

ACID MINE DRAINAGE TREATMENT WITH A COMBINED WETLAND/ANOXIC LIMESTONE DRAIN: GREENHOUSE AND FIELD SYSTEMS¹

by

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Abstract: The most common methods for treating acid mine drainage (AMD) involve applying a strong base to neutralize the acidity and to precipitate metals. Because of the enormous expense of chemical treatment, passive treatment systems have been installed on many sites to treat AMD. Constructed wetlands have been used for over a decade on hundreds of sites. Wetlands remove acidity and metals from AMD under most conditions, but problems arise when acid and metal loads are too great for wetland size or as metal hydroxides fill the wetland, restricting substrate and water contact. Passive systems often incorporate limestone, which is a very cost effective acid neutralizer, to treat AMD. Complications also arise in limestone systems because ferric iron (Fe^{3+}) in AMD coats the limestone (armoring) reducing limestone's contact with acid water and because aluminum (Al) and Fe hydroxides plug limestone pores decreasing water flow. Limestone use in AMD treatment has been largely confined to anaerobic wetlands, anoxic limestone drains (ALDs) and open limestone channels. If Fe^{3+} and Al could be removed from AMD before introduction into limestone systems, then the use of limestone for AMD treatment could be greatly expanded. We developed and monitored a passive AMD system to determine if AMD containing Fe^{3+} and Al could be pre-treated by flowing through a wetland making it more suitable for introduction into an underlying limestone drain, similar to a vertical flow wetland. Theoretically, pre-treatment by wetlands could reduce Fe^{3+} to ferrous iron (Fe^{2+}) through Fe reduction and precipitate Fe^{2+} as ferrous sulfides (FeS_x) through sulfate reduction. Further, Fe and Al may be adsorbed to organic matter in the wetland thereby eliminating the formation of metal hydroxides with subsequent plugging of limestone pores. A field scale wetland/anoxic limestone drain (WALD) system located at Douglas, WV exported net alkaline water (mean of 127 mg/L as $CaCO_3$) for one year. However, dissolved oxygen and Fe data suggest that poor hydraulic conductivity caused this system to act as an Fe-oxidizing system, rather than an Fe-reducing system. As such, the system's long term effectiveness for treating AMD was compromised. After five years of operation, the system still reduces the acidity of the water from about 500 mg/L as $CaCO_3$ to about 150 mg/L. A small scale Greenhouse system performed more like an Fe-reducing system, decreasing acidity for seven months and exporting Fe^{2+} , although the water exiting the wetland did not contain excess alkalinity. While complications arose in our systems due to high flows in the Douglas system and high acidity in the Greenhouse system, pre-treating AMD with organic material can improve the condition of the water for proper treatment by an ALD or underlying limestone. For low to moderate flows (<400 L/min) and low Fe concentrations (<50 mg/L), a passive system that pre-treats AMD with organic substrates and then directs the water into limestone may be effective for many years.

Additional Key Words: aluminum, iron, iron coating of limestone, limestone treatment, passive treatment, metal precipitation

¹1999 National Meeting of the American Society for Surface Mining and Reclamation, Phoenix, AZ, August 13-19, 1999.

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Introduction

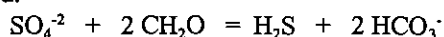
Acid mine drainage (AMD) forms when sulfide minerals such as pyrite and marcasite (FeS_2) are exposed to oxygen and water during mining and other large scale land disturbances. Acid mine drainage is characterized by high sulfate concentrations, high levels of dissolved metals, and $\text{pH} < 4.5$. In 1995, the Environmental Protection Agency (USEPA 1995) estimated that about 10,000 km of streams were impacted by AMD in the northern Appalachian area of the US (PA, MD, OH, and WV), and a 1996 study showed that 17 of 51 priority streams in WV were affected by AMD (Faulkner and Skousen 1998). Historically, AMD treatment is accomplished by adding a strong base to neutralize acidity, raise pH, and precipitate metals. Lime (in various forms), sodium hydroxide, sodium carbonate, and anhydrous ammonia are the four primary chemicals used for AMD treatment. Although effective, chemical treatment is expensive when the cost of equipment, chemicals, and manpower is considered (Skousen 1991), and responsibility for treatment may be a long term and possibly never-ending liability. In 1990, the United States coal industry spent over \$1 million per day on active treatment of AMD (Kleinmann 1990). Consequently, there has been much interest in the use of passive systems employing limestone as a more cost effective means of treating AMD (du Plessis and Maree 1994, Hedin et al. 1994b, Maree et al. 1992).

The primary passive technologies include aerobic or anaerobic constructed wetlands, anoxic limestone drains (ALD), vertical flow wetlands such as successive alkalinity producing systems (SAPS), and open limestone channels. Natural wetlands are characterized by water-saturated soils or sediments with supporting vegetation adapted to reducing conditions in their rhizosphere. Constructed wetlands are man-made ecosystems that mimic their natural counterparts. Often they consist of shallow excavations filled with flooded gravel, soil, and organic matter to support wetland plants, such as *Typha*, *Juncus*, and *Scirpus*. Treatment depends on dynamic biogeochemical interactions as contaminated water travels through the constructed wetland. Aerobic wetlands promote oxidation and hydrolysis in the surface water of the wetland. In anaerobic wetlands, the metabolic products of sulfate-reducing bacteria, usually accompanied by limestone dissolution, are major reactants in raising pH and precipitating metals as sulfides, hydroxides and/or carbonates. The bacteria use organic substrates and sulfate as nutrients; plants are not required but are often helpful in mediating the reactions.

