

IMPLICATIONS OF SULFATE-REDUCTION AND PYRITE FORMATION PROCESSES  
FOR WATER QUALITY IN A CONSTRUCTED WETLAND: PRELIMINARY OBSERVATIONS<sup>1</sup>

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Abstract--Preliminary observations of water chemistry in a recently constructed *Typha* wetland indicate significant improvements in water quality in areas where reduction processes are occurring. Where the organic substrate was black and loose, sulfate concentrations were 16-59 pct less than inflow, iron concentrations were 52-98 pct lower, and pH was 2-3 units higher. Ninety-six pct of the iron in these areas was in the reduced, ferrous form. Where the organic substrate was blanketed with orange iron oxyhydroxides, water chemistry was similar to inflow, and dissolved iron was predominantly in the oxidized, ferric form. Analyses of the organic substrate (mushroom compost) showed an enrichment of elemental sulfur in all samples. One substrate sample, collected 15 cm beneath the surface, contained both elemental sulfur and pyrite. Removal of iron from acid mine drainage (AMD) through pyrite formation and storage in anoxic sediments may be preferable to removal by oxidation and hydrolysis because of pyrite's density, negligible solubility in acid water, and placement in the substrate. Researchers should consider designs that would emphasize movement of AMD through organic-rich, anoxic substrates and thus maximize sulfate reduction and pyrite-forming processes.

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## INTRODUCTION

Dissimilatory sulfate reduction and pyrite formation are biogeochemical processes that conceptually can contribute significantly to the effectiveness of constructed wetlands in treating acid mine drainage (AMD). In the absence of oxygen, bacteria such as *Desulfovibrio* oxidize organic matter using sulfate as an electron

acceptor and subsequently reducing it to hydrogen sulfide (see reactions in Table 1). When released into the water column, hydrogen sulfide either bubbles away as a gas (the common rotten eggs odor of many wetlands) or is retained in the wetland as sulfides, polysulfides, elemental sulfur, iron monosulfides (FeS) and pyrite (FeS<sub>2</sub>). The reduction process produces alkalinity, which decreases acidity and raises pH. Formation of metal sulfides removes iron from solution. Because such changes in water chemistry are the primary goals of most AMD treatment systems, a better understanding of reducing reactions might result in significant improvements in the constructed wetland technology.

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Sulfate reduction is a common anaerobic, microbial decomposition process. Its occurrence is dependent on the presence of sulfate and suitable organic matter in an anoxic, aquatic environment. In marine systems sulfate levels are very high, and sulfate reduction is only limited by the presence of suitable organic matter in anoxic sediments (Bernier 1984). In most freshwater systems, sulfate reduction is limited by very low sulfate concentrations and microbially-mediated methanogenesis is the more important anaerobic, decomposition process (Cappenberg 1974, Lovley and Klug 1986). Because the formation of iron sulfides is primarily dependent on the presence of reduced sulfur, freshwater sediments typically have very low pyrite levels (Bernier and Raiswell 1983).

Wetlands constructed for the treatment of AMD have none of these limitations. During the first several years of operations, they contain a huge amount of high-quality organic matter. The systems typically consist of at least a thousand cubic meters of fertile, composted organic matter that is spread 15-30 cm deep in a shallow pit, flooded, and overlain by 10-20 cm of slowly flowing AMD water. Aerobic decomposition of the organic matter at the water/substrate interface promotes anoxic conditions within the flooded organic substrates. The acid mine drainage flowing through these wetlands is enriched with dissolved sulfate and iron. Thus, all the conditions for high rates of sulfate reduction and pyrite formation exist.

The expectation that reduction processes could be important in constructed wetlands is not without precedent. Tuttle et al. (1969) studied an AMD-polluted stream in Ohio that flowed through a sawdust dam and was effected by reduction processes within the sawdust pile. Water samples collected below the dam had sulfate concentrations 60 pct lower and iron levels 50 pct less than samples collected above the dam. Herlihy and Mills (1985) and many of their students have studied a reservoir in Virginia that receives AMD from abandoned pyrite mines. Summer sulfate reduction rates in sediments near the AMD inflow are consistently at least a magnitude higher than control areas. Acid volatile sulfide concentrations, which are assumed to represent iron monosulfides, are always a magnitude higher in the AMD impacted sediments than in the control sediments.

