ACID MINE WATER TREATMENT USING ENGINEERED WETLANDS

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ABSTRACT

During the last two decades, the United States mining industry has greatly increased the amount it spends on pollution control. The application of biotechnology to mine water can reduce the industry's water treatment costs (estimated at over a million dollars a day) and improve water quality in streams and rivers adversely affected by acidic mine water draining from abandoned mines.

Biological treatment of mine waste water is typically conducted in a series of small excavated ponds that resemble, in a superficial way, a small marsh area. The ponds are engineered to first facilitate bacterial oxidation of iron; ideally, the water then flows through a composted organic substrate that supports a population of sulfate-reducing bacteria. The latter process raises the pH. During the past four years, over 400 wetland water treatment systems have been built on mined lands as a result of research by the U.S. Bureau of Mines. In general, mine operators find that the wetlands reduce chemical treatment costs enough to repay the cost of wetland construction in less than a year.

Actual rates of iron removal at field sites have been used to develop empirical sizing criteria based on iron loading and pH. If the pH is 6 or above, the wetland area (m^2) required is equivalent to the iron load (grams/day) divided by 10. Theis requirement doubles at a pH of 4 to 5. At a pH below 4, the iron load (grams/day) should be divided by 2 to estimate the area required (m^2).

INTRODUCTION

Mining companies, reclamation groups and various researchers are currently cooperating in a number of studies to evaluate the use of constructed wetlands as low-cost, low-maintenance treatment systems for acid mine drainage (AMD). As a result of observations at natural wetlands (Huntsman, Solch and Porter, 1978; Wieder and Lang, 1982), subsequent pilot-scale tests (Kleinmann and others, 1983; Burris, Gerber and McHerron, 1984) and full-scale field trials, over 400 wetland water treatment systems have been built on mined lands. Early constructed wetlands were planted with *Sphagnum*, in an attempt to simulate natural bog-type wetlands. Experience gained in the field has led to the more prevalent use of emergent plants, especially cattails (*Typha*), and greater consideration of the biogeochemical processes that occur in the substrate materials.

Most of these biological water treatment systems have been constructed to treat acidic coal mine drainage, as opposed to the effluent water from metal mines. The principal contaminants of concern have been excessive acidity, iron, manganese and aluminum. The processes that take place within the constructed wetlands include: adsorption and ion exchange, bioaccumulation, bacterial and abiotic oxidation, sedimentation, neutralization, sulfate reduction and possibly formation of carbonate minerals. In general, these processes have been quite effective in removing iron, but inconsistent with respect to other water quality parameters. The removal of most of the iron eliminates much of the need for chemical treatment, but does not, by itself, eliminate its necessity. Indeed, only about 20 pct of the constructed wetland systems discharge water that completely meets the U.S. effluent limits of no net acidity, pH 6-9, average total iron $\leq$ 3 mg/L and average total manganese $\leq$ 2 mg/L. At most sites, supplemental chemical treatment is necessary, but the chemical treatment costs are much lower than they would be if biological treatment had not been utilized. In fact, most operators find that the costs of constructing the wetlands are recovered within one year through savings in chemical usage.

Most constructed wetlands include a 15-45 cm thick layer of an organic substrate in which the emergent plants can root. Organic material should be well composted before emplacement. Spent mushroom compost, a waste product of mushroom farming, has become a widely utilized organic substrate.

Constructed wetland systems usually consist of a series of several shallow pits or cells. This design makes flow control much easier than with a single large wetland. The cells are filled with organic substrate, planted with *Typha*, and flooded with mine drainage. In most systems, water depth is 5-15 cm above the substrate and most flow is above the substrate. Hay bales and logs are sometimes used as flow barriers to promote a serpentine flow pattern, prevent channelization, and increase the contact of AMD with the wetland substrate and vegetation.

The size and design of constructed wetlands depends on the flow volume and chemistry. Initially, 5 m^2 of wetland was thought necessary to treat each L/min of drainage but in a survey of the effectiveness of 1-2-year-old constructed wetlands, it was observed that the best performing systems had 15 m^2 of wetland for every L/min flow (Girts, Kleinmann and Erickson, 1987). This ratio was based on mine water with total iron concentrations less than 50 mg/L. As wetlands are now being built to receive much higher iron loadings, it has become necessary to consider the interaction of flow, pH and metal concentrations. Work still in progress indicates that at pH 6, 100 m^2 of wetland area is required to remove 1 kg of iron per day. At a pH of 4 to 5, twice as much area is required for an equivalent loading rate. At pH 3, this requirement increases to 500 m^2 per kg of iron per day (Hedin and Nairn, 1990). It should be emphasized that these values are based on conventional surface flow wetland systems designed primarily to remove iron. If the wetland is also expected to improve pH and/or lower manganese concentrations, even more space is required.