Anaerobic Wetlands

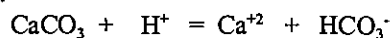
Anaerobic wetlands encourage interaction of water with organic-rich substrates. The wetland substrate may contain a layer of limestone in the bottom of the wetland or the limestone may be mixed within the organic matter. Wetland plants are transplanted into the organic substrate. These systems are used when the water has net acidity, so alkalinity must be generated in the wetland and introduced to the net acid water in order to accomplish significant precipitation of dissolved metals.

The alkalinity can be generated in an anaerobic wetland system in two ways (Hedin and Nairn 1990). Certain bacteria, *Desulfovibrio* and *Desulfotomaculum*, utilize reactions between organic substrate (CH_2O , a generic symbol for organic carbon) and sulfate as a source of energy for their metabolism. The bacteria require relatively simple organic compounds, so only part of the organic matter is normally usable by them, or they require action by fermenting or other bacteria to degrade complex compounds. In the bacterial conversion of sulfate to hydrogen sulfide, bicarbonate alkalinity is produced:



The sulfate-reducing bacteria function best in the pH range 6 to 9 (Widdell 1988) and can function down to about pH 5. However, the bacteria can control their microenvironment so that successful sulfate reduction has been reported at influent pH as low as 2.0 to 2.8 (Bolis et al. 1991, Gusek 1998, Tuttle et al. 1969). However, if the rate of acidity input exceeds the neutralization capacity of the system, pH will decrease and sulfate reduction will stop (Eger 1994).

Alkalinity can also be generated as the limestone under the organic material reacts with acidity in the wetland:



The limestone continues to react when kept in an anaerobic environment because ferrous iron (Fe^{2+}) is relatively soluble at pH 7 in anoxic water and ferrous hydroxide does not form and coat the limestone. If ferrous iron is oxidized, forming ferric iron (Fe^{3+}), then the ferric iron will precipitate as a coating of ferric hydroxide on the limestone. Bacterial sulfate reduction and limestone dissolution produce water with higher pH and add bicarbonate alkalinity for metal removal.

The surface water in anaerobic wetlands is oxidized, so oxidation and precipitation of Fe and manganese (Mn) are promoted in this zone to the extent that alkalinity is available. Organic matter and the resulting bacterial reduction of O_2 and Fe create reducing

conditions in the subsurface zone. Sulfate reduction and limestone dissolution in this zone consume acidity, produce alkalinity and cause Fe-sulfide precipitation. Increase of pH also causes Al hydrolysis and precipitation. Some alkalinity is transported to the surficial zone by diffusion and minor flow, promoting hydrolysis and precipitation. Iron, Al and H⁺ may also be transported into the anaerobic subsurface zone for precipitation and neutralization.

Several treatment mechanisms are enhanced in anaerobic wetlands compared to aerobic wetlands, including formation and precipitation of metal sulfides, metal exchange and complexation reactions, microbially-generated alkalinity due to reduction reactions, and continuous formation of carbonate alkalinity due to limestone dissolution under anoxic conditions. Microbial mechanisms of alkalinity production are likely to be of critical importance to long term AMD treatment. However, Wieder (1992) documents that the mechanism and efficiency of AMD treatment varies seasonally and with wetland age. Like their aerobic counterparts, anaerobic wetlands are most successful when used to treat small AMD flows of moderate water quality.

Five anaerobic wetland systems in WV receiving 4 to 98 L/min of net acid water (110 to 2400 mg/L acidity as CaCO₃ and Fe from 10 to 376 mg/L) reduced acidity by 3 to 76% and Fe concentrations by 62 to 80% (Faulkner and Skousen 1994). These wetlands were generally much smaller in area than that recommended by early formulas published by the U.S. Bureau of Mines based on Fe loads. For example, one of these wetlands, Keister, reduced the acidity of a 17-L/min flow from 252 to 59 mg/L as CaCO₃ (76% reduction) and increased pH from 3.1 to 5.4. Iron was reduced from 23 to 9 mg/L (62%), Mn from 23 to 20 mg/L (11%), and Al from 27 to 13 mg/L (52%). The Pierce wetland used an organic substrate over limestone and treated a 98-L/min flow. Influent pH was 3.3, acidity was 118 mg/L as CaCO₃, Fe of 10 mg/L, Mn of 8 mg/L, and Al of 9 mg/L. Outflow pH was 4.4, acidity was reduced to 57 mg/L as CaCO₃ (52%), Fe decreased to 2 mg/L (80%), Mn was reduced by 11%, and Al by 25%.

A wetland system consisting of six wetland cells (total area of 2500 m²) and a sedimentation basin each received a small flow (5 L/min) of AMD with pH of 3.0, acidity of 217 mg/L as CaCO₃, Fe of 27 mg/L, Al of 12 mg/L, and Mn of 2 mg/L (Hellier 1996). At this site in Pennsylvania, the effluent after passing through the wetland was raised to pH 5.1, and the water contained a net acidity of 16 mg/L as CaCO₃, with about 46% Fe removal, and 56% Al removal.

