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Treatment of Acid Mine Drainage Using Fishbone Apatite II^{TM}

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TREATMENT OF ACID MINE DRAINAGE USING FISHBONE APATITE II^{TM}[1]

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ABSTRACT. In 2000, a reactive barrier was installed on the East Fork of Ninemile Creek near Wallace, Idaho to treat acid mine discharge. The barrier was filled with fishbone derived Apatite II^{TM}[4] to remove the contaminants of concern (Zn, Pb, and Cd) and raise the pH of the acidic mine discharge. Metal removal has been achieved by a combination of chemical, biological, and physical precipitation. Flow for the water ranges from 5 to 35 gallons per minute. The water is successfully being treated, but the system experienced varying degrees of plugging. In 2002, gravel was mixed with the Apatite II^{TM} to help control plugging. In 2003 the Idaho National Laboratory was ask to provide technical support to the Coeur d'Alene Basin Commission to help identify a remedy to the plugging issue. Air sparging was employed to treat the plugging issues. Plastic packing rings were added in the fall of 2005, which have increased the void space in the media and increased flows during the 10 months of operation since the improvements were made.

Additional Key Words: reactive barrier, heavy metals, mining

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[4] Product Disclaimer:
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BACKGROUND

The Coeur d'Alene Basin of Northern Idaho is known as Silver Valley because of the huge volume of silver mined in the area in the early 1900s. As a result, thousands of acres of land and miles of streams have been contaminated with metals from the mining and milling activity (Gillerman 2002). Stabilizing stream banks and tailings piles that are sources of sediment and particulate metals in the creeks is one cleanup activity that is being implemented in the Coeur d'Alene Basin. In some locations, tailings have been piled on the canyon floors and cover the original creek channels. Water now flows through the tailings, where it picks up dissolved and suspended metals (Figure 1). The Success Mine site was identified as the largest remaining source of metals loading in the Ninemile Creek drainage (EPA 2002). Zinc, cadmium and lead concentrations are significantly higher in this area than background areas. During high flows in the spring, sediments that were trapped during low flow periods are resuspended and carried downstream. The pH of the water is also lower in this area due to the presence of pyrite formations (Golder Associates Inc., 2002).

Figure 1.0 Ground and Surface Water Passing through Mine Tailings

Groundwater flows from the adjacent hillsides and comes up in various locations in the canyon floor. Portions of this water comes up through the tailings pile and flows down gradient until it enters the creek, again carrying with it increased levels of dissolved and suspended metals with a lowered pH level.

INTRODUCTION

In 2000, a 45 foot long 12 foot deep reactive barrier was constructed to treat acid mine drainage resulting from surface and groundwater passing through mine and mill tailings at the Success Mine on the East fork of Ninemile Creek near Wallace, Idaho. The reactive barrier was constructed having two separate sides, each 6 foot wide, 12 feet deep, and 45 feet long (See Figure 2). On each side of the reactive barrier, water flows over and under alternating baffles to create as much contact between the media and contaminated water as possible. Each side of the reactive barrier has 5 cells separated by these alternating baffles (Figure 2).

The reactive barrier was filled with fishbone Apatite II^{TM} as a media to remove the metal contaminants and to raise the pH of the water. Apatite II^{TM}, derived from fish bones, stabilized a wide range of metals, including Zn, Pb, and Cd (Write et al., 1995). Depending on the metal concentration and water chemistry, the Apatite II^{TM} works by four possible processes: heterogeneous nucleation, pH buffering, chemisorption, and biological stimulation (Wright and Conca 2005). From the start, the reactive barrier successfully removed metals from the contaminated discharge, as well as early on, the system began experiencing plugging problems.

Figure 2.0. Construction of the Reactive Barriers at the Success Mine Site.

Gravel was added in 2001 to help control plugging. This provided only a short benefit and plugging was again an issue. The INL received funding in 2003 to assist the Coeur d'Alene Basin Commission in remediating the plugging issues associated with the reactive barrier. Chemical and biochemical analysis was performed on the media to determine the forms of metal precipitates, biological conditions, and physical and chemical conditions of the media.

In May of 2005, the compressed air was injected into the Apatite II^{TM} to break up sediments deposited in the media in order to increase flow through the media. MSE Technology Applications, Inc., in Butte, Montana had demonstrated that injecting air into a similar reactive barrier at the Stewart Mine on Pine Creek had successfully increased flow in the Apatite II^{TM} media at that location (McCloskey et al., 2006).

In November 2005, the old gravel/ Apatite II^{TM} mixture was removed and disposed onsite to make room for the new Apatite II^{TM} /plastic packing ring mixture. New Apatite II^{TM} media mixed with plastic packing rings was used to replace the plugged media in the East side of the reactive barrier. The plastic packing rings were used to increase the void space in the media and alleviate the plugging problem.

