USE OF STAGED WETLANDS FOR MITIGATION OF ACID MINE DRAINAGE

FY 95 319(H) C9-996100-03-0

TASK #800

First Draft Final Report

Submitted to:
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ACKNOWLEDGEMENTS

The author expresses sincere appreciation to the Oklahoma Conservation Commission for providing support for this work. The author is especially grateful to Mr. Jim Leach, Oklahoma Conservation Commission for his guidance, understanding and appreciation. Special thanks are also due to Mr. William Battles and Ms. Mindy Ledbetter, the landowners who graciously allowed us to complete our study on their private lands. Other partners in this effort included the Latimer County Conservation District and many students of the University of Oklahoma School of Civil Engineering and Environmental Science. Also providing in-kind assistance or donations were Boral Material Technology Company, Brazil Creek Minerals, Global Stone Corporation, Hertz Equipment Rental Company, McAlester Rental And Sales, Oklahoma Forestry Services, and Oklahoma City Blue Thumb volunteers.

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EXECUTIVE SUMMARY

Acid mine drainage (AMD) is a major nonpoint source pollution concern in many former mining regions. AMD forms due to the oxidizing action of air and water on exposed sulfidic strata and is characterized by elevated concentrations of metals (especially iron and aluminum), acidity and sulfate. In Oklahoma, AMD impacts from abandoned coal mining activities are most prevalent in the Gaines Creek watershed of Pittsburg and Latimer Counties. As part of a Clean Water Act Section 319 grant, The University of Oklahoma constructed a four-cell passive treatment wetlands system in the summer of 1998 to treat a portion of a large AMD flow. Of the dozen or more identified discharges in this watershed, waters emanating from the #40 Gowen site have the greatest impact on the stream. Previous reclamation efforts at #40 Gowen resulted in the collection of the AMD flow in an artesian discharge. The mean discharge rate is approximately 850 liters per minute and mean water quality is pH 3.4, 250 mg L^{-1} iron, 36 mg L^{-1} aluminum, 14 mg L^{-1} manganese, 1000 mg L^{-1} sulfate and 660 mg L^{-1} net acidity as $CaCO_3$ eq.

Traditional mine drainage treatment technologies are not viable options at abandoned mines due to their laborious and cost-intensive nature. Passive treatment technologies, i.e., those that rely on natural biogeochemical and microbiological processes to ameliorate AMD, do provide viable treatment alternatives. Treatment wetland systems require less operational and maintenance labor and have lower initial costs but require larger land areas than traditional active chemical treatment systems. At #40 Gowen, a Successive Alkalinity Producing System-type wetland treatment process was implemented (Figure 1). Treatment occurs in a four-cell system of alternating vertical flow wetlands (VF) and surface flow aerobic ponds (SF). AMD is sequentially treated by charging the waters with alkalinity in the first VF then providing near-optimum conditions for precipitating metals in the first SF. Alkalinity consumed by metal hydrolysis in the first SF is recharged to the waters in the subsequent VF, thus allowing further metals precipitation in the final SF.

All water flows through the treatment wetlands are gravity-driven. Only a portion of the entire discharge (approximately 20 liters per minute) flows through the demonstration project due to constraints on available area. Each VF includes three verticals sections (Figure 2). The top layer (standing water) provides water head necessary to drive water through the underlying substrate. A maximum of 1.5 m vertical elevation (water depth) is provided, including 0.3 m freeboard. The middle layer is designed to generate alkalinity via biotic and abiotic means. This section consists of a 1-m thick mixture of spent mushroom substrate, limestone and hydrated fly ash in a 20:10:1 ratio by volume. The bottom layer is a gravel under drain that acts as a highly permeable zone to transmit water leaving the system through a network of drainage pipes. The treatment cells were planted with native wetland vegetation. Chemical water quality and quantity and wildlife use have been monitored every two weeks for two years. In addition, several short-term projects have examined substrate leachability, biotic health and biodiversity, and substrate metal sequestration and fractionation.

The treatment wetlands have successfully improved water quality to within applicable regulatory guidelines for over two years. Concentrations of Fe, Al, and Mn decreased significantly and pH and alkalinity concentrations increased significantly. The final effluent of the system has maintained a net alkaline condition (> 150 mg L^{-1}) with pH > 6, iron and aluminum < 0.5 mg L^{-1} iron, and manganese < 5 mg L^{-1}. (In wetland treatment systems, efficient manganese removal is not expected and at active sites, manganese is regulated as a “surrogate ion” for trace metals.) Trace metals concentrations were either near detection limit at all sampling locations (barium, cadmium, chromium, copper and lead) or were retained completely by VF1 (nickel and zinc) to less than detection limit.

In the vertical flow wetlands, alkalinity was produced by a combination of processes, including limestone and fly ash dissolution and bacterial sulfate reduction (BSR), to over 250 mg L^{-1}. Final effluent concentrations were net alkaline on all sampling dates, i.e., alkalinity was greater than mineral acidity plus proton acidity. The combination of spent mushroom substrate, limestone and hydrated fly ash has a substantial effect on acidity removal, and, if these acidity removal rates are sustainable, resultant design criteria could lead considerable savings in passive treatment system construction and land acquisition costs. Initial effluent water quality characterization indicated the potential for leaching of substrate nutrients and anions. However, all effluent samples since January 1999 have not been significantly different from inflows. Characterization of the substrate via a sequential extraction process indicates that substantial metal loads are being retained in the deep substrate and sequestered from the environment. Metal fractionation demonstrates the probability of long-term treatment success.

Observations during water quality sampling events indicate considerable wildlife use of the treatment wetlands. Several species of amphibians (e.g., bullfrogs, leopard frogs, and salamanders) reptiles (e.g., snapping turtles, garter snakes), birds (e.g., red winged blackbirds, killdeer, great blue herons) and mammals (e.g., moles, voles, coyotes) use the site. Biological assessments in the summer of 2000 indicated healthy populations of fish and macroinvertebrates in three of the four cells. Macroinvertebrate community structure indicates a trend from tolerant to less tolerant species with flow through the wetland system. In the final surface flow cell alone, 314 bluegill fingerlings and 7 bluegill adults were seined.

The #40 Gowen treatment wetlands demonstration project represents a sustainable and cost-effective solution for the devastating impacts of AMD on the environment. In these ecologically engineered ecosystems, natural processes improve the quality of contaminated water and critical habitat is restored. This demonstration project represents the first and only successful passive AMD treatment system in Oklahoma. As of November 2000, work at the #40 Gowen demonstration project has resulted in 12 professional presentations, two refereed journal articles, five conference proceedings papers, one master’s thesis and four undergraduate theses.

Perhaps the most exciting aspect of the #40 Gowen demonstration project is the transferability of this technology to other mining impacted watersheds. Already, the

#40Gowen treatment wetland design is being applied to problems at the Tar Creek Superfund Site in Ottawa County, Oklahoma and is being investigated for application in several other watersheds nationwide. The Tar Creek site is part of a former lead and zinc mining area known as the Tri-State Mining District and is ranked #1 on the National Priorities List. Approximately 94 million cubic meters of contaminated water exist in underground mine voids. Metal-rich waters discharge to the surface at several locations. Coupled vertical flow wetland and surface flow pond designs are applicable to these waters and represent the only treatment methodology that has been considered viable for improvement and restoration of the waters of Tar Creek.

1.0 INTRODUCTION

Acid mine drainage (AMD) is a major nonpoint source pollution concern in many former mining regions. AMD forms due to the oxidizing action of air and water on exposed sulfidic strata and is characterized by elevated concentrations of metals (especially iron and aluminum), acidity and sulfate. In Oklahoma, AMD impacts from abandoned coal mining activities are most prevalent in the Gaines Creek watershed of Pittsburg and Latimer Counties. As part of a Clean Water Act Section 319 grant, The University of Oklahoma constructed a four-cell passive treatment wetlands system in the summer of 1998 to treat a portion of a large AMD flow. Of the dozen or more identified discharges in this watershed, waters emanating from the #40 Gowen site have the greatest impact on the stream. Previous reclamation efforts at #40 Gowen resulted in the collection of the AMD flow in an artesian discharge. The mean discharge rate is approximately 850 liters per minute. Mean water quality is pH 3.4, 250 mg L^{-1} iron, 36 mg L^{-1} aluminum, 14 mg L^{-1} manganese, 1000 mg L^{-1} sulfate and 660 mg L^{-1} net acidity as $CaCO_3$ eq.

1.1 Mine Drainage Chemistry.

AMD is a significant water pollution problem that has drastically degraded thousands of miles of streams and creeks across the country. This problem has plagued the environment since humans began mining operations. Although federal action has been taken to prevent future pollution from current operations, past mining practices have left a legacy of closed mines that continue to defile local ecosystems.

In underground coal mine drainage pools, chemical reactions occur between seeping meteoric or ground water and surrounding geologic formations. Due to the pyritic nature of associated strata (often sandstones) and impurities associated with the coal, acidic water develops. Acidic mine water has several constituents that may adversely affect the aquatic environment. Oxidation of the pyritic material liberates specific metals in toxic concentrations. Also, the acidic nature of the water results in the dissolution of other metal-rich minerals that may be associated with the surrounding strata. Many of these metals are toxic at various levels and damage aquatic life directly or synergistically. Common examples include iron, manganese, zinc, copper, and aluminum.

When acid mine water reaches the ground surface, it becomes AMD. The acidic water further undergoes abiotic and/or biotically mediated chemical reactions with oxygen and surrounding minerals. This usually results in a lowering of pH and significant amounts of metal precipitation. It is the ubiquitous iron precipitates that give AMD its distinctive red-orange color.

Acid mine water reaches the surface primarily due to variations in piezometric pressure. As is often true, mine workings in the study area are readily recharged by surface water and runoff. Water fills the excavated rooms and saturates the remaining coal seam. Gradually, the water level rises within the mine and coal seam to a point above the floor of the basin; thus creating a head pressure. The extent of this piezometric pressure is assumed to be limited to the geologic integrity of the overlying material. Water pressure will increase until an "exit" point is reached. Common discharge points include ventilation shafts and drill holes, but fractured rock strata also serves this purpose. These points of weakness form acidic water springs. Discharge from these springs varies in magnitude, from a few gallons to hundreds of thousands of gallons per day. Depending on the specific site, the receiving ecosystem is often devastated.

1.2 Mine Drainage Impacts.

The ecological impact of an AMD discharge to uncontaminated receiving waters can be severe. Potential impacts to the surrounding environment from AMD include the degradation of surface water quality, habitat stability and aquatic community structure (e.g., Sistani et al., 1995; Diamond et al., 1993; Short et al., 1990). The chemistry of AMD can be broadly characterized by a depressed pH, low dissolved oxygen (DO), elevated mineral acidity (acidity associated with hydrolyzable metals) and high metal (especially iron, aluminum and manganese) and SO_4^{-2} concentrations (Evangelou and Zhang, 1995; Kleinmann et al., 1995; Hedin et al., 1994a). When AMD rich in Fe^{+2} is exposed to the atmosphere, ferric iron (Fe^{+3}) may precipitate as insoluble hydroxides and oxyhydroxides, coating the bottom of receiving waters with an iron rich ochre (Hedin et al., 1994a), making the habitat unsuitable for macroinvertebrate community development. Elevated metal concentrations, net acidic conditions, habitat loss due to precipitation of iron and combined synergistic effects are known to have detrimental impacts on biological communities ranging from the individual to ecosystem level (e.g., Manyin et al., Short et al., 1990). As the ochre develops on the stream substrate, biological communities and interdependencies between species may become altered, changing biotic composition toward more metal tolerant organisms, resulting in low diversity or the complete prevention of aquatic populations for some distance downstream (Gray, 1997; Short et al., 1990). Kleinmann et al., (1995) determined that over 6,400 km of streams were degraded by mine discharges in Appalachia alone, while Skousen et al., (1996), concluded that AMD has degraded approximately 20,000 km of streams and rivers in the United States.

This problem is particularly evident in the southeastern portion of Oklahoma. This region has a rich history of coal mining that began in the late 1800's and continues to this day. Although mining has not been a significant part of the local economy for some time, the impacts from the numerous mines in the area have greatly affected the citizens. Problems triggered by subsidence, water pollution, and physical health hazards have instigated citizen concern.

In particular, a multitude of mines near the towns of Hartshorne and Gowen have severely degraded the water quality of the Pit Creek watershed. Several mines have been discharging acidic water for decades. This constant assault has ravaged the immediate ecosystem and has significantly impacted aquatic habitat for miles down stream. Studies conducted by the Oklahoma Water Resources Board (1992) have determined that discharge from these mine seeps is adversely affecting the water quality. Parameters of concern are toxic levels of metals (particularly iron, manganese, and zinc), pH, sulfate, low alkalinity and low dissolved oxygen. These pollutants and adverse environmental conditions are derived directly and indirectly from the oxidation of the geologic materials associated with the coal, primarily pyrite. The result is manifested in several miles of streams with substandard water quality. In fact, a report by the Oklahoma Department of Wildlife Conservation concluded that: "...mining influences...appear to seriously impair fish and wildlife propagation in Pit Creek and partially impair this beneficial use in a portion of Gaines Creek."

Furthermore, a study of the Gaines Creek arm of Lake Eufaula (Wagner 1997) concludes, "preventing or treating AMD should result in noticeable improvements in receiving streams." The site chosen for this demonstration project discharges into Pit Creek, and, subsequently, Gaines Creek. The demonstration of an effective treatment method for AMD will encourage and support activities that will significantly improve natural waters in the area.

A significant amount of attention has been focused on this region because of the degraded quality of Pit Creek and its subsequent impact on other receiving streams and water bodies. Analysis of surface water indicated that pH levels were as low as 2.5 near seep sites, and metal loading exceeded tolerable levels in many areas. Biological assessment of the site has indicated that there has been a disappearance of several species and an overall decrease in the aquatic biological diversity (Oklahoma Water Resources Board, 1992).

The Pit Creek watershed contains approximately 12 square miles in the townships 4N and 5N and range 17E IM. Roughly 21 miles (Oklahoma Water Resources Board, 1992) of streams are included in this area, with about a third of them directly influenced by AMD. Water drains from the basin into Gaines Creek, which subsequently flows into Lake Eufaula (see Map 2), a major drinking water reservoir and recreational area. Recently there has been heightened concern for the quality of this lake with respect to nonpoint source pollution, with attention focused on recent and past mining impacts in the Pit Creek watershed.

This region is formed in a shape of a bowl, with the Hartshorne syncline traversing through the center in a northeasterly direction. The watershed is located in the Arkoma Basin, just north of the Choctaw Fault. Major geologic outcroppings are associated with the Pennsylvanian Age, excluding deposits that occurred during the Pleistocene and more recently. Most of early deposits were composed of alternating layers of alluvial material originating from streams. The coal of primary interest is associated with the two seams of Hartshorne coal, upper and lower. The lower Hartshorne is approximately 50 feet above the Hartshorne sandstone, and ranges in depth from a few feet to over 500 feet below the surface. Early operations extensively mined this seam throughout the area.

High sulfur coal seams were actively mined throughout Latimer and Pittsburgh Counties between the early 1900’s and circa 1930, and were abandoned near that time. Mining operations ranged in size from a few acres to several hundred. One report estimated that over 3,869 acres of coal have been mined underground (Bigda, 1976). Most of the deep coal operations were discontinued by the mid to late 1930's, resulting in the abandonment of the mines. Over time, the underground workings filled with surface and groundwater, resulting in the formation of large subsurface reservoirs. Bigda (1976) estimated that there is approximately 7,738 acre feet of water stored in these mines.

The most evident AMD discharge is located in the SW ¼, SW ¼ Section 23, Township 5 N, Range 17 E, Latimer County, Oklahoma, near the town of Gowen. The #40 Gowen discharge is an AMD seep from an abandoned underground mine, operated in the early part of the twentieth century by the Rock Island Improvement Company. At the #40 Gowen seep upwelling water is retained in a small retention pond behind an earthen dam constructed by researchers from The University of Oklahoma, Health Science Center. Acid mine drainage at Gowen #40 ultimately flows into Gaines Creek and Lake Eufaula, a popular lake for outdoor recreation. The seep discharges at a mean of 800 L min^{-1}, with a mean acidity of 633 mg L^{-1} as $CaCO_3$ equivalent, pH of 3.44, 215 mg L^{-1} total Fe, 36 mg L^{-1} Al, 13.5 mg L^{-1} Mn, and 1131 mg L^{-1} SO_4^{-2}.

1.3 Passive Treatment of Mine Drainage.

Traditional mine drainage treatment technologies are not viable options at abandoned mines due to their laborious and cost-intensive nature. Passive treatment technologies, i.e., those that rely on natural biogeochemical and microbiological processes to ameliorate AMD, do provide viable treatment alternatives. Treatment wetland systems require less operational and maintenance labor and have lower initial costs but require larger land areas than traditional active chemical treatment systems.

Two independent research projects in the 1970s and 1980s found that passive treatment of mine discharges could potentially be achieved using natural *Sphagnum* (peat) wetlands (Wieder and Lang, 1982; Huntsman et al., 1978). These conclusions led to the possibility that wetlands could be constructed for the explicit purpose of water quality improvement at abandoned mine sites where passive treatment enabled the restoration of water quality at abandoned mine sites for a reasonable cost (Nairn and Hedin, 1992). Many of these first wetlands failed to accomplish the desired goals of industry and researchers within a relatively short period of time, leaving some doubting that wetlands could treat AMD successfully.

The process involved in the passive treatment of AMD is two fold. First, alkalinity must be imparted to the water in sufficient amounts, such that the pH is raised adequately and both proton and mineral acidity are neutralized. Alkalinity generation should be accomplished first, because the circumneutral pH associated with bicarbonate dominance ensures that reactions proceed more rapidly (Limpitlaw, 1996; Hedin et al., 1994b). Then, metal removal must occur, minimizing biological impacts due to metal toxicity in receiving waters.

