

EVALUATION OF A TWO-STAGE PASSIVE TREATMENT APPROACH FOR MINING INFLUENCED WATERS¹

L. Figueroa², A. Miller, M. Zaluski, and D. Bless

Abstract: A two-stage passive treatment approach was assessed at a bench-scale level using two Colorado Mining Influenced Waters (MIWs). The first-stage was a limestone drain with the purpose of removing iron and aluminum and mitigating the potential effects of mineral acidity. The second stage was a sulfate reducing bioreactor composed solely of 50% corn stover and 50% walnut shells by volume. The primary difference in the two MIWs was the concentration of zinc 5-7 mg/L for the National Tunnel Adit drainage (NTA) vs. 65-75 mg/L for the Silver Cycle Adit drainage (SCA). The limestone pretreatment columns reduced the zinc in the NTA MIW to 1-2 mg/L and the SCA MIW to 38 - 56 mg/L. The two SCA biocolumns had similar zinc removal but different sulfate removal with time. The sulfate reduction rate (SRR) for the SCA columns peaked at day 50 but at 0.5 mol S/m³/d for column 1 and 0.3 mol S/m³/d for column 2. Average SRR after day 50 was 0.24 and 0.13 mol S/m³/d for columns 1 and 2, respectively. The NTA columns (3 and 4) sustained an averaged SRR of 0.3 mol S/m³/d for days 30-130. The effluent zinc after startup from the two systems were < 0.1 mg/L and <2 mg/L for the NTA and SCA treatment systems, respectively. Other significant results included startup of sulfate reduction in both sets of bioreactors without the typical “manure” inoculum. The time to start up was not negatively affected by the lack of a designated inoculum. Another important result was the longer start up time required and the overall lower sulfate reduction observed for the higher zinc MIW.

Additional Key Words: MIW, acid mine drainage, water treatment, sulfate reduction, bioreactor, limestone

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Introduction

There are 51,700 abandoned mine land (AML) sites in EPA Region 8 and 22000 which are located in Colorado (WGA 1998). Most of these sites are on private lands where the ownership is either unknown or the owner does not have the resources to pay for problems associated with the mine lands. AML sites in Region 8 are also characterized by remote and diffuse location, small sites and periodic problems (WGA 1998). For example, water from snowmelt can cause the production of metal-laden drainage from mine tunnels and mine and mill tailings. As a result, streams and groundwater aquifers are affected by mining impacted waters (MIWs) with potential impacts to human and aquatic health.

Mine drainage components of concern are acidity or acid producing potential and toxic metals (e.g., As, Cu, Pb and Zn). Point sources of water (where treatment systems are usually implemented) are typically downstream of metal and acidity sources. Water flow at point sources can be high and typically active processes that require significant operation and maintenance are implemented. This is a problem for the remote and diffuse sites such as those found in EPA Region 8 where access year round is an issue. In contrast, passive systems (e.g. passive bioreactors and permeable reactive barriers) can be implemented at the foot of a tailing pile or at seeps to intercept a smaller flow of water at the contaminant source. Passive systems can also be used to implement biologically and chemically mediated processes. Little operation and maintenance is required which is advantageous for remote sites.

Many mine drainage waters require removal of acidity, acid generating potential, and/or metals. Passive bioreactor system promoting sulfate reducing bacterial activity can mitigate all three of these issues. However, the presence of Fe and Al in MIWs influent to passive bioreactor systems has historically cause problems with clogging by Fe and Al(OH)₃ precipitates (Zaluski et al. 2006). Clogging of passive bioreactor systems can result in failure long before the organic substrate in the bioreactors has been depleted. Hedin et al. (1994) recommend pretreatment for MIWs containing O₂, Fe and Al concentrations above 1 mg/ prior to treatment using wetlands or vertical flow reactors (similar systems in terms of design). One strategy to mitigate the clogging of bioreactors by Fe(OH)₃ and Al(OH)₃ is to pre-treat the water with a limestone drain. The dissolution of limestone results in reactions that consume protons and thus increase both alkalinity and pH. There are two major types of limestone systems commonly in use that have different chemistry and also different mechanisms for metal removal. Anoxic limestone systems (ALS) are used when the mine water to be treated is in a chemically reduced state, with little to no dissolved O₂, or if the water can be intercepted before being exposed to atmospheric conditions (Skousen, 1991). The anoxic water conditions force the metals present to stay in their reduced forms. Most importantly Fe will be predominantly present in the Fe²⁺ state, and Mn in the Mn²⁺ state. Aluminum is not affected by the redox potential of the water. It is only affected by the pH change caused by the limestone. For waters with a pH greater than about 4.5, the Al changes from dissolved to particulate.

