EVALUATING LONGEVITY OF VERTICAL FLOW BIOREACTORS THROUGH WATER QUALITY ANALYSIS[1]

Beatriz E. Santamaria[2] and Robert W. Nairn

Abstract. Past studies have shown the importance of carbon sources and microbial inocula on the effectiveness of microbially-based passive systems for acid mine drainage treatment. It is clear that a mixture of labile and recalcitrant carbon sources is necessary to have efficient, long-term metal removal and alkalinity generation in these systems. However, almost all studies have been performed in columns or batch experiments using known mixtures of fresh substrates, rather than comparing field-scale passive treatment systems operating for different periods of time. For this study, a batch experiment using substrate cores from existing passive treatment systems of different ages was completed. Passive treatment systems included Mayer Ranch, OK; Hartshorne, OK; Red Oak, OK and SR109, PA. Batch experiments were set up under controlled conditions and the experiment run for 168 days with a weekly change of influent synthetic AMD. In terms of pH, it was determined that the reactors received AMD with 5.5 ± 0.4 initially. Influent dissolved concentrations were 181 ± 14 mg/L Ca; 0.09 ± 0.03 mg/L Cd; 67.8 ± 8.3 mg/L Fe; 65.3 ± 4.7 mg/L Mg; 7.3 ± 1.0 mg/L Mn; 44.8 ± 5.5mg/L Na; 0.26 ± 0.08mg/L Pb; 3.9 ± 0.6mg/L Zn; and 817 ± 80 mg/L SO_4. The oldest substrate (>10 years) had a decrease in pH to 4.9 ± 0.3. However, pH increased with younger substrate age reaching 7.3 ± 0.2 in the youngest substrate. Similar results were observed with alkalinity, where the older system had an alkalinity of 6.0 ± 2.9 mg $CaCO_3$/L eq. and the youngest provided 830 ± 615 mg $CaCO_3$/L eq. Younger systems had higher sulfate reduction rates when compared to older systems. However, the rate decreased over time of the experiment. Results suggest that the performance of reactors declines with age of substrate. Chemical characterization of the organic substrates will provide insight into processes that account for observed differences in water quality.

Additional Key Words: acid mine drainage, batch reactors, passive treatment, organic substrate, sulfate reduction rates

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Introduction

Mining activities including extraction and beneficiation cause detrimental impacts to the environment which are exacerbated when mines are no longer profitable leading into abandonment. Mine abandoned prior to passage of environmental regulations, often carry with them great amounts of waste and polluted water as well as open pits and mine shafts. Once abandoned, underground mines can fill up with water leading to the oxidation and dissolution of minerals present on the mine surfaces creating what is commonly referred to as acid mine drainage (AMD) (Banks et al., 1997; Watzlaf et al., 2004). AMD, which often has low pH and elevated trace metals concentrations, can flow out of the underground mine through open shafts and pits. AMD has been documented to pollute groundwater aquifers, damage lakes' and rivers' aquatic life and habitat as well as cause land exposure through plant metal toxicity (EPA, 2004).

In United States alone there are approximately 200,000 abandoned hard rock mines (EPA, 2004), and yet more abandoned coal mines. Cleanup of the abandoned mines has proved to be an economic burden. According to EPA (2004) it has been estimated that it costs around $22 million on average to remediate one hard rock mining site. Cleanup efforts include removal and disposal of mining waste and treatment of AMD. Treatment of AMD can be done by two ways, active or passive (Johnson and Hallberg, 2005; Watzlaf et al., 2004; Younger et al., 2002). Active treatments are often not suitable for abandoned mines since these are often located in remote areas and these systems need constant operation and maintenance. An alternative for active treatment began to develop in early 1980s (Younger et al., 2002; Watzlaf et al., 2004). Passive treatment relies on natural processes for the attenuation of AMD. Passive treatment requires less operation and maintenance when compared to active treatments making them the preferred choice in difficult to access areas (Johnson and Hallberg, 2005).

Vertical flow bioreactors (VFB), also known as reducing and alkalinity-producing systems, (RAPS) are one of the most important units of passive treatment (Johnson and Hallberg, 2005; Watzlaf et al., 2004). These anaerobic cells rely on organic substrates for the supply of carbon for microbial activities. Sulfate reducing bacteria (SRB) use the carbon supplied in the substrate to reduce sulfate to sulfide and enhance the precipitation of metals as metals sulfides (Watzlaf et al., 2004). Previous research have compared different organic substrates and their long term efficiency (Waybrant et al., 1998; Cocos et al., 2002; Waybrant et al., 2002; Figueroa et al.,

2004; Watzlaf et al., 2004; Pruden et al., 2007). However, there is still discussion as to which is the optimum mixture of substrates. Additionally although the decline of efficiency with time has been documented there is no systematical study comparing the effectiveness of substrates from systems of different ages. Therefore, substrates from different aged systems were compared for their improvement of water quality under controlled laboratory conditions. This paper describes the changes of water quality for each system analyzed. It was hypothesized that the water quality improvement will decline with time as each substrate "ages".

Methodology

<u>Site Description</u>

<u>SR109, Pennsylvania.</u> SR109 is located in Slippery Rock Creek Watershed on Pennsylvania Game Lands No. 95 in Washington Township, Butler County, Pennsylvania. SR109 was built in September 1998 to treat coal mine drainage from what appears to be an old mine portal. The discharge is collected by a small check dam and pond flowing into a rock lined channel, followed by a VFB (VFP-1) (Fig. 1). Water flows from the VFB into a wetland (WL) discharging later into a rock lined channel that flows into an unnamed stream. The 0.12ha VFB was built to contain a 0.30 m thick layer of spent mushroom compost over 1 m layer of AASHTO #1 limestone (Stream Restoration Incorporated pers. comm.). Substrate samples were collected from this cell. Water quality samples were collected by the Pennsylvania Department of Environmental Protection (PA DEP) or Stream Restoration Inc./Biomost and analyzed by either the PA DEP laboratory or by G&C Coal Analysis lab. Water from the discharge varies from net acidic to net alkaline, with acidic pH and elevated concentrations of sulfate, Fe, Al and Mn.
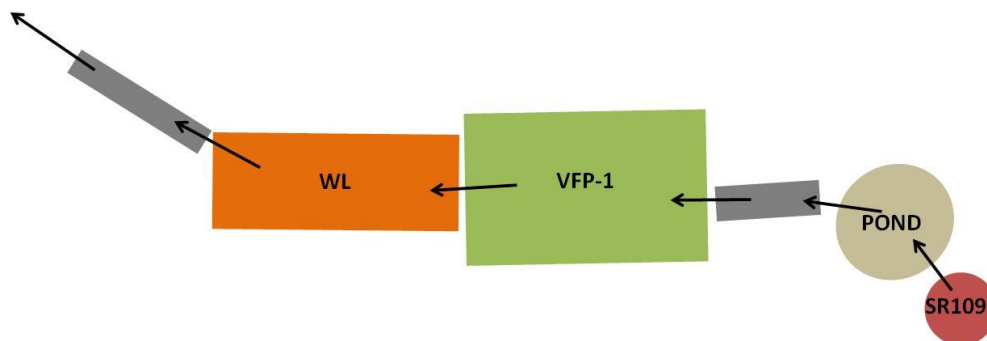

Figure 1. Diagram of SR109 passive treatment system showing the direction of flow.