Despite these observations, the role of reduction processes in constructed wetlands has received very little attention. Most research has focused on uptake of iron by plants, or microbially-mediated metal oxidation processes (e.g. Kleinmann et al. 1983, Gerber et al. 1985, Wieder and Lang 1986, Kearney and Wieder, elsewhere in these proceedings, Webster et al., elsewhere in these proceedings). In the only published studies that specifically looked for reduced sulfur compounds (and found minor amounts), either the samples were collected from the top 20 cm of peat in a natural *Sphagnum* wetland (Wieder and Lang 1986) or laboratory mesocosms were only 20 cm deep (Tarleton et al. 1984). Such shallow depths are not conducive to development of the permanent anoxic conditions that are necessary to promote pyrite accumulation.

The wetland monitored in this study is located in Westmoreland County, Pennsylvania about 16 km (10 mi) north of Latrobe. The wetland was constructed in the spring of 1987 to treat drainage from recently strip-mined coal spoils (Figure 1). It is a cattail-dominated (*Typha*) community growing on a substrate of 15 cm (6 in) of crushed limestone, covered with 45 cm (18 in) of mushroom compost<sup>3</sup>. Water depths over the substrate are 5-20 cm (2-8 in). Baffles were constructed in each cell with bales of hay to promote a serpentine flow path. By September, 1987 a dense stand of cattails had developed. Seepage drains from the reclaimed mine spoils at flows of 40 to 120 L/min (10 to 30 gals/min). It is collected in a shallow pit, which was also filled with substrates and planted with cattails, and then flows 30 m (100 ft) over limestone rip-rap into the wetland.

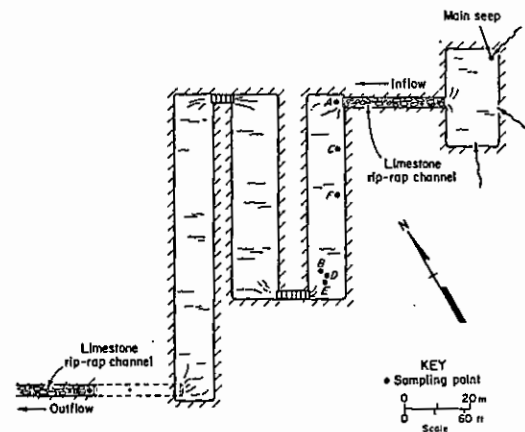


Figure 1.--Plan view of the constructed wetland.

## METHODS

The wetland was examined and sampled in autumn of 1987. Chemical measurements were made directly in the field and in Bureau of Mines' laboratories at the Pittsburgh Research Center. Numerous pH determinations were made using a temperature-compensated, field pH meter (Orion Model 230) with a Ross combination electrode. The electrode and meter were calibrated and measurements were subsequently made by placing the probe directly into wetland water. Dissolved oxygen (DO) was measured on October 7 with a portable polarographic sensor and field meter (Extech Model 9070). Because this DO probe could not be completely submerged, measurements reflect DO only to a depth of about 5 cm (2 in) beneath the water surface.

<sup>3</sup> Mushroom compost, a waste product of local mushroom growers, is produced by aerobically composting a mixture of spoiled hay, agricultural wastes, and animal manure.

Table 1.--Important chemical reactions in anaerobic, sulfate-rich environments

Reaction description	Reaction	Ref <sup>2</sup>
1. Sulfate reduction	$SO_4^{2-} + 2CH_2O^* \rightarrow H_2S + 2HCO_3^-$	(1)
2. hydrogen sulfide ionization	$H_2S \rightarrow HS^- + H^+$ $HS^- \rightarrow S^{2-} + H^+$	(2)
3. formation of elemental sulfur	$HS^- + 1/2O_2 + H^+ \rightarrow S^0 + H_2O$	(2)
4. polysulfide formation	$HS^- + (x-1)S^0 \rightarrow S_x^{2-} + H^+$	(2)
5. iron monosulfide formation	$Fe^{2+} + HS^- \rightarrow FeS + H^+$	(4)
6a. pyrite formation	$FeS + S^0 \rightarrow FeS_2$	(4)
6b. pyrite formation	$Fe^{2+} + S^0 + H_2S \rightarrow FeS_2 + 2H^+$	(3)
6c. pyrite formation	$Fe^{2+} + S_x^{2-} + HS^- \rightarrow FeS_2 + S_x^{2-} + H^+$	(3)

<sup>1</sup>CH<sub>2</sub>O represents organic matter.

