5-1-2010

EVALUATION OF THE TAB-SIMCO ACID MINE DRAINAGE TREATMENT SYSTEM: WATER CHEMISTRY, PERFORMANCE AND TREATMENT PROCESSES

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Recommended Citation
Segid, Yosief Teklehaimanot, "EVALUATION OF THE TAB-SIMCO ACID MINE DRAINAGE TREATMENT SYSTEM: WATER CHEMISTRY, PERFORMANCE AND TREATMENT PROCESSES" (2010). *Theses.* Paper 203.

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by

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B.S., University of Asmara, Eritrea, 2001

A Thesis
Submitted in Partial Fulfillment of the Requirements for the
Masters of Science Degree

Department of Geology in the Graduate School
Southern Illinois University Carbondale
May, 2010

THESIS APPROVAL

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in the field of Geology

Approved by:

Dr. Liliana Lefticariu, Chair

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Graduate School
Southern Illinois University Carbondale
March 31st, 2010

AN ABSTRACT OF THE THESIS OF

YOSIEF TEKLEHAIMANOT SEGID, for the Masters of Science degree in GEOLOGY, presented on 3/31/2010, at Southern Illinois University Carbondale.

TITLE: EVALUATION OF THE TAB-SIMCO ACID MINE DRAINAGE
TREATMENT SYSTEM: WATER CHEMISTRY, PERFORMANCE AND
TREATMENT PROCESSES

MAJOR PROFESSOR: Dr. Liliana Lefticariu

Evaluating the performance of an acid mine drainage treatment system, and the biogeochemical processes that occur within it, can be vital for improving the performance and longevity of the treatment system, and in designing new effective long-term treatment systems. In this study, the performance of the Tab-Simco treatment system and the biogeochemical processes that occur within it, were investigated by analyzing water samples from the site. The Tab-Simco treatment system comprises an anaerobic sulfate-reducing bioreactor and an oxidation pond. Results indicated that the treatment system increased the pH of the acid mine drainage (AMD) from 2.8 to 6.3 and decreased the mean acidity from 3,386 to 74 mg/l, SO_4^{2-} from 4,589 to 2,021 mg/l, Fe from 884 to 3.5 mg/l, Al from 207 to 2 mg/l and Mn from 34.5 to 26.4 mg/l. The average $\delta^{34}S$ value of the SO_4^{2-} in the untreated AMD was 7.3 ‰. This value was similar to the $\delta^{34}S$ values of the pyrite in the coal seams, indicating that the oxidation of the pyrites was the cause of the AMD. In the bioreactor, $\delta^{34}S$ value of dissolved SO_4^{2-} increased from an average of 6.9 to 9.2 ‰, confirming the presence of bacterial sulfate reduction processes. Alkalinity production calculations for the bioreactor revealed that roughly about 60% of the alkalinity was produced by bacterial sulfate reduction whereas, the remaining 40% was produced by limestone dissolution.

ACKNOWLEDGMENTS

First of all, I would like to thank my advisor, Dr. Liliana Lefticariu, for her continuous assistance and advice during my thesis work. Dr. Lefticariu provided me with the materials I needed for analyses, guided me during sample analyses, assisted with the editing process, and was always available to answer my questions. I will always be indebted to her for her support and advice.

Secondly, I would like to give my deepest appreciation to Mr. Paul Behum from the Office of Surface Mining Reclamation and Enforcement (OSMRE) and his office, for the unreserved cooperation they extended to me during the period of my thesis study. OSMRE allowed me to use their instruments to measure field parameters and were cooperative in analyzing my samples for certain parameters. Mr. Behum taught me how to take field measurements and was very helpful in finding information regarding the treatment system. Without his guidance and support, this thesis would not have reached this stage.

In addition, I thank the Illinois Department of Natural Resources, Land Reclamation Division, and the landowners, for allowing me access to the site in order to evaluate their state-of-the art AMD treatment system.

I am also grateful to Dr. Steven Esling (department head) and Dr. Scott Ishman (graduate coordinator) for serving as my committee members, proof reading and commenting on my thesis, and for their advice.

Finally, I would like to use this opportunity to thank the Department of Geology at Southern Illinois University Carbondale, along with all its faculty and staff members, for allowing me to pursue my master’s degree and providing me with an excellent education.

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1. INTRODUCTION

Acid mine drainage (AMD) is contaminated water characterized by low pH and high concentrations of dissolved metals and sulfate (SO_4^{2-}) (Blowes et al., 2003; Tsukamoto et al., 2004; Neculita et al 2008a). AMD is a serious and widespread environmental hazard that occurs primarily at coal and metal mining sites as a result of the oxidation of sulfide minerals such as pyrite and pyrrhotite. Because of its high acidity and high concentrations of dissolved metals and SO_4^{2}, AMD can cause various environmental problems including contamination of the surface and groundwater drinking supplies, disruption of the growth and reproduction of aquatic plants and animals, acid corrosion of the infrastructure such as wastewater pipes, and degradation of outdoor recreation and tourism sites (US Environmental Protection Agency website: http://www.epa.gov/reg3wapd/nps/mining/mines.htm#acid). The precipitation of ferric (oxy)hydroxide minerals, commonly known as “yellow-boy” at AMD sites can destroy vegetation by covering the soil layer and clogging the substrate interstices (Gray, 1998).

In the USA, AMD contamination has been reported in Pennsylvania, West Virginia, Ohio, Kentucky, Maryland, Indiana, Illinois, Oklahoma, Iowa, Missouri, Kansas, Tennessee, Virginia, Alabama, and Georgia (Appalachian Regional Commission, 1973). According to the US Environmental Protection Agency (1995), about 20,000 km of streams and rivers in the eastern United States are degraded by AMD.

Currently, different treatment methods are used to remediate AMD. When designed properly, anaerobic sulfate-reducing bioreactors have proved their effectiveness in treating AMD with low pH and high concentration of metals and SO_4^{2-}. However, studies have shown that the performance and longevity of an anaerobic sulfate-reducing bioreactor can be affected by different factors such as changes in amount of organic matter, hydraulic retention time, quality and flow rate of the AMD, and hydraulic properties of bioreactor due to pore clogging by the precipitated materials (Neculita et al. 2008a). The treatment efficiency of an anaerobic sulfate-reducing bioreactor might also vary seasonally due to variations in air temperature that can affect the biological activities of the bioreactor (Neculita et al., 2007).

Evaluating an acid mine drainage treatment system can be very important in understanding the performance of the system in removing acidity, dissolved metals and SO_4^{2-} from the AMD, the conditions inside the treatment system and the treatment processes that occur within the treatment system. Moreover, the evaluation can be helpful in understanding the short-and long-term temporal variations in the performance of the system. Understanding the bioreactor performance and treatment processes, in turn, can be critical in improving the performance and longevity of the system. Furthermore, this information is crucial in designing new effective long-term treatment systems using minimal resources. Consequently, evaluation of acid mine drainage treatment systems is currently an active research topic in AMD treatment.

In this study, the Tab-Simco AMD treatment system was evaluated to understand the performance of the treatment system in treating the AMD and the chemical and biological treatment processes that take place in the treatment system.

2. OBJECTIVES OF THIS STUDY

The main objectives of this study are:

1. To evaluate the performance of the Tab-Simco treatment system in removing acidity, dissolved metals and SO_4^{2-} from the AMD.
2. To understand both the chemical and biological processes which occur at the Tab-Simco AMD treatment system.
3. To study the chemical characteristics of the Tab-Simco AMD along the flow direction.
4. To study seasonal variations in the chemistry of the untreated AMD and the performance of the Tab-Simco sulfate-reducing anaerobic bioreactor.
5. To determine the amount of alkalinity production by limestone dissolution and bacterial sulfate reduction (BSR) in the Tab-Simco sulfate-reducing anaerobic bioreactor.
6. To investigate the source(s) of the sulfide minerals that cause the AMD at the site.
7. Finally, based on the results found, recommendations are presented to improve the performance of the Tab-Simco and similar anaerobic sulfate-reducing bioreactors.

3. BACKGROUND

3.1 Formation of AMD

AMD is mainly generated when sulfide minerals such as pyrite (FeS_2) oxidize due to exposure to water (H_2O) and oxygen (O_2) (Kalin et al., 2005; Ziemkiewicz, 2003). In natural systems, the oxidation of sulfide minerals occurs through combinations of abiotic and biotic processes, which result in waters with low pH level and high concentrations of dissolved metals and SO_4^{2-}. The oxidation process involves several reaction steps (Rimstidt and Vaughan, 2003) and begins with oxidation of sulfide minerals by O_2 as shown below (Nordstrom, 1982; Garrels et al., 1960; Kalin et al., 2005; Neculita et al., 2007).

$$2FeS_2\ (s) + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \qquad (3.1)$$

This process oxidizes the sulfide minerals such as pyrite and releases ferrous iron (Fe^{2+}), SO_4^{2-} and hydrogen ion (H^+). Next, the Fe^{2+} may be oxidized to ferric iron (Fe^{3+}).

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad (3.2)$$

At low pH level, without bacterial involvement, the rate of reaction 3.2 is slow. However, in a natural environment, iron oxidizing bacteria such as *Acidithiobacillus Ferrooxidans (syn-thiobacillus ferrooxidans)* can accelerate the rate of the reaction by factors greater than 10^6 (Singer et al., 1970; Zagury et al., 1997; Brown et al., 2002). At pH level above about 3.0-3.5, Fe^{3+} is unstable and reacts with H_2O to form ferric (oxy)hydroxides (Perez-Lopez et al., 2007b; Hedin et al., 1994), which precipitate as red to yellow colored compounds commonly referred to as “yellow-boy.” During the reaction (Reaction 3.3), three moles of H^+ are released in solution for every mole of Fe^{3+}.

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \tag{3.3}$$

At pH level less than 3.0-3.5, Fe^{3+} remains in solution and can oxidize FeS_2 according to the following reaction (Stumm and Morgan, 1996; Rimstidt and Vaughan, 2003; Hedin et al., 1994; Kalin et al., 2005):

$$FeS_2\ (s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{3.4}$$

During the reaction (Reaction 3.4), for every mole of FeS_2, sixteen moles of H^+ are released into the solution. The rate of FeS_2 oxidation by Fe^{3+} (Reaction 3.4) is much higher than the rate of pyrite oxidation by O_2 (Reaction 3.1) (Neculita et al., 2007).

The overall FeS_2 oxidation reaction under aerobic conditions is given by the following reaction (Bonnissel-Gissinger et al., 1998):

$$FeS_{2(s)} + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_{3(s)} + 2SO_4^{2-} + 4H^+ \tag{3.5}$$

Factors that control AMD generation include types of sulfide minerals, mineral surface area, environmental conditions (example, pH level, temperature and dissolved O_2 concentration), and bacterial activity (Berghorn et al., 2001).

3.2 AMD Treatment Methods

In order to restore AMD contaminated sites and avoid further environmental damage, the contaminated waters must be properly handled and treated. Currently, there are several commonly applied treatment methods to remediate AMD sites. The methods are categorized as active or passive treatment methods (Skousen et al., 2005; Ziemkiewicz et al., 2003).

Active treatment methods involve addition of manufactured chemicals to AMD to treat the contaminated water. The chemicals commonly used in active treatment include hydrated lime, $Ca(OH)_2$, caustic soda, NaOH, ammonia, NH_3, pebble quicklime, CaO, and soda ash, Na_2CO_3 (Skousen et al., 2005; Ziemkiewicz et al., 2003). Active treatment methods can be reliable and effective but they need continuous monitoring and maintenance, which makes them more expensive than passive methods (Ziemkiewicz et al., 2003). Another drawback of active treatment methods is handling the huge volume of sludge from precipitation, which needs high disposal cost to prevent possible environmental impact (Ziemkiewicz et al., 2003).

Passive treatment methods use naturally occurring materials such as limestone and organic matter to neutralize the acid and remove the metals and SO_4^{2-}. They are less expensive and do not require continuous follow up like active treatment methods (Hedin et al., 1994). However, passive treatment techniques may require longer retention time and larger treatment areas. There are different types of passive treatment methods including: (1) aerobic and anaerobic wetlands, (2) sulfate-reducing bioreactors, (3) anoxic limestone drains (ALD), (4) open limestone channels, (5) settling ponds, and (6) vertical flow systems (also known as successive alkalinity producing systems (SAPS)) (Ziemkiewicz et al., 2003; Skousen et al., 2005).

Selecting and designing an efficient treatment method for a specific AMD site depends on chemistry and flow rate of the contaminated water, site characterization, environmental goal, and available technologies (Hedin et al., 1994; US EPA, 2005; Doshi, 2006). For example, ALD is effective in treating AMD waters with low pH and low concentrations of Fe^{3+} and Al^{3+}, whereas anaerobic sulfate-reducing bioreactor and vertical flow systems have proven their efficiency in treating AMD waters with higher metal concentrations.

3.3 Anaerobic Sulfate-reducing Bioreactors

Anaerobic sulfate-reducing bioreactor is a type of passive treatment method that uses mainly sulfate reducing bacteria (SRB) to treat AMD. Sulfate-reducing bioreactors have advantages over active treatment methods because they can remove metals from low pH AMD with lower costs and minimal energy consumption and generate more stable sludge (Zaluski et al., 2003). An anaerobic sulfate-reducing bioreactor consists of a thick layer of selected organic matter mixed with limestone and often, a thin layer of limestone is set below the organic matter layer to produce additional alkalinity and provide bedding for a network of under draining pipes (Fig.1). The AMD flows vertically through the organic matter and limestone layers and is discharged through the pipelines.

In the organic matter layer, sulfate-reducing bacteria reduce the SO_4^{2-} in the contaminated water to hydrogen sulfide (H_2S) and oxidize the organic matter (CH_2O) to bicarbonate ions (HCO_3^-) as shown in the reaction below (Reaction 3.6) (Hedin et al., 1994; Watzlaf et al., 2004).

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \qquad (3.6)$$

The interaction of the AMD with the limestone within the bioreactor results in limestone dissolution according to reaction 3.7 and to produce additional HCO_3^- and calcium (Ca^{2+}) ions.

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \quad (3.7)$$

The produced HCO_3^- then reacts with H^+ to produce carbon dioxide (CO_2) and H_2O.

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2 \quad (3.8)$$

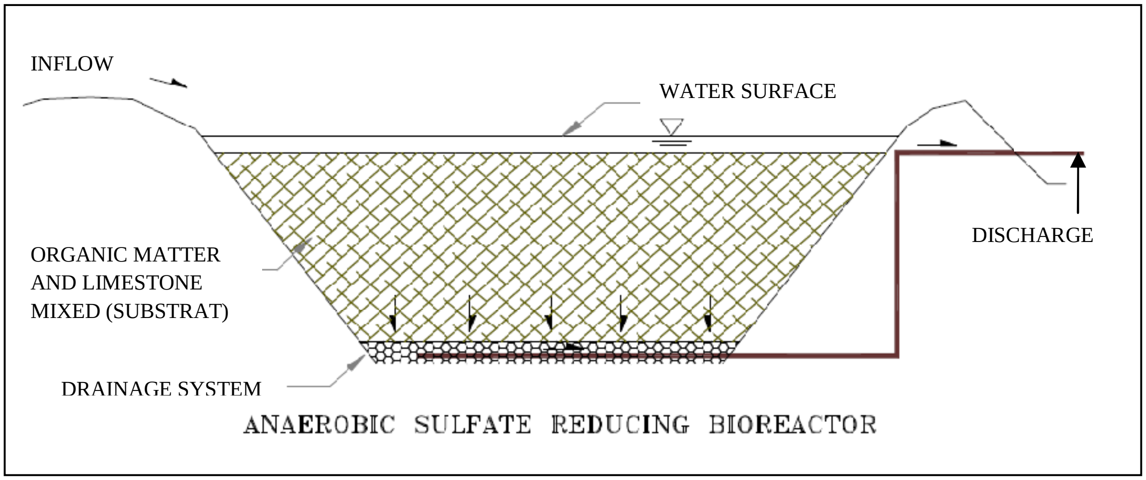


Figure 1. A section view of an anaerobic sulfate-reducing bioreactor. (Gusek, 2004). Reprinted by permission.

The consumption of H^+ contributes to the increase of the water's pH. As the pH increases, depending on the amount of dissolved O_2, dissolved metals in the AMD start to precipitate in the form of sulfides, (oxy)hydroxides, and/or carbonates. The dominant metal removal process in anaerobic bioreactors is precipitation of metals in the form of metal sulfides (Watzlaf et al., 2004). During the precipitation process, dissolved metals in the water react with HS^- to form metal sulfide precipitates as shown below.

$$HS^- + M^{2+} \rightarrow MS + H^+ \quad (3.9)$$

In reaction 3.9, M^{2+} represents divalent metals such as Fe^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} whereas MS represents the produced metal sulfide. The precipitation of dissolved metals in the form of metal sulfides depends on pH, solubility product of the specific metal sulfide, and the concentrations of the reactants (Hedin et al., 1994).

Metals might also precipitate in the form of (oxy)hydroxides and carbonates through oxidation and hydrolysis reactions as shown in reaction 3.3 and in the examples below (Watzlaf et al., 2004):

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (3.10)$$

$$Fe^{2+} + 0.25O_2 + 1.5H_2O \rightarrow FeOOH + 2H^+ \quad (3.11)$$

$$Mn^{2+} + 0.25O_2 + 1.5H_2O \rightarrow MnOOH + 2H^+ \quad (3.12)$$

$$Mn^{2+} + HCO_3^- \rightarrow MnCO_3 + H^+ \quad (3.13)$$

$$Fe^{2+} + HCO_3^- \rightarrow FeCO_3 + H^+ \quad (3.14)$$

During the processes described above, acidity, dissolved metals and SO_4^{2-} concentrations decrease improving the quality of the AMD water to an environmentally acceptable level.

4. THE STUDY AREA

4.1 General Description

The Tab-Simco is an abandoned coal mining site, located about 6 km southeast of Carbondale, Illinois, USA, (Fig. 2). The site is a “U” shaped upland about 37 meters above the surrounding lowland, and consists of approximately 12 hectares (30 acres) of underground mine works in two coal seams (Smith, 2002) (Fig. 3). The coal mining activities in the area exposed sulfide minerals to oxygenated rainwater, which caused oxidation and the production of low pH water with high SO_4^{2-} and metal content. The low pH water severely impacted the biological resources in the discharge area by destroying vegetation and nearly eliminating aquatic life around the site. In 1996, the Tab-Simco site was reported as one of the highly contaminated AMD sites in the mid-continent region (Smith, 2002). Starting in 1996, considerable reclamation works took place to restore the site and finally, in 2007, an anaerobic sulfate-reducing bioreactor was constructed at the site by the Illinois Department of Natural Resources Land Reclamation Division (IDNR-LRD) with the assistance of the Office of Surface Mining Reclamation and Enforcement Mid-Continent Region (OSMRE-MCR) to treat the AMD. The Abandoned Mine Land (AML) fund administered by OSMRE funded this reclamation activity.

