Iron Removal from Acid Mine Drainage by Wetlands[1]

by

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Abstract: Neutralization of acid mine drainage (AMD) in man-made cattail (*Typha*) wetlands was investigated over a four-year period utilizing experimental models (480 x 60 x 60 cm) constructed in a greenhouse. A naturally occurring AMD (430 mg/L Fe, 5 mg/L Mn, 2900 mg/L sulfate, pH 2.75) was collected in the field and added to the greenhouse wetlands at 60.5 L/day. Monthly water samples were collected at the wetland influent and effluent at 35 cm depth. Sediments and sediment pore water samples from four depths (10, 20, 30, and 40 cm) were obtained from the influent, midpoint, and effluent locations of the wetland. During the first year of AMD treatment, near neutral pH (6.5) and anoxic conditions (-300 mV) were observed in subsurface sediments of wetlands. The wetlands retained an estimated 65% of the total applied iron in the first year, primarily in the exchangeable, organically bound, and oxide form. During later years, 20 to 30% of the influent iron was retained predominantly as precipitated oxides. Iron sulfides resulting from sulfate reduction accounted for less than 5% of the iron retained, and were recovered primarily as monosulfides during the first year and as disulfides in the fourth year. Improvement in effluent pH was primarily attributed to limestone dissolution in the anaerobic subsurface sediments, which decreased with time. Constructed wetlands exhibit finite lives for effective AMD treatment and provisions should be made for their periodic rejuvenation or replacement.

Additional Key Words: aluminum, limestone, manganese, metal retention, passive treatment systems, sulfate reduction

Introduction

Control of acid mine drainage (AMD) from both active and abandoned surface mines is one of the biggest problems facing the coal mining industry in the eastern U.S. coal region. Nearly 4,000 km of streams in West Virginia are affected by AMD, and similarly impacted streams occur in Pennsylvania, Maryland, and Ohio. Operators are required by law to chemically treat AMD before release into receiving streams and are faced with this cost indefinitely. The use of *Typha* wetlands for removal of metals and acidity from AMD can provide an treatment occurs. Two construction styles currently alternative to conventional chemical treatment. The design of a *Typha* wetland ultimately affects how water predominate. Aerobic wetlands consist of *Typha* and other wetland vegetation planted into shallow (<30 cm), relatively impermeable sediments comprised of clay or mine spoil. Water treatment in aerobic wetlands results primarily from chemical and microbial oxidation reactions. Anaerobic wetlands consist of *Typha* and other wetland vegetation planted into deep (>30 cm), permeable sediments comprised of soil, peat moss, spent mushroom compost, sawdust, manure, hay, or a variety of other organic mixtures which are often underlain or admixed with limestone. Water treatment in anaerobic wetlands occurs by oxidation reactions in the shallow aerobic surface layer, and also by chemical and microbial reduction reactions in the anaerobic subsurface. Metal complexation and exchange occur in both systems, however anaerobic wetlands present a much greater reaction surface area due to subsurface flow.

Insoluble precipitates such as oxyhydroxides, carbonates, and sulfides represent a major sink for metal

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retention in wetlands (Wieder, 1993). Long term retention and stability of iron sulfides and iron oxyhydroxides in a wetland are not yet well understood. Unlike exchange and complexation reactions, retention of metal precipitates has no theoretical maximum, but in reality is limited by the physical density and volume of the material produced. For example, compared to diffuse amorphous iron oxyhydroxides, iron monosulfides and disulfides are compact and form dense precipitates, which occlude less wetland pore space volume per given amount of iron retained.

AMD often contains a mixture of ferrous and ferric iron . Oxyhydroxide formation depends both on the availability of dissolved oxygen and on the initial oxidation state of iron in the AMD. Oxygen must be present for ferrous iron oxidation. After ferric iron is formed, then oxygen is unnecessary for further hydrolysis to the oxyhydroxide. Ferric oxyhydroxides can be reduced with time to ferrous iron by anaerobic iron-reducing bacteria (Lovely and Phillips, 1986). Similarly, the use of ferric iron as a pyrite oxidant under anaerobic conditions would result in ferrous iron in wetland effluents.

