

# IRON REMOVAL FROM ACID MINE DRAINAGE IN WETLANDS BY OPTIMIZING SULFATE REDUCTION<sup>1</sup>

by  
Martin C. Rabenhorst, Bruce R. James, Mark C. Magness  
and Joey N. Shaw<sup>2</sup>

**Abstract.** Mesocosm scale wetlands were constructed to evaluate the efficiency of iron removal by sulfate reduction under various acid mine drainage (AMD) flow rates. Based on the results of previous experiments to evaluate the optimal wetland substrate for sulfate reduction, the mesocosms were filled with a mixture of barley straw and composted manure. A simulated AMD with pH 3.0 and Fe levels of 1 mM was passed through the mesocosms at flow rates of 1, 3, and 10 cm/day (which corresponded to approximately 6000, 2000, and 600 ft<sup>2</sup>/gallon/min, respectively.) The AMD was forced to flow through the wetland substrate using a gravity flow system. Various chemical parameters were measured periodically on porewater samples collected at incremental depths from the interior of the mesocosm, as well as on the effluent. These analyses included pH, pe, Fe, and soluble S<sup>2-</sup>. Porewater analyses indicated that all mesocosms had a more oxidized and acid zone near the surface, the thickness of which became greater as the flow rate increased. Sulfide levels of up to 5 mM were measured in the lower portions of the columns which corresponded to conditions of higher pH and lower pe. In zones where sulfide was abundant, soluble Fe levels dropped below 1 ug/mL, thus Fe added in the influent was being effectively removed. Dissection and visual examination of the sediments confirmed that Fe sulfides had formed in the sediments. Under the fastest flow rate (10 cm/day), the thickness of the acid-oxidized zone became progressively greater with time as an "oxidizing front" appeared to progress down the mesocosm. After approximately 12 months, the oxidizing front had extended nearly to the bottom of the mesocosm (100-135 cm) and Fe levels in the effluent began to rise. Under the slower flow rates, Fe continued to be completely removed by sulfidization.

## Introduction

Over the last decade, reclamation researchers have been constructing wetlands to treat acid mine drainage (AMD) but have met with mixed results. The wetland processes previously identified as having potential for removing metals from AMD include: ionic sorption of metals; biologic plant uptake of metals; complexation of metals by organic materials; formation and precipitation of metal

"oxides" (oxides or oxy-hydroxides); precipitation of metals as sulfides through microbial reduction of sulfate to sulfide (Kleinmann 1987; Hedin 1989).

The only two processes which have any long-term potential for metal removal are precipitation as either oxides or sulfides, the others having been shown to be relatively insignificant or to have a finite capacity (Sencindiver, and Bhumbala, 1988; Henrot and Wieder, 1990; Wieder, 1988; Wieder, and Lang, 1986). Recent efforts at utilizing oxidation and precipitation of iron as oxy-hydroxides as a mechanism for treating acid mine drainage has focused on the use of anoxic limestone drains (Skousen, 1991; Nairn et al., 1992). Because of the typically low redox potentials associated with wetlands and wetland sediments, they provide a poor environment for the formation of iron oxides. It was therefore the underlying premise of this project, that if wetlands have any serious future for treating AMD, they must utilize sulfate reduction.

<sup>1</sup>Paper presented at the 1993 National Meeting of the American Society for Surface Mining and Reclamation, Spokane, Washington, May 16-19, 1993.

<sup>2</sup>Martin Rabenhorst is Associate Professor of Pedology, Bruce James is Associate Professor of Soil Chemistry and Mark Magness and Joey Shaw are Graduate Research Assistants, Dept. of Agronomy, Univ. of Maryland, College Park, MD 20742.

