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Wetland Design for Mining Operations

Thomas Wildeman

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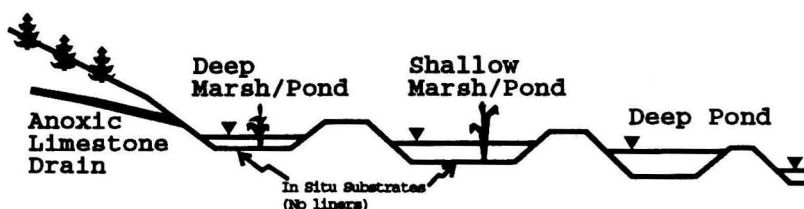
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Wetland Design for Mining Operations



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PREFACE

This volume is the fusion of two projects using constructed wetlands for the treatment of mine drainage. At the Tennessee Valley Authority, Greg Brodie and Cindy Britt have successfully developed surface style wetlands that emphasize aerobic removal processes. Also, they have developed the use of anoxic limestone drains for pretreatment of acidic waters. In Colorado, the research group at the Colorado School of Mines led by Tom Wildeman has developed subsurface wetland systems. These emphasize anaerobic processes and are useful for the treatment of drainages from metal mines that contain significant concentrations of other contaminant metals. The two wetland systems are complimentary, and use of one system or the other should be considered within the context of the specific problem.

This volume is divided into four sections. The first section concerns subsurface systems. Much of the work comes from a project at the Big Five Wetlands in Idaho Springs, Colorado that was supported by the Emerging Technologies Program of the U. S. Environmental Protection Agency. The handbook in this first section is the final report for that project. The many participants in that project are listed on the second page of the handbook. Ed Bates of the Risk Reduction Engineering Laboratory deserves special mention for his support of a technology that was unproven.

The next two sections of the volume contain the experiences of the TVA team on the development and construction of surface systems. Again, the second section is the handbook that Greg Brodie has prepared to help others construct surface style wetlands. The third section contains recent papers that he and Cindy Britt have written to update the handbook. Of particular note in this section, is the paper on anoxic limestone drains.

The fourth section contains recent papers written by the CSM group. These papers are an extension of the handbook in section I to aerobic wetlands, passive bioreactors, and systems operating in cold climates. A paper by Judy Bolis gives a good analysis of hydraulic conductivity in anaerobic reactors. Also a paper by Barb Filas gives an analysis of the regulatory aspects of wetland construction with specific reference to the Big Five Project.

This is a new technology. Developments are occurring rapidly. We anticipate that much of what is contained in this volume will be out of date in two years. Anoxic limestone drains are a good example of the type of developments that we hope will occur. Concepts, procedures, and methods introduced in this volume may or may not be useful for a specific problem situation. As a consequence, this volume was intentionally packaged in a binder so that papers that will be published within the next few years can be added to the package. These papers can be obtained from the publisher or the authors.

To use this document, we suggest to first study the table below.

WETLANDS COMPARISON

AEROBIC	ANAEROBIC
1. EMPHASIZE OXIDATION	1. EMPHASIZE REDUCTION
2. SURFACE FLOW OF WATER	2. SUBSURFACE FLOW OF WATER
3. OXIDE PRECIPITATES	3. SULFIDE PRECIPITATES
4. PROCESSES CAN LOWER pH	4. PROCESSES CAN RAISE pH
5. OPERATE BEST AT pH > 5.5	5. CAN BE EFFECTIVE AT pH ~ 2.5
6. MIGHT FREEZE IN THE WINTER	6. CAN OPERATE THROUGH THE WINTER
7. REMOVES Fe QUITE WELL	7. REMOVES OTHER HEAVY METALS QUITE WELL.

From the table it can be seen that for treatment of metals-contaminated waters, the two types of constructed wetlands compliment rather than compete. Aerobic systems are most applicable to seeps that are above a pH of 5.5 and primarily contain Fe and Mn. These conditions are often found around coal-mining operations. Anaerobic systems will work at lower pHs and have a better ability to remove heavy metals such as Cu, Zn, Cd, and Pb. These conditions are often found around metals-mining situations. In addition, aerobic systems will remove contaminants from metals-mining waters if the pH is above 6, and anaerobic systems will remediate severely contaminated coal mine waters that have pHs below 3. Depending upon the treatment situation, begin with the aerobic or anaerobic handbook.

In the anaerobic handbook, Section 2 is a review of the chemistry of acid rock drainage, and Section 3 is a review of wetland processes. Turn to these chapters if ideas on chemical fundamentals are needed. Because engineering design is different for aerobic and anaerobic systems, the methods on how to proceed should initially be taken from the appropriate section. However, in both handbooks the hints on design and construction are useful and do not overlap. Consequently, when beginning a project, read the design sections from both handbooks. Jim Gusek approaches design and construction in a different manner than does Greg Brodie. Studying the contrasting styles is quite instructive.

Finally, there are concepts that are so new that time has not allowed the ideas to be integrated into the handbooks. The principles behind how an anoxic limestone drain operates, and construction and design of such structures is a good example. A paper on these drains is included in SECTION III. This section has recent papers from the TVA group. In SECTION IV, the paper by on removal of manganese contains a recently developed method on how to do laboratory and bench-scale studies on aerobic systems. Consequently, staged design can be performed on anaerobic or aerobic systems. Also, a recently completed study on how hydraulic conductivity of substrates in anaerobic systems changes with time is the most extensive project on this topic to date. The preliminary results of this study are contained in SECTION IV. Papers published after the beginning of 1993, can be obtained from the authors or the publisher.

All the participants in these wetland projects have had an exciting time developing a technology that helps the environment in two ways, by remediating one resource while creating another resource. It is a strongly interdisciplinary activity. We hope that you have as great a time learning and interacting with your colleagues as we have had.

GENERAL CONTENTS

SECTION I: ANAEROBIC CONSTRUCTED WETLANDS HANDBOOK

Final Report EPA-ETP Big Five Wetland Project. Edited by Thomas Wildeman
The complete Table of Contents, including Figures and Tables are on pp. iii - xiii of that section.

SECTION II: AEROBIC CONSTRUCTED WETLANDS HANDBOOK

Staged, Aerobic, Wetlands-Based Acid Drainage Treatment Systems: Design, Construction, and Operation. Written by Gregory A. Brodie
The complete Table of Contents is on p. ii of that section.
The Appendices are in Section III.

SECTION III: SUPPLEMENTARY PAPERS FOR THE AEROBIC CONSTRUCTED WETLANDS HANDBOOK

1. Staged, Aerobic, Constructed Wetlands to Treat Acid Drainage - Case History of Fabius Impoundment I and Overview of the Tennessee Valley Authority's Program; G. A. Brodie
2. Anoxic Limestone Drains to Enhance Performance of Aerobic Acid Drainage Treatment Wetlands - Experiences of the Tennessee Valley Authority; G. A. Brodie, C. R. Britt, T. M. Tomaszewski, and H. N. Taylor

SECTION IV: SUPPLEMENTARY PAPERS FOR THE ANAEROBIC CONSTRUCTED WETLANDS HANDBOOK AND RECENT PAPERS ON NEW WETLAND CONCEPTS

1. The Use of Bench Scale Permeameters for Preliminary Analysis of Metal Removal from Acid Mine Drainage by Wetlands; J. L. Bolis, T. R. Wildeman, and R. R. Cohen,
2. Determination of the Rate of Sulfide Production in a Constructed Wetland Receiving Acid Mine Drainage; J. S. Reynolds, S. D. Machemer, T. R. Wildeman, D. M. Updegraff, and R.R. Cohen,
3. Hydraulic Conductivity of Substrates used for Passive Acid Mine Drainage Treatment; J. L. Bolis, T. R. Wildeman, and H. E. Dawson.
4. The Aerobic Removal of Manganese from Mine Drainage by an Algal Mixture Containing Cladophora; L. A. Duggan, T. R. Wildeman, and D. M. Updegraff.
5. The Use of Wetlands for Improving Water Quality to Meet Established Standards; B. A. Filas, and T. R. Wildeman.
6. Constructed Wetlands that Emphasize Sulfate Reduction: A Staged Design Process and Operation in Cold Climates; T. R. Wildeman, L. A. Duggan, J. L. Bolis, and J.J. Gusek.

Wetland Design for Mining Operations

Section I

FINAL DRAFT, FEBRUARY 1, 1993

**HANDBOOK FOR CONSTRUCTED WETLANDS
RECEIVING ACID MINE DRAINAGE**

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FINAL DRAFT, FEBRUARY 1, 1993

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John Dietz: Section 6

Susan Morea: Section 8

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PART A

THEORETICAL DEVELOPMENT

SECTION 1

INTRODUCTION

In the summer of 1987, a pilot constructed wetland was built at the Big Five Tunnel in Idaho Springs, CO. This is among the first pilot systems to receive metal-mine drainage. Accounts of the first year of operation are contained in recent publications of the wetlands research group at the Colorado School of Mines (3, 4, 5, 6, 7, 8, 9, 10, 11, 12). The second and third year of operation of this wetland was funded by the U. S. Environmental Protection Agency under the Emerging Technologies Program. One of the objectives of this EPA project is to publish a practical handbook on the theory, design and construction of wetlands for receiving mine drainages.

In 1988, two milestone conferences were held on mine drainage and constructed wetlands. In April of 1988 a conference on Mine Drainage and Surface Mine Reclamation was held in Pittsburgh. The program chairman, R. L. P. Kleinmann assembled an excellent group of mine drainage and constructed wetlands papers that were published as U. S. Bureau of Mines Circular 9183 (1). In June of 1988, the International Conference on Constructed Wetlands for Wastewater Treatment was held in Chattanooga, TN. Dr. Donald A. Hammer served as the program chairman for this conference. The proceedings of this conference were published in late 1989 (2). The groups from the U. S. Bureau of Mines and the Tennessee Valley Authority should be considered among the founders in the use of constructed wetlands for mine drainage.

The monographs by Kleinmann and Hammer have made the production of this handbook quite a bit easier. Much of what is contained in the following pages is an assimilation of the individual papers in those two monographs. The primary contribution from the Big Five Study is to put into practice on a metal-mine drainage the ideas that were developed during those conferences. Also, we find that our study has generated much fundamental research on wetland processes and design, and these results are integrated into this handbook. Finally, many triumphs and pitfalls have been encountered during this project and it is hoped that our experiences will smooth the route for the others who are considering constructing a wetland.

What is contained in this handbook is evolutionary. The comments and criticisms of others in the field of wetlands research and construction are most appreciated.

HANDBOOK ORGANIZATION

The text is divided into two broad sections:

- o Part A - Theoretical Development,
- o Part B - Design Considerations.

Although the above titles designate the material in each part, there are other differences between them. Part A represents the effort to initiate the project and comprehend the meaning of contradictory results.

Whereas Part B dictates how to carry out the project given 20/20 hindsight. Because of this, Part A appears to have gaps in the experiments, data, and results. On the other hand, Part B looks much more polished. These gaps in Part A are real because it relates how things happened. Determining predominant removal processes in a wetland is difficult because the system is not easy to sample and processes are interrelated. If, in the course of reading Part A, inconsistencies appear, take heed. They mark places where much discussion and positioning among the members of the research team took place before the proper insight was gained. It's presumed that others might have problems similar to those encountered on this project. These gaps mark places where caution should be exercised. If there is another edition of this handbook, the technology will probably have advanced to the point where it looks as if there are no problems in designing wetland treatment systems. By writing Part A in the style of how things happened, this handbook records those problems.

In addition to a more narrative style for Part A, other features have been included to broaden the scope of the handbook. Among these features are:

- o A review of mine drainage chemistry in SECTION 2 that emphasizes the similarities between coal and metal-mine effluents.
- o A review in SECTION 3 of aerobic and anaerobic wetland removal processes that gives extensive references.
- o An exposition in SECTION 7 of the units associated with wetlands technology that includes how loading factors are determined within different disciplines.

The exposition on units is an admission that no matter how hard the technical community tries, people from different disciplines will use units that give them the best grasp of the fundamental properties. When a technology is reasonably comprehended, then proper units will be established. Until then, a development of the differences is helpful.

In the latter sections of Part A and through all of Part B the focus is on removal of metals by precipitation of sulfides through the activity of sulfate-reducing bacteria. Design of aerobic wetlands that emphasize the oxidation of Fe and Mn and their subsequent precipitation as hydroxides is not included in this handbook. To investigate the design of aerobic systems, the reader is best advised to refer to the papers by Brodie and Britt (55, 68, 69, 72, 117).

SECTION 2

CHEMISTRY OF ACID MINE DRAINAGE

Acid mine waters are not new. Their production was noted in Roman times, and their possible toxicity was reported by Agricola in De Re Metallica (Nordstrom, U. S. Geological Survey, personal communication, 1989). Research on the refinement of the causes for acid mine drainage production is also not new. Most of the important ideas on the mechanism of production were generated in the 1960's and 1970's. The primary reactants are pyrite, water, and ultimately oxygen; and important catalysts are bacteria, particularly Thiobacillus ferrooxidans. Since many of the ideas on the cause of acid mine drainage were established about a decade ago, they can be found in texts and monographs that are often easier to locate than the primary literature sources. This review will draw extensively on these secondary sources so that the reader can more readily augment this paper. For each section, the useful monographs will be cited.

To define the subject, Table I shows the concentrations of constituents that are routinely determined in coal mine drainages, the constituents in a comparable metal mine drainage, the abundance ranges of these elements in coals, and the maximum contaminant levels for public drinking water. The references to the data are noted at the bottom of Table 1. For the coal information, the monographs by Bouska (13) and Valkovic (14) are useful. Manahan (15) gives a good explanation of the environmental effects of each constituent.

Although, from different regions and geologies, it is reasonable to consider that the drainage chemistries of the waters in Table 1 are similar. For the coal mine drainages, the concentrations of the major contaminants are quite similar in the Illinois and Kentucky coal regions and these compare well with the values for the whole United States. In the EPA document on effluent limitations for coal mining (16), tests were made on whether drainages from Western U. S. coal mines and anthracite mines should be separate categories, and no case could be made for subcategories. The Big Five Tunnel (3) is a metal-mine drainage and the concentration of most of the constituents fall well within the ranges for United States coal-mine drainages. Consequently, there appears to be reasonable cause to group all acid mine drainages together rather than split the waters into a number of categories. If this is done, then differences from the usual chemistry can be more successfully investigated.

Prodan, Mele, and Schubert (17) give means, standard deviations, minimum values, and maximum values for 110 effluents from abandoned coal refuse sites in Illinois and the numbers give a good indication of how far waters range from the median values and the ranges reported in Table 1. For the metal and coal mine drainages, the concentrations of Fe, Mn, Al, and $\text{SO}_4^{=}$ are in the same range. For a coal seam, the possibility of large abundances of Cu, Zn, Cd, Pb, and As exists. However, other than the EPA document (16), data on concentrations of these constituents in effluents are difficult to find. These

heavy metals do exist in metal mine drainages, and Wildeman (20) reviews the possibility of heavy metals in coal mine drainages.

In this section the geochemistry of the weathering of pyrite will be developed and this will be

Table 1. Concentrations of environmentally important constituents in acid mine drainages and in coal. For waters, the concentrations are in mg/L; for coal, in ppm.

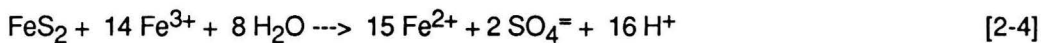
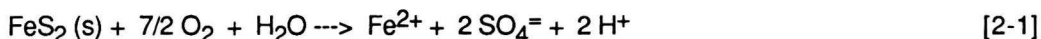
Substance	Coal Mine Drainage				Drinking	
	United States	Illinois	Kentucky	Big Five Tunnel	Water Standards	Coal
Al	--	37	—	18	—	14000
Fe	0.6 - 220	57	50 - 500	50	0.3	16000
Mn	0.3 - 12	6.4	—	32	0.05	100
Cu	0.01 - 0.17	—	—	1.6	1.0	19
Zn	0.03 - 2.2	—	—	10.	5.0	39
Cd	0.01 - 0.10	—	—	0.03	0.01	1.3
Pb	0.01 - 0.40	—	—	0.01	0.05	16
As	0.002 - 0.20	—	—	0.02	0.05	15
pH	3.2 - 7.9	3.0	1.8 - 3.5	2.6	6.5 - 8.5	---
SO ₄ ⁼	--	1300	500 - 12000	2100	250	---
Ref.	1	2	3	4	5	6

1. The 10 to 90 % concentration range of 23 acid drainages from coal mines throughout the United States taken from the EPA effluent limitations document (16).
2. Median of 110 drainages from coal refuse disposal sites in Southern Illinois compiled by Proudman, Mele, and Schubert (17).
3. Regional estimates from Caruccio and co-workers (18).
4. A typical metal mine drainage from the Front Range Mineral Belt of Colorado collected by Wildeman and Laudon (3).
5. Compiled from the U. S. Code of Federal Regulations (19). For mine drainages, effluent limits in mg/L are: Fe, 7.0 daily maximum, and 3.5 monthly average; Mn, 4.0 daily maximum, and 2.0 monthly average; pH between 6.0 and 9.0 at all times. For the other substances in the table, there are no written restrictions (16).
6. Average of United States coal compiled by Valkovic (14).

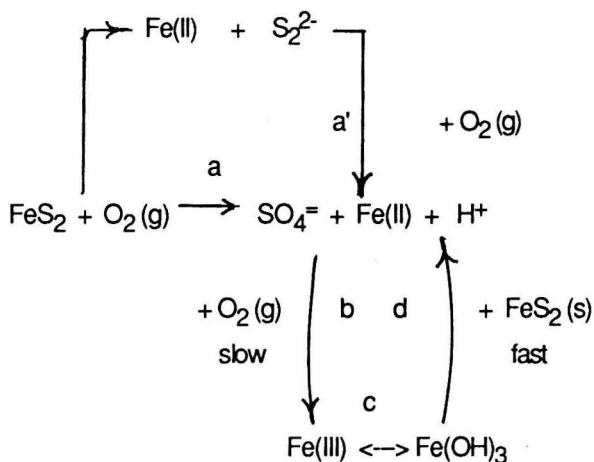
related to the weathering reactions of the minerals responsible for the other contaminants in mine drainage. The chemistry of mine drainages from the Central City Mining District in Colorado will be used as an example of how the weathering reactions are interrelated. Finally, the role of hydrology in the production of acid mine drainage will be reviewed.

PYRITE OXIDATION

In coal mining situations, pyrite is the mineral that is responsible for acid drainage problems. This same mineral is also the cause of the problems in metal mining situations. Understanding how pyrite weathers is essential to understanding the causes of the problem and the relations between coal and metal-mining pollution problems. Stumm and Morgan (21) review the chemistry of pyrite weathering and the following description is summarized from their text. The overall stoichiometric reactions are:



The accepted reaction path for the dissolution of pyrite is:



Key features of the stoichiometry and reaction path are:

- 1) Weathering is by oxidation. Since pyrite formation only occurs in a reducing environment, oxygen

gas from outside the deposit is the ultimate oxidant.

- 2) Hydrogen ions are produced by the oxidation. For every mole of pyrite oxidized, two moles of H^+ are produced by the oxidation to sulfate (Reaction 1), and two moles of H^+ are produced upon the precipitation of ferric hydroxide (Reactions 2 and 3).
- 3) Since ferric hydroxide is so insoluble, pyrite oxidation is among the most acid producing of all weathering reactions.
- 4) The slow step in the reaction path is oxidation in solution of Fe(II) to Fe(III). Sulfur oxidation is relatively rapid.
- 5) Once the weathering has produced Fe(III), this species can rapidly oxidize pyrite as shown in Reaction 4 and Step d of the reaction path. Therefore, Fe(III) cannot persist in the presence of pyritic minerals.
- 6) Step a and step d can be separated in time and space to enable the production of acid drainage from different environments.

Microorganisms can significantly catalyze the rate of Steps a and d in the mechanism. The monograph by Erlich (22) is a good review of how weathering reactions can be mediated by bacteria. Thiobacillus ferrooxidans can accelerate the rate of Step d by orders of magnitude. Thiobacillus thiooxidans can catalyze Step a. Bacteria are necessary to increase the rate of pyrite weathering to the extent that pollution problems will occur (23, 24).

Recent studies on the stable isotope geochemistry of the sulfate in acid mine drainage have added some refinements to the pyrite weathering mechanism (23, 24). Reaction 4 is found to be a major cause of sulfide oxidation and this reaction does not directly use molecular oxygen. Therefore, flooding mine workings to eliminate air-pyrite contact may not necessarily stop pyrite weathering. Weathering could continue by bacterial mediation of Reactions 1 and 2 in the unsaturated zone in the soil, and then by reaction 4 in the flooded workings. In addition, where pyrrhotite is present along with pyrite, production of acid drainage is apparently more widespread (Kalin, Boojum Research Ltd., personal communication, 1988).

INCONGRUENT WEATHERING

The concept of congruent and incongruent reactions is important to pyrite weathering and to reactions that form other constituents in acid mine drainage (25). To demonstrate incongruence, consider manganese in coal which exists as rhodochrosite, $MnCO_3$ (14). Below pH 4, the $MnCO_3$ will react accordingly:

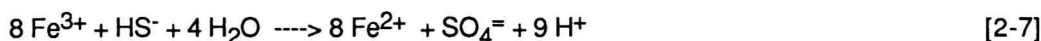


CO₂ gas can escape since it is slightly soluble in water and if this occurs, MnCO₃ can not be reprecipitated in an acidic solution. This is an example of incongruent weathering. Some other reaction or severe altering of solution conditions is necessary to cause reprecipitation of the reaction products. Reaction 5 is the basis for how Mn exists in coal mine drainages as Mn²⁺. Reactions 1 through 4 show that Fe(III) and SO₄⁼ in mine drainage cannot be changed back to pyrite through the reversal of a simple reaction.

Other sulfide minerals can weather by congruent reactions. A possible reaction for the weathering of sphalerite, ZnS, is:



However if ferric ion is present, it can oxidize the bisulfide ion in the same way as in the dissolution of pyrite:



In contact with an acid mine drainage solution, ZnS will also be weathered in a manner that cannot be easily reversed.

Tables 1 and 2 list the chemistry of some acid mine drainages. Fe, Mn, and SO₄⁼ dominate the constituents in coal mine drainages; Reactions 1-5 explain their presence. In drainages from metal and coal mines, Cu, Zn, Cd, Pb, and As are often present in amounts detrimental to the environment. Reaction 6 explains the presence in solution of these base metal cations. The presence of Al in mine drainages is best explained by acidic solutions causing the dissolution of clays (26). Groundwater hydrology, fluctuations in rainfall, and the manner of ore deposition can also affect mine drainage chemistry (27). The model for the chemistry of the Argo Tunnel is an example of what these other factors can do (26). However, Reactions 2-1 through 2-7 are basic to the system and the other factors cause secondary changes in the rate and extent of these reactions.

MINERAL ACIDITY

Of all the environmental problems related to mine drainage, the low pH is the most troublesome. Not only do the pHs of the drainages shown in Table 1 fall far out of bounds from the drinking water standards, but also increasing the pH to within the drinking water standards is necessary for long term removal of all the other pollutants. Consequently, most every pollutant removal method relies on raising the pH (3, 27). In addition, for acid-base stability of most natural water, buffering by the carbonic acid-bicarbonate-carbonate system is the most likely method (21). This begins to occur at a pH of between 5 and 6. Any effluent that is released into natural surface waters should be at a pH above 6 to insure that it will not harm the existing ecosystem.

However, the low pH is not just caused by the presence of H^+ ions. Examination of Reaction 3 shows that $Fe(III)$ hydrolyzes forming $Fe(OH)_3$ precipitate and H^+ . $Fe(III)$ should be considered an acid the same as H^+ . $Al(III)$ and $Mn(IV)$ will also strongly hydrolyze forming H^+ . Because the pH of an acid drainage depends on all these chemical factors, the term mineral acidity or just acidity is given to the situation. Acidity is operationally defined by how the analysis is conducted (29). In the analysis, hydrogen peroxide is added, the solution is boiled, and then titrated with standard sodium hydroxide to a pH of 8.2. If the water contains appreciable concentrations of Fe, Mn, and Al, the solubility products of these metal hydroxides will determine which constituents will hydrolyze by a pH of 8.2 and contribute to the acidity.

Using solubility product data from Lindsay (30), $Al(III)$, $Fe(III)$, and $Mn(IV)$ will completely hydrolyze by this pH of 8.2, but $Fe(II)$ and $Mn(II)$ at the concentrations encountered in mine drainages will still be in solution. However, $Fe(II)$ can oxidize according to Reaction 2 and $Mn(II)$ can do likewise. These constituents should be considered potential contributors to the acidity. Since the acidity analysis calls for addition of hydrogen peroxide and boiling, it is certain that $Fe(II)$ and $Mn(II)$ are oxidized to some extent and counted in the measure of mineral acidity.

Step b in the reaction path shows that the oxidation of $Fe(II)$ to $Fe(III)$ is slow and experience with the treatment of mine drainages shows the oxidation of $Mn(II)$ to be even slower (28, 31). This slow oxidation implies a long time release of mineral acidity that can cause the reversal of some treatment methods that rely on hydroxide precipitation (31). Slow oxidation is also responsible for the persistence of mine drainage conditions long after the water has breached the surface. For example, the red and roily nature of surface waters associated with mining is caused by the slow oxidation of $Fe(II)$ and its subsequent precipitation as $Fe(OH)_3$.

HEAVY METALS IN MINE DRAINAGES

The studies by Wildeman and co-workers (26, 27, 32) on the Central City Mining District in Colorado give some perspective on how pyrite affects the concentrations of contaminants in mine drainages. This district is a typical example of a zoned hydrothermal deposit of gold and base metal ores (33). The distribution of minerals from the high temperature Central Zone to the lower temperature Peripheral Zone is shown in Figure 1. The chemistry of drainages emanating from mines in the various zones is summarized in Table 2. The striking feature about the chemistry of these waters is that Cd, Zn, and Pb are in lowest concentration in the Peripheral Zone even though the ore minerals for these metals are in highest abundance in that zone. The concentration of all the contaminant metals in the drainages correlates with the abundance of pyrite in the ore. $Fe(III)$ and H^+ in the groundwater catalyze the dissolution of the other sulfides to such an extent that they become important constituents in the drainage from a metal mine even though the base metals may be in low abundance in the deposit.

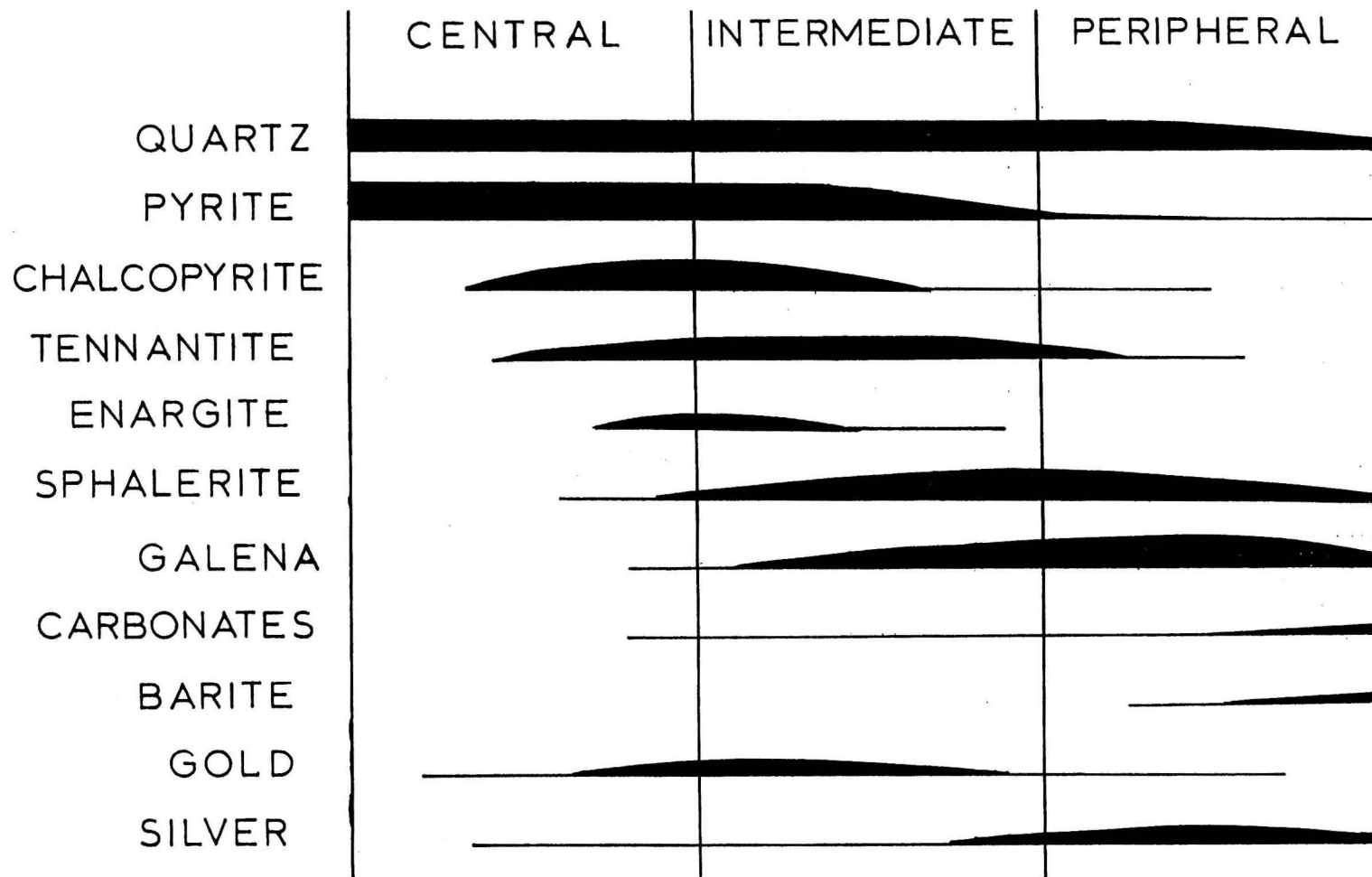


Figure 1. Minerals in the ore zones of the Central City Mining District.

Table 2. Dissolved Constituents in Mine Drainages of the Central City Mining District from Wildeman et al (32) and Wildeman (27). All concentrations are in mg/L except pH; n. d. means not detected.

Constituent	MINE DRAINAGES		
	Central Zone	Intermediate Zone	Peripheral Zone
Al	25 - 100	n. d.	n. d.
Fe	200 - 700	2 - 170	0.5 - 4
Mn	90 - 120	20 - 40	1.0 - 5.0
Cu	6 - 60	0.1 - 5	< 0.01 - 0.11
Zn	60 - 400	7 - 100	0.3 - 8.0
Cd	0.2 - 2.9	< 0.01 - 0.20	< 0.01 - 0.04
Pb	0.1 - 0.5	< 0.01 - 0.20	< 0.01 - 0.06
As	0.2 - 2.7	< 0.001 - 0.01	< 0.001
SO ₄ ⁼	2300 - 4000	900 - 1300	240 - 800
pH	2.1 - 2.7	4.0 - 6.0	5.4 - 6.9

When coal deposits are considered, all the heavy metals listed in Table 1 are associated with the pyrite and other sulfide minerals in coal and associated overburden (13, 14). Consequently, when the pyrite weathers, the products of that weathering are highly likely to release trace heavy metals from the coal. Other than the EPA document (16), it is difficult to find information on concentrations of heavy metals in coal drainages. However, Watzlaf (31) gives some insight into why trace heavy metals have generally not been measured. In the treatment of acid drainages, manganese is the most difficult metal to remove. Investigations by the Environmental Protection Agency (16) found heavy metals in untreated coal mine drainages. However, it was found that if Mn was reduced to 2 mg/L in the effluent, the heavy metals were also reduced to acceptable levels. Therefore, limitations on these metals were not promulgated, and a limitation on Mn of 2 mg/L was established. Watzlaf (31) has determined that this guideline is reasonable. However, the sludge produced is quite unstable and subject to resolubilization.

HYDROLOGY RELATED TO ACID MINE DRAINAGE

Although the presence of pyrite is definitely the key factor that determines mine drainage quality issuing from underground adits, there have been some studies that show how groundwater hydrology is involved. In a long term study of the Argo Tunnel drainage in Idaho Springs, Colorado, Wildeman (26) found that the chemistry of the water varied little with the seasons and precipitation events. To explain the

findings he used aquifer models developed to explain the chemistry of carbonate springs in Pennsylvania (34, 35). Two simple models for groundwater systems are generated: the conduit flow system and the diffuse flow system. These two models can be treated as the end members of all recharge systems. The properties that distinguish the two systems are given in Table 3. In both aquifers, recharge is from the

Table 3. Differences between Diffuse and Conduit Aquifers from Wildeman (26).

=====	
DIFFUSE	CONDUIT
=====	
1. No response to climatological change.	1. Responds to climatological changes.
2. Little fluctuation in flow.	2. Obvious fluctuations in flow.
3. No suspended solids in the water.	3. Carries suspended solids at times of high runoff.
4. Water temperature may not change throughout the year.	4. Water temperature changes with the seasons.
5. Parameters indicative of concentration such as conductivity (umho/cm) and hardness do not change with the climate.	5. Parameters indicative of concentration such as conductivity (umho/cm) and hardness show obvious changes with storms and runoff.
6. Specific concentrations of ions show little change with the climate.	6. Specific concentrations of ions show obvious changes with storms and runoff.
7. Residence time of months for the water in the aquifer.	7. Residence time of days for the water in the aquifer.
=====	

surface, through the soil vadose zone, and down to the ground water table (26). The Argo Tunnel drainage is an example of a primarily diffuse aquifer with some characteristics of a conduit aquifer.

A surprising characteristic of a diffuse aquifer is that when annual recharge occurs in spring and the flow of water does rise slightly, some constituents in the water will increase in concentration. Wildeman (26) found that all the metals associated with pyrite dissolution increased in concentration during the spring recharge. He suggested that pyrite weathering is a slower reaction than carbonate and silicate weathering. If the weathering products are retained in microfaults in the vadose zone above the water table, then the reaction is most favored. This water is then released from the faults during spring recharge.

Many of the adits in Colorado that Wildeman studied are regional systems that serve to lower the ground water and expose deeper deposits. Some adits in Eastern United States are of this type, but the greater concern is with overburden exposed during strip mining and with coal refuse piles. Caruccio and coworkers have done extensive research related to this problem (18, 36, 37).

During studies on how overburden related to acid mine drainage, Caruccio (36) noted that the weathering reactions that produced acidity appeared to be much slower than those that produced alkalinity. The slow rate suggests that pyrite oxidation is kinetically controlled; whereas the faster rate for carbonate dissolution suggests it is controlled through equilibrium processes. He suggested that situations that produced frequent flushing intervals of the overburden should reduce acid mine drainage. Recently, Snyder and Caruccio (37) tested a comparable hypothesis on two surface coal mine backfills. Through careful monitoring of the water budget, they were able to separate the shallow subsurface flow that is associated with rapid recharge from the slow, deep ground water recharge. They found that the baseflow associated with deep ground water carries the acidity. This water is associated with the spring recharge which sustains the acid mine seeps for the rest of the water year. The results of the hydrology studies in Colorado and the Eastern United States correlate quite well.

SUMMARY

Whether from coal- or metal-mining situations, the nature of acid mine drainage production is the same. Pyrite is weathered through oxidation by oxygen with water being a necessary reactant. Even though base metals such as Cu, Zn, Cd, Pb, and As may be in relatively low abundances in the deposit, the pyrite oxidation catalyzes the weathering of the sulfides with which these base metals are associated. As a consequence, environmentally significant concentrations of heavy metals often occur in acid mine drainages.

The slow kinetics of pyrite dissolution dictates certain environments where the problem will be most severe. If the pyrite zone is in an unsaturated overburden that contains low amounts of carbonate minerals, chances for an acid mine problem are significant. Also, if the hydrology is dominated by long term base flow as opposed to short term recharge, then the possibility for acid mine drainage is increased.

SECTION 3

REMOVAL PROCESSES IN CONSTRUCTED WETLANDS

This section reviews the removal processes that can operate in a wetland. Much of the information is edited from the reviews by Klusman and Machemer (28) and Wildeman and Laudon (3). Previous reviews of the removal mechanisms operating in wetlands suggested that removal by humic material adsorption or through uptake by plants subsequently harvested could be important metal removal processes (38, 39, 40). Recently, it's been suggested that removal through microbial activity, both aerobic and anaerobic, may be the dominant removal mechanism (3, 41). Whatever the mechanism, there are reasons why a constructed wetland may remove metals better than a natural one.

OVERVIEW OF REMOVAL PROCESSES

Figure 2 is a model of a typical wetland. Low cost immobilization of pollutants for long time periods is the goal of using wetlands for mine drainage treatment. Klusman and Machemer (28) list the removal processes operating in a wetland in the following sequence of decreasing priority:

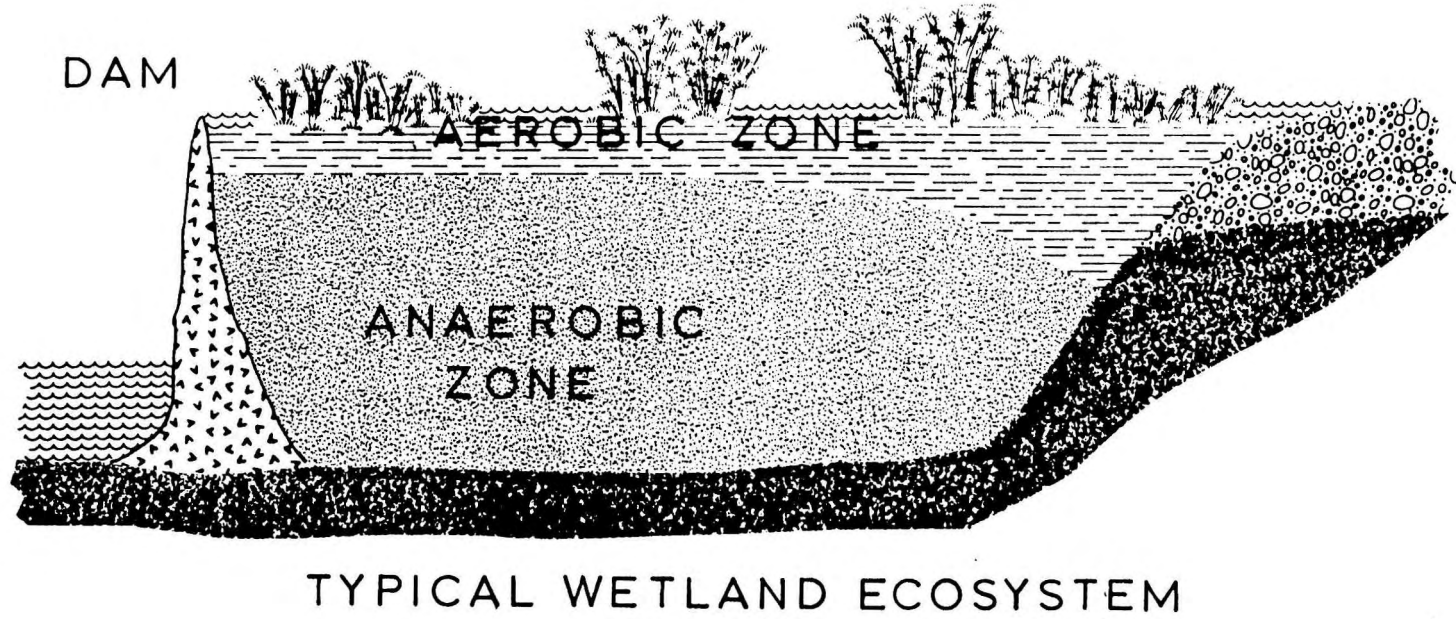
- 1) Exchange of metals by an organic-rich substrate, which is usually peat in natural wetlands.
- 2) Sulfate reduction with precipitation of iron and other sulfides.
- 3) Precipitation of ferric and manganese hydroxides.
- 4) Adsorption of metals by ferric hydroxides.
- 5) Metal uptake by living plants.

Others would add the following to this list (3, 42):

- 6) Filtering suspended and colloidal material from water.
- 7) Neutralization and precipitation through the generation of NH_3 and HCO_3^- by bacterial decay of biologic matter.
- 8) Adsorption or exchange of metals onto algal materials.

The first five processes will be considered in detail. Filtration is a physical process associated with wetlands used for polishing treatment. Neutralization is certainly an important process in wetlands used for municipal treatment (42). It is an unknown factor in wetlands used for mine drainage. There is growing evidence that algae do remove metals from mine drainages (43, 44, 45). The significance of processes 7 and 8 needs further study. However, all these processes should also be examined with regard to how a constructed wetland can be used for mine drainage cleanup.

Geochemical study of the metal removal suggests that removal processes 2, 3, 4, 7 and 8 should be made dominant. This suggestion is based on what happens to a wetland over geologic time (21, 30, 46, 47, 25), on recent wetland studies (41, 48, 67), and on recent experience at the Big Five Tunnel site (8). The basis for this suggestion is explained below.



3-2

Figure 2. Diagram of a typical free surface flow wetland.

If a wetland were buried, upon diagenesis, it would eventually become a bog deposit, coal, or black shale. (46, 47). Reviewing metals occurrence in these sediment types that have undergone early diagenesis may identify the metal forms with long term stability. The rationale is that mineral forms for manganese, iron, and the other base metals in these sediments represent the most thermodynamically stable phases of these elements. In sediments formed by chemical precipitation, the stable iron minerals are hematite (Fe_2O_3), pyrite (FeS_2), or siderite (FeCO_3); stable manganese minerals are pyrolusite (MnO_2), and rhodochrosite (MnCO_3) (21, 30, 46, 47). Trace elements such as Co, Ni, Cu, Zn, Ag, Cd, Au, Hg, and U occur as sulfides, oxides, and carbonates. The same is true in lignite and coal deposits. With the possible exception of V and Ni, metals are not retained by the organic fraction in organic-rich reducing sediments (14, 21, 46).

The importance of these observations lie in determining the role of organic material in a wetlands system. If the above observations do indeed point to sulfides, oxides, and carbonates as the most stable form of trace element precipitates, then immobile organic forms of these elements are intermediate products that will eventually undergo diagenesis to inorganic precipitates. This implies that the strategy for optimizing a wetlands system is to concentrate on the formation of inorganic precipitates and use the organic portions of the system to develop conditions that promote the formation of inorganic precipitates. Removal processes 2, 3, 4, 7, and 8 are those that promote inorganic precipitate formation. Chemically, this approach to metals removal by a wetland amounts to reversing Reactions 2-1 through 2-7 listed in SECTION 2 and making an ore deposit adjacent to the mine portal.

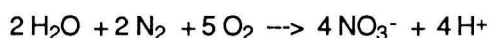
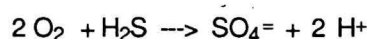
In the Big Five study, emphasis has been made on the formation of sulfides and oxides. Part of this section will review the progress made in emphasizing this one process. Other studies that have also concentrated on specific removal processes in natural and constructed wetlands will be reviewed where appropriate.

CONSTRUCTED VERSUS NATURAL WETLANDS

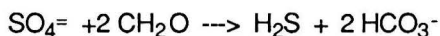
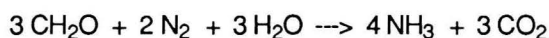
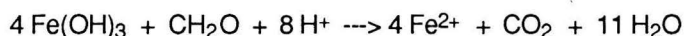
There are a number of reasons why use of a natural wetland for mine drainage treatment is not preferred. It's quite likely that a natural wetland is not available to receive mine drainage. Even if a natural wetland is available, it may have been receiving mine drainage for such a long period that it is close to saturation (49). In natural wetlands that have peat as the primary substrate, the flow is primarily across the surface and transmission of water through the substrate is limited. Surface flow diminishes the possibilities of the anaerobic processes. Also, a natural wetland may be rich in humic acids that limit the capability to neutralize the acid drainage (28, 42, 50). Finally, there's the possibility of destroying the natural ecosystem by the addition of contaminated waters (39, 48). Although natural wetlands have been used for removal of metal pollutants (51), a constructed system offers more promise for treatment of heavily contaminated water.

In the last decade, engineers began to use wetlands for the removal of contaminants from water (2, 52). In some instances, natural wetlands were used. However, a natural system will accommodate all the above removal processes and probably will not operate to maximize a certain process. If a wetland is constructed, it can be designed to maximize a specific process suitable for the removal of certain contaminants from water. Engineering as well as ecological reasons lead to the choice of constructing a wetland for contaminant removal rather than using an existing natural ecosystem.

As an example of constructing a wetland to maximize specific removal processes, consider the bacterial processes that are items 2, 3, and 7 in the above list. Typical microbial mediated reactions that are possible in the aerobic zone of a wetland include:



Typical microbially mediated reactions that are possible in the anaerobic zone of a wetland include:



In these reactions, "CH₂O" is used to symbolize organic material in the substrate.

It is apparent that the anaerobic reactions are approximately the reverse of the aerobic reactions. Both zones exist in a wetland. If removal involves aerobic processes, then the wetland should be constructed so the water remains on the surface. If removal involves anaerobic processes, then the wetland should be constructed so the water courses through the substrate. In a natural wetland, the water typically remains on the surface. Also, note that the aerobic reactions generate hydrogen ions and the anaerobic reactions consume hydrogen ions. In the important area of microbially mediated removal, the wetland must be constructed to maximize removal reactions and minimize competing reactions. In the case of removing contaminants from acid mine drainage, it is clear that removal processes should consume hydrogen ions, consequently anaerobic processes are emphasized (3, 41). The research and development at the Big Five Tunnel site in Idaho Springs, Colorado has concentrated on understanding the chemistry and ecology involved in removal and designing structures from readily available materials that maximize these processes.

EXCHANGE OF METALS ONTO ORGANIC MATTER

Exchange of dissolved metals with the humic and fulvic acids in the substrate is a likely mechanism whereby the metals are temporarily retained in a wetland (50, 53). Humic and fulvic acids are poorly characterized natural organic materials that are found in large abundances in wetland substrates, especially peat. Under acidic conditions, humic acids will be insoluble in water, fulvic acids will be soluble. Both groups of compounds have carboxyl and phenolic acid groups attached to a larger organic molecule. The organic acid groups can also be attached to larger humin particles. Since they have an organic acidic nature, the humic and fulvic acids will dissolve in basic solutions, humin will not. The exchange with metals is primarily controlled by these acid functional groups and can be described by the following reactions (28):



The acid portion is represented by the carboxylic group, -COOH, that dissociates to the carboxyl ion, -COO⁻, and hydrogen ions (Reaction 1). The R- represents the inert, organic portion of humic or fulvic acid or humin. Upon dissociation, the carboxyl ion can react with metal ion M²⁺ forming a complex. The reactions are comparable to how lactic or citric acid react with metals in solution. The double arrows in the two reactions signify that these are equilibrium reactions that can easily be shifted by changes in the concentrations of substances.

There are a number of factors important to the operation of this system in nature. They all are to be connected to the concept that the reactions are an equilibrium system. The pK_a for acid dissociation of humic materials averages approximately 4.2. In a mine drainage with a pH of 3, the dominant species in solution will be carboxylic acid which will not complex the metal ion. Efficient complexation begins between a pH of 4 and 6 depending on the metal ion (53). Some other process in the wetland is required to raise the pH of the acid drainage to a more neutral situation. At pH 4.7, the following order from 100 % complexed to 10 % was found (53): Hg = Fe = Pb = Cu = Al = Cr > Cd > Ni = Zn > Co > Mn. Since Reaction 2 is also an equilibrium situation, two consequences are possible when a mine drainage interacts with humic materials. If the peat had sufficient ionization of the acid groups, then when it came in contact with a solution laden with metal ions, Reaction 2 would be strongly shifted to the complexed metal product. On the other hand, if a peat that had high concentrations of metals came in contact with an acidic solution, reaction 2 could be reversed, releasing the metals.

In the study of the interaction of mine drainage with natural organic humic materials, the works by Weider and co-workers are quite important (40, 48). In one study, they performed sequential extraction procedures on peat from four wetlands (40). The results are listed in Table 4. Red Lake is a peatland that

receives virtually all its mineral matter from precipitation (rain and snow). Buckle's and Big Run Bogs are intermediate but receive appreciable mineral matter from precipitation. Tub Run Bog receives most of its mineral matter from an acid mine drainage. In Table 4, the pyrophosphate extractable step releases the metals that are bound to the humic and fulvic acids. For Fe, Al, and Mn in all four peats, the majority of the metal is associated with the organic acids regardless of the ecosystem.

Since the humic acid is a solid, Reaction 2 can be represented by a Langmuir adsorption isotherm. Weider and Lang tried this for iron on three of the peats and the results are shown in Figure 3. Use of an adsorption isotherm allowed them to calculate the maximum amount of iron retained on the peat and this ranged from 42 to 88 micro moles of Fe per gram of dry peat mass. Upon Fe adsorption, Ca, Mg, Na, K, and H⁺ were desorbed (48).

Two important ideas come from these adsorption studies: 1) Adsorption of a metal ion also implies desorption of another metal or hydrogen ion. 2) There is a limit to the amount of metal adsorption by humic materials. Nevertheless, Weider suggests that in a man-made Sphagnum wetland, adsorption onto organic matter will be the dominant removal process followed by formation of amorphous iron oxides (48).

These studies and others generate a number of conclusions and speculations on removal of contaminants by adsorption onto organic materials in a constructed wetland:

- 1) Adsorption works best at pHs that are higher than those encountered in the mine drainages in Table 1. Some other process and not the adsorption process has to raise the pH.
- 2) A large mass of humic acid acts as a tremendous acid-base buffer adjusting any incoming water to a pH of about 4. This is probably responsible for the rise in pH when acidic water encounters peat. However, this also implies that raising the pH to drinking water limits using a peat wetland is difficult.
- 3) If conditions change, then Reaction 2 can be reversed, desorbing the metals.
- 4) Removal of Mn, Zn, and Cd (metals often associated with mine drainages) by organic adsorption will be difficult.

Currently, it's suggested that organic exchange sites could serve for temporary retention of the metal cations on the substrate of the wetland (7, 28). This increases residence time for microbially-mediated metal removal processes to operate. An organic-rich substrate also produces nutrients for microbes and reducing conditions necessary for sulfate reducing bacteria. However, without additional processes, the capacity of a wetland to increase pH and retain metals would soon be saturated.

Table 4. Sequential extraction results for Fe, Al, Mn, and S and organic matter concentration surface (0-20 cm) peat; means \pm standard errors (from Weider (40)).

	Red Lake, MN	Buckle's Bog, MD	Big Run Bog, WV	Tub Run Bog, WV
Fe ($\mu\text{mol/g}$ dry mass)				
Total (HCl extractable)	45 \pm 8	101 \pm 17	300 \pm 46	869 \pm 96
Pyrophosphate extractable	23 \pm 6	47 \pm 10	269 \pm 44	484 \pm 44
Oxalate extractable	8.4 \pm 1.1	17 \pm 2	45 \pm 9	299 \pm 42
Dithionite extractable	8.7 \pm 1.8	24 \pm 4	17 \pm 2	186 \pm 29
FeS ₂	2.4 \pm 0.2	2.1 \pm 4	6.1 \pm 0.5	7.6 \pm 0.8
FeS	1.0 \pm 0.3	0.3 \pm 0.04	3.2 \pm 1.0	3.1 \pm 0.3
Al ($\mu\text{mol/g}$ dry mass)				
Total (HCl extractable)	65 \pm 11	109 \pm 16	159 \pm 26	243 \pm 12
Pyrophosphate extractable	35 \pm 5	61 \pm 8	140 \pm 24	109 \pm 12
Oxalate extractable	6.2 \pm 1.5	11.2 \pm 0.9	12.4 \pm 2.2	31.9 \pm 1.9
Dithionite extractable	2.9 \pm 1.3	7.4 \pm 2.0	9.3 \pm 0.7	20.4 \pm 1.6
Mn ($\mu\text{mol/g}$ dry mass)				
Total (HCl extractable)	1.5 \pm 0.3	5.3 \pm 0.8	2.5 \pm 0.4	4.9 \pm 2.0
Pyrophosphate extractable	1.3 \pm 0.2	4.7 \pm 0.7	2.2 \pm 0.3	2.5 \pm 0.8
Oxalate extractable	0.4 \pm 0.04	0.7 \pm 0.2	0.2 \pm 0.05	1.2 \pm 0.6
Dithionite extractable	0.06 \pm 0.03	0.6 \pm 0.03	0.2 \pm 0.02	1.1 \pm 0.3
S ($\mu\text{mol/g}$ dry mass)				
Total	48.6 \pm 2.5	87.2 \pm 5.4	134 \pm 8	108 \pm 6
Organic	41.2 \pm 2.1	77.2 \pm 5.4	114 \pm 8	83.9 \pm 4.7
FeS ₂	4.9 \pm 0.5	4.3 \pm 0.8	12.2 \pm 1.0	15.1 \pm 1.5
FeS	1.0 \pm 0.3	0.3 \pm 0.04	3.2 \pm 1.0	3.1 \pm 0.3
SO ₄ ²⁻	1.5 \pm 0.3	5.5 \pm 0.6	5.2 \pm 0.5	5.8 \pm 0.5
Organic matter (%)	84.1 \pm 1.4	86.3 \pm 2.3	89.6 \pm 2.3	55.9 \pm 2.8

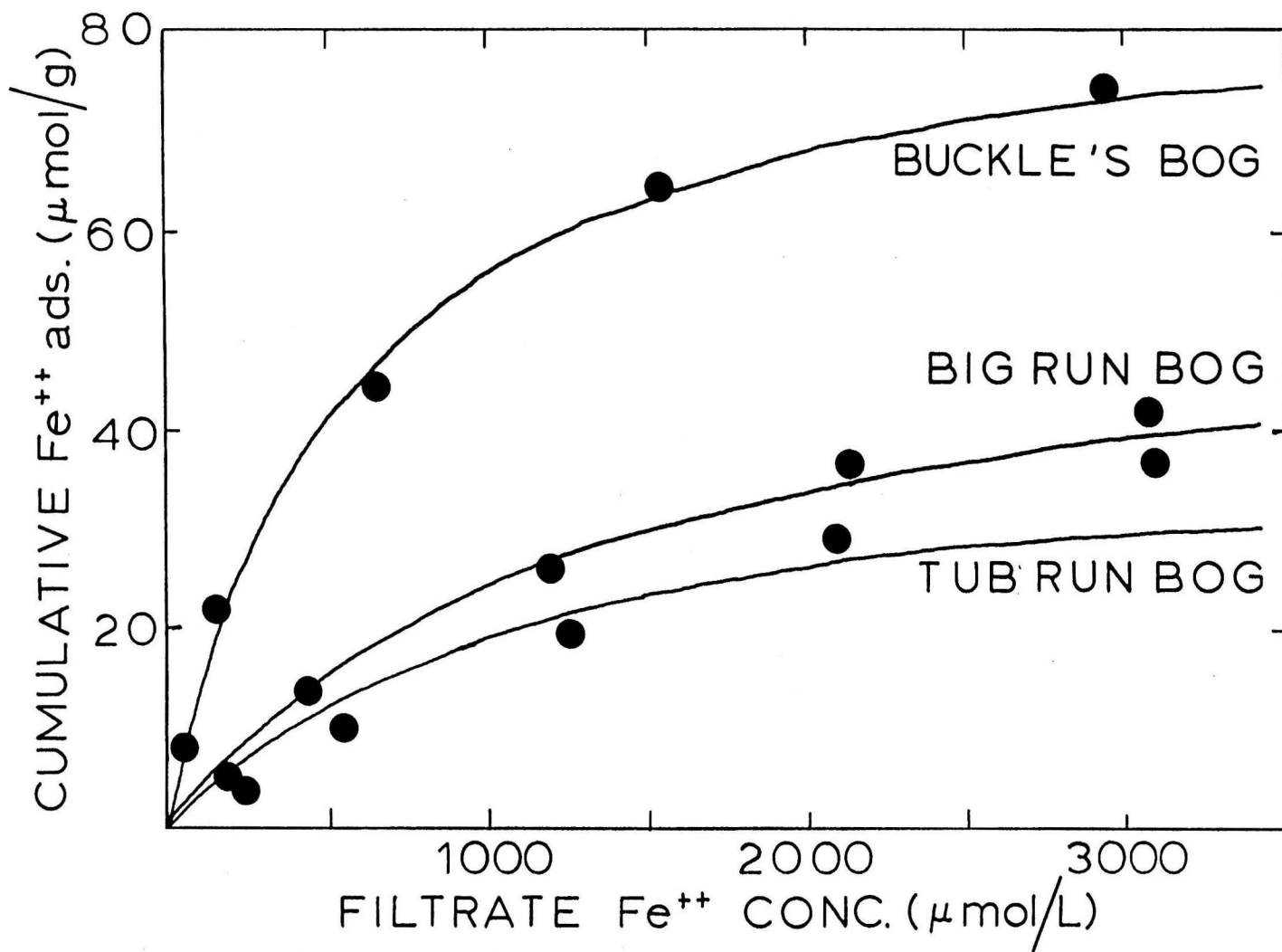
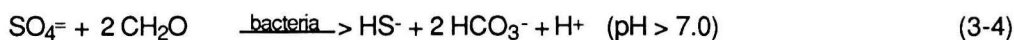
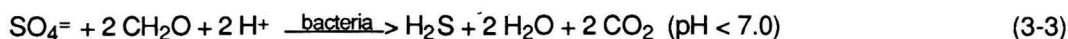


Figure 3. A Langmuir isotherm for iron adsorption onto wetland peat.

SULFATE REDUCTION CATALYZED BY BACTERIA

Generally, microorganisms survive in nature by catalyzing chemical reactions that are far from equilibrium and that can release energy to the organism upon reaction (15). For example, the formation of acid mine drainage is significantly promoted by bacteria that subsist on the energy generated by the oxidation of pyrite (21, 23).

The distribution of sulfur species with redox conditions (better known as an Eh-pH diagram) is shown in Figure 4 (21). For sulfate reducing bacteria to operate, Eh and pH conditions have to be maintained in the field in Figure 4 where sulfide species are stable. This implies acidic waters that are reducing are most favored, just the conditions that occur in a wetland. The presence of decaying organic matter in the peat substrate of the wetland rapidly depletes the oxygen and creates acidic soil waters. The sulfate reduction can be schematically written as follows:



The bacteria most capable of carrying out the catalysis are in the Desulfovibrio family (54). They need an organic nutrient and this is symbolized by CH_2O in the reaction. Lactic acid and cellulose material are the best for this (54). Other than this requirement, the bacteria are quite hardy. They will tolerate temperatures below -5°C and above 50°C , and pH's below 5 and to 9.5. The only environment the bacteria cannot tolerate is long periods of aerobic conditions. Also, if the pH falls below 5, the activity of sulfate-reducing bacteria is severely repressed (54). Note that by reactions 3-3 and 3-4 the anaerobes create their own microenvironment. If the pH becomes too low, H_2S and CO_2 will exsolve limiting the pH decrease. If the pH is too high, H_2S and H_2CO_3 will neutralize the base. To limit the environment from becoming too reducing, a source of Fe is sometimes necessary. Precipitation of FeS and FeS_2 prevents excess sulfide buildup.

In a wetland receiving mine drainage, sulfate reducing bacteria are helpful in two ways. Reaction 3-3 consumes hydrogen ions, so if the water is highly acidic, the loss of H_2S raises the pH. This results in the rotten egg smell sometimes associated with wetland bottom sediments. If the microenvironment is less acidic, then reaction 3-4 generates HS^- and this will form highly insoluble sulfide precipitates with Cu, Pb, Zn, Cd, and Fe. It should be noted that MnS is more soluble and not as easily removed by sulfide precipitation.

The study of sulfide precipitation in reducing environments is an important field in sedimentary geochemistry (21, 22, 25, 46). Much of the research focuses on the formation of pyrite. This can occur directly:



or indirectly through iron monosulfide:

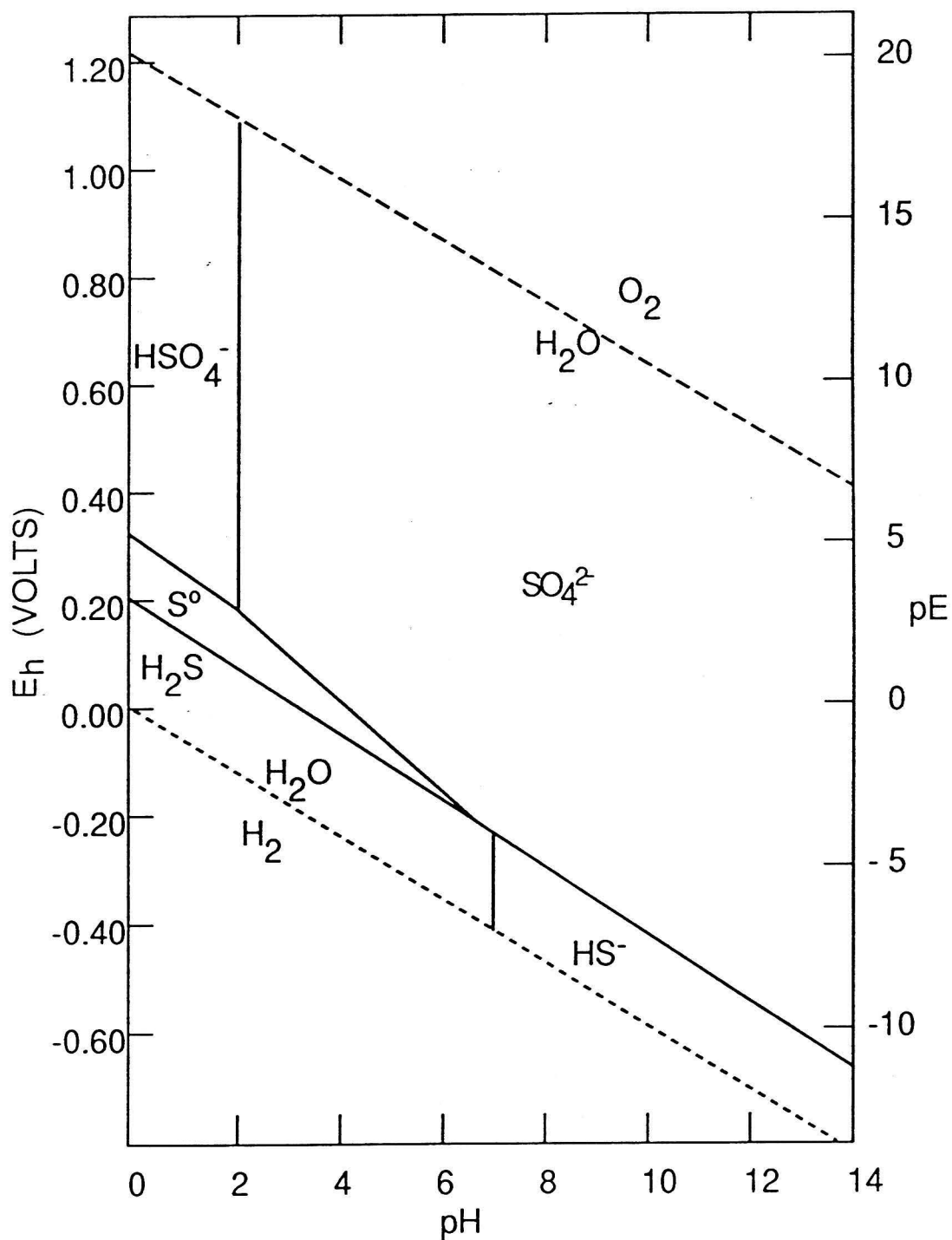
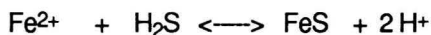


Figure 4. Eh-pH diagram for sulfur species in water.



There is an alternate mechanism that produces highly reactive framboidal pyrite (8). Examination of Eh-pH diagrams of Fe - S systems show that pyrite is the most stable iron sulfide in typical reducing environments (21, 28). This is corroborated by how common pyrite is in sediments formed in reducing environments.

In a review of sulfate reduction, Laudon (8) made these observations:

- 1) Pyrite formation is limited by the rate of sulfate reduction or by iron availability. Sulfate reduction in turn is limited by the supply of sulfate or useable organic material. In marine systems, reduction is limited by organic matter and in freshwater systems, by sulfate availability.
- 2) Since all mechanisms for pyrite formation require elemental sulfur, pyrite formation is also affected by the availability of slightly oxidized sulfur. Because of this, prime environments for pyrite formation are at the oxic-anoxic interface and around the oxidizing root zones.
- 3) In freshwater wetlands and salt marshes, seasonal variations in sulfide formation and sulfate retention are observed. As sulfate becomes a limiting reagent or as redox conditions change, sulfides oxidize and become a source of sulfate.

Laudon (8) and Hedin (41, 65) came to the same conclusions on how sulfate reduction and sulfide retention should be favored in a wetland receiving mine drainage. Water levels and chemistries do not fluctuate throughout the year, and a deep reducing zone is maintained. The supply of sulfate and reactive Fe(II) from the acid drainage is abundant as well as the supply of organic matter from the substrate. Also, the availability of sulfate reducers does not seem to be a problem. As shown in Table 5, in all four substrate materials used in the Big Five wetland, sulfate reducers were present even after the material was dried and stored for three months (5).

In the study of a constructed wetland receiving coal mine drainage, Hedin and co-workers (41, 66, 67) found all the properties of sulfate reduction operating. The wetland was made of mushroom compost with hay bales used to increase the path length of the water. In various spots in the wetland and especially behind the hay bales, black areas showed high pH and low sulfate and iron concentration. In the soil, pyrite and elemental sulfur were present. Also, in the water from these areas, Mn and Al were greatly reduced relative to the mine drainage. Hedin concluded (41, 65, 66) that in a wetland, sulfate reduction and sulfide retention have important advantages over other contaminant removal processes.

In the Big Five wetland study, sulfate reduction has been extensively studied (3, 4, 5, 7). Figure 5 is a diagram of this site. Three different substrates were used; Cell A contains mushroom compost, Cell B contains a blend of equal portions of peat, aged steer manure, and decomposed wood product, Cell C contains six inches of limestone cobbles overlain by the same substrate as in Cell B. Mine drainage

Table 5. Bacterial Populations ($\times 10^{-5}$ bacteria per gram) in the Substrates in the Cells in the Big Five Wetland during the first year of operation.

Type of Substrate	Pop. of Iron Oxidizers	Pop. of Sulfate Reducers	Pop. of Iron Oxidizers	Pop. of Sulfate Reducers
Initial Components, October 1987				
Aged Manure	0	0.9		
Wood Product	0	0.03		
Mushroom Compost	0	5		
Peat	0.002	0.03		
Peat/Manure/Wood	0	0.2		
Big Five Drainage	0.002	0		
Cell	Well		Cell	Well
15 cm depth January, 1988			90 cm depth, January 1988	
A	3	0.2 100	A	3 0.3 100
A	5	10 300	A	5 6 100
B	3	0.05 100	B	3 0.1 50
B	5	0.08 100	B	5 0.02 20
C	1	0.4 100	C	1 0.04 80
C	4	0.05 90	C	4 0.2 90
15 cm depth, June, 1988			90 cm depth June, 1988	
A	3	0.01 10	A	3 0.01 20
A	6	0.02 5	A	6 0.02 20
B	1	0.04 4	B	1 0.01 4
B	6	0.01 2	B	7 0.008 10
C	1	0.03 8	C	1 0.008 10
C	5	0.01 2	C	5 0.01 10
15 cm depth, August, 1988			90 cm depth, August, 1988	
A	3	0.08 1	A	3 0.008 20
A	6	0.02 5	A	6 0.01 70
B	1	0.01 6	B	1 0.002 20
B	6	0.004 80	B	6 0.02 80
C	1	0.01 30	C	1 0.02 80
C	5	0.002 200	C	5 0.01 50
15 cm depth, November, 1988			90 cm depth, November, 1988	
A	3	2.7 3	A	3 4 150
A	6	13 7	A	6 2 50
B	1	.4 8	B	1 .4 4
B	6	.4 60	B	6 .03 30
C	1	1.4 20	C	1 .2 110
C	5	.4 60	C	5 .4 100

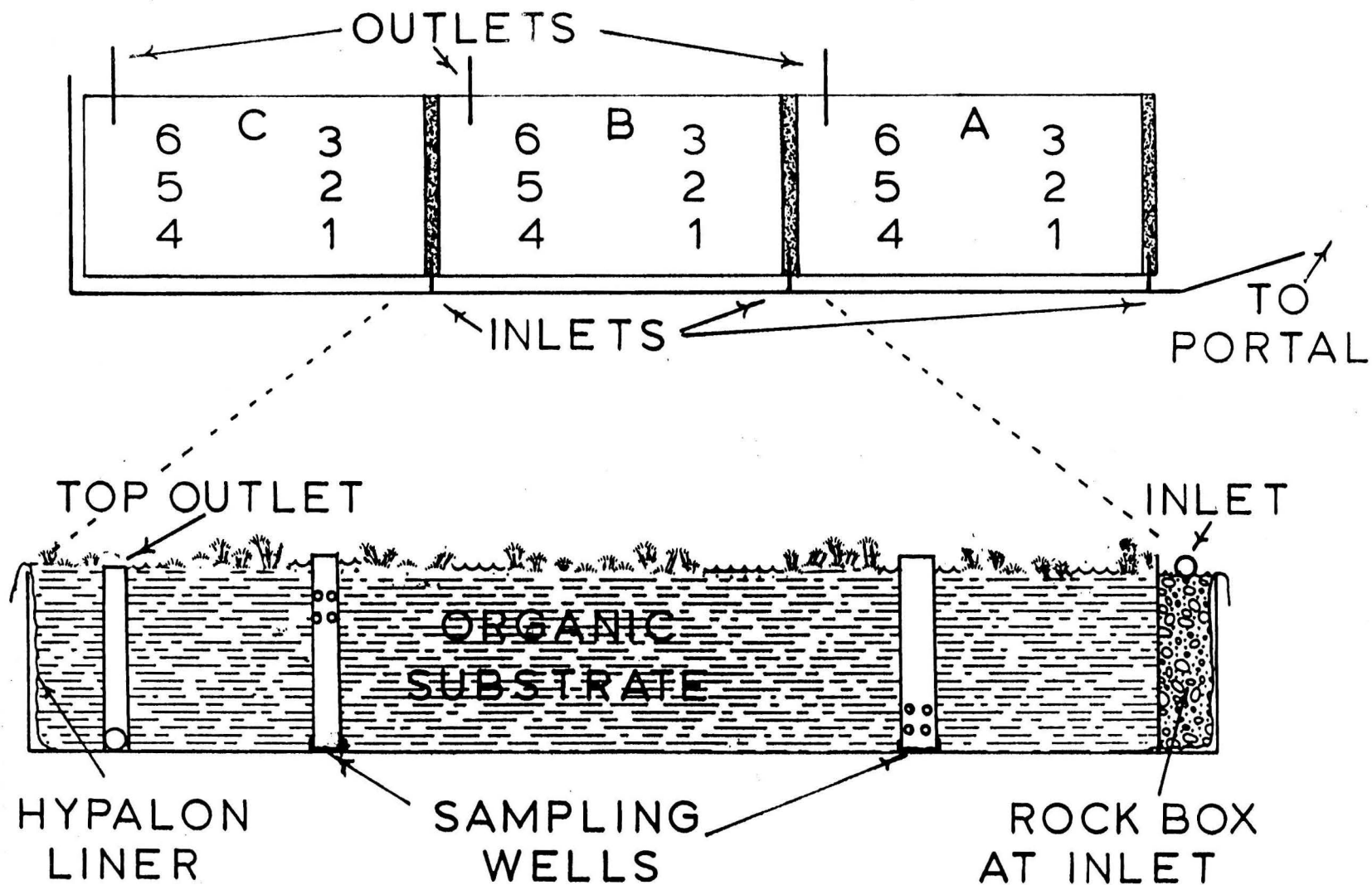


Figure 5. Plan view and cross section of the Big Five Tunnel wetland. Sampling location wells for Tables 5, 6, and 7 are shown for each cell.

Table 6. Bacterial Populations ($\times 10^{-5}$ bacteria per g) in the top 1 cm of depth in the Big Five Wetland cells over 1988-89.

Cell	Well	Pop. of Oxidizers	Pop. of Reducers	Cell	Well	Pop. of Oxidizers	Pop. of Reducers	Cell	Well	Pop. of Oxidizers	Pop. of Reducers
August, 1988				November, 1988				January, 1989			
A	3	2	0.02	A	3	200	30	A			
A	6	0.3	40	A	6	2	9	A			
B	1	0.5	0.5	B	1	200	40	B	1	90	20
B	6	0.02	0.6	B	6	2	8	B	6	7	20
C	1	0.6	20	C	1	7	7	C	1	0.7	0.2
C	5	0.2	20	C	5	20	20	C	5	10	7.

Table 7. Bacterial Populations ($\times 10^{-5}$ bacteria per g) in the Big Five Wetland cells over 1988-90. For the B Cells in 1990, (n) is the north part of the cell, and (s) is the south.

Cell	Well	Pop. of Iron Oxidizers	Pop. of Sulfate Reducers	Cell	Well	Pop. of Iron Oxidizers	Pop. of Sulfate Reducers
15 cm depth, January, 1989				90 cm depth, January, 1989			
B	1	.5	.8	B	1	.2	4
B	6	.13	.9	B	6	.1	1.
C	1	1	20	C	1	6	2.
C	5	1.1	5	C	5	.6	1.
15 cm depth, July, 1989				90 cm depth, July, 1989			
A	3	<2	200	A	3	20	1000
A	6	<2	200	A	6	2	400
B	1	16	300	B	1	.1	100
B	6	-	200	B	6	-	100
C	1	<2	300	C	1	1.	300
C	5	<2	300	C	5	.4	100
15 cm depth, January, 1990				90 cm depth, January, 1990			
A	6	3	100	A	6	6	3.
B(n) by inlet		5	5	B(n) by inlet		.2	5
B(n) by outlet		.04	300	B(n) by outlet		.2	3.
B(s) by inlet		2	100	B(s) by inlet		.6	1.
B(s) by outlet		.1	.6	B(s) by outlet		.3	4
C	5	.5	600	C	5	.4	300
E middle		.1	300	E middle		2	30
15 cm depth, August, 1990				90 cm depth, August, 1990			
A	6	1.	300	A	6	5	40
B(n) by inlet		<.02	80	B(n) by inlet		.4	2.
B(n) by outlet		<.01	30	B(n) by outlet		.2	10
B(s) by inlet		<.01	1	B(s) by inlet		.1	2
B(s) by outlet		.04	.5	B(s) by outlet		.1	3
C	5	.9	40	C	5	.08	20
E middle		<.01	30	E middle		.2	7.

started flowing through the system in October of 1987, and almost immediately, Cell A became more efficient at removing contaminants than the other two cells. Since the system started in the winter when the plants were dormant, many possible processes were eliminated. During the first five months of operation, the water soil interface in Cell A changed from one that was oxidizing and orange in color to one that was black and reducing.

Determining the level of sulfate reduction in a wetland is difficult (118,119,120), however one method of gaining some insight is to monitor the population of sulfate reducers. Tables 5, 6 and 7 show the levels of bacteria in the cells of the Big Five site from start-up in October 1987 through July 1990 (5, 10). The positions of the cells and the sampling wells are noted in Figures 5 and 11. The populations were determined by the most probable number method and the factor of confidence is 3.3. This implies the results are orders-of-magnitude estimates (5, 10).

The population of sulfate reducers is high and ubiquitous throughout the substrate throughout the substrate. Populations appear high in Cell A in the first six months of operation. However, the difference is not statistically significant. As stated above, the surface of Cell A soon turned anaerobic. However, populations of sulfate reducers in the first 15 cm of the substrate and, in August of 1988, in the top 1 cm of the substrate (see Table 6) do of Cell A do not appear much higher than in Cells B and C. It appears that populations of sulfate-reducing bacteria alone are not a strong indication of the amount of sulfide being produced. Comparing Tables 6 and 7 indicates that the populations of sulfate reducers is maintained in 1989 and 1990, whereas the population of iron oxidizers decreases from the levels of 1988. Measuring populations of sulfate reducers will give indications of whether the proper environment is being maintained on a long term basis.

The Big Five wetland will be discussed in greater detail in the SECTION 4; the case for sulfate reduction will be elaborated in SECTION 5. For now it can be said that the maintenance of high populations of sulfate-reducing bacteria over three years is a good indication that sulfate reduction is occurring in these constructed wetland sites. It appears that this process may have been responsible for the better initial performance of Cell A.

In conclusion, sulfate reduction and sulfide retention are processes that do operate in wetlands and generate preferred modes of contaminant removal. Sulfate concentration is reduced, pH is increased, and the metals are removed by the formation of highly insoluble precipitates. Since this process has only recently been investigated in a formal manner in constructed wetlands, the complete nature of the removal process is still uncertain. Two key factors that will determine the success of this process are the need for the drainage to flow through the anaerobic portion of the wetland and the need for continuous flooding of the wetland so that the products of reduction are not oxidized.

OXIDATION AND OXYHYDROXIDE PRECIPITATION CATALYZED BY BACTERIA

In SECTION 2, it was noted that the mechanism for pyrite oxidation favors the use of Fe(III) for further oxidation and thus, mine drainage has a significant concentration of Fe(II). Also, manganese is in the +2 oxidation state instead of +4. The hydroxides of Fe(II) and Mn(II) are far more soluble than those of the higher oxidation states (30). At pH = 8, both the +2 ions have solubilities of greater than 1000 mg/L. On the other hand, Fe(III) and Mn(IV) are highly insoluble. At pH = 5, their hydroxide solubilities are less than 1 mg/L. Efficient removal of Fe and Mn by hydroxide precipitation requires oxidation. In a wetland, this is most readily achieved by microbial catalysis in the aerobic zone.

The geomicrobiology of iron and manganese is reviewed by Erlich (22). There are a host of bacteria that oxidize iron. The most important of these is the Ferrooxidans family that starts the oxidation of pyrite. It is one of the few bacteria that can tolerate a pH less than three and can exist on the inorganic nutrients of Fe(II), CO₂, and NH₄⁺. In addition, when the pH of a system reaches 5, a large number of species of bacteria are capable of oxidizing Fe(II). These bacteria require organic material as a nutrient source.

As shown in Table 5, Ferrooxidans were found in the Big Five drainage and in the peat which had recent contact with natural waters. Analysis of Tables 5, 6, and 7 gives some insight on the role of these bacteria in the oxidation of iron. As shown in Table 5, there was a high original concentration of Ferrooxidans in all three cells at the Big Five site. These bacterial populations were maintained or perhaps increased, even at a depth of 90 cm into the substrate, through November, 1988. However, as seen in Table 7, populations started to fall in 1989 as the cells remained anaerobic. By 1990, it was difficult to find Ferrooxidans at depths of 90 cm. Analysis of Table 6 shows that, as expected, the highest populations of Ferrooxidans are in the top layer of substrate in the wetland.

For manganese, oxidation is more difficult. Mn(II) is stable to higher pHs than Fe(II) (21); and thus, bacteria that can use the oxidation of Mn(II) as a source of energy have to operate in systems with higher pHs. Bacteria that directly use the oxidation of Mn as a source of energy do not seem significant in acidic wetland environments. Bacteria that indirectly oxidize Mn(II) are most readily found in environments above a pH of 7 (22). Further reasons for the resistance of Mn (II) to microbial oxidation is the high activation energy for the reaction and the complexity of the mechanism.

The Tennessee Valley Authority currently is operating seven and planning eight constructed wetland systems for treating coal mine drainage (68, 69). The primary design for these wetlands is a surface treatment system using whatever substrate is readily available. The systems are large, typically contain a number of stages, and closely resemble a natural wetland. In these systems it is suggested that microbially catalyzed oxidation processes are the primary removal processes. Five of the operating wetlands have produced effluents meeting all discharge limits. These five systems are associated with moderate inflow quality (Fe = 11-69 mg/L and Mn = 5-14 mg/L), relatively large Mn to Fe ratios (average

Mn/Fe = 0.44), and significant inflow alkalinity as evidenced by the pH of the inflow being above 5.5 (68). As explained in SECTION 7, the treatment area requirements for these systems range from 0.6 to 3.4 m²/mg/min.

Reactions 2 and 3 in SECTION 2 show the oxidation and precipitation of iron. The comparable reactions for Mn are:



As in the case of iron, precipitation generates hydrogen ions, and this limits the extent of oxidation and precipitation.

The importance of oxidation and precipitation in wetlands is considerable, especially for Mn. In natural wetlands where the water is primarily flowing across the surface, Weider considers it just as significant as adsorption by organic material for the removal of iron (48). However, the inefficiency of the process for manganese removal is one of the great frustrations in the use of wetlands for contaminant removal. Klusman (28) reviewed this frustration. In active mine drainage treatment systems he states that although the rates of oxidation of Mn and Fe are both pH dependant, iron oxidation occurs at an acceptable rate at pH values near 7. The rate of Mn oxidation cannot be brought into an acceptable range without raising the pH above 9.0.

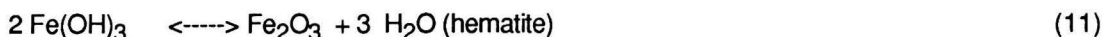
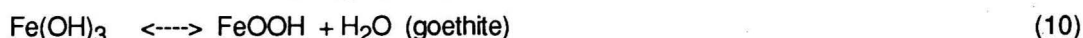
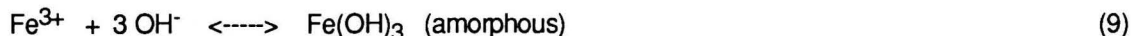
Based upon these ideas, some conclusions can be made concerning the use of oxidation and precipitation in wetlands.

- 1) Since the oxidation and precipitation sequence generates hydrogen ions, the reactions will be self limiting. Some other process has to be operating to raise the pH.
- 2) In peat wetlands, where soil waters remain acidic, there is little possibility of Mn removal.
- 3) Sulfate reduction and metal oxidation are mutually exclusive processes. One requires anaerobic conditions; the other aerobic. In constructed wetlands, this implies the design should be a staged system. Since sulfate reduction raises the pH, the stage promoting this process should be first.
- 4) Even though it is difficult to remove Mn by oxidation, this process has the best chance of success since MnS is relatively soluble. However as shown in SECTION 7, it does appear that manganese can be removed in an anaerobic cell. It is hypothesized that MnCO₃ is being formed.
- 5) Most of the area in a constructed wetland will be dedicated to the removal of Mn. Brodie and co-workers (55) suggest the area needed per milligram of Mn is about 2.5 to 3.5 times that needed per milligram of Fe.

ADSORPTION OF METALS BY OXYHYDROXIDES

When Fe(III) and Al precipitate as hydroxides, the solid is quite gelatinous. The scavenging properties of these precipitates have long been used in wastewater treatment (15). In addition, these two metal hydroxides as well as the Mn(IV) oxyhydroxide have a strong capability of adsorbing other metal ions onto their surface (21). Consequently, if the process of oxidation and precipitation occurs, a side benefit of further removal of contaminants by the precipitates will also occur.

When these precipitation reactions occur, the products are not simple crystals. For iron, the reaction sequence is roughly as follows (30):



The amorphous hydroxide is the first form that precipitates. It has some polymeric properties as does aluminum hydroxide and this causes the gelatinous appearance. As the hydroxide ages it turns into crystalline hematite in dry conditions or goethite in moist situations. The hematite and goethite have better capabilities of adsorbing other trace metals (21). There are a number of theories of how the surfaces of oxyhydroxides adsorb metals (21). Basically, the surface operates as a weak acid which attracts hydroxide ions making a negative surface. The negative surface of the particles attracts the positive metal ions. In this explanation, the hydroxide surface changes from positive to negative as the pH increases. The pH where there is no surface charge can be measured and this is called the pH of zero point of charge (zpc). For manganese (IV) oxyhydroxides the pH of zpc ranges from 3 to 7; for aluminum oxyhydroxides the pH of zpc ranges from 5 to 9; and for iron oxyhydroxides the range is from 6.5 to 8.5 (21). Since the surface of the manganese oxyhydroxide turns negative at lower pHs, it is generally a better absorber of cations than the other two solids. This is verified in studies of trace element relations with Mn and Fe oxyhydroxides (31, 56, 57).

The process of metal adsorption can be used in a wetland in the polishing and buffering stages. In the final portions of a wetland where hydroxide precipitation may be significant, these hydroxides will help to coagulate suspended material in the water. At the same time, these precipitates will help remove the final metal contaminants.

A common feature seen in mine drainages is the accumulation of oxyhydroxide precipitates by algae. There is a question of whether this is assimilation or preferred precipitation but nevertheless some strains of algae become quite orange with Fe(III) hydroxide coatings. Some projects have been carried out to investigate how algae can help the removal process. In Ontario, Kalin is using algae to increase surface areas for better Fe(III) precipitation and is also studying whether algae assimilate metals. In Missouri, Wixon (43) has used algae to polish mine waters that are discharged from a settling

pond. Kepler (45) is studying whether algae ponds are better than cattail ponds for removing Fe and Mn from coal mine drainage. Further work is needed to determine the relative amount of assimilation compared to precipitate accumulation. However it appears that algae are helpful in accelerating the final removal processes that are associated with oxyhydroxide precipitation.

UPTAKE OF METALS BY PLANTS

In the earlier studies using wetlands to treat acid mine drainage, it was presumed that uptake by plants was an important process (38, 39, 41). However, recent results have shown that uptake by the stems and leaves of plants account for only 1 to 5 % of metal accumulation (49, 58, 59). Metal removal by the roots and rhizomes of plants may be significant. The roots themselves do not seem to accumulate metals (49, 58, 59), but they do generate microenvironments that promote the reduction and oxidation processes. In one case it was observed that the soil below Typha roots was more reducing (58). Also it's been found that oxygen can be respired down the stems of Typha causing the precipitation of Fe(III) around the roots (60). This property of oxygen transpiration to the soil could be used to advantage in wetlands that rely on oxidation and precipitation.

Another significant role of the plant material in a wetland is to provide the biomass necessary for the other processes. Decayed plant material produces the organic matter that will be capable of removing metals by adsorption and exchange. The cellulose in plants provides the nutrients for the sulfate reducing microbes. Also, even a constructed wetland should be considered an ecosystem where the plants provide the long term nutrients and vegetative cover for the substrate which is providing the treatment.

The studies on plants in The Big Five wetland is summarized in SECTION 6.

OTHER PROCESSES

Are there any processes still to be discovered that will be important to the contaminant removal process? Based on the explosion of studies on water treatment by wetlands, it's certain that new and significant processes will be uncovered. Also, since much of the recent research is on microbial processes, it's quite likely that new microbial processes will be discovered. In the area of metals removal, an important process that is still uncertain is the increase in pH. Earlier, it was suggested that sulfate reduction is responsible for this pH rise. However, that has not been verified. It is highly likely that microbes are involved in this process.

Two microbial processes deserve mention as possible candidates. In the microbial degradation of protein, NH_3 is generated which will hydrolyze to NH_4OH . This process will raise the pH. The proteins would be part of the substrate materials. Another more speculative microbial process is suggested as part of the microbial reduction process. Apparently, microbes exist that generate H_2 gas from hydrogen ions (Dr. D. R. Updegraff, Colorado School of Mines, 1989, personal communication). These bacteria live in concert with sulfate reducers and methane generators which use the H_2 as a

nutrient. If these microbes do indeed exist in a wetland, their use in raising the pH is obvious.

SUMMARY

Upon review of the possible wetland processes some guidelines do become clear. Among the most important is that almost all removal processes are associated with the wetland substrate. However, little is known about that substrate. In particular, knowledge about the substrate as a nutrient for growth of microbes important to metals removal processes is sparse. Also few advances have been made in determining how to use the substrate as a vehicle for increasing the pH.

On the question of which processes are or are not important, the answer is all processes are important. The wetland design problem then becomes how to develop stages that will take advantage of the group of processes that will best do the specific metals removal process. The design of stages and separation of processes is readily divided into those that operate in an anaerobic system and those that best operate in an aerobic system. This question of design of stages is being investigated at the Big Five site and preliminary results will be developed in the next section.

SECTION 4

BIG FIVE WETLAND: DESIGN, CONSTRUCTION, OPERATION, AND RESULTS

INTRODUCTION

The Idaho Springs-Central City mining district in the Front Range has massive waste rock dumps, mill tailings piles, and abandoned mine shafts and tunnels from precious metal ore production (33). Tunnel drainage typically has low pH and high metal concentrations that affect the regional aquatic resources. Table 1 is typical of the chemistry of the drainage water. The Clear Creek site, which includes the Big Five Tunnel, is on the National Priorities List under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA or Superfund). When CERCLA was amended in 1986, Congress placed a special emphasis on the use of alternative treatment technologies for cleaning up hazardous waste sites. As part of the Feasibility Studies required by the Superfund Program, it was recommended that passive treatment by a constructed wetland be considered as a cost-effective option for treatment of acid mine water associated with the Clear Creek site (71). To assess the feasibility of wetland treatment, the Big Five Tunnel Pilot wetland site was constructed in the summer of 1987.

From June 1987 through September 1988, study of the wetland was funded through Region VIII of the EPA. Beginning in October, 1988, funding of modifications and monitoring of the Big Five site was through the Emerging Technologies Program (ETP) of the U.S. EPA Superfund Innovative Technology Evaluation Program (SITE). This handbook was written as part of that (ETP) project. Table 8 is a chronology of activities at the Big Five Tunnel. Table 9 is a list of the analyses performed during the project. In the 1987-88 portion of the project, the analyses were performed under the Contract Laboratory Program (CLP) of Superfund. Under the ETP Project, a Quality Assurance Project Program (QAPP) specific to the project was established. The analyses were performed at the Colorado School of Mines and at the laboratories of U.S. EPA Region VIII. A separate report on Quality Assurance/Quality Control that includes all the data on water and soils is available (121).

During 1987-88, monthly routine sampling of the wetland effluents, quarterly sampling of cell wells, and six month sampling of cell soils was performed. Under the ETP project, routine sampling of cell effluents was performed bimonthly and soils were sampled twice a year. The analyses performed on a routine basis are listed in Table 9. In addition to the routine studies, a number of special research studies were performed. During the summer of 1988, a study was conducted of how flow affects concentrations of metals in the effluents. Laudon (8) studied the forms of sulfur in the substrates in the wetland cells. Batal (10) studied the changes in microbial populations in the cells. Lemke (9) studied how hydraulic properties of the substrates affect the operation of the wetland cells. Machemer (7) has been studying the role of sulfate reduction in the operation of the wetland cells. Dietz has been studying the role of plants in the wetland cells and these results are presented in Section 6. In this section, the significant results from routine sampling are presented. The results of the special studies are also summarized.

Table 8. Chronological list of activities at the Big Five Wetland Site.

1987

Jun. 15-Aug. 15:	Sampling, selection, and analysis of candidate substrate materials. Selection of sites to secure plants.
Aug. 1-22:	Preparation of site, installation of plumbing, cells, and substrates.
Aug. 25-Sep. 30:	Substrate soaked with municipal water. Transplanting and sampling of sedges, rushes, and cattails.
Oct. 13-15:	Sampling of mine drainage, cell effluents, and cell wells to establish baseline conditions.
Oct. 25:	Flow of mine drainage into cells initiated.
Nov. 3:	Routine sampling of effluents, wells, and substrates initiated.