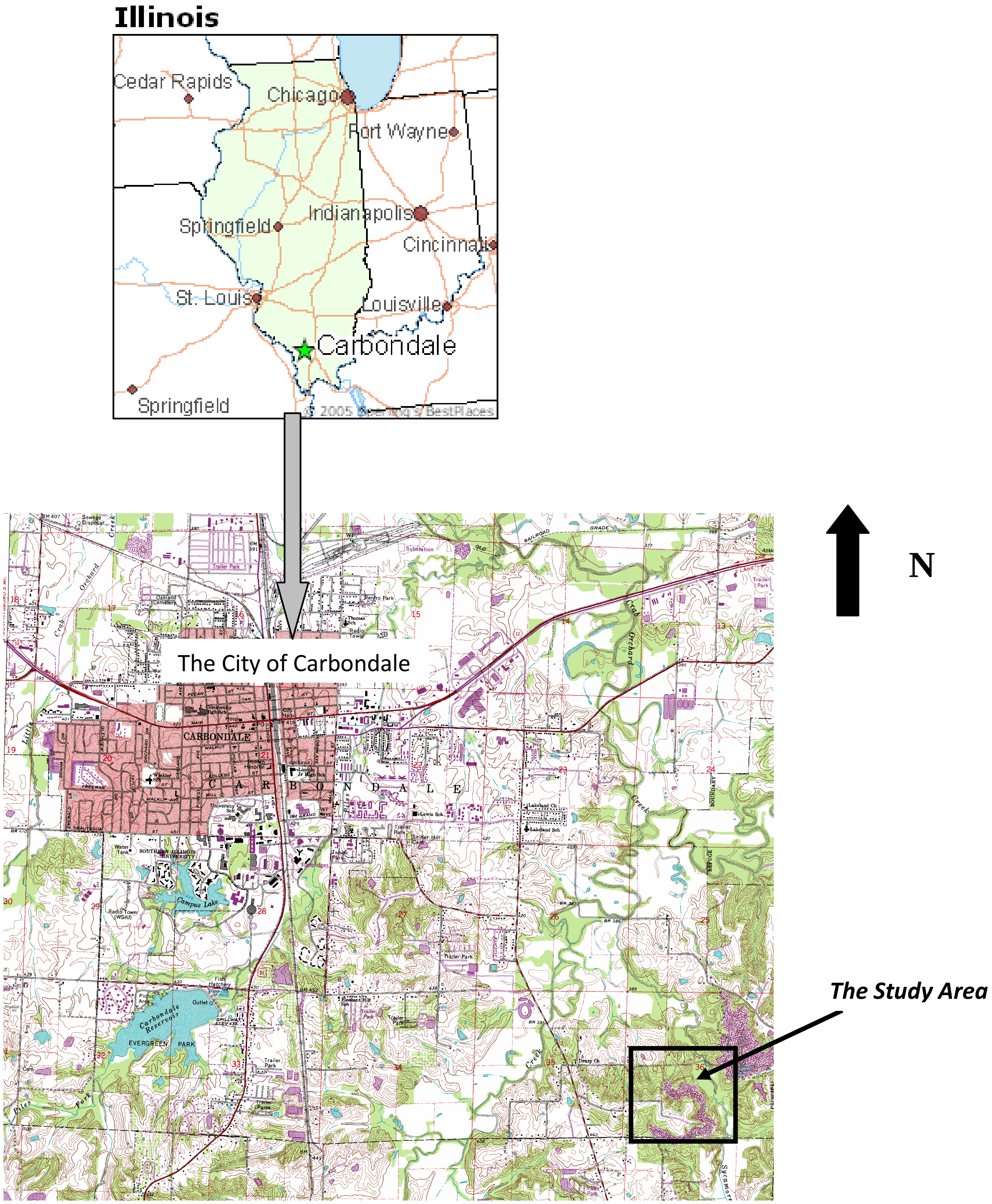


Figure 2. Location map of the study area (the Tab-Simco site), *Map downloaded from USGS website http://www.usgs.gov/, Carbondale, IL, 7.5 minute quadrangle*

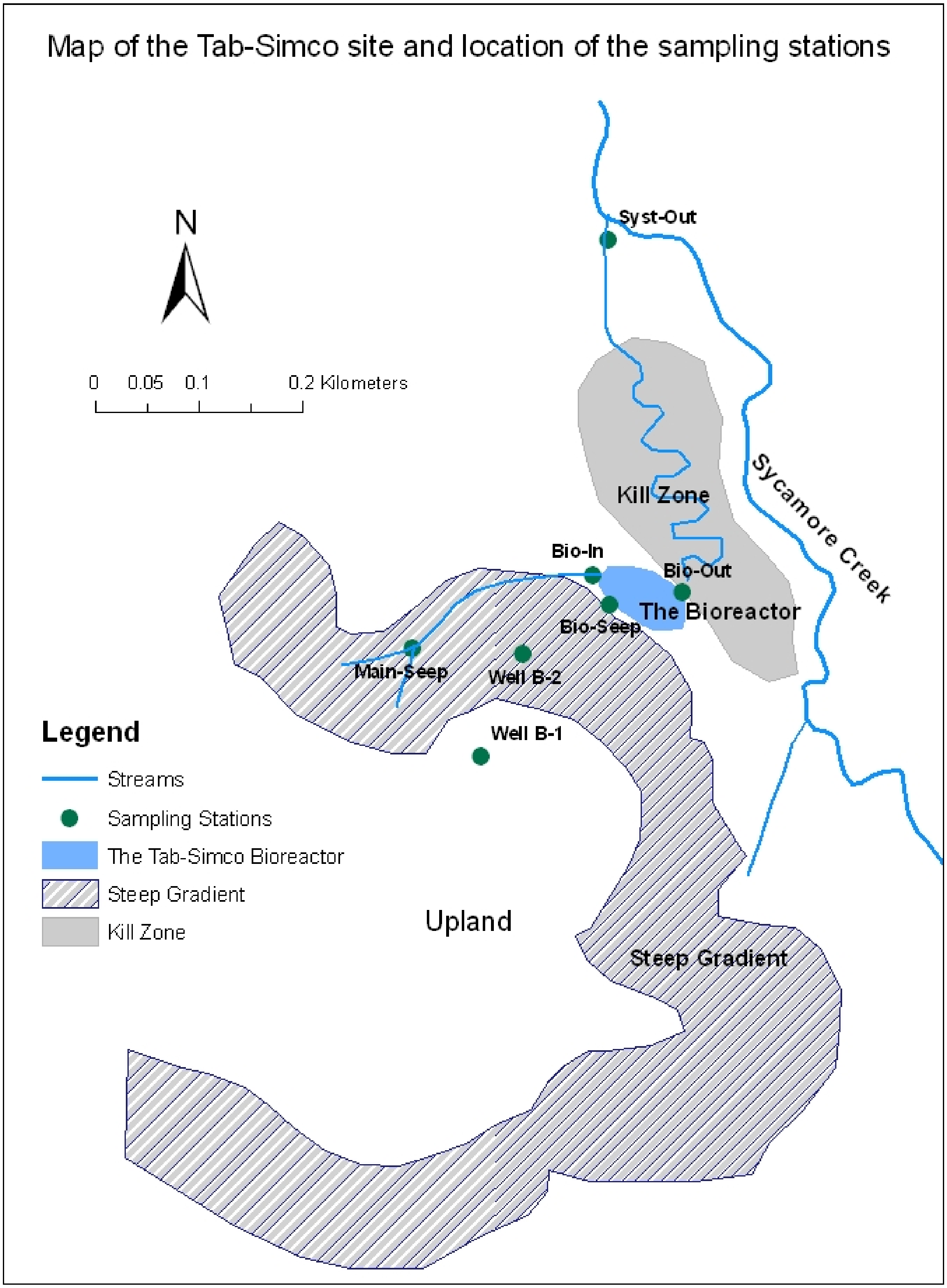


Figure 3. Map of the Tab-Simco site and the location of sampling stations.

4.2 Geology and Mining History of the Study Area

The Tab-Simco site is located within the Mt Vernon Hill Country sub-section of the Till Plains Section in the Central Lowlands Physiographic Province. The geology of site is characterized by the presence of a thin layer of superficial deposits of soils and loess underlain by Pennsylvanian rocks that dip gently to the north-northeast (Patrick Engineering, 1998). According to a comprehensive site investigation report by IDNR-LRD contractor Patrick Engineering in 1998, the Pennsylvanian rocks that underlie the area are part of the Spoon Formation. Spoon Formation rocks include alternating sandstone, shale, siltstone and

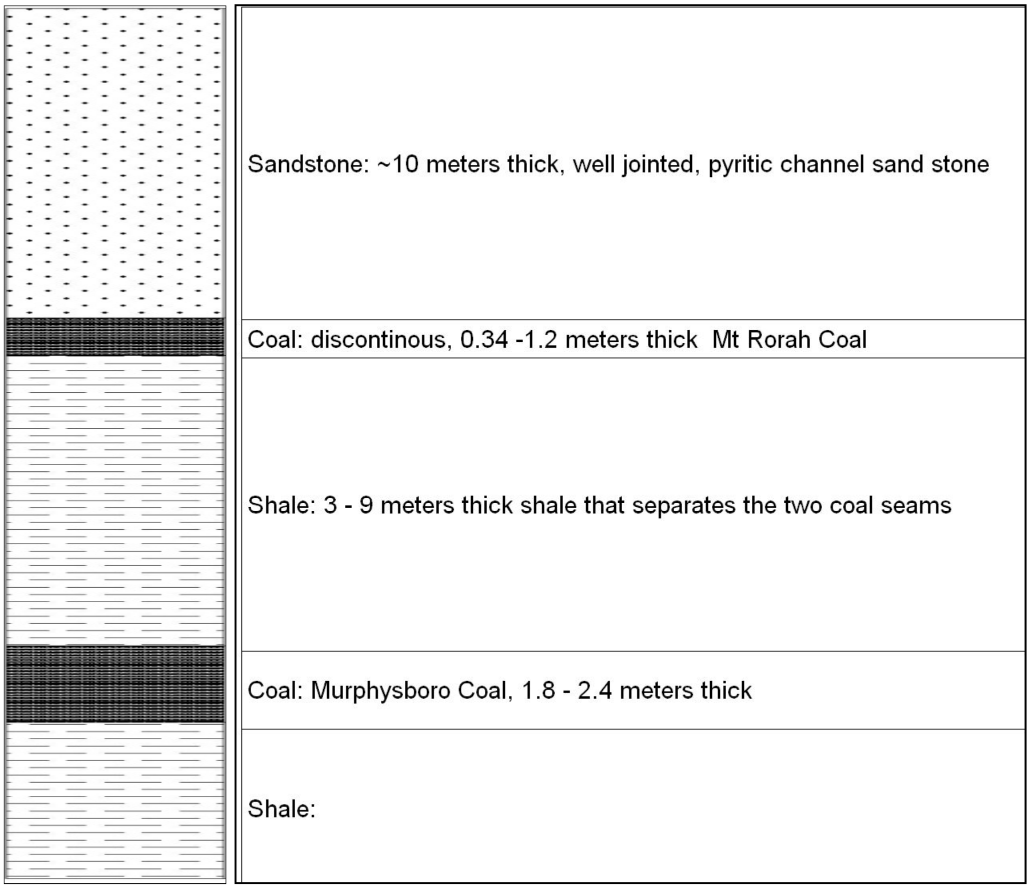


Figure 4. Typical stratigraphic column of the Tab-Simco site geologic units

claystone with occasional inter-layers of coal and limestone beds. The Pennsylvanian rocks in the study area, from top to bottom, are (1) a fine to medium grained, well jointed, pyritic channel sandstone up to 10 meters thick, (2) the discontinuous Mount Rorah Coal, which has thickness that ranges from 0.34 to 1.2 meters, (3) about 3 to 9 meters of a shale layer (4) the Murphysboro Coal that has thickness ranging from 1.8 to 2.4 meters (Patrick Engineering, 1998) and (5) a shale layer underlaying the Murphysboro coal. Figure 4 shows a typical stratigraphic column of the geologic units at the Tab-Simco site.

Underground and surface coal mining activities were performed in the area to mine the two coal seams, the Murphysboro (the lower seam) and the Mount Rorah. Underground coal mining occurred between 1890 and 1955 (Smith, 2002). An estimated 18 hectares (45 acres) were mined during this period (Lewis, 2008), although the full extent of this mining has not been identified. Strip mining of both coal seams along the south, east and north fringes of the mining site began in 1960 and ceased in 1975 (Lewis, 2008). It removed about 6 hectares (15 acres) of the older underground works, and has left large masses of spoil and numerous “break throughs” into the older underground mine works (Smith, 2002). In addition to this, the strip mining left about 1524 meters long steep, potentially hazardous, high-walls along the sides of the mining site (Lewis, 2008). Figure 5 shows a north-south cross-section through the mining site.

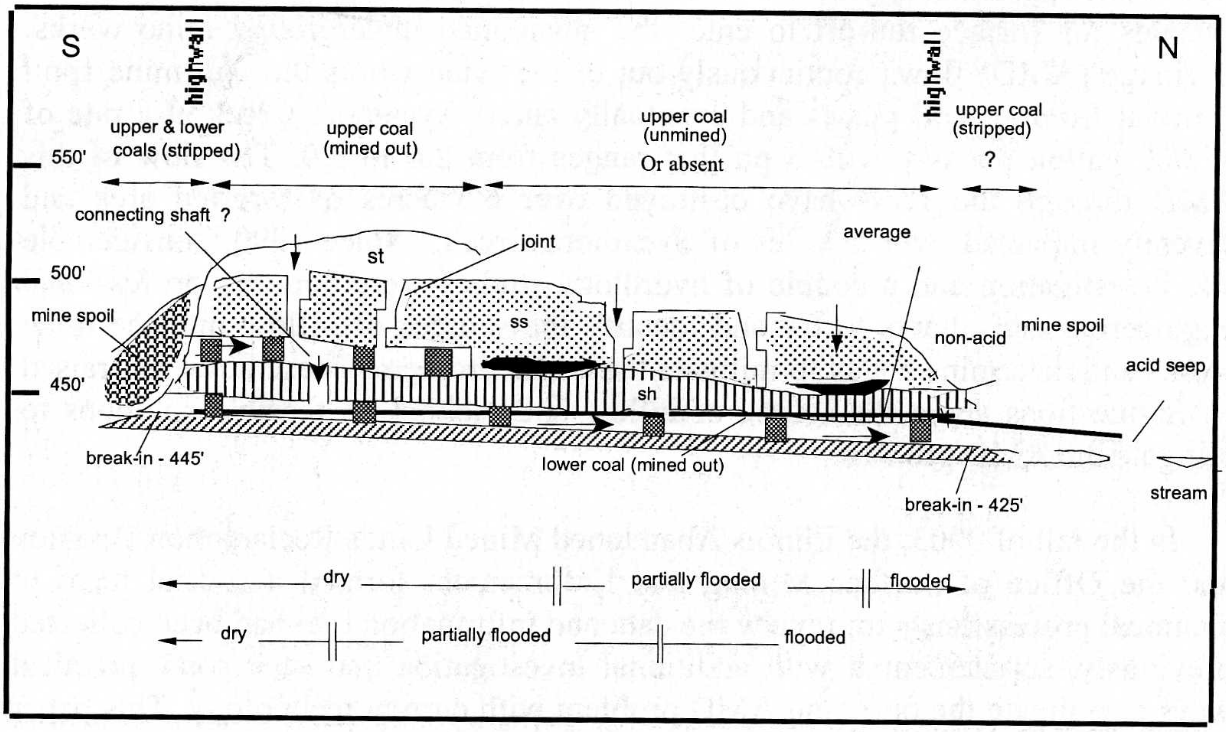


Figure 5. North-south cross-section through the mining work. (*Smith, 2002)*

4.3 AMD Development and Its Environmental Impact at the Tab-Simco Site

The coal mining activities in the study area exposed sulfide minerals in the rocks to oxygenated water. The exposure of sulfide minerals to H_2O and O_2 initiated oxidation of the sulfide minerals leading to the development of low pH acid water in the spoil and the underground mine works. Subsequently, acid mine pools were formed within the underground mine works (Smith, 2002). AMD from these pools flow from south to north following the dip of the underground mine works and discharges through a series of seeps located primarily in the northern part of the site (Smith, 2002). The acid water discharge, then, flows along a small tributary that runs north before discharging into the receiving stream, Sycamore Creek.

Recharge replenished the acid mine pool by infiltration through the jointed sandstone that overlies the upper coal seam and from run-off through “break ins”, and abandoned shafts and boreholes from the mine works. Consequently, the water level of the mine pool and volume of acid water discharge to the ground surface vary with the amount of precipitation water that reaches the acid mine pool. Prior to reclamation, the acid pool within the underground works discharged about 132,489 liters per day (35,000 gallons per day) of AMD with pH ranging from 2.6-3.0 (Lewis, 2008).

In the years between the cessation of mining activities (1975) and the construction of the anaerobic sulfate-reducing bioreactor at site (2007), the AMD caused severe environmental destruction on about 4 hectares of forest area, known as the “kill-zone” (Smith, 2002). The low-pH waters destroyed the vegetation and its ecological systems completely. It also severely degraded the Sycamore Creek for over 3.2 km (2 miles) downstream of the AMD site, destroying its aquatic life (Lewis, 2008).

4.4 Reclamation Efforts

Considerable efforts have been taking place at the site to minimize the adverse environmental impact from AMD and restore the site. These efforts comprise of a series of site investigations and reclamation works aimed at minimizing the amount of AMD, treating it and restoring the site.

Between 1996 and 1998, Patrick Engineering, Inc. (PEI) conducted a detailed site investigation that included drilling core, installing monitoring wells, sampling soil and water, and measuring hydrologic parameters. This study was done in three phases and provided the basis for the understanding of the underground mine work system, geology, hydrology and flow system, the geochemical characteristics of the AMD and other important aspects of the site (Patrick Engineering, 1998). In 1996 and1997, IDNR-LRP, the state's AML program, took steps to seal the mine opening to minimize water entering the underground mine works and back filled about 427 meters of the dangerous high-wall left from the strip mining (Lewis, 2008).

Investigation for site restoration design at the site started in 2003 by a technical team from the Illinois state AML program, OSMRE-MCR and the Southern Illinois University Carbondale's Cooperative Wildlife Resource Center. The team was composed of professionals from mining and civil engineering, geology, chemistry and hydrology (Lewis, 2008). The investigation took place in three phases. During the first phase, reclamation followed the recommendations of the previous study. The drainage system of the site was improved by constructing trenches that directed run-off water away from the site, and all isolated impoundments were backfilled. These efforts were undertaken to minimize the run-off water that enters the mine works and thereby reduce the AMD. During the second phase, in 2005, about 519 meters (1900 feet) long of the high-wall was backfilled to reduce its slope. Possible susceptible infiltration sites were sealed and the site was regraded, and lime and fertilizer were added on over 8 hectares (20 acres) to the site (Lewis, 2008). During the final phase in 2007, the remaining 518 meters (1,700 feet) of the high-wall were backfilled and 7.7 hectares (19 acres) of the site were seeded. Most importantly, a sulfate-reducing anaerobic bioreactor was constructed to treat the AMD and reduce the acidity and concentration of SO_4^{2-} and metals to acceptable standards (Lewis, 2008).