Material and Methods

Biological Analysis of the Apatite II^{TM} Media

The Apatite II^{TM} media was sampled to determine if sulfate reducing bacteria (SRB) were active in the barrier. These bacteria are responsible for precipitating metal ions found in acid mine drainage. SRBs are a ubiquitous group of prokaryotic microorganisms found in anaerobic environments. In the process of anaerobic respiration these organisms can use a variety of electron donors (AH_2) and can couple oxidation of those compounds to reduction of sulfate and elemental sulfur as shown in the following equation:

$$4\ AH_2 + SO_4^{-2} + H^+ \rightarrow 4\ A + HS^- + 4\ H_2O$$

It is in the anaerobic zone that the remediation takes place. The sulfide produced then precipitates with the soluble metals (such as Fe, Cu, Mn, Zn, Pb, and Cd) as insoluble metal sulfides, and the net consumption of protons due to formation of hydrogen sulfide gas generates bicarbonate alkalinity, which raises the pH of the waste stream.

The media used to isolate and identify SRB was Bacti control bottles API Anaerobic media which includes ammonium phosphate, dipotassium phosphate, yeast extract yeast extract, sodium lactate and magnesium sulfate and a nail to provide iron manufactured by Sherry Laboratories. Water samples were collected from each cell in both sides of the reactive barrier and from the outflow. One mL of each water sample was injected into a Bacti vial, using sterile methods. Each sample was collected in triplicate and diluted out to 10^{-8}. Medium used for heterotrophic and enteric bacteria was 2% PTYG Agar (2% Peptone-Tryptone-Yeast Extract-Glucose and 1.5 % agar) and Luria-Bertani Agar (10 g tryptone, 5 g yeast extract, 5 g NaCl, and 15 g agar per liter of water). One mL and 0.1 mL samples were plated in duplicate on both medium. Eh and pH of water samples were also taken.

Chemical Analysis of the Apatite II^{TM} Media

Apatite II^{TM} samples were collected from below the water level in each side of the reactive barrier to be representative of the conditions where chemical and biological reactions occur. The samples were collected and stored in polypropylene containers and put on ice until they were received at the laboratory.

Both the sediments and the Apatite II^{TM} were oven dried for 24 hours at 90º C. The samples were sieved to separate the sediments from the Apatite II^{TM} media. The Apatite II^{TM} media was also washed with tap water (tap water) to remove any surface attached material from the fish bones. The samples were pulverized with a mortar and pestle in preparation for analysis. The samples were analyzed for both metal concentrations and speciation using Powder X-Ray Diffraction and XRF and by Scanning Electron Microscopy.

Injection of Compressed Air to Improve Flow

The covers to the reactive barriers were removed to provide access to the media. A 10 foot galvanized hollow wand was fabricated to inject compressed air deep into the media. Compressed air was injected in at least two locations in each of the 5 cells for both the East and West side of the reactive barrier (See Figure 3).

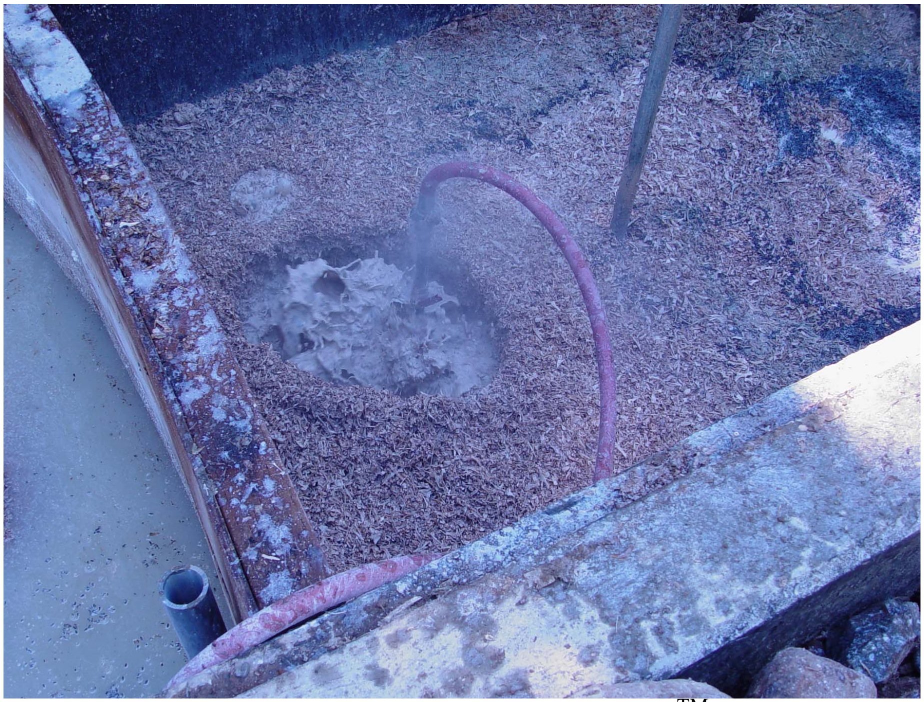

Figure 3. Injecting Compressed Air in the Apatite II^{TM} Media.