1988

Jan. 1:	Routine sampling under the Region VIII project continued.
Jun. 15-Jul. 20:	Special flow rate versus effluent concentration study conducted.
Jul. 1-Aug. 31:	Special sampling and analyses for forms of sulfur in the substrates conducted.
Oct. 1:	ETP Project begins.
Nov. 1:	Routine sampling under the ETP project initiated.
Dec. 1-15:	Reconstruction of Cell A carried out.

1989

Jan. 1:	Routine sampling and analyses under the ETP project continued.
Jan. 1:	Studies on hydrologic properties of substrates initiated.
Jun. 15-Aug. 1:	Special studies on the role of plants conducted.
Aug. 1-31:	Reconstruction of Cell B and construction of Cells D and E carried out.
Sep. 1-Dec. 1:	Special studies on substrate processes conducted.

1990

Jan. 1:	Routine sampling and analyses under the ETP project continued.
Jun. 1-Sep. 15:	Special study of the sulfate reduction process conducted.
Jun. 15:	Bench scale studies on Quartz Hill and National Tunnels initiated.

Table 9. Analyses Performed on Waters, Substrates, and Plants.

During 1987-88 under the CLP Program

<u>Waters</u>		<u>Substrates</u>	<u>Plants</u>	<u>Field</u>
RAS*	NH ₃	RAS*	RAS*	pH
CO ₃ ²⁻	TSS	B	B	Eh
HCO ₃ ⁻	TDS	NH ₃		cond.
Cl ⁻	B	N _{tot}		flow
F ⁻	TOC	C _{tot}		temp.
SO ₄ ²⁻	acidity	P _{tot}		
NO ₃ ⁻ /NO ₂ ⁻		S _{forms}		

During 1988-90 under ETP Project

<u>Waters CSM</u>	<u>Waters EPA</u>	<u>Substrates CSM</u>	<u>Substrates EPA</u>	<u>Plants</u>	<u>Field</u>
Mn	RAS*	Mn	RAS*	RAS*	pH
Fe	Cl ⁻	Fe	NH ₄	B	Eh
Cu	F ⁻	Cu	N _{tot}	P	cond.
Zn	SO ₄ ⁼	Zn	P _{tot}		Flow
SO ₄ ⁼	NO ₃ /NO ₃ ⁻	S			temp.
	NH ₄ ⁺				

*RAS (Routine Analytical Services) includes: Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Ag, Na, Tl, V, and Zn.

DESIGN AND CONSTRUCTION OF THE PILOT TREATMENT SYSTEM

The completed design of the pilot treatment system was a reinforced concrete structure with dimensions of 0.61 m (2 ft) in depth, 3.05 m (10 ft) in width, and 18.3 m (60 ft) in length. For the initial investigations, the structure was divided into three 6.1 m (20 ft) sections, with provisions to divide the box into six 3.05 m (10 ft) sections at some later time if this were to be desired (Figure 5).

The concrete sections were separated by walls constructed from 5 x 15 cm (2 x 6 in.) treated wood. Aluminum channels were grouted into void tubes in the concrete walls to allow the addition of lumber to form sidewalls and endwalls of adjustable height. In the initial study, the walls were built up to a height sufficient to allow the total depth of the cells to be 1.22 m (4 ft).

Each cell was fitted with two drains, one active and one reserve. The reserve drains were installed so that the number of cells could be changed from three to six if desired, and to drain the cells at the end of the study. The drains were built using 15 cm (6 in.) i.d. polyvinyl chloride (PVC) pipe, and the active drains consisted of standpipes initially set at a depth of about 1 m (3 ft). The drains deliver the overflow water to an existing runoff pond. A 0.76 mm (30 mil) Hypalon™ liner was used to line the cells so that they would be separated from one another and to prevent chemical reactions between the treated wood, concrete or aluminum channels and the organic substrates and mine drainage.

Rock baskets were constructed at the upstream end of each of the cells to allow the mine drainage to contact as much of the upstream cross-section of the organic substrate as possible. These baskets, approximately 30-45 cm (12-18 in.) thick, were built using expanded plastic fence and extended to the full depth and width of each of the cells. Washed 10-15 cm (4-6 in.) river rock was used to fill the baskets. Plastic curtains were suspended from supports just above the substrates on the downstream side of the rock baskets. These curtains extended down to 1/2 to 2/3 of the total depth to force the flow downward into the cells. Six access wells were installed in each cell to allow sampling of interstitial water. the location and the number of the wells is shown in Figure 5. These sample wells were made from 15 cm (6 in.) i.d. PVC and completed to allow water to enter from the lowest, middle, and the upper 30 cm (1 ft) of the organic substrates. Holes in the sample tubes were covered with nylon screen to prevent clogging with the substrate material. Two wells of each completed depth were placed in each of the 3 cells, for a total of 18 sample wells.

A small concrete dam was constructed just inside the tunnel portal to provide enough head to distribute water to the system cells 50 feet away and 2 feet downgradient. Water was piped from the portal to each of the cells through 2 inch diameter PVC lines, reduced in size through the system, and fitted with valves to control the total flow and the flow to each individual cell. Due to the harsh winter climate of the location, all plumbing had to be insulated. Water is distributed across the entire width of each cell by allowing it to flow into the rock baskets through 10 cm (4 in.) i.d. PVC perforated drain pipe, which extends from one side of the cell to the other. Excess water from the tunnel is allowed to drain into an adjacent pond, which percolates into nearby Clear Creek.

Once the sample wells were placed and the rock baskets were completed, the sections were filled with the organic substrates to a depth of about 1 m (3 ft). The first cell was filled with fresh, unused mushroom compost, which consisted of approximately 50 percent animal manure and 50 percent barley mash wastes from a local brewery. The second cell received a mixture of equal parts of peat, aged steer manure, and decomposed wood shavings and sawdust. The third cell was filled with the same mixture as the second cell, except that the third cell was filled to a depth of 15 cm (4-6 in.) with 5-8 cm (2-3 in.) of limestone rock before the cell was filled with the organic mixture. These substrates were chosen because they met with some success in constructed wetlands treating coal mine drainages (39, 41, 48). Other information on these substrates is contained in SECTIONS 5, 7, and 10. Initially, the organic substrates were saturated with municipal water to reduce stress on the transplanted vegetation.

TRANSPLANTING VEGETATION TO THE DEMONSTRATION SITE

The transplanting of cattail, sedge, and rush species was initially envisioned to be a moderately easy process of taking clumps of the plants about 30 cm in diameter and transplanting them to the treatment beds. In practice, however, separating the root systems around and underneath a section of plants to detach them proved to be very difficult since the root systems of these species are extremely intertwined and the soil quite heavy in some cases. The sizes of the vegetation clumps were ultimately determined by the weight that two people could lift without causing the bundle to disintegrate. The practical method was to cut the intertwined roots around a section of plants and to lift the edges of the clump while other workers separated the vegetation from the underlying soil or gravel. Once free, the samples were lifted onto plastic tarpaulins to prevent them from falling apart and to facilitate lifting them into the trucks. Vegetation bundles were then hauled to the mine drainage demonstration site and placed in the treatment cells, which had been previously saturated with municipal water.

Several different species of aquatic plants were transplanted into the treatment cells. Cattails (*Typha angustifolia*, *T. latifolia*), and sedges (*Carex utriculata*, *C. aquatilis*) were transplanted from an area of similar elevation near the northeast shore of a mountain lake in Grand County, Colorado. Since this site was on public land, a required permit was obtained from the U.S. Forest Service before vegetation was transplanted from this site. Four light trucks were used, six workers were involved, and the work took about ten hours. This effort included the travel time, and extracting and transplanting the cattails and sedges. About 25-30 percent of each of the treatment beds were covered as a result of this work.

On September 5, sedges (*C. aquatilis*) and rushes (*Juncus arcticus*) were transplanted from a wetland about 6.5 km (4 mi) up Stanley Road from the demonstration site. A one-ton stake bed truck with a hydraulic lift was used, which greatly facilitated the loading and unloading of the vegetation samples. About 50 percent of the treatment beds were covered at that time.

The remaining transplanting was done on September 18. Cattails were transplanted from a foothills wetland in Mount Vernon Canyon, and sedges were transplanted from a wetland adjacent to the demonstration site. The effort took about eight hours using two trucks and four workers. As a result of this transplanting, about 85 percent of the treatment beds were covered with species of either cattails, sedges or rushes. Figure 6 shows the general location of the different species of vegetation in the treatment cells.

After the transplanting was completed, municipal water was run through the system until October 25, 1987 when acid mine drainage was diverted into each of the cells. The initial flow rate was 3.8 liters/min (1 gpm) which was equivalent to a loading factor of 200 ft²/gpm.

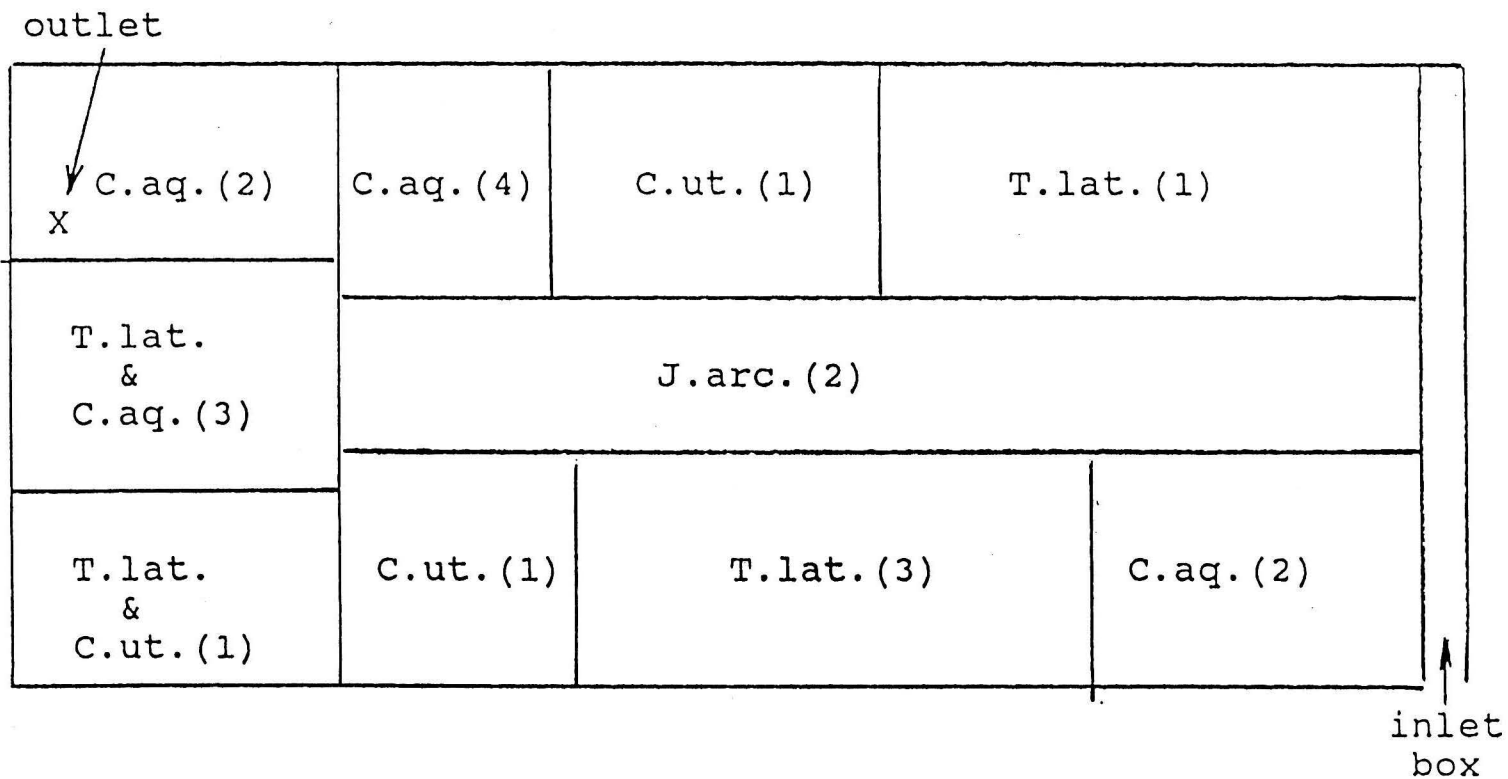


Figure 6. Typical location of plant species in each cell.

GENERAL OPERATION OF THE SYSTEM

Basic Structure of System

The basic structural components of the Big Five system appear to be functioning as designed. The concrete structure and the separating walls held by the aluminum channels are performing well. The 30 mil Hypalon^R liner used to line the cells remains intact and no leakage from the system has been observed. Recently, the liner withstood a severe hailstorm that shredded 10 mil polyethylene.

Mine Drainage Distribution System

The dam and plumbing constructed inside the Big Five adit continues to function adequately in diverting the desired portion of flow to the cells, although the area behind the dam is slowly filling with metal hydroxide sediment. The PVC lines that distribute the mine drainage to the individual cells are insulated adequately, since no freezing of the inflow water has been observed through two winter seasons. The standpipe drains continue to work well in all three cells and clogging has not been observed.

Metal hydroxide precipitates, however, occasionally clog the mine drainage inflow lines. Even though taken from the surface of the impoundment inside the portal, the incoming flow still retains enough metal hydroxide sediments to clog the lines. The lines have to be periodically flushed to remove the sediments in order to maintain the desired flow rates to each of the cells. The reason for the clogging appears to be a trap created by the requirement for installing a vertical section of pipeline to lift the flow to the top of the cells. The problem could be alleviated by avoiding sharp turns and vertical sections in the incoming lines. The clogging of the lines turned out to be serendipitous, however, in that much larger increases in pH values are found when the flow is reduced. This observation led to further studies to quantify the metal removal efficiencies and increases in pH values under different flow rates and retention times.

The rock baskets fill with metal hydroxides after a few months of operation and possibly reduce the opportunity for the mine drainage to contact the entire cross-section of the substrate. The layer of limestone rock in Cell C appears to be somewhat more effective in distributing the flow through the lower part of the substrate. This may not continue, however, as the interstices in the limestone layer become clogged with sediment.

Some of the nylon screens covering the openings in the sample wells become clogged with organic matter, resulting in very slow recharge once the wells are pumped down. These wells are pumped first during sampling to allow time for recharge. The clogging was due to the substrate and not to a buildup of precipitates. In general, metal sulfide precipitates cause much less clogging than metal hydroxide precipitates.

The method of delivering wastewater to the treatment cells depends on the overall system configuration, objectives, and costs. In general, a simple and inexpensive system is preferred over complex plumbing and pumping arrangements.

Vegetation

The vegetation transplanted in the fall of 1987 has recovered well in Cells B and C. The plants in

Cell A do not appear to be quite as vigorous, possibly due to the differences in the substrate and microbiological processes believed to be occurring in this cell. The speculation is that the level of ammonia was initially too high in the fresh mushroom compost. The health of the plants in Cell A appears to be improving as the decomposition processes continue. Metal uptake by the plants is measurable (around 1%) but remains insignificant when compared to metal removal through the activity of bacteria present in the organic substrate.

Some channelization of surface water is caused by the hasty placement of the transplanted vegetation with respect to maintaining appropriate water levels in the system. Channelization may reduce contact between the acid mine drainage and the organic substrates and thereby reduce the efficiency of the system. Careful placement of the different species of vegetation may be more effective in reducing the channelization. However, by the beginning of the second growth season, the cattails dominated the wetland and prevented channelization.

Thus, the presence of vegetation appears to be more important for stabilization of the substrate, reduction of channelization in the surface flow, and continual additions to the biomass of the system than for metal uptake. Metal uptake by plants was also found to be insignificant in comparison to metal removal through other processes by *Sagittaria* and *Bombina* (58). The choice of the species of vegetation, therefore, is not of primary importance, as long as they are able to tolerate the conditions of the acid mine drainage and local climate. If the objective is to have the vegetation emulate a natural ecosystem, complexity may be favored rather over simpler ecosystems (69).

INITIAL PERFORMANCE

From the beginning, removal of heavy metals occurred in all cells, and Cell A with mushroom compost was most effective in removing contaminants and raising the pH. For the first year of operation, selected values for the mine drainage input and the cell outputs are shown in Table 10. Mn, Fe, Cu, and Zn are the primary metal contaminants and also give excellent indication of the removal processes that are operating. Figures 7 and 8 plot the concentrations of Fe and Cu respectively in the mine drainage, Cell A effluent, and Cell B effluent for the first year of operation. In the first year an attempt was made to hold the loading rate at 200 square feet/gallon/minute.

During June and July of 1988, a study was made on how removal changed with flow rate. Because the size of the cell is fixed at 18.6 m², (200 ft²), the wetland loading in ft²/gpm is inversely proportional to the flow rate. The results of that study are given in Table 11. Changes in effluent concentration for Zn and Fe plotted against the loading factor in square feet/gallon /minute are plotted in Figures 9 and 10. Note that for copper in Cell A, 100 % removal began at about 400 square feet/gallon /minute. The best results during this period were for Cell A at a loading rate of 600 square feet/gallon/minute. Removal of Cu and Zn was 100 %, removal of Fe was 63 %, and pH increase was from 3.0 to 6.2. Mn was not removed. The removal patterns and results from other experiments gave convincing evidence that the important removal process was bacterial reduction of sulfate dissolved in the mine drainage to hydrogen sulfide and subsequent precipitation of the metals as sulfides. The case for sulfate reduction will be presented in SECTION 5.

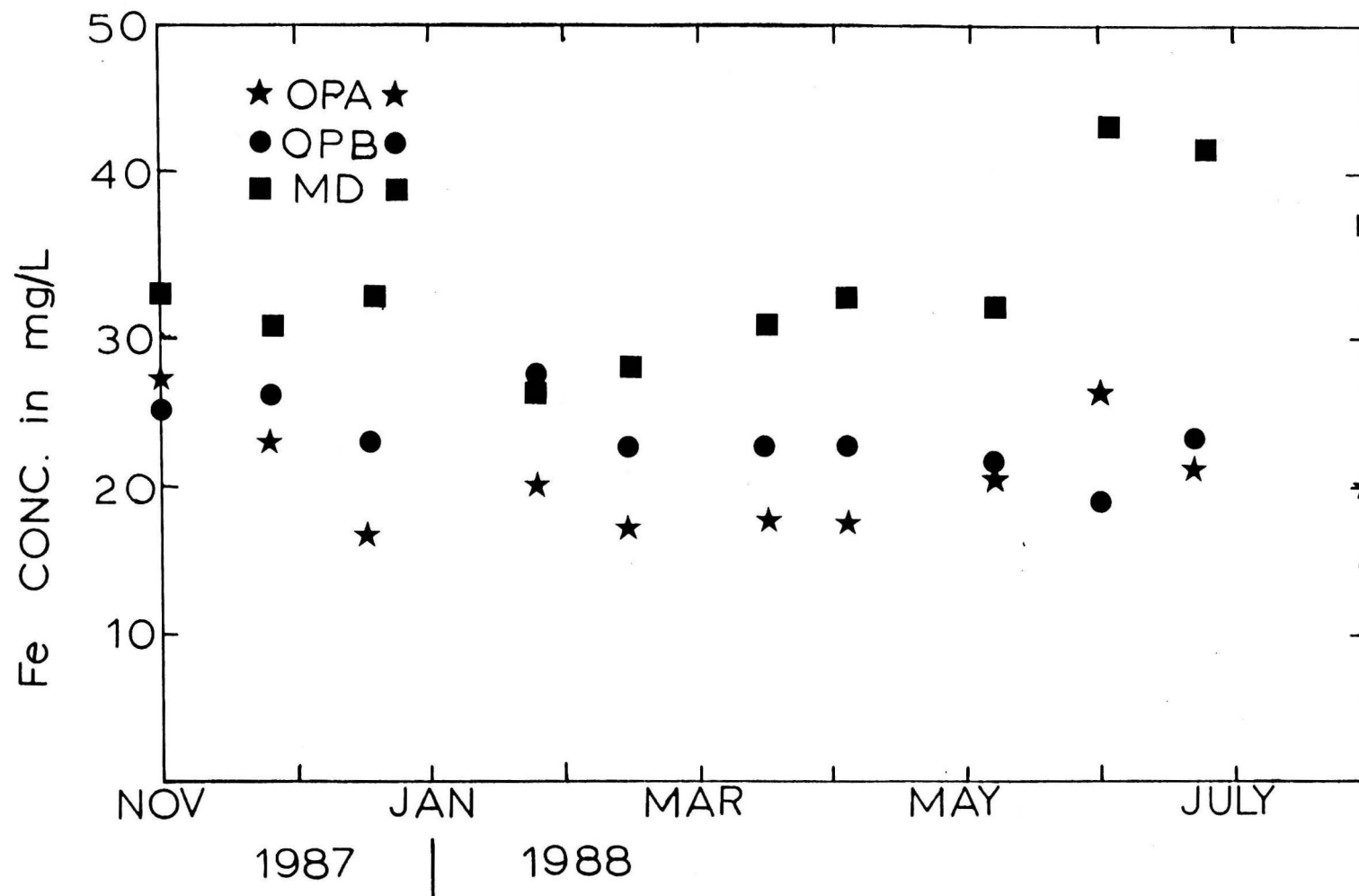


Figure 7. Iron removal in the Big Five Cells over 1987-88. In the figure, OPA is effluent from Cell A, OPB is effluent from Cell B, and MD is the mine drainage

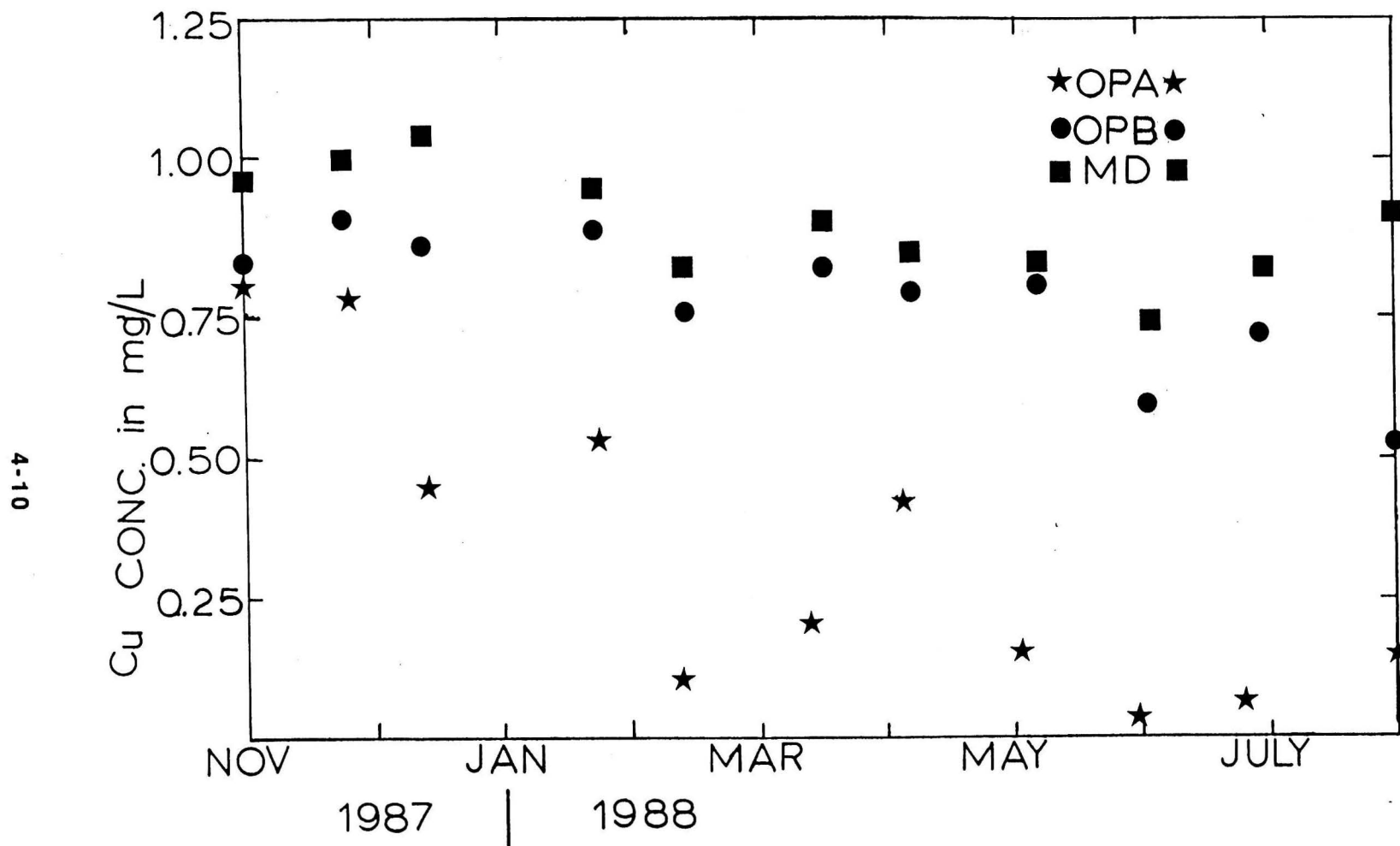


Figure 8. Copper removal in the Big Five Cells over 1987-88. In the figure, OPA is effluent from Cell A, OPB is effluent from Cell B, and MD is the mine drainage

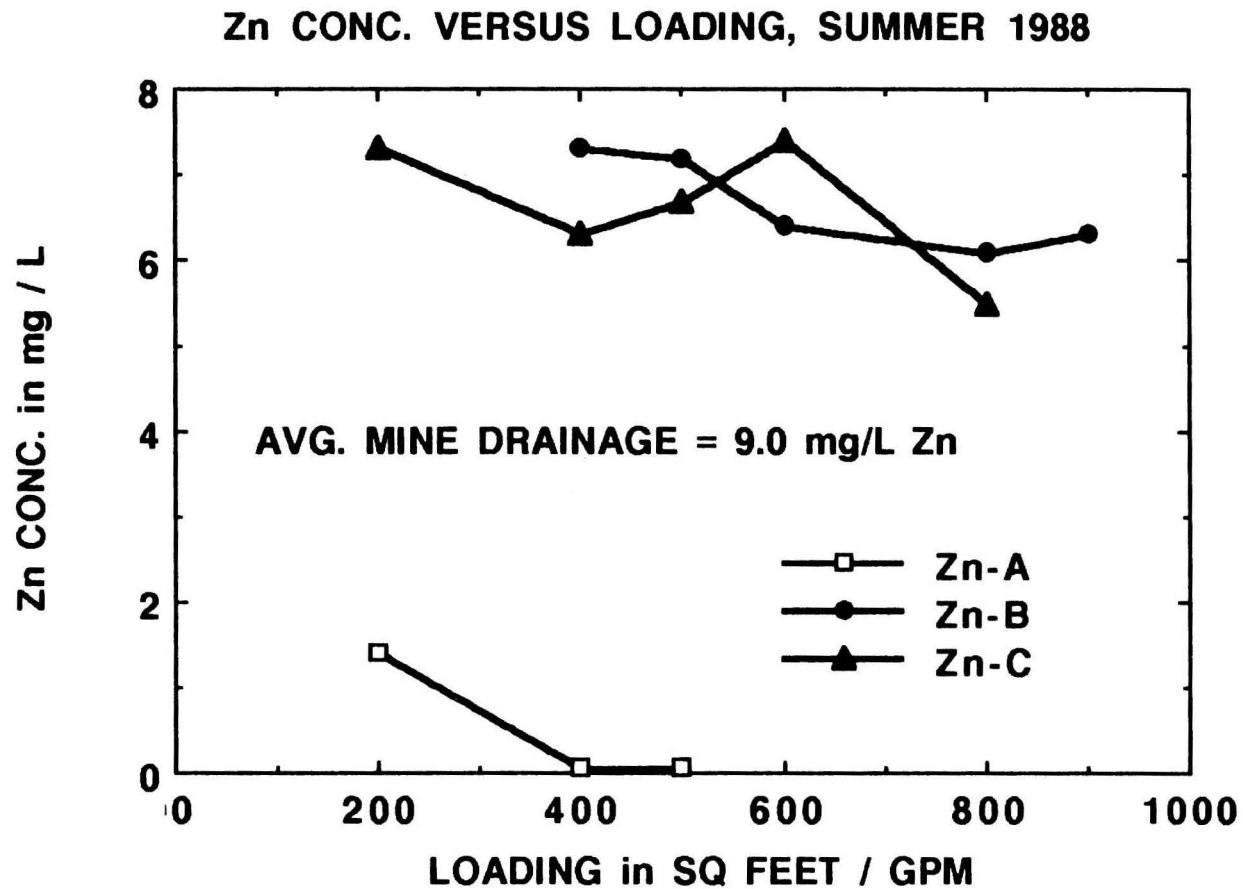


Figure 9. Zinc concentration versus loading factor for June & July 1988.

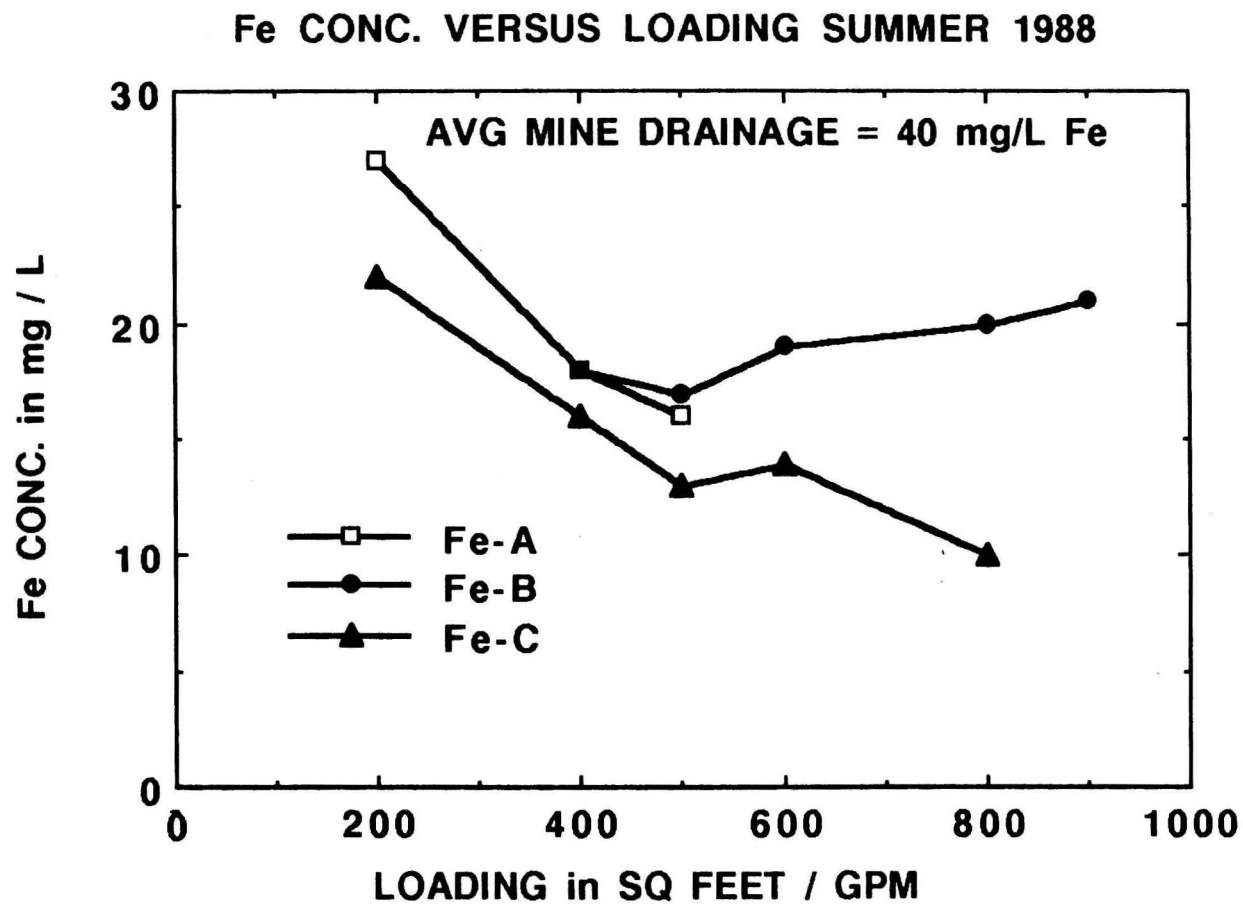


Figure 10. Iron concentration versus loading factor for June & July 1988.

TABLE 10. Concentrations (mg/L) of metals, percent reduction of metals, pH, and flow rates (liter/minute) in the Big Five Mine Drainage and wetland cell output waters during 1987-88.
The area of Cells A, B, and C is 200 ft².

Water Sample	Mn	% red.	Fe	% red.	Zn	% red.	Cu	% red.	pH	flow rate
November 3, 1987										
Mine Drainage	35		33		9.6		0.98		2.8	
Cell A	40	-14	27	18	8.4	12	0.81	17	3.1	3.8
Cell B	33	6	26	21	8.7	9	0.86	12	2.8	3.8
Cell C	34	3	26	21	8.3	13	0.82	16	3.1	3.8
December 11, 1987										
Mine Drainage	32		33		10.6		1.07		2.8	
Cell A	27	16	18	44	7.8	26	0.44	59	4.6	3.8
Cell B	33	-3	24	27	9.8	8	0.89	17	3.1	3.8
Cell C	34	-6	22	33	9.6	10	0.91	15	3.3	3.8
February 13, 1988										
Mine Drainage	28		28		8.2		0.86		3.3	
Cell A	27	3	18	35	5.9	28	0.14	84	5.2	3.8
Cell B	28	0	23	18	7.6	7	0.77	10	3.6	3.8
Cell C	28	0	25	11	7.9	4	0.87	0	3.6	3.8
March 9, 1988										
Mine Drainage	30		32		9.5		0.93		2.8	
Cell A	29	3	19	41	6.8	28	0.21	77	4.2	3.8
Cell B	30	0	24	25	8.6	9	0.83	11	3.2	3.8
Cell C	30	0	26	19	8.8	7	0.85	9	2.9	3.8
April 2, 1988										
Mine Drainage	29		34		9.1		0.88		3.2	
Cell A	29	0	19	44	6.7	26	0.43	51	4.2	3.8
Cell B	29	0	24	29	8.4	8	0.80	10	3.1	3.8
Cell C	28	3	25	26	8.2	10	0.79	10	3.2	3.8
May 31, 1988										
Mine Drainage	25		44		8.1		0.75		3.0	
Cell A	26	-3	28	36	5.5	32	0.02	97	4.3	3.8
Cell B	25	0	17	61	7.4	10	0.64	15	3.0	3.8
Cell C	25	0	21	52	7.7	5	0.68	9	3.0	3.8
June 27, 1988										
Mine Drainage	27		43		8.4		0.85		3.0	
Cell A	27	0	22	49	0.12	98	0.06	93	4.9	3.8
Cell B	28	-3	25	42	7.6	7	0.75	12	2.9	3.8
Cell C	27	0	23	46	7.6	7	0.69	19	3.0	3.8
July 29, 1988										
Mine Drainage	26		37		8.1		0.91		2.9	
Cell A	25	3	20	46	0.03	100	0.17	81	5.5	1.9
Cell B	26	0	16	57	6.4	21	0.57	33	3.3	0.90
Cell C	25	3	11	70	5.8	28	0.38	58	3.4	1.3

Table 11. Loading factor (ft²/gal/min) versus effluent concentration in mg/L at the Big Five wetland cells in June and July 1988. Area / Flow is in square feet/gallon/minutes

Date	Cell	Area/Flow	pH	Mn	Fe	Zn	Cu
6-23:	A	933	6.65	---	---	---	---
6-23:	B	6600	6.25				
6-23:	C	8400	6.70				
--Changed Flows on A, B, & C on 6-23--							
6-27:	A	200	4.95				
6-27:	B	200	3.95				
6-27:	C	200	3.0				
6-27:	MD	---	3.0				
--Changed Flows on A * B on 6-27--							
6-30:	A	400	6.25	26.	20.	<0.05	<0.03
6-30:	B	400	3.20	29.	18.	7.3	0.54
6-30:	C	200	3.0	29.	23.	7.5	0.73
7- 4:	A	400	6.1	26.	15.	<0.05	<0.03
7- 4:	B	460	3.1	29.	18.	7.4	0.58
7- 4:	C	200	3.1	29.	20.	7.3	0.79
7- 7:	A	380	6.05	26.	16.	<0.05	<0.03
7- 7:	B	450	3.05	28.	19.	7.5	-
7- 7:	C	200	2.95	28.	22.	7.2	0.75
7- 7:	MD	---	3.05	28.	40.	8.6	0.95
--Changed Flows on A, B, * C on 7-7--							
7- 8:	A	200	4.6	27.	25	0.8	<0.03
7- 8:	B	600	3.10	27.	18.	6.4	0.49
7- 8:	C	400	3.10	28.	16.	6.3	0.56
7- 9:	A	200	4.65	27.	25.	1.3	<0.03
7- 9:	B	600	3.15	27.	16.	6.3	0.49
7- 9:	C	400	3.15	28.	16.	6.3	0.56
7-10:	A	200	4.50	27.	29.	2.3	<0.03
7-10:	B	600	3.05	27.	16.	6.7	0.45
7-10:	C	450	3.15	28.	13.	7.0	0.56
7-14:	A	200	4.6	26.	23.	1.4	<0.03
7-14:	B	600	3.25	28.	19.	6.1	0.46
7-14:	C	500	3.35	28.	15.	6.3	0.37
7-14:	MD		2.95				
--Changed Flows on B & C on 7-14; On A on 7-17--							
7-18:	A	400	5.95	26.	21.	<0.05	<0.03
7-18:	B	800	3.55	29.	20.	6.1	0.32
7-18:	C	650	4.30	28.	13.	7.4	-
7-21:	A	600	6.20	25.	16.	<0.05	0.04
7-21:	B	900	3.90	28.	21.	6.3	0.54
7-21:	C	800	4.05	28.	9.7	5.5	0.31

In Tables 10 and 11, there are large variations in removal even though the flow is constant. This is because the loading capacity of the cells, as determined by the amount of sulfate that can be reduced, was exceeded. How loading affects removal will be developed in SECTION 7.

SUBSEQUENT MODIFICATIONS

As pointed out in Table 8, a number of modifications and additions were made to the pilot plant cell in 1988 and 1989. Figure 11 is a diagram of the current configuration of the Big Five site. The changes and the results of those changes are discussed in this section.

Cell A Modification

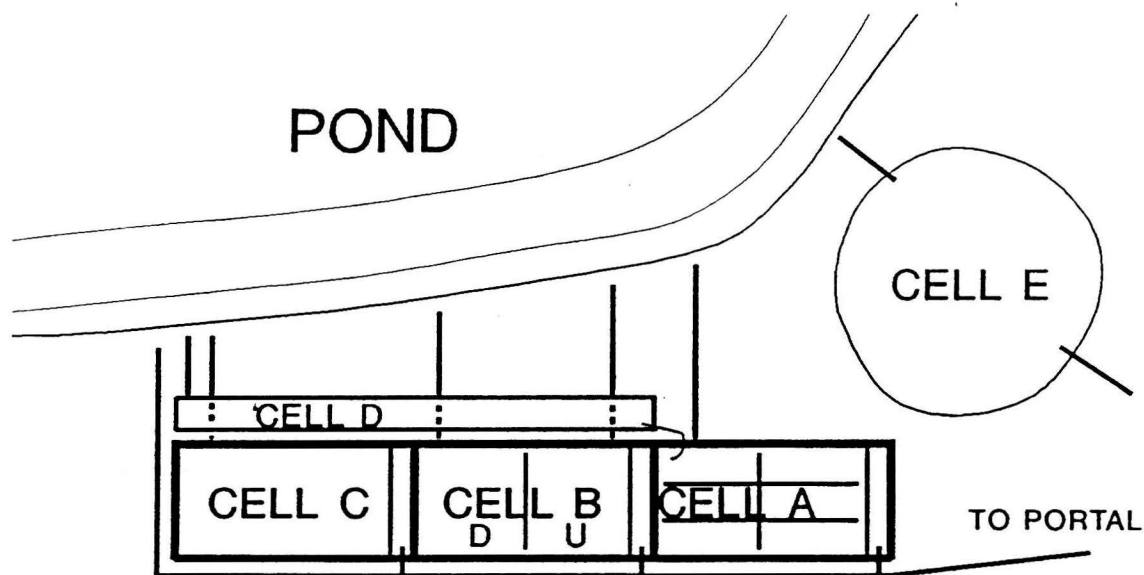
The first redesign concentrated on the issue of increasing the contact of the drainage with the substrate, especially in the anaerobic zone. This was accomplished by the addition of: a) Two walls running the length of the cell to increase the flow path length by a factor of three, and b) Six redistribution baffles to collect water flow from the top surface and redistribute it to the bottom of the substrate. This was done on Cell A and a cut-a-way view of the redesign is shown in Figure 12. Essentially, Cell A was redesigned to be a six segment plug-flow reactor (70).

Although the initial structure was amenable to major changes, the results of the redesign were discouraging. The desired plug flow (ideally, horizontal flow at all depths in the substrate) from segment to segment through the lower part of the substrate was not achieved. Considerable water flowed across the top of cell segments and leaked from one segment to others. When the cell was modified, the original mushroom compost was removed, stockpiled, and returned to the cell after the remodeling. It was speculated that through this handling, substrate permeability significantly decreased. Subsequent experiments on new and used mushroom compost from Cell A verified that permeability decreased from 3.0×10^{-3} to 9.2×10^{-5} cm/sec (9). Selected values on removal and changes in pH from the cells during this phase are shown in Table 12.

As a result of this setback, a laboratory and bench scale program was developed to determine how well typical soil tests could be adapted to this highly organic substrate. Especially important were the development of methods to determine hydraulic conductivity that could give reasonable indications of what to expect in a constructed wetland (9). Other tests on substrate materials included the determination of specific gravity, bulk density, size fractions, and percent moisture. The processes that cause the permeability of the substrate to change with time will be discussed in more detail in SECTION 10.

Plug-Flow, Upflow, and Downflow Cells

The initial constructed wetland designs for the Big Five Cells used the concept of plug flow. Basically, plug flow is similar to pipe flow in that the water is meant to travel through a cross-sectional area that is small relative to the length of travel in the substrate. In the case of wetlands, plug flow was meant to be essentially horizontal flow throughout the entire thickness of the wetland, as shown in Figure 12. In operation, however, most of the flow ends up being at or near the surface, due to the compaction-caused rapid decrease of permeability with depth in the wetland and having the outlet at the surface of the cell.

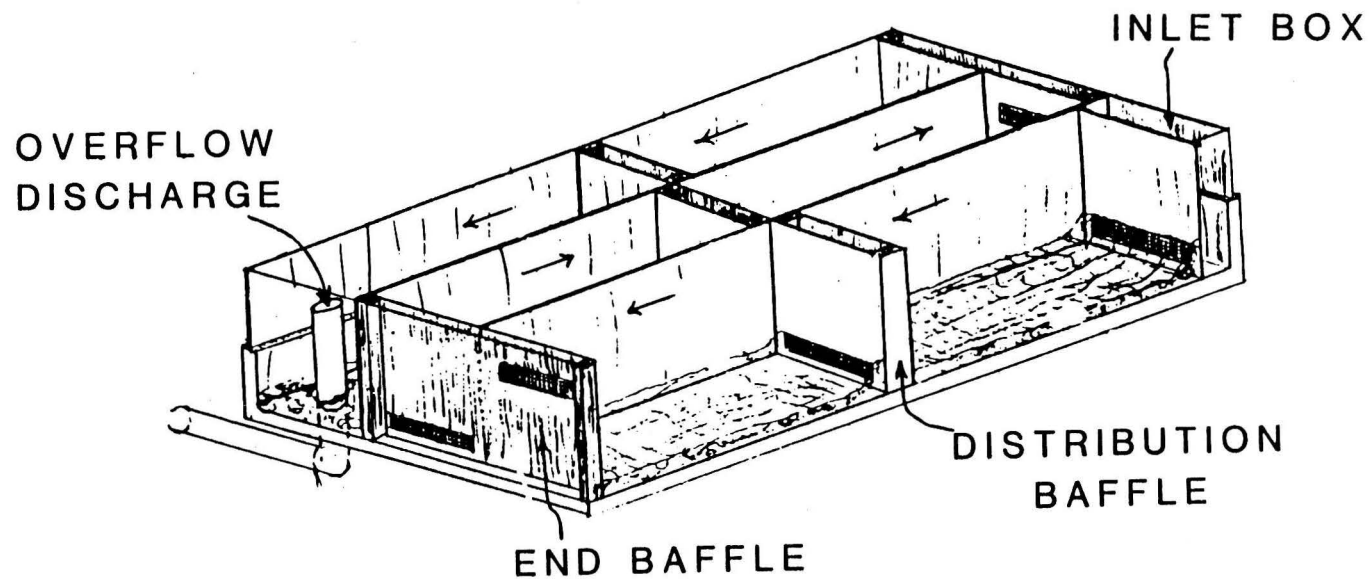


SCHEMATIC OF TREATMENT CELLS BIG-FIVE PILOT SYSTEM

SURFACE AREAS	square feet	square meters
Cell A	200	18.6
Cell B - <u>U</u> pflow	100	9.3
Cell B - <u>D</u> ownflow	100	9.3
Cell C	200	18.6
Cell D	~100	~9.3
Cell E	~100	~9.3

Figure 11. Present Big Five Site configuration.

CUT-A-WAY VIEW WETLANDS PILOT SYSTEM



4-17

Figure 12. A cut-a-way diagram of the Cell A redesign.

TABLE 12. Concentrations (mg/L) of metals, percent reduction of metals, pH, and flow rates (liter/minute) in the Big Five Mine Drainage and wetland cell output waters during 1988-89.
The area of Cells A, B, and C is 200 ft².

Water Sample	Mn	% red.	Fe	% red.	Zn	% red.	Cu	% red.	pH	flow rate
December 18, 1988										
Mine Drainage	29		38		9.2		0.80		3.0	
Cell A	28	3	31	18	8.6	6	0.62	22	3.4	4.5
Cell B	28	3	30	21	7.8	15	0.74	8	3.2	4.3
Cell C	28	3	28	26	7.7	16	0.69	14	3.3	4.7
January 21, 1989										
Mine Drainage	25		31		10.9		0.91		2.8	
Cell A	33	-32	32	-3	10.8	0	0.61	33	3.3	4.6
Cell B	34	-36	26	16	10.8	0	0.60	34	3.1	3.6
Cell C	33	-32	25	19	10.5	3	0.60	34	3.1	3.8
February 21, 1989										
Mine Drainage	23		38		9.0		0.72		3.0	
Cell A	28	-22	19	50	4.9	46	<0.05	100	5.1	1.0
Cell B	31	-34	39	-2	5.6	38	0.48	33	3.4	1.2
Cell C	25	-10	31	18	7.2	20	0.26	64	3.5	1.2
March 19, 1989										
Mine Drainage	22		40		8.3		0.73		3.0	
Cell A	24	-9	23	42	0.28	100	<0.05	100	6.5	0.21
Cell B	29	-32	7.3	82	3.9	53	0.21	71	5.7	0.36
Cell C	28	-27	7.3	82	2.0	76	<0.05	100	6.3	0.60
April 16, 1989										
Mine Drainage	29		39		9.8		0.70		2.7	
Cell A	32	-10	31	20	8.5	15	0.47	33	3.9	2.1
Cell B	32	-10	18	54	6.6	33	0.34	51	3.6	0.94
Cell C	30	-3	40	-2	9.6	2	0.66	57	3.9	1.4
May 21, 1989										
Mine Drainage	44		48		10.5		0.85		3.3	
Cell A	41	7	31	35	9.4	10	0.58	32	3.8	2.3
Cell B	37	16	0.46	100	0.22	100	<0.05	100	5.7	2.2
Cell C	35	20	24	50	8.9	15	0.62	27	3.2	2.3
June 16, 1989										
Mine Drainage	29		48		7.6		0.76		3.0	
Cell A	34	-17	26	46	4.4	42	<0.05	100	4.6	1.7
Cell B	29	0	30	38	7.9	4	0.60	21	3.0	2.2
Cell C	35	-21	26	46	5.7	25	0.46	39	3.0	2.4
July 14, 1989										
Mine Drainage	30		41		8.9		0.72		3.0	
Cell A	30	0	17	59	0.25	100	<0.05	100	5.7	1.2
Cell B	33	-10	17	59	7.1	20	0.36	50	3.3	1.1
Cell C	33	-10	13	68	2.2	75	<0.05	100	5.1	1.0

Plug flow design is suitable for aerobic wetlands because the aerobic layer is at the surface. In anaerobic wetlands, it is desirable to maximize flow through the subsurface anaerobic layers. Therefore, upflow and downflow cells were designed to maximize vertical flow, as shown in Figure 13. In upflow and downflow designs, which are similar to conventional trickling filters in concept, the cross-sectional area of substrate perpendicular to flow is large compared with the length of travel of fluid in the substrate.

Cell B Modification

Results of laboratory and bench-scale permeability experiments led to the modification of Cell B into upflow and downflow cells to monitor and evaluate permeability at the pilot scale. The original cell was divided into two lined, identical cells so individual variables could be tested. All features needed to determine soil permeability in the cell were included. A special feature in the design was inclusion of a plenum beneath each subcell for even distribution of drainage in the upflow configuration and even collection when used as a downflow cell. Each cell could be operated in the upflow or downflow configuration. Figure 13 is a cut-a-way diagram of the downflow operation.

There are a number of features in this modification that should improve contact with the substrate. When operating either as an upflow or downflow cell, the mine drainage is forced through the substrate before discharge. This configuration is comparable to a trickling filter process instead of the plug flow reactor design in the Cell A modification (70). Also included in the modification, was the addition in series of two 150 gallon stock tanks before the inlets of the subcells. Figure 13 shows the placement of one of the tanks. The tanks serve the purpose of completing the precipitation of ferric hydroxides before drainage enters the subcells so that plumbing, plenums, and filter fabrics do not become clogged. In both the upflow and downflow parts of the new Cell B, plants were not used. Instead, the substrate was covered with 25 cm of hay and then 6 mil black plastic to provide insulation during the winter.

Remodeling of Cell B was completed in August, 1989. The two subcells were filled with fresh mushroom compost to a depth of 0.61 m. This substrate material was selected because it appeared to provide the best metal removal performance among the three substrates used in the original cells. Flow of mine drainage through the subcells was initiated on September 1. One subcell (Cell B-North, or B-N) was operated in the upflow configuration, the other (Cell B-South or B-S) downflow. The positions of these cells is shown in Figure 11. Upflow permeability measured 1.3×10^{-3} cm/sec, and downflow permeability measured 3.1×10^{-4} cm/sec (9). The average permeability of substrate in cells operating in the upflow mode is expected to be higher than permeability of substrate in cells using downflow or plug flow. The increased permeability probably occurs because the upward driving force required under upflow conditions counters the downward compressive force due to the effect of gravity on overlying layers of substrate, so that compaction of the substrate would be less. The development of laboratory and bench-scale methods for predicting permeability in actual constructed wetlands has proven successful.

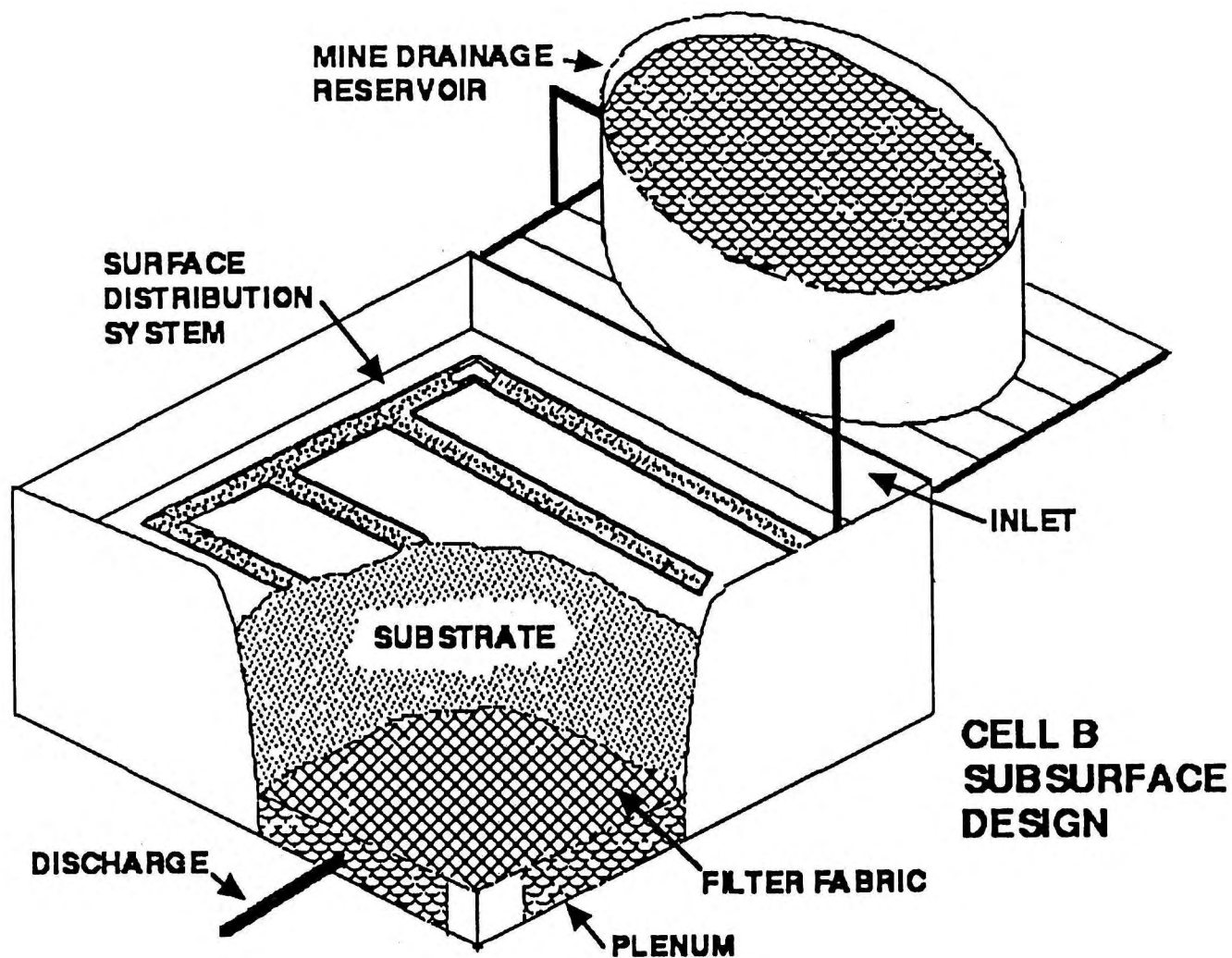


Figure 13. A cut-a way diagram of the Cell B redesign in the downflow mode.

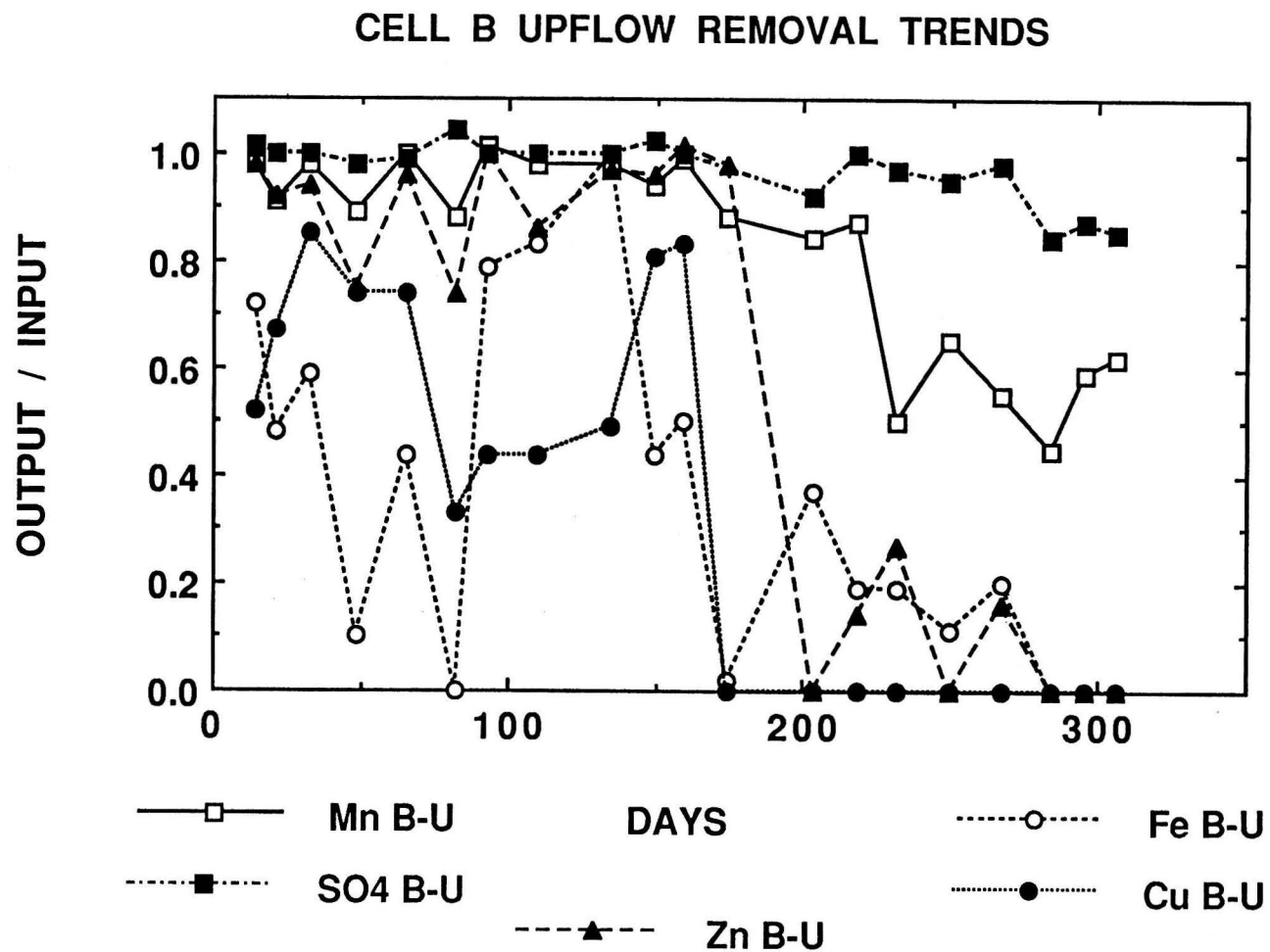


Figure 14. Removal of contaminants in Cell B Upflow over 1989-90.

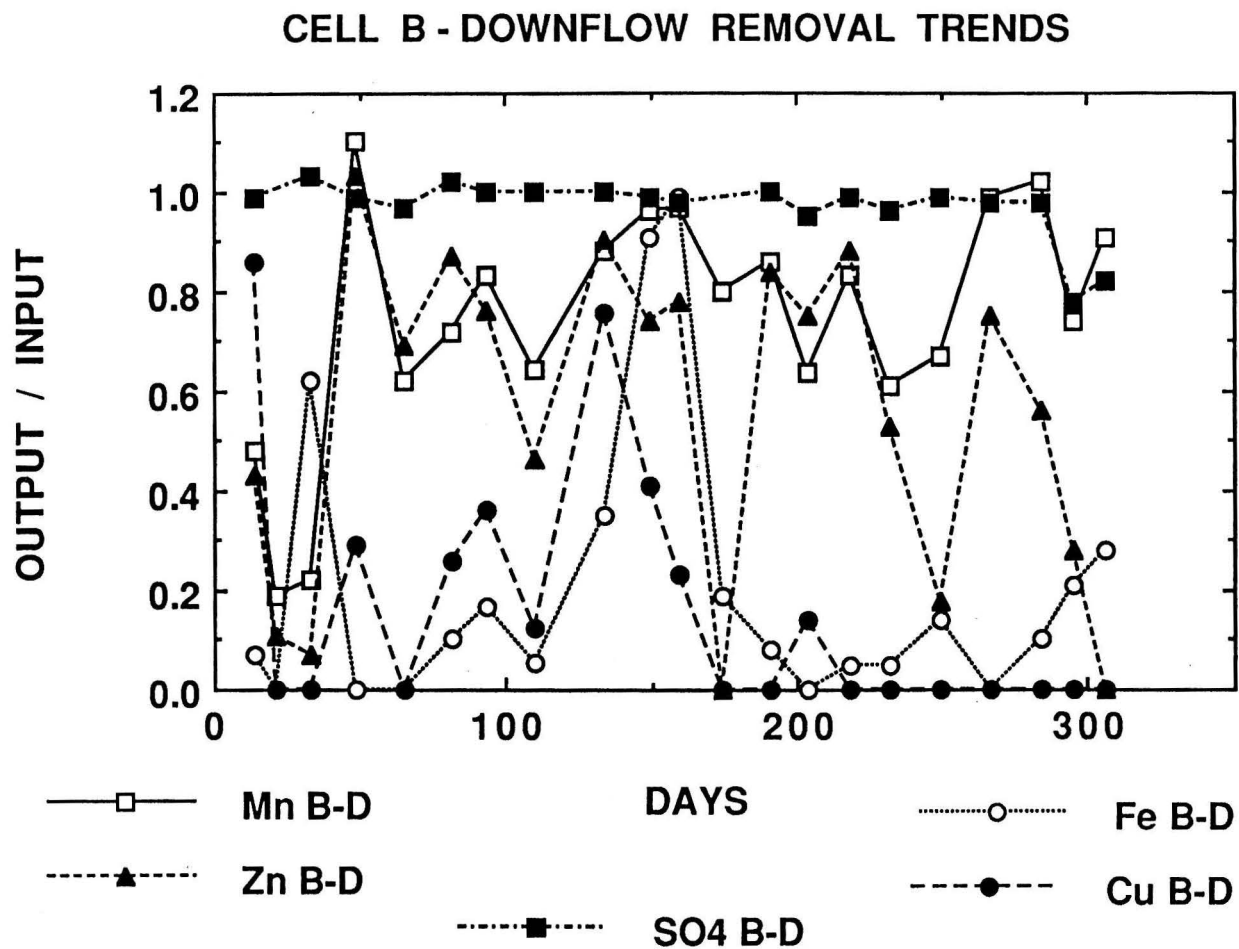


Figure 15. Removal of contaminants in Cell B Downflow over 1989-90.

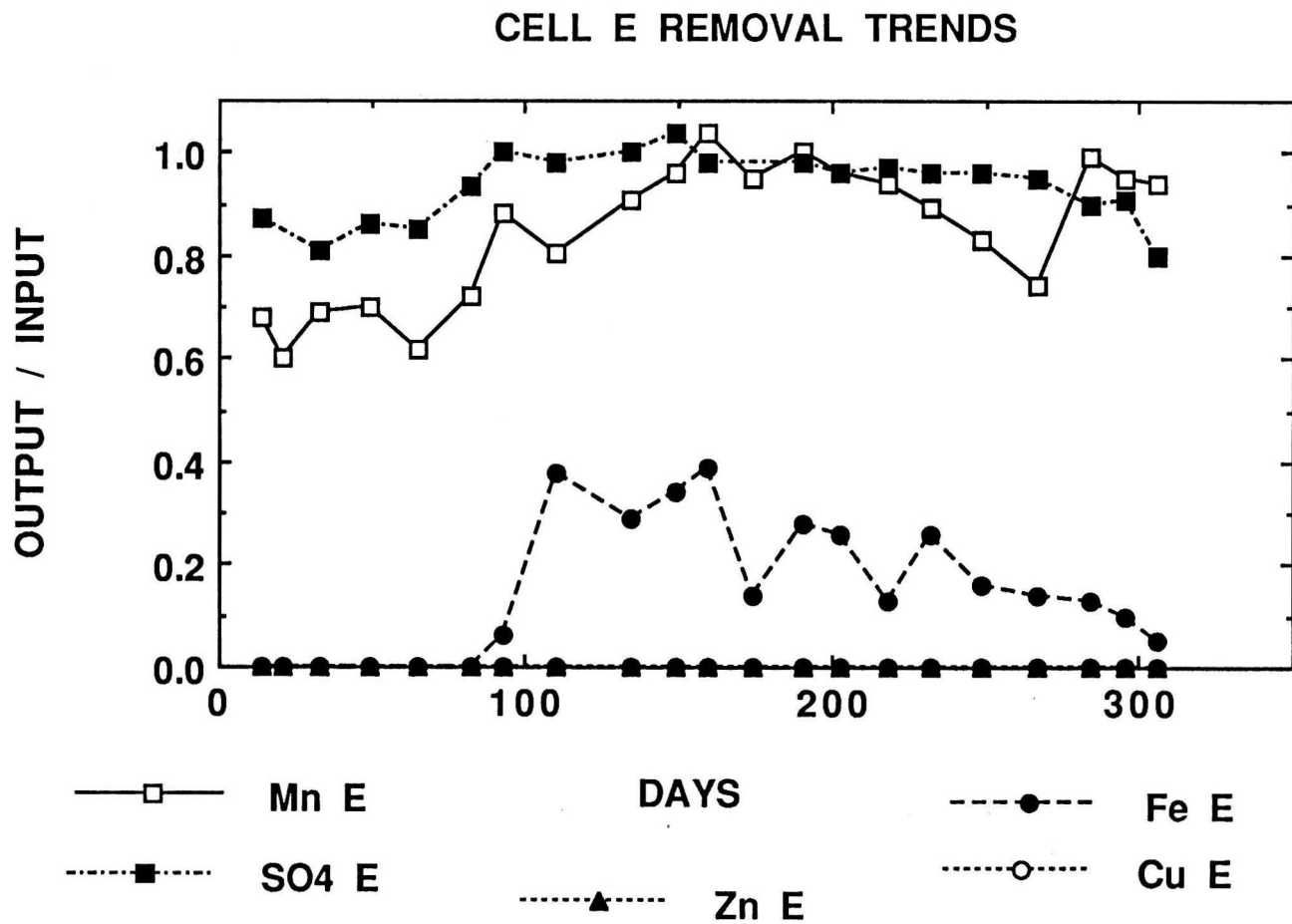


Figure 16. Removal of contaminants in Cell E over 1989-90.

Table 13. Concentrations (mg/L) of metals, percent reduction of metals, pH, and flow rates (liters/minute) in the Big Five Mine Drainage and wetland cell output waters during 1989-90*.

Water Sample	Mn	% red.	Fe	% red.	Zn	% red.	Cu	% red.	pH	flow rate
October 3, 1989										
Mine Drainage	35		46		9.9		0.66		3.2	
Cell A	35	0	31	33	2.2	78	0.07	89	5.1	0.98
Cell B-Up	34	3	39	15	9.3	6	0.59	11	3.5	1.1
Cell B-Down	7.7	78	23	50	0.76	92	<0.05	100	6.5	0.60
Cell C	36	-3	29	37	7.8	21	0.22	67	3.5	0.79
Cell D	32	8	24	48	<0.05	100	<0.05	100	6.1	0.32
Cell E	24	31	0.5	100	<0.05	100	<0.05	100	6.3	0.71
November 5, 1989										
Mine Drainage	32		38		8.7		0.61		2.9	
Cell A	32	0	27	29	8.2	6	0.49	20	3.5	2.0
Cell B-Up	31	3	17	55	8.4	3	0.48	21	3.6	0.83
Cell B-Down	20	38	0.36	100	6.0	31	<0.05	100	5.9	0.72
Cell C	32	0	27	29	8.2	6	0.52	15	3.5	1.4
Cell D	29	9	16	58	0.77	91	<0.05	100	5.7	2.6
Cell E	20	38	0.29	100	<0.05	100	<0.05	100	6.5	0.42
December 3, 1989										
Mine Drainage	30		43		9.0		0.58		3.0	
Cell A	30	0	21	51	1.3	85	<0.05	100	6.0	1.1
Cell B-Up	30	0	34	21	9.0	0	0.44	24	3.5	1.4
Cell B-Down	25	17	7.1	83	6.8	24	0.21	64	4.1	1.1
Cell C	30	0	32	26	8.5	5	0.52	10	3.4	1.3
Cell D	30	0	17	60	0.07	100	<0.05	100	6.2	0.57
Cell E	26	13	2.6	94	<0.05	100	<0.05	100	6.3	0.42
January 13, 1990										
Mine Drainage	31		33		9.0		0.60		2.9	
Cell A	31	0	26	21	7.4	18	0.36	40	3.3	1.5
Cell B-Up	30	3	33	0	8.9	0	0.49	18	3.2	0.79
Cell B-Down	27	13	12	64	8.1	10	0.44	27	3.2	0.76
Cell C	42	35	31	6	5.5	39	<0.05	100	6.0	2.1
Cell E	28	10	9.8	70	<0.05	100	<0.05	100	6.0	.38
February 6, 1990										
Mine Drainage	31		36		9.0		0.53		2.8	
Cell A	33	-6	20	44	4.8	47	0.17	68	3.8	0.57
Cell B-Up	30	3	36	0	7.0	22	0.12	77	3.3	0.45
Cell B-Down	31	0	18	50	9.1	0	0.44	17	3.2	0.49
Cell E	32	-3	14	61	<0.05	100	<0.05	100	5.8	0.76
March 10, 1990										
Mine Drainage	29		60		9.0		0.52		3.2	
Cell A	28	-3	36	40	2.0	78	<0.05	100	5.4	0.87
Cell B-Down	25	14	4.9	92	7.6	16	<0.05	100	6.0	NA
Cell E	28	-3	17	72	<0.05	100	<0.05	100	6.4	0.83

The area of Cells A, B, and C is 200 ft²; the area of Cells B-Up, B-Down, D and E is 100 ft².

Table 13. continued

Water Sample	Mn	% red.	Fe	% red.	Zn	% red.	Cu	% red.	pH	flow rate
April 6, 1990										
Mine Drainage	31		55		8.7		0.48		3.0	
Cell A	30	3	31	44	1.5	83	<0.05	100	5.2	0.91
Cell B-Up	27	13	11	80	1.2	86	<0.05	100	6.6	0.26
Cell B-Down	26	16	2.9	95	7.7	11	<0.05	100	6.0	0.15
Cell C	29	6	16	71	0.08	100	<0.05	100	6.6	1.30
Cell D	22	29	9.9	82	<0.05	100	<0.05	100	6.8	0.68
Cell E	29	6	7.1	87	<0.05	100	<0.05	100	6.2	0.41
May 7, 1990										
Mine Drainage	30		45		9.5		0.54		2.9	
Cell A	28	7	33	27	1.5	84	0.05	100	5.4	0.83
Cell B-Up	19	37	5.1	89	0.08	100	<0.05	100	6.8	0.19
Cell B-Down	20	33	6.3	86	2.8	70	<0.05	100	6.3	0.30
Cell C	28	-6	7.0	84	6.7	29	0.30	44	4.1	0.76
Cell D	20	33	5.9	87	<0.05	100	<0.05	100	6.6	0.23
Cell E	25	17	7.0	84	<0.05	100	<0.05	100	6.4	0.42
June 11, 1990										
Mine Drainage	32		40		8.8		0.59		3.0	
Cell A	33	-3	36	10	2.5	72	<0.05	100	4.9	0.79
Cell B-Up	14	56	0.42	100	0.08	100	<0.05	100	6.6	0.45
Cell B-Down	33	-3	3.9	90	5.0	43	<0.05	100	5.5	0.41
Cell C	33	-3	NA	-	4.6	48	NA	-	3.8	0.15
Cell E	31	5.2	<0.05	87	<0.05	100	<0.05	100	6.0	0.68
July 3, 1990										
Mine Drainage	30		38		9.4		0.55		3.1	
Cell A	29	3	26	31	5.0	45	<0.05	100	4.0	1.0
Cell B-Up	18	40	1.8	95	<0.05	100	<0.05	100	7.0	0.26
Cell B-Down	27	10	11	71	0.78	92	<0.05	100	6.3	0.15
Cell C	32	-6	13	66	6.3	32	0.07	87	4.0	0.79
Cell D	26	13	4.8	87	<0.05	100	<0.05	100	6.2	0.94
Cell E	28	7	1.8	95	<0.05	100	0.08	85	6.2	0.11
August 13, 1990										
Mine Drainage	34		47		9.2		0.54		3.0	
Cell A	35	-3	19	60	2.6	72	<0.05	100	5.0	0.87
Cell B-Up	25	26	3.9	92	<0.05	100	<0.05	100	6.8	0.57
Cell B-Down	45	32	21	55	3.7	60	<0.05	100	6.7	0.34
Cell C	36	-6	8.2	82	6.0	35	<0.05	100	5.0	0.76
Cell D	34	0	6.0	87	<0.05	100	<0.05	100	6.4	0.53
Cell E	35	-3	2.0	96	<0.05	100	<0.05	100	6.2	0.53

*The area of Cells A, B, and C is 200 ft²; the area of Cells B-Up, B-Down, D and E is 100 ft².

Values on removal of Mn, Fe, Cu, and Zn and increases in pH for Cell B-Upflow and Cell B-Downflow are given in Table 13. Just as for the original Cell A design, removal has occurred from initiation of flow. Figure 14 shows output/input over time for Cell B in the upflow mode; Figure 15 shows the same for Cell B downflow.

Initially, removal from the downflow system was better than from the upflow, however, flows through the cells have not always been equal. Also, the pattern of removal of Zn and Mn with little or no removal of sulfate, indicates that the initial removal in the downflow cell is by organic complexation instead of sulfate reduction (7). After 3 months, removal in the downflow cell is not as good as during the first month. This is particularly the case for Mn and Zn. This implies that the sites for organic complexation are being saturated after about three months (7). Organic complexation compared with sulfate reduction will be discussed further in SECTION 5. In the upflow cell, poor initial removal is attributed to ponding and oxygenation of water on the surface of the substrate and an excessive loading factor. In March of 1990, after about 180 days of operation these problems were rectified. Since then, removal of heavy metals from the upflow cell has been excellent. That the adjustments worked gives important evidence that sulfate reduction processes can recover if loading factors are not exceeded. Also, to keep an upflow cell anaerobic, effluent has to be taken from the cell before it breaches the surface.

Cells D and E Design, Construction, and Operation

When Cell B was remodeled, Cells D and E were constructed using the original substrate from Cell B. Their positions and configuration in the site are shown in Figure 11. Cell D was designed to polish discharges from anaerobic cells by using aerobic processes. Features of the design include a shallow depth (0.50 m) and a length to width ratio of 10. Substrate and plants from the original Cell B were used. It has been receiving the discharge from Cell A. Removal of Cu, Zn, and Fe is completed in Cell D and the pH is raised to above 6.

Cell E was designed to operate as a downflow, subsurface wetland. Construction was completely accomplished with materials found locally. It is approximately 9.3 m² and the substrate is 0.61 m deep. As in Cell D, substrate and plants from the original Cell B were used. Subsurface flow is achieved by flow through landscape fabric into 2.5 cm gravel and subsequent discharge into a tube on the downflow end. For this system, results have been excellent.

Flow of mine drainage through Cell E was initiated on September 1, 1989. From the beginning, removal of Cu, Zn, and Fe has been 100 %, pH has increased to 6.5, and Mn removal has averaged 25 %. Removal results are given in Table 13 and are shown in Figure 16. Laboratory experiments have confirmed that sulfate reduction with subsequent precipitation of metal sulfides is the predominant removal process in Cell E (7).

The removal successes with Cells D and E confirm that it was not the chemical or microbiological characteristics of the peat/manure/decomposed wood substrate that caused Cell B to operate more poorly than Cell A. Rather, the poor performance was caused by the low permeability of the substrate. Products of microbial reactions occurring within the substrate couldn't come in contact with the metals in the mine drainage.

OPERATIONS DURING THE WINTER

The last four winters have allowed observations on how well wetland cells operate during the winter. Not all of the cells have kept operating during the winter. Two key factors allow winter operation: The mine drainage water is about 12 to 15 °C the year round, and portions of the site are in winter sun throughout the day. Below, the winter success of each cell is described.

Cell A has operated continuously through all four winters. This is the case even when the flow was cut back from 4 L/min to 1 L/min. Three reasons can be given for the winter success of Cell A:

1. It is continuously in the sun.
2. Compared with Cells B and C, more of the water flows through the substrate rather than across the surface and thus the surface is less prone to freezing.
3. The inlet is small and insulated so the energy within the water is not lost.

When the flow into Cell C was cut back to 1 L/min, it has frozen over the last two winters. This cell is more shaded during the winter. The dense growth of Typha in Cell C inhibits solar radiation from reaching the substrate-water interface. In addition, Cell C still has the original rock box inlet. This inlet allows much of the water energy to be lost.

Cell D was built in the summer of 1989 and in both winters it has frozen. This is primarily a surface flow cell and the depth of the substrate is only 0.5 meter. Also it is not well insulated.

Cell E has worked well over the last two winters. It is shallow, but is a subsurface flow cell and the surface is always in the winter sun. An important feature that keeps Cell E operating during the winter is that excess water enters the cell, flows across the surface, and over the spillway. This excess water, at 12 to 15 °C, provides thermal energy for the substrate.

The modified B Cells have operated over the winter primarily because the surface of the cells was insulated with hay and plastic. In fact, the temperature of the outlet only dropped 4 to 5 °C during January and February. On Cell B-Upflow the new outlet installed in the spring of 1990 was not insulated. It froze in December, 1990 and the cell had to be turned off for the winter. Cell B-Downflow did have an insulated outlet, and it has continued operations throughout both winters.

Guidelines for Winter Operation

From these observations, a number of guidelines can be established for insuring the operation of wetland systems in cold winter climates.

- o Use the thermal energy within the mine drainage water to best advantage. Insure that delivery systems are insulated. Keep inlet structures small and insulated.
- o Place wetland cells so they receive winter sun. If this cannot be completely achieved, at least insure that outlets are in winter sun.
- o Insulate the top of the cell with hay and plastic as in the B Cells or have excess surface flow as in Cell E.

- o Insulate wetland outlets and provide a method for the effluent to flow away from places where it could cause freezing problems. This is especially important if winter sampling is planned. Chopping ice from sampling outlets is tedious and damaging.
- o If possible, design subsurface flow systems such as Cells B and E. The thermal energy within the substrate will aid operation, whereas in a surface flow system the waters are exposed to the elements.

CONCLUSIONS

Using constructed wetlands for wastewater treatment is still a developing technology. However, the results from the Big Five Pilot Wetland that was funded by the Emerging Technology Program (ETP) of the U. S. EPA shows promising removal of heavy metals and increase of pH for acid mine drainage. Conclusions from the project include:

1. On a three year basis, toxic metals such as Cu and Zn can be removed and the pH of mine drainage can be increased.
2. The major removal process is sulfate reduction and subsequent precipitation of the metals as sulfides. Exchange of metals onto organic matter can be important during the initial period of operation.
3. A downflow, trickling filter style of configuration achieves the best contact of the water with the substrate.
4. Removal efficiency depends strongly on loading factors. In the Big Five wetland, factors above 1,000 feet² per gallon/minute are needed for reasonable removal. A more definitive method for establishing the loading rate for an anaerobic cell is given in SECTION 7.
5. Permeability of the substrate is a critical design variable for successful operation. Using laboratory and bench-scale tests, a good indication of the soil permeability in a constructed wetland can be determined.
6. Solutions to problems such as plugging of plumbing by ferric hydroxides and freezing of discharge lines during winter have to be designed and constructed into the passive nature of wetlands to achieve long term operation.
7. Eventual removal of precipitated metal sulfides for metal recovery or disposal must be included in the operating plan. Estimates of how long the substrate will last are included in SECTIONS 8 and 12.

SECTION 5

EVIDENCE FOR SULFATE REDUCTION

INTRODUCTION

Using wetlands to treat acid mine drainage has only been studied for a little over a decade (71). During the first few years of this research, biologists and ecologists dominated studies (39). As a result, constructed wetland studies concentrated on the surface ecosystem as the key to removal processes. Key wetland features in such a constructed wetland are:

1. If an ecosystem is needed, the smallest pilot system should be about 200 square feet.
2. Plants are necessary in a constructed wetland.
3. Aerobic processes are the key to removal.
4. Peat as a substrate would be desirable.

Typical constructed systems that were built using these guidelines are those in the Tennessee Valley (72), the Simco #4 wetland (73), the natural wetland along Peru Creek in Colorado (74), and the Tracy wetlands in Montana (75).

In some cases, removal of contaminants was achieved (39, 72). However, In most cases Fe was only partially removed (72, 73) and manganese and sulfate were generally not removed. In some cases the pH increased (72, 73), but just as often the pH decreased (72, 74). In some cases (74) it was feared that the drop in pH would release metals from the wetland system. From the discussion of wetland removal processes in SECTION 3, the drop in pH and release of metals might be expected. Aerobic processes oxidize ferrous to ferric and its precipitation definitely lowers the pH of the effluent. If the peat removes metals through some organic adsorption process, then increasing the concentration of hydrogen ions definitely shifts the adsorption equilibrium to release metals.

At the American Society for Surface Mining and Reclamation Meeting in 1988, the first suggestions that sulfate reduction may be an important process were made (41, 76, 77). In the same year, these suggestions were expanded at the Constructed Wetlands Conference sponsored by the TVA (3, 65). Since then, research efforts on sulfate reduction in constructed wetlands have centered on the studies done by the Colorado School of Mines group and by the U. S. Bureau of Mines group (41, 65, 66, 67). This section explores the evidence from the Big Five Pilot Wetland for sulfate reduction and sulfide precipitation as a removal process in a constructed wetland. The evidence follows the thought chronology while the project developed. It includes: Wetlands functioning immediately even during the winter; the pH of the effluent increasing; sulfide in the substrate; the metal removal pattern; and finally, sulfate decreasing in the effluent.

IMMEDIATE OPERATION EVEN DURING THE WINTER

Design and construction of the Big Five Wetland was met with a number of delays because the site was on the national CERCLA (Superfund) list. Transplanting of vegetation took place in September of 1987 and mine drainage first flowed through the wetland starting on October 21, 1987. There was concern that, because of the late starting time, no immediate removal would occur and plants would not survive the winter. Surprisingly, removal of contaminants and increase in pH occurred within the month. Table 10 and Figures 7 and 8 document this immediate removal. Cell A containing mushroom compost was particularly effective in contaminant removal. In Cell A, the surface of the wetland turned from rust colored to gray-black within five months. This was a strong clue that anaerobic processes were responsible for contaminant removal. In wetlands that were effective in Pennsylvania, Hedin noticed the same change to anaerobic conditions (41).

During the initial operation of Cell B-Downflow and Cell E contaminant removal patterns and changes in pH were closely monitored (7). Both these systems operated as downflow subsurface wetlands so comparisons should be on the chemistry and not the physical design. There are differences in the substrates. Cell E substrate was taken from the original Cell B and was peat/manure/and decomposed wood product laden with active sulfate reducers. In Cell B, new mushroom compost was used and mine drainage was immediately applied to the dry compost with no presoaking. In this case, the activity of sulfate-reducing bacteria should be low.

Laboratory Adsorption Studies

Examining the list of removal possibilities in SECTION 3 reveals that removal of contaminants by adsorption processes onto the organic or inorganic sites could occur immediately. Since the substrate is highly organic, it is assumed that adsorption by humic acids would be the predominant process. If this is the case, then the ideas in SECTION 3 concerning the role of pH and the order of metal adsorption should reveal whether adsorption is occurring. In particular, it has been found that Fe and Cu are more strongly adsorbed than Zn and Mn (53).

First, a laboratory adsorption test was conducted. To determine the extent of the adsorption of metals from the mine drainage by organic material in the substrate, a set of experiments was conducted that tested the adsorbing capability of fresh mushroom compost using the Big Five Tunnel mine drainage collected on October 19, 1989. First, 10 mL of a 1000 mg/L solution of SeO_4^- was added to 0.100 g of the substrate used in Cell B-Downflow to inhibit sulfate reducing bacteria (54). Second, various volumes of mine drainage (10, 20, 30, 40 mL) were added to shaker tubes containing the substrate and SeO_4^- . Next, the pH was adjusted to 4.5 with HNO_3 and NaOH, and the volume of the solution was adjusted to 50 mL with deionized water. The tubes were shaken for three days and the pH checked and adjusted to 4.5 each day. Next, the concentration of Mn, Fe, Cu, and Zn was determined in each of these solutions. The results are given in Table 14. A blank containing no mine drainage showed no metals extracted from the

Table 14. Results of the laboratory experiment testing
adsorption of metals onto a substrate of fresh
mushroom compost during equilibrium with mine drainage
at a pH of 4.5. I

mL of mine drainage in 50 mL total volume	10	20	30	40
Initial mmol/L of Mn, Fe, Cu, & Zn	0.32	0.63	0.95	1.3
Mn mg/L initial	6.9	14	21	28
Mn mg/L final	1.1	11	18	25
Mn micromol adsorbed	5.3	2.9	2.9	2.3
Fe mg/L initial	8.9	18	27	36
Fe mg/L final	0.04	0.2	0	0
Fe micromol adsorbed	8.0	16	24	32
Cu mg/L initial	0.12	0.25	0.37	0.50
Cu mg/L final	0	0	0.04	0.08
Cu micromol adsorbed	0.10	0.20	0.26	0.32
Zn mg/L initial	16.9	3.8	5.8	7.7
Zn mg/L final	0.22	2.3	4.6	6.7
Zn micromol adsorbed	1.1	1.2	0.89	0.75

Note: In this experiment, the mine drainage was tested at four different dilutions. The initial and final concentrations of Mn, Fe, Cu, and Zn in solution are given along with the sum of these four metal concentrations in the initial solution. The amount of Mn, Fe, Cu, and Zn adsorbed onto 0.10 gram of fresh mushroom compost is given in micromoles. The error in these data is less than 10 percent.

original compost. The test which contained 20 mL of mine drainage was run in duplicate and the results were confirmed to within 10 %. Similar experiments were also conducted with 0.1 g of substrate and an adjusted pH of 5.5, and with 1.0 g of substrate at pH's of 4.5 and 5.5 and essentially all of the metals were adsorbed onto the substrate under these conditions.

Data from this experiment show that competition for sorption sites on the substrate is significant. Figure 17 shows the ratio of Mn, Fe, Cu, and Zn concentrations in the final solution to those in the initial solution versus the sum of the concentration of the four metals in the original solution. These results are similar to those from Kerndorf and Schnitzer (53) where, at a pH of 4.7 and 5.8, the amount sorbed for Fe, Cu, Zn, and Mn is as follows:

$$\text{Fe} = \text{Cu} \gg \text{Zn} = \text{Mn}$$

An important difference between the results of Kerndorf and Schnitzer (53) and this experiment is that the

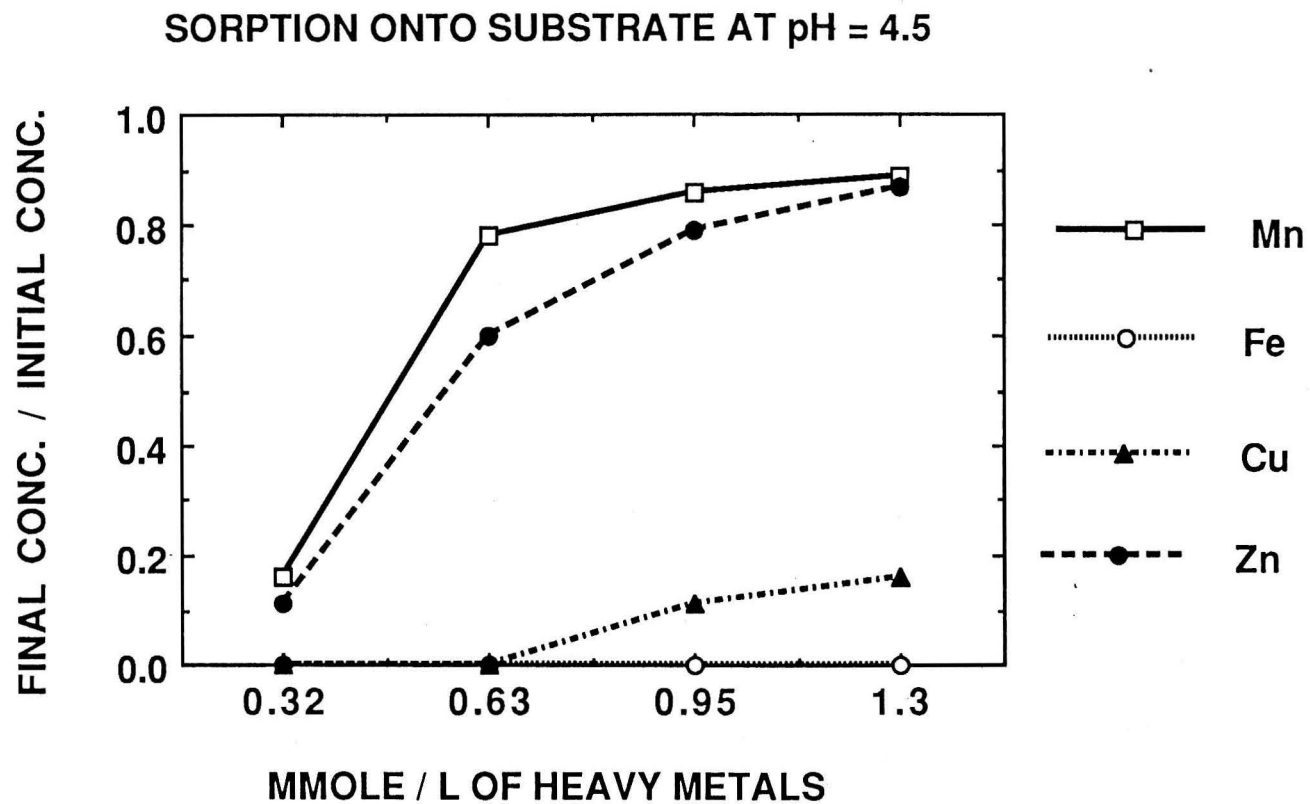


Figure 17. Adsoption of Mn, Fe, Cu, and Zn versus concentration in the mine drainage.

metals here are in test solutions at various concentrations up to those typical of the Big Five mine drainage. At higher total metal concentrations, the percent of Mn and Zn adsorbed decreases as Fe and Cu are preferentially adsorbed onto the most available sites. At a pH of 4.5, it is possible that Fe (III) may have precipitated as $\text{Fe}(\text{OH})_3$, though no typical orange coloration from such a precipitate was observed. However, the other metals, Mn, Zn, and Cu, are very soluble at mine drainage concentrations and a pH of 4.5 (21), suggesting that the most likely metal removal process occurring is metal adsorption onto organic material.

Field Evidence for Adsorption Versus Sulfide Precipitation

In Table 15 the effluent concentrations for all the sampling episodes for the first four months of operation of Cell B-Upflow, Cell B-Downflow, Cell E, and the Big Five drainage are given. In Figures 18 and 19 the removal data for Cell B-Downflow and Cell E are presented; and in Figure 20, the pH of the effluents are plotted.