The other main type of limestone systems are systems that are open to the atmosphere or for waters with large amounts of oxidized metal species, and are thus called oxic limestone systems (OLS) (Ziemkiewicz, et al., 1997, Ziemkiewicz, at al., 1994, Cravotta and Trahan, 1999). In this type of system the pH and alkalinity additions happen concurrently with metal precipitation. As

the pH in an OLS increases Fe^{3+} and Al will precipitate, and can accumulate on the limestone surface thus forming an armored coating. Although the armoring does not stop limestone dissolution completely, it can slow the rate of dissolution, which, can be taken into account in the design of the OLS. (Ziemkiewicz et al., 1997, Letterman, 1995). The conglomeration of Fe^{3+} and Al precipitates in the drain will eventually cause clogging, preferential flow paths, and short-circuiting. These effects also can be integrated in the design to ensure the OLS achieves the desired design life.

Anaerobic passive bioreactor systems have been constructed at numerous sites in the United States and Canada. The success of these systems has been mixed. The performance efficiency of constructed anaerobic wetlands receiving mine drainage has been observed to vary seasonally and with wetland age (Wieder 1992). Ordonez et al. (2000) were unable to achieve SO_4 -reducing conditions in a pilot-scale wetland. A field-scale passive bioreactor constructed in West Fork Missouri has effectively removed lead from the mine water. However, periodic roto-tilling and back flushing has been required to keep the cells from clogging (Gusek et al. 2000). In addition, experiences at sites in Colorado and Wyoming (Reisinger et al. 2000, Farmer et al. 1995) suggest that special problems do occur when water at near freezing temperatures is treated in a passive treatment system. It appears that the system will operate reasonably well for a certain period of time and then, when there is a stress put upon the system, the sulfate-reducing capability ceases: subsequent efforts to restart SO_4 reduction prove difficult. Permeable reactive barriers are designed to include a significant fraction of gravel to ensure good hydraulic conductivity. Three permeable reactive barrier systems installed between 1995 and 2000 in Canada have been performing as designed since installation (Blowes 2001).

One issue for passive bioreactor treatment systems is a lack of consensus on design criteria. The lack of specifications for organic substrate and inorganic material fractions and physical, chemical and biological characteristics are an example. The system design by Ordonez et al. used only undefined compost for organic substrate where as Blowes (2001), Wildeman (2001), and Zaluski et al. (2006) recommend mixtures of organic substrates. There is a need for systematic physical, chemical and biological characterization of the organic substrates used in these passive bioreactor systems relative to SO_4 reducing activity and metal removal efficiency. This would allow the development of design criteria related to organic substrate specification.

This study examined the treatment of MIWs from two sources using a two-stage limestone pretreatment and anaerobic bioreactor system. The sources of MIWs were the Silver Cycle Adit (SCA) at Idaho Springs, CO, and National Tunnel Adit (NTA) at Black Hawk, CO. An OLS was used for pretreatment followed by an anaerobic biocolumn containing a mixture of corn stover and walnut shell. The organic substrate was selected to address the hydraulic conductivity concerns and substrate sustainability.

