NUISANCE CONSTITUENTS IN PASSIVE WATER TREATMENT SYSTEMS– A SPECIFIC CASE STUDY[1]

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Abstract: While passive treatment has been proven effective at removing heavy metals and adding alkalinity to mining influenced water (MIW), many forms of passive treatment result in the production of "nuisance" constituents that must be addressed prior to discharge. Such "nuisance" constituents include reduced compounds (such as ammonia, hydrogen sulfide, and total organic carbon) that contribute to biochemical oxygen demand and chemical oxygen demand. Each of these constituents may be regulated necessitating secondary or tertiary treatment prior to discharge.

The focus of this paper addresses the "nuisance" constituents that have formed in a specific anaerobic bio-geochemical reactor: how these constituents formed, the length of time they may persist, and ways in which they may be treated. The passive treatment system analyzed is located on a confidential mine site in central Montana. The system consists of a biochemical reactor and an aerobic polishing cell; it was constructed in the fall of 2007 and has run continuously since.

Additional Key Words: passive treatment, mining influenced water, nuisance parameters, BOD, COD, hydrogen sulfide, ammonia

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Introduction

Passive treatment of mining influenced water (MIW) is a technology that has been proven to be an effective alternative to traditional active treatment. While it may not be appropriate for all MIW sites, passive treatment can typically resolve MIW problems at a lower cost than traditional methods (e.g., lime dosing) when systems are properly designed and operated. Passive treatment is also considered a sustainable "green" technology that uses natural organic substrate and has a low/near neutral carbon footprint. For these reasons and others, passive treatment of MIW with anaerobic and aerobic technologies is an option that should be considered in MIW treatment situations. However, the use of passive treatment can create unique design challenges, including the creation of "nuisance" constituents, which have not received much attention in the literature.

Passive treatment, particularly via biotic anaerobic systems such as biochemical reactors (BCRs) (aka sulfate reducing bioreactors), successive alkalinity producing systems (SAPS), and reducing alkalinity producing systems (RAPS), often results in the generation of a variety of "nuisance" constituents that must be addressed prior to discharge. Most biotic anaerobic passive treatment systems add hardness, alkalinity, and organic matter to the MIW, all of which can be beneficial to overall water quality and aquatic life (Blumenstein et al., 2006). While their anaerobic bio-geochemical environment is a prime reason they are successful at adding alkalinity and removing target constituents such as heavy metals and other compounds that can otherwise be difficult to remove (Postgate, 1979, Wildeman, et al., 1993, Gusek, 2000, Gusek et al., 2000, Gusek, 2001, Busler et al., 2002, Thomas and Romanek, 2002, Seyler et al., 2003, Gusek et al., 2006, Faulkner et al., 2007), that same environment also causes oxygen depletion, producing "treated" water that has low levels of dissolved oxygen (DO).

The degradation of organic substrates also results in the discharge of reduced compounds (such as NH_3, H_2S, and total organic carbon) that contribute to biochemical oxygen demand (BOD) and chemical oxygen demand (COD); these are often regulated in surface water discharge and municipal waste water permits. Consequently, biotic anaerobic system effluents must receive secondary and/or tertiary treatment prior to discharge. Polishing treatment alternatives include: aerobic lagoons, aerobic digesters, and free water surface constructed wetlands. This paper is a case study, focusing on the nuisance constituents associated with one particular biotic anaerobic passive treatment system. Key issues include the expected persistence of these parameters and what remedies might be employed to address them.

The site is a confidential historic gold mine that is using a BCR to remove Tl, Se, and NO_3^- present in the MIW there (Blumenstein et al., 2008). In the geochemically reducing conditions typically present in the BCR, biogenic sulfide is believed to combine with dissolved Tl to form insoluble metal sulfide precipitates (e.g., TlS, Tl_2S, and Tl_2S_2) (Nriagu, 2003). Thallium is typically found in nature as a substituting ion in pyrite; previous unpublished research at this site suggested that a sacrificial source of iron facilitated Tl removal. Additionally, the reducing conditions in the BCR will reduce the Se present as selenate (Se^{+6}) to selenite (Se^{+4}) and then to elemental selenium (Se^0) (Gusek et al., 2008). After a successful three month bench test showed that ≥ 99% removal of Tl, Se and other heavy metals (Zn, Cu, etc.) was possible, a demonstration-scale passive treatment system (PTS) was built. This unit comprises the first half of a full-scale system; it was constructed in November 2007and has been operational since then.

The demonstration-scale PTS consists of a BCR, an aerobic polishing cell (APC), and all the requisite pipes and valves to allow a gravity feed. In the first two years of operation, this system has achieved near complete removal of all heavy metals, including Tl (influent: 1.3 mg/L to < 2 µg/L effluent) (Blumenstein, 2009). While the BCR is performing well at removing the heavy metals present, there have been a variety of nuisance constituents that have persisted in the BCR effluent.