Red Oak, Oklahoma. Coal mining in the Bache and Denman underground mine occurred from 1907 until 1925 when it was abandoned (Nairn, 2004). The Red Oak system (RO) is located near Red Oak in eastern Latimer County, Oklahoma. RO has a total of 5 cells consisting of an oxidation pond (OP), two VFBs and two surface-flow (SF) ponds (Fig. 2). Surface areas for individual cells vary and the first VFB has an approximate surface size of 0.075 ha (Nairn, 2004). Construction of the system was finalized in October 2001 but problems delayed AMD flow until October 2002 and it has been flowing ever since. A high alkaline coal combustion product (CCP) was injected into the mine in 1997 and 2001 significantly changing mine water quality from the seep (Nairn, 2004; Winfrey et al., 2008). Before injection water from the seep was net acidic, with low pH and higher metal concentration changing into higher alkalinity, circumneutral pH with lower metal concentrations after CCP injection (Winfrey et al., 2008). Substrate samples were collected from the first VFB. The cell consists of a top layer of 1 m of standing water, a middle layer with 1 m of stable waste mix and limestone, and a 0.60 m bottom layer of gravel (Nairn, 2004). The middle layer was built in an approximate 2:1 ratio by volume of horse manure/sawdust mix with high quality limestone (Nairn, 2004). Water quality analysis was completed by the OU Center for Restoration of Ecosystems and Watersheds (CREW) biweekly starting November 2002 until December 2003 and then monthly until December 2004. Water entering the first cell has circumneutral pH and elevated concentration of sulfate, Fe, Mn and Al (Nairn, 2004).

Rock Island #7, Oklahoma. Rock Island Coal Company #7 mine passive treatment system (RI7) is located near Hartshorne, Pittsburg County in Oklahoma. The mine was abandoned in the 1930s and mine drainage starting flowing through an open fan shaft (LaBar et al., 2008). Extreme variations in water quality parameters was observed during late 1990s and early 2000s, but in general the mine drainage was net acidic with elevated concentrations of iron and manganese (LaBar and Nairn, 2009). This 12 cell system is more complex than the previous two systems. Mine water flows through a vertical anoxic limestone drain (VALD) into a series of three oxidation ponds further divided by re-aeration berms (Cell 1, 3 and 5), two VFBs (Cell 2 and 4), and a polishing wetland (PW) (Fig. 3). Construction of the system was finished by summer 2005 but water did not start flowing into the system until January 2007 due to a severe drought that affected Oklahoma (LaBar and Nairn, 2009). Samples were collected from the fist VFB (Cell 2), or the first VFB. The cell has an approximate surface area of 0.064 ha with a

bottom layer of 1 m of high calcite limestone covered by 0.5 m of spent mushroom compost (LaBar and Nairn, 2009). Water quality was monitored periodically from January 2007 until June 2008. Water from the VALD continues to be net acidic with elevated metals concentrations, sulfate and chloride with values varying greatly (LaBar and Nairn, 2009).
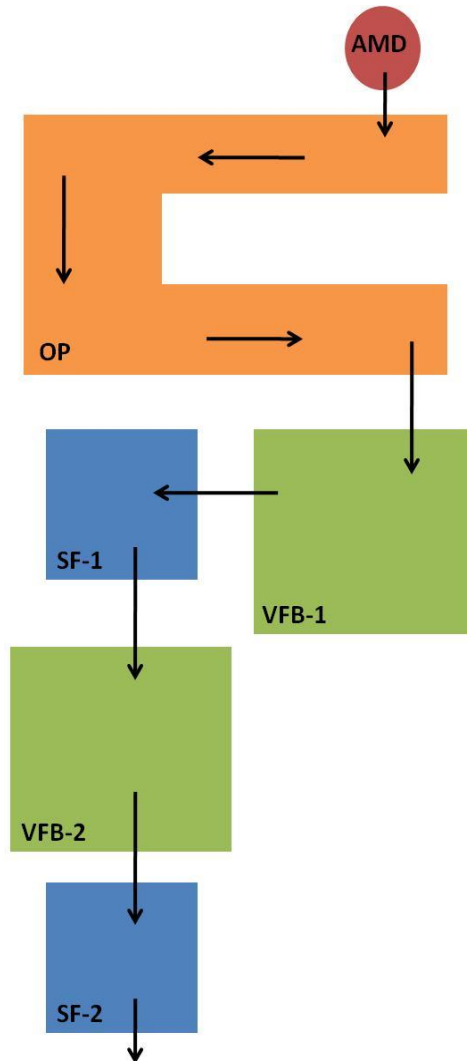

Figure 2. Diagram of RO passive treatment system showing the direction of flow.
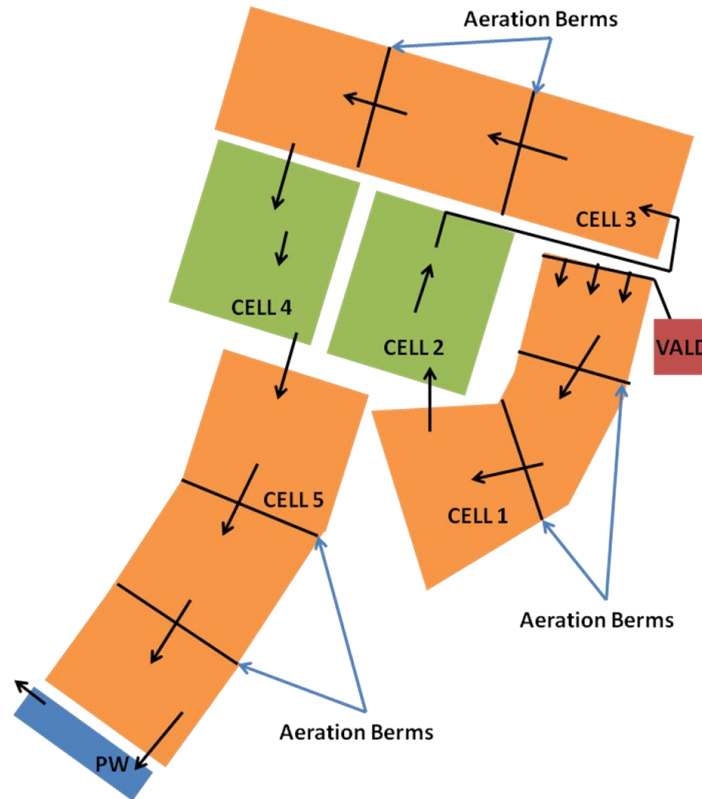
Figure 3. Diagram of RI7 passive treatment system showing the direction of flow.