Anoxic Limestone Drains

Anoxic limestone drains (ALDs) are buried cells or trenches of limestone into which anoxic water is introduced. The limestone dissolves in the mine water and adds alkalinity (Watzlaf and Hedin 1993). Under anoxic conditions, the limestone does not coat or armor with Fe hydroxides because Fe²⁺ does not precipitate as ferrous hydroxide at pH <8.0. The effluent pH of ALDs is typically between 6 and 7.5. The sole function of an ALD is to convert net acidic mine water to net alkaline water by adding bicarbonate alkalinity. The removal of metals within an ALD is not intended and has the potential to significantly reduce the permeability of the drain resulting in premature failure. The maximum alkalinity in effluents from 21 ALDs studied by Hedin et al. (1994b) was 469 mg/L as CaCO₃, with effluent values commonly between 150 and 300 mg/L as CaCO₃. Based on experiments with limestones of differing purity, Watzlaf and Hedin (1993) showed that limestones with >82% CaCO₃ differed little from purer limestones in their effectiveness in neutralizing acid.

Faulkner and Skousen (1994) reported both successes and failures among 11 ALDs treating mine water in WV. In all cases, water pH was raised after ALD treatment, but three of the sites had pH values <5.0, indicating that the ALDs were not fully functioning or that the acid concentrations and flow velocities were too high for effective treatment. Acidity of water in these drains, varying from 170 to 2200 mg/L as CaCO₃, decreased 50 to 80%, but Fe and Al concentrations in the outflow also decreased from influent values. With Fe and Al decreases in outflow water, some coating or clogging of limestone is occurring with Fe and Al hydroxides inside the ALD.

At the Howe Bridge and Morrison ALDs, alkalinity in effluents increased by 128 and 248 mg/L, respectively, over influent water, CO₂ pressures were near 0.1 atm and calcite was at about 10% of saturation (Hedin et al. 1994a). For the past eight years, the effluent from the ALD-wetland system at Morrison has always met effluent criteria (pH 6-9, and Fe <3 mg/L). At Howe Bridge, the ALD-wetland system has removed an average of 70% of the Fe over the past seven years.

At the Jennings Env. Center in Slippery Rock, PA, an ALD was constructed to document the reduction in permeability due to Al hydroxide precipitation within the drain. The system, which received 21 mg/L Al at a flow rate of 92 L/min, began to have permeability problems within three months and plugged with Al hydroxide after about 6 months (Watzlaf et al. 1994).

At the Brandy Camp site in PA, an ALD was employed to treat AMD with a pH of 4.3, acidity of 162 mg/L as CaCO₃, Fe of 60 mg/L, Mn of 10 mg/L, and Al of 5 mg/L (Hellier 1996). After passage through the ALD, the effluent had a pH of 6.0, net alkalinity of 10 mg/L as CaCO₃, Fe of 50 mg/L, Mn of 10 mg/L, and Al of <1 mg/L. Most of the Fe and Mn passed through this system and precipitated in subsequent wetlands, while Al was precipitated inside the drain. Like wetlands, ALDs may be a solution for treating specific types of AMD or for a finite period after which the system must be replenished or replaced.

Longevity of AMD treatment is a concern for ALDs, especially in terms of water flow through the limestone. If appreciable dissolved Fe³⁺ and Al are present in influent water, precipitation of Al and Fe hydroxides causes clogging of limestone pores (Faulkner and Skousen 1994, Watzlaf and Hyman 1995). For waters with high sulfate (>1,500 mg/L), gypsum (CaSO₄) may also precipitate (Nairn et al. 1991). In ideal situations, dissolved Fe³⁺, Al, and oxygen should not be present in the AMD. The presence of any Fe³⁺, Al, or oxygen in the mine water may significantly decrease the effective life of the ALD. Selection of the appropriate water and conditions is critical for long term alkalinity generation in an ALD.

Vertical Flow Wetlands or SAPS

Any strategy or system which could inexpensively raise pH while removing Al, and either precipitating Fe³⁺ or reducing Fe³⁺ to Fe²⁺ prior to entering an ALD may broaden treatment application. Ferrous iron is not thought to armor limestone at the pH values attained in ALDs (Turner and McCoy 1990). Such a system was developed by Kepler and McCleary (1994) and called a successive alkalinity producing system (SAPS) or vertical flow wetland. In a typical SAPS, acid water is ponded from 1 to 3 m over 0.1 to 0.3 m of an organic compost, which is underlain by 0.5 to 1 m of limestone. Below the limestone is a series of pipes that drains the water into an aerobic pond where metals are precipitated. The hydraulic head drives ponded water through the anaerobic organic compost, where oxygen is consumed and ferric iron is reduced to ferrous iron. Sulfate reduction and Fe sulfide precipitation can also occur in the compost. After aeration and metal precipitation in a pond or wetland, water retaining net acidity can be passed through additional SAPS. Compared with horizontal flow anaerobic wetlands, vertical flow systems greatly increase the interaction of water with organic matter and limestone.

Kepler and McCleary (1994) reported on initial successes for three SAPS in PA. The Howe Bridge SAPS reduced acidity from 320 mg/L to 93 mg/L as CaCO₃, and removed 2 mg/L ferric iron. The REM SAPS decreased acidity from 173 to 88 mg/L as CaCO₃, and exported more ferrous iron than entered. The Schnepf Road SAPS decreased acidity from 84 to 5 mg/L as CaCO₃, but removed all 19 mg/L ferric iron, with only 1 mg/L ferrous iron exiting the SAPS.

