# DESIGNING A BIOCHEMICAL REACTOR FOR SELENIUM AND THALLIUM REMOVAL, FROM BENCH SCALE TESTING THROUGH PILOT CONSTRUCTION<sup>1</sup>

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<u>Abstract:</u> Water treatment is often required at active and inactive mine sites to remove heavy metals and other contaminants of concern (COCs) prior to discharging water. Traditional water treatment can be expensive and impractical at some sites due to excessive energy, manual labor, and operations and maintenance (O&M) requirements. Passive treatment has emerged as a way to treat such waters inexpensively by requiring minimal amounts of O&M and little to no external energy. One form of passive treatment technology that has been developed over the last twenty years is the biochemical reactor (BCR), also known as a sulfate reducing bioreactor (SRBR). As its name would suggest, a BCR treats water by way of biological and chemical reactions. A BCR uses a combination of organic substrate materials and microbial activity to remove heavy metals, remove other COCs, and stabilize pH in mining influenced water (MIW). Additionally, a BCR adds hardness, alkalinity, and organic matter to the MIW, all of which are beneficial to overall water quality and aquatic life.

A historic gold mine in Montana is using passive treatment in the form of a BCR to remove selenium (Se), thallium (Tl), and nitrate  $(NO_3^{-1})$  from its MIW. Selenium is a metal common to MIW and can be difficult to remove with traditional technologies, while Tl is a metal of which very little is known, but has extremely low discharge standards throughout the United States. The first step in this process was designing and conducting a three-month bench-scale test using a variety of different organic substrate mixtures. After steady state conditions were reached in the BCR, benchscale testing demonstrated  $\geq$  99% removal of Tl and Se as well as for traditional heavy metals (Zn, Cu, Fe, etc.). Average influent Tl concentrations of 1.40 mg/L were removed to an average concentration of 0.008 mg/L; concurrently, average influent Se concentrations of 0.011 mg/L were removed to below the detection limit Using the bench-scale testing results; design began on a at 0.0025 mg/L. demonstration-scale passive treatment system which is half of the size of a full-scale system. Design and construction of the demonstration-scale passive treatment system was performed so that scaling up to a full-scale system will be easy in the future.

Additional Key Words: biochemical reactors, passive treatment, heavy metals, mining influenced water, design and construction

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#### **Introduction**

Active and inactive mine sites are often required to perform water treatment to remove heavy metals and other contaminants of concern (COCs) prior to discharging water. Traditional water treatment can be expensive and impractical at some sites due to excessive energy, manual labor, and operations and maintenance (O&M) requirements. Passive treatment of such waters has emerged as a way to treat such waters inexpensively by requiring minimal amounts of O&M and little to no external energy. One form of passive treatment technology that has been developed over the last twenty years is the biochemical reactor (BCR), also known as a sulfate reducing bioreactor (SRBR). As its name would suggest, a BCR treats water by way of biological and chemical reactions. A BCR uses a combination of organic substrate materials and microbial activity to remove heavy metals, other COCs, and stabilize pH in mining influenced water (MIW). Additionally, a BCR adds hardness, alkalinity, and organic matter to the MIW, all of which are beneficial to overall water quality and aquatic life.

A historic gold mine in Montana is using passive treatment in the form of a BCR to remove thallium (Tl), selenium (Se), and nitrate (NO<sub>3</sub><sup>-</sup>) from its MIW. In the reducing state of the BCR, sulfide is produced via sulfate (SO<sub>4</sub><sup>2-</sup>) reduction and it is believed that selenium and thallium will precipitate out as insoluble metal sulfides (SeS<sub>2</sub> and TlS, Tl<sub>2</sub>S, and Tl<sub>2</sub>S<sub>2</sub>). Because little is known regarding the treatment and preferential removal of Tl, a three month bench-scale test using a variety of different organic substrate mixtures was conducted to determine how Tl would best be removed in a BCR. After steady state conditions were reached in the BCR, bench-scale testing demonstrated  $\geq$  99% removal of Tl and Se as well as for traditional heavy metals (Zn, Cu, Fe, etc.). Using the bench-scale testing results; design began on a demonstration-scale passive treatment system (PTS) which is half of the size of a full-scale system. Design and construction of the demonstration-scale passive treatment system.

This paper discusses the results of the bench-scale testing, pilot-scale construction, and considerations for future BCR PTS design and construction.

#### **BCR Bench-Scale System**

## **Bench-Scale Construction**

A BCR system was constructed for bench-scale testing by Golder Associates Inc. (GAI) on August 3<sup>rd</sup>, 2006. The bench-scale test consisted of four nitrate-reducing BCR cells to treat residual drainage from a gold (Au) heap-leach pad. Each of the four BCR cells contained a unique mixture of organic and inorganic materials. The mixtures, hereafter referred to as substrate, were placed in four 200-liter (55-gallon) drums and labeled: BCR Cell 1, BCR Cell 2, BCR Cell 3, and BCR Cell 4. The purpose of the bench-scale test is to determine the most effective BCR substrate mixture for removal of the COCs in the heap leach pad water. If successful, the process would be applied at other MIW sources at the mine with similar COC issues.

A "baseline" substrate mixture was placed in BCR Cell 1. This mixture has a long record of success in other studies of similar scope. However, due to the relatively narrow range of COCs in the source water (i.e.,  $NO_3^-$ , Tl, and Se with little if any Fe, Zn, or Mn), the authors hypothesized that the substrate required a source of sacrificial metal to prolong substrate effectiveness, especially with respect to Tl removal. That is, the naturally inherent mass of metals contained in the baseline substrate would be completely consumed prior to consumption of the organic fraction. The organic fraction has typically been found to be the limiting factor in estimating substrate longevity.

Three sacrificial media sources were evaluated; two sources (zero valent iron [ZVI] and magnetite  $[Fe_3O_4]$ ) provided a source of sacrificial iron; a single manganese source (MnO<sub>2</sub>) was evaluated. Slightly varying amounts of the different sacrificial media were mixed into the substrates. BCR Cell 2 received ZVI; BCR Cell 3 received magnetite sand; and BCR Cell 4 received MnO<sub>2</sub>. The substrate mixtures are shown on Table 1. A schematic drawing of all four BCR Cells is shown as Fig. 1.

Material	Cell 1	Cell 2	Cell 3	Cell 4
Pyrolox (MnO <sub>2</sub> )	0%	0%	0%	3.3%
Wood Chips	50%	48%	46%	46.7%
Limestone	30%	30%	30%	30%
Zero Valent Iron	0%	2%	0%	0%
Hay	10%	10%	10%	10%
Magnetite Sand	0%	0%	4%	0%
Animal Manure	10%	10%	10%	10%
Total	100%	100%	100%	100%
Logic	Baseline no sacrificial media	ZVI	Magnetite	MnO <sub>2</sub>

Table 1. Cell mixtures on an as-received by weight basis.



Figure 1. Bench-Scale Test BCR Cell Schematic.