In passive AMD treatment with sequential alkalinity producing systems (SAPS), the primary means for alkalinity production are the dissolution of calcium carbonate ($CaCO_3$), or limestone, and bacterial sulfate reduction (BSR). Using limestone as a method to effectively buffer the acidity has been common practice in passive technologies due to the low cost of limestone and its efficiency in increasing alkalinity when used under the proper environmental conditions. At low pH with anaerobic conditions, the dissolution rate of limestone is extremely rapid, being limited primarily by the rate of transport between the solution and the mineral surface (Stumm and Morgan, 1996). SAPS are systems designed to force water through a layer of compost, creating an anoxic environment and increasing the contact time between AMD and the compost (Nairn et al., 1999; Kepler and McCleary, 1994). Successive alkalinity producing systems combine anoxic limestone drain (ALD) treatment with anaerobic wetland technologies into one system, forcing water vertically through compost overlying a limestone bed (Kepler and Mc Cleary, 1994). The biological oxygen demand (BOD) associated with the compost causes the substrate to become anaerobic, enhancing limestone dissolution without concerns associated of armoring. SAPS were initially designed for a compost layer to be placed over the top of a limestone layer, creating two distinct components, but the evolution of SAPS technology has incorporated limestone into the organic layer in compost wetlands (Nairn et al., 1999, 2000). This design may have allowed sulfate-reducing bacteria (SRB) to tolerate more acidic waters than generally accepted by creating a microclimate of circumneutral pH values around the limestone (Hedin, 1996).

After alkalinity has been generated, iron (Fe), aluminum (Al) and manganese (Mn) retention is generally accomplished via oxidation and hydrolysis. Oxidation and hydrolysis reaction rates are a function of DO concentrations, pH, and retention time in the system (Hedin et al., 1994a). Because pH influences both solubility of metal solids and oxidation/hydrolysis kinetics, it is of particular importance (Stumm and Morgan, 1996; Hedin et al., 1994a). At circumneutral pH values, Al is removed almost immediately via hydrolysis reactions, and with sufficient DO the oxidation of Fe and Mn occurs rapidly (Nairn and Hedin, 1992). Aerobic ponds generally serve the purpose of providing long retention times under aerated conditions, thereby allowing physical retention of Fe and Mn by promoting metal oxidation.

The applicability and efficacy of passive treatment of AMD is limited by the ability of the systems to produce adequate alkalinity to buffer mineral and proton acidity present in the AMD, or proton acidity produced via metal oxidation and hydrolysis (Nairn and Hedin 1992). The dominant treatment processes in aerobic wetlands (metal oxidation, hydrolysis, precipitation and settling) make them applicable only to net alkaline mine drainages. The use of anoxic limestone drains is limited to AMD containing negligible Al^{+3} or Fe^{+3} concentrations because of armoring and clogging concerns with $Al(OH)_3$ or $Fe(OH)_3$. Organic substrate wetlands may provide sufficient alkalinity production capacity in those cases where contact of the AMD with the substrate is maximized and sufficient land areas are available. However, acidity removal rates in surface flow organic substrate systems are limited by passive diffusion of alkalinity from the substrate to the water column.

Successive alkalinity producing systems (SAPS) are coupled vertical-flow wetlands and aerobic ponds. Their performance relies on alkalinity production in wetland cells through bacterial sulfate reduction (BSR) and mineral (predominately limestone or $CaCO_3$) dissolution, followed by subsequent metal removal in aerobic ponds via oxidation, hydrolysis, precipitation and settling (e.g., Kepler and McCleary 1994; Jage et al. 2000; Watzlaf et al. 2000). If sufficient alkalinity is produced in the vertical-flow wetlands, proton acidity produced by aerobic metal removal mechanisms in the ponds will be buffered and waters may be discharged to receiving waters. If sufficient buffering capacity is not introduced, AMD may be directed into another series of vertical-flow wetlands and aerobic ponds. This sequence may then be reproduced as necessary to reach water quality improvement objectives. SAPS have been used throughout the coalfields of central and northern Appalachia, USA, in the last five years and have recently been implemented in other mining areas**.**

Biological alkalinity generation in vertical-flow wetlands is provided by BSR, and, to a lesser degree, by other microbially mediated processes. In temperate regions, the contribution of biological processes to overall alkalinity production is seasonal (Watzlaf 1996; Watzlaf et al. 2000) and abiotic processes occur at a relatively constant rate year round. Most operating SAPS rely solely on limestone dissolution for abiotic alkalinity generation. Limestone is an inexpensive source of neutralizing capacity and is often available in close proximity to mining areas. The use of alternative alkaline materials in the substrate of vertical-flow wetlands has received little attention. Some traditional mine water treatment chemicals are available in solid form (e.g., $Ca(OH)_2$), but are cost-prohibitive and caustic, thus causing environmental and human health concerns in wetlands. Alkaline coal combustion products (CCPs) may provide an inexpensive and readily available source of alkaline materials. In general, the utility of AMD treatment using CCPs has been examined by injecting grouts into underground mines (e.g., Canty and Everett, 1998). However, they have not been used as an alkalinity source in passive treatment systems.

Amendments to the Clean Air Act (CAA) in 1977 and 1990 mandated substantial changes in the quality of coal burned, as well as the pollution emitted at coal-fired power plants (Hower et al., 1999). When high sulfur coal is burned in power plants, technologies are required which reduce the amount of SO_2 and NO_x emitted. These technologies have successful at decreasing air emissions, but the trade off is the production of greater solid waste material. Although several ash types exist, coal combustion products (CCPs) generally refer to high volume residues produced during energy production. The type and quality of CCPs produced depend on the type and quality of coal used, the calcium and sulfur content of the coal, boiler type and emission control strategies (Stewart, 1999; Tishmack, 1996). There are seventeen potentially toxic elements found in ashes (Fitzgerald, 1996), including aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, copper, lead, manganese, mercury, molybdenum, nickel, selenium, vanadium and zinc.

The use of certain alkaline CCPs for the treatment of AMD has become a topic of recent research, because about one-half of the bed ashes contain calcium oxides (CaO and CaOH) which are strong forms of alkalinity (Aljoe and Renninger, 1999; Ziemkiewicz and Skousen, 1996). This results from the addition of lime within the boiler to act as a sorbent with SO_x (Stewart, 1999). Most commonly, CCPs have been used as an *in-situ* treatment technology, whereby some slurry ash mix is pumped into an abandoned mine in an attempt to neutralize AMD (Aljoe and Renninger, 1999; Canty and Everett, 1998), control subsidence or as an attempt to seal the acid-producing strata within the mine (Aljoe and Renninger, 1999). In addition, research has been completed into the use of CCPs as an alkaline amendment to SAPS substrates.

In waters with very high acidity concentrations, SAPS may be unable to generate the alkalinity required to neutralize acidity and precipitate metals from solution. A demonstration project was conducted in Latimer County, Oklahoma to show that supplementing SAPS with alkaline CCPs sufficiently increased the ability of the treatment system to function without compromising the ecological integrity of the receiving waters. This study addressed concerns relating to the potential leaching of heavy metals from the CCPs, and to validate the their use in treatment wetlands. Knowledge of how this system might truly impact the downstream ecology will allow a better evaluation of CCP amendments to SAPS for AMD treatment.

2.0 MATERIALS AND METHODS

A treatment wetlands demonstration project was constructed at the #40 Gowen discharge by The University of Oklahoma. A four-cell passive treatment wetlands system was built in the summer of 1998 to treat a portion of the large AMD flow. Chemical monitoring was ongoing for approximately two years and was supplemented with biological and substrate sampling and analysis.

2.1 Site construction.

At #40 Gowen, a SAPS-type wetland treatment process was implemented in summer 1998 (Figures 2.1 and 2.2). Based on the chemical nature of the AMD (high dissolved Al concentrations), a SAPS supplemented with alkaline CCPs was determined to be the best

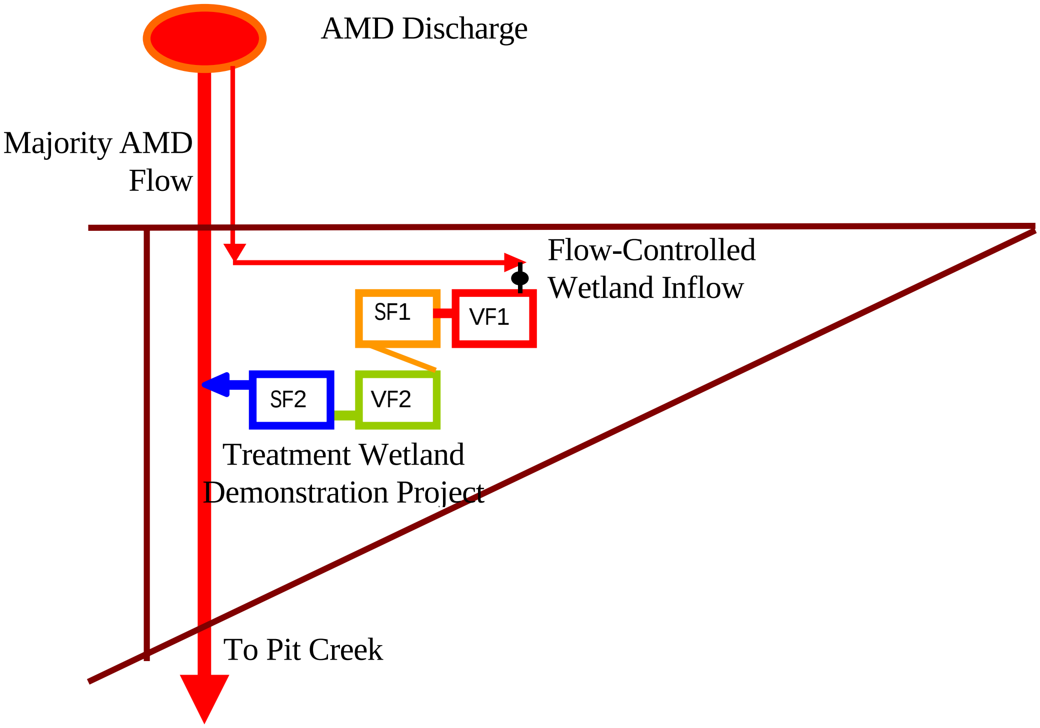

Figure 2.1. Plan view diagram of the #40 Gowen Treatment Wetlands Demonstration Project. Note that only a fraction of the total volume of the discharge is directed to the treatment system due to constraints on available land area.

Figure 2.2. Aerial photograph of the #40 Gowen Treatment Wetlands Demonstration Project. Note the proximity to Highway 270 and production agricultural lands..

passive treatment option at #40 Gowen. The innovative treatment system was designed with four alternating approximately 185 m^2 vertical flow wetlands (VFs) and aerobic settling ponds (SFs.). Construction of the wetland treatment system began June 8, 1998, and completed August 25, 1998, due to wet conditions in the month of June. Drought conditions during July and August and a subsequent lowering mine pool elevation, caused the system not to be flooded until late September.

Construction implementation occurred as a multi-phase process, requiring a variety of equipment and much manual labor. Heavy equipment, including bulldozers, front-end loaders, backhoes and small excavators were used to excavate the treatment cells. The design called for each VF cell to be approximately 2-2.5 m deep and 2.5-3 m for each SF, and each 12 m by 15 m in area. The bulldozer was expected to do the bulk of the excavation, with the author serving as the operator. The proposed timeline for this task was 3-4 days if no major problems were encountered. Cells 3 (VF2) and 4 (SF2) were completed in about one and one-half days; however, several delays were encountered while attempting to excavate VF1 and SF1. First, a “muck” (approximately 0.75 m thick) layer from a buried stock pond was unearthed in the bottom of both VF1 and SF1 during excavation. This layer consisted of heavy organics, decreasing the traction of the bulldozer. At this point, the excavation was delayed several hours. From this point forward, excavation within cell 1 and 2 were completed using a backhoe. Secondly, several times (June 10, 11 and 18, 1998), heavy precipitation stopped work completely for multiple days due to muddy conditions.

After the excavation phase was complete, about 15 cm fluidized bed ash (FBA) was placed in the bottom of each pond using front-end loaders. Fluidized bed ash has cementious properties, theoretically creating an impervious layer beneath the alkaline generating substrate to help ensure the pond would not leak. Historically, the use of bed ashes has been in concrete, soil stabilization, and road base because of its self-hardening properties (Brazil Creek Minerals, Inc., 1998; Pflughoeft-Hassett, 1996). Because a secondary seep was discovered in cells 1 and 2 during construction, roughly 30 cm of FBA was placed into the bottom of VF1 and SF1 as an attempt to keep water from leaking. Class C FBA was obtained from Brazil Creek Minerals, Inc., Fort Smith, Arkansas. A breakdown of the chemical characteristics in FBA and HFA can be found in Table 1.1. The FBA was stored on the ground until needed. Unfortunately, moisture from precipitation caused the FBA to harden, decreasing its value in retarding leaks. No other changes were made to the SFs, with the exception of 10 cm schedule 40 PCV pipe placed to transfer water between ponds.

In each VF, 30 m of perforated agricultural type piping was buried in 12-15 cm of limestone (73% $CaCO_3$, 21% SiO_2) (Dolese Brothers quarry, Hartshorne, Oklahoma) was placed on top of the FBA. The perforated drain pipe measured 10 cm inside diameter, was moderately flexible, and had three holes (~1 cm) drilled around the circumference every 12-15 cm along its length. The purpose of the pipe network was to collect water after passing through the alkaline generating substrate, so that it could then be piped into the SFs. The drain pipe was then connected to a 10 cm inside diameter schedule 40 PVC using a metal fastener, and rotated 90^o upward to exit the cell. The schedule 40 PVC was connected to another piece of 10 cm schedule 40 PVC which ran parallel to the ground.

Table 1.1 - Summary of the percentage of chemical characteristics within the HFA and FBA used in the 40 Gowen AMD wetland treatment system (From Nairn et al., 1999).

Constituents	HFA	FBA
SiO_2	31	15.6
CaO	28.2	39.8
Al_2O_3	19.3	11.3
MgO	6.4	2.2
Fe_2O_3	5.8	9.4
SO_3	2.2	18.4
Other	7.1	3.3

surface using a 45^{o} elbow. This design served two purposes. First, the water level in each cell was maintained by the outflow pipe elevation. Second, water was moved between cells passively, requiring no outside power sources to maintain flow between the cells.

On top of the drainage layer was an approximately three-quarter meter thick alkaline generating layer, composed of spent mushroom substrate (SMS), limestone (>90% $CaCO_3$), and hydrated fly ash (HFA) in a 2:1:0.1 ratio. The SMS was obtained from JM Farms, Miami, Oklahoma, after being used as a substrate for mushroom farming. SMS varies regionally, and the SMS utilized in this study contained chicken litter, wheat straw, cotton seed meal, soybean meal and gypsum ($CaSO_4$) (JM Farms, 1998). The limestone (>90% $CaCO_3$) and HFA were purchased from the Marble City quarry and Oolaga Power Station, respectively. To provide enough head pressure to force water through the alkaline generating layer, the design called for roughly 1.5 m of standing water to be maintained at all times. Water flow within the system was completely gravity driven, with water levels in each cell maintained by the outflow pipe elevation at approximately 0.25 m above downstream cells. Cattail (*Typha spp.*) seed heads were dispersed with each VF cell on November 6, 1998, but aquatic vegetation was not established by the conclusion of this study.

While the vertical flow systems were designed to impart alkalinity to the system, the aerobic (surface flow) ponds were designed to increase retention time and available oxygen to precipitate metals in an insoluble solid form (i.e., FeOOH). These cells were lined with 15 cm of FBA and planted with a few *Typha spp.*, with no other amendments being made to the cells. At the conclusion of construction, the berms of all cells were planted with annual rye and fertilized to help control erosion. It was also hypothesized that bermuda grass would spread from surrounding areas where bermuda growth is dense, further providing ground cover. Several times during the sampling period, maintenance was done on the treatment system. Leaks were detected at multiple locations around the system. To control the leaks, FBA was placed on the outside of the berm, which was covered with approximately 15 cm of topsoil and planted with grass seed.

Water from the seep upwelling was transferred to VF1 by pipe with minimal influence on the chemistry of the AMD. Roughly 6 m of 10 cm schedule 40 PVC pipe ran from the earthen dam directly to the seep upwelling in an attempt to attain AMD which had been influenced little by surface atmospheric conditions. Water was transported approximately 200 m from the seep upwelling to VF1, where flows were controlled using a wheeled gate valve. The water level in the seep pond was maintained 15 cm higher than VF1 using three 10 cm PVC standpipes, allowing gravity flows to VF1 strictly through head pressure and elevational differences. The outflow pipe of each cell was placed 15 cm below the inflow pipe, maintaining the water level 15 cm below the inflow elevation, allowing gravity to move water through the system. Schedule 40 PVC was used between all ponds because of its strength and ability to resist photodegradation.

Treatment occurs in a four-cell system of alternating vertical flow wetlands (VF) and surface flow aerobic ponds (SF). AMD is sequentially treated by charging the waters with alkalinity in the first VF then providing near-optimum conditions for precipitating metals in the first SF. Alkalinity consumed by metal hydrolysis in the first SF is recharged to the waters in the subsequent VF, thus allowing further metals precipitation in the final SF.

