COLUMN STUDY OF ORGANIC SUBSTRATES: PASSIVE ACID MINE DRAINAGE TREATMENT

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ABSTRACT: The Hughes Borehole is a 3,500 gpm (maximum) acid mine drainage (AMD) discharge located in Pennsylvania that has significantly impacted water quality in the Little Conemaugh River via its uncontrolled discharge. A column study was initiated to evaluate the feasibility of passive treatment of the discharge utilizing sulfate-reducing bacteria (SRB). Two six-foot long, six-inch diameter PVC columns were developed for the study. One column was packed with a dry weight mix of 80% saw dust and 20% cow manure (100% column) and the second with a volumetric mixture of 50% limestone and 50% of the above organic substrate (50/50 column). Four sampling ports were installed in each column; one in the influent tubing (raw water), two in the columns at 2 feet and 4 feet from the top, and one in the effluent tubing. Discharge from the borehole was collected on a regular basis and delivered to the laboratory for use in the study. After incubation to establish anaerobic conditions, the columns were operated in downflow at a regulated flow rate of approximately 5 milliliters per minute. Results show that the 50/50 substrate was more effective in treating the AMD discharge than the 100% substrate. In the 50/50 column, pH increased from an average influent level of 3.2 to an average effluent level of 5.8. Additional results such as decreased metals concentrations, decreased oxygen and oxidation-reduction potential, and generation of alkalinity and sulfide indicated that SRB were present. Data from the 100% column indicated that treatment was occurring, but at a much less effective rate. Additionally, a steady decline in treatment efficiency in the 100% column indicated questionable long-term effectiveness of the 100% substrate. Pre- and post-study substrate metals concentrations were also determined to evaluate metals loading rates and its impact on the substrates.

INTRODUCTION

The Hughes Borehole is a deep mine acidic discharge (pH 3.5 to 4.5) located in a wide valley formed by a meander in the Little Conemaugh River in Portage Township, Cambria County, Pennsylvania. Originally drilled to lower the water level and relieve pressure within the Hughes #2 Lower Kittaning Mine, the Borehole has affected the Little Conemaugh sub-basin of the Kiskiminetas river basin for over 40 years. With a flow that ranges from 1,890 liters per minute ($L\ m^{-1}$) to 13,250 $L\ m^{-1}$ (500 to 3,500 gallons per minute [gpm]), the Borehole discharges an average of 8,300 pounds of heavy metals and other pollutants into the Little Conemaugh River every day, comprising 8 percent of the total pollution load carried by the sub-basin (Barbin, 1995). Reportedly, where the Borehole discharge enters the Little Conemaugh River, no aquatic life is present, and this condition continues for three miles to the Borough of Portage (Barbin, 1995).

A column study was initiated to evaluate whether a passive treatment system utilizing sulfate-reducing bacteria (SRB) was feasible for treating Hughes Borehole acid mine drainage (AMD). The objectives of the column study were to evaluate the following indicators of SRB treatment:

- Increase in influent pH to near or above 6.0;
- Reduction in acidity and generation of alkalinity;
- Increase in sulfides and reduction in sulfates; and
- Removal of heavy metals.

COLUMN TEST SET-UP

The selection of appropriate organic substrates was controlled primarily by economics and availability. Only substrates that were locally available in large quantities and at low costs were considered based on the estimated size of a full-scale treatment system. Based on inquiries of locally-available substrate components and the aforementioned constraints, cow manure and sawdust were determined to be the most appropriate substrate components. Limestone was also considered as a substrate component. Two substrates mixes were developed for the study, one for each of the two columns operated. The substrate mixes were as follows:

- 100% Organic Substrate (100% Column)
  - 80% sawdust by wet weight
  - 20% cow manure by wet weight.

- 50% Limestone/50% Organic Substrate (50/50 Column)
  - 50% limestone (½" to 1") by volume
  - 50% organic substrate by volume.

Six-inch diameter, six-foot long poly-vinyl chloride (PVC) pipes were used to construct the columns. One column was filled with the organic substrate (100% column) and the second was filled with the organic/limestone substrate (50/50 column). Each of the substrates were placed into the columns in lifts and compacted with a wooden 2' x 4' to mimic in-situ compaction characteristics resulting from placement with standard construction equipment. Four sampling ports were installed in each column; one in the influent tubing prior to entry into the column (port 1), two in the column sidewall at two feet and four feet from the top of the column (ports 2 and 3, respectively), and one in the effluent tubing following passage through the column (port 4).

COLUMN TEST OPERATION

Water from the Borehole discharge was collected approximately once per week (or as necessary to keep a constant supply of water for the study) using 5-gallon Low Density Polyethylene (LDPE) collapsible containers. Approximately 95 liters (25 gallons) of water was obtained during each collection event and was delivered to the laboratory. The laboratory stored the collapsible containers in a refrigerator until use. Once ready for use, the active container was placed in an iced cooler approximately five feet above the top of the columns and the water was introduced into the columns by gravity. Flow rate in the columns was controlled by raising or lowering the effluent tubing out of the columns.

At the start of the study and following installation of the substrates, both columns were filled with untreated Borehole water and allowed to incubate. Eh, pH, and dissolved oxygen (DO) were monitored daily by collecting a sample from port 3 in each column to determine when anaerobic, sulfate-reducing conditions had been established (i.e., DO < 0.5 milligrams per liter [mg L^{-1}], Eh < approx. -250 mV). The data from the incubation phase of the column study indicated that anaerobic conditions were achieved within approximately 48 hours of saturation in both columns. Following a total of 6 days of incubation, Borehole water was introduced to both columns at a flow rate of approximately 4.7 milliliters per minute (mL min^{-1}). The selection of this flow rate was based on a desired retention time and the feasibility of delivering water from the remote Borehole location to the laboratory on a weekly basis.

The study (post-incubation) was operated continuously as described for a total of 50 days. Near the middle of the study, the flow rates were adjusted, as described in the results section, to evaluate treatment efficiency versus retention time.

COLUMN TEST SAMPLING

On the 36 weekdays within the 50-day study duration, the following sampling and analyses were performed:

- Eh, pH, and DO daily for all ports on both columns.

- Alkalinity, sulfide, sulfate, iron, manganese, aluminum, and calcium from port 1, port 2, port 3, and port 4 (both columns) on consecutive days (i.e., port 1 of both columns was sampled on Day 1, port 2 of both columns was sampled on Day 2, etc.).

- Several archived samples were analyzed for total acidity following the column study.

The analytical methods and instrumentation used during the study are provided in Table 1.

TABLE 1. Hughes Borehole Column Study Analytical Methods.

Parameter	Method No.	Instrumentation
Acidity	SM 2310B	HACH Meter No. EC20
Alkalinity	SM 2320B	HACH Meter No. EC20
Aluminum	EPA 200.8	Perkin Elmer ICP/MS
Calcium	EPA 200.8	Perkin Elmer ICP/MS
Iron	EPA 200.8	Perkin Elmer ICP/MS
Manganese	EPA 200.8	Perkin Elmer ICP/MS
Sulfide	EPA 376.2	HACH DR/4000
	SM 4500-S^{2-}D	Spectrophotometer

TABLE 1. Hughes Borehole Column Study Analytical Methods (Continued).

Parameter	Method No.	Instrumentation
Sulfate	EPA 375.4	HACH DR/4000
	SM 4500-SO_4^{2-}F	Spectrophotometer
Eh	SM 2580B	HACH ISE Meter No. EC20
Dissolved Oxygen	SM 4500-O G	YSI 1500 Dissolved Oxygen Meter - Standard Calomel Electrode (SCE)
pH		HACH ISE Meter No. EC20

RESULTS AND DISCUSSION

The following observations and interpretations were made based on the column study data. It should be noted that on Day 21, influent flow to the 50/50 column was increased (to approximately 9 mL min^{-1}) and flow to the 100% column was decreased (to approximately 3 mL min^{-1}). The purpose of this adjustment was to evaluate if treatment efficiency decreased (50/50) or increased (100%) at these rates and to find a retention time “break point” (i.e., the flow at which treatment is no longer effective).