4.5 The Tab-Simco Anaerobic Sulfate-reducing Bioreactor

The Tab-Simco anaerobic sulfate-reducing bioreactor was constructed by IDNR to treat the AMD at the site to prevent further environmental degradation. The bioreactor is located on the northern edge of the site at a lower elevation compared to the seepage points (Fig. 3). The bioreactor was constructed on an area of approximately 300m^2 (0.75 acres). The Tab-Simco bioreactor comprises, from top to bottom, a 0.3-meter (1 foot) standing acid water impoundment, a 2-meter (six-foot) thick organic layer underlaying the standing water, and a 0.3-meter (one-foot) limestone layer. Within the limestone layer are perforated 6” PVC pipes that help to collect and discharge the treated water. The 2-meter (6 foot) organic layer is composed of 53% woodchips, 27% straw mulch, 11% seasoned compost and 9% agricultural ground limestone. The bioreactor was completed in October 2007 and started to work in by the beginning of 2008 (Lewis, 2008).

AMD enters the bioreactor in two ways: (1) from groundwater seepage directly into the bioreactor and (2) from surface flow through the bioreactor inlet (Fig. 3). The AMD that enters the bioreactor from surface flow reaches the bioreactor after seeping upstream through constructed subsurface French drains filled with chert into an open trench that runs to the bioreactor. The water then flows vertically through the organic matter and limestone layers, reaches the PVC pipes and leaves the system after flowing horizontally through the pipes.

As the water flows through the organic matter, sulfate-reducing bacteria in the organic matter are expected to reduce dissolved SO_4^{2-} to H_2S and produce HCO_3^-(Reaction 3.6). Additional HCO_3^- is also expected to be produced from limestone dissolution both in the organic and the limestone layers. Then, the HCO_3^- produced neutralizes the acid in the AMD, increasing the pH level. As the pH of the water increases, dissolved metals react with hydrogen sulfide to form metal sulfide precipitates as shown in reaction 3.9. Dissolved metals can also precipitate in the form of (oxy)hydroxides and carbonates as shown in reactions 3.3 and 3.10-3.14. During these processes, acidity and dissolved SO_4^{2-} and metals decrease significantly and the quality of the AMD is improved.

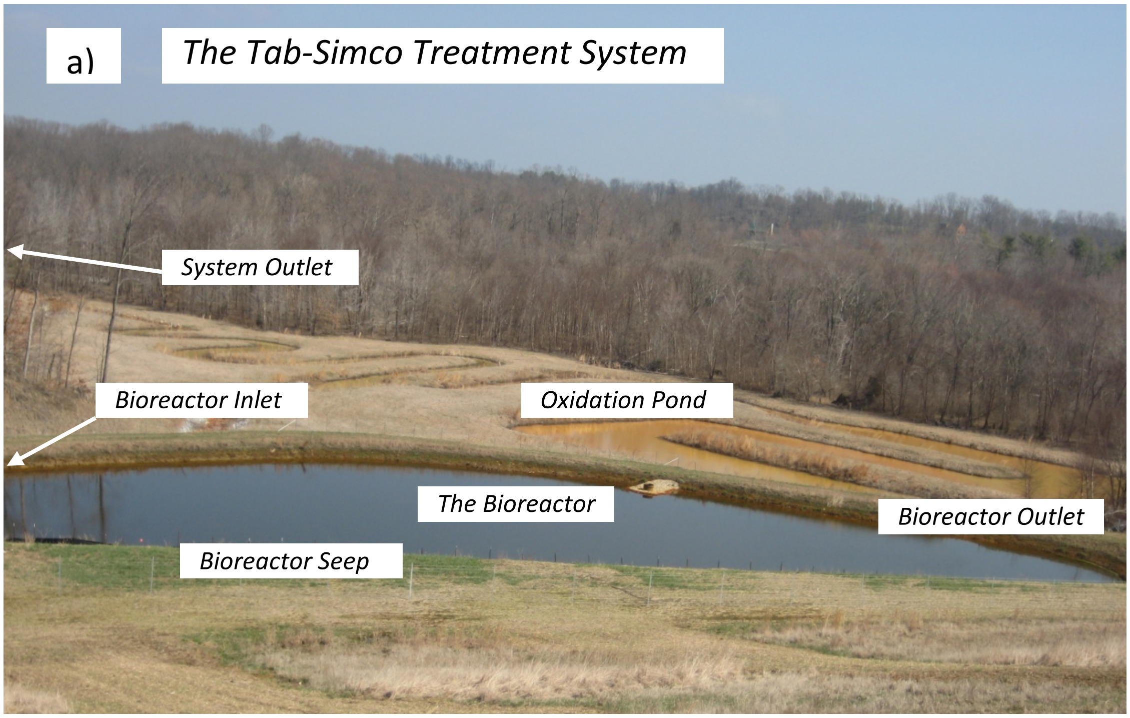
After leaving the bioreactor, the treated water enters an oxidation pond (settling pond) located immediately below the bioreactor. In the oxidation pond, metals such as Fe and Mn can be oxidized and removed in the form of (oxy)hydroxide precipitation. The treated water then continues to flow slowly downstream in an open limestone channel, a winding open trench lined with limestone, until it joins the north flowing Sycamore Creek (Fig. 3).

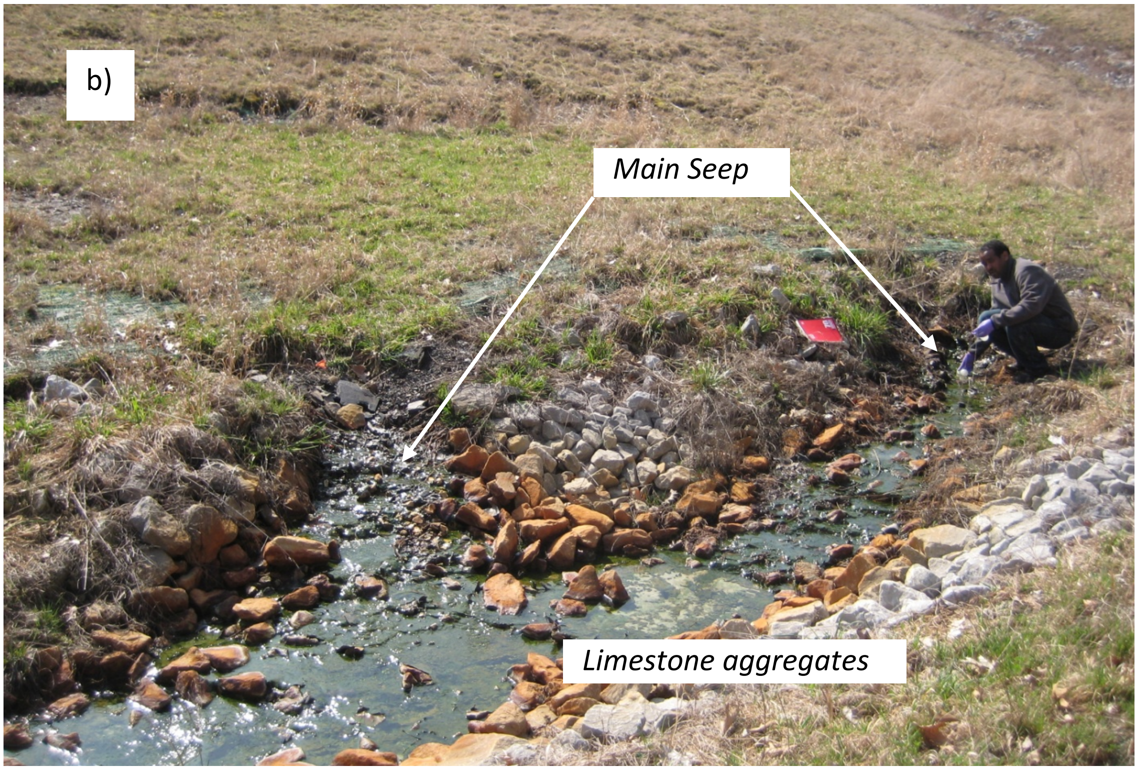
5. METHODS AND MATERIALS

5.1 Water Sampling

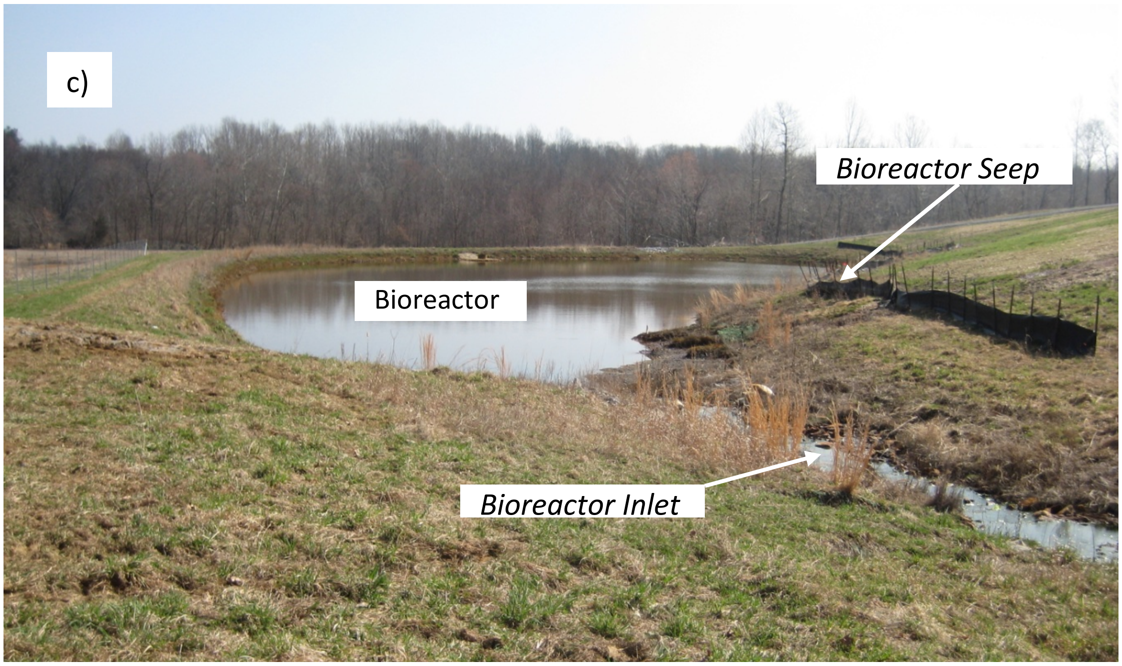
Water samples for chemical and isotopic analyses were collected from the study area between July 2008 and Sept 2009. Samples were taken from seven sampling stations at the study area (Fig. 3). The sampling stations were located at: (1) groundwater monitoring well B-1, a well drilled into the underground acid pool, (2) well B-2, a well located between the underground acid pool and the bioreactor, (3) the bioreactor seep, where AMD from groundwater seeps into the bioreactor, (4) the main seep, a site where most of the AMD seeps to the surface upstream the bioreactor, (5) the bioreactor inlet, a point where the AMD enters the bioreactor from surface flow, (6) the bioreactor outlet, a point where the treated water leaves the bioreactor, and (7) the system outlet, a point where the treated water leaves the entire treatment system and enters Sycamore Creek. Figure 6a-f show photos of the Tab-Simco treatments system, and the sampling stations.

At each station, duplicate water samples were collected in 125 ml bottles. One of the water samples was used for metal analyses and the other water sample was used for SO_4^{2-}, alkalinity, and ferrous and total Fe analyses. Immediately after sampling, the samples were stored in ice in an insulated cooler until they were taken to the laboratories.

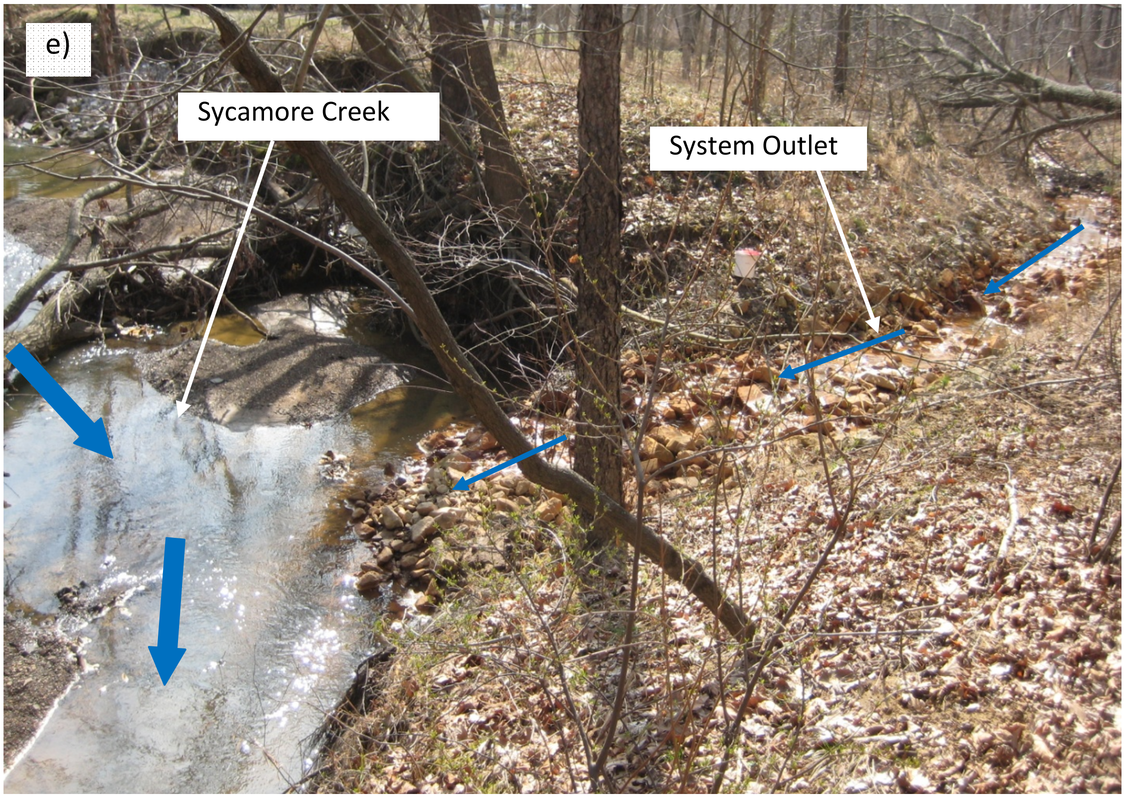


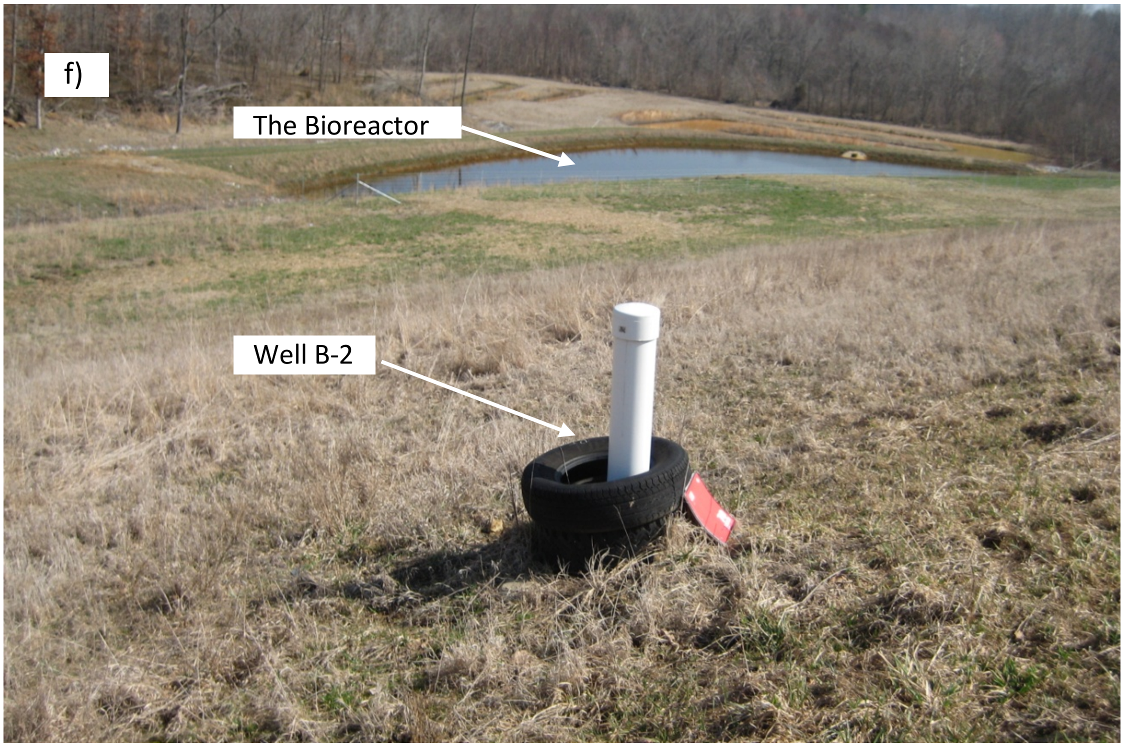


Figures 6a & 6b. (a) The Tab-Simco treatment system. Photo was taken looking northeast. (b) The Main Seep sampling station. Photo was taken looking southwest.



Figures 6c & 6d. (c) The Bioreactor inlet and Bioreactor seep sampling stations. (d) The Bioreactor outlet sampling station. Both photos were taken looking east.





Figures 6e & 6f. (e) The System Outlet sampling station. Photo was taken looking south. (f) Well B-2 sampling station. Photo was taken looking northeast.

5.2 Field Measurements

At each sampling station, I measured the following in situ parameters: pH level, specific conductance (Sc), dissolved oxygen (DO), oxidation reduction potential (ORP) and flow rate. A Hach (Loveland, CO) HQ40D pH/ conductivity/ DO meter was used to measure pH level, Sc and DO values of the acid water. A Fisher (Pittsburgh, PA) Accumet® instrument with a platinum electrode was used to measure the ORP. The flow rates at the bioreactor inlet and bioreactor outlet were measured using a bucket and a stopwatch. The flow rate of the AMD that seeped from groundwater was then determined by subtracting the bioreactor inlet flow rate from that of the bioreactor outlet flow rate.

5.3 Laboratory Analyses

Chemical analyses: Immediately after arriving at the laboratory, the water samples were filtered using pre-baked and dried 0.22 μm pore-size quartz-fiber filters (Whatman, QM-A). Samples for metal analyses were then acidified to pH below 2.0 using 50% nitric acid (HNO_3) and were refrigerated until chemical analyses were performed. The duplicate samples were analyzed for total alkalinity, dissolved ferrous and total Fe, and SO_4^{2-} concentrations immediately.

Researchers from the OSMRE-MCR, Alton, Illinois determined alkalinity, Fe^{2+} and total Fe concentrations. The concentrations of the dissolved metals (Fe, Ca, Al, Mn, Mg, Na and K) and SO_4^{2-} were determined in the Geochemistry Laboratory at Southern Illinois University Carbondale (SIUC). In addition to the analyses in the SIUC laboratory, SO_4^{2-}, Mn and Al concentrations were also measured at OSMRE-MCR laboratory.

