chitin Reactor Results

The chitin reactor influent water was BCR effluent water. This reactor is an additional process to treat the BCR effluent anaerobically in order to reduce metals concentrations further. The discussion of chitin results includes field variables and Mn removal.

Chitin Reactor Field Results

Flow Rate. As previously discussed, chitin flow rates were not measured directly; chitin flow rates are shown on Fig. 13. The average flow rate to the reactor was 0.8 gpm.

pH. Chitin reactor effluent pH ranged from 7.0 to 8.2 s.u. Generally, the chitin reactor effluent pH was slightly greater than the influent pH, except for measurements collected on 10/2/08. Chitin reactor effluent pH was consistently within the water quality criteria range of 6.5 to 9 s.u.

Temperature. Chitin effluent temperature varied from 4.6 to 13.1 ^{o}C. Effluent temperature was usually comparable to the influent temperature. It appeared that the chitin reactor did not contain material that creates an exothermic reaction.

Oxidation Reduction Potential. The BCR effluent water was conveyed to the chitin reactor through pipes with limited exposure to the air. Chitin effluent ORP measurements were consistently less than -100 mV and were similar to chitin influent ORP values. The chitin reactor maintained the anaerobic conditions of the BCR effluent water.

Manganese Removal. The goal of the chitin reactor was to remove Mn from the BCR effluent. Influent total and dissolved Mn concentrations were practically identical during the monitoring period (Fig. 13), which was the start-up period for the reactor. Dissolved influent concentrations ranged from 7.5 to 14.7 mg/L, with an average concentration of 11 mg/L. Chitin effluent total and dissolved Mn concentrations were similar during the monitoring period. Dissolved effluent concentrations ranged from 1.1 to 16 mg/L. Effluent samples collected on 07/30/08 and 08/07/08 contained Mn concentrations below the water quality standard of 1.65 mg/L. The other effluent samples contained Mn concentrations above water quality standards. The highest effluent Mn concentrations were observed during the final two sampling events of 2008; these samples contained total and dissolved Mn concentrations greater than influent concentrations suggesting that previously removed Mn was being released from the reactor. The average percent removal of Mn was 23%; the maximum percent removal was 90%.

