BIOCHEMICAL TREATMENT OF MINE DRAINAGE THROUGH A REEDGRASS WETLAND

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Abstract. Treatment of pre-law acid mine drainage with lime neutralization facilities is an expensive and short-term solution for a chronic problem. Processes associated with microbiological sulfate reduction have long been recognized as a potential technique for acid water treatment. The value of biochemical treatment of mine drainage was demonstrated through the management and monitoring of a wetland treatment unit established at the Peabody Will Scarlet Mine in southeastern Williamson County, Illinois. More than 60 million gallons of acid water was directed through an existing 27-acre non-acid wetland during April 1988 through February 1989, to evaluate biochemical treatment capabilities of the receiving wetland. Monitoring of surface and groundwater quality documented chemical, and hydrological characteristics within the oxidized surface zone, and the wetland anaerobic substrate of a reedgrass (<u>Phragmites</u> <u>australis</u>) wetland subjected to chronic acid input.

Introduction

Mine associated wetlands in the midwest have long been recognized as valuable assets rather than liabilities (Klimstra and Nawrot 1982). Water quality of the majority of mine impoundments in Illinois is adequate to support many industrial, agricultural, recreational, and biological uses (Klimstra and Nawrot 1986). However, in some regions pre-law mining practices have contributed to phytotoxic spoil areas and acid runoff. Although mine drainage treatment plants are effective in addressing the problems of acid generation, treatment of symptoms can become a perpetual and expensive commitment (Nawrot et al. 1988). Abatement of acid sources rather than perpetual treatment is the only long term solution; however, in areas of extensive acid generation, complete abatement is not always possible. Chronic acid seeps may persist and water quality of inadequately buffered impoundments may remain acidic.

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Many pre-law acid impoundments have recovered through natural processes. Recovery of poorly buffered acid mine impoundments is contingent upon development of physical and chemical conditions conducive to sulfate reduction (King et al. 1974). The capacity of an acid impoundment to attain neutral conditions depends upon organic matter input from the surrounding watershed as vegetation density increases; thereby, providing an organic substrate for sulfate reducing bacteria (Brugam et al. 1983). Microbial sulfate reduction has long been recognized as a potential treatment for mine drainage; it was suggested that with addition of organic matter through sewage sludge, waste paper, algae, aquatic weeds, etc., conditions for sulfate reduction could be greatly enhanced (Tuttle et al. 1969a). Hedin (1988) suggested sulfate reduction mechanisms are an important design consideration for current AMO treatment wetlands.

Introduction of organic matter can enhance the sulfate reduction process in AMD treatment. Organic matter decomposition promotes the establishment of anaerobic conditions conducive to heterotrophic bacteria such as <u>Desulfovibrio</u> which convert sulfuric acid to hydrogen sulfide (Rice and Rabolini 1972). Organic carbon associated with decomposing wetland plants or sewage sludge provides an electron source (energy) for sulfate

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reduction. Sulfate reduction is most effective when a pH of ≥ 5.5 is maintained and temperatures are above $10^{\circ}C$ (a reaction rate increase of 4x occurs at 37°C) (Rice and Rabolini 1972). However, sulfate reduction has been recorded at a pH of 3.0 (Tuttle et al. 1969b). As hydrogen sulfide forms, acidity decreases, and pH increases as the hydrogen sulfide gas is lost to the atmosphere (King et al. 1974). For every equivalent of sulfate reduced and precipitated (as iron sulfide), one equivalent of alkalinity should be produced (Brugham et al. 1983). As sulfate reduction proceeds, ferrous and other metallic ions form metallic sulfides. Although large amounts of hydrogen sulfide are produced in the anaerobic zone of submerged wetland soils, the concentration of water soluble hydrogen sulfide should remain negligible due to removal of sulfide in insoluble forms (Ponnamperuma 1972). The role of sulfate reduction in AMD amelioration, is a beneficial geochemical process that has been well documented in the rice growing regions of Asia where seasonal and planned inundation of acid sulfate soils promotes sulfate reduction and alkalinity generation (Moorman and van Breeman 1978).

Algae blooms resulting from nutrient additions such as sewage sludge can also promote bicarbonate alkalinity and anaerobic substrate conditions (Stowell et al. 1981). As pH increases, metallic ions precipitate, forming black deposits of FeS. Additional metallic ions can be removed by absorption (physical-chemical, and bio-floculation) to extracellular polymers produced by sulfate reducing bacteria (slime layers) (Dugan 1970).