Nuisance Constituent Sources in the BCR

The degradation of organic substrates present in biotic anaerobic passive treatment systems can result in the discharge of reduced compounds (such as NH_3, H_2S, and total organic carbon) that contribute to BOD and COD; these are often regulated in surface water discharge and municipal waste water permits. This system in specific has elevated levels of NH_3, H_2S, and total organic carbon, which contributes to elevated levels of BOD and COD.

Reasons for Elevated Levels of Reduced Organic Compounds

Three primary reasons are suspected of causing elevated concentrations of reduced organic compounds present in the Montana PTS effluent. They are:

- Addition of cow manure at start-up as an inoculum
- Over sizing of the BCR

- Under sizing of the APC

Reduced Compounds Present Due to Manure Addition. The manure was added to the BCR as a source of microbial inoculum during initial substrate mixing and placement. After an incubation period of approximately four weeks, the water was released from the BCR which flowed into the APC. While the BOD/COD increase due to the manure being flushed out of the BCR only lasted on the order of a few months, the reduced organics were flushed into the APC, leaving a thick, black BOD solids sludge in all of the APC cells. This bio-solid sludge was removed from the APC cells using a vacuum truck approximately six months after start-up. Subsequent testing at other mining sites has shown that a BCR could be started with far less microbial inoculum, whether the inoculum is manure or another source such as mushroom compost. The BCR at the Montana site used an inoculum of 10% manure by weight, whereas recent BCR start-ups have used anywhere from 2% by weight to no inoculum at all, with positive preliminary results (unpublished data).

Reduced Compounds Present Due to Over Sizing of the BCR. Due to space constraints, the demonstration-scale BCR was designed to remove nitrate as well as thallium, selenium, and other heavy metals. While nitrate could be efficiently removed in an APC, it needed to be removed first in the BCR to create conditions that would allow microbial sulfate reduction to occur. There was insufficient space at the site to remove the nitrate present in the MIW with an APC prior to the BCR. Sizing the BCR for nitrate removal also ensured that all of the selenium would be removed in the BCR. Subsequent research (unpublished data) has shown that selenium can be removed in a BCR with a hydraulic retention time (HRT) of 1 to 2 days, but that was not known at the time of this system's design. As such, the demonstration-scale BCR was designed for a molar removal rate of 0.06 moles/m^3/day of nitrate.

The result is that the HRT in the BCR is between 7 and 10 days, which is more than sufficient for thallium (average of 1.2 mg/L) and selenium (average of 0.015 mg/L) removal to levels below analytical detection limits, but also results in excessive breakdown of organic substrate, leading to elevated concentrations of BOD, COD, TOC, etc. in the BCR effluent.

The resulting HRT of 7 to 10 days, however, has allowed sulfate reduction and soluble carbon degradation in excess of what is required for thallium, iron, copper, and zinc removal. Because of the excess sulfate reduction (from sulfate, S^{+4}, to sulfite, S^{+2}, to sulfide, S^{-2}) there is more sulfide present than is necessary for metal sulfide precipitation and co-precipitation. Although some of the sulfide converts to elemental sulfur (S_0), there is still a small amount of sulfide that binds with free protons (H^{+1}) to form hydrogen sulfide gas (H_2S). H_2S is extremely dangerous and can cause serious health implications at elevated concentrations. The H_2S created in the BCR water has been eliminated as a health concern at this site because the levels are low (they have not registered on a multi-gas meter) and the BCR is out in the open with ample ventilation. The potential presence of hydrogen sulfide gas must be considered, however, when designing enclosures and BCRs in the future.

An example of this is a pilot BCR in Alberta, Canada that was operated through the winter of 2009-2010 (unpublished data). This system was installed in a shipping container so that it could be run in parallel to an active treatment system through the winter. A build up of H_2S occurred in the container that was high enough to trigger an alarm in a multi gas meter (~40 mg/L) and cause an employee become light-headed. The employee was taken to a hospital for observation.

The 7 to 10 day HRT also results in excess consumption of organic substrates by microbial organisms. Because of the long HRT and resulting elevated organic substrate degradation, the BOD/COD concentration (composed primarily of ammonia, and total organic carbon) in the BCR effluent is higher than the APC was designed to handle.

Reduced Compounds Due to Under Sizing of APC. Because the BOD/COD concentrations exhibited in the BCR effluent were very high at start up (200-500 mg/L), and near 100 mg/L after two years of operation, the APC was undersized for the load. Rather than being sized to reduce BOD from 20 mg/L to less than 5 mg/L, the APC would have needed to be significantly larger to handle influent BOD concentrations on the order of 100 mg/L, which may or may not be a temporary condition.