Replacing the Media in the Reactive Barrier with Apatite II^{TM} and Plastic Packing Rings

Attempts to improve flow on the East side of the reactive barrier were only temporarily successful. The addition of gravel to the media did not improve flow through the system. Aerating the Apatite II^{TM} media was successful for a short time, but it soon returned to the original flows. As a result, an alternative mixture of Apatite II^{TM} and plastic packing rings was used to help increase the percent of void space in the reactive barrier. Plastic packing rings (produced by Jaeger Products Inc.,) are used in many aspects of water treatment to increase the surface area for microbial attachment and increase the reactive area of the media. They are also used to increase the void space in the media (Figure 4).

Figure 4. Plastic Packing Rings.

Results and Discussion

Water samples were taken at the discharge of both sides (East and West) of the reactive barrier to determine if SRBs were present in the discharge. Water was also sampled in each of the 5 cells on each side of the reactor. The Apatite II^{TM} was plugged on the East side and required mechanical mixing and injection of compressed air to get water flowing again through the reactive barrier. This would have affected the true Eh values being measured in the field at the time. Table 1 shows the results of the field measurement for pH and Eh and Table 2 shows the laboratory results for the SRB counts.

Table 1. Field Measurements for Eh, pH, and SRB Counts.

Sample	Eh	pH
Inflow water	468	4.5
Cell 1 West	211	7
Cell 2 West	-48	6
Cell 3 West	245	6
Cell 4 West	238	6
Cell 5 West	-199	7
Outflow West	150	7
Cell 1 East	236	6
Cell 2 East	310	6
Cell 4 East	Not sampled	Not sampled
Cell 5 East	Not sampled	Not sampled
Outflow East	224	7
E.fork Nine Mile Creek	550	

Table 2. Sulfate Reducing Bacteria Counts.

Sample	Sulfate Reducing Bacteria
Cell 1 West	3 X 10^4 /mL
Cell 2 West	3 X 10^4 /mL
Cell 3 West	4 X 10^4 /mL
Cell 4 West	4 X 10^3 /mL
Cell 5 West	7 X 10^5 /mL
Outflow West	1 X 10^2 /mL
Outflow West	present
Cell 1 East	1 X 10^5 /mL
Cell 2 East	7 X 10^3 /mL
Cell 3 East	Not Done
Cell 4 East	1 X 10^3 /mL
Cell 5 East	7 X 10^3 /mL
Outflow East	1 /mL
Outflow East	Present

The most obvious finding is that there was in fact SRBs present in the reactive barrier as expected, so some treatment (precipitation) of should occur. The Eh values indicate that most samples are not anaerobic (negative value). This is probably due to the low levels of water in the barrier, which was a consequence of the time of year and weather conditions. Several locations in the West cells had negative Eh values, indicating that the water was deep enough in the barrier and anaerobic activity was present. However, not all location in the West cells had negative Eh values. The micro anaerobic zones did exist throughout the barrier, as shown by the presence of SRB's in most samples. If more water was present in the barrier, a larger anaerobic zone could be created and a larger population of SRB would be present (1 X 10^8 /mL). This would hopefully lead to complete precipitation of the metal and an increase of the pH to neutral (7.0). The East cells had little to no water flow and no anaerobic zones as indicated by the positive Eh values. It is not likely that treatment was occurring in this cell. If flow can be maintained, and anaerobic zones created, SRB should grow and metal precipitation and pH increase should occur.

Chemical Analysis of the Apatite II^{TM} Media

The presence of zinc, cadmium and lead were measured in the Apatite II^{TM} using scanning electron microscopy (SEM). The SEM provided a relative concentration for each metal. Figure 5 shows the relative weight percents observed in the Apatite II^{TM} for each of the metals of concern. In addition, the concentration of sulfur was also measured. Sulfate is present in the feed water. Under anaerobic conditions, the metals form insoluble sulfide precipitates. The presence or absence of sulfur can be used to determine if metal sulfides are being formed under the conditions present in the reactive barrier. In the Apatite II^{TM} samples, there was no appreciable amount of sulfur detected (Figure 5).