Data gathered since the flow of mine drainage into the new cells was started indicate that saturation of organic adsorption sites in the fresh mushroom compost occurred within months after Cells B-Upflow and B-Downflow began receiving flow. Figure 18 shows the ratio of metal concentrations in the outflow to those in the inflow for Cell B-Downflow. Mn and Zn are almost completely removed from the mine drainage during the first 30 days. Afterwards, the concentration of these two metals dramatically increases, suggesting that Mn and Zn may be less preferentially adsorbed onto the substrate material after enough adsorption sites become filled. The concentration of Cu and Fe, however, remains low for over 100 days before starting to rise, implying that Fe and Cu may be more competitive for adsorption sites than Mn or Zn. The rise in metal concentrations after about four months may indicate that adsorption sites in the substrate are becoming saturated. The pattern of metal concentration ratios for Cell B-Downflow is similar to the data trend from the sorption experiment as shown in Figure 17. Notice that the sulfate concentration in Cell B-Downflow is essentially the same as in the mine drainage for the entire time period, showing, along with the high Eh's and lack of measurable sulfide in the output waters, that no significant sulfate reduction is taking place.

Metal concentrations in the outflow from Cell E-Downflow show a much different pattern. The Cell E-Downflow substrate was used for two years in the original Cell B. In this used substrate there were substantial populations of sulfate reducing bacteria (10). Figure 19 shows the ratio of metal concentrations in the outflow to those in the inflow for Cell E-Downflow. The difference between the pattern of metal removal in Cell B-Downflow and Cell E-Downflow is substantial. Copper and Zn are completely removed for the entire period. In the first 80 days, Fe is completely removed, Mn is removed 30 to 40 percent, and sulfate is removed 10 to 20 percent. The consistency in metal and sulfate removal through the first 80 days followed by a trend of decreasing removal which is similar for sulfate, Fe, and Mn,

Table 15. Metal and sulfate concentrations (mg/L), pH, Eh (mV), and water temperature (°C) of the Big Five mine drainage (MD) and of the output waters from Cells B-Upflow, and B-Downflow, and E-Downflow since September 1, 1989. Flow rates, in liters/minute, are given for the input flow to the cells as well as for the output flow for Cell E-Downflow due to some loss of water over its spillway.

SAMPLING DATE	14-Sep-89	22-Sep-89	03-Oct-89	19-Oct-89	05-Nov-89
MINE DRAINAGE	MD-1101	no water	MD-1201	MD-1218	MD-1301
Cu (mg/L)	0.647	sample	0.660	0.624	0.614
Fe (mg/L)	36.8	taken	45.9	44.3	38.3
Mn (mg/L)	30.4		34.9	34.5	31.8
Zn (mg/L)	8.5		9.9	9.6	8.7
SO ₄ (mg/L)	1750		1670	1690	1740
pH	2.9	2.9	3.2	3.0	2.9
Eh (mV)	655	630	605	660	510
Temperature (C)	13.5	14.5	13.3	13.0	13
OUTPUT B-UPFLOW	B1-1105	B1-1110	B1-1205	B1-1219	B1-1305
Cu (mg/L)	0.543	0.445	0.590	0.400	0.482
Fe (mg/L)	26.6	17.9	39.4	4.59	17.1
Mn (mg/L)	29.9	27.5	34.3	30.4	31.4
Zn (mg/L)	8.6	8.5	9.3	7.2	8.4
SO ₄	1720	1550	1730	1650	1720
pH	3.3	3.3	3.5	3.7	3.6
Eh (mV)	545	580	585	510	660
Temperature (C)	11	13	9.6	11	6
Input flow (L/min)	1.7	1.1	1.1	1.0	0.83
OUTPUT B-DOWNFLOW	B2-1106	B2-1113	B2-1206	B2-1220	B2-1306
Cu (mg/L)	0.558	<0.05	<0.05	0.180	<0.05
Fe (mg/L)	2.69	<0.5	22.9	0.603	<0.5
Mn (mg/L)	14.8	6.29	7.7	37.6	20.1
Zn (mg/L)	3.79	1.0	0.76	9.9	5.97
SO ₄ (mg/L)	1730	1700	1720	1680	1680
pH	5.1	6.4	6.5	5.5	5.9
Eh (mV)	475	475	330	530	490
Temperature (C)	11.5	14	12.5	8	6
Input flow (L/min)	0.83	0.61	0.61	0.72	0.91

Table 15. - continued

SAMPLING DATE	14-Sep-89	22-Sep-89	03-Oct-89	19-Oct-89	05-Nov-89
OUTPUT E-DOWNFLOW	OE-1109	OE-1111	OE-1209	OE-1222	OE-1309
Cu (mg/L)	<0.05	<0.05	<0.05	<0.05	<0.05
Fe (mg/L)	0.627	0.304	0.530	0.603	<0.5
Mn (mg/L)	20.6	19.6	24.0	24.2	19.7
Zn (mg/L)	<0.05	<0.05	<0.05	<0.05	<0.05
SO ₄ (mg/L)	1340	1370	1350	1450	1480
pH	6.5	6.4	6.3	6.4	6.5
Eh (mV)	5	-5	15	140	-40
Temperature (C)	13	14	14	10.0	10
Input flow (L/min)	0.72	2.8	2.5	0.93	2.3
Output flow (L/min)	0.31	missing	0.72	0.41	0.41
SAMPLING DATE	21-Nov-89	03-Dec-89	20-Dec-89	13-Jan-90	27-Jan-90
MINE DRAINAGE	MD-1310	MD-1401	MD-1410	MD-1501	MD-1510
Cu (mg/L)	0.85	0.578	0.606	0.590	
Fe (mg/L)	35.1	42.7	38.2	33.3	
Mn (mg/L)	31.4	29.5	31.1	30.7	
Zn (mg/L)	9.3	9.0	9.5	9.0	
SO ₄ (mg/L)	1690	1700	1660		
pH	2.9	3.0	2.85	2.9	3.0
Eh (mV)	710	680	695	668	690
Temperature (C)	13.5	7.3	12.0	13	10.3
OUTPUT B-UPFLOW	B1-1311	B1-1405	B1-1411	B1-1505	B1-1512
Cu (mg/L)	0.284	0.440	0.439	0.489	
Fe (mg/L)	<0.5	33.7	31.8	33.3	
Mn (mg/L)	27.7	29.8	30.5	29.9	
Zn (mg/L)	6.85	9.0	8.2	8.9	
SO ₄ (mg/L)	1760	1690	1670		
pH	5.5	3.5	3.15	3.25	3.55
Eh (mV)	515	460	595	535	670
Temperature (C)	7	6.4	6.0	6.3	2.7
Input flow (L/min)	0.29	1.4	0.55	0.81	0.54

Table 15. - continued

SAMPLING DATE	21-Nov-89	03-Dec-90	20-Dec-89	13-Jan-90	27-Jan-90
OUTPUT B-DOWNFLOW	B2-1312	B2-1406	B2-1412	B2-1506	B2-1513
Cu (mg/L)	0.217	0.209	0.077	0.442	
Fe (mg/L)	3.51	7.2	2.05	11.7	
Mn (mg/L)	22.5	24.7	20.0	26.9	
Zn (mg/L)	8.1	6.84	4.41	8.1	
SO ₄ (mg/L)	1730	1700	1680		
pH	5	4.1	5.7	3.25	3.3
Eh (mV)	530	560	385	660	740
Temperature (C)	8	2.6	4.5	7.7	5.8
Input flow (L/min)	clogged	1.1	0.18	0.76	0.59
OUTPUT E-DOWNFLOW	OE-1314	OE-1409	OE-1414	OE-1509	OE-1514
Cu (mg/L)	<0.05	<0.05	<0.05	<0.05	
Fe (mg/L)	1.42	2.65	14.5	9.8	
Mn (mg/L)	22.5	26.0	25.1	27.7	
Zn (mg/L)	0.220	<0.05	0.125	<0.05	
SO ₄ (mg/L)	1580	1700	1630		
pH	6.7	6.3	6.5	6.0	6.25
Eh (mV)	135	25	305	140	345
Temperature (C)	11	7.1	3.0	6.3	4.0
Input flow (L/min)	0.28	0.58	missing	missing	missing
Output flow (L/min)	missing	0.43	missing	0.39	2.5

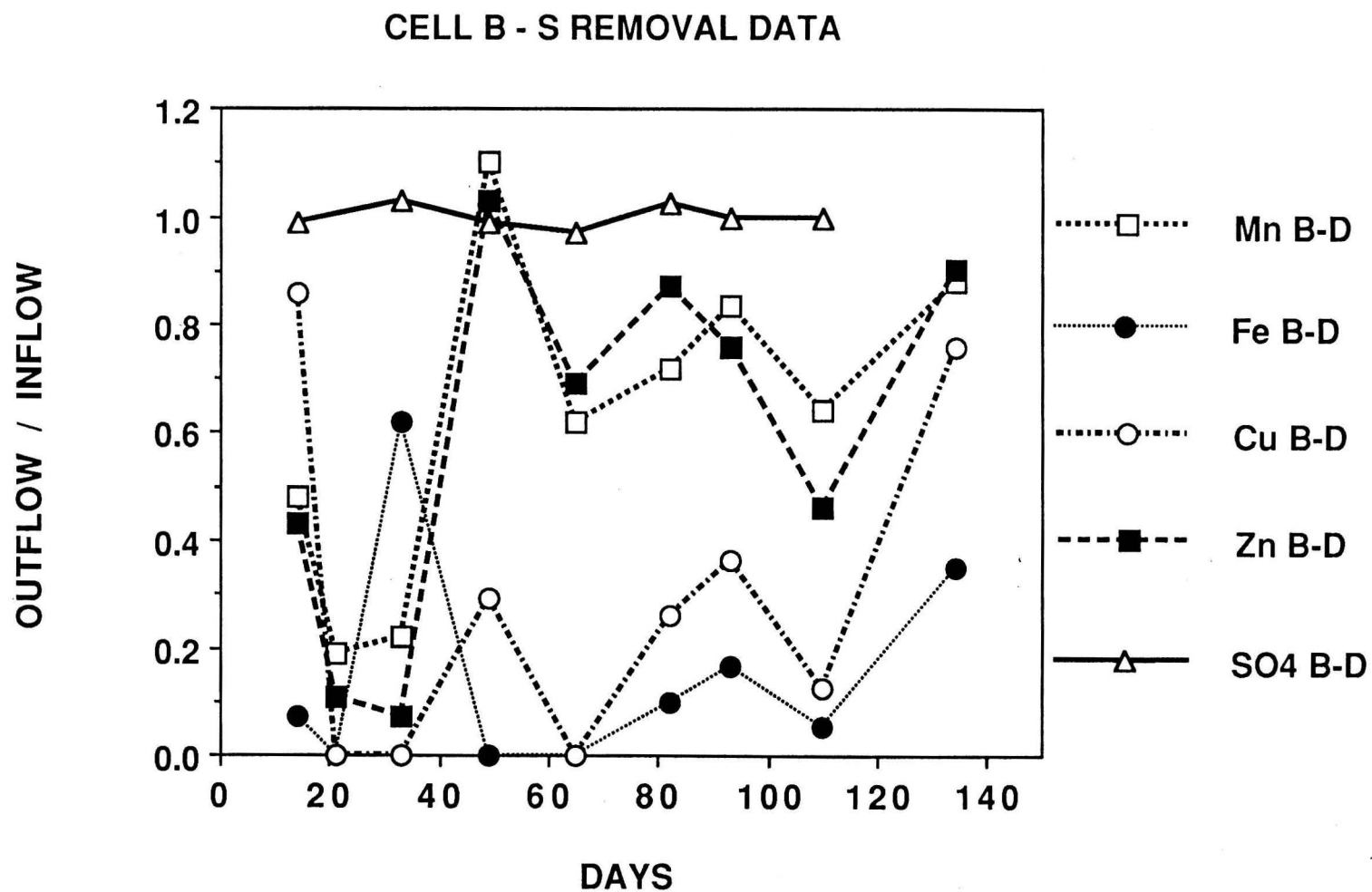


Figure 18. Removal of contaminants in Cell B Downflow over the first four months of operation.

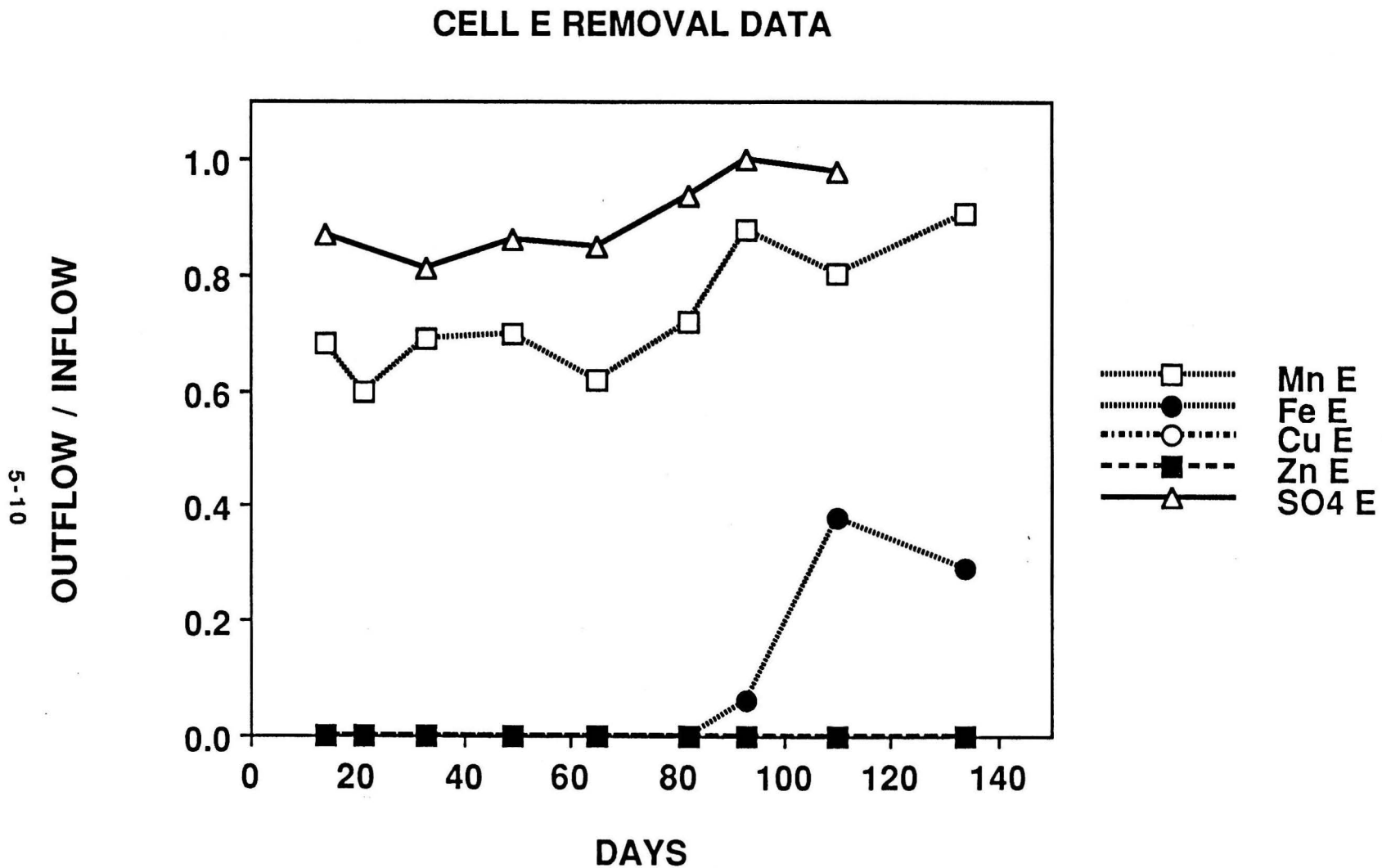


Figure 19. Removal of contaminants in Cell E over the first four months of operation.

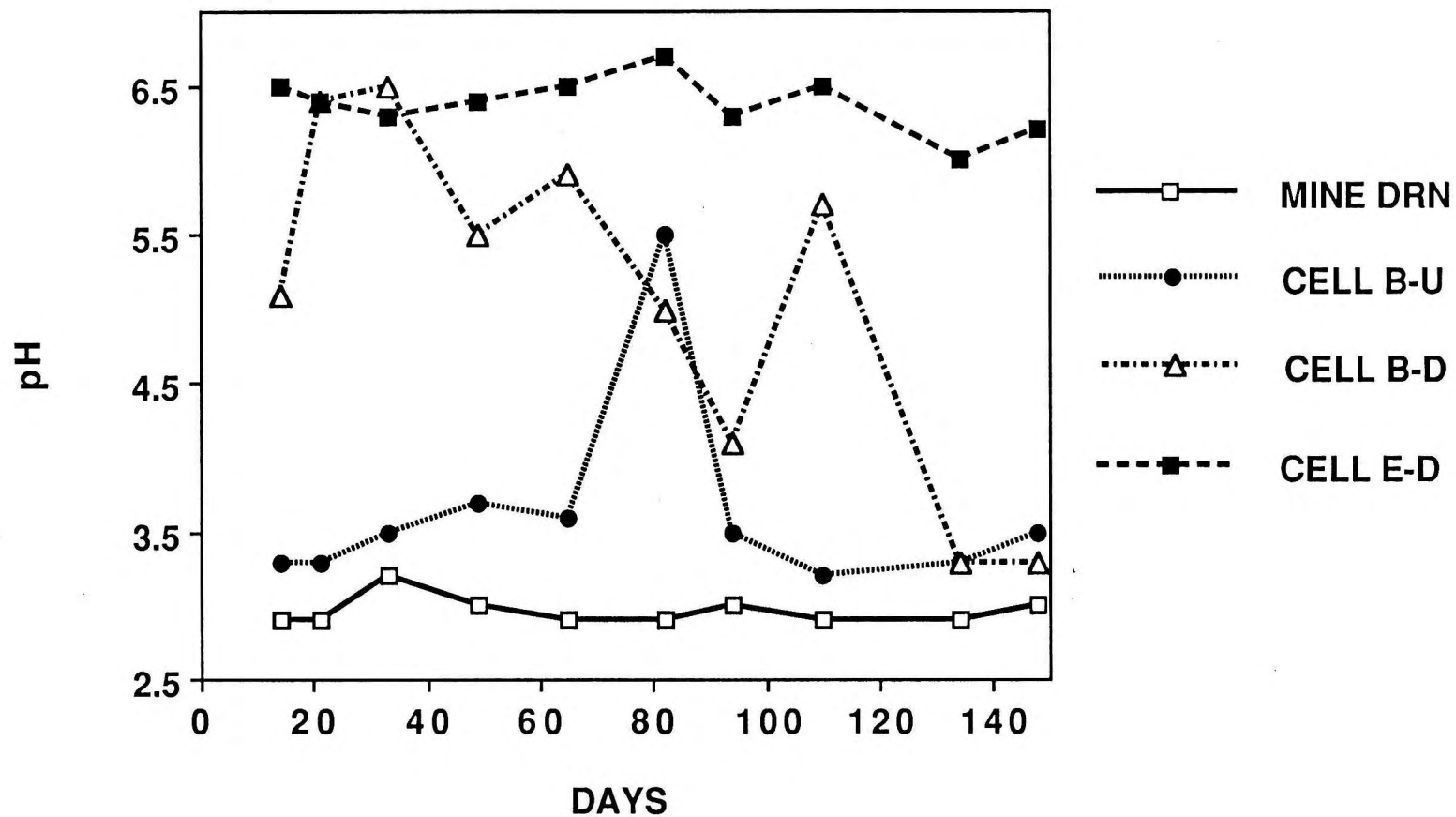


Figure 20. Effluent pH for Cells B Upflow, B Downflow, and E over the first four months of operation.

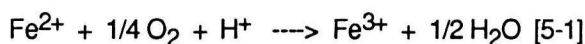
suggests that metal and sulfate removal are linked. This, along with the expected saturation of adsorption sites in the substrate due to its prior two year exposure to mine drainage, suggests that adsorption is not the major metal removal process. The relatively high removal of sulfate along with the measurement in the output waters of 0.5 millimole per liter of sulfide and generally low Eh's indicate that significant sulfate reduction is occurring. This pattern of sulfate and metal removal is explained by sulfate reduction and the precipitation of metal sulfides. Sulfate concentrations are expected to decrease significantly as sulfide is produced. Copper and Zn sulfides are expected to precipitate most readily followed by Fe sulfides and, finally, Mn sulfides are expected to precipitate least readily. This pattern follows the trend in K_{sp} 's for these metal sulfides: $CuS < ZnS < FeS < MnS$ (21).

Fluctuations of pH during this period for the mine drainage and for Cells B-Upflow, B-Downflow, and E-Downflow are shown in Figure 20. The pH for the mine drainage tends to be relatively consistent around 2.9. For Cell B-Upflow, the pH remains relatively low, around 3.5, reflecting an absence of an effective neutralizing process. The pH for Cell B-Downflow, however, shows a decreasing trend from over 6 to below 3.5, indicating the presence of a neutralizing process that becomes less effective over time. Adsorption may not be a consistent neutralizing process due to available sorption sites becoming filled over time. The removal of metals in Cell B-Downflow varies with the fluctuation of pH in the outflow water and is probably the effect of pH on the adsorption of metals onto the substrate material. Hydrogen ions are expected to be more competitive for adsorption sites than metal ions, causing less adsorption of metals and higher dissolved metal concentrations at lower pH's. As noted above for the adsorption experiment, it is unlikely that significant metal hydroxide was formed. This is because no typical orange coloration from a ferric hydroxide precipitate was observed and because Mn, Zn, and Cu are very soluble at mine drainage concentrations and pH's below 6.5 (21).

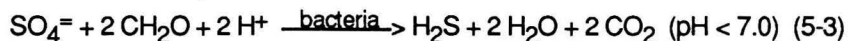
The output water for Cell E-Downflow has a consistently high pH, between 6.0 and 6.7, suggesting the presence of a consistent process acting to neutralize the mine drainage. Sulfate reduction may be a more consistent neutralizing process than adsorption due to the pairing of hydrogen ions with continuously produced sulfide ions. There does not appear to be a trend between pH and metal removal similar to that between the removal of sulfate and metals, implying that pH is not as important as sulfide precipitation in removing metals from solution. Although the pH is relatively high, it is unlikely that significant metal removal is the result of metal hydroxide precipitation due to the reducing conditions of the system and high metal solubilities (21).

pH INCREASE OF THE EFFLUENT

The consistently high pH of the effluent from Cell E shown in Figure 20 cannot be due to removal of iron by oxidation. As shown in reactions 5-1 and 5-2 below, precipitation of $Fe(OH)_3$ releases 2 moles of H^+ for every mole of Fe oxidized and precipitated as $Fe(OH)_3$.

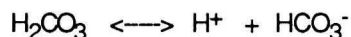
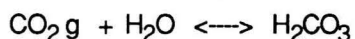


On the other hand, generation of H_2S can increase the pH.



It appears that in a wetland in which oxidation and precipitation of iron is the predominant removal process, the pH of the effluent should decrease. Indeed, a few case studies have shown this to be the case (73, 74, 75). On the other hand, in a wetland in which sulfate reduction is the predominant process, the pH of the effluent can increase. However, there are two situations that confuse this analysis.

The first situation in which pH might not be lowered even though $\text{Fe}(\text{OH})_3$ is precipitated is when the pH of the mine drainage is above 5.5. This is because the water is neutral enough to be buffered by the bicarbonate system. Consider the following two equilibrium reactions:



If the pH of the water is high enough to maintain carbonic acid in solution instead of CO_2 exsolving, then the pH of the water can be maintained at slightly below 7 by atmospheric carbon dioxide dissolving in the water. The necessary minimum pH is about 5.5. Brodie (68) finds that if the pH of a mine drainage is above 5.5, then treatment by a surface flow wetland will be effective. In this situation, precipitation of $\text{Fe}(\text{OH})_3$ is the predominant removal process. The pH of the treated effluent remains above 5.5.

The second situation not related to sulfate reduction that can raise the pH is buffering by the wetland substrate. In natural peat wetlands, the humic acid material will maintain the soil at a pH of about 4 (50). At this low pH, sulfate reducers will have a difficult time surviving and removal of heavy metals through sulfide precipitation will be retarded. Indeed, this retarded the removal efficiency of the Big Five Cells in the first year of operation. Choosing a more basic substrate will promote these reactions. In addition, if the soil has a large buffering capacity, then basic conditions will be maintained until the wetland substrate has time to generate a neutral pH suitable for sulfate reduction. For the four original materials used in the Big Five cells, the acid-base characteristics are given in Table 16.

Since the peat is primarily composed of humic acids, its initial pH shows it to be quite acidic. On the other hand, the other three materials have initial pH's that are basic. For the manure and decomposed wood product, the odor of ammonia was readily apparent. This was caused by microbial breakdown of the amino acids in the material. If basic substrate material is used, then the pH of the effluent during the initial three to four months of operation may be controlled by the buffering capability of the substrate.

In many respects, use of a substrate whose soil pH is above 7 is almost essential to the success of sulfate reduction as a removal process. The sulfate reducing microbes operate best in the pH range

between 5 and 9.5. If the substrate has a soil pH between these ranges, and has some buffering capacity, then the ability of the sulfate-reducing bacteria to create their own microenvironment will help to maintain the substrate pH around 7. At the Big Five site, the well waters within the cells give a good indication of the pH of the substrate waters. Before mine drainage was introduced into the cells, the pH of well waters ranged between 5 to 7.5. The pH of the well waters in Cell A were the lowest, ranging from 5 to 6.6. After 10 months of operation, the pH of the well waters in Cell A ranged from 5.8 to 7.6 and at this time the pH's in Cell A effluent ranged from 6.2 to 7.3. The substrate in Cell C is underlain by six inches of limestone cobbles. However, after 10 months, the pH in the well waters in Cell C were lower than those in Cell A, ranging from 5.8 to 7.0. Some of this ability of Cell A to maintain a high pH has to be attributed to the sulfate-reducing bacteria.

Table 16. Acid-base characteristics of some substrate materials

Substrate Material	Split	Initial pH	Buffering Capacity ^a
Mushroom Compost	11	8.05	0.769
	17	8.30	0.672
Grant Bog Peat	8	3.10	0.192
	4	3.10	0.197
Aged Manure	1	8.55	1.18
	11	8.05	1.05
Decomposed Wood	5	8.60	0.987
	17	8.65	0.987

^aMillimoles of HCl needed to titrate one gram of substrate to a pH of 2.5.

SULFUR FORMS IN THE SUBSTRATE

In the summer of 1988 when it was speculated that sulfate reduction was the important removal process, Laudon initiated research on the forms of sulfur in the substrates of the Big Five wetland cells (8). Analytical results on forms of sulfur in the substrate done by ASTM test D-2492 (78) suggested a significant increase in sulfate sulfur from initiation in October 1987 to the first substrate sampling in January 1988 (61). This seemed confusing since if metal sulfides were precipitated, they would form pyrite or metal monosulfides. This discrepancy led Laudon to conduct an extensive sequential extraction procedure for the various forms of sulfur on the selected substrates.

The extraction sequence is shown in Figure 21 and was modified after procedures used by Tuttle (79) and Wieder (80). Substrate cores were taken, sealed, and immediately transported under wetland water to the laboratory. The sequential analysis was started within two hours of sampling. The forms of sulfur determined included:

Acid volatile sulfur (AVS): Sulfur in metal monosulfide precipitates such as FeS, CuS, and ZnS.

Elemental Sulfur (S^0)

Sulfate Sulfur: Sulfur primarily in pore waters.

Pyritic Sulfur: Sulfur as FeS_2 .

Organic Sulfur: Sulfur bound in insoluble organic compounds.

A separate analysis is made of total sulfur by the Eschka Method (81). In addition, total soluble sulfide in nearby well waters was determined on site by an electrochemical titration method using 0.0001 M $AgNO_3$ (7). The description of the sample sites is in Table 17; the well locations are shown in Figure 5. Table 18 contains the results of the sequential analyses and the total sulfur analysis. In Table 18, all values are given as percent of sulfur in the total sample. The values in each subcategory should add up to the total sulfur value. Table 19 contains the results of the soluble sulfur titrations. These concentrations of H_2S are estimates of the sulfide concentration in the pore waters within the cores.

Original substrate materials and those samples collected in January of 1988 were air dried and stored in partially sealed polyethylene bags. Because acid volatile sulfides (AVS) can oxidize rapidly, it was assumed that a separate AVS fraction could not be recovered. In these cases AVS is reported as $AVS + S^0$. Laudon also performed duplicate analyses and recovery tests and these are discussed in her thesis (8). The sum of the fractions agreed with the total sulfur analysis to within 20 % in all cases except the core from Cell C and the NBS coal. The relative standard deviations on total sulfur analyses were within 10 %. Large deviations occurred on duplicates of the sequential extractions especially when the form of sulfur was only present in minor amounts.

Figures 22 and 23 show, in Cells A and B respectively, the changes in sulfur content in the substrates over the first 10 months of operation. The results show increases in the AVS in the substrates, especially in those from Cell A which was the best performing cell in 1987-88. Certainly in this cell, the removal mechanism is formation of metal sulfides by dissimilatory sulfate reduction. In Cells B and C there is an increase in the amount of acid volatile sulfides but one could not assert that removal through sulfate reduction was the predominant process.

Two other conclusions from the results of Laudon's research should be pointed out. In Cell A, the system that has the greatest sulfur increases, there is no apparent increase in organic or pyritic sulfur. In Cell B, there may be an increase in these two sulfur forms. The lack of pyritic sulfur formation is contrary to the expectation was that pyrite would form immediately or, at least, some of the acid volatile sulfide would change to pyrite. Upon review of the literature (82), it is not unusual to form significant amounts of AVS

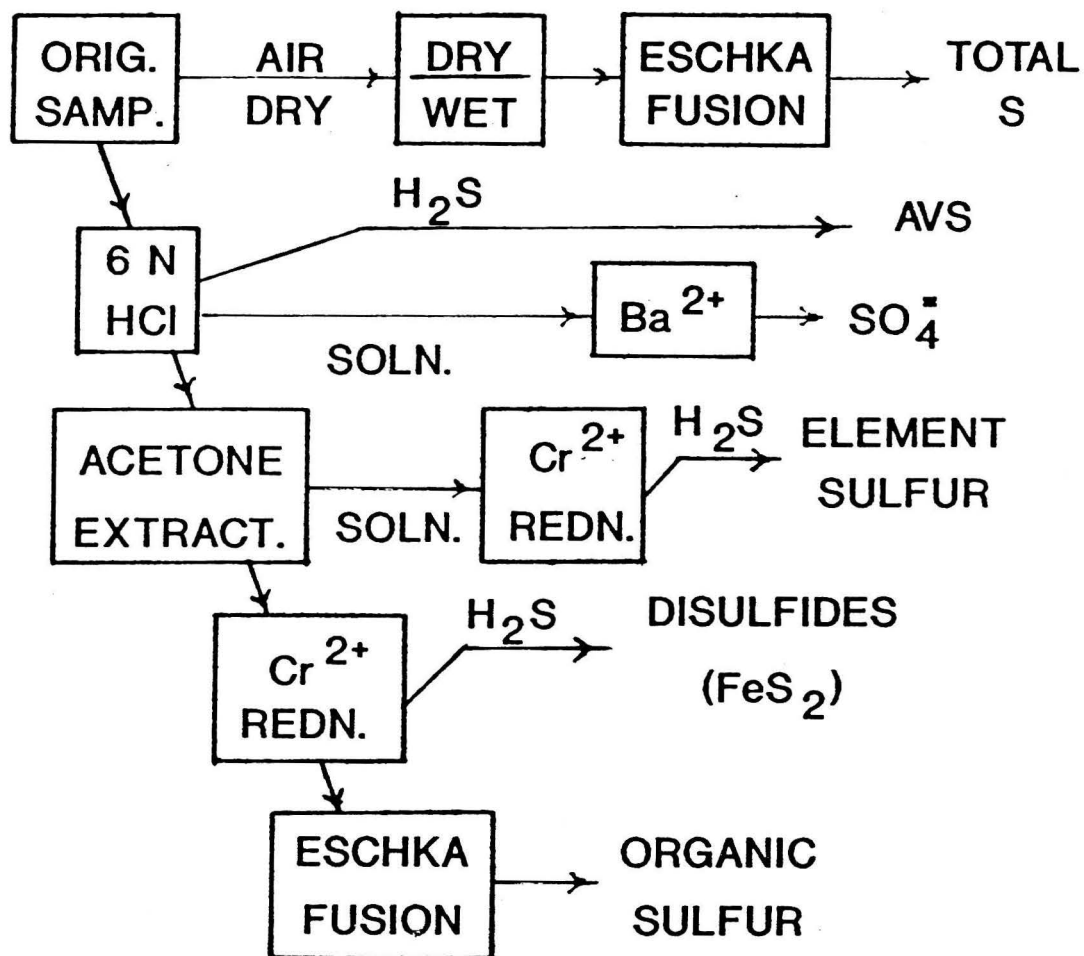


Figure 21.

Extraction sequence for the forms of sulfur determination.

Table 17. Locations of sample used in the sequential sulfur extraction.

Abbreviation	Description
CS	Compost substrate (initial material used in cell A).
TA5	Top 6" of substrate collected near well A5.
#1(A2)	First core collected (near well A2).
#2(A5)	Second core collected (near well A5).
P/M/WP	Peat, manure, wood products (initial material in cells B and C).
TB5	Top 6" of substrate collected near well B5.
B(B5)	Core collected in cell B near well B5.
C(C5)	Core collected in cell C near well C5.

Table 18. Forms of S in substrate samples and NBS Coal 1635. All values are in %S in total sample.

Sample	Date Collected	S _{TOT}	S _{AVS}	S _{S°}	S _{FeS₂}	S _{ORG}	S _{SO₄}
TA5	1/88	0.83		0.45*	0.05	0.21	0.17
#1(A2)	7/88	1.61	0.31	0.49	0.24	0.35	0.07
#2(A5)	7/88	1.39 [#]	0.83	0.16	0.09 ⁺	0.22 ⁺	0.08 ⁺
P/M/WP	1/87	0.61	<0.02	0.05	0.34	0.14	0.16
TB5	1/88	0.59	-	0.09*	0.25	0.15	0.15
B(B5)	7/88	0.67 [#]	0.08	0.09	0.42 ⁺	0.20	0.02
C(C5)	7/88	0.73 ⁺	0.19	0.13	0.40	0.19	0.07
NBS Coal	1635	0.32	<0.03	0.02	<0.02	0.35	<0.02

*AVS + S°

[#]average of 3 values⁺average of 2 valuesS_{TOT} = Total SulfurS_{AVS} = Acid volatile sulfurS_{S°} = Acetone soluble sulfurS_{FeS₂} = DisulfidesS_{ORG} = Organic sulfurS_{SO₄} = SO₄²⁻ sulfurTable 19. Results of H₂S titration on well water samples.

Well	Screened Interval	mg/L S as H ₂ S
A	3'	20
A4	1'	<1
A5	2'	79
B4	1'	49
C5	3'	9

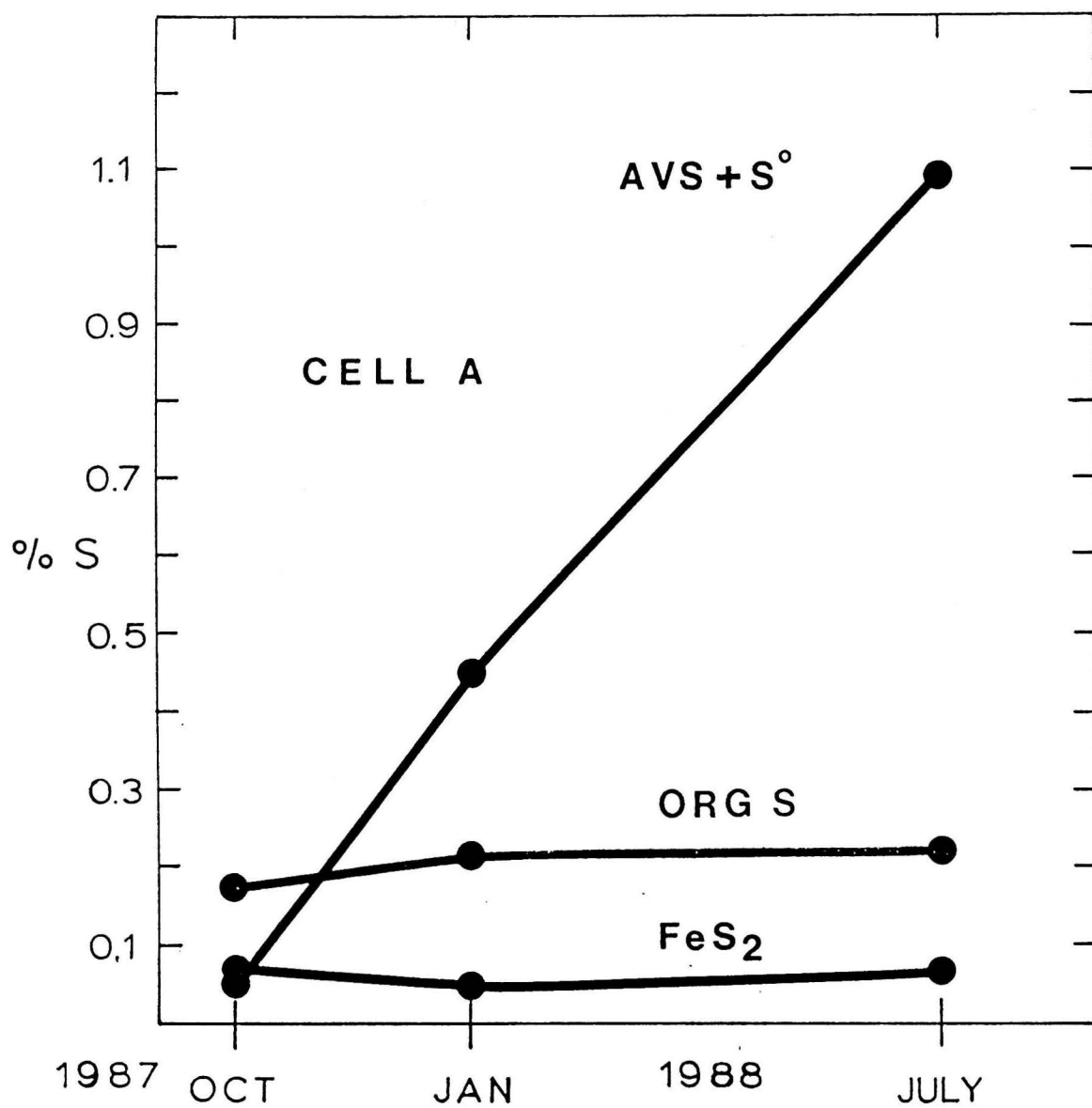


Figure 22. Changes in sulfur content and forms within the substrate in Cell A over the first 10 months.

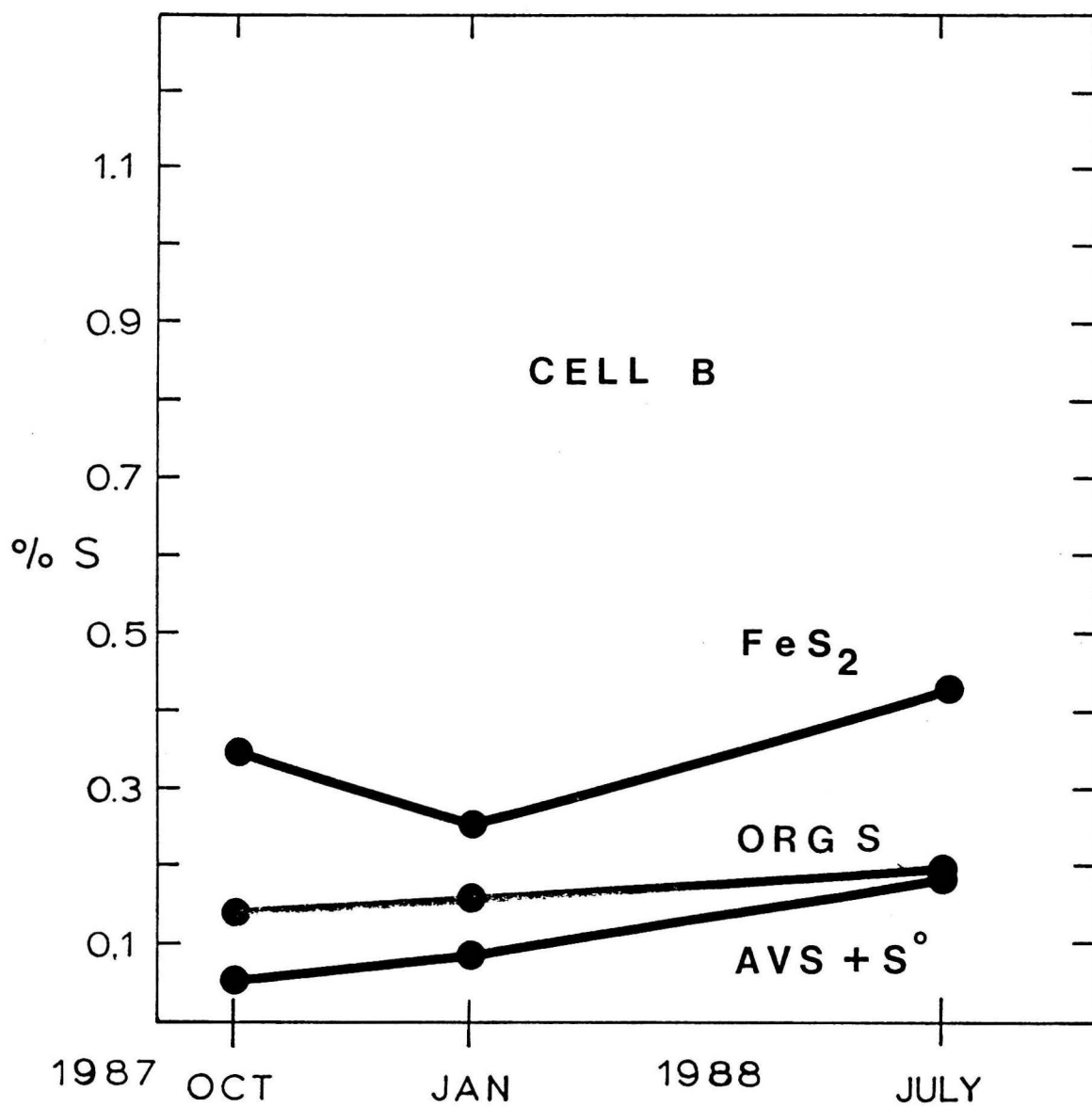


Figure 23. Changes in sulfur content and forms within the substrate in Cell B over the first 10 months.

with little formation of pyrite. Acid volatile sulfides form under conditions that are strongly reducing and remain that way. Also, there is little diagenesis of acid volatile sulfides to pyrite. Pyrite formation requires the presence of elemental sulfur or polysulfides. These will be present under more oxidizing conditions or in areas where there is periodic incursion of oxygen (82, 83). Apparently in Cell A, the vigor of sulfate reduction coupled with the highly anaerobic conditions account for acid volatile sulfides being the predominant product.

FORMS OF HEAVY METALS IN THE SUBSTRATE

Since research on sulfur forms points to the formation of metal sulfides in the substrate, the next logical step is to investigate where the heavy metals are accumulating in the substrate. It was hoped that this could be done by some spectroscopic method thus giving an atomic confirmation of the presence and molecular form of the metal sulfides. Since sulfur is present in abundances greater than one percent, x-ray diffractometry should detect pyrite or iron monosulfide crystals. To enhance the concentration of the heavy metal sulfides, the substrate samples were screened and x-ray diffractometry was performed on the fraction that was less than 200 mesh. Quartz, feldspar, illite, and gypsum were identified but no metal sulfides or oxides could be conclusively identified. Apparently, if precipitates are formed, they are amorphous. Mossbauer spectroscopy is an excellent method for detecting and measuring the concentrations of pyrite and other iron oxides in solids (84). Often this spectroscopy can detect iron minerals that are amorphous to x-ray diffractometry. Two fresh sediments were taken from Cell A, packed in sealed sample containers, and analyzed by Mossbauer spectroscopy. There was some Fe(II) mineral present in small amounts, but no pyrite or FeS was detected. Again the precipitate is so fine grained that it was amorphous to Mossbauer spectroscopy.

Because spectroscopy does not reveal how the heavy metals are bound to the substrate, it was decided to perform sequential extraction studies on the heavy metals. These procedures would be comparable to the studies of the forms of sulfur. As reviewed by Chao (85), the objective of a sequential extraction is to chemically determine the forms of metal compounds in a soil or sediment. Bound forms of metals typically tested for include:

- o Easily extracted cations loosely bound to the sediment;
- o Metals bound by organic complexes, usually humic acids;
- o Metals adsorbed onto manganese (IV) oxides;
- o Metals adsorbed onto iron (III) oxides;
- o Metals precipitated as sulfides or oxides;
- o Metals bound in silicate or other resistant minerals.

Because of the sequential nature of the extraction, a number of uncertainties are inherent in the

experiment. First it is obvious that errors accumulate and so one can only expect correspondences to within 20 percent for duplicate analyses. One method for determining the success of an experiment is to compare the sum of abundances in the extraction with a separate total metal analysis. If the two compare within 20 %, the experiment is considered successful. Related to the general experimental error is the fact that the more steps in an extraction sequence, the greater the chance for systematic or accidental error.

There also are chemical problems that are sometimes unavoidable. The extraction steps assume discrete phases have been formed (86), especially for the oxides and sulfides. In the case of Big Five substrates, the targeted phases are x-ray amorphous, and so the chances for discrete phases in the substrate is diminished. The experimental design assumes that the chemical agents in each step will attack and release the metals from only that phase and also do this completely. Complete separation is unlikely, especially for the organically bound metals (87, 88) and for the Mn and Fe oxides (89, 90, 91). Finally, it is assumed that a metal released in a certain step will not be resorbed when the solid is separated from the extract. This is a controversial assumption especially with regard to the first steps of the extraction sequence (92, 93).

In summary, sequential extractions to determine how metals are bound or contained in sediments require careful interpretation. Perhaps the best way to interpret the results is that the tests show the tendency of metals held by the substrate to be released. The first steps in the sequence use relatively mild reagents and continue to more aggressive reagents in the final steps. If a metal is released in an early step, it is relatively mobile and the possibility of it being released back into the environment is high. If a metal remains until the final extraction steps, it is in a more resistant site in the substrate and the possibility of release is diminished.

Two different sequential experiments were performed on substrates from the Big Five cells: a six step sequence, and a five step sequence. The six step sequence was the first method tried. The first steps in this sequence are quite aggressive in terms of pH changes. The acetic acid buffer is used to release carbonates as well as easily extracted metals. The pyrophosphate step uses a relatively high pH to dissolve humic acids and the metals associated with them (50, 87). The five step sequence uses methods for releasing easily extractable metals and organically bound metals that are more mild in terms of pH changes. However the sodium hypochlorite used to attack organic sites may oxidize metal sulfides. Also, this sequence has no step specific to metal sulfides.

Six-Step Extraction Sequence

Figure 24 shows the steps in the six step sequence. This sequence was tried on substrate samples taken from the top of Cell A in July 1988, about the same time samples for the forms of sulfur extraction were taken. They were chosen because they had accumulated the highest amounts of metals.

The samples were air dried and stored until the analyses were performed in March, 1989. Some of the acid volatile sulfides may have oxidized during air drying and storage. Table 20 gives the results of the six step sequential extraction experiments. Figures 25 through 28 compare the metal speciation in the original mushroom compost to speciation in the average of the three Cell A samples.

For manganese and zinc the experiments show that the metals were held in sites where they could be easily released. Iron is distributed throughout all the sites but mostly is contained in an organic form. Copper is strongly held. It persists until the step that would release crystalline oxides and sulfides. These experiments indicate that the heavy metals are held to the substrate on sites where release is quite possible. Oxidation during storage may account for some of this mobility. However if the substrate was removed from Cell A and prepared for disposal, it likely would be subject to some oxidation. It may be that the acetic acid in the first step causes the dissolution of poorly formed oxides or sulfides. For this reason, the five step sequence was tried.

Five-Step Extraction Sequence

Figure 29 shows the steps in the five step sequence. This sequence was also tried on the same substrate samples taken from the top of Cell A in July 1988. The analyses were performed by Sellstone (94) in the fall of 1989 as part of his thesis project. Again, some of the acid volatile sulfides may have oxidized during air drying and storage. Table 21 gives the results of the five step sequential extraction experiments. Figures 30 through 33 compare the metal speciation for the original mushroom compost to speciation on the average of the three Cell A samples. Due to an analytical problem, the absolute abundances for zinc in each step were lost.

The first step of this sequence uses no acid and assumes that magnesium replaces the easily extracted metal on the substrate. As can be seen in Figures 30 through 33, now only Mn is appreciably released in the first step. All the other metals are held until the last two steps. The idea that the acetic acid in the first step of the first extraction sequence released metals from acid sensitive sites appears to be reasonable.

Metal Extraction Summary

The metal extractions could not definitively show the sites where heavy metals were bound onto the wetland substrates. Since there also is no spectroscopic evidence, it is not certain where metals are bound after all the organic sites are occupied. The metal extraction experiments do give an indication of the tendency of heavy metals to be released from the substrate. It appears that mobilization could be initiated by mild acids, probably due to the formation of AVS. This suggests that the substrate could be classified as a hazardous waste once it is removed from the wetland. we are presently considering experiments in which deeper, less organic-rich wetlands will be tested to treat the same volume of mine drainage. The aim of these experiments is to control the redox potential and rate of sulfate reduction in order to maximize the ratio of pyrite-to-AVS that is produced.

SEQUENTIAL METALS EXTRACTION

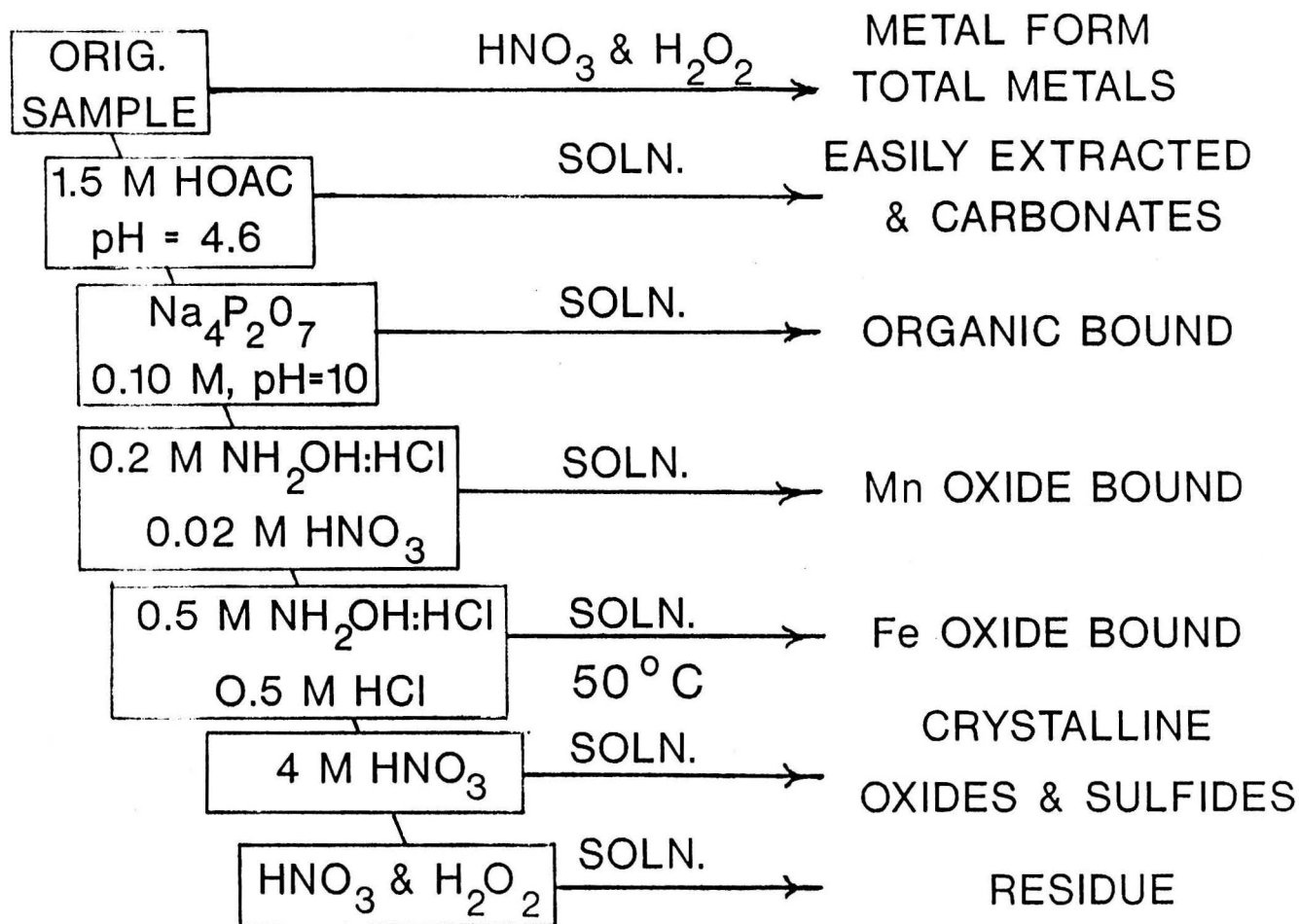


Figure 24. Six step sequential extraction for metal speciation in substrate samples.

Table 20. Results of the Six-step Metal Extraction Sequence
on Substrates from the Top of Cell A.

Step	Orig. Compost		Soil A4, 6"		Soil A6, 6"		Soil A3, 6"		Avg Soil
	pm	%	ppm	%	ppm	%	ppm	%	%
Manganese									
1	228	68	562	86	837	85	1008	86	85
2	23	7	24	4	48	5	54	5	4
3	13	4	5	1	18	2	20	2	2
4	23	7	21	3	36	4	46	4	4
5	9	3	9	1	12	1	14	1	1
6	36	12	35	5	35	4	32	3	4
Total ^a	334	-	656	-	987	-	1173	-	-
Act Tot ^a	359	93	609	108	1013	97	1327	88	-
Copper									
1	5	6	4	3	5	2	6	3	2
2	5	7	22	16	46	14	46	26	18
3	0	0	26	19	12	4	27	15	10
4	9	12	26	19	100	30	29	16	24
5	34	47	39	29	135	40	43	24	34
6	20	28	18	14	36	11	27	15	13
Total	73	-	138	-	334	-	179	-	-
Act Tot	57	128	165	83	474	70	182	98	-
Iron									
1	261	3	2900	14	3280	19	1030	5	13
2	273	3	8000	40	5900	35	8450	44	40
3	273	3	2190	11	300	2	1930	10	8
4	1260	15	1280	6	1540	9	1580	8	8
5	930	11	1280	6	1000	6	1280	7	6
6	5230	64	4600	23	4900	29	4850	25	25
Total	8220	-	20200	-	17000	-	19100	-	-
Act Tot	9640	85	23600	86	20900	81	23080	83	-
Zinc									
1	53	42	711	59	1860	53	723	69	57
2	18	14	284	24	971	28	197	19	25
3	13	10	64	5	93	3	42	4	3
4	23	18	107	9	442	13	59	6	11
5	8	6	17	1	106	3	8	1	2
6	12	9	13	1	24	1	13	1	1
Total	127	-	1197	-	3490	-	1040	-	-
Act Tot	127	100	1398	86	3950	88	1180	88	-

^aThe total = sum of the partial extractions.

The Act Total = results of a separate total analysis.

The percent next to Act Tot. = (Total/Act Total) x 100

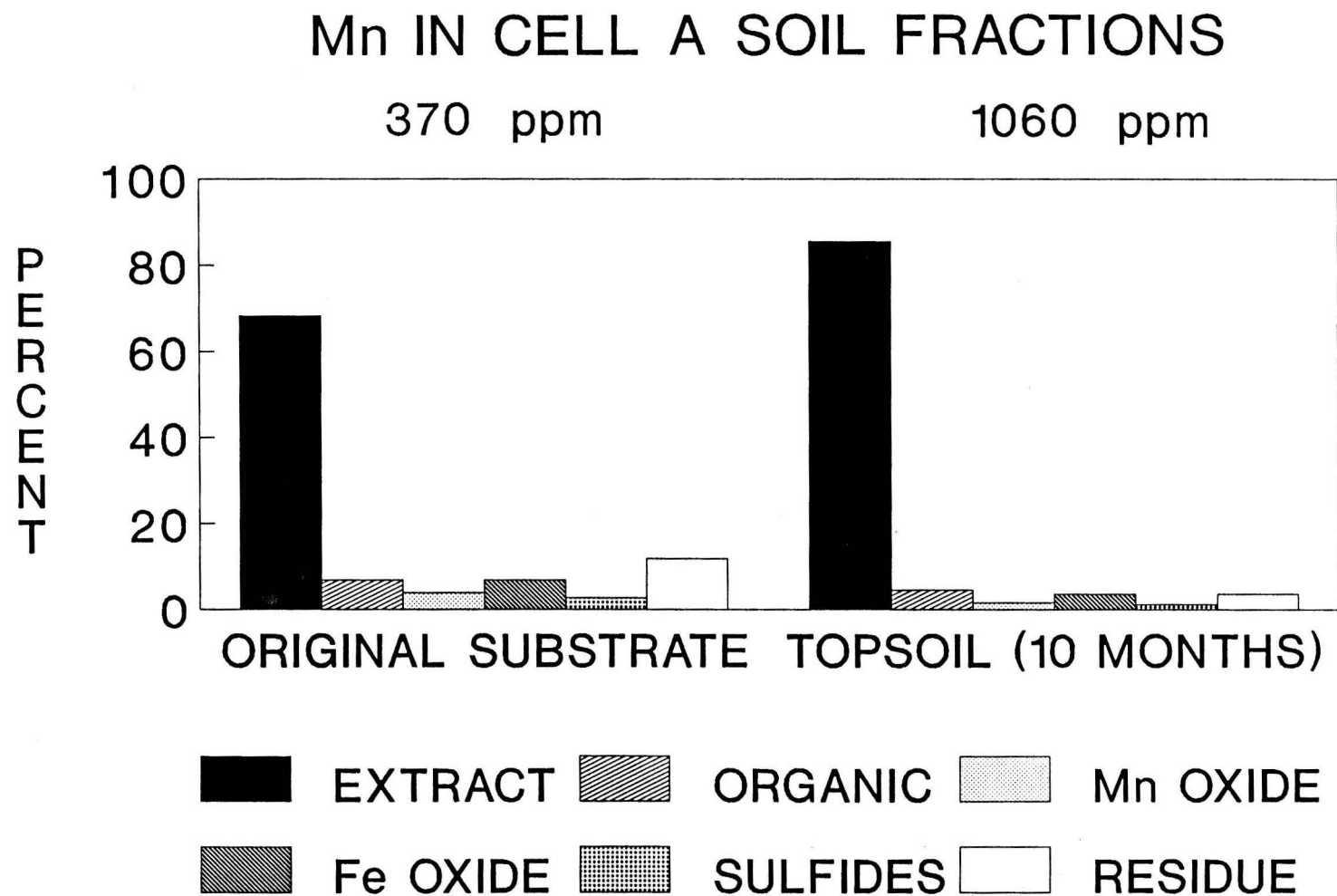


Figure 25. Six step manganese speciation in original mushroom compost and in substrate from the top of Cell A after 10 months.

Zn IN CELL A SOIL FRACTIONS

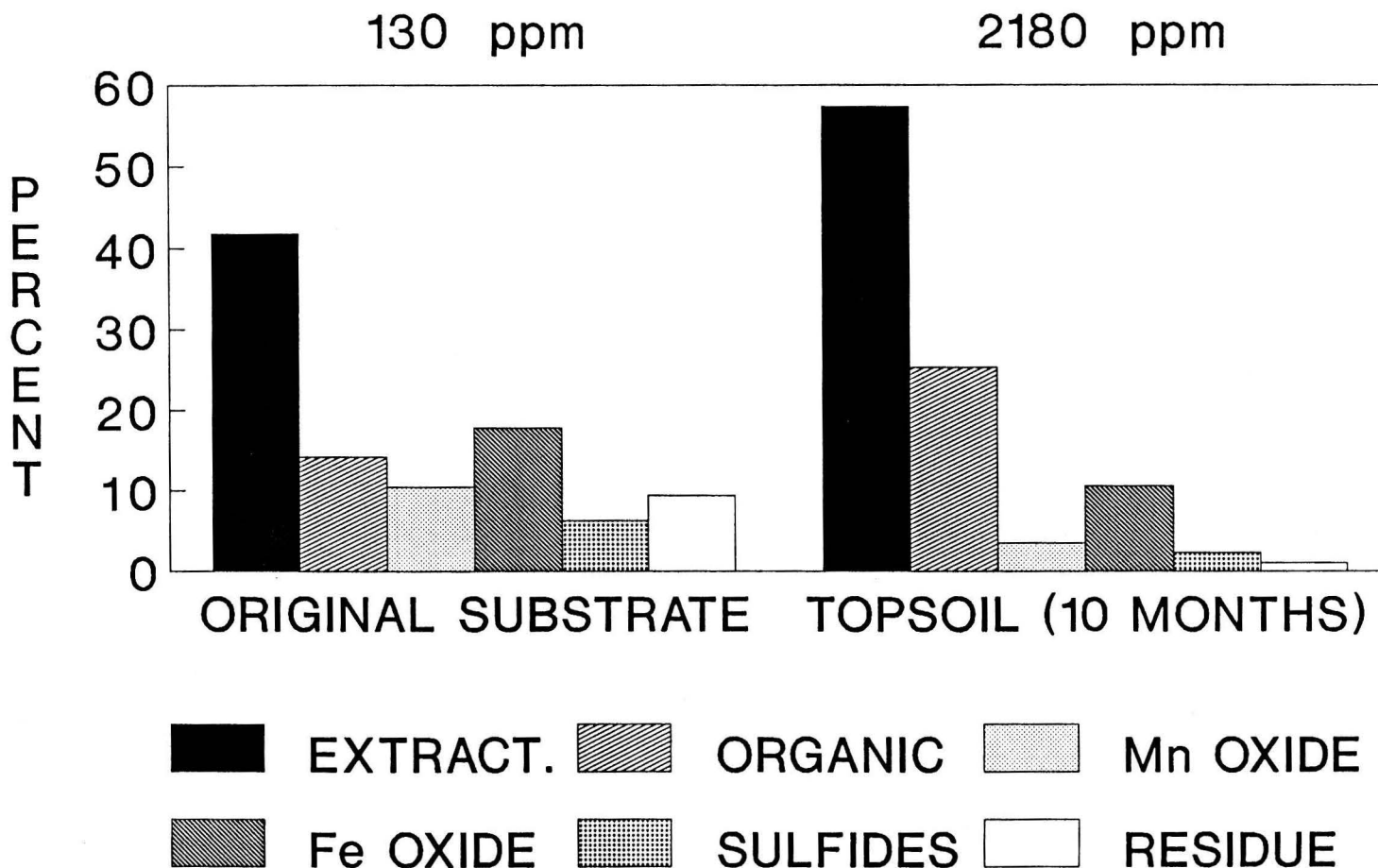
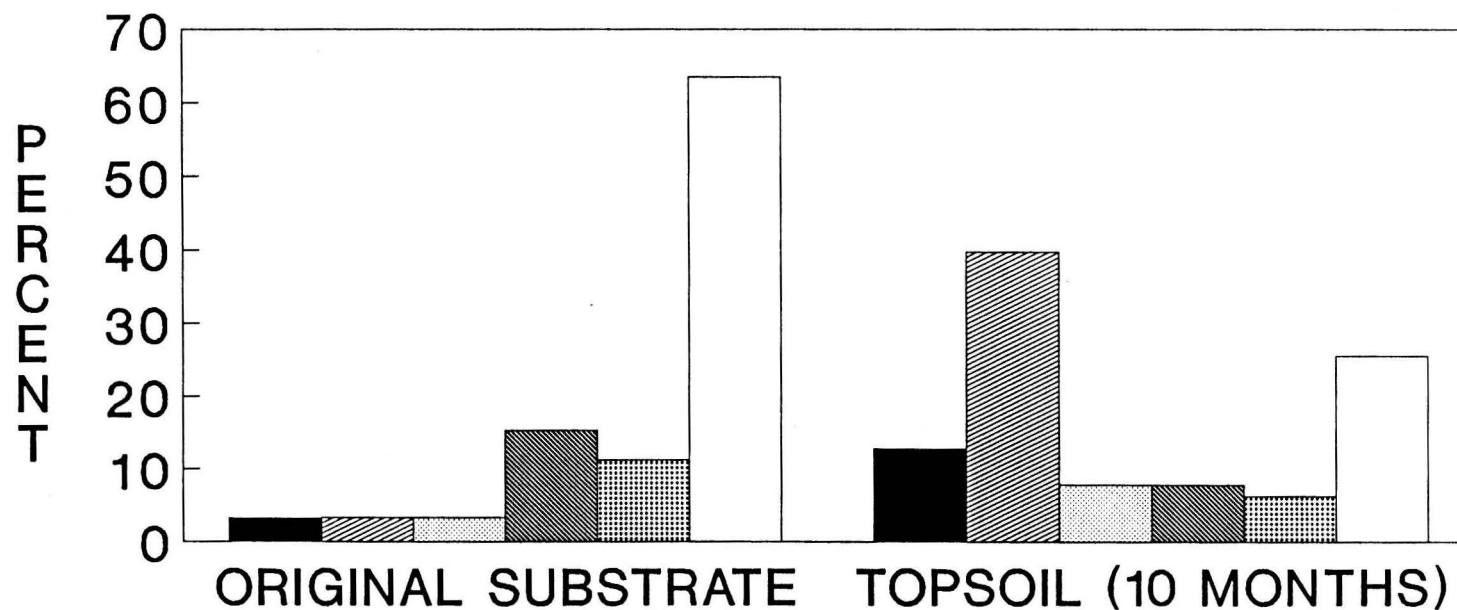


Figure 26. Six step zinc speciation in original mushroom compost and in substrate from the top of Cell A after 10 months.

Fe IN CELL A SOIL FRACTIONS

0.96 %

2.25 %



EXTRACT.
 ORGANIC
 Mn OXIDE
 Fe OXIDE
 SULFIDES
 RESIDUE

Figure 27. Six step Iron speciation in the original mushroom compost and in substrate from the top of Cell A after 10 months.

Cu IN CELL A SOIL FRACTIONS

58 ppm

270 ppm

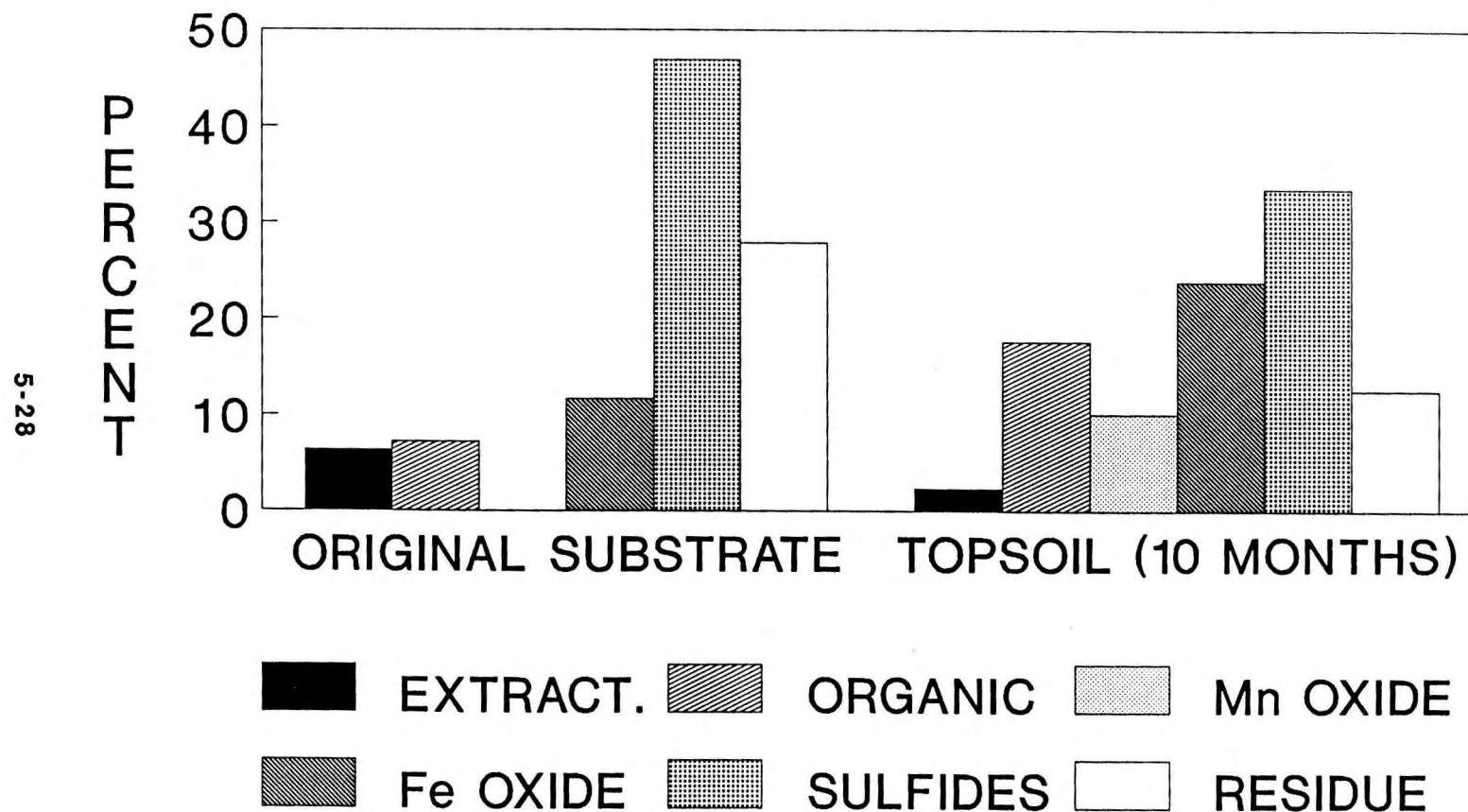
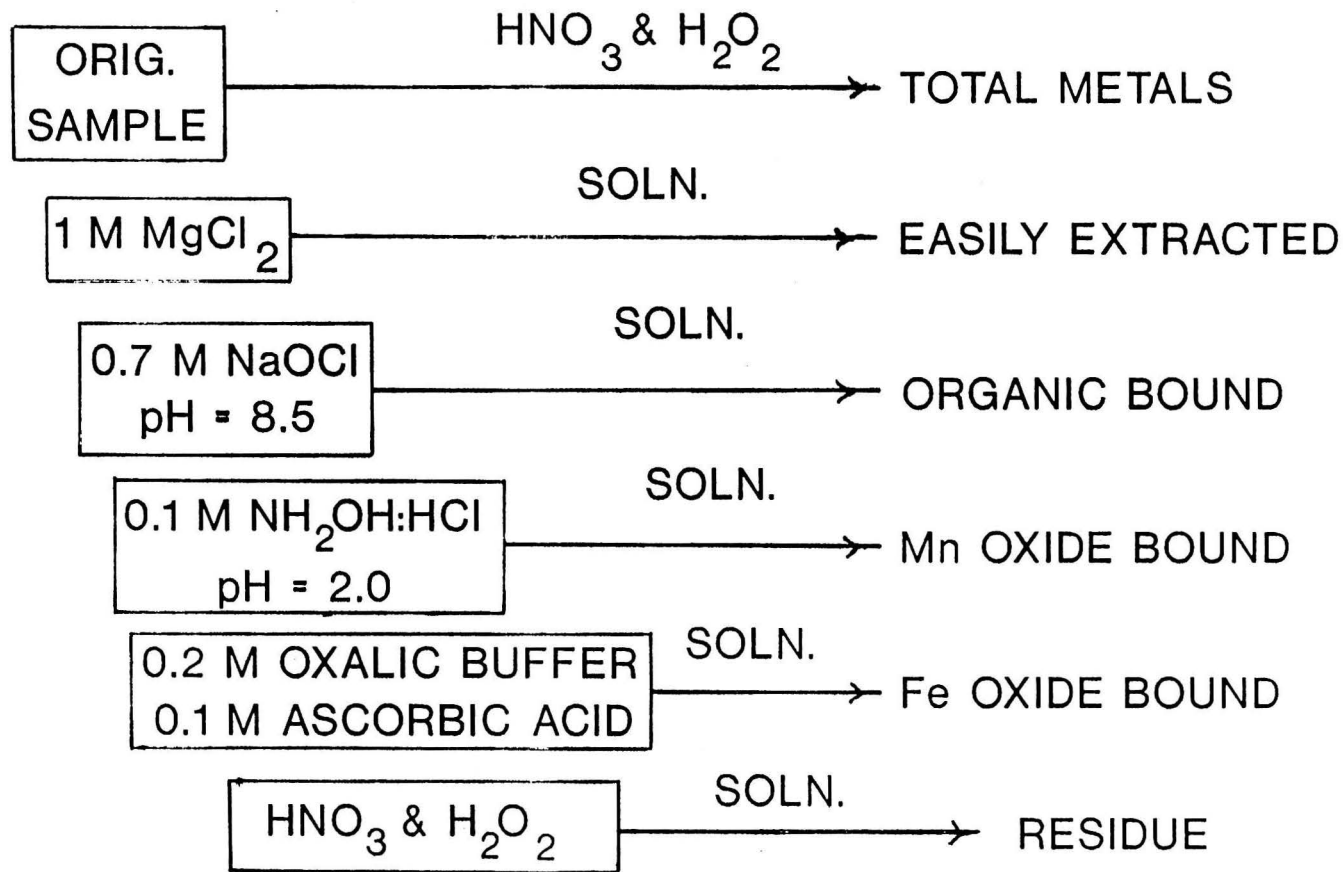


Figure 28. Six step copper speciation in the original mushroom compost and in substrate from the top of Cell A after 10 months.

SEQUENTIAL METALS EXTRACTION "II"

METAL FORM



5-29

Figure 29. Five step sequential extraction for metal speciation in substrate samples.

Table 21. Results of the Five-step Metal Extraction Sequence
on Substrates from the Top of Cell A.

Step	Orig. Compost		Soil A4, 6"		Soil A6, 6"		Soil A3, 6"		Avg Soil
	pm	%	ppm	%	ppm	%	ppm	%	%
Manganese									
1	35	6	470	44	390	34	720	45	44
2	29	6	160	14	116	10	210	13	14
3	217	41	67	15	220	19	290	18	15
4	121	23	68	15	240	21	260	16	15
5	127	24	101	13	182	16	170	11	13
Total	529		1070		1153		1660		
Act Tot	490	108	1160	92	1400	82	1600	103	-
Copper									
1	0	0	0	0	0	0	0	0	0
2	0.9	0	2.1	1	1.0	0	0	0	0
3	0	0	9.6	2	0	0	0	0	0
4	9.9	15	36	8	13	9	13	10	9
5	47	89	410	90	135	91	123	90	90
Total	58		458		149		136		
Act Tot	54	107	390	116	170	88	130	105	-
Iron									
1	8	0	200	0	0	0	10	0	0
2	35	0	370	0	60	0	80	0	0
3	71	1	620	3	310	2	320	2	2
4	7540	56	11200	59	13200	60	14300	64	61
5	5840	43	7300	38	8200	38	7800	32	37
Total	13500		19700		21800		22500		
Act Tot	12000	112	19000	107	20000	109	17000	132	-
Zinc									
1	-	0	-	17	-	3	-	3	8
2	-	3	-	18	-	4	-	5	9
3	-	4	-	26	-	23	-	23	24
4	-	54	-	20	-	51	-	48	40
5	-	38	-	20	-	18	-	20	20
Total	-		-		-		-		
Act Tot	-	-	-	-	-	-	-	-	-

Mn IN CELL A SOIL 2nd EXTRACTION

490 ppm

1300 ppm

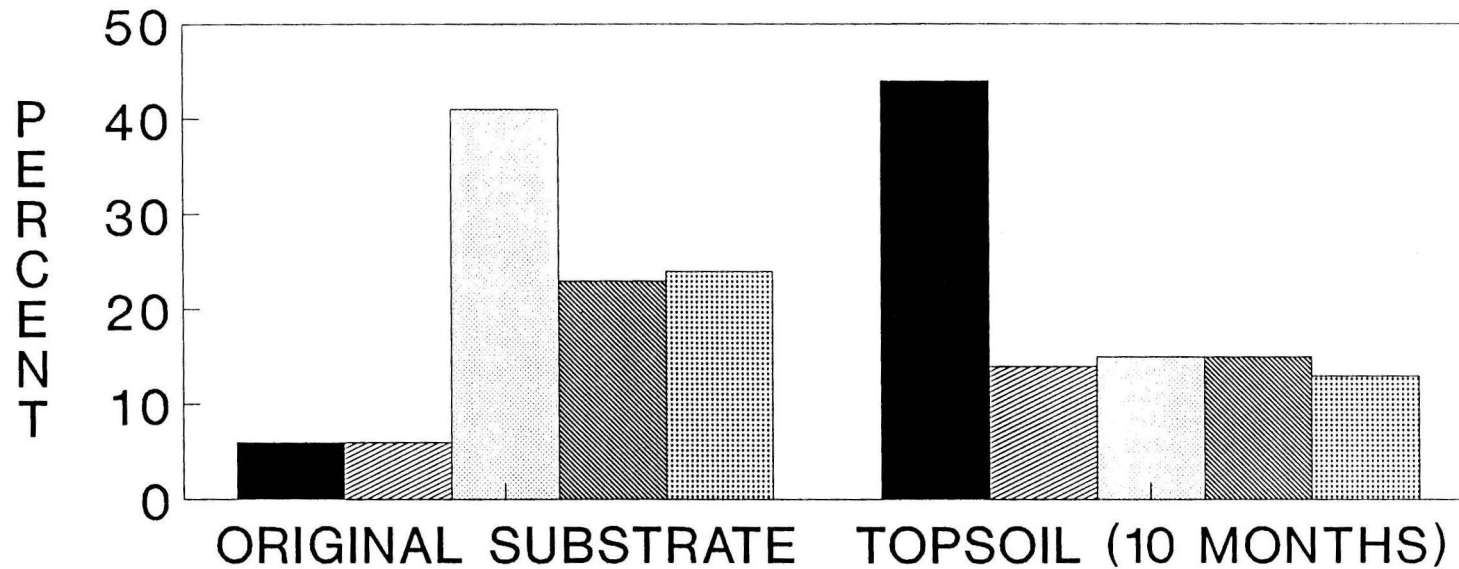


Figure 30. Five step manganese speciation in the original mushroom compost and in substrate from the top of Cell A after 10 months

Zn IN CELL A SOIL 2nd EXTRACTION

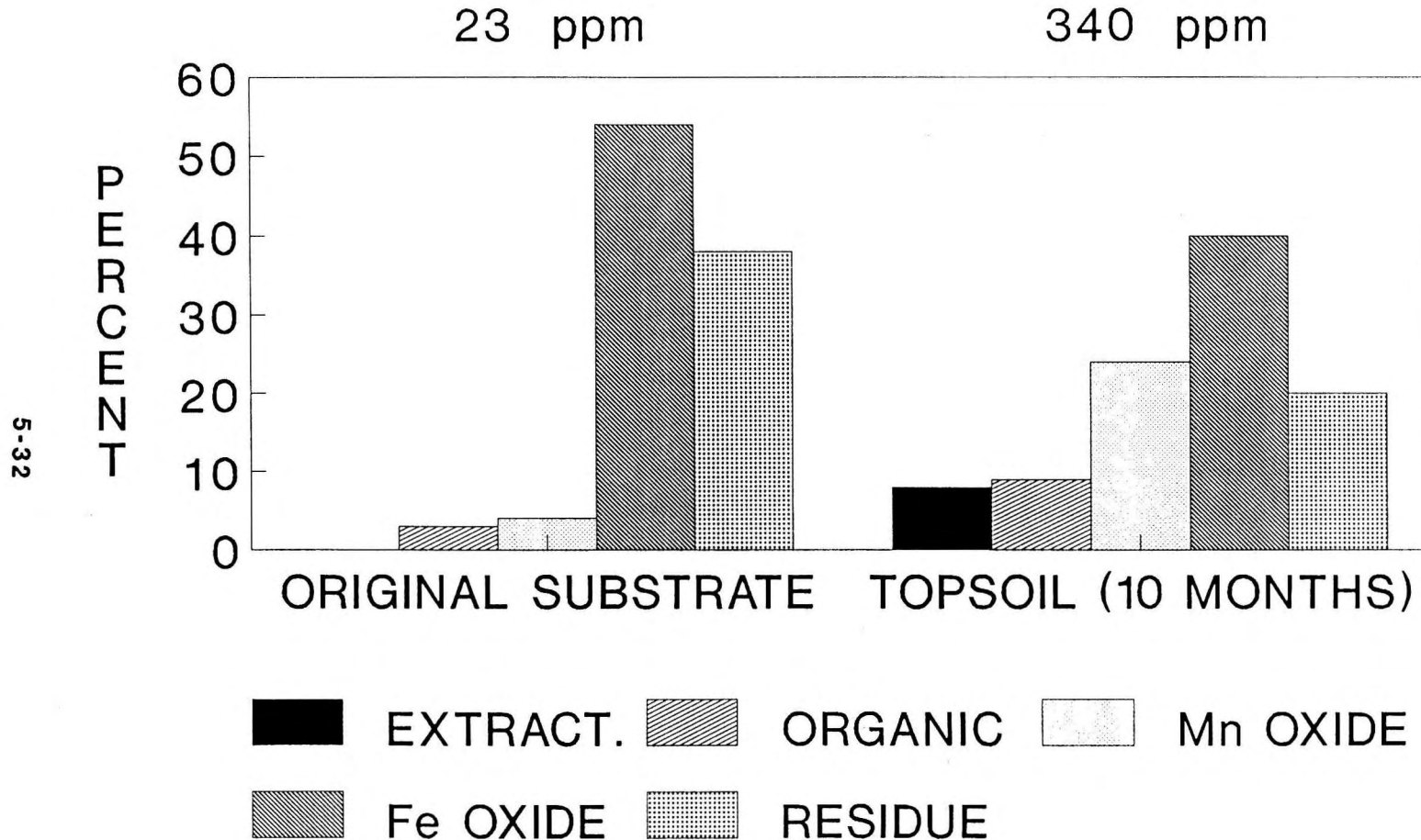


Figure 31. Five step zinc speciation in the original mushroom compost and in substrate from the top of Cell A after 10 months.

Fe IN CELL A SOIL 2nd EXTRACTION

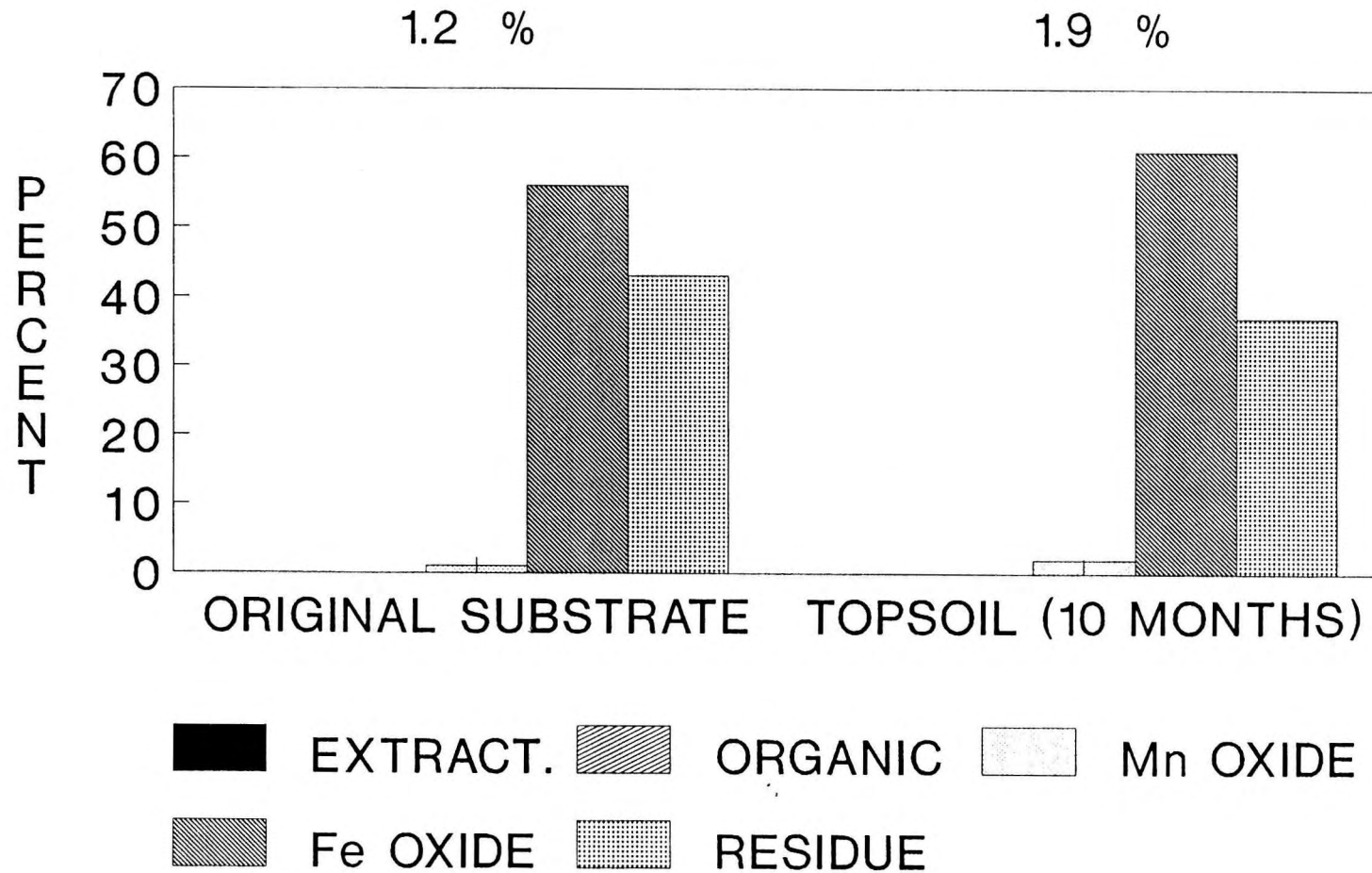


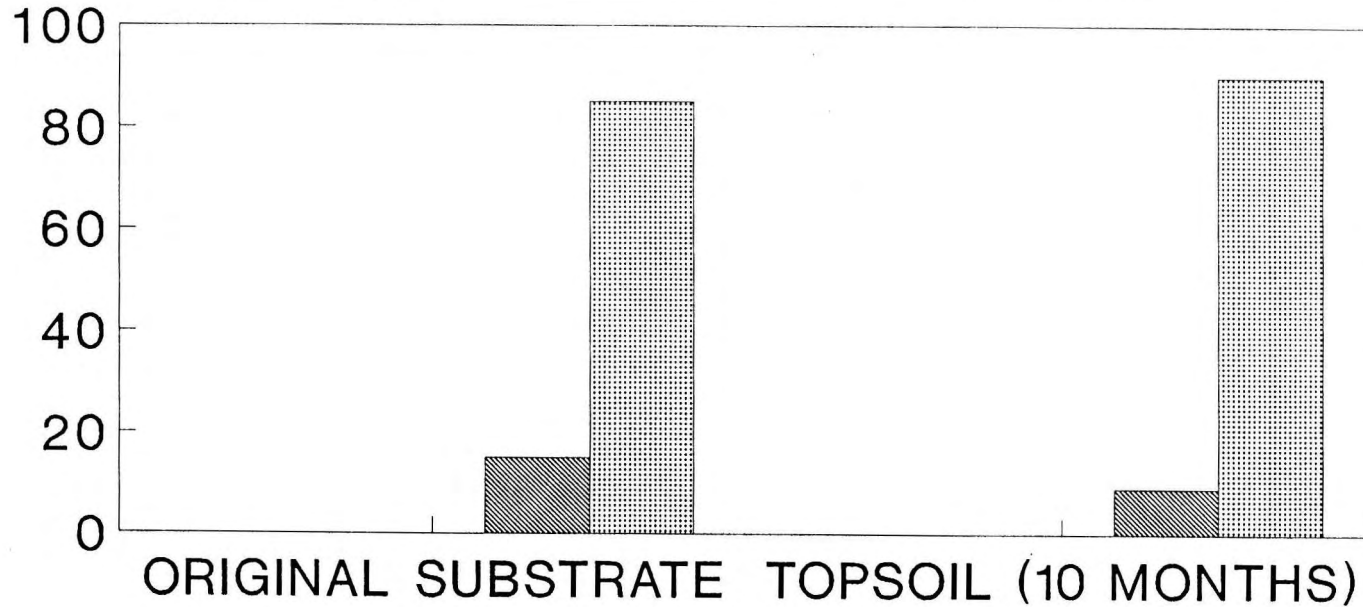
Figure 32. Five step iron speciation in the original mushroom compost and in substrate from the top of Cell A after 10 months.

Cu IN CELL A SOIL 2nd EXTRACTION

54 ppm

220 ppm

PERCENT



EXTRACT.
 ORGANIC
 Mn OXIDE
 Fe OXIDE
 RESIDUE

Figure 33. Five step copper speciation in the original mushroom compost and in substrate from the top of Cell A after 10 months.

DECREASE OF SULFATE IN THE EFFLUENT

If by reactions 5-3 and 5-4 sulfate is reduced to sulfide, and it is precipitated as a metal sulfide; then the concentration of sulfate should decrease in the effluent leaving a wetland cell. However, this decrease can be difficult to verify. As Laudon reviewed in her thesis (7), it is quite easy to oxidize the precipitated sulfides by using the bacteria that oxidize pyrite. Wieder (40, 48) observed that Big Run Bog, West Virginia was a source of $\text{SO}_4^{=}$ to receiving streams during periods of low flow and a sink for $\text{SO}_4^{=}$ during high flow periods corresponding to the water saturation status of the wetland.

Based on seasonal studies of saltmarsh sediments, Cutter and Velinsky (122) interpreted that in spring to early summer, photosynthesis injects O_2 into the upper 15 cm of sediment that oxidizes Fe sulfides and precipitates Fe oxides and elemental sulfur. Then in autumn, O_2 infusion slows and sulfate reduction predominates, Fe oxides and elemental sulfur are reduced and reprecipitated as Fe sulfides. Finally in winter, oxidation and reduction rates slow but Fe sulfides continue to precipitate due to upward diffusion of H_2S and Fe(II) .

It appears that in natural wetlands, sulfate concentration could be higher or lower than the average value depending on climatic conditions. In the first year, it was not clear that a change in sulfate concentration would occur.

Sulfate Reduction Evidence

When the Emerging Technologies Project started, sulfate analyses started to be performed by the Eschka method (81). Since this method uses a sulfate precipitation and the concentration of sulfate in the Big Five waters is quite high, the precision of duplicate analyses was well within 5 %. The first analyses by this method were through late fall and winter in 1988-89. In Table 22, the sulfate concentrations and pH of the mine drainage, Cell A, and Cell C are reported. It is obvious that the difference in sulfate concentration between the mine drainage and the cell effluents is minimal. However in February, the pH in Cell A effluent increased and the sulfate decreased beyond the analytical error. Also in February, the sulfate concentration in Cell C effluent increased to a level definitely above the concentration on the mine drainage. It appears that sulfate concentration can increase or decrease depending on whether sulfide is stable in the wetland substrate. In the case of sulfate decrease, the pH appears to increase.