<u>Mayer Ranch, Oklahoma.</u> The Mayer Ranch system (MR) is located in Ottawa County near Commerce, Oklahoma. It is part of the Tar Creek Superfund Site, the Oklahoma portion of the Tri-State Lead-Zinc Mining District. Pb and Zn ores were mined in the Tar Creek area from early 1900s until it ceased in early 1970s (Nairn et al, 2009). The passive treatment system receives water from three borehole discharges (SA, SB and SD) and was designed with a common oxidation pond followed by two parallel trains to allow for maintenance redundancy and experimentation (Fig. 4). Construction was completed late 2008 with a total of 10 cells. Water from the seeps flows into an oxidation pond. Water is equally divided at the outflow of this pond flowing into pairs of surface flow wetland/ponds (C2S and N), VFBs (C3S and N), re-aeration ponds (C4S and N) and horizontal-flow limestone beds (C5S and N). Water is combined at the outflow of the limestone beds flowing into a polishing wetland and then into an unnamed tributary (C6). The VFBs sampled (referred to as MR3S and MR3N in results) were built by using a mixed compost layer containing 45% spent mushroom compost, 45% hardwood

chips and 10% manufactured limestone sand (Nairn et al., 2009). Water quality in Tar Creek and its tributaries has been monitored from 1998 with a monthly sampling schedule beginning in 2004 (Nairn et al., 2009). AMD entering the system is net alkaline with elevated concentrations of Fe, Zn, Pb and Cd.
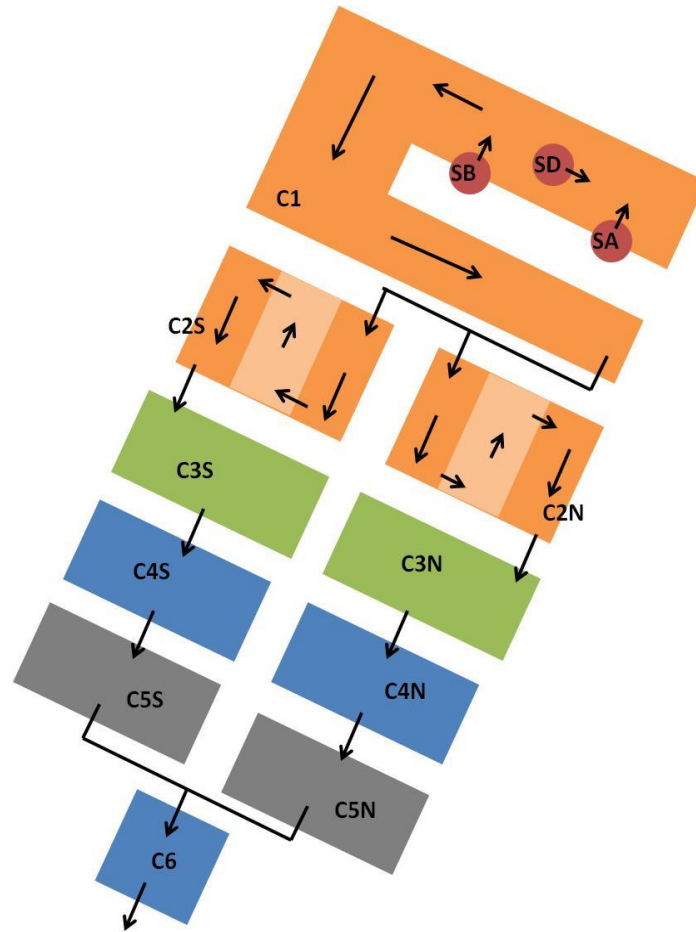

Figure 4. Diagram of MR passive treatment system showing the direction of flow.

Impacted Volunteer Wetland, Oklahoma. The impacted cattail marsh (MRF) was located in Ottawa County near Commerce, Oklahoma. Mine water flowed though the wetland discharging into an unnamed tributary. The wetland was removed for the construction of the MR system in July 2008. Water from the seeps had circumneutral pH, net alkalinity and elevated concentrations of Fe, Zn, Pb and Cd.

Substrate Collection

Substrate was collected from five different sites, four of which were passive systems. In each site, a composite sample was collected and used for experimental analysis. Care was taken

in order to maintain anaerobic conditions at all times, since oxygen can affect the microbial composition of the organic substrates. Of the five systems, four were from VFBs belonging to RAPS, and one from a contaminated zone from the Tar Creek Superfund Site (Table 1). Samples from each site were collected by different methods (Table 1). The samples were collected into 0.5 L Whirl-Pack® sterile bags. Air was removed from the bags to ensure anaerobic conditions. The sample bags were then put into a cooler with ice and taken to University of Oklahoma CREW laboratories for analysis and construction of reactors.

Construction of Batch Reactors

   Batch reactors were built with substrate from a single site in quadruplicate by using 1-L cubitainers. Each reactor contained approximately a 1:2 AMD:substrate ratio. Substrate dry weight was determined in triplicate prior to the construction of the batch reactors. Approximately 5 g of wet substrate was weighed and dried at 105˚C for 24 hours. Since more than one bag was collected for each substrate a composite sample was prepared inside an anaerobic chamber by using the collected moist material, accounting for the dry weight for each bag. The reactors were rinsed with simulated mine drainage from a common source for seven weeks to allow for establishment of substrates. After seven weeks, effluent samples were collected on a monthly basis for 20 weeks. The reactors were incubated at room temperature (~20° C) taking care to minimize head space in the cubitainers after the addition of AMD.

Mine Water Formulation

   All substrate reactors received synthetic mine drainage from a common source. Synthetic AMD was prepared weekly based on values previously reported in the literature (Pruden et al., 2007) as well as using average values for coal mines as reported in Watzlaf et al. (2004). Simulated AMD was prepared by adding 150mg/L Na_2SO_4, 5mg/L NH_4Cl, 15mg/L $ZnSO_4 \cdot 7H_2O$, 0.4 mg/L $Pb(NO_3)_2$, 20mg/L $MnSO_4 \cdot H_2O$, 600mg/L $MgSO_4 \cdot H_2O$, 500mg/L $CaSO_4$, 0.1 mg/L $CdSO_4 \cdot {}^{8}/_{3}H_2O$ and 240 mg/L $FeSO_4 \cdot 7H_2O$ to deionized water. Resulting synthetic AMD contained in 181 ± 14 mg/L Ca; 0.09 ± 0.03 mg/L Cd; 67.8 ± 8.3 mg/L Fe; 65.3 ± 4.7 mg/L Mg; 7.3 ± 1.0 mg/L Mn; 44.8 ± 5.5mg/L Na; 0.26 ± 0.08mg/L Pb; 3.9 ± 0.6mg/L Zn; and 817 ± 80mg/L SO_4.

Table 1: Sample site classification, characteristics and method of collection.

Category	System	System ID	Method of collection
Senior (>10 yrs)	SR109, PA	SR109	Cell drained overnight. Substrate collected with 6-in PVC pipe
Adult (5-10 yrs)	Red Oak, OK	RO	Substrate collected with soil auger and Shelby tubes from a canoe
Adolescent (1-5 yrs)	Hartshorne, OK	RI-7	Substrate collected with a Russian peat auger
New Born (<1 yr)	Mayer Ranch, OK	MR3S & MR3N	Substrate was collected at the time of construction using a shovel
Contaminated Site	Tar Creek, OK	MRF	Substrate collected with a Russian peat auger

Water Quality Analysis

Water from the reactors was analyzed for dissolved oxygen (DO), pH, specific conductance (SC), total alkalinity, total and dissolved metals and anions on a monthly basis. SC, DO and pH were measured by using an Accumet AR60 bench top multimeter. Alkalinity was measured by titrating 25 mL of sample to the end point of bromocresol green/methyl red indicator (pH 4.5) with 1.6 N H_2SO_4 acid by following HACH 8203 Methods. Dissolved metals were collected by passing samples through a 0.45μm filter. Dissolved and total metals were digested by EPA Method 3015 and then analyzed by Varian Vista-PRO® ICP-OES (Inductively-coupled Plasma, Optical Emission Spectrometer) following EPA method 6010. Anions were analyzed by EPA Method 300 on a MetrOhm® 761 compact ion chromatograph.