Until the last couple of years, most researchers studying AMD wetlands have largely discounted sulfate reduction as an important mechanism (Wieder, 1988; Henrot, et al., 1989; Henrot and Wieder, 1990; Stillings, et al., 1988; Wieder and Lang, 1986; Wieder and Lang, 1985). More recently researchers have begun to demonstrate the role of sulfate reduction in wetlands designed to treat AMD. Using mainly columns and reactors, several researchers have been focusing on the removal of trace metals such as Co, Cu, Cd, Ni, Pb, and Zn, as sulfides (Staub and Cohen, 1992; Eger, 1992; Hammack and Edenborn, 1991; Dvorak et al., 1991). Others are now invoking sulfate reduction as important in field scale wetlands, although direct evidence is not always available (Duddleston et al., 1992.) The factors necessary for sulfate reduction have been well documented and include sulfate reducing bacteria, a source of sulfate, a source of organic matter for bacterial metabolism, and a reducing environment (Pons et al, 1982; Rickard, 1973).

The objectives of this project were: 1) to develop laboratory scale model wetlands to evaluate the potential of sulfate reduction for treating AMD in wetlands; and 2) to evaluate the impact of influent AMD flow rate on metal removal efficiency through sulfidization.

### Methodology

#### **Mesocosm Design and Sediment Type**

The laboratory scale wetlands (mesocosms) were constructed from PVC tubing 0.30 m in diameter and 1.5 m high. The substrate used for the wetland "sediment" was a 1:1 straw:manure mixture (on dry weight basis). On a volume basis, the bulk of the mixture comprised barley straw with a relatively small component of a composted, and partially dehydrated cow manure. Details concerning the composition of the straw and manure are given in Rabenhorst et al. (1992). The mixture of materials was packed to approximate the density and porosity of straw bales and the mesocosms were filled to a depth of 1.35 m at a dry density of 0.12 Mg/m<sup>3</sup>. Sampling ports were installed to allow the extraction of the sediment porewater at depths of 5, 10, 15, 20, 30, 40, 50, 75, 100, and 135 cm.

#### **AMD Composition and Flow Rates**

A simulated acid mine drainage (AMD) was prepared in the lab which contained 1 mM Fe, 10 mM SO<sub>4</sub><sup>2-</sup>, and which had a pH of 3.0. The simulated AMD was passed through the mesocosms following the schedule shown in Table 1. The rates were chosen to bracket the flow rates commonly

recommended in design criteria (Girts and Kleinmann, 1986; Hedin and Nairn, 1990).

#### **Sampling and Analytical Procedures**

Sediment porewater was basically collected at two week intervals, although some analyses were conducted at a greater or lesser frequency. Porewater samples were analyzed for pH (by glass electrode), pe (using a Pt electrode), sulfide (using colorimetric procedures of Cline (1969), and APHA (1985) and soluble iron was determined by atomic absorption spectroscopy.

### Results and Discussion

#### **Iron Levels in Sediment Porewater**

Pronounced trends with depth were evident in the levels of soluble Fe measured in the sediment porewaters. These trends were also related to the system flow rate and to time. The soluble Fe depth functions for the mesocosms under the different three flow rates and at five different times are shown in Fig. 1, 2, and 3. In nearly all instances, the soluble Fe concentrations were greatest near the surface where the influent entered the system, and then decreased with depth. At the slowest flow rate of 1 cm/day (Fig. 1), fairly high Fe levels (10-30 ug/mL) were maintained with depth throughout the first 50 days. After 100 days, however, the levels of soluble Fe were quite low. The presence of measurable soluble sulfide (Figs. 4 and 5) suggested that the reason for the decrease in Fe levels was the precipitation of the Fe in a solid sulfide phase.

The depth at which the Fe level approached zero increased with time, going from 10 cm to 15 cm to 20 cm at 100, 200, and 300 days respectively. This trend suggested a slowly advancing "front" which may have represented a boundary between an oxidized zone (where the Fe-sulfides were not stable) and reduced portion of the mesocosm (where the Fe-sulfides were stable).

As the flow rate increased, there was a corresponding increase in the rate at which the Fe levels dropped within the mesocosms. This suggested that there may have been some component which leached from the system which allowed the Fe to be removed from solution. In earlier work (Rabenhorst et al., 1992) it was similarly noted that greater flow (and leaching) rates enhanced sulfate reduction in columns filled with hay and straw in the early stages of operation. Figures 4 and 5 similarly illustrate that, particularly at greater depths (75 and 100 cm), the levels of soluble sulfide were dramatically higher under the

Table 1. Flow rates used in this experiment and their various equivalent flow parameters.

cm/d	L/min/m <sup>2</sup>	L/day <sup>a</sup>	m <sup>2</sup> /L/min	ft <sup>2</sup> /gal/min	MRT <sup>b</sup> days	Fe loading gdm <sup>c</sup>
10	0.069	7.070	14	586	11	5.6
3	0.021	2.121	48	1953	36	1.7
1	0.007	0.707	144	5860	108	0.6

<sup>a</sup>This is based on use of a 30 cm diameter mesocosm.