In October, 1989, to further test the sulfur budget, total sulfide in Cell E pore waters was determined by electrochemical titration at the time of monthly water sampling. The balance of sulfur is shown in Figure 34. In this balance, it was assumed that all of Mn, Fe, Cu, and Zn were precipitated as sulfides. If this is the case, only 1.08 millimole / liter (100 mg/L) of sulfate is needed to completely precipitate all the metal sulfides. The Big Five mine drainage is a gypsum water as are most mine drainage. There is an excess of sulfate in the water. Another important feature of this balance is that when sulfate concentration in the effluent is decreased, there is a definite presence of sulfide in the wetland pore

waters. Both these experiments confirm that if sulfate-reducing bacteria are operating and sulfide precipitation is an important removal process, then the sulfate concentration should decrease.

When Cells B and E were started in September, 1989, changes in sulfate concentration as well as heavy metals were closely monitored. In Figures 18 and 19 sulfate removal as output / input is plotted for the first four months of operation. In Figure 20 pH is plotted. Note that in Cell B-downflow sulfate has not decreased and the pH of the effluent has not risen above 4 even though metals are removed. As discussed earlier in this section, removal in this cell was by adsorption onto organic phases. On the other hand, sulfate is being removed from Cell E and the pH is around 6. In laboratory experiments, Machemer (7) found the same pattern of concentration change when sulfate-reducing bacteria were vigorously growing. Reduction in the concentration of sulfate is a reliable indicator of removal of metals by bacterial reduction of sulfate and precipitation of sulfides.

Table 22. Sulfate concentrations and pH's in the Big Five Cells in the Autumn and Winter of 1988-89.

=====		NOV	DEC	JAN	FEB
WATER					
DRAINAGE	SO ₄ ⁼	1750	1710	1690	1780
	pH	2.9	3.0	2.8	3.0
CELL A	SO ₄ ⁼	1690	1710	1670	1660
	pH	3.3	3.4	3.3	5.1
CELL C	SO ₄ ⁼	1740	1700	1720	2000
	pH	3.2	3.3	3.1	3.5
=====					

Changes in Sulfate Concentration with Flow

Another indication that continuous bacterial reduction of sulfate is manifested by a reduction in sulfate concentration is the change in chemistry of effluent water with the flow through the wetland cell. From 1987 through 1989, changes in chemical parameters in Cell A effluent were compared with flow into the wetland cell (11). For metal concentrations, correlations were not obvious. However the concentration of sulfate in Cell A effluent did decrease as the flow decreased. A graph of the change is shown in Figure 35. A linear regression analysis on the data points produced a correlation coefficient of 0.82. In addition, the Eh decreased as the sulfate decreased. The graph is shown in Figure 36. In this case the correlation coefficient is 0.78.

As discussed in SECTION 3, sulfate-reducing bacteria require reducing conditions. The two

chemical variables that are most directly related to sulfate-reducer activity do change in the expected manner. Removal of heavy metals requires that sulfide, the product of sulfate reduction, comes in contact with the mine drainage. Apparently in Cell A, this does not always happen. However, the results of Cell E as shown in Figures 16 and 19 prove that proper design can make this removal linkage be effective.

SUMMARY

Through all the experiments performed on the Big Five Cells, the case for sulfate-reducing activity being linked to metals removal has been established. Proving sulfate reduction and sulfide precipitation from field evidence becomes difficult because of the complexity of a wetland. To further establish that sulfate reduction, sulfide precipitation, and removal of metals are linked, an extensive series of laboratory tests on the substrate from Cell-B Upflow were conducted. Preliminary results (118, 119, 120) show a direct correlation in the reduction of sulfate concentration with the increase in acid volatile sulfides in the precipitate. Metal removal correlates with the amount of acid volatile sulfide (120). However, the results suggest a source of metals other than those from the mine drainage. It appears that metals previously adsorbed onto the organic Cell-B substrate are the most likely additional source.

With this laboratory confirmation of the field evidence, the case for sulfate-reducing activity being linked to metals removal has been reasonably shown. This being the case, the most direct effect of sulfate reduction--decrease in sulfate concentration in the effluent--appears to be the best indicator of sulfate reducing activity. In addition, decrease of the Eh in the effluent compared to influent helps confirm sulfate reducing activity. The direct correlation of these two variables in Cell A is shown in Figure 36.

Now that it has been shown that sulfate concentration should be consistently lower, this along with the Eh can be used to monitor the removal efficiency of a wetland removal system.

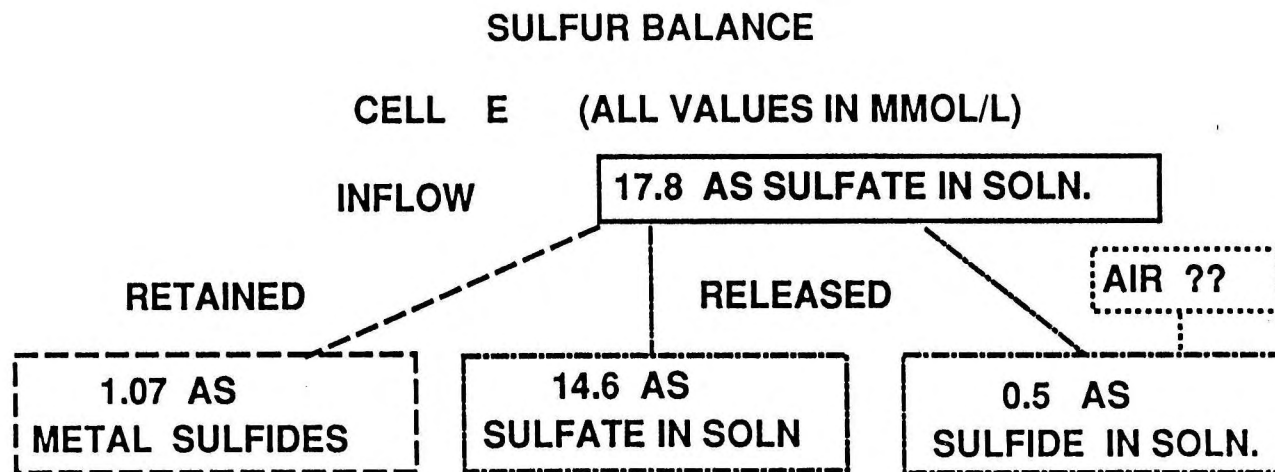


Figure 34. Sulfur balance in Cell E in October, 1989.

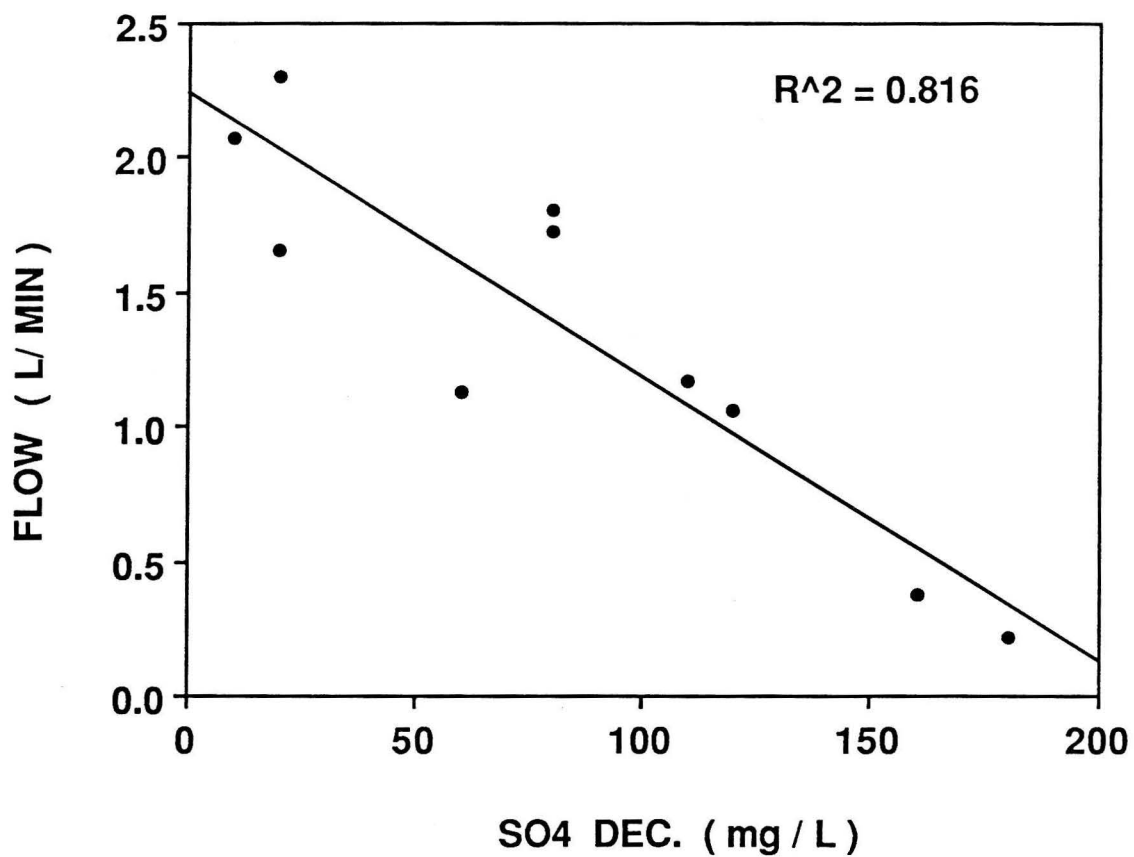


Figure 35. Change in sulfate concentration versus flow in Cell A.

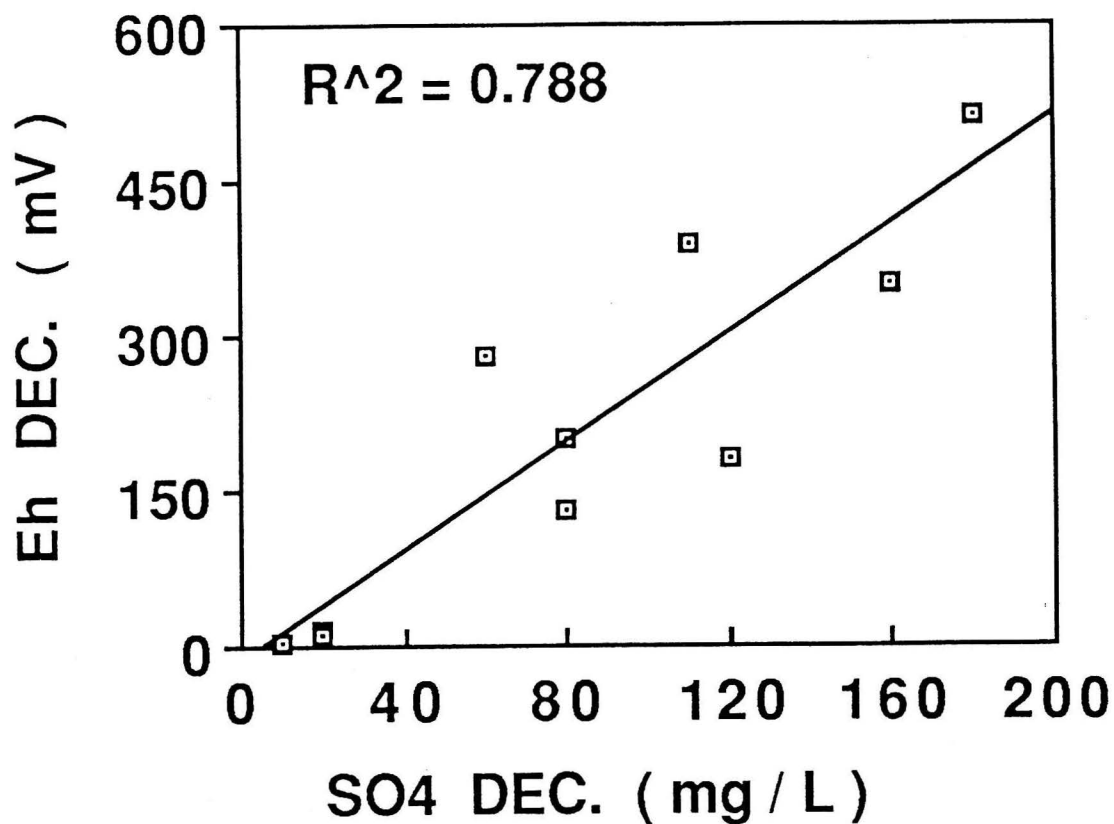


Figure 36. Decrease (DEC.) in Eh versus decrease (DEC.) in sulfate concentration in Cell A effluent compared to influent.

SECTION 6
ECOPHYSIOLOGICAL CONSIDERATIONS OF PLANTS
AT THE BIG FIVE CONSTRUCTED WETLAND, IDAHO SPRINGS, COLORADO

INTRODUCTION

One component of the pilot-scale treatment system at the Big Five tunnel is emergent wetland vegetation. The role and importance of the vegetation to the metal-removal efficiency of the system is not entirely known. However there is documentation at other constructed wetland sites of improved removal of some metals in systems with emergent vegetation, when compared to similar systems without vegetation. Among the proposed/speculated effects the wetland vegetation has upon the treatment system are:

- o oxygenation of the substrate;
- o provision of nutrients to microorganisms living within the substrate, both by exudation of chemical substances from the plant roots and rhizomes that are used by certain microbes (e.g. sugars), and by addition of biomass;
- o alteration of the permeability and hence the flow dynamics of the substrate, in the upper part of the substrate;
- o effects upon the water budget of the system, through evapotranspiration;
- o aesthetic enhancement

The primary objectives of the study of the emergent vegetation at the Big Five system were: 1) to further the understanding of the role that emergent vegetation has upon the dynamics of the treatment system (e.g. addition of organic material, oxygenation, evapotranspiration); and 2) to examine the health of the emergent plants by such means as monitoring of elemental uptake, visual appraisal, and comparison of annual mapping.

QUANTIFICATION OF BIOMASS

One effect the vegetation has upon the treatment system is by addition of organic material as biomass to the wetland substrate, providing additional nutrient source for microorganisms. The addition of such biomass might extend the life of the substrate within a cell, by possibly providing more sites for complexation of metals, as well as nutrients for microbial processes. An attempt was made to quantify the amount of material added to the substrate by the plants. Because of limitations on the total amount of plant material, and because of a concern that destructive sampling might affect cell performance, methods that were largely nondestructive were used to estimate biomass.

The measurements were made on Cell C in summer 1989, as this cell had been undisturbed from the beginning of the project, and had essentially total vegetation cover. This quantification was made by the following method:

- 1) Visual appraisal that *Typha* (cattail) biomass comprised on the order of 75% by volume of total biomass of plants in the cell (based on the estimates of four different workers at the site)
- 2) Mapping and counting of the number of *Typha* plants within the cell.
- 3) Estimation of total *Typha* leaf area, by taking the mean of leaf area measurements for several plants. This leaf area was then multiplied by average dry weight per area for *Typha* leaves, resulting in total dry weight of leaves.
- 4) Estimation of total below-ground biomass. This component has appreciable uncertainty. Dry weights of above/ below-ground biomass were compared for several plants, with the below-ground including roots and rhizomes. Results indicated more dry weight biomass below ground level, on the order of 1.75 to 2 times as much as above. Other reports (58) indicate commonly 50% of *Typha* biomass is below ground, with variation. As a conservative compromise, a figure of 1.5 times as much below-ground biomass as above ground was used.
- 5) Assumption that the remaining 25 % by volume of *Carex aquatilis*, *Carex utriculata*, and *Juncus arcticus* has the same biomass as the *Typha*.

This method resulted in the following estimate:

767 total *Typha* plants in Cell C X 33.5 g dry weight leaves per plant = 25.69 kg total leaves

Biomass below water level: 1.5 X 25.6 kg = 38.53 kg

Total *Typha* biomass: 64.22 kg

Total biomass estimate for all species (estimating *Carex aquatilis*, *Carex utriculata*, and *Juncus arcticus* to comprise 25% of total) in Cell C: 85.62 kg (rounded to 86 kg).

Assumption 4 on the amount of below ground biomass and 5 on the biomass of the other species probably make this an overestimate.

This figure is an approximation of the dry weight amount of organic material contributed to Cell C in the 1989 growing season. Analysis of the plant samples in 1989 showed an average dry weight of 31.07% carbon content. Using these figures, (total biomass X percent carbon), an estimated 27 kg carbon was represented by the biomass of Cell C in 1989. For Cell C, with an area of 18.6 m², this would be 1.4 kg/ m² of carbon. For natural wetlands, an average figure is often near 1 kg/m². Over the course of years, all of the above-ground, and perhaps half of the below-ground biomass will senesce and contribute to the soil organic matter. This would represent approximately 70 percent of the total carbon in the biomass entering into the organic carbon pool. For Cell C this would amount to about 1 kg / m² of carbon. This amount may be insufficient to meet most of the microbial carbon demands of sulfate-

reducing bacteria (65); and could, in fact, become a limiting factor on the system once the carbon in the original substrate is depleted.

EFFECT OF PLANT RESPIRATION ON Eh VALUES

Another effect of the emergent vegetation upon the treatment system is from the diffusion of oxygen from the roots into the surrounding substrate. The result is the creation of localized oxidizing zones within the substrate, which should be conducive to removal of some metals by oxidation (primarily iron). This is probably a contributing factor to the seasonality of metals removal reported in other constructed wetlands (73). Batal (10) reports increased populations of iron- and manganese- oxidizing bacteria during summer 1988, and decreased populations of sulfate-reducing bacteria during that summer, at the Big 5 wetland. Data for 1989-90 in Table 7, however, show that the populations of iron-oxidizing bacteria apparently have decreased steadily since 1988 in Cells A and C particularly in the 90 cm depth in the substrate. Along with temperature, this release of oxygen from plant roots probably affects the microbial populations particularly at shallow depths in the substrate.

A simple experiment was conducted to examine some of the effects of plants upon the oxidation potential values in the substrate. Eh measurements were made under controlled conditions, where a microprobe could be used to measure directly next to plant roots. Substrate from Cell A was placed in a 30-gallon glass tank in an indoor growing chamber and roots and rhizomes of *Typha* plants (cattails) were transplanted into the tank. Big Five mine drainage water was used to keep the substrate below water level, simulating conditions at the treatment site. After one month, several *Typha* plants had grown to a height of 1-1.5 meters, and the first set of measurements was made. Over 50 Eh measurements were made at varying depths within the tank, making one set of measurements within a centimeter of plant roots, and one set 10-15 cm. away from plant roots (Table 23).

Table 23. RESULTS OF FIRST Eh MEASUREMENTS IN GROWING CHAMBER

Measurements under plants/ or next to visible roots (millivolts)					Eh measurements away from plants (millivolts)				
Depth	Mean	High	Low	Std Dev	Depth	Mean	High	Low	Std.Dev
1.5 cm	+131	+240	+60	56	1.5 cm	+110	+150	+40	38
4 cm	+94	+150	+20	41	4 cm	+70	+130	-70	67
12 cm	+78	+170	-60	67	12 cm	-53	+60	-200	126

Not enough measurements were made for rigorous statistical testing. However there is a distinct qualitative difference in the oxidation potential near plant roots where oxygen is diffusing from the roots to the surrounding substrate, compared to measurements in substrate away from plant roots. In every case of paired measurements (under/away from plant roots), Eh values were higher underneath the plants. At the deeper depth, the mean difference was more than 100 mv, indicating small, localized oxygenated zones due to the presence of the roots. The experiment was later repeated using two tanks, one completely filled with *Typha* plants, and one with no cattails. Slightly greater differences were seen between the Eh measurements of the two tanks, with a mean difference at 12 cm depth of 133 mv higher in the tank with plants. These results show an oxygenation effect of the plants within and near the root zones that should affect metal removal by bacterial processes.

Other research (60) has compared the amount of oxygen diffusion (termed radial oxygen loss) from roots of five different wetland plants from a constructed wetland in Tennessee, and found *Typha* to have the highest oxygen loss of those compared.

EVAPOTRANSPIRATION MEASUREMENTS

Transpiration from the wetland vegetation has an effect upon the water budget of the treatment system. To estimate the magnitude of this component, measurements were made, at different times of the growing season, of total evapotranspiration (ET) by measuring the difference in flow between input and output to each cell. Evaporation was also estimated by use of evaporation pans, and the amount of surface evaporation from the cell calculated. The difference between evaporation and total water loss was taken as the transpiration component. These measurements were taken at regular intervals over 24 hours to assess the diurnal variation. Again, data for Cell C were used, as it had virtually a complete vegetation cover for the entire growing season.

During summer, the transpiration component was found to be greater than the evaporation component, by almost an order of magnitude. Figure 37 shows one measurement of evapotranspiration taken at peak growing season. For Cell C, the water loss in mid-afternoon was 0.13 gpm, or almost 20% of the inflow of 0.66 gpm; surface evaporation accounted for only approximately a 1.5% loss of the inflow, with the remaining 18% loss from transpiration. However, the water loss at pre-dawn measurements, when transpiration was at a minimum, was only 2%. Averaged over a 24- period, the water loss was 8-9% of total inflow.

An important consideration in such calculations is the incoming flow rate. Presumably, the evapotranspiration will remain approximately the same, no matter what the flow rate, as long as the substrate remains sufficiently moist, and the increased concentration of salts does not present an osmotic barrier to the plants. With a flow rate of half as much, as has been used at the Big 5 system at times, this

Diurnal variation in evapotranspiration, August 21/22, 1989

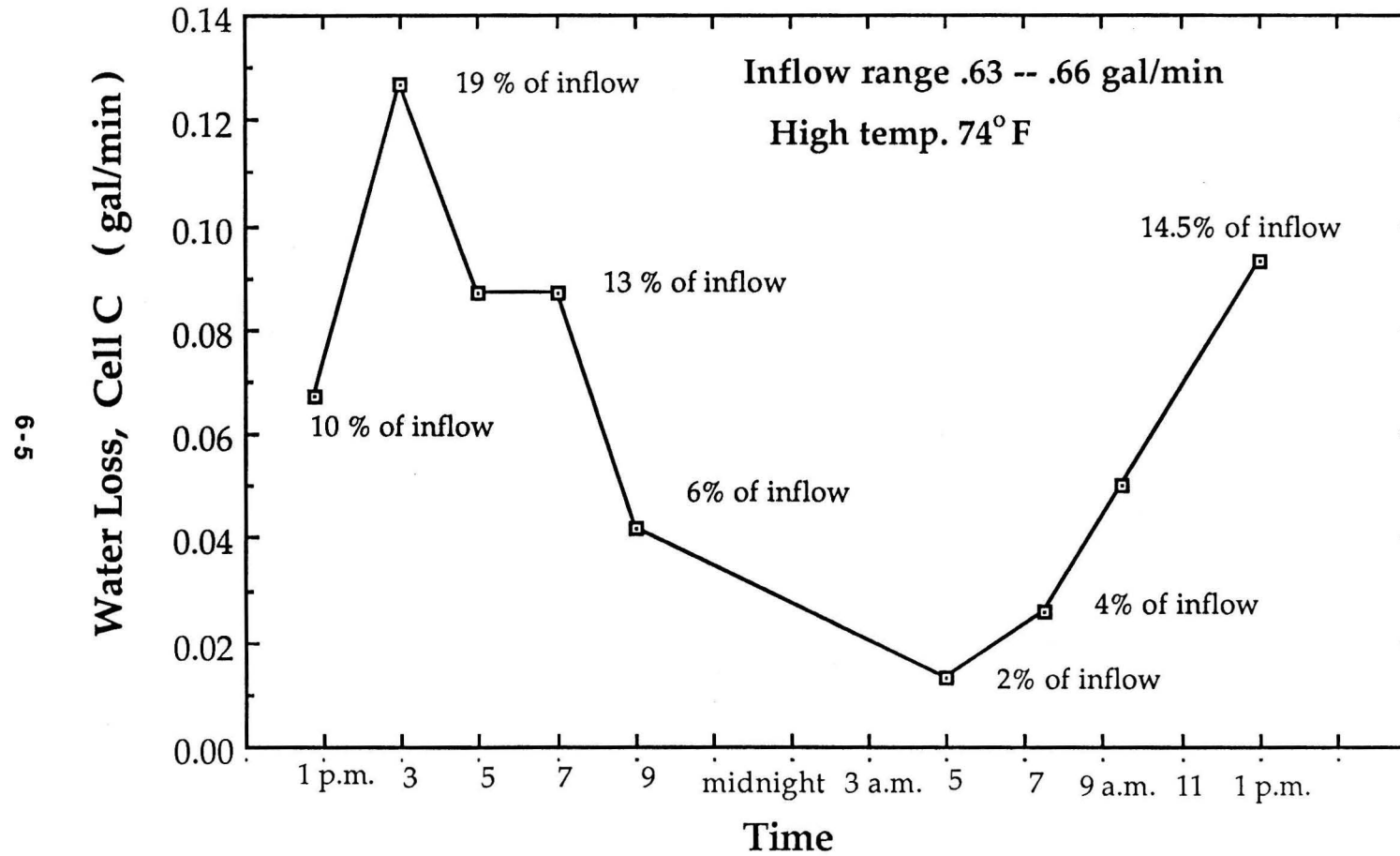


Figure 37.

Diurnal variation in evapotranspiration from Cell C over a 24 hour period, August 21 / 22, 1989.

evapotranspiration percentage would double. Flow measurements by Lemke (pers. communication, 1989) show water loss as high as 50% from Cell C, at peak ET times and low flow rates. Conceivably, at very low flow rates and peak ET rates, the evapotranspiration could account for most of the flow. Evapotranspiration should be considered in terms of ET per area, rather than as percentage of flow rate.

At these times of high water loss, there will be an increased concentration of substances dissolved in the drainage water flowing through the wetland cell. This raises the question of how this affects the treatment system's ability to remove the materials desired when they are present in the concentrated amounts, and whether this leads to periods during the day when treatment performance goals may not be met. We do not believe that this should be a problem. In SECTIONS 3,4, and 7, it was shown that removal efficiency apparently depends on the total amount of base metal in the inflow per day, and not on the relative concentration.

ELEMENTAL ANALYSIS OF PLANTS

A program of vegetation sampling was conducted in 1987, 1988, and 1989. Among the objectives of this sampling were:

- o Monitoring of elemental uptake, to provide a baseline database for use in evaluating the health of the vegetation in this and future treatment systems, and for predictions of longevity of the vegetation in such systems.
- o Monitoring of seasonal partitioning of various elements in the vegetation.
- o Further understanding of the metal removal budget within the treatment system.
- o Documentation of elemental concentrations of the vegetation growing in the system, because of concern for possible entry of heavy metals into the food chain should large-scale systems become operational.

Procedure

Destructive sampling of the three primary emergent plant species, *Carex utriculata*, *Carex aquatilis* (both sedge species), and *Typha latifolia* (cattail) was performed. Samples were washed with deionized water, oven-dried, and sent to EPA laboratories in Oregon and Cincinnati for ICP analysis. For comparison, in the 1989 growing season, samples were also collected at three 'control' sites, which are mountain wetlands in Colorado not directly impacted by mine drainage. These sites were:

- 1) Big Meadow, in Rocky Mountain Park; (*C.utriculata* and *C.aquatilis*. only)
- 2) Deer Creek, near the Keystone resort (*C.aquatilis* only);
- 3) Shadow Mountain Lake, near the west side of Rocky Mountain Lake, which was one of the sites from where the original plants for the Big Five system were obtained (all three species).

Results

Carex aquatilis is the species that was collected at all the sites not impacted by acid mine drainage. The abundance of Cu and Zn in *C. aquatilis* roots from the different locations is given in Figures 38 and 39 respectively. In these figures, DC stands for Deer Creek, BM stands for Big Meadow, and SM stands for Shadow Mountain Lake. For both elements, there is an increase of over a factor of ten in roots taken from the Big Five Cells. One might argue that these metals may be strongly adsorbed to the surfaces of the roots. Nevertheless, the high concentrations of these two metals in the water cause high abundances of these metals in or on the roots.

With respect to how the plants have changed over time, Cell C has remained undisturbed since construction in 1987. Plant samples were taken in October, 1987, when the vegetation was transplanted, and again in October, 1988 and 1989. By October, the leaves of the plants had gone into dormancy. Figures 40 and 41 show the abundance distributions of Cd and Pb in various plant parts from Cell C. Metal concentrations in both the leaves and the roots for *Typha*, *C. aquatilis*, and *C. utriculata* are shown in these figures. In general, the abundances of these two metals in all the plant parts have increased over the course of two growing seasons. For the first two samplings, the concentrations were higher in roots than leaves. However in 1989, the abundances in the two plant parts are about equal. This equality of abundances in plant parts is manifested in all three species. This suggests that high metal concentrations in the water start to be reflected in all three of these wetland plants after two years. Also, shifting contaminants to senescing leaves at the end of the growing season is a known strategy for plant survival in contaminated locations. This is seen in the large increase of Cd in the leaves of all three species.

Cell C is the only pilot system that has remained undisturbed over the course of the project. In 1990, the growth of plants in Cell C was just as vigorous as in previous years. Even though the abundances of microcontaminants may be increasing in the plants, it has not as yet affected growth and production of biomass. This is especially true of the *Typha* species that has taken over and forced out the *Carex* and *Juncus*.

Finally, root and leaf samples of *Typha* were taken in both July and August of 1988 to see if abundances of metals increased during the growing season. In Figure 42, Fe and Mn abundances in *Typha* leaves and roots are shown. Fe is known to precipitate at the root surfaces in *Typha* (60); while Mn doesn't precipitate and is taken into the leaves. For both July and August, this situation is seen for Mn and Fe. In all cases, abundances of the metals are higher in August than in July. However, the increases are within or just beyond the bound of analytical uncertainty. Abundances of these microcontaminants show small increases during the height of the growing season.

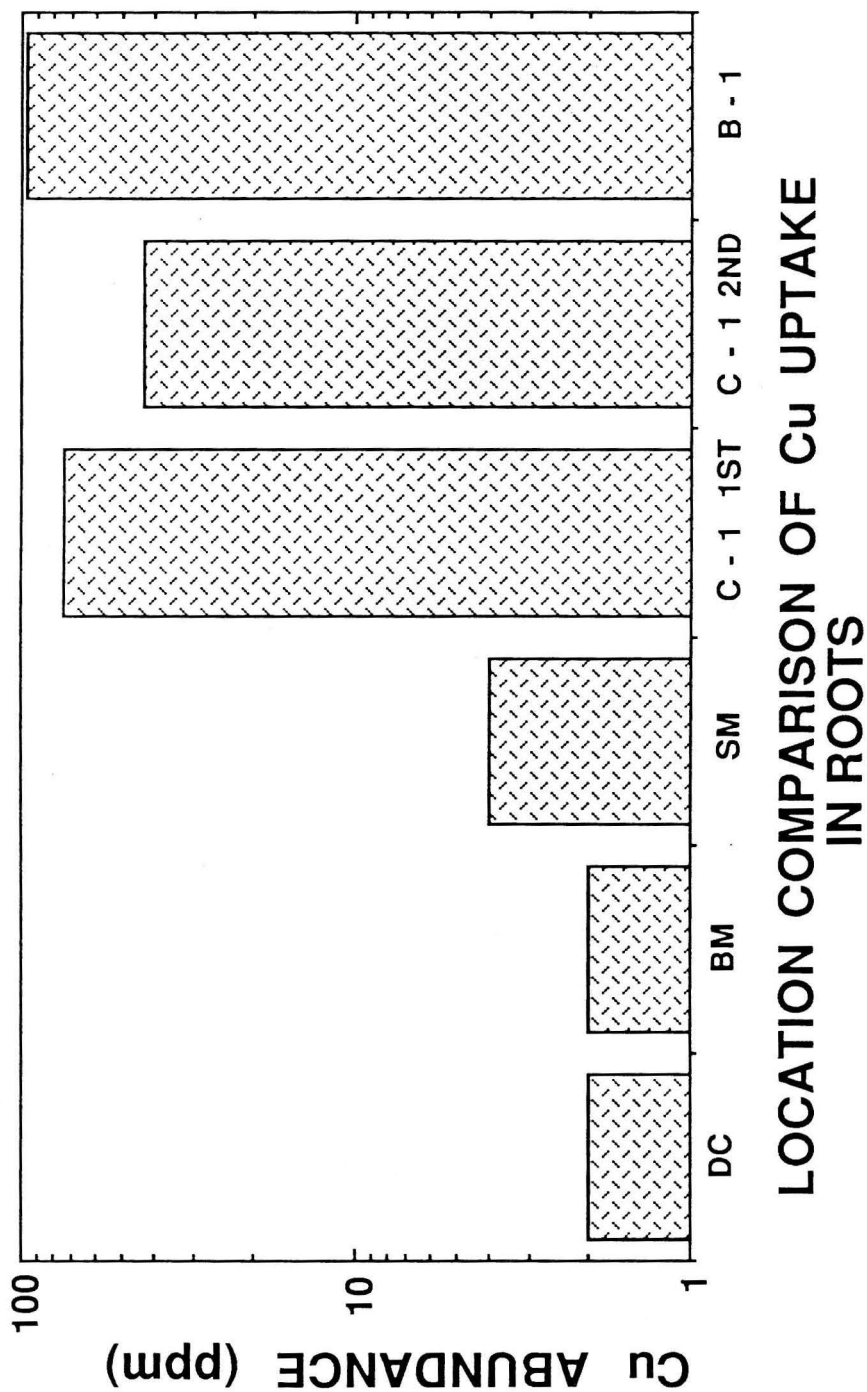


Figure 38. Comparison of Cu in *C. Aquaticus* roots from wetland sites not impacted by mine drainage and from Cells B and C. The locations are: Deer Creek (DC), Big Meadow (BM), Shadow Mountain Lake (SM), the front of Cell B (B-1), and the front of Cell C (C-1).

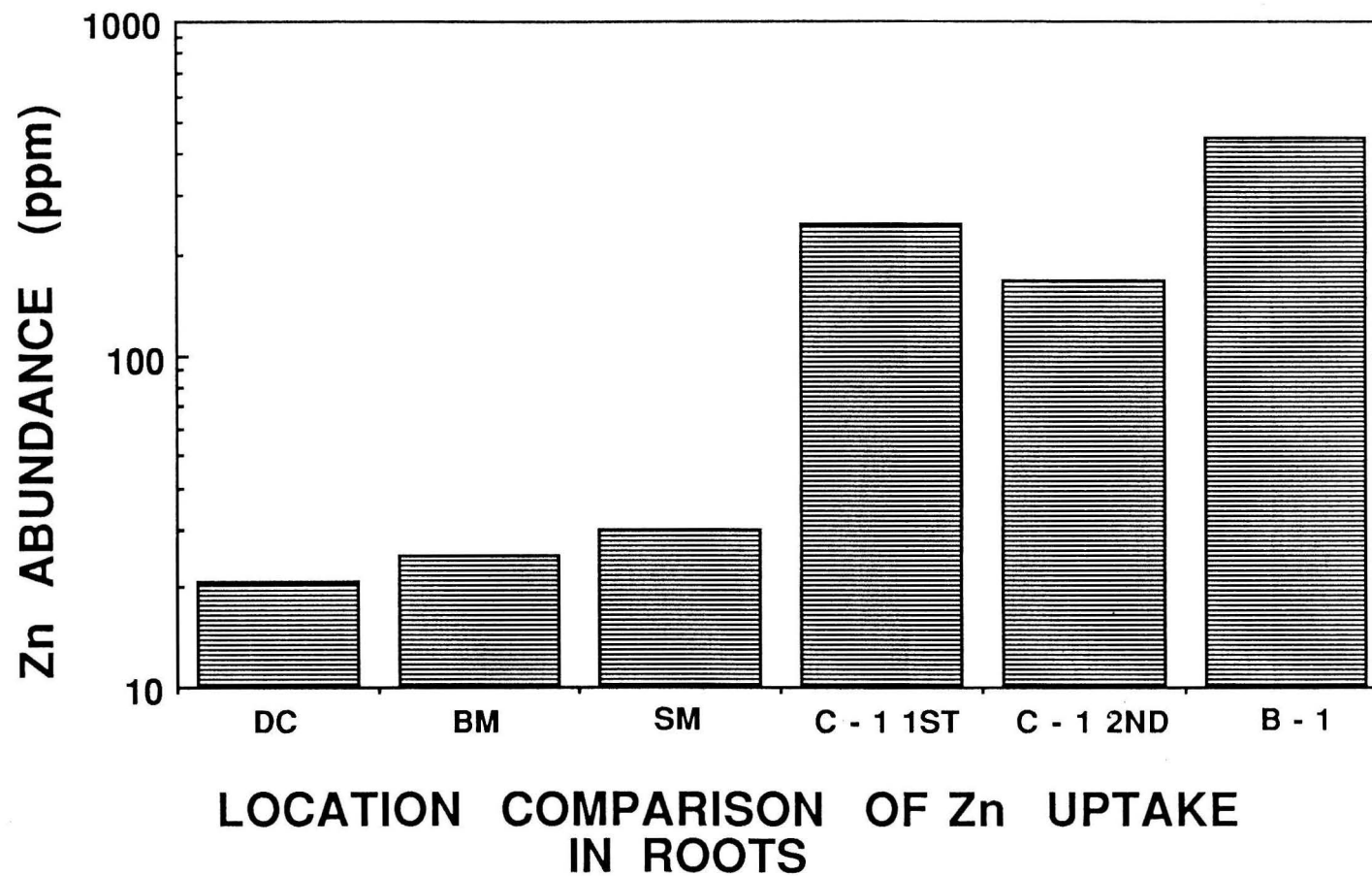


Figure 39. Comparison of Zn in *C. Aquatilis* roots from wetland sites not impacted by mine drainage and from Cells B and C. The locations are: Deer Creek (DC), Big Meadow (BM), Shadow Mountain Lake (SM), the front of Cell B (B-1), and the front of Cell C (C-1).

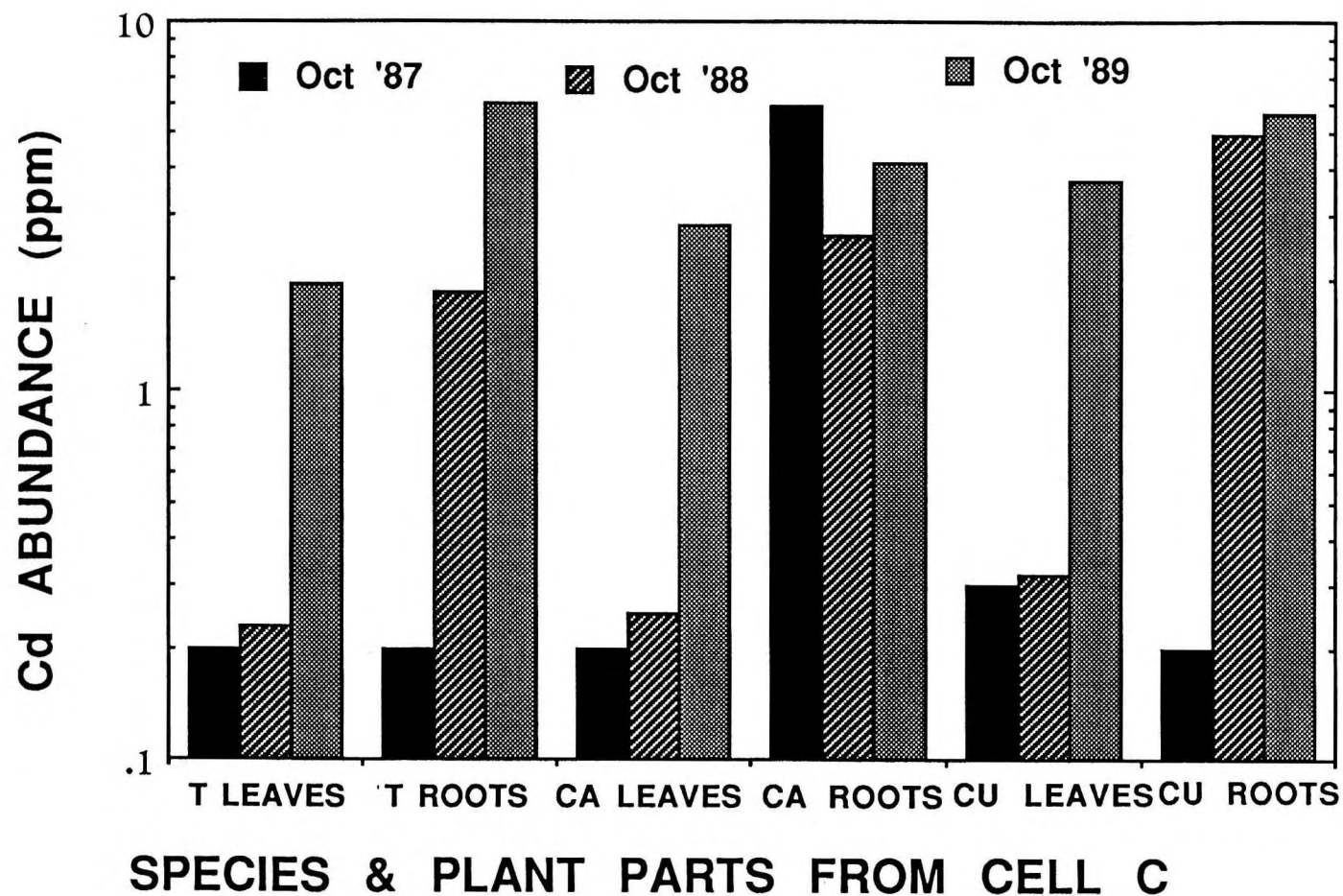


Figure 40. Uptake of Cd into roots and leaves of the plant species in Cell C from October 1987 through October 1989. The plants are: *Typha* (T), *Carex aquatilis* (CA), and *Carex utriculata* (CU).

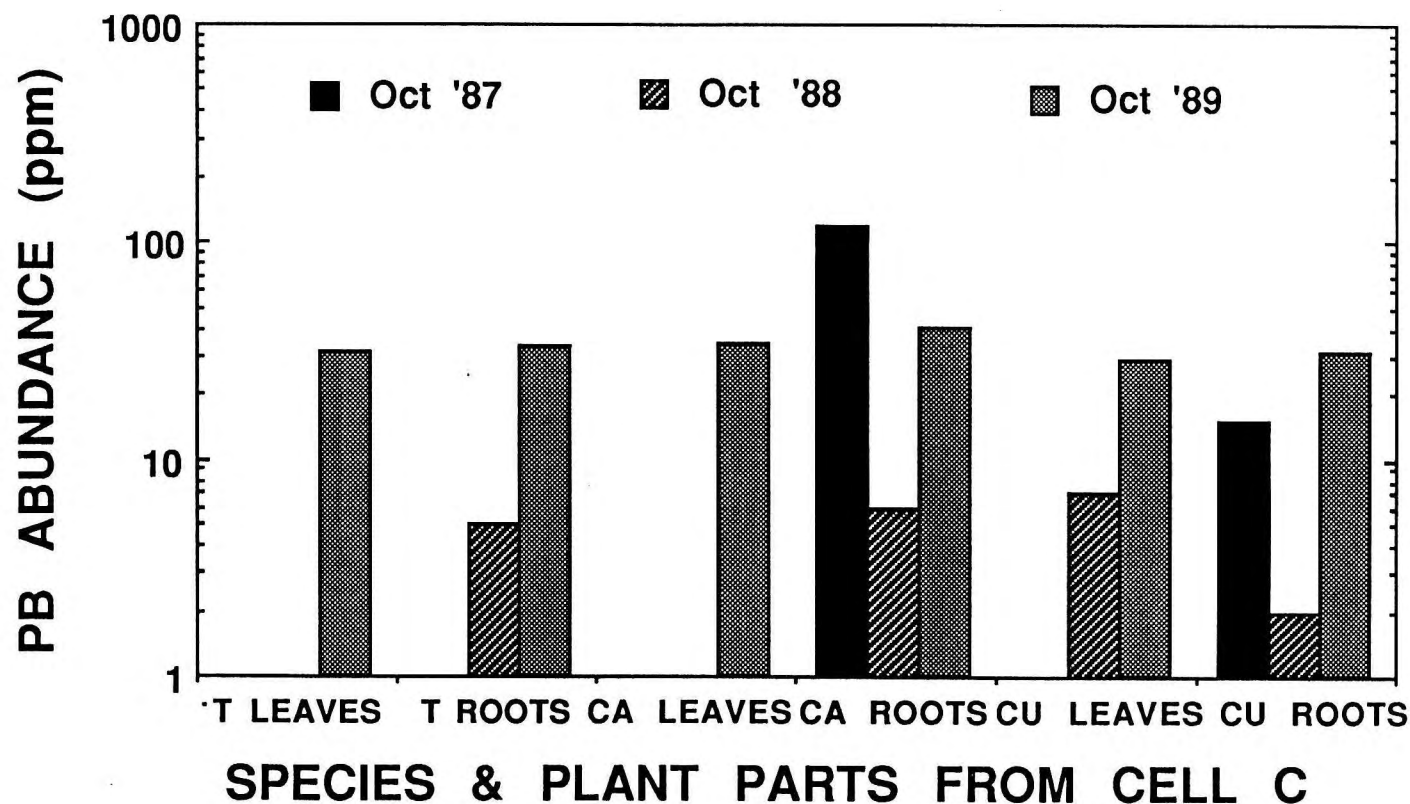


Figure 41. Uptake of Pb into roots and leaves of the plant species in Cell C from October 1987 through October 1989. The plants are: *Typha* (T), *Carex aquatilis* (CA), and *Carex utriculata* (CU).

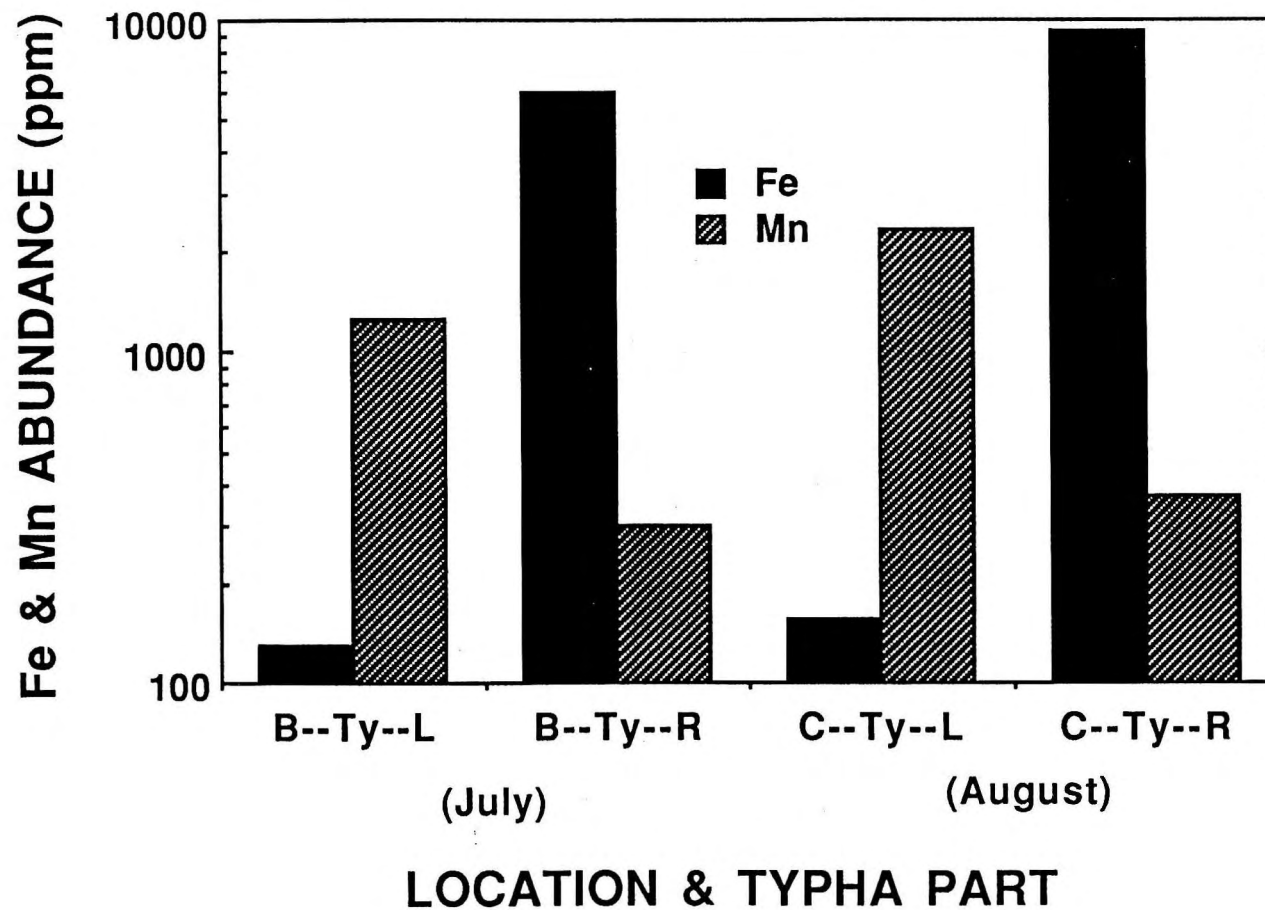


Figure 42. Uptake of Mn and Fe in Typha roots and leaves in July and August, 1988.

OTHER CONSIDERATIONS

Changes in Vegetation

As one means of qualitatively assessing the health of the wetland plants, vegetation mapping was done in 1988 and in 1989, to help chart the changes as the wetland matured. Figure 6 is the diagram of the original distribution of plants in all three cells. The most obvious change with time was the spread of the *Typha* plants. The cattails have been by far the most successful of the original transplanted species (*Carex aquatilis*, *Typha latifolia*, *Carex utriculata*, and *Juncus arcticus*), spreading from their original transplanted locations to virtually all parts of the cells. In Cell C, numbers of cattail plants increased from less than 500 in 1988 to more than 750 in 1989. A similar increase occurred in Cell B. There is no visual evidence of dieback of the *Typha*. It is estimated that the *Typha* plants account for perhaps 75-80% of the total plant biomass.

Of the other species, the sedges (*C. aquatilis* and *C. utriculata*) show some sign of dieback in Cell C. In 1989 some patches of the sedges were dead, and in 1990 other patches of the sedges were less dense within Cell C compared to the previous year, although there are still healthy stands of sedges in certain locations. The rush species, *Juncus arcticus*, increased in cover area in Cell C in 1989 compared to 1988.

Physical Effects

Wetland vegetation has an effect upon the flow dynamics of the cells by altering the permeability of the substrate, at least as deep as the roots penetrate. When the substrate was removed from Cell B in August 1989, zones of unequal flow and removal reaction were observed in the substrate below the root zone. Such zones may cause a problem in a wetland designed for aerobic treatment. For a sulfate reducing system, flow through the substrate underneath the roots is the important criterion.

Another beneficial consideration of a plant cover might be the reduction of erosion by wind at times when the water level drops below the level of the substrate.

Aesthetic Considerations

An important contribution of emergent vegetation in a constructed wetland system is its aesthetic value. In a scaled-up treatment system, a vegetation-covered design would be more visually appealing than a barren site. This could be especially desirable in the case of a treatment system for the Big Five and Argo tunnels, as the system would likely be in a location of high visibility, e.g. close to the I-70 highway. The presence of a plant community in at least part of the system would contribute to more favorable public opinion of such a treatment option.

Effects on Fauna

One question that should be considered is whether the uptake of metals by plants could affect animals. There are two possible problems if animals forage on the plants:

- o Ingestion could cause mortality;
- o Ingestion by lower forms of animal life could be magnified up the food chain.

An analysis by John Emerick (personal communication) suggests that these problems will not happen. The animals that forage in wetlands typically have a wide food range. Even if the metal abundances in the plants were dangerous, these plants would be only a small part of the animals diet. Magnification or disease would be circumvented by the diverse diet of the animals that would use the wetland.

CONCLUSIONS

Emergent vegetation can be an important component of a metals-removal system for treatment of acid mine drainage, particularly with respect to addition of biomass for bacterial nutrition, oxygenation of the substrate, and aesthetic considerations. Brodie (69) considers plants to be essential component of an aerobic constructed wetland. For a sulfate-reducing treatment system, where the primary removal processes are occurring in the substrate, aesthetic considerations may be the most important consideration.

The result of the calculation of biomass contribution on an annual basis for Cell C was modest (~60 kg dry weight/year, for an area of 200 sq. ft.). Calculations in SECTION 12 lead to a similar conclusion. For an unvegetated system, a simple procedure such as adding hay to the treatment cells might provide an effective substitution. However, for a large scaled-up design, such an addition could be a large and moderately expensive task; the natural addition of biomass by the vegetation helps keep the concept of a low-cost, minimal-maintenance wetland.

The zone of oxygenation from plant roots is only a fraction of the depth of the cells, probably less than 25 cm below the surface. Oxygenation of the substrate by plants may not be wanted for all parts of the system. For cells that are designed to be anaerobic for metals removal by sulfate reduction processes, a plant cover might be counter-productive. For the specific circumstances at the Big Five site, it may be that only the final cells would be designed to be aerobic, for final 'polishing' removal of iron and manganese as hydroxides. (There are indications that plants may have a more important role in constructed wetlands for treating waters that are not as acidic, e.g. in eastern U.S. coal country, where aerobic conditions are more important for metal-removing goals.) Still, even if the vegetation was used for the final 'polishing' cells in future, larger designs, these cells might comprise half of the surface area of the design.

After three years of operation, indications are that the vegetation can withstand the conditions of this system; and that it can have a minor role in the treatment process. Through time, the vegetation is likely to become increasingly *Typha*-dominated.

SECTION 7

AREA REQUIREMENTS AND LOADING FACTORS

DISCUSSION OF UNITS

This research is necessarily interdisciplinary. Unfortunately, scientists from different disciplines use different units to describe the same properties. This typically causes confusion and in the case of wetlands research the confusion is compounded. English units are mixed with metric units. Environmental scientists designing wetlands use the reciprocal of the properties that sanitary engineers use in their design equations (39, 42, 55). This section is not an attempt to settle on the proper units. Technical people work with the units that are comfortable to them and only grudgingly change. What follows is only an attempt to put the units for various parameters in one place for easy reference.

The important parameters are volume, concentration, flow, and a loading factor. Units and conversion factors will be discussed for each parameter.

Volume

For chemical analysis purposes, the standard volume is a liter (L). However, for wastewater treatment situations handling large volumes, cubic meters (m^3) is preferred. For many mine drainages, volume estimates in gallons (gal) seem to be the easiest and consequently this unit sneaks into the literature (see Figures 9 and 10).

$$1 \text{ L} = 0.001000 \text{ m}^3 = 0.2642 \text{ U. S. gallons}$$

$$1 \text{ m}^3 = 1000. \text{ L} = 264.2 \text{ U. S. gallons}$$

$$1 \text{ U. S. gallon} = 3.785 \text{ L} = 0.0003785 \text{ m}^3$$

Concentration

For this property, the units are fairly standard. Concentration in milligram/liter (mg/L) is the accepted unit. For large volumes gram/ cubic meter (g/m^3) is sometimes used. For water solutions, parts-per-million (ppm) is sometimes substituted for mg/L.

$$1 \text{ mg/L} = 1 \text{ g/m}^3 = 1 \text{ ppm aqueous solution}$$

Flow

Here units become less standardized because different disciplines use units comfortable to them. Liters per second (l/s) is the primary units, but gallons per minute (gal/min), cubic meters per second (m^3/s), cubic feet per second (ft^3/sec), and millions of gallons per day (mgd) are all used to some extent.

$$1 \text{ L/s} = 0.001000 \text{ m}^3/s = 15.85 \text{ gal/min} = 0.03531 \text{ ft}^3/s$$

$$1 \text{ m}^3/s = 1000 \text{ L/s} = 15850 \text{ gal/min} = 35.31 \text{ ft}^3/s = 22.82 \text{ mgd}$$

$$1 \text{ mgd} = 0.04381 \text{ m}^3/s = 1.547 \text{ ft}^3/s = 43.81 \text{ L/s} = 694.4 \text{ gal/min}$$

Loading Factor

The loading factor or flux, describes the amount of water or contaminant that enters an area of the wetland per unit time. Since it is a combination of all the above units, the confusion is compounded. In addition, environmental scientists usually consider loading factors in area per flow; while sanitary engineers consider the reciprocal, that is in flow per area. Since flow is volume per time, flow per area can also be expressed length per time. Sometimes the amount of contaminant is used instead of flow. In this case a mass loading factor would be in area times time over mass or the reciprocal would be mass over area times time.

For the environmental scientists, typical hydraulic loading factors would have the units of square meters X second/ liter ($\text{m}^2/\text{L/s}$), square feet X minute/ gallon ($\text{ft}^2/\text{gal/min}$), hectares X days over 1000 cubic meters ($\text{ha}/1000 \text{ m}^3/\text{day}$), and acres X days over millions of gallons (acre/mgd). For the sanitary engineer, typical hydraulic loading factors would have the units of cm per day (cm/day),. Typical mass loading factors have the units of square meters X minute/ milligram ($\text{m}^2/\text{mg/min}$), grams X days over square meters ($\text{g}/\text{m}^2/\text{day}$) and kilograms X days over hectares ($\text{kg}/\text{ha}/\text{day}$).

$$1 \text{ gm}/\text{m}^2/\text{day} = 10 \text{ kg}/\text{ha}/\text{day} = 1/1.440 \times 10^6 \text{ m}^2/\text{mg/min}$$

$$1 \text{ m}^2/\text{L/s} = 0.001157 \text{ ha}/1000 \text{ m}^3/\text{day} = 0.6788 \text{ ft}^2/\text{gal/min} =$$

$$= 0.01082 \text{ acre}/\text{mgd} = 1/8640 \text{ cm}/\text{day}$$

A curious arithmetic quirk sets up the following conversion measure: $200 \text{ ft}^2/\text{gal/min} = 294 \text{ m}^2/\text{L/s}$, which is the reciprocal of $29.4 \text{ cm}/\text{day}$. The initial loading rate for the Big Five constructed wetlands was $200 \text{ ft}^2/\text{gal/min}$.

A way to consider the reciprocal loading factors is as follows: If one gallon per minute flowed into a 200 ft^2 container, the water in the container would rise 29.4 cm in one day. If the container were larger in area, then the water would not rise as high in one day. Table 24 gives conversions for typical loading factors discussed in SECTION 7.

Table 24. conversions of loading factors used in this section.

ENVIRONMENTAL SCIENTISTS (Area / Flow)			SANITARY ENGINEERS (Length per Time)
$\text{ft}^2 / \text{gal} / \text{min}$	acres / mgd	$\text{m}^2 / \text{L} / \text{sec}$	cm / day
200	3.2	294	29.4
680	10.8	1,000	8.6
800	12.8	1178	7.3
2920	46.5	4300	2.0
8560	136	12,600	0.68
10,000	160	14,700	0.59

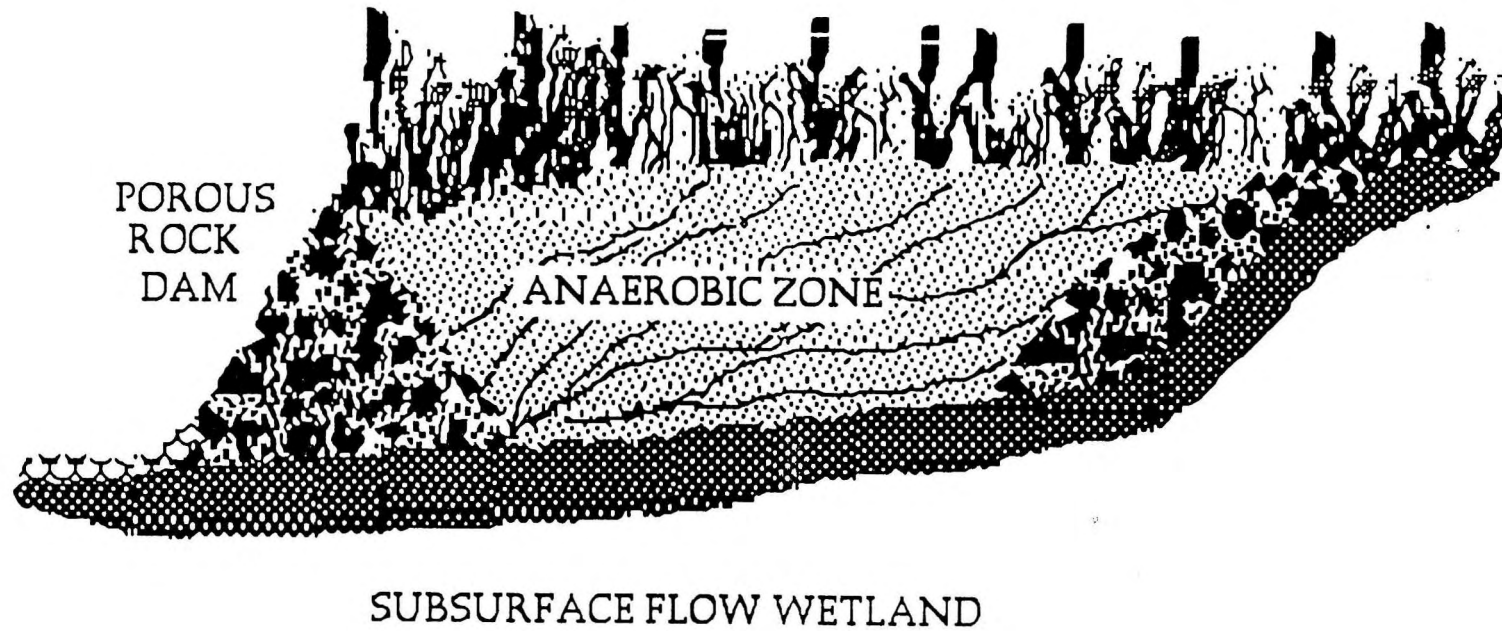


Figure 43. A diagram of a typical subsurface flow wetland.

SURFACE FLOW SYSTEMS AND SUBSURFACE FLOW SYSTEMS

An important division has been established in wetlands used for municipal wastewater treatment and this distinction will be important to the design of wetlands used for mine drainages (42, 52). This is between surface flow systems and subsurface flow systems. A good explanation of wetlands technology for wastewater treatment is contained in Reed, Middlebrooks, and Crites (52) and their categorization of wetlands will be used here. The surface flow system is also called the free water surface system by Reed et al (52). Since free water is shown on the surface, Figure 2 is a diagram of a surface flow system. The depth of water is from 5 to 30 cm. Soil or another suitable medium is used to support the vegetation that emerges through the water and provide nutrients other than carbon. Significant treatment of wastewater is by microorganisms in the soil and water column (52). To insure plug flow conditions, as discussed in SECTION 4, the basins or channels are long and narrow. Typically the length to width ratio is above 10 to 1. Almost all mine drainage wetland systems built before 1986 are designed for surface flow (39, 40, 41). The aerobic wetlands designed by Brodie are surface flow systems (69). Cells A and C in the present Big Five wetland (Figures 5 and 11) are surface flow systems.

A subsurface flow system, also called a vegetated submerged bed, has had greater development in Europe (39, 52). There they have been described as root-zone method, hydrobotanical systems, soil filter trench, biological-macrophytic, and marsh beds by wastewater scientists. The substrate includes rock or crushed stone, gravel, and different soils used alone or in combination. The water flows laterally through the substrate. Figure 43 is a diagram of a subsurface flow system. In municipal systems, plants may be desirable because oxygen is conveyed down the plant, into the roots and rhizomes, and out into the soil. The subsurface is saturated and consequently anaerobic, but the oxygen supplied by the plants creates aerobic microenvironments next to the roots and rhizomes (60). In a subsurface system, plug flow is maintained as long as the water flows through the substrate and not across the surface, thus the length to width is quite smaller, usually around 2 to 1. Cells B-Upflow, B-Downflow, and E in the present Big Five wetland configuration (Figures 11 and 13) are subsurface flow systems.

REVIEW OF LOADING FACTORS FOR MUNICIPAL WETLANDS

References 42 and 52 give provide good reviews of constructed wetlands treating municipal wastewaters. Table 25 is a summary of the current estimates of loading rates for treatment of municipal wastewaters taken from the review by Watson and others (42). A number of considerations have gone into producing the numbers. First, it is assumed that surface flow systems are less efficient than subsurface systems. Consequently loading factors are higher for subsurface systems. Also treatment objectives vary considerably for municipal systems. Table 25 is twice divided by treatment. A first division is by basic (handling of raw waste with no settling or clarifying), secondary (handling the effluent from

Table 25. Hydraulic Loading Rates for the Preliminary Design of Constructed Wetlands for Treating Municipal Wastewaters taken from Watson et al. (42).

Treatment Objectives

Use	Secondary Treatment				Advanced Treatment/Multiple Objectives			
	Surface Flow		Subsurface Flow		Surface Flow		Subsurface Flow	
	cm/day	acres/mgd	cm/day	acres/mgd	cm/day	acres/mgd	cm/day	acres/mgd
Basic treatment	a	a	2.3-6.2	40-15	a	a	≥3.1	≥30
Secondary treatment	1.2-4.7	75-20	4.7-18.7	20-5	≥1.9	≥50	≥4.7	≥20
Polishing treatment	1.9-9.4	50-10	4.7-18.7	20-5	≥3.1	≥30	≥4.7	≥20

a This use has not yet been demonstrated. Surface flow systems constructed to date are preceded by at least primary treatment units (septic tanks, clarifiers, lagoons, etc.).

primary operations), or polishing stages (handling the effluent after it has gone through primary and secondary processes). A second division by treatment objectives determines whether the wetland was built to handle one stage of the treatment process or multiple stages.

Designers of municipal systems (42) stress that "current information is adequate to design systems that substantially reduce targeted contaminants but inadequate to optimize the design and operation for consistent compliance." Two suggestions are made to cope with the uncertainty. The first is to use multiple cells in series, parallel, or combination to optimize treatment processes. The first suggestion was also made for mine drainage situations by Howard and others (6). This parallel and series design configuration can be called a modular design. Figure 44 is a diagram of the modular concept. An important aspect of this type of design is that the route from a pilot system to complete treatment can be made in stages. A complete, monolithic wetland never has to be constructed. Also, maintenance on the modules would be much easier than on one large system. The second suggestion on municipal wetlands is to take two approaches to the loading factor question. Design very conservatively with low loading rates to avoid future problems. The alternative approach is to use higher loading rates and don't expect great performance. In the latter case, plan for expansion so that upgrades can be made based on experience and actual performance data.

In summary, study of municipal loading factors indicates that the initial Big Five Wetland loading rate of 200 ft²/gal/min (29.4 cm/day) is highly optimistic for a wetland treating mine drainage comparable in chemistry to the waters in Table 1. Even a subsurface system requires lower loading factors than 29

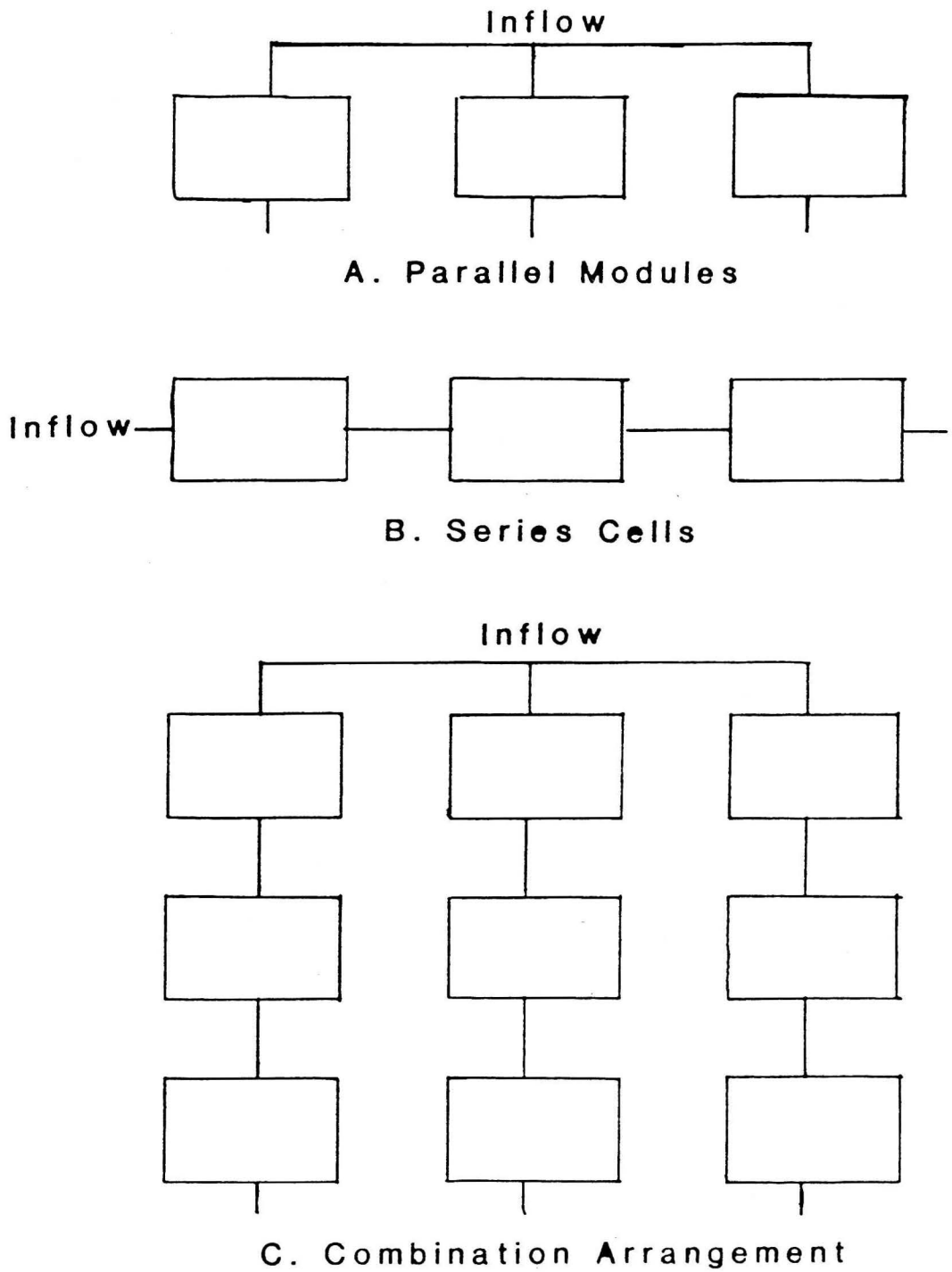


Figure 44. Different possibilities for modular wetland configurations.

cm/day. Results from municipal systems also suggest that for surface flow systems receiving mine drainage, a loading factor of 1000 m²/L/s (8.6 cm/day) may be a bit optimistic. Although treatment objectives are quite different, applying municipal design guidelines on a mine drainage treatment system would suggest a loading factor in the neighborhood of 4300 m²/L/s for a surface system. Experience from municipal systems provides some good ideas on how to cope with the uncertainty in determining wetland size.

REVIEW OF LOADING FACTORS FOR MINE DRAINAGE WETLANDS

Early Concepts on Loading Factors

There have been a number of estimates of the loading factor for a wetland receiving acid mine drainage. From the first suggestions made in the early 1980's, until now, the area requirement per unit of flow has increased significantly. The first rule-of-thumb, proposed for wetlands receiving coal mine drainage in Appalachia, was 200 ft²/gal/min (33). In the design of the Big Five pilot wetland, the standard cell size of 18.6 m² (200 ft²) was chosen using this rule of thumb.

Girts and Kleinmann (39) in their review of constructed wetlands for treatment of acid mine drainage found the following size and flow ranges: Sizes ranged from 93 to 6070 m² with a mean of 1550 and a median of 929 m². Flows ranged from 0.06 to 13 L/s with a mean of 1.3 and a median of 0.5 L/s. Loading factors ranged from 61 to 10700 m²/L/s with a mean of 2390 and a median of 928 m²/L/s. Watson et al. (42) noted that most wetland systems rely on surface removal and have minor interaction of the drainage with the substrate.

Recently, the wetland research group at the Tennessee Valley Authority made estimates of loading factors based upon the systems they have installed (55). The estimates are mass loading factors and take into account the pH of the drainage, the amount of Fe, and the amount of Mn. The desired discharge requirements for the constructed wetland were selected as 3 mg/L or less for iron and 2 mg/L or less for manganese. The loading factor for Fe is 2 m²/mg/min if the pH of the drainage is less than 5.5 and 0.75 m²/mg/min if the pH is greater than 5.5. The loading factor for Mn is 7 m²/mg/min if the pH of the drainage is less than 5.5 and 2 m²/mg/min if the pH is greater than 5.5. Note that the loading factors take into account the greater difficulty of Mn removal compared to Fe. The area calculation is made separately for Fe and Mn and the largest area is chosen. Gross estimates on the average mine drainage can be made from Table 1 of about 100 mg/L of Fe, 30 mg/L of Mn, and a pH of approximately 3. Using these, loading factors are 100 x 2 x 60 = 12000 m²/L/sec for Fe and 30 x 7 x 60 = 12600 m²/L/sec for Mn. The selected size would be 12600 m²/L/sec (8560 ft²/gal/min) of drainage. Again, these estimates relate to surface flow systems and not subsurface flow systems.

In summary, it appears that the early rule-of-thumb of 294 m²/L/s (200 ft²/gal/min) was highly optimistic. If surface flow systems are considered, a better estimate of the loading factor would be some

where around 1000 m²/L/s. No estimates have been made on subsurface flow systems. Cell A in the Big Five wetland had significant flow through the substrate and the results shown in SECTION 4 suggest that a loading factor of about 800 m²/L/s would be sufficient for removing heavy metals and raising the pH to between 5 and 6. As developed in SECTION 12, this value depends on the thickness of the anaerobic zone.

Area Adjusted Loadings and Removals

In 1990, Hedin suggested a new method for sizing and performance of constructed wetlands (95); and a number of research groups used his suggestion to evaluate their wetland operations (11, 96, 97). Hedin's suggestion was based on the following analysis:

1. If one looks at wetland efficiency based on percent removal or on outflow/inflow (Figures 14, 15, and 16), this does not take into account the flow of water going into a wetland. Presumably, a wetland with a bad removal efficiency but receiving a high flow could be removing a large absolute amount of contaminants.
2. If one looks at wetland loading only from the viewpoint of what is entering and the areal size, then the loading factor doesn't contain a good measure of what was removed.
3. The best situation is to combine both measures into what would be called a wetland area-adjusted loading and removal factor. The units for this factor are grams of contaminant removed / day / square meter (abbreviated as gdm).
4. The calculation of the area-adjusted loading and removal factor is by the following formulas in which Fe is the contaminant removed:

$$\text{Fe in (g/day)} = 1.44 \times \text{inflow (L/min)} \times \text{Inflow Fe Conc (mg/L)}$$

$$\text{Fe out (g/day)} = 1.44 \times \text{outflow (L/min)} \times \text{Outflow Fe Conc (mg/L)}$$

$$\text{Fe rem (g/day/m}^2\text{)} = \text{Fe gdm} = [\text{Fe in} - \text{Fe out}] / \text{area (m}^2\text{)}$$

In the case where outflow = inflow, such as the Big Five Cells, then:

$$\text{Fe gdm} = \frac{1.44 \times \text{Flow (L/min)} [\text{Inflow Fe conc} - \text{Outflow Fe Conc}]}{\text{area (m}^2\text{)}}$$

Looking at the formulas it can be seen that an area-adjusted loading and removal factor (gdm) does combine the loading factor with the removal efficiency. Design calculations using this method are developed in SECTION 12 in the subsection Area/Flux Method.

Using gdm's as an analytical tool, Hedin suggested that what would happen in a constructed wetland is at low gdm's Fe-rem ought to increase as Fe-in is increased (95). Then, when the removal capacity of the wetland is met, the Fe-rem gdm would reach a plateau and not increase as the Fe-in gdm is increased. The plateau value would be the maximum Fe gdm for that wetland. This analysis worked for

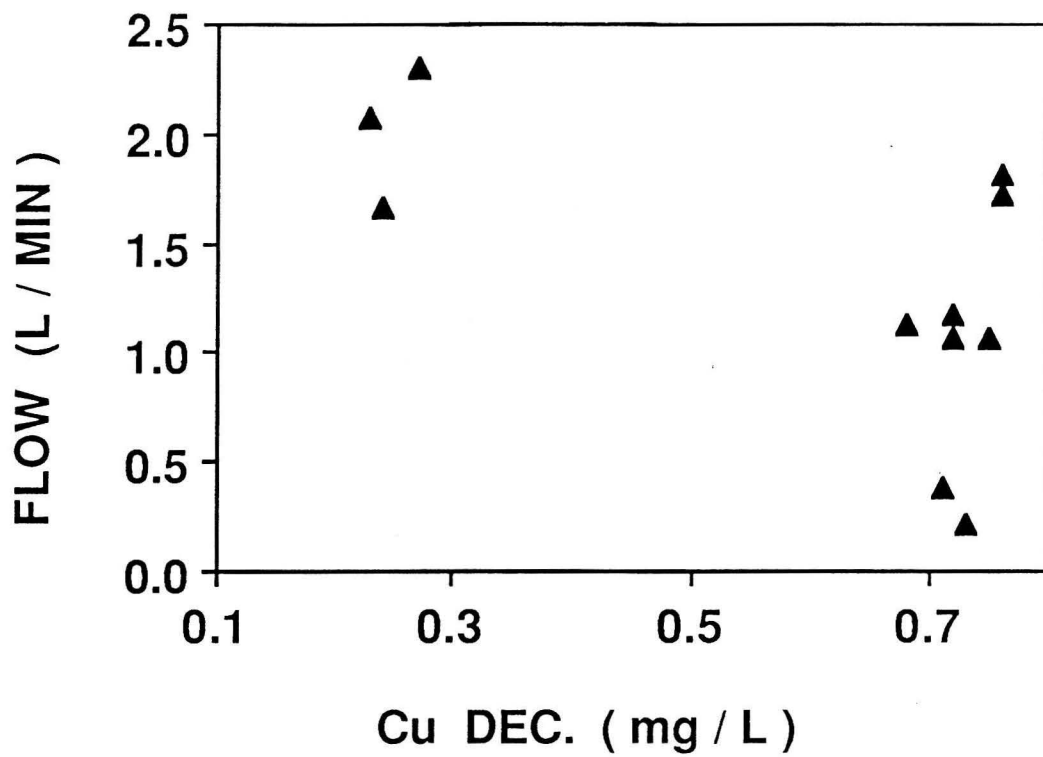


Figure 45. Decrease in copper concentration in Cell A versus Flow for 1989.

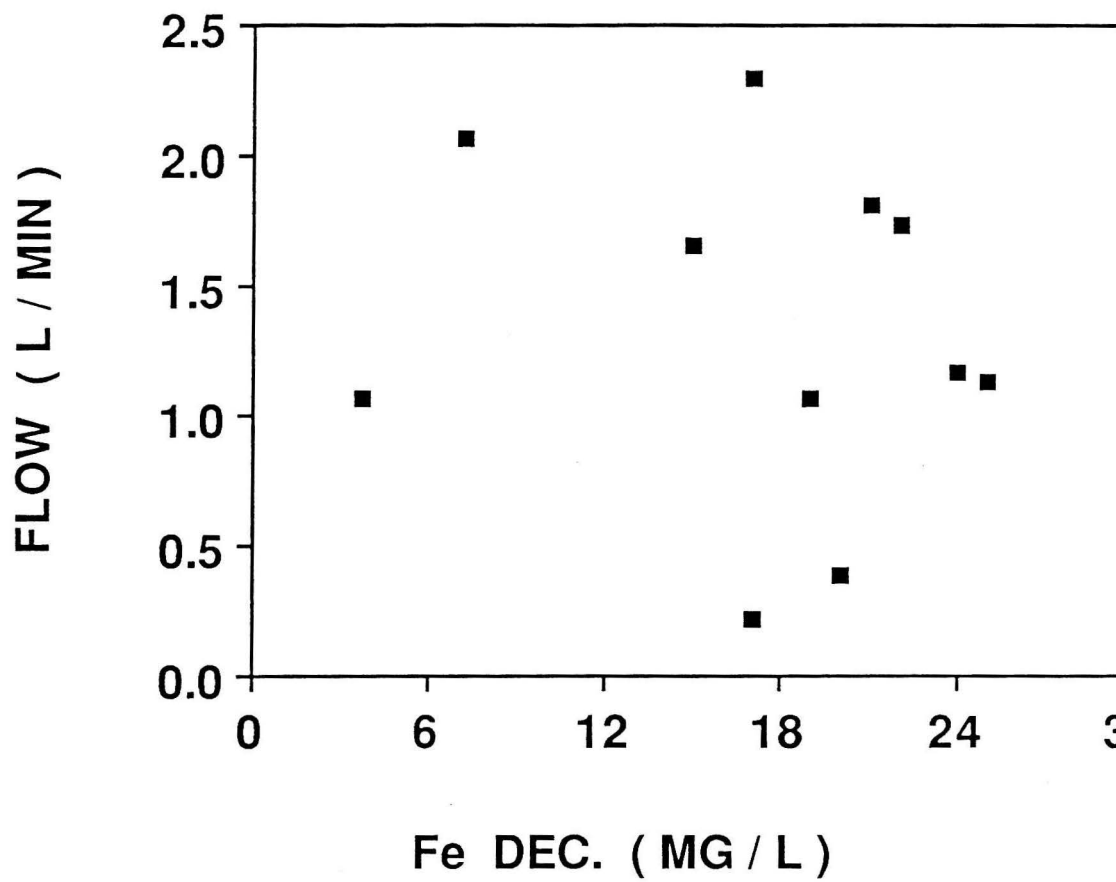


Figure 46. Decrease in iron concentration in Cell A versus Flow for 1989.

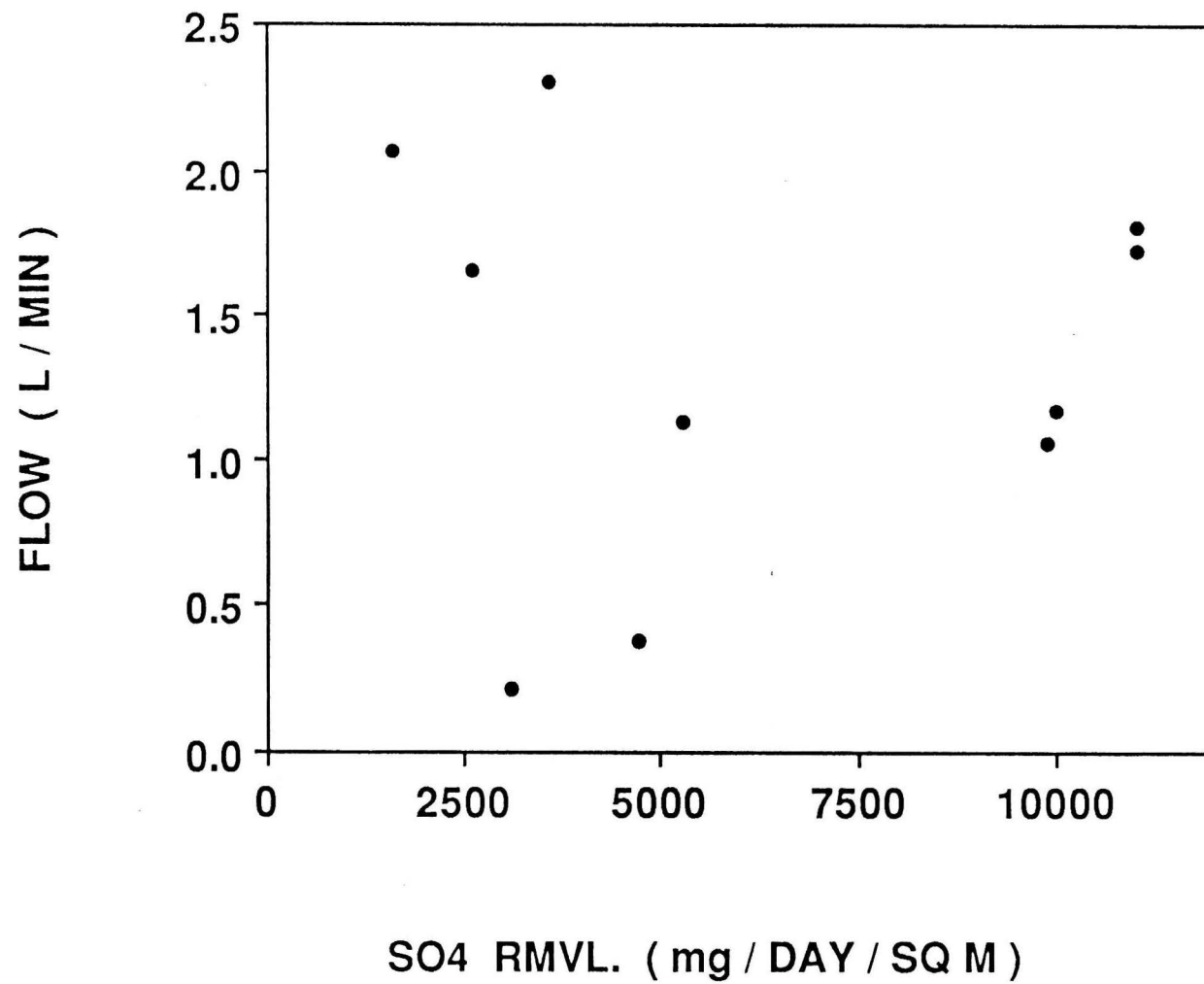


Figure 47.

Area adjusted removal factor (gdm) for sulfate versus flow in Cell A for 1989.

the Somerset Wetland, but produced mixed results for the Latrobe and Friendship Wetland. None of the three wetlands achieved complete removal of iron.

Based on his analysis, Hedin made suggestions on iron loading factors for constructed wetlands. He estimated that if a wetland is receiving mine drainage whose pH is 3 or less, then a wetland can remove 4 gdm of iron. If the pH of the mine drainage is 4 or more, the wetland can remove 10 gdm of iron. The average mine drainage in Table 1 has a pH of 3 and a concentration of Fe of 100 mg/L. Assuming outflow equals inflow and using a removal factor of 4 gdm, the loading factor calculates to be $2160 \text{ m}^2 / \text{L} / \text{sec}$ ($1466 \text{ ft}^2 / \text{gal} / \text{min}$). Over 1989, for Big Five Cell A when it was operating in an assumed plug flow mode, area-adjusted loading and removal factors for iron ranged from -1.5 to 4.4 gdm; the average was 1.8 gdm. For Big Five Cell E a subsurface system, the flow out averages about 0.4 L/min, Fe concentration averages 40 mg/L and is completely removed, and the wetland size is about 10 m^2 . The Fe gdm for Cell E calculates to be 2.3 gdm.

Brodie (69) has recently analyzed the area-adjusted loading and removal rates for TVA wetlands. He found the range for Fe gdm to be from 0.5 to 10; the average was 1.25 gdm. He suggested 10 gdm to be the practical limit for Fe removal by wetlands. For Mn, the area adjusted loading and removal factors were quite a bit lower, and he suggested 2 gdm to be the practical upper limit.

In the case of the Big Five Wetland, it was difficult to analyze the performance of the cells based on area-adjusted loading and removal factors (11). As shown in Figures 35 and 36, sulfate and Eh decreases are directly related to the flow. However, for the heavy metals this correlation doesn't always work. Figures 45 and 46 show how decreases in the effluent concentration of copper and iron change with flow in Cell A. For copper removal is complete at low flows and sporadic at high flows. For iron, there is no obvious correlation. Since sulfate showed such a good removal trend with flow, a sulfate gdm was calculated for Cell A over 1989. The result is show in Figure 47. Sulfate removal in gdm has no correlation with flow, even though decrease in sulfate concentration did correlate. For Big Five Cell A, lack of correlation of removal with flow was disturbing. Failure of the cell to provide consistent removal was even more disturbing. Yet, excellent removal results were being provided by Cell E (Figure 16). Also when the flows on Cell B-Upflow and B-Downflow were cut so the loading remained constant at around $800 \text{ ft}^2 / \text{gal} / \text{min}$, removal of Fe, Cu, and Zn was nearly 100 % (Figures 14 and 15). This led us to determine loading factors for wetlands emphasizing sulfate reduction by a completely different method described below, that considers reaction rates and the volume rather than the area of the wetland.

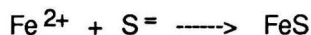
LOADING FACTORS FOR SULFATE REDUCING WETLAND CELL

The Limiting Reagent Concept

In our experiences, at the Big Five site, typical measures of loading factor do not seem to explain the removal of metals even though heavy metals such as Cu and Zn are reduced by greater than 99 %

(12). We have discovered that a key factor in sulfate reduction is to insure that the optimum microenvironment for sulfate-reducers is maintained. The most important environmental factors are reducing conditions and a pH of around 7. Since the wetland cell is receiving mine drainage with pH below 3 and Eh of above 700 mV, the water can easily overwhelm the microenvironment established by the anaerobic bacteria. This leads to the limiting reagent concept for determining how much water can be treated, as an alternative to the use of typical loading factors.

Consider the following precipitation reaction:



At high flows of mine drainage through the substrate, sulfide will be the limiting reagent, the microbial environment will be under stress to produce more sulfide, the pH of the microenvironment will drop, and removal will be inconsistent. At low flows of mine drainage through the substrate, iron will be the limiting reagent, the excess sulfide will insure a reducing environment and a pH near 7, the microbial population will remain healthy, and removal of the metal contaminants will be consistent and complete. Using this concept, loading factors should be set to insure that the heavy metal contaminants are always the limiting reagents. The question then is how much sulfide can a colony of sulfate-reducing bacteria produce per cubic cm of substrate per day?

Studies by the U. S. Bureau of Mines wetlands group suggest that a reasonable figure for sulfide generation is 300 nanomole sulfide / cubic cm / day (0.3 mole sulfide/m³/day) (65, 67). This number, the volume of the wetland cell, and the metals concentrations in the mine drainage are used to set the flow of mine drainage through the wetland cell. Using this concept in a subsurface wetland cell to determine the loading factor has resulted in year round complete removal of Cu and Zn, a nearly complete removal of Fe, and a rise in pH from 3 to 6 that is seen in Cells B-Upflow, B-Downflow, and E. Design of wetlands using this method is discussed in SECTION 12 in the subsection Sulfate-Reducing Stoichiometry Method.

Volume Loading Factors

This volume loading factor will be used extensively in SECTION 12 in the subsection on Volumetric Loading Method. For now, consider how it was used to set the desired flow into the redesigned B Cells. The depth of the B Cells is about 1 meter, this makes the volume of substrate to be about 8 m³. Using the volume loading factor, 2.4 moles of sulfide will be produced in the cell per day. Using the limiting reagent concept, heavy metals flowing into the cell should not exceed 2.4 moles per day. Big Five mine drainage has 40 mg/L Fe, 30 mg/L Mn, 10 mg/L Zn, and 1 mg/L of Cu for a total 81 mg/L of heavy metals. Using the atomic weight of manganese (55 g/mole) as the average atomic weight of the metals, the total concentration of heavy metals in the drainage is about 1.5 millimoles/L. Consequently, flow into the cell should be limited to 1600 L/day or about 1.1 L/min. This works out to a traditional loading factor of about 430 m²/L/s or 290 ft²/gal/min. As a safety factor, over 1990, the flows at the Big Five Cells have been set so the loading factor is 800 ft²/gal/min. Note that with an area of Cell B of

9.3 m², if all the heavy metals were removed and the flow rate was 1.1 L/min, the gdm of heavy metals would be 14, since half the heavy metal concentration is iron, the Fe gdm would be 7.