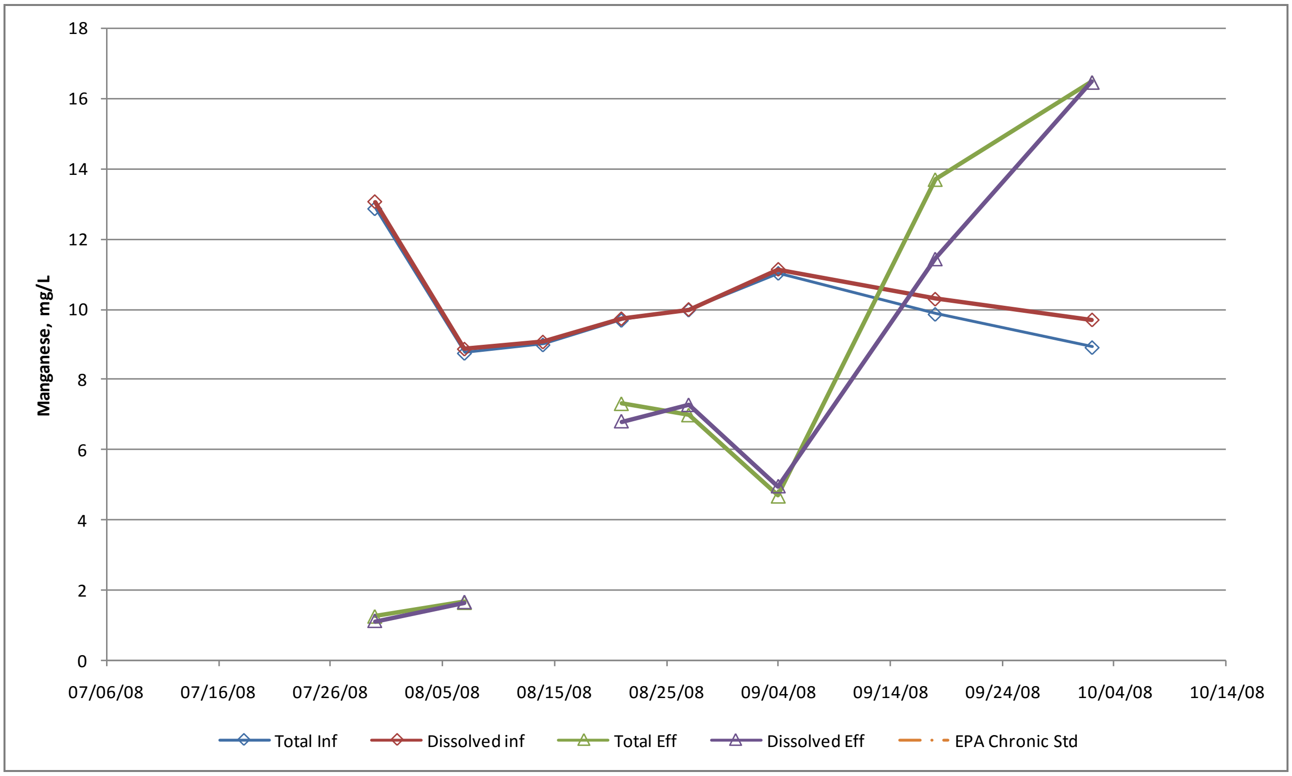


Figure 13. Chitin Reactor Manganese Concentrations

Other Metals. In addition to Mn, the chitin reactor influent contained Fe and Zn. The chitin reactor reduced the concentrations of these metals until mid-September 2008 when effluent concentrations of Fe and total Zn increased to levels greater than influent concentrations. This upset condition is consistent with the increased Mn concentrations and an increase in conductivity.

Modeling of Chitin Reactor Results

The chitin reactor used Chitorem™ in the substrate sand mixture. This new technology has a limited history of field applications for treating MIW. Manganese removal in a chitin reactor had been observed during bench-scale studies at the National Tunnel in Blackhawk, Colorado (Venot et al., 2008). The geochemical thermodynamic model PHREEQC was used to evaluate possible Mn removal mechanisms in the chitin reactor through thermodynamic speciation of the chitin reactor influent and effluent water qualities. The PHREEQC model is a well-established thermodynamic model published by the USGS (Parkhurst and Appelo, 1999) that can be used to "speciate" water quality to determine mineral saturation indices (SI) for a solution. The SI values indicate which minerals are under-saturated, super-saturated, or at equilibrium in a given solution. Geochemical modeling used water quality data from the chitin reactor with the Minteq database. Redox conditions within the model were controlled by the difference in the sulfide and sulfate concentrations measured in influent and effluent water quality and supported by measured ORP measurements.

The geochemical model indicated that the chitin effluent was at or near equilibrium with respect to rhodochrosite ($MnCO_3$), with SI values ranging from -0.5 to 0.5 (a value of zero indicates perfect equilibrium). Given these SI values, it was likely that rhodochrosite was present within the chitin reactor. The calculated SI values for manganese sulfide were much lower, ranging from -1.7 to -5.5 depending on the effluent solution and the particular manganese sulfide form. These low SI values indicate that the effluent solution was under saturated with respect to manganese sulfide. The undersaturated SI values indicate that if the mineral were present, it would not be stable in contact with the solution and would dissolve. As such, manganese sulfide is not likely to be the removal mechanism in the chitin reactor because the mineral is not stable based on the effluent chemistry. These results agree with conventional wisdom from the literature, which indicates that manganese sulfide has a higher solubility relative to other sulfides and requires a greater pH to precipitate in anaerobic conditions (Walton-Day, 2003).

Discussion

Ability of BCR to Meet Water Quality Standards for Metals

The BCR has achieved high levels of metal removal for Cd, Cu, Pb, and Zn since startup with little variation in effluent quality. The cold winter temperatures and flow interruptions did not significantly affect the metal removal rates. It should be noted that the flow interruptions were system related and not process related. Most BCR systems do not include pumps. The BCR achieved average removal percentages for Cd, Cu, Pb, and Zn approximating 98%. Copper was consistently removed to concentrations below the chronic water quality standard. The detection limits for Cd and Pb were not low enough to verify compliance with water quality standards. Effluent Zn concentrations were consistently above the chronic water quality standard. The high removal rates for Cd, Cu, Pb, and Zn were consistent with those measured in other BCR systems (Gusek et al., 2008). The BCR Fe removal rate was 65%, and the Mn removal rate was 4%. Iron and Mn are not consistently removed under anaerobic conditions but can be removed in an aerobic polishing process such as an aerobic wetland.

Chitin Results

The chitin reactor was constructed and put in place for Mn treatment. During the first two months of operation, the chitin reactor achieved Mn removal percent ranging from 85% to 90%, with an average Mn removal rate of 23%. During the last few sampling events, the chitin effluent Mn concentration was greater than the influent concentration indicating that Mn was being released from the reactor and the removal percentage was negative. One possible explanation for the low Mn removal rate was that the flow rate to the cell was greater than the design flow rate. Continued operation and monitoring of the chitin reactor is recommended to better understand the treatment process.