Applicability of microbiological processes for acid water treatment through sulfate reduction has been recognized for almost 20 years; however, only recently have these principles been applied in the eastern coal fields. Initial laboratory studies and plot demonstrations have emphasized the wetland treatment capability of <u>Sphagnum</u> bogs in the eastern United States (Weider and Lange 1982, Kleinmann et al. 1983). Currently, wetland treatment systems emphasize cattails (<u>Typha</u>) established in organic substrates using a compartmentalized cell design (Hedin 1989).

Constructed wetlands have provided valuable data regarding specific hydrologic physical, chemical, and vegetation relations of man-made systems receiving mine drainage (Brodie et al. 1988). However, performance of all constructed wetlands has not been consistent. Sizing and loading factors are variables that are currently being investigated by many state and federal organizations.

To determine the acid loading capacity and treatment capability of a pre-law wetland, a field demonstration was conducted at the Peabody Will Scarlet Mine in southeastern Illinois. This paper briefly summarizes flow, acid loading data, and receiving water quality data which were collected during low volume and high volume discharge trials. These data were derived from a portion of a wetland treatment study supported by the Illinois Mines and Minerals Resource Institute (USBM Grant G118-4117). Data used in this paper were part of a field and laboratory study conducted by Mark Guetersloh, Research Assistant.

Methods

To demonstrate the potential value of wetlands as treatment units for acid mine drainage, monitoring and documentation of water quality and substrate characteristics were conducted on two wetlands located at the Peabody Will Scarlet Mine "Old Works" area, southeastern Williamson County, Illinois. The treatment unit (IC1) is a 27-acre reedgrass wetland with a large length to width ratio (1,750 feet long, 600 feet wide) (Figure 1). A rectangular notch weir was installed between IC1 and an adjacent 18-acre acid (pH 3.3 to 3.8) impoundment (IC2) to regulate the introduction of acid water into the wetland.

Monitoring of IC1, IC2 was conducted at 21 sampling stations (1a, 1b in IC2, and 2-20 in IC1) (Figure 1). Surface water sampling was conducted monthly (April 1988-February 1989) at each sampling station (1a/1b-20). Surface water analyses included pH, eH (redox potential), dissolved oxygen, and conductivity. Interstitial water sampling was conducted monthly at sample stations 1a, 1b, 3, 9, 15, and 20; analyses included pH, eH (redox potential), dissolved oxygen, and conductivity.

Six groundwater wells, constructed of 2 inch Brainard-Kilman Triloc slotted (.010 inch slot size) PVC monitor pipe were installed in IC1 and IC2 (sample stations 1a, 1b, 3, 9, 15, and 20). Slotted wellpipe extended from the sediment surface to a depth of 30 inches with brown pea-gravel installed around the slotted section to prevent excessive sedimentation. Dissolved oxygen, pH, eH and conductivity within wells were determined in-field with portable meters (probes lowered to a depth of 4 inches below sediment-water interface within each well). Water samples were evacuated from each well (from a depth of 4 inches below sediment water interface) with a hand operated peristaltic pump. Acidity of surface and interstitial water was determined by hydrogen peroxide boiling procedure (ASTM D1067-70, Method B), and alkalinity by electrometric sodium hydroxide procedure (ASTM D1067-70, Method A) (American Society for Tests and Materials 1979).

During April 1988 through February 1989 more than 60 million gallons of acid water (pH 3.3) were introduced into IC1 from IC2 through a rectangular notch weir. Flow measurement was determined by standard methods (ASTM D2305, American Society for Testing and Materials 1979).

Results and Discussion

Managing and monitoring of discharge events were conducted to identify the biochemical threshold of a naturally established reedgrass wetland receiving chronic acid mine drainage. The goal of this field demonstration was simply to identify the operational limits (i.e. maximum flow and/or allowable duration of acid input) of an established (~ 15 years old) wetland that had previously served (~ 1984-1987) as a natural "treatment" system for polishing chronic acid runoff prior to off-site discharge. Observation and monitoring by mine personnel of outflow quality below the reedgrass wetland during the mid-1980's



Figure 1. Location of groundwater wells and sampling sites in wetland areas IC1 and IC2 at the Peabody Will Scarlet Mine, Williamson County, Illinois.

established the ability of the reedgrass wetland to function as a supplemental treatment system if operational limits could be better defined.

However, prior to initiation of pre-law acid soils reclamation in the upslope watershed in 1983, water quality within the reedgrass wetland was unacceptable for discharge without chemical (i.e. hydrated lime) treatment. Water quality within ICl was generally acidic (pH \leq 3.2; acidity (0.480 to 1,300ppm CaCO₃). Following the initiation in 1983, of reclamation of approximately 175 acres of upslope acid slurry disposal areas, and alkaline flushing of the reedgrass wetland (ICl), water quality within ICl returned to acceptable levels. By fall 1987, surface and interstitial water within ICl had returned to an acceptable equilibrium characterized by excess alkalinity within both the oxidized surface zone and the anaerobic interstitial zone (Table 1).