Presence of Manganese and Arsenic in BCR Effluent. Two other parameters that are present in the BCR effluent at this site are Mn and As. The Mn is present from two sources: a small amount of Mn leaches from the organic substrate used in the BCR (approximately 0.2-0.3 mg/L), and the anaerobic BCR does not remove any manganese present in the influent (approximately 0.1 mg/L). While Mn can be removed in a passive treatment system, it is difficult to remove anaerobically (Gusek, 2002). While there are emerging technologies that suggest Mn removal can be accomplished anaerobically with the use of chitinous materials such as crab shells (Venot, et al. 2008), it can also lead to an increase in arsenic and BOD, and further research and long-term application is necessary to fully understand its use. More traditional passive treatment of Mn includes Mn removal beds and using algae to raise the pH and create manganese oxides (e.g. – pyrolusite) and manganese hydroxides.

The As is present in the BCR effluent because of an unforeseen material substitution that occurred during construction and start-up of the BCR. Because the MIW at this site lacks dissolved Fe, an iron-bearing ore was added to the substrate mixture as a "sacrificial media" to encourage Tl removal. During bench testing a local magnetite was used with good results, but at the time of demonstration-scale BCR construction, the magnetite used during bench testing was unavailable. A different iron ore was used commission the BCR before winter: crushed basalt from a mine approximately 100 miles from the site. The basalt was immediately mixed with the organic substrate and placed in the cell. Since bench testing was not conducted using the basalt, its elevated levels of arsenic were not readily apparent. Because of this, As in the BCR effluent is present at a higher concentration than the influent. At most sites where arsenic is present, it is a primary contaminant of concern (COC) rather than a nuisance constituent; it is considered a nuisance constituent at this site.

Persistence of Nuisance Constituents in a Biotic Anaerobic System

The persistence of a nuisance constituent in a biotic anaerobic passive treatment system varies from site to site and MIW to MIW source. For the BCR and APC system in Montana, the manganese and arsenic concentrations are somewhat introduced and are expected to eventually decrease in the BCR effluent. Consequently, they are considered nuisance constituents. Because they are leaching from the BCR organic substrate under normal operating conditions, however, the Mn and As are expected to be present for an extended period. This situation dictates that they must be treated and removed aerobically prior to surface discharge just as if they were a COC (as As and Mn are often identified).

The first step in determining if aerobic treatment of the anaerobic effluent is necessary is to identify how long the nuisance constituents will persist at the site. Once that is established, design of the aerobic treatment can begin, if necessary. For the Montana site, data regression modeling was conducted to estimate the time required until the nuisance constituents would drop to levels that could be treated in the existing APC. Results of this modeling are presented in

Fig. 1. The BOD regression model used in the analysis predicts future BOD concentrations using a ratio of pore volumes treated (PV) divided by the HRT of the bioreactor at the operational flow rate of 5 gpm.

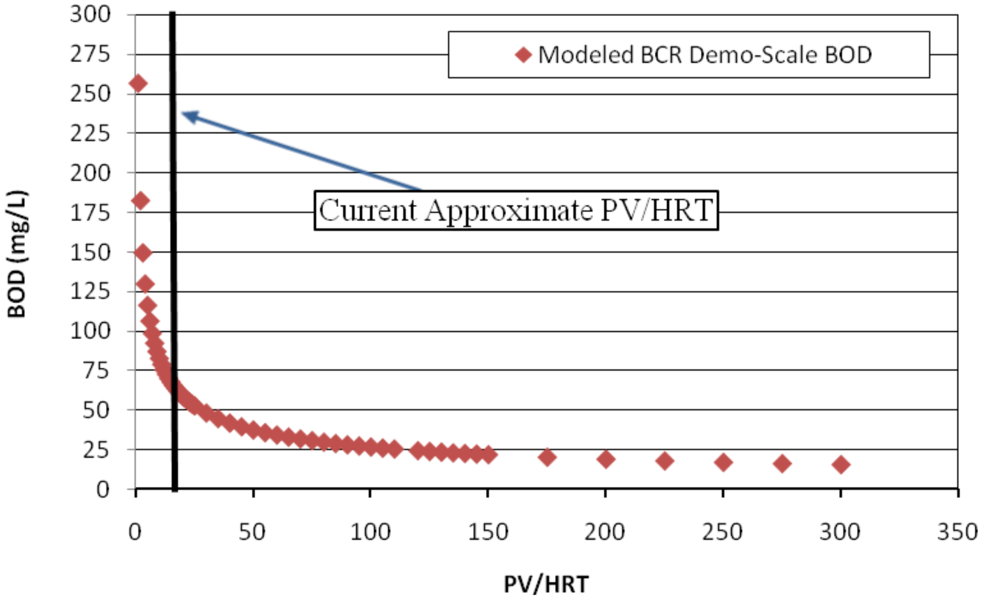

Figure 1 - Modeled BOD Projection for Anaerobic Demonstration-Scale PTS

Translated to table form (Table 1), the BOD regression modeling clearly indicates that the nuisance constituents at the Montana site will persist for a significant period of time, which necessitated the development of an aerobic process step to treat the anaerobic BCR effluent.