Materials and Methods

Limestone reactors

Four bench scale limestone reactors were constructed from 4-liter (L) polypropylene jugs. A hole was drilled in each reactor at a volume of 2L where the outflow tubing was connected. The reactors were filled with a limestone size of approximately 0.75-inch. The jug was filled with limestone by volume up to the 2L mark. Thus when filled with water, the limestone was in

contact with the water for the entire time that the water was in the reactor. The remaining 2L of headspace in the reactor were open to atmospheric gasses, but were lightly capped to minimize particle intrusion. Two limestone reactors were fed SCA MIW and two limestone reactors were fed NTA MIW. The influent tube from the peristaltic pump was placed so that the influent entered the reactor at the very bottom and exited from a 1/4-inch hole drilled at the 2L mark. It was assumed that the general water flow regime was as a vertical plug flow reactor. Two 10-liter reservoirs were used to separately collect the effluent from the SCA and the NTA limestone reactors

The flow rate to the limestone reactors was set at a nominal rate of 1000mL/day that corresponded with 0.6 days residence time assuming porosity of the medium of 0.3. Periodic sampling (approximately weekly) was performed to measure pH, alkalinity, dissolved and total metals. The pH was measured using a standard pH probe, and the alkalinity was determined by colorimetric titration with a HACH digital titrator. Samples for metals analysis were passed through a 0.45-micron filter (“dissolved metals”). All samples for metals analysis were acidified prior to ICP-AES analysis with concentrated HNO₃. The concentrations and properties of the influent mine water collected from the SCA and NTA are presented in Table 1.

Table 1- Typical mine water composition

Constituent	Silver Cycle	National Tunnel
Sulfate, mg/L as S	700	300
Zinc, mg/L	65-75	5-7
Iron, mg/L	40	40
Aluminum, mg/L	< 1	< 1
pH	5.0-5.5	6.0-6.5

Biocolumns

The four columns were constructed out of 30 cm long by 5 cm diameter acrylic tubes. Square flanges (4 inches) were constructed from 1/4-inch thick acrylic plates and were glued to the column tubes. Square flat acrylic plates (4-inches) were ported for 1/4 inch threaded influent and effluent fittings. A rubber gasket was used to seal the flange plates to the column flanges. A nylon screen was placed on the inside of the influent side to prevent the flow of bulk material exiting the column. A threaded (male) tube fitting was screwed into each end plate. Peristaltic pumps were used to feed either 30 mL or 60 mL per day to the biocolumns.

The columns were packed with 17 grams of corn stover and 194 grams of walnut shells (equal volumes), i.e. the substrate introduced by Zaluski et al (2006). The influent water (effluent from limestone reactors) was pumped from the bottom to the top of the biocolumn. The nominal flow rates of 30 and 60mL/day to the biocolumns, corresponded to 10 days and 5 days hydraulic residence times assuming porosity of the medium of 0.5. Periodic sampling was performed to measure outflow, pH, alkalinity, dissolved and total metals. Outflow rate was measured thorough the use of a graduated cylinder and a stopwatch. Due to the small flow rate, the effluent volume was monitored for several hours to get a significant sample volume. Alkalinity, pH and metals were measured as described previously.

Results and Discussion

Limestone reactors

All limestone reactors decreased influent iron to less than 0.1 mg/L. Effluent Zn from the limestone reactors was 45 to 55 mg/L for the SCA MIW and 1 to 2 mg/L for the NTA MIW. Effluent pH increased slightly for both sets of limestone reactors. Silver Cycle Adit MIW increased from an average pH of 5.2 to 5.8. NTA MIW increased from an average pH of 6.3 to 6.5. The effluent from the limestone reactors was fed into their respective duplicate SO_4 -reducing biocolumns. The limestone reactors were capable of Zn removal of approximately 20 mg/L for the SCA MIW and 5 mg/L for the NTA MIW. The pH and alkalinity of the treated water was not conducive to the formation of $\text{Zn}(\text{CO})_2$ or $\text{Zn}(\text{CO}_3)_2$. The removal of Zn and Cu in limestone systems has been documented (Cravotta and Trahan 1999, Watzlaf et al. 2004, Lee et al. 2002), but their fate, and method of removal remains a largely unexplored topic. Potential mechanisms of Zn removal are sorption to limestone or $\text{Fe}(\text{OH})_3$ surfaces or co-precipitation with $\text{Fe}(\text{OH})_3$ (Stumm 1992). The effluent pH of the water for the limestone reactors precludes the removal of Zn as a carbonate or hydroxide precipitate. Miller et al. (2006) observed that Zn can be removed in open limestone systems and the removal is a function of Zn to Fe ratio, Zn concentration and effluent pH. Thus, an OLS can be used to for partial Zn removal and in the case of the NTA MIW, Zn is reduced to below secondary drinking water standards (5 mg/L). The removal of Zn also serves to reduce the potential toxicity of the treated MIW to the bioreactors.