## Bench-Scale BCR Sampling and Analysis

System influent (BCR INF) and effluent (BCR Cell 1 EFF, BCR Cell 2 EFF, BCR Cell 3 EFF, and BCR Cell 4 EFF) samples were collected every week by mine site personnel and sent to Energy Laboratories, Inc. in Billings, MT for metals (Tl, Se, Zn, Fe, Mn, Ca, and Mg), anions  $(NO_3^{-7}, SO_4^{-2^{-7}}, and alkalinity)$ , sulfide, biochemical oxygen demand, and fecal coliform analysis. Field parameters (pH, oxidation-reduction potential, conductivity, temperature, odor, and color) were also measured on a weekly basis as per instructions in the sampling and analysis plan (SAP) submitted to the mine site personnel prior to start-up of the bench study. A three-week

incubation period followed the construction of the BCR cells to allow the bacterial suite to adjust to the unique chemistry at the site. This paper includes field parameters and analytical results from samples collected from 8/22/2006 to 11/07/2006. Sampling dates are shown on Table 2.

Week	Date (of week)	Influent (BCR INF)							Cells 1,2,3,4 BCR Effluent (BCR EFF1, BCR EFF2, BCR EFF3, BCR EFF4)						
		$\mathbf{F}^1$	$SML^2$	LML <sup>3</sup>	$A^4$	$S^5$	$BOD^6$	$FC^7$	F	SML	LML	А	S	BOD	FC
1	08/22/06	Х	-	-	-	-	-	-	Х	-	-	-	-	-	-
2	08/29/06	Х	Х	-	Х	Х	-	-	Х	Х	-	Х	Х	Х	-
3	09/05/06	Х	Х	-	Х	-	-	-	Х	Х	-	Х	-	Х	-
4	09/12/06	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х	Х
5	09/19/06	Х	Х	-	Х	-	-	-	Х	Х	-	Х	-	Х	-
6	09/26/06	Х	Х	-	Х	Х	-	-	Х	Х	-	Х	Х	Х	Х
7	10/03/06	Х	Х	-	Х	-	-	-	Х	Х	-	Х	-	Х	-
8	10/10/06	Х	Х	Х	Х	Х	-	-	Х	Х	Х	Х	Х	Х	Х
9	10/17/06	Х	Х	-	Х	-	-	-	Х	Х	-	Х	-	Х	-
10	10/24/06	Х	Х	-	Х	Х	-	-	Х	Х	-	Х	Х	-	Х
11	10/31/06	Х	Х	-	Х	-	-	-	Х	Х	-	Х	-	-	-
12	11/07/06	Х	Х	Х	Х	Х	-	-	Х	Х	Х	Х	Х	-	Х

 Table 2.
 Bench-scale test sample collection schedule

Notes:

<sup>1</sup> (F) Field Parameters (pH, oxidation-reduction potential, conductivity, temperature, odor, color)

<sup>2</sup> (SML) Short Metals List (Ca, Fe, Mg, Mn, Se, Tl, Zn)

<sup>3</sup> (LML) Long Metals List (31 element ICP-AES analysis at the Colorado School of Mines)

<sup>4</sup> (A) Anions (alkalinity, sulfate, nitrate)

<sup>5</sup> (S) Sulfide

<sup>6</sup> (BOD) Biological Oxygen Demand, until concentrations lower (<5 mg/L)

<sup>7</sup> (FC) Fecal coliforms

#### Bench-Scale Results

During the course of bench testing, the heap leach pad effluent water typically exhibited a pH of about 7.7 and a consistently positive oxidation-reduction potential (ORP). The influent MIW had average concentrations of:

•	$NO_3$ as N - 9.6 mg/L,	• Se	-	0.010 mg/L,

• Tl - 1.28 mg/L, • Zn - 0.085 mg/L.

During the first one to two pore volumes of water treated, a "flushing-maturation" condition was observed in which heavy metal removal was poor. After the cell's microbiological community matured and the labile organics and TSS were flushed out of the system, each of the four BCR cells performed well in reducing nitrate to a level equal to or less than 1.0 mg/L NO<sub>3</sub><sup>-</sup> as N; this performance level was typically maintained throughout the balance of the test. More importantly, approximately 99% of the Tl and Se were typically removed over the final month of the test; i.e., Tl and Se were both removed to levels at or below the detection limit of 0.005 mg/L. More complete bench-scale testing results are displayed in Table 2. It is important to recognize that only about three pore volumes were sent through the bench-scale BCR cells before the end of testing; past experience with BCR systems indicate that if the test had been run longer, metals removal would have increased and effluent water quality would have improved further. It is important to note that these results do not reflect the beneficial effects of secondary treatment, such as an aerobic polishing cell (APC), which is typically added on the end of a BCR for BOD, Fe, and Mn removal.

<u>Field Parameters</u>. As reported in Table 2, pH, flow rate, oxidation-reduction potential, temperature, and electric conductivity were monitored throughout bench-scale BCR testing. Details of each of the field parameters are discussed below.

<u>pH</u> – The influent pH values were relatively constant, ranging from 7.2 to 8.3. Effluent pH values from BCR Cells 1, 3, and 4 ranged from 5.2 to 5.4 during the first seven weeks of operation, while the effluent pH values from BCR Cell 2 ranged from 5.8 to 6.0 during the same period. While the pH values decreased, they did not appear to decrease to levels at which the microbial consortium present in the BCR cell substrate would be adversely affected. The depressed pH values were likely due to the formation of organic acids in the organic matter of the substrate; this effect was countered by the commonly-included limestone component of the substrate mixtures. After Week 7 (10/3/2006), the flow rate was increased to 5.0 L/day, and the effluent pH values from all four cells increased until the end of the bench study at Week 12 (11/7/2006). Observed pH values at the end of the study were 6.3 for BCR Cell 1; 6.8 for BCR Cell 2; 6.1 for BCR Cell 3; and 6.1 for BCR Cell 4.