Table 1. Predicted BOD Concentrations at Montana Site Using the Current PV/HRT Model at 5 gpm

BOD (mg/L)	PROJECTED DATE
100	November 1, 2009
75	March 2010
50	September 2010
40	May 2011
30	February 2012
25	June 2013
20	December 2014
15	January 2019

The following methods section will outline the methods used to create an aerobic treatment process step for the Montana mine demonstration-scale PTS.

Methods

When an aerobic treatment step is required to remove nuisance constituents, there are several options to chose from, ranging from APCs and free water surface constructed wetlands to aerobic lagoons and aerobic digesters. As was mentioned above, space at this site is limited and it prevents the expansion of the existing APC or the introduction of a constructed wetland. To reduce the footprint required for the aerobic treatment step, an aerobic lagoon concept was selected for lab testing.

An aerobic lagoon utilizes an external source of aeration/mixing that increases the kinetics of the biological and chemical reactions present, decreasing the necessary HRT and footprint of the aerobic treatment step. In order to properly size an aerobic lagoon, lab testing was conducted to determine the appropriate HRT to effectively remove the BOD (including ammonia, sulfide, and TOC) present in the Montana BCR effluent.

Sample Collection.

In preparation for the lab tests, personnel from the Montana mine site collected approximately 57 liters (15 gallons) of BCR effluent and shipped it to the Golder water treatment laboratory (WTL). Field parameters recorded at the time of sample collection are provided in Table 2.

Table 2. Field Parameters at Collection of First 57 Liters of BCR Effluent

Sample Date	Time	Temperature	pH	ORP	Conductivity
Monday, April 20th	0945	7.7˚ C	7.15 s.u.	-230 mV	2.59 mS/cm

During aerobic lagoon bench testing, preliminary results indicated that a one-day HRT lagoon would be insufficient to fully remove the nuisance constituents. At this point, additional BCR effluent was collected so the testing could be completed. Field parameters recorded at the time of sample collection are shown in Table 3.

Table 3. Field Parameters at Collection of Final 19 Liters of BCR Effluent

Sample Date	Time	Temperature	pH	ORP	Conductivity
Monday, May 18th	1100	11.4˚ C	6.97 s.u.	-257 mV	2.30 mS/cm

Laboratory Equipment Used.

Over the course of aerobic lagoon lab testing, several types of laboratory equipment were used in accordance with the following general protocols. Samples were collected with a washed and clean sampling device (e.g. – syringe, plastic beaker, glass beaker); field measurements were recorded within 15 minutes of sample collection. Any probes used to measure field parameters were rinsed after each use in preparation for the next sampling event. Laboratory equipment used is presented below:

- pH Readings – ORION 230A+ laboratory meter and probe and a HANNA pH/ORP pen probe.
- ORP Readings – OAKTON pH 110 Series field meter and probe and a HANNA pH/ORP pen probe
- DO Readings – OAKTON DO300 field meter and probe.
- Conductivity Readings – OAKTON CON400 Series field meter and probe.
- COD Readings – HACH DRD200 digester block and HACH DR 2800 spectrophotometer.
- Temperature Readings – All of the above meters and probes have temperature outputs that were averaged for reported temperature readings.

Development of Aerobic Sludge Seed.

Before testing began, an aerobic sludge seed needed to be developed. 4.0 liters (L) of BCR effluent was placed in a bucket and aeration began. Nitrogen and P were also added to the water at a ratio in accordance with that required from the expected biochemical oxygen demand (BOD) level of approximately 100 mg/L. The appropriate ratio of nutrients for an aerobic lagoon is approximately 10-12 grams of N and 5-6 grams of P per 100 grams of BOD (Tchobanoglous, 2003). Nitrogen was added in the form of urea ($[NH_2]_2CO$) and K was added in the form of potassium phosphate (K_3PO_4).

Over the next two and one-half weeks the aerobic sludge seed was developed. BCR effluent was added to make up for evaporative losses and N andP were added every few days. Over that period, suspended solids began to develop and increase in concentration. Field data was recorded and samples were collected for COD analysis to determine when the aerobic sludge seed would be ready for aerobic lagoon lab testing. The following parameters were used to determine when the aerobic sludge seed had effectively acclimated to the BCR effluent:

- The COD consistently drops each time the water is sampled,
- the dissolved oxygen (DO) is at or above 2.0 mg/L, and
- the TSS levels increase over those initially recorded.