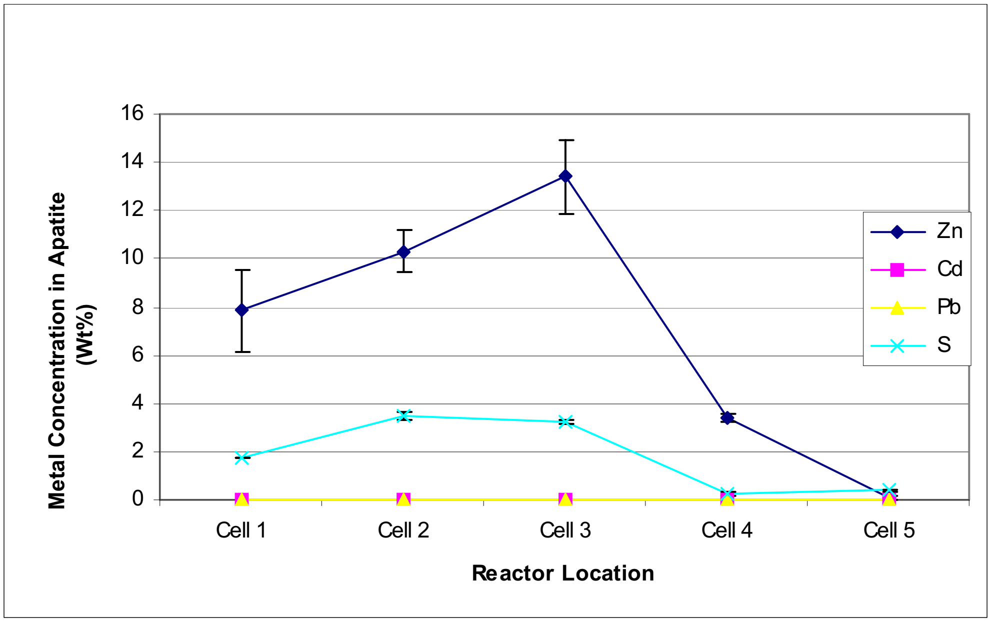

Figure 5. Metal concentration in the Apatite II^{TM} material from the West Side of the Reactive Barrier.

The sediments around the Apatite II^{TM} were also analyzed for metal concentration. Slightly higher concentrations of zinc and lead were present in the sediment than in the Apatite II^{TM}. There was also a notable amount of sulfur present in the sediment. This suggests that the metal precipitates formed in the sediments were resulting at least in part due to metals sulfides being formed under anaerobic conditions.

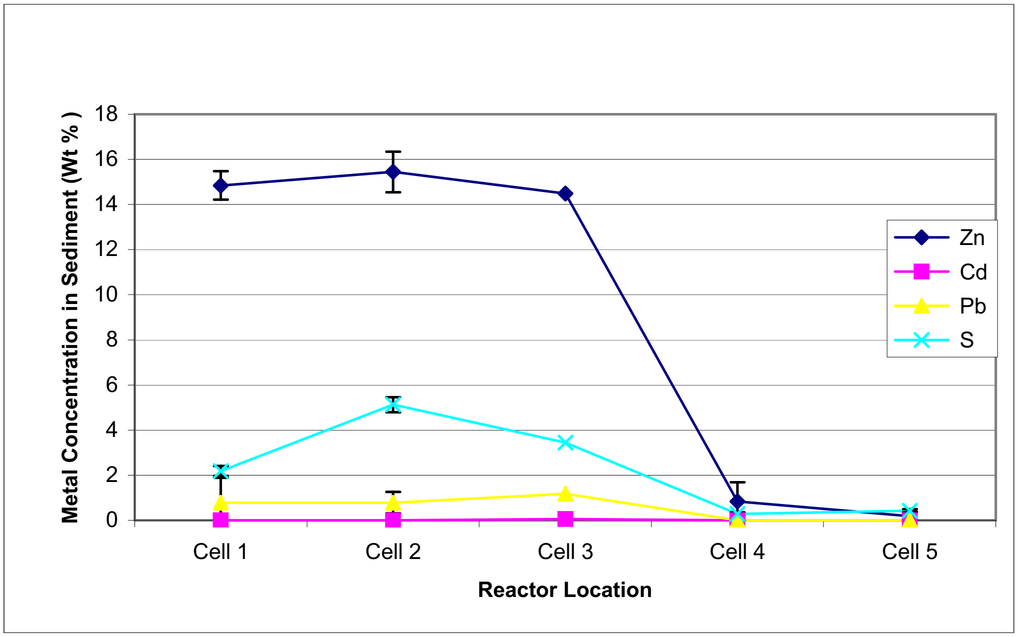

Figure 6. Metal concentrations in the sediment of the West Reactive Barrier.

The same analysis was performed on the East side of the reactive barrier. Figure 7 shows the zinc, cadmium, lead and sulfur concentrations found in the Apatite II^{TM} from the East side of the reactive barrier. This figure shows that the concentrations of the contaminant metals were lower in the East side than the West side. It also shows that most of the reaction occurs in the first two cells and that the subsequent cells are not removing metal from the contaminate water.