<sup>b</sup>MRT=Mean residence time of AMD in the mesocosms; this is based on a 1.35 m height, an assumed porosity of 80%, and piston type flow.

<sup>c</sup>gdm = grams of Fe per day per m<sup>2</sup>; based on prescribed flow rates and Fe concentrations of 1 mM (56 mg/L.)

faster flow regime. After approximately 200 days, the trend reversed, presumably after inhibitory compounds were finally leached from the more slowly flowing mesocosm.

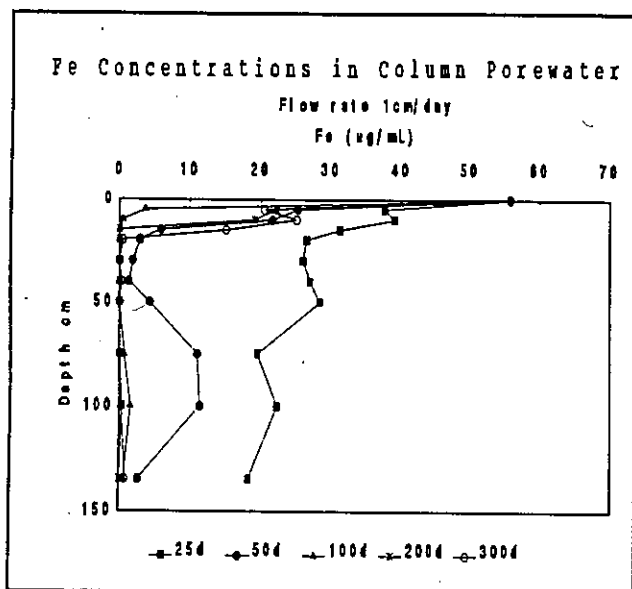


Figure 1. Iron concentrations in column porewater under a flow rate of 1cm/day as measured at various points in time.

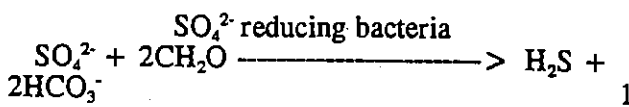
The downward progression of what appears to be an acidic oxidation front, is best illustrated in Fig. 3. There appeared to be a strongly pronounced boundary above which the Fe level approached that of the influent, and below which it dropped precipitously. This boundary appeared to be moving steadily downward and occurred at approximately 25 cm, 40 cm, 75 cm, and 100 cm at 25, 50, 100, and 200 days, respectively. This system had a flow rate of 10 cm/day. In fact, the rapid rate at which the front moved through the mesocosm suggested that for AMD with a pH of 3.0 and an Fe content of 1 mM, this rate is too great for the system to maintain effective long-term treatment.

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### pH and pe in Sediment Porewater

The trends in porewater chemistry described for Fe and sulfide concentrations, were also reflected in the parameters of pH and pe. These data are presented in Fig. 6, 7, 8, and 9. In the earlier stages of the experiment and at greater depths within the mesocosms, the pH of the porewater rose from 3.0 to values between 6 and 6.5. Under slower flow conditions (Fig. 6), these high pH values persisted (approaching 400 days) deeper in the mesocosms while they became more acid at shallower depths (after 100 to 200 days). In the high flow system (Fig. 7), the pH dropped quickly in the upper portion of the mesocosm, and even at the 75 cm depth, the pH began to drop after 200 days. These data are consistent with the idea of a downward-progressing acidic front.