Based on the chemical nature of the AMD (high dissolved Al and acidity concentrations), a SAPS supplemented with alkaline CCPs was determined to be the most viable passive treatment option at the #40 Gowen discharge (Figure 2.3.) The treatment system was designed to incorporate four alternating, 185 m^2 vertical-flow wetlands (VFs) and surface-flow aerobic settling ponds (SFs). Construction of the treatment system was completed from June-September 1998. The design called for each VF cell to be approximately 2-2.5 m deep and 2.5-3 m for each SF, and each 12 m by 15 m in area. A layer (15 cm thick) of Fluidized Bed Ash (FBA) was placed in the bottom of each cell as a means of minimizing water loss due to leaking. Like HFA, FBA is a product of coal-fired power plants. In each VF, 30 m of perforated agricultural type pipe was buried in 25-30 cm of limestone (73% $CaCO_3$, 21% SiO_2). The perforated drainpipe measured 10 cm inside diameter, was

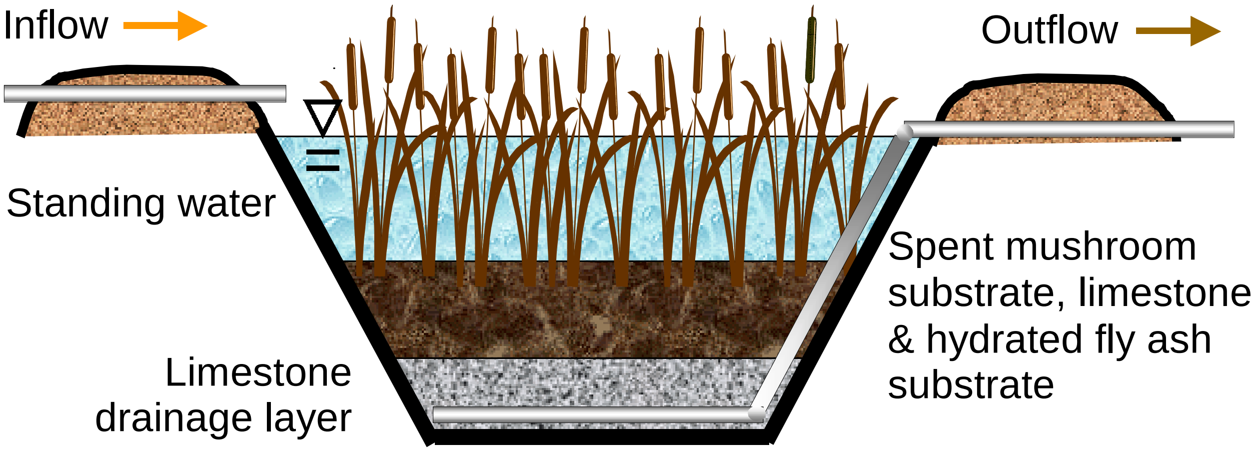

Figure 2.3. Cross-section of one of the #40 Gowen Treatment Wetland Demonstration Project vertical-flow cells.

moderately flexible, and had three holes (~1 cm) drilled around the circumference every 12-15 cm along its length. The drainpipe served to collect water after passing through an alkaline generating substrate, and was connected to 10 cm schedule 40 PVC so it could then be piped into the SFs. On top of the drainage layer was an approximately three-quarter meter thick alkaline generating layer, composed of spent mushroom substrate (SMS), limestone (>90% $CaCO_3$), and hydrated fly ash (HFA) in a 20:10:1 ratio by volume. While SMS varies regionally, the SMS utilized in this study contained chicken litter, wheat straw, cotton seed meal, soybean meal and gypsum ($CaSO_4$) (JM Farms, 1998). The limestone (>90% $CaCO_3$) and HFA were purchased from the Marble City quarry and Oolaga Power Station, respectively. To provide enough head pressure to force water through the alkaline generating layer, the design called for roughly 1.5 m of standing water to be maintained at all times. While the VF cells were designed to impart alkalinity to the system, the SF cells were designed to increase retention time and available oxygen. Under circumneutral conditions, with sufficient oxygen, iron will precipitate in an insoluble solid form (i.e., FeOOH) relatively quickly.

All water flows through the treatment wetlands are gravity-driven. Only a portion of the entire discharge (approximately 20 liters per minute) flows through the demonstration project due to constraints on available area. The top layer (standing water) provides water head necessary to drive water through the underlying substrate. A maximum of 1.5 m vertical elevation (water depth) is provided, including 0.3 m freeboard. The middle layer is designed to generate alkalinity via biotic and abiotic means as described above, and consists of a 1-m thick mixture of spent mushroom substrate, limestone and hydrated fly ash in a 20:10:1 ratio by volume. The bottom layer is gravel underdrain that acts as a highly permeable zone to transmit water leaving the system through a network of drainage pipes. The treatment cells were planted with native wetland vegetation, predominantly *Typha latifolia* L.

It is important to note that the #40 Gowen discharge underwent a dramatic hydrologic change during early September 2000. The Oklahoma Abandoned Mine Lands Program's reclamation efforts in the early 1990s resulted in a single AMD discharge pond on an adjacent landowner's property that collected the artesian flow. The university had installed a piping system during summer 1998 that brought a portion of this flow to our treatment wetlands system on William Battle's land. Flow to the wetland cells was completely driven by hydraulic head differences and was dependent on water levels maintained by stand pipes in the AMD discharge pond. Mean flow out of the discharge pond was approximately 250 gallons/minute. By September 11, 2000 (as noted by Paul Behum and Jeff Zingo of the Office of Surface Mining, Reclamation and Enforcement) the original point of discharge had ceased to flow and the mine drainage was now apparently surfacing into the bottom of a (formally freshwater) stock pond on William Battles' land.

On September 22, the Principle Investigator visited the site with Matt Mercer (Oklahoma Conservation Commission Wetlands Coordinator and OU MES graduate who had completed his MES on the #40 Gowen treatment wetlands). The original discharge pond and the receiving channel that flows south through Battles' land and under Highway 270 was found to be dry. Approximately 6-8" of standing water were found in the discharge pond, well below the outflow stand pipes. The water source from the mine (the entry) was visible but not flowing. Inflow to the wetland cells was therefore zero and water levels in treatment wetland cell #1 were down approximately one foot. All wetland cells were maintaining water but were assumed to be losing water to evapotranspiration.

Water quality in the formerly fresh stock pond was degraded (pH 3.4.) Flows in the channelized portion of the outflow were estimated via bucket and stopwatch to be ~ 70 gpm. A substantial fish kill had occurred (largemouth bass, several species of sunfish, etc.) in the former stock pond. This event effectively removed the inflow to the wetlands demonstration project and caused the project to end approximately one month prematurely.

2.2 Field water quality monitoring.

Field sampling began October 2, 1998, and occurred weekly through November 25, 1998, then bi-weekly through September 7, 2000. Water samples and flow rates were collected at eight locations including the inflows and outflows of each of the four cells (W1, W2, W3, W4 and W5), the artesian discharge (L1) and two downstream locations (L1 and L2). During each sampling event qualitative and quantitative field data were collected along with water samples. Upon arriving at #40 Gowen, field observations were taken, including approximate any other important observations.

In situ field measurements were conducted as follows: pH and temperature with a calibrated Orion SA290 portable pH/ISE meter, dissolved oxygen with a calibrated YSI Model 55 DO meter and conductivity with an Oakton Conductivity/TDS meter. In addition, an Orion 1230 Multiparameter meter was also used for Ph, temperature, conductivity and dissolved oxygen. Alkalinity was determined in the field with a Hach Digital Titrator using 1.6 N H_2SO_4.

Water flow rates were measured at all sampling locations with a calibrated bucket and stopwatch. Three to six measurements of the time necessary to collect a known volume of water were made and the mean reported.

2.3 Laboratory water quality analyses.

Raw and acidified (concentrated HCl) samples were collected in high density polyethylene (HDPE) bottles at each sampling point. Each sampling event included at least one field duplicate and one blank for quality control purposes. One sample from each location per event was preserved with 2 ml of concentrated HCl to ensure that the ratio of redox metals did not change before analysis could be completed. Samples were immediately placed on ice in an insulated cooler and returned to the Ecosystem Biogeochemistry and Ecology Laboratory at the University of Oklahoma in Norman within 24 hours of collection. Raw samples were stored at $<4^{o}C$ and acidified samples were stored at room temperature until analysis.

In the laboratory, acidified samples were digested via a modified nitric acid technique including the addition of 2 mL of H_2O_2 after completion to ensure complete oxidation of residual organic matter (APHA 1995). Total metals concentrations (Fe, Mn, Al, Mg, Ca, Na, Zn, Ni, Cu, Cr, Cd, Pb, and Ba) were then analyzed on the digested samples using a Buck Scientific Model 210 (October 1998-April 1999) or Perkin Elmer 5100 Atomic Absorption Spectrometer. Concentrations of sulfate, nitrate, phosphate and chloride were determined on a Dionex Model AI 450 Ion chromatography system after filtering through a 0.2 um filter to prevent clogging. Acidity was determined by calculation using hydrolyzable metals concentrations and pH (Hedin et al. 1994).

Loading rates were calculated by multiplying the concentration, in mg L^{-1}, of a particular metal species with the flow rate where the sample was collected (Equation 4)

$$\text{Loading (g day}^{-1}\text{)} = 14.4 * [M^{+}] * \text{Flow Rate (L minute}^{-1}\text{)}$$

(where the multiplier 14.4 converts the loading from mg minute^{-1} to g day^{-1}). Flow rates fluctuated substantially between sample dates, and therefore do not provide a complete assessment of the loading. However, these data can provide useful information into how the system in performing. Loading data were used to calculate area adjusted removal rates by subtracting the outflow concentration from the inflow concentration and dividing by the area (Equation 5). Although volume

$$\text{Area Adjusted Removal Rate (g m}^{-2}\text{ day}^{-1}\text{)} = (\text{Load}_{\text{Inflow}} - \text{Load}_{\text{Outflow}})/\text{Area}$$

adjusted removal are more indicative of the ability of the system to perform under load limited conditions, area adjusted removal rates are more commonly used in the literature as a measure of the efficiency of the system.

2.4 Substrate and Vegetation Analyses

In March-April 2001, samples were collected to determine the fate of the sequestered metals via VF substrate sample collection and analysis. The metals may have been retained in several forms, including oxides, carbonates, or sulfides. To further evaluate the success of this demonstration project and the long-term viability of this technology, sampling and analysis of substrates of the VFs was conducted to quantify and fractionate the metal forms sequestered over the last two years. Limited microbiological sampling and analyses of the substrates was conducted to further identify metal retention pathways.

The purpose of this amendment to the original project was to characterize metal quantities, metal forms and microbiological activity, in the substrates of the vertical flow wetlands after two years of water throughput. This information will then be used in developing refined and optimized treatment wetland designs. Results of sequential extraction and analyses of adequate number of substrate cores from each vertical flow wetland helped to determine the forms of metals and the total quantity of metal sequestered in the substrate of the vertical flow wetlands. In addition, determination of microbiological functional groups and activity helped to evaluate the magnitude of microbiological activity in the substrate of the vertical flow wetlands.

Nine substrate-sampling locations were positioned in each vertical flow wetland (approximately 150 m^2 substrate surface area) on a regular grid spacing to adequately characterize the heterogeneity of the substrate. At least two cores (for metals and microbial determinations, respectively) were collected at each location. Substrate cores were depth-profiled at two depths. No EPA or standard technique exists for retrieval and analysis of substrates cores for mine drainage treatment wetlands, so reliance has been placed on Csuros (1994) and refereed literature techniques (Knaus 1986, Knaus and Cahoon 1990, Cahoon et al. 1996). Upon return to the laboratory, sub-cores were sequentially extracted and the resulting extracts analyzed for concentrations of iron, manganese, zinc, calcium, magnesium and aluminum as previously described. Separate sub-cores were analyzed for iron and sulfur related bacteria. Field duplicates equal to at least 33% of the sample size were collected. All laboratory duplicate and spiking procedures for water quality analyses in the original QAPP were adhered to for analysis of substrate extracts.

After draining each wetland cell to a water depth of approximately 15 cm, substrate samples for metals analysis were obtained by the use of a soil auger with a polybutyrate liner (25 cm x 8 cm) inside the auger head. Immediately upon obtaining the sample, the liner was removed from the auger head and capped on both ends to minimize exposure to the atmosphere. Removal of substrate from around the first liner allowed for the insertion of a second liner in the same location in order to obtain the second sample at a depth below that of the first core. Depths were field-determined. The second sample was obtained using the same technique as the first sample. After capping, the substrate core was placed in a mesh bag and frozen to –30°C in a mixture of dry ice (solid carbon dioxide) and methanol in a field cooler. After the core was completely frozen, it was placed in a plastic storage container packed in dry ice until placement in a 0^{o}C freezer in EBEL, where it remained until analysis. The auger head was decontaminated thoroughly with deionized water between samples. Duplicate samples were taken randomly at three of the nine sample locations. In the laboratory, sub-cores were freeze-dried and a sequential extraction procedure will be performed to fractionate metal forms and determine concentrations of metals in the forms described in Table 2.1 (Wieder et al. 1991).

Table 2.1. Metal fractions analyzed in substrate samples.

Metal fraction	Extractant
Water soluble	Deionized water
Exchangeable	KNO_3
Organically-bound	$Na_4P_2O_7$
Carbonate	EDTA
Oxide or oxide-bound	$Na_3C_6H_5O_7$ and $NaHCO_3$
Residual (including sulfides)	HNO_3

Cores for microbial analysis were obtained in an identical manner to that of cores for metals analysis. Immediately upon obtaining the sample the liner wase removed from the auger head and placed in a sealed and anaerobic container, flushed with nitrogen gas. Sealed containers were transported back to the EBEL under these anaerobic conditions and placed in an anaerobic hood until microbial analysis was performed. The substrate samples were then subjected to an extraction procedure and analyzed for bacterial concentration using most probably number (MPN) and plating techniques. Enumeration needed to occur within thirty days of sampling and biological activity within twenty-one days per standard methods.

In January 2001, representative *Typha* spp. plants were obtained in cells 1, 2, and 3. Plant stem height and basal width was measured and evidence of fruiting from the previous season noted. Samples were then washed in Liquiniox and air-dried for approximately one week, and oven-dried at 60-75^{o}C until constant mass was achieved. Dry mass of above and below ground biomass was thereby recorded.

Samples were then ground using stainless steel grinding apparatus until material passed a 1.0 mm sieve. Samples were wet-ashed (Campbell and Plank, 1998), diluted with 2.0% HNO3, and deionized water, filtered through a 0.45 um filter and analyzed for metal content as previously described.

3.0 RESULTS AND DISCUSSION

3.1 Performance Summary

The treatment wetlands have successfully improved water quality to within applicable regulatory guidelines for two years. Concentrations of Fe, Al, and Mn decreased significantly and pH and alkalinity concentrations increased significantly. The final effluent of the system has maintained a net alkaline condition (> 150 mg L^{-1}) with pH > 6, iron and aluminum < 0.5 mg L^{-1} iron, and manganese < 5 mg L^{-1}. (In wetland treatment systems, efficient manganese removal is not expected and at active sites, manganese is regulated as a "surrogate ion" for trace metals.) Trace metals concentrations were either near detection limit at all sampling locations (barium, cadmium, chromium, copper and lead) or were retained completely by VF1 (nickel and zinc) to less than detection limit.

In the vertical flow wetlands, alkalinity was produced by a combination of processes, including limestone and fly ash dissolution and bacterial sulfate reduction (BSR), to over 250 mg L^{-1}. Final effluent concentrations were net alkaline on all sampling dates, i.e., alkalinity was greater than mineral acidity plus proton acidity. The combination of spent mushroom substrate, limestone and hydrated fly ash has a substantial effect on acidity removal, and, if these acidity removal rates are sustainable, resultant design criteria could lead considerable savings in passive treatment system construction and land acquisition costs. Initial effluent water quality characterization indicated the potential for leaching of substrate nutrients and anions. However, all effluent samples since January 1999 have not been significantly different from inflows. Characterization of the substrate via a sequential extraction process indicates that substantial metal loads are being retained in the deep substrate and sequestered from the environment. Metal fractionation demonstrates the probability of long-term treatment success. Metal uptake by vegetation was significant only for iron.

Casual observations during water quality sampling events indicate considerable wildlife use of the treatment wetlands. Several species of amphibians (e.g., bullfrogs, leopard frogs, and salamanders) reptiles (e.g., snapping turtles, garter snakes), birds (e.g., red winged blackbirds, killdeer, great blue herons) and mammals (e.g., moles, voles, coyotes) use the site. Biological assessments in the summer of 2000 indicated healthy populations of fish and macroinvertebrates in three of the four cells. Macroinvertebrate community structure indicates a trend from tolerant to less tolerant species with flow through the wetland system.

In the final surface flow cell alone, 314 bluegill fingerlings and 7 bluegill adults were seined.

3.2 Fulfillment of Project Goal and Objectives

In the original Work Plan for this project, it was noted that, due to the drastic impacts associated with AMD, this form of water pollution has received extensive attention for several decades. Numerous mitigation methods have been attempted to treat this problem and attained varying degrees of success. Most strategies fell short of curing the problem primarily because the pollution was not eliminated, but was simply relocated from one site to another. Compounding this situation are financial considerations. Active control technologies are often expensive, elaborate, and require regular attention resulting in increased overall costs due to operation and maintenance expenses. Thus, many active control techniques are impractical in the treatment of AMD. Ideally, the cause of the pollution should be addressed; or at the very least, the pollution should be treated in such a manner that it does not pollute another site.

This project sought to incorporate this premise in a holistic approach. In the future, water quality problems in the Pit Creek watershed will be addressed in a manner that emphasizes passive biological and physical/chemical processes. This treatment wetland project was employed to demonstrate this technology. The specific goal identified in the original Work Plan was to implement a “system would reduce pollution in the treated water through passive biological and chemical/physical processes, and result in a noticeably improved aquatic environment capable of supporting indigenous species.”