Iron sulfides form as a result of microbial sulfate reduction in the presence of an oxidizable carbon source (Rabenhorst et al., 1992). Theoretically under continual anoxic conditions and in the absence of soluble ferric iron, pyrite should remain stable. In addition to its metal removal potential, sulfate reduction consumes acidity and raises water pH (Hedin and Nairn, 1992). High sulfate concentrations (500 to 2000 mg/L) are not uncommon in AMD and availability of this anaerobic electron acceptor results in selective enrichment for sulfate-reducing bacteria. Wieder (1992) reported transitory activity of sulfate-reducing bacteria during the first year of wetland operation, but found the bacteria to be distributed throughout the entire wetland, including near surface sediments. McIntyre and Edenborn (1990) and Calabrese et al. (1994) report sulfate-reducing bacteria activity for longer periods, particularly in deep sediments adjacent to zones of subsurface limestone dissolution.

This study was designed to examine chemical and microbiological mechanisms by which constructed *Typha* wetlands treat AMD and to examine sustainability of these treatment mechanisms. Over a period of four years, we measured iron retention and export from scale-model wetlands constructed in a greenhouse. We also examined formation and retention of sulfides resulting from bacterial sulfate reduction.

Materials and Methods

Four wetlands were constructed in a greenhouse (Figure 1). Each wetland had dimensions of 480 x 60 x 60 cm (L x W x D), and were sloped to about 2% and lined with 40-mil thick plastic. Wetland substrate consisted of a bottom layer of limestone gravel (15 cm) covered with 40 cm of a 90:10 mixture of commercial *Sphagnum* peat moss and soil. Each wetland was inoculated with four liters of a mixed sediment slurry collected from a volunteer *Typha* wetland that was successfully treating AMD on a nearby surface mine and saturated for four weeks with tapwater. The purpose of the inoculum was to introduce microorganisms adapted to AMD prior to planting *Typha* in the wetland systems. Each wetland was planted with 32 plants of *Typha latifolia* in rows to maximize wetland coverage. The cattails established and grew for a period of six months prior to addition of AMD. The six-month establishment period provided for the development of extensive root systems and helped stabilize the microbial communities in these man-made systems.

Tapwater or AMD was added to the wetlands by timer-controlled, peristaltic pumps fed from plastic barrels. Inflow rates were fixed at 60.5 L/day. Based on an estimated 35% pore volume in the substrate and a 5-cm layer of surface water, the water retention time was 12 days. Untreated AMD was collected weekly at a point discharge from an abandoned deep mine blowout, transported to the greenhouse, and pumped into the barrels feeding the wetlands. Composition of the AMD averaged 438 mg/L total iron, 4 mg/L total manganese, 2900 mg/L sulfate, 1835 mg/L total acidity ($CaCO_3$ equivalent) , and pH 2.75. Greater total iron and acidity were found in the AMD during later years of the study.

From August 1989 through July 1992 (24 months), two of the wetlands received AMD (designated AMD Only and AMD/Water) and the other two served as controls (Water Only and Water/AMD) receiving freshwater at 60.5 L/day. In July 1992, one of the AMD wetlands (AMD/Water) began receiving freshwater, while one of the freshwater wetlands (Water/AMD) began receiving AMD. The other two wetlands continued as they began.

Influent water samples were collected at the inlet, and effluent water samples were collected from a plexiglass/PVC exit port installed at the 35-cm depth in each wetland. Pore water was collected from small wells on 90-cm by 11-cm, high density, polyethylene interstitial water samplers (Calabrese et al., 1991). The small wells were filled with sterile, degassed, Milli-Q water, then a