In general, there appears to be an inverse relationship between the pe and the pH of the systems, with the redox potential (pe) of the porewater being much lower under the slower flow (Fig. 8) than under the high flow (Fig. 9) conditions. This is also well illustrated in Fig. 9 where the most oxidizing conditions (high pe) are associated with the shallowest depths where the pH is generally low (Fig. 7). This is a generally acknowledged phenomenon and, in these systems, can be partially attributed to the generation of bicarbonate during the sulfate reduction process (eq 1). Variations in pe measured with using Pt electrodes may be due partially to variations in pH, since Pt electrode voltages are affected by [H<sup>+</sup>].



### Conclusions

As simulated acid mine drainage moved through the mesocosm scale wetlands used in this study,

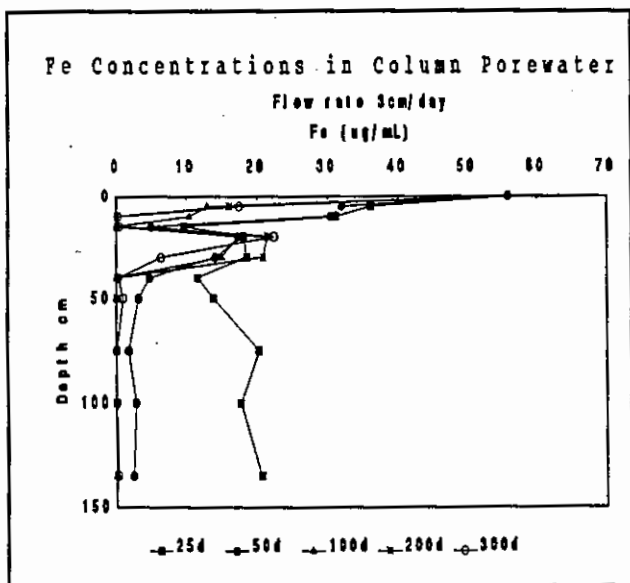


Figure 2. Iron concentrations in column porewater under a flow rate of 3cm/day as measured at various points in time.

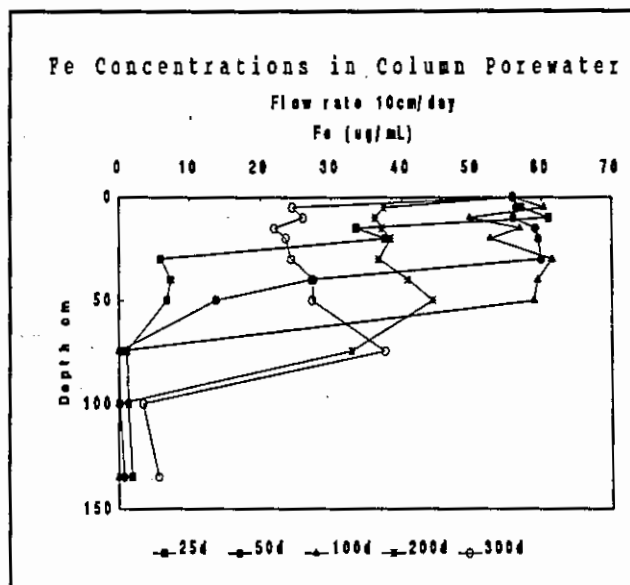


Figure 3. Iron concentrations in column porewater under a flow rate of 10cm/day as measured at various points in time.

reducing conditions developed and sulfate reducing microorganisms produced soluble sulfide. One of the effects of this process was the generation of alkalinity and an accompanying rise in pH. Because of the low solubility of Fe sulfides, soluble Fe precipitated as sulfides thereby lowering concentrations of porewater Fe. Thus, in these systems, sulfate reduction appeared to be a viable mechanism for the treatment of Fe-bearing acidic waters.