Results and Discussion

pH and Alkalinity

Results for changes in pH and alkalinity can be observed in Fig. 5 and 6, respectively. Younger systems had a higher pH increase when compared to the oldest operating system. In contrast, alkalinity generation was stable for older systems through the time of experimentation decreasing over time for MR3 systems. Differences in the changes in pH and alkalinity could be due to incorporation of limestone into the substrates of MR3N, MR3S, RO and RI7. Ca values increased in the effluent during the time of experimentation suggesting that limestone dissolution

was a contributor for pH and alkalinity generation (see below). Whenever possible, bigger sizes of limestone were removed at time of experimental set-up, however the MR3 systems had sand size limestone which made its removal difficult. These results could be explained by the nature of the organic substrates including the acid neutralization capacity (ANC) of the soil, sulfate reduction rates and organic ligand exchange (Wieder, 1993; Waybrant et al., 1998, 2002).

Dissolved Oxygen

Change in DO values over time are identified in Fig. 7. DO was below 2mg/L for all reactors. Older systems had lower decrease in DO when compared to new systems. DO stripping is a key function for VFB performance, promoting microbial and chemical reactions that enhance alkalinity generation. As noted by Watzlaf et al. (2004) the anoxic conditions generated in the organic layers of VFBs are created through biotic and abiotic oxygen demand components of the substrate which may have been limited in SR109, RI7 and MRF.
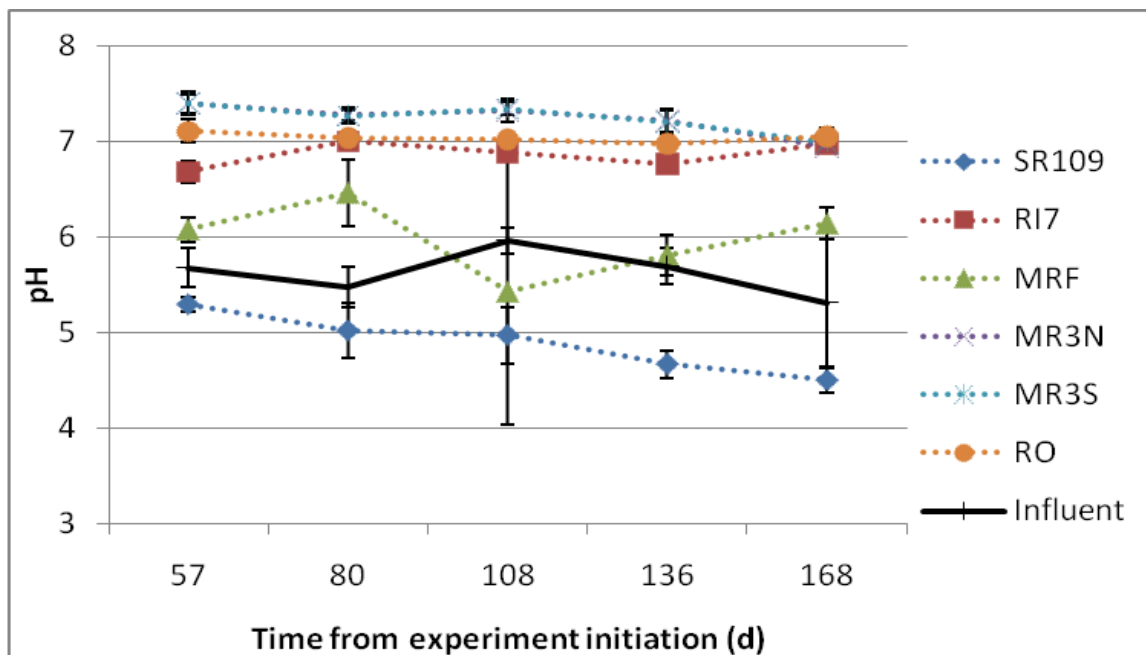

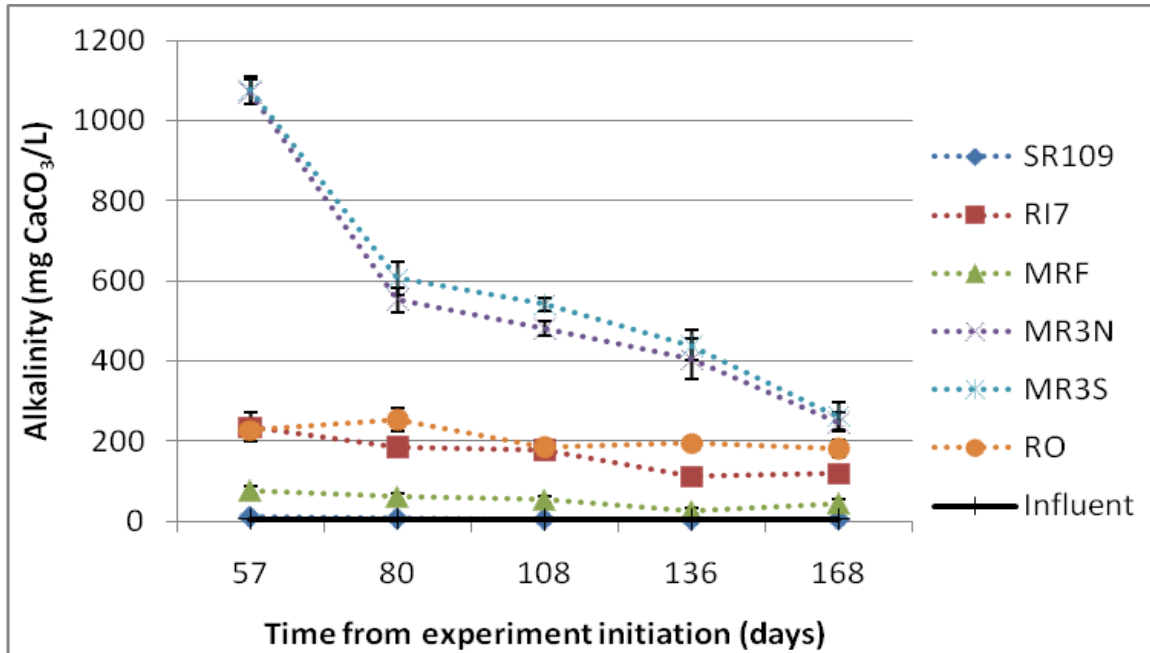Figure 5. Changes in pH for different mine drainage reactors.