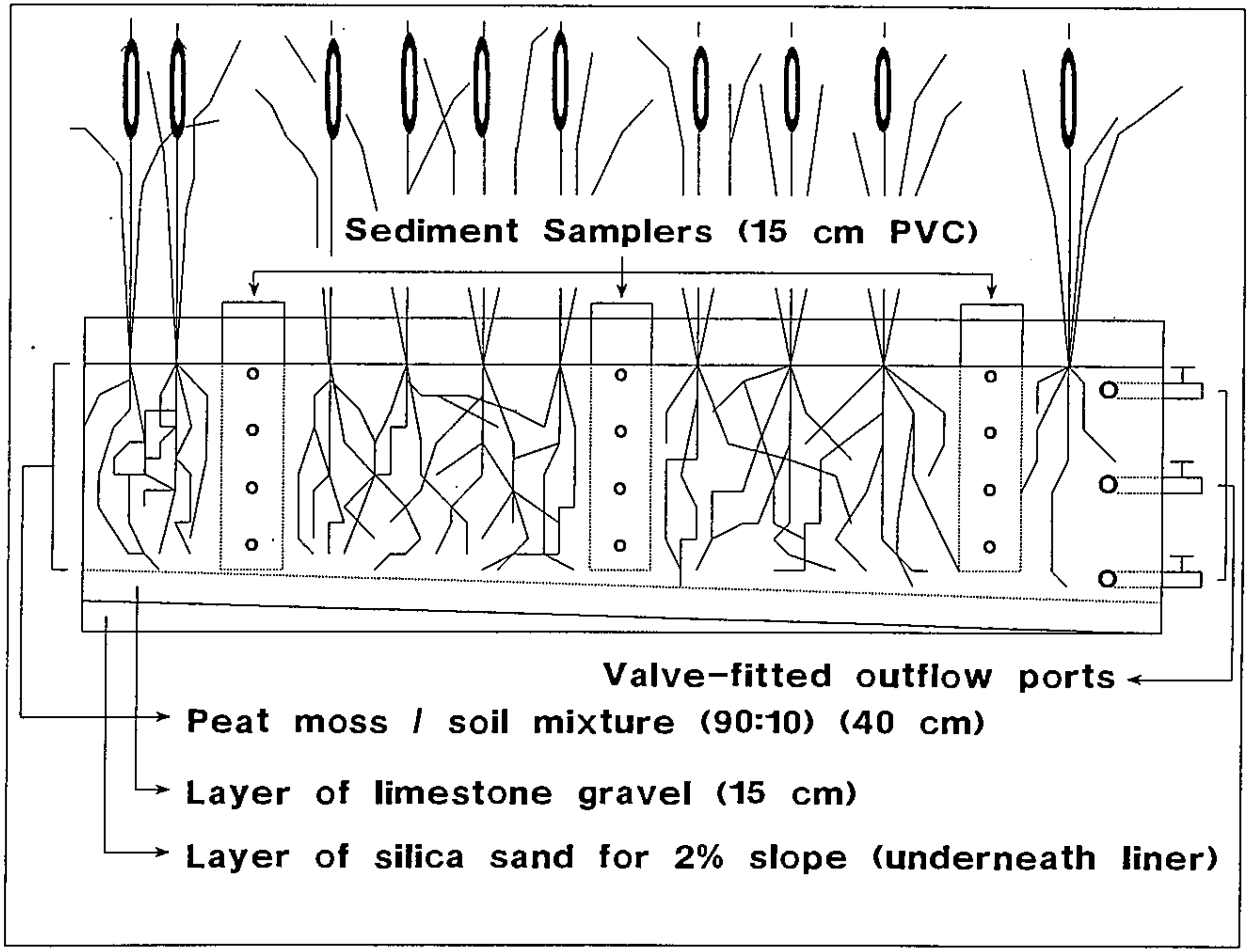

Figure 1. Cross-sectional diagram of a typical greenhouse wetland showing locations of exit ports and substrate sampling devices.

0.4-um filter membrane was placed over the wells and secured by a retaining plate. Pore water samplers were inserted into the wetland sediments where they were allowed to equilibrate for a minimum of two weeks prior to pore water sampling. Pore water samples were maintained under anaerobic conditions for Eh and pH determinations using a platinum electrode paired with a Ag/AgCl double junction electrode (YSI Model 3530 and 3540). Total iron and calcium were determined by a Perkin Elmer model 403 Atomic Absorption Spectrophotometer. Sulfate was determined by single column ion chromatography (Varian).

Sediment samplers were installed at three locations (designated as influent, midpoint, and effluent) within each wetland and were used to collect sediments. These samplers consisted of bottom-capped 15 x 60 cm (Dia x L) PVC pipes where four ports were drilled on each side of the pipe at 10, 20, 30, and 40 cm depths. The 16 ports were closed with rubber stoppers and the PVC sediment samplers were submerged in the sediment. The use of these samplers provided for minimal disturbance when sampling the substrate and also allowed a technique where anoxic conditions could be maintained during sampling (Calabrese et al., 1991). Sediment/slurry samples were collected by attaching a hose to a sampling port in the sampler and extracting sediment and water through the hose into a collection flask by the use of a hand pump. Both the inside of the sampler and collection flask were continuously sparged with argon. Excess water was poured off from the collection flask and the resulting slurry was maintained under argon at 4°C prior to use.

