Lab-Scale Bioremediation Treatability Studies for Legacy Mines and Lessons Learned

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Abstract

This paper presents results and lessons learned from lab-scale treatability studies evaluating passive bioremediation as a potential treatment strategy for mining-influenced water (MIW) emerging from two legacy mines in Montana, USA. MIW influent from both mine sites was acidic with a mean pH of 2.46 and 4.01, had low to moderate total dissolved solids, and contained constituents of concern (CoCs) such as Al, As, Be, Cd, Cu, Fe, Pb, Tl, and Zn that exceed potentially applicable water quality benchmarks. Passive, biologically-based water treatment can be a cost-effective technology for treating MIW, particularly at legacy mine sites. The primary goal of these studies was to assess the effectiveness of sulfate-reducing biochemical reactors (SRBRs) and treatment wetlands for improving the quality of MIW discharges from two historical mines. SRBRs can increase pH and alkalinity of MIW while producing sulfide, which, in turn, removes aqueous metal ions through precipitation as metal sulfides. Constructed treatment wetlands can be designed to promote oxic and aerobic conditions thereby improving the quality of SRBR-treated water. Laboratory-scale SRBRs and wetlands were evaluated for their ability to improve the quality of MIW collected from both mines. The studies were conducted with oversight by the U.S. Environmental Protection Agency and Montana Department of Environmental Quality.

Each stage of the treatment systems effectively removed potential CoCs for MIW from each mine site by promoting the necessary geochemical and biological processes. The conditions necessary for biological sulfate reduction and metal sulfide precipitation were maintained in the SRBRs operated at design flow rates, while the conditions necessary for the oxidation of biochemical oxygen demand and manganese, and removal of residual CoCs, were maintained in the treatment wetlands. Treatment systems operating at design flow rates provided ample sulfate reduction, sulfide generation, metal sulfide precipitation, and alkalinity to significantly improve MIW quality. Despite a change in performance associated with

increasing flow rates in some SRBRs, the treatment wetlands were able to continue removing residual CoCs from SRBR effluents.

Introduction

Passive, biologically-based water treatment can be a cost-effective and low maintenance technology for treating MIW, particularly for remotely located legacy mine sites. This paper describes two lab-scale treatability studies developed with oversight by the US Environmental Protection Agency and Montana Department of Environmental Quality, with the goal of assessing passive bioremediation as a potential treatment option for MIW emerging from two historical mine sites. The Danny T Mine adit (referred to as the Danny T Mine), is located within the Barker Hughesville Mining District (BHMD) Superfund Site in Cascade and Judith Basin Counties, Montana. The Haystack Creek Mine (referred to as the Haystack Creek Adit), is located within the Carpenter Snow Creek Mining District (CSCMD) Superfund Site in Cascade County, Montana. Mining activities in the region occurred from the later part of the 19th and early 20th centuries until the mid-20th century after silver, lead, and zinc deposits were discovered in the districts.

The focal technologies considered were biologically-based and included sulfate-reducing biochemical reactors and constructed treatment wetlands. Biological sulfate reduction accomplished by sulfate-reducing bacteria increases alkalinity and pH of MIW while producing sulfide anions, which, in turn, remove aqueous metal ions through precipitation as metal sulfides (see Sheoran et al. 2010 for a review). Treatment wetlands, on the hand, can be designed to target removal of other metals not removed by SRBRs, such as manganese (Hedin and Nairn 1993, Kadlec and Wallace 2009). Bioremediation technologies, such as the two evaluated here, can potentially reduce operation, maintenance, and monitoring costs compared to active MIW treatment strategies, while potentially achieving water quality objectives. Ultimately, these evaluations provide critical information for determining whether passive bioremediation treatment strategies are feasible for implementation, as well as providing insight into potential design of full-scale systems.

Methods

MIW was collected from the two mines during the summer of 2017 in 55-gallon barrels, which were then sealed and transported to a testing laboratory in Tucson, Arizona. The MIW was held in climate-controlled storage until ready for use in the lab-scale study.