Following three more months (February through April 1988) of baseline monitoring, acid discharges (from IC2) into the reedgrass wetland (1C1) were initiated. A series of 11 discharge events were monitored between 12 April 1988 through 9 February 1989 (Table 2). Discharge events included high flow (>13,000 gpm) and short duration (5 hours) acid discharges, as well as moderate to high flow (500 to 2,500 gpm) in association with moderate (1 day) to prolonged durations (greater than 30 days). Monitoring of surface sample locations documented pre- and post-discharge water quality changes during the 11 treatment events (Table 2).

More than 60 million gallons of acid water (pH @ 3.3, 262ppm acidity) were discharged into the reedgrass wetland during the 10-month period of acid loading. Volume of water discharged ranged from slightly more than 1 million gallons during a 20-hour period in August 1988 to more than 30 million gallons during a 1-month period in late winter 1989. These various loadings reflected an attempt to determine the biochemical threshold of the receiving wetlands' natural buffering system. At some point simple dilution by the chemical buffering capacity of the receiving wetland should have been exceeded as based upon physical factors of flow rates, and retention time.

Determination of chemical buffering capacity (based on total volume and average alkalinity) of the receiving wetland indicated the ability of IC1 to dilute and 'treat' approximately 22 million gallons of acid water (average acidity @ 70ppm CaCO₃) assuming sufficient retention time to allow complete mixing. As input quality of IC2 acid discharge averaged 250ppm acidity, 5 to 6 million gallons would be the maximum acid loading before exhaustion of alkalinity would be expected. Depletion of alkalinity within the receiving wetland should have occurred during the December 1988 or January 1989 discharge when more than 10 million gallons of acid water were introduced in less than a 20-day period. During this mid-winter discharge, acid loading exceeded the "dilution" ability of the receiving wetland by more than 10 million gallons. During this high loading period (500,000 gallons/day) of 17 December to 6 January 1989, significant depletion of alkalinity was noted in the inlet monitoring station (Station #3) compared to the outlet station (Station #20) within the receiving wetland (Table 2).

Following temporary cessation of acid input to allow sampling of surface and interstitial zones, a final discharge event introduced approximately 1 million gallons of acid water per day for 34 days. Acid discharge was terminated on 9 February when alkalinity had been depleted in both the inlet and outlet stations of the receiving wetland (Table 2). During this discharge event dilution capabilities were exceeded by more than 65 million gallons. As recovery of surface alkalinity values were documented after this and all previous acid discharge events (Figure 2) it can be assumed that biochemical amelioration contributed to alkalinity restoration.

Maintenance and restoration of surface water alkalinity in the 'treatment' wetland (1C1) can be seen in the graphic summarizations of monthly water quality monitoring data (Figure 2, 3, and Water pH values for the acid source (IC2) 4). during October 1987 through July 1989, illustrated the ability of the reedgrass wetland to maintain acceptable water quality despite acid input totalling more than 60 millions gallons (Figure 3). Alkaline buffering capacity of the reedgrass wetland throughout the acid loading trials was severely stressed only during the final high volume input event of December 1988 through January 1989 (Figure 2). Only during this extreme attempt at "overloading" (and the April 1988 7.4 million gallon loading) was alkalinity significantly reduced within the anaerobic interstitial zones. Subsequent sampling showed a recovery of the wetland treatment surface water to pre-discharge alkalinity levels of 70ppm (Table 3, and Figure 4). As suggested by other wetland research (Hedin 1988), restoration of surface water alkalinity could be occuring due to interaction with alkaline (~ 300 ppm @ CaCO₃) water in the anaerobic sediment zone. Restoration of alkalinity within previously stressed (i.e. depleted) anaerobic wetland sediment zones (of IC1) following acid discharge events, can be attributed to naturally occuring biochemical processes such as sulfate reduction.

This monitoring project emphasized documentation of effects associated with a large-scale field demonstration of acid loading. Monitoring of trial discharge events documented the response of a natural wetland that had been subjected to similar accidental acid loadings for the previous 5 to 7 years. Many hydrologic variables, such as mixing, flow paths, retention time, etc. are acknowledged as having an influence on wetland treatment performance of the receiving wetland. However as the acid loading factor greatly exceeded the dilution capability of the treatment wetland, this demonstration empirically demonstrated wetland biochemical treatment as a potentially effective method for continued amelioration of chronic acid drainage at this site.