Iron in sediments was separated into various fractions by sequential extractions followed by 1M perchloric acid digestion: exchangeable (1M KCl), organically complexed (0.1N KP_2O_7), oxide or oxide-bound (0.3N $Na_3C_6H_5O_7$ + 1.0M $NaHCO_3$ + 1 g $Na_2S_2O_4$), and residual iron (Shuman, 1985). Sulfides in sediment slurries were fractionated according to the methods of Stover et al. (1976). Conventional aerobic extractions were found to overestimate oxide formation by 10 to 20% compared with similar extractions performed under anaerobic conditions (Bhumbla et al., 1990), therefore anaerobic extractions were employed throughout this study.

Small samples of sediment slurries were transferred to an anaerobic Coy glove box where the sediments were used to measure sulfate-reduction rates. Sulfate reduction rates were determined by adding 2 uCi of $^{35}SO_4^{-2}$ to sediment samples and placing them in anaerobic Torbal jars for 48 hrs at 25°C with subsequent freezing at -20°C to terminate microbial activity. Samples were thawed under 2M NaOH and transferred to digestion flasks for sulfide determinations. Using a Nishita apparatus, pyritic sulfides (chromium reducible sulfides, CRS) and iron monosulfides (acid volatile sulfides, AVS) were liberated and trapped in sulfide antioxidant buffer (SAOB: 0.2M disodium EDTA, 0.2M ascorbic acid, and 2M NaOH). Four mls from each SAOB trap were transferred to vials for scintillation counting (Andersen and Jorgensen, 1989).

Results and Discussion

During their first year of operation (August 1989-June 1990), the experimental wetlands treated AMD by removing iron and buffering effluent acidity (Calabrese et al., 1991). While the effluent water would have required further treatment to meet legal discharge limitations (4 mg/L Fe), the cost of chemical treatment would have been substantially reduced. Analysis of sediment pore water revealed that the surface layers of the wetlands were oxidizing (Eh > +400 mv) and acidic (pH < 3) due to hydrolysis and precipitation of dissolved iron (Figure 2). However, reducing conditions (Eh < -200 mv) and circumneutral pH prevailed in subsurface sediments. Water exited the wetlands from the 35-cm depth at pH 6.5 and 150 mg/L iron compared with pH 2.5 and 450 mg/L iron in the influent water. Amelioration of pH was attributed primarily to continuous dissolution of subsurface limestone (> 500 mg/L Ca).

Approximately 65% of the iron applied to the wetlands was retained during the first year of operation. Oxides and exchangeable iron were predominantly retained in surficial sediments, while exchangeable and organically complexed iron predominated in subsurface sediments (Table 1). In a laboratory simulation, Henrot and Wieder (1990) previously observed that organic complexation in peat microcosms retained 50 to 80% during initial AMD application, but saturated at 12 mg Fe/g dry peat. Iron monosulfides (AVS) were measurable in subsurface sediments (Table 2) due to active sulfate reduction (range 60 to 250 nmoles S/cm^3/day).

Originally, our experimental design included replicated AMD treatment wetlands. During the second year of operation (July 1991 to July 1992), we noted decreased *Typha* growth and increased iron export in both replicates. However, by early 1992 water treatment in the two replicate systems began to diverge. One of the AMD wetlands exported 250-350 mg/L iron and 250-350 mg/L calcium at pH 3-5 compared with 300-500 mg/L iron and 400-600 mg/L calcium at pH 5-6.5 from the other AMD wetland (Table 3). Decreased iron export and calcium