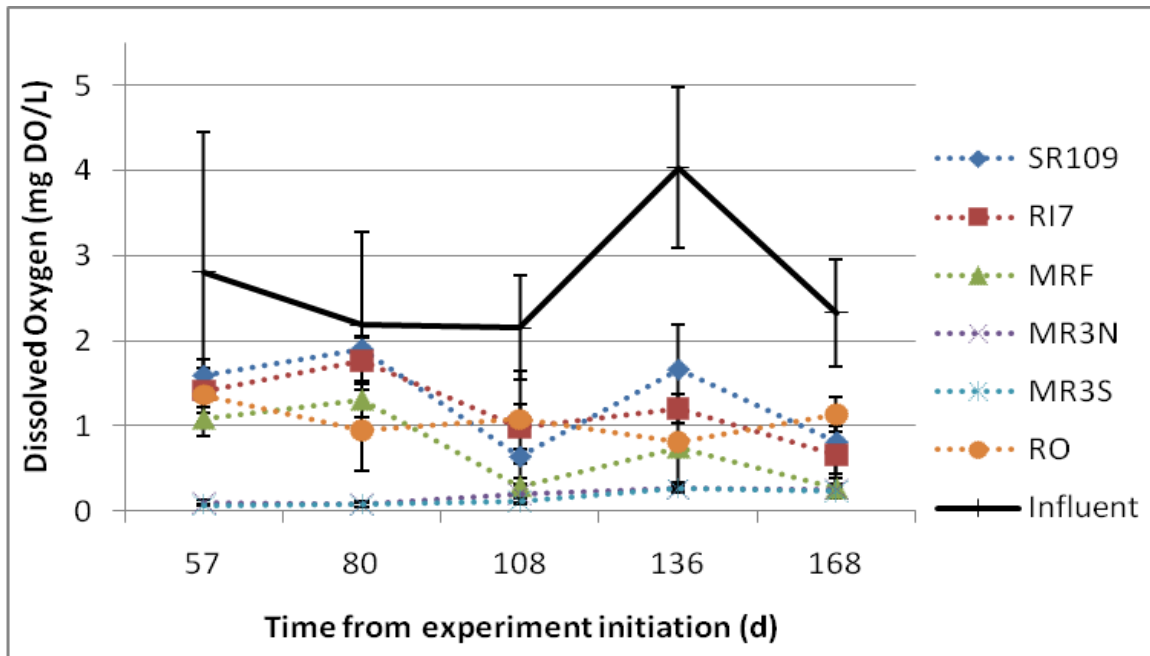Figure 6. Changes in alkalinity for different mine drainage reactors.

Figure 7. Dissolved oxygen concentration for different mine drainage reactors.

Sulfate reduction rates

   Influent and effluent concentrations of sulfate can be observed in Fig. 8. MR3N and MR3S had the lowest sulfate concentrations which increased through the time of experiment. Sulfate

reduction rates (SRR) were also calculated (Fig. 9). RO, MR3N and 3S had higher SRR. Neculita et al. (2007) reports that the optimal SRR observed in the field is 0.3 mol/m^3-d. However, laboratory batch reactors using different reactive mixtures observed a SRR of 0.5 to 0.75 mol/m^3-d (Waybrant et al.; 2002). Field experiments using pilot scale bioreactors built with spent mushroom compost carried by Dvorak et al. (1992) found a SRR similar to those reported by Neculita et al. (2007), 0.214 to 0.33 mol/m^3-d. As pointed out by Neculita et al. (2007) batch reactors usually have higher SRR when compared to column and field VFBs which can be due to the differences in hydraulic retention times and variability of initial sulfate concentrations.

Past studies have shown that columns built with organic wastes need time to reach a pseudo steady-state (Pruden et al., 2007; Waybrant et al., 1998, 2002; Zagury et al., 2006). These results suggest that MR3N and 3S reactors were still adapting to the influent AMD although they were rinsed for 7 weeks prior to starting analysis. The decline in sulfate reduction could be explained by the use of the labile organic substrates by SRB. It has been shown in previous experiments that organic wastes contain a higher amount of simple sugars that are depleted over time (Waybrant et al., 1998, 2002). Older systems like SR109, RI7 and RO had higher sulfate effluent concentration that at points were higher than the influent concentration suggesting lower SRB activity. Zagury et al. (2006) observed a similar behavior when doing batch reactors experiments with single substrates attributing the results to inhibitory characteristics of the substrates. As shown in previous studies, SRB thrive in an environment with pH 5 to 8 and a Zn concentration of <40mg/L (Neculita et al., 2007). Influent Zn concentrations were 4.01+0.52 mg/L, considerably lower than inhibitory levels. SRB are heterotrophic or autotrophic bacteria that need an anoxic to anaerobic environment with redox potential lower than -100 mV (Neculita et al., 2007).

DO values suggest that older systems with DO values >1 mg/L may have had an inhibitory effect on SRB. However, microenvironments created within the substrate may be responsible for the sulfate reduction observed in some of the older systems (Fortin et al., 1996; Stockdale et al., 2009). As observed in the field, the organic layer in the VFBs creates the anaerobic conditions favorable for SRB through the oxidation of organic substrates (Watzlaf et al., 2004). Additionally, as mentioned above decreases in sulfate reduction rates in older systems may also be accompanied by a reduction in the simple organic sugars initially present in the organic

wastes (Waybrant et al., 1998, 2002); suggesting that this may also had an effect in sulfate reduction rates in older systems.
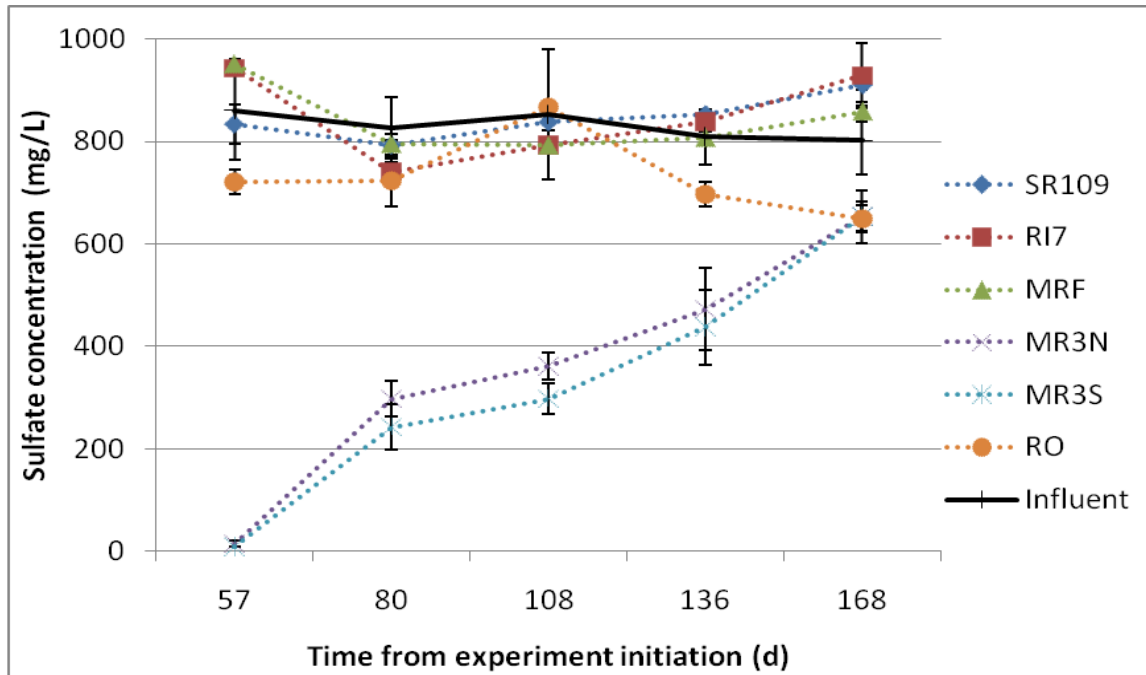