One important feature of this volume loading factor is that a poorly acting cell will recover if the volume loading factor is cut back to below the value of 300 nanomole/cubic cm/day. Over the course of the last year both the B Cells developed problems. Correcting the problem and adjusting the flow to within the proper range allowed the cells to recover. By the end of the testing period, both cells were removing heavy metals quite well.

Recent Example of the Use of the Volume Loading Factor

In a bench scale study just recently completed, garbage cans filled with substrate to a depth of about 60 cm were used to determine whether using the sulfide generation figure of 300 nanomole sulfide / cubic cm of substrate / day could be used to set the conditions for treating severely contaminated effluent that flows from the Quartz Hill Tunnel in Central City, CO. Contaminant concentrations for this drainage are shown in Table 26. Using the limiting reagent concept described above and the amount of substrate contained in the garbage can, flow could not exceed one milliliter / minute to insure that sulfide would always be in excess. Contaminant concentrations from the outputs of three different bench scale cells are shown in Table 26. For cell A the mine drainage was passed through the cell with no delay. For cell B the substrate was soaked with city water for one week before mine drainage started passing through the cell. For cell C, the substrate was inoculated with an active culture of sulfate-reducing bacteria and soaked with city water for one week before mine drainage started passing through the cell. Preparations on cells B and C were done to insure that there would be a healthy population of sulfate-reducing bacteria

Table 26. Constituent concentrations in mg/L in the Quartz Hill Tunnel mine drainage and in effluents from the bench scale tests.

Sample	Days Operated	Mn	Fe	Cu	Zn	SO ₄	pH
		<-----	Concentration in mg/L			----->	
Mine Drainage	24	80.	630	48	133	4240	2.4
Cell A	24	0.94	1.6	0.06	0.27	450	7.4
Cell B	24	0.91	1.9	<0.05	0.17	770	7.5
Cell C	24	0.99	1.0	<0.05	0.16	412	7.4
Mine Drainage	43	80.	640	50	135	4300	2.5
Cell A	43	0.97	0.87	<0.05	0.18	1080	7.2
Cell B	43	0.64	0.96	<0.05	0.24	660	7.4
Cell C	43	1.6	0.46	<0.05	0.14	1180	7.2
Mine Drainage	71	70.	820	70.	101	NA	2.6
Cell B	71	0.48	0.40	<0.05	0.21	NA	8.0
Cell C	71	1.6	0.40	<0.05	0.25	NA	7.9

before mine drainage flowed through the substrate. All cells were run in a downflow mode of the mine

drainage through the substrate. In all three cells removal of Cu, Zn, Fe, as well as Mn is greater than 99 %. The increase in pH is from about 2.5 to above 7. These results were consistently maintained for over ten weeks of operation (123, 124). In addition, the concentration of sulfate has significantly decreased at the 24 and 43 day sampling period. Eh measurements also indicate that sulfate reduction is occurring (124).

The substrate used was a mix of 3 / 4 cow manure and 1 / 4 planting soil. The results from cells B and C show that the cow manure has an indigenous population of sulfate-reducing bacteria that are quite active. Inoculation with an active culture of bacteria is not necessary in this case. Also, since the results from cell A are comparable to those of cells B and C, the population of sulfate reducers can withstand immediate exposure to severe mine drainage and still produce sufficient quantities of sulfide. The key to good initial activity is to insure that the flow of mine drainage is low enough that its low pH does not disturb the micro-environment established by the bacteria.

Another feature of the results shown in Table 26 is that Mn is removed in all three cells. Typically, Mn is the most difficult contaminant in mine drainage to remove (3, 4, 5, 6, 7, 8). It is usually presumed that removal of Mn has to be achieved by raising the pH to above 7, and then introducing the effluent into an aerobic wetland cell so that Mn will be oxidized to MnO_2 (28, 69). Removal in an anaerobic cell must be as Mn(II) (28). Analysis of possible species at a pH above 7, suggest that removal could be as MnS or MnCO_3 (21, 28). In this case, it is hypothesized that MnCO_3 is the precipitate because it is more insoluble than the sulfide (21). In either case, a key to Mn removal in an anaerobic cell appears to be the ability to raise the pH of the effluent above 7. If raising the pH to above 7 can be consistently achieved, then all the contaminants in mine drainage can be removed in one anaerobic cell. In a project supported by the U. S. Bureau of Mines, these hypotheses on how manganese can be removed from mine drainage are currently being tested (123, 125).

For the garbage cans, the volume is 0.114 m^3 , and the surface area is 0.204 m^2 (2.2 ft^2). For the Quartz Hill drainage, the sum of heavy metal concentration is about 1060 mg/L or 19.3 millimole/L. With a flow of 1.0 mL/min, the area adjusted removal rate is 7.6 gdm. For Fe, it is 5.9; for Mn, it is 0.50 gdm. In one day, the generation of sulfide would be 0.034 moles, and the loading of heavy metals would be 0.027 moles. The areal loading factor is $14,700 \text{ m}^2/\text{L}/\text{sec}$ ($10,000 \text{ ft}^2/\text{gal}/\text{min}$) for a wetland thickness of about 60 cm. Comparing the figures, it appears that an area-adjusted removal factor of between 5 and 10 gdm for Fe is the maximum for mine drainages with a pH below 3. This loading is based on the amount of sulfide generated in the wetland substrate. As shown in Table 1, iron is the most abundant contaminant in mine drainage. This typically determines wetland size even if the objective is to remove other heavy metals.

An interesting hypothesis derived from this work is that downflow and upflow cells combined with anaerobic processes may allow wetlands to be built with greater effective thicknesses. Experiments are currently being planned (Filipek, pers. communication, 1991) to both increase the thickness and

permeability and decrease the concentration of organic matter in the substrate. It is hoped that this combination will allow increased formation of pyrite relative to acid-volatile sulfides throughout virtually the entire substrate column.

SUMMARY

In the past few years, suggested loading factors for constructed wetlands treating acid mine drainage have become much more conservative than the 200 square feet/gallon/minute used in the early 1980's. For a highly effective wetland Hedin's area-adjusted removal rate estimates of 4 gdm for mine drainages of pH less than 3 and 10 gdm for mine drainages with pH greater than 4 appear to be appropriate. However prudence would suggest building a safety factor of 2 into the design.

For downflow and upflow wetland cells using microbial sulfate reduction as the primary removal process, a volume loading factor appears to work well. Using the value of 300 nanomole/ cubic cm / day as the amount of sulfide generated and the concentration of heavy metals in the drainage, the flow should be adjusted so that sulfide is always in excess. This volume loading factor has worked well on bench scale and pilot scale tests.

PART B

DESIGN CONSIDERATIONS

SECTION 8

REGULATORY ISSUES

The regulatory issues associated with the construction of passive treatment systems for acid/metal drainages can be categorized into 1) pre-construction, and 2) operation and decommissioning components.

DISCLAIMER

Because this is an emerging technology, regulation of the technology is still being developed. What is contained in this chapter is a discussion of possible issues and not a definitive statement of regulatory intent. Some regulatory precedent has been set. The use of passive constructed wetlands has been included in the Record of Decision at two CERCLA sites. In these two cases, success has come from including the appropriate regulatory agencies in all the decision processes. What follows is an attempt to state what regulatory issues may become important during the design, construction, and operation of a passive treatment system.

PRE-CONSTRUCTION ISSUES

Pre-construction issues involve those regulations that are not exclusive to constructed wetlands and typically apply to many types of construction. Pre-construction regulatory issues for passive treatment systems may include:

- o Environmental Review (National Environmental Policy Act, 1969)
- o NPDES Permit (Clean Water Act, 1972)
- o Mining Reclamation Permit (Surface Mining Control and Reclamation Act, 1977)
- o Air Quality/Construction Permit (Clean Air Act, 1967)
- o Archeological Survey (National Historic Preservation Act, 1966)
- o Protected Species or Habitat (Endangered Species Act of 1973)
- o Floodplain and Wetland Considerations (Executive Orders 11988 & 11990, respectively)
- o Water Rights (State Water Laws)

These regulatory issues and similar local laws that may vary from state to state should be considered in siting any passive treatment system. As these and similar issues are not unique to the permitting of a passive treatment facility, they will not be discussed further.

OPERATION AND DECOMMISSIONING ISSUES

After a passive treatment facility is permitted and constructed, the regulatory issues appear to be more complex. Operation and decommissioning regulatory issues encompassing constructed wetlands may include:

- o RCRA - Resource Conservation and Recovery Act
 - Hazardous Waste Characteristics of Substrate
 - Bevill Amendment (Mining Exclusions)

- o NPDES - Discharges are excluded from RCRA but not while being treated, stored, etc. Water treatment sludges are not excluded from RCRA.
 - o Floodplains and Wetlands Considerations
 - o State Water Rights
 - o Endangered Species Act
 - o Reclamation Bond Release (post-mining land use)
- Each of these issues is considered in the following narrative.

RCRA WASTE

A major issue determining the design of the passive systems and the disposal of the saturated wetlands substrate is whether the substrate would be classified as a RCRA hazardous waste. Two of the RCRA classification criteria are expected to apply to this material: TCLP toxicity and reactivity. The loading rate and metal suite at a particular wetland site will determine when (or if) the substrate would be considered TCLP (toxicity characteristic leaching procedures) toxic according to the RCRA definition.

Under RCRA, a waste can be defined as reactive if it meets any of the following eight criteria (CFR 261.23):

- (1) It is normally unstable and readily undergoes violent change without detonating.
- (2) It reacts violently with water.
- (3) It forms potentially explosive mixtures with water.
- (4) When mixed with water, it generates toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.
- (5) It is a cyanide or sulfide bearing waste that, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.
- (6) It is capable of detonation or explosive reaction if it is subjected to a storing initiating source or if heated under confinement.
- (7) It is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.
- (8) It is a forbidden explosive as defined in 49 CFR 173.51, or a Class A explosive as defined in 49 CFR 173.53, or a Class B explosive as defined in 49 CFR 173.88.

Of these criteria, only number five potentially applies to the passive substrate material since hydrogen sulfide gas would be generated at a pH of 2 (EPA SW846-Sect 7.3.4.1). However, at higher pHs the material may be expected to be stable and its disposal may pose little, if any, threat to human

health or the environment.

The "Bevill Amendment" exclusion [40 CFR 261.4 (b)(7)] of "mining wastes" from RCRA hazardous waste classification may or may not apply to the substrate within passive treatment systems. The Bevill Amendment excludes the following materials from RCRA Subtitle C regulation, which pertains to hazardous wastes:

Solid waste from the extraction, beneficiation, and processing of ores and minerals (including coal, phosphate rock and overburden from the mining of uranium ore)...

For the purposes of 261.4 (b)(7), beneficiation of ores and minerals is restricted to the following activities: Crushing; grinding; washing; dissolution;...ion exchange;... precipitation;...

Waste from the treatment of an excluded waste may also be excluded from hazardous waste regulations.

The exclusion provided by the Bevill Amendment is currently in effect. However, regulations on mining wastes are being considered by the EPA that may eliminate the Bevill exclusion. Mining wastes will then be regulated as a special category of solid waste.

The disposition of used passive treatment system substrate materials from a mining operation will be a function of their chemical and physical characteristics. However, it appears that used substrate is not really a "mining waste"; it is more likely to be classified as a "waste water treatment sludge" which is regulated by RCRA Subtitle C.

When coal mining regulations are considered, used substrate may be considered an unsuitable material requiring burial on-site. For example, Colorado coal mining regulations require the covering of coal and "acid and toxic-forming materials" in accordance with the following regulation:

4.14.3 (1) COVER.

- (a) A person who conducts surface coal mining operations shall insure that all debris, acid-forming materials constituting a fire hazard are treated or buried and compacted or otherwise disposed of in a manner approved by the Division and are designed to prevent contamination of ground or surface waters...
- (b) Where necessary to protect against ... formation of acid or toxic seeps, to provide an adequate depth for plant growth, or otherwise meet local conditions, the Division shall specify an appropriate amount of cover using non-toxic material or special compaction and isolation from ground water contact.

From a geochemical standpoint, an argument can be made that the precipitated metals in a constructed wetland could be viewed as a mineral resource and theoretically, metals could be recovered from the used substrate using conventional metallurgical techniques. The residue after this "processing" could be currently viewed as a "Bevill Waste", or a waste that would be regulated under Subtitle D and assumed to be suitable for landfill disposal. The term "mineral resource" introduced above should not be

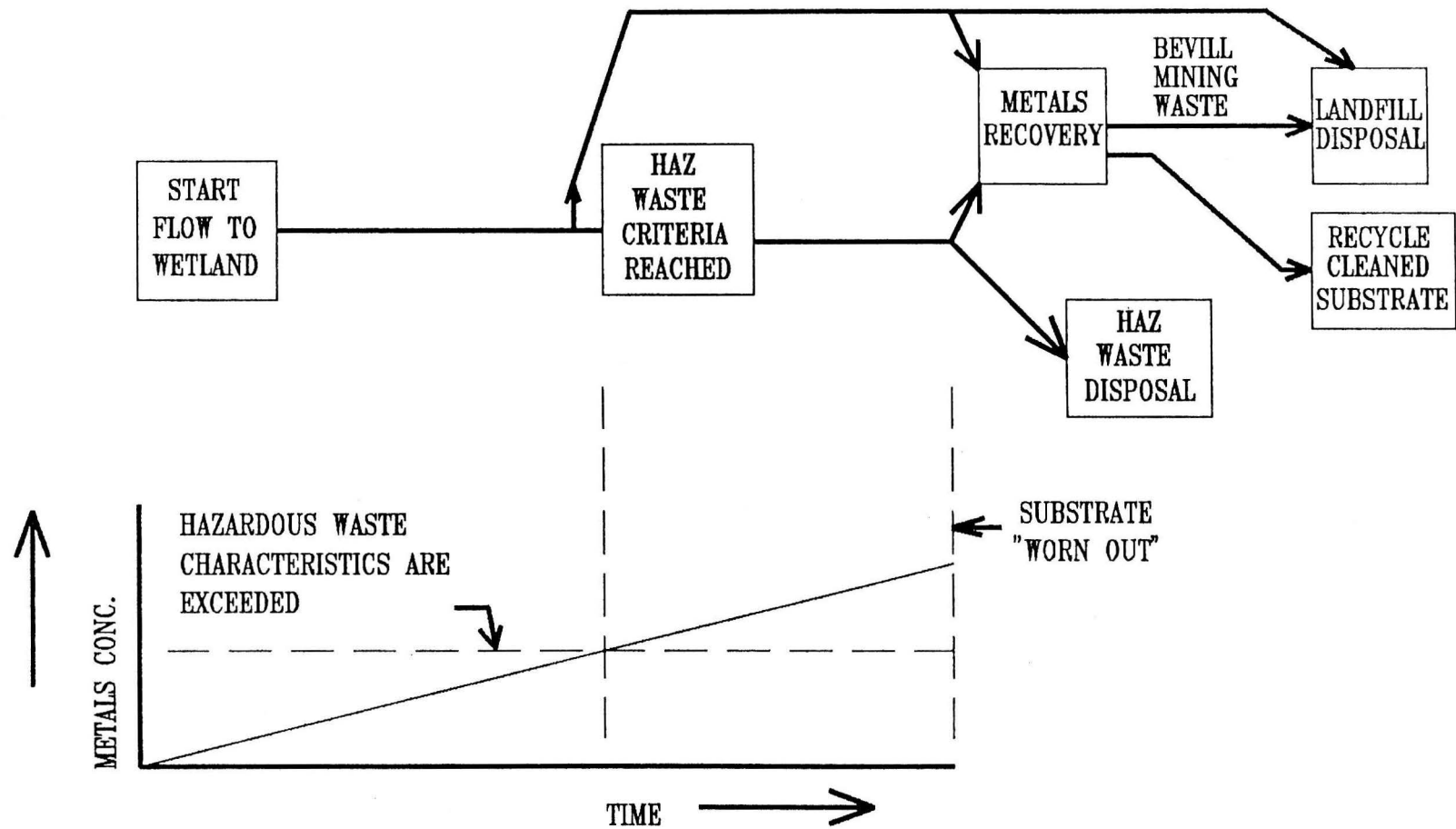


Figure 48 Changes in used substrate disposal alternatives with time and concentrations of metals.

interpreted to mean "ore". The accepted definition of "ore" recognized by the mining industry is a mineral resource that can be recovered, processed, and sold at a profit. It is not certain that the recovery of metals from wetland substrate can be accomplished at a profit. However, the material handling and processing cost associated with metals recovery may be less than the cost of disposal of the material at a hazardous waste site.

Thus, the long term operational policy of a passive treatment system will influence the disposal options for used substrate from the facility and the design of the facility itself. From the first operation of the facility, the substrate is by definition a Subtitle C waste, which is unlikely to be hazardous at first. If the substrate is allowed to become a Subtitle C hazardous material through metals accumulation, the passive treatment facility would have to meet RCRA design criteria as discussed below. Thus, as the substrate ages and is loaded with metals, metals recovery may be a logical option to avoid the high costs of disposal of used substrate as a hazardous waste.

This regulatory situation results in several alternatives for the disposal or regeneration of used substrate material as illustrated on Figure 48. The most likely operational/ disposal scenario is the exhumation or in situ processing of the substrate prior to its becoming classified as hazardous and the processing of the material to yield a "mining waste" residue and possibly a saleable by-product (metals). This is supported by the discussion of the complicated and expensive design criteria for a RCRA Subtitle C facility in subsequent paragraphs. In any event, if landfill disposal of residue or Bevill Waste is performed, steps should be taken to isolate these materials from other wastes in case regulations governing their disposal are changed at some future date.

If the substrate will be allowed to become a RCRA hazardous waste, the passive treatment system would be designed to comply with the RCRA criteria for surface impoundments. The passive treatment systems would be designed to prevent the migration of "leachate" within the wetland to the surrounding soils. The containment system might consist of a 40 mil high density polyethylene (HDPE) liner covered by 6 inches of coarse sand in turn covered by a second HDPE liner and 6 inches of coarse sand. The wetland substrate would be placed on top of a geotextile overlaying these four layers. To collect any water which escapes the first HDPE layer, the system would be sloped to the effluent end of the cells to convey leachate in the first sand layer for collection in a nearly horizontal, perforated leachate collection pipe.

In accordance with RCRA surface impoundment requirements, the system designs would incorporate berms adequate to protect the systems from the 25-year, 24-hour storm event. In addition, the integrity of the passive systems would be inspected weekly in accordance with RCRA.

The proposed passive treatment systems could result in two types of material that would contain high concentrations of heavy metals and would have to be managed accordingly. These materials would consist of accumulated metal precipitates (primarily iron hydroxides) in the settling basins used as an aerobic pretreatment step and metal laden substrate within the anaerobic wetlands.

The metal precipitates from the settling basins may be classified as a RCRA hazardous waste, and as such, the operational cost of the facility should include disposal of these materials at a RCRA landfill. Also, the anaerobic substrate from the wetlands would contain metals that were removed from the mine discharges. The disposal option for this alternative assumes the substrate is classified as hazardous. This option would entail placing the material in appropriate containers and transporting it to a RCRA hazardous waste landfill.

WATER QUALITY DISCHARGE STANDARDS AND THE CLEAN WATER ACT

Wetlands constructed to improve the quality of the discharge function as waste water treatment facilities. Their discharge which generates a point source load may have to be regulated under Section 402 of the Clean Water Act National Pollution Discharge Elimination System Permit (NPDES).

Technology Based Limitations

The 1972 amendments of the Clean Water Act established a two-step program for the reduction of the discharge of pollutants into the nation's waters. First, categories of industrial dischargers were required to meet a level of pollutant control based on the across-the-board application of "best practicable control technology currently available" (BPT) by July 1, 1977. The second level of effluent limitations, to be achieved by July 1, 1983, was to be based on the "best available technology economically achievable" (BAT).

Technology-based standards are now the foundation of the industrial effluent limitations program, although recently both Congress and EPA again have placed renewed emphasis on water quality.

The BAT standards do not apply to conventional pollutants (BOD, TSS, fecal coliform, pH, and oil and grease). In 1977, Congress decided that full application of the BPT standards provided adequate protection from conventional pollutants and that more stringent control of these pollutants would, in many cases, yield only marginal benefits. Accordingly, in its 1977 "mid-course corrections" to the Act, Congress enacted Section 301(b)(2)(E), which required the application of a more lenient "best conventional pollutant control technology" (BCT), rather than BAT, for conventional pollutants by July 1, 1984.

The Water Quality Act of 1987 extended the compliance deadlines for most technology-based requirements to "as expeditiously as practicable" but not later than three years after the requirement is established, and in no case later than March 31, 1989.

BPT deals primarily with traditional pollutants of concern -- BOD, oil and grease, pH, TSS, some metals, etc. BAT, by contrast, deals primarily with toxics, (e.g., organics and heavy metals). In determining what level of treatment constitutes BAT, EPA has more latitude to depart from the usual technologies employed by the industry than when setting BPT standards. EPA may consider process controls, as well as end-of-pipe treatment, and it may base its standards on transfer technology or pilot plant data, although it must meet the "economically achievable" test in the statute.

The BAT determination does not involve even a limited cost-benefit analysis, although cost is one of the statutory factors EPA is directed to consider. In essence, BAT represents the maximum feasible pollution reduction. BAT treatment requirements are considered "economically achievable" so long as their imposition would not force the closure of a large portion of the plants in a category or subcategory of an industry. Cost is thus relevant, but there is no explicit weighing of the benefits against the costs. As a practical matter, however, EPA will be influenced by a showing that substantial additional costs will produce only minor incremental pollution reductions.

From another viewpoint, it appears that the application of BPT/BAT limitations are not applicable to a newly constructed wetland. Typically, BPT/BAT standards apply to existing water sources. A new facility would have to meet new source performance standards or water quality based stream standard limitations. Consequently, it may best to concentrate on new source standards and not worry about BPT/BAT limitations.

Water Quality-Based Limitations

Under the Clean Water Act, where technology-based limitations are insufficient to ensure that water quality standards for the receiving stream will be met, water quality-based limitations are incorporated into a discharger's NPDES permit. Water quality standards consist of two elements: (1) use classifications, and (2) water quality criteria.

The Clean Water Act requires each state to classify all of the waters within its boundaries according to intended use. In establishing the classifications, states are to consider the value of waters for public drinking supplies, propagation of fish and wildlife, recreational purposes, and industrial, agricultural and other purposes. EPA's regulations require that all classifications that do not provide for protection and propagation of fish and wildlife and water recreation must be reexamined to determine whether new developments warrant an upgrading to attain such protection.

Where a state has identified water quality-limited segments, it must adopt permit limitations that will ensure the standards for the water quality of each segment are met. For heavy metals and other pollutants whose effect on water quality is not complicated by biodegradation or other reactions over time, these limitations are usually set in a straightforward manner calculated to ensure that the concentrations in excess of those allowed by the standard are not exceeded at the point of discharge. Heavy metals precipitated in passive treatment facilities will react over time only if the ambient environment changes, thus a stable wetlands operational environment (constant substrate saturation) helps to assure discharge compliance.

For pollutants such as BOD or ammonia, whose effect on water quality varies in a complex manner over time, the setting of water quality-based limitations is much more complicated, requiring the use of models, or alternatively, reliance on conservative assumptions which may restrict discharges much more than is necessary to comply with the standards.

Setting water quality-based limitations is further complicated where more than one facility discharges into the segment and the burden of effluent reduction must be allocated among dischargers.

States may grant variances from compliance with water quality standards on a case-by-case basis. Such variances are considered by EPA to involve amendments to state water quality standards and, therefore, must follow the same procedures and meet the same basic requirements, including approval by EPA. Even in states where EPA administers NPDES programs, variances are not available directly from EPA.

EPA will approve a variance on a showing of "substantial and widespread economic and social impact." EPA recommends that a state adopt a variance, rather than change a designated use, if the state believes the use can eventually be attained.

Individual Control Strategies for Point Sources Causing "Toxic Hot Spots"

The Water Quality Act of 1987 created a new program intended to further the goal of achieving water quality standards. This new program does not substantially change the pre-existing water quality program, but establishes a tight timetable for achievement of state water quality standards. Within two years after enactment of the Act (by February 4, 1989) each state must prepare and submit for EPA approval a list of those waters within the state which will not meet water quality standards or maintain beneficial uses due to point source discharges of toxic pollutants, despite the implementation of technology-based limitations. For each such segment, referred to as "toxic hot spots," the state is to identify the sources of the discharges causing the impairment and the amount of pollutants from each source.

States must also develop and implement an "individual control strategy" for each point source identified which, in combination with other controls on point and nonpoint sources, will result in achievement of the applicable water quality standard within three years after the strategy is established.

EPA must approve or disapprove state lists and strategies within 120 days after February 4, 1989. If a state fails to submit information or EPA disapproves a strategy, EPA will, within one additional year, implement the requirements for listing and strategies for such state.

The states are to adopt specific numerical criteria for all toxic pollutants which could be expected to interfere with the designated uses of the water segment. Where numerical criteria are not available for a pollutant, the state is to adopt criteria based on biological monitoring or assessment methods.

FLOODPLAINS AND WETLANDS CONSIDERATIONS

Executive Orders 11988 and 11990 require federal agencies to take action to avoid adversely impacting floodplains and wetlands, respectively. Executive Order 11990 requires the minimizing of wetlands destruction and the preservation of wetland values. These orders apply only to existing, natural wetlands and not to constructed wetlands with one exception. Current federal policy on constructed

wetlands appears to hinge on whether the wetlands is constructed for water treatment or for other uses. Water treatment type constructed wetlands are not as controlled or protected as wetlands constructed for other purposes such as flood control or those created coincidentally with earthwork projects that intersect the water table.

However, it is possible that constructed wetlands for water treatment may evolve, in the long term, to exhibit many beneficial features of natural wetlands. At this point, the intent of Executive Orders 11988 and 11990 may be argued in the legal arena on a case by case basis if significant changes (such as the replacement of substrate or the decommissioning of a constructed wetland) to these systems are proposed. For example, new, more efficient technologies or the depletion of finite metal sources may allow the decommissioning of constructed wetlands. It is likely that each site will be handled on an individual basis. It is possible, however, that the operators of a constructed wetland may be required to replace it with a similar facility in the case of closure or may have to take extraordinary precautions in maintaining it (substrate replacement) to preserve its natural benefits.

EPA's Wetlands Protection Policy

Recent revisions (1991) of the definition of wetlands has reopened debate on this sometimes emotional issue. Constructed wetland systems may be included within the current definition despite the fact that these systems function as water treatment systems that are not naturally connected hydraulically to sources of water. Constructed wetland systems may fall under this purview since the term wetlands means "those areas that are inundated by surface or ground water with a frequency sufficient to support and under normal circumstances does or would support a prevalence of vegetative or aquatic life that requires saturated or seasonally saturated soil conditions for growth and reproduction". Wetlands typically include swamps, marshes, bogs, and similar areas such as sloughs, potholes, wet meadows, river overflows, mud flats, and natural ponds.

Whether or not a constructed wetland is included in the new category of wetlands, these systems should not impact existing "natural wetlands", if it is avoidable.

STATE WATER RIGHTS

Since each state has its own body of laws governing ground and surface waters, it is not possible to provide a complete discussion of this subject. A water "right", as legally defined, is not legal title to the water, but the legal right to use it in a manner dictated by law. It may be difficult to determine whether water exiting from an underground adit is a ground water withdrawal or the headwaters of surface water. For the purposes of discussion, the later is assumed as a mine water discharge enters a larger surface body of water. The right to that water may be appropriated to some downstream user. As discussed in SECTIONS 6 and 12, evapotranspiration can contribute a significant amount of water volume loss from a constructed wetland. If evapotranspiration losses from a new constructed wetland facility are significant enough to

affect downstream water rights, the operator of the facility may be required by water law to purchase or replace those rights. In surplus water years, the downstream effects of a constructed wetland may not be felt. However, in a drought year, the wetland may be considered a "junior" user and may have to compensate a more senior, downstream user for significant evapotranspiration losses.

In another instance, a feed water source to a wetland (for example, a discharging adit) may be controlled/throttled or eliminated by means such as underground bulkheads. The consequences of this action on downstream senior water rights would also have to be considered.

ENDANGERED SPECIES ACT

The construction of passive treatment systems may consequently create an ideal wildlife habitat. Eventually, an ecosystem may develop that could include endangered species in the flora or fauna populations. This event could complicate typical maintenance operations, restrict the operation of the facility and perhaps affect facility decommissioning. Occurrences of endangered species at passive treatment sites will undoubtedly be handled on an individual basis. It is likely that relocation to more protective sites may be preferred for endangered fauna. Endangered floral occurrences, which may be more sensitive to relocation, may need to be protected in situ, with protective measures developed specifically at each site in concert with regulatory agency guidance.

RECLAMATION BOND RELEASE (POST-MINING LAND USE)

The goals of constructed wetlands include the immobilization of metals in the substrate and the positive adjustment of pH. As such, passive treatment systems function as water treatment plants. This may be the basis of reported current federal policy which appears to preclude the employment of constructed wetlands as a post mining land use. Although changes to this policy are reportedly being sought, it is likely that long term, historical, performance of passive treatment systems will be required before agency policy change is observed. In summary, it appears that passive treatment systems remaining on a mine site after closure of other aspects of the operation may preclude "total" bond release. A nominal portion of the bond may be retained to provide funds for maintenance and decommission/reclamation of the passive treatment system until its operation is no longer required.

SUPERFUND ACT

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980, commonly known as Superfund, was passed by Congress to address the nation's abandoned and inactive hazardous waste sites. In the event that constructed wetlands are chosen as the preferred alternative for treating wastes from a Superfund site, it is likely that some, if not all, of the regulations listed earlier in this SECTION would apply.

CERCLA as it was passed in 1980, did not contain a specific requirement pertaining to the compliance of on-site CERCLA actions with other laws. CERCLA §105, which authorizes EPA to prepare the National Contingency Plan (NCP) for hazardous substance response, says only that the NCP shall include "methods and criteria for determining the appropriate extent of removal, remedy, and other measures." EPA, however, stated in the NCP (as revised in 1985) and in its policy memorandum on CERCLA compliance with other environmental statutes, which was attached to the preamble to the 1985 NCP, that it would attain or exceed applicable or relevant and appropriate Federal environmental and public health standards in CERCLA response actions unless one of five specifically enumerated situations was present.

CERCLA §121, added by Congress in the Superfund Amendments and Reauthorization Act (SARA) in 1986, in effect codifies EPA's existing approach to compliance with other laws. Section 121 establishes cleanup standards for remedial actions under §§104 and 106 of CERCLA. Remedial actions must attain a general standard of cleanup that assures protection of human health and the environment, must be cost effective, and must use permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable. In addition, for any material remaining on-site, the level or standard of control that must be met for the hazardous substance, pollutant, or contaminant is at least that of any applicable or relevant and appropriate standard, requirement, criteria, or limitation under any Federal environmental law, or any more stringent standard, requirement, criteria, or limitation promulgated pursuant to a State environmental statute.

CERCLA §121(e) provides that no Federal, State, or local permit shall be required "for the portion of any removal or remedial action conducted entirely on site," when the action is selected and carried out in compliance with the cleanup standards requirements in §121. EPA interprets "on-site" to include the "areal extent of contamination and all suitable areas in very close proximity to the contamination necessary for implementation of the response action." As a matter of policy, this definition would be implemented with certain limitations. Generally, best professional judgement should be used to determine that the area is within "very close proximity" to the contamination and is necessary for implementation of the portion of the response action addressing the nearby contamination.

Finally, §121(d)(4) provides that under six specific circumstances legally applicable or relevant and appropriate requirements can be waived. However, the requirement that the remedy be protective of human health and the environment cannot be waived.

SECTION 9

SITE CONSIDERATIONS

SOURCES

The sources of acid drainage from a metal mining-affected environment can be diverse. They are dependent on site geology, hydrogeology, mining methods and mining/milling waste disposal policies. In the case of abandoned sites, acidic site runoff may be derived from non-point sources such as scattered occurrences of waste rock or mill tailings mixed with indigenous soils.

Typically, acid drainage from mining sites manifests itself in the following features:

- o Adit/tunnel portals. For these easily identified point sources, discharge rates may range from seeps of fractions of a gallon per minute to several cubic feet per second; flow rates may be responsive to local precipitation/runoff/snowmelt events; the portals may be caved or in unsafe condition; caved roof occurrences at the portal or deeper into the adit/tunnel are likely to impound water.
- o Waste rock piles. These features may have been formed by the filling of ravines or large valleys; in older facilities, precipitation infiltrating through waste rock piles may follow buried drainage features but may exit as a non-point source into ground water; in recently-constructed facilities, infiltration may follow planned drainage features within the piles and drainage may exit as point sources.
- o Impounded Mill Tailings. Many of the characteristics of waste rock piles, above, apply to tailings storage facilities; differences in material permeability typically render drainage discharge rates from tailings facilities underdrains less sensitive to precipitation events.
- o Inundated Pits. Mined out pits often fill with water from runoff or ground water sources; site hydrogeology and final reclaimed topography may result in a steady discharge through a low point in the highwall of the pit.
- o Shafts. These features comprise an unlikely source of acid metal mine drainage; however, some shafts may have encountered artesian conditions which bring acidic water to near-surface aquifers or drainages.
- o Inclines. Like shafts, these features are an unlikely source of acid mine drainage.
- o Seeps "associated" with any of the above features. Hydrologic connections may be difficult to defend. These may be naturally-occurring seeps that may have been affected by nearby mining activities or seeps that are naturally acidic and/or metal-bearing.

FLOW RATE VARIABILITY

Determining the typical or average flows that the wetland and conveyances will normally experience is an important task to complete prior to beginning wetland design. Historical data, if not already available, should be developed over at least a year to determine seasonal fluctuations in discharge quantity and quality. As discussed in a subsequent section, mass loading rates will influence wetland sizing.

The wetland site flow data should be correlated to historical flow data from other sources/nearby sites to expand the wetland source database. For example, the gathering of quality and flow data for receiving streams and meteorologic data for the site watershed may allow correlation of variations in source flows (from adits, etc.) to larger databases such as those from USGS water gaging stations. Thus, projections of adit/source flow variability beyond those immediately observed for the site may be derived.

On the effluent end of the wetland, flow variability of the receiving stream may affect the loading and sizing of the wetland. Changes in water use, water rights, and allocations should be considered in determining the "base" flow of the stream. This "base" flow may play a role in sizing the wetland to assure compliance with stream standards.

If a large variability in discharge flow rates is observed, it is typically an indication that surface water is intruding directly into the hydrologic system. It may be reasonable to attempt to abate the intrusion by source control measures which may stabilize the discharge rates.

Some sources, particularly long drainage tunnels/adits, are subject to dramatic but short-lived increases in flow that may have catastrophic effects on downstream wetlands. The source of these flow increases, referred to subsequently as "surge flow events", is likely to be the erosion and subsequent catastrophic failure of underground rooffall related "dams" that impound significant amounts of acid water. Drainage features whose flows exhibit close correlation to surface precipitation/runoff events appear to be more likely to experience surge flow events. It is suspected that extraordinary surface runoff reporting to underground mine workings could create stress on roof fall dams, increasing erosion and accelerating catastrophic failure.

The following mine/tunnel characteristics should be evaluated in order to provide a relative indication of surge event potential for the mine/tunnel systems providing water to wetland treatment installations:

- o Length of tunnel. The volume of water impounded behind a roof fall is proportional to a tunnel's length, ignoring the workings connected to the tunnel.
- o Extent of connected workings. A tunnel is typically connected to other workings. These additional connected workings are capable of providing additional hydrostatic head and volume to a surge event. The more connected workings there are, the higher the likelihood of a surge event volume being impounded.
- o Reports of water, either at the portal or underground. These reports, either in the literature or by personal observations, contribute to the likelihood of water being impounded underground and being released in a single event.
- o Stopes or multiple shafts intersecting the surface. These mining-related characteristics provide multiple pathways for surface water inflows into the mine workings.

A means of objectively assigning a relative risk of a surge event to mine/tunnel systems considered for wetland treatment should be developed. Discharge features with high surge event risk

for wetland treatment should be developed. Discharge features with high surge event risk may require controls such as underground structures/impoundments to throttle surge flow event flows so that wetland treatment systems are not overwhelmed or damaged.

In essence, the flows expected at the portal of a mine/tunnel/ waste rock pile system will be a function of the system's hydrology. As discussed in SECTION 2, the hydrology of mining features may be broadly characterized into "diffuse" and "conduit" systems. Features with "diffuse" hydrology are less likely to experience surge flow events and their discharge water quality does not change with climate.

Minimal flow values (drought conditions) will also be important to quantify prior to the wetland design. Wetland substrate chemical stability appears to be sensitive to desiccation (99). As discussed in SECTION 3, desiccation of substrate may subsequently result in the re-mobilization of precipitated metal sulfides that oxidize during desiccation. Ivanov (100) observed that dewatered peat lost permeability as a result of compression forces generated when the buoyant effect of the water was removed. These changes in the substrate could dramatically impact the performance of the wetland.

Changes in minimal loading conditions also need to be considered. In areas where snowmelt provides a significant portion of the acid drainage, flow rates and loading rates are typically not equivalent. While flow rates to the wetland may decrease after the initial melt, loading rates may remain constant or actually increase until spring runoff "flushes" accumulated contaminants resulting in a temporary loading rate spike.

FLUID COLLECTION ALTERNATIVES

Metal hydroxide formation in conveyances due to oxidation of mine waters can interfere with efficient transport of water to the wetland. Therefore, fluid collection strategies should attempt to reduce formation of hydroxides by limiting seepage exposure to oxygen. This can be accomplished by intercepting fluids as close to their source as possible to minimize air contact. Previously flooded and subsequently rehabilitated underground workings with acid drainage exhibited a reduction in metal hydroxide accumulations in areas with mine atmospheres deficient in oxygen. Otherwise, underground workings would tend to "self seal" with hydroxide accumulations.

Fluid collection alternatives that conform to a reduced oxygen exposure strategy follow. They include underground impoundments, portal impoundments, rock/pipe galleries and open ponds.

Underground Impoundments

Besides reducing acid water exposure to oxygen, underground full-face bulkheads provide several advantages in collecting fluids to be diverted to constructed wetlands:

- o Impounded water may provide driving head energy necessary to convey acid drainage to wetland sites far removed from the tunnel/adit portal location.
- o Bulkheads can provide protection from surge event flows by throttling such flows through pipeline conveyances equipped with valves.

- o Bulkheads allow the utilization of the mine workings themselves as reservoir space. This could permit the temporary suspension of drainage to allow periodic maintenance of conveyances or other wetland components.

Bulkhead design considerations include:

- o The site geology, particularly the faulting patterns in the underground workings
- o Stability of the underground opening, for safety during construction and reduction of grouting requirements,
- o Maximum anticipated static pressures and potentially dynamic heads developed from surge events; dynamic pressures can be reduced through the construction of a raised air chamber upstream from the bulkhead,
- o Bulkhead locations that provide geostatic pressures above the bulkhead site equal or greater to the potential combined static and dynamic (surge) pressures,
- o Multiple bulkheads to insure containment of fluids within underground workings; i.e, prevent impounded water from rising to form a new point source discharge on the surface,
- o Impacts on adjacent mines or surface facilities,
- o Allowable leakage around bulkheads, fracture flow around bulkheads,
- o Contact with acid mine drainage water,
- o Allowance for pipes or other conveyances that permit the passage of water through them either for maintenance or as a standard operating condition,
- o Long-term durability; i.e., 50-plus year design life

Underground bulkheads have probably been used in some form to control water since underground mining began. Bulkheads installed in deep South African gold mines appear to provide the most contemporary design and construction experience applicable to the construction of bulkheads to collect acid drainage.

Data on the construction of underground bulkheads in deep gold mines in South Africa (101) indicate that:

- o Leakage through wall rock fractures adjacent to the bulkhead, which is related to the pressure behind the bulkhead, is the primary design criterion rather than plug/wall resistance to thrust. Data indicate that the bulkhead should have at least one foot of thickness for every 25 to 40 psi of static water pressure exerted on the plug.
- o The plug may be constructed of concrete formed by emplacement of a cement grout into clean, strong angular rock fragments (up to boulder size) that have been previously packed between forms.
- o If indicated by drilling and water pressure tests, the rock surrounding the bulkhead should be grouted through boreholes ring-drilled to a minimum depth of 20 feet deep. Grout pressures

should be at least equal to the local lithostatic pressure.

- o Plugs may not need to be hitched into the wall rock, tapered nor constructed with reinforcing bars. The plug/wall rock friction from normal rock irregularities may be sufficient to maintain plug stability as long as the leakage/pressure criteria above are met.
- o Leakage adjacent to the finished bulkhead is usually observed in the floor and back (roof), even at low pressures. The flow paths are created at the concrete/wall rock contact due to concrete weeping in the curing process, air pockets and entrained mud. These leakages can be sealed by standard grouting techniques.

Testing for rock in-situ permeabilities and flow paths should occur prior to, or commensurate with, the plug design. Rock grouting should be an integral part of plug installation. The harsh chemical environment that may exist in the tunnel or the rock should be considered for all materials to be placed. A logical extension of underground bulkheads includes underground excavations (including horizontal and inclined boreholes) that collect acid drainage.

Portal Impoundments

Portal impoundments include bench or weir type installations that do not completely fill the mine/tunnel opening. Portal impoundments should only be considered for mining features where risk of surge flow events is low or cost prohibits the rehabilitation of the workings to allow the safe construction of a full face bulkhead.

If an existing portal is collapsed, a natural impoundment condition may exist. This condition should be approached with extreme caution; earth and rock in a collapsed portal should not be considered adequate substitutes for an engineered, constructed portal impoundment. The region beyond the collapsed zone should be dewatered with caution before the collapsed material is totally excavated for construction of impoundment facilities.

Portal impoundment design should consider most criteria applicable to the full-face bulkhead with the obvious exception of geostatic pressures. Typical portal impoundment facilities should be constructed of acid-resistant reinforced concrete.

Portal impoundments are typically constructed near the entrance to the underground workings. Therefore, designers should consider additional measures to reduce the exposure of impounded water to oxygen. One method is installing brattice curtains to reduce air movement/oxidation of water. Brattice curtains of acid-resistant material or masonry walls with underflow conveyances could be hung from/attached to the roof and walls of the mine opening. In addition, mine timbers could be placed behind the brattice; the timbers would slowly rot and consume oxygen. These oxygen-depletion measures will decrease, but probably not totally prevent, hydroxide sludge accumulations.

Rock/Pipe Galleries

These installations may be constructed as an integral part of waste rock or tailings facilities or retrofitted as a toe/embankment extension for completed facilities lacking underdrainage. Designs should

typically include "french drain" type components such as gravel/rock seepage zones contained in permeable geofabric envelopes, gas traps, perforated acid-resistant piping or rigid geomembrane/ geofabric composites that eliminate gravel/rock requirements.

Designers should assume that any pipe, either with full pipe flow or open channel flow, will eventually clog with iron hydroxide precipitate even if oxygen exposure is eliminated. Valves, low points in the pipe route and bends will clog even faster. Thus, cleanout provisions should be included in every design.

In past experience, the use of limestone or other acid-neutralizing rock in the construction of rock/pipe galleries resulted in rock armoring with hydroxide precipitates and the subsequent failure of the system as a collection/treatment device. Recent advances reported by Brodie and Britt (117) indicate that the total exclusion of oxygen from a limestone rock gallery prevents the formation of precipitate armoring. Brodie's term for such a facility is an "Anoxic Limestone Drain" or ALD. Total oxygen exclusion features of a typical ALD include geosynthetic/plastic and clay soil covers and gas traps. The consumption of limestone may pose a long-term maintenance consideration. Brodie estimated that typical ALD's installed by the TVA have operational lifetimes on the order of decades. Thus, the design of a rock/pipe gallery should consider the eventual replacement of limestone if that particular rock type is used. As discussed in SECTIONS 3 and 4, limestone may be used as a component of anaerobic wetland substrate. Oxygen exclusion in a rock/pipe gallery is a design challenge with few obvious solutions. Impoundment of fluids within an embankment can cause slope failures. The employment of inverted pipe traps and minimum soil/geomembrane covers over galleries appear to be the best apparent strategies for minimizing oxygen exposure to water in rock/pipe galleries. However, traps may be maintenance problems because they may be difficult to clean if they become plugged.

Open Ponds

These water collection features may include inundated mine pits or excavated wide channels with little, if any, gradient. The exposure of the drainage to air is unavoidable in this circumstance; it is likely that metal hydroxides will form, posing a long-term maintenance problem. Further, the orange/red precipitates are not aesthetically pleasing. On the other hand, if the mine drainage is issuing from a tunnel that historically has a high surge potential, some structure such as an open pond may be necessary to prevent catastrophic destruction of the wetland from surge flow.

The wetland designer should consider converting the open pond situation to an in-place wetland if land use or regulatory restrictions allow it. From a geomorphologic viewpoint, lakes and ponds naturally tend to become wetlands as sediments and vegetation accumulate in the lake bottom. Thus, conversion of open water to shallow wetlands may: 1) provide a more stable hydrologic environment, 2) increase site aesthetics and 3) provide water quality improvements.

If total conversion of an open pond collection feature is not practical, shoreline wetland features that may include wetland treatment cells should be considered.

SECTION 10

CONSTRUCTABILITY - METHODS AND MATERIALS

SUBSTRATE FROM NATURAL SOURCES

Substrate materials may consist of mixtures of organic and inorganic soils and typically include animal waste in the form of manure. Substrate component materials have included:

- o depleted mushroom compost (50% manure/50% barley mash waste)
- o peat moss
- o aged manure
- o decomposed wood products
- o limestone
- o planters mix soil (topsoil)
- o straw

Data suggest that wetland removal performance is closely linked to how the acid metal drainage flows through the substrate materials. Substrate materials may be selected initially based on local availability and reasonable cost, then amended (if necessary) to produce a composite substrate material for a particular application.

A substrate material that has demonstrated good performance for both metals removal and flow characteristics at the Big Five Tunnel Project is mushroom compost (3, 6). Mushroom compost is a mixture of manure and brewery waste. Some physical characteristics of the mushroom compost substrate follow (9):

Specific Gravity of Solids	1.66 to 1.78 grams/cubic centimeter
Bulk Density, Wet Substrate	1.23 to 1.33 grams/milliliter
Porosity by Volume	25% (typical)
Bound Water by Weight	3.7%
Permeability (down-flow)	10^{-3} to 10^{-5} centimeters/second
Grain Size Distribution	58.5% passing a No. 10 sieve; 15% passing a No. 200 sieve
Ash Content	71.5% (typical)

Hydraulic Conductivity

Hydraulic conductivity is an important wetland design parameter because the hydraulic performance of the wetland is particularly sensitive to this variable. Hydraulic conductivity, "K", is a cornerstone variable in Darcy's Law and other hydrologic relationships typically utilized to predict the hydrologic performance of wetlands.

For the Big 5 Tunnel Project, hydraulic conductivity (permeability) values of wetland substrates were measured in laboratory and field permeameters by Lemke (9). Laboratory methods have been developed and documented in the Peat Testing Manual (102) and Fetter (103); methods include

constant and falling head test procedures for permeameters with down-flow and up-flow configurations. Permeameter configurations are presented in Figures 49 and 50. Laboratory procedures are addressed in SECTION 14.

Laboratory permeameters are typically clear plastic tubing about two inches (5 cm) in diameter fed by constant head or falling head measurement plumbing. Laboratory measurements may typically employ distilled or de-ionized water or other fluids. There may be some debate as to whether this is representative of actual field conditions; i.e., acidic, metal bearing drainages.

In-situ measurement techniques for permeability in constructed wetland installations typically involve falling or rising head testing at shallow depths (102). However, dewatering of substrate may result in compression of lower layers, reducing permeability and yielding erroneously lower values than what may actually exist in-situ (100).

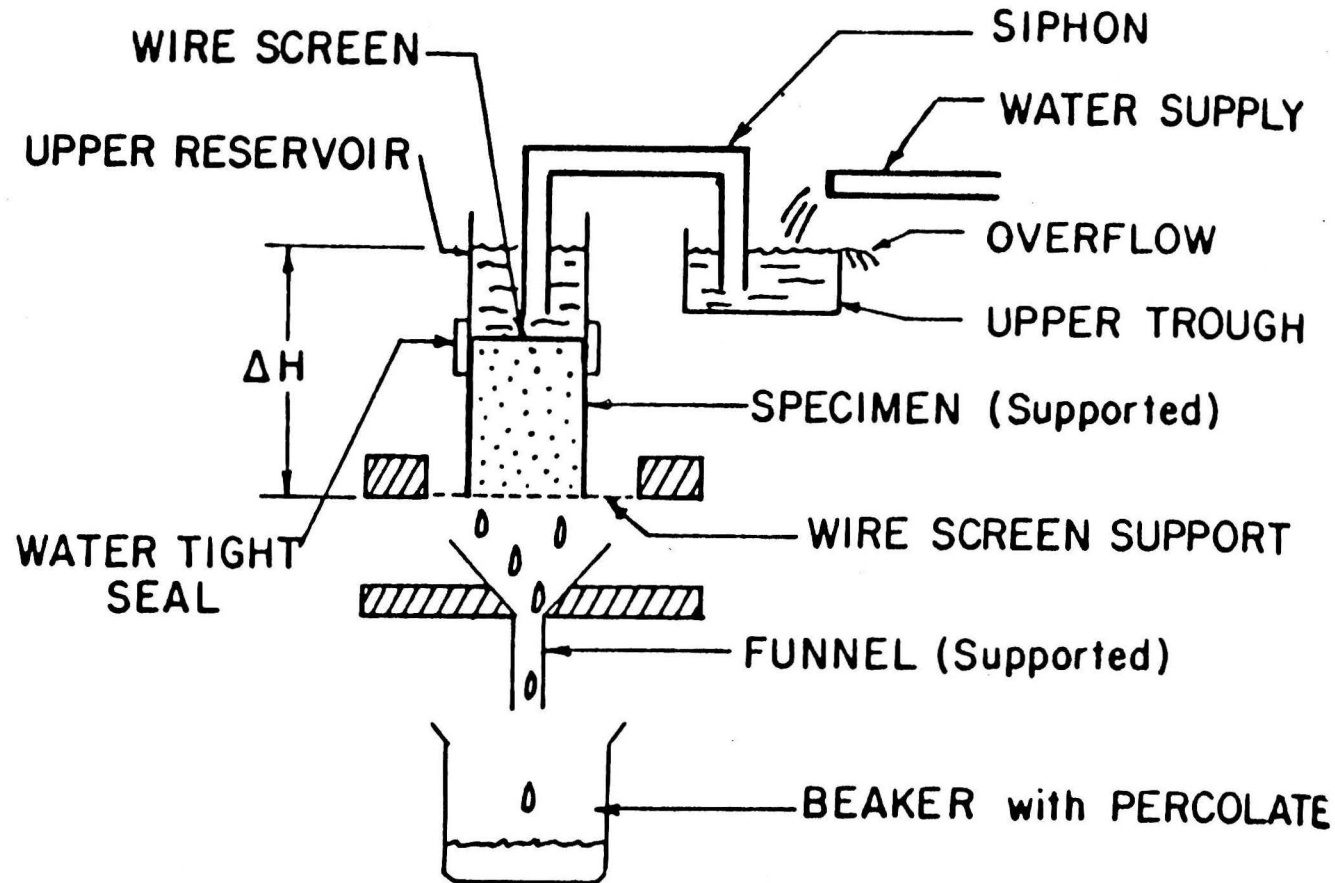
Field permeameters constructed with 30 gallon (120 liter) capacities have provided data that correlate well with laboratory scale permeameters (9). However, caution must be employed in the construction of field permeameters to insure that hydroxide precipitation in feed plumbing does not interfere with hydraulic conductivity determinations. A typical field permeameter is depicted in Figure 51.

Lemke reported wetland substrate hydraulic conductivity values (mushroom compost) from 10^{-3} to 10^{-5} cm/sec for "fresh" and "used" (submerged for about one year), respectively. Laboratory permeabilities for wetland substrate appeared to vary with the following parameters:

- o Age (Humification)
- o Wetted condition
- o Size distribution
- o Flow direction (up-flow versus down-flow)

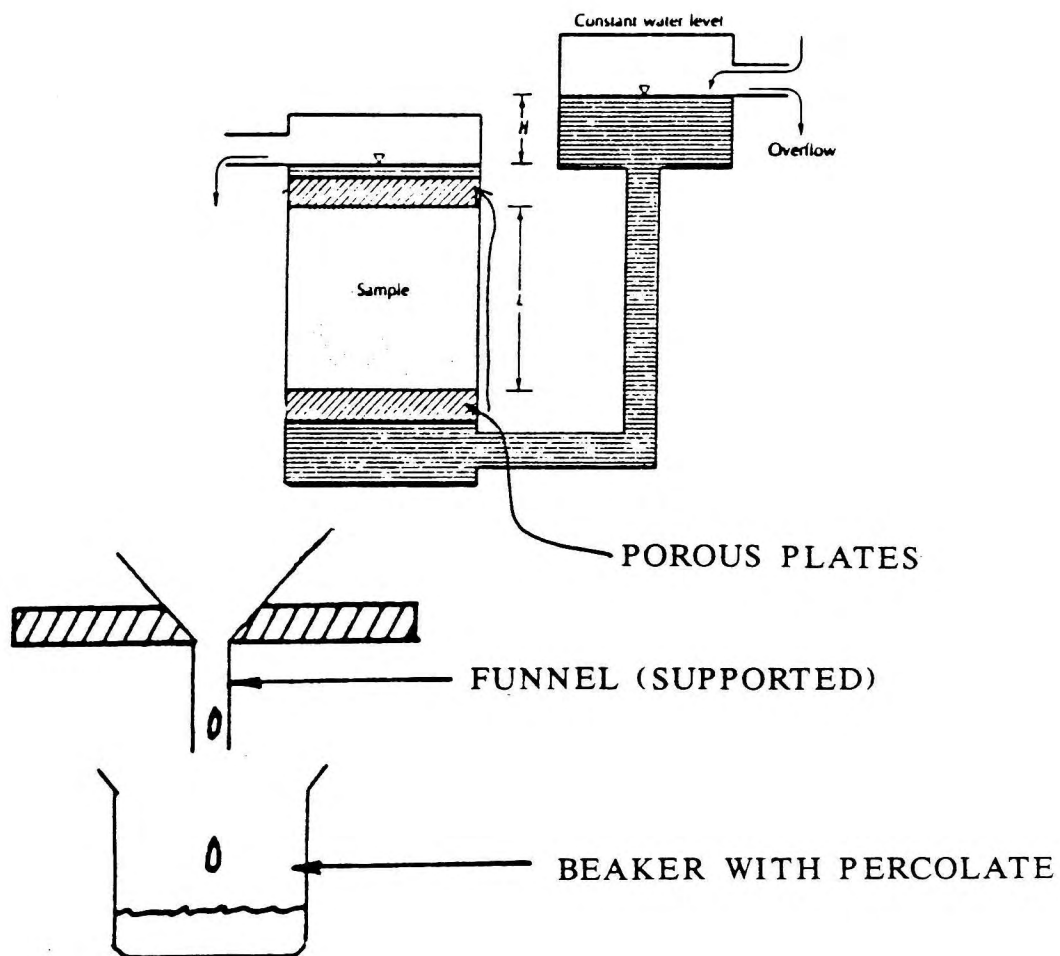
Lemke (9) observed that permeability was a function of wetted condition. Used mushroom compost that had been allowed to dry typically had permeability values nearly equal to unused mushroom compost that was obtained in a dry condition. Drying of used mushroom compost appeared to allow the recovery of about one order of magnitude of permeability when compared to the wet condition. Various mechanisms may be responsible for this phenomenon; a likely one is the adherence of small particles to larger particles upon drying. Studies have shown that permeability values for dry mushroom compost decrease as soon as submergence begins and approach typical "wet" permeability values after about three months (99).

Winneberger (104) gives a detailed discussion of the changes in permeability of soils as they are inundated with water. Winneberger points out that in 1922, a soil scientist named E.V. Winterer observed that inundated soils go through three phases of permeability change. During Phase I (about 10 days), infiltration rates decrease rapidly. This initial decrease is explained as the result of "slaking" of the soil; i.e., changes in the affinity of the soil surfaces for water and the decrease of the cohesive forces that hold the soil particles together [Winterkorn, 1942 and Christiansen, 1942, referenced in (104)].



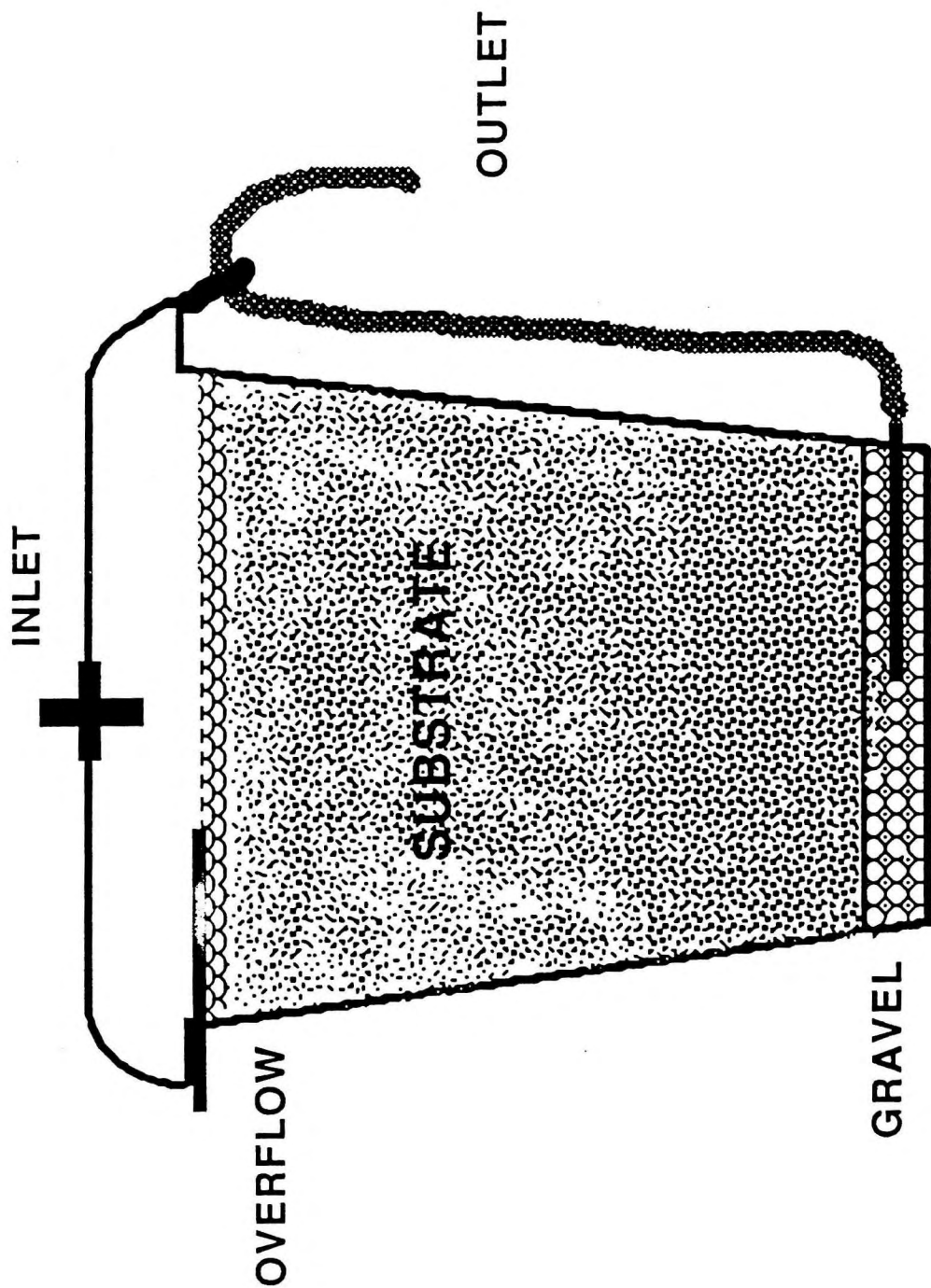
ΔH = TOTAL HYDRAULIC HEAD DIFFERENCE
ACROSS SPECIMEN.

Figure 49. A diagram of a typical downflow laboratory scale permeameter.



H = TOTAL HYDRAULIC HEAD DIFFERENCE
ACROSS SPECIMEN.

Figure 50. A diagram of a typical upflow laboratory scale permeameter.



BENCH SCALE WETLAND MODULE DOWNFLOW MODE

Figure 51. A diagram of a bench scale permeameter.

In Phase II, which lasts about 25 days, the permeability increases again, due to removal by dissolution of air trapped in soil pores. Phase III is a slow (several month) decrease in permeability due to biological activity [Allison, 1947 in (104)].

According to Winneberger (104), "With numerical variations, such a (three-phase) curve has been observed of essentially all inundated soils whether tested in a laboratory or in the field." Further, the three phases appear to compress in time when sewage or waste water is applied due to the addition of high concentrations of bacteria and their food source.

In addition to the phenomena described above, decreases in substrate permeability with age/use/submergence (9) may be due to the biochemical decay and disintegration of organic fractions in the substrate. Theories on the formation of coal (105, 106) suggest that stagnant flow conditions in naturally occurring wetlands promote the preservation of organic matter. Conversely, "dilution" of stagnant conditions resulting from water movement through the wetland appears to promote organic decay or humification.

TABLE 27. HUMIFICATION EFFECTS ON COEFFICIENT OF SEEPAGE
VALUES OF DIFFERENT KINDS OF PEAT FROM REF (100)

Type of Peat in Natural Deposit and Degree of Humification	Coefficient of Seepage (cm/s)	
	Average Value	Limits of Variation
Fen peat (Hypnum-sedge, sedge, sedge-Sphagnum)		
Slightly humified (25-30%)	0.005	0.002 - 0.01
Moderately humified (40-55%)	0.0008	0.0002 - 0.002
Bog peat		
Very slightly humified (up to 10%)	0.015	0.01 - 0.025
Slightly humified (10-20%)	0.004	0.002 - 0.007
Moderately humified (35-45%)	0.0005	0.00025 - 0.001
Much humified (55-65%)	5×10^{-5}	2×10^{-6} - 8×10^{-5}

Thus, inundation in a reducing environment appears to slow, but does not halt the humification of wetland substrate. Ivanov (100) observed that "coefficient of seepage" (permeability) is a function of the degree of humification and not a function of peat type. Table 27 presents permeability values for two types of peat as a function of humification.

Day, et. al. (102, Appendix C) contains a classification of degree of humification. The distinction among the 10 grades of humification appears to be a function of "muck" content, plant remains,

consistency and the color of water extracted when the sample is hand-squeezed. Thus, degree of humification appears to be a relatively subjective characterization.

Further, the accumulation of metallic precipitates in substrate void spaces will also tend to decrease permeability with continued use. Thus, it appears likely that the permeability of substrate will change (decrease) as a constructed wetland is operated and may become a maintenance consideration.

Permeability of granular materials is universally accepted to be a function of particle size distribution. The smaller the particles and the more evenly distributed (as opposed to uniform-sized particles) a granular material (substrate) is, the less permeable it will be. Data from Hough (107) as presented in Table 28 support this.

Permeability values appear to be a function of flow direction for some wetland substrate materials (9). Permeability measurements in a down-flow configuration are significantly different from up-flow measurements. The phenomenon is probably due to suspension of fine-grained particles in the upward flowing fluid compared to clogging of flow passages with finer-grained particles in a down-flow configuration. These permeability differences have been noted in bench-scale (30 gallon container) experiments, and in larger pilot-scale (100 square feet) wetland configurations over short time frames. However, after the pilot-scale upflow cell had been operating for 10 months, permeability decreased to about the same as in the downflow cell. Flow velocity through the substrate materials in up-flow conditions appears to be the key criterion that needs consideration.

Particle Size Distribution

Hydraulic conductivity is directly related to particle size distribution of substrate materials. Particle size distribution requirements for substrate are typically easier for a design engineer to specify in construction bid documents than hydraulic conductivity.

The discussion of particle size distribution is another case in which the distinctive vocabularies of different disciplines (in this case civil engineers and geologists) can lead to confusion. For example, to describe a collection of particles of primarily a single size, civil engineers use the term "uniform". For the same collection of particles, geologists use the term "well-sorted", based on hydrological sorting processes, or "well-graded", because the particles all lie within the limits of a single "grade".

At the other extreme is a collection of particles of various sizes, in which all sizes are approximately equally represented. Civil engineers use the term "evenly graded" or "well-graded" for this collection. By this term, they signify that a uniform mixture, of "gradation" of particle sizes exist. Geologists use the term "graded" in the opposite sense, so that they would term this same mixture of particles "poorly sorted" or "poorly graded".

The geological perspective is the three-dimensional context in which the particles were deposited in a sedimentary environment, based on the different settling rates of different-sized particles. In geological terms, a "graded bedding" is a sedimentary deposit "in which each layer displays a gradual and progressive change in particle size, usually from coarse at the base of the bed to fine at the

TABLE 28. TYPICAL VALUES OF PERMEABILITY COEFFICIENTS
FROM HOUGH (107) AND FETTER (103)

Material	Particle Size Range				*Effective* Size		Permeability Coefficient-k
	Inches		Millimeters				
Civil Engineering Terminology (107)	D _{max.}	D _{min.}	D _{max.}	D _{min.}	D ₂₀ in.	D ₁₀ mm.	Cm./sec.
Derrick STONE	120	36	-	-	48	-	100
One-man STONE	12	4	-	-	6	-	30
Clean, fine to coarse GRAVEL	3	1/4	80	10	1/2	-	10
Fine, uniform GRAVEL	3/8	1/16	8	1.5	1/8	-	5
Very coarse, clean, uniform SAND	1/8	1/32	3	0.8	1/16	-	3
Uniform, coarse SAND	1/8	1/64	2	0.5	-	0.6	0.4
Uniform, medium SAND	-	-	0.5	0.25	-	0.3	0.1
Clean, well-graded SAND & GRAVEL	-	-	10	0.05	-	0.1	0.01
Uniform, fine SAND	-	-	0.25	0.05	-	0.06	40 x 10 ⁻⁴
Well-graded, silty SAND & GRAVEL	-	-	5	0.01	-	0.02	4 x 10 ⁻⁴
Silty SAND	-	-	2	0.005	-	0.01	10 ⁻⁴
Uniform SILT	-	-	0.05	0.005	-	0.006	0.5 x 10 ⁻⁴
Sandy CLAY	-	-	1.0	0.001	-	0.002	0.05 x 10 ⁻⁴
Silty CLAY	-	-	0.05	0.001	-	0.0015	0.01 x 10 ⁻⁴
CLAY (30 to 50% clay sizes)	-	-	0.05	0.0005	-	0.0008	0.001 x 10 ⁻⁴
Colloidal CLAY (-2u ≥ 50%)	-	-	0.01	10A°	-	40A°	10 ⁻⁹
Hydrogeologists Terminology (103)							Conductivity (cm/sec)
Clay	-	-	-	-	-	-	10 ⁻⁹ - 10 ⁻⁶
Silt, sandy silts, clayey sands, till	-	-	-	-	-	-	10 ⁻⁶ - 10 ⁻⁴
Silty sands, fine sands	-	-	-	-	-	-	10 ⁻⁵ - 10 ⁻³
Well-sorted sands, glacial outwash	-	-	-	-	-	-	10 ⁻³ - 10 ⁻¹
Well-sorted gravel	-	-	-	-	-	-	10 ⁻² - 1

top" (Glossary of Geology, Bates and Jackson). Each layer of this deposit would be "well-sorted" (or "uniform" in civil engineering terminology). Only if a slice of this deposit, through all layers, were stirred or homogenized in some way, would that slice become "well-graded" in civil engineering terms.

In this report, we will use the term "sorted" whenever possible. If the term "graded" is used, it will be in the civil engineering context.

The relationship of particle size distribution to hydraulic conductivity has been extensively studied. It is generally accepted that the more uniform the particle size is in a collection of materials, the higher the void ratio and the higher the hydraulic conductivity when compared to a well-graded or non-uniform collection of particles. For example, a group of uniform spheres of a certain size diameter "T" will have a higher hydraulic conductivity than a group of spheres which have evenly distributed diameters between diameter T and a significantly smaller diameter "t". The small diameter particles fit within the voids between the larger particles, thus reducing overall volume of voids and lowering the permeability.

Thus, if a high permeability is required, a material with relatively uniform size particles of a size T would be specified. If a low permeability is required, a poorly-sorted size distribution would be specified between particle diameter sizes T and t. Table 28 presents relative size distributions (standard soil classifications) and estimated permeabilities. The first part of Table 28, which gives hydraulic conductivity values for various particle size collections, is from a civil engineering text (107). The second part is from a hydrogeology text (103).

Particle size measurements for substrate are typically performed by either dry sieving (ASTM D2977) or wet sieving (102). These methods were developed for "peat" materials. While some substrate materials do not satisfy the definition of peat, these testing protocols appear to provide sufficient data for substrate particle size characterization. As with all laboratory methods, revisions should be considered to fit individual materials and situations.

Day, et al (102) summarize the dry sieving method:

A representative test specimen of air-dried peat is separated into four designated fractions by means of an 8-mesh and 20-mesh sieve. The fractions are: (1) foreign matter, removed manually from the 8-mesh sieve; (2) coarse fibre, retained on the 8-mesh sieve; (3) medium fibre, passed through the 8-mesh sieve but retained on the 20-mesh sieve; and (4) fines, passed through the 20-mesh sieve retained in the bottom pan. The mass percentage of each fraction is calculated on the as-received basis.

Day, et al, (102) summarize the wet sieving method:

A shaken mixture of peat and distilled water is wet sieved through the standard soil sieves. The residue on each sieve is oven-dried at 105°C and its mass weighed to determine the percentage of each of the four particle sizes.

Due to the likelihood that finer particles may adhere to larger particles as long as the substrate material is dry, wet sieving methods are probably more representative of actual particle size distribution

within the inundated wetland. Slaking effects noted by Winneberger could be evaluated for dry substrate samples by observing variations in permeability with "presoaking" time periods. Presoaking times on the order of weeks should be considered. Also, if excessive substrate depths are being considered, triaxial cell permeability determinations should be conducted.

There is no "recommended" size distribution for "typical" wetland substrate. The desirability of a given substrate material will be a function of how closely it provides a desired hydraulic conductivity and how stable the size distribution remains with prolonged submergence. Table 29 (9) presents permeabilities determined for mushroom compost that was used in Cell B at the Big Five Wetland. At the bottom of Table 29 is the size distribution of the substrate used in Cell A of the Big Five Wetland Site (9).

From a practical standpoint, it may be desirable to mechanically sieve or physically amend a substrate material to provide a size distribution that will ultimately yield a given hydraulic conductivity. Lemke (9) examined mechanical separation of finer size fractions and amendments to adjust permeability of used mushroom compost with measurable but marginal changes (increases) in permeability.

TABLE 29. PERMEABILITIES (VARYING SCALE & FLOW PATH)
AND SIZE FRACTIONS FROM CELL A MUSHROOM COMPOST FROM REF (9).

PERMEABILITIES		
SCALE	FLOW PATH	K (cm/sec)
Lab	Downflow	3.50×10^{-3}
Intermediate	Downflow	3.14×10^{-3}
Pilot	Downflow	2.96×10^{-4}
Lab	Upflow	6.65×10^{-2}
Intermediate	Upflow	1.44×10^{-2}
Pilot	Upflow	1.38×10^{-2}

SIZE FRACTIONS			
SIEVE	RETAINS	% DRY WT	CUMULATIVE %
10	2 mm	25.8	28.5
20	0.85 mm	21.1	46.9
100	0.15 mm	32.6	79.5
200	0.075 mm	4.5	84.0
PAN	<0.075 mm	16.0	100.0

Substrate particle size distribution (and hydraulic conductivity) at a given vertical zone within the wetland may change with time due to several factors:

- o Addition of coarser particles from the development of plant root systems and dead stalks.
- o Disintegration of organic fractions due to decomposition/ humification, which is inevitable with extended submergence .
- o Gravity migration of heavier or larger particles toward the bottom of the wetland.
- o Migration of lighter particles in the direction of flows.
- o Precipitation of mineral species in interstitial voids.
- o Compaction of the substrate under its own weight.

Bio-Compatibility

Substrate bio-compatibility is an important design consideration. If sulfate-reducing bacteria do not thrive in the media, the wetland may not meet performance expectations even though it may be properly designed in accordance with other criteria.

The presence of naturally-occurring sulfate-reducing bacteria in candidate substrate materials is a strong indication that bacteria will thrive in acidic/metallic drainage. Tests for the presence of sulfate reducing bacteria are discussed by Batal, et. al. in (10). Many animal manures have naturally-occurring sulfate reducing bacteria populations. At a minimum, laboratory scale tests with substrate candidates and effluent samples should be conducted.

A 1:1 ratio of substrate to effluent sample (30 grams solid : 30 grams liquid) has been shown to be sufficient in developing significant sulfate-reducing bacteria populations in as little as two weeks (99) of incubation. Qualitative indicators such as the occurrence of black precipitates in test containers are used to denote the presence of sulfate reducing bacteria.

Offensive Smells and B.O.D. Considerations

If the substrate material contains manure, offensive smells, high Biological Oxygen Demand (B.O.D.) and ammonia may be observed. These problems can be minimized if the substrate materials are composted well before use in a wetland. Composting methods have been well developed and documented in the literature (108). Composting is an accepted method of encouraging the biochemical degradation of the organic fraction of solid waste material; having a humus-like substance as an end product. Aeration and moisture control of composting materials are important parameters for the successful use of the technique. Typical composting time varies from two to ten weeks, depending on initial carbon to nitrogen and carbon to phosphorus ratios in the feed stock.

If composting of manure-rich substrate materials is not practical, polishing steps provided by additional constructed wetlands downstream from the metal-removing wetlands may be required. The design and construction of wetlands for municipal waste water treatment are well documented in the literature (109).

Organic Content

Minimum organic content requirements to "fuel" biochemical reactions have not been established. A discussion of organic content stoichiometry in relation to sulfate reduction is presented in SECTION 12. Lemke (9) measured organic contents of 28.5% and 29.0%, respectively, for "fresh" and "used" mushroom compost materials. Statistical uncertainty or organic additions from plant sources may have been the cause of the apparent net gain in the substrate's organic content with one-year's use/submergence.

However, Lemke noted that the size distribution of organic material did change with use; the medium size fractions experienced an increase in organic content, suggesting organic material disintegration or humification.

Carbonate Sources

Carbonate is required in the substrate to provide buffering capacity and a source of anions for the removal of manganese as a carbonate. Limestone is the preferred carbonate source due to its typical low cost and wide availability.

Size distribution of limestone amendments, when required, should be consistent with overall substrate characteristics. The heavier density of limestone (2.6 grams per cubic centimeter [g/cc]) when compared to substrate (1.6 g/cc [9]) could induce the settlement of limestone particles to the bottom of the wetland. A finer grind of limestone (tempered by permeability considerations) should be considered to counteract this effect and provide more surface area for geochemical reactions.

Minimum carbonate content requirements in substrate materials should be established based on the stoichiometry of each wetland system and field trials.

Substrate from Synthetic Sources

The US Bureau of Mines has developed a "synthetic" substrate material it has named "Bio-Fix" beads (110). The material consists of sphagnum peat moss surrounded by pervious long chain polymers that make the peat moss more durable and more reusable. The beads function in the same way as ion-exchange resins and thus are limited to a narrow operating range in pH and loading rate.

At a significant sacrifice in a system's passive treatment nature, the beads may provide a suitable downstream polishing step to a constructed wetland. The beads are reusable; i.e., metals can be stripped from them using dilute sulfuric acid.

Proper sizing of the polishing cell using Bio-Fix beads may allow the stripping of beads to coincide with scheduled periodic wetland maintenance, thus preserving the passive aspect of remediation of water quality problems with wetlands. However, since the USBM estimates that approximately 80 bed volumes at relatively dilute metals concentrations will load the system and require the subsequent stripping of the Bio-Fix media, this is not an extended enough time to allow the truly "passive" operation of a wetland using this substrate. A typical substrate loading would be completed in about 240 days.

CONTAINMENT STRUCTURES

From a cost perspective, substrate containment structures for constructed wetlands should take advantage of local conditions; i.e., on-site materials should be employed if practical and designs should consider the availability of specialized materials.

There are four basic construction alternatives available to contain substrate. These are:

- o Natural soil-lined excavation: While typically economical, this approach allows some seepage losses to local ground water, which may not be an acceptable condition, even if the seepage meets quality criteria.
- o Geosynthetic lined excavation: While seepage losses are minimized, substrate maintenance considerations may further increase cost. For example, the liner needs to be protected if the substrate has to be periodically removed/replaced/rejuvenated.
- o Structural concrete: This high capital cost alternative provides a durable, maintainable facility. System flexibility may be sacrificed, however. Some components will require acid-resistance or acid protection.
- o Prefab coated metal/fiberglass tanks: These might be considered for situations where waters have dilute metal concentrations that allow "column" configurations and adequate hydraulic head is available to drive the system. Metal surfaces should be coated with rubber or other inert material to provide protection from corrosion.

MODULAR UNIT CONCEPTS

A modular unit design philosophy should be considered to allow system operational flexibility. Here, a balance must be struck between the concept of a single large wetland treating all the acid/metal drainage effluent and a multitude of smaller cells that each receive a proportion of the effluent.

The basic problem with large modules is that they may be difficult to control, slow to respond to changing conditions and difficult to adapt if redesign is necessary. The same problem might apply to balancing flows and conditions among many small modular units. Clearly, there should be a typical "range" of module sizes that fulfill the criteria.

Overall wetland size will be governed by design criteria and methods developed in SECTION 12. However, overall effluent flow rate and the minimum "manageable" flow rate will probably be the governing criteria to module size.

Minimum module size will probably be governed by the overall flux criteria and a unit flow rate of one gpm through the module. One gpm is probably the lowest practical flow rate value that can be managed without sophisticated flow metering/controlling devices. Thus, if a design flux rate of 800 square feet per gpm is required for metals removal, a minimum module size might be 800 square feet or a square with 28.3 foot side lengths.

Assuming one large single module, the maximum module size is governed by the overall system requirements. Here, site considerations may take precedence, assuming that acid/metal drainage

effluent flow rates are held relatively constant by controls installed at the source or within the collection systems.

Among the criteria that will influence the size of the wetland cell are:

- o Ease of performing maintenance functions, such as cleaning of pipes and adding organic materials to the substrate and aspects of long term reliability.
- o Hydrology of flow distribution. Large flow rates may need to be allocated among several wetland cells to allow reasonable distribution pipe sizes.
- o Site configuration. The topography and hydrology of the site may limit wetland cell dimensions.
- o Need for additional removal process cells. As discussed in SECTION 3, aerobic processes can release what was removed by anaerobic processes. Separate cells may be necessary to isolate processes.
- o Need for a substrate materials handling area. New substrate materials may need to be stored and mixed. Old substrate materials may need to be stored or dried prior to disposal. These operations may have to be done on the site.

An "optimum" cell size is difficult to define because each of the above criteria may be satisfied by different configurations. It seems logical to at least divide the flow into from five to ten equal and parallel streams. More than a dozen cells might be difficult to control. If treatment of acid drainage must be highly reliable; i.e., system availability must be near 100 percent, the minimum number of cells might be two, each large enough to handle the entire flow from the source. Thus, if maintenance needs to be performed on one cell, the other functions as a backup.

The long term reliability of wetland performance has yet to be established since it appears that few man-made systems have been operated for more than five years. As evidenced by peat bog accumulations in many parts of the world, the stability of natural systems has been measured in centuries (111), given constant climate conditions and constant rates of land subsidence and water recharge.

SECTION 11

CONVEYANCES/FLOW CONTROL

Ideally, wetland treatment systems should be located as close as possible to the collection systems or sources of acid/metal discharges. Site restrictions such as land ownership or land use, however, may prohibit the utilization of otherwise ideal wetland sites. Thus, acid/metal drainage may need to be conveyed some finite distance to the constructed wetland site.

PIPES AND PIPELINES

Pipes are the logical first-choice conveyance method. In keeping with the "oxygen-exclusion" philosophy developed in SECTION 9 to limit the formation of clogging metal-hydroxide precipitates, conveyances should be designed to be fully enclosed. Piping of water certainly satisfies this criteria; full-pipe flow satisfies it to a greater extent. However, open channel flow within an enclosed pipe may offer advantages as discussed subsequently in this section.

Besides meeting the typical pipe design criteria related to flows and pressures, pipeline materials should be acid/chemical resistant and, if they will be exposed to the elements, ultraviolet light resistant. Many plastic and fiberglass pipe materials satisfy these criteria. Stainless steel also satisfies the criteria, but exorbitant costs will probably limit its use to relatively short reaches. As periodic pipe cleaning will probably occur, the materials/linings should be selected to withstand such treatment.

To insure year-round operation in sub-freezing climates, pipes should be buried below the frost line. In rocky terrain, this requirement may increase installation costs, but system maintenance headaches from freezing pipes will be minimized. Pipe burial also provides security from other forms of surface damage.

If elevated mine water temperatures are the norm and flows are constant, pipe insulation may substitute for below frost line burial.

The most critical aspect of pipe utilization is the maintenance consideration of metal-hydroxide precipitation accumulation. Pipeline configurations that convey feed waters to wetlands should avoid low points, valves and sharp bends, as these features may induce hydroxide accumulations. Pipes should be installed to allow for easy inspection and cleanout. If precipitate accumulation is a serious problem, several approaches might be considered to alleviate it, none of which is totally satisfactory:

- 1) Settling of precipitates in a holding pond prior to entering the pipeline. The pond may require periodic cleaning, which lessens the passive nature of the installation and increases operating cost. Sludge disposal needs to be considered.

- 2) Installing a parallel/backup pipeline to allow uninterrupted flows from the collection system to the wetland during periodic cleaning. The increase in capital cost for the extra pipe would need to be compared to other alternatives.
- 3) Design for partially filled conduits (open channel flow). While the flows are exposed to oxygen, the excess cross sectional area that is available for precipitation buildup may prolong the time interval between required cleanings. However, utilization of hydraulic head is very limited in open channel flow situations.

For pipeline conveyances, the diameter of the pipe should be selected to promote full-pipe flow and to provide scouring velocities (2.5 feet/sec) to limit the accumulation of metal-hydroxide precipitate. Excessive headlosses may preclude the employment of scouring velocities to maintain precipitate-free pipes.

Anywhere that precipitation is anticipated within the wetland piping system, traditional flow controls like valves should be avoided if possible. The precipitate can foul valve mechanisms such as gates or valve seats. If valves must be used, they should be "full flow" types such as ball valves or valves designed for slurry pipeline application.

Headloss through a "partially-closed valve" should be avoided as a flow control technique. Again, this is due to the accumulation of precipitate in the high turbulence areas of the valve body, especially for flows below scouring velocity. Flow rates can be adjusted by modifying headlosses with unrestricted full pipe flow methods such as a flexible tube whose discharge elevation is varied. An example of this type of flow control is shown as Figure 52.

From experience in handling mine drainages over the last five years, the following guidelines indicate when precipitate buildup in pipes will be a problem:

- o The most troublesome precipitate is ferric hydroxide. Any water with over 1 mg/L of dissolved iron can potentially cause a problem.
- o Analysis of stability diagrams of iron species in water (20) reveal that mine drainage with pH > 3.25 is certain to cause problems because, above pH 3.25, ferric hydroxide is the stable form. Waters with pH < 2.75 will cause fewer problems because dissolved ferrous iron is the stable form. However, these low pH waters will be quite corrosive.
- o Mine drainages whose flows fluctuate because of the invasion of shallow subsurface water will cause problems because the mixing of the waters will drive the pH above 3.25. Problems will appear a week or two after invasion.
- o With waters below pH 2.75, a coating of precipitate will eventually adhere to the wall of pipes-even plastic pipes. Once this occurs, monthly maintenance is a necessity. The key maintenance points are partially closed valves.

OPEN CHANNEL FLOW CONVEYANCES

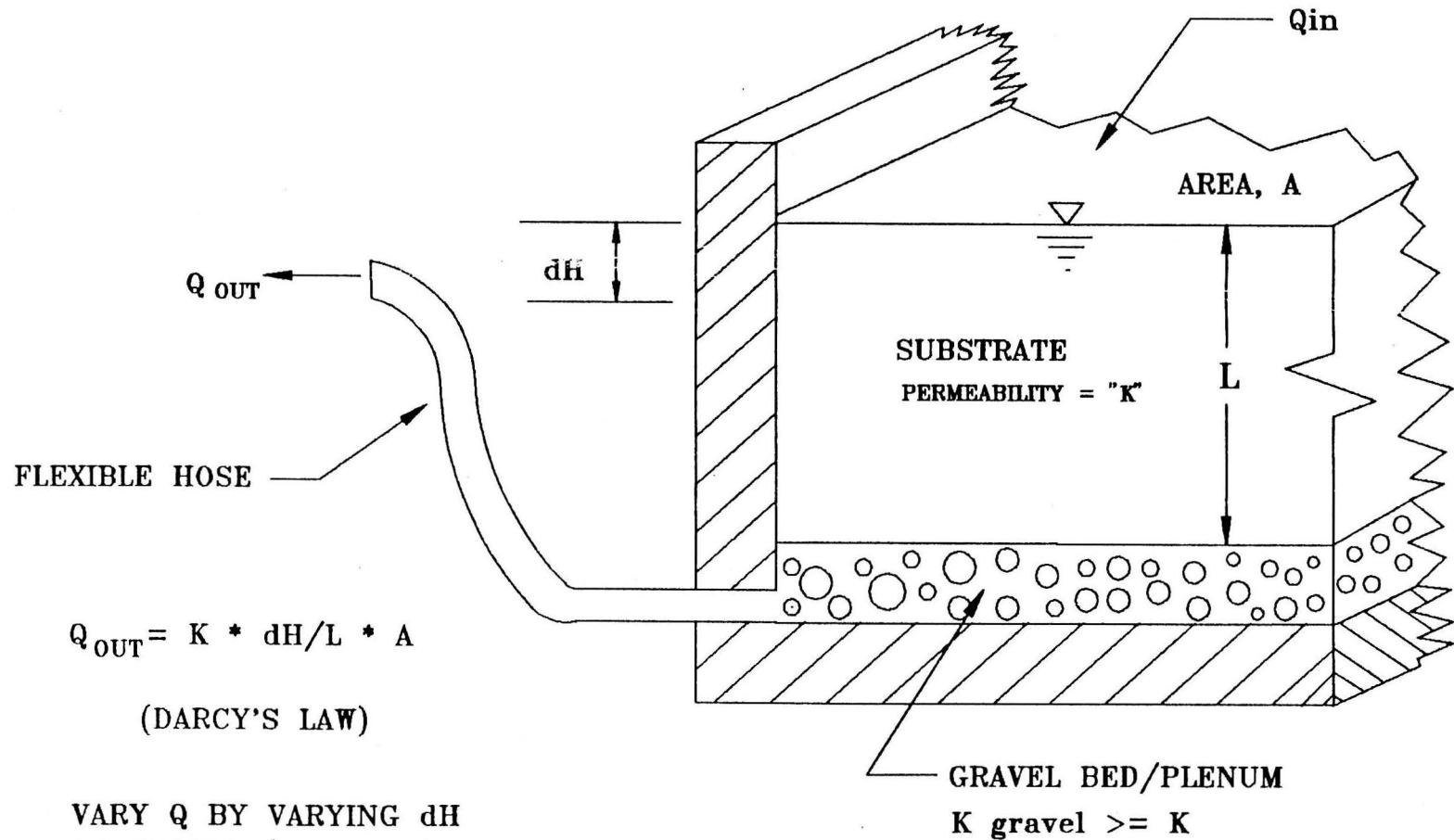
Open channel conveyances like ditches and flumes are one alternative to pipe flow. Alternately, as suggested earlier, open channel flow in partially-filled conduits should also be considered.

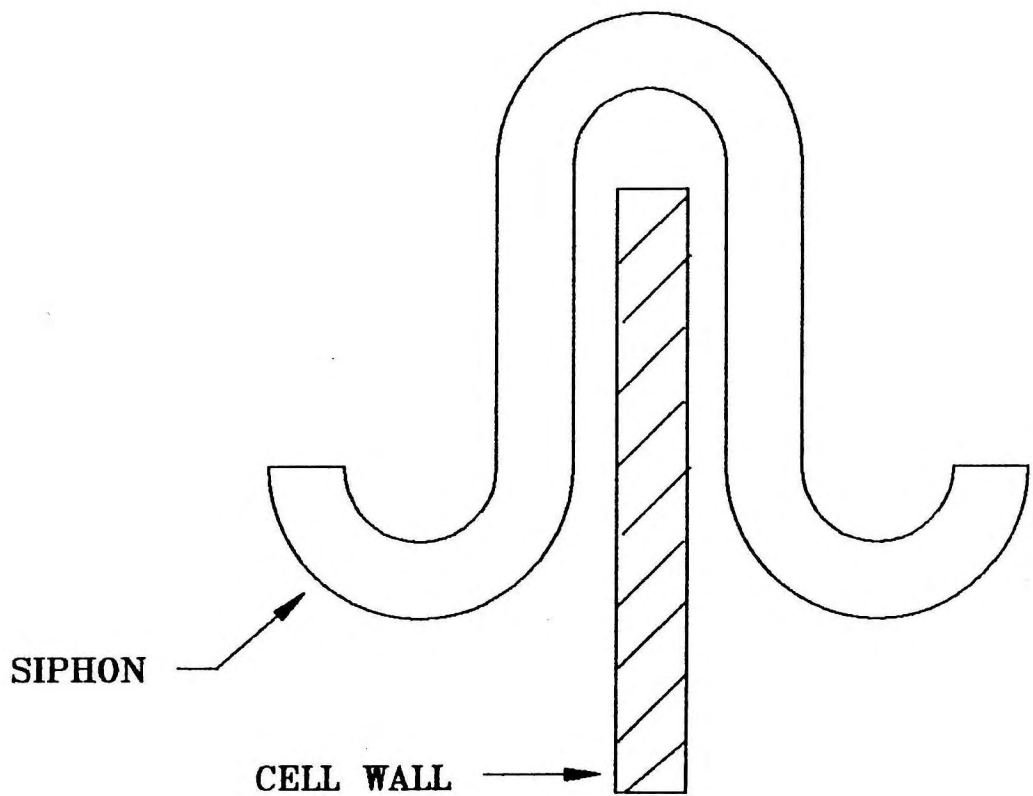
A distinct disadvantage of open channel flow conveyances is the sacrificing of hydraulic head that may be available to force feed water through wetland substrate with a low hydraulic conductivity. However, open channels such as ditches and flumes may offer maintenance advantages. First, these conveyances are easy to inspect; they do not require elaborate monitoring appurtenances such as test spools or inspection ports. Second, if open channel conveyances are sized to allow for the accumulation of hydroxide precipitate, the time period between conveyance cleaning may be extended to perhaps decades. For example, if an open ditch will carry water from the collection system to the wetland, the bottom width and depth of the ditch should be "over-designed" to allow for the accumulation of precipitate without compromising the flow capacity of the conveyance. The same applies to over-sized pipes carrying drainage flows in an open-channel flow mode.

Freezing conditions may preclude open-channel flow conveyances. If the installation of open-channel covers is considered, one might as well opt for a buried pipe conveyance, in open-channel or full pipe flow mode.