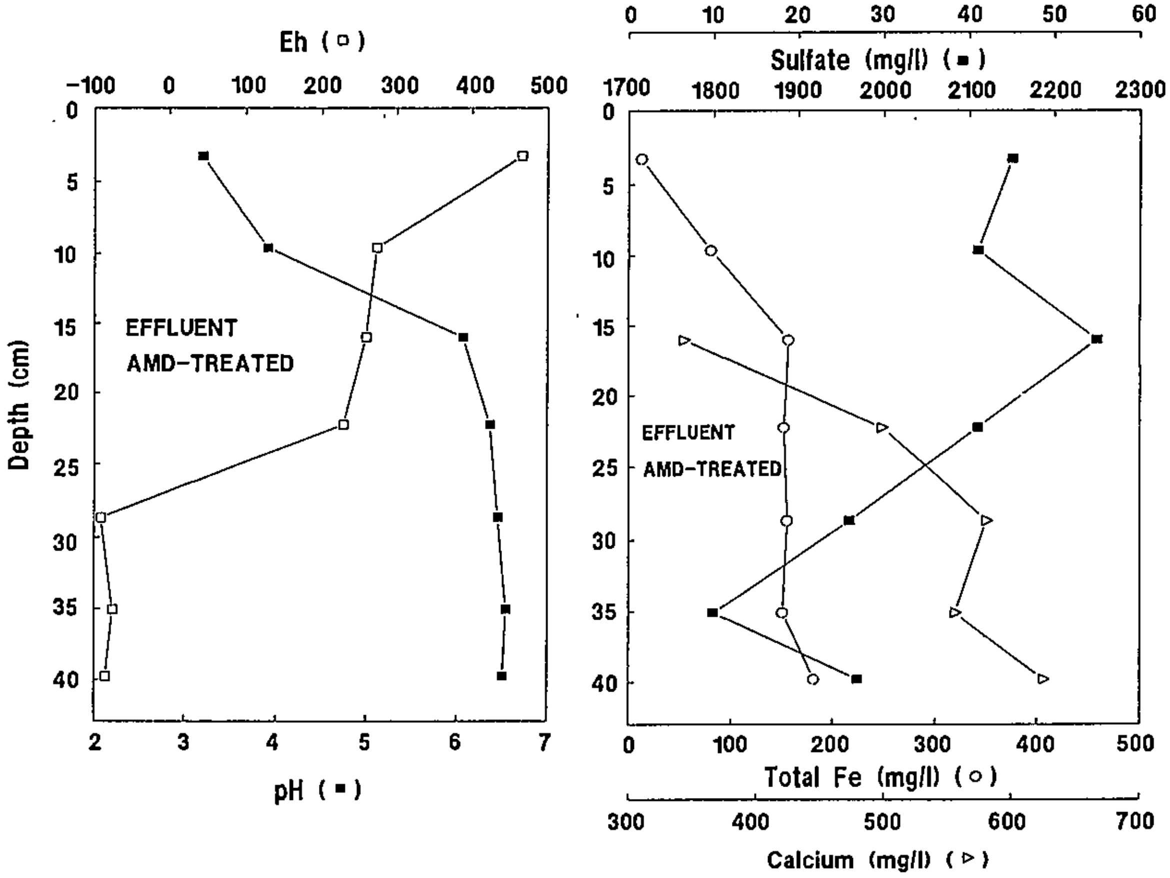

Figure 2. Depth profiles of porewater pH, Eh, iron, calcium, and sulfate from effluent of the AMD Only wetland in 1990.

Table 1. Total iron in sediments (mg Fe/g dry weight) and the extractable form of iron in AMD wetlands during 1990, the first year of operation. The sediment samples for iron fractionation were taken at the midpoint of the wetland at depths of 10 and 20 cm.

Sample Depth (cm)	Total Fe (mg Fe/g dry wt.)	Fe Oxides	Exchangeable Fe	Organic Fe	Sulfide Fe
		(%)			
10	39.1	57.6	34.7	5.2	2.4
20	17.9	6.5	45.8	28.3	19.4

Table 2. Total sulfides in sediments (ug S/g dry weight) and the form of sulfide [acid volatile (AVS) vs chromium reducible (CRS)] in AMD wetlands in 1990, the first year of operation. The sediments for sulfide determinations were taken from three depths (10, 20 and 30 cm) and at the influent, midpoint and end of the wetland (Inf, Mid, End).