100% Column

- For the first six days of the study, effluent pH was raised to above 5.5 from a pH of 3.0 to 3.5 in the influent. However, effluent pH steadily declined over the duration of the study. From Day 6 to Day 20, effluent pH dropped from 5.52 to 4.73. On Day 21, influent flow was decreased from approximately 4.7 mL min^{-1} to approximately 3 mL min^{-1}; it was expected that decreased flow may reverse the decreasing trend in pH and allow for more retention time. However, pH continued to decrease at a steady rate. By the latter stages of the study, pH in the effluent dropped below 4.0 and did not recover.

- Figures 1, 2, and 3 present the trends in pH, retention time, and Δ pH (i.e., the increase in pH between the ports and the influent) for port 2, port 3, and port 4 of the 100% column, respectively. Retention time (days) was calculated by dividing the volume of the column at the respective sampling port by the influent flow rate. The key observation from Figures 1, 2, and 3 is the decreasing trend in pH and ΔpH in all ports, even as retention time of water at each port increased at Day 21.

Figure 1
Graph of 100% Column Port 2 Results (pH, Retention Time, Δ pH)

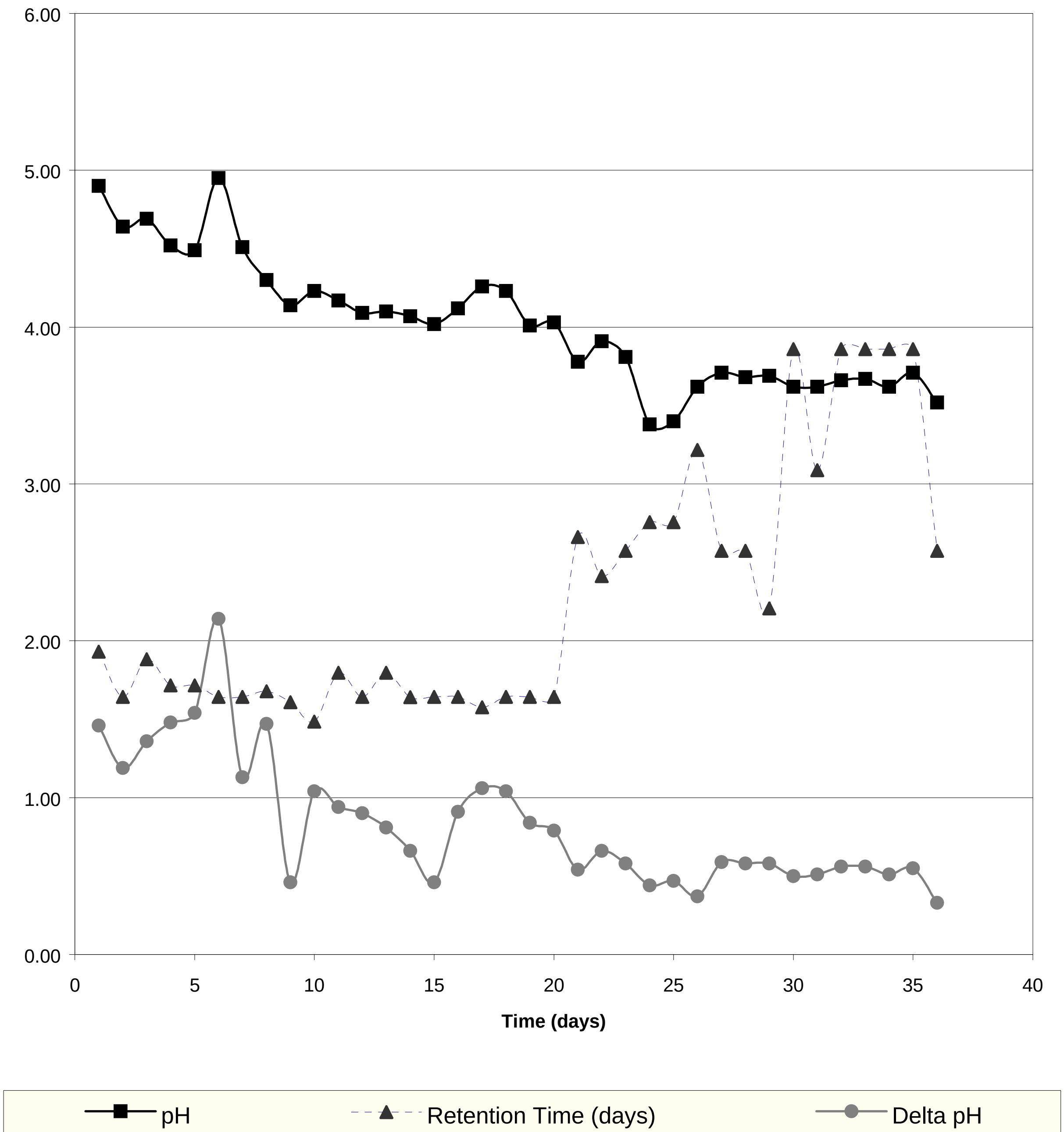


Figure 2
Graph of 100% Column Port 3 Results (pH, Retention Time, Δ pH)