		INF		BCR EFF1		BCR EFF2		BCR EFF3			BCR EFF4					
Parameter	Units	Ave.	First 8 Weeks	Final Month	Ave.	First 8 Weeks	Final Month	Ave.	First 8 Weeks	Final Month	Ave.	First 8 Weeks	Final Month	Ave.	First 8 Weeks	Final Month
рН		7.7	7.8	7.5	5.6	5.3	6.2	6.2	5.9	6.6	5.6	5.3	6.0	5.5	5.3	5.9
Conductivity	(mS/cm)	4.1	5.0	2.9	7.8	10.5	3.7	9.4	12.6	4.7	8.5	11.2	4.4	7.8	10.4	4.5
Temp	°C	12.8	13.5	11.7	13.8	16.0	10.1	13.4	15.5	9.6	14.0	16.1	10.2	14.5	16.6	9.7
Oxidation- reduction potential	millivolt	75	98	35	23	55	-34	-76	-81	-69	38	48	19	39	45	29
Flow	L/day	4.25	2.92	6.25	4.09	2.86	6.25	4.09	2.86	6.25	4.09	2.86	6.25	4.09	2.86	6.25
Nitrate, N-NO <sub>3</sub>	mg/l	9.6	9.7	9.3	0.8	0.6	1.0	0.7	0.5	1.0	0.6	0.6	0.7	0.7	0.6	0.7
Selenium, Se	mg/l	0.0095	0.0080	0.0120	0.0057	0.0076	0.0025	0.0040	0.0049	0.0025	0.0053	0.0069	0.0025	0.0060	0.0080	0.0025
Thallium, Tl	mg/l	1.28	1.22	1.38	0.0299	0.044	0.005	0.028	0.043	0.003	0.031	0.045	0.008	0.034	0.045	0.014
Zinc, Zn	mg/l	0.085	0.064	0.121	0.379	0.551	0.076	0.064	0.094	0.010	0.465	0.664	0.118	0.468	0.650	0.150
Calcium, Ca	mg/l	391	381	409	1,338	1,739	636	1,012	1,360	404	1,357	1,763	647	1,308	1,668	678
Iron, Fe	mg/l	0.0	0.0	0.0	30.8	41.1	12.8	1,885	2,581	667	57.9	75.8	26.5	27.5	33.3	17.2
Magnesium, Mg	mg/l	146	141	156	221	263	148	213	266	120	207	253	128	225	266	154
Manganese, Mn	mg/l	0.007	0.006	0.009	18.1	25.7	4.8	35.5	51.1	8.2	19.7	28.0	5.2	108.9	124.5	81.8
BOD	mg/l	3	3	3	8,244	11,400	1,933	9,870	13,000	2,567	9,620	12,714	2,400	9,060	11,743	2,800
Fecal coliform	counts / 100 mL	1	1	1	310.0	N/A	310	80.0	N/A	80	34.8	25.3	49.0	549.6	282.7	950.0
Alkalinity, as CaCO <sub>3</sub>	mg/L	286	296	268	3,020	4,150	1,043	5,143	6,714	2,393	3,228	4,299	1,353	3,139	4,104	1,449
Sulfate	mg/l	1,343	1,280	1,453	837	679	1,114	217	169	301	693	600	856	698	595	878
Sulfide	mg/l	0.6	0.6	0.5	5.2	7.0	0.8	10.2	13.0	3.3	4.4	6.0	0.5	3.5	4.4	1.3

Table 3. Influent and effluent for BCR cells 1, 2, 3, and 4 average, early results, and final month

Notes: N/A – not applicable

<u>Flow Rate</u> – After nominally three weeks of incubation, the design flow rate of 2.5 L/day was delivered to each cell. This flow was derived from the nitrate and heavy metals loading rate expected based on historic heap leach pad seep (BCR INF) water chemistry. Accounting for substrate porosity, this initial flow rate was equivalent to a 49-day hydraulic residence time (HRT) in the 55-gallon drums. This initial flow rate and retention time was determined assuming a molar  $NO_3^-$  loading rate of 0.03 moles of  $NO_3^-$  per day per cubic meter of substrate. This value had been observed in tests of similar MIW at different sites.

The incubation time of three weeks was significantly longer than the one week that the authors typically observed prior to cell commissioning. An initial incubation period of two weeks was conservatively recommended to allow the bacterial suite to adjust to the unique chemistry at this site but was extended a week due to administrative issues associated with laboratory schedules and finalizing sampling plans.

After the Week 7 sampling on 10/3/2006, flow through the cells was increased to 5.0 L/day because all four of the cells were removing NO<sub>3</sub><sup>-</sup> to levels below the detection limit of 1.0 mg/L NO<sub>3</sub><sup>-</sup> - N. At a flow of 5.0 liters per day, the HRT in the 55-gallon drums was approximately 24.5 days. After three weeks of sampling when the flow rate was 5.0 L/day, influent NO<sub>3</sub><sup>-</sup> was still being reduced to non-detect levels (<1.0 mg/L as N). Because of this, flow was increased again to a rate of 7.5 liters per day during Week 10 (10/25/2006) which resulted in a corresponding HRT of approximately 16.3 days. This rate was maintained through the remaining two weeks of the test.

In mid-November, the mine site personnel reported that the flow to the cells was suspended because of sub-freezing conditions within the test building due to an especially frigid arctic cold front that engulfed the site.

<u>Oxidation-Reduction Potential (ORP) and Average Effluent Temperature</u> – Negative ORP values are indicative of anaerobic-reducing conditions. These are conducive to robust sulfate- and nitrate-reducing bacteria health. Effluent ORP values for BCR Cells 1, 3, and 4 were slightly above or slightly below zero but usually less than influent ORP values and close to zero. Effluent ORP values for BCR Cell 2, on the other hand, were always well below zero throughout the bench test. It was encouraging that ORP values did not increase, but actually decreased, after the flow was increased to 5.0 and then 7.5 L/day. This is a sign that microbial populations in the cells responded positively to increased flow rates during the last four weeks of the test.

The average influent water temperature was 14.1°C, although that varied significantly from a high of 27.5 °C at the beginning of the test to a low of 5.6 °C during a cold spell in Weeks 8 and 9 (10/10/2006 and 10/17/2006). The influent temperature never varied substantially from the effluent temperature of the four BCR cells. Temperature values less than 10° C are sub-optimum for bacterial growth. As a rule of thumb, bacterial population reproduction rates typically double for every 10° C of water temperature increase. The cells were incubated and began operating in late August, when the weather was warm. As the testing progressed, temperatures dropped in the influent and effluent waters, however, the performance of all four cells actually improved during that time. The strong performance of the cells during the cold weather is a good indication that future BCR systems at the site will also likely perform well throughout the year. Improved performance may occur in a pilot scale or full scale system if the system is constructed below ground and is well insulated.

<u>Conductivity</u> – The average influent conductivity was 4.1 milli-Siemens per centimeter (mS/cm). There was a conductivity spike in the influent in Week 4. Average effluent conductivity values ranged from 7.8 mS/cm (BCR Cell 1 and BCR Cell 4) to 9.4 mS/cm (BCR Cell 2). As expected, the effluent water experienced a flushing event at start-up which caused high effluent conductivity values as mobile ions in the substrate were released. Effluent conductivity values gradually decreased until they approached the influent value in Week 11 (10/31/2006). Based on experience with similar BCR systems, effluent conductivity values would have eventually matched influent values had the BCR effluent been sent through an APC for secondary treatment and polishing.

<u>Analytical Parameters</u>. As reported in Table 2, NO<sub>3</sub>, Se, Tl, Zn, Ca, Fe, Mg, Mn, biochemical oxygen demand (BOD), Fecal coliform, alkalinity (as CaCO<sub>3</sub>),  $SO_4^{2^-}$ , and sulfide (S<sup>-</sup>) were monitored throughout bench-scale BCR testing. Details of each of the analytical parameters are discussed below.

<u>Nitrate Concentrations</u> – Nitrate concentrations averaged 10.8 mg/L as  $NO_3^-$  -N in the influent water. Effluent  $NO_3^-$  concentrations for all four BCR cells were routinely observed to be at or below the detection limit of 1.0 mg/L. The only period in which all four cells had measurable  $NO_3^-$  concentrations in their effluent waters was during Weeks 11 and 12. This likely occurred in response to the increased flow rates established after the Week 7 sampling (to 5.0 L/day) and

during Week 10 (to 7.5 L/day). It must be noted that the discharge limit for nitrate at this site is  $< 10 \text{ mg/L NO}_3^-$  -N; the primary reason for monitoring the removal of NO<sub>3</sub><sup>-</sup> is because it must be removed from the influent before SO<sub>4</sub><sup>2-</sup> reduction can commence in the BCR.