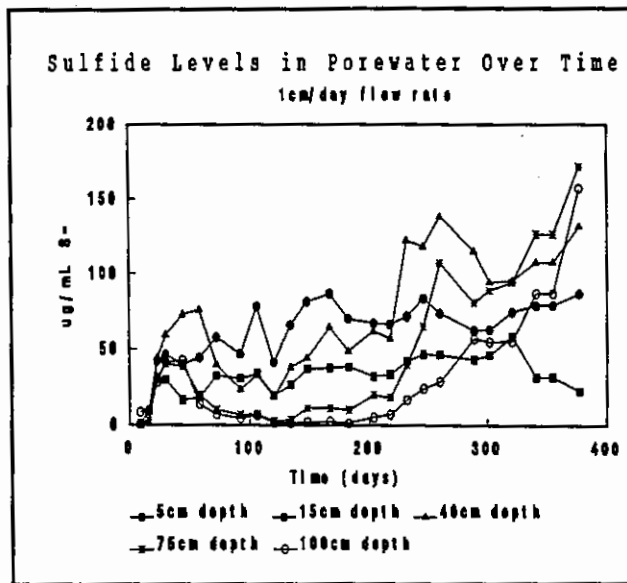


Figure 4. Sulfide levels in column porewater under a flow rate of 1cm/day. Measurements were taken at various depths over time.

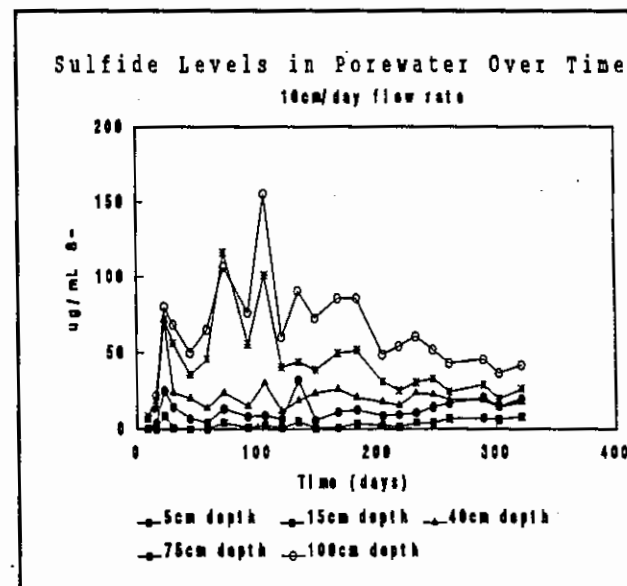


Figure 5. Sulfide levels in column porewater under a flow rate of 10cm/day. Measurements were taken at various depths over time.

Especially under high rates of porewater flow, there was evidence of an acidic oxidation front, which progressed downward through the sediment. Under the slower flow rates this effect was less pronounced. Because sulfate reduction is important within the reduced zone, but would be expected to be minimal in the oxidized zone, the observation of this front has serious implications design specifications to achieve long term viability of the wetlands.

Influent pH or metal concentrations other than those used in this experiment would also be expected to affect the efficiency of wetland operation and the development and progression of acidic oxidation fronts which warrants further investigation of these parameters.

### Acknowledgements

This work was supported in part by grants from the Maryland Water Resources Research Center and the Maryland Department of Natural Resources - Bureau of Mines. The authors also wish to thank Julie Cartron, Ahmed Hussein, and Sandy Schneider who assisted in the project.

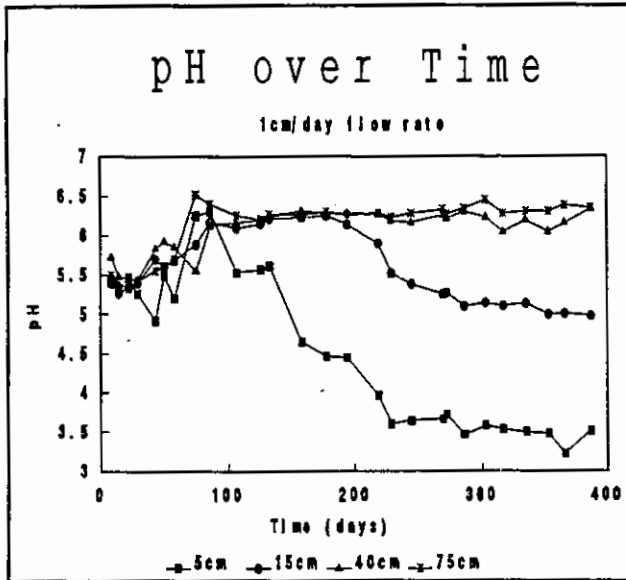


Figure 6. Solution pH in column porewater under a flow rate of 1cm/day. Measurements were taken at various depths over time.