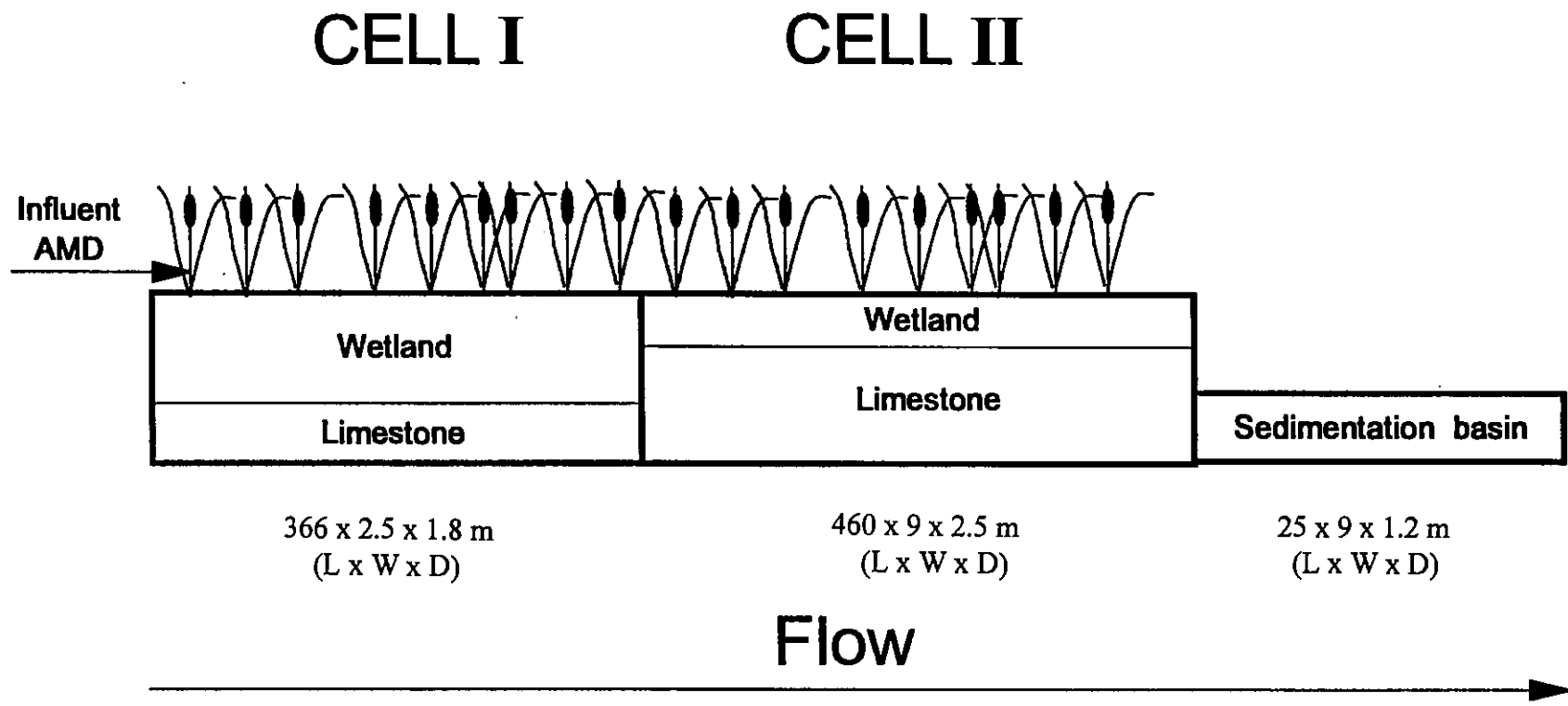
Kepler and McCleary (1997) also reported the use of SAPs in OH, PA, and WV. In all cases, Al in AMD precipitated in their systems. Their drainage design incorporates a flushing system called the 'Aluminator.' This allows for the precipitated Al to be flushed from the pipes thereby maintaining hydraulic conductivity through the limestone and pipes. The Buckeye SAPS received 3 L/min of pH 4.0 water with acidity of 1989 mg/L as CaCO₃, Fe of 1005 mg/L, and Al of 41 mg/L. Over a two-year period, the effluent had a pH of 5.9, net acidity concentration of about 1000 mg/L, Fe of 866 mg/L, and <1 mg/L Al. The Greendale SAPS received 25 L/min, and increased the pH from 2.8 to 6.5, changed the water from a net acid water (925 mg/L as CaCO₃) to a net alkaline water (150 mg/L as CaCO₃), and reduced Fe from 40 to 35 mg/L and Al from 140 to <1 mg/L.

At the Brandy Camp site in PA, a SAPS was employed to treat AMD with a pH of 4.3, acidity of 162 mg/L as CaCO₃, Fe of 60 mg/L, Mn of 10 mg/L, and Al of 5 mg/L (Hellier 1996). After passage through the SAPS, the effluent had a pH of 7.1, net alkalinity of 115 mg/L as CaCO₃, Fe of 3 mg/L, Mn of 10 mg/L, and Al of <1 mg/L. The system effectively increased alkalinity, but retained most of the Fe and Al inside the system.

This paper reports the treatment effectiveness and longevity of two passive systems (combining a wetland with an ALD, termed a WALD) that treat two different AMD solutions. One of the WALD systems was a small system built in a greenhouse and it received a small flow of AMD with very high acid and metal concentrations. A second WALD was a large system built on an abandoned mine land reclamation project and it received a large flow of AMD with moderate acid and metal concentrations.

Materials and Methods

Two WALD systems (same design but different scale) were constructed and monitored for several years. The field system, 826 m in length, was constructed at the Douglas Highwall Abandoned Mine Land (AML) site near Douglas, WV (Figure 1). The second system, 11.6



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Figure 1. Schematic representation of the Douglas wetland/anoxic limestone drain.

m in length, was constructed in the Plant Sciences Greenhouse at West Virginia University (Figure 2).