Maintenance of the open channel is an important design consideration. Open channel routes should provide for heavy equipment access during routine maintenance operations such as mucking out precipitates or other conveyance cleaning tasks.

Continuously-primed siphons (CPS) may be used within a compartmentalized wetland to control short circuiting or to provide low-tech passive flow or level control. Such devices, as shown on Figure 53, may be used to balance or distribute flows among various wetland components. The upper "U" of the CPS should be protected against freezing; the only other constraint to operation is that the elevation of the lower "U's" must be equal.





NOT TO SCALE

Figure 53. A cross-section view of a constant-prime siphon

SECTION 12

WETLAND DESIGN METHODOLOGIES

This section concentrates on the design of anaerobic wetland systems in which the best treatment occurs when contaminated water flows through the substrate. On the other hand, aerobic wetland treatment relies on the water flowing across the surface of the system. There are large differences in design of aerobic and anaerobic systems. For design ideas on aerobic systems, referral to the papers by Brodie (55, 68, 69, 72, 117) is strongly suggested. For anaerobic systems, this chapter uses the key principles associated with sulfate that were developed in the THEORETICAL DEVELOPMENT part of this handbook and applies them to design of passive bioreactors.

Besides the basic hydrologic design approach (storm/runoff routing) that is necessary to assure that a wetland can handle design flows, other methodologies may be applied to satisfy geochemical/bacteriological constraints.

Design size/configuration of wetlands may be based on:

- o Area/flux - this is based on Darcy's Law.
- o Precipitated metal mass loading - independent of void ratio, substrate should be capable of daily loadings of about 300 nanomoles of metals per cubic centimeter. pH values associated with mass loading above this value may overwhelm sulfate-reducing bacteria.
- o Precipitated metal volumetric loading - filling of void spaces in the substrate.
- o Self sustaining capability - surface area is large enough to allow dying plants to replenish organic material to support a suitable void ratio.
- o Water balance - evapotranspiration can contribute to wetlands metal removal efficiency in warmer climates.
- o Sulfate reducing stoichiometry and its effects on substrate carbon content.

A brief discussion of each design methodology follows.

AREA/FLUX METHOD

The application of Darcy's Law is the physical foundation of wetland design, as the typical wetland flows can be characterized as laminar flow through porous, saturated media (substrate).

Darcy's Law (see equation below) relates the flow (Q) to the cross sectional area (A) perpendicular to the fluid flow direction, the hydraulic gradient (i) and the permeability of the media (K) as follows:

$$Q = K * i * A = K * (dH/L) * A$$

where: Q is flowrate (cubic centimeters per second)

K is hydraulic conductivity (centimeters [cm] per second)

dH is value of constant head, cm, needed to maintain a sustained flowrate, Q

L is the length of the specimen, cm

A is cross section area perpendicular to the flow path (square cm)

Ivanov (100) reported that permeability varies with depth in the wetland, but since flow directions are perpendicular to the wetland surface, the effects of minor variations are masked and the flow of water is restricted by the smallest permeability value in the substrate column. Typically, permeability would be expected to decrease with depth, as the pore/void spaces in the substrate are influenced by increasing static pressure from overlying substrate. Ivanov reported that humification of the substrate also significantly affects substrate permeability as shown in Table 27.

The hydraulic gradient is a variable that is a function of the depth of substrate, L, and the loss of driving head from friction, dH, as the flow passes through the substrate media.

The value of L for wetlands typically ranges from two to five feet, the nominal substrate depth; the value of K for substrate ranges from 10^{-2} to 10^{-5} cm/sec for upflow or downflow cells; the area, A is the surface area of the wetland; i, the hydraulic gradient across the substrate, is typically assumed to be no greater than 1.0 because ponding on the surface of the wetland should be avoided to preserve anaerobic conditions. However, hydraulic considerations in a "closed" system could require a hydraulic gradient greater than 1.0 while anaerobic conditions are preserved by other means.

Table 30 presents a mathematical application of Darcy's Law using typical wetland design parameters. The "spreadsheet" presentation of Darcy's equation allows the evaluation of many possible incremental changes in the variable parameters of flow, permeability, substrate depth and surface area. Lotus 123™ was used for the spreadsheet calculations. Cell formulas are included on the Tables to allow designers to develop similar tools.

Table 30 includes several derived parameters, including flow flux, F, otherwise called the hydraulic loading factor (SECTION 7). Many wetland researchers employ this flow flux as a key indicator of wetland performance. A dimensional analysis of flux units as presented in Table 30; i.e., square feet per gallon per minute (sf/gpm), reveals that the flux unit is the reciprocal of velocity, as discussed in SECTION 7. On the other hand, the unit for permeability is velocity (cm/sec). In Table 30 at a hydraulic gradient of 1.0, flux units are actually the inverse of permeability. For example, 800 sf/gpm can be converted mathematically to the value $1 / 8.5 \times 10^{-5}$ cm/sec (1/K).

Caution should be exercised in comparing flux values for aerobic and anaerobic wetlands. The surface area cited in aerobic system flux discussions is the area of the wetland. However, the flux of water is across and not through this surface. A Darcian analysis of flow is usually not included in aerobic wetland design (55, 68, 69, 72, 117). If a Darcian analysis of an aerobic system was to be done, the appropriate

TABLE 30 ESTIMATE OF PRESSURE DROP ACROSS AND UPFLOW OR DOWNFLOW
WETLAND CELL USING DARCY'S LAW

Deltas ----->		1 gpm		90 %		0 ft		800 sq-ft			
(SEE NOTE 1)		*=variables									
	*			*	*				*	S	D
	Q	Q	F	K	L	dH	dH	i	A	SQUARE	CIRCLE
NOTES	FLOW	FLOW	FLUX	PERMEABLTY	DEPTH	HEADLOSS	HDLOSS	GRADIENT	AREA	SIDE L	DIA
	gpm	cfs	sf/gpm	cm/sec	feet	feet	inches	ft/ft	sq-ft	ft	ft
=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====
Initial value	1.0	2.2E-03	800	3.5E-04	6.0	1.46	17.5	0.24	800	28	32
	2.0	4.5E-03	800	3.2E-04	6.0	1.62	19.4	0.27	1600	40	45
	3.0	6.7E-03	800	2.8E-04	6.0	1.80	21.6	0.30	2400	49	55
	4.0	8.9E-03	800	2.6E-04	6.0	2.00	24.0	0.33	3200	57	64
	5.0	1.1E-02	800	2.3E-04	6.0	2.22	26.6	0.37	4000	63	71
	6.0	1.3E-02	800	2.1E-04	6.0	2.46	29.6	0.41	4800	69	78
	7.0	1.6E-02	800	1.9E-04	6.0	2.74	32.9	0.46	5600	75	84
	8.0	1.8E-02	800	1.7E-04	6.0	3.04	36.5	0.51	6400	80	90
	9.0	2.0E-02	800	1.5E-04	6.0	3.38	40.6	0.56	7200	85	96
	10.0	2.2E-02	800	1.4E-04	6.0	3.76	45.1	0.63	8000	89	101
	11.0	2.5E-02	800	1.2E-04	6.0	4.17	50.1	0.70	8800	94	106
	12.0	2.7E-02	800	1.1E-04	6.0	4.64	55.6	0.77	9600	98	111
	13.0	2.9E-02	800	9.9E-05	6.0	5.15	61.8	0.86	10400	102	115
	14.0	3.1E-02	800	8.9E-05	6.0	5.72	68.7	0.95	11200	106	119
	15.0	3.3E-02	800	8.0E-05	6.0	6.36	76.3	1.06	12000	110	124
	16.0	3.6E-02	800	7.2E-05	6.0	7.07	84.8	1.18	12800	113	128
	17.0	3.8E-02	800	6.5E-05	6.0	7.85	94.2	1.31	13600	117	132
	18.0	4.0E-02	800	5.8E-05	6.0	8.73	104.7	1.45	14400	120	135
	19.0	4.2E-02	800	5.3E-05	6.0	9.70	116.3	1.62	15200	123	139
	20.0	4.5E-02	800	4.7E-05	6.0	10.77	129.3	1.80	16000	126	143
	21.0	4.7E-02	800	4.3E-05	6.0	11.97	143.6	1.99	16800	130	146
	22.0	4.9E-02	800	3.8E-05	6.0	13.30	159.6	2.22	17600	133	150
	23.0	5.1E-02	800	3.4E-05	6.0	14.78	177.3	2.46	18400	136	153
	24.0	5.3E-02	800	3.1E-05	6.0	16.42	197.0	2.74	19200	139	156
	B	C	D	E	G	H	I	J	K	L	M
CELL FORMULAS											
COLUMNS	INITIAL VALUES (ROW 14)				VARIABLE VALUES (ROW 15, ETC.)						
=====	=====				=====						
B	1				+B14+\$B\$7						
C	+B14*0.002228				+B15*0.002228						
D	+K14/B14				+K15/B15						
E	0.00035				+E15*\$E\$7/100						
G	6				+G15+\$G\$7						
H	+C14*G14/(K14*(E14/30.48))				+C15*G15/(K15*(E15/30.48))						
I	+H14*12				+H15*12						
J	+C14/((E14/30.48)*K14)				+C15/((E15/30.48)*K15)						
K	800				+K15+\$K\$7						
L	=SQRT(K14)				=SQRT(K15)						
M	=SQRT(4*K14/\$PI)				=SQRT(4*K15/\$PI)						

NOTE 1: DELTA VALUES ARE INCREMENTAL VALUES ADDED TO OR MULTIPLIED BY THE INITIAL
VALUES TO GENERATE VARIABLE VALUES AND HENCEFORTH THE TABLE

* = USER INPUT INITIAL AND DELTA VALUES

area to us would probably be calculated by multiplying the depth of the wetland by the breadth (109). The area value in anaerobic system flux calculations (using upflow or downflow) and Darcian analysis is the same; i.e., the surface area of the wetland, which is perpendicular to fluid flow direction.

Other derived parameters in Table 30 include uniform shape (square and circle) wetland dimensions of side length, S, and circle diameter, D, respectively. These provide a rough perception of wetland cell dimensions.

An explanation of flow flux rate nomenclature is appropriate at this point for clarification. For the purposes of discussion, flux rates associated with high flow velocities through substrate are defined as "high flux rates". Flux rates associated with low flow velocities through substrate are defined as "low flux rates". Numerically, the opposite is true. Thus, a flux rate of 400 sf/gpm is a high flux rate when compared to a flux rate of 800 sf/gpm because the flow velocity associated with 400 sf/gpm is higher than the flow velocity associated with 800 sf/gpm for an identically-sized wetland.

Flow flux rate adjusted by metals concentration may provide a benchmark criterion for wetland performance with respect to sulfate reducing bacterial efficiency. However, the mechanism responsible may not be metals concentration alone; it appears that the viability of sulfate reducing bacteria is sensitive to substrate pH. pH values of less than 5 standard units cause stress in sulfate-reducing bacteria (99). High fluxes, especially those with acidic characteristics, may result in a dilution of more-neutral waters in the substrate which are favorable to sulfate-reducing bacteria and a reduction in metals reduction efficiency.

Dissolved metals concentration in acidic drainage is closely related to pH. Typically, the lower the pH of the water, the more metals in solution. Accordingly, some workers have focused on metals concentration effects on wetland performance, as discussed in SECTION 7, in the subsection Area Adjusted Loadings and Removal.

Therefore, wetland performance from a chemical perspective may be a function of total metals concentration/pH flux because sulfate reducing bacteria may be overwhelmed by the metals toxicity/pH changes and not perform optimally. For example, in the Big Five Wetlands (99), sulfate reducing bacteria performance appears to decrease when exposed to flux rates less than 800 sf/gpm at about 80 mg/liter total dissolved metals.

From a physical/hydrologic perspective, the lower limit of flux rate will be a value necessary to preclude substrate desiccation. The maximum achievable flux rate may be a function of the practical working permeability of the substrate. For example, the nominal flux is inherently low for a substrate with a low permeability; this flux may satisfy wetland design criteria if the metals content is excessively high (with accompanying low pH) in the feed water. For substrate with a high predicted permeability, flux may need to be physically controlled by varying area and/or unit flow rates to the cell to satisfy chemical criteria as described in the preceding paragraphs.

TABLE 31 ESTIMATE OF PRESSURE DROP AND METAL LOADING ACROSS
UPFLOW OR DOWNFLOW WETLAND CELLS OF VARIOUS DEPTHS

Deltas -----> (SEE NOTE 1)	0 gpm									METAL LOADING * CRITERIA		
	100 % 0.1 ft									0 sq-ft total		
										metals-> 100 mg/liter		
NOTES	Q	Q	F	K	L	dH	dH	i	A	V	Lm	Qm
	FLOW	FLOW	FLUX	PERMEABTY	DEPTH	HEADLOSS	HDLOSS	GRADIENT	AREA	VOLUME	nanomoles/	Qm
	gpm	cfs	sf/gpm	cm/sec	feet	feet	inches	ft/ft	sq-ft	cc's	day	(Lm/V)
=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====
Initial value	1.0	2.2E-03	800	3.5E-04	1.0	0.24	2.9	0.24	800	2.3E+07	9.9E+09	437
	1.0	2.2E-03	800	3.5E-04	1.1	0.27	3.2	0.24	800	2.5E+07	9.9E+09	398
	1.0	2.2E-03	800	3.5E-04	1.2	0.29	3.5	0.24	800	2.7E+07	9.9E+09	364
	1.0	2.2E-03	800	3.5E-04	1.3	0.32	3.8	0.24	800	2.9E+07	9.9E+09	336
	1.0	2.2E-03	800	3.5E-04	1.4	0.34	4.1	0.24	800	3.2E+07	9.9E+09	312
-----	1.0	2.2E-03	800	3.5E-04	1.5	0.36	4.4	0.24	800	3.4E+07	9.9E+09	292
THESE CONFIGS	1.0	2.2E-03	800	3.5E-04	1.6	0.39	4.7	0.24	800	3.6E+07	9.9E+09	273
WOULD WORK	1.0	2.2E-03	800	3.5E-04	1.7	0.41	4.9	0.24	800	3.9E+07	9.9E+09	257
BASED ON	1.0	2.2E-03	800	3.5E-04	1.8	0.44	5.2	0.24	800	4.1E+07	9.9E+09	243
METAL LOADING	1.0	2.2E-03	800	3.5E-04	1.9	0.46	5.5	0.24	800	4.3E+07	9.9E+09	230
	1.0	2.2E-03	800	3.5E-04	2.0	0.49	5.8	0.24	800	4.5E+07	9.9E+09	219
	1.0	2.2E-03	800	3.5E-04	2.1	0.51	6.1	0.24	800	4.8E+07	9.9E+09	208
	1.0	2.2E-03	800	3.5E-04	2.2	0.53	6.4	0.24	800	5.0E+07	9.9E+09	199
	1.0	2.2E-03	800	3.5E-04	2.3	0.56	6.7	0.24	800	5.2E+07	9.9E+09	190
	1.0	2.2E-03	800	3.5E-04	2.4	0.58	7.0	0.24	800	5.4E+07	9.9E+09	182
	1.0	2.2E-03	800	3.5E-04	2.5	0.61	7.3	0.24	800	5.7E+07	9.9E+09	175
	1.0	2.2E-03	800	3.5E-04	2.6	0.63	7.6	0.24	800	5.9E+07	9.9E+09	168
	1.0	2.2E-03	800	3.5E-04	2.7	0.65	7.9	0.24	800	6.1E+07	9.9E+09	162
	1.0	2.2E-03	800	3.5E-04	2.8	0.68	8.1	0.24	800	6.3E+07	9.9E+09	156
	1.0	2.2E-03	800	3.5E-04	2.9	0.70	8.4	0.24	800	6.6E+07	9.9E+09	151
-----	1.0	2.2E-03	800	3.5E-04	3.0	0.73	8.7	0.24	800	6.8E+07	9.9E+09	146
TYPICAL	1.0	2.2E-03	800	3.5E-04	3.1	0.75	9.0	0.24	800	7.0E+07	9.9E+09	141
DEPTHS	1.0	2.2E-03	800	3.5E-04	3.2	0.78	9.3	0.24	800	7.3E+07	9.9E+09	137
COLUMNS-->	B	C	D	E	G	H	I	J	K	M	N	O

CELL FORMULAS

PARAMETER	COLUMNS	INITIAL VALUES (ROW 14)	VARIABLE VALUES (ROW 15, ETC.)	COMMENTS:
=====	=====	=====	=====	=====
Q, FLOW, gpm	B	1	+B14+\$B\$7	CONSTANT Q, F, A, K
Q, FLOW, cfs	C	+B14*0.002228	+B15*0.002228	VARY L
F, FLUX, sf/gpm	D	+K14/B14	+K15/B15	OBSERVE Qm < 300
K, cm/sec	E	0.00035	+E15*\$E\$7/100	
L, DEPTH, ft	G	1	+G15+\$G\$7	
dH, HDLOSS, ft	H	+C14*G14/(K14*(E14/30.48))	+C15*G15/(K15*(E15/30.48))	
dH, HDLOSS, in	I	+H14*12	+H15*12	
i, GRDNT, ft/ft	J	+C14/((E14/30.48)*K14)	+C15/((E15/30.48)*K15)	
A, AREA, sq-ft	K	800	+K15+\$K\$7	
V, VOLUME, cc's	M	+K14*G14*1000/0.03531	+K15*G15*1000/0.03531	
Lm, LOADG, nm/d	N	+B14*5450.4*\$N\$8/(55*0.000001)	+B15*5450.4*\$N\$8/(55*0.000001)	
LOAD/VOLUME	O	+N14/M14	+N15/M15	

NOTE 1: DELTA VALUES ARE INCREMENTAL VALUES ADDED TO OR MULTIPLIED BY THE INITIAL
VALUES TO GENERATE THE TABLE

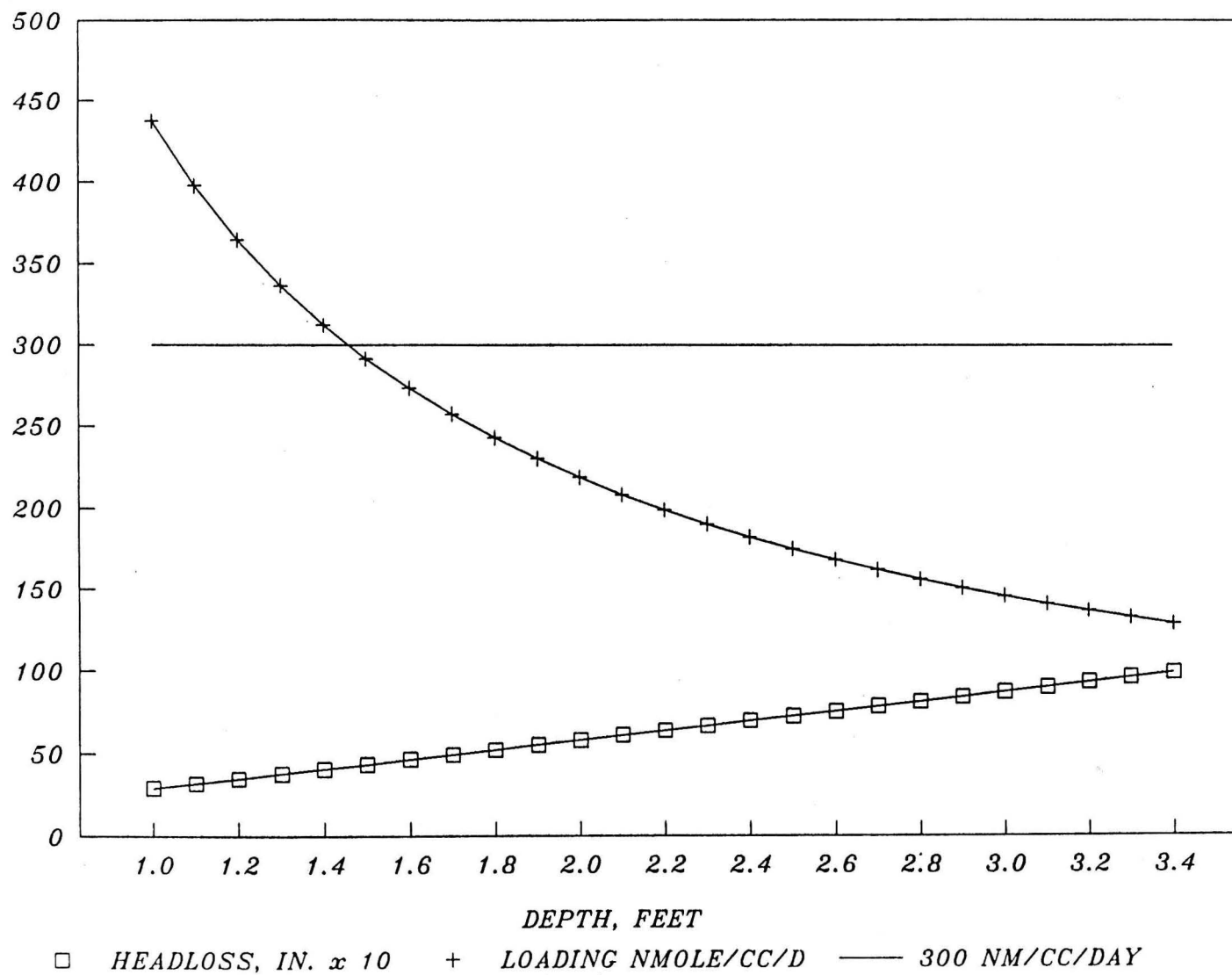


Figure 54. Changes in loading and head losses as depth varies in substrate. The values plotted are from Table 31.

TABLE 32 MODIFICATION OF TABLE 31 TO DETERMINE MINIMUM PERMEABILITY

Deltas -----> (SEE NOTE 1)										METAL LOADING CRITERIA * total metals-> 100 mg/liter		
0 gpm 90 % 0 ft 0 sq-ft												
NOTES	* Q FLOW gpm	* Q FLOW cfs	* F FLUX sf/gpm	* K PERMEABILITY cm/sec	* L DEPTH feet	dH HEADLOSS feet	dH HDLOSS inches	i GRADIENT ft/ft	* A AREA sq-ft	V VOLUME cc's	Lm nanomoles/ day	Qm (Lm/V) (Lm/V)
=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====
Initial value	1.0	2.2E-03	800	3.5E-04	1.5	0.36	4.4	0.24	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	3.2E-04	1.5	0.40	4.9	0.27	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	2.8E-04	1.5	0.45	5.4	0.30	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	2.6E-04	1.5	0.50	6.0	0.33	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	2.3E-04	1.5	0.55	6.7	0.37	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	2.1E-04	1.5	0.62	7.4	0.41	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	1.9E-04	1.5	0.68	8.2	0.46	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	1.7E-04	1.5	0.76	9.1	0.51	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	1.5E-04	1.5	0.85	10.1	0.56	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	1.4E-04	1.5	0.94	11.3	0.63	800	3.4E+07	9.9E+09	292
THESE CONFIGURATNS WOULD WORK	1.0	2.2E-03	800	1.2E-04	1.5	1.04	12.5	0.70	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	1.1E-04	1.5	1.16	13.9	0.77	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	9.9E-05	1.5	1.29	15.5	0.86	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	8.9E-05	1.5	1.43	17.2	0.95	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	8.0E-05	1.5	1.59	19.1	1.06	800	3.4E+07	9.9E+09	292
THESE CONFIGURATNS WOULD NOT WORK, HEADLOSS IS GREATER THAN L	1.0	2.2E-03	800	7.2E-05	1.5	1.77	21.2	1.18	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	6.5E-05	1.5	1.96	23.6	1.31	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	5.8E-05	1.5	2.18	26.2	1.45	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	5.3E-05	1.5	2.42	29.1	1.62	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	4.7E-05	1.5	2.69	32.3	1.80	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	4.3E-05	1.5	2.99	35.9	1.99	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	3.8E-05	1.5	3.32	39.9	2.22	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	3.4E-05	1.5	3.69	44.3	2.46	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	3.1E-05	1.5	4.10	49.3	2.74	800	3.4E+07	9.9E+09	292
	1.0	2.2E-03	800	2.8E-05	1.5	4.56	54.7	3.04	800	3.4E+07	9.9E+09	292
COLUMNS-->	B	C	D	E	G	H	I	J	K	M	N	O
CELL FORMULAS												
PARAMETER	COLUMNS	INITIAL VALUES (ROW 14)			VARIABLE VALUES (ROW 15, ETC.)					COMMENTS:		
=====	=====	=====			=====					=====		
Q, FLOW, gpm	B	1			+B14+\$B\$7					CONSTANT Q, F, A, Qm		
Q, FLOW, cfs	C	+B14*0.002228			+B15*0.002228					VARY K		
F, FLUX, sf/gpm	D	+K14/B14			+K15/B15					OBSERVE i <= 1		
K, cm/sec	E	0.00035			+E15*\$E\$7/100							
L, DEPTH, ft	G	1.5			+G15+\$G\$7							
dH, HDLOSS, ft	H	+C14*G14/(K14*(E14/30.48))			+C15*G15/(K15*(E15/30.48))							
dH, HDLOSS, in	I	+H14*12			+H15*12							
i, GRDNT, ft/ft	J	+C14/((E14/30.48)*K14)			+C15/((E15/30.48)*K15)							
A, AREA, sq-ft	K	800			+K15+\$K\$7							
V, VOLUME, cc's	M	+K14*G14*1000/0.03531			+K15*G15*1000/0.03531							
Lm, LOADG, nm/d	N	+B14*5450.4*\$N\$8/(55*0.000001)			+B15*5450.4*\$N\$8/(55*0.000001)							
LOAD/VOLUME	O	+N14/M14			+N15/M15							

NOTE 1: DELTA VALUES ARE INCREMENTAL VALUES ADDED TO OR MULTIPLIED BY THE INITIAL VALUES TO GENERATE THE TABLE

* = USER INPUT INITIAL AND DELTA VALUES

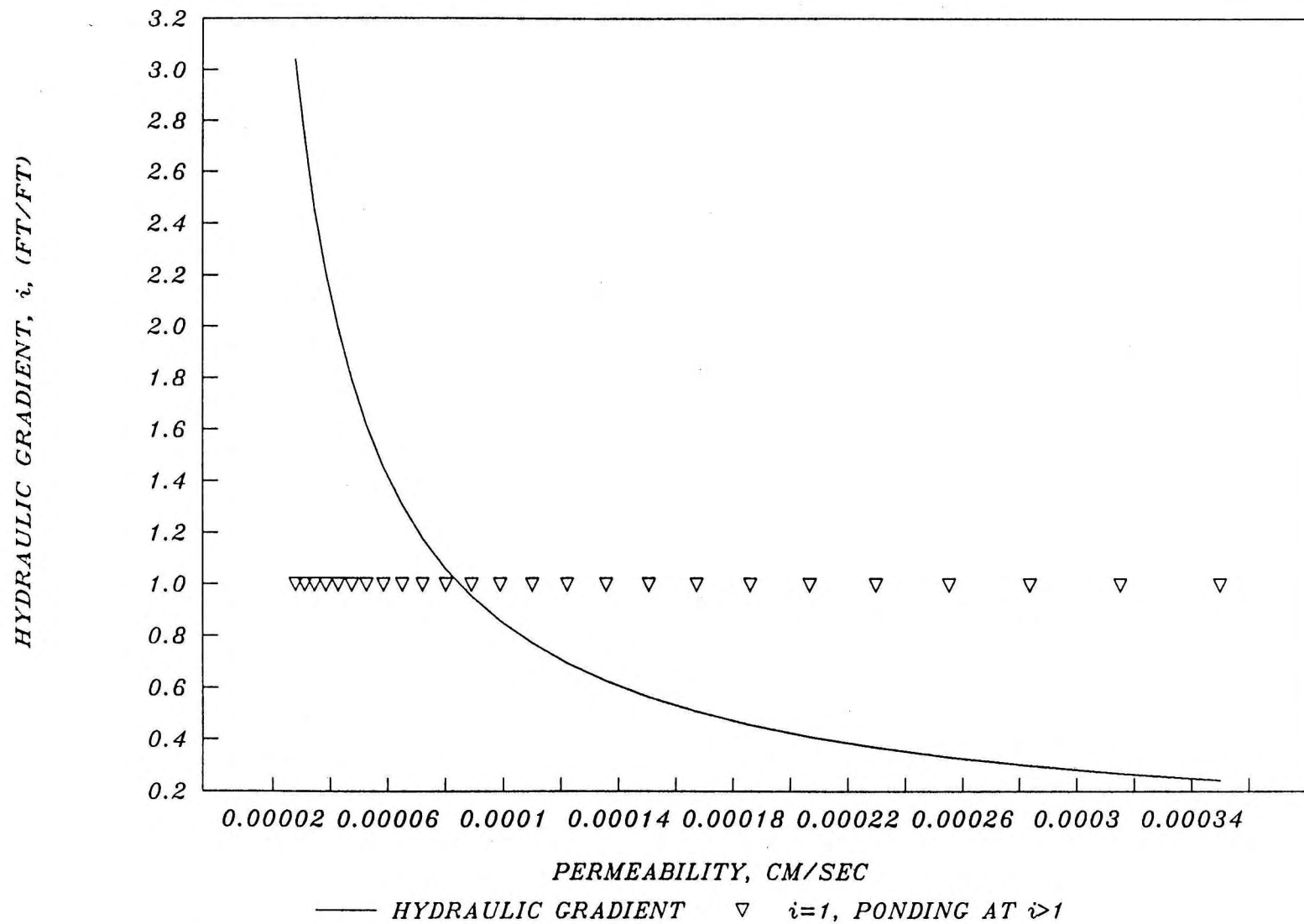


Figure 55. Changes in hydraulic gradient with varying permeability. The values plotted are from Table 32.

TABLE 33 MODIFICATION OF TABLE 31 TO A DEPTH OF 3 FEET

										METAL LOADING CRITERIA		
										* total		
										metals-> 100 mg/liter		
										* 0 sq-ft		
										0 gpm		
										90 % 0 ft		
										Deltas -----> (SEE NOTE 1)		
NOTES	Q	Q	F	K	L	dH	dH	i	A	V	Lm	Qm
	FLOW	FLOW	FLUX	PERMEABLT	DEPTH	HEADLOSS	HDLOSS	GRADIENT	AREA			
	gpm	cfs	sf/gpm	cm/sec	feet	feet	inches	ft/ft	sq-ft	cc's	nanomoles/day	(Lm/V)
=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====
Initial value	1.0	2.2E-03	400	3.5E-04	3.0	1.46	17.5	0.49	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	3.2E-04	3.0	1.62	19.4	0.54	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	2.8E-04	3.0	1.80	21.6	0.60	400	3.4E+07	9.9E+09	292
THESE	1.0	2.2E-03	400	2.6E-04	3.0	2.00	24.0	0.67	400	3.4E+07	9.9E+09	292
CONFIGURATNS	1.0	2.2E-03	400	2.3E-04	3.0	2.22	26.6	0.74	400	3.4E+07	9.9E+09	292
WOULD WORK	1.0	2.2E-03	400	2.1E-04	3.0	2.46	29.6	0.82	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	1.9E-04	3.0	2.74	32.9	0.91	400	3.4E+07	9.9E+09	292
THESE	1.0	2.2E-03	400	1.7E-04	3.0	3.04	36.5	1.01	400	3.4E+07	9.9E+09	292
CONFIGURATNS	1.0	2.2E-03	400	1.5E-04	3.0	3.38	40.6	1.13	400	3.4E+07	9.9E+09	292
WOULD NOT	1.0	2.2E-03	400	1.4E-04	3.0	3.76	45.1	1.25	400	3.4E+07	9.9E+09	292
WORK, HEADLOSS	1.0	2.2E-03	400	1.2E-04	3.0	4.17	50.1	1.39	400	3.4E+07	9.9E+09	292
IS GREATER	1.0	2.2E-03	400	1.1E-04	3.0	4.64	55.6	1.55	400	3.4E+07	9.9E+09	292
THAN L	1.0	2.2E-03	400	9.9E-05	3.0	5.15	61.8	1.72	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	8.9E-05	3.0	5.72	68.7	1.91	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	8.0E-05	3.0	6.36	76.3	2.12	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	7.2E-05	3.0	7.07	84.8	2.36	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	6.5E-05	3.0	7.85	94.2	2.62	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	5.8E-05	3.0	8.73	104.7	2.91	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	5.3E-05	3.0	9.70	116.3	3.23	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	4.7E-05	3.0	10.77	129.3	3.59	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	4.3E-05	3.0	11.97	143.6	3.99	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	3.8E-05	3.0	13.30	159.6	4.43	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	3.4E-05	3.0	14.78	177.3	4.93	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	3.1E-05	3.0	16.42	197.0	5.47	400	3.4E+07	9.9E+09	292
	1.0	2.2E-03	400	2.8E-05	3.0	18.24	218.9	6.08	400	3.4E+07	9.9E+09	292
COLUMNS-->	B	C	D	E	G	H	I	J	K	M	N	O

CELL FORMULAS

PARAMETER COLUMNS INITIAL VALUES (ROW 14)

=====

Q, FLOW, gpm	B	1
Q, FLOW, cfs	C	+B14*0.002228
F, FLUX, sf/gpm	D	+K14/B14
K, cm/sec	E	0.00035
L, DEPTH, ft	G	3
dH, HDLOSS, ft	H	+C14*G14/((K14*(E14/30.48))
dH, HDLOSS, in	I	+H14*12
i, GRDNT, ft/ft	J	+C14/((E14/30.48)*K14)
A, AREA, sq-ft	K	400
V, VOLUME, cc's	M	+K14*G14*1000/0.03531
Lm, LOADG, nm/d	N	+B14*5450.4*\$N\$8/(55*0.000001)
LOAD/VOLUME	O	+N14/M14

VARIABLE VALUES (ROW 15, ETC.)

=====

+B14+\$B\$7
+B15*0.002228
+K15/B15
+E15*\$E\$7/100
+G15+\$G\$7
+C15*G15/((K15*(E15/30.48))
+H15*12
+C15/((E15/30.48)*K15)
+K15+\$K\$7
+K15*G15*1000/0.03531
+B15*5450.4*\$N\$8/(55*0.000001)
+N15/M15

COMMENTS:

=====

CONSTANT Q, Qm, V
VARY K,
HALVE AREA, A
DOUBLE DEPTH, L
OBSERVE i < /= 1

NOTE 1: DELTA VALUES ARE INCREMENTAL VALUES ADDED TO OR MULTIPLIED BY THE INITIAL VALUES TO GENERATE THE TABLE

* = USER INPUT INITIAL AND DELTA VALUES

TABLE 34 MODIFICATION OF TABLES 31 AND 33 ALLOWING
FLOW AND FLUX TO VARY

Deltas -----> (SEE NOTE 1)										1 gpm	100 %	0 ft	400 sq-ft	* total metals-->	METAL LOADING CRITERIA 100 mg/lit
NOTES	* Q FLOW gpm	* Q FLOW cfs	* F FLUX sf/gpm	* K PERMEABILITY cm/sec	* L DEPTH feet	dH HEADLOSS feet	dH HDLOSS inches	i GRADIENT ft/ft	* A AREA sq-ft	V VOLUME cc's	Lm nanomoles/ day	Qm (Lm/V (Lm/V			
=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====			
Initial value	20.0	4.5E-02	400	1.9E-04	3.0	2.68	32.2	0.89	8000	6.8E+08	2.0E+11	29%			
	21.0	4.7E-02	400	1.9E-04	3.0	2.68	32.2	0.89	8400	7.1E+08	2.1E+11	29%			
	22.0	4.9E-02	400	1.9E-04	3.0	2.68	32.2	0.89	8800	7.5E+08	2.2E+11	29%			
ALL	23.0	5.1E-02	400	1.9E-04	3.0	2.68	32.2	0.89	9200	7.8E+08	2.3E+11	29%			
CONFIGURATNS	24.0	5.3E-02	400	1.9E-04	3.0	2.68	32.2	0.89	9600	8.2E+08	2.4E+11	29%			
WOULD WORK	25.0	5.6E-02	400	1.9E-04	3.0	2.68	32.2	0.89	10000	8.5E+08	2.5E+11	29%			
	26.0	5.8E-02	400	1.9E-04	3.0	2.68	32.2	0.89	10400	8.8E+08	2.6E+11	29%			
	27.0	6.0E-02	400	1.9E-04	3.0	2.68	32.2	0.89	10800	9.2E+08	2.7E+11	29%			
	28.0	6.2E-02	400	1.9E-04	3.0	2.68	32.2	0.89	11200	9.5E+08	2.8E+11	29%			
	29.0	6.5E-02	400	1.9E-04	3.0	2.68	32.2	0.89	11600	9.9E+08	2.9E+11	29%			
	30.0	6.7E-02	400	1.9E-04	3.0	2.68	32.2	0.89	12000	1.0E+09	3.0E+11	29%			
	31.0	6.9E-02	400	1.9E-04	3.0	2.68	32.2	0.89	12400	1.1E+09	3.1E+11	29%			
	32.0	7.1E-02	400	1.9E-04	3.0	2.68	32.2	0.89	12800	1.1E+09	3.2E+11	29%			
	33.0	7.4E-02	400	1.9E-04	3.0	2.68	32.2	0.89	13200	1.1E+09	3.3E+11	29%			
	34.0	7.6E-02	400	1.9E-04	3.0	2.68	32.2	0.89	13600	1.2E+09	3.4E+11	29%			
	35.0	7.8E-02	400	1.9E-04	3.0	2.68	32.2	0.89	14000	1.2E+09	3.5E+11	29%			
	36.0	8.0E-02	400	1.9E-04	3.0	2.68	32.2	0.89	14400	1.2E+09	3.6E+11	29%			
UPPER LIMIT	37.0	8.2E-02	400	1.9E-04	3.0	2.68	32.2	0.89	14800	1.3E+09	3.7E+11	29%			
DESIGN FLOWS	38.0	8.5E-02	400	1.9E-04	3.0	2.68	32.2	0.89	15200	1.3E+09	3.8E+11	29%			
----->	39.0	8.7E-02	400	1.9E-04	3.0	2.68	32.2	0.89	15600	1.3E+09	3.9E+11	29%			
	40.0	8.9E-02	400	1.9E-04	3.0	2.68	32.2	0.89	16000	1.4E+09	4.0E+11	29%			
	41.0	9.1E-02	400	1.9E-04	3.0	2.68	32.2	0.89	16400	1.4E+09	4.1E+11	29%			
	42.0	9.4E-02	400	1.9E-04	3.0	2.68	32.2	0.89	16800	1.4E+09	4.2E+11	29%			
	43.0	9.6E-02	400	1.9E-04	3.0	2.68	32.2	0.89	17200	1.5E+09	4.3E+11	29%			
	44.0	9.8E-02	400	1.9E-04	3.0	2.68	32.2	0.89	17600	1.5E+09	4.4E+11	29%			
COLUMNS-->	B	C	D	E	G	H	I	J	K	M	N	O			
CELL FORMULAS															
PARAMETER	COLUMNS	INITIAL VALUES (ROW 14)				VARIABLE VALUES (ROW 15, ETC.)				COMMENTS:					
=====	=====	=====				=====				=====					
Q, FLOW, gpm	B	20				+B14+\$B\$7				CONSTANT F, Qm, L, K, dH, i					
Q, FLOW, cfs	C	+B14*0.002228				+B15*0.002228				VARY Q & A					
F, FLUX, sf/gpm	D	+K14/B14				+K15/B15				OBSERVE ALL					
K, cm/sec	E	0.00019				+E15*\$E\$7/100				CRITERIA SATISFIED					
L, DEPTH, ft	G	3				+G15+\$G\$7									
dH, HDLOSS, ft	H	+C14*G14/(K14*(E14/30.48))				+C15*G15/(K15*(E15/30.48))									
dH, HDLOSS, in	I	+H14*12				+H15*12									
i, GRDNT, ft/ft	J	+C14/((E14/30.48)*K14)				+C15/((E15/30.48)*K15)									
A, AREA, sq-ft	K	400				+K15+\$K\$7									
V, VOLUME, cc's	M	+K14*G14*1000/0.03531				+K15*G15*1000/0.03531									
Lm, LOADG, nm/d	N	+B14*5450.4*\$N\$8/(55*0.000001)				+B15*5450.4*\$N\$8/(55*0.000001)									
LOAD/VOLUME	O	+N14/M14				+N15/M15									

NOTE 1: DELTA VALUES ARE INCREMENTAL VALUES ADDED TO OR MULTIPLIED BY THE INITIAL VALUES TO GENERATE THE TABLE

* = USER INPUT INITIAL AND DELTA VALUES

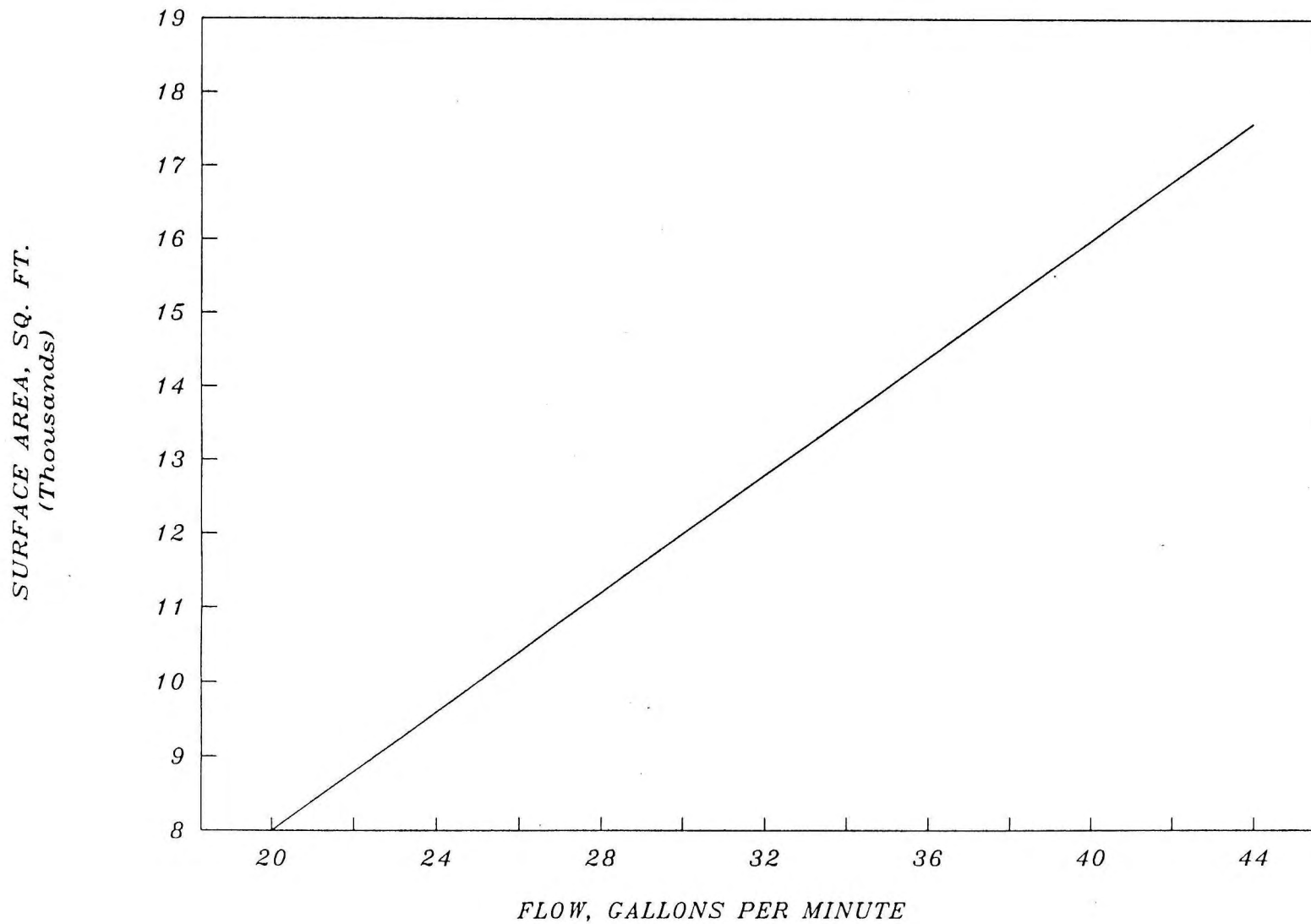


Figure 56. Changes in flow with area keeping all other variables constant. The values plotted are from Table 34.

METAL LOADING CRITERIA

CELL FORMULAS

PARAMETER	COLUMNS	INITIAL VALUES (ROW 14)	VARIABLE VALUES (ROW 15, ETC.)	COMMENTS:
=====	=====	=====	=====	=====
Q, FLOW, gpm	B	20	+B14+\$8\$7	VARY K, 1% LOSS FROM
Q, FLOW, cfs	C	+B14*0.002228	+B15*0.002228	COMPRESSION PER
F, FLUX, sf/gpm	D	+K14/B14	+K15/B15	ADDTNL 0.1 FT OF L
K, cm/sec	E	0.00019	+E15*\$E\$7/100	
L, DEPTH, ft	G	3	+G15+\$G\$7	
dH, HDLOSS, ft	H	+C14*G14/(K14*(E14/30.48))	+C15*G15/(K15*(E15/30.48))	
dH, HDLOSS, in	I	+H14*12	+H15*12	
i, GRDNT, ft/ft	J	+C14/((E14/30.48)*K14)	+C15/((E15/30.48)*K15)	
A, AREA, sq-ft	K	8000	+K15+\$K\$7	
V, VOLUME, cc's	M	+K14*G14*1000/0.03531	+K15*G15*1000/0.03531	
Lm, LOADG, nm/d	N	+B14*5450.4*\$N\$8/(55*0.000001)	+B15*5450.4*\$N\$8/(55*0.000001)	
LOAD/VOLUME	O	+N14/M14	+N15/M15	

12-12

* = USER INPUT INITIAL AND DELTA VALUES

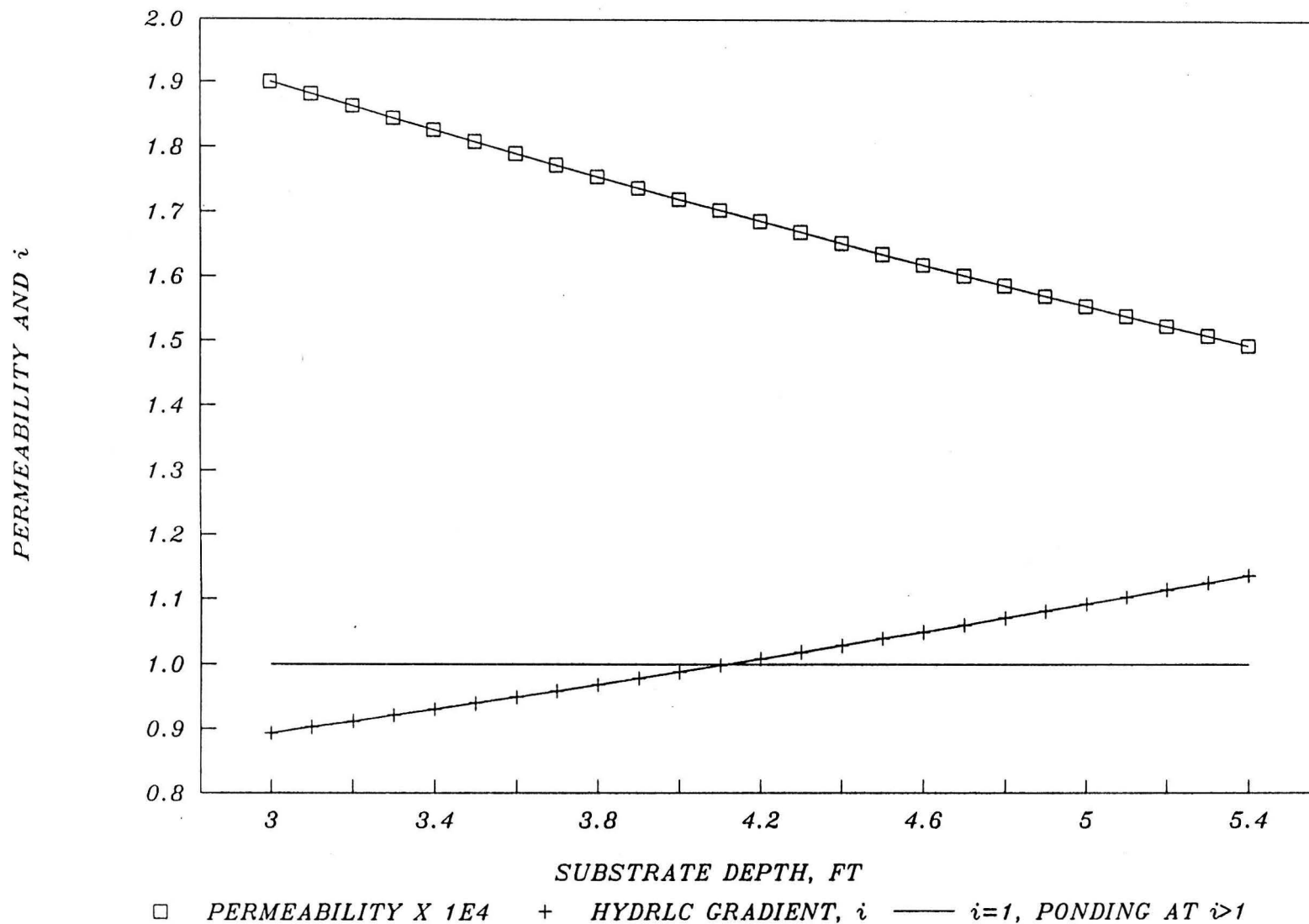


Figure 57. Decrease in permeability by one percent for each 0.1 feet of depth of substrate. When the hydraulic gradient is greater than one, ponding on the surface occurs. The values plotted are from Table 35.

TABLE 36 MODIFICATION OF TABLE 35 TO ALLOW FOR CHANGES IN
FLOW AND PERMEABILITY WITH VARYING DEPTH

METAL LOADING
CRITERIA

Deltas ----->	-0.1 gpm	99 % 0.1 ft							0 sq-ft	total	metals->		100 mg/lit
(SEE NOTE 1)													
	* Q FLOW gpm	* Q FLOW cfs	* F FLUX sf/gpm	* K PERMEABILITY cm/sec	* L DEPTH feet	* dH HEADLOSS feet	* dH HEADLOSS inches	* i GRADIENT ft/ft	* A AREA sq-ft		V VOLUME cc's	Lm nanomoles/ day	Qm (Lm/V) (Lm/V)
NOTES	=====	=====	=====	=====	=====	=====	=====	=====	=====		=====	=====	=====
Initial value	20.0	4.5E-02	400	1.9E-04	3.0	2.68	32.2	0.89	8000		6.8E+08	2.0E+11	29
	19.9	4.4E-02	402	1.9E-04	3.1	2.78	33.4	0.90	8000		7.0E+08	2.0E+11	28
	19.8	4.4E-02	404	1.9E-04	3.2	2.89	34.7	0.90	8000		7.3E+08	2.0E+11	27
	19.7	4.4E-02	406	1.8E-04	3.3	2.99	35.9	0.91	8000		7.5E+08	2.0E+11	26
	19.6	4.4E-02	408	1.8E-04	3.4	3.10	37.2	0.91	8000		7.7E+08	1.9E+11	25
	19.5	4.3E-02	410	1.8E-04	3.5	3.21	38.5	0.92	8000		7.9E+08	1.9E+11	24
	19.4	4.3E-02	412	1.8E-04	3.6	3.31	39.8	0.92	8000		8.2E+08	1.9E+11	23
	19.3	4.3E-02	415	1.8E-04	3.7	3.42	41.1	0.93	8000		8.4E+08	1.9E+11	22
	19.2	4.3E-02	417	1.8E-04	3.8	3.53	42.4	0.93	8000		8.6E+08	1.9E+11	22
	19.1	4.3E-02	419	1.7E-04	3.9	3.64	43.7	0.93	8000		8.8E+08	1.9E+11	21
	19.0	4.2E-02	421	1.7E-04	4.0	3.75	45.1	0.94	8000		9.1E+08	1.9E+11	20
	18.9	4.2E-02	423	1.7E-04	4.1	3.87	46.4	0.94	8000		9.3E+08	1.9E+11	20
	18.8	4.2E-02	426	1.7E-04	4.2	3.98	47.8	0.95	8000		9.5E+08	1.9E+11	19
	18.7	4.2E-02	428	1.7E-04	4.3	4.09	49.1	0.95	8000		9.7E+08	1.9E+11	19
	18.6	4.1E-02	430	1.7E-04	4.4	4.21	50.5	0.96	8000		1.0E+09	1.8E+11	18
	18.5	4.1E-02	432	1.6E-04	4.5	4.32	51.9	0.96	8000		1.0E+09	1.8E+11	18
	18.4	4.1E-02	435	1.6E-04	4.6	4.44	53.3	0.97	8000		1.0E+09	1.8E+11	17
	18.3	4.1E-02	437	1.6E-04	4.7	4.56	54.7	0.97	8000		1.1E+09	1.8E+11	17
	18.2	4.1E-02	440	1.6E-04	4.8	4.68	56.1	0.97	8000		1.1E+09	1.8E+11	16
	18.1	4.0E-02	442	1.6E-04	4.9	4.80	57.6	0.98	8000		1.1E+09	1.8E+11	16
	18.0	4.0E-02	444	1.6E-04	5.0	4.92	59.0	0.98	8000		1.1E+09	1.8E+11	15
WATER PONDING	17.9	4.0E-02	447	1.5E-04	5.1	5.04	60.4	0.99	8000		1.2E+09	1.8E+11	15
AT L=5.4 FEET	17.8	4.0E-02	449	1.5E-04	5.2	5.16	61.9	0.99	8000		1.2E+09	1.8E+11	15
Q=17.6 GPM	17.7	3.9E-02	452	1.5E-04	5.3	5.28	63.4	1.00	8000		1.2E+09	1.8E+11	14
	17.6	3.9E-02	455	1.5E-04	5.4	5.40	64.9	1.00	8000		1.2E+09	1.7E+11	14
COLUMNS-->	B	C	D	E	G	H	I	J	K		M	N	O

CELL FORMULAS

PARAMETER	COLUMNS	INITIAL VALUES (ROW 14)	VARIABLE VALUES (ROW 15, ETC.)	COMMENTS:
=====	=====	=====	=====	=====
Q, FLOW, gpm	B	20	+B14+\$B\$7	VARY K, 1% LOSS
Q, FLOW, cfs	C	+B14*0.002228	+B15*0.002228	FROM COMPRSN PER
F, FLUX, sf/gpm	D	+K14/B14	+K15/B15	0.1 FT OF L,
K, cm/sec	E	0.00019	+E15*\$E\$7/100	DECREASE FLOW
L, DEPTH, ft	G	3	+G15+\$G\$7	
dH, HDLOSS, ft	H	+C14*G14/(K14*(E14/30.48))	+C15*G15/(K15*(E15/30.48))	
dH, HDLOSS, in	I	+H14*12	+H15*12	
i, GRDNT, ft/ft	J	+C14/((E14/30.48)*K14)	+C15/((E15/30.48)*K15)	
A, AREA, sq-ft	K	8000	+K15+\$K\$7	
V, VOLUME, cc's	M	+K14*G14*1000/0.03531	+K15*G15*1000/0.03531	
Lm, LOADG, nm/d	N	+B14*5450.4*\$N\$8/(55*0.000001)	+B15*5450.4*\$N\$8/(55*0.000001)	
LOAD/VOLUME	O	+N14/M14	+N15/M15	

NOTE 1: DELTA VALUES ARE INCREMENTAL VALUES ADDED TO OR MULTIPLIED BY THE INITIAL
VALUES TO GENERATE THE TABLE

* = USER INPUT INITIAL AND DELTA VALUES

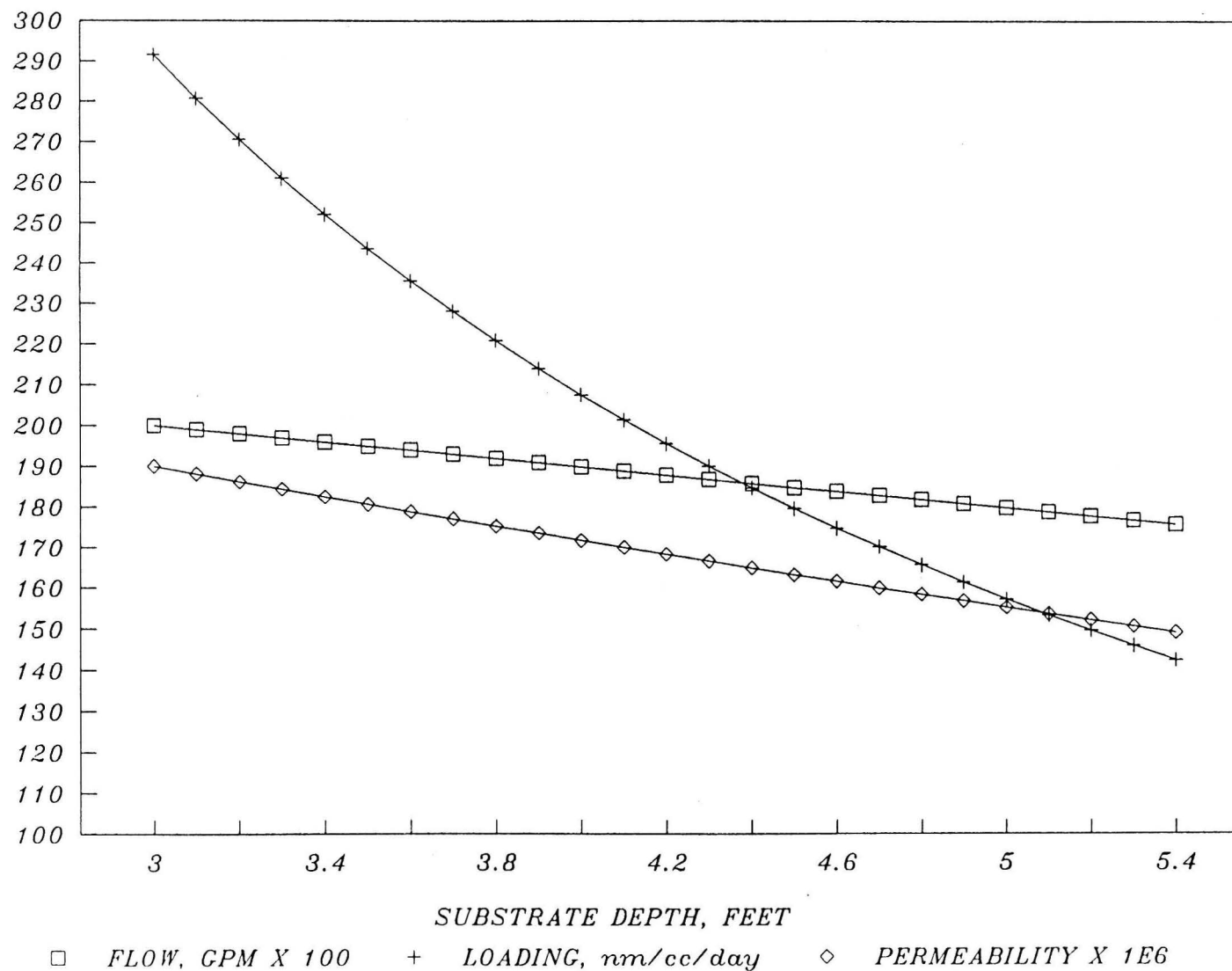


Figure 58. Changes in flow, permeability, and loading with increasing depth. Note the restriction that the hydraulic gradient has to be ≤ 1 . The values plotted are from Table 36.

MASS LOADING METHOD

U.S. Bureau of Mines studies (65, 67) have shown that the reaction rate of sulfate-reducing bacteria may have a limiting effect on wetland performance. For the US Bureau of Mines Friendship Hill wetland, a maximum sulfate reduction activity of nanomoles per cubic-centimeter per day (nmole/cc-day) was found. According to the discussion in SECTION 7, the loading of metals delivered to the wetland substrate should not exceed this value of 300 (nmole/cc-day). The Table 31 spreadsheet "sliderule/nomograph" can be used to select the size a particular "example" wetland using a particular metals loading value, which is Q_m in the Table.

The key input/operating parameters for the example site are:

- o 100 mg/liter of dissolved metals in feed water stream (iron/lead/copper/zinc/cadmium/manganese)
- o 20 to 40 gallons per minute of flow
- o Substrate initial permeability of 3.5×10^{-4} cm/sec
- o Flux may vary from 400 to 800 sf/gpm
- o Depth may vary from 3 to 6 feet based on topography
- o Site topography is not constraining (area available is large)
- o 300 nmoles/cc-day is the maximum mass loading rate - assume that metals average 55 grams/gram-mole (a conservative assumption). This is related to mg/liter of metal in the drainage.
- o To preserve anaerobic conditions, no ponding on the surface of the wetland is allowed; i.e., hydraulic gradient is less than 1.0
- o For each 0.1 foot of depth increase above 3 feet, permeability drops by one percent.

In Table 31, the flow rate, flux, area (by definition) and permeability are held constant; depth is varied to observed the configurations required to provide less than 300 nmoles/cc-day of loading (Q_m) in the last column). The spreadsheet assumes 100 percent removal of metals, which should be verified in lab or field scale tests. Figure 54 graphically presents some of the variables changing in Table 31. Table 31 shows that depths greater than 1.5 feet would satisfy this criteria. The Table indicates that the depth range of 3 to 6 feet, as chosen for our example wetland above, and labeled "Typical Depths" in the first column satisfies the loading rate criteria.

In Table 32, the flow rate, flux, area, depth, and mass loading rate are held constant and permeability is varied to determine the lower bound of permeability values that would yield a gradient of less than 1.0. Figure 55 graphically presents some of the variables changing in Table 32. Table 32 shows that a substrate with a K value of less than 8.9×10^{-5} cm/sec would produce ponding with a substrate thickness (depth) of 1.5 feet (that is headloss is greater than depth).

In Table 33, the flow rate, mass loading and wetland volume are again held constant; but the depth is doubled to 3 feet. The mass loading is kept constant by halving the surface area to 400 square feet. Permeability is again varied to determine the lower bound of permeability values that would yield a gradient of less than 1.0. Table 33 shows that a substrate with a K value of less than 1.9×10^{-4} cm/sec would produce ponding.

In Table 34, flux, mass loading rate, depth, permeability (at the lowest acceptable value) and gradient are held constant; flow rate and surface area are varied. Figure 56 graphically presents some of the variables changing in Table 34. Table 34 shows that for flows of 20 gpm to 44 gpm, wetland areas from 8,000 to 16,000 square feet, respectively, would be required.

In Table 35, flow rate, flux and surface area are held constant with values consist with a 20 gallon per minute cell. Figure 57 graphically presents some of the variables changing in Table 35. Depth and permeability are varied to show the one percent decrease in substrate permeability for every 0.1 foot of depth. Table 35 shows that water ponds on the surface at a depth of 4.1 feet when the permeability of the substrate reaches 1.7×10^{-4} cm/sec (gradient equals 1.0). The mass loading rate proportionately decreases with the increase in substrate depth and volume.

In Table 36, the conditions of Table 35 are used and the flow rate is incrementally lowered to observe what depth increases might be gained in this situation. Figure 58 graphically presents some of the variables changing in Table 36. Table 36 shows that if the flow could be reduced to 17.6 gpm, the wetland depth could be increased to 5.4 feet. The design example could be carried further by increasing the cell area to carry the required minimum 20 gallons per minute and verifying that all design parameters are satisfied or optimized.

Tables 31 through 36 and Figures 54 through 58 illustrate the utility of the Lotus 123™ spreadsheet format for estimating wetland configurations. However, other computer codes that are more user-interactive may be preferable to some designers. The purpose of the illustration was to show a comprehensive design methodology that incorporates hydrology and substrate geochemistry.

VOLUMETRIC LOADING METHOD

Bacterial action results in the precipitation of metal sulfide minerals. Consequently, the pore/void spaces within the wetland substrate will become filled. Lemke (9) estimated that void space in mushroom compost accounted for approximately 25 percent of the substrate volume. This design method assumes that the filling of void spaces within the substrate is a key limiting factor to wetland performance as a acid/metal drainage treatment system.

This method allows the estimation of the ultimate size of a wetland (substrate volume) based on the following assumptions:

- o The substrate has a lab- or field-measurable void ratio of which a significant percentage is available for the precipitation of metal sulfides.

TABLE 37 PROJECTED WETLAND VOLUME REQUIREMENTS BASED ON VOID SPACE
AVAILABILITY FOR METAL SULFIDE AVAILABILITY PRECIPITATE FORMATION

METAL LOADING RATES					SOURCE FEED RATE		PERCENT VOIDS AVAILABLE FOR METAL SULFIDE PRECIPITATION			
IRON	65 Mg/Liter				50 GPM					
COPPER	6 Mg/Liter				=====					
OTHER HEAVY METALS	4 Mg/Liter				15 % VOIDS					
TOTAL LOADING	75 Mg/Liter				=====					
MINERAL LOADING RATES										
FeS	0.27 CU-FT/DAY									
COVELLITE, CuS	0.02 CU-FT/DAY									
OTHER SULFIDES (Xxs)	0.01 CU-FT/DAY									
TOTAL LOADING	0.30 CU-FT/DAY									
DRY SUBSTRATE CONCENTRATIONS BY WEIGHT AT DESIGN LIFE										
WETLAND AREA (ACRES)	SUBSTRATE DEPTH (FT)	WETLAND VOLUME (CU-FT)	WETLAND VOLUME (CU-YDS)	VOID VOLUME (CU-FT)	LIFE OF WETLAND (DAYS)	LIFE OF WETLAND (YEARS)	TOTAL WETLAND DRY MASS (KG)	IRON (%)	COPPER (%)	OTHER (%)
0.25	3	32670	1210	4901	16515	45	627,264	46.6%	4.3%	2.9%
0.25	4	43560	1613	6534	22020	60	836,352	46.6%	4.3%	2.9%
0.25	5	54450	2017	8168	27525	75	1,045,440	46.6%	4.3%	2.9%
0.25	6	65340	2420	9801	33030	90	1,254,528	46.6%	4.3%	2.9%
0.5	3	65340	2420	9801	33030	90	1,254,528	46.6%	4.3%	2.9%
0.5	4	87120	3227	13068	44040	121	1,672,704	46.6%	4.3%	2.9%
0.5	5	108900	4033	16335	55050	151	2,090,880	46.6%	4.3%	2.9%
0.5	6	130680	4840	19602	66060	181	2,509,056	46.6%	4.3%	2.9%
1	3	130680	4840	19602	66060	181	2,509,056	46.6%	4.3%	2.9%
1	4	174240	6453	26136	88080	241	3,345,408	46.6%	4.3%	2.9%
1	5	217800	8067	32670	110099	302	4,181,760	46.6%	4.3%	2.9%
1	6	261360	9680	39204	132119	362	5,018,112	46.6%	4.3%	2.9%
2	3	261360	9680	39204	132119	362	5,018,112	46.6%	4.3%	2.9%
2	4	348480	12907	52272	176159	483	6,690,816	46.6%	4.3%	2.9%
2	5	435600	16133	65340	220199	603	8,363,520	46.6%	4.3%	2.9%
2	6	522720	19360	78408	264239	724	10,036,224	46.6%	4.3%	2.9%
A	B	C	D	E	F	G	H	I	J	K
CELL FORMULAS										
PARAMETER	COLUMNS			INITIAL VALUES (ROW 24)			NOTE 1: (AFTER LEMKE, 1989) WETLAND SUBSTRATE BULK DENSITY = 1.28 g/cc; S.G. SOLIDS OF SUBSTRATE = 1.7 YIELDS 53% DRY SOLIDS BY WEIGHT AND DRY DENSITY OF 19.2 Kg/CF			
=====	=====			=====						
AREA, ACRES	A			0.25						
DEPTH, FEET	B			3						
VOL, CU-FT	C			+A24*43560*B24						
VOL, CU-YDS	D			+C24/27						
VOID VOL, CU-FT	E			+\$J\$10*C24/100						
WETLAND LIFE, DAYS	F			+E24/\$D\$17						
WETLAND LIFE, YEARS	G			+F24/365						
WETLAND DRY MASS, Kg	H			+C24*19.2 (SEE NOTE 1)						
ULTIMATE Fe CONC., %	I			(+ \$C\$8*\$F\$9*1440*3.785*\$F24/\$H24)/1000000						
ULTIMATE Cu CONC., %	J			(+ \$C\$9*\$F\$9*1440*3.785*\$F24/\$H24)/1000000						
ULTIMATE Other CONC., %	K			(+ \$C\$10*\$F\$9*1440*3.785*\$F24/\$H24)/1000000						

- o An average daily mineral loading rate can be estimated in terms of mass and volume of metals sulfides.

Table 37 is an example spreadsheet that employs this substrate volume sizing methodology. Mass loading rates from water balance and metals concentration perspectives were assumed to be constant over the life of the wetland.

Note that the Table 37 spreadsheet includes an estimate of the concentrations of key metals accumulated in the substrate at various design lives. These data are useful in determining temporal points after which the substrate might be considered a hazardous waste. Since final metals concentration in the substrate is a function of void space, all the configurations in Table 37 have identical metals concentrations; "total" metals amounts would be different for each unique wetland volume/life span.

To determine wetland "life" (at a given substrate depth and surface area) whereby the metal-laden substrate would not be considered a hazardous waste, void space is incrementally varied until the hazardous material criteria are met. If the void space percentage required to make the material "hazardous" is greater than the maximum void space physically available, the life of the wetland will probably not be governed by hazardous material criteria.

The wetland lifetimes generated in this VOLUMETRIC LOADING METHOD analysis extend far beyond the lifetimes of any currently operating subsurface wetland. At this time, what will limit the life of such a system is purely speculative. However optimists hope a wetland can be a walk-away treatment system that will operate in perpetuity. There are at least two other factors that could limit wetland lifetime: The volume of biomass added to the wetland, and the amount of biomass available to the sulfate-reducing bacteria. These considerations, are taken up in the next two sections

VOLUMETRIC BIOMASS ACCUMULATION METHOD

In the previous section, the lifetime of a wetland is limited by the volume of substrate available to hold the metal sulfides that are precipitated. However, wetland substrate mass/volume may be incrementally increased through accumulation of dead vegetation. Biomass accumulation rates are a function of climate. For example, researchers have estimated that biomass accumulation rates in tropical primeval coal swamps approached one foot every 10 years (105). In "forest mires of the temperate zone" (100), biomass accumulations have been measured to be on the order of one foot every 300 years.

There is a dearth of data on biomass accumulations in constructed wetland facilities for metal mine drainage treatment in typical temperate climates. However, assuming that new substrate from vegetation is added to the wetland at a rate of one foot every 100 years, the availability of void space for metal-hydroxide or sulfide precipitation in the wetland may become self-perpetuating. As shown on Table 38, the self-perpetuating threshold design area for a flow of 50 gpm appears to be about 1.275 acres, whereby additional operating life due to bioaccumulation equals the original life of the wetland.

TABLE 38 EFFECT OF BIOMASS ACCUMULATION AND SULFIDE PRECIPITATION
AS SOURCES AND SINKS OF VOID SPACE ON WETLAND CELL DESIGN LIFE

METAL LOADING RATES					SOURCE FEED											
IRON		65 Mg/Liter			RATE											
COPPER		6 Mg/Liter			50 GPM											
OTHER HEAVY METALS		4 Mg/Liter			=====											
TOTAL LOADING		75 Mg/Liter				15 % VOIDS AVAILABLE FOR METAL SULFIDE PRCN										
					=====											
MINERAL LOADING RATES																
FeS		0.20 CU-FT/DAY														
COVELLITE, CuS		0.02 CU-FT/DAY														
OTHER SULFIDES (XxS)		0.01 CU-FT/DAY														
TOTAL LOADING		0.23 CU-FT/DAY														
(1)																
WETLAND AREA (ACRES)	SUBSTRATE DEPTH (FT)	WETLAND VOLUME (CU-FT)	WETLAND VOLUME (CU-YDS)	VOID VOLUME (CU-FT)	LIFE OF WETLAND (DAYS)	LIFE OF WETLAND (YEARS)	ADDITNL DEPTH (FT)	ADDITNL BIOMASS (CU-FT)	ADDITNL VOID VOL (CU-FT)	ADDITNL LIFE (YRS)	ADDITNL LIFE (YRS)	TOTAL LIFE (YRS)				
=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====				
0.25	3	32670	1210	4901	21435	59	0.59	6395	959	11		70				
0.25	4	43560	1613	6534	28580	78	0.78	8527	1279	15		94				
0.25	5	54450	2017	8168	35725	98	0.98	10659	1599	19		117				
0.25	6	65340	2420	9801	42870	117	1.17	12790	1919	23		140				
0.75	3	98010	3630	14702	64304	176	1.76	57557	8634	103		280				
0.75	4	130680	4840	19602	85739	235	2.35	76742	11511	138		373				
0.75	5	163350	6050	24503	107174	294	2.94	95928	14389	172		466				
0.75	6	196020	7260	29403	128609	352	3.52	115114	17267	207		559				
1	3	130680	4840	19602	85739	235	2.35	102323	15348	184		419				
1	4	174240	6453	26136	114319	313	3.13	136431	20465	245		558				
1	5	217800	8067	32670	142899	392	3.92	170539	25581	307		698				
1	6	261360	9680	39204	171478	470	4.70	204646	30697	368		838				
1.275	3	166617	6171	24993	109317	299	2.99	166339	24951	299		599				
1.275	4	222156	8228	33323	145757	399	3.99	221786	33268	399		798				
1.275	5	277695	10285	41654	182196	499	4.99	277232	41585	498		998				
1.275	6	333234	12342	49985	218635	599	5.99	332678	49902	598		1197				
A	B	C	D	E	F	G	H	I	J	K		L				
CELL FORMULAS																
PARAMETER	COLUMNS				INITIAL VALUES (ROW 14)											
=====	=====				=====											
AREA, ACRES	A				0.25				NOTE 1: ASSUMES 1 FOOT OF BIOACCUMULATION PER 100 YEARS							
DEPTH, FEET	B				3											
VOL, CU-FT	C				+A24*43560*B24											
VOL, CU-YDS	D				+C24/27											
VOID VOL, CU-FT	E				+J\$10*C24/100											
WETLAND LIFE, DAYS	F				+E24/\$D\$17											
WETLAND LIFE, YEARS	G				+F24/365											
ADDITIONAL DEPTH, FT	H				+G24/100											
ADDED BIOMASS, CU-FT	I				+H24*A24*43560											
ADDED VOIDS, CU-FT	J				+I24*J\$10/100											
ADDITIONAL LIFE, YEARS	K				(+J24/\$D\$17)/365											
TOTAL LIFE, YEARS	L				+K24+G24											

TABLE 39 PROJECTED WETLAND VOLUME REQUIREMENT BASED ON THE
STOICHIOMETRY OF THE SULFATE-REDUCING BACTERIA REACTION

SOURCE			METAL CONCENTRATIONS									
FEED RATE												
GPM	50		LOADING RATE, IRON		65 mg/liter							
=====			LOADING RATE, COPPER		5 mg/liter							
			LOADING RATE, OTHER		5 mg/liter							
			TOTAL LOADING		75 mg/liter							
ORGANIC MATTER			METAL LOADINGS					METAL LOADING FORMULAS				
CONTENT IN			LOADING RATE, Fe		17.7 Kg/DAY	<--	+\$B\$8*3.785*1440*G8/1000000					
ORIGINAL			LOADING RATE, Cu		1.4 Kg/DAY	<--	+\$B\$8*3.785*1440*G9/1000000					
SUBSTRATE	30 %		LOADING RATE, OTHER		1.4 Kg/DAY	<--	+\$B\$8*3.785*1440*G10/1000000					
=====			TOTAL LOADING		20.4 Kg/DAY	<--	\$SUM(J14..J16)					
(1)			(2)			(3)						
WETLAND AREA (AC)	WETLAND DEPTH (FT)	WETLAND VOLUME (CU-FT)	WETLAND DRY MASS (Kg)	ORGANIC MASS (Kg)	METAL LOAD RATE (Kg/DAY)	LIFE OF WETLAND (DAYS)	LIFE OF WETLAND (YEARS)	ADDITIONAL BIOMASS (Kg)	ADDITIONAL DEPTH (FT)	ADDITIONAL LIFE (YRS)	TOTAL LIFE (YRS)	AREA FLUX SF/GPM
=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====
1	3	130680	2.5E+06	7.5E+05	20	7,365	20	6E+04	0.07	1.6	22	871
1	4	174240	3.3E+06	1.0E+06	20	9,821	27	8E+04	0.10	2.2	29	871
1	5	217800	4.2E+06	1.3E+06	20	12,276	34	1E+05	0.12	2.7	36	871
1	6	261360	5.0E+06	1.5E+06	20	14,731	40	1E+05	0.15	3.3	44	871
2	3	261360	5.0E+06	1.5E+06	20	14,731	40	2E+05	0.15	6.6	47	1,742
2	4	348480	6.7E+06	2.0E+06	20	19,641	54	3E+05	0.20	8.8	63	1,742
2	5	435600	8.4E+06	2.5E+06	20	24,552	67	4E+05	0.24	11.0	78	1,742
2	6	522720	1.0E+07	3.0E+06	20	29,462	81	5E+05	0.29	13.1	94	1,742
12	3	1568160	3.0E+07	9.0E+06	20	88,386	242	9E+06	0.88	237	479	10,454
12	4	2090880	4.0E+07	1.2E+07	20	117,848	323	1E+07	1.17	316	638	10,454
12	5	2613600	5.0E+07	1.5E+07	20	147,310	404	1E+07	1.47	394	798	10,454
12	6	3136320	6.0E+07	1.8E+07	20	176,772	484	2E+07	1.76	473	958	10,454
A	B	C	D	E	F	G	H	I	J	K	L	M
CELL FORMULAS												
PARAMETER	COLUMNS FORMULAS (ROW 24)											
=====	=====											
AREA, ACRES	A	1										
SUBSTRATE DEPTH, FT	B	3										
WETLND VOL, CU-FT	C	+A24*43560*B24										
WETLND DRY MASS, Kg	D	+C24*19.2										
ORGANIC MASS, Kg	E	+\$C\$16*D24/100										
TOTAL LOADING, Kg/DAY	F	+\$G\$17										
WETLAND LIFE, DAYS	G	(+E24/(\$F24*2.5))*0.50										
WETLAND LIFE, YEARS	H	+G24/365										
ADDITIONAL BIOMASS, Kg	I	+A24*43560*0.093*H24*0.75										
ADDITIONAL DEPTH, FT	J	(I24/19.2)/(A24*43560)										
ADDITIONAL LIFE, YEARS	K	(+I24/(\$F24*2.5)*0.5)/365										
TOTAL LIFE, YEARS	L	+K24+H24										
AREA FLUX, SF/GPM	M	+A24*43560/\$B\$8										
NOTE 1: (AFTER LEMKE, 1989) WETLAND SUBSTRATE BULK DENSITY = 1.28 g/cc SOLIDS OF SUBSTRATE = 1.7 YIELD DRY SOLIDS BY WEIGHT AND DRY DENSITY = 19.2 Kg/CF												
NOTE 2: LIFE OF WETLAND IS BASED ON 50% OF CARBON IN ORIGINAL SUBSTRATE IS CHEMICALLY AVAILABLE (IN THE LONG TERM) DUE TO HUMIFICATION.												
NOTE 3: ACCUMULATION BASED ON DATA OF HEDIN, ET. AL. IN HAMMER, 1989; METAL CARBON IS .093 (Kg/yr)/SF OF WHICH IS AVAILABLE TO SULFATE REDUCERS.												

NOTE 1: (AFTER LENKE, 1989) WETLAND
SUBSTRATE BULK DENSITY = 1.28 g/cc; S.G.
SOLIDS OF SUBSTRATE = 1.7 YIELDS 53%
DRY SOLIDS BY WEIGHT AND DRY DENSITY OF
19.2 Kg/CF

NOTE 2: LIFE OF WETLAND IS BASED ON 2.5
GRAMS ORGANIC MATTER ARE NECESSARY FOR
EVERY GRAM OF METAL REDUCTION AND ONLY
50% OF CARBON IN ORIGINAL SUBSTRATE MASS
IS CHEMICALLY AVAILABLE (IN THE LONG
TERM) DUE TO HUMIFICATION.

NOTE 3: ACCUMULATION BASED ON DATA IN
HEDIN, ET. AL. IN HAMMER, 1989; NPP OF
CARBON IS .093 (Kg/yr)/SF OF WHICH 75% IS
AVAILABLE TO SULFATE REDUCERS.

It is assumed that the added substrate from the vegetation die-off would have the same characteristics as the original substrate. It is also assumed that there is allowance for increasing thickness of the constructed wetland system. The extension on operating life would occur only if the submergence of the biomass was maintained. That is, the hydraulic level controls would have to be adjusted infrequently to allow for increased water depth.

The 300 year design life for a three-foot deep wetland in Table 38, however, is probably unrealistic. Biomass accumulation rates significantly greater than one foot every 100 years would have to be achieved in order for a wetland designed with respect to other criteria to be self-perpetuating from a volumetric perspective.

As discussed below, typical wetland substrate organic content may need to be maintained to satisfy stoichiometric criteria. Even with plant accumulations, maintenance actions such as periodic additions of beneficial materials like hay or other organic-rich supplements may be required. Organic addition is likely to be a site-specific maintenance consideration.

SULFATE-REDUCING STOICHIOMETRY METHOD

Hedin, Hyman and Hammack (65) present a discussion of sulfate-reducing bacteria stoichiometry and its relationship to carbon content in the substrate. Stoichiometrically, one mole of sulfate is reduced to hydrogen sulfide for every two moles of carbon oxidized. Further, one mole of sulfate is required to precipitate iron as "FeS" as discussed in SECTION 5. Thus, two moles of carbon are required for every mole of ferrous iron in the wetland feed water. Most other metals (Cu, Zn, Cd, Ni and Hg) tend to follow the 1:1 metal to sulfur stoichiometry. Thus, they also require two moles of carbon for every mole of metal. Assuming "organic matter" [O.M.] in substrate has the chemical formula CH_2O (molecular wt = 30 grams), 60 grams of organic matter would be required per mole of metal precipitation.

However, the formation of a mole of pyrite (FeS_2) requires an additional two moles of carbon. Pyrite is more stable in acid solution than FeS, so it would be desirable to optimize conditions for pyrite, rather than acid-soluble FeS. The formation of pyrite in a wetland environment may need to be induced by other process mechanisms. Nevertheless, for every mole of pyrite formed, four moles of carbon are required stoichiometrically.

The other heavy metals (with the exception of Mn) have larger atomic weights than Fe--from 1.14 times (for Cu) to 3.6 times (for Hg) the weight of Fe. However, the Fe concentration is generally at least an order of magnitude larger in acid drainage than that of the next most concentrated metal. Therefore, as a first approximation, the concentrations of all the heavy metals, in mg/l, can be added. Then, the atomic weight of iron and the stoichiometry of the pyrite reaction can be used to estimate substrate "life" based on available carbon/organic matter. Biomass accumulations from a carbon source perspective can also be used to estimate whether a particular wetland configuration will become self-perpetuating.

Table 39 presents constructed wetland life estimates based on the following assumptions:

- o Wetland substrate dry density is 1.77 g/cc (9).

- o The concentrations, in mg/l, of Fe, Cu, Zn, Cd, Ni, and Hg are added and assumed to be equal to the concentration of a hypothetical metal with atomic weight of 55.
- o Four gram-moles of carbon are required for each gram-mole of this hypothetical metal.
- o Thus, 0.83 grams of carbon are needed to reduce 1 gram of dissolved metal to sulfide.
- o 40 percent of organic matter is "stoichiometrically available" as carbon ($12 \times 4 \text{ gram C} / 120 \text{ grams OM} = 0.4$), thus 2.5 grams of OM are required per gram of metal.
- o 50 percent of the carbon in the original substrate is rendered unavailable to sulfate reducing bacteria due to the cumulative long-term effects of humification.
- o Carbon accumulation from plants occurs at a rate of $1 \text{ kg/m}^2\text{-yr}$ or $0.093 \text{ Kg/square foot per year}$ (65 and SECTION 12).
- o 75 percent of the accumulated plant carbon is available for sulfate precipitation (65)

Table 39 results suggest that a one acre, four-foot-deep wetland with a nominal metal loading of 75 mg/liter in a flow rate of 50 gpm should last about 27 years. Additional biomass accumulations could add about two years to the life of the facility for a total life of 29 years. The associated area flux value of 871 sf/gpm is within nominal limits for this variable.

As an academic exercise, the wetland size in Table 39 was expanded to determine when a wetland treating this mine drainage would be self-perpetuating. The analysis suggests that at the given loading rates, a self-perpetuating wetland system might develop for a nominal 12-acre site. However, there are far too many unanswered questions concerning wetlands technology to attach much credence to this estimate.

The associated flux value of 10,454 sf/gpm is significantly higher than the limits for this variable used in Tables 31-37. Cost trade-offs between annual operating costs and front-end capital costs should be examined to establish minimum overall system costs. In addition, if lifetime estimates of a wetland are extended to these high values, The question of how long the acid mine drainage will last should also be studied.

The availability of "bacteria-usable" carbon in the substrate needs to be further addressed to allow reasonable use of this wetland design methodology. Further, the amount of carbon that is actually used by sulfate-reducing bacteria is unknown. Also, the sulfate-reducing bacteria may compete with other bacteria for organic carbon.

Lemke (9) measured "organic matter" contents of about 30 percent in mushroom compost. Lemke did not measure carbon content that is stoichiometrically available to sulfate-reducing bacteria. Data presented in SECTION 6 indicate that 31% of Typha (cattail) plant mass is carbon. The chemical makeup of "typical" organic matter in candidate substrates should be established before this methodology is used to design constructed wetlands (see SECTION 14).

TABLE 40 NET EVAPOTRANSPIRATION LOSSES AT A HYPOTHETICAL
CONSTRUCTED WETLAND SITE

INFLOWS (SEE NOTE 1):

	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	TOTALS
RAINFALL(IN)	1.29	1.50	2.26	4.00	4.47	4.35	2.56	2.21	1.83	1.76	1.68	1.49	29.40 INCHES
EVAPORATN(IN)	0.81	1.23	2.18	3.26	4.79	5.84	6.54	5.95	4.06	2.62	1.18	0.77	39.23 INCHES

OUTFLOWS:

WETLAND FACTOR 1.8 (SEE NOTE 2)

		, NET LOSSES (-), GAINS (+) IN GALLONS PER MINUTE												
WETLAND ACRES	WETLAND SQ-FT	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	AVERAGE
=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	=====
0.5	21,780	-0.1	-0.2	-0.5	-0.6	-1.3	-1.9	-2.9	-2.7	-1.7	-0.9	-0.1	0.0	-1.1
1	43,560	-0.1	-0.4	-1.0	-1.2	-2.6	-3.9	-5.8	-5.3	-3.4	-1.9	-0.3	0.1	-2.2
1.5	65,340	-0.2	-0.7	-1.6	-1.8	-3.9	-5.8	-8.7	-8.0	-5.2	-2.8	-0.4	0.1	-3.2
2	87,120	-0.2	-0.9	-2.1	-2.3	-5.2	-7.7	-11.6	-10.7	-6.9	-3.7	-0.6	0.1	-4.3
2.5	108,900	-0.3	-1.1	-2.6	-2.9	-6.5	-9.7	-14.5	-13.4	-8.6	-4.6	-0.7	0.2	-5.4
3	130,680	-0.3	-1.3	-3.1	-3.5	-7.8	-11.6	-17.4	-16.0	-10.3	-5.6	-0.8	0.2	-6.5
3.5	152,460	-0.4	-1.6	-3.7	-4.1	-9.1	-13.6	-20.3	-18.7	-12.1	-6.5	-1.0	0.2	-7.6

NOTE 1: TYPICAL RAINFALL AND PAN EVAPORATION DATA FROM BLACK HILLS, SD

NOTE 2: WETLAND FACTOR IS THE MULTIPLYING FACTOR APPLIED TO PAN EVAPORATION RATES
DUE TO PLANT EVAPOTRANSPIRATION. TYPICAL WETLAND FACTOR IS 2.0 OR LESS.

The stability of the carbon in the substrate with respect to bacterial utilization is another area worthy of further study. Data from natural systems may suggest the extent that humification modifies organic matter to the point that sulfate-reducing bacteria cannot use it.

EVAPOTRANSPIRATION LOSSES

Evapotranspiration losses from natural wetlands have been measured at levels several times that of natural pan evaporation (58). This is consistent with evapotranspiration results from the Big Five constructed wetland reported in SECTION 6.

In design considerations of wetlands with plants, an evapotranspiration rate of 1.8 times that of standard pond evaporation might be assumed without raw data. Using this assumption in a sample water balance analysis (see Table 40), net evaporation/evapotranspiration losses from a one acre wetland ranged from 4 gpm to 6 gpm in the summer months to negligible amounts in the winter months. Similar analyses were performed for wetland areas up to 3.5 acres in size with proportionate results; the maximum net evapotranspiration loss from a 3.5 acre wetland was about 20 gpm.

This amount could provide a significant reduction in net wetland output in the summer months and may impact water rights. However, the water budget of a typical wetland will probably not result in a zero-discharge facility. As discussed in SECTION 5, substrate desiccation is to be avoided due to the likelihood of oxidation of precipitated sulfides and re-mobilization of heavy metals. Thus, in certain circumstances, evapotranspiration effects can work against the goals of a constructed wetland.

SUMMARY

This section establishes how the primary parameters used to design an anaerobic wetland system are interrelated. First, a surface flux of 400 to 800 sf/gpm was chosen for storm and runoff stability. Using Darcy's Law, reasonable permeabilities for the substrate were established. Then using the criteria that 300 nanomoles/cc-day is the maximum rate of sulfide generation, various depth and flow configurations were tested to develop a reasonable wetland size. Using this size, the configuration was tested to see how changes in permeability, flow, and flux would affect the design. Such a mental exercise is probably not necessary for the design of all anaerobic bioreactors. However, it is strongly suggested that it be tried at least once to gain an appreciation for how geotechnical considerations interact with biogeochemical criteria for the design of this type of wetland/bioreactor.

Once a design is decided upon, the question arises on how long the system will last. Three methods to test the design lifetime were tested:

- o Precipitated metal volumetric loading
- o Addition of organic matter to help increase the volume and thus the lifetime of the wetland
- o Determining when the supply of organic matter for the sulfate-reducing bacteria would be

depleted.

Although quite speculative, all three methods give lifetimes of over 20 years. What this implies is that the lifetime of a wetland will probably be determined by the disposal options of the substrate as discussed in SECTION 8. This preliminary analysis suggests that filling of void spaces by sulfides or depletion of the biomass will not be the factors that limit the life of an anaerobic wetland/bioreactor.

SECTION 13

DESIGN CONFIGURATIONS

It has been said that an anaerobic constructed wetland that treats acid/metal drainage is a "bioreactor with a green toupee", referring to the organic substrate where most of the bioreactions occur and the collection of plants that grow on the surface of the wetland. As discussed in SECTIONS 3 and 6, studies have shown that plant uptake does not contribute significantly to water quality improvements in anaerobic wetlands. However, plants can replenish the wetland with organic material and add aesthetic appeal.

The design methods discussed in SECTION 12 will yield key design parameter values such as surface area and substrate volume and depth as well as system hydrology constraints such as flux and minimum acceptable hydraulic conductivity of the substrate.