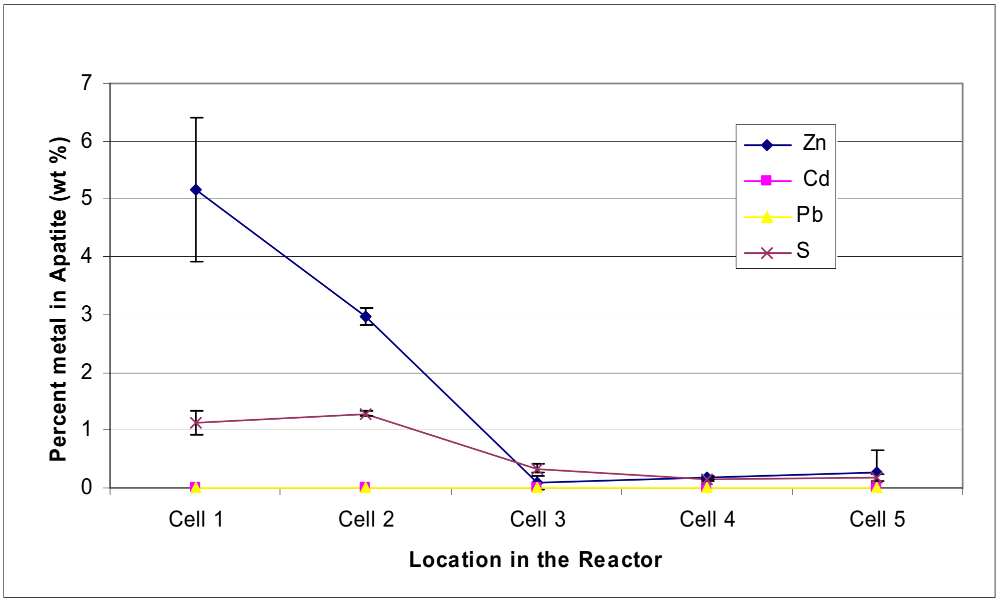

Figure 7. Metal concentration in the Apatite II^{TM} from the East side of Reactive Barrier.

Figure 8 illustrates the concentrations of the metals of interest in the sediment of the East side of the reactive barrier. Most of the precipitation that does occur, takes place within the first two cells of the barrier. The concentration is about half the measured values observed in the West side of the reactive barrier.

<u>Injection of Compressed Air</u>

The reactive barrier was constructed in 2000 and the first Apatite II^{TM} was placed in the barrier in January of 2001. Other than adding new media to the East side of the reactive barrier in 2002, nothing had been done to deal with the plugging issues associated with the reactive barrier. The cause of the plugging was a combination of sediment buildup from the influent stream and sedimentation occurring from the breakdown of the Apatite II^{TM}. Figure 9 illustrates the sediment buildup that had occurred in the West side of the reactive barrier. Note the buildup of sediment in the Apatite II^{TM} and notice how the water has formed preferential paths in the media resulting in inefficient contact of water and the reactive media.

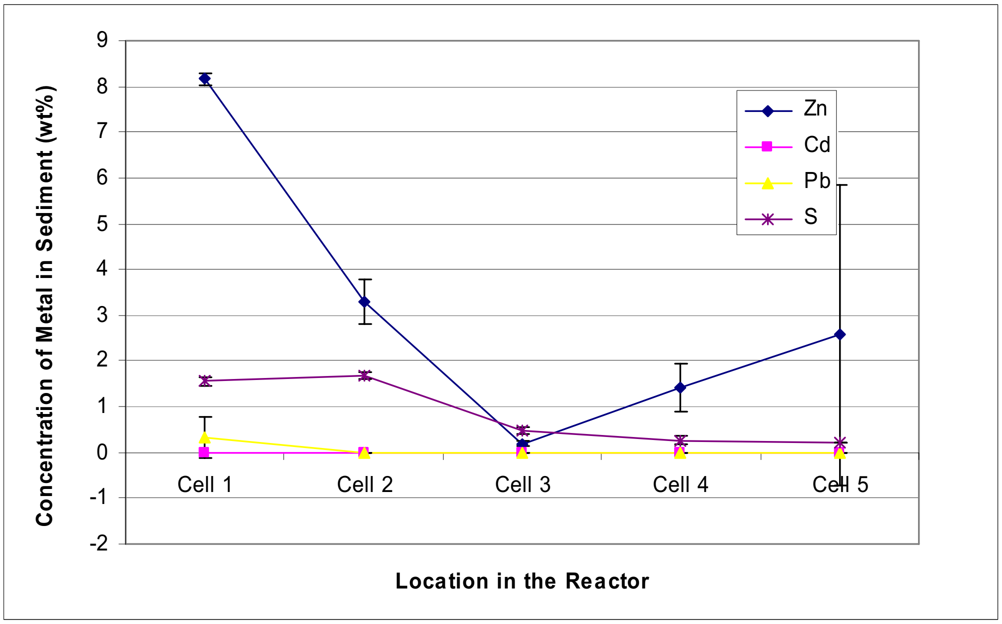

Figure 8. Metal Concentration in the Sediment of the East side of the reactive barrier.