Douglas System

The Douglas WALD is located near Douglas, Tucker County, WV, on a 25-ha AML site reclaimed by the West Virginia Division of Environmental Protection in 1991-1993 (Skousen 1995). One deep mine portal discharges large volumes of AMD into the North Fork of the Blackwater River. A concrete bulkhead at the mine portal diverts 900 L/min (240 gpm) of AMD into the constructed WALD and the AMD flows into the wetland portion of the system (Cell I). Dimensions of Cell I are 366 x 2.5 x 1.8 m (L x W x D) and the cell consists of a 0.6-m base of high-quality (>90% CaCO₃) limestone (2- to 4-cm size) covered by 1.2 m of organic matter (peat:hay:soil; 50:30:20 ratio). The limestone and organic matter are separated by a permeable erosion-control geotextile to limit transport of organic matter into the limestone. Cell I was also equipped with top and bottom baffles installed in an alternating pattern every 30 m that caused the water to flow up and down through the organic substrate. Cell II is 460 x 9 x 2.5 m (L x W x D) and consists of 1.5 m of limestone (10-cm size) covered by 1.0 m of organic matter separated by filter fabric. Top barriers were installed every 90 m starting at the beginning of Cell II to force water down into the limestone. The entire system contains about 15,000 tons of limestone and 6,000 m³ of organic material, and was lined with 60-mil PVC plastic. The WALD was planted with *Typha* and other wetland species and was later extensively colonized by volunteer species. The Douglas system was allowed to equilibrate with metal-free river water for two months prior to introduction of about 900 L/min of AMD starting in July, 1994. The water exited the WALD through a weir and water samples were collected at the weir. A sedimentation basin designed to collect metal hydroxide flocs is located immediately downstream of Cell II. Its average dimensions are 25 x 9 x 1.2 m (L x W x D).

Greenhouse System

A Greenhouse scale model of the Douglas system was also constructed and its dimensions were 11.6 x 0.5 x 0.8 m (L x W x D; Figure 2). The frame of the WALD was constructed of lumber and lined with four layers of polyethylene sheeting. The WALD was sloped to 1% and had two cells. Cell I was 4.9 m long and consisted of a 0.25-m base of high quality limestone (2- to 4-cm size) covered by 0.65 m of organic material. Cell II was 6.7 m long and consists of a 0.65 m base of limestone (10-cm size) covered by 0.25 m of organic

material. The organic material consisted of a mix of peat moss, hay and soil (40:40:20). During mixing, the organic material was inoculated with anaerobic sediments from an AMD treatment wetland. Landscape cloth separated the organic matter from the underlying limestone. Cell I had a system of five alternating top and bottom baffles to divert water up and down in the organic substrate. A 0.5-m top baffle divided Cell I from Cell II. Within Cell II, a series of four evenly-spaced, 0.4-m deep top baffles directed water to the limestone. The system was planted with *Typha* rootstocks and other wetland plants including *Phragmites*, which eventually dominated the system. The Greenhouse system was also colonized by volunteer species from adjacent constructed wetlands.

The Greenhouse system was allowed to equilibrate with tap water for one month prior to AMD introduction. AMD was collected weekly from Madsville, WV and transferred to a polyethylene tank for introduction to the WALD. AMD was introduced sub-surface via a peristaltic pump at a rate of approximately 208 L/day (0.14 L/min). Water exited the ALD at the median depth of the limestone (water samples taken here) and entered a series of two sedimentation basins via limestone rip rap.

Sampling and Analysis

The Douglas WALD was sampled monthly from June till November 1994, quarterly until September 1995, then at periodic intervals since then. The Greenhouse system was sampled monthly from August 1994 until September 1995. Water samples were taken by allowing water to flow into a container prior to pumping through a YSI Model 3500 sample chamber (Yellow Springs Instruments, Yellow Springs, OH) equipped with Eh, pH, EC and temperature probes. Water samples for metal analyses were filtered (0.45 μ m filters), acidified with HCl (0.24M final concentration), and stored in sealed vials at 4°C until analyzed. Total Fe, Mn, Al, Ca and Mg were analyzed using a Perkin Elmer Plasma 400 Inductively Coupled Plasma Spectrometer (ICP). Ferrous iron was quantified using a modification of the ferrozine procedure (Stookey 1970). Standards were prepared using FeSO₄ · 7H₂O prepared in 0.25M HCl. Ferric iron was calculated by difference as Fe(total) - Fe²⁺. Sulfate was measured using a Varian model 2510 HPLC pump equipped with a Vydac 3021C 4.6 anion column, an Alltech 28069 anion guard column, and a Milton Roy LDC Conductometer. Total acidity and alkalinity were determined by fixed endpoint titration to pH values of 8.3 and 4.2, respectively, using a Titralab VIT-90 automatic titrator (Radiometer-America, Westlake, OH).