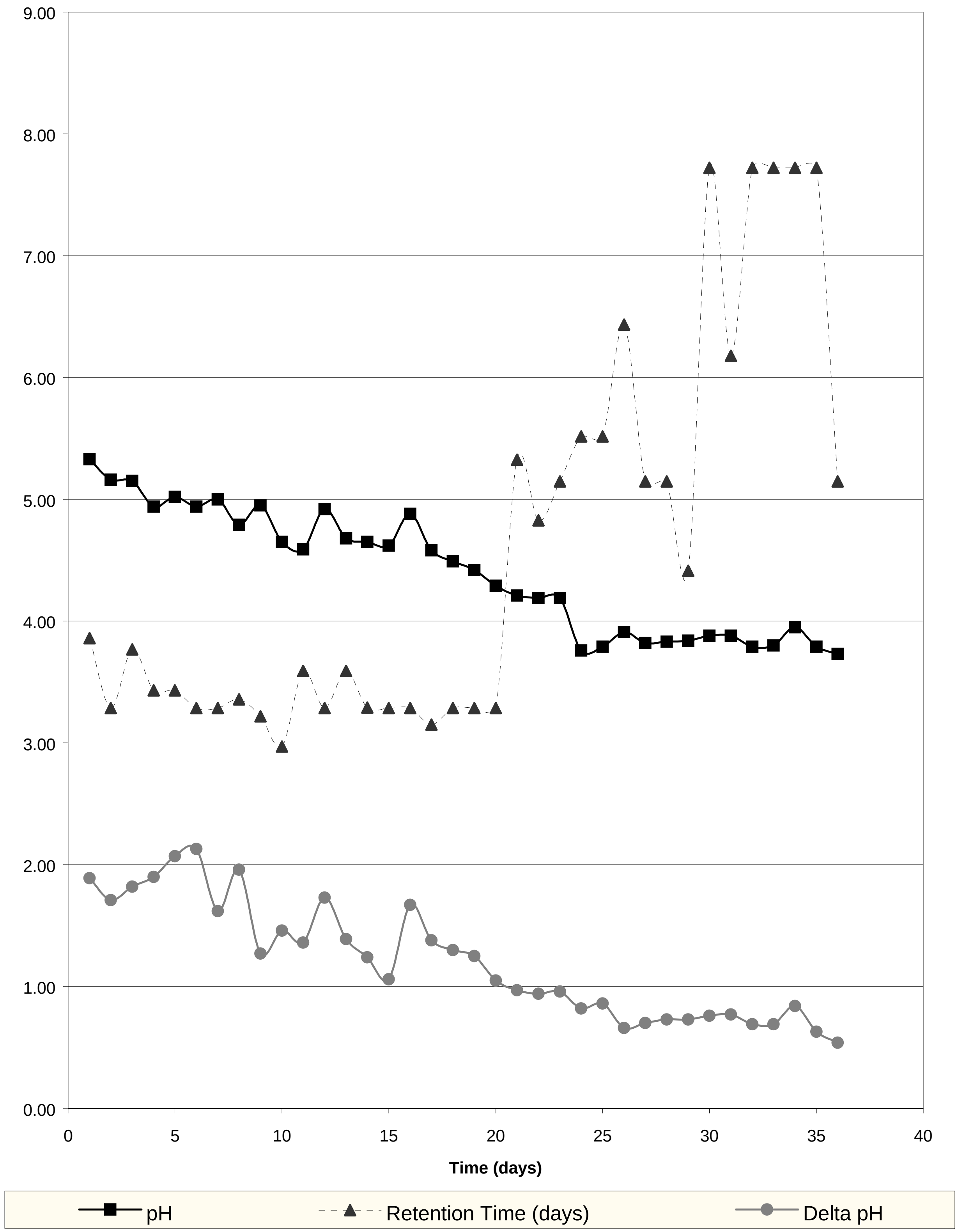
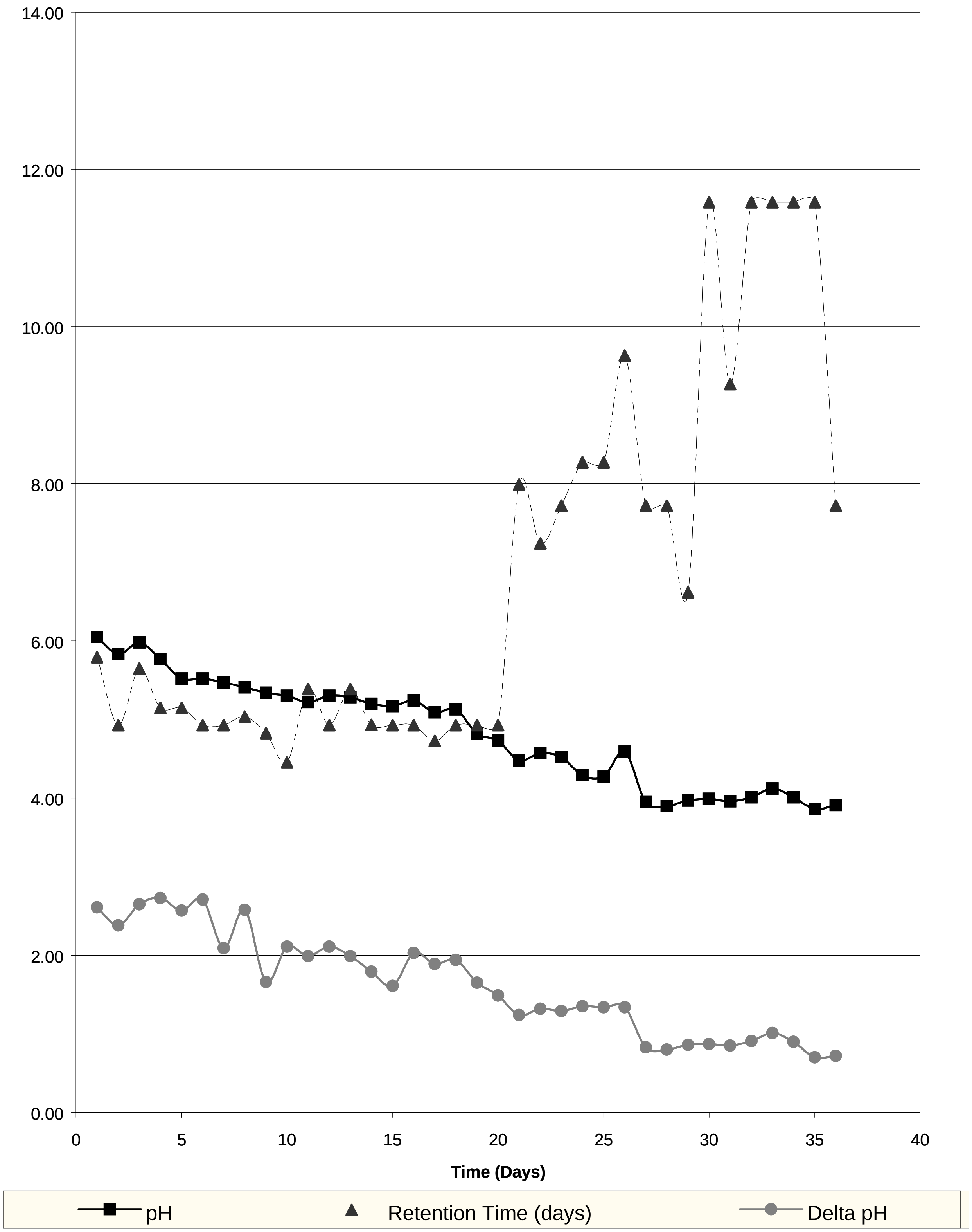


Figure 3
Graph of 100% Column Port 4 Results (pH, Retention Time, Δ pH)



- Eh and DO of the effluent initially indicated anaerobic conditions and potential SRB activity; however, moderate increases in effluent Eh and DO throughout the study indicated that anaerobic conditions (and potential SRB activity) seemed to decline.

- On Day 6 of the study, the laboratory reported a leak in the column. Following the restoration of this leak, SRB activity, if present, appeared to have declined (decreases in pH and increases in Eh and DO). The potential purging of the column may have caused a permanent decline in SRB activity, if it were ever present.

- Concentrations of manganese and calcium increased during the study (420% and 200% increases, respectively, in effluent as compared to influent). This is likely due to the liberation of these metals from the substrate to the low pH water. Conversely, levels of iron and aluminum decreased during the study (64% and 84% decreases, respectively, in effluent as compared to influent). Thus, there appears to have been accumulation of iron and aluminum in the 100% column, which is favorable for effluent water quality (but may influence the service life of a full-scale system).

- The 100% column demonstrated a progression of alkalinity increases from port to port and an effluent alkalinity increase of 760% (averages of 40 mg/l as $CaCO_3$ in influent to 347 mg/l as $CaCO_3$ in effluent). However, this alkalinity may have been due more to the activity of iron-reducing bacteria than by alkalinity generated by SRB (as suggested by Eh values above the range typical for SRB activity). In what appears to be an erroneous result, acidity increases were also observed (i.e., acidity and alkalinity should not increase simultaneously).

- Sulfide concentrations in the column effluent, a significant indicator of SRB activity, were generally low (except for Day 14), and decreases in sulfate concentrations were not generally observed (overall there was an increase in sulfates). These results appear to confirm that SRB activity was low in the 100% column.

- The 100% column was cut open following the study. It appeared as though most of the manure component of the substrate was exhausted. Black staining of the saw dust substrate was apparent only for the first foot of the column profile, followed by the remainder of the substrate remaining a normal sawdust color. The lack of black discoloration in most of the column (indicating little deposition of metal sulfides) and redox potentials (Eh) above -100 mV suggest that iron reduction rather than sulfate reduction may have been the dominant biological process in the 100% column (Tarutis et. al, 1992).

50/50 Column

- Samples collected from port 2 of the 50/50 column from Day 1 to Day 20 (influent flow rate approximately 4.7 mL min^{-1}) indicated consistent increases in pH, from approximately 3.0 to 3.5 in the influent to 5.7 to 6.2 in port 2 effluent. This indicates that little retention time is required to treat Borehole water using the 50/50 substrate. On Day 21, influent flow was increased to approximately 9 mL min^{-1} to evaluate if treatment efficiency would decline and to identify a retention time "break point." The results show that pH in port 2 effluent declined slightly (to approximately 5.0 to 5.5); however, the column effluent (port 4) pH remained stable at approximately 6.0. These results indicate that retention times at both flow rates are adequate to provide the treatment required to increase effluent pH to 6.0. The "break point" (i.e., the flow and retention time at which treatment is no longer effective) was not identified in this study.