Sample Depth (cm)	Total Sulfide (ug S/g dry weight)			Acid Volatile Sulfides (%)			Chromium Reducible (%)		
	Inf	Mid	End	Inf	Mid	End	Inf	Mid	End
10	260	700	1475	92	57	77	8	43	23
20	495	2040	4603	95	77	69	5	23	31
30	1035	2217	9960	94	80	77	6	20	23

dissolution, coupled with lower effluent pH suggested precipitation of iron hydroxides and armoring of the underlying limestone in the AMD wetland (AMD/Water). In contrast, the second AMD wetland (AMD Only) exported over 75% of the influent iron at pH>5 suggesting that this wetland was functioning in a manner similar to an anoxic limestone drain; i.e., there was sufficient alkalinity in the effluent water to help buffer acidification due to post-wetland precipitation of iron (Nairn et al., 1991). Considering that the wetlands were identical in design, received identical AMD, and experienced nearly identical climatic conditions in the greenhouse, the variability in AMD treatment between these two AMD wetlands is not readily explainable and highlights the difficulty in predicting the performance of complex biological treatment systems.

Due to the impending failure of AMD treatment in the first AMD wetland (AMD/Water), we changed the inflow water type of two of the wetlands beginning in July 1992. The failing AMD wetland was switched to receive freshwater (AMD/Water) in order to test stability of iron previously retained by this wetland. One of the freshwater wetlands was switched to receive AMD (Water/AMD) in order to compare its response to receiving AMD back to the first year of operation of the previous AMD wetlands. The remaining two wetlands continued to receive AMD or freshwater (AMD Only and Water Only). Responses to these treatment are presented through June 1993 when regular monthly sampling of the wetlands was terminated (Table 3).

Effluent chemistry from the Water Only control wetland remained consistent throughout the entire 47 months of water treatment (pH 6.5 to 7.4, Fe < 5 mg/L, Ca 20-190 mg/L). Most notable in these data are the lower levels of limestone dissolution compared to wetlands actively treating AMD. The AMD Only wetland remained relatively unchanged over the 47-month treatment period documenting continuous improvement of water quality. An additional sample taken from this wetland in December 1993 (data not shown) exhibited diminished water treatment (effluent Fe of 127 mg/L at pH 2.4). These latter data document that

Table 3. Influent and effluent chemistry in all wetlands (Water Only, AMD Only, Water/AMD, and AMD/Water) from January 1992 through June 1993.

			Wetland Treatment																
Type		Influent	Jan-92	Feb-92	Mar-92	Apr-92	May-92	Jun-92	Jul-92	Aug-92	Sep-92	Oct-92	Nov-92	Dec-92	Jan-93	Feb-93	Mar-93	Apr-93	My-93	Jun-93
Water Only	pH	7.4	6.6	6.8	6.8	6.8	6.9	6.7	6.6	6.7	6.7	6.6	6.7	6.6	6.6	6.7	6.6	6.7	6.8	6.8
	Fe	1.3	4.6	4.6	2	3.4	0.3	1	0.3	1.5	0.1	0.1	0.1	0.6	0.1	0.2	0.4	0.2	0.3	0.8
	Ca	32	79	111	73	55	70	103	65	95	118	124	171	183	156	167	187	151	169	168
AMD Only	pH	2.9	5.1	5.9	5.0	6.1	6.2	6.2	6.0	6.2	6.3	6.3	6.5	6.1	6.1	6.2	5.7	5.8	6.1	6.4
	Fe	455	317	373	382	368	437	523	536	543	556	484	594	500	354	349	349	352	306	319
	Ca	293	401	623	512	472	602	571	510	664	527	484	574	610	426	378	465	153	500	477
Water/ AMD[1]	pH	7.6, 2.8	6.5	6.8	6.8	6.7	6.8	7.1	6.2	6.2	5.7	5.2	5.9	4.8	5.2	5.1	5.6	5.8	6.1	6.2
	Fe	2.9, 372	1.2	6.9	3	3.7	2.2	3.5	161	283	290	292	319	335	303	292	343	317	285	396
	Ca	25, 295	40	98	83	61	71	93	526	707	541	430	568	539	393	331	474	528	467	445
AMD/ Water[2]	pH	2.7, 7.5	5.6	3.8	4.7	3.2	3.0	4.7	5.3	5.9	6.1	6.0	6.3	5.9	6.0	5.9	6.2	6.3	6.3	6.5
	Fe	428, 0.8	385	294	309	265	347	351	76.7	109	29.5	29.3	17.9	59.1	52.2	42.7	40.8	47.7	50.9	70.8
	Ca	311, 38	341	502	492	333	454	397	178	304	119	146	116	504	410	345	404	527	455	428

The Water/AMD wetland received water for 24 months (until July 1992), then it was switched to receiving AMD after July 1992.