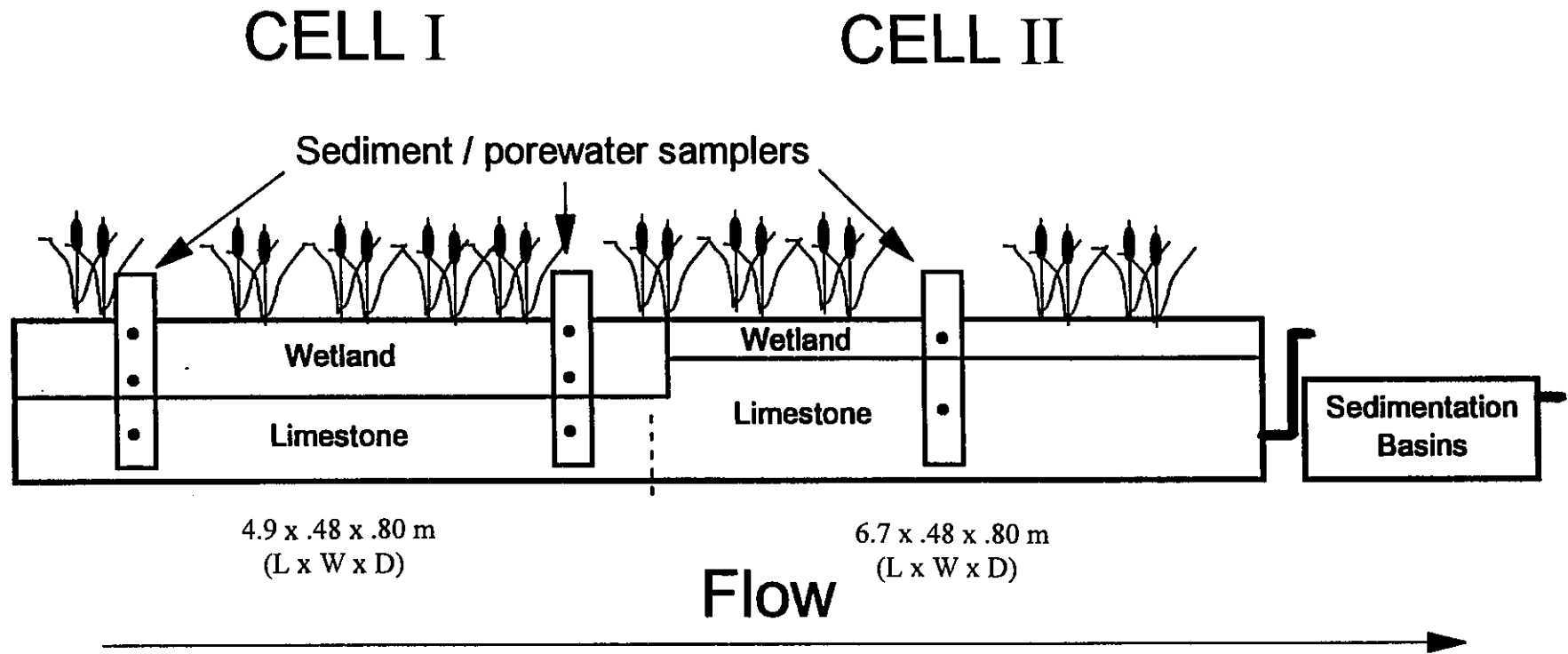


Figure 2. Schematic representation of the Greenhouse wetland/anoxic limestone drain system at West Virginia University.

Results and Discussion

Douglas WALD System

This system raised pH of the 900-L/min flow from an average of 3.2 to a maximum of 7.3 during the first year (Table 1). After one year, effluent pH declined from 5.2 after 13 months to 3.0 after 19 months. Effluent pH after approximately four years of operation has been about 3.5. Acidity decreased from 500 mg/L as CaCO₃ to an average net alkalinity of 127 mg/L as CaCO₃ during the first year. During the last three years, acidity values have averaged 169 mg/L as CaCO₃. Even though alkalinity is not measurable in the water, continued precipitation of metals in the system has caused a reduction in total acidity.

Iron and Al, the metals of primary concern, did not exit the WALD system during the first year and ferrous iron was not generated in the system by iron-reduction reactions. Manganese was also removed by the system during the first year and this was probably due to co-precipitation of the Mn with Fe and Al hydroxides. The pH and mV values measured in the wetland should not have been high enough for Mn precipitation by itself, but Mn is often reduced in treatment systems where Fe and Al are being precipitated (Kleinmann et al. 1985). Calcium increased in effluent water due to limestone dissolution, whereas Mg was unchanged. Sulfate appeared to decrease during the first year and sulfate compounds containing Fe, Al and Ca may have formed and precipitated.

The high mV and dissolved oxygen readings in water throughout the WALD system confirmed our observations of water flow in the system (data not shown). Most of the water flowed across the surface of the WALD in Cell I, rather than migrating downward through the organic matter. The low permeability of the organic substrate lead to short circuiting of the flow and little contact with organic matter was attained with the majority of the water. These data and our observations suggest that the Douglas WALD system acted as an aerobic, Fe-oxidizing system rather than an anaerobic, Fe-reducing system as originally intended.

After a few months of operation (in November 1994), we attempted to reduce the surface flow and encourage ponding and downward movement of the water into the organic substrate by installing a series of hay bale dikes every 10 m in Cell I. However without an outlet for the water below the limestone and organic substrate (a drainage system), the water simply ponded behind the dikes and exited at the dike's lowest point.

Although the effluent water quality was improved during the first year, the longevity of the system was compromised since Fe and Al in the water precipitated in the system. The system has not generated measurable alkalinity, but metals are continuing to precipitate in the system thereby reducing the acidity of the water and the metal load to the river. Assuming the average influent acidity value was 430 mg/L as CaCO₃ and the average effluent acidity value was 170 mg/L as CaCO₃ at the 900-L/min flow, an acid load reduction can be estimated. Approximately 227 tons of acid per year entered the river before treatment, while 90 tons of acid per year enter the river after passing through the WALD. This represents 137 tons less acid per year, and multiplying that amount for the past three years equals more than 400 tons of acid that have not entered the river. The system may continue to reduce the acidity of the water to this level for many more years. So while the system may not be introducing net alkaline water into the river, a significant amount of acid and metals are not entering the river.