<sup>2</sup>References are: (1) Berner 1984; (2) Chen and Morris 1972; (3) Altschuler et al. 1983; (4) Berner 1967.

Table 2. Changes in water Quality between the main seep and wetland inflow on October 27, 1987

	pH	Acidity	Sulfate	Fe	Fe <sup>2+</sup>	Al	Mn	Na	Ca	Mg
main seep	3.04	1000	2125	227	146	49	36	4	188	134
inflow	3.02	909	2075	203	62	51	38	4	209	139

Acidity is mg/L of CaCO<sub>3</sub> equivalent; all other values, except pH, are mg/L.

Water samples were collected at various locations (Fig. 1) and analyzed in the laboratory for pH, acidity, sulfate, Fe<sup>tot</sup>, Fe<sup>2+</sup>, Mn, Al, Ca, Mg, and Na using standard methods (e.g. Watzlaf 1986). Substrate samples were collected in plastic bottles which were filled to capacity, capped, and refrigerated. In the laboratory, these samples were centrifuged to separate solids from liquid, and the supernatant was either analyzed or discarded. The solids were dried under vacuum and stored under argon. Total sulfur was determined using a LECO SC-32 Sulfur Determinator. Sulfur forms were distinguished using evolved gas analysis (EGA) and X-ray photoelectron spectroscopy (XPS) (Hammack, elsewhere in these proceedings). X-ray diffraction was used to corroborate EGA and XPS results. The acid-soluble metal content of solids was determined by boiling a weighed sample in aqua regia (a mixture of hydrochloric and nitric acids) and measuring the metal concentrations of the acid extract after filtering it through a Whatman No. 42 filter.

## RESULTS

When first examined five months after construction, the limestone rip-rap in the ditch preceding the wetland was coated with iron oxy-

hydroxides and had little effect on drainage chemistry (Tab. 2). On several other occasions we measured the pH of water in the pit and at the inflow and never found substantial differences. The only major change in water chemistry between the main seep and the wetland inflow was partial oxidation of the ferrous iron (Fe<sup>2+</sup>). Thus, on all sampling dates we have collected wetland inflow samples from the end of the riprap (location A in Fig. 1).

Since September, 1987, the wetland has displayed a variable appearance. In some areas the organic substrate is coated with about 1 cm of an orange precipitate that is sometimes hard and crusted. In other areas the substrate is black and loose. We have visually estimated that black areas represent about 20 pct of the wetland area, while orange areas represent the rest. Occasionally the substrates in black areas are covered with a fine, white precipitate. Many of the black areas are located in stagnant water behind haybales, while orange-colored areas tend to be on the upstream sides of haybales and in the central, main-flow area. Density of living cattails does not appear to be substantially different between the areas.

The dissolved oxygen (DO) concentrations of surface water were lower in black areas than in orange areas (Tab. 3). The highest DO value, 10.1 mg/L or 99% of saturation (water temperature = 13<sup>o</sup> C, saturation = 10.2 mg/L (Truesdale et al. 1955)), was found overlying an orange area near the inflow. Downstream of the first row of hay bales in the first cell, the DO of surface water in an orange area was 9.0 mg/L. A black area, only 1 meter away, had a surface DO content of 5.0 mg/L. By the time water reached the outflow pipe at the end of the third cell, DO levels were depressed everywhere. However, surface water in black areas still had 1.2-1.9 mg/L lower DO concentrations than nearby orange areas (Tab. 3). Losses of dissolved oxygen were likely due to consumption of oxygen by aerobic decomposition of organic matter at the substrate/water interface, as well as aerobic oxidation of ferric iron by chemical and microbial processes. The lower values in black areas could have resulted from higher oxygen consumption, less mixing with oxygenated water, or both. Nowhere did we find surface water DO levels low enough to be considered anoxic. We suspect, based on sulfur and iron analyses (to be discussed), that anoxic conditions existed several cm beneath the water/organic substrate interface.

