



# WETLAND TREATMENT FOR TRACE METAL REMOVAL FROM MINE DRAINAGE: THE IMPORTANCE OF AEROBIC AND ANAEROBIC PROCESSES

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## ABSTRACT

When designing wetland treatment systems for trace metal removal, both aerobic and anaerobic processes can be incorporated into the final design. Aerobic processes such as adsorption and ion exchange can successfully treat neutral drainage in overland flow systems. Acid drainage can be treated in anaerobic systems as a result of sulfate reduction processes which neutralize pH and precipitate metals.

Test work on both aerobic and anaerobic systems has been conducted in Minnesota. For the past three years, overland flow test systems have successfully removed copper, cobalt, nickel and zinc from neutral mine drainage. Nickel, which is the major contaminant, has been reduced around 90 percent from 2 mg/L to 0.2 mg/L. A sulfate reduction system has successfully treated acid mine drainage for two years, increasing pH from 5 to over 7 and reducing concentrations of all metals by over 90 percent.

Important factors to consider when designing wetlands to remove trace metals include not only the type of wetland required but also the size of the system and the residence time needed to achieve the water quality standards.

## KEYWORDS

Copper, cobalt, nickel, zinc; ion exchange; sulfate reduction; adsorption; acid mine drainage; passive treatment.

## INTRODUCTION

Acid mine drainage is a serious environmental problem. Thousands of miles of streams have been affected by acid drainage from both coal and metal mines (U.S. Bureau of Mines 1985). Acid drainage associated with metal mines contains elevated concentrations of the metals associated with the ore body. These metals, in addition to the acid, can pose dangers to downstream human and aquatic communities. Although this type of drainage can be chemically treated in an active treatment plant, this is an expensive and longterm commitment, particularly since drainage problems can persist for over a hundred years.

An alternative approach to chemical treatment is the development of "passive" technologies. These types of treatment systems tend to be lower in cost and maintenance and often employ natural processes to remove contaminants. Wetland treatment of mine drainage is a common example of passive treatment. Wetlands have been effective in removing iron from coal drainage, and metals from metal mine drainage.

In wetlands, a variety of processes are responsible for metal removal. These include a mixture of chemical, biological, and microbiological reactions which occur in the aerobic and anaerobic zones of wetlands. Mine drainage can be treated with both aerobic and anaerobic processes in constructed wetlands, although the type of drainage that can be treated and the resulting water quality will vary. This variation in results is due to the different processes that occur in the aerobic and anaerobic zones. This paper will discuss the aerobic and anaerobic processes as they relate to the treatment of metal mine drainage using results from test systems constructed in Minnesota.

### AEROBIC PROCESSES

In most wetlands where there is free water surface, aerobic conditions exist throughout the water column, but conditions quickly change to anaerobic below the soil surface. However, if the water level is below the soil surface, the area of the soil above the water level is also aerobic. In addition, when vegetation is present, an aerobic zone exists around the roots of each plant as the plant transports oxygen to its roots (Grosse 1989, Michaud and Richardson 1989). This occurs even when the roots of the plant are totally submerged.

In coal mining applications, wetlands are typically constructed so that flow occurs across the surface of an organic substrate which has been planted with cattails; and treatment occurs in the aerobic zone (Wieder 1989, Hedin 1989). Iron removal primarily occurs through the oxidation of ferrous iron to ferric iron and the subsequent removal as a ferric oxyhydroxide. Although this reaction removes iron, it also reduces pH.

For neutral metal mine drainage, wetland systems similar to those used for coal drainage can effectively remove low levels of metals from the drainage (Eger 1992). Removal occurs primarily in the aerobic zone through a variety of reactions including adsorption, chelation, and ion exchange. Ion exchange reactions often involve the exchange of a hydrogen ion for the metal ion, therefore causing pH to decrease. As pH decreases, the efficiency of the aerobic processes decreases. In laboratory studies, metal removal decreased by over 50% as pH decreased from 7.4 to 4.0 (Lapakko and Eger 1988).