After approximately three weeks, the aerobic sludge seed had effectively reduced the COD from the original 240 milligrams per liter (mg/L) by 50% to 120 mg/L. Additionally, the DO maintained a concentration above 5 mg/L and the TSS levels were significantly higher than those initially observed. At that point, it was decided that the aerobic sludge seed had sufficiently acclimated to the BCR effluent and lab testing was ready to commence.

Initially, aerobic lagoon lab testing consisted of three components conducted in parallel: a one day HRT lagoon, a two day HRT lagoon, and a four day HRT lagoon. A fourth aerobic lagoon eight day HRT component was added to more completely characterize the decay rate and required HRT of a full-scale aerobic lagoon. Each of the different HRT aerobic lagoon tests were conducted in the same manner outlined below.

Aerobic Lagoon Lab Testing

When the aerobic sludge seed had sufficiently acclimated to the BCR effluent, testing commenced. At the beginning of aerobic lagoon lab testing, aquarium air pumps and diffusers were added to the 1 day HRT, 2 day HRT, and 4 day HRT lagoon buckets (Fig. 2). Then the aerobic sludge seed was split into three equal (approximately 0.9 L each) volumes and added to each of the lagoon buckets with 3.0 L of BCR effluent for an approximate total volume of 4.0 L per lagoon.

Figure 2 - Aerobic Lagoon Lab Test Experimental Setup

At that point, the air pumps were engaged and aeration began in all three aerobic lagoon tests. Initial samples were collected for COD analysis, field parameters were recorded, and nitrogen and phosphorus were added shortly after aeration began. Figure 3 displays the aerobic lagoons' appearance prior to and after aeration began.

Figure 3 - Aerobic Lagoons Before and After Aeration (left to right: 1 day HRT, 2 day HRT, and 4 day HRT)

Between sampling events, lids were placed loosely on the top of the aerobic lagoon buckets to minimize evaporative loss, as this would skew results of this small-scale study. After about a day of testing, it appeared that the air diffusion alone was not enough to keep the solids suspended in the aerobic lagoons. To remedy this, a submersible pump was added to each aerobic lagoon test bucket to re-circulate the water and keep the solids suspended (Fig. 4).

Figure 4 - Aerobic Lagoon Before and After Inserting Recirculating Pump for Solids Suspension

A description of the sampling schedules and the steps followed during each sampling event are provided in the sections below. While only the one-day HRT testing process is provided, each of the four HRT set-ups was tested similarly, with only the sample collection frequency changing.

One Day HRT Aerobic Lagoon Bucket Lab Testing –

1) A 0.5 L sample was collected from the one day HRT aerobic lagoon bucket every 3 hours.
2) The same volume of water that was removed from the bucket (0.5 L) was replaced with raw BCR effluent. As a result, the full volume of the BCR effluent was replaced every day (eight 0.5 L samples every 3 hours), simulating a one day HRT aerobic lagoon.
3) If a sampling event was missed, the volume of water removed from the bucket and replaced with raw BCR effluent was doubled, from 0.5 L to 1.0 L.
4) At each sampling event, field parameters (pH, ORP, temperature, and conductivity) were recorded and entered in a spreadsheet to monitor for trends. Once per day, the COD was determined for the sample removed from the bucket. Urea and potassium phosphate were added to ensure there were residual concentrations of N and P present in the water. COD was measured by allowing the solids to settle out of the sample, and then collecting a decanted sample of the water to add to a HACH COD vial. The vial was then placed in the HACHDRD200 digestion block. After digestion, the vial was placed into a HACH DR2800 spectrophotometer to measure a COD value for that water sample. All of the data, including COD, DO, pH, ORP, temperature, and conductivity, are summarized in Table 4 below.
5) This process occurred over five days for the one day HRT aerobic lagoon. This allowed the equivalent of five pore volumes of BCR effluent to be treated in the 1 day HRT aerobic lagoon test unit.
6) For the final sampling event, a sample was collected and sent to Energy Labs in Casper, Wyoming. This sample was analyzed for BOD, COD, sulfide, As, Fe, Mn, Se, and Tl.

Results of Lab Testing to Optimize Aerobic Lagoon System

Field Parameters

Over the course of the aerobic lagoon lab testing, field parameters were recorded during each sampling event. A summary of the field parameters recorded throughout lab testing is provided in Table 3.