- Figures 4, 5, and 6 present the trends in pH, retention time, and Δ pH for port 2, port 3, and port 4 of the 100% column, respectively. Retention time (days) was calculated by dividing the volume of the column at the respective sampling port by the influent flow rate. The key observations from Figures 4, 5, 6 are: 1) pH in ports 2 and 3 were relatively stable throughout the column study, even as retention times decreased; and 2) effluent pH (port 4) increased despite a significant decrease in retention time (see previous bullet).

Figure 4
Graph of 50/50 Column Port 2 Results (pH, Retention Time, Δ pH)

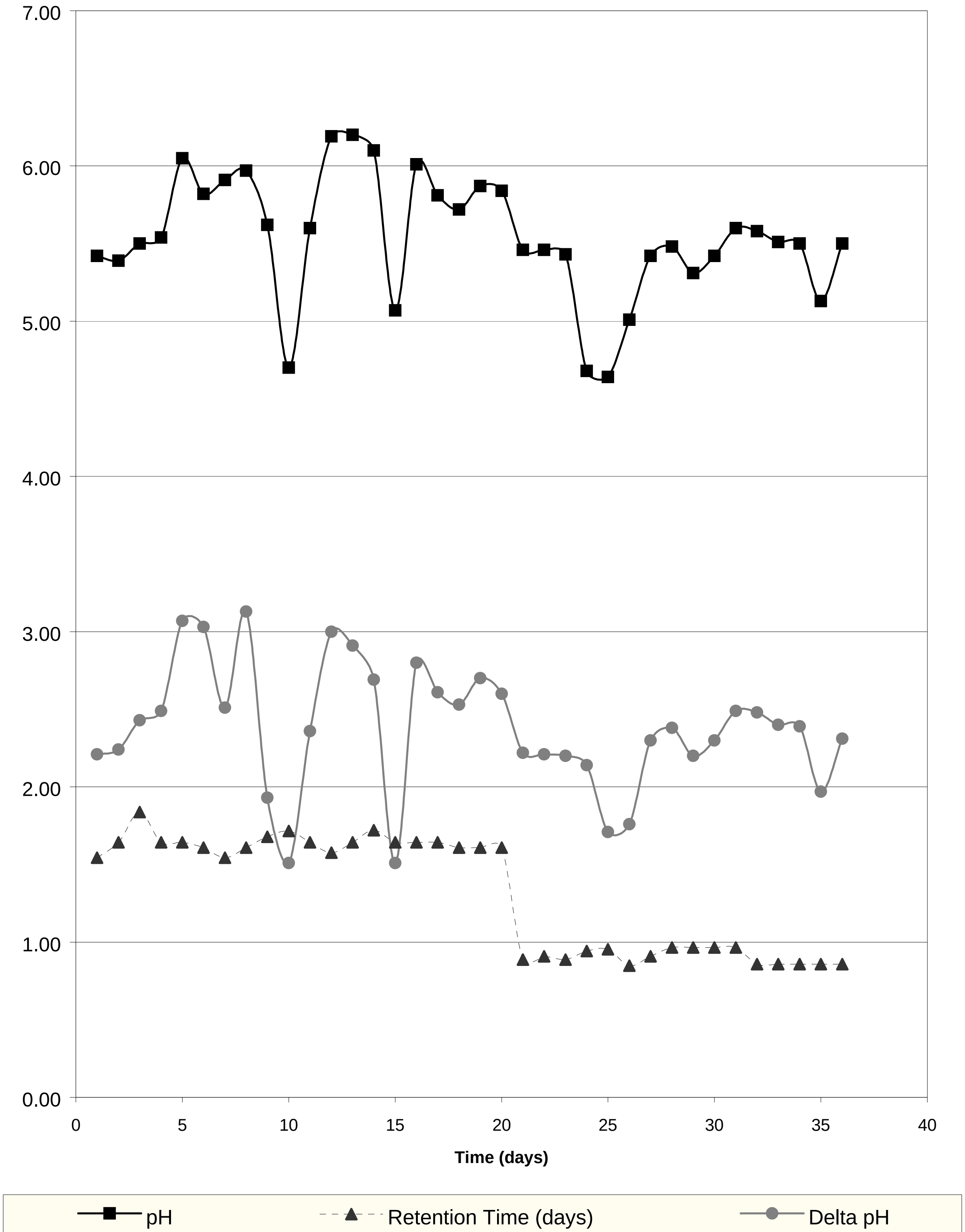


Figure 5
Graph of 50/50 Column Port 3 Results (pH, Retention Time, Δ pH)