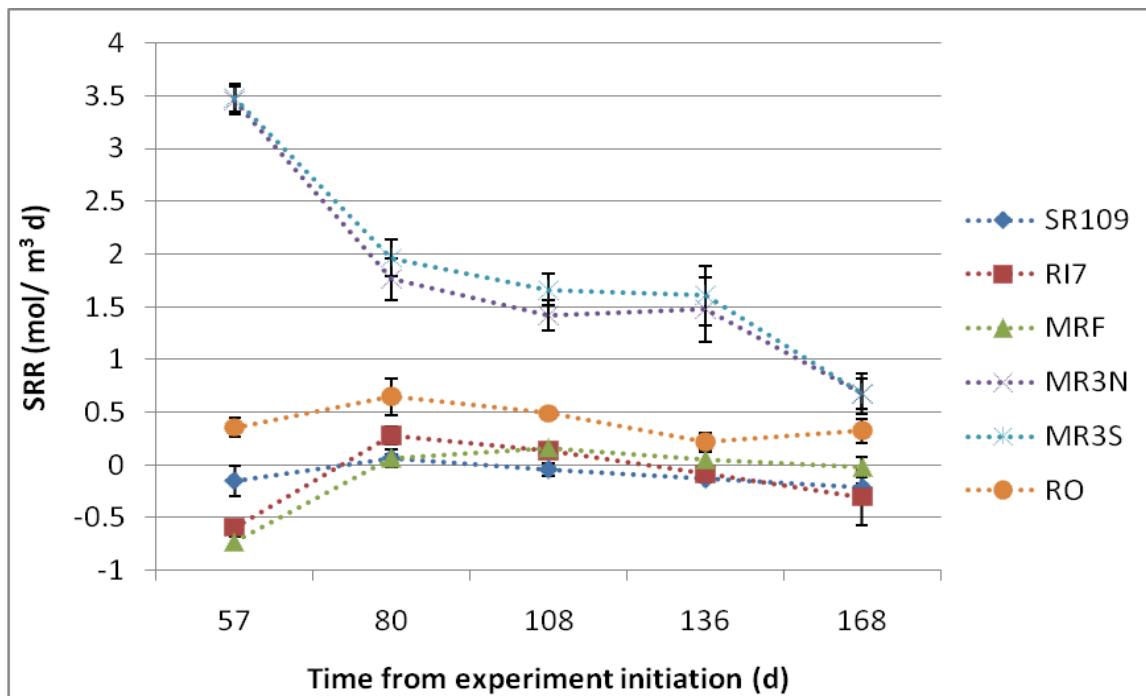Figure 8. Influent and effluent concentration of sulfate for different mine drainage reactors.

Figure 9. Sulfate reduction rates for different mine drainage reactors.

Calcium removal

Ca increased to up to 80% in RI7 reactors (Fig. 10). However, MR3N and S reactors had lower Ca values at the first point increasing through the time of experimentation (Table 2). MRF, RI7 and RO elevated concentrations of Ca could be due to accumulation of Ca in substrates overtime as shown by substrate analysis of Ca (data not shown). This increase could be due to the precipitation of Ca as calcite, aragonite and gypsum in the substrates over time (Waybrant et al., 1998, 2002; Zagury et al., 2006). Additionally, limestone dissolution may have increased the concentrations of Ca in the effluent as indicated by the increase of pH and alkalinity. Past studies in passive treatments have observed an increase in Ca in the effluent water due to dissolution of limestone (Athay, 2003). Furthermore, Hedin et al. (1994) observed that the increase in alkalinity in AMD is closely followed by Ca concentration in the effluent water attributed to calcite dissolution.
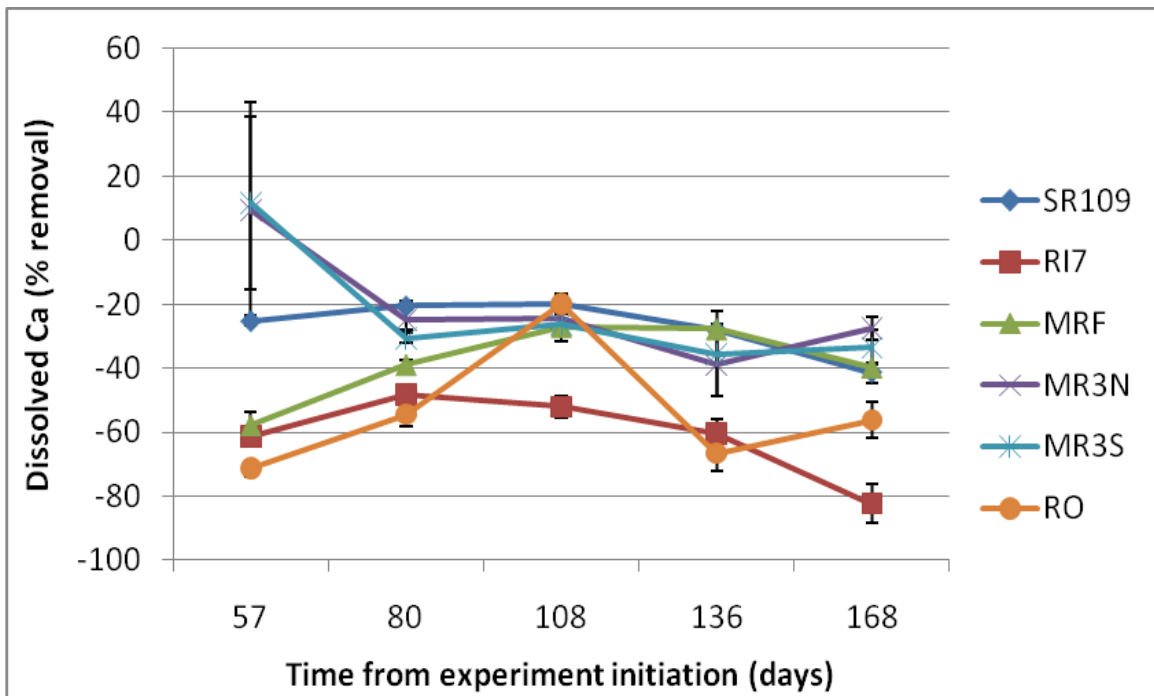

Figure 10. Percent removal of Ca for different mine drainage reactors.

Table 2: Influent and effluent values of Ca for reactors at different times. All values in mg/L.

Time Point	Influent		SR109		RI7		MRF		MR3N		MR3S		RO	
	mean	Std Dev	mean	Std Dev	mean	Std Dev	mean	Std Dev	mean	Std Dev	mean	Std Dev	mean	Std Dev
57	170	3	232	3	298	1	292	8	156	57	152	47	287	4.
80	180	8	229	4	281	4	264	2	218	5	228	3	273	7
108	178	12	230	6	291	6	243	4	213	6	216	10	303	2
136	202	44	232	3	291	8	232	2	238	16	233	23	284	10
168	182	13	256	6	330	11	253	1	249	7	260	10	264	10

Cadmium removal

Cd was removed in all reactors below detection limits (BDL).   Influent Cd concentrations were 0.07 ± 0.02mg/L with effluent values below 0.01mg/L for all reactors. Cd can be removed through precipitation as CdS (Hedin et al., 1994; Watzlaf et al., 2004), adsorption to Fe(III)-hydroxides (Olivie-Lanquet et al., 2001; Carroll et al., 1998) and adsorption to organic ligands (Fristoe and Nelson, 1983). The high removal rates of Fe and the observation of Fe precipitates suggests that adsorption to Fe(III)-hydroxides may have occurred in all reactors. Adsorption to organic ligands is most favorable in pH 4-5 suggesting that this mechanism may have occurred in the SR109 reactors which had a pH in this range.   Finally, sulfate values suggest that precipitation as CdS most likely occurred in MR3N and 3S as well as RO.