The naturally established (>15 year-old) mined-land wetland was able to process chronic

Sample Location	Depth	рН	Acidity (ppm CaCO ₃)	A'lka'linity (ppm CaCO ₃)	Conductivity (µmhos/cm)	Oissolved Oxygen (ppm)	Redox. Potential (MV)
3	Surface Interstitial	7.4 6.6	0.0	72.0 340	3,700 2,600	2.7 0.0	-175
9	Surface Interstitial	6.9 6.6	0.0	70.5 228	2,100 3,100	7.9 0.0	 -52
15	Surface Interstitial	8.0 6.2	0.0	96.0 204	2,200 3,950	g.2 0.0	-52
20	Surface Interstitial	7.6 6.2	0.0	76.0 116	2,200 2,200	8.4 0.0	 -5
MEAN	Surface Interstitial	7.5 6.4	0.0	71.9 220	2,550 2,962	7.1 0.0	-71

Table 1. Pre-treatment water quality¹ for surface and interstitial zones of a 27-acre naturally established reedgrass mine drainage treatment wetland (IC1) at the Peabody Will Scarlet Mine, Williamson County, Illinois.

1. Surface water quality samples collected 7 October 1987. Interstitial water quality samples collected 12 January 1988.

Table 2. Water quality summary data1 for discharge of acid water (IC2) into non-acid wetland (IC1) at the Peabody Will Scarlet Old Works area. for the period 12 April 1988 through 9 February 1989.

		Flow		Acid Wetland (IC2)		Non-Acid Wet Inlet-Station 3		land (IC1) Outlet-Station 20	
Date(s)	Duration (hours)	Rate (GPM)	Total (Galx10 ⁶)	<u>рН2</u>	Acidity ² (ppm CaCO ₃)	pH	Alkalinity (ppm CaCO ₃)	pH	Alkalinity (ppm CaCO ₃)
12 April 1988	5	13,124	3.9	3.5	268	7.0	64	7.2	72
21-22 April	25	2,747	4.1	3.5	260	6.8	68	6.8	90
28-29 April	20	2,747	3.3	3.6	256	6.8	52	6.2	132
26-27 Aug.	25	1,087	1.6	3.3	300	7.3	80	7.3	210
29-30 Aug.	20	898	1.1	3.2	272	7.0	76	7.2	208
5-7 Sept.	42	700	1.8	3.2	232	7.4	108	7.0	120
7-9 Sept.	50	557	1.7	3.2	244	7.0	100	7.0	212
25-28 Sept.	72	492	2.1	3.1	264	7.2	68	7.2	160
25 Oct5 Nov.	192	180	2.0	3.2	272	6.6	48	7.2	152
17 Oec6 Jan.3	989458	377	11.0	3.5	248	5.6	16	6.6	56
6 Jan9 Feb.	815	6D7	30.0	3.6	256	5.8	12	5.5	16

¹Summary: 62.6 million gallons (documented; actual >90 million gallons) @ pH ~3.3 and 262 (ppm CaCO₃) acidity. ²Average value based on initial and final water quality.



Figure 2. Acid discharge loading volumes and alkalinity response of surface and interstitial water in a 27-acre naturally established reedgrass mine drainage treatment wetland at the Peabody Will Scarlet Mine, Williamson County, Illinois.



Figure 3. Surface water pH values for a 27-acre naturally established reedgrass wetland (IC1) receiving input from a pre-law acid wetland (IC2). Acid discharge (pH 3.3, acidity @ 262 ppm) exceeded 60 million gallons during April 1988 through February 1989.



Figure 4. Surface and interstitial zone pH values for a 27-acre naturally established reedgrass wetland subjected to acid loading (62.6 million gallons; pH 3.3, acidity 262 ppm) during April 1988 through February 1989.