Remote Monitoring

The ISCO™ Stratolink transmitters did not operate consistently. Typically, transmissions from only one of the two transmitters were received at a time. When it was operational, the advantage of the Stratolink system was that field variables and flow data could be viewed on an Internet web page within several hours of their observation. This was a valuable tool because the daily cell performance could be monitored closely from a remote location. In the summer 2008, ISCO™ decided to abandon the use of the Stratolink transmitters because of the operational and accessibility issues at this site and others and replaced the transmitters with satellite phones. During the first few months of operation, data retrieval using the satellite phones was also problematic. Overall, remote monitoring of the pilot system was a significant challenge and warrants further study.

Conclusion

To date, a BCR and a chitin reactor were constructed at the Standard Mine Superfund site to test their ability to operate at a high-altitude, low-temperature, remote site. An aerobic polishing cell (APC) was also built near the end of the summer of 2008, but data were not collected during the study period. The pilot BCR was in operation for the longest period, approximately 13 months. Despite influent water temperatures as low as 1°C (33.8°F) and ambient temperatures as low as -28 °C (-18.4°F), the startup and operation of the BCR process was successful as most of the metals were removed in the BCR, and metal removal rates for Cd, Cu, Pb, and Zn were, on average, 98% for the treatment period. The pilot performance demonstrated that passive, biological treatment of MIW may be feasible at cold, remote sites but that remote monitoring still remains a challenge. Despite the high removal rate, the BCR effluent exceeded the stringent Colorado water quality standards for Cd, Pb, and Zn. Results from the first two months of chitin reactor showed inconsistent Mn removal rates; further monitoring of the reactor is recommended.

Acknowledgements

This paper has undergone peer and EPA review and has been approved for publication. Work on this project was conducted under an EPA contract with Golder Associates, Inc. (David Reisman, Project Officer). Mention of company trade names or products does not constitute endorsement for use. The authors would like to thank Ms. Christina Progess and Ms. Gina Andrews of EPA Region 8 for their assistance on the site, as well as several EPA site contractors working under their direction, including URS / UOS for their sampling assistance. The authors would also like to acknowledge the work of Jay and Lena from Nunatak for their assistance on the solar system and wiring, as well as their skiing and digging efforts at the site. Without the efforts and desire of these important people, this project would not have been possible.

Literature Cited

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).

Gusek, J.J. 2000. "Reality Check: Passive Treatment of Mine Drainage As Emerging Technology or Proven Methodology?", *In:* Procedings of the 2000 Society for Mining Engineers Annual Meeting, Salt Lake City, UT, February 28, 2000.

Gusek, J.J., 2002. Sulfate-Reducing Bioreactor Design and Operating Issues: Is This the Passive Treatment Technology for Your Mine Drainage? *In*: Proceedings of the National Association of Abandoned Mine Land Programs, Park City, Utah, September 15-18, 2002.

Gusek, J.J., T. Rutkowski, E. Blumenstein, and B. Shipley. 2008, Two-year Sulfate Reducing Bioreactor Pilot Test Results at the Golinsky Mine, California, Proceedings America Society of Mining and Reclamation, 2008 pp 424-441. http://dx.doi.org/10.21000/JASMR08010424.

Korte, K.M., C.E. Newcombe, and R.A. Brennan. 2008, Evaluation Of Three Different Purities Of Crab-Shell For The Remediation Of Mine Impacted Water, Proceedings America Society of Mining and Reclamation, 2008 pp 510-524. http://dx.doi.org/10.21000/JASMR08010510.

Parkhurst, D.L. and C.A.J. Appelo. 1999. User's Guide to PHREEQC (Version 2)—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geological Survey Water Resources Investigations Report 99-4259.

Postgate, J.R. 1979. The Sulphate-Reducing Bacteria. Cambridge University Press. Cambridge, Great Britain.

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

America Society of Mining and Reclamation, 2008 pp 892-909. http://dx.doi.org/10.21000/JASMR08010892.

Ruiz, A., L. Figueroa, M. Zaluski, and D. Bless. 2008, Substrate Degradation and Metal Removal Performance of a 1,500-Gallon Sulfate-Reducing Bioreactor for Mining-Influenced Water Treatment, Proceedings America Society of Mining and Reclamation, 2008 pp 950-968. http://dx.doi.org/10.21000/JASMR08010950.

Thomas, R.C. 2002. Passive Treatment of Low pH, Ferric Iron-Dominated Acid Rock Drainage. Doctoral Thesis. University of Georgia.

Venot, C., L. Figueroa, R.A. Brennan, T.R. Wildeman, D. Reisman, and M. Sieczkowski. 2008, 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.

Walton-Day, K. 2003. Passive and Active Treatment of Mine Drainage. *In:* Environmental Aspects of Mine Wastes, Mineralogical Association of Canada, Short Course Series Volume 31, J.L. Jambor, D.W. Blowes, and A.I.M. Ritchie, editors.