Another similar site in the Coeur d'Alene basin is using Apatite II^{TM} to treat acid mine drainage at the Nevada Stewart Mine. At this location, compressed air is injected into the media combat the effects of plugging on the reactive barrier. This results in temporarily increased flow in the media at the Nevada Steward Mine site. For the reactive barrier at Success, a ten-foot hollow wand was constructed to inject air deep into the media at the Success Mine reactive barrier. Figure 10 shows the workers injecting air into the media at the Success Mine.

Figure 9. Sediment buildup in the Reactive Media.

Figure 10. Injection of Compressed Air into the Reactive Media.

The result of the injection of compressed air into the media was an immediate increase in flow through the reactive barrier, primarily on the West side. The presence of the gravel on the East side made it difficult to get the metal wand into the media to successfully inject the air into the media. This resulted in only limited success on the East side of the reactive barrier.

Figure 11 shows the flow rate measured at the discharge of the reactive barrier. Note that before injecting air into the reactive media, there was a steady stream of water measured in the overflow for the system. Following the air injection, the flow through the reactive media increase and the overflow went to zero meaning that the system was again treating all of the water. The flow rates in general continued to decrease over time following the air injection, but this is primarily due to a seasonal decrease in flow. Note that there was no flow observed in the overflow following the air injection and that the flow in the West side increased again in the Spring of 2006 when flows came back up. Flow on the East side also increased at that time, but it should be noted that the increase in flow on the East side could be directly attributed to the addition of new media in November of 2005. From this it can be observed that injecting compressed air into the media does provide at least temporary improvement to flow in the Apatite II^{TM} media.

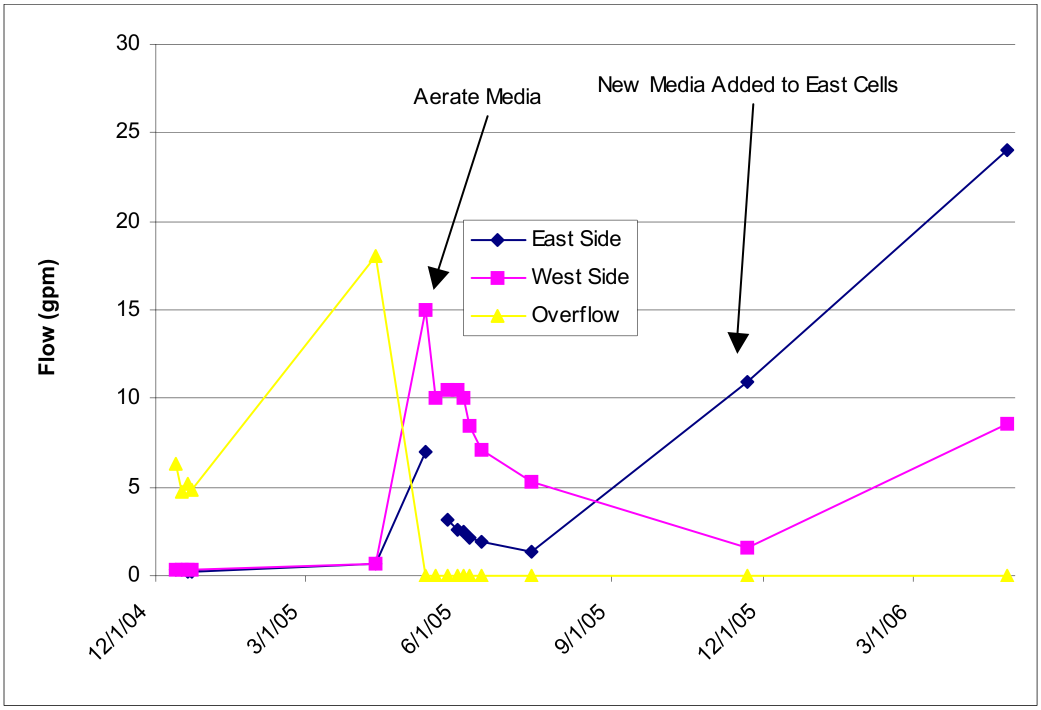

Figure 11. Flow rates measured in the outlet and overflow of the reactive barrier.