Greenhouse WALD System

The AMD used in this experiment had very poor water quality from a nearby Pittsburgh coal underground mine. The average influent water pH of 2.7 was increased for the first six months to around 6.0 in effluent water (Table 2). After six months, the pH gradually declined over time to around 3.0. Anoxic conditions also seemed to be present during this initial six months. Total acidity of the water passing through the WALD decreased by an average of 50% during the first six months, but this system never generated net alkaline effluent water. Near the end of the first year, the effluent acidity concentration approached influent acidity concentration. Iron was completely removed by the system during the first three months of operation, after which the effluent Fe concentration increased to influent levels. The system retained an average of 10% of the total Fe load, compared with total retention in the Douglas system. Aluminum concentrations in effluent water were lower than influent water throughout the experiment, but effluent concentrations approached influent concentrations toward the end of the experiment. Effluent sulfate concentrations were lower than influent concentrations and the concentrations of sulfate and Ca were sufficient for gypsum and other Fe and Al sulfate compounds to form. Redox potentials in sediment and limestone pore water progressed from negative mV readings (-150 mV) due to anoxic conditions to strongly positive readings (> +100 mV) with time as the ferric iron overwhelmed the treatment capacity of the WALD.

Table 1. Average influent water chemistry and effluent chemistry from August 1994 to November 1998 for the Douglas WALD System.

Parameter ¹	Average Inflow	EFFLUENT SAMPLING DATE									
		8/94	11/94	3/95	6/95	9/95	11/95	3/96	6/96	3/97	11/98
pH	3.2	7.3	7.0	6.8	6.8	5.2	4.5	3.0	3.3	3.0	3.7
mV	497	-110	70	238	180	300	---	---	---	---	---
EC	900	200	1400	1050	1120	1040	980	970	910	970	880
Acidity	430	20	0	23	45	54	87	165	198	165	147
Alkalinity	0	75	231	112	160	10	5	0	0	0	0
Total Fe	20	0.3	0.3	0.0	0.2	0.3	3.8	12.3	14.0	11.5	1.8
Ferrous Fe	5	0.0	0.0	0.0	0.0	0.0	---	---	---	---	---
Manganese	6	0.1	0.2	1.2	14	5.3	5.6	5.5	4.8	5.8	4.9
Aluminum	35	0.3	0.0	0.1	1.5	1.8	23.9	21.0	18.8	22.5	15.1
Calcium	64	132	195	170	278	142	148	135	145	138	90
Magnesium	42	19	42	32	33	39	38	34	37	35	41
Sulfate	530	249	625	423	393	503	569	490	415	460	480

¹Units for parameters: pH = standard unit; mV = millivolts; EC = electrical conductivity, dS/cm; Acidity = mg/L as CaCO₃; Alkalinity = mg/L as CaCO₃; All the remaining are in mg/L.

Table 2. Average influent water chemistry and effluent chemistry from August 1994 to September 1995 for the Greenhouse WALD System.

Parameter ¹	Average Inflow	EFFLUENT SAMPLING DATE								
		9/94	12/94	3/95	4/95	5/95	6/95	7/95	8/95	9/95
pH	2.7	5.6	6.3	6.3	4.4	3.9	5.0	3.2	3.1	3.4
mV	415	51	-17	-27	190	270	44	372	386	360
EC	4700	1200	2500	4300	4400	4200	1200	4400	4500	4300
Acidity	2400	818	856	1005	1145	1014	592	1190	1552	1738
Alkalinity	0	25	100	115	5	0	12	0	0	0
Total Fe	660	0.0	606	725	682	497	367	738	463	531
Ferrous Fe	444	0.0	435	427	445	187	294	287	452	460
Manganese	5.0	7.8	10.0	7.0	8.4	6.2	8.2	15.1	8.3	7.6
Aluminum	173	0.6	1.1	0.7	30.1	17.3	1.3	27.7	102.3	126.1
Calcium	450	445	950	615	777	1308	1472	658	565	595
Magnesium	171	164	244	180	134	176	210	138	202	177
Sulfate	3010	2552	1625	2614	2536	2836	2757	3165	2481	2499

¹Units for parameters: pH = standard unit; mV = millivolts; EC = electrical conductivity, dS/cm; Acidity = mg/L as CaCO₃; Alkalinity = mg/L as CaCO₃; All the remaining are in mg/L.

With a more controlled system in the greenhouse, AMD treatment was enhanced for a short period by passage through the Greenhouse WALD system compared to the Douglas system. The reasons for enhanced treatment in the Greenhouse were: 1) the AMD

influent water was introduced subsurface into the organic material and not to the surface of Cell I, 2) the hydraulic conductivity of the organic material was more suitable for water flow, and 3) the low flow introduced to this system allowed greater detention time and contact with organic

matter and limestone. Calculated water retention times were 6.3 days in the Greenhouse system vs 4.0 days in the Douglas system. The low water flow introduced into the Greenhouse system was such that the water did not flow across the surface but permeated through the organic matter into the underlying limestone. The Greenhouse WALD system functioned in a manner more like the intended design.