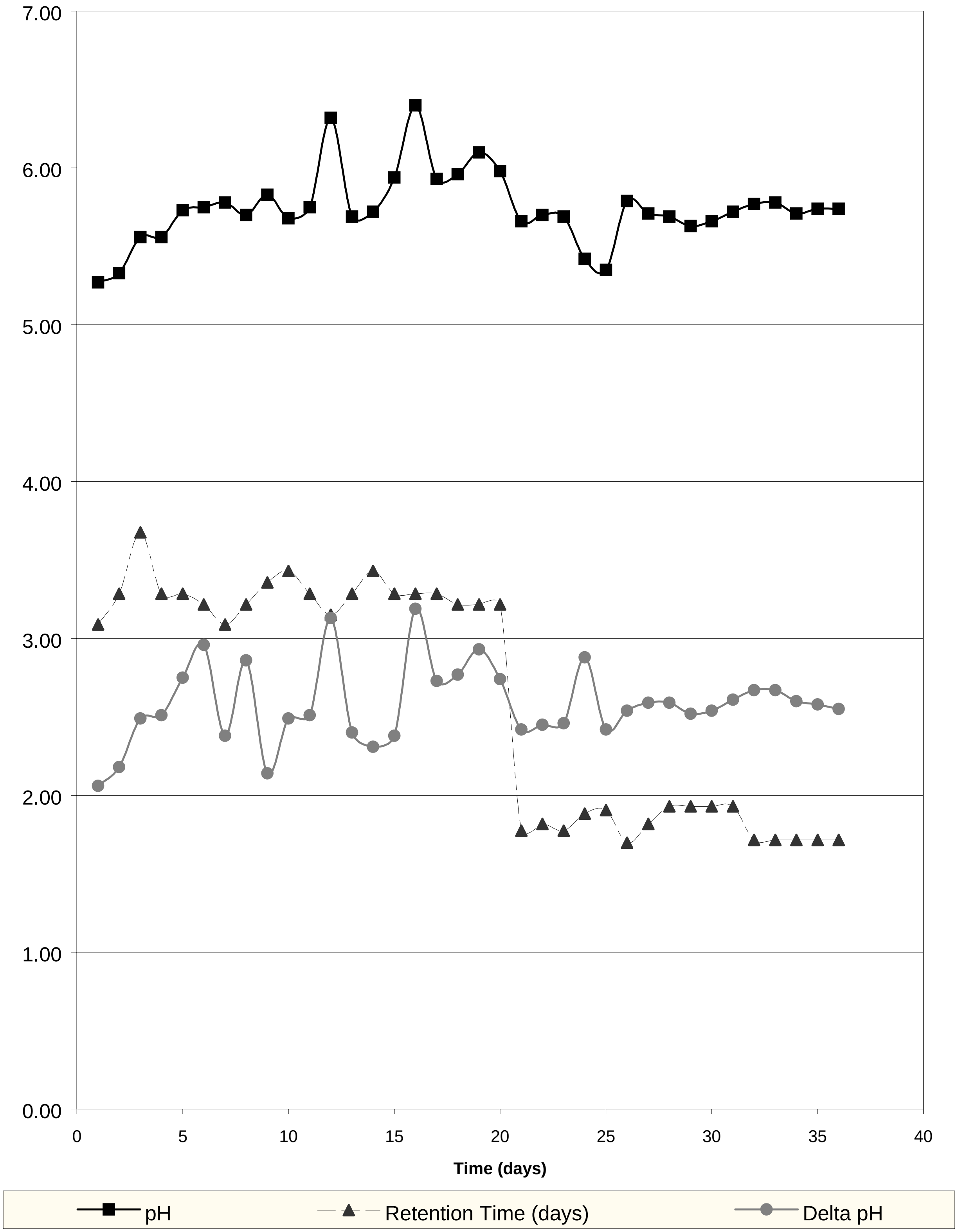
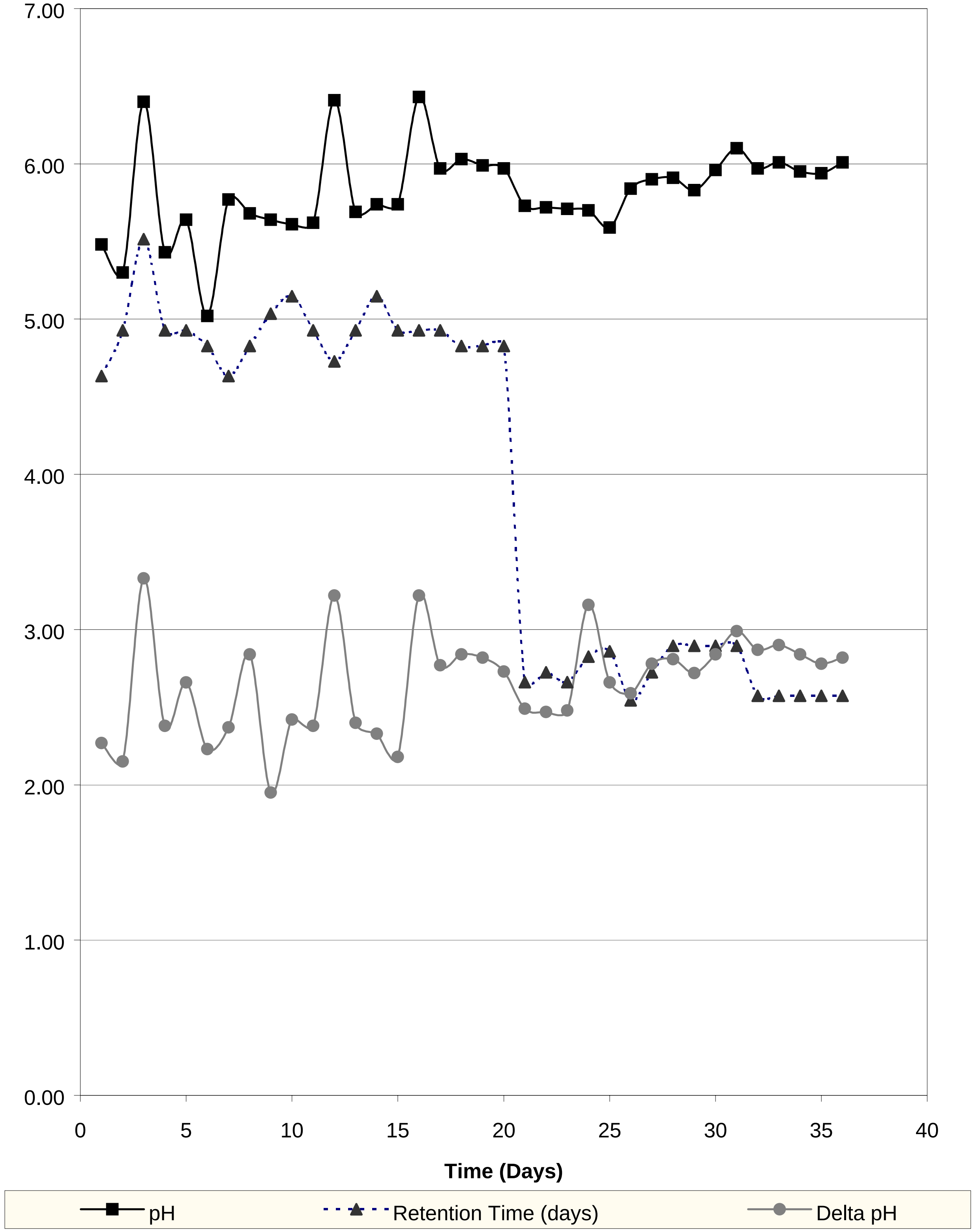


Figure 6

Graph of 50/50 Column Port 4 Results (pH, Retention Time, Δ pH)



- Eh and DO of the effluent for the first 20 days indicated significant SRB activity. After flow was increased on Day 21, Eh and DO levels initially increased but original levels were soon restored.

- Concentrations of calcium increased during the study (220% increases in effluent as compared to influent). This is expected due to the dissolution of limestone in this column. Conversely, levels of iron, manganese and aluminum decreased during the study (93%, 27% and 98% decreases, respectively, in effluent as compared to influent). Thus, there appears to have been accumulation of iron, manganese and aluminum in the 50/50 column, which is favorable for effluent water quality (but may influence the service life of a full-scale system).

- The 50/50 column demonstrated a progression of alkalinity increases from port to port and an effluent alkalinity increase of 1880% (averages of 40 mg/l as $CaCO_3$ in influent to 797 mg/l as $CaCO_3$ in effluent, with a maximum of 1440 mg/l as $CaCO_3$ in effluent). The generation of significant levels of alkalinity are likely a result of a combination of limestone dissolution and SRB activity (Hedin et. al, 1988). As expected, the generation of alkalinity resulted in reductions of acidity.

- The formation of sulfides by SRB was significant, as observed by a 5700% increase in sulfides (averages of 0.23 mg/l in influent to 13.35 mg/l in effluent). Sulfates were reduced by 54% in effluent as compared to influent (averages of 884 mg/l in influent to 406 mg/l in effluent). These results appear to confirm that SRB activity was high in the 50/50 column.

- The 50/50 column was cut open following the study. Slight orange staining was present for the first foot of the column on the limestone and the interior of the PVC. Despite this observation, SRB activity appeared to be high within the first two feet of the column (as suggested by the results from port 2). The bottom five feet of the column exhibited no staining, and the manure component appeared to be mostly exhausted.

Comparison Between 100% and 50/50 Columns

Figures 7 and 8 present the linear regression of effluent pH data (from ports 2, 3 and 4) and projected treatment cell size (based on the column study retention times, an assumed Borehole flow rate of 1500 gpm, and a cell depth of 6 feet) for the 100% and 50/50 columns, respectively. The purpose of these figures was to visually present the correlation (or lack thereof) between the potential land area required for treatment and the expected pH of the effluent from cells with each of the substrates evaluated in this study. The coefficient of correlation (R^2) values and the linear regression equation (Figure 8 only) are presented on the figures. The reader should be advised that the size of a full-scale treatment cell(s) may be significantly different than the sizes presented here.