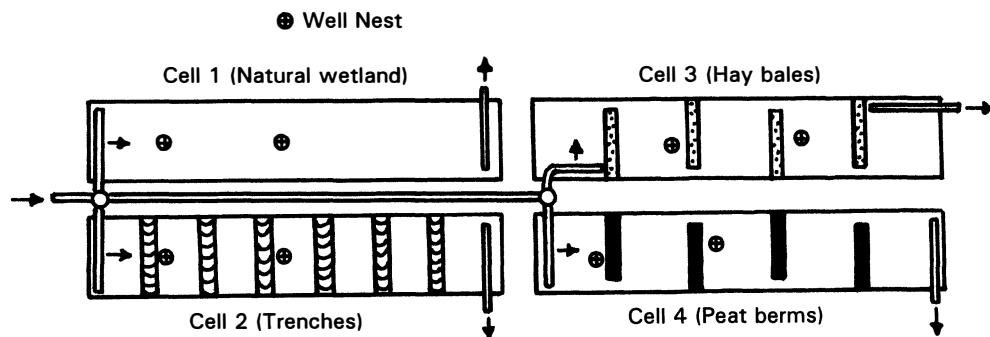


Fig. 1. Design schematic of wetland treatment cells.

A study to investigate the ability of natural wetland systems (free water surface wetlands) to remove trace metals, primarily nickel, from neutral mine drainage was initiated in 1989 at the Dunka Mine in northeastern Minnesota. Four cells were designed so that a variety of water levels, vegetation, and flow regimes could be tested (Figure 1). Each cell was 6 metres wide x 30.5 metres long and was surrounded by a compacted peat berm. To hydrologically isolate the cells, a sand-bentonite cutoff ditch was installed in the center of the berms surrounding each cell (Eger *et al.*, 1991a, 1991b).

Nickel concentrations into the cells have ranged from 0.11 to 3.8 mg/L. In 1991 the average nickel concentration of the input water was 2.0 mg/L. The drainage has an average hardness of around 2300 mg/L as  $\text{CaCO}_3$  and a pH range of 6.5-7.9. Copper and zinc generally meet water quality criteria, while cobalt and nickel routinely exceed the criteria, sometimes by more than an order of magnitude.

## Results

The purpose of this paper is to summarize some of the results and relate metal removal to aerobic processes occurring in the wetland. A more detailed discussion of the results can be found in earlier reports (Eger *et al.*, 1991a, 1991b, 1992).

TABLE 1. Nickel Removal in Wetland Treatment Cells, 1989-1990

Cell	Description	Vegetation	Water Level (cm)	Outflow Concentration (mg Ni/L)	Concentration Reduction %	Mass Removal %
1	unmodified natural wetland	primarily grasses and sedges	5	0.10	85	83
2	modified wetland with trenches	primarily grasses and sedges	5	0.09	87	86
3	modified wetland serpentine flow straw addition	cattails with open water	15	0.23	66	68
4	modified wetland serpentine flow	dense stand of cattails	15	0.46	32	40

Mean input nickel concentration 0.66 mg/L (range 0.11-2.1 mg/L).

Nickel, which was the major contaminant in the drainage, was removed in all cells. In general, removal increased as the depth of water above the peat surface decreased and the residence time in the cell increased. When the water level was on the order of 5 cm and residence time exceeded 24 hours, nickel concentrations were generally reduced by 80-90%, and the overall mass removal of nickel exceeded 80% (Table 1).

When the water depth was about 15 cm, there was insufficient contact between the stockpile drainage and the peat. Tracer studies conducted with a rhodamine dye demonstrated that there was much less interaction with the surface in the deep water cells than in the shallow cells (Figure 2). Since the rhodamine is surface active, the lower recovery of dye in the shallow cells indicated a higher degree of surface interaction in the shallow water cells.

As the water flowed through the cells, the outlet pH was about 0.1-0.2 pH units below the inlet pH. This decrease is due in part to the exchange of metal ions for hydrogen ions on the peat surface. In laboratory adsorption experiments conducted with mine drainage and peat, pH decreased by as much as 3 pH units (Lapakko *et al.* 1986).