Comparison Between Systems

Despite a similar design, the Douglas and Greenhouse systems performed differently. The Douglas system improved water quality due to the massive size of the system and the large amount of limestone contained in Cell II, but did not function according to the intended design. The purpose of placing a wetland or organic material prior to an ALD was to remove dissolved oxygen and remove ferric iron either as mineral precipitates or by chemical or microbial reduction to ferrous iron. The intent was to extend the use of ALDs to treat AMD containing high ferric iron and Al, not typically considered suitable for this technology. During the study period, extensive short-circuited flow was observed at Douglas indicating that permeability of the organic substrate was low. This undoubtedly limited exposure of AMD to oxygen-consuming and metal-reducing reactions in Cell I. All Fe entering the WALD at Douglas was retained in the system, most probably as precipitated ferric hydroxides. Continued precipitation of metal hydroxides within limestone pore spaces will cause an eventual failure of the system to where there is no reduction in acidity, in a manner similar to that observed in previous ALDs (Faulkner and Skousen 1994).

Conversely, relatively little of the Fe introduced into the Greenhouse system was retained after the first two or three months after installation. Since the influent Fe passed through the Greenhouse WALD and precipitated in a subsequent settling pond, the limestone pores were not becoming clogged with ferric hydroxide precipitates. However, the observation of high ferric iron concentrations in circumneutral effluents was puzzling, since ferric iron at this pH should precipitate within the system. One possible explanation for this phenomenon is that ferric iron was chelated by organic acids leached from the substrate or exuded by plant roots (Jones et al. 1996). If this speculation is valid, Fe chelation might increase drain life by preventing ferric iron precipitation and armoring in the drain. Chelation has been shown to enhance ferric iron availability for microbial reduction (Lovley et al. 1996).

In separate anaerobic experiments, we measured

ferric iron reduction rates for Douglas and Greenhouse sediments and found them to be very similar (about 0.05 mg ferrous iron reduced/day/gram of sediment slurry (Skousen et al. 1997). Despite our ability to measure microbial Fe reduction in laboratory assays, water chemistry data do not support net Fe reduction in this treatment system. Unlike the Douglas system which exhibited short-circuited flow, the Greenhouse system appears to have exhibited preferential flow through the limestone drain. Anaerobic conditions were always found in the organic matrix but not in the limestone, suggesting that water flow in the organic matrix was slower than that in the limestone. Yet the retention time was not long enough to realize net Fe reduction. It is also possible that Fe reduction was masked by ferrous iron re-oxidation in the aerobic rhizosphere of the wetland plants (Michaud and Richardson 1989).

The Greenhouse WALD was challenged with very acidic and metal-laden AMD which eventually overwhelmed the treatment capacity of the system. Prior to introduction of AMD, the labile carbon (hay and plant roots) helped drive microbial metabolism, which created strongly reducing conditions and the production of sulfides. Over time, the labile carbon was depleted, which limited the capacity to maintain strongly reducing conditions in the WALD sediments. When AMD was introduced, residual redox buffering capacity was quickly depleted in part due to auto-oxidation of sulfides by ferric iron (Stumm and Morgan 1981, Vile and Wieder 1993). It is possible that the redox buffering capacity was depleted as labile carbon and other chemical conditions unfavorable to growth limited heterotrophic microbial activity. Nutrient amendment or carbon supplementation may be required to increase net Fe reduction rates to practical levels.

Summary and Conclusions

Two WALD systems were monitored for their ability to treat AMD. The Douglas system was a very large system constructed at an abandoned mine land reclamation site, while the Greenhouse system was designed similarly but much smaller in scale. Net alkaline effluent resulted from the Douglas system for the first year, but effluent water quality declined over the next three years to a near constant level five years after construction. Despite decreased effluent water quality near the end of the study, the Douglas system still has untapped neutralization potential in limestone and organic matter. The system still causes precipitation of Fe and Al thereby reducing the acidity and metal load that enter the Blackwater River. The Douglas WALD acted as an Fe-oxidizing system where metals precipitated as

oxyhydroxides, rather than an Fe-reducing system as was originally intended.

Unlike the Douglas system, the Greenhouse WALD performed in a manner more like an Fe-reducing system only retaining 10% of the total Fe input. This phenomenon may have been due to better hydraulic conductivity of the organic substrate and to the low flow of AMD introduced into the system. Due to the very high acidity and metal content of the AMD, the Greenhouse system never achieved net effluent alkalinity. Despite retaining only 10% of total Fe input, the Greenhouse system never showed a clear pattern of net Fe reduction. Treatment of AMD by the use of a WALD may still be a valid technique even though complications arose in our systems. For low to moderate flows (<400 L/min) and low Fe (<50 mg/L) and low Al (<20 mg/L) concentrations, a WALD system may be effective for many years.

Acknowledgments

The authors gratefully acknowledge the West Virginia Division of Environmental Protection (WVDEP) who originally contacted researchers at West Virginia University to help design a passive acid mine drainage treatment system at the Douglas Highwall Abandoned Mine Land Project. The design and subsequent construction of the system was the basis for submitting a proposal to the U.S. Bureau of Mines for monitoring the effectiveness of treatment. Special thanks are extended to David Callaghan, David Broschart and David L. Smith of WVDEP. Breckenridge Corporation was the contractor on the site and thanks go to Alan Shreve and Tim Stump for allowing WVU employees on the site during construction. We also appreciate help from U.S. Bureau of Mines; namely, Gerry Puskar, George Watzlaf, and Robert Hedin. Funding for this research project was obtained from the U.S. Bureau of Mines (Contract No. 1432-H0339009) and the National Mine Land Reclamation Center (Project No. WV66).

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