Table 3. Dissolved Oxygen Content of Surface Water in Various Environments

Area description	DO (mg/L)
Seep collection pit.....	8.7
<u>First Cell</u>	
Inflow, after riprap.....	9.2
Orange area upstream of first haybales.....	10.1
Orange area downstream of first haybales.....	9.0
Black area downstream of first haybales .....	5.0
<u>Third Cell</u>	
Water entering outflow pipe....	5.0
Orange area near outflow pipe...	5.3
Black area near outflow pipe....	3.4
Black area near outflow pipe....	4.1

The orange precipitate that coats much of the organic substrate in this wetland was 21% iron (Tab. 5) and appears to be an iron oxyhydroxide that commonly forms when dissolved iron in AMD is oxidized and hydrolyzed. In the first cell, the chemistry of surface water flowing through orange areas was very similar to inflow water. Numerous pH measurements in the first cell (not detailed here) consistently found values only several tenths of a unit higher than the inflow. The chemistry of water collected at the substrate/water interface in an orange area at the end of the first cell is shown in table 4 (sample B). Despite having flowed through 60 m of wetland, the chemistry was quite similar to the inflow (sample A). The only notable chemical changes were a decrease in total iron of 34 mg/L (19 pct of inflow) and an equivalent loss of ferrous iron.

This loss of dissolved ferrous iron, combined with the presence of iron oxyhydroxide precipitates, indicates the predominance of oxidizing reactions in these areas. Because abiotic oxidation of ferrous iron is quite slow at low pH, the changes in Fe<sup>2+</sup> in orange areas were presumably mediated by iron-oxidizing bacteria. These bacteria may also be involved in the removal of iron from solution as oxyhydroxides (Gerber et al. 1985). The fact that a significant portion of this wetland is covered with iron oxyhydroxides indicates the historic importance of oxidizing reactions to overall iron removal. However, it is also important to note that the current activity of these orange areas appears to be limited. Iron is only slightly decreased, while all other chemical parameters are virtually unchanged.

Areas in which the substrate surface were black had markedly different water chemistry than the inflow, or even orange-colored areas located less than one meter away. These differences are readily seen in table 4 by comparing samples C, D and E to A and B. All three samples were collected from the substrate/water interface in black areas in the first cell (fig. 1). Samples from black areas had dissolved iron concentrations that were much less than samples at the inflow or nearby orange areas. The dissolved iron concentration in sample D was only 3 pct of inflow. Over 95 pct of the dissolved iron that was observed in black areas was in the reduced ferrous form. This contrasted markedly with the inflow sample, which was 40 pct ferrous, and the nearby orange area sample, which was only 27 pct ferrous.

Table 4. Water Chemistry for Samples Collected October 7, 1987

#	SAMPLE LOCATION	CHEMICAL MEASUREMENT									
		pH	Acidity	Sulfate	Fe	Fe <sup>2+</sup>	Al	Mn	Na	Ca	Mg
A	Inflow	2.86	872	2050	181	73	50	36	4	194	133
B	Orange area	2.96	777	2000	147	39	47	36	5	223	139
C	Black area	4.75	10	1725	30	28	bd	58	5	404	159
D	Black area	5.39	5	850	3	3	bd	11	6	214	82
E	Black area with white precipitate	4.60	159	1000	87	84	bd	20	4	171	75

Acidity is mg/L of CaCO<sub>3</sub> equivalent; all other values, except pH, are mg/L; "bd" is below detection level of instrument (<0.4mg/L).

Table 5. Acid Soluble Metal Content of Substrate Samples Collected at the Water/Substrate Interface on October 7, 1987

#	SAMPLE LOCATION	METAL CONTENT (% OF DRY WEIGHT)					
		Fe	Mn	Al	Ca	Mg	Na
B	Orange Area	21.4	<0.1	<0.1	<0.1	<0.1	<0.1
E	Black Area with white precipitate	0.2	<0.1	9.8	<0.1	<0.1	<0.1

Percentages do not sum to 100% because of carbon, oxygen, hydrogen, sulfur and acid-insoluble metals.