Table 3. Summary of Field Parameters Recorded During Aerobic Lagoon Lab Testing

Parameter (Units)	1 day HRT			2 day HRT			4 day HRT			8 day HRT		
	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.
DO (mg/L)	5.8	4.0	7.4	5.5	3.1	6.9	5.6	3.2	7.3	4.0	3.5	4.6
pH (s. u.)	8.1	7.0	9.2	8.5	7.3	9.3	8.3	7.4	9.1	8.4	7.8	9.0
ORP (mV)	17	-140	116	-30	-114	90	-29	-94	99	-44	-85	16
Temp (°C)	17.4	14.0	20.0	20.3	14.0	26.3	20.3	14.0	26.5	23.4	18.9	25.0
Cond (mS/cm)	1.9	1.7	2.4	1.9	1.7	2.5	2.0	1.7	2.6	2.1	1.8	2.3

<u>DO</u> – The average DO levels were 5.8, 5.5, 5.6, and 4.0 mg/L for the 1 day, 2 day, 4 day, and 8 day HRT, respectively. DO levels started to drop over the last week of testing. This is suspected to have been caused by the DO probe's failure during this period. The DO probe was calibrated every three days and could not be successfully calibrated over the last week of testing. With the exception of the last week, DO levels were maintained above 3.0 mg/L at all times throughout aerobic lagoon lab testing.

<u>pH</u> – The average pH levels were 8.1, 8.5, 8.3, 8.4 standard units for the 1 day, 2 day, 4 day, and 8 day HRT, respectively. The pH levels typically behaved consistently over the aerobic lagoon testing effort. The BCR effluent reported an initial pH that was near neutral. Over the course of aeration, the pH in each of the aerobic lagoon buckets increased approximately one standard unit, from about 7.0 standard units to just above 8.0 standard units.

<u>ORP</u> – The average ORP levels were 17, -30, -29, and -44 mV for the 1 day, 2 day, 4 day, and 8 day HRT, respectively. As noted in the sample collection section above, the ORP values recorded at the lab varied from the field readings recorded at the site. It is suspected that the lab ORP probe may need replacement, which results in the low ORP values. ORP values did not affect the results of the aerobic lagoon lab testing because DO levels were also monitored to ensure aerobic conditions prevailed during testing.

<u>Temperature</u> – The average observed temperatures were 17.4, 20.3, 20.3, and 23.4 ºC for the 1 day, 2 day, 4 day, and 8 day HRT, respectively. The ambient temperature was lower during the first few days of aerobic lagoon testing and increased during the final week of testing. This

can be seen in the relatively lower temperatures recorded in the one day HRT aerobic lagoon test unit compared to the elevated temperatures recorded in the eight day HRT aerobic lagoon test unit.

Conductivity – The average conductivity values were 1.9, 1.9, 2.0, and 2.1 mS/cm for the 1 day, 2 day, 4 day, and 8 day HRT, respectively. Conductivity values generally did not change significantly during testing but did drop slightly from initial start-up until steady state conditions were reached.

COD Trends

Over the course of the aerobic lagoon lab testing, samples were collected for COD analysis from each of the aerobic lagoon buckets approximately once per day. Figure 5 displays how the samples appeared after they were collected and after they were allowed to settle for 24 hours.

Figure 5 - Samples Immediately after Sample Collection and After 24 Hours of Settling

A summary of the COD readings recorded throughout lab testing is provided in Table 4. The different HACH COD vials used, and the sample preservation protocols used follow.

- HACH High Range COD Vials – The high range (HR) COD vials were used for the majority of COD analysis throughout the aerobic lagoon lab testing. HACH HR COD vials have a range of 0-1,500 mg/L COD. HR COD results have been subdivided into two categories:

- *HR COD* – For these results, the samples were collected and kept in the garage where the lab test was performed until they could be taken to the lab and digested for COD readings.
- *HR Lab COD* – For these results, the samples were collected and immediately refrigerated until they could be taken to the Golder WTL and digested for COD readings.
- HACH Low Range COD Vials – The low range (LR) COD vials were primarily used during the second half of the aerobic lagoon lab testing. HACH LR COD vials have a range of 0-150 mg/L COD. LR COD results have been subdivided into two categories:
    - *LR COD* – For these results, the samples were collected and kept in the garage where the lab test was performed until they could be taken to the lab and digested for COD readings.
    - *LR Lab COD* – For these results, the samples were collected and immediately refrigerated until they could be taken to the Golder WTL and digested for COD readings.

Table 4. Summary of COD Measurements Recorded During Aerobic Lagoon Lab Testing

Parameter (Units)	1 day HRT			2 day HRT			4 day HRT			8 day HRT		
	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.
HR COD (mg/L)	116	59	159	106	61	162	97	48	139	--	--	--
HR Lab COD (mg/L)	78	63	92	74	63	90	73	45	111	61	52	74
LR COD (mg/L)	112	96	137	102	114	89	97	87	105	--	--	--
LR Lab COD (mg/L)	--	--	--	45	42	48	47	44	50	45	43	46

1 day HRT COD. The average COD results for the one day HRT aerobic lagoon were 116, 78, and 112 mg/L for HR COD, HR Lab COD, and LR COD vials, respectively. The samples that were immediately refrigerated until being taken to the lab for digestion typically resulted in lower COD concentrations for the HR Lab COD vials. This is because the garage-stored samples had additional bacterial growth before digestion, resulting in false high COD

concentrations. The HR Lab COD values should be considered the most representative results for the one day HRT aerobic lagoon.