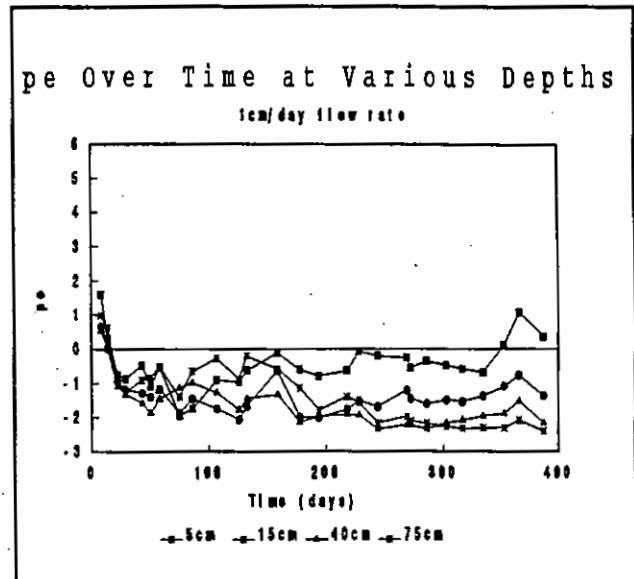


Figure 8. Solution pe in column porewater under a flow rate of 1cm/day. Measurements were taken at various depths over time.

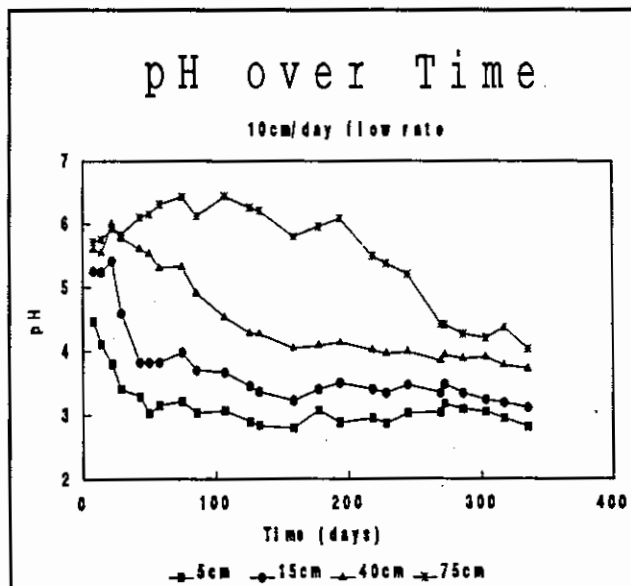


Figure 7. Solution pH in column porewater under a flow rate of 10cm/day. Measurements were taken at various depths over time.

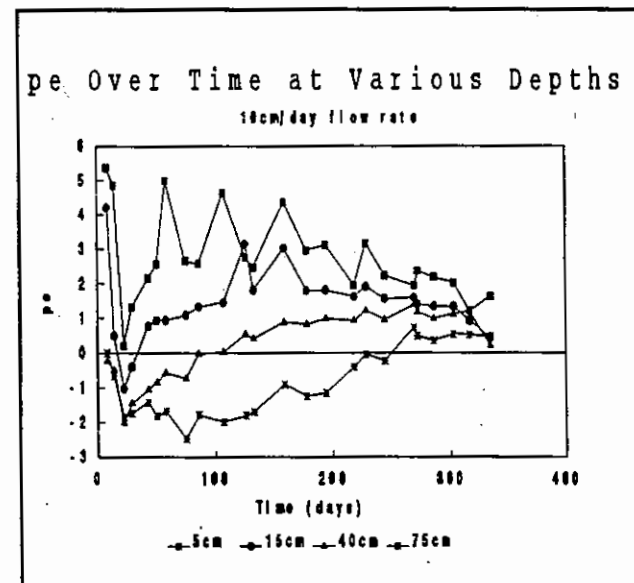


Figure 9. Solution pe in column porewater under a flow rate of 10cm/day. Measurements were taken at various depths over time.

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