The aluminum and ferric iron typically found in MIWs may lead to clogging within SRBRs due to precipitation of aluminum and iron hydroxide and oxide minerals. This fouling may render the SRBR less effective, require increased levels of maintenance, and shorten the longevity of the treatment system. Therefore, we evaluated the need for, and effectiveness of, limestone pre-treatment by operating a subset of SRBRs with and without pre-treatment. The pre-treatment stage was designed to increase pH above 4.5 s.u. to promote the precipitation and removal of Al and Fe (oxy)hydroxides. Reactors were filled with 1-1.5-inch diameter limestone. Half of the Danny T SRBRs were provided with limestone pre-treated water and the other half of the SRBRs were provided raw MIW. The SRBRs receiving raw MIW were larger to accommodate a higher acidity and metal loading thus they were constructed from 8-inch diameter PVC pipe fashioned into 46-inch tall columns (Figure 1). The bottom 4 inches of the column was filled with pea gravel (for increased hydraulic conductivity at the effluent port), followed by 36 inches of substrate mixture, and finally at least 2 inches of MIW at the top (inflow side of the column) will be maintained during operations. The four SRBRs receiving pre-treated water, as well as the Haystack Creek SRBRs, were smaller due to the reduced acidity and metal load and were constructed from 4-inch diameter PVC pipe fashioned into 46-inch tall columns. The bottom 4 inches of the column was similarly filled with pea gravel (for increased hydraulic conductivity at the effluent port), followed by 36 inches of substrate mixture, and finally at least 2 inches of MIW at the top. All SRBRs contained a mixture of labile and recalcitrant carbon sources, which serve as electron donors for the sulfate-reducing bacteria, as well as limestone as an alkalinity source. Additionally, a small amount of manure was added to the reactor as an inoculant to stimulate biological colony growth. Two SRBR organic substrate mixtures were evaluated, differing only in the amounts of woodchips and walnut shells. The mixtures consisted of alfalfa hay (10% wt.), woodchips and sawdust (10 or 30% wt.), walnut shells (30 or 50% wt.), and limestone (30% wt.).

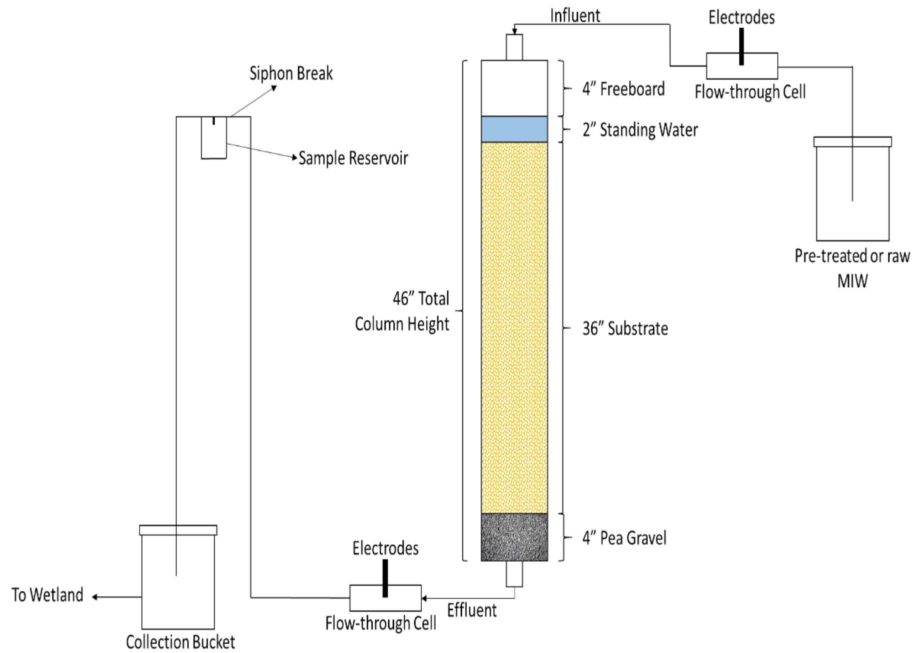

Figure 1. Schematic of the 4 in. and 8 in. diameter SRBR columns used in the treatability studies. Depicted here is a Danny T SRBR as indicated by the SRBR-treated water being directed to a VFW.