<u>Selenium Concentrations</u> – Influent Se concentrations averaged 0.010 mg/L. Prior to increasing the flow to 5.0 L/day on 10/3/2006, Se removal was minimal. A week after increasing the flow rate (10/10/2006) dissolved effluent Se concentrations in all four cells were below the detection limit of 0.005 mg/L through the end of the test.

<u>Thallium Concentrations</u> – The average influent TI concentration was 1.28 mg/L. Thallium was not detected at concentrations above the laboratory reporting limit of 0.10 mg/L in samples collected from BCR cell effluent. In an effort to lower the laboratory reporting limit, samples were filtered with a 0.45  $\mu$ m filter starting in Week 8. The detection limit for dissolved TI was 0.005 mg/L, greatly improving the accuracy and lowering the observed TI concentrations of the effluent waters. The TI level observed in BCR Cell 2 effluent was below the dissolved detection limit of 0.005 mg/L for all samples collected. BCR Cells 1, 3, and 4 typically showed a decreasing TI concentration trend approaching and below the 0.005 mg/L detection limit from Weeks 8 to 12, with the exception of BCR Cell 4 in Week 12 (0.030 mg/L).

The dissolved Tl detection limit used was above the regulatory standard of 0.0017 mg/L. Reasoning for the elevated Tl detection limit was three-fold:

1) This bench-scale study was designed as a proof-of-concept experiment whose main goal was to prove that the BCR cells were capable of removing Tl from the heap leach pad drainage water. This was demonstrated by the observed Tl removal from an average influent concentration of ~1.3 mg/L to an average effluent concentration of 0.005 mg/L (observed at the end of the bench test). The approximate average effluent concentration of 0.005 mg/L is reasonably close to the 0.0017 mg/L regulatory discharge level.

2) The BCR cells investigated during this bench-scale study are intended to operate as one component of a full-scale or pilot-scale system. A pilot-scale treatment system would be (and was) designed to incorporate an aerobic polishing cell (APC) or reactor, which would be installed down-gradient of the BCR. It is anticipated that the APC would provide for the removal of additional TI removal and removal of other metals. Thus, the TI removal observed in the BCR cells in the bench study displays only the first phase of

TI removal in the proposed pilot or full-scale system. The observed BCR average effluent TI concentration of 0.005 mg/L is considered an indicator of acceptable BCR performance.

3) The regulatory TI discharge limit of 0.0017 mg/L is well below the normal ICP-MS detection limit for total TI of 0.10 mg/L. The regulatory level is also below the normal ICP-MS detection limit for dissolved TI of 0.005 mg/L. Specialized analytical protocols and low detection limit analyses would have been required to demonstrate regulatory compliance for TI. The additional cost burden was considered unreasonable for a bench-scale study. Consequently, low-detection TI analyses required to demonstrate regulatory compliance will probably be incorporated into pilot or demonstration study sampling protocols.

Zinc Concentrations – The average influent zinc concentration was 0.11 mg/L. Effluent Zn concentrations for BCR Cells 1, 3, and 4 were substantially higher than influent Zn concentrations for the first eight weeks of the bench study (which is the amount of time it took for one pore volume to pass through the BCR cells). It is suspected that Zn was eluted from the manure that had been mixed into the substrate for bacterial inoculation. When the majority of the manure appeared to be flushed out of the cells and flow was increased, effluent Zn concentrations in BCR Cells 1, 3, and 4 decreased significantly and were lower than influent concentrations from Week 10 (10/24/2006) through the end of the study. Alternatively, any Zn introduced to the system by way of manure may have been precipitated by rising sulfide concentrations as the BCR matured. BCR Cell 2 was effective at removing zinc from the water throughout the entire bench test, probably because ZVI was the sacrificial media. ZVI had been observed to be effective at removing Zn from MIW in BCR units at other sites studied by the authors.

<u>Calcium Concentrations</u> – The average influent calcium concentration was 435 mg/L. Through the first five weeks of the study, the average Ca level in the effluent of BCR Cells 1, 3, and 4 was around 2,000 mg/L, while the Ca level in BCR Cell 2 effluent was around 1,400 mg/L. All the cells appeared to exhibit conditions supporting limestone dissolution. Starting in Week 6, however, the Ca level in all of the cells began to decline rapidly and Ca concentrations were only slightly above the influent Ca concentration by the end of the study. During the final six weeks of the study, the Ca concentration in BCR Cell 2 remained below that of the other three cells, with the exception of Week 8. Limestone dissolution appears to be a brief but necessary phenomenon in startup as it helps to maintain the pH at levels supportive of robust bacterial activity.

<u>Iron Concentrations</u> – The average iron concentration in the influent water was 0.019 mg/L. All of the cells had Fe in the effluent water samples at concentrations above influent concentration samples. BCR Cell 1, which had no sacrificial media present, and BCR Cell 4, which used  $MnO_2$  as the sacrificial media, exhibited effluent iron concentrations of 40-50 mg/L during the first six weeks of the study. BCR Cell 3, which used magnetite sand (Fe<sub>3</sub>O<sub>4</sub>) for a sacrificial media, averaged an effluent iron concentration of 88.2 mg/L during the same period.

It is suspected that the manure component of substrate was the common source of the elevated Fe levels in the cell effluents, as was also hypothesized for the elevated Zn levels. This theory was further supported when Fe levels began to drop as the flow increased and the system was flushed after the first pore volume had passed through the NRBR cells. In Week 12, iron concentrations in BCR Cells 1 and 4 were approximately 10 mg/L and were 20 mg/L in BCR Cell 3. As discussed in the Zn section, any Fe introduced to the system by way of manure may have been precipitated by rising S<sup>-</sup> concentrations as the BCR matured.

BCR Cell 2, which had ZVI as its sacrificial media, had an average effluent Fe concentration of 2,660 mg/L over the first six weeks of the bench test. This is problematic because Fe present in BCR effluent will need to be removed in an aeration channel prior to discharge in a pilot scale or full scale system. Iron concentrations of this magnitude would require a very large aeration channel to remove the Fe to discharge levels. As observed with the other cells, Fe concentrations in BCR Cell 2 decreased as the flow increased and the system was flushed out but remained near 200 mg/L in Week 12.

<u>Magnesium Concentrations</u> – The average influent Mg concentration was 161 mg/L. In concert with Ca concentrations, the effluent Mg concentrations for all cells averaged just over 300 mg/L for the first four weeks of the study and then dropped until they were near the influent concentration in Week 7. The effluent Mg levels remained at or slightly below the influent level for the remainder of the study.

<u>Manganese Concentrations</u> – Influent Mn concentrations averaged 0.007 mg/L and were observed at or above the detection limit of 0.01 mg/L only three times throughout the study. Similar to Fe, all of the cell effluents contained elevated levels of Mn; however, these slowly decreased as the manure organic component was consumed and flow rate increased. The three cells in which sacrificial Mn was absent in the substrate, BCR Cells 1 2, and 3, exhibited effluent average Mn levels of 32.3 mg/L, 46.5 mg/L, and 38.3 mg/L, respectively, over the first four weeks of the study. BCR Cell 4, the cell that received MnO<sub>2</sub> as a sacrificial media, averaged 148 mg/L over the first four weeks. By Week 12, Mn concentrations in BCR Cells 1, 2, and 3 had all decreased to around 4 mg/L, while Mn concentrations in BCR Cell 4 had only decreased to 72.8 mg/L, about an order of magnitude higher.