<u>Replacing the Media in the Reactive Barrier with Apatite II^{TM} and Plastic Packing Rings</u>

In November of 2005, the media in the East side of the reactive barrier was replaced with new Apatite II^{TM} mixed with plastic packing rings at a ratio of 30 volume % plastic packing rings. Two inch Jaeger plastic packing rings were used to provide an increase in void volume in the reactive barrier. The increase in void volume was desired to provide more area for water to flow through in the Apatite II^{TM} media and to provide more volume for sediments and precipitates to form without impacting the flow. Figure 4 is a picture of the packing rings used in the reactive barrier. By themselves, the plastic rings have a void volume of 92%. Information on the void space of Apatite II^{TM} was not available, but had noticeably less void volume than the plastic rings alone.

Prior to the removal of the old Apatite II^{TM} /gravel mixture and the placement of the new Apatite II^{TM} /plastic packing ring mixture, the flow from the East side of the reactive barrier was less than 1.5 gallons per minute. After replacing the media, the flow increased to over 10 gallons per minute in December of 2005. It further increased to 24 gallons per minute in April of 2006 (primarily due to high Spring water runoff). This is the highest flow produced from the East side of the reactive barrier since it was constructed. In June of 2006 the flows had gone back down to just over 5 gallons per minute, but there was no water flowing out the overflow. This still was the highest flow from the East side of the reactive barrier since May of 2002. Figure 12 illustrates the flow rates through the reactive barrier since it was constructed. Since the change out of the

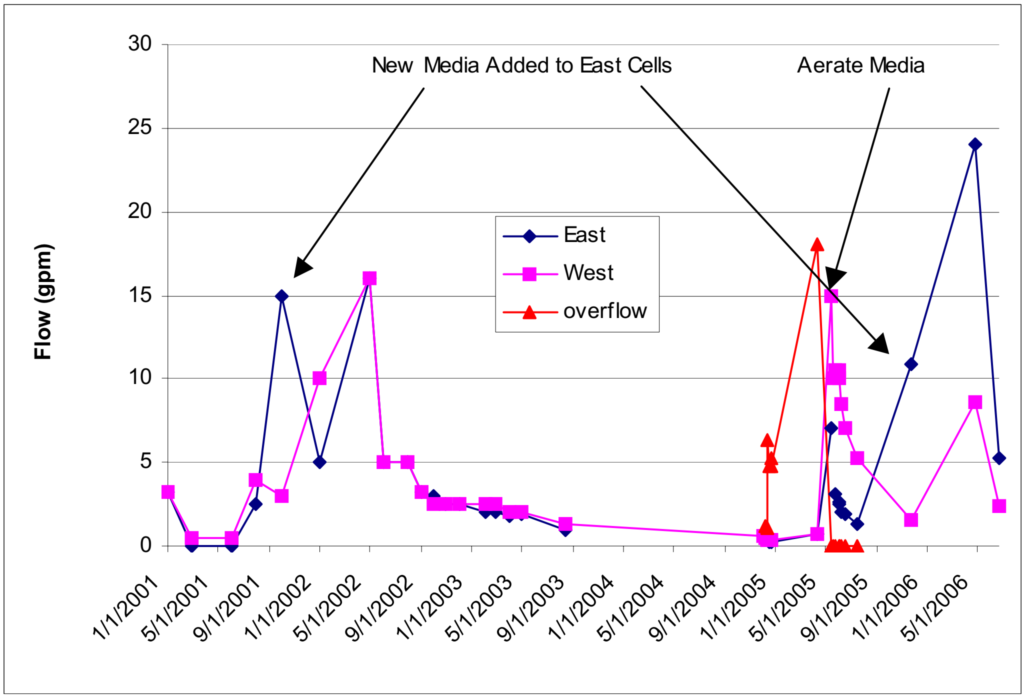

Figure 12. Flow rate (gallons per minute) for the Success Reactive Barrier.
*data from 1/1/2001 to 9/1/2003 was taken from Golder 2003 – overflow data was not always collected

media in the fall of 2005, the East side of the reactive barrier has produced higher discharge flow rates than the West side of the reactive barrier for a longer period of time since the barrier was constructed.

Ph was measured from November 2004 through September of 2005. The pH of the water has been improved by treatment with the Apatite II^{TM} media. Influent pH levels average 4.8. Effluent pH values average 6.7 in the West side of the reactive barrier and 6.6 from the East side of the reactive barrier.

Removal efficiency

The average concentration of the metals of concern in the influent to the reactive barrier are 0.52 mg/L Cd, 1.01 mg/L Pb, and 83.6 mg/L Zn. The average concentration in the discharge for the West side of the reactive barrier is 0.007 mg/L Cd, 0.014 mg/L Pb, and 1.06 mg/L Zn. On the East side of the reactive barrier the outlet average outlet concentration is 0.002 mg/L Cd, 0.005 mg/L Pb, and 0.374 mg/L Zn. The removal efficiencies for the metals are presented in Figure 13. In each case, the removal efficiency is greater than 98% removal.