Iron removal

Fe was removed in all reactors during the experiment (Table 3). MRF exhibited the lowest percent removal (Fig. 11). Removal mechanisms for Fe include formation of Fe-hydroxides (Hedin et al., 1994; Watzlaf et al., 2004), FeS (Kolmert and Johnson, 2001), combination with organic ligands (Fletcher and Beckett, 1987) and co-precipitation with phosphate (Omoike and Vanloon, 1999). The presence of DO as well as the observation of orange precipitates in MRF, RI7 and SR109 reactors indicate that dissolved Fe was most likely removed as Fe(III)-hydroxide. Furthermore, Hedin et al. (1994) and Watzlaf et al. (2004) showed that Fe(II) in the presence of oxygen oxidizes and precipitates, which was the case for all reactors. Sulfate reduction values suggest that FeS may have been observed in MR3N and 3S reactors.   The observed concentrations of phosphate in MR3N and 3S reactors (data not shown) suggest that Fe may have been removed through this mechanism as well.
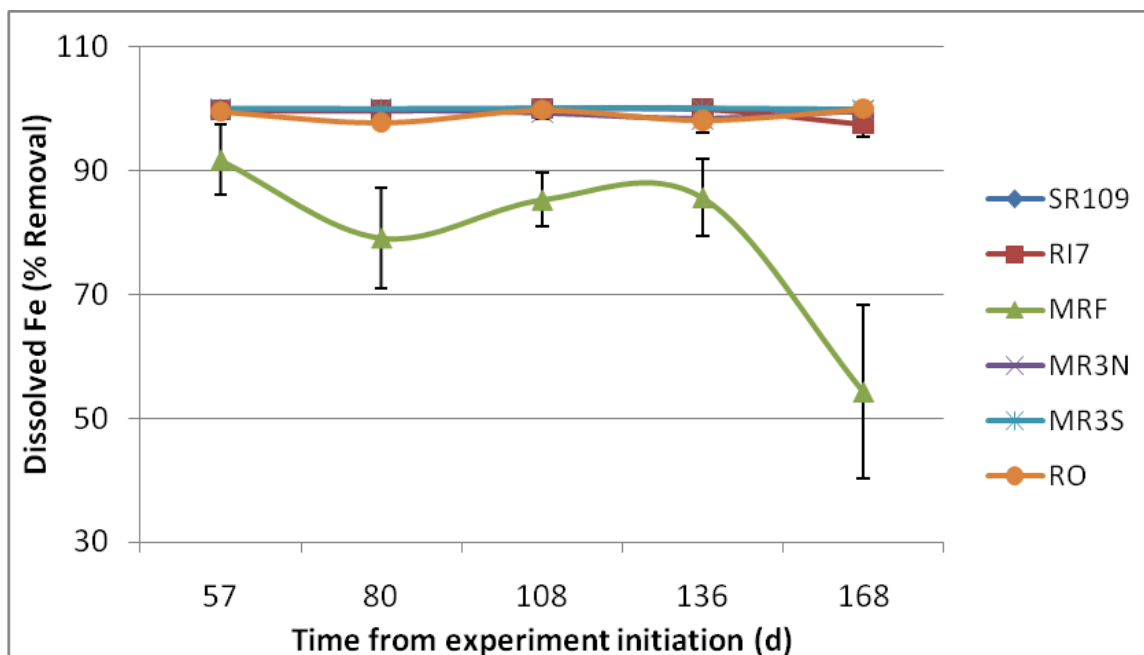
Figure 11. Percent removal of Fe for different mine drainage reactors.

Table 3: Influent and effluent values of dissolved Fe for reactors at different times. All values in mg/L.

Time Point	Influent		SR109		RI7		MRF		MR3N		MR3S		RO	
	mean	Std Dev	mean	Std Dev	mean	Std Dev	mean		mean	Std Dev	mean	Std Dev	mean	Std Dev
57	68	6	0.12	0.088	0.11	0.09	5.0	3.5	0.08	0.08	0.02	0.04	0.26	0.21
80	71	6	0.20	0.126	0.23	0.16	16.0	6.3	0.09	0.03	0.05	0.014	1.46	0.17
108	64	14	<0.004	N/A	<0.004	N/A	11.1	3.4	0.43	0.66	<0.004	N/A	0.12	0.03
136	67	1	<0.004	N/A	<0.004	N/A	9.5	4.2	1.08	0.66	<0.004	N/A	0.88	1.012
168	64	11	0.34	0.14	1.67	1.43	31.3	9.5	0.18	0.09	0.12	0.04	<0.004	N/A

N/A not applicable

Lead removal

Most Pb concentrations decreased to below detection limits (BDL) throughout the experiment (Table 4). In general RO had the lowest removal of Pb throughout the experiment followed by MRF (Fig. 12). MR3N and MR3S had similar removal rates which stayed constant through the time of experiment. SR109 and RI7 had a similar behavior having a drop in the percent removal at the last data point. Pb can be removed through formation of PbS (Hedin et al., 1994; Watzlaf et al., 2004; Younger et al., 2002), adsorb and co-precipitate with Fe(III)-

hydroxides (Carroll et al., 1998), and by absorbing to organic ligands (Fletcher and Beckett, 1987). Data from this experiment suggest that Pb is removed as PbS in reactors with sulfate reduction like MR3N and S, co-precipitating with Fe(III)-hydroxides as well as adsorption to the organic substrate in all reactors.
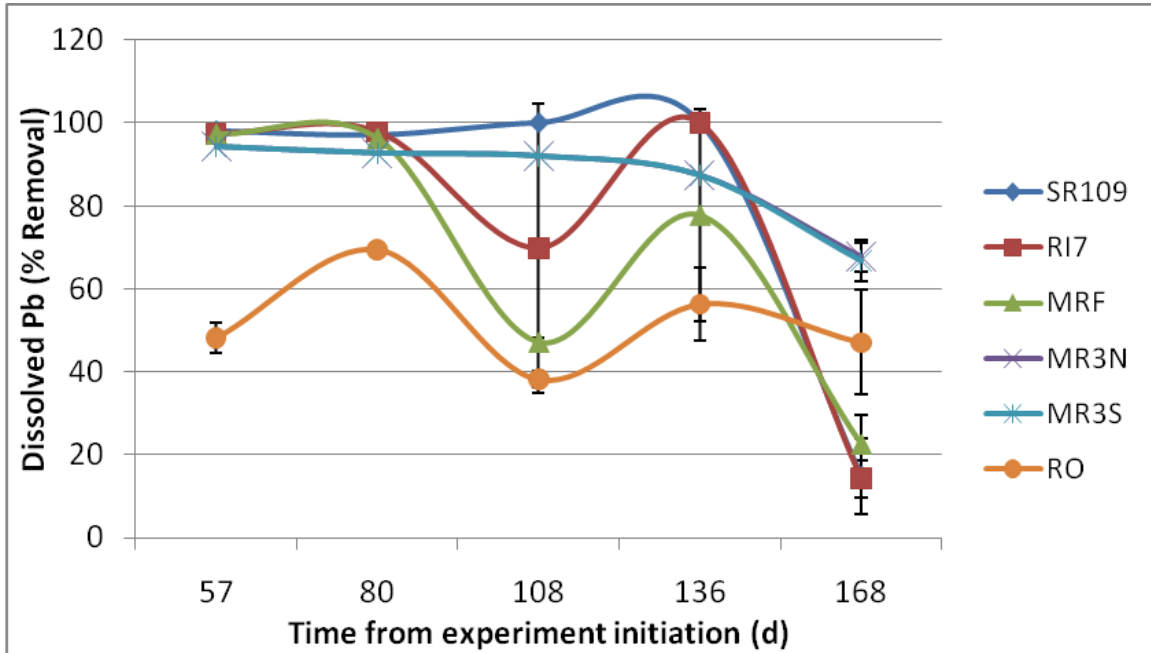

Figure 12. Percent removal of Pb for different mine drainages reactors.