Nickel removal occurs primarily through the interaction of the drainage with the peat surface. Preliminary data collected on the peat in the test cells demonstrated that nickel concentrations have increased substantially since the study began. Prior to the study, nickel concentrations in the top 20 cm of the wetland were on the order of 100-200 mg/kg, while in the samples collected in 1991, concentrations had increased to over 1000 mg/kg. Additional samples were collected during the winter of 1992. These will be segmented and extracted sequentially to determine the depth and form of metal removal occurring in the wetlands.

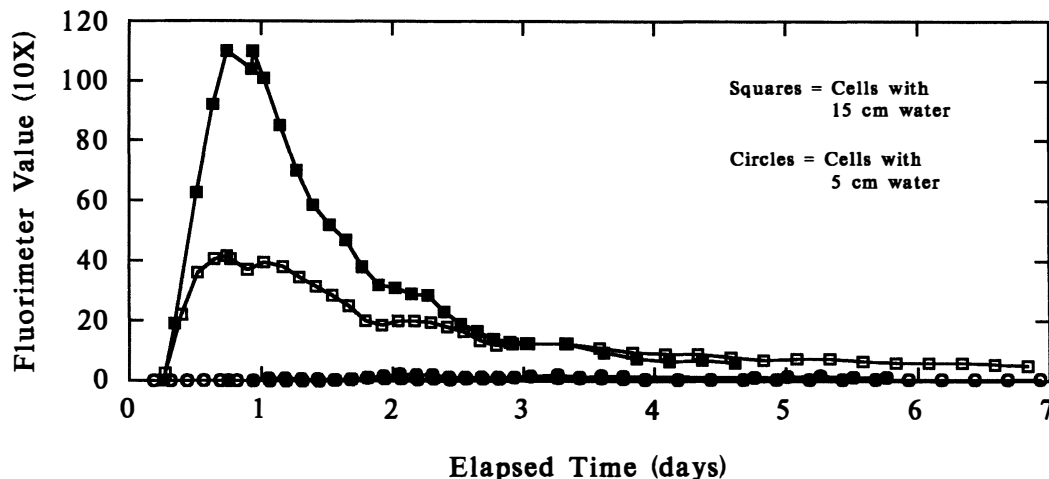


Fig. 2. Results from 1990 dye study of wetland treatment cells.

Metal concentrations were also measured in the vegetation in the test cells. Average nickel concentrations in cattails ranged from 15 mg/kg in the leaves to 247 mg/kg in the roots. In general, those concentrations are similar to those found around the Inco Smelter in Sudbury (Taylor and Crowder 1981). Although vegetation does accumulate metals, most of the metal removal in these systems occurs through interaction with the peat substrate. Mass balance calculations for a white cedar (*Thuja occidentalis*) wetland, which also received stockpile drainage at the Dunka mine, indicated that over 90% of the metals removed were associated with the peat, while less than 1% were associated with the vegetation (Eger and Lapakko 1988).

Anaerobic zones do exist in free water surface wetlands, but metal removal reactions are concentrated in the aerobic zone primarily because of the limited transport of contaminants to the deeper anaerobic zones of the wetland. In general, most of the flow in wetlands occurs across the surface or within the upper 30 cm of the wetland (Romanov 1968). There is generally little to no hydraulic gradient down into the peat, and the hydraulic conductivity of the peat decreases as depth and degree of decomposition increases. Transport into the anaerobic zone is controlled by diffusion and is very slow.

#### Designing free water surface wetlands

Designing aerobic wetlands to treat mine drainage requires characterization of the drainage to be treated, the wetland, and operational constraints (for example, regulatory standards). Metal removal capacities must be determined for the metals of interest, either through laboratory studies or through field investigations.

In our study, annual nickel removal rates varied from 22 to 66 mg/m<sup>2</sup>/day. Metal removal occurred at residence times as low as 18 hours, but to meet water quality standard consistently, residence times greater than 48 hours were required.

Using data generated from the test cells, two full-scale free water surface wetlands were designed to treat drainage at the Dunka Mine (Eger and Melchert 1992, Frostman 1992). The area of the wetland was determined from the following:

$$\text{Area of wetland (m}^2\text{)} = \frac{\text{nickel load from stockpile (mg/day)}}{\text{nickel removal rate in wetland (mg/m}^2\text{/day)}}$$

For a neutral drainage with 5 mg/L nickel and an average flow of 76 L/min, an area of 6300 m<sup>2</sup> would be required.