For the Danny T MIW, a third treatment stage was evaluated; vertical flow wetlands (VFWs) for removing BOD and Mn were added after the SRBRs (Figure 2). VFWs were constructed using 45-gallon polyethylene tanks (24 in. x 24 in. x 18 in.) containing 16 in. of media consisting of 8 inches of washed coarse sand placed on top of 8 in. of round, washed gravel (0.2-0.5 in. diameter). Influent water was distributed across the surface of the sand and gravel bed planted with wetland vegetation. Wetland plants promote an environment conducive to microbes that passively treat water, and root systems help maintain hydraulic conductivity of the media. This type of wetland has the added advantage of maintaining activity during the winter because water is distributed below the surface of the topmost media, thereby helping to maintain temperatures above freezing (Kadlec and Wallace 2009), which would be important for any full-scale system to be considered for the site.

Treatability of the adit discharge was assessed by quantifying metal removal efficiency and changes in concentrations of the primary constituents of concern (CoCs) based on multiple aqueous chemical and physical parameters. Aqueous samples were routinely collected from the influent feed and from the effluent feeds of each treatment system stage and analyzed for pH, electrical conductance (EC), oxidation-reduction potential (ORP), dissolved oxygen (DO), and temperature. Samples were also analyzed for total and dissolved cations, anions, alkalinity, acidity, and biochemical oxygen demand (BOD). A set of probes were installed in a flow-thru cell to record field chemistry parameters in real-time, but later discontinued because of fouling issues. Routine sampling continued throughout the study. For the purposes of this paper, emphasis will be placed on results at end of pipe rather than individual treatment stages.

Figure 2. Lab-scale treatability study setup. *Left*: Sample reservoirs, multi-meters, and flow-through cells on the back side of the rack. *Right:* Columns are on the front side of the rack and treatment wetlands on the right.

Results and Discussion

Danny T Mine MIW is acidic with a mean pH of 2.9, has moderate total dissolved solids, and contains concentrations of Al, As, Be, Cd, Cu, Fe, Pb, Tl, and Zn that exceed identified water quality benchmarks. The Haystack Creek MIW is milder, but still acidic with a mean pH of 4.0, has low total dissolved solids, and contains concentrations of Al, Be, Cd, Cu, Fe, Pb, and Zn. Results from historical periodic monitoring at both sites indicate seasonal variation in adit water quality, which is likely related to seasonal changes in flow rates associated with spring runoff.

The Danny T passive treatment system without pre-treatment markedly improved the quality of the MIW influent. Water quality indicator parameters (e.g., DO, ORP) indicate that anoxic and anaerobic conditions were maintained in all SRBRs, as required for sulfate reduction, and oxic and aerobic conditions were restored in the VFWs (Figure 3). Water treated by this two-stage system was circumneutral and net alkaline. Treated effluent was also characterized by metal concentrations at or below the identified potentially applicable benchmarks, with the exception of total arsenic, copper, and strontium.

Concentrations for these metals did not decrease below the identified benchmark until the latter half of the study or they occasionally exceeded the identified benchmark. It is worth noting that strontium is not an identified CoC at the site; it was, however, leached from the substrates used in the study, highlighting the importance of characterizing potential substrates to better understand what might be added to treated water.

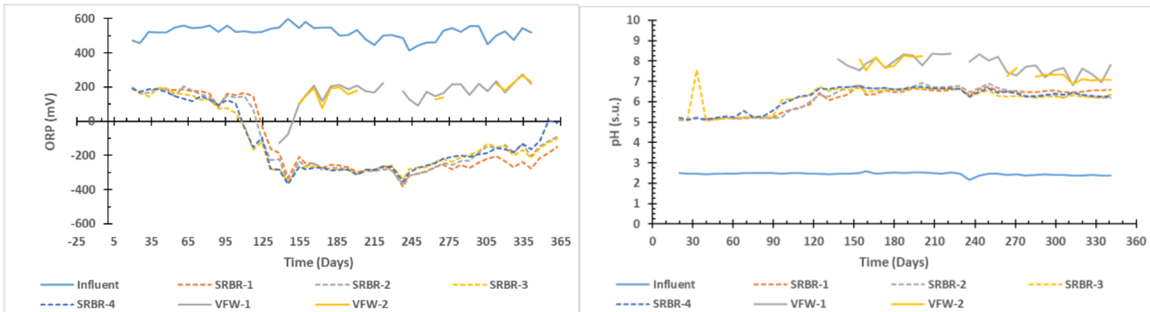

Figure 3. Oxidation-reduction potential (ORP; *left*) and pH (*right*) readings recorded during weekly sampling events in MIW influent (blue line), SRBRs (dashed), and VFWs (solid) from two-stage system (i.e., without pre-pretreatment).