The AMD/Water wetland received AMD for 24 months (until July 1992), then it was switched to receiving water after July 1992.

this wetland finally failed like the other AMD wetland, but maintained treatment effectiveness for twice the time as the other AMD wetland.

Effluent pH from the Water/AMD wetland was lower (4.8 to 6.2) and effluent iron was higher (283 to 396 mg/L) compared to the AMD wetlands (AMD Only and AMD/Water) during their first year of treatment. Less iron retention in this system may be due to the strongly anaerobic character established in this mature wetland and ineffective iron retention by exchange reactions (see below).

The AMD/Water wetland effluent improved dramatically after AMD addition ceased (pH 5.9 to 6.3 and dissolved calcium 350 to 500 mg/L). This wetland exported iron at much lower levels (17 to 109 mg/L) than during active AMD treatment and the effluent iron concentration remained about the same over time. To our knowledge, no previous study has documented post-treatment stability of iron retained by wetlands once AMD additions have ceased. These data demonstrate that iron within the wetland matrix was not extensively re-mobilized and imply that wetlands may serve as a long term sink for this metal pollutant.

Data from 1990 (Table 1) suggested that exchange and binding to the organic substrate were initially important sinks for iron retention within the wetlands. However, long term AMD treatment in wetlands cannot rely primarily on these reactions, which are subject to saturation (Wieder, 1988). Natural inputs of organic matter occur annually at plant senescence replenishing exchange sites. However, plant biomass and growth rate decreased with increasing exposure time to AMD (Roxanne Bessette, unpublished data), further reducing the availability of renewable organic matter. Substantial artificial inputs of organic matter have been suggested as a successful strategy to temporarily renew exchange capacity when a decline in wetland performance is observed (Eger and Melchert, 1992; Haffner, 1992; Stark et al., 1991).

Iron fractionation at the end of the four-year treatment period varied within and among the wetlands (Table 4). After four years, 40 to >90% of the total extractable iron from the wetland sediments was in the form of ferric oxyhydroxides. In the Water Only control wetland, little total iron (0 to 8 mg/g) was extractable from the sediment, and the iron was recovered predominantly in the oxide and organically complexed fractions. The greatest total iron measured in the AMD/Water wetland sediment (12 to 231 mg/g) was recovered toward the effluent end of the wetland where iron oxides predominated in both surface and subsurface sediments. In Water/AMD and AMD Only wetlands, oxides were the predominant iron form in sediments, especially near the influent area of the wetland. However, exchangeable and organically complexed iron were also significant in midpoint and effluent areas of the wetland. Even after four years of continuous operation, the AMD Only wetland still retained between 20 to 30% of the influent iron load, demonstrating the potential long term, low-maintenance treatment benefit.

After four years of AMD addition, bacterial sulfate reduction rates (SRR) were higher than those measured in the first year (range from 10 to 2800 nmoles S/cm^3/day) and were similar in magnitude to those reported by McIntyre and Edenborn (1990). Despite apparent higher rates of SRR activity, the relative accumulation of sulfides in AMD wetlands was unchanged. During 1993 (Table 5), the amount of total sulfides in sediments was similar to that found in 1990 (range from 500 to 2,500 ug S/g dry weight). Sulfides generally represented less than 5% of the total extractable iron in all wetlands (Table 4) and were often most prevalent in deep sediments toward the effluent. During the first year (1990), sulfides accumulated primarily as transitory monosulfides (AVS), similar to reports by Taddeo (1991) and Rabenhorst et al. (1992). However, by 1993 the extractable sulfides were recovered as disulfides (CRS), except in the Water/AMD wetland to which AMD had been newly introduced (Table 5). These data suggest that although sulfide pools were not significantly greater in magnitude with long term AMD addition, they were probably more stable.