The final configuration of a constructed wetland will in most respects rely on the land space available and the topography of the site. Given that mining sites are typically found in rugged topography where level land has been already allocated to other land uses, wetland sites may have to be developed by excavation and earthwork. For example, excavated terraces or stabilized/reclaimed tailings or waste rock dump surfaces might be considered as potential wetland sites.

Maintenance access will also influence configuration. As will be addressed in SECTION 15, maintenance functions such as long term rejuvenation of substrate organic content and the possible removal/ replacement of expended substrate need to be considered.

If the design criteria are satisfied, the bacteria that populate the wetland substrate should flourish and the performance of the wetland as a bioreactor should meet design effluent concentrations. It is up to the individual design engineer to incorporate "safety factors" where appropriate, based on parameter uncertainties. For example, if flow rate fluctuations are expected, wetland surface area and volume requirements (and other accompanying parameters) may need to be increased proportionately.

GENERAL CONFIGURATIONS

The fact that the bacteriologic processes flourish anaerobically and in the absence of large living plants offers the design engineer more flexibility/creativity in the selection of a wetlands configuration. Without plants, a wetland can be configured in two general ways: as a conventional/natural wetland system or as a "stacked plate" system.

In both configurations, the water to be treated essentially makes "one pass" through the dissolved-metals-removing wetland. Unless additional wetland polishing to remove B.O.D. or ammonia is

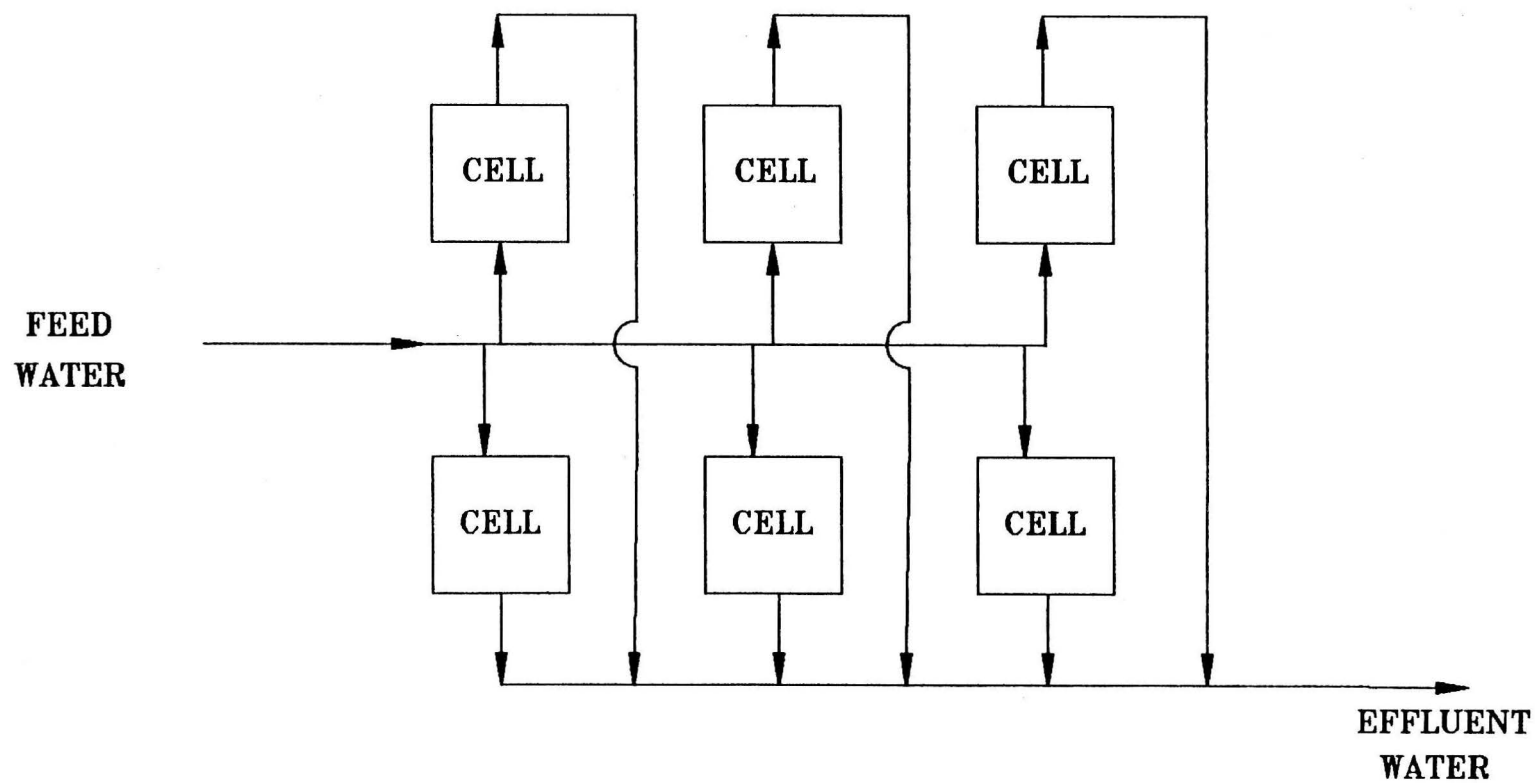


Figure 59

A schematic plan view of a conventional wetland configuration.

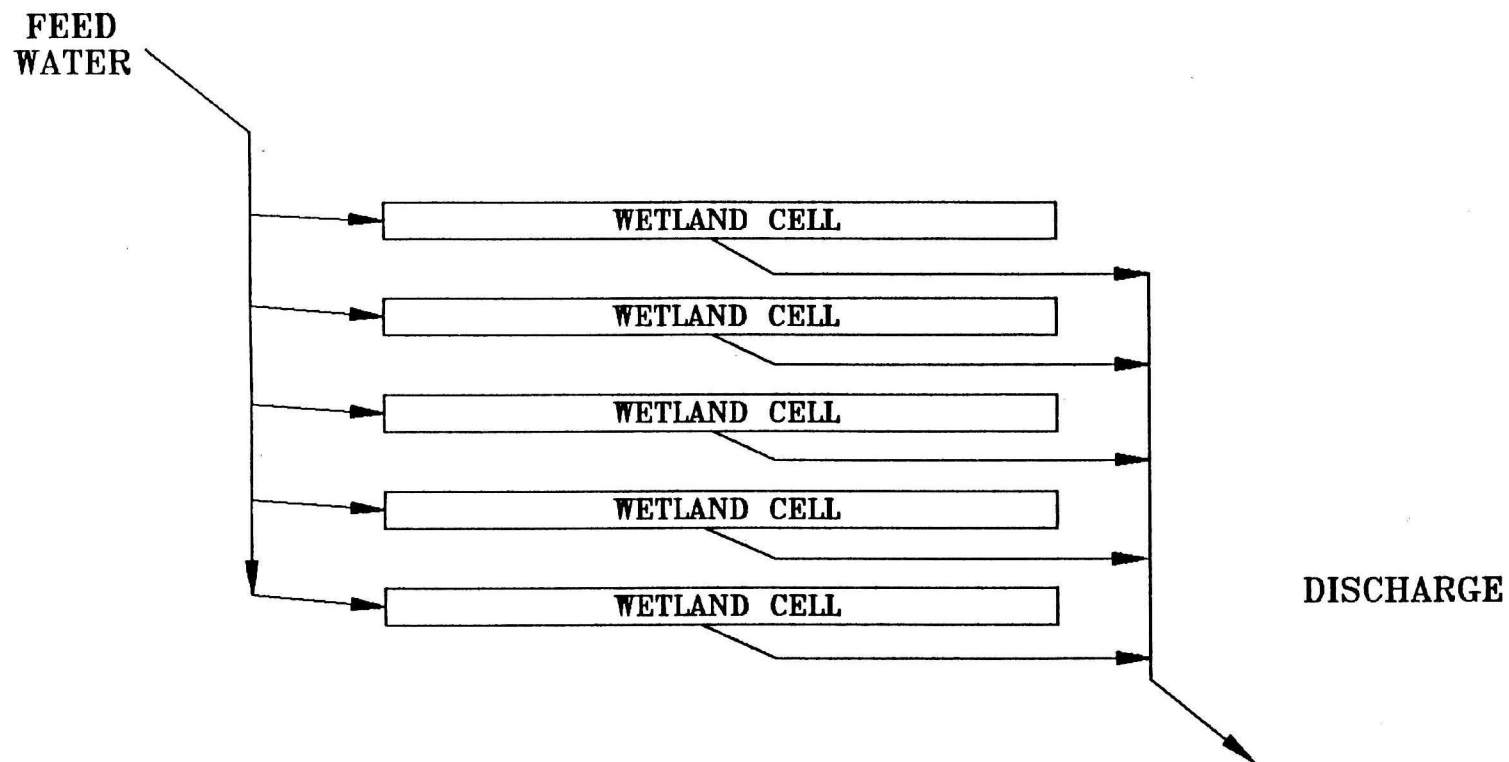
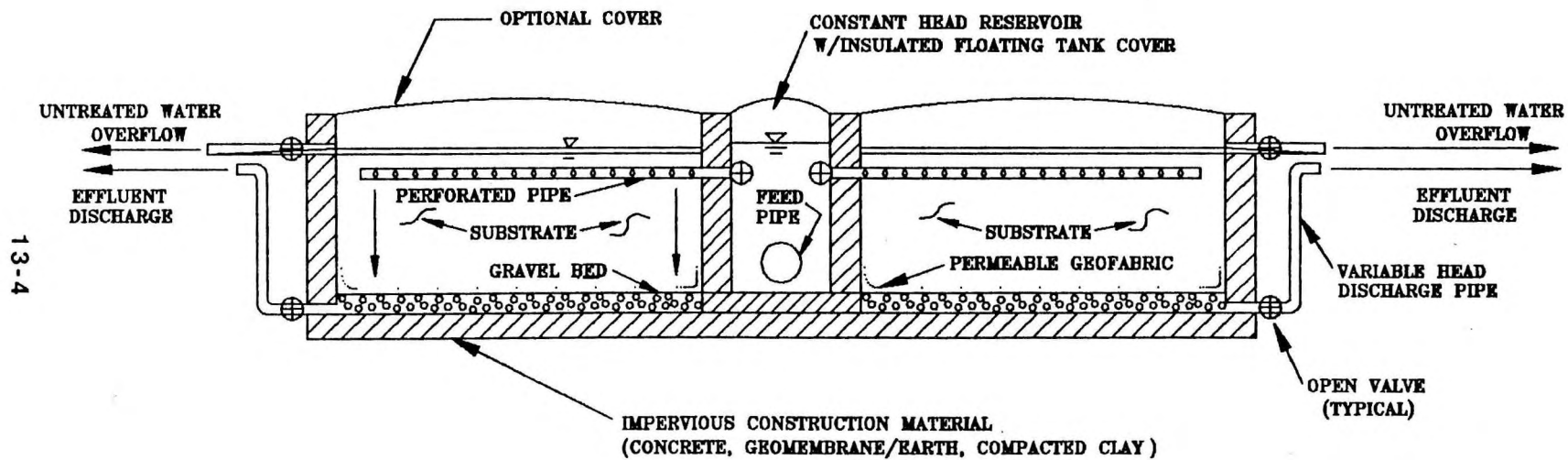


Figure 60. A schematic cross-section view of a stacked wetland configuration.



13-4

required, the treated water only passes through a wetland cell once. In the following discussions, additional polishing steps are assumed to be unnecessary. However, minor amounts of wetland effluent may pass through several down-gradient cells to replenish evaporation losses and insure substrate saturation.

Natural/Conventional Configuration

Given a site situation with abundant land area, the design engineer may employ a "conventional" configuration that appears to be a natural system as shown in Figure 59. A conventional configuration could be used regardless of plant usage policies in the wetland. Brodie of the TVA (55,68,69) has been quite successful at building these types of systems, although the systems are shallow and promote aerobic bacterial reactions and fluid flow over the surface. Anaerobic "conventional" wetland systems have deeper cell depths and vertical fluid flow.

From a construction materials perspective, a conventional configuration would allow the use of a broad range of materials such as earthen berms, geomembranes, compacted clay with reinforced concrete and piping as required. From a visual perspective, such a configuration might resemble a natural wetland or a series of tiered settling ponds.

The addition of plants in the wetlands could provide a more natural appearance. Even if plants are not directly introduced at the completion of wetland construction, it is likely that volunteer plants will establish themselves with the passage of time. Thus, unless some plant control measures (such as geomembrane/geotextile covers over open wetland areas) are installed, one might as well plant acceptable flora species to avoid the ultimate invasion of noxious ones.

Stacked Plate Configuration

Given a site situation with inadequate land area for the design flows and the decision not to use plants, the design engineer may employ a "stacked plate" configuration as shown in Figure 60. From a construction materials perspective, a stacked configuration would compel the use of rigid materials such as reinforced concrete or coated/lined compartmentalized tanks. From a visual internal perspective, such a configuration might resemble a multi-storied automobile parking garage. Externally, the facility might appear to be a concrete water tank. Such a facility should be considered a passive bioreactor instead of a constructed wetland.

In such a configuration, anaerobic conditions could be easily maintained. However, substrate maintenance may require extraordinary procedures that render the configuration impractical.

Excavated underground workings near the portal of a discharging tunnel may provide the necessary "land area" for a passive bioreactor without plants in a stacked plate configuration. The apparently simpler legalities and hidden aesthetics of developing underground excavations to house plantless wetland facilities could result in capital cost savings when compared to the land acquisition costs and the securing of conveyance rights of way for alternative surface sites. Further, the "buried" nature of the facility is unlikely to produce public opposition fueled by "not in my backyard" attitudes.

In areas of exorbitant land acquisition costs or restrictive site topography, use of a stacked plate wetland configuration should be considered.

DETAILED CONFIGURATIONS

Flow Directions

Anaerobic wetland bench and pilot scale testing has employed both up-flow and down-flow configurations with nearly equal success. The development of up- and down- flow systems was prompted by a desire to maintain a relatively high hydraulic conductivity of mushroom compost substrate in order to vary loading rates.

Work with field permeameters (99) has shown that the physical operation of up-flow systems presents numerous problems that include flow control and short circuiting. In pilot scale systems (cells B north and south at the Big Five Site), the differences in hydraulic conductivity between up-flow and down-flow decreased significantly (99). From a hydraulic perspective, up-flow systems require a driving head at least double the thickness of the substrate layer and as permeability decreases, short circuiting becomes more likely.

Thus, while up-flow systems appear to be useful on bench and pilot scale experiments, they appear to be of limited application in full scale systems and will not be discussed further.

Conceptual Cell Design

A conceptual wetland down-flow cell detail is shown in Figure 61. The key aspects of the cell include:

- o Surface coverings (above perforated inlet pipes) to promote anaerobic reactions and protect pipes in seasonal subfreezing climatic conditions (assuming no plants).
- o Compartmentalization to provide for flow control/maintenance
- o Subsurface collection of effluent in a gravel bed and pipe network.
- o Paired cells adjacent to a single central feed pipe to minimize feed water exposure to oxygen.
- o Separation of substrate and gravel bed/plenum with permeable geofabric.
- o Overflow weir or pipe for untreated effluent to pass to the next down-gradient cell.
- o Covered central "constant head reservoir" that contains a buried feed pipe for providing source head and flow control within each cell.
- o Floating reservoir cover to reduce oxygen contact with feed water.
- o Variable height discharge line for differential head control; i.e., flow control.
- o Impervious construction materials for cell containment could include concrete, geomembrane/earth berms, compacted clay.

- o Full-section valves for cell operational control/maintenance. The valve positions would normally be fully open or completely closed. The valves could be used for flow throttling on a short-term basis only.
- o Groups of cells would be cascading in as much as site topography allows; i.e., the elevation of the underflow from an up-gradient cell pair would be slightly higher than the overflow from a down gradient cell pair. Thus, an "idle" cell will automatically remain inundated from upgradient sources.

Figure 62 shows the grouping of several pairs of wetland cells in a conceptual wetland treatment facility. Note that the overflow streams of untreated water from up-gradient cell pairs are routed to the central reservoir feeding the down-gradient cell pairs.

Furthermore, the underflow from up-gradient cells is routed (via constant prime siphons with check valves, if necessary) to the top of down-gradient cells. This design feature is a means of keeping down-gradient cell substrate mass saturated if the facility operates unattended and feed flow rate decreases. If the substrate mass is allowed to desiccate, sulfide precipitates could become oxidized and would be released when flows to the cell returned. Desiccation could also result in substrate permeability losses from compression of lower layers of the cell.

If the wetland facility is inspected on a regular basis, manual adjustments in cell discharge rates could balance the flows among the cell pairs; constant-prime siphons would not be required. Still, gravity flow configurations should be included in the installation for routing the underflow from up-gradient cells to the tops of down-gradient cells.

Figure 63 shows a cross section through a group of cell pairs that highlights the anti-desiccation features of the conceptual design.

The dimensions of individual cells will be estimated using methods discussed in SECTION 12. The key criteria to successful cell operation should be the maintenance of flows through the cells and the uninterrupted saturation of the substrate.

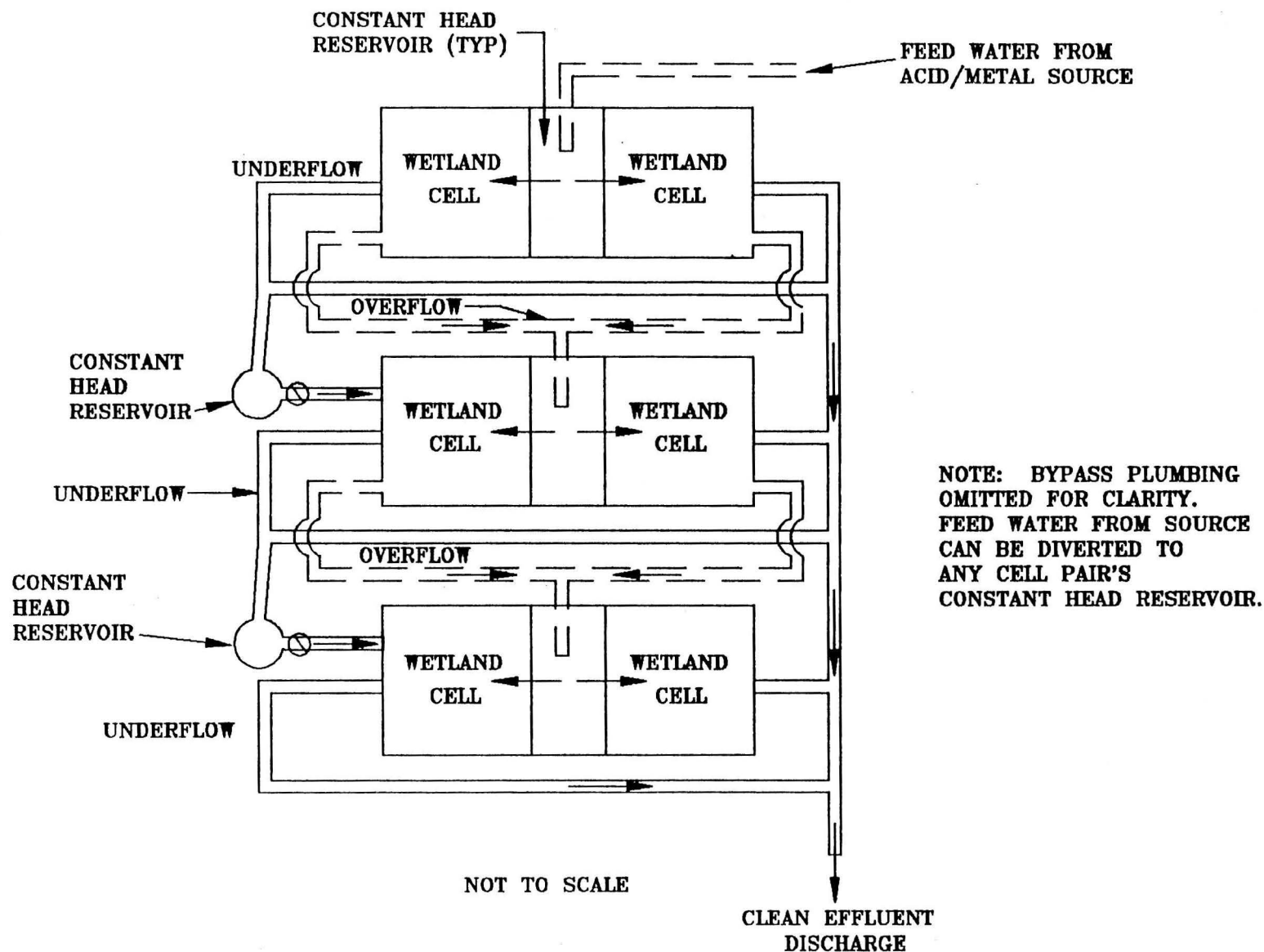
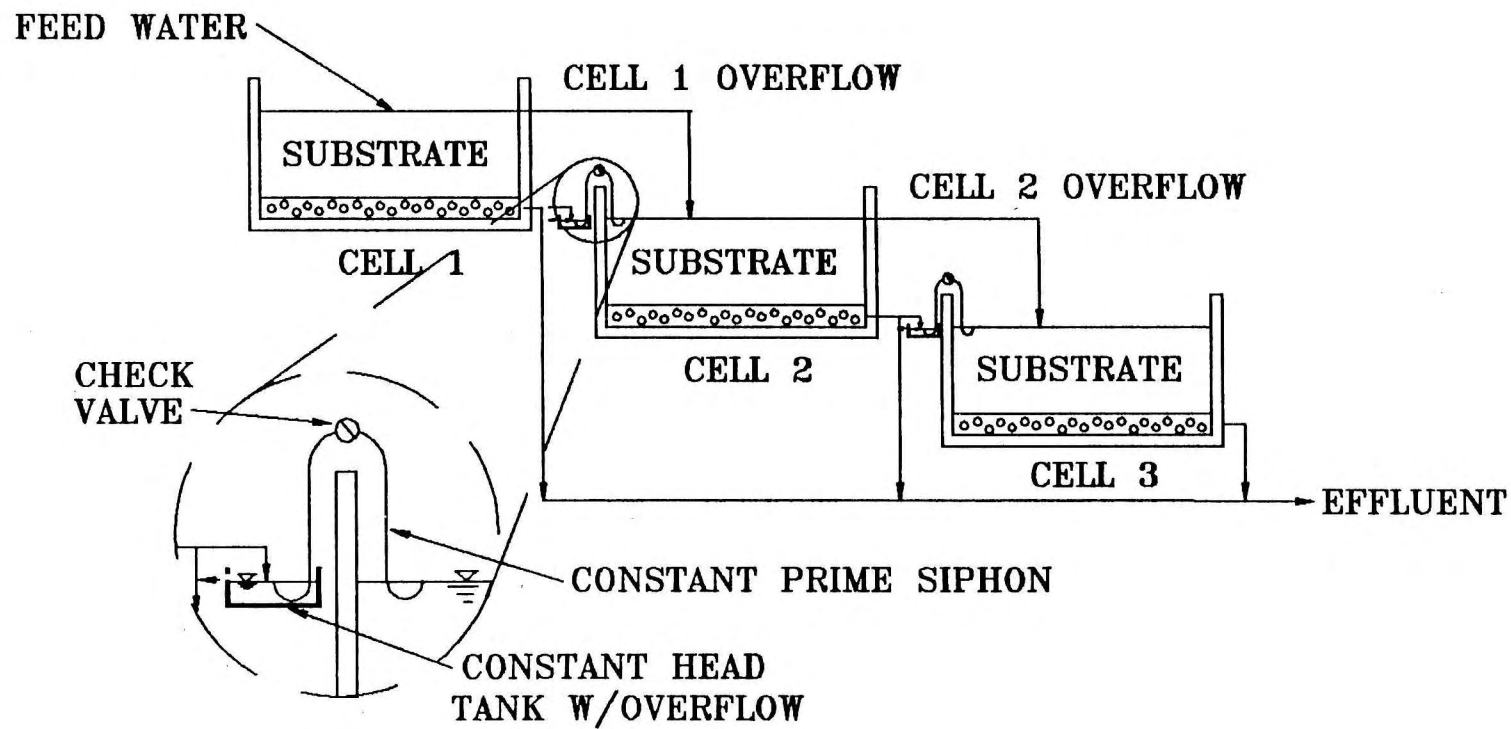


Figure 62 A schematic plan view of a downflow wetland configuration



NOT TO SCALE

Figure 63. A schematic cross-section view of a downflow wetland installation.

SECTION 14

INSTRUMENTATION/PERFORMANCE EVALUATION

Effluent water quality is the ultimate indication of anaerobic wetland performance in removing dissolved metals and neutralizing acid conditions. However, because the technology may not be accepted as a totally "proven" method by some governmental agencies, documentation of all performance parameters is recommended.

Prior to the startup of a constructed wetlands system, a Sampling and Analysis Plan (SAP) and a Quality Assurance Project Plan (QAPP) should be written specifically for the site. These plans should assure the consistent gathering and analysis of samples from the wetland and provide documentation on wetland performance. The testing results could provide information useful in optimizing wetland performance as operating experience is gained.

WETLAND CELL INSTRUMENTATION

For the entire site, a continuous chart recorder should monitor flow rate from the acid/metal source. Flow meter selection should be influenced by the probability that metal hydroxide precipitates may form in the conveyance section and disrupt flow measurements. Non-contacting flow meters such as ultrasonic and magnetic units are recommended.

Periodic sampling of source water quality should be conducted in concert with the monitoring of effluent water quality. Automated samplers that can retrieve composite samples should be considered after wetland performance has stabilized.

At a minimum, the following data should be periodically obtained from each wetland cell:

- o Differential head ("dH", Figure 52) between the water level on top of the substrate and the underflow (effluent) pipe outlet. This measurement may be obtained with manometers or pressure transducers. It is recommended to monitor at least one cell in an installation with a continuous chart recorder for the first few years of operation.
- o Average depth of substrate in the cell ("L", Figure 52), determined by survey after construction, checked periodically for signs of substrate compression.
- o Effluent flow rate ("Qout", Figure 52), measured with a calibrated flow meter. At a minimum, it is recommended to monitor the cumulative effluent flow rate from all cells with a continuous chart recorder and totalizer. Ideally, each cell would be continuously monitored for these data, so that the organic matter content of the substrate in the cell could be correlated to the cumulative flow and metal loading that the cell treated. As the quality of the effluent will probably not be corrosive, flow meter construction materials need not be as chemical resistant as those used in measuring source flow rates. Assuming no seepage losses, evapotranspiration losses can be estimated using source and effluent flow rate values.

- o Substrate samples for laboratory testing. The frequency of sampling and testing will be driven by the performance of the system. Also, substrate disposal considerations may dictate some of the sampling methodology. Recommended sampling procedures and test parameters are discussed in the next two subsections.

Sampling points should be standardized to reduce sampling bias. From an academic perspective, piezometers may be installed at various substrate levels to monitor the progress of bacterial treatment as the water passes through the substrate. Water quality results may be correlated with other substrate parameters such as organic matter or carbon content.

SAMPLING SUBSTRATE FOR PHYSICAL TESTING

Baseline Sampling of Candidate Substrate Materials

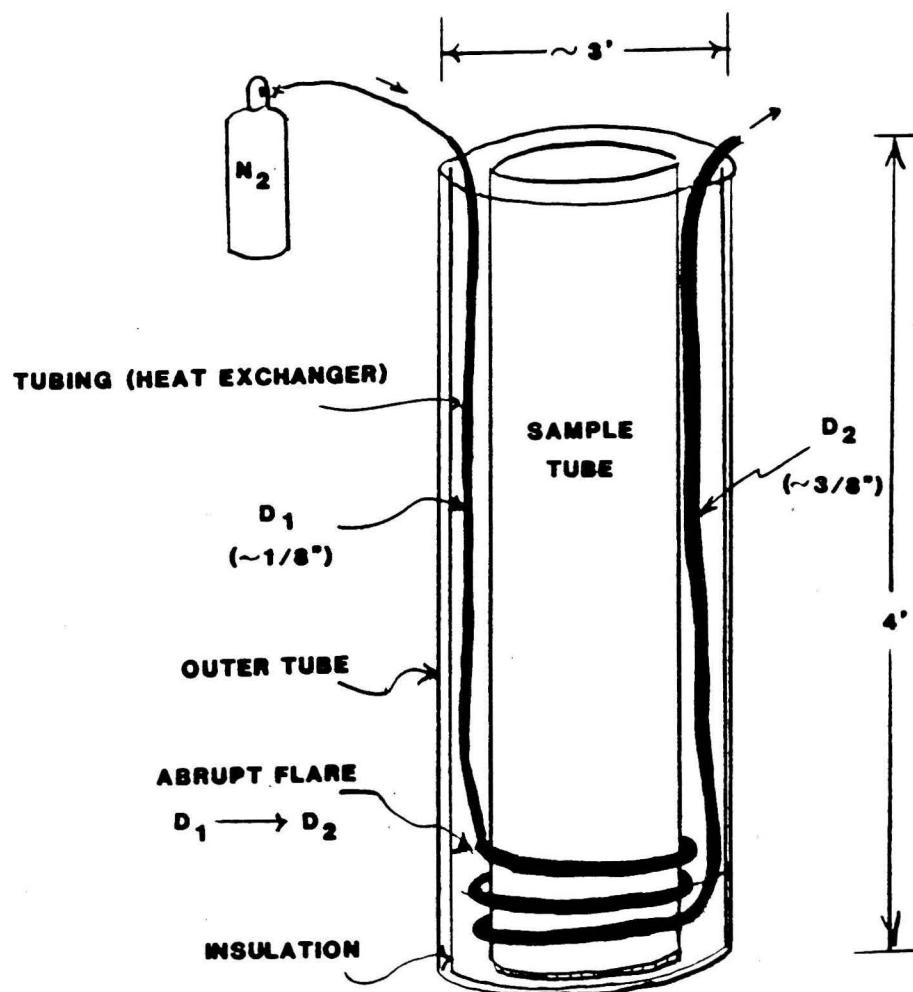
Candidate substrate materials should be sampled using methods that provide truly "representative" samples. Statistical evaluation of important substrate characteristics such as permeability and carbon/organic matter content should be considered. As with all soils, sample mass/volume should be a function of material size distribution; i.e., the larger the maximum particle size, the larger should be the mass of the sample. The number of samples might be governed by confidence interval requirements or other statistical parameters.

Sampling In-Situ Materials

It is desirable to obtain relatively undisturbed samples of in-situ substrate to adequately characterize it. There are a number of mechanical devices described in the literature on testing of peats and organic soils. Some "undisturbed" sampling procedures have been attempted for substrate with soupy consistency at the Big Five Wetland (114) such as closing the head end of the sampling tube and/or creating a suction at the back end of the sampling tube, but there has been little or no undisturbed sample retrieval success.

A thin wall sampling tube, such as specified in the American Society of Testing Materials (ASTM) Method D 1587, with extremely sharp (possibly serrated) leading edges may be used to delineate a relatively undisturbed sample. Recovering the sample, however, would be difficult due to its unconsolidated, nearly liquid nature. The use of a small heat exchanging device has been recommended to freeze the lower three or more inches of sample within the tube, effectively creating a temporary plug with which to extract the practically undisturbed sample. In practice, the heat exchanging device would be inserted and activated after the thin wall sampling tube had been driven a desired distance.

The heat exchanging device might consist of copper tubing coiled to just fit over the outside of the thin walled sampling tube as shown in Figure 64. The coil would be protected by an outer tubing and a layer of insulation to prevent freezing of the sample tube to a large volume of surrounding material. The outer tubing with coil would be put in place after placement of the sampling tube.



NOT TO SCALE

Figure 64. A prototype substrate sampling device.

The heat exchange source could be a tank of compressed gas, such as carbon dioxide or nitrogen, which would be connected to the tubing. The gas would be released and allowed to expand at the bottom of the heat exchanging device. To assist in the gas expansion, the diameter of the coil would be abruptly enlarged (for example, from 0.125 inches to 0.375 inches) in the area required to be frozen.

After extraction, the tube would be kept in an upright position and the ends of the thin wall sample tube would be covered with flexible plastic caps or similar devices.

The preservation of the sample after extraction could be completed in the following ways:

- o Allowing for expansion, the entire sample could be frozen, then shipping short distances in insulated containers would be possible;
- o With caps on both ends, the samples could be moved short distances (from the site to the lab) in a rack that kept the sample tubes oriented vertically. Freezing could be accomplished at the lab, if desired. Alternately or in addition to an airtight cap, a hot paraffin plug might be placed on top of the sample to further preserve sample integrity.

If it can be shown that freezing does not disrupt sample material characteristics, freezing the entire sample as soon as possible should be considered. As discussed in the next subsection, this approach offers a variety of advantages in testing procedures.

PHYSICAL TESTING

The following physical properties are considered important for classification and comparison of this research with other constructed wetlands research, furtherance of understanding of the treatment processes, and selection and development of values for design parameters:

- o Material Classification
- o Hydraulic Conductivity
- o Moisture-Density/Compaction Relations
- o Moisture-Density vs. Hydraulic Conductivity

The primary characteristic of a substrate material necessary for a number of other determinations is the specific gravity of the solid components in the substrate. Given that the "muck" in the wetlands is actually a mixture or slurry of solid substrate and acid mine water, knowing the specific gravity of the solids would allow estimations of moisture contents by measuring the specific gravity (bulk density) of samples. The specific gravity of the solids and bulk density of the mixture provide data from which the following characteristics can be calculated:

- o Porosity
- o Moisture content
- o Volume of solids in the mixture (for a given vol. or wt.)
- o Weight of solids in the mixture (for a given vol. or wt.)
- o Void ratio

- o Compaction
- o Concentration of solids by weight
- o Concentration of solids by volume

Field measurements immediately after sample collection may allow the estimation of sample gas content.

If the entire sample is frozen, adjustments for the density of water as a liquid and water as a solid would have to be made. However, the freezing of the entire sample would allow ease of sample splitting, either axially or laterally. It may be possible to make polished sections of frozen samples to evaluate compaction mechanisms, gas content and other phenomena.

Specific Gravity of Solids

The following alternative methods require evaluation:

- o Landva, et. el. (112, p. 48), subscribe to a method proposed by Akroyd:

Essentially it involves the placing of the pulverized peat sample in a flask or bottle, covering it with de-aired filtered kerosene, and applying a high vacuum until air bubbles cease to be emitted from the sample. The container is then filled with kerosene and permitted to reach a constant temperature. The specific gravity (Gs) may be calculated from the equation:

$$G_s = \frac{\text{Wt. of Dry Sample}}{\text{Wt. of Kerosene Displaced}} \times \text{Spec. Grav. of Kerosene}$$

- o There is no specific ASTM method for determining the specific gravity of peat. ASTM method C 128 applies to fine aggregate and uses water as the displaced medium but does not specify the de-airing and filtering as stated above.

The above methods both involve the same principle proposed by Archimedes. The first method is probably more accurate, and should be performed on a number of samples. The second method may be more appropriate to determine the effects of entrained air on the apparent specific gravity of the solids. A comparison of results between the two methods may be informative.

Bulk Density of Substrate/Water Mixtures

ASTM method D 4531 (113) was evaluated as it may apply to the bulk density determinations of either frozen or unfrozen samples recovered from constructed wetlands. Method D 4531 utilizes two different approaches, one which assumes a consolidated core material whose volume can be determined by direct measurement and a second approach that requires dipping a less easily measured sample in hot paraffin and the measuring of volume by submersion.

The first approach is probably more applicable than the second for both frozen and unfrozen samples. Assuming that the weight of the sample tube has been predetermined and that the volume of

the sample in the tube can be accurately measured, a bulk density of the mixture could be calculated. Corrections for frozen conditions would have to be made as necessary. In addition, some adjustment for gas content would have to be made as the mixture actually consists of solid, liquid and gas components.

Alternately, ASTM method D 4380 (113) may be used if a sample may be disturbed. This method, developed to test the density of bentonitic slurries, utilizes a mud balance and a measured volume to determine the bulk density of the mixture. De-gassification of samples would assist in determining true solids/liquid content of samples using this method.

Material Classification/Ash Content

Most contemporary references agree that "peat" consists of material with ash contents of less than 25% of dry weight. Considering the sources of the materials in a typical substrate might be composted manure, soil and other organics, (which probably contain significant mineral ash forming material), it is likely that the mushroom compost would not be classified as a peat. Nonetheless, since the organic content is a key substrate performance parameter due to its role in the sulfate-reducing bacteria's health, this parameter would be a useful material characteristic to measure. The organic content of a sample is calculated as follows:

$$\text{Organic Content} = 1 - (\text{Ash Content, expressed as a decimal}).$$

For the determination of ash content, Landva, et. al. (112, p. 45) recommend the ASTM method D 2974 modified by lowering the muffle furnace temperature to 440 degrees C (from 550 degr. C) and firing the sample for five hours. As this recommendation was made primarily to preserve the characteristics of mineral clays in samples, the modification is not required if very little clay is present in the material. Typically, ash content of substrate samples may be determined using method D 2974, unmodified.

It is interesting to note that Landva, et. al. (112, p. 44) draw a relationship between ash content and specific gravity for organic samples. However, the anticipated range of values for typical substrate materials might be expected to be different from reported values for peat.

Carbon Content (Ultimate Analysis)

The Ultimate Analyses procedure is typically applied to coal samples but can be applied to any material with combustible components such as wetland substrate. An ultimate analysis (ASTM D-3176) of a substrate sample is the determination of the ash and the elements of carbon, hydrogen, nitrogen, sulfur, and oxygen as products of complete combustion. To insure that organic carbon content is reported in the ultimate analysis results, samples should be digested in mild acid (HCl) and then thoroughly rinsed to remove mineral carbonate materials, an inorganic source of carbon that would not be available to sulfate-reducing bacteria.

Material Classification/Size Distribution

There are three general ASTM methods of classifying peats which may be applied to substrate materials by their size distributions and other factors:

D 2607 This method is a classification system based on five major material types according to generic origin and fiber content (Sphagnum, Hypnum, etc). Fibers are defined as materials retained on an ASTM No. 100 (0.15 mm) sieve, consisting of stems, leaves, or fragments of bog plants, but containing no particles larger than 0.5 inches (12.7 mm). It excludes fragments of other materials such as stones, sand and gravel.

D 2977 This method separates peat material into arbitrary fractions based on particle size. Physical separation of peat material according to particle size provides a useful indicator of the properties of the peat specimen such as pore space, decomposition, etc. It also provides a means of determining the amount of foreign matter. The four fractions are:

- o Foreign matter consisting of ash-forming material such as rocks and shells is removed manually from the 8 mesh sieve,
- o Coarse fiber is retained on the 8 mesh sieve,
- o Medium fiber is retained on the 20 mesh sieve and,
- o Fine fibers and fines are passed through the 20 mesh sieve and retained in the pan.

D 4427 This classification method standardizes naming peat products on the basis of fiber content (see D 2607, above), ash content (D 2974), acidity (D 2976), absorbency (D 2980) and botanical composition based on inspection.

A modified version of method D 4427 is recommended by substituting method D 2977 for size distribution in lieu of D 2607 as recommended in D 4427 unmodified. It is believed that the modified version offers more data of a physical nature compared to unmodified D 4427 which provides biological/geological data.

Volume Weights. Water Holding Capacity. Air Capacity of Saturated Peat

Ivanov (100) discusses "bound" and "free" water in peats and draws a relationship between the volume of bound water and the active or effective porosity and the hydraulic conductivity of peat. Research has indicated that the "immobilized" water in peat varies between 300% to 400% of the weight of solid matrix. In effect, the presence of bound water may increase the relative velocity of water through a wetlands system, thus reducing the residence time and adversely affecting chemical processes.

Preliminary estimates of residence time, using approximate data in Ivanov and the dimensions of the Big Five wetlands cell (114), indicate that actual residence time might be about 60% of the estimated residence time if bound water volume is ignored. Reed, et. al. (52) appear to have ignored the effects of bound water in calculations and projections.

Ivanov (100) reported that bound water estimates were derived from radioactive tracer data. A method that may closely approximate the amount of bound water in a sample is ASTM D 2980. This method sets up standardized conditions for measuring the volume and weight of water-saturated peat. From these data, saturated volume weights, water-holding capacity on a weight and volume basis, dry substrate volumes, and air volumes can be determined. The method provides useful information in evaluating substrate materials. If large air spaces are present, high water penetration and aeration exist. If air spaces are smaller, water retention is increased. Water retention would be greater in humified substrate materials (smaller air spaces), whereas water penetration would be greater in unhumified substrate. This test method may provide useful design data as to when the substrate needs to be periodically replaced to provide the optimum water treatment capacity.

Lemke (9) reported a 3.6 to 3.8 percent bound water content (as measured by drying at 105 °C) in dry mushroom compost; a free water content (as measured by drying at 25 °C) of 69.5 percent was found for mushroom compost used for one year in Cell A.

Measurement of a sample's bound water may provide useful data for the comparison of candidate substrate materials with those that have shown to be adequate. Further, the data may be useful in developing modifying existing design methodologies. Perhaps sulfate reducing bacteria reaction rates may be a function of bound/free water contents in substrate materials.

Hydraulic Conductivity. Laboratory Methods

The goal of hydraulic conductivity measurements is to be able to simulate in the laboratory actual flow conditions that might occur in the field wetlands environment. Thus, laboratory measurements would allow the evaluation of critical design parameters that might be encountered in a scale up of bench or pilot scale experiments. Standard ASTM methods provide a stable frame of reference from which to formulate an appropriate method that would approach the above goal.

ASTM method D 4511 yields the hydraulic conductivity of essentially saturated peat under constant head conditions (see Figure 49). This method is similar to ASTM method D 2434 for the permeability of granular soils under constant head. The principal distinction between the two methods is the way of measuring of pressure differential, which is a function of the range of expected hydraulic conductivity values.

Method D 2434 uses a fully saturated permeameter with the sample confined between two porous plates and a differential manometer to measure a wide range of values, from about 10^{-2} to 10^{-10} cm/sec.

Method D 4511 uses a partially saturated permeameter with the sample confined between two 40 mesh screens and a measured height difference between the top of the feed reservoir and the bottom of the permeameter to measure a range of values greater than 10^{-5} cm/sec.

Both methods assume laminar flow through a porous media as an ideal test condition so that Darcy's law (see SECTION 12) can apply.

The laboratory configuration prescribed by method D 4511 is probably more applicable to the field wetlands configuration due to the use of the 40 mesh screen rather than porous plates. The screen might be considered analogous to the layer of coarse rock in the bottom of the existing pilot plant. However, the partially saturated condition of method D 4511 may need to be modified to a fully saturated condition to be more representative of field conditions. Such a modification is shown on Figure 65.

Further, method D 4511 attempts to provide flow conditions with the void spaces saturated with water and no air bubbles in the voids. The likelihood of gas being generated in the substrate (from sulfate-reducing reactions) suggests that gas concentrations in the D 4511 permeameter should be allowed to remain as close as possible to in situ concentrations during hydraulic conductivity measurements to better simulate field conditions. Measurements with and without ambient gas concentrations may provide useful design data.

ASTM reports that the K of peat is very sensitive to changes in bulk density and that even under light compression, K can change by several orders of magnitude. This observation would probably apply to typical substrate materials. From a laboratory and field perspective, then, care must be observed to be able to adjust for changes in bulk density. Given that the sampling method proposed will provide relatively undisturbed samples, minor changes in bulk density might be desirable to achieve more correlatable results among samples; i.e., compare the hydraulic conductivity for many samples at the same bulk density.

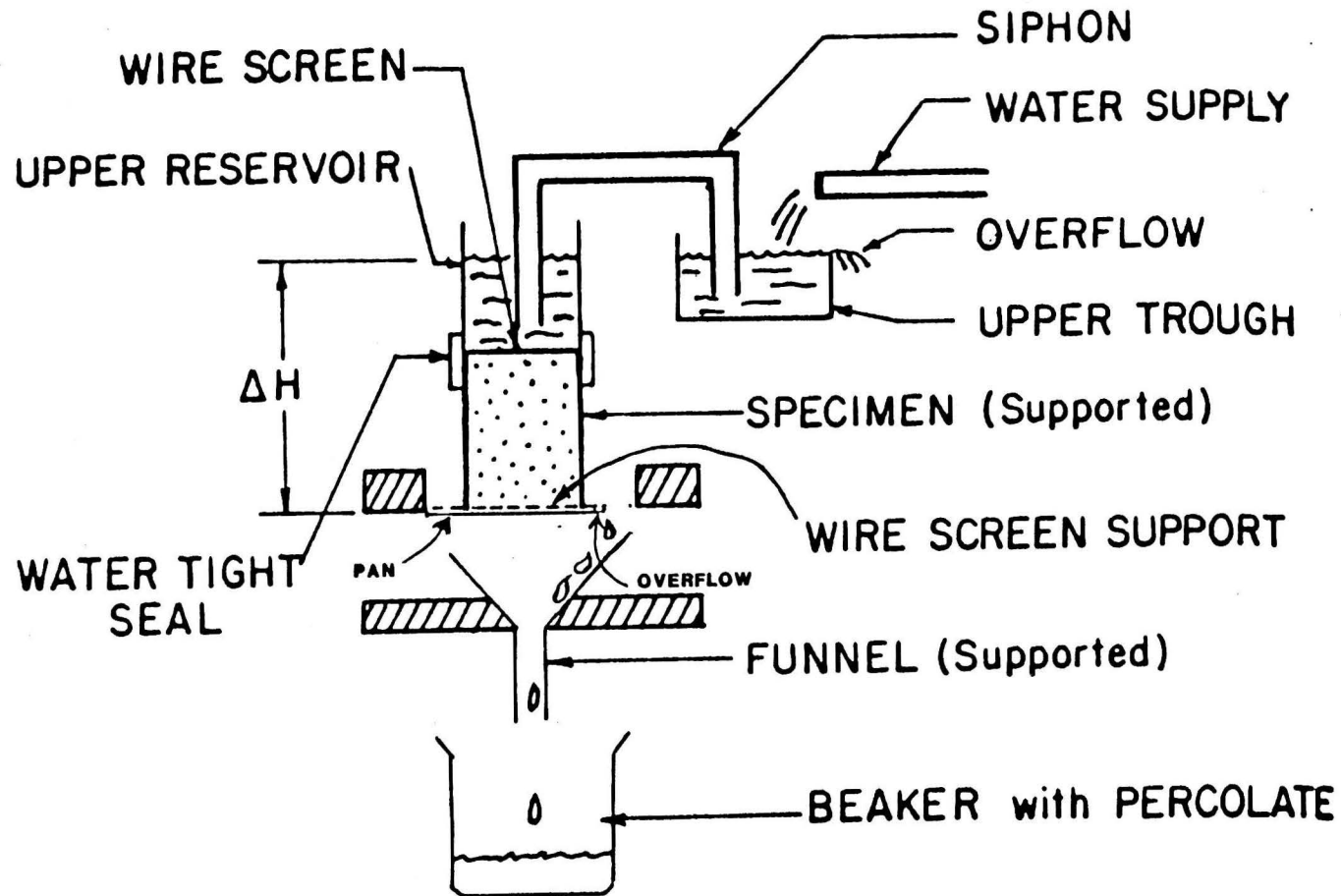
The effects of Stokes law of settling may allow the minor adjustments to bulk density suggested above. In order to achieve this, the permeameter configuration in D 4511 might be changed to allow water inflow from the bottom upwards instead of the top down (see Figure 50). If the upper 40 mesh screen were allowed to float freely to a level of a desired bulk density, and the flow through the permeameter temporarily adjusted into the turbulent range to generate "quicksand" conditions, the sample material might adjust to the new available bulk volume to provide a "standard" or repeatable bulk density. Thus, changes in hydraulic conductivity at a given location within the wetlands cell could be correlated to either bulk density or actual material characteristics or both. Other methods of adjusting bulk density might be subject to more error and sample disturbance.

The concept of bound water might be considered at this point. The amount of bound water may be a direct function of size distribution and bulk density. The modified D 4511 permeameter configuration provides a means of testing these hypotheses.

Hydraulic Conductivity, Field (In Situ) Methods

There is no ASTM method of measuring field hydraulic conductivity of saturated soils although methods are available for measuring in situ permeability of rock (ASTM D 4630). An applicable method that should be considered is either a falling head or constant head permeability test (102).

Falling head tests would be conducted in a boring completed in a wetland cell by either raising the water level in the boring above the static level of the wetland cell level and observing the fall of the water level in the boring as a function of time, or by pumping water from the boring so the water level in the



ΔH = TOTAL HYDRAULIC HEAD DIFFERENCE
ACROSS SPECIMEN.

Figure 65.

A downflow laboratory permeameter modified for full saturation.

boring is below the static level of the cell and then observing the recovery of water in the boring as a function of time. Given the fairly liquid nature of the substrate in the cell which might be sucked into the casing, the first approach is preferred; that is, observing the fall in water level from some level above static.

The boring would be cased with perforated PVC pipe, with the perforations located in the zone of interest. Due to boundary conditions, a small diameter, say 1 inch (2.54 cm), boring is preferred. Various shape factors and other parameters influence the final calculations, but the data acquisition would be fairly rapid considering the site configuration.

Constant head tests could be conducted in a similar manner and are subject to the same limitations and comments as above. The primary difference, as the name implies, is that the head of water in the casing is kept constant by the addition of a known volume of water. Hence, for practical purposes, this test can only be performed with the head of water in the casing above the static level of the wetland cell.

To maintain a constant head of water in the casing, the use of a volumemeter or similar device is required.

SECTION 15

SYSTEM OPERATION AND MAINTENANCE

SUBSTRATE MAINTENANCE

The substrate is a key component in any functioning constructed wetland treating acid/metal drainage. Like any mechanical/ chemical/biological treatment system, declining effluent characteristics will indicate that system maintenance is required. Design methodologies and physical testing of engineering parameters have established a foundation for determining which aspects of the wetland operation may need attention/correction.

Whether substrate materials can "wear out" remains a central issue in wetlands design, operation and maintenance. From the perspective of carbon content available for bacterial utilization, the substrate has a "useful life" imposed by chemical stoichiometry adjusted by the effects of humification.

Summarizing, wetland substrate will be subjected to stresses that tend to decrease its performance with use. These stresses include:

- o Precipitation of metal sulfides in void spaces
- o Consumption of organic matter/substrate carbon
- o Humification of organic matter
- o Loss of permeability which may be related to organic matter conditions and/or compaction from settlement

The effects of the stresses are typically irreversible, but mitigation measures could provide minor extensions of substrate usefulness. Mitigation measures include:

- o Maintenance of a plant community on the surface of the wetland to provide a source of organic matter/carbon
- o Periodic additions of organic matter as a solid on the surface of the wetland (straw added using mulch-spreading machines such as those employed in reclaiming disturbed land)
- o Periodic removal of finer-grained materials that could lower substrate permeability; precipitated metals in amorphous form may be removed simultaneously
- o Continuous maintenance of substrate saturation, even if the wetland cell is "idle". Permeability restoration by allowing the substrate to dry out is only temporary and will result in the oxidation of precipitated sulfides and the remobilization of metals when flows are re-established. Furthermore, Ivanov (100) points out that drying accelerates organic material breakdown and decreases substrate permeability due to compression.
- o Prohibition of machinery/personnel on substrate (this may require additional construction to allow periodic sampling without impacting substrate)

Ultimately, perhaps after decades of operation, the substrate may require total replacement. Given that the wetland system has been designed properly, substrate removal should not impact other subsystems of the wetland cells such as underdrains, gravel layers and system plumbing. Substrate replacement in a "stacked" configuration would need to be considered in the initial design of the facility.

Assuming that the substrate material is totally humified and mucky, slurry pumping/dredging technology might be considered in its removal and replacement. For a conventional configuration wetland, substrate could be removed from inundated cells with a shallow-draft dredge and replaced with the same craft in almost a continuous process. For a stacked configuration, flushing mechanisms and bottom or side drains and launders/flumes could be employed to remove/replace spent substrate.

Dewatering and disposal of the spent substrate material or removed fines will be governed by site-specific substrate characteristics and governmental regulations (see SECTION 8). However, consideration should be given to the resource potential of the metals contained in the substrate. Bog iron ore in naturally-occurring wetland metal deposits was developed as a valuable resource by the early American iron industry. Sulfide minerals could be concentrated using flotation methods for ultimate recovery by smelting or other processes.

Data suggest (41, 65) that partial substrate replacement by mixing old substrate with new materials should be attempted with great care because the mixing process would infuse oxygen into the substrate. The alteration of anoxic conditions in the substrate would result in the oxidation of metal sulfides and the re-mobilization of metals. However, mobilized metal-laden water could be temporarily routed to a still-functioning wetland cell (perhaps by pumping) or to a metals recovery system. Alternately, the rejuvenated cell could be allowed to "lay fallow" without fresh inflows to allow the sulfide-reducing bacteria to re-establish anoxic conditions and reduce any oxidized metals present in the substrate. Thus, the total removal of substrate could be delayed or circumvented entirely. Also, as seen in Cell A, substrate disturbance may have irreparably altered the permeability of the new/old substrate mix.

Land disposal of substrate without metals recovery may follow two process options in accordance with hazardous or solid waste handling regulations:

- o The substrate would have to be maintained in a saturated condition, otherwise oxidation of sulfides could produce new acid drainage.
- o Dried substrate would have to be maintained in a dry environment, perhaps secured beneath an impermeable soil/geomembrane cap.

MAINTENANCE OF CONVEYANCES AND FLOW CONTROLS

Pipeline Maintenance

The precipitation of metal hydroxides and the corrosion of metal components are likely to comprise the typical maintenance problems associated with the operation of a constructed wetland.

Periodic inspections of the installation should include measurements associated with flow rates and pressures. Headlosses in pipes should be calculated to determine if metal hydroxides are reducing the cross sectional areas of pipes. The net effect of this phenomenon would be increases in pipeline flow velocities and headlosses and accompanying decreases in flow rates.

Plugging of measuring points may result in erroneous pressure data readings. Thus, measuring points (pipeline taps) should be designed to allow flushing with fresh water prior to measurements. This requirement applies to continuous recording pressure and velocity probes as well. These probes need to be periodically inspected, cleaned and calibrated to insure that they are operating properly.

To obtain a tangible observation of internal pipeline conditions, test spool sections should be considered. Spool sections can be removed and measured to obtain qualitative data on pipeline conditions such as corrosion or precipitation plugging. Thus, internal pipeline conditions can be physically documented. A typical spool arrangement is shown on Figure 66.

Pipelines should be cleaned as needed before hydroxide deposits significantly or completely fill the pipe cross section. Theoretically, scouring effects from higher flow velocities could maintain a stable pipe cross sectional area. However, low pressure heads available at a site may limit the effects of scouring. Maintenance of design flows should not rely entirely on scouring effects unless the factors controlling scour are well understood.

Pipeline "pigs" are normally used to clean the interiors of pipes with detrimental accumulations. Pigs are commercially available and should be used periodically on a site-specific schedule based on experience. The pig's construction material should be compatible with the acidic conditions that will be encountered.

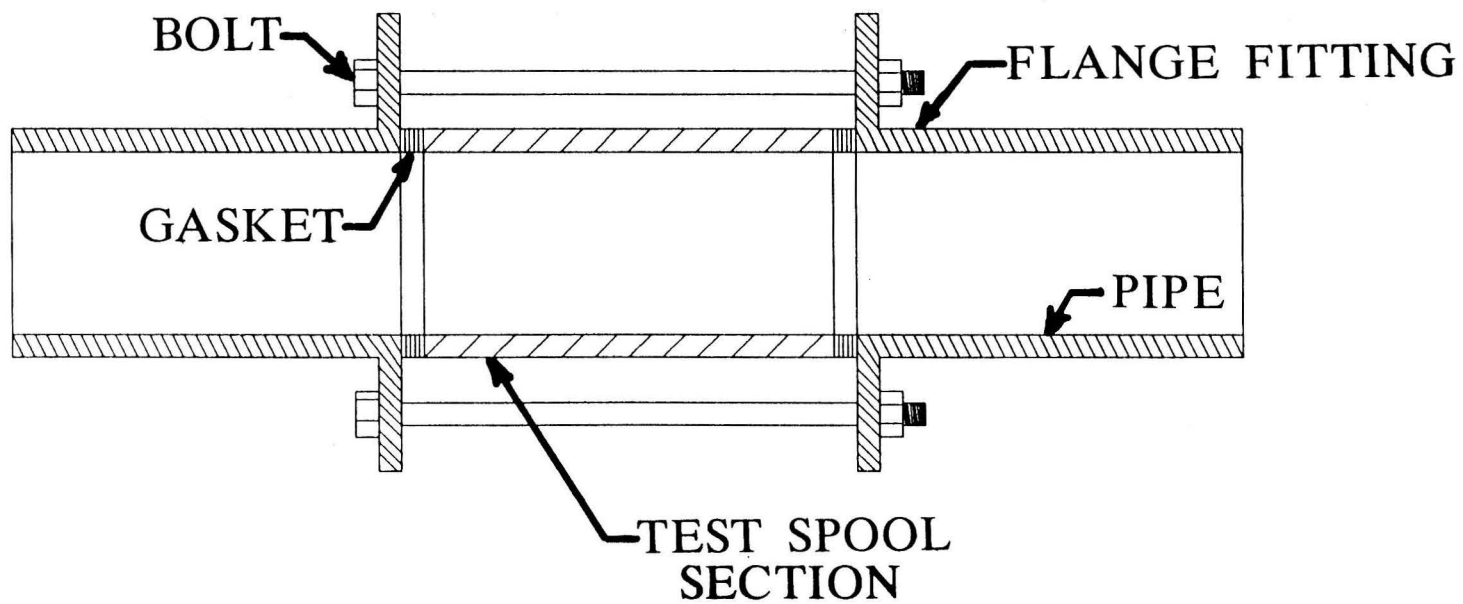
Provision should be made to divert metal hydroxide sludges resulting from pipeline cleaning operations away from wetland cell distribution systems. Holding/evaporation ponds or containment berms may be required to complete this periodic maintenance task.

As shown in Figure 67, valves should be installed with clean-out plugs at tee- or wye- intersections to allow periodic cleaning with brushes or similar tools.

Surface Conveyance/Wetland Containment Maintenance

Surface conveyance maintenance will probably consist of the removal of metal hydroxide deposits from the conveyance invert and possibly the removal/replacement of substrate material lining the surface conveyance. Other maintenance tasks may include repairs from burrowing animals or damages from storm events. Earthmoving equipment such as backhoes or small bulldozers would typically be used to complete these types of repairs.

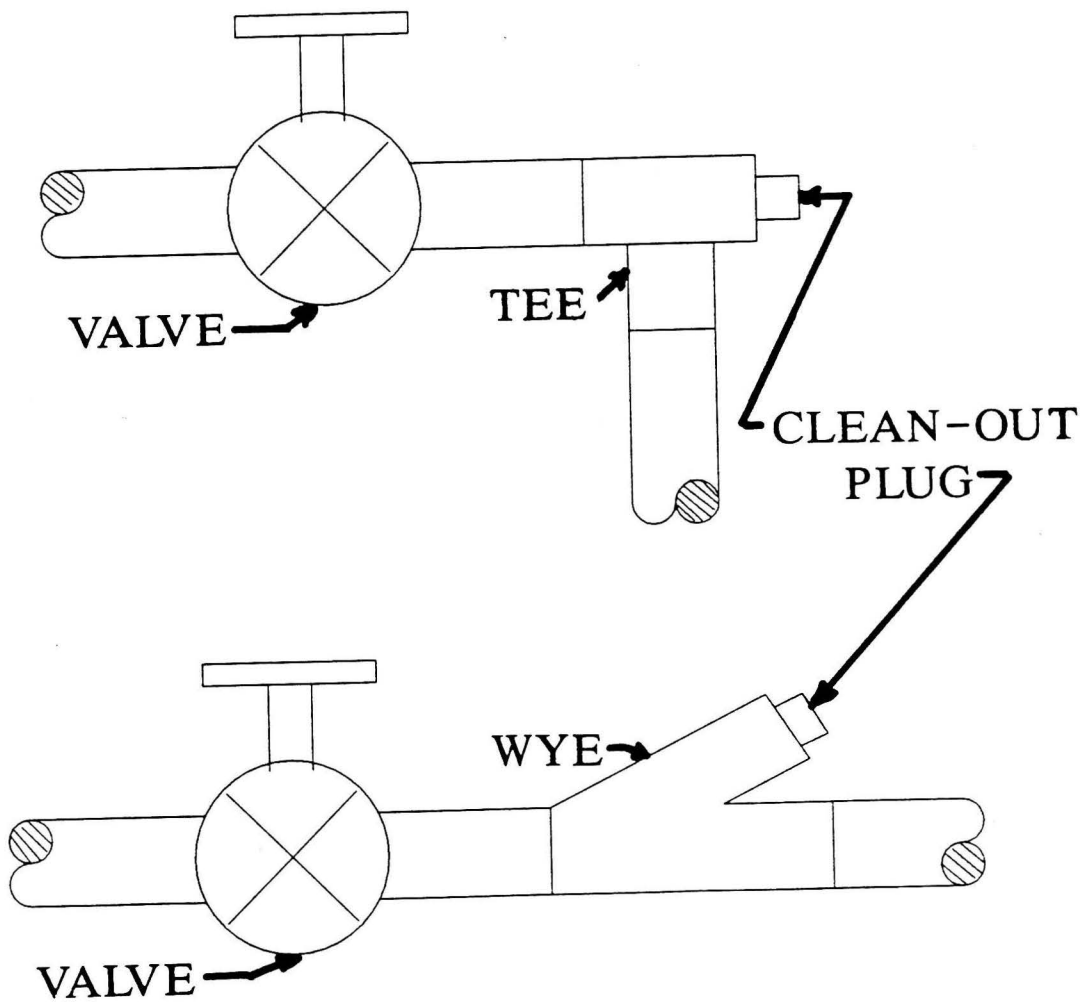
Burrowing animals can impact wetland operations. Other workers (69) have addressed mitigation measures against burrowing animals. These include covering embankment or channel surfaces with chain-link fence and/or rip-rap and installing drop-pipe spillways.



15-4

NOT TO SCALE

Figure 66. A typical spool arrangement used to monitor internal pipeline conditions.



NOT TO SCALE

Figure 67. A diagram of the pipe cleaning valve arrangement used at tee-intersections.

SECTION 16

COST ESTIMATING

Typical costs of constructing wetlands have been reported in the literature (2, 69, 109). Due to the wide variation in siting and construction conditions, no "typical" unit costs for constructing wetlands are presented herein. This section provides an outline of typical cost components associated with the construction and operation of a constructed wetland.

Actual cost estimates for a specific project can be generated by summing the cost values of individual components. Unit construction cost data are available from private-sector publications such as the Means Cost Data (115) or Blue Book Equipment Costs (116).

CAPITAL/CONSTRUCTION COSTS

The major components of capital cost for constructed wetlands include:

- o Preliminary Engineering and Testing
- o Environmental Baseline Studies, Permits
- o Land Acquisition
- o Rights of Way Access
- o Final Engineering Design and Construction Specifications
- o Construction

The entire scope of the project should be included in the capital cost estimate, from the design and construction of a collection system, to the acquisition of land for conveyances and the wetland itself and finally to the construction of the designed facility.

Preliminary Engineering and Testing

Given that a source of acid/metal-laden water has been identified and characterized, preliminary engineering and testing are appropriate. Preliminary engineering and testing comprise those rudimentary activities that help to determine the feasibility of utilizing wetlands technology for a particular site. Typical activities include but are not limited to:

- o Lab scale "bottle testing" of different combinations of source water and candidate substrates. These tests take several weeks to complete.
- o Physical testing of candidate substrate materials as detailed in SECTION 14. These tests can be completed while bottle testing is underway.
- o Field scale testing with 30 gallon (120 liter) "mini-cells" to establish candidate substrate long-term permeability, viable loading rates and flux capacities. These tests should be continued until "mini-cell" geochemistry and hydrology is completely understood. This may require six to 12 months of monitoring and testing.

- o Preliminary wetland designs. If loading constraints require a land area that is not practical and a "stacked" configuration has been eliminated due to cost considerations, wetland treatment may not be feasible compared to other alternatives. This activity should be conducted as soon as reliable field scale testing data are available.
- o Pilot scale testing with cells at least 10 square meters in size using preliminary wetland designs. Pilot scale testing would verify the "mini-cell" results and investigate the feasibility of typical construction components such as conveyances, valves, source collection systems and scaled-up substrate masses. Pilot scale tests should be conducted for at least a year. Pilot scale facilities could become a "module" in the eventual full-scale system.
- o Hydrologic investigations to establish source flow rate variation, if any. This effort may involve rehabilitation of underground workings to evaluate potential bulkhead locations. The effort may require up to a year of flow rate monitoring unless flow rate/hydrologic data are available.

The costs of conducting these activities will vary significantly for each site. Typically, both preliminary engineering and testing and final engineering design (SECTION 9) may amount to from six to ten percent of a project's total capital cost (115).

Environmental Baseline Studies, Permits

Baseline environmental studies will be required prior to the siting and permitting of a constructed wetland. The extent of the studies will be a function of the volume of existing data. For example, regulatory agencies may not require background air quality studies if an adequate database already exists, and complex air quality modeling may not be necessary if there are no significant thermal emissions or large material stockpiles. It should be assumed that air quality, water quality and geosciences aspects of the project will require some level of investigation. In addition, cultural resources, vegetation and wildlife, land use and socio-economic aspects of the project will need to be addressed.

In summary, key environmental issues include:

- o air quality
- o climatology
- o water quality and water use (surface and groundwater)
- o soils and geology
- o vegetation, wildlife, threatened and endangered species
- o used substrate "waste" characterization
- o land use and visual impacts
- o cultural resources
- o socio-economic impacts

SECTION 8 addresses regulatory/permit aspects of constructed wetlands. Cost estimates for environmental baseline studies and permits should consider time for professional representatives of the project to meet with regulators.

Land Acquisition

For sites with significant private land holdings, land acquisition costs can amount to a significant percentage of overall project capital cost. For example, land acquisition costs for the Arcata, CA wetland installation amounted to nearly 15 percent of the total project cost (109). At the same site, land acquisition represented about 32 percent of the construction cost and was greater than preliminary engineering (plan of study), permit and right of way access combined.

Nominal increases in construction and operations costs by considering "stacked" wetland configuration may be more than offset by savings in land acquisition costs.

Rights of Way Access

If the wetland site is a significant distance from the acid water source, significant rights of way access may be required. The routing of pipes, open channels and power lines (assuming that recording instruments may require a non-battery power source) may be required through lands not necessarily included in the wetland proper. The further the source water is from the wetland installation, the higher these costs are likely to be.

Rights of way access costs may consist of crossing fees imposed by entities such as railroads or private land owners but more than likely will involve professional fees to negotiate and finalize agreements for the acquisition of rights of way.

Final Engineering Design and Construction Specifications

Final engineering design involves the employment of methodologies developed in SECTION 12 and standard engineering approaches to produce the details of wetland construction.

Minor field investigations to determine the geotechnical and hydrologic characteristics of the site are included in this effort. The field investigations may include the installation of additional ground water monitoring wells (to supplement those installed in the environmental studies) and the gathering of geotechnical data associated with available soils on site or at nearby soil borrow sites. These data are typically acquired by drilling of geotechnical borings.

Final designs are used to generate construction specifications or plans which include text and shop drawings, detailing what will be built, how it will be built and, if necessary, how a contractor would be paid to build it. Construction specifications are typically organized by construction task.

An Engineer's Cost Estimate is usually included with construction specifications.

As stated earlier, preliminary and final engineering can amount to from six to ten percent of total project costs (115). Attempts to economize in engineering may result in higher operating costs when systems do not perform as intended and must be subsequently re-designed and re-built.

Construction

A construction cost estimate is typically included with the documents provided by the project engineering staff. Construction cost items are typically distributed among discrete tasks and may be estimated on a lump-sum or unit price basis.

specifications. Construction management insures that no shortcuts in installation procedures are taken nor substitution of materials made that could compromise the design of the facility. Typically, construction management costs comprise approximately six percent of the total construction cost.

OPERATING COSTS

Operating costs are clearly distributed between two major categories, nominal maintenance and inspection and major overhauls.

Nominal maintenance tasks typically should include:

- o Periodic, scheduled inspections
- o Sampling events, maintenance of instruments and chart recording devices
- o Cleaning of conveyances
- o Flow adjustments and balancing flows among cells

The costs of nominal maintenance should include the preparation of periodic reports, management of sampling and testing quality assurance activities and the costs of sample analysis.

Major overhauls may include periodic substrate rejuvenation or total replacement. Cost components may include:

- o Removal of existing substrate materials
- o Removal of some aspects of cell plumbing/water distribution system
- o Removal and preservation of plants
- o Treatment of removed substrate materials (drying, stabilization processing, metals recovery)
- o Containerization of removed substrate materials
- o Transportation and disposal of removed materials
- o Purchase of rejuvenation materials or replacement substrate raw materials
- o Transportation of raw materials to the site
- o Preparation of materials prior to installation
- o Installation of prepared, rejuvenated or new substrate materials
- o Replanting of vegetation
- o Temporary treatment or rehandling of untreated effluents (may include pumping or temporary impoundment of source water)

Costs associated with the above tasks may be partially offset by revenues derived from metals recovery. Metals recovery from substrate materials could provide two distinct advantages:

- o Spent substrate materials may not be considered hazardous and may be disposed in a municipal landfill or used in another beneficial use (soil amendment)
- o Recovered metals may be processed to yield a saleable product.

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Wetland Design for Mining Operations

Section II

STAGED, AEROBIC, WETLANDS-BASED ACID DRAINAGE TREATMENT SYSTEMS
DESIGN, CONSTRUCTION, AND OPERATION

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INTRODUCTION

Staged, aerobic, constructed wetlands-based systems offer a potential low-cost, natural, low-maintenance, and long-term alternative to conventional treatment of acid drainage (Brodie, 1992a, Appendix 1). Guidelines for design and construction of treatment wetlands exist but, although useful for general planning purposes, should not be considered comprehensive due to the rapidly evolving constructed wetlands technology (Brodie, 1989, 1990, 1991c; Brodie et al, 1988; Hammer, 1989; Karathanasis, 1991; Kleinmann et al, 1990; Pesavento, 1984; Reed et al, 1988; U.S. EPA, 1985; Wildeman et al, 1991; WPCF, 1990). This workshop is designed to present current guidelines on the processes of preliminary considerations, design, operation, and maintenance of staged, aerobic constructed wetlands for treating acid drainage. The design concepts discussed are therefore primarily oriented to acid water treatment and are probably not optimal for other types of wetlands construction on mined lands (e.g., mitigation wetlands). However, because the types of systems described in this report are efficient at removing suspended solids, the designs may be useful for managing small to moderate flows of stormwater.

Using wetlands for water pollution control began in Europe where research and applications involving wetlands and vegetative waste treatment date back to the early 1950's. In the U.S., experimental application of wastewater was tested in wetlands during the 1970's. However, treatment of acid drainage did not evolve from wastewater treatment but rather from water quality studies at sites where acid mine drainage was flowing into natural Sphagnum moss bogs.

The first of these studies, by a group at Wright State University, found Sphagnum recurvum growing in pH 2.5 water in Ohio's Powelson Wildlife Area. Iron, magnesium, sulfate, calcium and manganese all decreased while pH increased from 2.5 to 4-6 s.u. as the water flowed through the bog. A natural outcrop of limestone located downstream provided sufficient neutralization to raise the effluent pH to between 6 and 7 s.u. (Huntsman et al, 1978).

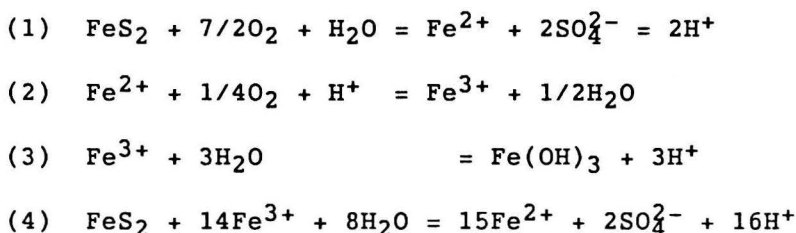
A similar study was conducted by a West Virginia University group at Tub Run Bog in northern West Virginia. They found that acid drainage flowing into the wetlands area rapidly improved in quality. In 20 - 50 meters, pH rose from 3.0 - 3.6 s.u. to 5.5 - 6.1 s.u., while only 10 - 20 meters of flow through the bog was needed to reduce sulfate concentrations from 210 - 275 mg/l to 5 - 15 mg/l and iron from 26 - 73 mg/l to less than 2 mg/l (Wieder et al, 1982).

WETLANDS PROCESSES

"Wetlands" is a generic term encompassing swamps, marshes, bogs, wet meadows, fens, etc. The term allows general discussion of at least two types, cattail marshes and peat moss bogs, which are dominated by plants that actually prefer slightly to moderately acidic water. These plants also tolerate levels of sulfate and various metals that would be toxic to most plant forms. Most important, these plants form the framework for a self-maintaining ecosystem that removes metals, mineral acidity, and sulfates.

Several physical, chemical, and biological processes contribute to changes of the chemistry of mine drainage as it flows through a constructed wetlands (Figure 1). The simplest mechanism is dilution. Wetlands are normally built on a hydrologically low site, and additional flows from surface drainage or non-target groundwater seeps are common. In some systems, major inflows of uncontaminated groundwater and storm runoff can cause changes in chemistry that might be mistakenly attributed to biological or chemical processes. Hedin (1992) has suggested a methodology using Mg concentrations as an adjustment factor which accounts for dilution effects in a constructed wetlands.

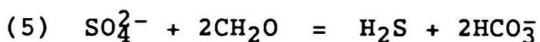
Probably the most important metal removing mechanisms in wetlands, as they are currently being constructed, are bacterially-catalyzed oxidation and hydrolysis reactions that cause dissolved iron to precipitate as insoluble iron, which is incorporated into the substrate. In one study of the metal chemistry of peat in a 10-month-old constructed wetlands, 93 percent of the accumulated iron and 27 percent of the manganese accumulation were in oxidized forms (Wieder et al, 1985). Other more recent studies substantiate Wieder's findings (Faulkner and Richardson, 1990; Tarutis and Unz, 1990). Iron oxidation and hydrolysis, however, is an acid-generating reaction which acts to lower pH. These reactions are summarized below (Stumm and Morgan, 1970).



Note that these reactions are catalyzed by the bacterium Thiobacillus ferrooxidans.

Faulkner and Richardson (1990a) also suggest that Mn sorption to Fe oxides is a likely, long-term Mn removal mechanism. Successful Mn removal at wetlands receiving excess alkalinity from anoxic limestone drains may be attributed to Mn coprecipitation (Brodie, 1992a). Biological rock filters for Mn removal may also be appropriate (Gordon, 1989; Meehan, 1991).

Another potentially important mechanism is bacterial sulfate reduction, which occurs in the anaerobic organic substrate (Dvorak et al, 1991; Hedin et al, 1989; McIntire and Edenborn, 1990). Wetlands constructed with a composted organic substrate show high rates of biological activity and very significant rates of sulfide production. The sulfide ion reacts with metals to form an insoluble precipitate, which remains buried in the organic mass. More important, is the fact that this reactions series consumes acidity and acts to raise pH.



Hydrogen sulfide will, depending on the chemical environment, react with dissolved metals and precipitate as a polysulfide or iron sulfides (FeS , FeS_2).

POLLUTANT REMOVAL MECHANISMS

Aerobic Constructed Wetlands

MAJOR MECHANISMS

- Abiotic & Bacterially-Mediated Fe & Mn Oxidation
- Fe Hydrolysis
- Mn Sorption & Coprecipitation
- Carbonate Buffering
- Sulfate Reduction
- Burial/Diagenesis

MINOR MECHANISMS

- Dilution/Aeration & CO₂ Stripping
- Plant Uptake
- Absorption
- Chelation
- Mn-Carbonate Formation
- Cation Exchange
- Organic & Inorganic Complexing
- Algae & Fungi-Mediated Oxidation & Oxygenation

FIGURE 1

The neutralization aspect of sulfate reduction is, at present, more important than metal removal because oxidation and hydrolysis is a more efficient way to remove iron and dissolved iron can interfere with sulfide production (iron reduction precedes sulfate reduction). Therefore, biological treatment systems that incorporate sulfate reduction should be designed to treat the water sequentially, so that most of the iron is removed aerobically before anaerobic processes predominate. Improvements in water quality may also result from the accumulation of metals in plants and in the organic substrate, and from microbially mediated reduction processes, and abiotic or microbially-catalyzed metal oxidation and hydrolysis reactions. Because wetlands have heterogeneous environmental conditions, these processes are intertwined.

Much of the original field and laboratory research with constructed wetlands focuses on the ability of plants to accumulate metals. Sphagnum has a well-established capability to accumulate iron (Burris et al, 1984; Gerber et al, 1985; Wenerick et al, 1988). However, except in low-flow, low-concentration situations ($\text{Fe} < 10 \text{ mg/l}$), metal accumulation in Sphagnum reaches a toxic level within a single growing season (Spratt and Wieder, 1988). Thus, although many of the original constructed wetlands were built with Sphagnum, few remain operational. Typha is much more tolerant of mine drainage than Sphagnum, probably because it does not accumulate metals to high, toxic concentrations. Although Typha is the dominant source of productivity and living biomass in most constructed wetlands, its role as an iron sink is negligible and probably accounts for less than 1 percent of the annual inflow iron load.

Certain algae have recently received attention from wetlands builders and researchers because of observations that algal blooms are sometimes associated with decreased dissolved manganese concentrations. Some wetlands builders have attempted to enhance algal growth with periodic fertilization and by creating open water ponds in which competition with emergent plants for sunlight is reduced. Unfortunately, like removal of iron by plant accumulation, removal of manganese by algal activity is probably minor and only useful at low contaminant concentrations.

The organic substrates sometimes used in wetlands construction can remove metals from solution by adsorption, chelation and cation exchange processes. Detailed investigation of adsorption and chelation processes in peat systems has shown that metal-removal capacities are limited. In most constructed wetlands, these capacities would be exhausted with several months of exposure to acid drainage. In aerobic wetlands, the substrates do not contribute greatly to the pollutant removal processes except to the extent that they support the growth of aquatic vegetation.

PRELIMINARY CONSIDERATIONS

General

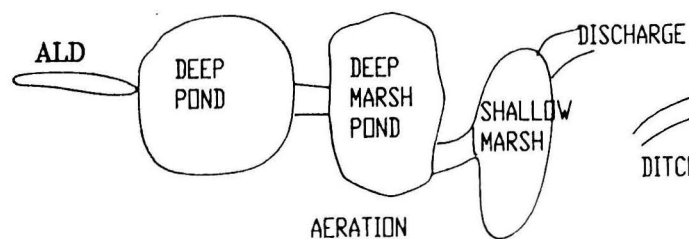
At the conception of a wetlands project, one should become familiar with existing and proposed regulations and guidelines regarding constructed wetlands. These requirements vary from state to state, but, in addition to potential local or regional requirements, could include the following.

<u>Regulation/Requirement</u>	<u>Federal Law</u>
Environmental Review	National Environmental Policy Act
National Pollutant Discharge Elimination System (NPDES) Permit	Clean Water Act
Mining/Reclamation Permit	Surface Mining Control and Reclamation Act
Air Quality/Construction Permit	Clean Air Act
Archaeological Survey	National Historic Preservation Act
Survey for Protected Species or Habitat	Endangered Species Act
Consideration of Floodplains and Existing Wetlands	Executive Orders 11998 (Floodplain Management) and 11990 (Protection of Wetlands)

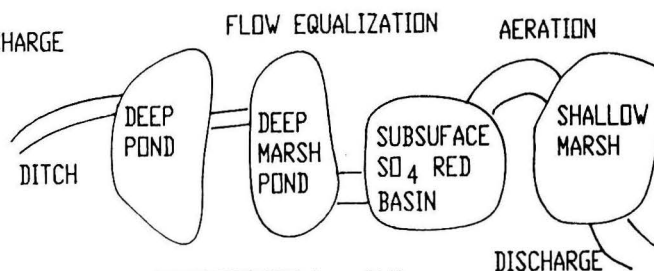
Site conditions that influence wetlands design and construction include hydrology, wastewater character, geology, soils, topography, access, land availability and use, and geotechnical attributes. Selection and evaluation of sites for constructed wetlands treatment systems has been detailed elsewhere (Brodie, 1988). It is recognized that siting a wetlands system is usually limited to the areas immediate to the acid water discharge, however, certain considerations should be adhered to for favorable results.

Hydrology

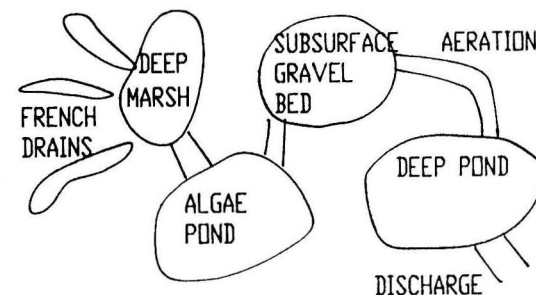
Surface and groundwater flow patterns, use, quantity, and chemistry should be determined sufficiently to properly design major hydraulically sensitive components of a wetlands (e.g., dikes, spillways, channels, retention basins). Maximum stormflow into a wetlands should be closely estimated because of the profound effects (scouring, flushing of sediments, overloading, structural failure) of surface runoff on a wetlands system. Conversely, periods of low or no flow should be determined. Acid inflows should be completely characterized chemically to determine the presence of major and hazardous constituents. Minimally, inflows to a proposed wetlands should be sampled and analyzed several times over the year for pH, dissolved oxygen, total and dissolved Fe, total manganese, aluminum, total sulfate, alkalinity, and acidity. A determination of the presence of toxic constituents (e.g., heavy metals, pesticides, organics) is recommended, especially if the source of the acid water is not well-defined or is a process waste (e.g., coal ash, gob). Nearby water wells, springs, or public water supplies should be sampled to document pre-wetlands water quality. Downstream water quality and biologic surveys may be useful in documenting stream recovery to support release from a permit.



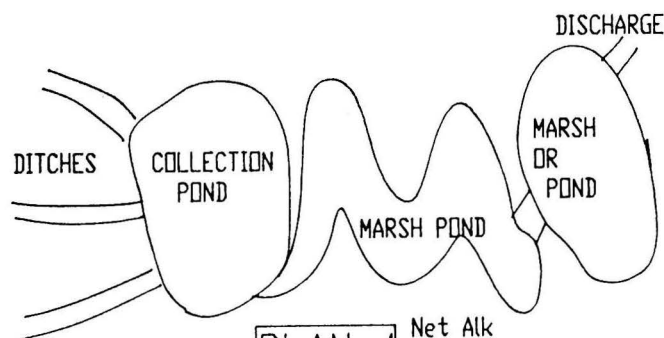
PLAN 1 Zero ALK
High Fe
Mod Mn



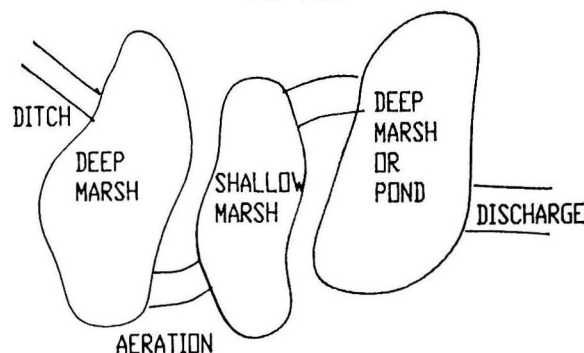
PLAN 2 Low ALK
High Fe
Var Flow



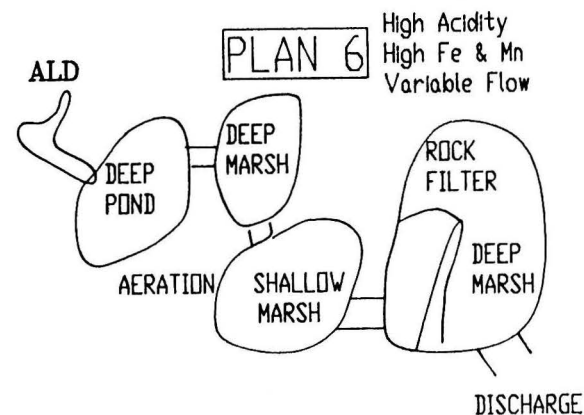
PLAN 3 Net ALK
Mod Fe
High Mn



PLAN 4 Net Alk
Mod Fe & Mn
Var Flow

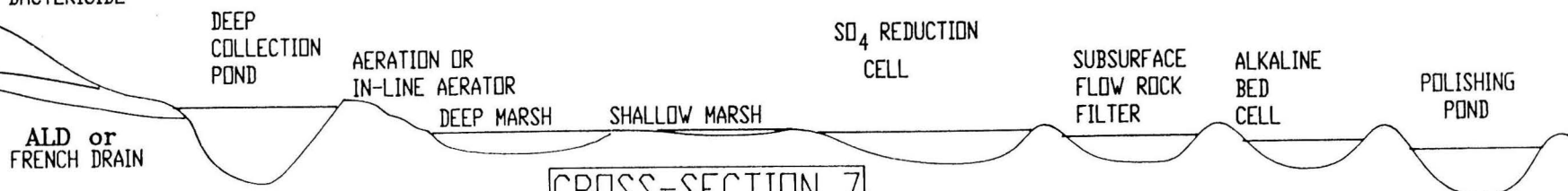


PLAN 5 Low Acidity
Low Fe & Mn

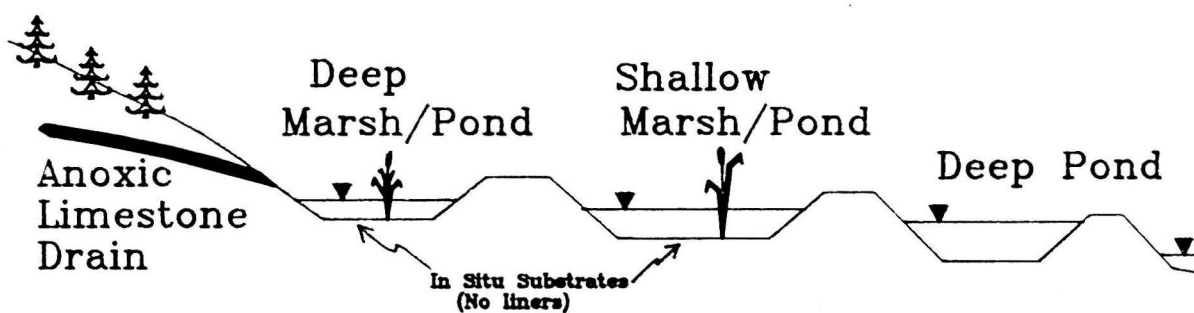
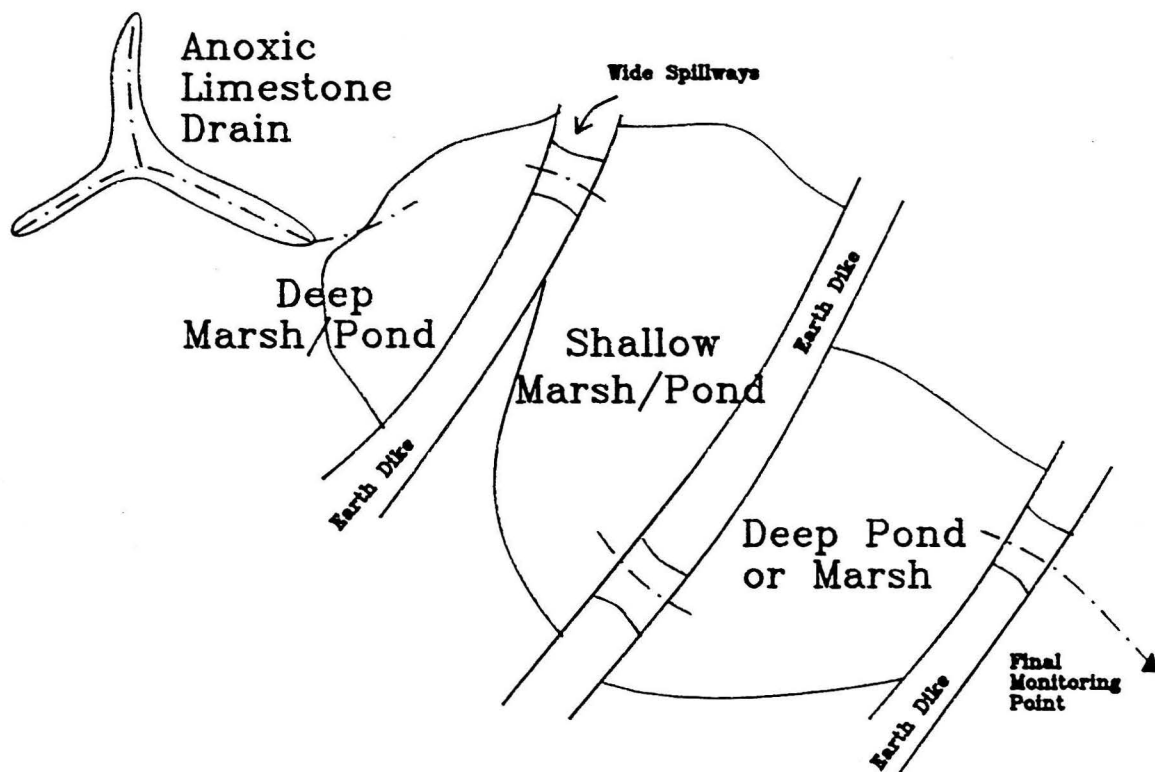


PLAN 6 High Acidity
High Fe & Mn
Variable Flow

ALKALINE RECHARGE
BACTERICIDE



CROSS-SECTION 7



TYPICAL STAGED, AEROBIC CONSTRUCTED WETLANDS

FIGURE 3

Simplified Flow Chart for Designing Staged, Aerobic Constructed Wetlands

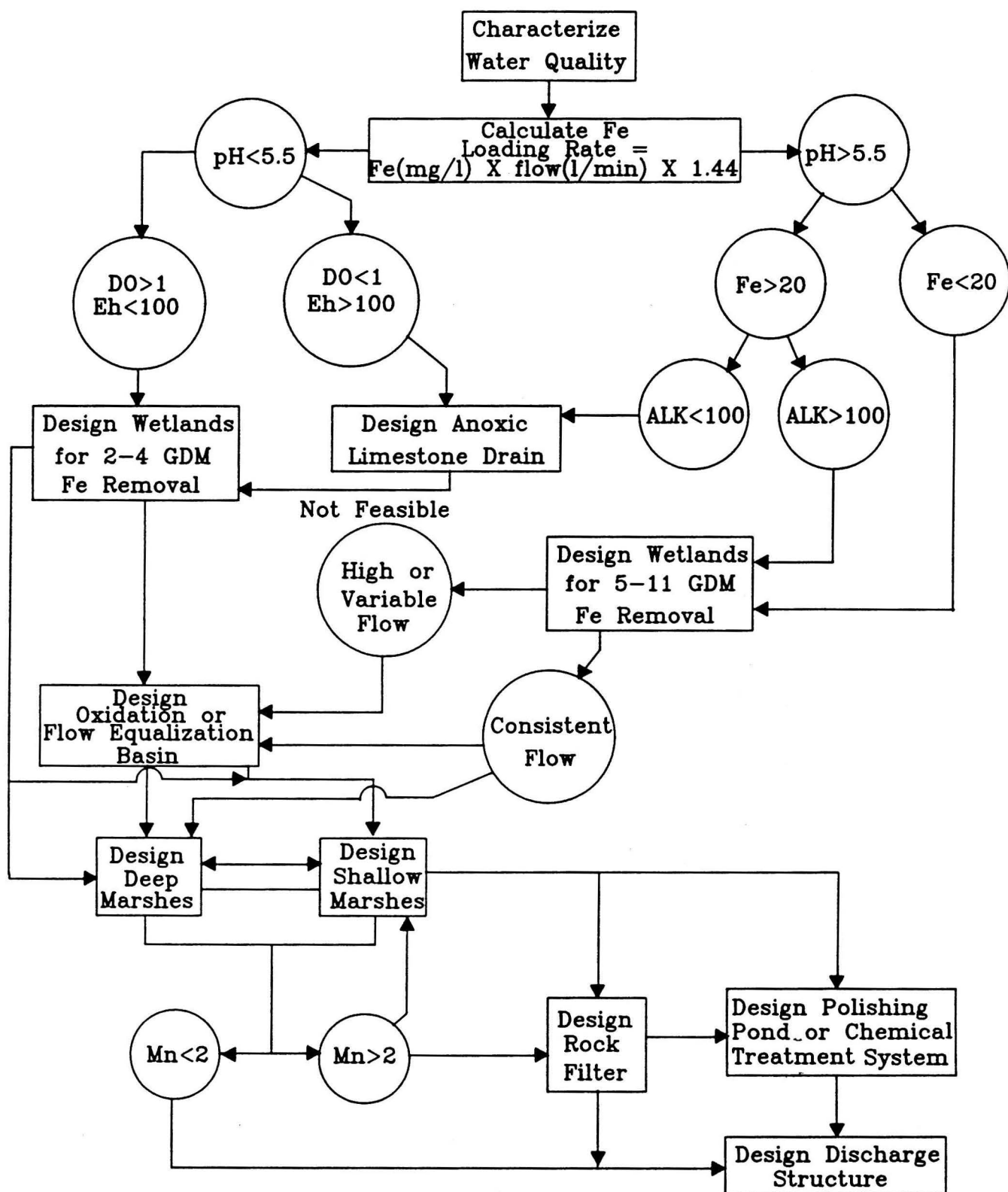


FIGURE 4

STAGED AEROBIC WETLANDS FOR ACID MINEWATER PURIFICATION (SaWAMP)

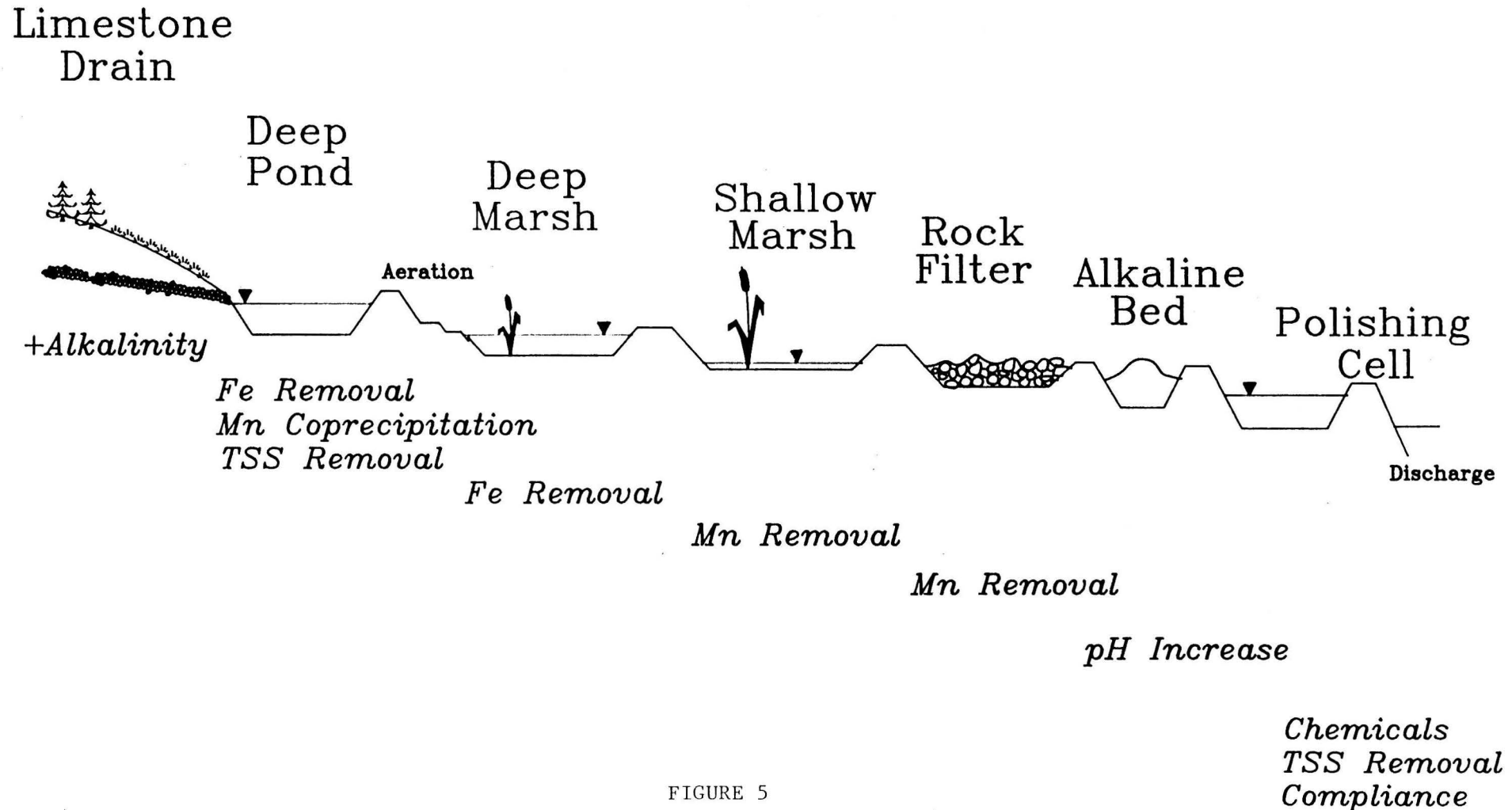


FIGURE 5

Geology

Soils and surface materials should be characterized for thickness, depth, classification and composition, use as a construction material, drainage characteristics, and erosion potential. Depth to bedrock should be determined to allow for various design considerations, although very shallow bedrock may preclude the use of constructed wetlands.