Alkalinity value in the AMD was determined by titration using Hach digital micropipette and pH meter. Samples were titrated using H_2SO_4 (sulfuric acid) to a pH of 4.5, and samples with pH less than 4.5 were considered to have zero alkalinity value (American Public Health Association, 1998b). Total acidity was then determined by calculation from pH, Fe^{3+}, F^{2+}, Al and Mn concentration values using the formula below (Hedin et al. 1994; Rose et al., 1998).

$$\textbf{Total Acidity} = 50*[2*(Fe^{2+})/56 + 3*(Fe^{3+})/56 + 3*Al/27 + 2*Mn/55 + 1000*10^{-pH}]$$

Finally, Net acidity was calculated by subtracting alkalinity from total acidity.

SO_4^{2-} concentrations were determined using a Dionex (Sunnyvale, CA) ICS-2000 ion chromatography with KOH eluent and an IonPack® AS18-HC column. Dissolved Fe^{2+} and total Fe concentrations were analyzed using colorimeter, Hach Ferrous (Method Number 8146) and FerroVer (Method Number 8008) methods, respectively*.* The acidified samples for metal analyses were analyzed for concentrations of Fe, Al, Mn, Ca, Mg, Na, and K using a Hitachi (Suite 500 Schaumburg, Illinois) Z-2000 Polarized Zeeman Atomic Absorption Spectrometer (AAS) flame test method.

Isotope analyses: Sulfur isotope values for dissolved SO_4^{2-} were measured at Indiana University using a Thermo Scientific (Waltham, MA) manufactured Finnigan/Mat Delta Plus® stable-isotope ratio mass spectrometer. The stable isotope ratios are expressed in standard $\delta^{34}S$ notations in parts per thousand ("per mil", ‰) relative to Vienna Cañon Diablo Troilite (V-CDT) standard (Craig, 1957):

$$\delta^{34}S = (R_{sample} - R_{standard}) / R_{standard} \times 1000\ (‰)$$

Where, R_{sample} and $R_{standard}$ refer to the $^{34}S/^{32}S$ ratios in sample and standard, respectively.

For the stable sulfur isotope analyses, first barium chloride (BaCl) solution was added to the samples to precipitate the SO_4^{2-} in the form of barium sulfate ($BaSO_4$). Then the $BaSO_4$ samples were dried in an oven. Then, from each sample, about 510 μg of the dried $BaSO_4$ were loaded into tin cups, mixed with 1-2 mg of V_2O_5, and combusted on-line in an EA 1,110 elemental analyzer at a flash temperature of 1,400 ℃. Combustion products were carried by a continuous flow of helium through a 1,010 ℃ oxidation-reduction column, through a $MgClO_4$ water trap, and a Costech (Valencia, CA) packed column (0.8 m) to purify SO_2. Sulfur isotopic calibration utilized international standards IAEA-S1 = -0.3‰, IAEA-S2 = +21.6‰, IAEA-S3 = -31.3‰, and NBS127 = +20.3‰ (SO_2-scale). The analytical uncertainty was better than ±0.05‰, whereas sample reproducibility was typically ±0.15‰.

5.4 Mass Balance Calculations

In order to assess the performance of the Tab-Simco bioreactor, and the overall AMD treatment system, the concentration rates of the acidity, dissolved SO_4^{2-} and metals that entered and left the bioreactor, and the entire treatment system were calculated. The concentration rates (loading) of the parameters that entered and left the bioreactor were determined by multiplying the concentrations in the influent and effluent by their respective flow rates (Barton et al., 1999). The removal rates of the acidity, dissolved metals and SO_4^{2-} were then determined by subtracting the concentration rates in the effluent from that of the influent (Riefler et al., 2008). Finally, removal rates were converted to kilogram per day.

The alkalinity that neutralized the AMD within the Tab-Simco bioreactor was produced from BSR and limestone dissolution (Barton et al., 1999; Riefler et al., 2008). To determine the amount of alkalinity produced by each of these processes, Ca^{2+} and SO_4^{2-} concentration differences in the effluent and influent were used. To calculate alkalinity produced from limestone dissolution, the increase in Ca^{2+} concentration within the bioreactor was considered to be solely from limestone dissolution (Riefler et al., 2008). The alkalinity production rate by limestone dissolution was then calculated considering the fact that limestone dissolution produces equal number of HCO_3^- and Ca^{2+} moles (Reaction 3.7).

The rate of alkalinity production by the BSR processes was determined using the decrease in SO_4^{2-} concentration within the bioreactor. It was assumed that all SO_4^{2-} loss within the bioreactor was due to the BSR (Riefler et al., 2008). During BSR for each SO_4^{2-} mole reduced, two moles of HCO_3^- are produced (Reaction 3.6). The alkalinity production rates from both processes were then added to find the total alkalinity production rate within the bioreactor.

The total alkalinity production rate within the bioreactor was also determined using an independent method from net acidity removal rates within the bioreactor (Riefler et al., 2008). In this case, the amount of acidity removed within the bioreactor was assumed to be equal to the amount of alkalinity produced. The total alkalinity production rate found from this method was then compared with the one determined from the BSR and limestone dissolution.

6. RESULTS

6.1 Field Parameters

The Tab-Simco AMD Field parameter results measured at seven sampling stations are presented in Table 1 and Figure 7. Figure 7 shows the trend of field parameter values along the AMD flow direction, using the average value for each parameter at each sampling station. The results indicate that, as the acid water flowed from the acid mine pool (well B-1) to the main seep, pH level and DO values decreased slightly, whereas Sc and ORP values showed a small increase. The lowest mean pH value in the Tab-Simco AMD, 2.8, was measured at the main seep sampling station. Between the main seep and the bioreactor inlet sampling stations, the trend was reversed, pH, DO and ORP values increased, whereas Sc value decreased.

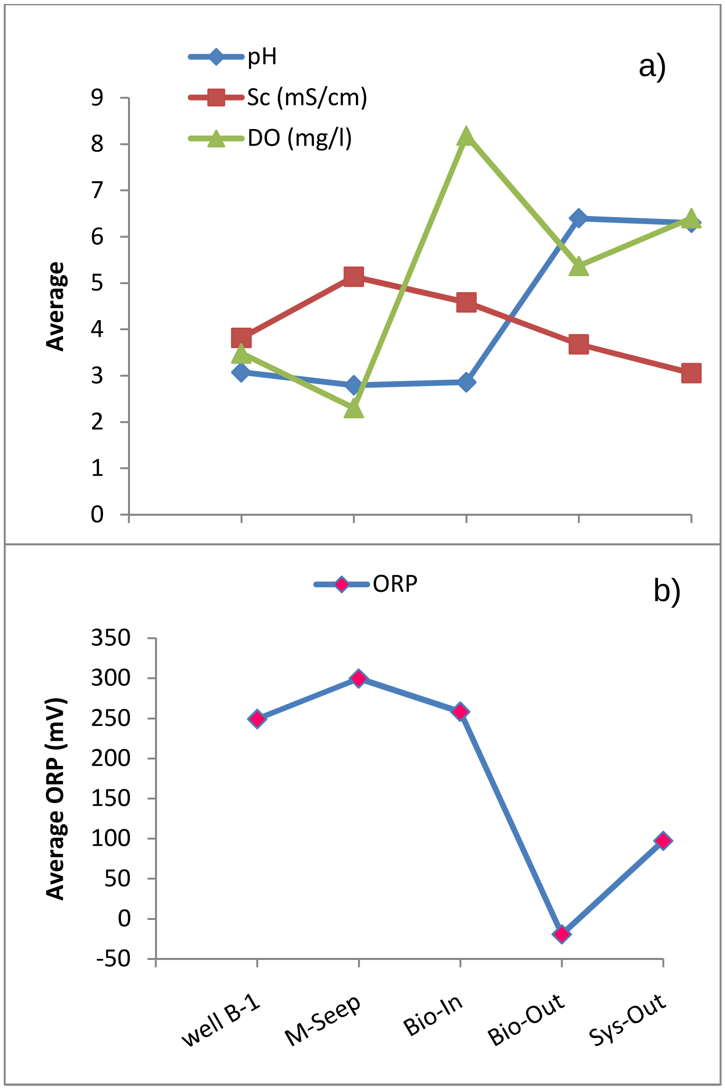
Analyses of groundwater samples from well B-2, which represents the chemical characteristics of the AMD that seeped directly into the bioreactor, showed similar mean pH value, 2.83, to the AMD that entered the bioreactor from surface flow through the bioreactor inlet, 2.86. However, the mean pH value at well B-2 was lower than the mean pH value at the mine pool, 3.07, suggesting pH decreasing processes between well B-1 and B-2. Mean Sc, DO and ORP values at well B-2 were similar to the values at Well B-1, although, the mean Sc and DO values at B-2 were lower compared to their values at the bioreactor inlet.

As the AMD flowed through the bioreactor, a sharp increase in pH was observed and the pH value of the water, at the bioreactor outlet, was increased to 6.40, whereas DO, Sc and ORP values of the AMD were decreased

Table 1: *Field measurement results from the Tab-Simco AMD.*

ID	Station	Date	pH	Temp (^{o}C)	Sc (mS/l)	DO (mg/l)	DO Sat. %	ORP (mV)	DTW (ft)
1	Well B-1	10/22/08	2.90	17.90	4.10	3.72	42.5	NM	NM
		12/01/08	3.03	10.40	4.10	NM	NM	323	78.12
		01/22/09	3.23	13.80	3.92	3.75	37.6	278	78.43
		03/12/09	2.71	14.70	3.97	1.61	14.8	278	78.00
		07/30/09	3.50	18.60	3.00	4.85	56.4	118	75.66
2	Well B-2	07/11/08	2.75	26.50	3.55	5.42	NM	392	23.40
		10/22/08	2.80	15.10	3.66	2.13	22.7	292	25.41
		12/01/08	2.70	12.80	4.42	NM	NM	348	25.90
		04/30/09	2.79	17.90	3.49	3.85	44.5	129	24.35
		07/30/09	2.82	17.60	2.99	3.64	43.5	96	23.40
		09/23/09	3.11	18.80	3.00	3.40	37.1	255	NA
3	Main Seep	10/22/08	2.80	16.10	4.63	2.05	22.0	280	NA
		12/01/08	2.66	12.30	5.53	3.10	NM	318	NA
		01/22/09	2.70	11.50	5.64	3.03	30.2	330	NA
		09/23/09	3.02	17.20	4.75	1.04	11.1	271	NA
4	Bioreactor Inlet	07/11/08	2.76	23.00	4.78	8.72	NM	NM	NA
		09/15/08	2.95	18.40	4.30	8.56	100.1	340	NA
		10/14/08	2.93	19.40	4.86	8.52	101.1	NM	NA
		10/22/08	2.90	12.60	4.36	10.50	105.3	326	NA
		12/01/08	2.90	7.10	4.81	9.72	81.0	306	NA
		01/22/09	2.99	11.90	4.72	7.45	65.2	345	NA
		03/12/09	2.60	7.00	4.85	8.61	75.3	308	NA
		04/30/09	2.87	23.30	4.46	9.22	116.2	101	NA
		07/30/09	2.71	23.10	4.40	3.74	40.2	122	NA
		09/23/09	2.99	24.60	4.30	6.79	81.8	219	NA
5	Bioreactor Outlet	07/11/08	6.39	27.10	4.52	4.89	NM	NM	NA
		09/15/08	6.42	22.50	3.56	4.61	57.8	18	NA
		10/14/08	6.40	20.90	4.20	5.63	68.2	NM	NA
		10/22/08	6.23	18.40	3.18	4.80	55.7	-20	NA
		12/01/08	6.38	11.90	4.40	6.92	66.2	24	NA
		01/22/09	6.27	9.80	3.67	5.94	72.5	66	NA
		03/12/09	6.89	9.05	3.29	7.28	67.0	35	NA
		04/30/09	6.34	17.40	3.21	5.68	62.9	-71	NA
		07/30/09	6.34	23.45	3.10	3.00	39.0	-93	NA
		09/23/09	6.32	23.90	3.63	4.96	60.0	-113	NA
6	System Outlet	10/14/08	6.55	20.90	3.47	4.13	50.0	NM	NA
		10/22/08	6.54	12.90	3.29	5.78	68.2	70	NA
		12/01/08	6.23	5.00	3.53	7.44	62.8	259	NA
		01/22/09	5.68	3.10	3.39	6.46	55.7	134	NA
		03/12/09	5.64	3.60	2.82	10.09	55.7	134	NA
		04/30/09	5.25	22.60	2.12	6.74	84.0	NM	NA
		07/30/09	7.45	26.60	2.79	3.14	42.6	37	NA
		09/23/09	7.07	25.00	3.04	7.43	91.1	-50	NA

Note: NM = Not Measured, NA = Not Applicable, DTW = Depth to Water.



Figures 7. Field measurement values along the flow direction at the Tab-Simco site using average values in each sampling station.

significantly (Fig. 7). In addition, a strong smell, which probably was produced by H_2S emissions (reaction 3.6) from the bioreactor, was detected at the bioreactor outlet.

Between the bioreactor outlet and the system outlet, DO and ORP increased significantly, while the pH remained relatively constant, and Sc continued to decrease (Fig. 7).

Flow rates: Influent and effluent flow rates within the bioreactor varied seasonally with considerable increase during spring and summer (Table 2). Total flow rate into the bioreactor, measured between 7/2008 and 9/2009, ranged between 40.0 and 128.6 l/min (excluding flow rate from 4/30/2009), with an average value of ~ 65 l/min (93,609 liters/day). The proportion of AMD that entered the bioreactor from surface flow to groundwater seep varied seasonally. The proportion of the AMD that entered from the groundwater seep increased significantly during rain seasons (spring and summer). During one of the sampling dates, 4/30/2009, after an overnight heavy rainfall, the effluent flow rate was abnormally high due to additional of water from run-off. When calculating the bioreactor performance for this sampling date, a reasonable flow rate, based on the flow rates from the previous sampling dates, was used for the AMD that seep from groundwater to avoid the effect of run-off water.

Table 2: *The Tab-Simco AMD flow rate measurements (liters per minute)*

Date	Bioreactor Outlet	Bioreactor Inlet (from surface flow)	Bioreactor seep (from groundwater seep)
07/11/08	80.00	48.00	32.00
10/22/08	40.00	33.00	7.00
12/01/08	40.00	33.00	7.00
01/22/09	45.00	30.00	15.00
03/12/09	60.00	30.28	29.72
04/30/09	171.43	45.00	90.00
07/30/09	128.57	58.54	70.03
09/23/09	60.00	40.00	20.00

6.2 Acidity and Alkalinity Values

Alkalinity, total acidity, and net acidity values for the Tab-Simco AMD are given in Table 3 and Fig. 8. The alkalinity and acidity values are expressed in mg/l as $CaCO_3$ equivalent. Since the pH values at well B-1, well B-2, bioreactor seep, main seep, and bioreactor inlet sampling stations were always below 4.5, alkalinity at these sampling stations was always zero. As the water flowed from the mine pool to the main seep, considerable increase in average acidity, from 1,735 to 3,386 mg/l, was observed (Table 3, Fig. 8). Between the main seep and the bioreactor inlet the average acidity decreased slightly. The highest average acidity value at the site was measured at the main seep sampling station. For the AMD that seeped from groundwater, the average acidity at well B-2, and bioreactor seep were similar to that of the acid mine pool (well B-1).

Within the bioreactor, a substantial amount of alkalinity was produced and the acidity showed a significant drop from an average of 2,766 mg/l, at the bioreactor inlet, to an average of 360 mg/l, at the bioreactor outlet (Fig. 8). Accordingly, the average net acidity at the bioreactor outlet was only 68 mg/l.

However, as the treated water flowed between the bioreactor outlet and the system outlet, additional acidity released from hydrolysis reactions and precipitation of metal hydroxides, such as $Fe(OH)_3$ and $Al(OH)_{3,}$ consumed more of the alkalinity. Consequently, the average alkalinity at the system outlet dropped to 45 mg/l as $CaCO_3$ equivalent (Fig. 8).

6.3 Sulfate Concentration

Table 4 lists dissolved SO_4^{2-} and metal concentration values from the Tab-Simco AMD. The trends of the SO_4^{2-} concentration along the flow direction using average values for each parameter in each sampling station is shown in Figure 8. The data indicate that SO_4^{2-} concentration in the AMD varied along the flow path from the acid mine pool to the system outlet. As the acid water flowed from the acid mine pool to the main seep, a substantial increase in SO_4^{2-} concentration,

Table 3: Alkalinity and Acidity Values in Tab-Simco AMD (mg/l as $CaCO_3$ equiv.)

ID	Sampling site	Sampling Date	pH (lab)	Total Alkalinity	Acidity	Net Acidity
1	**Well B-1**	12/01/08	3.03	0.0	2182.0	2182.0
		01/22/09	3.23	0.0	2144.5	2144.5
		07/30/09	3.50	0.0	877.7	877.7
2	**Well B-2**	12/01/08	2.70	0.0	1989.4	1989.4
		04/30/09	2.79	0.0	1880.7	1880.7
		07/30/09	2.82	0.0	1577.9	1577.9
		09/23/09	2.92	0.0	1312.1	1312.1
3	**Bioreactor Seep**	03/22/09	2.81	0.0	2036.7	2036.7
		04/30/09	3.00	0.0	1772.7	1772.7
		09/23/09	2.89	0.0	1404.1	1404.1
4	**Main Seep**	12/01/08	2.66	0.0	3366.0	3366.0
		01/22/09	2.70	0.0	3553.8	3553.8
		03/22/09	2.70	0.0	3397.36	3397.36
		09/23/09	2.91	0.0	3233.3	3233.3
5	**Bioreactor Inlet**	10/14/08	2.93	0.0	2492.2	2492.2
		12/01/08	2.90	0.0	2870.3	2870.3
		01/22/09	2.99	0.0	2714.9	2714.9
		03/22/09	2.81	0.0	2865.4	2865.4
		04/30/09	2.87	0.0	2702.6	2702.6
		07/30/09	2.71	0.0	2924.6	2924.6
		09/23/09	2.87	0.0	2791.7	2791.7
6	**Bioreactor Outlet**	10/14/08	6.38	336.0	216.1	-119.9
		12/01/08	6.38	350.0	403.0	53.0
		01/22/09	6.27	215.2	346.5	131.3
		03/22/09	6.34	289.0	367.0	78.0
		04/30/09	6.34	241.6	422.3	180.7
		07/30/09	6.34	320.0	406.0	86.0
		09/23/09	6.32	300.0	551.5	251.5
7	**System Outlet**	10/14/08	6.55	111.0	56.3	-54.7
		12/01/08	6.23	5.0	51.5	46.5
		01/22/09	5.66	32.0	134.1	102.1
		03/22/09	5.72	82.4	90.6	8.2
		04/30/09	5.25	6.4	49.3	42.9
		07/30/09	7.45	36.0	64.7	28.7
		09/23/09	7.22	56.0	33.7	-22.4

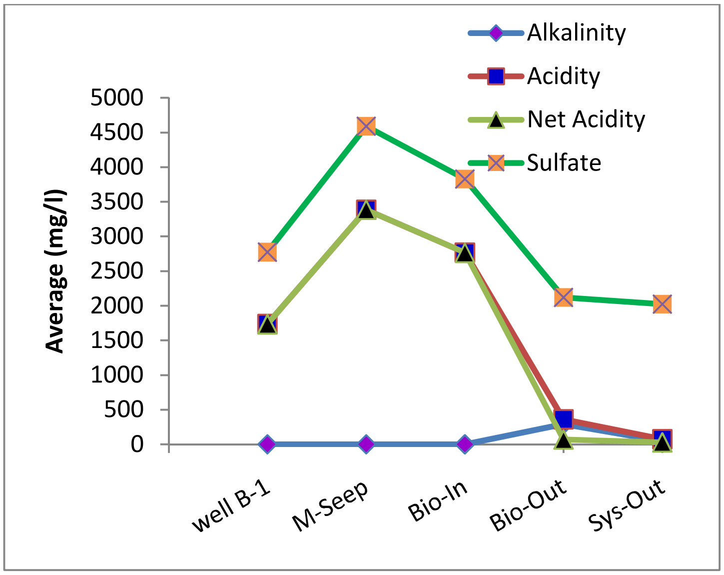


Figure 8. Sulfate, acidity and alkalinity values along the flow direction at the Tab-Simco site using average values in each sampling station.

from an average of 2,774 to 4,589 mg/l, was observed (Table 4, Fig. 8) and the pH value reached its maximum measured average value along the flow path. Then, between the main seep and the bioreactor inlet sampling stations, average SO_4^{2-} concentration displayed a relatively smaller decreased. On the other hand, the average SO_4^{2-} concentration in the AMD that seeped from groundwater was similar to the average SO_4^{2-} concentration in the acid mine pool (Table 4). Therefore, as the AMD entered the bioreactor the average SO_4^{2-} concentration of the AMD from surface flow was higher compared to its concentration in the acid groundwater seepage (Table 4).