The primary objectives of this project were to (1) install and (2) demonstrate the effectiveness of an AMD passive treatment wetland system. After the appropriateness of this technology was proven at one particular site, applications at other sites in the watershed may be implemented with the ultimate goal of improving the water quality of the entire area. Specifically, a system of treatment cells was to be established directly below an AMD discharge point to intercept degraded water and treat it through a progression of unit processes designed specifically to address the particular water quality problem of that seep. As identified by the Oklahoma Water Resources Board (1992), the project treatment scheme was tailored to the pollutants of concern, and had treatment objectives producing the following results:

a) Iron and manganese concentrations < 3.5 mg/l, and < 2 mg/l respectively, on a monthly average or significant reduction in loadings from baseline levels
b) Nontoxic levels of zinc and other heavy metals;
c) pH in the range of 6.0 to 9.0;
d) Improved alkalinity such that the effluent water has a sufficient buffering capacity;
e) Increased dissolve oxygen content-- at least to a level capable of supporting aquatic biota;
f) Reduced levels of sulfates--ideally below secondary drinking water standards.

The first objective was the design and construction of a passive treatment system consisting of a series of unit processes that individually addressed specific contaminants in the AMD. The basic premise behind the system was that biological and chemical processes would remove the pollutants associated with the AMD. Based on the specific water quality problems associated with the seep of concern, a series of unit processes was designed, sized and constructed to adequately achieve the treatment goals stated above. Sizing and design was based on criteria produced by the U.S. Bureau of Mines (1994). Specifically, the systems was design for acidity removal at a rate of 20 g m^{-2} day^{-1} in the vertical flow cells and iron removal rate of 20 g m^{-2} day^{-1} in the surface flow cells.

Each of the wetland constituents provided a specific purpose. The alkaline material neutralized some of the acidity, adsorbed some metals, and improved water pH. The organic matter chemically and physically bound metals as well as provided substrate for sulfate reducing bacteria and nutrients for vascular plants. Anaerobic bacteria used sulfate as an alternative electron acceptor, resulting in the production of hydrogen sulfide. The hydrogen sulfide caused the precipitation of metals as insoluble sulfides. Other reactions with hydrogen sulfide produced excess alkalinity. Vegetation stabilized the organic substrate, and once established, served as a continual supply of organic matter. Cattails (*Typha* sp.) were used because they are hardy plants known to flourish in AMD affected environments, and also because they have been shown to remove zinc. The primary purpose of the wetland vegetation was a continuing supply of organic substrate for the sulfate-reducing bacteria. Thus, the establishment of native species, which may occur naturally over time, is an acceptable outcome. However, due to the nature of the water at the #40 Gowen site, *Typha* spp. remained the primary species in the wetlands. This was also an acceptable outcome. The SAPS-type treatment process implemented provided treatment in a four-cell system of alternating vertical flow wetlands (VF) and surface flow aerobic ponds (SF). AMD was sequentially treated by charging the waters with alkalinity in the first VF then providing near-optimum conditions for precipitating metals in the first SF. Alkalinity consumed by metal hydrolysis in the first SF is recharged to the waters in the subsequent VF, thus allowing further metals precipitation in the final SF. Therefore, treatment processes were primarily microbiological or physical/chemical.

Treatment of the entire discharge with the land area available was not feasible. Therefore, the system was sized to demonstrate effective treatment of a portion of the flow. Based on contaminant loadings of approximately 18,000 and 7,000 g day^{-1} of acidity and iron, respectively, and anticipated removal rates of 20 g m^{-2} day^{-1} of acidity from published data and the column studies, the system was designed with a surface are of approximately 750 m^2.

Implementation of the water delivery system and four-cell wetland passive treatment system with associated piping, flow control, and sampling stations was begun in late May and completed in mid-August 1998, completely by volunteer labor. Due to a prolonged and severe summer drought, mine pool elevations decreased to a level insufficient to provide a flow of water to the system. Mine pool elevations did not increase sufficiently until after substantial late September rains and the system first received water on September 28, 1998.

The second objective of the study was to include extensive monitoring of the passive treatment system. Although monthly measurements of specific parameters were proposed in the original Work Plan, monitoring actually occurred at a minimum of every two weeks. Monitoring was conducted at the seep (before any treatment), before and after each unit process and before and after discharge of the treated water to the receiving stream. Parameters of interest included discharge rate, metals concentrations, pH, temperature, specific conductance, alkalinity, sulfate, and dissolved oxygen. It was hoped that the information generated from this continual analysis will be invaluable for future technology implementation (e.g., future installation of passive systems), estimating biological impacts (based on the long-term quality of the effluent from the system), and as an indicator of trends in water quality. If a serious effort is to be made in restoring stream ecosystems, then basic water quality data was considered essential for background comparison and project assessment.

3.3. Water Quality Performance

This section of the final report was taken whole or in part from the MES thesis of Matthew N. Mercer, entitled Enhancing the performance of acid mine drainage treatment wetlands with coal combustion products and alternative organic substrates” and completed as a part of this demonstration project.

The efficiency of 40 Gowen was analyzed based on three parameters: i) the ability of the treatment system to effectively buffer the acidity in AMD (i.e., increase alkalinity), ii) the subsequent increase in pH, and iii) changes in metals of interest (i.e., Fe, Al, and Mn) concentration (Appendix A). Changes in Ca and SO_4^{-2} concentrations were used to help determine the source of alkalinity production with the system. Magnesium (Mg) concentrations were used to make determinations of dilution effects at the site. The intent of this study was to determine if supplementing SAPS with CCPs has a significant beneficial effect on the performance of the system at treating common mine water quality issues (e.g., Fe, Al, Mn, pH, acidity), justifying further research into CCP use in passive AMD treatment.

3.3.1 Acid Neutralization Capacity

The untreated mine drainage contains zero alkalinity to buffer against the depressed pH values and mineral acidity. Alkalinity significantly increased in VF1 ($p<0.05$), with mean inflow and outflow concentrations of zero mg/L and 244 +/-4.1 mg L^{-1}, respectively, which created a net alkaline environment entering SF1. Although net alkaline waters were measured at W2, the oxidation of dissolved Fe within SF1 produced H^+, decreasing the alkalinity measured at W3 to 108 +/-3.8 mg L^{-1}, as $CaCO_3$ equivalent. Net alkalinity (i.e., Total Alkalinity – Acidity) refers to any alkalinity which would remain if all acidity in the sample could be neutralized. In other words, alkalinity is greater than acidity concentrations at this specific time and place. As a result, the net alkalinity in SF1 significantly decreased ($p<0.05$) to approximately 60 mg L^{-1}, as $CaCO_3$ equivalent, increasing the alkalinity concentration at an area adjusted rate of 14.4 +/-3.5 g m^{-2} day^{-1} from solution. Alkalinity significantly increased ($p<0.05$) in VF2 to 141 +/-2.0 mg L^{-1}, and remained steady through SF2 at 134 +/-3.0 mg L^{-1}. The net alkalinity released after treatment was 122.2 mg L^{-1}, providing a total area-adjusted alkalinity production rate of 57.7 +/-17 g m^2 day^{-1}.

Alkalinity generation occurred in both vertical flow cells via three primary processes; HFA and limestone dissolution and theoretically BSR, although this was not be determined. Determination of exactly how alkalinity production occurred within the system is difficult at best, considering increases in calcium concentration can be attributed to the release of gypsum in SMS, the dissolution of limestone, and calcium oxides found in HFA. Calcium concentrations significantly increased in VF1 ($p<0.05$) to a mean of 391 +/-10.8 mg L^{-1} from 30.1 +/-1.6 mg L^{-1} at W1. Concentrations significantly decreased in SF1 ($p<0.05$) to 359 +/-15.1 mg L^{-1}. There were no significant changes in VF2 and SF2, which had mean effluent concentrations of 371 +/-12 and 336 +/-32.6 mg L^{-1}, respectively. Calcium was released from VF1 at an average area adjusted rate of 203 +/-68 g m^{-2} day^{-1}, while SF1, VF2, and SF2 are retaining 39 +/-31.7, 17 +/-49, and 41 +/-37 g m^{-2} day^{-1}, respectively.

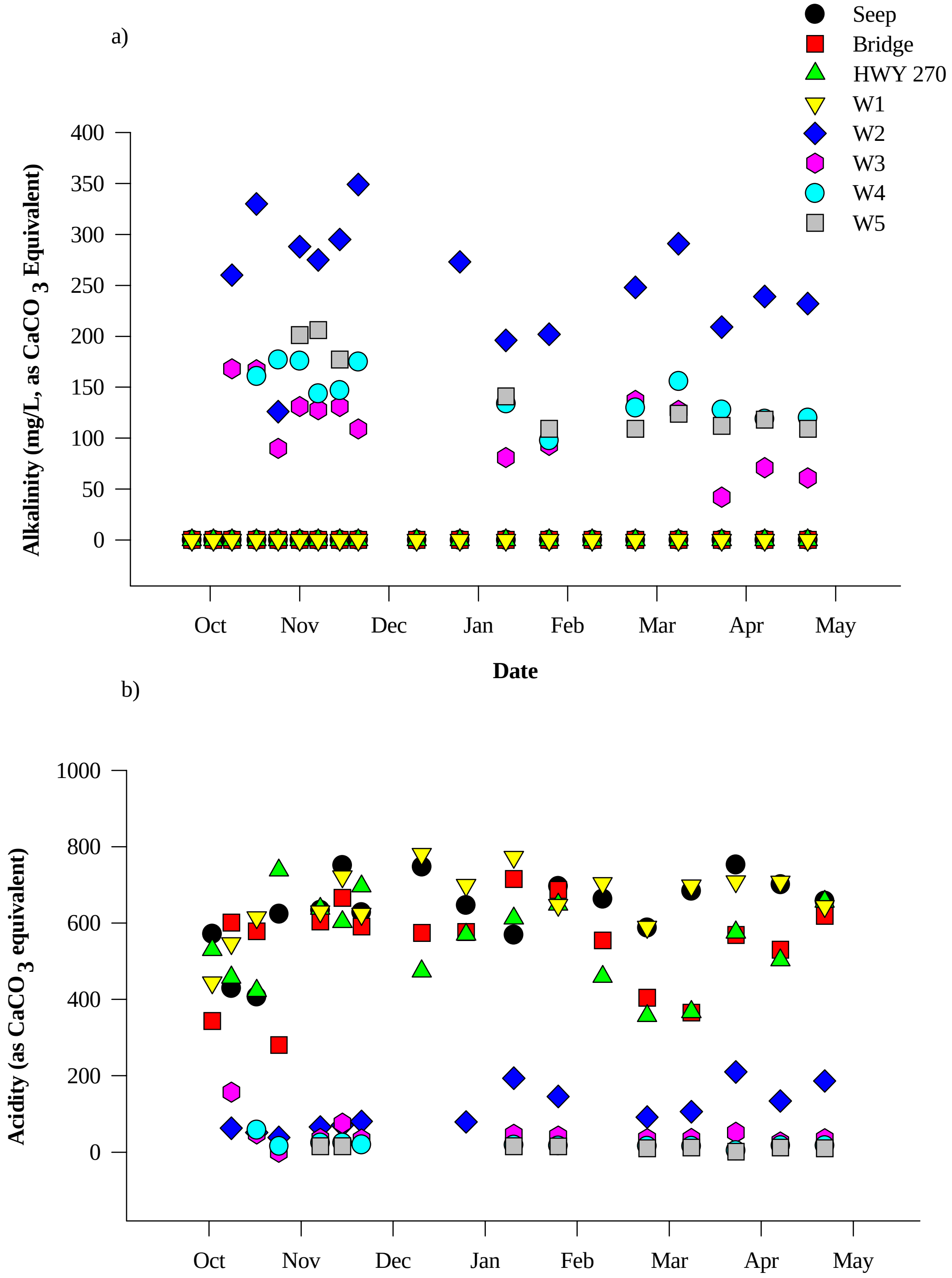

Figure 3.1. Temporal changes in the a) alkalinity and b) acidity concentrations for all sampling locations at the 40 Gowen treatment wetlands.

Table 3.1. Statistical summary of mean pH, acidity (mg L^{-1}), alkalinity (mg L^{-1}), and net alkalinity (mg L^{-1}) concentration +/- standard error at each sample location.

	pH		Acidity		Alkalinity		Net Alkalinity
	Mean	Std. Error	Mean	Std. Error	Mean	Std. Error	Mean
L1	3.51	0.08	632.8	24	0	0	-632.8
L2	3.46	0.13	544.6	30	0	0	-544.6
L3	3.31	0.11	547.7	27	0	0	-547.7
W1	3.27	0.09	658.7	21	0	0	-658.7
W2	6.42	0.09	108.5	15	244	4.1	135.5
W3	6.95	0.23	48.1	10	108	3.8	59.9
W4	7.17	0.17	21	4	141	2	120
W5	7.69	0.35	11.8	1.5	134	3	122.2

Table 3.2. Statistical summary of the mean (+/- standard error) area adjusted rates of alkalinity production and acidity removal. Total refers to the entire treatment system. Data are presented as g m^{-2} day^{-1}. NA means not applicable.

	Alkalinity		Acidity	
	Mean	Std. Error	Mean	Std. Error
VF1	14.4	3.5	65.4	21.6
SF1	-8.3	2.2	4.1	2.6
VF2	62.2	16.8	-4.0	2.7
SF2	-11.5	12.4	3.0	1.0
Total	56.8	NA	68.5	NA

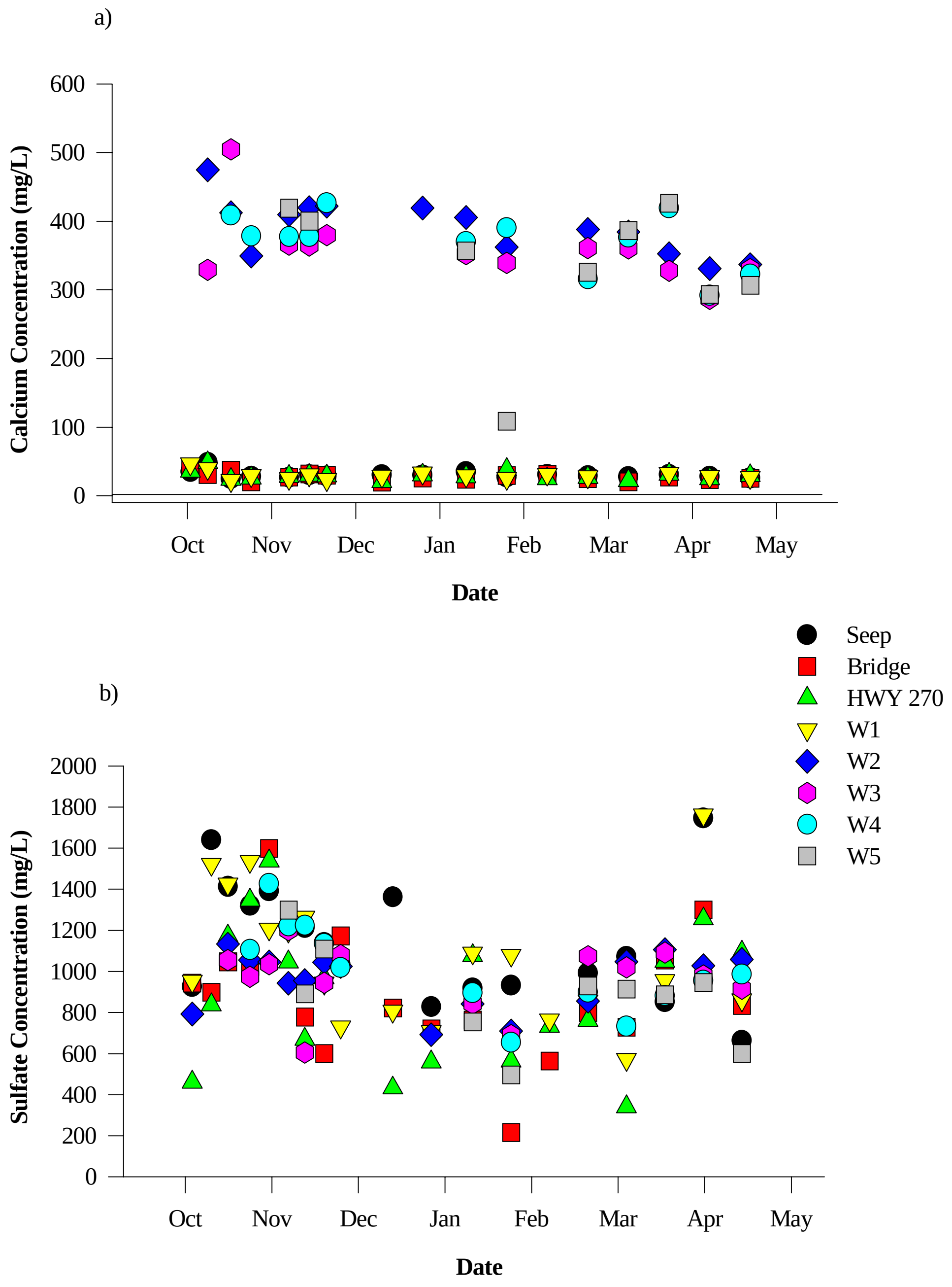

Figure 3.2. Changes in the a) calcium and b) sulfate concentration with time at the 40 Gowen treatment wetland system.

Table 3.3. Statistical comparison of the mean (+/- standard error) sulfate and calcium concentrations at each sampling location. Data are presented as mg L^{-1}.

	Sulfate		Calcium	
	Mean	Std. Error	Mean	Std. Error
L1	1131.2	64.82	30.24	1.31
L2	876.2	76.06	27.57	1.42
L3	912.9	81.23	29.07	1.63
W1	1044.5	73.91	30.09	1.64
W2	969.6	34.04	390.59	10.81
W3	964.9	42.94	358.51	15.09
W4	1010.7	58.79	371.18	11.98
W5	882.16	72.78	335.75	32.64

As a result, the system is loading 28.2 +/-9.4 kg day^{-1} of calcium into the drainage channel, which could alter the hardness of the water, and therefore the bioavailability of some heavy metals. The criteria maximum concentration (CMC) of several of the EPA listed priority metals is hardness dependent (Federal Register, 1998). This release rate had no significant impact on the calcium concentration at downstream locations, and therefore did not impact the total hardness of these waters. However, if implemented at a scale large enough to treat the entire discharge, impacts at downstream locations might be observed. Determining the exact source of calcium production was not accomplished in this study, and therefore assessing which chemical processes released calcium (which has been used as an estimate of alkalinity production in other SAPS) is unknown.