Biocolumns

Zinc and sulfate removals for the SCA biocolumns are shown in Fig. 1 and 2. The variations in initial Zn removal between the SCA biocolumns may reflect the 30-day lag in startup of the second biocolumn. Influent concentration and temperature were therefore not the same when examined with respect to startup time. The reduction of Zn to < 1 mg/L occurred for SCA biocolumns in 3 to 6 weeks for Columns 1 and 2, respectively. The maximum rate of SO_4 reduction occurred in both columns after 50 days of operation. Column 1 initial SO_4 reduction rate was almost twice the rate observed for Column 2. The lower initial sulfate reduction rate for Column 2 may have been responsible for the longer time from startup observed for significant Zn removal. Column 1 always removed more SO_4 than Column 2 over the duration of the experiments. One possibility is that early differences in temperature and flow conditions including a loss of flow between 12/29/05 and 1/04/05 caused the development of a different microbial community structure. The lack of flow would result in depletion of SO_4 and a synergistic community of fermenters, acidogens and methanogens developed in the absence of SO_4 . Column 1 had already established a healthy population of SO_4 reducer and thus was less affected by the loss of flow. Lower rates of SO_4 reduction for Column 2 may have been the result of the establishment of a competitive utilizer of soluble organic acids.

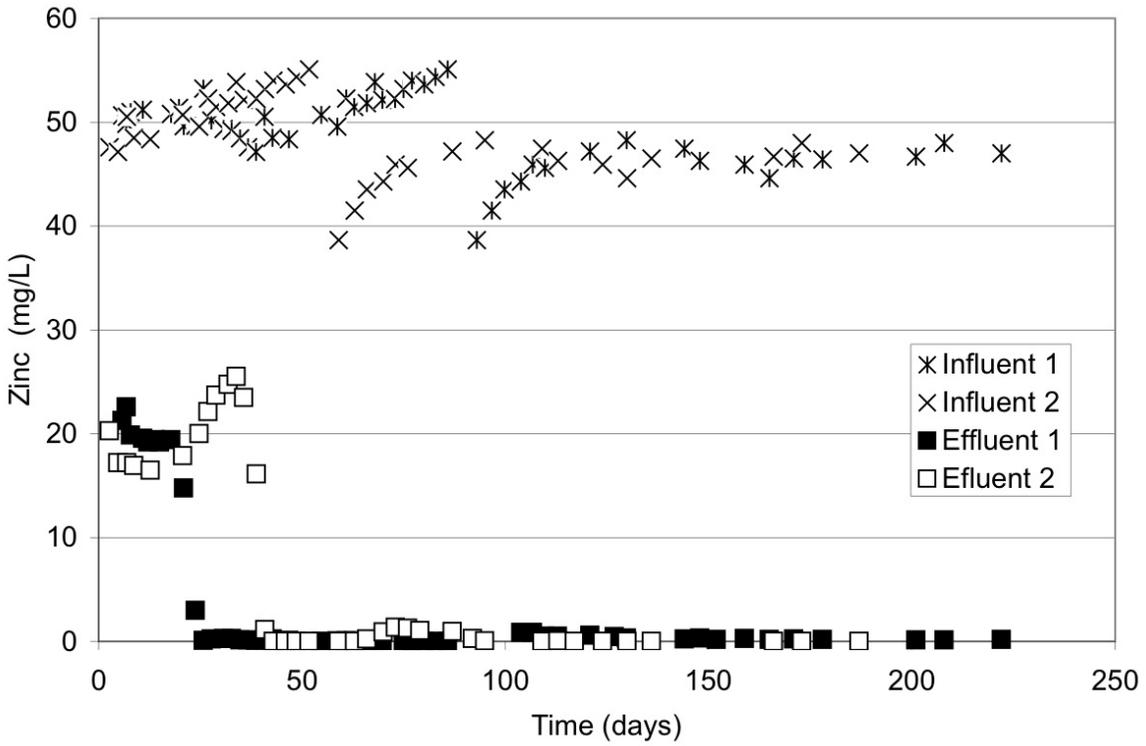


Figure 1. Influent and effluent Zinc Concentrations with Time for Silver Cycle Biocolumns

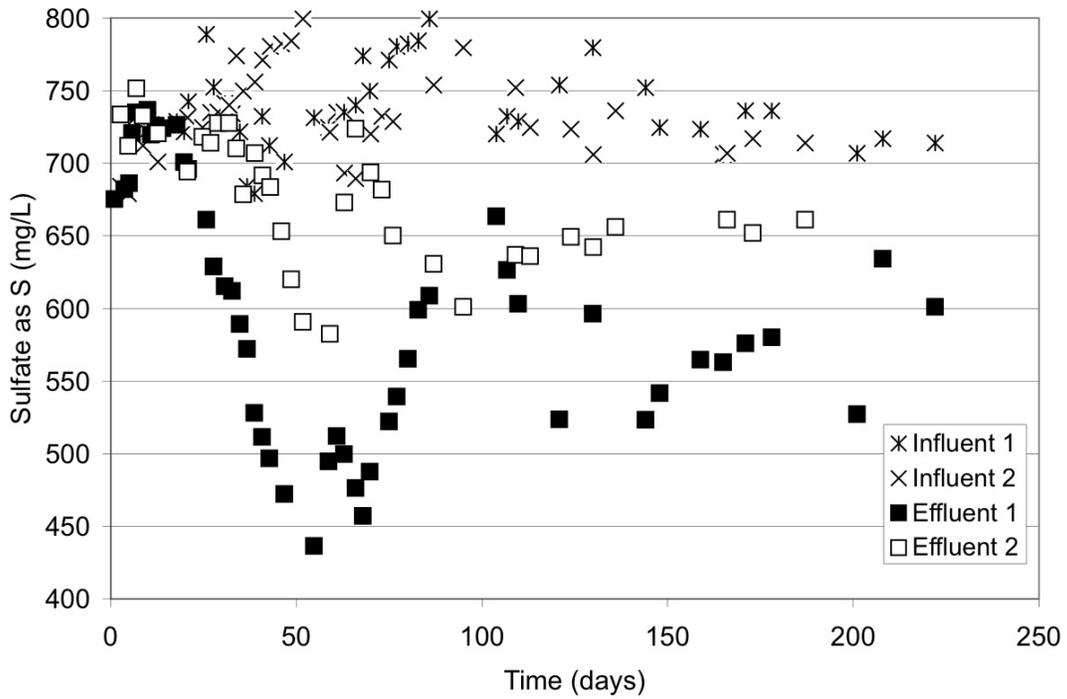


Figure 2. Influent and Effluent Sulfate Concentrations with Time for Silver Cycle Biocolumns

Zinc and sulfate removals for the NTA biocolumns are shown in Fig. 3 and 4. The reduction of zinc to < 0.1 mg/L occurred for the NTA biocolumns within 3 weeks for both columns. Sulfate removal for the two NTA biocolumns was similar as shown in Fig. 4. After one month, the sulfate reduction rate was stable at approximately 0.28 mol S/ m^3 /d. This amount of SO_4 removal rate was similar to the average amount of SO_4 removal rate observed for SCA biocolumn 1, 0.24 mol/ m^3 /d after 50 days. The average rate of SO_4 removal for SCA biocolumn 2 was only 0.13 mol/ m^3 /d after 50 days. Sulfate reduction rate was also more variable for the SCA biocolumns than for the NTA biocolumns. One hypothesis is that the system was under more stress from the higher influent Zn concentration. Zinc has been shown to inhibit the growth of both cellulolytic fermenters (Ruhs et al. 2003) and sulfate reducers (Utigikar et al. 2003).