The goal of intentionally elevating Mn in the BCR effluents is to provide a steady supply of this metal to support an aerobic algae-based eco-community. The biologically-facilitated deposition of  $MnO_2$  in the aeration channel could further sequester Tl that may have evaded removal in the BCR cells. Without sacrificial Mn, however, this treatment process would not be feasible at this mine site; due to the low Mn concentrations in the MIW.

Elevated manganese concentrations in the initial samples may influence system startup protocols. If the  $MnO_2$  sacrificial media were used in a larger-scale system, a recycling or polishing treatment of the BCR effluent water during start-up (perhaps for two or more pore volumes) would be necessary. After the initial treatment, however, both Mn and Fe levels may be low enough to allow BCR effluent water to flow into the aeration channels for algae-facilitated polishing prior to discharge.

<u>Biochemical Oxygen Demand (BOD) Concentrations</u> – When measured in Week 4, the influent BOD concentration was 4.0 mg/L. Through Week 6, all of the cell effluents had elevated levels of BOD ranging from a low of 11,000 mg/L to a high of 19,000 mg/L. It is suspected that these elevated BOD levels were a combined result of the organic material used to form the substrate (manure, hay, and wood chips), the prolonged incubation time, and the long HRT of 49 days. The long contact time with organic substrate of about 60 days, including incubation, resulted in unusually high BOD levels during this part of the test. As the manure component decomposed and the flow rates were increased, the effluent BOD began decreasing in Week 7 and it continued to decline throughout the remainder of the study. In Week 12, all four of the observed BOD concentrations were between 1,000 mg/L and 1,300 mg/L. BOD levels are expected to be reduced to levels far below 1,000 mg/L in a pilot or full scale system when there is an appropriately sized APC to treat the BCR effluent water.

The high levels of BOD in the initial pore volume (through Week 8) of MIW through the BCR cells is another indication that the BCR effluent water should be recycled or treated during the start-up of a pilot or full scale system.

<u>Fecal coliform Concentrations</u> – There were no fecal coliform counts in the influent sample collected on Week 4. All of the fecal coliform counts conducted on BCR Cell 3 effluent were below 63 counts/100 mL. The first two fecal coliform counts conducted on BCR Cell 4 water were below 71 counts/100 mL, while the next count increased to 720 counts/100 mL. After declining to 400 counts/100 mL in Week 10, the fecal count increased to 1,500 in Week 12. Increases in fecal coliform concentration correspond to an increase in flow rate. It is likely that increased flow rates increased linear fluid velocity through the cell, which would purge manure particulates and increase fecal coliform counts.

As mentioned earlier in the report, the flow was doubled at the end of Week 7 sampling. This increase in flow appeared to cause a direct increase in fecal coliform counts in Week 8 samples. The fecal coliform count level was decreasing until the flow was increased again during Week 10; this again seemed to result in an increase in fecal coliform count as observed in Week 12, resulting in the highest fecal coliform counts observed during the test. If a pilot or full scale system were allowed to run at a constant flow rate and reach steady state conditions, the fecal coliform counts would be expected to decrease to levels seen through Week 6 of the study and remain below 100 counts/100 mL. These levels would likely decrease further in a commissioned aerobic polishing cell located downstream from the BCR.

<u>Alkalinity Concentrations</u> – The average influent alkalinity concentration was 286 mg/L, while average effluent alkalinity concentrations from BCR Cell 3 were 3,228 mg/L. BCR Cell 3 effluent alkalinity concentrations during the first eight weeks of the bench testing were 4,299 mg/L, and declined to 1,353 mg/L in the final month. This indicates that the alkalinity being added to the BCR effluent was proportional to the flow through the cell; the increased flow in the final weeks of testing resulted in a lower alkalinity concentration.

<u>Sulfate Concentrations</u> – The average influent  $SO_4^{2-}$  concentration was 1,475 mg/L. The average effluent  $SO_4^{2-}$  concentrations from BCR Cells 1, 2, 3 and 4 were 840 mg/L, 220 mg/L, 700 mg/L

and 700 mg/L, respectively. Effluent  $SO_4^{2^2}$  concentrations began increasing in Week 10 samples, which may have been in response to increasing the flow rate or to decreasing ambient temperatures (decreasing microbial processes). The decline of  $SO_4^{2^2}$  reduction did not appear to affect the observed Tl or Se removal rates of the cells. This observed decline in  $SO_4^{2^2}$  reduction is not a concern for the bench study because  $SO_4^{2^2}$  was not identified as a parameter of concern that needed to be removed from the MIW. Monitoring  $SO_4^{2^2}$  reduction is a way of determining whether the BCR cells have the appropriate chemistry to remove metals from the influent MIW via metal S<sup>-</sup> precipitation. Since the MIW has limited metals present, the BCR cells should be capable of removing influent target metals concentrations to regulatory levels, as long as  $SO_4^{2^2}$  reduction and other biochemical reactions occur, even at modest kinetic rates.

<u>Sulfide Concentrations</u> – The detection limit of S<sup>-</sup> was 1.0 mg/L throughout the test; S<sup>-</sup> was not detected in samples collected from the influent water. BCR cell effluent samples exhibited S<sup>-</sup> concentrations ranging from 6 to 13 mg/L in the first six weeks of the study; they gradually decreased from Weeks 6 through 12. In Week 12, S<sup>-</sup> concentrations were below the detection limit of 1.0 mg/L for all of the four effluent samples. This may suggest that to the degree that S<sup>-</sup> was being generated microbially in concert with s SO<sub>4</sub><sup>2-</sup> concentration reductions was being sequestered by complexing with the sacrificial metals and/or TI.

#### Bench-Scale Substrate Longevity Analysis.

Longevity calculations for organic substrate, limestone, and sacrificial media were performed to estimate the designed operational lifespan of the bench cells and/or a full scale system with the same substrate and loading rates.

<u>Carbon Longevity</u> – The authors estimate organic substrate longevity based on the amount of carbon required to support the  $SO_4^{2^-}$  reduction occurring in the bench cells. Loss on ignition and moisture values were assumed for the wood chips, hay, and manure used in the substrate mixture to estimate the carbon (C) content of each BCR cell, based on experience with similar projects. The loss on ignition value is the sum of cellulose and lignin in the organic fraction of the substrate. Cellulose is much more bio-available than lignin. Wood fiber is typically 15% to 25% lignin. The C longevity analysis assumes that lignin is eventually consumed. Actual values may be slightly lower than those calculated if portions of the lignin are not fully bio-degraded and leave the system as organic acids.