The impacts that changes in sulfate concentration incur were impossible to evaluate as SMS and HFA may have released sulfate into solution, while BSR should theoretically decrease sulfate concentrations. There were no significant changes ($p<0.05$) in sulfate concentration

Table 3.4. Statistical comparison of the mean loading (L1 and W1-W5) and area adjusted removal rates at the 40 Gowen treatment system. Loading rates are given in kg/day and area adjusted removal rates are in g m^{-2} day^{-1} ("T" stands for total removal within the system). Negative numbers represent release rates as opposed to removal rates.

	Sulfate					Calcium				
	Loading			Removal			Loading			Removal	
	Mean	Std. Error		Mean	Std. Error		Mean	Std. Error		Mean	Std. Error
L1	13,845	3,297.0				L1	360.6	54.6			
W1	282.1	118.4	VF1	930.8	648.0	W1	8.6	4.1	VF1	-203.2	68.1
W2	109.9	29.0	SF1	-32.9	51.5	W2	46.2	12.1	SF1	37.8	31.7
W3	116.0	26.5	VF2	155.4	118.3	W3	39.0	9.5	VF2	17.4	49.0
W4	87.3	20.6	SF2	120.7	75.3	W4	35.8	9.7	SF2	41.3	37.1
W5	64.9	18.9	T	1,174	658.9	W5	28.2	9.4	T	-105.7	57.2

within the vertical flow cells, although there was a significant decrease ($p<0.05$) in sulfate throughout the treatment system. A substantial decrease in sulfate concentration occurred in VF1 (74 mg L^{-1}), although the opposite occurred in VF2, where sulfate concentrations increased 46 mg L^{-1}. Based on changes in sulfate concentration in VF1, the expected alkalinity increase due to BSR would be 148 mg L^{-1} (2 bicarbonate ions produced per sulfate reduced; reaction 5), although due to the complexity of sulfate chemistry with VF1, it is unknown actually how much of the alkalinity imparted to the water is due to BSR. It can be assumed that sulfate is leaching from the SMS in VF2, as concentrations increased from 964.9 +/- 42.9 mg L^{-1} at W3 to 1010.7 +/-58.8 mg L^{-1} at W4. Sulfate concentrations significantly decreased ($p<0.05$) in SF2 to 882.2 +/-72.8 mg L^{-1}, loading the receiving drainage with 64.9 +/-18.9 kg day^{-1} on average. Although present environmental laws do not regulate SO_4^{-2} as a pollutant, proposed regulations may require operators not only to meet metal and pH standards, but SO_4^{-2} concentrations as well (Reinsel, 1999). The proposed regulations will place standards on drinking water for SO_4^{-2} that current effluent concentrations at W5 would not meet. Although water quality improvements are being made, if regulations were placed on SO_4^{-2} the implementation of this type of vertical-flow SAPS on a large scale may be impractical.

There are three main forms of acidity found in mine discharge, including proton acidity (pH), organic acidity (associated with dissolved organic carbon), and mineral acidity (associated with hydrolyzable metals) (Hedin et al., 1994a). Hedin et al. (1994a) state that the concentration of dissolved organic carbon in mine water is low, therefore contributing little to the overall acidity of the system. Mineral acidity in mine water and receiving streams is generally very high due to elevated concentrations of Fe^{+2}, Al^{+3}, and Mn^{+2}. The main hydrolyzable metals in AMD, adding considerably to the acidity loading of the system. Significant decreases in acidity concentration occurred at each treatment sample location. The mean acidity concentration at the seep was calculated to be 632 +/-24 mg L^{-1}, as $CaCO_3$ equivalent, loading the stream with 706.8 +/-126 kg day^{-1} total mineral acidity. This was primarily the result of high Fe concentrations in the mine water and a depressed pH. At both downstream sampling locations, acidity levels were significantly lower than the seep ($p<0.05$), with mean concentrations of 545 +/-30 and 548 +/-27 mg L^{-1}, respectively. The area-adjusted acidity removal rate in VF1 was 61.5 +/-20.6 g m^{-2} day^{-1} (, significantly decreasing ($p<0.05$) the mean acidity concentration from 658.7 +/-21 to 108.5 +/-15 mg L^{-1}. This decrease in acidity, combined with the generation of alkalinity in VF1, produced net alkaline waters (135 mg/L) entering SF1. Acidity was further reduced ($p<0.05$) in SF1 to 48 +/-10 mg L^{-1}, loading VF2 with 739.8 g day^{-1} acidity. Decreased acidity concentrations in SF1 were primarily the result of Fe oxidation and hydrolysis, as well as elevated bicarbonate (HCO_3^-) concentrations. Metal precipitation, although releasing H^+ and thus decreasing the alkalinity, results in a lower mineral acidity in solution, and therefore a decrease in the total acidity as well. Significant decreases ($p<0.05$) in the acidity concentration occurred in VF2 and SF2, resulting in mean concentrations of 21 +/-4 and 11.8 +/-1.5 mg L^{-1}, respectively. Acidity removal rates in VF2 were significantly lower ($p<0.05$) than those in VF1. This occurred because acidity in VF2 became load- limited. In other words, the acidity entering VF2 was low enough that the system could

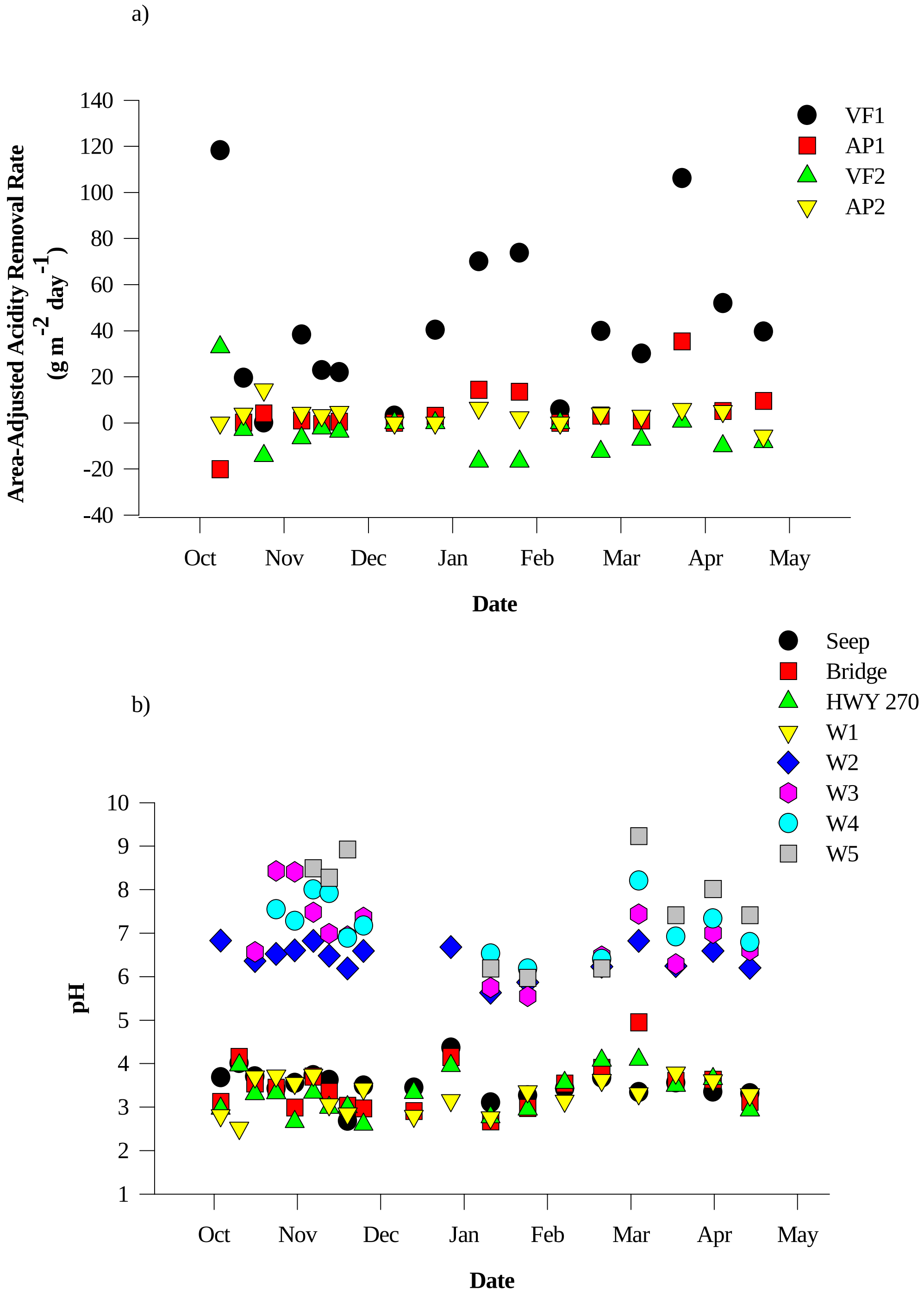

Figure 3.3 - Temporal changes in the a) acidity area-adjusted removal rate and b) pH value for all sampling locations at the 40 Gowen treatment wetlands from October 1998 through April 1999.

Table 3.5 - Statistical summary of the mean acidity and alkalinity loading rates in kg day^{-1} at the seep and within the treatment system.

	Acidity		Alkalinity	
	Mean	Std. Error	Mean	Std. Error
L1	706.8	126	0.00	0.00
W1	12.8	3.9	0.00	0.00
W2	1.49	0.5	2.81	0.64
W3	0.74	0.35	1.28	0.37
W4	1.49	0.34	12.79	3.15
W5	0.93	0.31	10.67	3.16

easily buffer the system. The true test of determining the ability of the system is to introduce more acidity than it can successfully buffer against, indicating maximum acidity removal capacity. The residual acidity in the water was primarily the effect of small amounts of Mn. The mean area-adjusted acidity removal rate for the treatment system was determined to be 68.5 g m^{-2} day^{-1}, which is higher than most reported in the literature. The WALD obtained success for approximately six months, decreasing acidity by approximately 103 g m^{-2} day^{-1} at a seep flowing at 900 L min^{-1} and averaging 430 mg L^{-1} acidity (Skousen et al., 1999). However, this elevated acidity removal rates was not sustained, and within one and one-half years the average area-adjusted acidity removal rate decreased to 66 g m^{-2} day^{-1}.

As a result of the alkalinity imparted to the AMD and the reduction in acidity concentrations via the vertical flow cells, especially VF1, mean pH values significantly increased. The mean seep pH value was 3.51 +/-0.08, and did not significantly change at either downstream location (L2 or L3). The pH of the AMD entering VF1 was 3.27 +/-0.09, and

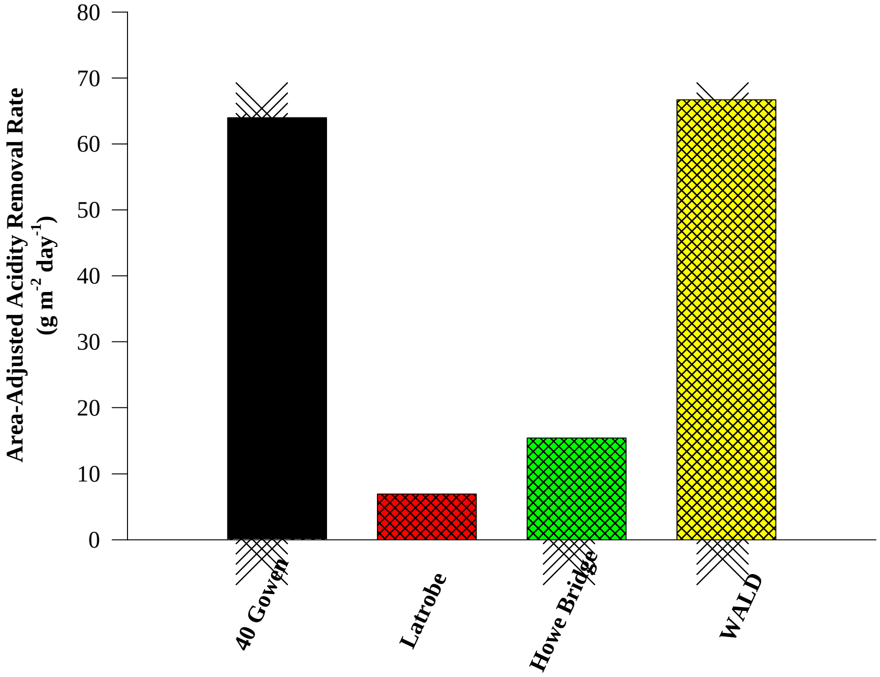

Figure 3.4– Comparison of 40 Gowen acidity removal rates with Latrobe surface-flow wetland (Hedin et al., 1994a), Howe Bridge SAPS (Kepler and McCleary, 1994) and the WALD system (Skousen et al., 1999).

increased significantly ($p<0.05$) at the VF1 outflow to 6.49 +/-0.30. This dramatic increase in pH resulted from the buffering capacity imparted by VF1. The mean pH value significantly increased ($p<0.05$) in SF1 to 6.95 +/-0.23. Increased pH values in SF1 were not expected, considering that iron oxidation increases the H^+ concentration. This increased pH may have resulted from photosynthesis in SF1, which can increase alkalinity if nitrates serve as the nitrogen source (reaction below)

$$106\ CO_2 + 16\ NO_3^- + HPO_4^{-2} + 122\ H_2O + 18\ H^+ \rightarrow C_{106}H_{263}O_{110}N_{16}P_1 + 138\ O_2$$

(where $C_{106}H_{263}O_{110}N_{16}P_1$ represents algae) (Stumm and Morgan, 1996). increased pH values may also have resulted from the dissolution of the FBA liner which has a pH near ?.Although substantial increases in pH occurred in VF2 (7.17 +/-0.17) and SF2 (7.69+/-0.35), no other significant changes ($p<0.05$) in pH were recorded throughout the remainder of the treatment system. Water discharged from SF2 was measured as having a pH below 6 one time (5.97 on 1/26/99), while all other values ranged between 6.19 and 9.23. The mean pH value substantially decreased during winter months. This change in pH can likely be attributed to one of two processes: i) lower water temperatures slowed the metabolism of SRB, thus decreasing the production of bicarbonate ions or ii) photosynthesis was no longer aiding in the capture of H^+. Although mean pH values in the water discharged from the treatment wetland was elevated to circumneutral levels, no significant improvement at downstream sampling locations in pH was observed.

The mean dissolved oxygen (DO) concentration at L1 (1.37+/-0.19 mg L^{-1}) and W1 (0.82+/-0.15 mg L^{-1}) were significantly different ($p<0.05$). Water surfacing from a mine shaft has very low DO concentrations. This was the reasoning behind collecting water directly over the upwelling before piping it to the treatment system. If DO levels were elevated, iron would precipitate in the pipe causing logistical difficulties. Since the water collected at W1 contained significantly less ($p<0.05$) O_2, it can be safely stated that elevated DO levels observed at the seep were most likely due to wind aeration of surface waters. Random sampling of O_2 concentrations at the surface of VF1 indicate that aeration (~3.7 mg L^{-1}) did occur in VF1 before entering the substrate. DO concentrations were recorded below 2.0 mg L^{-1} on ten occasions indicating that waters in VF1 were more desirable for the elevated BSR rates useful in this type of passive treatment. Unfortunately, BSR rates in VF2 may have been limited by the DO concentrations measured at W4 to be 5.01 +/-1.35 mg L^{-1}. The primary means for iron removal in most SAPS is oxidation and hydrolysis in an aerated retention pond. Therefore, elevated DO levels in SF1 and SF2 was desirable. Initially, there were some concerns that wind aeration would not sufficiently aerate the waters in the retention ponds. The mean DO concentration in these cells was 12.48 +/-1.48 and 11.87 +/-1.42 mg L^{-1},

Table 3.6 Statistical summary of the mean dissolved oxygen concentration (mg L^{-1}), flow rates (L min^{-1}) and temperature (^{o}C) at 40 Gowen, Latimer County, Oklahoma (NA means that flows were not taken at that location).

	Dissolved Oxygen		Flow		Temperature	
	Mean	Std. Error	Mean	Std. Error	Mean	Std. Error
L1	1.37	0.19	781.3	104.1	17.2	0.3
L2	6.93	0.25	NA	NA	16.2	0.5
L3	7.21	0.28	NA	NA	16.2	0.5
W1	0.82	0.15	15.5	5.4	15.7	0.6
W2	2.55	0.83	8.8	1.9	14.7	0.9
W3	12.08	1.48	8.7	1.8	14.4	1.2
W4	5.01	1.35	6.7	1.6	13.4	1.0
W5	11.87	1.42	6.1	1.8	13.3	1.3

respectively. This aeration was completely passive, being accomplished by wind aeration and photosynthesis. At the outflow of SF2, DO ranged from 8.00 to 12.17 mg L^{-1}, indicating that wind action is sufficiently aerating the cell.