HOW CONSTRUCTED WETLANDS FUNCTION

In most of the constructed systems, the principal metal-removal mechanism appears to be bacterially-catalyzed oxidation of iron. Subsequent hydrolysis precipitates the metal as the familiar orange sludge that quickly blankets the substrate surface. Manganese-oxidizing bacteria are also present and active in the wetland system, but generally have negligible effect on manganese concentrations unless the pH is above 6. Aluminum is generally only removed when the pH is raised sufficiently to initiate hydrolysis.

The processes of adsorption, ion exchange and complexation with organic material also play a role in metal removal. Wieder and Lang (1986) estimated that adsorption and organic complexation processes can remove 33 mg of iron per gram (dry weight) of *Sphagnum*. During the first few months of operation of a new wetland system, adsorption and complexation by the substrate helps compensate for limited initial biological activity. However, once these capabilities are exhausted by saturation, only the addition of new organic material by plant growth supplements this mechanism of metal removal. This productivity is not sufficient to remove a significant amount of metals in currently sized wetlands.

Accumulation of metals by growing plants varies considerably depending on the metal and the plant in question. *Sphagnum* has a tremendous ability to accumulate iron, but if exposed to even moderate concentrations of iron, it absorbs so much metal that it petrifies (Spratt and Weider, 1988). *Typha* is much more tolerant of mine water precisely because it is not as efficient in accumulating metals. Sencindiver and Bhumbla (1988) calculated that the bioaccumulation of 19,506 μg of iron per gram of *Typha* rhizome at a site receiving 10 mg/L Fe accounted for only 0.2 pct of total annual inflow of iron. Bioaccumulation of manganese by *Typha* was even less significant.

Algae also accumulate iron and manganese. When calculated on a dry weight basis, the resultant accumulated concentrations appear to be quite impressive. Kepler (1986) measured concentrations as high as 56,000 mg of manganese per kg (dry weight) of algae in samples of *Oscillatoria*. We have collected numerous *Microspora* samples that contain, on a dry weight basis, 30,000 - 90,000 mg/kg of manganese. However, algae biomass in a wetland is very limited, so that its contribution to metal removal will rarely reach significant levels.

Calculations show that very productive algal systems accumulating manganese at 50,000 mg/kg would still only remove 4 mg/L of manganese from AMD, assuming currently-sized wetland systems (Hedin, 1989).

Plants and organic substrate do, however, provide sites for bacterial attachment and colony development. In addition, the large surface area to volume ratio of most wetlands enhances aeration of surface waters, which is often a prerequisite for the bacterial oxidation of metals. Emergent plants are also capable of aerating the sediments by releasing oxygen from their roots. *Typha* roots are often coated with iron oxyhydroxides, which some researchers believe is due to plant-induced oxygenation of the rhizosphere and the activity of iron-oxidizing bacteria (Taylor, Crowder and Rodden, 1984; Sencindiver and Bhumbla, 1988). Finally, the organic detrital material and the carbon excreted by plants provide food for heterotrophic metal-oxidizing bacteria in the aerobic zone and for sulfate-reducing bacteria in the anaerobic bottom waters. Bacterial sulfate reduction and metal sulfide formation in the organic-rich substrate can contribute significantly to improvements in water quality.

The relative importance of sulfate reduction was uncertain for some time due to contradictory observations in *Sphagnum* wetlands and constructed *Typha* wetlands. The sulfide and elemental sulfur content of *Sphagnum* peat substrate exposed to AMD for 30 years was determined to be only 0.58 mg/g (Wieder and Lang, 1986). In contrast, much higher concentrations have been found in *Typha* wetlands constructed with a composted organic substrate. At one site, after only eighteen months of operation, the anaerobic substrate contained 8.5 mg/g reduced sulfur, most of which was in the iron monosulfide form. The iron content of these reduced substrate samples averaged 40 mg/g. Dissolved sulfide concentrations in the pore waters ranged up to 500 mg/L.

Bacterial sulfate reduction is potentially very important to the long term prospects for constructed wetlands. As opposed to the voluminous blanketing sludge that results from the oxidation and hydrolysis of the iron, iron sulfide precipitates are more dense and form within the substrate. The processes involved are the reverse of pyrite oxidation; in fact, acidity is consumed. Finally, unlike bacterial oxidation processes, which are not effective in removing most heavy metals, hydrogen sulfide produced by bacterial sulfate reduction reacts with many metals to form virtually insoluble sulfide compounds. This makes it possible to extend biological treatment to mine water contaminated with various heavy metals.