Dissolved aluminum was decreased to undetectable levels (<0.4 mg/L) in all samples from black areas. Sample E represented an attempt to collect a fine white precipitate that covered the black substrate in several areas. Large amounts of black substrate were unavoidably included in the sample. Analysis of the acid-soluble constituents of this material revealed an aluminum content of almost 10 pct (tab. 5). Based on the color and this analysis, it appears that the white precipitate was aluminum hydroxide, which commonly forms when the pH of Al-containing water rises above 3.5. Note that, unlike the substrate sample taken only one meter away in an orange area, iron was a minor component of the substrate solids. Despite the fact that dissolved iron was very low in the black areas, its loss was not due to precipitation and accumulation on the surface of the organic substrate.

Samples in black areas were much less acidic than the inflow or nearby orange area samples. Additional pH measurements have indicated that the surface water in black areas generally has a pH between 4.0 and 4.5, while the water within the organic substrate often has a pH greater than 6.0. This decreased acidity cannot be entirely attributed to the neutralizing effect of underlying limestone. Two of the three samples had dissolved calcium concentrations very similar to the inflow. Only sample C had higher calcium levels, but the increase over inflow, 5.25 mm/L (millimoles per liter), was not enough to explain the 8.6 mm/L decrease in acidity (CaCO<sub>3</sub> equivalents).

Presumably, part of the decreased acidity resulted from sulfate reduction (eq.1, tab. 1). Dissolved sulfate concentrations of samples C, D, and E were lower than samples from both the inflow and orange areas (Tab. 4). Sample D had only 41 pct of the inflow sulfate concentration. When disturbed, sediments in virtually every part of the wetland released considerable emissions of gas bubbles and the characteristic odor of hydrogen sulfide was evident. This combination hydrogen sulfide production and decreased dissolved sulfate and acidity is very strong evidence for sulfate reduction.

Once released into the water column by sulfate-reducing bacteria, H<sub>2</sub>S has several possible fates. In acidic water, ionization is low (Eq. 2 in Tab. 1) and H<sub>2</sub>S can escape from the wetland as a gas. Under alkaline conditions, ionization potentially results in significant concentrations

of both HS<sup>-</sup> and S<sup>2-</sup>. These dissolved sulfides can be oxidized to elemental sulfur by oxygen (Eq. 3) or react with ferrous iron to form monosulfides or pyrite (Eq. 5 and 6c, respectively). Secondary reactions of elemental sulfur can result in polysulfides (Eq. 4) and pyrite (Eq. 6a and 6b). All of these products precipitate and thus remove iron and sulfide from solution. Iron monosulfides oxidize very quickly in aerobic environments and decompose in acidic solutions to ferrous iron and hydrogen sulfide (reverse of eq. 2 and eq. 5). Pyrite and elemental sulfur also oxidize to sulfate if oxic conditions develop, but neither is soluble in the sulfuric acid that gives AMD its acid character.

Currently, judgments about the relative importance of each of these sulfur-containing compounds in this constructed wetland cannot be made. However, it is certain that sulfide reduction in excess of that required for iron sulfide formation is occurring. Water samples in black areas had, on average, 2.5 mm/L (millimoles per liter) less iron than inflow water. If all this iron was removed by formation of monosulfides and pyrite, 2.5-5.0 mm/L of sulfide would have been required. Sulfate concentrations in the black areas averaged 9.0 mm/L less than inflow samples. Thus, at least 4.0 mm/L of reduced sulfur must have been either released as gaseous H<sub>2</sub>S, or retained in the wetland in a reduced form not associated with iron.