## ANAEROBIC PROCESSES

In most wetlands anaerobic conditions develop in the saturated zone, below the soil/water interface. Although exchange reactions can still occur in the anaerobic zone, the primary reaction of importance for metal removal is sulfate reduction. Sulfate reduction reactions cannot only remove metals but can also increase pH, and therefore can treat acid mine drainage effectively. The reactions involved can be represented as follows:



Complex organics are reduced to simpler organics by bacteria. These simpler organic compounds can then be utilized by the sulfate reducing bacteria. Sulfate reducing bacteria are ubiquitous and tolerate a wide range of environmental conditions. Their optimal pH range has been reported to be from 5 to 9, but they can control their microenvironment even when the bulk solution pH is below 5. Successful sulfate reduction has been reported for a drainage with a pH as low as 2.6 (Bolis *et al.* 1991). Although anaerobic zones exist in natural wetlands, the peat material itself breaks down very slowly. Therefore, although sulfate reduction reactions occur, they are quite slow. By constructing a wetland within a more reactive organic substrate, reaction rates can be increased significantly. This organic substrate has typically been waste material.

TABLE 2. Water Quality Results, Sulfate Reduction Treatment, 1990-1991

Row	Average Concentrations <sup>1</sup> , mg/L					Water Quality Standards
	Input	1	2	3	4	
Organic Substrate	NA	municipal compost	composted yard waste	manure+ sawdust <sup>2</sup>	compost, sawdust <sup>3</sup>	NA
Parameter						
pH	5.2	7.4	7.6	7.2	7.2	6.5-8.5
alkalinity	4	1360	440	620	1110	NA
acidity	50	160	40	130	150	NA
copper	7.3	0.10	0.05	0.06	0.06	0.023
nickel	24.5	0.12	0.12	0.12	0.11	0.21
cobalt	1.2	0.04	0.04	0.04	0.04	0.05
zinc	1.4	0.13	0.04	0.05	0.06	0.34
sulfate	820	250	630	580	370	NA

<sup>1</sup> By titration; recent data indicates that these values are low since metal precipitation is not instantaneous, and neutralization reactions were not complete when acidity was measured.

<sup>2</sup> 10 kg. horse manure to 1 kg sawdust, wet weight basis.

<sup>3</sup> 2 barrels municipal compost followed by 1 barrel sawdust.

NA Not applicable.

Spent mushroom compost has been commonly used in constructed wetlands in the eastern United States (Wieder 1989). Recent experiments in Colorado and Arkansas have used other local waste products such as steer manure, rice hulls, and chicken litter as the substrate (Howard *et al.*, 1989, Gross *et al.*, 1991). The U.S. Bureau of Mines is also investigating the use of waste materials for supplementing the substrate and thereby increasing the rate of sulfate reduction (Hammack 1991).

A pilot scale sulfate reduction system was installed in northeastern Minnesota to treat acid mine drainage in 1990. Four different local organic materials were selected for this test: 45-day-old municipal compost, screened composted yard waste, mixed hardwood sawdust, and horse manure. These materials were chosen for their suspected ability to support sulfate reduction, their availability, and their lack of contaminants.

Mine drainage with a pH of around 5 and containing 26.0 mg/L of nickel, 7.7 mg/L of copper, 1.2 mg/L of cobalt, and 1.4 mg/L of zinc was used as the input to the system. Sulfate concentrations were on the order of 800 mg/L. This drainage was fed to four rows of three 55-gallon barrels (connected in series), each containing organic material.

By maintaining the organic substrates in a saturated condition and forcing the mine drainage to flow through the substrate, anaerobic processes can dominate the treatment. Although all substrates supported sulfate reduction, the highest rate occurred in the municipal compost where removal rates ranged from 7 to 27 g/day. All substrates not only supported sulfate reduction but also elevated pH and removed trace metals. The pH of the drainage was increased from around 5 to greater than 7 while trace metal concentrations were decreased by over 90% (Table 2). Although other processes may be responsible for removing metals, the sulfate reduction reaction is responsible for the overall change in drainage quality.