Within the bioreactor, SO_4^{2-} concentration decreased significantly from an average of 3,830 to 2,119 mg/l. However, as the treated water flowed between the bioreactor and the system outlet, SO_4^{2-} concentration did not show significant changes (Fig. 8).

6.4 Metal Concentrations

Metal concentrations along the flow direction showed different patterns (Fig. 9). Dissolved Fe and Al concentrations displayed similar patterns (Fig. 9a and 9b), in which an increasing trend was first observed between the mine pool and the main seep sampling station, and then the concentrations decreased continuously to the system outlet. The highest Fe and Al concentration drops along the flow path were measured within the bioreactor, where the average total concentrations were decreased from 778 to 154 mg/l for Fe and from 153 mg/l to below the detection limit for Al. Average dissolved Fe and Al concentrations in the acid groundwater that seeped to the bioreactor were similar to their values in the acid mine pool (Table 4). However, compared to the Fe and Al concentrations in the AMD that entered through the bioreactor inlet, which had average concentrations of 778 mg/l Fe and 153 mg/l Al, the Fe and Al concentration values in the acid water that seeped from groundwater to the bioreactor were much lower, 479 mg/l Fe and 106 mg/l Al.

As the AMD flowed from the acid mine pool to the bioreactor inlet, dissolved Mg, Na and K concentration trends in the AMD showed similar patterns with that of dissolved Fe and Al concentration trends (Table 4 and Fig. 9b and 9c). The average concentrations of the dissolved Mg, Na and K in the AMD increased from 156, 23.6 and 1.2 mg/l at the acid mine pool (well B-1) to reach their maximum measured values of 199, 29.4 and 5.0 mg/l at the main seep, respectively. As the water flowed to the bioreactor inlet sampling station, the concentration of these metals dropped slightly to reach 186, 25.9 and 3.1 mg/l,

Table 4: *Dissolved SO_4^{2-} and Metal Concentrations (mg/l) in the Tab-Simco AMD*

ID	Samp site	Samp. Date	SO_4^{2-}	Total Fe	Fe(III) %	Fe(III)	Fe(II)	Al	Mn	Ca	Mg	Na	K
1	**Well B-1**	12/01/08	3236.7	614.4	96.1	590.6	23.8	NM	34.1	222.2	158	21.10	0.92
		01/22/09	2765.0	621.8	62.0	385.7	236.1	108.0	33.2	211.8	156	24.65	1.22
		07/30/09	2319.7	244.6	33.0	80.6	164.0	53.6	30.4	250.6	154	21.95	1.59
2	**Well B-2**	12/01/08	3297.9	517.6	68.0	351.8	165.8	NM	33.1	194.8	159	20.90	0.54
		04/30/09	2714.1	480.4	65.5	314.7	165.7	107.5	34.2	173.8	156	22.55	0.56
		07/30/09	2048.8	315.0	52.1	164.1	150.9	131.6	34.2	192.4	129	20.80	0.70
		09/23/09	2236.6	326.6	57.5	187.8	138.8	80.0	31.2	163.8	143	22.00	0.66
3	**Bioreactor Seep**	03/22/09	3261.9	558.8	67.0	374.4	184.4	NM	34.9	260.4	147	21.55	0.91
		04/30/09	2977.1	447.4	67.0	299.8	147.6	NM	35.8	283.8	150	22.35	0.56
		09/23/09	2398.1	432.0	41.3	339.2	482.1	63.0	35.2	199.6	151	22.55	1.03
4	**Main Seep**	12/01/08	5099.4	844.6	70.7	597.2	247.4	NM	34.6	166.4	200	30.25	4.26
		01/22/09	4515.9	872.4	67.3	587.2	285.2	236.0	33.4	146.6	194	27.25	5.69
		03/22/09	4957.5	860.4	70.7	608.4	252.0	NM	36.2	139.4	201	28.85	4.92
		09/23/09	3781.8	958.8	47.4	454.4	504.3	178.7	33.7	134.3	201	31.05	5.11
5	**Bioreactor Inlet**	10/14/08	NM	772.2	39.7	306.4	465.8	162.0	35.4	217.2	181	24.80	2.71
		12/01/08	4229.2	754.0	70.2	529.5	224.5	166.3	35.4	226.0	192	26.45	3.00
		01/22/09	3622.5	759.8	61.8	469.5	290.3	147.7	37.1	178.7	183	24.70	2.81
		03/22/09	4076.2	771.8	67.4	519.9	251.9	158.1	37.0	221.0	185	25.90	2.70
		04/30/09	3900.8	786.8	50.4	396.4	390.4	146.0	35.8	186.8	187	25.45	2.94
		07/30/09	3493.3	783.0	79.0	618.9	164.1	146.5	34.3	187.2	182	27.00	3.55
		09/23/09	3655.6	821.3	53.1	436.1	385.2	144.8	35.2	166.4	192	26.65	3.72
6	**Bioreactor Outlet**	10/14/08	NM	83.4	13.3	11.1	72.3	0.01	31.4	851.5	176	21.50	3.68
		12/01/08	2483.7	153.9	47.5	73.1	80.8	0.90	31.8	733.0	143	20.00	3.53
		01/22/09	2247.0	147.6	18.2	26.8	120.8	0.31	31.5	842.0	180	17.65	3.19
		03/22/09	2074.0	154.9	29.2	45.2	109.7	0.0	27.5	749.0	136	16.15	2.62
		04/30/09	2036.7	177.1	35.0	62.1	115.0	0.0	27.8	712.5	131	15.85	2.36
		07/30/09	1708.8	158.4	43.3	68.6	89.8	3.6	23.0	726.5	135	17.90	3.81
		09/23/09	2165.3	203.5	37.0	75.3	128.2	12.4	28.6	765.0	169	22.55	3.55
7	**System Out**	10/14/08	NM	0.9	0.0	0.0	0.9	0.01	3.0	643.2	158	20.10	5.80
		12/01/08	2575.8	0.0	0.0	0.0	0.0	NM	23.9	854.0	168	19.15	3.86
		01/22/09	2214.7	18.9	36.1	6.8	12.0	5.40	35.3	859.5	158	20.25	4.41
		03/22/09	2061.9	4.6	10.0	0.5	4.1	NM	30.4	586.5	138	20.45	3.12
		04/30/09	1387.2	0.0	90.4	0.0	0.0	1.2	23.3	462.0	92	15.00	2.54
		07/30/09	1803.1	0.0	93.2	0.0	0.0	3.9	23.7	685.0	135	17.25	4.03
		09/23/09	2086.0	0.0	0.0	0.0	0.0	0.0	18.5	629.3	164	22.20	4.92

NM = Not Measured. Zero values represent concentrations below the detection limit.

respectively. In the acid groundwater that seeped into the bioreactor, the average concentrations of dissolved Mg, Na and K measured at the bioreactor seep sampling station were 149, 22.2 and 0.8 mg/l, respectively. The results indicated that the concentrations of dissolved Mg, Na and K in the acid groundwater that seep into the bioreactor were lower as compared to their values in the AMD that reaches the bioreactor from surface flow through the bioreactor inlet. Within the bioreactor, a slight decrease in Na and Mg concentration and significant increase in K were observed. In the remaining course, K continued to increase at a lower rate.

Dissolved Mn concentrations showed relatively little changes along the flow path (Table 4, Fig. 9c). A small increase in Mn concentration was observed as the acid water flowed from the acid main pool to the bioreactor inlet sampling station. Within the bioreactor, Mn concentration decreased from an average of 35.7 mg/l at the bioreactor inlet to 28.8 mg/l at the bioreactor outlet (Table 4, Fig. 9c). However, the amount of reduction in Mn concentration was very small compared to the percentage reduction in Al and Fe concentrations. Unlike the other metals, average Mn concentration in the AMD which seeped to the bioreactor was similar to its value in the AMD from surface flow (Table 4). Between the bioreactor outlet and the system outlet, average Mn concentration showed a slight decrease (Fig. 9c).

Calcium (Ca) concentration trend along the flow course displayed the opposite of most other metals (Fig. 9a). First, the concentration decreased slightly as the AMD flowed from the acid pool to the main seep, and then a small increase was observed between the main seep and the bioreactor inlet (Fig. 9a). Within the bioreactor, the average Ca concentration increased significantly from about 198 to

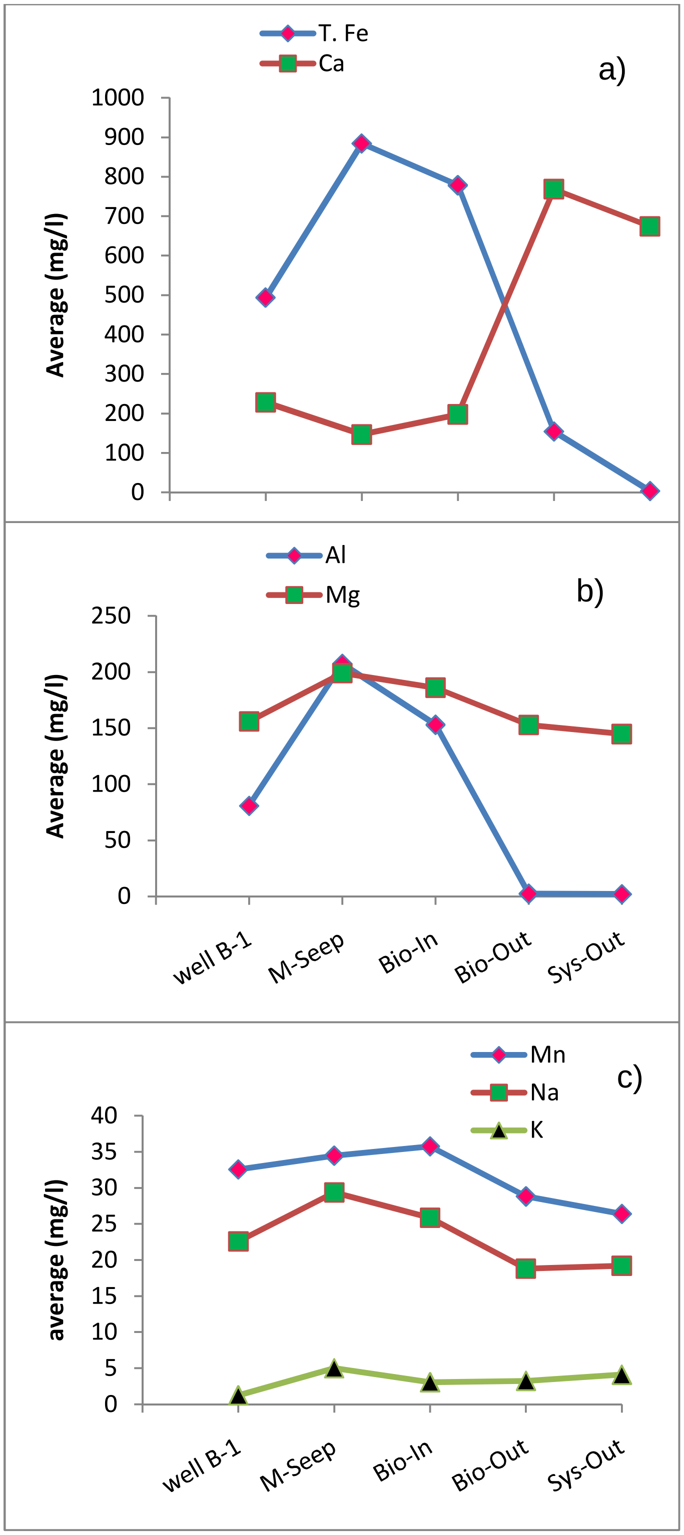


Figure 9. Metal concentrations along the flow direction at the Tab-Simco site using average values in each sampling station.

769 mg/l. Between the bioreactor outlet and the system outlet, average Ca concentration remained almost constant with a slight tendency to decrease. Comparison of Ca concentrations in the AMD from surface flow and groundwater seepage into the bioreactor indicated that the Ca concentration in the water which comes from groundwater seepage had a higher concentration than the AMD from surface flow (Table 4).

6.5 Sulfur Isotope Results

Sulfur stable isotope results of dissolved SO_4^{2-} in the Tab-Simco AMD are given in Table 5 and plotted on Figure 10. Results from sampling stations, well B-1, well B-2 and the main seep, represent the $\delta^{34}S$ values of the dissolved SO_4^{2-} in the AMD before reaching the treatment system. The $\delta^{34}S$ values of the dissolved SO_4^{2-} in the AMD were varied between 7.2 and 7.4 ‰. Slight decrease in the $\delta^{34}S$ value (6.9 ‰) was measured at the bioreactor inlet station relative to its value at the main seep sampling station. Within the bioreactor, $\delta^{34}S$ values increased from an average of 6.9 ‰ at the bioreactor inlet to 9.2 ‰ at the bioreactor outlet suggesting the presence of ^{34}S enriching process in the bioreactor. Between bioreactor outlet and system outlet no significant change was observed.

Table 5: *Sulfur isotope values of the dissolved SO_4^{2-} in the Tab-Simco AMD*

Sampling Date	**Sampling Station**	**$\delta^{34}S$**
12/1/2008	Well B-1	7.403
	Well B-2A	7.355
	Main-Seep	7.314
	Bioreactor-Inlet	6.979
	Bioreactor-Outlet	9.578
	System-Outlet	9.961
1/22/2009	Well B-1	7.347
	Main-Seep	7.176
	Bioreactor-Inlet	6.862
	Bioreactor-Outlet	8.806
	System-Outlet	7.880

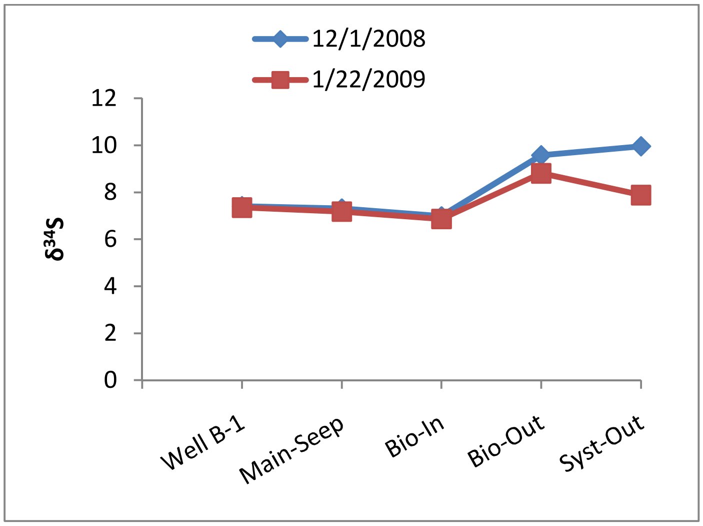


Figure 10. The trend of $\delta^{34}S$ value of dissolved SO_4^{2-} in the Tab-Simco AMD along the flow direction using average values in each sampling station.

7. DISCUSSION

7.1 The Tab-Simco AMD Water Chemistry

Field parameters and chemical analyses results from seven sampling stations (well B-1, well B-2, main seep, bioreactor seep, bioreactor inlet, bioreactor outlet, and system outlet) at the Tab-Simco site are given in Tables 1, 2, 3 and 4. The results from sampling stations, well B-1, well B-2, main seep, and bioreactor inlet, represent the quality of the Tab-Simco AMD before it entered the sulfate-reducing bioreactor. The results indicated that the Tab-Simco AMD is low pH water with high concentrations of dissolved SO_4^{2-} and metals. As the AMD reached the surface at the main seep sampling station, average concentrations of the parameters were about 3,386 mg/l of acidity, 4,589 mg/l of SO_4^{2-}, 884 mg/l of Fe, 207 mg/l of Al, 34.4 mg/l of Mn, with average pH of the water 2.8.

Variations along the flow path and possible processes: As the AMD flowed between the acid mine pool and the Tab-Simco bioreactor, noticeable changes were measured in the chemical characteristics of the AMD waters (Figures 7, 8 and 9). The results indicated that the concentrations of acidity, dissolved SO_4^{2-} and metals in the AMD were always higher at the main seep sampling station than their values in the acid mine pool (well B-1). The increase in acidity, dissolved SO_4^{2-} and metal concentrations, as the acid water flowed from the acid mine pool (W-B1) to the main seep sampling station could be due to (1) oxidation of additional sulfide minerals as the water flows through the mine spoils and/or

(2) mixing of the AMD from W-B1, with AMD from other acid mine pools that have higher concentrations of, acidity, dissolved metals and SO_4^{2-}.

As the AMD flowed from the main seep to the bioreactor inlet sampling station, acidity, SO_4^{2-} and most metal concentrations dropped slightly, whereas Ca^{2+} and Mn^{2+} concentration values showed a slight increase (Figures 7, 8, and 9). The drop in the concentrations of acidity, dissolved SO_4^{2-} and most metals could suggest dilution of the AMD by fresh water which contained lower concentrations of these parameters. Furthermore, reddish precipitate, covering the bottom bed of the trench through which the AMD flowed, was observed during some of the sampling dates (at pH around 2.9), suggesting the presence of Fe (oxy)hydroxides (e.g $Fe(OH)_3$ and FeOOH) precipitating processes as the AMD flowed between the main seep and bioreactor inlet sampling stations.