The Danny T three-stage passive treatment system (with limestone pre-treatment) similarly improved the quality of the MIW influent with each stage of the three-stage system effectively removing potential CoCs as intended. Following pre-treatment, pH increased from a mean of 2.9 s.u. in the MIW to a mean of 6.6 s.u. due to alkalinity generated during the dissolution of limestone. Increased pH and reduced acidity following pre-treatment likely improved environmental conditions for sulfate-reducing bacteria, as well as other essential fermenters and methanogens within the SRBRs (Johnson and Hallberg 2005, Sheoran et al. 2010). Pre-treatment of the MIW largely removed Al and Fe while also decreasing As, Be, Cu, and Pb concentrations. Potential CoCs relatively unaffected by the increased pH during pre-treatment were Ni, Se, Cd, Tl, Mn, and Zn. Water quality indicator parameters (e.g., DO, ORP) indicate that anoxic and anaerobic conditions were maintained in all SRBRs and oxic and aerobic conditions were restored in the VFWs throughout the study. The conditions necessary for biological sulfate reduction and metal sulfide precipitation were maintained in the SRBRs operated at design flow rates, while the conditions necessary for the oxidation of BOD and Mn, and removal of residual CoCs were maintained in the VFWs. In fact, incorporating pre-treatment allowed the SRBRs to achieve operating conditions approximately 60 days earlier than the two-stage treatment system. Water treated by the three-stage system was circumneutral and net alkaline. Treated effluent was also characterized by metal concentrations below the identified benchmarks during the latter half of the study.

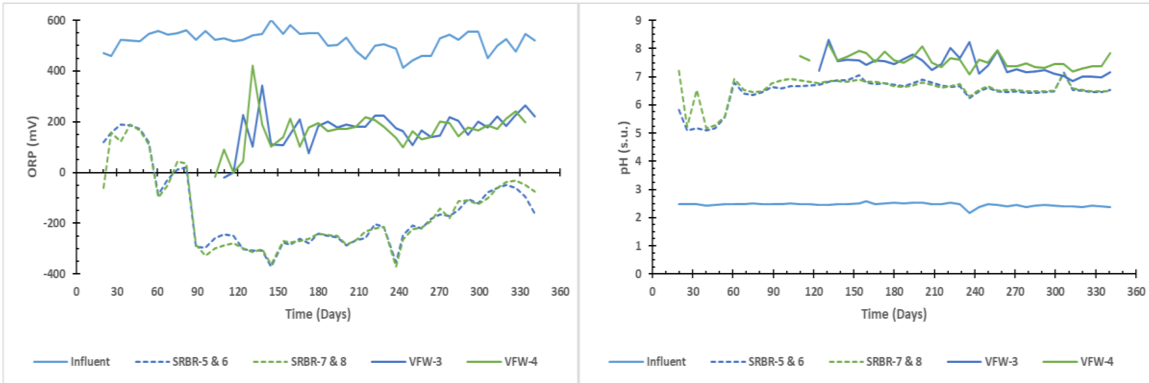

Figure 4. Oxidation-reduction potential (ORP; left) and pH (right) readings recorded during weekly sampling events in MIW influent (blue line), SRBRs (dashed), and VFWs (solid) from three-stage system (i.e., with pre-pretreatment).

The Haystack Creek SRBRs, which lacked pre-treatment and post-treatment wetlands, also successfully treated the relatively milder MIW, producing effluent that was net alkaline with a mean pH of 6.9 s.u. and metal concentrations that were at or below the identified benchmarks, with the exception of total Zn. Zinc particulates are very small and likely were incompletely filtered out by the SRBRs. Results from the Danny T two- and three-stage systems, however, show that VFWs are an effective filtering mechanism for the total iron and zinc particulate material that was not effectively removed or retained by the SRBRs (see Figure 5 for an example).