Summary and Conclusions

Acid mine drainage passing through anaerobic wetlands was effectively treated to circumneutral levels during wetland operation. Up to 66% of the iron introduced into the wetland was retained during the first year, followed by a 20 to 30% retention during later years. Iron was retained in primarily oxide, exchangeable, and organic forms. Oxide forms became increasingly important with time. Sulfides were not major sinks for metal retention despite measurable rates of bacterial sulfate reduction.

Constructed wetlands of our design have finite lifetimes (1 to 4 years) for effective treatment of AMD, and the efficiency and mechanism of AMD amelioration may change with the age of the wetland. Provision should be made for periodic rejuvenation or replacement of constructed wetlands treating AMD. There are significant treatment advantages to wetlands underlain

Table 4. Total iron in sediments (mg Fe/g dry weight) and the percentages of the iron in oxide, exchangeable, organic, and sulfide forms (%O,E,Or,S) in the four experimental wetlands in 1993. Sediments were taken at influent (I), midpoint (M), and ends (E) of the wetlands at four depths (10, 20, 30 and 40 cm).

Sample	AMD/Water		Water/AMD		Water Only		AMD Only	
	Total Fe	(%O,E,Or,S)	Total Fe	(%O,E,Or,S)	Total Fe	(%O,E,Or,S)	Total Fe	(%O,E,Or,S)
I10	15	(74,14,12,0)	52	(91,3,5,1)	4	(74,3,19,6)	6	(81,11,7,1)
I20	24	(87,5,8,0)	60	(91,3,5,1)	3	(67,4,28,0)	3	(55,20,21,3)
I30	47	(96,2,2,0)	27	(81,3,9,8)	1	(69,9,22,0)	23	(71,17,10,2)
I40	64	(93,2,2,4)	24	(84,4,11,1)	1	(60,7,33,1)	15	(69,27,4,0)
M10	13	(87,4,5,4)	22	(100,0,0,0)	1	(4,13,83,0)	60	(99,0,1,0)
M20	12	(82,4,12,2)	41	(52,49,0,0)	3	(2,7,89,2)	70	(99,0,1,0)
M30	32	(94,2,3,1)	83	(99,0,0,1)	8	(1,4,17,79)	28	(88,8,4,0)
M40	29	(92,2,5,2)	58	(98,0,1,1)	2	(10,14,75,1)	15	(74,14,11,1)
E10	231	(99,1,1,0)	129	(97,1,1,1)	2	(41,8,51,0)	16	(20,65,4,11)
E20	199	(99,1,1,0)	121	(99,1,0,0)	3	(50,6,45,0)	12	(26,72,1,1)
E30	93	(96,2,2,0)	17	(46,11,18,25)	3	(45,1,54,0)	20	(47,47,3,41)
E40	82	(96,2,2,0)	15	(57,13,22,8)	1	(89,3,5,3)	31	(49,49,1,1)

Table 5. **Total sulfide in sediments (ug S/g dry weight) and the percentages of the sulfide in acid volatile sulfides (AVS) and chromium reducible sulfides (CRS) in three experimental wetlands that received AMD in 1993. Sediments were taken at influent (I), midpoint (M), and ends (E) of the wetlands at four depths (10, 20, 30 and 40 cm).**

Sample	AMD/Water		Water/AMD		AMD Only	
	Total S	(%AVS,CRS)	Total S	(%AVS,CRS)	Total S	(%AVS,CRS)
I10	23	(1,99)	438	(0,100)	93	(0,100)
I20	69	(2,98)	753	(3,97)	94	(0,100)
I30	163	(5,95)	2828	(29,71)	375	(0,100)
I40	2543	(5,95)	323	(37,63)	1	(0,100)
M10	1170	(54,46)	523	(11,89)	541	(0,100)
M20	234	(1,99)	237	(1,99)	239	(0,100)
M30	260	(4,96)	947	(0,100)	69	(1,99)
M40	620	(5,95)	362	(1,99)	167	(1,99)
E10	72	(1,99)	845	(4,96)	1294	(29,71)
E20	133	(9,91)	175	(16,84)	104	(1,99)
E30	63	(4,96)	3405	(0,100)	705	(5,95)
E40	190	(2,98)	984	(0,100)	411	(3,97)

with limestone and to those that incorporate deep subsurface flow of water through anoxic sediments. Such designs maximize physical retention of iron and subsurface water buffering, both of which promote microbial activity and post-system precipitation of iron without re-acidification.

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