In addition to dilution, other possible factors which could have decreased the concentration of SO_4^{2-} as the AMD flowed to the bioreactor inlet are: (1) BSR processes (Webb et al., 1998; Watzlaf et al., 2004) and (2) precipitation of SO_4^{2-} minerals such as gypsum ($CaSO_4.2H_2O$) and jarosite ($KFe_3(SO_4)_2(OH)_6$) (Neculita, 2008a; Blowes et al., 2003; Willow and Cohen, 2003). During BSR, SO_4^{2-} molecules containing ^{32}S are preferentially reduced over SO_4^{2-} molecules containing ^{34}S. Consequently, BSR results in progressive enrichment in ^{34}S value of the dissolved SO_4^{2-} (Ohmoto et al., 1997). However, the Tab-Simco sulfur isotope results (Table 5, Fig. 10) showed a decreasing trend in $\delta^{34}S$ value as the water flowed from the main seep to the bioreactor inlet sampling station, suggesting that BSR did not occur or was a minor process.

The increase in Ca^{2+} concentration and decrease in acidity of the AMD could be due to limestone dissolution (reaction 3.7) as the water flowed toward the bioreactor inlet. During reclamation work at the site, all the areas around the bioreactor, both up and down gradient of the bioreactor, including the trenches through which the AMD flow, were lined with limestone aggregates. Therefore, limestone dissolution was the most probable cause for the increase in Ca^{2+} concentration and decrease in acidity.

On the other hand, the chemical characteristics of the acid groundwater which seeped to the bioreactor showed similar chemical characteristics with the water in the acid mine pool (Tables 1, 3 and 4). The groundwater seep had lower acidity, SO_4^{2-}, and metal concentrations than the AMD from surface flow at the bioreactor inlet (Table 4). The slight improvement in the water quality from the acid water that seeped from the groundwater to the bioreactor is mainly due to the addition of alkalinity from limestone dissolution, and subsequent precipitation of metals as the water continued towards the bioreactor. Overall, the acid water that reached the bioreactor from groundwater seepage had slightly better water quality than the surface flow influent (Tables 1, 3 and 4).

7.2 The Bioreactor and Overall System Performance and Treatment Processes

The performance of the Tab-Simco bioreactor and the overall Tab-Simco treatment system in removing acidity, dissolved SO_4^{2-} and metals from the AMD, which reached the treatment system, were evaluated by analyzing the measured concentrations of the contaminants (acid, SO_4^{2-} and metals) in the influent and effluent. The performance results are summarized in Table 8a. The results are expressed in terms of removal rates and percentage removals for both the bioreactor and the overall treatment system. Overall, the Tab-Simco AMD treatment system provided an excellent removal of acidity and most metals. In the following sections, the performance of the bioreactor and overall treatment system with respect to each parameter and the treatment processes are discussed.

7.2.1 Field parameters

The Tab-Simco field measurement results, before and after passing through the bioreactor, are given in Table 1 and Fig. 7. One of the most significant changes in the AMD parameters was the increase in pH value as the water passed through the bioreactor. As the AMD entered the bioreactor, the average pH of the acid water that seeped from groundwater was 2.83, whereas that of the AMD that reached from surface flow through the bioreactor inlet was 2.86. After passing through the bioreactor, the average pH of the water at the bioreactor outlet increased up to 6.4. Within the bioreactor, a substantial amount of alkalinity was produced from BSR and limestone dissolution. The increase in the average pH value of the AMD within the bioreactor was, therefore, mainly due to neutralization reaction. Between the bioreactor outlet and system outlet, the average pH value of the treated water that left the bioreactor did not show significant change (Fig. 7a).

Other than the increase in pH value, average ORP, Sc and DO values were decreased within the bioreactor. The decrease in ORP and DO values can be explained by the high O_2 demand in the organic layer by certain bacteria, whereas the Sc decrease was attributed to the precipitation of metals within the bioreactor.

7.2.2 Acidity removal

The performance of the Tab-Simco treatment system in removing acidity is shown in Table 6a. On average, the bioreactor received about 257 kg/day of acidity as $CaCO_3$ equivalent. The measured average acidity removal rate by the bioreactor was 241 kg/day. This removal rate accounts for about 94% of the acidity that reached the bioreactor. The large drop in acidity within the bioreactor was mainly due to the neutralization of the acidity by alkalinity produced within the bioreactor. The alkalinity production was due to BSR processes (reaction 3.6) and limestone dissolution (reaction 3.7) within the bioreactor. This was revealed from the considerable increase in the alkalinity of the AMD, from zero at bioreactor outlet to an average of 292 mg/l at the bioreactor inlet (Table 2).

In contrast to the bioreactor behavior, as the treated water flowed from the bioreactor outlet to the system outlet, a decline in the average amount of alkalinity in the water was measured. This decline was because of the consumption of alkalinity to neutralize the acidity released from hydrolysis and precipitation of metal oxy-hydroxide (Reactions 3.3 and 3.10-3.12) (Neculita, 2008a). The average acidity removal rate by the entire treatment system from the Tab-Simco AMD in this study was 98.5%.

7.2.3 Sulfate removal

The Tab-Simco bioreactor and the overall treatment system performance in removing dissolved SO_4^{2-} from the Tab-Simco AMD are shown in Table 6a. The measured average mass rate of dissolved SO_4^{2-} that reached the bioreactor from surface flow and groundwater seepage was 366 kg/day, whereas the bioreactor's average SO_4^{2-} removal rate for the period of study was 121 kg/day (Table 6a). On average, the bioreactor removed about 35% of the dissolved SO_4^{2-} in the AMD. As the treated water flowed to the system outlet, an additional drop in the concentration of SO_4^{2-} was observed. Thus, the Tab-Simco AMD treatment system removed, on average, 145 kg/day of dissolved SO_4^{2-}, which represents 39%. The dissolved SO_4^{2-} removal rate measured at the Tab-Simco AMD treatment system is similar to the rates of SO_4^{2-} removal reported from other passive AMD treatment sites (e.g. Barton et al., 1999).

There are different processes that can occur within the bioreactor which can contribute to the decrease in SO_4^{2-} concentration. One process that can produce a decrease in SO_4^{2-} concentration is BSR in the organic layer (Reaction 3.6). During BSR, sulfur isotopic fractionation can result in an increase of 2 to 46‰ in the $\delta^{34}S$ values of the dissolved SO_4^{2-} (Bruchert et al. 2001). In the Tab-Simco, as the AMD passed through the bioreactor, the $\delta^{34}S$ value of the dissolved SO_4^{2-} increased from an average of 6.9 to 9.2‰, suggesting that the BSR processes were active. During sulfate mineral precipitation, the $\delta^{34}S$ value of the dissolved SO_4^{2-} remains unchanged (Seal, 2003). The presence of a strong hydrogen sulfide (H_2S) smell and black sulfide sludge (precipitates) at the bioreactor outlet was also another good indication of BSR processes within the bioreactor.

Another process that can contribute to the decrease in SO_4^{2-} concentration within the bioreactor is the precipitation of sulfate minerals such as gypsum, $CaSO_4.2H_2O$, and jarosite, $KFe_3(SO_4)_2.(OH)_6$ (Blowes et al., 2003; Thomas et al., 2002b). To determine the possibility of gypsum precipitation within the bioreactor, the gypsum saturation index within the bioreactor was calculated. The results indicated that gypsum had an average saturation index of 24. A saturation index of greater than one indicates that the solution is oversaturated with respect to the ion under consideration. Thus, the saturation index for gypsum suggests that gypsum precipitation occurs within the bioreactor.

However, studies reveal that gypsum precipitation in anaerobic conditions is limited and that BSR is the main process that removes dissolved SO_4^{2-} in bioreactors (Barton et al, 1999). For this reason, and based on the sharp increase in $\delta^{34}S$ value within the bioreactor, the dominantly black sulfide sludge observed and the strong sulfide smell detected at the bioreactor outlet, BSR was considered as the main process that caused a decrease in dissolved SO_4^{2-} concentration in the Tab-Simco bioreactor.

The slight decrease in SO_4^{2-} concentration between the bioreactor outlet and the system outlet could be either due to dilution or precipitation of sulfate minerals.

7.2.4 Metal removals

The Tab-Simco bioreactor removed a significant amount of the metals in the AMD that reached the bioreactor (Table 6a). Previous studies have shown that metal removal in bioreactors occurs mainly due to precipitation of metals in the form of sulfides, (oxy)hydroxides and carbonates (Neculita et al., 2007). Adsorption of dissolved metals onto the organic compounds is also an important removal process during the initial stages of the bioreactor (Gibert et al., 2005a). Finally, metals can also be co-precipitated with Fe and Mn (oxy)hydroxides (Neculita et al 2008b).

Iron (Fe)**:** On average, the Tab-Simco bioreactor received about 64 kg/day of dissolved Fe, both from surface flow and groundwater seepage (Table 6a). The measured Fe removal rate by the bioreactor for this study was about 46 kg/day. This rate accounts for 75% of the Fe received by the bioreactor. Additional Fe was removed outside the bioreactor, as the treated water flowed between the bioreactor outlet and the system outlet. At the system outlet, the mean dissolved Fe concentration, for most of the sampling dates, was below the detection limit. Overall, 99.5% of the Fe that reached the bioreactor was removed by the Tab-Simco treatment system.

In passive treatment systems, Fe removal can occur through precipitation of Fe in the form of sulfides (e.g FeS, FeS_2), Fe (oxy)hydroxides (e.g. Fe hydroxide, $Fe(OH)_3$, goethite, FeOOH, and schwertmannite ($Fe_8O_8(OH)_{4.8}(SO4)_{1.6}$), and/or carbonates (e.g $FeCO_3$) (Hedin et al., 1994; Riefler et al., 2008). The removal of Fe under oxidizing conditions is primarily through oxidation of Fe^{2+} to Fe^{3+} followed by hydrolysis and precipitation of Fe (oxy)hydroxides as shown in reactions 3.3 and 3.11 (Hedin et al., 1994). Fe oxidation processes in oxidizing conditions can be abiotic or mediated by bacteria depending on the pH level of the AMD. Bacterial Fe oxidation is the dominant process in waters with pH levels between 2 and 3, whereas abiotic Fe oxidation becomes the dominant process in waters with neutral pH values (Hedin et al., 1994). Precipitation of $Fe(OH)_3$ from AMD is also pH dependent and occurs only when the pH is above ~3-3.5 (Pérez-López et al., 2007; Hedin et al., 1994). In anaerobic systems that contain organic substrate, Fe oxidation is limited by the absence of O_2 and microorganisms (Fe oxidizing bacteria). Consequently, precipitation of Fe in the form of Fe^{3+} (oxy)hydroxides can be limited to the upper surface of the bioreactor (McCauley et al., 2009). In such environments, Fe removal occurs mainly through precipitation of Fe monosulfides (FeS), and to some extent, Fe disulfides such as pyrite (FeS_2) (Watzlaf et al., 2004).

At the Tab-Simco AMD treatment system, Fe removal within the bioreactor was mainly through precipitation in the form of Fe sulfides. This was confirmed by the predominantly black sulfide sludge observed in the discharge at the bioreactor outlet.

After the treated water left the bioreactor, it entered the oxidation pond where metal oxidation and precipitation took place (Neculita, 2008a), and then flowed slowly to the system outlet. Fe removal between the bioreactor outlet and system outlet was primarily due to precipitation of Fe in the form of Fe oxy-hydroxide minerals.

Aluminum (Al): For most of the sampling period, Al was the only metal which was removed to the level below the detection limit within the bioreactor. Average Al mass rate into the Tab-Simco bioreactor during the study period was about 14 kg/day (Table 6a). In most of the effluent samples (bioreactor outlet station), the concentration of Al dropped below the detection limit. Overall, the bioreactor removed 98% of the Al received.

In aquatic systems, Al is present in only one oxidation state, Al^{+3}, and it does not undergo an oxidation or reduction process (Hedin et al. 1994; Drever, 1997). As a result, Al removal in passive treatment systems does not need O_2 or oxidizing bacteria, and occurs mainly through hydrolysis reactions in the form of aluminum hydroxide (gibbsite), $Al(OH)_3$ (Hedin et al., 1994). To some extent, Al can also be removed in the form of Al hydroxysulfates such as felsobanyaite (basaluminite), $Al_4(SO_4)(OH)_{10}.4H_2O$, hydrobasaluminite, $Al_4(SO_4)(OH)_{10}.15H_2O$ and alunite, $KAl_3(SO_4)_2(OH)_6$ (Blowes et al., 2003; Bigham et al., 2000). The main factor that determines the removal of Al is the pH of the AMD. At pH levels between 5 and 8, $Al(OH)_3$ is highly insoluble and usually precipitates to remove the concentration of dissolved Al to below 1g/l (Hedin et al., 1994). However, at lower pH levels, $Al(OH)_3$ is highly soluble and most of the Al exists as ions in solution and thus no significant Al precipitation occurs.

In the Tab-Simco bioreactor, the pH of the AMD that left the bioreactor was always above 6. Therefore, the reduction of Al to below the detection limit within the bioreactor can be attributed to the precipitation of Al in the form of $Al(OH_3)$ and/or hydroxysulfates minerals.

Manganese (Mn): Mn retention in the bioreactor was very small compared to Fe and Al. The bioreactor, on average, received ~3.6 kg/day of dissolved Mn and dispatched ~0.58 kg/day of it (Table 6a). This means only ~15.1% of the dissolved Mn was removed from the AMD in the bioreactor. Between the bioreactor outlet and the system outlet, no significant change was observed in Mn concentrations. The overall system removal rate measured at the system outlet was 22.5%. Low Mn removal rates by sulfate-reducing bioreactors, similar to that of the Tab-Simco bioreactor, are widely reported in many previous bioreactor performance studies (Neculita et al. 2008a; Zaluski et al., 2003; Hallberg et al., 2005; Kuyucak et al., 2006).

Similar to Fe^{2+}, dissolved Mn^{2+} in aerobic conditions undergoes oxidation and hydrolysis reactions to precipitate in the form of Mn (oxy)hydroxide minerals (Watzlaf et al., 2004). Mn^{2+} in AMD may be oxidized either to Mn^{+3} or Mn^{+4} through abiotic or bacterial processes. However, Mn^{2+} oxidation reactions are highly pH dependent. The abiotic oxidation is very slow at the pH level below 8 (Hallberg et al., 2005). The biological oxidation of Mn^{2+} is limited to aerobic conditions with a pH level greater than 6 (Nealson, 1983b). In addition, biological oxidation of Mn^{2+} does not proceed rapidly in the presence of Fe^{2+}, and thus no significant Mn removal occurs where the concentration of Fe^{2+} exceeds 1 mg/l (Nairn et al., 1993).

Mn removal in an aerobic environment occurs mainly through precipitation of (oxy)hydroxides (e.g. MnO_2 and MnOOH) and carbonates (e.g. $MnCO_3$) (Hedin et al., 1994). However, MnO_2 solubility is highly pH dependent and it can only precipitate from waters with pH values greater than 6 (Hedin et al., 1994). $MnCO_3$ can precipitate but only from alkaline waters (Watzlaf et al., 2004). Moreover, the presence of a high Fe^{2+} concentration in an AMD inhibits the precipitation of $MnO_{2,}$ and might dissolve what is already precipitated (Hedin et al., 1994). In anaerobic conditions, Mn^{2+} oxidation is limited because of the lack of oxidizing agents (O_2 and Mn^{2+} oxidizing organisms). Thus, in anaerobic conditions, Mn removal in the form of (oxy)hydroxides is insignificant (Watzlaf et al., 2004). Because of their high solubility compared to other metal sulfides, manganese sulfide minerals also do not form to a great extent in bioreactors until the concentrations of the other metals become very low (Hallberg et al., 2005; Gusek, 2002; Watzlaf et al., 2004). Therefore, Mn removal in anaerobic sulfate-reducing bioreactors is often less efficient as compared to Fe and Al (Waybrant et al., 2002).

Accordingly, the low Mn removal rate by the Tab-Simco anaerobic bioreactor could be explained by the limitation in Mn^{2+} oxidation and the high solubility of the potential manganese sulfide minerals. However, some Mn was removed within the bioreactor possibly by (1) adsorption of Mn^{2+} onto the surface of the substrate, (2) co-precipitation with Fe and Al hydroxides, and/or (3) precipitation in the form of $MnCO_3$.

Between the bioreactor outlet and the system outlet, despite aerobic conditions and AMD pH levels above 6, no significant amount of Mn^{2+} was removed from the AMD water. This could be due to the inhibition of the MnO_2 precipitation process caused by high concentrations of Fe^{2+} or other metals in the AMD.

Magnesium (Mg): In acid mine treatment systems, Mg can be considered as a conservative ion and it’s concentration remains unaffected by treatment processes (Hedin et al., 1994). This is because the potential solid precipitates of Mg, such as magnesium sulfate (Epsom salt), $MgSO_4$, magnesium hydroxide, $Mg(OH)_2$, magnesium carbonate (magnesite), $MgCO_3$ and dolomite, $CaMg(CO_3)_2$, are unlikely to form in the Mg concentrations and pH levels found in AMD treatment systems (Hedin et al., 1994). Likewise, Mg concentration in the Tab-Simco AMD did not show significant changes as the AMD passed through the bioreactor. On average, the measured Mg mass rate that entered the Tab-Simco bioreactor was 17.4 kg/day. The average calculated Mg removal rates were 1.1 kg/day for the bioreactor and 2.7 kg/day for the entire treatment system (Table 7a). These account for the removal of only 7.2% and 13.2% of the received Mg mass rate, respectively.

Calcium (Ca) and Potassium (K): Unlike most other metals, Ca and K concentration levels of the AMD increased within the bioreactor (Table 4 and Fig. 9c). On average, the mass rate of Ca that entered the bioreactor from the influent was about 23 kg/day (Table 6b). After passing through the bioreactor, the mass rate of Ca that left the bioreactor increased to 84 kg/day. The increase in the Ca level was primarily attributed to limestone dissolution within the bioreactor. As the AMD passed through the bioreactor, limestone dissolution released Ca^{2+} and HCO_3^- to the AMD, increasing the Ca^{2+} concentration (Reaction 3.7). However, Ca^{2+} can also be removed, to some extent, through precipitation of Ca^{2+} containing minerals such as gypsum (Neculita, 2008a; Blowes et al., 2003; Willow et al., 2003). This was confirmed by the high gypsum saturation index, 24, within the bioreactor. Also, some Ca^{2+} might have been added to the solution from the organic substrate (Neculita, 2008a).

Despite the low K concentration in the Tab-Simco AMD, the mass rate of K increased within the bioreactor. The average mass rate of K in the AMD that reached and left the bioreactor was 0.21 and 0.35 kg/day, respectively (Table 6b). These results revealed a 60% increase in the mass rate of K. As the treated water flowed between the bioreactor outlet and the system outlet, the K concentration continued to increase. At the system outlet, the K mass rate was increased to 0.42 kg/day.

Sodium (Na): Na flux in the AMD decreased by 20% as the AMD passed through the bioreactor. The bioreactor received 2.5 kg/day of Na from the AMD out of which the bioreactor removed 0.49 kg/day. One possible reason for the decrease in Na concentration is the precipitation of Na containing minerals such as natrojarosite, $NaFe_3(SO_4)_2(OH)_6$, which is frequently reported from AMD sites (Blowes et al., 2003).