3.3.2 Metals Dynamics

At circumneutral pH values with sufficient dissolved oxygen (DO), iron will readily oxidize and hydrolyze, precipitating from solution. Samples collected downstream of the seep upwelling indicate that total iron concentrations were significantly lower ($p<0.05$) than those at the seep. This was the result of some iron precipitation which will occur slowly within the stream if the pH is greater than 3. The mean total iron loading in the AMD at 40 Gowen was determined to be 252 +/-47.1 kg day^{-1}. Total iron concentrations at L1 and W1 sample locations were not significantly different, averaging 215 +/-9.9 and 223 +/-8.8 mg L^{-1}, respectively. Within VF1, iron concentrations significantly decreased ($p<0.05$) to 46 +/- 7.5 mg L^{-1}, providing a mean area-adjusted removal rate of 18.3 +/-5.2 g m^{-2} day^{-1}. At the Lick Run Demonstration Wetland in Athens County Ohio, Mitsch and Wise (1998) observed iron removal rates of 4.76 g m^{-2} day^{-1}, while Hedin et al. (1994a) present removal rates ranging from 2.2 to 8.6 g/m^2-day at various sites in their research with the Bureau of Mines. Retention within the vertical flow cells may have occurred through cation exchange, physical filtration, organic complexation with the substrate, oxidation at the surface or via precipitation as an iron sulfide (Rose, 1999). Observations taken during sampling indicate that iron hydroxide precipitation is occurring at the surface of VF1, and thus some iron removal in VF1 is being accomplished via oxidation.

Table 3.7 - Statistical comparison of the mean concentration (+/- standard error) for iron, aluminum, manganese and magnesium. Mean concentrations are provided as mg L^{-1}.

	Iron		Aluminum		Manganese		Magnesium	
	Mean	Std. Error	Mean	Std. Error	Mean	Std. Error	Mean	Std. Error
L1	215.5	9.9	36.2	1.7	13.5	0.4	51.8	2.2
L2	182.7	10.2	30.1	1.8	11.5	0.5	47.0	2.6
L3	180.8	7.9	29.8	1.5	10.8	0.5	47.2	1.8
W1	223.4	8.8	35.3	1.8	12.7	0.6	53.6	2.4
W2	46.1	7.5	0.15	0.04	14.0	1.3	58.8	3.9
W3	12.4	5.6	0.36	0.06	15.4	0.9	63.0	4.5
W4	3.1	1.6	0.18	0.04	8.6	0.6	57.4	2.0
W5	0.77	0.2	0.18	0.05	5.8	0.3	51.9	4.7

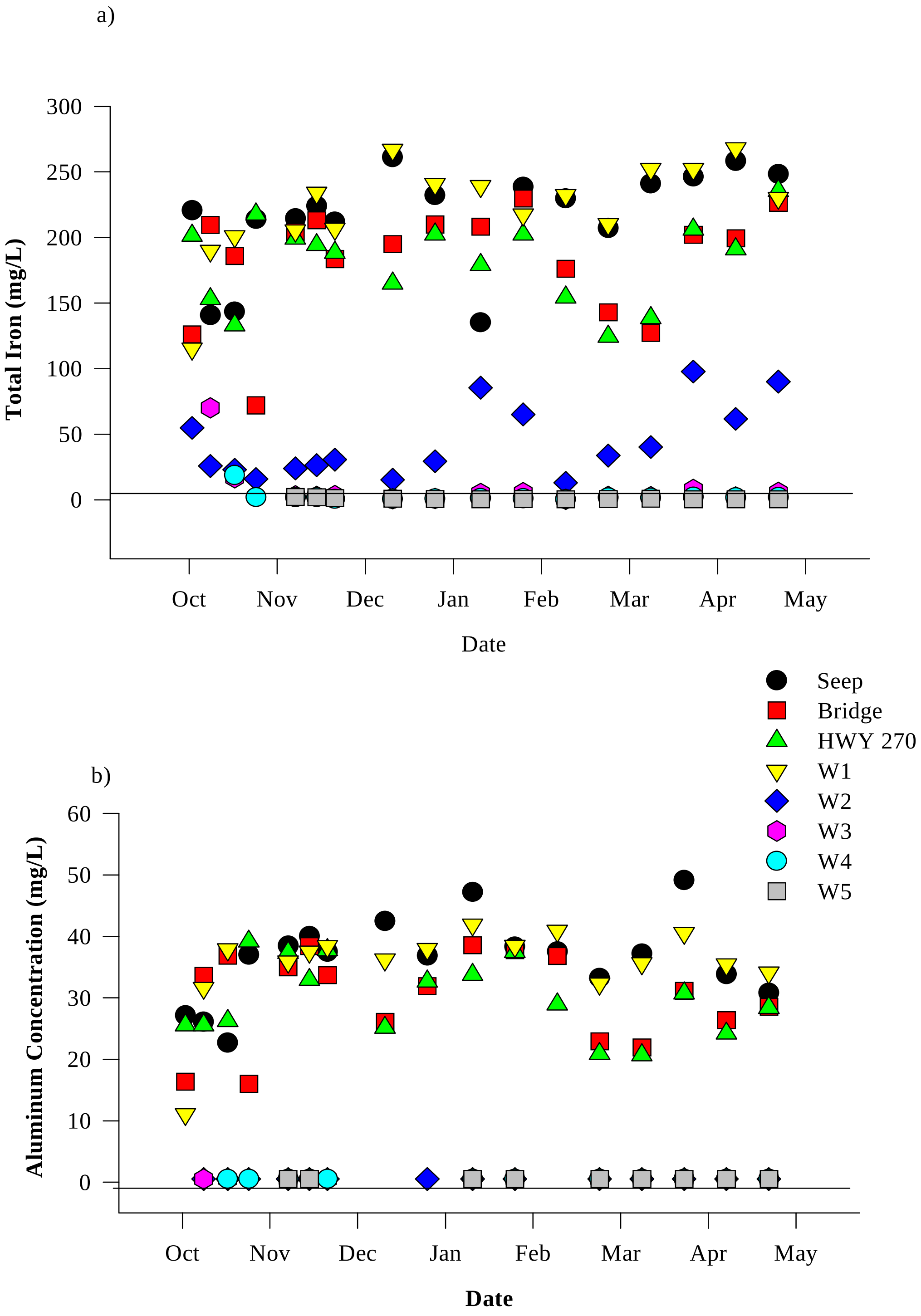

Figure 3.5 - Temporal changes in the a) iron and b) aluminum concentration for all sampling locations at the 40 Gowen treatment wetlands.

Table 3.8 - Statistical summary of the mean loading (+/- standard error) of iron, aluminum, manganese and magnesium at specified locations. Loadings are provided in kg day^{-1}.

	Iron		Aluminum		Manganese		Magnesium	
	Mean	Std. Error	Mean	Std. Error	Mean	Std. Error	Mean	Std. Error
L1	252.1	47.1	39.1	5.6	15.4	2.1	63.0	9.0
W1	416	1.1	0.59	0.13	0.24	0.06	0.94	0.2
W2	0.65	0.23	0.001	0.001	0.19	0.05	0.72	0.2
W3	0.21	0.16	0.004	0.002	0.19	0.05	0.55	0.1
W4	0.18	0.05	0.001	0.001	0.06	0.02	0.47	0.1
W5	0.06	0.01	0.0002	0.0001	0.04	0.02	0.42	0.1

Table 3.9 - Statistical summary of the mean (+/- standard error) area-adjusted removal rates (g m^{-2} day^{-1}) for iron, aluminum, manganese and magnesium at 40 Gowen.

	Iron		Aluminum		Manganese		Magnesium	
	Mean	Std. Error	Mean	Std. Error	Mean	Std. Error	Mean	Std. Error
VF1	18.29	5.17	3.20	0.7	0.27	0.25	1.168	1.12
AP1	2.75	1.39	-0.02	0.01	0.00	0.13	0.964	0.99
VF2	0.21	0.92	0.02	0.01	0.72	0.27	0.384	0.12
AP2	0.66	0.19	0.01	0	0.09	0.04	0.276	0.42
Total	21.80	5.8	3.21	0.7	1.04	0.35	2.792	1.26

Research at 40 Gowen indicates that iron in the substrate is primarily (~64%) of the oxide form, with residual iron (likely a sulfide complex) accounting for another 25% (Lipe and

Nairn, 2000), which was similar to the findings of Wieder et al. (1990). Iron sulfides can form as a result of microbial sulfate reduction (Sexstone et al., 1999; Rabenhorse et al., 1992). In fact, Lyew and Sheppard (1997) state that free sulfides will readily bind with iron, precipitating as an insoluble iron sulfide. Additionally, the precipitation of metal sulfides will provide long-term metal removal capabilities as long as they are kept under anaerobic conditions (Sobolewski, 1996). The removal of iron sulfide is possible only because the concentration of iron is significantly greater than that of other metals in solution. Based on the solubility constants, copper, cadmium, nickel, and zinc (log k = 36.1, 27, 26.5, and 24.7, respectively) sulfides would form more rapidly than iron (log k = 18.1). Seasonal fluctuations in iron concentration were observed. The mean iron concentration at the outflow of VF1 between October 2, 1998 and December 28, 1998, was significantly lower ($p<0.05$) than that observed from December 28, 1998 and April 20, 1999. Iron removal was significant within SF1 ($p<0.05$), most likely removing iron in the form of hydroxides or oxyhydroxides, providing a mean outflow concentration of 12.4 +/-5.6 mg L^{-1}. Decreases in iron concentration in VF2 and SF2 were substantial, reaching 3.1 +/-1.6 and 0.77 +/-0.2 mg L^{-1}, respectively. Total area adjusted iron removal within the treatment system was determined to be 21.8 g m^{-2} day^{-1}. These results indicate that the 40 Gowen treatment system is as efficient at iron removal as other passive technologies constructed for AMD treatment.

Seep aluminum concentration averaged 36.2 +/-1.7 mg/L, loading the stream with 39.1 +/-5.6 kg day^{-1}, but significantly decreased ($p<0.05$) by downstream sample locations. The mean Al concentration at L2 was 30.1 +/-1.8 mg/L, with L3 averaging 29.8 +/-1.5 mg/L. The mean aluminum concentration at W1 was 35.3 +/-1.8 mg/L, and was decreased ($p<0.05$) to levels which were below detection limit (BDL) in VF1 (0.15 +/-0.04 mg/L) and remained at that level throughout the treatment system. In fact, any aluminum removal which may have occurred within the system after VF1 was not significant. This observation was not surprising as aluminum is insoluble at pH > ~4.5, and was thus retained in the first

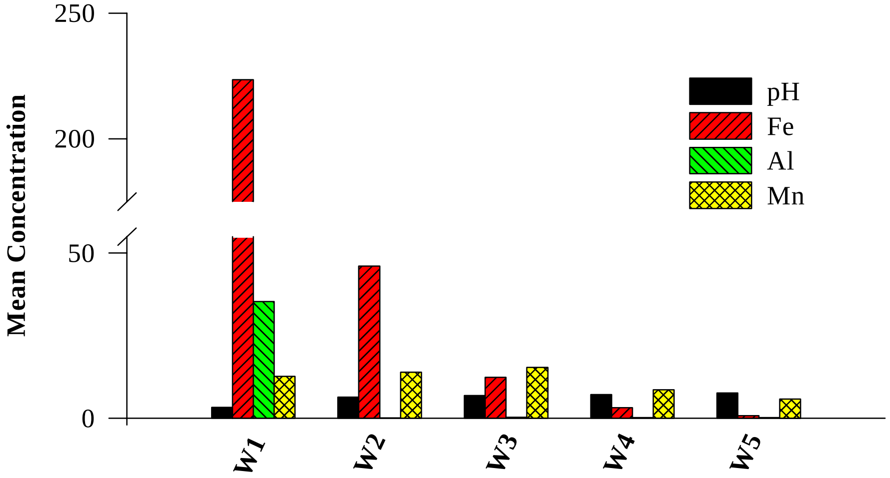

Figure 3.6 – Mean pH and Fe, Al and Mn concentration within the treatment system showing the change at each sample location.

cell most likely as an aluminum hydroxide, $Al(OH)_3$. Based on average area-adjusted removal rates, the total mass of aluminum was calculated to be 118 kg. The retention of aluminum at high concentrations may create long-term hydraulic conductivity issues or cause short circuiting to occur through paths of least resistance.

Significant retention of manganese ($p<0.05$) at the 40 Gowen treatment site did not occur until VF2. The mean Mn concentration at the inflow of VF1 and SF1 measured 12.7 +/-0.6 and 14.0 +/-1.3 mg/L, respectively. The lack of Mn retention may have resulted due to the continued presence of ferrous iron in the system, which causes instability in manganese oxides (Tarutis and Unz, 1995; Hedin et al., 1994a). Essentially, Mn (IV) will oxidize iron as long as dissolved iron exists. When iron concentrations decreased, manganese oxide stability increased, thus allowing the removal of manganese from solution. Hedin et al., (1994a) state that Fe and Mn are sequentially removed from mine waters in passive treatment systems, as iron oxidizes and precipitates more rapidly than manganese. Once oxidized forms of iron (i.e., FeOOH) are present in water, co-precipitation may occur as it may offer an adsorption site for Mn^{+2}. This hypothesis was observed in VF2 and SF2, where significant removal of manganese ($p<0.05$) occurred, providing resultant mean concentrations of 8.6 +/-0.6 and 5.8 +/-0.3 mg/L, respectively. Apparently, with dissolved Fe removed from solution, manganese oxides can form and maintain a stable status within the treatment system. The total area-adjusted removal rate of manganese in the 40 Gowen treatment system was calculated at 1.04 +/-0.35 g m^{-2} day^{-1}. In a mesocosm study assessing various substrates for use in compost wetlands, Wieder (1993) concluded that only SMS was successful at Mn retention. Although treatment did not meet regulatory requirements for Mn, the intent of the law was met. Manganese is used in mine drainage treatment as an indicator that other metals are only found in trace concentrations, as these metals generally form stable solids before Mn in chemical treatment systems. The mean manganese concentration at the seep and downstream locations (L2 and L3) were 13.5 +/-0.4, 11.5 +/-0.5, and 10.8 +/-0.5 mg/L, respectively.

Magnesium is a conservative base cation, and therefore will not readily be removed from AMD through passive treatment. Testing Mg concentrations was completed not to determine if Mg removal was occurring, but instead was done to evaluate if Mg was leaching from FBA, HFA, and SMS used in construction, and as a means to determine dilution effects. Magnesium concentrations in the raw seep water were fairly high, averaging 51.8 +/-2.2 mg/L, and did not change significantly at downstream locations. Changes in the Mg concentration would not have been expected downstream unless dilution was occurring from precipitation runoff water entering through the runoff channel created by AML during land reclamation. Magnesium concentrations increased in VF1 from 53.6 +/-2.4 mg/L at the inflow to 58.8 +/-3.9 mg/L at the outflow. No significant increases were observed within any one cell of the treatment system, however, the Mg concentration at W3 (63.0 +/-4.6 mg/L) was significantly greater than W1. Because there is such a large increase in Mg, it is quite possible that the secondary seep exposed during construction is releasing untreated AMD into SF1. Unexpectedly, magnesium concentrations declined in VF2 (57.4

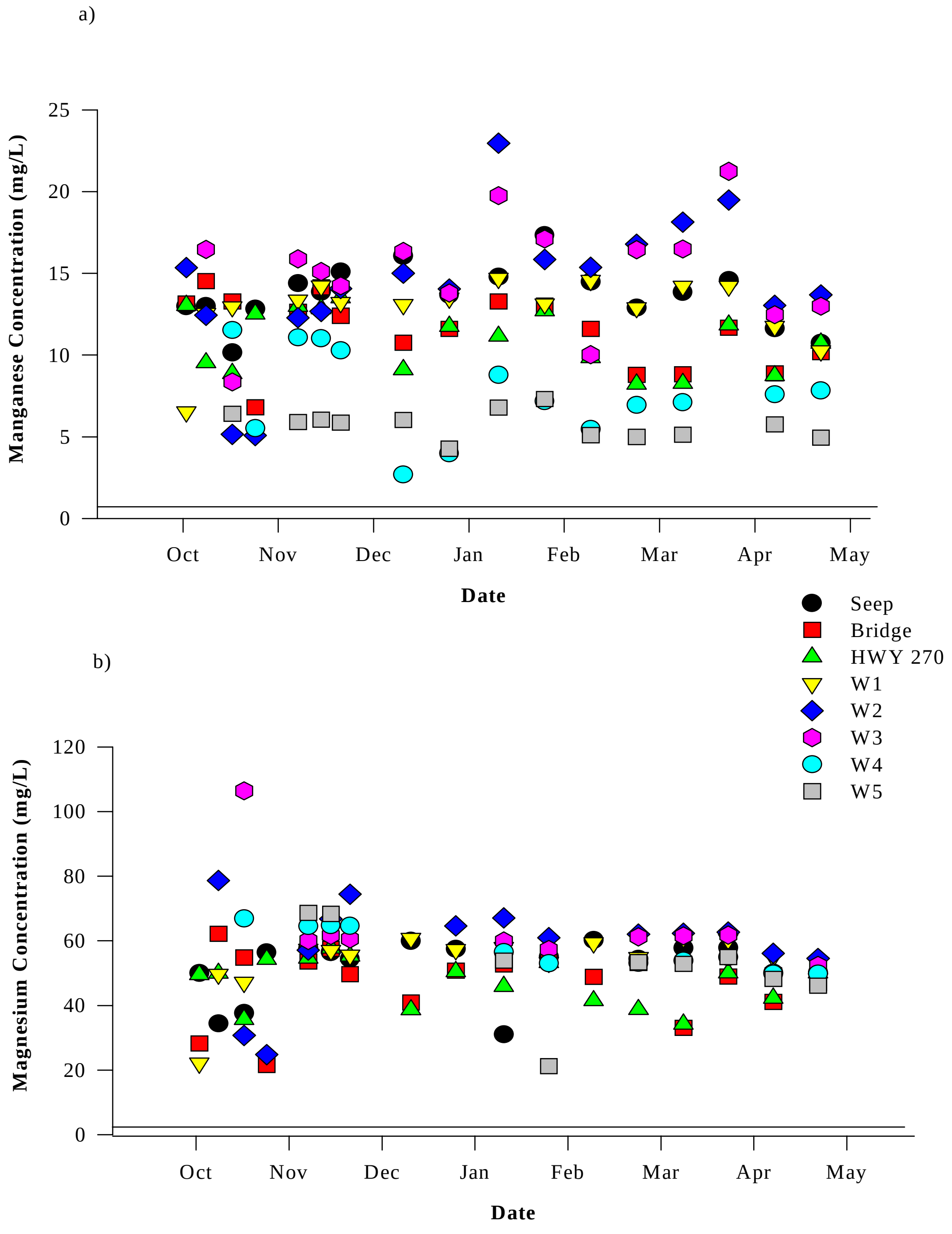

Figure 3.7 - Temporal changes in the a) manganese and b) magnesium concentration for all sampling locations at the 40 Gowen treatment wetlands. Solid line represents the detection limit.