2 day HRT COD. The average COD results for the two day HRT aerobic lagoon were 106, 74, 102, and 45 mg/L for HR COD, HR Lab COD, LR COD, and LR Lab COD vials, respectively. The samples that were immediately refrigerated until being taken to the lab for digestion resulted in lower COD concentrations for the HR Lab COD and LR Lab COD vials. This is due to the same reasons cited above for the one day HRT COD. The HR Lab COD and LR Lab COD values should represent most accurate results for the two day HRT aerobic lagoon.

4 day HRT COD. The average COD results for the four day HRT aerobic lagoon were 97, 73, 97, and 47 mg/L for HR COD, HR Lab COD, LR COD, and LR Lab COD vials, respectively. The samples that were immediately refrigerated until being taken to the lab for digestion resulted in lower COD concentrations for the HR Lab COD and LR Lab COD vials. This is due to the same reasons cited above for the one day HRT COD. The HR Lab COD and LR Lab COD values should be considered the most representative results for the four day HRT aerobic lagoon.

8 day HRT COD. The average COD results for the eight day HRT aerobic lagoon were 61 and 45 mg/L for the HR Lab COD and LR Lab COD vials, respectively. All samples were immediately refrigerated until they were taken to the lab for digestion. Both the HR Lab COD and LR Lab COD values should be considered accurate results for the eight day HRT aerobic lagoon.

Energy Labs Analytical Results

As previously mentioned, the final sample collected from each aerobic lagoon test unit was split and sent to Energy Labs for analytical testing, as well as used to digest for COD analysis in the testing lab as had been done throughout the testing program. The final Energy Labs analytical data is presented in Table 5.

The Energy Labs analytical data suggest that a majority of the BOD and COD is removed in the first day of aeration (approximately 70% of the BOD and approximately 57% of the COD). Because a one day HRT is too short for good development of active biomass, any BOD or COD that is being removed from the BCR effluent in the first 24 hours is not a result of biological degradation, but rather the result of off-gassing of volatile materials. This is not surprising as there is 66 mg/L of sulfide in the raw BCR effluent water, as well as other volatile compounds such as NH_3.

Table 5. Final Analytical Results from Montana Site Aerobic Digester Lab Test

Sample ID	Parameter							
	BOD	COD	Sulfide	Arsenic	Iron	Mang.	Selenium	Thallium
	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L
BCR Eff.	165	188	66	101	170	500	1	***< 2***
1 day HRT	47	80	0.05	81	***< 5***	250	1	***< 2***
2 day HRT	4	43	***< 1***	95	***< 30***	140	< 1	***< 2***
4 day HRT	< 6	39	***< 1***	92	30	90	1	***< 2***
8 day HRT	< 6	39	0.05	82	***< 70***	30	1	***< 2***

Blue Italics = Below Detection Limit

This conclusion is supported by the results from oxidation testing performed in May of 2008. In these results, the BOD decreased from 201 mg/L to 93 mg/L after just four hours of aeration using an aquarium pump with a diffuser stone. In a different portion of that same test, the BOD dropped from 201 mg/L to almost 100 mg/L in two separate cells that were aerated for just under 24 hours. Neither of these experiments cultured an activated sludge seed prior to testing.

These two instances, corroborated by the data provided in this lab test, suggest that a majority of the BOD and COD present in BCR effluent is present as volatile compounds that are essentially air stripped and off-gassed within the first 24 hours of aeration. While biological degradation can occur in the first 24 hours of aeration, it is minimal compared to what was seen during this test. This is a favorable condition as it influences the full-scale design of an aerobic lagoon for the Montana demonstration-scale PTS because the removal of volatile compounds is only slightly affected by decreasing temperature. This suggests that a majority of the BOD and COD will not need to depend on solely on biological degradation and should be removed via off-gassing in the first 24 hours of aeration.

In addition to BOD and COD, sulfide also appears to be completely removed in the first 24 hours of aeration. It is suspected that the conditions described in the previous paragraph are responsible. That is, it appears that the sulfide is being off-gassed upon its exposure to aeration.

Some of the sulfide may also be precipitating as white colloidal native sulfur; this was not confirmed by testing.