In most of the wetlands constructed to treat coal mine drainage, flow is predominantly above the substrate, so that only a small fraction of the water passes through the anaerobic zone. The water in the substrate is markedly different from the overlying surface water a few centimeters higher. For example, in the pore waters, the pH is 3-5 units higher and dissolved iron concentrations can be 50-99 pct lower. The Bureau of Mines is currently experimenting with wetland designs that utilize subsurface flow to expose a higher proportion of the water to be treated to the anaerobic zone. Preliminary results from a site with water of pH less than 3, acidity values of 1,000 mg/L (as $CaCO_3$), and iron concentrations of 150-200 mg/L, indicate that promoting flow through the anaerobic zone raised the pH of the water to near-neutral, generated alkalinity (up to 500 mg/L), and decreased iron concentrations to 20 mg/L. Sulfate reduction rates were determined to be approximately 200 nmol/cm^3 per day, which is comparable to rates found in coastal marine sediments (McIntyre and Edenborn, 1990). Engineering problems associated with inducing subsurface flow must be resolved if this process is to be incorporated into the constructed wetland technology.

POTENTIAL APPLICABILITY TO METAL MINE DRAINAGE

When extending the results from coal mines in the eastern United States to the possible treatment of metal mine effluent waters, one consideration is the effect of high metal concentrations on wetland performance. Regarding tolerance, the literature is encouraging. *Typha latifolia* can tolerate copper concentrations up to 50 mg/L and nickel concentrations greater than 150 mg/L without difficulty (Taylor and Crowder, 1983a). *T. latifolia* shoots grown in a solution of 100 mg/L Cu (as an EDTA complex) accumulated 127 $\pm$ 28 g/g Cu in their leaves and 2,364 $\pm$ 209 g/g Cu in their roots, but displayed reduced leaf growth when the copper concentrations in the leaves reached 80 g/g (Taylor and Crowder, 1983b; Taylor and Crowder, 1984). *Typha* has been reported growing in a mine water marsh where the sediment contained 3,738 g/g Cu and 9,372 g/g Ni (Taylor and Crowder, 1983b). Kalin and Van Everdingen (1987) have successfully demonstrated that *Typha* can be transplanted into acid water with a pH range of 2.9 to 5.7, a mean zinc concentration of 221 mg/L and a mean copper concentration of 21 mg/L. However, hydroponic transplantation has been unsuccessful (Kalin, 1988). Other wetland plants may be somewhat less metal-tolerant. For example, cadmium retarded the growth of *Sphagnum fimbriatum* at 0.1 mM (11 mg/L) but not at 0.01 mM. Lead at 1 mM (207 mg/L) strongly retarded the growth of *Sphagnum fimbriatum* but was tolerated at this concentration by *Fetusca ovina* and *Hordeum vulgaris* (Gignac and Beckett, 1986; Lee, Jonasson and Goodfellow, 1984). Certain algal species can also tolerate significant concentrations of lead, copper and zinc (Gale, 1985; Kalin, 1988).

Bioaccumulation of metals, though potentially significant in slightly contaminated waters, is biomass-limited. Metal uptake by wetland plants has been reviewed by Chan and others (1982); cited plants include pickleweed (*Salicornia pacifica*), which can remove 0.016 to 0.024 kg Cd/ha, reed canary grass (*Phalaris arundinacea*), which can remove 0.69 kg Cu/ha and a sedge (*Carex stricta*) which can remove 0.67 kg Ni/ha. For the more toxic metals, bioaccumulation may actually cause problems, for it could result in the chronic poisoning of foraging animals.

Metal removal by sulfate reduction appears to be much more promising. Although sulfate reducing bacteria are inhibited at low pH, their activity increases the pH in their immediate environment, allowing their activity in the sediments beneath extremely acidic waters (Herlihy and others, 1987; Satake, 1977). Recent work in our laboratory indicates that sulfate reducing bacteria are also tolerant of high heavy metal concentrations. Preliminary screening tests indicate that the sulfate-reduction potential is not inhibited by nickel, lead or zinc concentrations as high as 60 mg/L. Important information about the sulfate reducing bacteria must still be determined, such as the rate of hydrogen sulfide generation, sensitivity to parameters such as temperature and water chemistry fluctuations, and the nature of organic compounds required for their activity. The latter is critical because partial breakdown of the organics by fermentative bacteria will probably be necessary; their tolerance and sensitivity may be important also.

It should be recognized that precipitation of sulfide minerals is only going to continue if there is sufficient organic matter to maintain an anaerobic environment. If seasonal decay of emergent species and the excretion of organic compounds by plants is inadequate, then periodic addition of selected organic materials may be necessary. The nature of this requirement will be tested in the near future. If, however, one can afford to periodically add organics, there are potential advantages to biological treatment without wetlands, especially for metal mine drainage. First, the areal requirements can be reduced, for instead of a shallow system, one can emphasize depth. For example, an abandoned pit could serve as the primary biological treatment basin. Second, seasonal variations in performance could be minimized. It may be possible to treat mine water in a pipeline-type reaction vessel filled with composted organic waste; presumably, this could even be done inside of an active or abandoned section of an underground mine. In regions with long, harsh winters or limited land surface, or if bioaccumulation becomes a concern, both approaches would be preferable to a constructed wetland approach. During the next few years, in addition to our wetland studies, we will be evaluating the feasibility of treating metal mine drainage biologically, without wetlands.

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