+/-2.0 mg/L) and SF2 (51.9 +/-4.7 mg/L), loading the receiving water with 423 +/-133 g day^{-1} of Mg.

All duplicate samples were within ten percent of the primary sample for iron concentrations with the exception of two (October 15, 1998 and October 23, 1998). It is suspected that the mine may have “burped” recently after equilibrium mine pool elevations were reached. On October 23, the duplicate Fe concentration was 12 percent greater than the primary sample as opposed to 10 percent. The trip blank mean Fe concentration was 0.1 mg/L. Duplicate Al samples were within 10 percent of the primary sample eight out of eleven, and four separate dates providing Al concentration which were BDL. Samples which were outside the appropriate range occurred on October 15, 1998 and October 23, 1998. Trip blanks ranged from 0.05 to 0.16 mg/L, well below the detection limit for Al. A sample (4/20/99) was spiked with 5 ml of 1000 mg/L Al^{+3}, which should provide a final concentration of 50.15 mg/L. However, the sample was measured as having 32.19 mg/L. Multiple laboratory Mn duplicate samples were measured for quality control purposes. Twenty out of twenty-six duplicate samples were within 10% of the primary sample, with all duplicates being within 20%. The Mn concentration of blank samples were determined twice. Each time the duplicate Mn concentration was less than 0.026 mg/L, which was significantly less than the detection limit.

3.3.3 Water Quality Conclusions

The innovative SAPS passive treatment system was successfully able to abate AMD at an abandoned underground upwelling near Gowen, Oklahoma. Success or failure was based on the ability of the system to effectively increase pH values to near-neutral, create net alkaline waters and retain Fe, Al and Mn within the system. Mean pH values (6.42 +/-0.09) significantly increased within the first vertical-flow wetland as a result of efficient alkalinity generation (240 +/-4.1 mg/L, as $CaCO_3$ equivalent). Area adjusted acidity removal rates were substantially higher than those reported in the literature to date, averaging 61.5 +/-20.6 g/m^2-day. Elevated alkalinity generation rates resulted in significant removal ($p<0.05$) of

Fe, Al and Mn, the three primary metals in mine drainages. Mean Fe concentrations at the W5 were near BDL at W5, while Al was BDL after passing through VF1. Although Mn concentrations at the outflow were greater than NPDES permits allow at active mine sites, the fact that Mn removal did occur indicates that all other metals have been removed from the water. Based on these data, the performance HFA as an alkaline supplement in SAPS offers promising results.

3.4. Substrate Characterization

This study explored the metal content of six fractions of the substrate of the wetlands in order to assess the different forms of the metals and the removal processes taking place in the system. This analysis will give insight into the sustainable nature of this passive treatment system.

The substrate samples were freeze-dried in the laboratory, and a sequential extraction procedure was performed on 2.5g of the freeze-dried material from each sample location. A duplicate sample from three of the sample locations was also analyzed for quality control purposes. Each fraction was obtained sequentially using a 24-hour centrifuge/shaker process with the addition of the following chemicals:

The metals in the water-soluble fraction were extracted in the first 24-hours through the use of deionized water. This fraction contains metals that are easily extractable, since they are located in the water directly surrounding the substrate material and are not chemically bound to the substrate. The exchangeable fraction contains metals that went through an exchange with the substrate surface. The organically bound metals were bound to the organic material in the substrate. The carbonate fraction contains metals that formed carbonates in the substrate. The oxide or oxide-bound metals are solid materials that develop upon oxidation in the water column or the substrate. The residual fraction contains any metals that could not be extracted from the other chemical additions. This includes any metals that are bound within the substrate in a metal-sulfide form.

The extracted substrate samples and the water samples were then digested in order to be sure the metals in the solution were in the form necessary for atomic absorption (AA) spectrophotometric analysis. Iron, magnesium, manganese, calcium, and zinc concentrations were obtained for all of the water samples and for each of the six substrate fractions at each sample location using AA analysis.

The majority of the iron and zinc are sequestered in the first wetland cell. The pH of the water in cell one is raised through limestone dissolution and microbial processes, which add alkalinity to the system. Calcium is added to the water in the cell through the limestone dissolution process. The concentrations of manganese and magnesium are not significantly changed in the first wetland cell and, therefore, this analysis will concentrate on the iron, zinc, and calcium concentrations that are present in the substrate. Iron decreases by 172 mg/L in cell one and is therefore the dominant metal in the substrate. Sixty-four percent of the iron in the substrate is in the oxide or oxide-bound fraction (Figure 3.8). Iron comes into the system as ferrous iron (Fe^{+2}). The oxide fraction of iron in the substrate is iron that has been oxidized, hydrolyzed, and has precipitated. The oxide fraction is a solid that has formed and is bound in the substrate. The high oxide fraction found at sample location A1 may be due to oxidation, hydrolysis, and precipitation that take place in the inflow pipe. This pipe is periodically physically flushed, which may result in an elevated amount of iron-oxide precipitate coming into the system and immediately depositing at A1.

The iron residual fraction is 25% of the total iron in the substrate. The residual fraction most likely represents iron sulfides (FeS), as seen in the following reaction:

$$Fe^{+2} + H_2S = FeS + 2\ H^{+}$$

If sample location A1 is discounted (due to the effect of the pipe flushing), then this fraction accounts for an amount very similar to the oxide fraction.

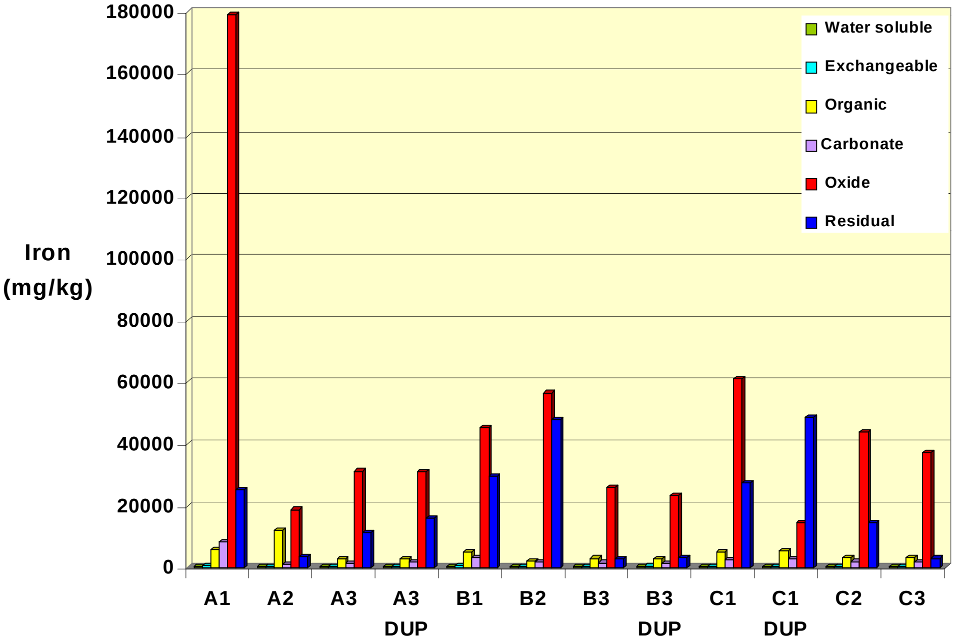

Figure 3.8: Iron Concentrations in the substrate of VF1.

The residual fraction is the dominant form of zinc in the substrate (Figure 3.9). The zinc is removed from the water as a sulfide (ZnS) in the following reactions:

$Zn^{+2} + H_2S = ZnS + 2\ H^+$

The removal of zinc as a zinc sulfide is a thermodynamically favorable reaction, but this reaction takes time to occur. The water must remain in contact with the hydrogen sulfide in the substrate for an extended time period in order for the reaction to occur. The water that comes into cell theoretically is dispersed evenly throughout the cell. The zinc data exhibits a trend that contradicts this theory of equal residence time for all of the inflowing water. The substrate samples from sample locations A3, B3, and C3, which are the greatest distance away from the inflow and outflow pipes, have greater zinc sulfide concentrations. This suggests that the water away from the inflow and outflow pipes has a greater residence time, and therefore more zinc sulfides are formed in the substrate in this area.

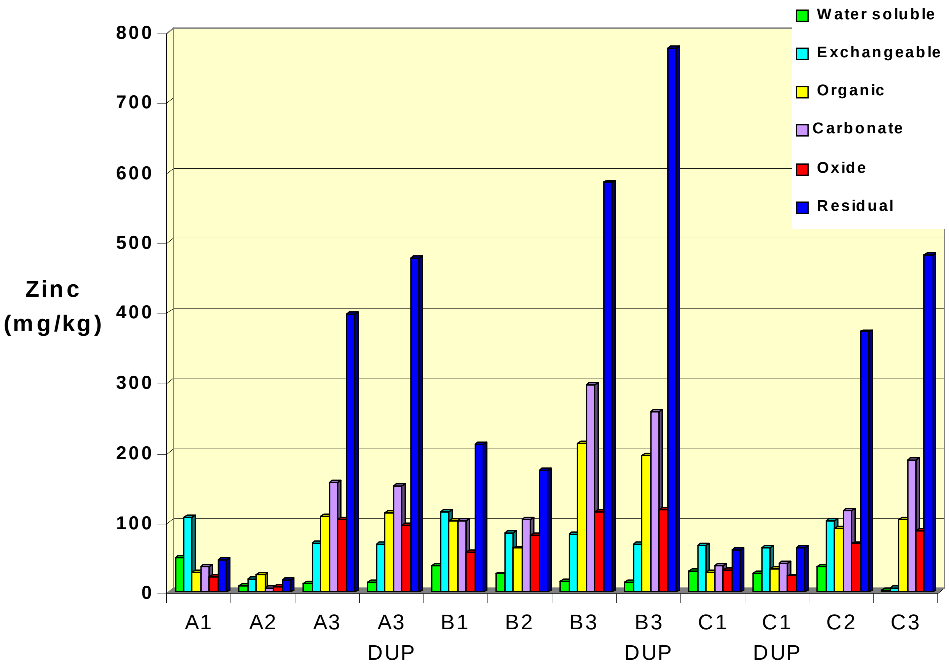

Figure 3.9: Zinc Concentrations in the Substrate

Calcium ions (Ca^{+2}) come into solution in the first wetland from limestone ($CaCO_3$) and hydrated fly-ash ($Ca(OH)_2$) dissolution processes. High concentrations of water-soluble and exchangeable fractions are seen in the substrate, because these fractions contain metals that are still in their ionic form (Figure 3.10). The water-soluble calcium ions are not chemically or physically bound to the substrate particles but are present in the water surrounding the substrate particles. These particles have been recently released from the limestone rocks and hydrated fly-ash and have yet to migrate up to the water column.

The exchangeable calcium ions have traded places with ions on the surface of the substrate particles. Theses metals are physically bound to the surface of the substrate particles but remain in their ionic form. The residual calcium fraction is found in elevated concentrations at sample locations A3 and B2, which may be due to hydrated fly-ash particles that were extracted with the substrate samples. The hydrated fly-ash compromises only 3% of the total substrate (by volume), and therefore it is expected that only two sample

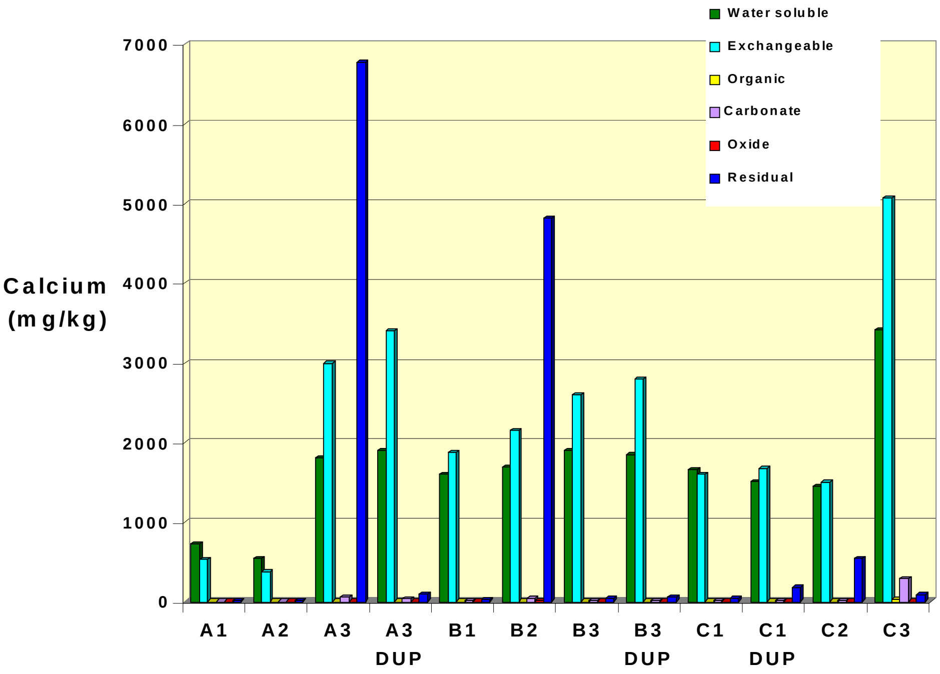

Figure 3.10: Calcium Concentrations in the Substrate

locations show elevated concentrations. The other sample locations did not have any hydrated fly-ash present in the 2.5g sub-sample that was used for analysis.

Much of the iron and zinc present in the AMD is sequestered into the substrate. Both the residual and oxide fractions are solids that form inside the substrate particle, and therefore metals are stabilized inside the substrate and are no longer in contact with the water. The residual fraction is a stable solid in the substrate, and the metals stabilized in this residual form are not expected to be released into solution with the existing conditions. Cell one appears to be stabilizing a majority of the zinc and high amount of iron in the substrate as sulfides, and thus extending the lifetime and metal capacity of the system.

The dissolution of calcium ions is also occurring in cell one. It is not thermodynamically favorable for these ions to form solids, and therefore the calcium in the substrate is predominantly in the water-soluble or exchangeable fraction. The calcium ions exchange with the surface of the substrate (exchangeable) or remain in the water surrounding the substrate particles (water-soluble). By remaining on the surface of the particle or in the surrounding water, the calcium ions remain in contact with the water. The calcium ions in the water aid in the alkalinity addition process and thus aid in elevating the pH.

In order to assess the lifetime of the system further investigations need to be conducted after the system has been operating for an extended period of time. This data could then be compared with the data in this study in order to assess patterns of metal accumulation in the substrate. The data in this study confirm that iron and zinc are accumulated in substrate in a contained form, and the system is successfully removing metals from the AMD and accumulating these metals in various forms in the substrate.

3.5. Vegetation Characterization

For all vegetation samples, metals other than iron were below the detectable limit, which corresponded to approximately 100-250 ug/g dry plant matter. This detection limit was greater than the minimum literature values of 1-100 ug/g dry plant matter reported as the range of plant requirements.

Iron concentrations of plants obtained from all three cells were variable, regardless of differences in iron concentration in the water. There was no statistical difference between absolute concentrations of iron between cells. When iron concentrations were adjusted by plant biomass, a relationship was seen and was more pronounced than that between absolute concentrations, but still not statistically different, most likely due to limited sample sizes. For both stems and roots, cell one had the highest amount of iron. Adjusting for biomass of samples helps adjust for size, which one can assume is correlated with vegetation age.

For stems, 2.75 +/- 2.76 mg Fe/g dry plant matter was determined. For roots, 122 +/- 62.4 mg Fe/g dry plant matter was determined. On average, the roots accumulated greater than 40 times the iron content of the stems. This supports the hypothesis that iron would be preferentially stored in plant roots. According to the literature, on uncontaminated sites, iron concentrations in all plant species ranges from 2 mg/g to 15 mg /g dry plant matter (Kalra 1998; Wang and Lewis, 1997) for both roots and stems. In this study, over 100 mg Fe /g dry plant matter was found in 7 of 10 root samples, with a maximum over 200 mg/g. There appears to be a definitive influence of AMD on phytoaccumulation of iron.

3.6. Completion of Tasks

Including revisions made in 2001, 15 tasks were identified in the revised project Work Plan. All 15 tasks were successfully completed as follows.

Task 1. Submit Quality Assurance Plan. OCC and EPA approved a Quality Assurance Project Plan (QAPP) in September 1996 and it was used throughout the project to guide all sampling and analysis activities.

Task 2. Identify appropriate seep site. . Of the dozen or more identified discharges in the Pit Creek watershed, waters emanating from the #40 Gowen site have the greatest impact on the stream. Previous reclamation efforts at #40 Gowen resulted in the collection of the AMD flow in an artesian discharge. The mean discharge rate is approximately 850 liters per minute and mean water quality is pH 3.4, 250 mg L^{-1} iron, 36 mg L^{-1} aluminum, 14 mg L^{-1} manganese, 1000 mg L^{-1} sulfate and 660 mg L^{-1} net acidity as $CaCO_3$ eq. Because of the severity of this impact, as well as it prominent location (next to State Highway 270), it was selected as the appropriate seep for treatment in 1997.

Task 3. Complete background analysis of geology and hydrology of immediate area. The background analysis was necessary for proper understanding, sizing and placement of the passive treatment system. This was also completed in 1997.