The bacteria-mediated reduction of  $SO_4^{2-}$  to S<sup>-</sup> requires two moles of C for every mole of  $SO_4^{2-}$  or 24 grams of C for every 96 grams of  $SO_4^{2-}$ . Using the maximum sulfate reduction rate seen in the bench BCRs, the authors calculated the lifetime of the BCR cell based on the available C and the C consumption rate to sustain this maximum  $SO_4^{2-}$  reduction rate. Nitrate was not included in these calculations because C consumption was being driven by  $SO_4^{2-}$  reduction for this site. Far more  $SO_4^{2-}$  reduction than  $NO_3^{-}$  reduction occurred in these cells. The carbon-controlled substrate longevity estimates for each cell are:

- BCR Cell 1 40.2 years
- BCR Cell 2 18.6 years
- BCR Cell 3 30.1 years
- BCR Cell 4 30.3 years

The C longevity analysis shows that in BCR Cells 1, 3, and 4, there is excess C available to provide food for the bacteria in the BCR cells for a 20-year system life. BCR Cell 2 falls just short of the 20-year C longevity at 18.6 years. All cells appear to have sufficient C for a 20-year life of a BCR system with the exception of BCR Cell 2, which would need slightly more C.

<u>Limestone Longevity</u> - The longevity of limestone in the cells is calculated based on influent and effluent Ca concentrations. Limestone longevity can be calculated in two ways: minimum longevity based on averaging Ca dissolution rates during startup, and maximum longevity based on Ca dissolution rates observed at the end of the bench study.

Calcium dissolution rates from Weeks 2 through 12 were averaged to determine an average daily limestone dissolution rate (grams per day). Alterations in flow rate were taken into account to ensure accurate grams per day dissolution rates were used (converted from moles per liter). Dividing the limestone content of each cell by dissolution rate yields a limestone longevity estimate for each cell. The resulting average limestone longevity for each cell is estimated to be:

- BCR Cell 1 10.4 years
- BCR Cell 2 16.4 years
- BCR Cell 3 8.9 years
- BCR Cell 4 8.5 years

BCR Cell 2 has the greatest limestone longevity estimate; it is also the cell that displayed depressed Ca concentrations during the last three weeks of the study. This is an indication that either calcite or gypsum was precipitating in the BCR. Additional maintenance may be necessary in a pilot or full scale system using the BCR Cell 2 substrate mixture. This is another reason that the authors would eventually like to perform 'autopsies' of the bench cells.

BCR Cells 1, 3, and 4 all have similar limestone longevity estimates between approximately 8.5 and 10.5 years. Typically, BCRs are designed to last at least 20 years. All four BCR cells fall below the 20-year target due to high limestone consumption in the first six weeks of the bench study. If limestone dissolution values were isolated to the final few weeks of the bench study, the resulting maximum limestone longevity estimates would exceed 20 years for all four cells:

- BCR Cell 1 41.3 years
- BCR Cell 2 25.9 years
- BCR Cell 3 26.3 years
- BCR Cell 4 30.2 years

It is believed the limestone longevity estimates based on calcium data collected during the final few weeks of the study more accurately represent limestone dissolution under steady-state conditions in the bench cells. For these reasons, the authors estimate that the current percentage of limestone used in the substrate mixture of future BCR systems at this mine site is sufficient for 20-year limestone longevity. This is consistent with the observation that limestone dissolution appears to be a vital substrate component during startup by providing alkalinity to buffer against acidity generated in organic degradation. Once  $SO_4^{2-}$  reduction biological reaction rates mature and biologically-derived alkalinity is generated, limestone dissolution should be become less important in maintaining pH.

<u>Zero Valent Iron Longevity</u> - The longevity of ZVI in BCR Cell 2 was calculated to be 272 days using the average ZVI displacement rate over the entire bench study and a maximum of 3.0 years using the ZVI displacement rate from Week 12. Longevity of ZVI was determined by subtracting the average of the Fe concentrations measured in BCR Cell 1 and BCR Cell 4 effluent samples (the two BCR cells that did not have Fe as a sacrificial media) from the Fe concentrations in BCR Cell 2 effluent samples. The difference resulted in the amount of ZVI displaced from the substrate mixture in BCR Cell 2. Because of the large dissolution rate of ZVI, the amount of Fe released from BCR Cell 2 was greater than 200 mg/L throughout the study. This amount of Fe would require a very large aeration channel to be removed in a pilot or full scale system. At either the average or the maximum rates of ZVI dissolution, the short longevity of ZVI in BK Cell 2 suggests that ZVI should not be used as a sacrificial media in future pilot or full scale BCR systems at this site.

<u>Magnetite Sand Longevity</u> - The magnetite sand placed in BCR Cell 3 as a sacrificial media displayed the lowest dissolution rate among the sacrificial media used in the bench study. Magnetite sand was estimated to have longevity of 87 years based on the average magnetite sand dissolution rate and 196 years based on the minimum dissolution rate observed at the end of the bench study. Either value exceeds the projected life of the carbon and limestone discussed in the previous sections. It is important to note that, because of the low magnetite sand dissolution rates, a relatively small amount of iron is being released in the effluent waters. This amount could be easily be removed in an appropriately sized APC.

The longevity determination is an estimate because the geochemical fate of the magnetite sand in BCR Cell 3 is uncertain. A portion of the magnetite sand may have been dissolved and re-precipitated as another solid (e.g.- FeS) within the cell. This situation could mask the actual dissolution rates of magnetite sand. Despite this, the authors believe that the ratio of magnetite sand used in the bench study is appropriate for use as a sacrificial media in any future BCR system constructed at this site.

<u>Manganese Dioxide Longevity</u> - Manganese dioxide longevity was determined by subtracting the average Mn concentrations of BCR Cell 1, BCR Cell 2, and BCR Cell 3 (the cells that did not have Mn as a sacrificial media) from the Mn concentration of BCR Cell 4. The resulting value was the concentration of Mn in the effluent thought to have been derived from  $MnO_2$ dissolution. The longevity of  $MnO_2$  in BCR Cell 4 was calculated to be 19.4 years using the average  $MnO_2$  displacement rate over the entire bench study and a maximum of 39.7 years using the  $MnO_2$  displacement rate from the end of the bench study. These longevity rates are reasonable when comparing them to the expected longevity of the C and limestone, but are not as long as those seen in BCR Cell 3 with magnetite sand. It is important to note that the effluent Mn concentration was equal to or greater than 73 mg/L throughout the bench study. To remove that amount of Mn would require a very large APC in a pilot or full scale system. Because of the above, and the fact that  $MnO_2$  is significantly more expensive than magnetite sand, it is not recommended that  $MnO_2$  be used as a sacrificial media in any future BCR systems at this site.

## Bench-Scale Conclusions and Summary

When analyzing results of BCR bench-scale testing, one of the most important parameters to study is that of heavy metal removal efficiency. Because the influent MIW at this particular site is relatively clean as far as heavy metals are concerned, this is a unique site to evaluate how successful BCR cells can be for removing unique heavy metals that are either hard to remove from process water (Se) or metals about which little is currently known (Tl). Consequently, combined Tl and Se removal are discussed below.

<u>Combined Thallium and Selenium Removal</u> – Combining TI and Se removal efficiencies into a single value provides an overall measure of system performance during the bench test. Combined TI and Se removal efficiency was consistently greater than 93% throughout the 12-week study. When dissolved concentrations were analyzed starting in Week 8, the detection limit of TI was reduced from 0.10 mg/L to 0.005 mg/L. Subsequently, the average combined TI and Se removal efficiencies averaged 99%. A week by week plot of combined TI and Se removal is presented in Fig. 2.



Figure 2. Combined thallium and selenium removal during bench-scale testing.