Sample Date	Depth	рН	Acidity ¹ (ppm CaCO ₃)	Alkalinity ¹ (ppm CaCO ₃)	.Conductívity (µmhos∕cm)	Dissolved Oxygen (ppm)	Redox Potential (MV)
10/87	Surface (n=4)	7.5	0	79	2,150	7.1	
11/87	Interstitial (n=4)	6.4			2,675	0.0	-48
1/88	Surface (n=19) Interstitial (n=4)	7.0 6.4	-16 27	74 222	2,142 2,962	9.6 0.0	-71
2/88	Surface (n=19) Interstitial (n=4)	7.3 6.6			1,821 2,675	0.0	-62
3/88	Surface (n=19)	7.3	- 15	68	1,505	10.0	+109
	Interstitial (n=4)	6.8	368	431	2,675	0.0	-70
4/88	Surface (n=19)	6.6	- 34	74	2,137	7.1	+46
	Interstitial (n=4)	6.1	328	356	3,075	0.0	-93
5/88	Surface (n=19)	7.2	-79	112	2,016	5.7	+25
	Interstitial (n=4)	6.4	235	319	2,800	0.0	-126
6/88	Surface (n=19)	6.9	-60	12 1	2,279	4.7	-31
	Interstitiaï (n=4)	6.2	246	256	2,825	0.0	-128
7/88	Surface (n=19)	7.5	-40	91	2,216	12.9	+43
	Interstitial (n=4)	6.2	414	283	2,925	0.0	-151
8/88	Surface (n=19)	7.8	-73	125	2,300	10.8	+16
	Interstitial (n=4)	5.9	334	291	2,975	0.0	-142
9/88	Surface (n=19)	7.4	-78	103	2,316	10.7	+44
	Interstitial (n=4)	6.2	328	333	2,875	0.0	-118
10/88	Surface (n≃19)	7.5	-78	106	2,245	10.4	+113
	Interstitial (n=4)	6.0	319	370	3,000	0.0	-92
11/88	Surface (n=19)	7.1	-49	109	2,032	10.2	+129
	Interstitial (n=4)	6.0	6	467	2,775	0.0	-78
12/88	Surface (n=19)	6.6	-41	59	1,874	11.9	+114
	Interstitial (n=4)	6.2	285	381	2,625	0.0	-67
1/89	Surface (n=5)	6.3	-11	30	1,870		
2/89	Surface (n=5)	5.0	76	14	2,080		
3/89	Surface (n=1)	6.5	21	24			
4/89	Surface (n=1)	6.5	22	30			
7/89	Surface (n=1)	7.0	- 32	72			

Table 3. Water quality summary data for surface and interstitial zones of a 27-acre naturally established reedgrass wetland (IC1) at the Peabody Will Scarlet Mine, Williamson County, Illinois.

1. n=4 for all depths except the 3, 4, and 7/89 samplings where n=1.

acid inputs as it had during the past 5 to 7 years. Factors contributing to the ability of this wetland to tolerate acid loading without permanent degredation of its alkaline buffering capacity suggested natural processes such as sulfate reduction can maintain an acceptable acidity-alkalinity equilibrium under field conditions if biochemical thresholds of the wetland systems are not exceeded.

Wetland treatment system can be viewed as a "biological shock absorber" capable of absorbing some environmental shocks and handling <u>normal</u> loads. However, subjecting an environmental system to constant abuse or even a short series of acute stressful events can sufficiently exceed the system's loading capacity and its ability to recover. Once a biological system has been degraded, time is required for natural recovery processes to restore a stable and healthy equilibrium. In the case of acid treatment wetlands, sizing and flow design must accomodate a reasonable constant and even distribution of acid flows (both quanitity and quality) to prevent deterioration of biochemical processing ability at the input point. Biological thresholds must be determined and upper limits of tolerance to acid loading can not be exceeded.

The wetland system will need to be well established and diverse to prevent disruption of fragile equilibriums characteristic of recently constructed wetlands. Natural productivity of above-ground biomass is required for natural recovery processes to restore a stable and healthy equilibrium. Natural productivity of above-ground biomass or introduction of other organic matter sources should be maximized to facilitate sulfate reduction in anaerobic substrates.

The previous recommendations represent a general description of the Will Scarlet treatment wetland (IC1) and other reclamation practices currently being implemented at wetland sites at Will Scarlet. Sewage sludge is being used as an organic substrate for alkaline capped (AMD sludge) slurry impoundments. Sewage sludge capped slurry wetlands are being designed to function as additional biochemical buffering systems for chronic acid runoff which originates from pre-law acid seeps. The overall reclamation goal of the Will Scarlet site will be to eventually (3 to 5 years) provide sufficient wetland buffering capacity to eliminate the need for chemical water treatment.

The acid-loading trials summarized in this paper served both as an empirical evaluation of wetland treatment potential of a naturally established wetland, and as a guideline for "not-to-exceed" loading rates for future design and operation of wetland treatment units at Will Scarlet. This demonstration did not control or accurately measure effects or functions of the many physical, vegetational, or chemical components operating within the treatment wetland. Wetlands will always be the most diverse and dynamic natural system ever established on mined lands, or ever used in the treatment process of mine drainage. Understanding or documenting the complexity of wetlands does not affect their intrinsic ability to perform their many functions. From waterfowl habitat enhancement to water quality improvement, wetlands will continue to serve a vital function in the reclamation of the Peabody Will Scarlet mine.

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