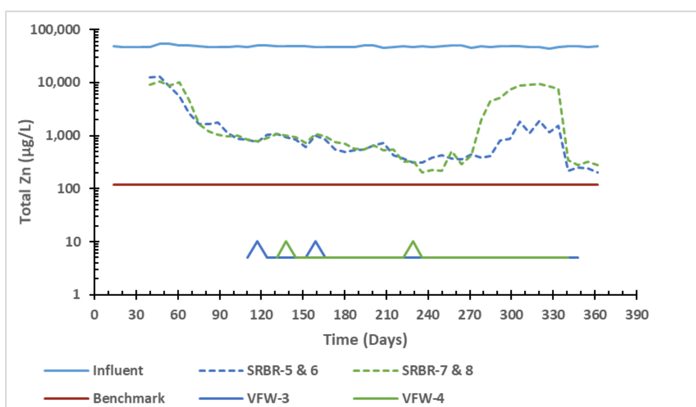

Figure 5. Total zinc concentrations (log scale) in MIW influent (blue line), SRBRs (dashed lines), and VFWs (solid lines) relative to the identified potential water quality benchmark (red lines). Zn was removed below detection levels by the VFWs.

A subset of SRBRs used for both sites were periodically subjected to increased flow rates while others were left as is. Metal removal rates increased with increasing flow rates, suggesting still greater capacity for metal removal. Yet, the SRBRs operated at the (unchanged) design flow rate exhibited the most strongly anoxic and anaerobic conditions while the SRBRs operated at higher flow rates showed signs of weakening anoxic and anaerobic conditions. For example, Danny T SRBRs 2 and 4 in Figure 3 exhibit the highest

ORP values during the final 40 days of the study when they were operated at a flow rate twice as high as the design flow rate. This observation suggests that the increased mass loading of oxygen inhibited sulfate reduction. Increased oxygen loading is the likely cause of the observed increase in DO and ORP and concomitant decrease in sulfate reduction rates (not shown). However, higher oxygen loading rates do not explain the similar, but less dramatic, increase in DO and ORP and decrease in sulfate reduction rates observed in SRBRs that remained at a constant flow rate (see SRBRs 1 and 3 in Figure 3 for an example). It is possible that these SRBRs shifted to a new pseudo steady-state condition as microbial communities matured or as the availability of critical nutrients shifted (Kleinmann et al. 2021).

Another objective of the study was to refine the mixture of organic and inorganic substrates used in each treatment system component. Proper characterization and selection of organic and inorganic substrates would mitigate the observed leaching of CoCs into the water being treated and would therefore increase the likelihood of meeting all treatment goals. Moreover, selecting the appropriate mix of organic substrates offers additional benefits to SRBR performance (Sheoran et al. 2010), as suggested by the improvement in SRBRs containing a higher percentage of wood chips and sawdust relative to walnut shells. The organic carbon associated with the woodchips and sawdust may have been more readily available to the microbial community to support sulfate reduction relative to what was available in walnut shells. It is possible that more substantial differences in substrate performance may have become evident later as the contribution of more recalcitrant organic matter sources becomes more important.

Conclusions

Overall, the passive treatment systems operating at design flow rates markedly improved the quality of MIW from both mines, producing effluent that was circumneutral and net alkaline. Incorporating pre-treatment allowed the SRBRs to achieve operating conditions approximately 60 days earlier than the two-stage treatment system. The three-stage system with pre-treatment also reduced CoCs below the identified benchmarks earlier in the study. Improvements in water chemistry following pre-treatment (increased pH and reduced acidity) likely improved environmental conditions for sulfate-reducing bacteria and therefore improved its performance.

The success of all treatment systems operated at the design flow rates suggests that the initial flow and mass loading calculations provided an appropriate starting point for design and operation. Results showing metal removal rates increasing in several SRBRs with increasing flow rates suggests still greater capacity for metal removal. However, the data also indicate that there are limits to metal removal. Differences in performance became evident as flow rates were increased to each treatment system. In the system without pre-treatment, anoxic and anaerobic conditions were maintained in all SRBRs throughout the study. In the system with pre-treatment, the SRBRs operated at the highest flow rate began exhibiting signs of failure, as indicated by a near complete, but potentially temporary, loss of anoxic conditions by the end of the study. Results suggest performance decreased in these high flow rate SRBRs due to excessive oxygen loading.

Overall, results from this study highlight the value in designing passive bioremediation systems with components that target different subsets of potential CoCs. In this study, the conditions necessary for biological sulfate reduction and metal sulfide precipitation were promoted in the SRBRs, while the conditions necessary for the oxidation of BOD and Mn, and removal of residual CoCs were promoted in the VFWs. CoCs targeted for removal by the SRBRs, but which were not completely removed, were subsequently removed by the VFWs.

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