<u>Combined Thallium, Selenium, and Zinc Removal</u> – Zinc was added to combined TI and Se removal efficiency estimate to convey the importance of either recycling or treating the initial pore volume of effluent from a pilot or full scale BCR system. Zinc is believed to have been elutriated from the manure component of the substrate in the bench cells as there was consistently more Zn in the effluent than in the influent, with the exception of BCR Cell 2, which contained ZVI. This situation has a significant impact on Fig. 3, which displays combined TI, Se, and Zn removal efficiencies. With the exception of BCR Cell 2, combined removal of these three metals does not reach 40% until the Week 8 sampling event.

This observation makes sense intuitively because the first pore volume of water exited the cells on approximately day 49 (HRT) which coincided with the Week 8 sampling event (flow was started on Week 1). This initial purging of water with three weeks of incubation contact with manure appeared to directly affect Zn removal efficiency. Based on previous research, increasing incubation time would typically result in better removal efficiency. However, for unknown reasons, it did not in this case as demonstrated by the apparent stripping of Zn from the manure which appeared to cease with the initiation of flow. From Week 8 until the end of the study at Week 12, the second pore volume passed through the BCR cells. During this time, the combined removal rates continued to improve, and all four of the cells had achieved 87% removal or better at the end of the study. Based on previous experience, it is likely that this improvement trend would have continued if the tests had concluded as planned on Week 16 (12/5/2006).



Figure 3. Combined heavy metals (Tl, Se, Zn) removal during bench-scale testing.

## **BCR and APC Demonstration-Scale System**

The positive overall results in the bench-scale phase of testing supported the development of a demonstration-scale system which would become a modular component of a full-scale system. For this site, the demonstration-scale system was designed to handle ½ of the potential maximum drainage from the heap leach pad. If the demonstration-scale results are promising, a second BCR will be added so the system can treat the full flow of MIW at the site.

## **Demonstration-Scale Design**

A substrate mixture was selected based on the bench-scale BCR test results. The bench-scale BCR Cell that was most effective at removing metals was BCR Cell 2, which used ZVI as a sacrificial media. However, the ZVI leached out of the cell at a very high rate, resulting in extremely high Fe concentrations in the effluent that would be difficult to remove in an APC. The short ZVI longevity was also of concern. The next two best performing BCR cells were the base-line recipe with no sacrificial media (BCR Cell 1), and the cell with the magnetite ore as the sacrificial media (BCR Cell 3). As discussed above, because of the concern of low Fe levels in

the influent once the BCR system completely flushed out, the substrate recipe with the magnetite ore sacrificial media was chosen.

Unfortunately, the source of the magnetite ore used in the bench-scale testing was unavailable at the time of material procurement for construction of the demonstration-scale PTS. Because of this, a last second substitution was made to use crushed basalt rather than magnetite ore. Basalt was chosen because of its chemical composition and its availability at the time of construction. The actual substrate recipe used in construction of the demonstration-scale BCR system is displayed in Table 4.

	te for demonstration scale Der eer
Material	Demonstration-Scale BCR Cell
Wood Chips	46%
Limestone	30%
Hay	10%
Crushed Basalt	4%
Animal Manure	10%
Total	100%

Table 4. Cell mixture for demonstration-scale BCR cell

In addition to the change in substrate mixture, an APC was also included in the demonstration-scale BCR PTS design. The APC was added to the BCR PTS to treat and polish the BCR effluent for removal of BOD, Fe, and Mn prior to discharge.

#### **Demonstration-Scale Construction**

As the design phase of the demonstration-scale BCR PTS came to a close, the mine site selected a contractor for construction of the system and began to assemble equipment and order substrate material. Permitting clearance issues delayed earthwork on the PTS until September, 2007. The foundation and compacted fill for the BCR cell were completed by the end of September (Fig. 4), and substrate was mixed and placed in the BCR cell during the first week of October (Fig. 5 and 6). Additional hay was mounded on top of the BCR cell to provide insulation against the cold air and wind in the winter months (Fig. 7). MIW was introduced to the BCR cell in the middle of October and allowed to incubate for approximately three weeks. While the BCR cell was incubating, earthwork and construction of the APC began (Fig. 8). The

BCR incubation was complete and the APC was constructed by early November of 2007 (Fig. 9).



Figure 4. Foundation and compacted fill construction for BCR cell.



Figure 5. Mixing of substrate materials for placement in BCR cell.



Figure 6. Construction of demonstration-scale BCR; placement of mixed substrate.



Figure 7. Additional hay mounded on top of BCR for winter insulation.



Figure 8. APC earthwork and construction activity.



Figure 9. Completed APC, with berms, spillways, and vegetation.

The BCR cell operation commenced in early November, with the effluent bypassing the APC and being sent directly to the mine site's lower pump back station for recirculation. The APC was bypassed until the BCR cell had flushed-matured such that the BOD was reduced to a reasonable level (> 1,000 mg/L). At that point, BCR effluent was diverted to the APC for polishing and secondary treatment for removal of any remaining BOD, iron, and manganese. The demonstration-scale BCR PTS is shown in Fig. 10.

Figure 10 also displays that, in addition to bypassing the APC (APC bypass vault), plumbing was installed to enable untreated MIW to be mixed with the BCR effluent water. Thus, residual treatment characteristics of the BCR effluent might be put to beneficial use. Any amount of raw water bypassing the BCR cell will increase the BCR cell life; this portion of the demonstration-scale BCR PTS is identified as the mixing vault. It is important to note that the mixing vault is an option for this system because the NO<sub>3</sub><sup>-</sup> discharge limit is < 10 mg/L, and so any NO<sub>3</sub><sup>-</sup> present in the water that bypasses the BCR does not need to be removed in the mixing vault. The beneficial treatment in the mixing cell would come from the utilization of any S<sup>-</sup> present in BCR effluent to precipitate Se, Tl, and any Fe or Mn present.

The final component of the demonstration-scale BCR PTS is the aeration cell (Fig. 10). After MIW has been treated by the BCR cell and polished in the APC, it reports to the aeration cell which is a concrete vault (three feet by three feet wide and four feet deep). Here, mechanical aeration can be introduced to the COC-stripped water if it is not adequately oxygenated after passage through the APC.

#### Preliminary Demonstration-Scale Results

Field parameters and flow data were recorded as soon as the BCR cell received MIW on a continuous basis. Analytical samples were also collected beginning in early January 2008. This paper provides the field parameters, flow data, and analytical results through early January 2008. Additional field parameters, flow data, and analytical results will be collected and developed over the coming months and will be discussed in detail during the ASMR presentation in June of 2008.

Field parameters were recorded one to two times per week starting in early November, as soon as flow was discharged from the BCR cell. Over the first two months of operation, a flushing-maturation process was observed similar to the bench performance. Over the first two pore volumes the demonstration-scale BCR cell received, the effluent pH increased while the ORP and electric conductivity dropped. A review of the field parameters from the first two months of BCR cell operation can be found in Table 5.



Figure 10. Process flow diagram of the demonstration-scale BCR passive treatment system.