Table 4: Influent and effluent values of dissolved Pb for reactors at different times. All values in mg/L.

Time Point	Influent		SR109		RI7		MRF		MR3N		MR3S		RO	
	mean	Std Dev	mean	Std Dev	mean	Std Dev	mean	Std Dev	mean	Std Dev	mean	Std Dev	mean	Std Dev
57	0.25	0.11	<0.01	N/A	0.01	N/A	<0.01	N/A	<0.01	N/A	<0.01	N/A	0.09	0.006
80	0.31	0.05	<0.01	N/A	0.01	N/A	<0.01	N/A	<0.01	N/A	<0.01	N/A	0.10	0.005
108	0.24	0.01	<0.01	N/A	0.07	0.07	0.119	N/A	<0.01	N/A	<0.01	N/A	0.10	0.003
136	0.21	0.09	<0.01	N/A	0.01	N/A	0.074	0.073	<0.01	N/A	<0.01	N/A	0.107	0.022
168	0.23	0.07	0.12	0.01	0.12	0.01	0.113	0.01	0.088	0.01	0.09	0.013	0.138	0.033

N/A not applicable

Zinc removal

Influent and effluent Zn concentration are documented in Table 5. Calculated Zn removal rates were over 80% for all reactors (Fig. 13). Zn can be removed from solution as ZnS (Hedin et al., 1994; Watzlaf et al., 2004; Younger et al., 2002), through adsorption to Fe(III)-hydroxides (Fletcher and Beckett, 1987; Norton et al., 2004; Gibert et al., 2005), and through adsorption to organic ligands (Fletcher and Beckett, 1987; Gibert et al., 2005; Machemer and Wildeman, 1992; Norton et al., 2004). ZnS formation was most likely observed in MR3N and 3S reactors where sulfate changes suggest sulfate reduction was occurring. Zn may have precipitated in reactors with Fe(III)-hydroxides formation. Adsorption to organic ligands may have played a smaller role in the removal of Zn for all reactors.
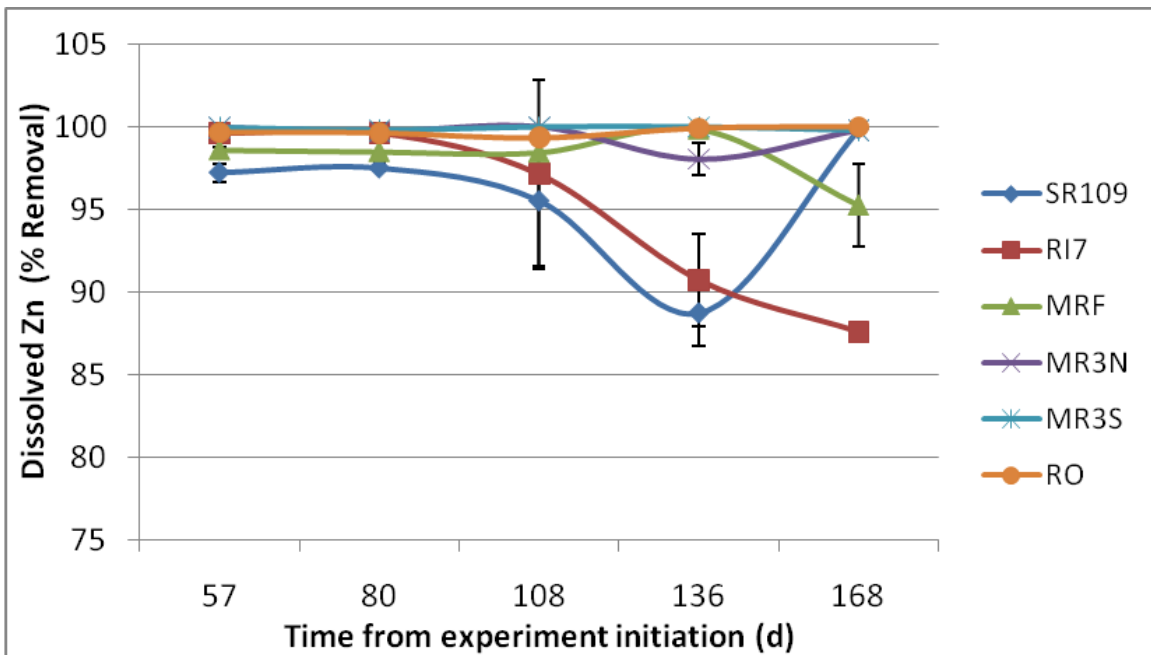

Figure 13. Percent removal of Zn for different mine drainage reactors.

Table 5: Influent and effluent values of dissolved Zn for reactors at different times. All values in mg/L.

Time Point	Influent mean	Influent Std Dev	SR109 mean	SR109 Std Dev	RI7 mean	RI7 Std Dev	MRF mean	MRF Std Dev	MR3N mean	MR3N Std Dev	MR3S mean	MR3S Std Dev	RO mean	RO Std Dev
57	3.96	0.08	0.12	0.02	0.016	0.003	0.061	0.008	0.003	0.003	0.002	0.002	0.013	0.001
80	4.20	0.38	0.12	0.01	0.016	0.008	0.069	0.030	0.011	0.007	0.007	0.001	0.014	0.004
108	4.00	0.68	0.21	0.19	0.13	0.27	0.071	0.021	<0.001	N/A	<0.001	N/A	0.025	0.004
136	3.64	0.31	0.37	0.07	0.005	0.008	0.31	0.09	0.072	0.037	<0.001	N/A	0.004	0.006
168	4.28	1.02	0.40	0.02	0.005	0.007	0.15	0.08	0.008	0.001	0.009	0.001	<0.001	N/A

Conclusions

The experiment demonstrates that alkalinity generation, pH increase and sulfate reduction rates and Pb removal may decrease with the age of VFBs. However, the results show that removal of Cd, Fe and Zn are not highly affected by decreased SRB activity. Other removal mechanisms may have taken place in reactors where sulfate reduction was at its lowest (e.g., SR109, RI7 and MRF) like adsorption to organic matter, organic ligands, anions and iron hydroxides. Sulfate reduction rates may have been affected by availability of simple sugars and the lack of completely anaerobic medium. Current studies include chemical and microbial analysis of substrates including metal concentration in the substrate, ANC, loss on ignition and SRB numbers. This analysis will help elucidate the processes occurring in batch reactors responsible for differences in the results shown in the water quality analysis presented here. Other studies should include geochemical analysis to estimate removal pathways for anions and metals. Additionally a sequential extraction could be performed to analyze the metals present in different fractions in the substrates.

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