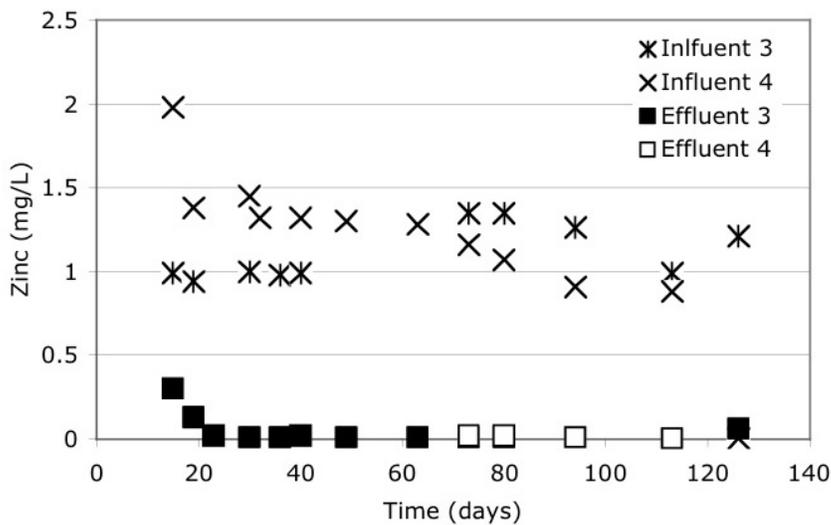


Figure 3. Influent and Effluent Zinc Concentrations with Time for National Biocolumns

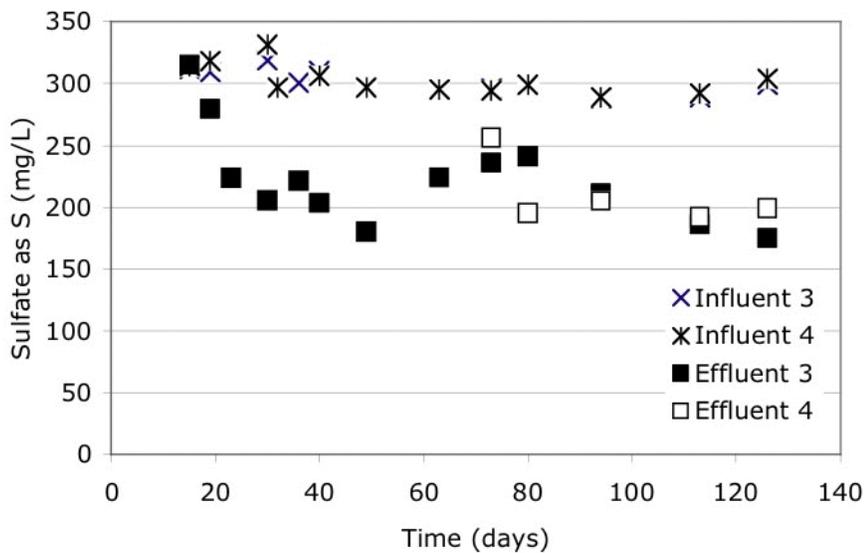


Figure 4. Influent and Effluent Sulfate Concentrations with Time for National Tunnel Biocolumns

The column flows on averaged were maintained at the target flow rates. A typical plot of measured outflow is shown for Silver Cycle Column 1 in Fig. 5, which was set to 30 mL/day. Previous column runs with more compressible and finer grain substrates have resulted in outflow reductions with time (Logan et al 2005). The limestone pretreatment system reduced the potential impact of iron hydroxides and the corn stover/walnut shell mixture facilitated the maintenance of flow.