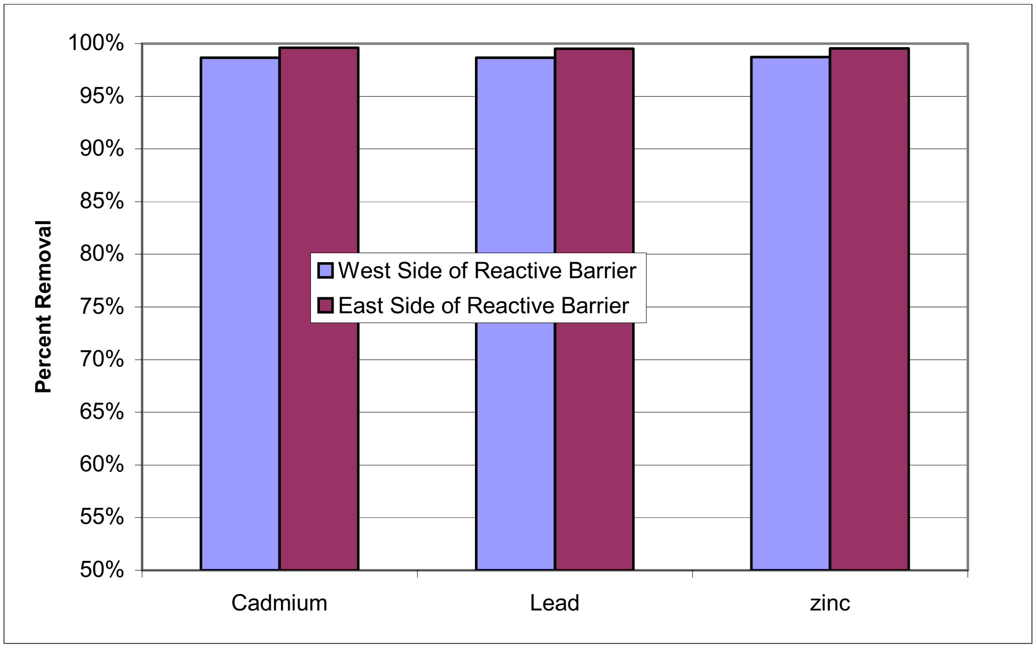

Figure 13. Removal Efficiency for Cd, Pb, and Zn from the Reactive Barrier.

Summary

The biological and chemical analysis of the Apatite II^{TM} showed that the reactive barrier is utilizing more than one single method to remove metal contaminants from the mine drainage, specifically both biological reduction and chemical sorption are causing the reduction in metal concentrations in the contaminated waters.

The injection of compressed air does improve the performance of the reactive barrier by breaking up preferential flow paths created over time in the media. The process of injecting compressed air will need to be reviewed on a case-by-case basis, but in this case annual injection of air would lengthen the life of the media.

Since the construction of the reactive barrier in 2001, the media in the East side of the reactive barrier has been replaced twice. It is not clear why the problem started so early on in the system when both sides of the barrier appeared to have been constructed in the same manner. It is apparent that mixing the Apatite II^{TM} with gravel does not improve the efficiency of the system. Two problems resulted from this. First, the addition of gravel to the Apatite II^{TM} did not have the desired effect of increasing the void space of the media; it simply reduced the amount of media present. Second, it created a media with a much higher bulk density. The two sides appear to have similar void volumes. Water entering the two sides of the reactive barrier enters from the same distribution box or manifold. Water naturally tends to flow to the path of least resistance which in this case is the side without the gravel.

Since the new Apatite II^{TM} mixed with plastic packing rings was put in the East side of the reactive barrier in November 2005, the flows in the East side of the reactive barrier have surpassed the West side for the longest period of time since construction. While continued monitoring needs to take place, we are optimistic that this will be a beneficial solution to the plugging experienced at the Success Mine.

Using the average flow rates and average concentrations in the source water and the treated water, it is estimated that the system has removed 44 pound of cadmium from the East side and 49 pounds of cadmium from the West side of the reactive barrier, 85 pounds of lead from the East side and 95 pounds of lead from the West side of the reactive barrier, and 7003 pounds of zinc from the East side and 7850 pounds of zinc from the West side of the reactive barrier over the 5 years of operation. While this paper discusses resolving plugging issues with the Apatite II^{TM} media, it should be noted that the systems has continued to successfully reduce metal concentrations in acid mine drainage to below drinking water standards and raise the pH to near neutral levels. With the addition of the plastic packing rings to the Apatite II^{TM}, it is anticipated that the system will continue to operate for several more years.

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