Task 4. Complete background analysis of seep water quality. Some preliminary water quality data were available, but regular sampling of the discharge began in 1998. Ongoing analysis of seep water quality continued throughout the project.

<u>Task 5.</u> Determine optimum ratio of fly ash to organic substrate. The optimum ratio of fly ash to organic substrate was determined in a series of small-scale laboratory experiments. In these experiments it was determined that 1) hydrated fly ash was preferred to fluidized bed ash due to its muted caustic alkalinity and 2) a mix of approximately 20:10:1 parts mushroom compost to limestone to hydrated fly ash seemed to provide adequate treatment coupled with minimal biological disturbance.

<u>Task 6.</u> Size passive treatment system to meet project objectives. Treatment of the entire discharge with the land area available was not feasible. Therefore, the system was sized to demonstrate effective treatment of a portion of the flow. Based on contaminant loadings of approximately 18,000 and 7,000 g day^{-1} of acidity and iron, respectively, and anticipated removal rates of 20 g m^{-2} day^{-1} of acidity from published data and the column studies, the system was designed with a surface are of approximately 750 m^{2}.

<u>Task 7.</u> Implement passive treatment system. Construction of the wetland treatment system began June 8, 1998, and was completed August 25, 1998, due to wet conditions in the month of June. Drought conditions during July and August and a subsequent lowering mine pool elevation, caused the system not to be flooded until late September. Therefore flow did not begin until September 28, 1998. It is important to note that this treatment wetland system was constructed solely by university personnel (the Principle Investigator and students) and therefore, considerable cost savings were realized, *freeing funds for two times the proposed monitoring requirement.*

<u>Task 8.</u> Establish biological component of the wetland. The wetland cells were planted twice – fall 1998 and spring 1999 – with local *Typha latifolia* L. The fall planting was conducted by breaking seed heads across the filling wetland cells. The spring planting included approximately 400 live plants and associated tubers. The biological component quickly established. By late summer 1999, volunteer vegetation of over 12 species had colonized the site, especially the wetland banks. Water primrose (*Ludwigia* spp.) was the

dominant species in cells two and three, providing nearly 100% cover of the formerly open water areas. The biological component of the wetland cells was well established and continues to grow and cover the cells by summer 2000. Emergent vegetation growth was extensive and abundant. In addition, floating-leaved aquatic vegetation and submergent vegetation had become well-established.

<u>Task 9.</u> Treat seep discharge. The treatment wetlands successfully improved water quality to within applicable regulatory guidelines for over two years. Concentrations of Fe, Al, and Mn decreased significantly and pH and alkalinity concentrations increased significantly. The final effluent of the system has maintained a net alkaline condition (> 150 mg L^{-1}) with pH > 6, iron and aluminum < 0.5 mg L^{-1} iron, and manganese < 5 mg L^{-1}. (In wetland treatment systems, efficient manganese removal is not expected and at active sites, manganese is regulated as a “surrogate ion” for trace metals.) Trace metals concentrations were either near detection limit at all sampling locations (barium, cadmium, chromium, copper and lead) or were retained completely by VF1 (nickel and zinc) to less than detection limit.

In the vertical flow wetlands, alkalinity was produced by a combination of processes, including limestone and fly ash dissolution and bacterial sulfate reduction (BSR), to over 250 mg L^{-1}. Final effluent concentrations were net alkaline on all sampling dates, i.e., alkalinity was greater than mineral acidity plus proton acidity. The combination of spent mushroom substrate, limestone and hydrated fly ash has a substantial effect on acidity removal, and, if these acidity removal rates are sustainable, resultant design criteria could lead considerable savings in passive treatment system construction and land acquisition costs. Initial effluent water quality characterization indicated the potential for leaching of substrate nutrients and anions. However, all effluent samples since January 1999 have not been significantly different from inflows. Characterization of the substrate via a sequential extraction process indicates that substantial metal loads are being retained in the deep substrate and sequestered from the environment. Metal fractionation demonstrates the probability of long-term treatment success.

Task 10. Conduct monthly monitoring of water quality of the seep, at several locations within the treatment system, and of the system effluent. This task was completed in conjunction with Task 9. However, monitoring was not conducted monthly *but rather twice as often on a bi-weekly basis for two years.*

Task 11. Submit final report. This report fulfills this task.

Task 12. Present results at conferences. Presentation and publication of the results from this demonstration project has been quite successful. As of the present time, 23 presentations (two international) and eight peer-reviewed publications (one invited) have resulted from this work. In addition, at least eight additional publications and at least four additional presentations are planned. This brings the total output for this project to 31 professional presentations and 12 publications.

Presentations based whole or in part on this project include:

23. Dec. 2001. Mines, Marshes, Microbes and Models: 20 Years of Treatment Wetlands in the U.S. University College Dublin, National University of Ireland, Special Department of Botany Seminar, Dublin, Ireland,
22. Oct. 2001. Treatment Wetlands to Solve Pollution Problems in Oklahoma. Oklahoma State University Wetlands Ecology Graduate Seminar, Stillwater, OK.
21. Sep. 2001. Treatment Wetlands: Working with Mother Nature to Solve Pollution Problems. Air and Waste Management Association and Oklahoma Society of Environmental Professionals, Oklahoma City, OK.
20. June 2001. Remediation Challenges and Opportunities at the Tar Creek Superfund Site, Oklahoma. American Society for Surface Mining and Reclamation, 18th Annual National Meeting, Albuquerque, NM.
19. June 2001. Remediation of a Drastically Disturbed Landscape Using Wetlands: Opportunities at the Tar Creek Superfund Site, Oklahoma. Society of Wetland Scientists, 22nd Annual Meeting, Chicago, IL (Poster)
18. April 2001. Working with Mother Nature: Land and Water Restoration through Ecological Engineering. University of Oklahoma Interdisciplinary Perspectives on the Environment Conversations on the Environment and 1st Annual Earth Day Conference, Norman, OK.
17. April 2001. Treatment Wetlands for Metal-Contaminated Waters: Two Decades of Experience in the USA: Phytoremediation of Trace Elements in Contaminated Soils and

Waters, European Union Cooperation in the Field of Scientific and Technical Research (COST) Action 837 Workshop, Madrid, Spain.

16. Feb. 2001. A Hard Rock Legacy: Environmental Restoration Challenges at the Tar Creek Superfund Site, University of Oklahoma School of Geology and Geophysics Shell Oil Colloquium Series, Norman, OK.
15. Dec. 2000. Treatment Wetland Possibilities and the "Wetlands Concept Plan" for the Tar Creek Superfund Site, Oklahoma Wetlands Working Group, Oklahoma City, OK.
14. Oct. 2000. Ecological Engineering of ecosystem and watershed functions: Examples of treatment wetlands in mining impacted landscapes, University of Oklahoma Division of Landscape Architecture Graduate Seminar, Norman, OK.
13. Oct. 2000. Development of Holistic Remediation Alternatives for the Catholic 40 and Beaver Creek, Oklahoma Society of Environmental Health Professionals Annual Meeting, Oklahoma City, OK.
12. Sep. 2000. Addressing Water Quality Issues at the Tar Creek Superfund Site, Governor Frank Keating's Tar Creek Superfund Task Force, Miami, OK.
11. Aug. 2000. Assessing ecosystem and watershed functions of treatment wetlands: Examples from mining impacted landscapes. Society of Wetland Scientists and Millennium Wetland Event, 21st Annual Meeting, Quebec, Canada.
10. June 2000. Alkalinity generation and metals retention in vertical flow treatment wetlands. American Society for Surface Mining and Reclamation, 17th Annual National Meeting, Tampa, FL.
9. May 2000. Passive Treatment of Mine Waters Using Wetlands. Fifth Annual U.S. Environmental Protection Agency Region 6 Nonpoint Source Watershed Conference, Angel Fire, NM.
8. April 2000. Passive Treatment of Mine Waters: Solving Environmental Pollution Problems with Mother Nature and Father Time as Partners. Second Annual Tar Creek Issues Conference and Sixth Fish Tournament and Toxic Tour, Miami, OK.
7. Aug. 1999. Passive treatment using coal combustion products: An innovative vertical flow constructed wetland field study. American Society for Surface Mining and Reclamation, 16th Annual National Meeting, Scottsdale, AZ.
6. Aug. 1999. Ecological engineering alternatives for remediation and restoration of a drastically disturbed landscape. American Society for Surface Mining and Reclamation, 16th Annual National Meeting, Scottsdale, AZ.
5. April 1999. Passive Treatment of Mine Waters: Solving Environmental Pollution Problems with Mother Nature and Father Time as Partners. National Conference on Tar Creek Abandoned Mine Reclamation, Miami, OK.
4. Mar. 1999. Functions and Values of Wetlands: Vital Components of the Land- and Waterscape. U.S. EPA Region 6 Volunteer Monitors Conference, Lake Texoma, OK.
3. Nov. 1998. Design and construction of an AMD passive treatment system. Abstracts, Oklahoma Academy of Sciences Annual Technical Meeting, Tahlequah, OK.
2. July 1998. The biogeochemistry of passive treatment system design. Mid-Summer Mine Water Meeting, University of Newcastle, Newcastle upon Tyne, United Kingdom.
1. May 1998. Passive treatment using coal combustion products: results of a column study. American Society for Surface Mining and Reclamation, 15th Annual National Meeting, St. Louis, MO.

Publications based whole or in part on this project include:

8. Nairn, R.W. and M.N. Mercer. 2001. Alkalinity generation and metals retention in a successive alkalinity producing system. *Mine Water and the Environment.* 19(2): 124-133.
7. Nairn, R.W., M.N. Mercer and S.A. Lipe. 2000. Alkalinity generation and metals retention in vertical flow treatment wetlands. *In*: W.L. Daniels and S.G. Richardson (eds.), A New Era of Land Reclamation, Proceedings, 2000 Annual Meeting of the American Society for Surface Mining and Reclamation, Tampa, FL, pp. 412-420.
6. Evenson, C.J. and R. W. Nairn.. 2000. Enhancing phosphorus sorption capacity with treatment wetland iron oxyhydroxides. *In*: W.L. Daniels and S.G. Richardson (eds.), A New Era of Land Reclamation, Proceedings, 2000 Annual Meeting of the American Society for Surface Mining and Reclamation, Tampa, FL, pp. 421-426.
5. Nairn, R.W., M.N. Mercer, and J.W. Everett. 1999. Passive treatment using coal combustion products: An innovative vertical flow constructed wetland field study. *In*: Mining and Reclamation for the Next Millenium, Proceedings, 16th Annual National Meeting, American Society for Surface Mining and Reclamation, Scottsdale, AZ.
4. Nairn, R.W., L. Hare., M. Mercer, K. Dresback, K. Pepple, A. Kirchner, D. Cseak, J. Lossing, C. Durham and B. Chen. 1999. Ecological engineering alternatives for remediation and restoration of a drastically disturbed landscape. *In*: Mining and Reclamation for the Next Millenium, Proceedings, 16th Annual National Meeting, American Society for Surface Mining and Reclamation, Scottsdale, AZ.
3. Mercer, M.N. and R.W. Nairn. 1999. Analysis of substrate leachate from an innovative vertical flow AMD passive treatment system. *In*: Mining and Reclamation for the Next Millenium, Proceedings, 16th Annual National Meeting, American Society for Surface Mining and Reclamation, Scottsdale, AZ
2. Mercer, M.N. and R.W. Nairn. 1999. Alternative organic substrates in constructed wetlands: preliminary results of a batch examination. *In*: Mining and Reclamation for the Next Millenium, Proceedings, 16th Annual National Meeting, American Society for Surface Mining and Reclamation, Scottsdale, AZ.
1. Nairn, R.W., T. Crisp, K.A. Strevett, J.W. Everett and B. Chen. 1998. Passive treatment using coal combustion products: results of a column study. Abstracts, 25th Anniversary and 15th Annual National Meeting of American Society for Surface Mining and Reclamation, St. Louis, MO.

Task 13. Wetland Substrate Autopsy – substrate sample collection. After approval of the supplemental QAPP, wetland substrate sample collection was completed in spring 2001. Nine locations in each cell were sampled at two depths on a regular grid system.

Task 14. Chemical and biological substrate sample analysis. Sequential extraction of the substrate samples demonstrated substantial accumulation of iron in the oxide fraction and zinc in the residual (sulfide) fraction with substantial spatial variability. Microbial analyses indicated that populations of sulfate reducing bacteria (SRBs) were greater in cell 3 than cell 1, and also demonstrated substantial spatial variability. It appears that viable populations of SRBs existed in the system and contributed to metal sequestration. Metals were removed via a significant contribution of physical, chemical and microbial processes.

<u>Task 15.</u> Excavation, regrading, planting and closure. All four cells of the treatment wetlands demonstration project were filled, regarded and planted in conjunction with an ongoing operation conducted at this site by the OCC Abandoned Mine Lands program in the summer of 2001. The site was returned to original condition to the satisfaction of the landowner.

4.0 CONCLUSIONS

The innovative SAPS passive treatment system was successfully able to abate AMD at an abandoned underground upwelling near Gowen, Oklahoma. Success or failure was based on the ability of the system to effectively increase pH values to near-neutral, create net alkaline waters and retain Fe, Al and Mn within the system. Mean pH values (6.42 +/-0.09) significantly increased within the first vertical-flow wetland as a result of efficient alkalinity generation (240 +/-4.1 mg/L, as $CaCO_3$ equivalent). Area adjusted acidity removal rates were substantially higher than those reported in the literature to date, averaging 61.5 +/-20.6 g/m^2-day. Elevated alkalinity generation rates resulted in significant removal ($p<0.05$) of Fe, Al and Mn, the three primary metals in mine drainages. Mean Fe concentrations at the W5 were near BDL at W5, while Al was BDL after passing through VF1. Although Mn concentrations at the outflow were greater than NPDES permits allow at active mine sites, the fact that Mn removal did occur indicates that all other metals have been removed from the water. Based on these data, the performance HFA as an alkaline supplement in SAPS offers promising results.

The #40 Gowen treatment wetlands demonstration project represents a sustainable and cost-effective solution for the devastating impacts of AMD on the environment. In these ecologically engineered ecosystems, natural processes improve the quality of contaminated water and critical habitat is restored. This demonstration project represents the first and only successful passive AMD treatment system in Oklahoma. Perhaps the most exciting aspect of the #40 Gowen demonstration project is the transferability of this technology to other mining impacted watersheds. Already, the #40Gowen treatment wetland design is being applied to problems at the Tar Creek Superfund Site in Ottawa County, Oklahoma and is being investigated for application in several other watersheds nationwide.

The treatment wetlands have successfully improved water quality to within applicable regulatory guidelines for over two years. Concentrations of Fe, Al, and Mn decreased significantly and pH and alkalinity concentrations increased significantly. The final effluent of the system has maintained a net alkaline condition (> 150 mg L^{-1}) with pH > 6, iron and aluminum < 0.5 mg L^{-1} iron, and manganese < 5 mg L^{-1}. (In wetland treatment systems, efficient manganese removal is not expected and at active sites, manganese is regulated as a "surrogate ion" for trace metals.) Trace metals concentrations were either near detection limit at all sampling locations (barium, cadmium, chromium, copper and lead) or were retained completely by VF1 (nickel and zinc) to less than detection limit.

In the vertical flow wetlands, alkalinity was produced by a combination of processes, including limestone and fly ash dissolution and bacterial sulfate reduction (BSR), to over 250 mg L^{-1}. Final effluent concentrations were net alkaline on all sampling dates, i.e., alkalinity was greater than mineral acidity plus proton acidity. The combination of spent mushroom substrate, limestone and hydrated fly ash has a substantial effect on acidity removal, and, if these acidity removal rates are sustainable, resultant design criteria could lead considerable savings in passive treatment system construction and land acquisition costs. Initial effluent water quality characterization indicated the potential for leaching of substrate nutrients and anions. However, all effluent samples since January 1999 have not been significantly different from inflows. Characterization of the substrate via a sequential extraction process indicates that substantial metal loads are being retained in the deep substrate and sequestered from the environment. Metal fractionation demonstrates the probability of long-term treatment success.

Observations during water quality sampling events indicate considerable wildlife use of the treatment wetlands. Several species of amphibians (e.g., bullfrogs, leopard frogs, and salamanders) reptiles (e.g., snapping turtles, garter snakes), birds (e.g., red winged blackbirds, killdeer, great blue herons) and mammals (e.g., moles, voles, coyotes) use the site. Biological assessments in the summer of 2000 indicated healthy populations of fish and macroinvertebrates in three of the four cells. Macroinvertebrate community structure indicates a trend from tolerant to less tolerant species with flow through the wetland system. In the final surface flow cell alone, 314 bluegill fingerlings and 7 bluegill adults were seined.

The #40 Gowen treatment wetlands demonstration project represents a sustainable and cost-effective solution for the devastating impacts of AMD on the environment. In these ecologically engineered ecosystems, natural processes improve the quality of contaminated water and critical habitat is restored. This demonstration project represents the first and only successful passive AMD treatment system in Oklahoma. As of November 2000, work at the #40 Gowen demonstration project has resulted in 12 professional presentations, two refereed journal articles, five conference proceedings papers, one master’s thesis and four undergraduate theses.

Perhaps the most exciting aspect of the #40 Gowen demonstration project is the transferability of this technology to other mining impacted watersheds. Already, the #40Gowen treatment wetland design is being applied to problems at the Tar Creek Superfund Site in Ottawa County, Oklahoma and is being investigated for application in several other watersheds nationwide. The Tar Creek site is part of a former lead and zinc mining area known as the Tri-State Mining District and is on the National Priorities List. Approximately 94 million cubic meters of contaminated water exist in underground mine voids. Metal-rich waters discharge to the surface at several locations. Coupled vertical flow wetland and surface flow pond designs are applicable to these waters and represent the only treatment methodology that has been considered viable for improvement and restoration of the waters of Tar Creek.

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