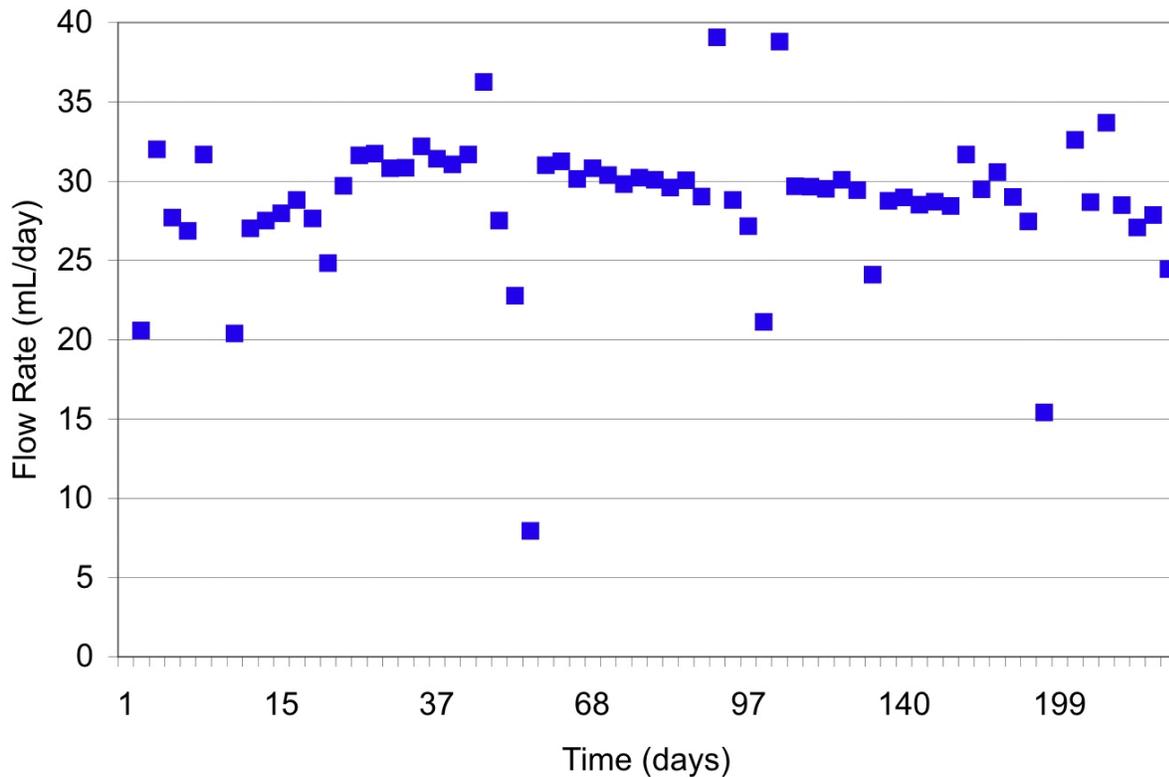


Figure 5. Measured outflow rate for Silver Cycle Column 1 with Time.

Another observation from these laboratory studies is that a designated inoculum is not required to start up sulfate reduction in bioreactors. These biocolumns only used corn stover and walnut shells as the reactive medium. Start up times for the NTA columns were comparable to times observed for biocolumns using manure as an inoculum (Logan et al 2005 and Figueroa et. al 2005). The longer start up times for biocolumns receiving SCA MIW is attributed to the inhibitory effects of Zn on the microbial community. Microbial community adaptation allowed for the establishment of comparable average sulfate reduction between the NTA columns and SCA column 1. However, the SCA columns were subject to more variation in SO_4 reduction.

Conclusions

An open limestone pretreatment of iron laden MIW can effectively reduce Fe to less than 1 mg/L. Thus, operation and maintenance issues typically associate with Fe in MIW can be avoided for anaerobic bioreactors by pretreating the MIW using OLS. A mixture of only corn stover and walnuts shells are an effective substrate and inoculum for establishing sustainable sulfate reduction. Influent zinc concentrations are important for start up time and bioprocess stability.

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