Table 6a: *The performance of the Tab-Simco treatment system in removing, acidity, SO_4^{2-} and metals*

Ion	Date	Mass Rates (kg/day)			Removal Rates (kg/d)		Mass Removal %	
		Bio-In	Bio-Out	Sys-Out	Bioreactor	Ent. Syst	Bioreactor	Ent. Syst
Net Acidity	12/1/08	156.45	3.05	2.68	153.40	153.77	98.05	98.29
	1/22/09	163.61	8.51	6.62	155.10	156.99	94.80	95.96
	3/12/09	212.11	6.74	0.71	205.37	211.40	96.82	99.67
	4/30/09	404.87	44.62	10.59	360.25	394.28	88.98	97.38
	7/30/09	405.66	15.93	5.32	389.73	400.34	96.07	98.69
	9/23/09	201.24	21.73	-1.94	179.51	203.18	89.20	100.96
SO_4^{2-}	12/1/08	226.95	145.60	143.51	91.16	85.85	35.84	36.76
	1/22/09	317.33	179.20	178.15	81.35	83.44	43.53	43.86
	3/22/09	638.61	502.85	342.50	138.14	139.18	21.26	46.37
	4/30/09	501.08	316.36	333.82	135.76	296.11	36.86	33.38
	7/30/09	279.63	187.08	180.23	184.71	167.26	33.10	35.55
	9/23/09	234.22	143.06	148.36	92.55	99.40	38.92	36.65
Fe	10/14/08	41.05	4.80	0.05	36.25	41.00	88.30	99.87
	12/1/08	41.05	8.86	0.00	32.18	41.05	78.40	100.00
	1/22/09	44.00	9.56	1.22	34.44	42.78	78.26	97.22
	3/22/09	57.57	13.38	0.40	44.18	57.17	76.75	99.31
	4/30/09	108.97	43.73	0.00	65.24	108.97	59.87	100.00
	7/30/09	97.77	29.33	0.00	68.44	97.77	70.00	100.00
	9/23/09	59.75	17.58	0.00	42.16	59.75	70.57	100.00
Al	10/14/08	8.67	0.00	0.00	8.67	8.67	99.99	99.99
	12/1/08	8.87	0.05	0.00	8.82	8.75	99.42	98.64
	1/22/09	8.71	0.02	0.35	8.69	8.36	99.77	95.98
	3/22/09	11.01	0.00	0.00	11.01	10.83	100.00	98.35
	4/30/09	23.39	0.00	0.30	23.39	23.10	100.00	98.73
	7/30/09	25.62	0.67	0.72	24.95	24.90	97.40	97.18
	9/23/09	10.15	1.07	0.00	9.08	10.15	89.45	100.00
Mn	10/14/08	2.01	1.81	1.73	0.198	0.280	9.86	13.94
	12/1/08	2.02	1.83	1.37	0.185	0.645	9.16	31.93
	1/22/09	2.33	2.04	2.29	0.290	0.040	12.46	1.72
	3/22/09	3.11	2.38	2.62	0.731	0.482	23.53	15.52
	4/30/09	6.95	6.87	5.75	0.086	1.202	1.23	17.28
	7/30/09	6.36	4.27	4.38	2.092	1.974	32.91	31.04
	9/23/09	2.96	2.47	1.59	0.487	1.363	16.47	46.09
Mg	10/14/08	10.12	10.14	9.10	-0.01	1.02	-0.14	10.10
	12/1/08	10.73	8.24	9.68	2.49	1.05	23.21	9.79
	1/22/09	11.08	11.66	10.24	-0.58	0.84	-5.26	7.60
	3/22/09	14.36	11.75	11.92	2.61	2.43	18.16	16.96
	4/30/09	31.56	32.34	22.72	-0.79	8.84	-2.49	28.02
	7/30/09	28.35	24.99	24.99	3.36	3.36	11.84	11.84
	9/23/09	15.41	14.60	14.17	0.81	1.24	5.23	8.04
Na	10/14/08	1.41	1.24	1.16	0.17	0.25	11.91	17.64
	12/1/08	1.47	1.15	1.10	0.32	0.36	21.50	24.84
	1/22/09	1.53	1.14	1.31	0.39	0.22	25.37	14.38
	3/22/09	2.05	1.40	1.77	0.66	0.28	31.99	13.88
	4/30/09	4.55	3.91	3.70	0.63	0.84	13.91	18.53
	7/30/09	4.37	3.31	3.19	1.06	1.18	24.23	26.98
	9/23/09	2.18	1.95	1.92	0.24	0.27	10.81	12.20

Table 6b: *Dissolved Ca and K concentration increase at the Tab-Simco treatment system*

Ion	Date	Mass Rates (kg/day)			Addition Rates (kg/day)		Mass Addition %	
		Bio-In	Bio-Out	Sys-Out	Bioreactor	Ent. Syst	Bioreactor	Ent. Syst
Ca	10/14/08	12.33	49.05	37.05	36.713	24.713	297.67	200.37
	12/1/08	12.70	42.22	49.19	29.520	36.487	232.38	287.23
	1/22/09	13.34	54.56	55.70	41.217	42.351	308.87	317.37
	3/12/09	20.78	64.71	50.67	43.933	29.893	211.41	143.85
	4/30/09	48.89	175.92	114.07	127.033	65.184	259.86	133.34
	7/30/09	35.18	134.50	126.82	99.322	91.639	282.30	260.46
	9/23/09	15.33	66.10	54.37	50.763	39.034	331.07	254.57
K	10/14/08	0.14	0.21	0.33	0.073	0.195	52.32	140.07
	12/1/08	0.15	0.20	0.22	0.055	0.074	37.38	50.22
	1/22/09	0.14	0.21	0.29	0.066	0.145	46.55	102.60
	3/22/09	0.16	0.23	0.27	0.070	0.113	44.48	72.06
	4/30/09	0.26	0.58	0.63	0.320	0.364	121.48	138.37
	7/30/09	0.37	0.71	0.75	0.336	0.376	90.72	101.74
	9/23/09	0.24	0.31	0.43	0.063	0.181	25.74	74.26

Key: Bio-in = Bioreactor Inlet, Bio-Out = Bioreactor Outlet, and Sys-Out = System Outlet Sampling stations, Ent. Syst = Entire system.

7.3 Seasonal Variations in the Untreated AMD Chemistry and the Bioreactor Performance

Variation in the chemistry of the untreated AMD: The chemical characteristics of the Tab-Simco AMD through time are plotted in Figure 11. In these graphs, most of the parameters (field parameters, acidity, SO_4^{2-} and metals) in the untreated AMD (Bio-In) display almost horizontal curves throughout the study period. This illustrates that the chemical characteristics of the untreated Tab-Simco AMD remained similar throughout the study period without any noticeable seasonal variations.

Variations in the bioreactor performance: Previous studies reported that the performance of anaerobic sulfate-reducing bioreactors decline significantly at low temperature conditions, which negatively affect the activities of SRB (Tucker et al., 1998; Benner et al., 2002; Doshi, 2006; Neculita, 2007; Tsukamoto et al., 2004). The low temperature inhibits the activities of SRB, leading to a decrease in BSR, which in turn causes a decline in the bioreactor treatment efficiency.

Results from this study indicate that the removal rates of the acidity, dissolved SO_4^{2-}, and metals, by the Tab-Simco bioreactor, were higher during the spring and summer compared to the fall and winter (Table 6a). The concentrations of different parameters (acidity, dissolved metals and sulfate) in the effluent were more or less the same during the study period (Figure 11) However, the flow rate of the AMD that enters the Tab-Simco bioreactor was higher during spring and winter than its values during fall and winter (Table 2). Consequently, when the removal rates of the parameters were calculated, by multiplying the differences in the concentrations of each parameter in the influent and effluent by the corresponding flow rates, higher removal rates for acidity, dissolved metals and sulfate were obtained during spring and summer compared to winter and fall (Table 6a).

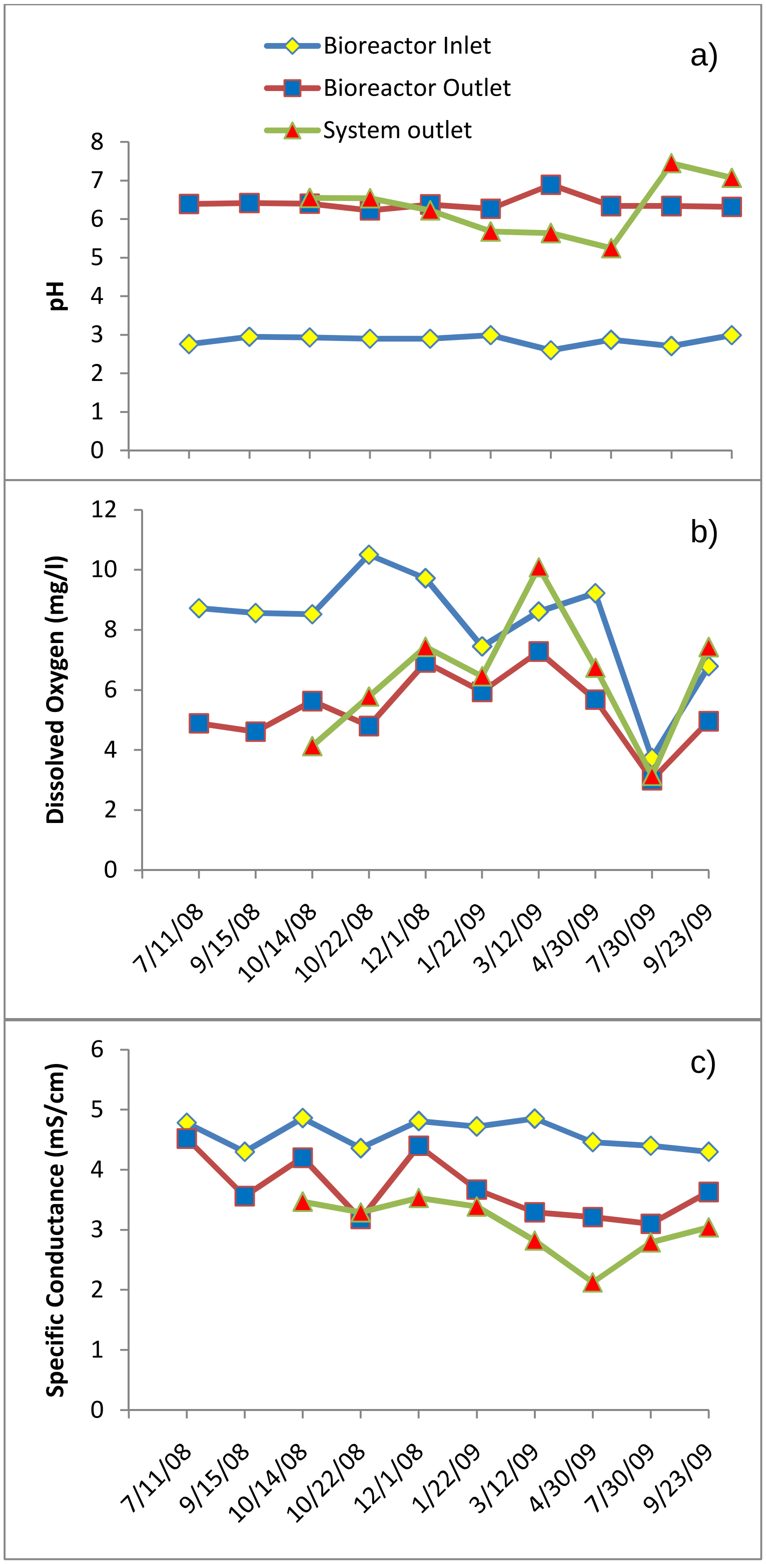


Figure 11. Field and laboratory measurement results through time in the Tab-Simco AMD at the bioreactor inlet, bioreactor outlet, and the system outlet sampling stations. Graphes continue to the next pages.

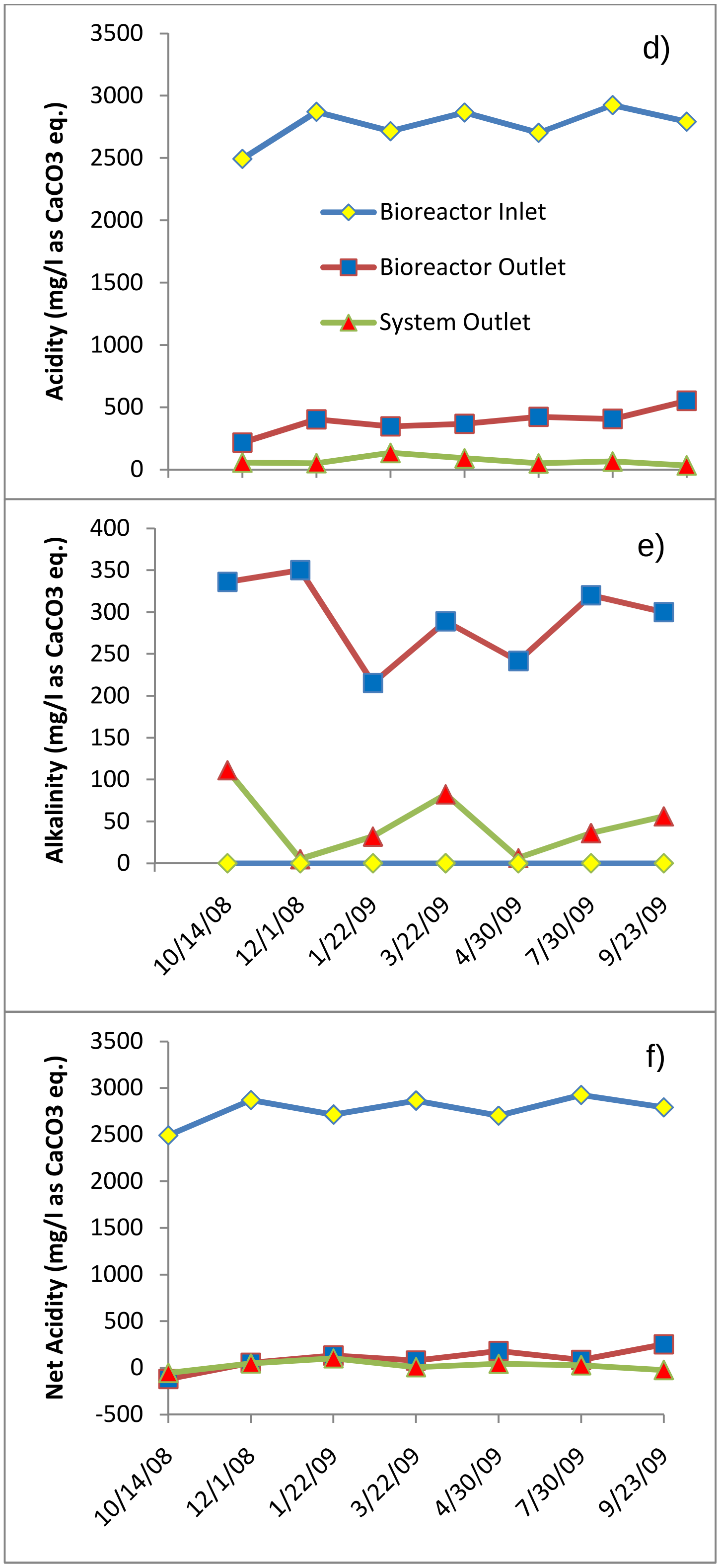


Figure 11 (Continued) (Caption shown on the previous page).

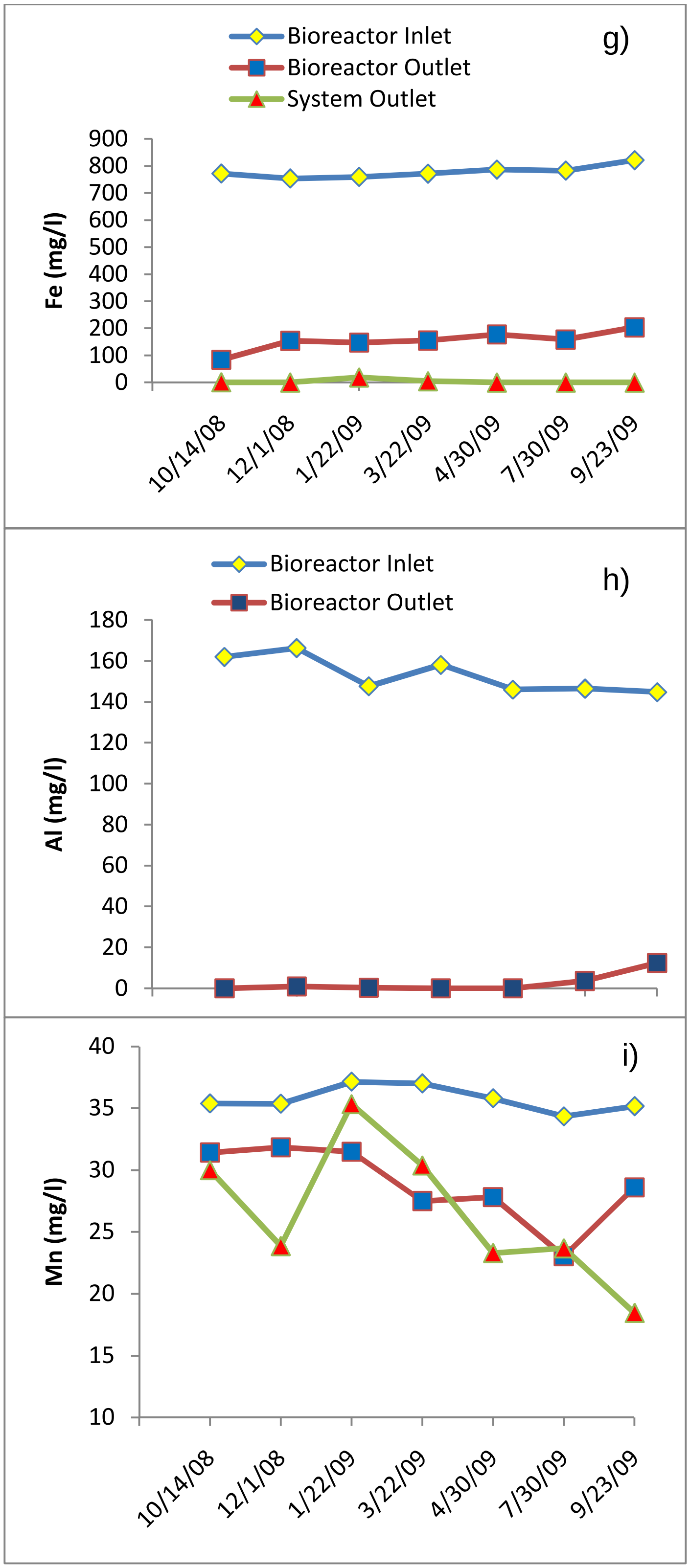


Figure 11. (Continued) (Caption shown on the previous page).