Except when we disturbed the sediments by walking in the wetland, we noticed little odor of hydrogen sulfide. This observation may be explained by the alkaline conditions that exist in the organic substrates and which should cause ionization of H<sub>2</sub>S to the dissolved sulfide forms. If losses of sulfide as H<sub>2</sub>S are not major, then retention and accumulation of reduced sulfur in the organic substrates must be occurring. We evaluated this hypothesis by analyzing samples of the organic substrate for sulfur content (LECO sulfur analyzer) and sulfur form (evolved gas analysis). Mushroom compost in its original form has a sulfur content of about 1.5 pct, most of which is in the sulfate form. All substrate samples collected from this wetland have contained more than 2.0% sulfur, and we have measured total sulfur contents as high as 10.2 pct for black particulates filtered from wetland water samples. The organic substrate filtered from sample D was 3.2 pct sulfur. Evolved gas analysis (Fig. 2) of this sample showed that most of the sulfur was elemental with subordinate

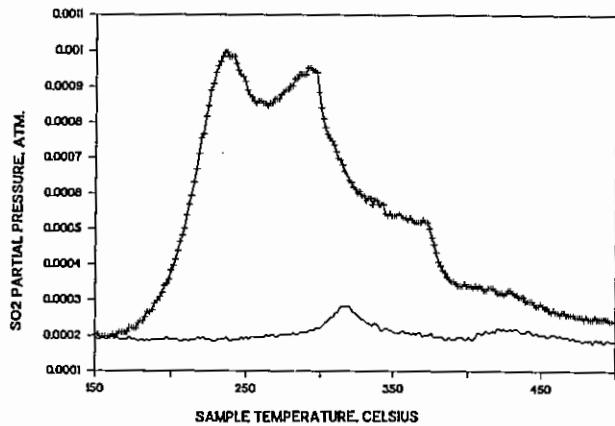


Figure 2.--Evolved gas analyses of fresh mushroom compost (lower line) and substrate samples collected from the constructed wetland (upper line). The wetland sample was collected from the substrate surface at location D. The plotted lines indicate evolution of  $\text{SO}_2$  as the samples were heated from  $50^\circ\text{C}$  to  $1000^\circ\text{C}$  (only the  $150\text{--}500^\circ\text{C}$  range is shown).  $\text{SO}_2$  evolution temperature ranges for important sulfur forms are: reduced and elemental sulfur,  $150\text{--}300^\circ\text{C}$ ; carbon-bonded sulfur,  $300\text{--}350^\circ\text{C}$ ; pyritic sulfur,  $375\text{--}425^\circ\text{C}$ ; sulfate,  $800\text{--}900^\circ\text{C}$ . The fresh compost sample had a very large peak in the sulfate range that is not shown.

amounts of organic sulfur that co-evolved with aliphatic hydrocarbons. The presence of elemental sulfur was confirmed with XPS and X-ray diffraction. Elemental sulfur was not present in the original compost material (Fig. 2). Pyrite, which is indicated by peaks between  $380^\circ\text{C}$  and  $420^\circ\text{C}$ , was not found. This was not unexpected because the samples were collected from the surface of substrates overlain by shallow oxygenated water. Authigenic pyrite (pyrite formed in place, not transported) is not stable in such an oxidizing environment.

Based on the high iron and reduced sulfur concentrations observed in the wetland, pyrite would be expected to form in anaerobic areas. We tested this prediction by collecting one sample from  $15\text{--}20\text{ cm}$  deep in the organic substrate (location F in Figure 1). The sampling area was a black pool, and the pH of disturbed water after sampling was greater than  $6.0$ . Evolved gas analysis of the solid organic material revealed the presence of large amounts of elemental sulfur, as well as a smaller amount of pyritic sulfur (Figure 3). The identification of pyrite was confirmed with X-ray diffraction analysis. Although we have not performed experiments yet to ascertain that this pyrite is authigenic (versus being washed in from surrounding spoils), we believe that the environmental conditions, as well as the pyrite's location in the organic substrate argue strongly for an authigenic origin.

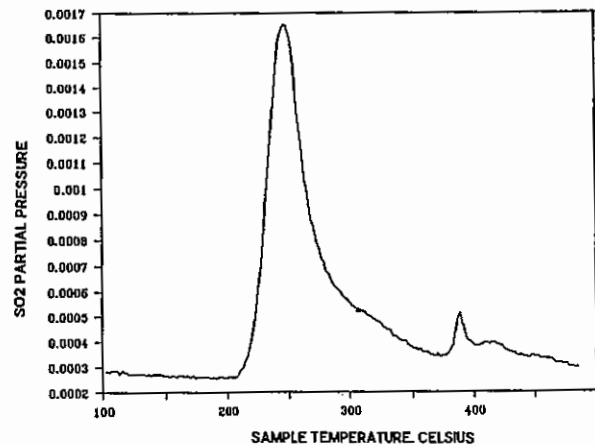


Figure 3.--Evolved gas analysis of organic substrate collected  $15\text{--}20\text{ cm}$  deep in the constructed wetland. The peak at  $390^\circ\text{C}$  indicates pyrite, while the larger one at  $250^\circ\text{C}$  is elemental sulfur.