Arsenic was not effectively removed in any of the aerobic lagoons during lab testing. The influent concentration of 101 µg/L was only reduced by 6-20%. A variety of conditions could be responsible for the poor As removal as discussed by Bednar, et al. (2001). One that may be particularly relevant to the Montana site may be the low iron levels present in the BCR effluent. Langmuir, et al. (1999) suggests that approximately five times as much Fe should be present in water compared to As to effectively co-precipitate the As as an arsenic-iron hydroxide. The Fe level present in the BCR effluent water was only approximately 1.7 times that of As. It is expected that the As would be removed in an aerobic lagoon if iron levels were in excess of five times those of As.

Manganese removal increased as the HRT of the aerobic lagoons increased. The Mn level decreased from 0.5 mg/L to 0.03 mg/L in the eight day HRT aerobic lagoon. Selenium and Tl levels were unaffected throughout the aerobic lagoon lab test. Throughout the testing program, Se remained at or less than 1 µg/L and Tl was below the detection limit (2 µg/L) in all of the aerobic lagoons.

Aerobic Lagoon Lab Test Conclusions

The field and analytical data from the aerobic lagoon lab test, presented above, provide sufficient data to estimate the appropriate size of a full scale aerobic lagoon at the confidential Montana mine site. At the temperatures present during lab testing, which average approximately 20 °C, a two day HRT aerobic lagoon would likely reduce BOD to levels that the APC could handle. The biological processes that degrade the BOD, however, are very susceptible to slower kinetics in colder temperatures. For this reason, even though a majority of the BOD present in BCR effluent appears to be volatile and off-gassed within 24 hours, the HRT of the full scale aerobic lagoon should be significantly longer than two days to effectively remove the BOD and provide a conservative design.

Before, during, and upon completion of the aerobic lagoon lab testing, research was carried out regarding aerobic lagoon design (Tchobanoglous, 2003, Crites, 2006, Middlebrooks, 2009). This research, in addition to the results provided from the aerobic lagoon lab test, have resulted in sizing the full scale aerobic lagoon with an HRT of 5.0 days. The size of this lagoon is based on the reaction rate constant (k) calculated from the various HRT aerobic lagoons in the lab test (k = 5.64/day). The reaction rate constant was then adjusted for winter conditions in equation 1:

$$k_T = k \times \theta^{(T_w - 20)} \qquad (1)$$

Where k_T = temperature adjusted reaction rate coefficient,
k = reaction rate coefficient at 20 °C,
θ = temperature coefficient, and T_w = temperature of the pond water.

For this application, $k = 5.64$, $\theta = 1.06$ (which is conservative as per Crites et al. 2006), and $T_w = 0.5$ degrees Celsius. This results in a $k_T \approx 1.81$. Next, the k_T is input into equation 2 to calculate the effluent BOD of the aerobic lagoon:

$$C_e = \frac{C_o}{(1 + k_T \times t)} \qquad (2)$$

Where Ce = effluent BOD,
Co = influent BOD,
k_T = temperature adjusted reaction rate coefficient, and
t = HRT of the aerobic lagoon.

After rearranging the equation to solve for HRT, a solution can be determined. Because of the volatile fraction of BOD in the BCR effluent, the following values were used: $Co = 50$ mg/L, $Ce = 5$ mg/L, and $k_T = 1.81$. This results in a $t \approx 5$ days.

Therefore, a HRT of five days was recommended for installation at the central Montana demonstration-scale passive treatment system. This aerobic lagoon should be situated at a hydraulic gradient such that the BCR effluent can flow via gravity to the influent of the aerobic lagoon and then on to the APC via gravity flow, should there be enough of a hydraulic gradient to allow it. Because the aerobic lagoon is operated as a completely mixed system, the aerobic lagoon effluent must transverse a settling pond where the solids will settle out of solution, before clarified effluent can report to the APC. This settling pond was designed for no less than a 48 hour HRT, to ensure maximum time for solids settling and clarification.

Conclusions

In summary, while passive treatment systems have proven to be effective at addressing many target contaminants, including heavy metals that are otherwise difficult to remove, many of these systems create nuisance parameters that must be removed prior to discharge to a surface water or municipal treatment plant. For biotic anaerobic passive treatment systems, such as the BCR, such nuisance parameters may include, but are not limited to: elevated levels of NH_3, BOD/COD, H_2S, and total organic carbon. These nuisance parameters may persist in the system effluent for a short time or they may be present on a long term basis. If they are present long term, they must be treated in one way or another prior to discharge. Options for treating nuisance parameters include constructed wetlands, APC, aerobic lagoons, aerobic digesters, and settling ponds.

Each biotic anaerobic passive treatment system produces a unique effluent that must be characterized to determine the best way to deal with the nuisance parameters present. Oftentimes anaerobic biotic reactors such as the BCR discussed in this paper are followed by aerobic unit processes. Based on the results seen at this site, it may be necessary to size these aerobic unit processes for the removal of nuisance constituents in addition to, or in lieu of, traditional constituents such as Fe and Mn.

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