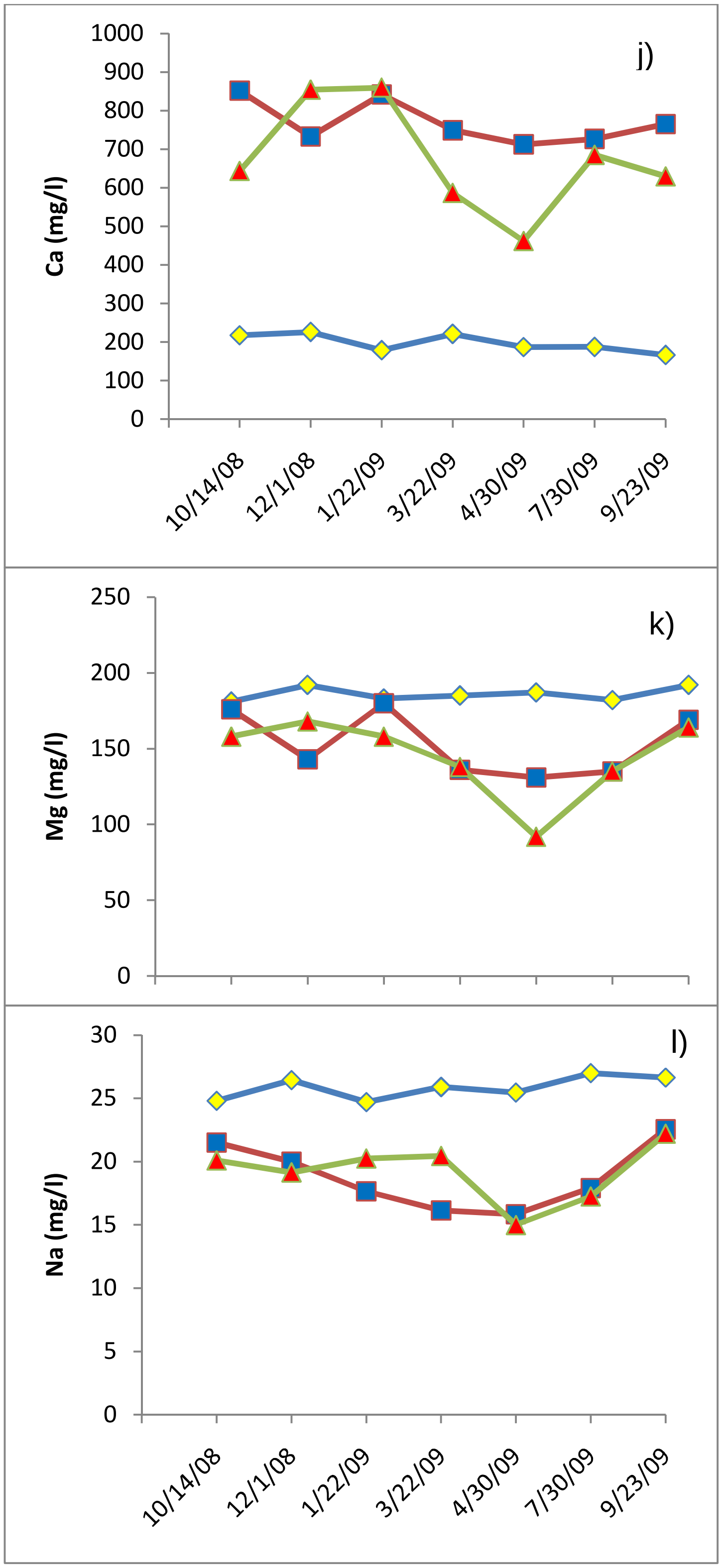


Figure 11. (Continued) (Caption shown on the previous page).

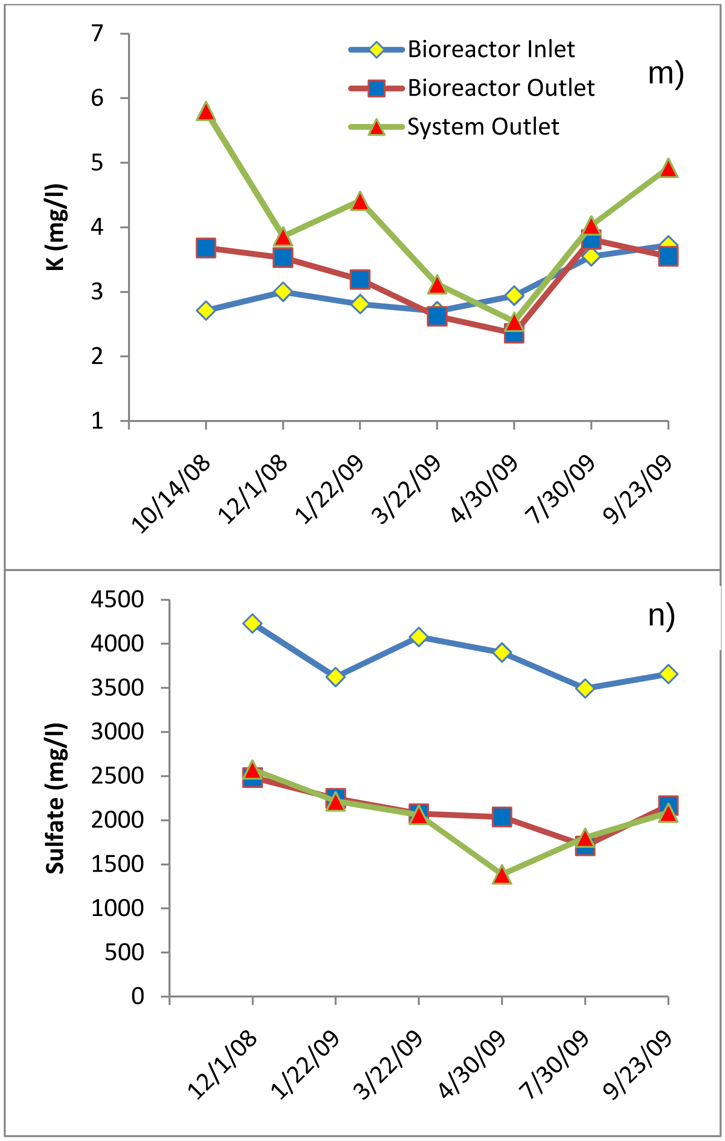


Figure 11. (Continued) (Caption shown on the previous page).

7.4 Alkalinity Production in the Tab-Simco Bioreactor

In the Tab-Simco anaerobic sulfate-reducing bioreactor, alkalinity can be produced by two main processes: (1) the BSR and (2) limestone dissolution. The alkalinity production by BSR can be estimated using the decrease in dissolved SO_4^{2-} concentration as the AMD passes through the bioreactor (Barton et al., 1999). The alkalinity produced from limestone dissolution can be determined by measuring the increase in Ca^{2+} concentration as the AMD passes through the bioreactor (Hedin et al., 1994; Barton et al., 1999).

In anaerobic sulfate-reducing bioreactors, BSR is considered to be the dominant process that decreases the amount of SO_4^{2-} concentrations (Barton et al., 1999; Riefler, 2008). To estimate the amount of alkalinity produced by BSR, it was assumed that the decrease in SO_4^{2-} concentration within the Tab-Simco bioreactor was exclusively due to BSR. The decrease in the SO_4^{2-} concentration, as the AMD passed through the bioreactor, was then used to estimate the total amount of alkalinity produced by BSR. The calculated rates of alkalinity production by BSR are given in Table 7. Calculations indicated the bioreactor produced an average of 147.3 kg/day of alkalinity from the BSR (Table 7).

On the other hand, limestone dissolution is the primary process that increases the Ca^{2+} concentration of AMD in sulfate-reducing bioreactors. To assess alkalinity production from limestone dissolution, the increase in the Ca^{2+} concentration within the bioreactor was considered to be caused solely by limestone dissolution. The Ca^{2+} concentration differences between the influent and effluent were then used to determine the amount of alkalinity produced from the limestone dissolution. The calculated results indicate that limestone dissolution in the Tab-Simco bioreactor produced on average about 99.6 kg/day of HCO_3^- (Table 7).

In the above calculations, the decrease in SO_4^{2-} and increase in the Ca^{2+} concentrations were assumed to be only from the BSR and limestone dissolution, respectively. However, minor addition or removal of SO_4^{2-} and Ca^{2+} could occur

Table 7: A*lkalinity production rates (kg/day) at the Tab-Simco bioreactor*

Date	Alkalinity from Limestone Dissolution	Alkalinity from Bacterial Sulfate Reduction (BSR)	Total Alkalinity from limestone Diss. and BSR	Total Alkalinity Determined using Net Acidity Removal Rate
12/1/08	45.02	115.85	160.86	153.40
1/22/09	62.86	103.38	166.23	155.10
3/22/09	67.00	175.55	242.55	205.37
4/30/09	193.73	172.52	366.25	360.25
7/30/09	151.47	234.74	386.21	389.73
9/23/09	77.41	81.67	159.09	179.51
Average	**99.58**	**147.29**	**246.87**	**240.56**

from other processes that take place within the bioreactor. For example SO_4^{2-} and Ca^{2+} can be removed in the form of insoluble minerals (Blowes et al., 2003; Thomas et al., 2002b), or might be added from the organic substrate (Neculita, 2008a), or from dissolution of already precipitated minerals. To check the accuracy of the alkalinity production rates from the above calculations, the sum of the alkalinity production rates (from BSR and limestone dissolution) was compared with the total alkalinity production rate for the bioreactor measured using other independent method. The total alkalinity production rate of the bioreactor was determined independently from the net acidity removal rate within the bioreactor. Using this method, the total alkalinity production rate in the Tab-Simco bioreactor was 241 kg/day as $CaCO_3$ equivalent (Table 7). Comparison of the sum of the alkalinity production rates from the BSR and limestone dissolution (247 kg/day), with the total alkalinity production rate determined from the net acidity removal rate (241 kg/day), shows that the total alkalinity production rate values determined by the two different approaches are very close to each other.

7.5 Limestone Dissolution and Bioreactor Longevity

Determining the limestone dissolution rate in a bioreactor could be helpful in estimating the amount of time before the limestone is dissolved completely, which thereby estimates the lifetime of the bioreactor. However, the lifetime of a bioreactor is affected by different factors, including the limitation of organic matter, hydraulic retention, changes in the chemistry and flow rate of the AMD, and hydraulic properties of the reactive mixture (such as clogging, armoring and compaction of the substrate) (Neculita et al., 2008a). According to Lewis (2008), about 1,500 tons (1,500,000 kg) of limestone was used in the construction of the Tab-Simco bioreactor. Considering the average limestone dissolution rate for the Tab-Simco bioreactor, which was 99.58 kg/day, it would take about 25 years for the limestone within the bioreactor to dissolve completely. However, previous studies have shown that complete limestone dissolution is not attainable because of armoring effects on the limestone by precipitated materials such as $Al(OH)_3$, $Fe(OH)_3$ and $CaSO_4.2H_2O$ (Kalin et al., 2005; Ziemkiewicz,1997).

7.6 Source(s) of the Sulfide Minerals That Cause the Tab-Simco AMD

Identifying the source of AMD could be very important in preventing AMD formation and predicting the amount of AMD to be produced. The source of AMD can be investigated by studying the sulfur isotope values of dissolved SO_4^{2-} in an AMD, and relating it with sulfur isotope values of sulfide minerals at the site. The oxidation of sulfide minerals to form SO_4^{2-} is accompanied by minor or no sulfur isotopic fractionation (Taylor et al., 1994; Taylor et al., 1984a; Toran et al., 1989). Therefore, if the oxidation of sulfide minerals had been the only reason for the formation of sulfate in AMD, a close correspondence between the sulfur isotopic values of dissolved SO_4^{2-} in the AMD and the sulfide minerals would be expected (Knoller et al, 2004).

Sulfur isotope values of dissolved SO_4^{2-} in the Tab-Simco AMD site for this study period are given in Table 5. Results from sampling stations, well B-1, well B-2 and the main seep, indicated that on average, the $\delta^{34}S$ value of the Tab-Simco dissolved SO_4^{2-} was 7.3 ‰ before it entered the treatment system. The source of the sulfide minerals that cause the AMD at the Tab-Simco site can be the coal seams and/or the shale layer at the site. Recently, Lefticariu et al. (2009) studied the sulfur isotope values of pyrite minerals in the Murphysboro and Mount Rorah coal seams in the surroundings of the Tab-Simco site. The study reported average $\delta^{34}S$ values of 6.2‰ and 10.6‰ for pyrite in the Mount Rorah and Murphysboro coal seams, respectively.

Comparisons between the average $\delta^{34}S$ value of the dissolved SO_4^{2-} and the $\delta^{34}S$ values of the pyrite in the Murphysboro and Mount Rorah coal seams indicated that the $\delta^{34}S$ value of the dissolved SO_4^{2-} was between the $\delta^{34}S$ values of pyrites from the two coal seams. This suggests that the cause for the Tab-Simco AMD was likely the oxidation of pyrite minerals both from the Murphysboro and Mount Rorah coal seams that occur at the site.

8. CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

1. The Tab-Simco AMD is highly contaminated water with average concentrations of acidity, 3,386 mg/l, dissolved SO_4^{2-} 4,589 mg/l, Fe 884 mg/l, Al 207 mg/l, Mn 34.5 mg/l and a pH level of 2.80 as the AMD reached the surface at the main seep sampling station.
2. The chemical characteristics of the Tab-Simco AMD showed slight variations as it flowed down gradient from the underground acid mine pool to the bioreactor. Between the acid mine pool and the main seep sampling stations, the concentrations of acidity, SO_4^{2-}, and most metals increased, and pH decreased slightly, indicating the possible presence of a sulfide mineral oxidation process and/or mixing of AMD from different acid mine pools. As the AMD flowed between the main seep and the bioreactor inlet sampling stations, slight improvement in water quality was observed. Acidity, SO_4^{2-} and most metal concentrations decreased slightly. Possible processes that caused the water quality changes in this part of the AMD system would be the mixing of the AMD with fresh water and / or precipitation in the form of metal (oxy)hydroxides and hydroxysulfates.
3. On average, the Tab-Simco treatment system removed 253 kg/day (98.5 %) of acidity, 145 kg/day (39%) of SO_4^{2-}, 64 kg/day (99.5%) of Fe, 13.5 kg/day (98%) of Al, 0.86 kg/day (22.5%) of Mn. The pH of the AMD that entered the bioreactor was increased from an average of 2.86 to 6.30. Measured concentrations in the discharge at the Tab-Simco site indicated that the

treatment system successfully removed the acidity and most metals from the AMD. However, the concentrations of Mn (26.4 mg/l) and SO_4^{2-} (2,021 mg/l) in the discharge were still elevated.

4. Treatment processes in the Tab-Simco bioreactor include production of alkalinity through BSR, and limestone dissolution followed by metal precipitation. The produced alkalinity neutralized the acidity, bringing it to lower levels and increasing the pH of the water. The BSR also decreased the SO_4^{2-} concentration in the AMD. Upon pH increase, a metal in the AMD precipitated mainly in the form of metal sulfides, oxides, and possibly carbonate and hydroxysulfates. The existence of BSR within the bioreactor was confirmed by an increase in $\delta^{34}S$ values, a decrease in SO_4^{2-} concentration in the effluent, a strong H_2S smell at the bioreactor outlet, and an observation of black sulfide minerals coming out with the effluent. The existence of limestone dissolution, on the other hand, was indicated by an increase in Ca concentration in the effluent.
5. In the Tab-Simco bioreactor, alkalinity production was by BSR processes and limestone dissolution. An attempt to determine the proportion of alkalinity contributed by each process using the decrease in SO_4^{2-} concentration and increase in Ca concentration within the bioreactor indicated that in the Tab-Simco bioreactor produced on average about 247 kg/day of alkalinity as $CaCO_3$ equivalent. Out of this, the 147.3 kg/day, 60% of the total alkalinity, was produced by the BSR processes, whereas the remaining 99.6 kg/day (40% of the total alkalinity) was produced from limestone dissolution.

6. A study for possible seasonal variations in the chemical characteristics of the untreated Tab-Simco AMD indicated that the chemical characteristics of the untreated Tab-Simco AMD measured at the bioreactor inlet sampling station was similar throughout the study period, indicating no significant seasonal variations in the untreated AMD existed. On the other hand, the bioreactor performance results indicated that the Tab-Simco bioreactor removed greater amount of acidity, SO_4^{2-} and metal during spring and summer compared to winter and fall.
7. Comparison of the $\delta^{34}S$ value of dissolved SO_4^{2-} in the Tab-Simco AMD with $\delta^{34}S$ values of pyrite minerals at the area indicated that the values are similar, suggesting that oxidation of pyrite minerals in Murphysboro and Mount Rorah coal seams was the most probable cause of the Tab-Simco AMD.

8.2 Recommendations

1. To avoid environmental impacts from high concentrations of Mn and SO_4^{2-}, the Tab-Simco treatment system could be amended to decrease the concentrations of these ions to acceptable levels. For example, the treated water that leaves the bioreactor could flow through a limestone bed inoculated with Mn-oxidizing bacteria to facilitate the Mn oxidation and precipitation by further increasing the pH level and introducing Mn-oxizing bacteria (Rose et al., 2003). To facilitate a higher removal rate of SO_4^{2-}, either the thickness of the organic layer or the surface area of the bioreactor can be increased. Increasing the thickness or surface area of the organic layer would increase BSR process resulting to a higher SO_4^{2-} removal rate which would

increase alkalinity production and pH level. An increase in pH level would in turn increase the Mn removal rate.

2. Further study that involves solid phase analyses and biological diversity should be undertaken to assess the conditions within the bioreactor, such as depletion of organic matter and, armoring and clogging of substrate material by precipitated metal oxides, which might affect its success rate and longevity. Identifying the mineralogy of the precipitates within the bioreactor using solid phase analyses is very helpful to understand the removal mechanisms and the geochemical conditions inside the bioreactor. Understanding the conditions inside the bioreactor in turn can be helpful in amending the bioreactor in a way that can increase its longevity and performance.
3. Periodic flushing of the bioreactor is also helpful in removing precipitates that can cause clogging of the substrate and pipelines within the bioreactor.
4. Finally, additional stable isotope (sulfur and oxygen) and mineralogical study of the sulfide minerals at the site is needed to identify the exact source and amount of the AMD causing sulfide minerals. Because identifying the source of the AMD causing sulfide minerals could be helpful in predicting and protecting the AMD formation.

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APPENDICES

APPENDIX A

Permission for Figure Reprinting

Mon, April 12, 2010 8:18:10 AM
RE: Asking permission
From: "Gusek, Jim"
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From: Yosief T Segid [mailto:yosief779@yahoo.com]
Sent: Saturday, April 10, 2010 9:47 AM
To: jgusek@knightpiesold.com; Gusek, Jim
Subject: Asking permission

Hi Gusek,
My name is Yosief Segid. I am a graduate student at Southern Illinois University Carbondale. I am evaluating an anaerobic sulfate-reducing bioreactor for my thesis. This is to ask your permission to use a FIGURE from your publication in my thesis. The figure shows Sulfate-Reducing Bioreactor Schematic and is indicated as Fig. 2 in the link
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Thank You

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