## DISCUSSION

Many biogeochemical processes interact to cause the amelioration of AMD chemistry as it flows through a natural or constructed wetland. Sulfate reduction and pyrite formation, though often cited as the desirable, ultimate sink for iron removal in constructed wetlands, have received little research attention. The results in this paper illustrate the dramatic chemical changes associated with reducing zones in a newly constructed wetland.

These processes also would appear to have important advantages over other mechanisms of AMD amelioration. Unlike oxidation processes, which produce acidity, sulfate reduction produces alkalinity (Eq. 1 in Tab. 1). Sulfate reduction and pyrite formation processes are not constrained by accumulation limits or toxic effects. Hydrogen sulfide is a waste product of dissimilatory sulfate-reducing bacteria that is expelled, not accumulated. Pyrite formation occurs for solubility reasons (Howarth 1979) or because of chemical transformations in existing inorganic sulfur compounds (Berner 1984, Altschuler et al. 1983). These processes contrast with bioaccumulation or chelation/adsorption processes. Many wetland plants can remove metals from solution, however, accumulation is generally limited by toxicity factors (Kearney and Wieder, elsewhere in these proceedings). Organic matter, such as peat, has a well documented tendency to accumulate metals, but it is constrained by adsorption limitations (Wieder and Lang 1986).

Pyrite may also be preferable over the iron oxyhydroxides that form by oxidation and hydrolysis reactions for several reasons. It accumulates within the organic substrates and is less likely than surface deposits of iron oxyhydroxides to be flushed out of the wetland during storm events. As

long as pyrite stays in a reducing environment, it is insoluble in AMD. Iron oxyhydroxides can be resolubilized if the drainage becomes more acidic. Pyrite is a quite dense compound whose accumulation would not be expected to change flow or mixing regimes. Iron oxyhydroxides are not as dense, and by accumulating on the surface can fill the wetland and deleteriously effect flow and mixing patterns.

Presently we are unable to estimate the importance of reducing reactions as compared to oxidizing reactions and plant uptake in this wetland. However, if reduction processes are to be maximized in constructed wetlands, it is likely that designs must be reconsidered. Currently, most constructed wetlands have very high surface:volume ratios which maximize aeration of water. The result is surface conditions that are conducive for oxidation and hydrolysis reactions and, potentially, the formation of voluminous iron oxyhydroxides on top of the organic substrate. This blanket must interfere with mixing of surface and subsurface water. Over time, oxidation and reduction processes likely become more disconnected, and the possibility exists that the importance of reducing reactions will decrease. Design features that maximized flow through anaerobic environments might be more effective in the long term. For example, if inflow pipes were positioned at the base of the wetland, water would be forced to rise through anoxic organic matter, presumably stimulating sulfate reduction and pyrite formation. When water reached the surface, it would then be "polished" by oxidation and hydrolysis reactions. This bottom flow system has natural analogies in the New Jersey Pine Barrens where sulfate entering *Sphagnum* wetlands in the groundwater is removed by reduction reactions before it reaches the surface (Spratt et al. 1987).

#### CONCLUSIONS

Reducing environments represent major iron and sulfur sinks that are not being exploited in most wetlands constructed to treat AMD. Compared to water in oxidized zones of this wetland, water in reducing zones has substantially lower concentrations of sulfate, iron, and acidity, while organic substrates are enriched with elemental sulfur and, at depth, are accumulating pyrite. However, these conditions do not exist throughout the wetland, and a considerable flow of water is through oxygenated, surface channels which do not markedly change water chemistry. Wetland builders should consider design features that increase flow through reducing environments, while researchers must determine what factors effect the rates of sulfate reduction and pyrite formation in these wetlands.

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