	рН		Tempe	erature	0	RP	Electric Conductivity		
Date	std.	std. units		Celsius	n	nV	mS/cm		
	BCR	BCR	BCR	BCR	BCR	BCR	BCR	BCR	
	INF	EFF	INF	EFF	INF	EFF	INF	EFF	
11/13/2007	N/A	6.09	N/A	10.8	N/A	-23.0	N/A	7.53	
11/15/2007	7.33	6.48	9.6	10.7	41.0	-29.0	2.89	3.80	
11/29/2007	7.57	6.44	11.9	21.0	38.0	-26.0	2.62	5.52	
12/10/2007	7.68	6.62	9.3	10.7	43.0	-29.0	3.23	3.59	
12/13/2007	7.53	6.37	5.5	9.0	13.0	-38.0	3.11	4.37	
12/20/2007	7.70	6.54	6.0	9.6	22.0	-39.0	2.32	4.35	
12/27/2007	7.77	6.74	5.7	8.6	-19.0	-79.0	3.23	3.79	
1/2/2008	7.93	6.85	6.6	8.9	-14.0	-99.0	2.68	3.13	
1/9/2008	7.70	6.92	6.2	8.3	26.0	-99.0	4.32	3.18	
1/11/2008	7.60	6.79	6.3	8.0	12.0	-108.0	2.64	3.76	

 Table 5. Field parameters from BCR over first two months of operation.

Over the first two months of operation, flow was also monitored into the demonstration-scale BCR cell via a flow totalizer and data are presented in Table 6.

	Flow	Flow	Flow Daried	Flow	Flow
Date	Totalizer	Totalizer	Flow Fellou	Rate	Rate
	gallons	liters	From – To	gpm	Lpm
11/13/2007	81,220	307,418	N/A	N/A	N/A
11/15/2007	96,770	366,274	11/3/2007 - 11/15/2007	5.40	20.4
11/29/2007	158,760	600,907	11/15/2007 - 11/29/2007	3.07	11.6
12/10/2007	186,780	706,962	11/29/2007 - 12/10/2007	1.77	6.7
12/13/2007	193,930	734,025	12/10/2007 - 12/13/2007	1.66	6.3
12/20/2007	205,690	778,537	12/13/2007 - 12/20/2007	1.17	4.4
12/27/2007	217,950	824,941	12/20/2007 - 12/27/2007	1.22	4.6
1/2/2008	227,220	860,028	12/27/2007 - 1/2/2008	1.07	4.1
1/9/2008	267,560	1,012,715	1/2/2008 - 1/9/2008	4.00	15.1
1/11/2008	278,130	1,052,722	1/9/2008 - 1/11/2008	3.67	13.9

Table 6. Flow measurements to BCR cell recorded over first two months of operation

The first analytical samples were collected in the first week of January 2008. The results were received in mid January and provided in Table 7.

			BCR
Parameter	Units	BCR INF	EFF
Ca	mg/L	440	436
Fe	mg/L	0.34	13.4
Mg	mg/L	155	152
Mn	mg/L	0.162	2.97
Se	mg/L	0.009	0.002
Tl	mg/L	1.45	0.002
Zn	mg/L	0.29	0.01
Alkalinity, as			
CaCO <sub>3</sub>	mg/L	344	720
$SO_4^{2-}$	mg/L	1,440	908
BOD	mg/L	5	600
Fecal coliform	counts / 100	13	4,600

Table 7. Analytical results for January 2<sup>nd</sup>, 2008 from Energy Labs for BCR cell.

Note: Italics indicate metal concentrations were below the detection limit.

It is important to note that at the time the samples analyzed by Energy Labs (displayed in Table 7) were collected, almost exactly three pore volumes (75,000 gallons) had been treated by the demonstration-scale BCR cell, which is equal to the number of pore volumes treated by the bench-scale BCR cells during the entire three-month bench-scale test. It seems appropriate to compare the field and analytical data from the January 2<sup>nd</sup>, 2008 sample collection to the field and analytical data from the final bench-scale sample collection on November 7<sup>th</sup>, 2007. While the data is fairly similar between the two sampling events, it differs slightly for the following reasons:

- The sacrificial media used in the bench-scale testing was magnetite ore while the sacrificial media used in the demonstration-scale BCR cell was crushed basalt (this is resulting in higher effluent Mn concentrations that would be seen from magnetite ore),
- the bench-scale system was constructed in early August and fully incubated by early September, while the demonstration-scale system did not begin incubating until the middle of October,

- bench-scale testing was completed by early November, while demonstrationscale testing did not begin until early November and will run through the winter, and
- there is always some uncertainty with scaling a bench-scale test up to a larger BCR system.

Despite the differences outlined above, the demonstration-scale BCR cell perform better than the bench-scale BCR cells at the conclusion of bench testing. This validates the importance of bench-scale testing in predicting the performance of a large BCR PTS and minimizing risk. The bench-scale testing helped in the selection of the best substrate mixture, increased understanding of the amount of MIW that should pass through a BCR cell until the 'flushing-maturation' process begins to subside, and increased understanding of substrate longevity for overall BCR cell life.

## **Conclusions**

During bench-scale testing, demonstration-scale design and construction, and demonstration-scale start-up, many lessons were learned. The following list highlights several of the most important conclusions:

- 1. Bench-scale testing at this site demonstrated that Se, a hard to remove heavy metal, and Tl, a heavy metal about which little is known can be removed in a BCR.
- Bench-scale testing did not definitively determine whether sacrificial media was effective at promoting co-precipitation of heavy metals in a BCR, because all bench-scale BCR cells contained Fe in the effluent.
- Bench-scale testing demonstrated that a BCR cell could effectively remove NO<sub>3</sub><sup>-</sup> at acceptable loading rates.
- 4. Bench-scale testing is an effective tool for determining the optimal sizing, flow rate, substrate mixture, and 'flushing-maturation' period for a scale-up to a larger BCR passive treatment system (PTS). The authors recommend conducting a bench-scale test (on site or in a lab) prior to the construction of any and all larger-scale BCR PTS.

- 5. A demonstration-scale (pilot-scale) BCR PTS can be constructed in two to four weeks, depending on the size, location, and complexity of the system; the permitting process is often much longer.
- 6. At least the first two pore volumes of BCR cell effluent should bypass polishing cells to prevent fouling of the polishing cells with elevated levels of BOD and/or fecal coliforms that are present during the 'flushing-maturation' stage of a BCR. The first two pore volumes of BCR effluent should either be pumped back to the top of a system (heap leach pad in the case of this site) or treated prior to discharge.
- 7. A demonstration-scale (pilot-scale) BCR PTS can operate through winter in extremely cold environments, such as central Montana, as long as 'winterizing' precautions are taken. Such precautions may include, but are not limited to: burying all piping below maximum frost line for that area, providing extra insulation on and around potential weak spots in the system (BCR surface, vaults, piping, etc.), and starting flow through the entire system (including polishing cells) prior to the onset of freezing conditions at the site, if possible.
- 8. It may be difficult to operate full polishing cells throughout the winter, even with optimal start-up conditions and design considerations. For this reason, it is prudent to include a means to bypass some or all of the polishing cells during the coldest periods of the year.

The demonstration-scale BCR PTS will continue to be monitored and sampled over the coming months. During this time, field and analytical samples will be examined and further operational hypotheses will be developed and tested. If the demonstration-scale system operates satisfactorily and meets MTDEQ guidelines, a second BCR cell will be constructed next to the original BCR cell and the system is expected to be able to treat water from the entire tailings drainage.