Figure 7
Linear Regression of pH Versus Cell Size for 100% Column

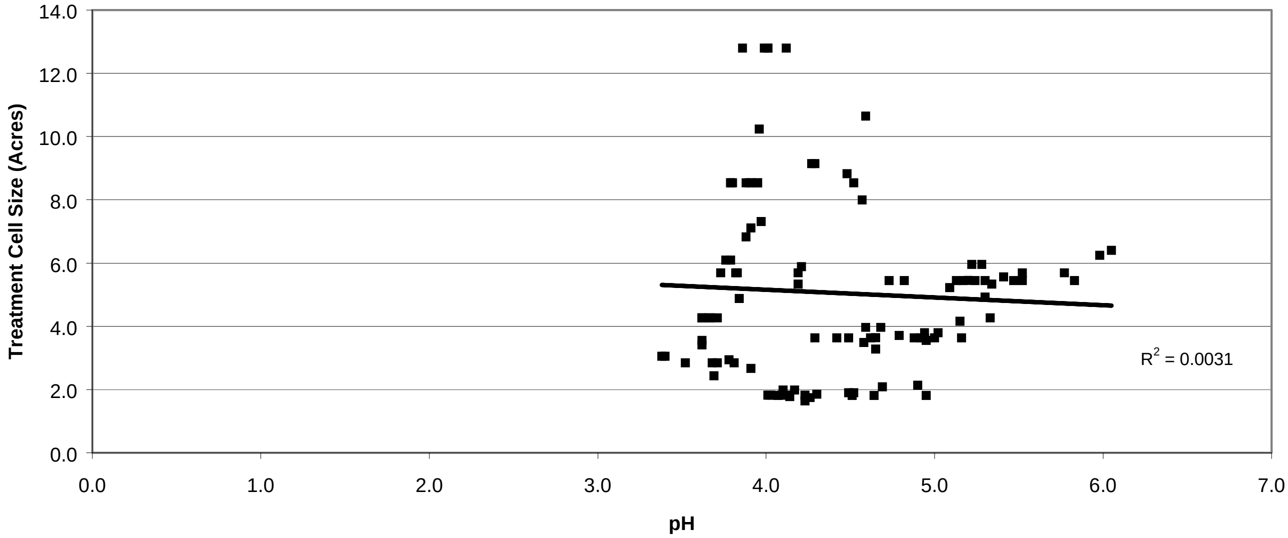


Figure 8
Linear Regression of pH Versus Cell Size for 50/50 Column

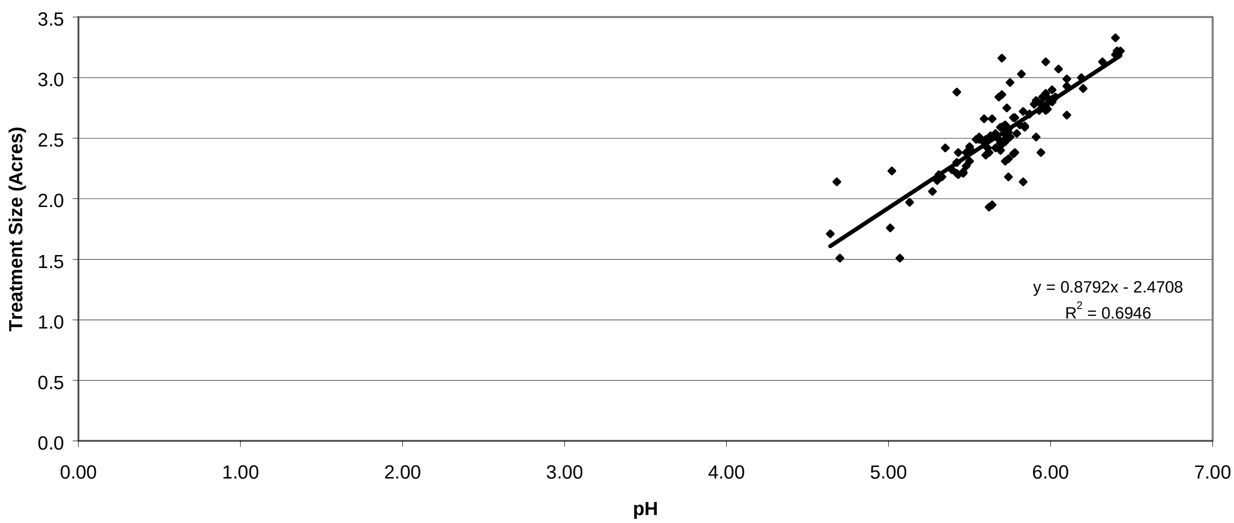


Figure 7 demonstrates a weak correlation ($R^2 = 0.0031$) between treatment cell size and effluent pH of a 100% substrate cell. It is not appropriate, based on the weak correlation, to estimate the land area required for treatment of Borehole AMD using the 100% substrate. Figure 8 shows a much stronger correlation ($R^2 = 0.695$) between treatment cell size and effluent pH of a 50/50 substrate cell. By solving the linear regression equation for a desired pH of 6.0, the required area for a 50/50 cell is 2.8 acres. The meaningfulness of this information should be viewed with caution considering the limited scope and duration of the column study.

Figure 9 presents a comparison of average pH and DO data for the influent and the 100% and 50/50 effluents (port 2 effluent for pH, port 4 effluent for DO). Port 2 effluent was used for the pH comparison to clearly indicate relative substrate effectiveness. While it is acknowledged that the use of average data for comparisons neglects the data variability which are of interest, this information is useful in evaluating overall treatment efficiency. Figure 9 shows that the 50/50 column was more effective in increasing pH, and significant decreases in DO levels in both columns suggest microbial activity (whether iron-reducing bacteria or SRB).

Figure 4-9
Average pH and DO Data for Influent and Column Effluent

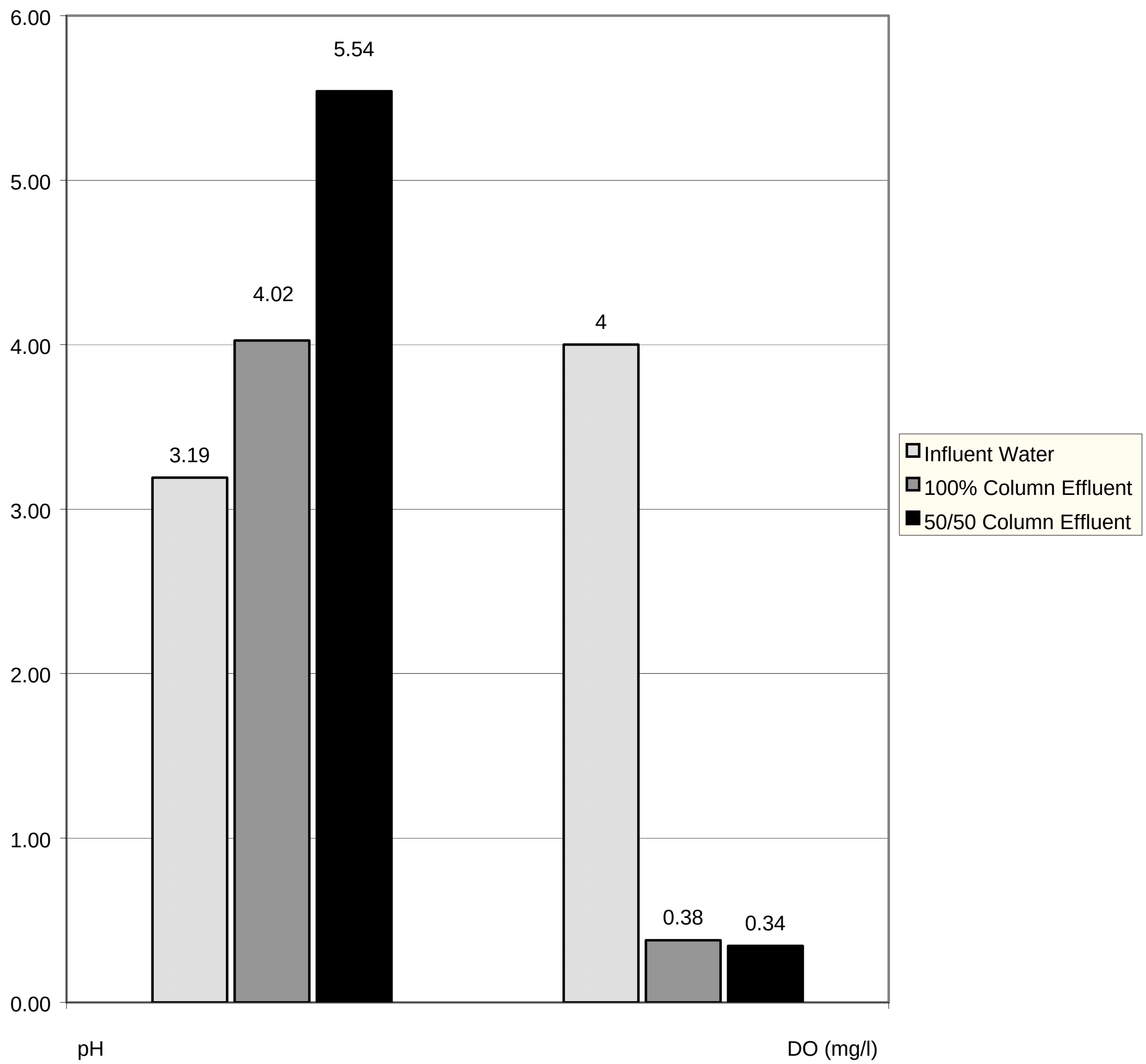


Figure 10 presents a comparison of average alkalinity and sulfate data for the influent and the 100% and 50/50 effluents (port 4). Alkalinity generation in the 50/50 column was more than twice that produced in the 100% column. Overall, sulfate concentrations increased in 100% effluent, indicating that SRB activity was inhibited, while sulfate concentrations decreased by over 50% in the 50/50 effluent.