#### Design of wetlands to promote sulfate reduction

For metal removal to occur in the anaerobic zone of a wetland, the wetland must be constructed to force flow through this zone. This generally requires a vertical flow either up or down through an organic substrate. Although water can be transmitted horizontally through a bed of organic substrate, it is more efficient to induce vertical flow, since the hydraulic head can be more easily controlled and is much larger in a vertical system. For a comparable sized wetland, a vertical system can be designed to transmit at least 10 times more water through the anaerobic zone than a similar sized horizontal system (Table 3). Typical hydraulic conductivity reported for organic substrates are in the range of  $10^{-3}$  to  $10^{-4}$  cm/sec but tend to decrease with time as decomposition occurs (Wildeman *et al.*, 1991). As the hydraulic conductivity of the substrate decreases, the hydraulic head would have to be increased to maintain the same flow through the system.

TABLE 3. Comparison of Flow Through the Anaerobic Zone of a Wetland

Flow	gradient	flow/unit cross-sectional area of wetland liters/minute/1000 m <sup>2</sup>
horizontal	0.01-0.02 <sup>a</sup>	8-16
vertical	.33 <sup>b</sup>	200

a gradient based on natural slope of wetland.

b gradient controlled by a head of water on the wetland, calculation assumes .33 meter of water on an anaerobic zone, 1 meter thick.

Once sufficient flow occurs through the anaerobic zone, a sulfate reduction wetland can be designed by balancing the rate of sulfate reduction occurring with the input rate of metal and acid. If the sulfate reduction system was 100 percent effective at removing metals, then one mole of sulfate would be reduced for each mole of divalent metal precipitated (Equations 1, 2). The removal of each mole of aluminium and ferric iron requires 1.5 moles of sulfate reduction. Aluminium does not form a stable sulfide in the presence of water, and therefore aluminium removal probably occurs due to the formation of a hydroxide:



To neutralize the acid generated by this reaction requires that 1.5 moles of sulfate be reduced (Equations 1, 2). Ferric iron ( $\text{Fe}^{+3}$ ) could be removed as a hydroxide, but removal probably occurs through the reduction of ferric iron to ferrous iron and subsequent precipitation as a divalent metal sulfide (Dvorak *et al.* 1991):



To remove one mole of ferrous iron, one mole of sulfate must be reduced; and to neutralize one mole of acid, one-half mole of sulfate must be reduced (Equation 1). Therefore, to remove all the metals and acid in the input, the required rate of sulfate reduction can be calculated from:

$$\text{Required rate of sulfate reduction} = \text{mmole divalent metals in input (M}^{+2}) + 1.5 \text{ mmole Al}^{+3}, \text{Fe}^{+3} + 0.5 (1000 \times 10^{-\text{pH}}) \quad (5)$$

For the drainage in this study, copper, nickel, cobalt, and zinc are the major contaminants. They account for about 90% of the total sulfate reduction required to treat the input water.

Designing a system to treat acid mine drainage successfully will require that the input load of metals and acid always be less than the sulfate removal rate. The minimum size of the system would be determined by:

$$\begin{aligned} \text{Volume of organic substrate} = & \frac{\text{input divalent metal load, mmole/day} \\ & + 1.5 \text{ aluminium and ferric iron load} \\ & + 0.5 \text{ input (m}^3\text{)acid load, mmole/day}}{\text{sulfate removal rate, mmole/day m}^3} \end{aligned} \quad (6)$$

In an actual design, a safety factor should be employed since sulfate removal, metal and acid input, and hydraulic conductivity will vary with time. For a well designed treatment system, both metal loading and hydraulic loading must be compatible with the size of the system.

## CONCLUSIONS

Aerobic processes occurring in wetlands can remove metals from neutral mine drainage. These processes are limited by the amount of available exchange sites in the substrate and by the transport of contaminants to these sites. Aerobic processes cause pH to decrease and are less effective at removing metals as solution pH decreases.

Anaerobic processes are effective in not only removing metals but also in elevating pH. This is the best treatment for acid mine drainage. Systems designed for anaerobic treatment can handle a higher volume of flow than similar sized aerobic systems, but flow rates through the substrate may decrease over time as the substrate decomposes.

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