Figure 10
Average Alkalinity and Sulfate Data for Influent and Column Effluent

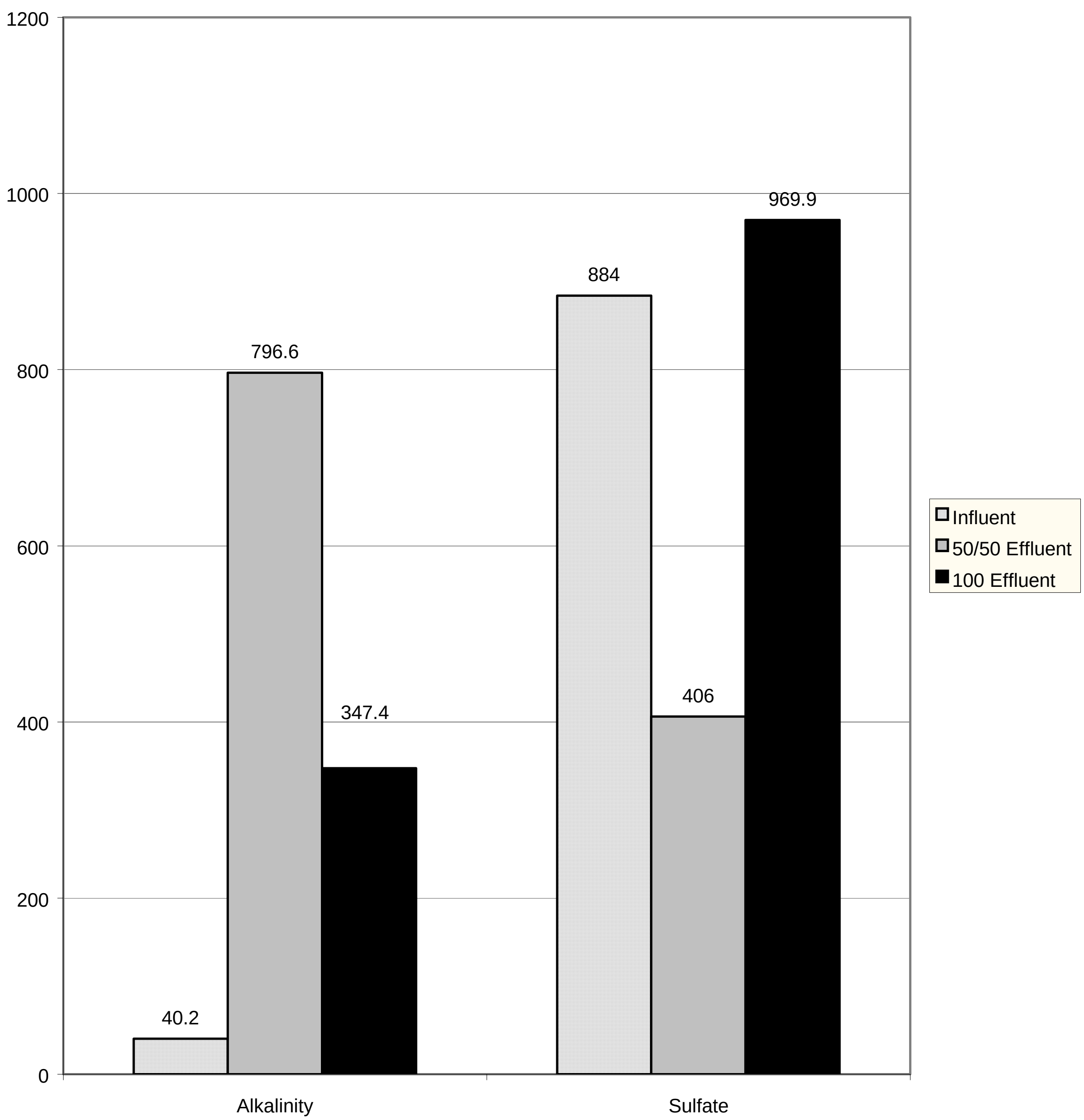


Figure 11 presents a comparison of average iron and manganese data for the influent and the 100% and 50/50 effluents (port 4). The 50/50 column was more effective than the 100% column in removing iron and manganese. Manganese concentrations increased in the 100% effluent, likely due to the presence of manganese in the 100% substrate.

Figure 11
Average Iron and Manganese Data for Influent and Column Effluent

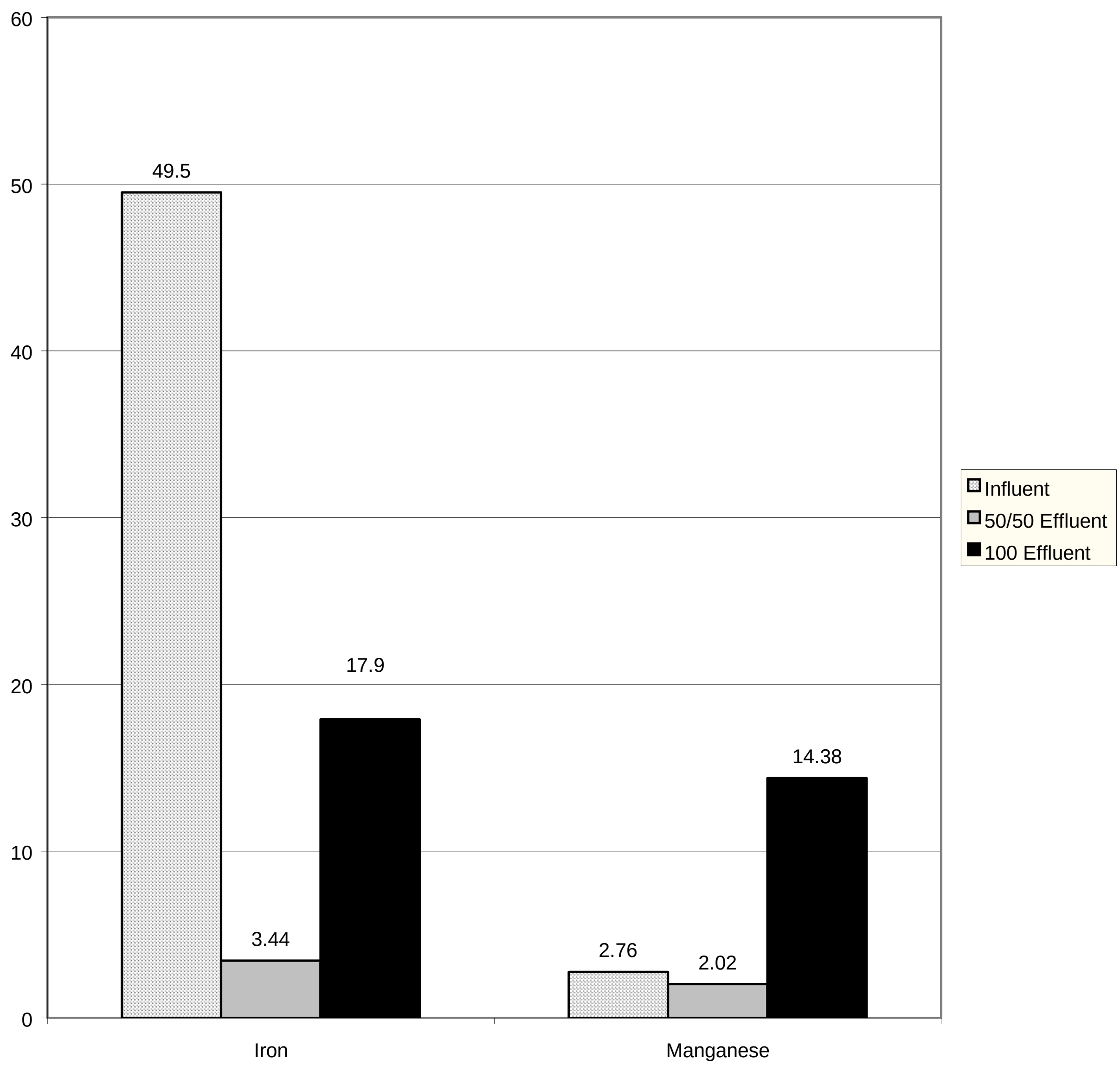
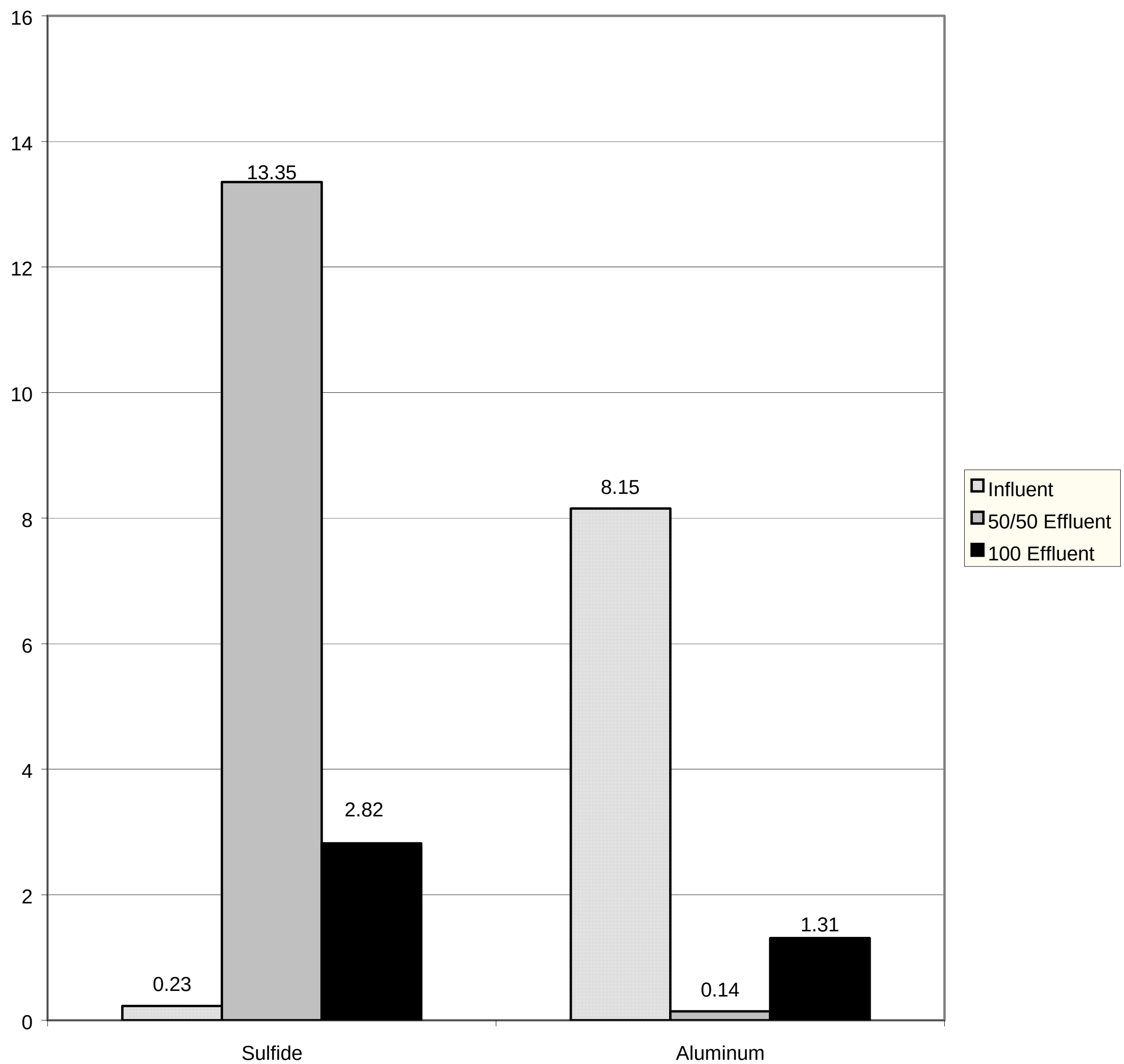


Figure 12 presents a comparison of average sulfide and aluminum data for the influent and the 100% and 50/50 effluents (port 4). Sulfide formation in the 50/50 column appeared, overall, significantly higher than in the 100% column. It should be noted that it is unclear whether sulfide production was actually higher in the 50/50 column since sulfides (associated with metals) may have precipitated out of solution in the substrates at a greater rate in the 100% column. Aluminum removal was effective in both columns.

Figure 12
Average Sulfide and Aluminum Data for Influent and Column Effluent



Concentrations of metals (iron, manganese, aluminum, and calcium) were analyzed in the 50/50 and 100% substrates following the study, and the results are presented in Table 2. The results show a significant accumulation of iron and aluminum occurring within the first foot of substrate in the 50/50 column. This has practical implications for the active life of a 50/50 treatment cell in the field (i.e., the first foot or more of substrate may require replacement often). Since the column study was only performed for a limited duration, there is no data to indicate the amount of time before the treatment efficiency of the 50/50 substrate may decline.

TABLE 2. Post-Study Substrate Concentrations.

Sample	Iron (mg/kg)	Manganese (mg/kg)	Aluminum (mg/kg)	Calcium (mg/kg)
50/50 Top 1'	5600	35	2400	19000
50/50 Bottom 1'	780	24	135	13000
100% Top 1'	800	12	380	1500
100% Bottom 1'	300	22	117	1600

CONCLUSIONS

Based on the results of the column study, the following fundamental conclusions are drawn.

100% Column. The 100% column was, considering the progressive decreases in pH, not efficient in treating the Borehole water. This finding relates directly to the objectives of the study whereby SRB was to be evaluated as an effective means of treating AMD at Hughes. The authors cite two possible explanations for the outcome:

- The substrates selected for this study (sawdust [80%] and aged cow manure [20%]) may not have provided the carbon content or other requirements for sustained SRB activity. Other substrates (or mix ratios), particularly mushroom compost, have consistently shown good results in other bench- and pilot-scale studies. Mushroom compost has been shown by several investigators (e.g., Wieder, 1993; Wildeman et. al, 1990; Vile and Wieder, 1993) to sustain significant rates of sulfate reduction and sulfide and alkalinity formation. Limestone mixed with mushroom compost appears to improve SRB activity and overall alkalinity generation; high limestone dissolution (and SRB-mediated alkalinity generation) rates were found in a constructed wetland where mushroom compost was supplemented with limestone (Hedin and Nairn, 1993).

- The SRB population in the 100% column, if present, may not have been able to overcome the potential purging of the column which occurred on Day 6 of the study (i.e., the leak). This is considered less plausible than the first explanation considering the steady decline in pH throughout the remainder of the study. If the SRB colony were indeed purged, pH decline would likely have been more rapid and would not have been characterized by a steady decline.

50/50 Column. The 50/50 substrate was moderately to very effective in treating Borehole AMD. In comparison to the 100% column, the organic/limestone mix was superior in treating Borehole AMD and was able to buffer the incoming pH to near or above 6.0. The data suggest that a combination of limestone dissolution and SRB activity was responsible for the generation of significant amounts of alkalinity in the study. Elevated concentrations of sulfides in effluent and decreases in sulfate levels by over 50% indicate high SRB activity. While sulfide levels in effluent may be undesirable for a receiving water body, an oxidation step following a treatment cell(s) would remove most sulfides. Removal of metals from the AMD was also successful with the 50/50 substrate.

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