Topography affects cut and fill requirements, drainage and erosion characteristics, and slope stability. Number of cells in a wetlands may be dictated solely on the basis of topography. Detailed topographic surveys are usually not needed to design a wetlands but are convenient planning bases.

DESIGN

Major components of a wetlands treatment system which require design include general configuration/staging, collection structures, aeration structures, dikes, spillways, basins or wetlands cells, and pre- or post-treatment systems. There are numerous potential stages of a wetlands system and uncounted potential variations and configuration of the various stages, each based on site-specific conditions. Possible stages in a system include French drains, buried limestone drains, deep basins, shallow marshes, deep marsh-ponds, wet meadows, subsurface marshes, rock filters, bogs, polishing or treatment ponds, aeration structures, algae ponds, and others. Figure 2 shows plan schematics of several different examples of staged wetlands systems. Figure 3 shows a typical scheme for a staged wetlands system consisting of an anoxic drain, a deep marsh/pond cell, and a shallow marsh/pond cell followed by a polishing pond. Figure 4 suggests a simplified flow scheme for designing a staged constructed wetlands treatment system. By no means should this flow chart be considered a complete guideline, but rather a method at which to arrive at a conceptual design which must be refined based on the numerous site-specific characteristics. Because of the many types of pollutants in acid drainage which require different treatment methodologies, constructed wetlands can consist of several "stages" and components. Figure 5 depicts the SaWAMP model with the important stages in an aerobic style wetlands-based system. Each of these stages and their components are discussed below.

Collection Structures

If very different acid drainage compositions are under consideration, then combining them together may or may not be desirable. For example, if there is a low flow, very strong acid drainage and a high flow, low strength drainage, then it may be desirable to combine them, because wetlands processes may not be able to adequately treat the strong drainage itself. If the converse is true, then combining the two waters will only result in more water being treated by a non-wetlands treatment system.

French drains in the toe area of spoil can be used to discharge water into the first wetlands treatment unit. The design of the drain system should minimize mixing with uncontaminated water so as to avoid flow surges to the wetlands system.

Pipes are chronic O&M problems in acid drainage environments. If pipes are necessary to collect the seepage, the use of a gas trap at the exit and clean-out plugs should minimize these problems. It is important to exclude oxygen to avoid the precipitation of iron oxyhydroxides that can constrict the flow in the pipe, eventually rendering it useless.

Seeps can be collected in strategically located collection ponds or contour ditches that discharge into a collection pond or the first wetlands treatment unit. These structures can also serve as pre- or primary treatment units. This includes precipitate settling and possible chemical treatment, if required. The advantages of a collection pond include flow surge control and relatively constant head to the wetlands system. Dams and/or diversion ditches can also intercept surface acid mine drainage.

Inflow surge and constant head control are particularly important where the inflow is from surface drainage and/or heavily influenced by runoff. Surges from seeps and underground mines are usually dampened relative to those from surface drainage. The maintenance of a relatively constant head on the inflow to the wetlands system will provide the wetlands system with a relatively constant inflow rate and simplify design considerations. The wetlands system will operate in a relatively constant, steady-state condition, which minimizes hydraulic, vegetative, and substrate stresses. A collection pond or ditch with an elevated diversion ditch, spillway, or riser pipe is appropriate. Ideally, these should be located upstream from the wetlands system to protect it from storm surges. The retention capacity of a collection pond can be sized to contain typical "flood" or storm events. Some wetlands designs have a spillway at the end of the last treatment cell, but this will not protect the body of the wetlands from the effects of a storm surge eroding sediments and substrate. A sediment settling pond upstream of the wetlands cells will also remove material not requiring treatment in the wetlands treatment cells. The reduction of incoming sediment loads to the wetlands system will contribute to maximizing the useful life of wetlands treatment cells.

An additional type of collection structure is the anoxic limestone drain (ALD). Because this structure is an important pretreatment stage, it is discussed later and as Appendix 2.

Sizing Wetlands

The simplest rule to follow in constructing wetlands is the bigger, the better. Increased surface area and increased retention time improves overall performance. Increasing the size also increases the cost, so the minimal wetlands size for effective water treatment is desirable.

Wetlands size is a major design consideration which is being investigated by several researchers. The first size design guideline, 200 square feet per maximum flowing gallon per minute, was based on hydraulic loading and neglected any consideration of water chemistry (Kleinmann et al, 1983; Pesavento, 1984). More recently, chemical loading rates based on wetlands area and iron and manganese influent concentrations have been suggested as better parameters for sizing wetlands (Brodie et al, 1988; Brodie, 1990; Hedin, 1990; Stark et al, 1990; Hedin and Nairn, 1990; Stark et al, 1990).

Fe Loading and Removal

TVA Constructed Wetlands

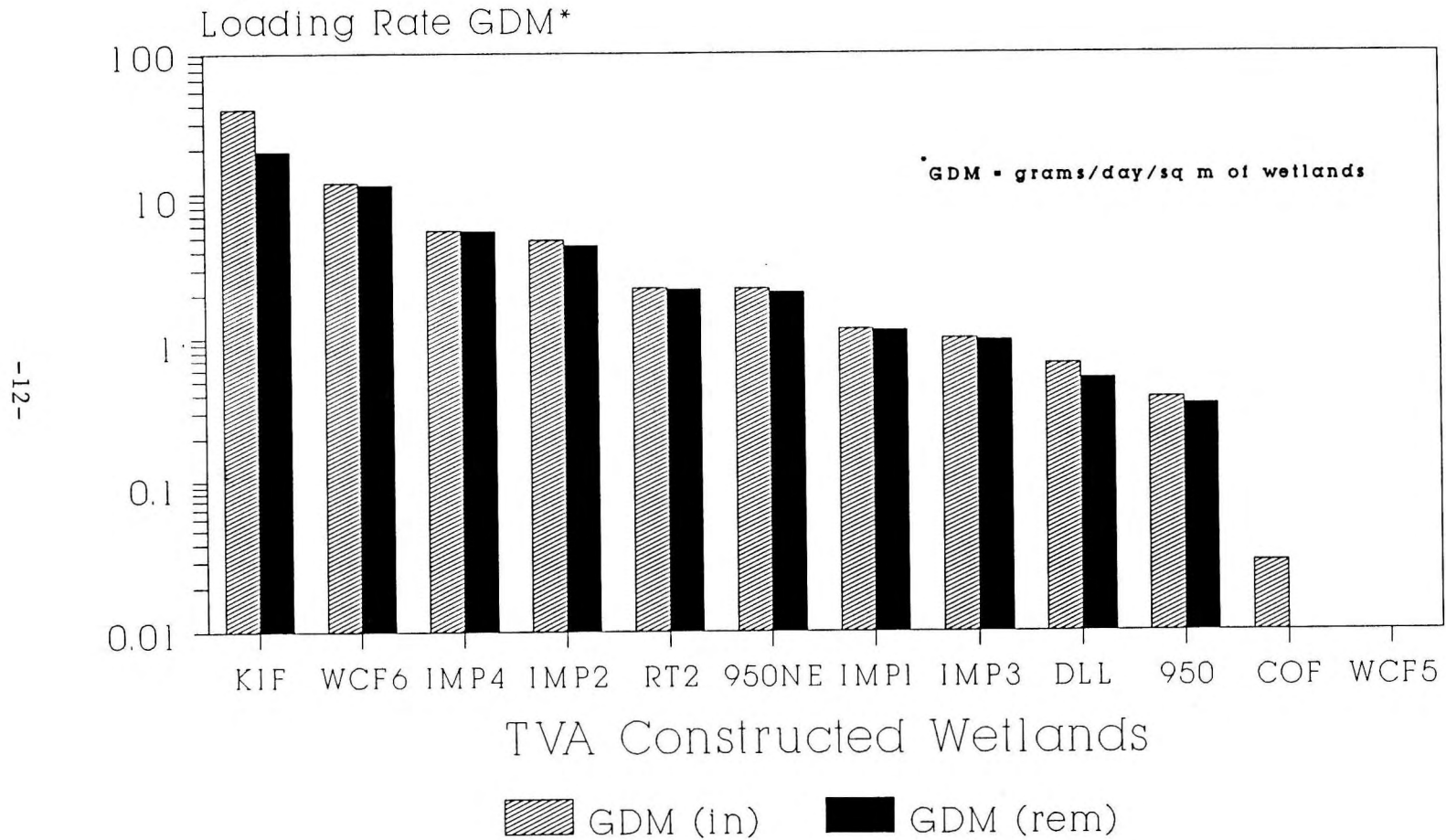


FIGURE 6

Wetlands sizing based on a single parameter (e.g., total Fe) is probably not appropriate because of the many active influences on pollutant active in a wetlands. These influences include influent pH, alkalinity and acidity, Fe concentration and form, Mn concentration, sulfate concentration, and average and maximum flow. Of these influences on wetlands sizing, the system must be designed to accommodate the maximum probable flow. Practically, this might correspond to the 100-year, 24-hour rainfall event being contained. However, with only preliminary chemical loading rate guidelines ranging from about 2.0 g/day/m² (GDM) to nearly 11 GDM of total Fe (see Figure 6), one can do a best practical estimate of wetlands size based on influent iron concentration and maximum probable flow. For example, a water with 50 mg/l Fe and a maximum flow rate of 150 l/min would be sized according to:

$$\text{Wetlands Area (A)} = \frac{[\text{Fe Conc. (mg/l)} \times \text{Flow (l/min)} \times 1.44]}{\text{Recommended Chemical Loading Rate (GDM)}}$$

$$\begin{aligned} A &= [50 \text{ mg/l} \times 150 \text{ l/min} \times 1.44] / 2.0 \text{ GDM} \\ &= 5400 \text{ sq. m} \end{aligned}$$

If significant alkalinity is present in the influent, the larger loading rate may approach a sizing guideline.

$$\begin{aligned} A &= [50 \text{ mg/l} \times 150 \text{ l/min} \times 1.44] / 11 \text{ GDM} \\ &= 982 \text{ sq. m} \end{aligned}$$

The Bureau of Mines has developed empirical sizing criteria, based on iron removal, that takes into account water chemistry as well as flow rates (Kleinmann et al, 1990). For influent water with a pH of 3.0-3.5 s.u., 1200 ft² of wetlands will remove, on average, a pound of iron a day. If the influent pH is 4-5 s.u. the wetlands is more efficient and less space is required: 500 ft² of wetlands will remove, on average, a pound of iron per day. If pH is > 6 s.u., and excess alkalinity is available, the efficiency doubles: 250 ft² will remove a pound of iron per day. For design purposes, a good rule of thumb is to double these area requirements to account for reduced effectiveness during winter and unexpected high loadings.

If the pH and/or manganese concentrations require treatment, additional space must be allotted to treat these parameters. The Tennessee Valley Authority estimates that, on average, to meet discharge criteria wetlands should be built 5 to 6 times larger than what the Bureau of Mines believes is required for iron removal alone.

Most wetlands have not been constructed as large as TVA would suggest is required, but most wetlands do not meet discharge criteria either. Approximately 80 % of the sites require chemical treatment to bring the effluent of the wetlands into compliance with regulatory limits (generally Fe ≤ 3 mg/l, Mn ≤ 2 mg/l, TSS ≤ 35 mg/l, and pH = 6-9 s.u.). However, even these wetlands are considered effective because they significantly decrease chemical treatment costs. Indeed, most wetlands constructed to treat acid mine drainage pay for themselves in less than a year by allowing the operator to use simpler, less expensive chemical treatment systems and/or to significantly reduce the amount of chemicals used.

Thus, sizing becomes a question of balancing available space and wetlands construction costs versus influent water quality and chemical treatment costs. Wetlands can be constructed as a biological pre-treatment step or as a potential alternative to chemical treatment; in either mode, wetlands can be effective, given the site conditions and the operating assumptions.

Depth

Depth of water in cells may vary according to the needs of the operator. Shallow (< 25 cm) marshes lend toward strong dissolved oxygen levels and oxidizing conditions but reduce lifespan of the cell, reduce retention capacity, enhance higher flow velocities, and may be subject to freezing in cold climates. Deeper cells (25-50 cm) decrease vegetation diversity, lend to lower dissolved oxygen levels and reducing conditions near the substrate, but increase the retention capacity and lifespan of the cell. Deeper cells may be most appropriate for moderate water quality or as the first stage in a wetlands system to accommodate rapid oxidation/precipitation of ferrous Fe.

Additionally, deeper cells, or deep spots within shallow cells, may enhance fish and wildlife habitat, provide recharge and wildlife refuge areas in the wetlands during dry periods, and improve hydraulic characteristics of the cell. Ideally, a cell should not be of a uniform depth, but should include shallow and deep marsh areas and a few deep (1 to 2 m) spots. Note that most readily available aquatic vegetation will not tolerate water depths greater than about 50 cm.

Wetlands Forms

Configuration of a staged wetlands system will vary depending on flow, water quality, and topography. Very large cells are subject to hydraulic short-circuiting and should be hydraulically chambered using simple, low or subsurface finger dikes, logs, riprap baffles or other structures. The most common flow path guides are hay bales. The theory is to maximize the contact volume or surface area and the effective detention time of the wetlands cell as well as avoid channelization or short-circuiting of the cell. An alternative is to have irregular or serpentine perimeters for the cells. Some wetlands have irregular islands in the cell. Preferably, a wetlands system should consist of several cells.

The geometry of the wetlands site, as well as flow control and water treatment considerations, may dictate the use of multiple wetlands cells. The intercell connections may also serve as aeration devices. If there are elevation differences between the cells, the interconnection should dissipate kinetic energy and not allow high energy water to enter a wetlands cell causing erosion and/or the mobilization of precipitates.

Multiple and sequential treatments, such as aerobic/anaerobic, may be required to treat low pH, high metal-content acid drainage. The order of dominant treatment cell mechanisms has been observed from a limited number of observations to be significant. Wetlands systems with anaerobic processes before aerobic processes have resulted in considerably diminished treatment effectiveness relative to using only aerobic processes. Data to date indicate that treatment cells dominated by aerobic processes should precede those dominated by anaerobic processes. Figure 3 depicts a consummate Staged Wetlands for Acid Minewater Purification (SWAMP).

Bottom slopes are not extremely critical to the operation of a wetlands. An exception may be a subsurface flow stage which uses deep beds of compost or other permeable organic material to induce sulfate reduction. Bottom slopes in these stages should be about 1-3 % upstream.

Cell length to width (L:W) ratios should be sufficient to prevent high velocities and channelization. Experience from municipal wastewater treatment wetlands suggests that $L:W < 1.0$ enhances treatment capabilities of a system.

Substrates

Substrates for a wetlands range from labor and cost-intensive crushed limestone/compost in sulfate reducing-type wetlands to lower cost in-situ materials such as mine spoil in aerobic wetlands. The Bureau of Mines has suggested a design for a treatment wetlands which uses about 30-50 cm of high calcium limestone covered by 20-30 cm of spent mushroom compost to induce sulfate reduction. The limestone enhances the alkalinity and buffering capacity of the wetlands flow, and the compost enhances sulfate reduction mechanisms in the system and provides a suitable growth medium for aquatic vegetation.

TVA has built numerous wetlands using only in-situ materials for substrates and primarily aerobic mechanisms for pollutant removals (Brodie, 1992a). These materials have included low organic sandy loams, silty loams, medium organic silty loams, and sandy to rocky mine spoils. Wetlands success at the TVA has not been correlated to the type of substrate used. The added expense of importing substrates is not recommended, but rather use of site, or in-situ materials to provide only a suitable growth medium.

To remove acidity, alkalinity must be generated by either limestone dissolution (as from an anoxic limestone drain) or bacterial sulfate reduction. The approach used in northern Appalachia is to route the aerobically-treated, low-iron effluent of a conventional constructed wetlands through composted organic substrate in a second series of wetlands, to use the acid-consuming activity of the sulfate-reducing bacteria. Although aerobic systems may be passively influenced by the presence of their substrate and associated biological activity, anaerobic processes dominate in the second system. The central themes in these treatment systems are substrates rich in organic matter to support sulfate reduction, vegetation to replace consumed organic matter, and a flow regime that is contained mainly in the substrate.

The common substrate is spent mushroom compost that is generally placed (not compacted) in a layer about 50 cm thick. Thicker layers cause densification at depth which reduces permeability to an ineffective level to promote transmissability of the acid drainage. Spent mushroom compost has a bulk density of about 0.65 g/cm^3 (1,100 pounds per cubic yard). A typical coverage for a .5 m (18 inches) thick substrate is about 3.2 m^2 per metric ton (3.5 square yards per ton). Other types of composted organic matter may be suitable as well.

Cattails or other emergent vegetation are planted in the substrate to stabilize it and provide organic matter to "fuel" the sulfate reduction process. As a practical tip, cattail plant/rhizomes should be planted well into the substrate prior to flooding the wetlands cell.

The flow regime in a sulfate reducing wetlands should be primarily within the substrate material. There are various ideas on inducing subsurface flow in the substrate, most of which have met with failure. Buried pipe systems have had limited operational life, but first demonstrated that significant water chemistry changes could be made on acid drainage using subsurface flow. While subsurface flow schemes are still in the experimental state, gravel packs to infuse and/or collect water in a wetlands cell have been used in some wetlands applications mostly for non-acid drainage wastewater. The greatest success, to date, has been at sites where the compost is sloped or piled a little higher than the free water surface of the wetlands cell, so that the water must flow through the compost. Water flows through the compost, eventually breaking out at the end, where it flows out of the first cell and into another cell.

In some cases (e.g., a groundwater recharge area), a liner may be required to protect groundwater resources and to simply retain water in the wetlands. Liners may be compacted clay soils (6-10 inches) or synthetic liners overlain by 8 or more inches of growth medium. Most aerobic wetlands are constructed using compacted clay and silt soils. The use of liners on a sand or soil base for the treatment cell may be rather expensive. There are occasional uses of plastic liners for ditches and intercell connections. Plastic liners have also been used on dam faces. The chemical resistance of plastic or rubber materials to aqueous hydrogen sulfide and the sulfate solutions of ferrous and ferric iron should be evaluated before use in a constructed wetlands. The use of bentonitic clays in some compositions of AMD may not result in the expected performance of the bentonite. There are different varieties of bentonites and these should be evaluated before use in an AMD environment.

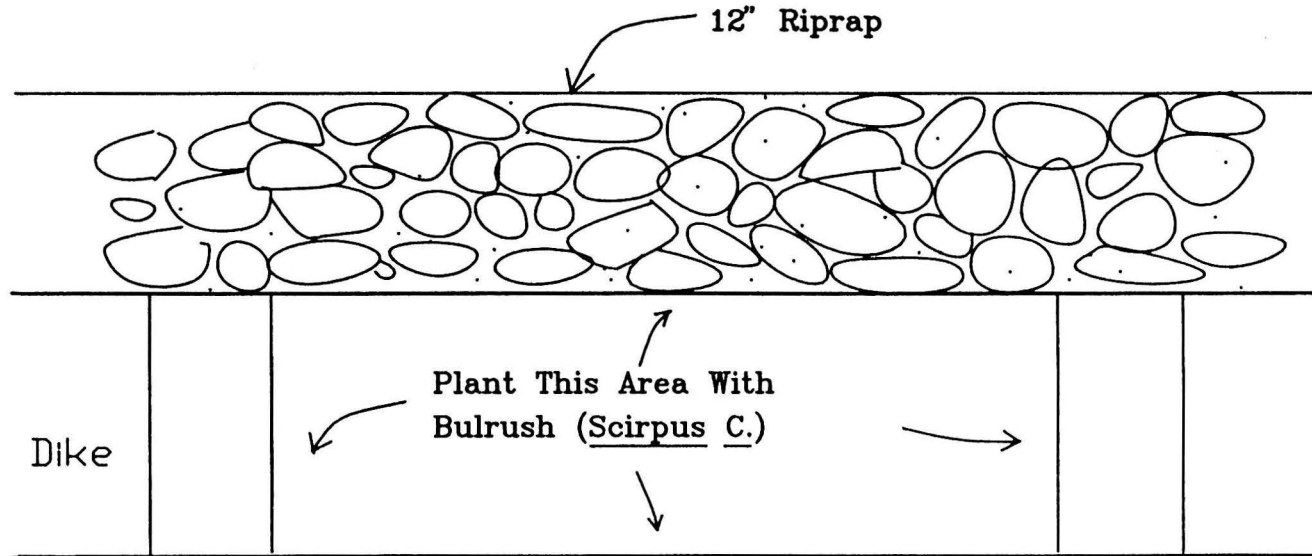
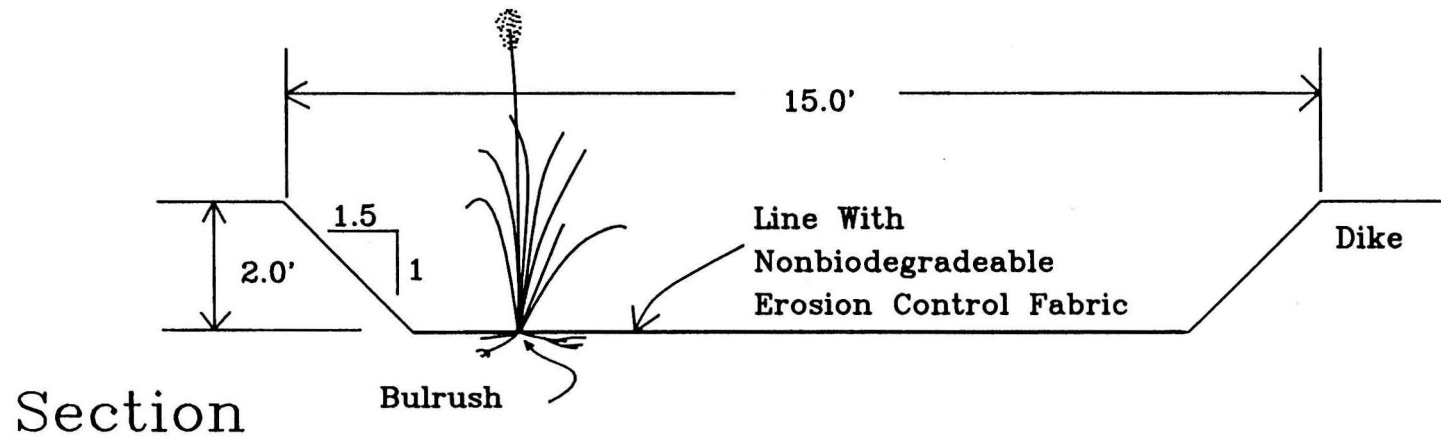
Dikes and Spillways

Dikes should be constructed of locally borrowed material (cell cuttings are ideal usually), adequately compacted and sloped minimally 2H:1V. Dikes tend to settle over several years and should therefore be constructed with about 2.5 ft. freeboard to ensure over the long term. Dike crest widths may vary. Wide dikes reduce wetlands area and increase the susceptibility to vehicular traffic. It is recommended to minimize dike widths and to place large tank bars at each end to discourage vehicles.

Spillways should be designed to pass the maximum probable flow. Figure 7 shows a typical design for a spillway. Spillways should consist of wide cuts in the dike with side slopes no steeper than 2H:1V, lined with non-biodegradable erosion control fabric, and coarse riprapped if high flows are expected. Proper spillway design can preclude high future maintenance costs due to erosion and/or failed dikes. Vegetated spillways overlying erosion control fabric provide natural and stable spillways. Other forms of spillways include pipes, risers, and various water level control structures. With best engineering design practices, most spillways will perform adequately. If pipes are used, small diameter (< 12") pipes should be avoided due to plugging from litter. Pipes should be PVC or coated for long-term stability. If desired, emergency spillways can be incorporated into the dike design.

Figure 7

TYPICAL CONSTRUCTED WETLANDS SPILLWAY



Pretreatment and Aeration

Aeration structures include simple splash areas, cascades, or more elaborate structures such as an in-line aeration system. Generally, the shallow depths in constructed wetlands, along with the spillway designs, provide for sufficient aeration to enhance metals removal and support aquatic life. If aeration structures are planned, their consumption of hydraulic potential should be considered. As aeration only provides enough oxygen to oxidize 50-70 mg/l ferrous iron to the more insoluble ferric form, acid drainage with higher concentrations of ferrous iron will require the operation of a series of aeration units-wetland cell combination. The wetlands cells are required to allow the oxygen in the aerated water to be consumed in oxidizing the ferrous iron and the resulting floc to settle out of suspension. At acid pH's, iron oxidation is primarily a function of bacterial activity but at circum-neutral pH's abiotic oxidation is also significant. A side effect of either oxidation process is a generation of acidity which in turn slows the oxidation process which is inversely proportional to pH. This acidity must be consumed and the pH raised in order to take better advantage of the next aeration/oxidation/precipitation stage. This acidity can be consumed by added alkaline materials or the alkalinity generated by bacterial sulfate reduction.

A new system which is being used in Tennessee to pretreat wetlands inflow is known as an anoxic limestone drain (ALD). These systems, which consist of limestone backfilled collection drains within the spoil, are covered with plastic and clay soil to maintain an anoxic state to prevent ferric iron armoring. Seepage through the trench picks up significant alkalinity which buffers the water against drastic pH decreases in the wetlands as ferrous iron oxidizes, hydrolyzes, and precipitates. Success with the systems is preliminary but impressive (Brodie et al, 1991).

Vegetation can be simply one species readily available from nurseries or nearby wetlands, or can be more exotic species adapted to a specific niche in the constructed wetlands. The least costly vegetation has been nursery stock planted in shallow water or saturated substrate. A more costly option is to transplant vegetation from nearby marshes. Preferably, a new system should be planted with several species, such as cattail (Typha sp.), bulrush (Scirpus), and rush (Eleocharis). Vegetation has traditionally been planted at about one-foot centers, but less dense planting may be acceptable, especially when using cattails. All dikes and disturbed areas should be revegetated immediately to minimize erosion and sedimentation into the wetlands.

A final note on design concerns the method of contracting a wetlands project. Set contracts, although good for planning purposes, are often less desirable because of the frequency of field changes in design of a system. Unless a wetlands has been thoroughly engineered and designed, it is usually cost-effective to complete a wetlands project through a contract operator on a cost-reimbursable basis, with adequate controls.

CONSTRUCTION

Heavy equipment used for constructing wetlands may vary, but usually consist of a small dozer and a larger dozer, a hydraulic excavator or backhoe, a loader, and a dump truck. Additionally, a hydroseeder may be useful.

After site mobilization of equipment, silt retention structures should be installed in and along the stream. The cells are then cleared and grubbed, rough graded, and the dikes are constructed. Emergency spillways are built, then the primary spillways. If flow or water level adjustment devices are not used, temporary pumping or delaying final spillway construction may be required to proceed with planting nursery stock. Full grown aquatic vegetation may be planted directly in deep (< .5 m) water as long as leaves are exposed to air. Planting cattails must be done carefully, setting the whole root ball into the substrate. Breaking the cattail stem at the water level prevents wind throw and stimulates root growth. Bulrush may simply be placed on the substrate. Wetlands have generally been fertilized once to get them going. A typical list of materials would include crushed limestone, spent mushroom compost, riprap, piping, erosion control fabric, wood, sacrete or concrete, seed, mulch, fertilizer, fencing, and aquatic vegetation. Labor requirements include a site engineer, two equipment operators, labor crew, and foreman.

OPERATION AND MAINTENANCE

During the initial start-up period (4 to 8 months), water levels should be closely monitored if nursery stock was used. Otherwise, the start-up period is shortened to weeks. Operational problems can be attributed to inadequate design, unrealistic expectations, pests, inadequate construction methods, or nature-induced problems. If properly designed and constructed, a wetlands treatment system can be operated with a minimum amount of attention and money.

Probably the most common maintenance problem is dike and spillway stability. Reworking slopes, rebuilding spillways, and increasing freeboard can all be avoided by proper design and construction using existing guidelines for such construction.

Pests often plague wetlands with operational problems. Muskrats will burrow into dikes, posing leakage and potentially catastrophic failure problems, and will uproot significant amount of cattails and other aquatic vegetation. Muskrats can be discouraged by linking dike inslopes with chain-link fence and/or riprap to prevent burrowing. Beavers cause water level disruptions due to damming and also seriously damage vegetation. They are very difficult to control once established. Small diameter pipes traversing wide spillways ("three-log structures") and trapping have had limited success in beaver control. Large pipes with 90-degree elbows on the upstream end have been used as spillways in beaver-prone areas. Otherwise, shallow ponds with dikes with shallow slopes toward wide, riprapped spillways may be the best design for a beaver infested system (i.e., learn to live with them).

If mosquitoes are a problem, mosquitofish (Gambusia affinis) may be introduced into the wetlands. Other insects, such as the armyworm, have devastated monocultural wetlands by their appetite for cattails (Snoddy et al, 1989). Planting numerous species in a system will minimize such problems, although it may be necessary to apply an insecticide such as Lorsban until natural predators control certain insect pests. Even bats may provide a means of insect control at remote sites (Tuttle, 1988).

COSTS

Figure 8 shows the major items contributing to the cost of a constructed wetlands. These include costs for land acquisition, engineering and design, construction (equipment, labor, and materials), and operation and maintenance. Costs will vary based on numerous factors which include geotechnical considerations (bedrock depth, availability of construction materials, liners, etc.), land acquisition costs, and labor and equipment rates. However, costs per square foot of wetlands generally range from about \$ 0.50 to \$ 3.00, and average just over \$ 1.00.

FINAL NOTES

The author, on behalf of the Tennessee Valley Authority, is pleased to share his experiences and background on constructed wetlands. Design and design concepts for constructed wetlands are relatively new technologies. Concepts, procedures, and methods introduced in this report may or may not be useful for a particular situation. Prospects for application of constructed wetlands should be examined by scientists and engineers with appropriate training and experience. When the application is viable, systems design and carefully staged, monitored, and documented development only by experienced persons are recommended. Further, because of the potential importance of wetlands-based technology to mitigate many serious water quality problems, it is essential that those who build and operate such systems document and report on their successes and failures in order that the scientific, engineering, and regulatory communities can advance the state-of-the-art of constructed wetlands based on knowledge and data.

TYPICAL COST BREAKDOWN

TVA Constructed Wetlands

DESIGN	\$6000
PERMITTING	1000
LAND ACQUISITION	6000
CONSTRUCTION	
- Equipment & labor	12,000
- Materials	6000
- Supervision	4000
OPERATION & MAINTENANCE	9000
MISCELLANEOUS	6000
TOTAL	\$ 50,000

FIGURE 8

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Wetland Design for Mining Operations

Section III

STAGED, AEROBIC CONSTRUCTED WETLANDS TO TREAT ACID DRAINAGE -
CASE HISTORY OF FABIUS IMPOUNDMENT 1
AND OVERVIEW OF THE TENNESSEE VALLEY AUTHORITY'S PROGRAM

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ABSTRACT

The Tennessee Valley Authority has constructed 14 staged, aerobic constructed wetlands to treat acid drainage at reclaimed coal mines, a coal preparation plant, and at coal-fired power plants. Nine systems produce consistent compliance quality discharges without chemical treatment. The other systems are either under development or are not in compliance due to high Fe and zero alkalinity in the inflow which result in low pH due to Fe oxidation and hydrolysis in the wetlands. These systems are being modified with anoxic limestone drains (ALD) to increase alkalinity of the inflow to buffer against pH decreases. One high Fe, zero alkalinity system has been in compliance since May 1990 when an ALD was added above the wetlands. TVA's wetlands rely on oxidative mechanisms in cattail (*Typha* sp.) marsh-pond type wetlands cells in addition to aeration structures and anoxic mechanisms in the ALDs. Systems are currently removing Fe at rates between 0.4 and 21.3 grams/day/m² of wetlands (GDM) and Mn at rates between 0.15 and 1.87 GDM. TVA's wetlands have been loaded at rates 0.03 - 41.5 GDM for Fe and 0.17 - 2.0 GDM for Mn. All of the wetlands meet compliance for total suspended solids. Based on TVA's operational results, design recommendations have been developed.

In May 1985, the Impoundment 1 wetlands was constructed to treat acid drainage emanating from an earthen dam impounding fine coal refuse at TVA's Fabius Coal Preparation Plant in Alabama. The system has consistently discharged compliance quality water and reduced total Fe from 69 mg/l to 0.9 mg/l and total Mn from 9.3 mg/l to 1.6 mg/l. Suspended solids has always been in compliance. The pH has effectively been increased from 3.5 to 6.8 primarily due to a limestone roadbed located under the earth dam. Aquatic flora and fauna in the constructed wetlands and receiving stream have shown rapid growth, expansion, and diversification.

INTRODUCTION

Staged, aerobic constructed wetlands offer an inexpensive, natural, low maintenance, and potentially a long-term solution to treating acid drainage without chemical additives.¹ Since 1985 the Tennessee Valley Authority (TVA), the Nation's largest electric utility, has constructed 14 wetlands systems for treating acid drainage at coal mining and processing facilities and coal-fired power plants. Twelve of these sites are now operational (one is under development and one was abandoned), and have been evaluated and manipulated in attempts to understand and refine the processes occurring in constructed wetlands. Nine of the 12 operational systems are meeting water discharge limitations without any form of additional treatment.

METHODOLOGIES

Guidelines for design, construction, and operation of aerobic acid drainage treatment wetlands have been developed.² These should be considered comprehensive due to the continued upgrading of the constructed wetlands technology and the need for site specific designs which often restrict the

use of standard engineering and construction methods. Detailed descriptions of the design, preliminary considerations, and construction of TVA's wetlands have been published elsewhere.^{1,2,3}

Design and construction

Figure 1 shows a typical plan for a constructed wetlands. TVA's aerobic wetlands generally consist of a pretreatment stage (anoxic limestone drain and/or oxidation basin) followed by several cells of shallow to deep (0.1 - 2.0 m) cattail (Typha sp.) marsh-ponds. Most of the systems have been constructed in groundwater gaining streams created by the acid drainage, although a few sites required diversions to rout the drainage to the wetlands system. Some systems are followed by a final polishing pond which may improve long-term capacity and minimize storm event flushing of Fe and Mn precipitates from a constructed wetlands.⁴

Based on TVA's results only, aerobic wetlands systems should be designed for 4.0 - 11.0 GDM of Fe removal depending on pH, alkalinity, and Fe concentrations of the inflow.² TVA's early wetlands systems (i.e., those before 1988) were sized hydraulically and then increased if the site allowed. Cell areas were arbitrarily increased in size if very poor quality water was to be treated. The most recent wetlands have been sized based on state-of-the-art guidelines,² but in most cases have been built larger than design size to increase the safety factor and lifespan of the systems.

To ensure long-term stability, dikes were sloped no steeper than 2:1 and riprapped or protected with erosion-control fabric on the slopes. Spillways were designed for handling the maximum probable flow with an ample safety factor and protected with either large (> 30 cm) riprap or non-biodegradable erosion-control fabric planted with species such as wool grass (Scirpus cyperinus), sedge (Carex sp.), or threesquare (Scirpus americanus).

Wetlands shapes varied and were dictated by existing topography, geology, and land availability. Irregular shapes for wetlands cells enhanced their natural appearance and provided hydraulic discontinuity. The number of cells was determined by site topography, hydrology, and water quality. Level sites were amenable to large cells hydraulically chambered with rock or earthen finger dikes, large logs, or vegetated hummocks. Steeper slopes required more grading, or a system of several cells terraced downgrade. Staged treatment using several cells probably provides a more efficient system since chemical and hydraulic overloading of all cells is minimized. One wetlands cell should be constructed for each 50 mg/l Fe in the inflow due to the need for reaeration after oxidation of this amount of Fe.

Average water depth in TVA's wetlands ranged from 15-30 cm with some deeper and shallower areas to provide for species diversification. Isolated deep pockets of up to 2.0 m were included in many cells to provide for aquatic fauna refuge in drought events.

Vegetation was hand dug to obtain complete root balls/rhizomes and planted

on the same day as digging. Cattail (Typha sp.) was set into the substrate at 0.3 m centers in early systems and 1.0 m centers in later ones. Stems were broken over at the water level to prevent windfall and to stimulate new growth from the rhizomes. Wool grass (Scirpus cyperinus), sedge (Carex sp.), and rush (Juncus effusus) clumps were simply placed in the desired location. Squarestem spikerush (Eleocharis quadrangulata) and scouring rush (Equisetum hyemale) were carefully set into the substrate. Complete wetlands installations were operating in 6 to 10 weeks depending on their complexity. Most wetlands were completed in early summer, although successful installations were completed as late as October. Wetlands were fertilized generally only once with a phosphorous-potassium fertilizer such as 0-12-12 at 400 kg/ha.

Mosquitos have not been a problem at TVA's wetlands, however, as a precaution mosquitofish (Gambusia affinis) were stocked in all wetlands. Several bat houses have been installed at TVA to investigate the use of bats for mosquito control. Additionally, various bird houses (martin, screech owl, wood duck, blue bird) were erected at the sites.

Post-construction activities included water quality monitoring, maintenance of dikes and spillways, and the addition of new ponds to further treat the wetlands discharge. Additional water, substrate, and vegetation sampling and biological monitoring was performed to quantify the wetlands development and treatment efficiencies.

Sampling and Analytical Techniques

NPDES monitoring requirements included pH, total Fe and Mn, and total suspended solids (TSS). Effluent samples from the wetlands were obtained during daylight hours generally within the second and fourth weeks of the month. Sampling was always initiated within two weeks of system startup. All samples were collected and analyzed according to standard methods.

Total metals samples were collected in 500 ml acid-rinsed polyethylene bottles, preserved with HNO₃ to a pH of greater than 2.0, usually by tilting the bottle gently into the seep. The sample was placed on ice and transported to the laboratory for analyses. Samples were digested with concentrated, redistilled HNO₃ and HCl, reduced to 20 ml, diluted back to volume, centrifuged or filtered depending on solids, and then analyzed by atomic emission or atomic adsorption.

Total suspended solids (TSS) samples were collected in one-liter cubitainers. All air was expelled from the cubitainer and the sample was stored on ice for transport to the lab. Samples were filtered through glass fiber filter, dried at 102 to 105°C with the difference of weight retained on filter and reported as TSS.

RESULTS

A summary of characteristics and water quality parameters for TVA's 14 constructed wetlands is presented in Table 1. Significant water quality

improvement has occurred at all of the 12 operating wetlands. Nine systems have produced discharges that consistently meet NPDES monthly average discharge limitations (pH = 6 - 9 s.u.; Fe < 3.0 mg/l; Mn < 2.0 mg/l; TSS < 35.0 mg/l) with no chemical treatment. Where regulatory limits were not entirely achieved, cost savings were realized as a reduction in chemicals needed for further metals precipitation or pH adjustment at IMP2, WCF6, and COF13. TVA's wetlands were, on average, hydraulically loaded between 0.02 - 0.24 l/day/m² of wetlands (LDM). Maximum hydraulic loading ranges were 0.06 - 1.47 LDM and averaged 0.42 LDM.

Ten of the 12 operating wetlands produce discharges in compliance with total Fe limitations, i.e., < 3.0 mg/l (Table 1). Figure 2 shows Fe loading in the systems ranges from 0.03 GDM to 41.4 GDM. Fe removed ranges from 0.0 GDM to 21.3 GDM, corresponding to 0 to 99 % Fe removal. Note that the 0 % removal is associated with very low Fe inflow (0.7 mg/l) at the COF wetlands; this data may be a result of sampling error or a lower limit of Fe removal possible at the COF wetlands. Fe removal in the wetlands is very efficient for loadings up to 13 GDM which occurs at the WCF6 wetlands. Fe removal is less efficient (51 %) at KIF where Fe loading exceeds 41 GDM. More data for Fe loadings between 13 GDM and 41 GDM is needed to better assess the Fe loading limit for a constructed wetlands. There is no correlation in TVA's wetlands between Fe removal and influent alkalinity, Fe removal and wetlands size, or Fe removal and hydraulic loading.¹

Figure 3 shows total Mn loading and removal in the TVA wetlands. Data for WCF5 is not available. Nine of the twelve operating wetlands produce discharges in compliance with total Mn limitations, i.e., < 2.0 mg/l (Table 1). Mn loading ranges from 0.17 GDM to 2.00 GDM. Mn removed ranges from 0.15 GDM to 1.87 GDM, corresponding to 0 to 96% Mn removal. The low removal rates are all associated with low pH (2.9 - 3.9 s.u.) systems. Mn removal in the wetlands is very efficient for loadings as high as 2.0 GDM, which occurs at the 950NE wetlands. There is no correlation in TVA's wetlands between Mn removal and wetlands size, and Mn removal and hydraulic loading. There is a good correlation between Mn removal and influent alkalinity and acidity concentrations (Figure 4).^{1,3} Systems with zero alkalinity have removed 0 to 16.5% Mn, while systems with alkalinity greater than 62 mg/l and with excess acidity as high as 248 mg/l have removed 85-97% of the Mn load. Inflows with zero alkalinity have always resulted in low pH in the wetlands. Low Mn removal is associated with zero alkalinity and thus, low pH in the wetlands. This data suggests that Mn co-precipitation on Fe-oxides at circum-neutral pH is a likely mechanism of Mn removal.⁵

Nine of the twelve systems increase or maintain inflow pH to produce discharges in compliance for pH, i.e., 6.0 - 9.0 (Table 1). Three systems cause pH reductions due to Fe oxidation and hydrolysis; these systems are being modified with anoxic limestone drains.³ All of the wetlands produce discharges in compliance with total suspended solids (TSS) limitations, i.e., < 35 mg/l.

Case History of Impoundment 1 Constructed Wetlands

Impoundment 1 (IMP1), constructed in June 1985, was TVA's first acid mine drainage treatment wetlands. The system treats acid seepage emanating from an earth dike impounding 16 ha of coal slurry at TVA's reclaimed Fabius Coal Preparation Plant in Jackson County, Alabama.

Since construction IMP1 has generally produced compliance-quality effluent. Figure 5 shows average water quality data during the period July 1985 to October 1991 for the wetlands inflow and the discharges from each of the four wetlands cells. Variations in flow from each cell were due, in part, to acid seeps encountered along a sandstone shelf underlying the site and in the leaky nature of the wetlands system. Effluent from the first cell alone has met discharge limitations 56 percent of the time. Figure 6 shows total Fe and total Mn concentrations in the effluent for the same period. From June to August 1988 and again from June to September 1989, total Mn concentrations increased to several times the IMP1 average discharge concentration of Mn. Similar but less drastic increases in Mn concentrations were noted in the summers of 1986 and 1987. When these anomalies were compared to rainfall records and wetlands flow, no correlations were apparent. Most of the other wetlands have exhibited similar patterns of Mn concentration variability. These increases are probably seasonally related and could be due to numerous factors, including temperature, degree of mixing, redox conditions, nutrient and/or carbon availability, or photosensitivity of Mn-oxidizing bacteria.

IMP1 is one of two constructed wetlands receiving inflow total Fe concentrations exceeding 50 mg/l that has successfully produced compliance-quality discharges without chemical treatment. Other wetlands receiving greater than 50 mg/l total Fe (Table 1) have been impacted by low pH, high acidity, and the resultant inability to remove Fe and/or Mn to meet discharge limitations. Investigations into differences among the wetlands revealed that IMP1 influent had an alkalinity often exceeding 250 mg/l. The three other high-Fe wetlands had influent alkalinity ranging from 0 to 26 mg/l with high acidity. Further investigations into the IMP1 characteristics disclosed that the leaking coal slurry impoundment dike was constructed in 1974 over an existing limestone coal mine haul road, which may represent the oldest, working anoxic limestone drain (ALD).³ Historically, local limestone has been quarried from the Monteagle Formation, an oolitic, high-calcium limestone. Apparently this road is the source of the IMP1 influent alkalinity.

Stability problems at IMP1 resulted from inadequate spillway and dike designs. Each dike was repaired in late 1989 to increase the freeboard to over 30 cm. The spillways were reconstructed to provide long-term, erosion-resistant stability. Six species were originally planted in IMP1: broadleaf cattail (*Typha latifolia*), wool grass (*Scirpus cyperinus*), rush (*Juncus effusus*), scouring rush (*Equisetum hyemale*), and squarestem spikerush (*Eleocharis quadrangulata*). Over 70 vegetative species have now been identified in IMP1, dominated by *Typha latifolia*, *Scirpus cyperinus*, *Juncus effusus*, *Eleocharis quadrangulata*, and rice cutgrass (*Leersia oryzoides*). The remaining stream of IMP1 originally was almost

biologically dead (less than 5 invertebrate species). The stream now contains over 30 species of invertebrates as well as mosquitofish (Gambusia affinis) and other minnow species.

Total cost of the IMP1 wetlands was \$43,000 (1985 dollars). Annual costs from 1985-1990 were about \$13,000 due to repairs on the prototype design and due to extensive monitoring. Operations and maintenance costs today are less than \$1,000 annually. Costs to chemically treat this acid drainage site instead of with wetlands treatment would have been approximately \$250,000 from 1985 to 1991.

SUMMARY AND CONCLUSIONS

TVA has constructed 14 and operates 12 aerobic, staged wetlands systems for treating acid drainage from coal mine spoil, coal slurry and gob, and coal ash. These systems offer a preferred alternative to conventional methods of treating acid drainage from various coal-related sources.

Nine wetlands systems now produce effluents meeting all discharge limitations without chemical treatment, four of which have been released from NPDES monitoring requirements. These 9 systems are associated with moderate inflow water quality (i.e., total Fe = 0.7 - 69 mg/l, total Mn = 5 - 17 mg/l), relatively high total Mn to total Fe ratios in the influent (average Mn/Fe = 0.44), significant inflow alkalinity (35 - 300 mg/l), and variable Fe loading (.03 - 6.13 GDM).

Five systems have experienced high acidity production and low pH within the wetlands due to Fe oxidation/hydrolysis. Four of these systems are associated with high influent Fe concentrations (40-170 mg/l), high Fe loads (5 - 41 GDM), and zero to very low influent alkalinity. Two of these wetlands discharges require NaOH treatment to achieve compliance quality. One system, Imp4, was modified with an anoxic limestone drain which has allowed cessation of chemical treatment and enabled the wetlands to produce compliance quality discharges. Another system, KIF6, has been modified with an anoxic limestone drain, but due to its recent completion (10/1/91), only preliminary data has been collected.

One system (COF) which has experienced very little metals reduction is associated with low Fe (0.7 mg/l) and higher Mn (5.3 mg/l). The performance of this wetlands may be related to absence or inhibition of Mn-oxidizing bacteria or lack of Fe-Mn coprecipitation. TVA is currently investigating the use of rock filters to lower concentrations of Mn in low Fe acid drainage.

Fe and Mn removal efficiencies and pH improvement in the TVA wetlands do not correlate well with wetlands treatment areas for total Mn or flow. This, in part, is probably due to the effect of Fe oxidation/hydrolysis overwhelming other wetlands system mechanisms.

Many factors affect the ability of wetlands to ameliorate acid drainage, including hydrology, Fe and alkalinity concentrations, and various wetlands

characteristics such as depth, area, hydraulics, vegetative and microbial species and extent, and substrate. Because of the interrelationships among these many factors and their effects on wetlands treatment efficiencies, it is difficult to develop treatment area design guidelines. Additionally, with the relatively new concept of the anoxic limestone drain, required areas and designs of wetlands to achieve compliance may be greatly affected. However, TVA's data show that even in the absence of alkalinity, wetlands are removing up to 21.3 GDM of Fe. Mn is being removed up to 1.9 GDM in the presence of alkalinity. TVA's experience suggests that these numbers may represent an upper limit sizing criteria for aerobic wetlands as they are currently designed and constructed.

TVA's encouraging results suggest that staged treatment wetlands systems are preferred designs potentially capable of treating poor-quality acid drainage. Such staged treatment may consist of: 1) an initial anaerobic limestone trench at the source of the seepage to passively add alkalinity; 2) a large, deep settling basin to accumulate oxidized and precipitated Fe sludges; and 3) a two or three cell constructed wetlands for Mn and further Fe removal. TVA is currently investigating the use of passive alkaline beds to increase the pH of constructed wetlands discharges in cases where pH remains below 6.0. TVA plans to continue its research and evaluation of operational and experimental wetlands treatment systems, especially regarding methods to passively increase buffering capacity and pH in wetlands influents and effluents. As more information is made available by TVA and other operating systems and research activities, design guidelines for the components of staged-treatment wetlands systems should be improved.

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TABLE 1

TVA ACID DRAINAGE WETLANDS TREATMENT SUMMARY

Wetlands System	Date Initiated Operation	Area m ²	Number Cells	Influent Water Parameters (mg/L)				Effluent Water Parameters (mg/L or L/min)						Loading g/day/m ²		1/day/m ² Ave Flow
				pH	Fe	Mn	TSS	pH	Fe	Mn	NFR	Flow		Fe	Mn	
												Ave	Max			
950	1-76	3400	3	5.7	12.0	8.0	20.0	6.5	1.1	1.6	5.4	83	341	.42	.28	.04
IMP1	7-85	5700	4	6.1	69.0	9.3	9.5	6.7	0.9	1.8	3.0	73	693	1.27	.17	.02
IMP4	11-85	2000	3	6.3	65.0	16.8	21.0	6.3	0.4	0.6	6.0	131	693	6.13	1.58	.09
WCF5	7-90	6600	4	-	-	-	-	8.4	2.2	0.7	-	973	2057	-	-	.21
WCF6	6-86	4800	3	5.6	150.0	6.8	-	3.9	6.4	6.2	-	289	1495	13.0	.59	.09
WCF19	6-86	25000	3	5.6	17.9	6.9	-	4.3	3.3	5.9	-	492	6360	.50	.20	.03
IMP2	6-86	11000	5	3.5	40.0	13.0	9.0	3.1	3.4	13.0	0.8	1016*	1540*	5.32	1.72	.13
IMP3	10-86	1200	3	6.3	15.8	4.9	21.4	7.0	0.5	0.7	9.0	58	250	1.10	.34	.07
RT2	9-87	7300	3	5.7	45.2	13.4	-	6.8	0.6	1.8	3.2	277	1155	2.47	.73	.05
950NE	9-87	2500	4	6.0	11.0	9.0	19.0	6.9	0.6	0.8	5.0	385	1386	2.44	2.00	.22
KIF6	10-87	9300	3	5.5	170.0	4.4	40.0	2.9	82.5	4.6	-	1574	2271	41.43	1.07	.24
COF	10-87	9200	5	5.7	0.7	5.3	-	6.7	0.7	3.5	-	288	408	.03	.24	.05
DLL	5-90	7550	4	6.2	10.0	5.5	23.0	6.4	2.1	2.2	10.0	385	7700	.73	.40	.07
HR000	UC**	40,000	5	4.5	40.0	17.0	-	-	-	-	-	4000	-	-	-	-

*Also receives pumpage from slurry lake up to 4800 l/min.

**Under Construction

Staged Aerobic Constructed Wetlands... Brodie.

1. General Schematic of Staged Aerobic Constructed Wetlands
2. Fe Loading and Removal in TVA Constructed Wetlands
3. Mn Loading and Removal in TVA Constructed Wetlands
4. Mn Removal vs Influent Alkalinity in TVA Constructed Wetlands
5. TVA Fabius IMP1 Constructed Wetlands Average Water Quality Data
6. TVA Fabius IMP1 Constructed Wetlands Effluent Fe and Mn Data

Limestone
Drain

Deep
Pond

Deep
Marsh

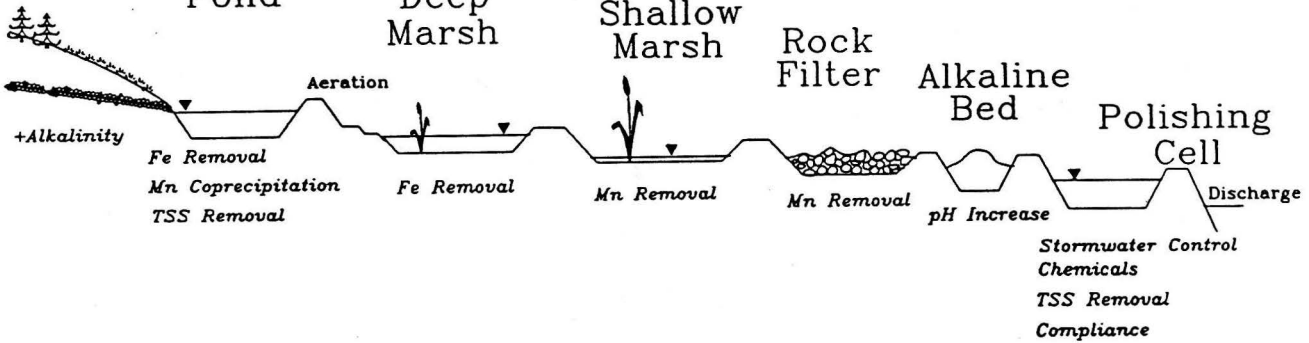
Shallow
Marsh

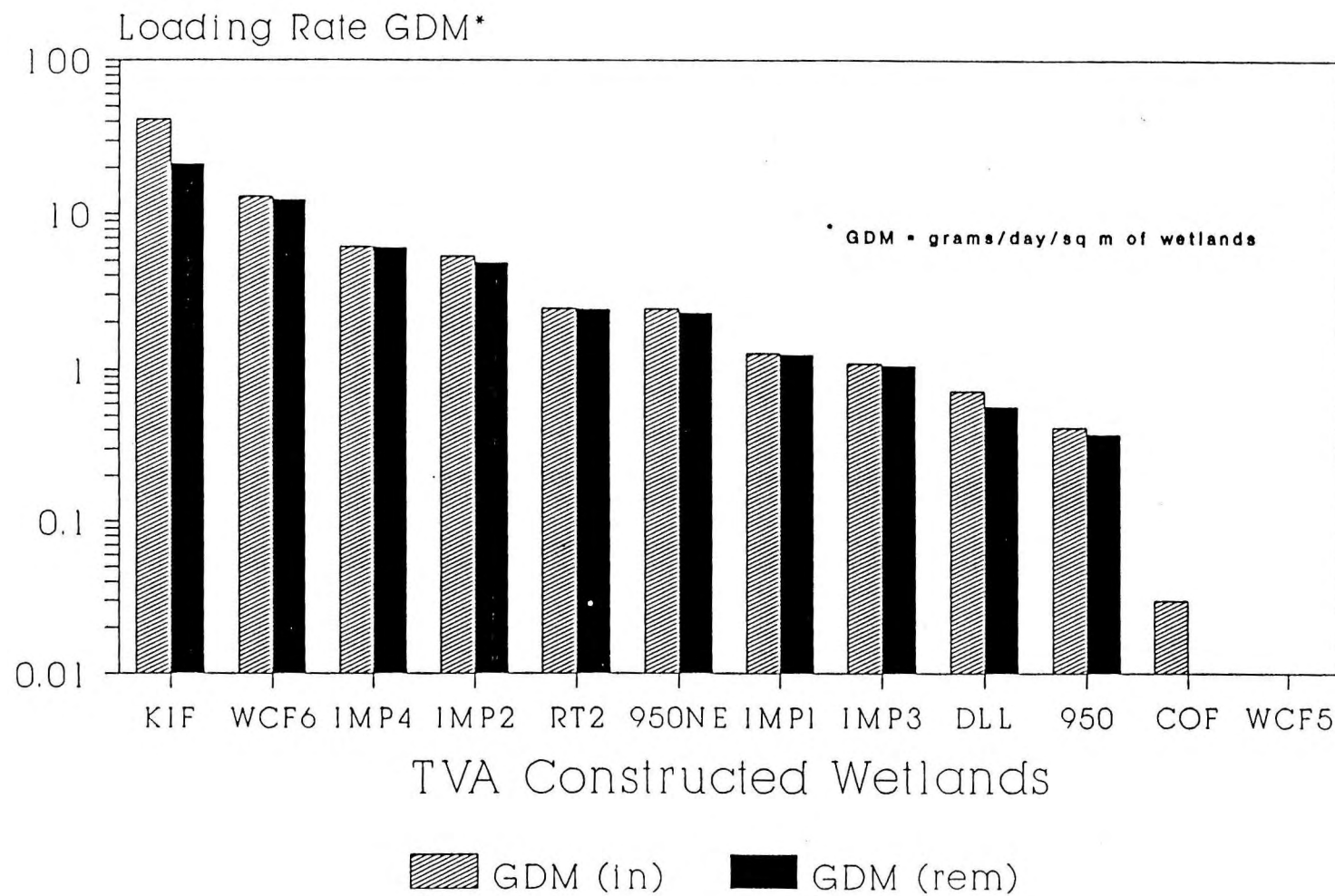
Rock
Filter

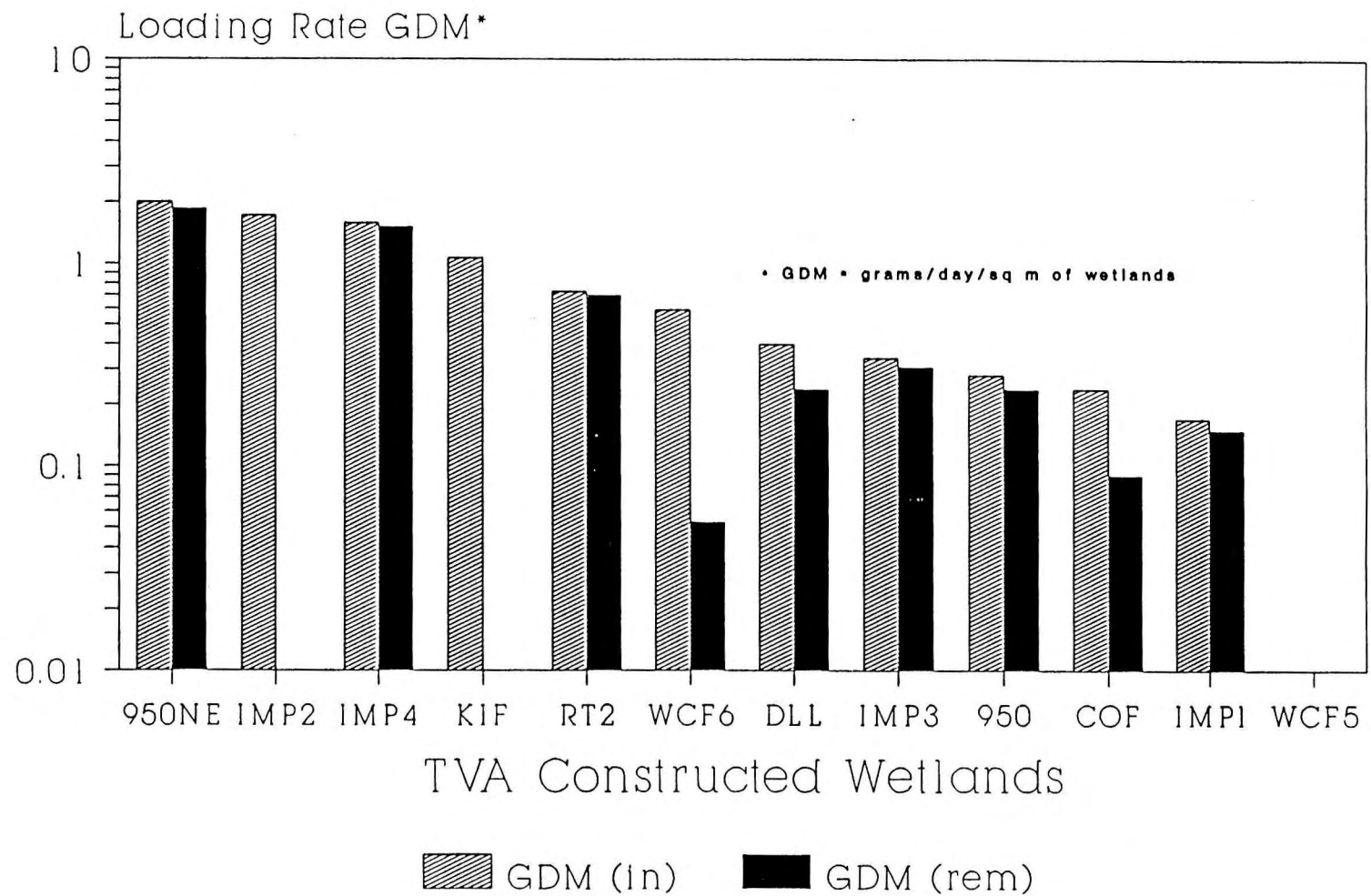
Alkaline
Bed

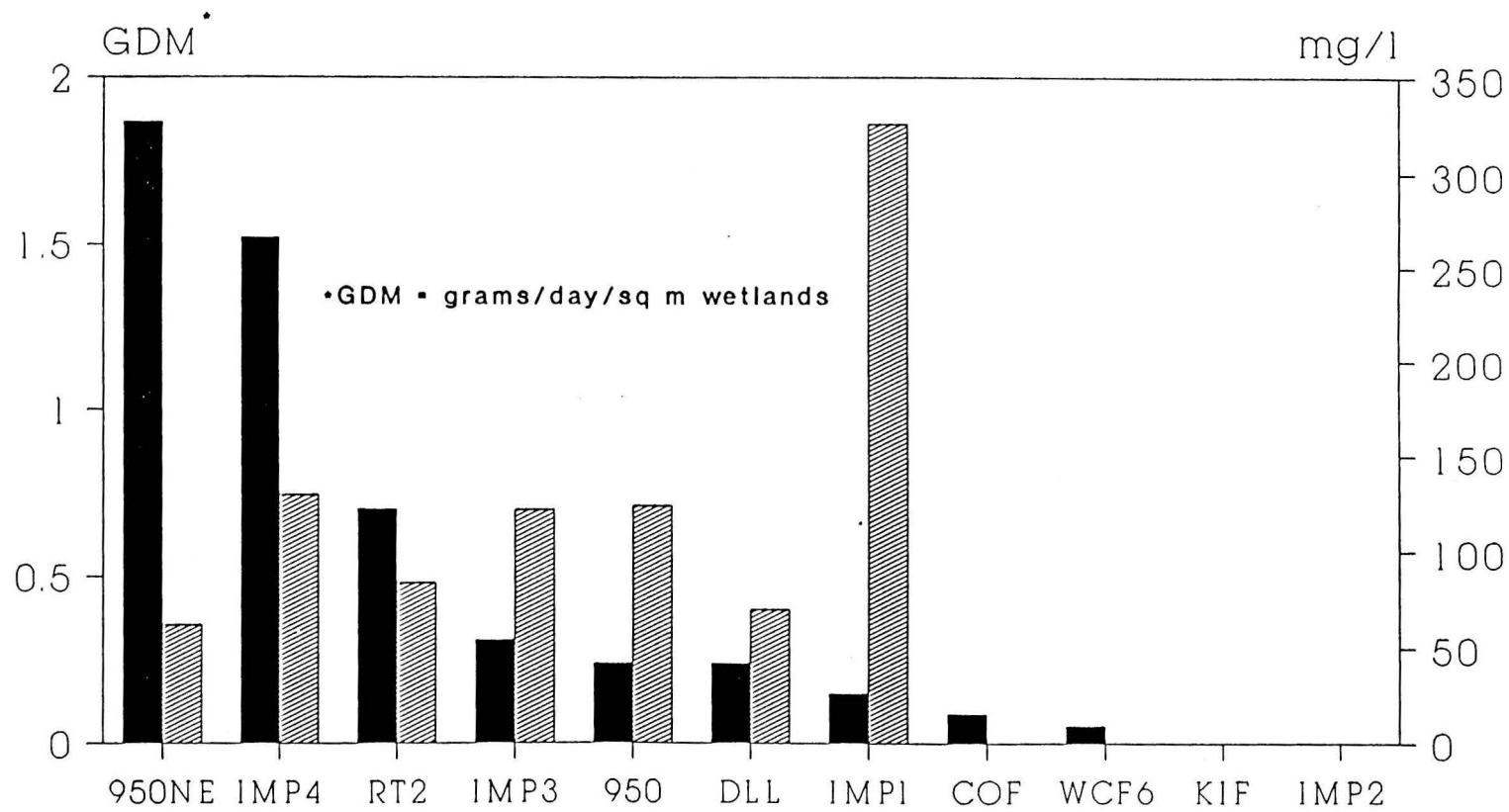
Polishing
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Discharge



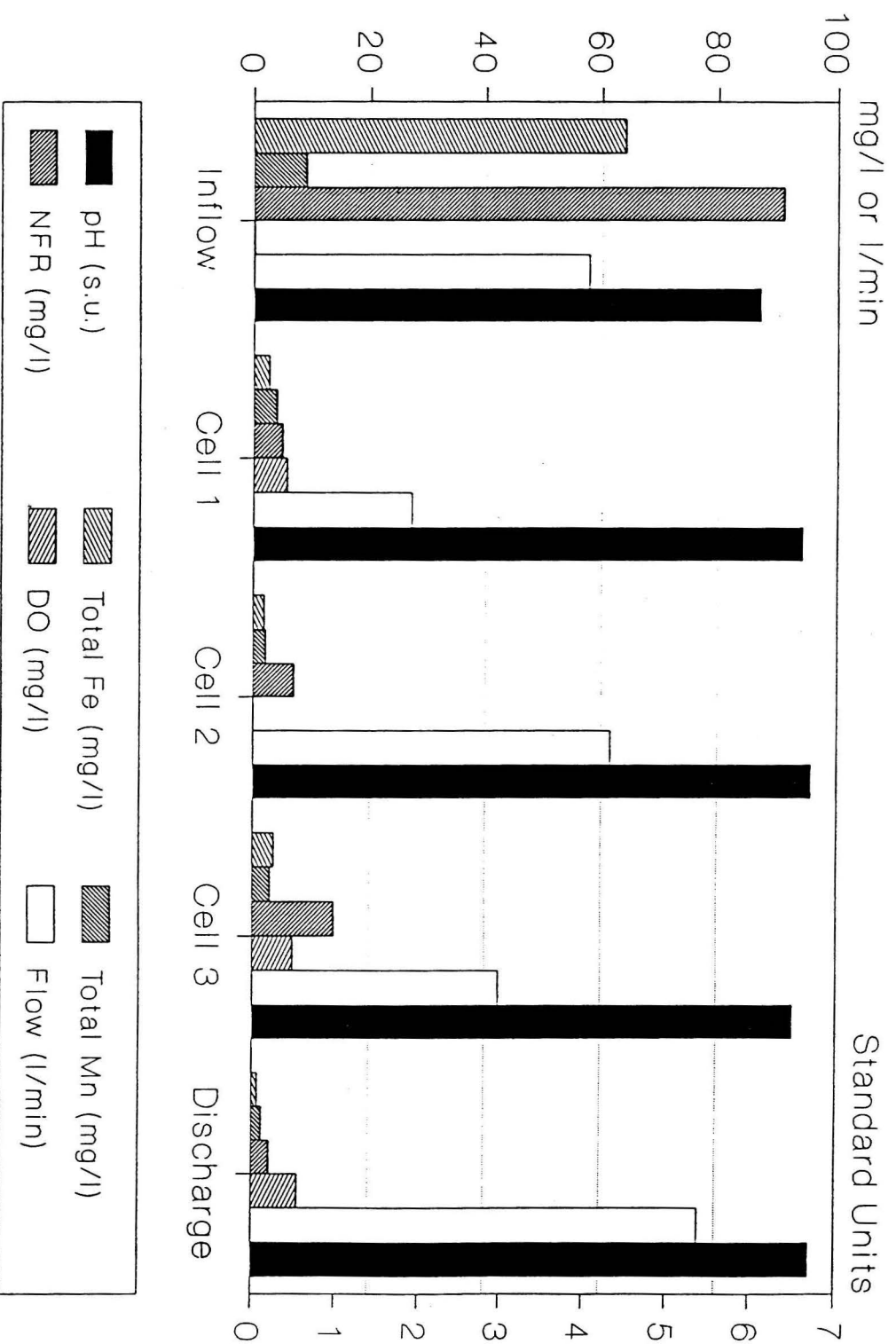


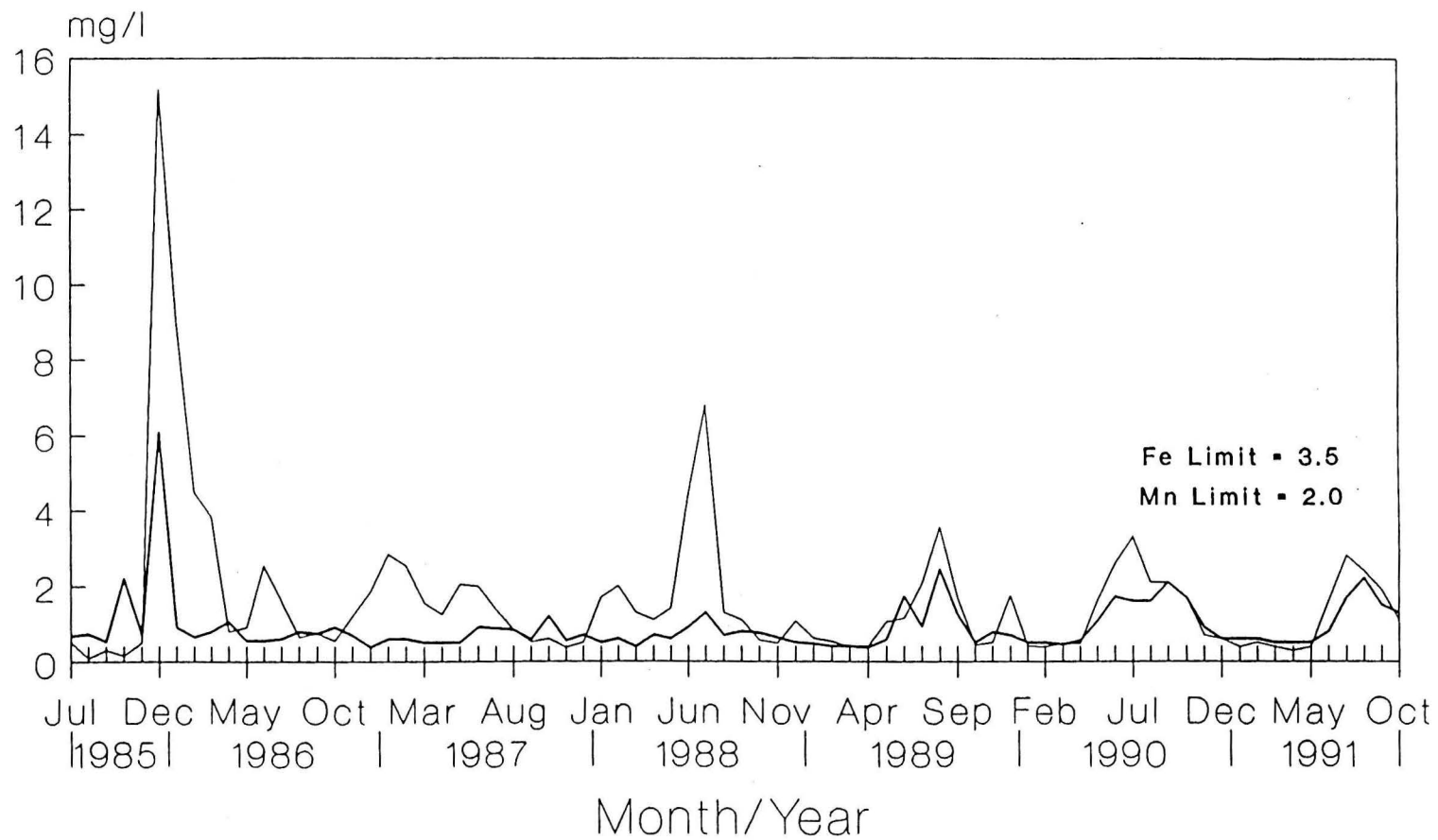




TVA Constructed Wetlands

■ GDM (rem) ▨ Alkalinity (mg/l)





— Total Fe — Total Mn

ANOXIC LIMESTONE DRAINS TO ENHANCE PERFORMANCE OF
AEROBIC ACID DRAINAGE TREATMENT WETLANDS -
EXPERIENCES OF THE TENNESSEE VALLEY AUTHORITY

G. A. Brodie, C. R. Britt, T. M. Tomaszewski, and H. N. Taylor

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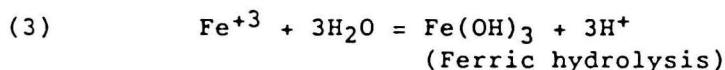
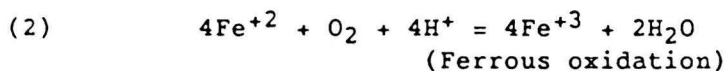
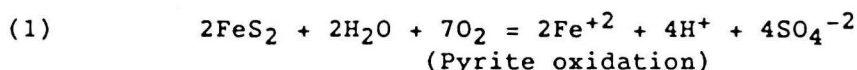
ABSTRACT

Constructed aerobic wetlands for treating acid drainage are preferred, low-cost, alternatives to conventional treatment. Drainage with high Fe (e.g., >50 mg/l) and zero alkalinity has not been amenable to treatment with wetlands alone, primarily due to Fe hydrolysis and resultant low pH. Anoxic limestone drains (ALDs) increase the alkalinity of the seep that is then routed to a constructed wetlands. Increased alkalinity buffers the aerobic wetlands system from pH decreases and enhances the effectiveness of wetlands treatment. The Tennessee Valley Authority (TVA) has modified two low-pH constructed wetlands with ALDs and has identified several "accidental" ALDs at its constructed wetlands sites. Results indicate aerobic wetlands with ALDs can meet effluent limitations without chemical treatment. ALDs consist of an excavated seepage-interception trench backfilled with crushed limestone covered with plastic and clay soil. Dissolution rates of limestone in operational and simulated ALDs have been measured to estimate design parameters and longevity of an ALD. Potential problems with ALDs include structural and hydraulic stability, plugging due to reaction products within the ALDs, and inadequate design and installation.

INTRODUCTION

Staged aerobic constructed wetlands are an effective means of treating certain qualities and quantities of acid drainage from various mine spoils and refuse, and from coal ash disposal areas.¹ Wetlands efficiencies are related primarily to flow rates, pH, and concentrations of dissolved oxygen (DO), Fe, Mn, acidity, and alkalinity. Foremost are the relationships among influent DO, Fe speciation, alkalinity, and influent/effluent pH.

Metals removal mechanisms in wetlands are variable and numerous, but it is probable that microbially-catalyzed Fe oxidation and hydrolysis are major reactions responsible for Fe removal in aerobic wetlands systems.² These reactions may dictate the ultimate success or failure of a wetlands system because of their acidity-producing natures, summarized below.



Reactions 1-3 all occur in the backfill while reactions 2-3 occur in the wetlands. Only reaction 3 acts to increase acidity in a wetlands. If sufficient buffering capacity is not present in the acid drainage, pH will decrease in a wetlands as ferric hydrolysis proceeds. Several TVA wetlands systems, although removing substantial amounts of Fe and Mn, have had influent pH near 6.0 and effluent pHs of less than 3.0.¹ TVA's 3-cell, 2.3 acre constructed wetland at the Kingston Fossil Plant in Roane County, TN receives, on average, 379 gpm of acid seepage from an ash disposal area with an influent

pH of 5.5 and total Fe of 170 mg/l. Effluent from the wetlands system has a pH of 2.9 and total Fe of 83 mg/l; thus the hydrolysis of about 87 mg/l of Fe is responsible for the decreased pH.

DISCUSSION

Numerous methods, primarily chemical treatment, for treating acid drainage have been used to meet effluent standards; however these methods are expensive and require constant attention to maintain compliance with effluent limitations. Also, many chemical additives have an adverse impact on aquatic biota in receiving streams. Limestone treatment has many advantages over conventional chemical treatment including lower sludge production, lower cost, and less potential for overdosing. However, the use of limestone rock as a buffering agent was abandoned because, in an oxidizing environment, Fe hydroxides coat the limestone surface and inhibit or eliminate the dissolution of the limestone, thus preventing effective buffering. This paper discusses a passive methodology of introducing alkalinity to acid drainages in order to buffer pH decreases in constructed wetlands due to Fe hydrolysis.

In 1988, the Tennessee Division of Water Pollution Control (TWPC) constructed and evaluated prototype passive anoxic limestone drains (ALDs) at 2 mine sites in Tennessee.³ At the same time, TVA recognized a correlation between alkalinity and DO of wetlands influent, and the relative success of TVA constructed wetlands, and conducted several relevant bench-scale studies on alkalinity enhancement to achieve NPDES compliance of acid drainage using passive aerobic wetlands systems.⁴

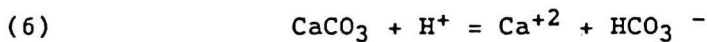
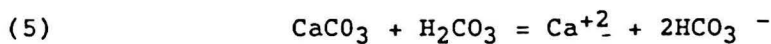
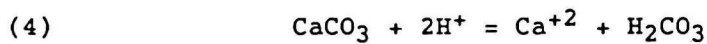
Results of a TVA study identified a correlation between wetlands influent alkalinity and effluent pH, Fe, and Mn. An "accidental" roadbed originated anoxic drain (AROAD) was identified at the TVA Impoundment 1 constructed wetlands, which treats high-Fe (> 100 mg/l) acid drainage emanating from a fine-coal refuse disposal area at the Fabius Coal Preparation Plant site in northeastern Alabama (Figure 1). Air photo investigations showed that a 1400-ft long, 25-foot high earth dam was constructed in 1974 over an existing coal haul road built of crushed rock that was presumably obtained from the local Monteagle formation, a high CaCO_3 , oolitic limestone. Although this limestone roadbed was not intended for water quality enhancement, it was hypothesized that it was pretreating acid drainage seeping through the dike by adding alkalinity and buffering capacity so that the wetlands was producing compliance-quality discharges. TVA drilled and sampled the dike and the AROAD, and confirmed the presence of a 4-11 inch roadbed consisting of gravel-sized limestone (peloid grainstones, peloid packstones, pellet packstones/grainstones, and coarse-grained bivalved grainstone) containing 46-58% Ca.⁵ Split spoon samples of the limestone showed no evidence of mineralization or coatings on the stone. Dissolution was evidenced by the rounded edges of the recovered crushed stone. Monitoring wells were drilled and are being sampled to determine the changes in water quality as the flow passes through the earth dam. Figure 2 depicts preliminary water quality data from six monitor wells completed in the dam at various locations relative to the AROAD, the slurry lake, and the seepage.

Over 50 ALDs have now been constructed in the eastern U. S.⁶ The ALD, which

consists of a shallow, limestone-filled trench excavated into the spoil and sealed from the atmosphere, passively introduces buffering capacity, as alkalinity, into the acid drainage. Changes in pH due to acid production from Fe hydrolysis in the wetlands are buffered due to the high alkalinity in the influent. Detailed design and construction guidelines have been previously published.⁷

The basic design of an ALD is shown in Figure 3. The ALD consists of an open, unlined trench or excavation backfilled with gravel-sized, crushed, high-CaCO₃ limestone. The limestone is covered with plastic to preclude oxygen infiltration and CO₂ exsolution. It is desirable to place geotechnical fabric over the plastic for protection of the plastic from puncture by equipment or manpower. A clay soil is then placed over the fabric.

It is assumed that the following reactions are applicable within the ALD:



Equation 4 reacts limestone with acidity (at pH <6.4) present in the mine drainage to form free calcium and dissolved carbon dioxide (carbonic acid). The carbonic acid further reacts with limestone in equation 5 to produce alkalinity. As reactions 4 and 5 act to increase pH above 6.4, equation 6 becomes the major reaction where bicarbonate is the dominant dissolved CO₂ species.⁸ Systems observed to date indicate that if the ALD is properly constructed, limestone in the ALD will not armour with Fe or Al precipitates and alkalinity can be significantly increased in the ALD effluent.

DESIGN GUIDELINES

Guidelines to determine the utility for an ALD are suggested as follows:

- Case 1: Alkalinity > 80 mg/l, Fe > 20 mg/l; an ALD may be beneficial, but a wetlands system based on previously reported chemical loading rates is probably adequate.¹
- Case 2: Alkalinity > 80 mg/l, Fe < 20 mg/l; an ALD is not necessary, only an adequately designed wetlands.
- Case 3: Alkalinity < 80 mg/l, Fe > 20 mg/l; an ALD is recommended and probably necessary as the initial stage in a constructed wetlands system.
- Case 4: Alkalinity < 80 mg/l, Fe < 20 mg/l; an ALD is recommended, but not necessary.
- Case 5: Alkalinity ≤ 0 mg/l, Fe < 20; an ALD will likely be necessary as Fe approaches 20 mg/l.

Case 6: Dissolved oxygen > 2.0 mg/l or Fe oxidizing conditions exist (e.g., pH > 6.0 , eH > 100 mv). An ALD should not be installed because of probable limestone armoring.

Case 7: Ferric iron present in appreciable concentrations in the unaerated seep sample; an ALD may not be appropriate due to potential limestone armoring.

In order for an ALD to perform successfully, unaerated mine drainage must come into contact with the buried limestone. Discrete seeps or boils from embankments are generally good starting points for excavation of the ALD into the backfill. Non-point seep areas may require more innovative means of collection, such as specialized rock drains or the construction of an embankment to contain the ALD. Underground mine adits could be sealed and flooded, routing the drainage via a pipe to an ALD, or a mine adit could be backfilled with limestone and thereby delineate the boundaries of the ALD.

Maximum expected flow through the ALD should be determined to prevent hydraulic failures and disruption of the sealed nature of the ALD. Because of the relative low cost of an ALD compared to conventional treatment systems, an oversized ALD is recommended to ensure hydraulic stability and to maximize longevity. In fact, desired longevity of the ALD will likely dictate a design size far in excess of the hydraulic design requirements. A suggested crude, but conservative, method for hydraulically designing the ALD is to calculate infiltration from the contributing drainage basin at the point source of the seepage and assume an attenuation factor based on the mine fill characteristics.

Another important preliminary consideration for ALD construction is water quality. The success of an aerobic wetlands system to meet effluent limitations is directly and primarily related to influent pH, acidity, alkalinity, Fe, and Mn concentrations. Alternatively, DO and oxidation-reduction potential (ORP) are critical for the proper operation of an ALD. All waters that would be routed through an ALD should be sampled and analyzed for the above mentioned parameters. Samples should be collected directly from the seep via methodologies precluding sample aeration (e.g., peristaltic pumps, large syringes, etc.). DO and ORP must be field measurements. Fe^{+2} and Fe^{+3} are good indicators of ORP (and possible armoring). If samples are immediately acidified with HNO_3 (or another non-oxidizing acid) Fe^{+2} can be determined accurately in the lab. Al precipitation within the ALD has also been proposed as a potential plugging problem,⁹ but has not been observed at TVA systems including the IMPl AROAD where total Al is greater than 10 mg/l.

Side slopes of the excavation are not critical to the operation of the ALD and are best made near vertical to facilitate construction. High-calcium limestone (i.e., $\geq 90\%$ available CaCO_3) should be used. TVA and TWPC have used 3/4 to 1-1/2 in crushed rock in existing ALDs because of its high hydraulic conductivity, large surface area, and ready availability; however, a different gradation, a well-graded mixture, or a layering of several grades of rock may be suitable. Larger rock size or more dolomitic (i.e., CaMgCO_3) stone is not recommended due to the loss of surface area in the ALD with the

large rock and the lower reactivity of dolomite. The depth of limestone backfill should be determined by (1) the need to accommodate the maximum probable flow, (2) the desired longevity of the ALD, and (3) a comfortable safety factor for both (1) and (2). Desired longevity is discussed below. TVA's and TWPC's ALDs have contained limestone depths of 2 to 5 ft. Because the very lowest portion of the backfill may be rendered ineffective due to its tendency to embed in the bottom of the excavation, about 6 inches additional depth of limestone should be included to account for this loss.

A minimum of 2 ft of soil cover should be placed and compacted over the plastic and fabric covered limestone backfill. Soil should be sufficiently impermeable to oxygen migration. If available and practicable, clay soil is recommended. Alternatively, a clay, clayey-silt, or silty-clay loam should be adequate. The final cover should be slightly crowned and protected with erosion control fabric or adequately waterbarred to prevent erosion. Crowning will allow for subsidence of the ALD over the years due to limestone dissolution. Ideally, the crowned ALD should be ripped or revegetated with species such as sericea (Lespedeza cuneata) or crownvetch (Coronilla varia), which will discourage the establishment of trees whose roots could penetrate the ALD and render it ineffective.

Prototype installations of ALDs have used 5-mil plastic and/or filter fabric covered with clay soil to seal the limestone from the atmosphere.³ More recent ALDs have used 20-mil plastic or double layers of 10-mil plastic which is significantly less expensive than 20-mil and is more readily available. Geotechnical fabric should be of quality sufficient to protect the integrity of the plastic from puncture under loads from equipment and workers.

An additional design recommendation is the use of an oxidation basin immediately after the seep discharges from the ALD and prior to routing that flow into a constructed wetlands. The purpose of an oxidation basin is aimed at high Fe influents (e.g., >50 mg/l). The basin allows the newly aerated and highly alkaline ALD discharge water to react and precipitate the majority of its Fe load, which can be achieved physiochemically and without the use of a constructed wetlands. The U.S. Bureau of Mines has suggested a general empirical guideline which states that about 50 mg/l Fe can be removed in an aerobic wetlands cell before reaeration is required.¹⁰ An oxidation basin will greatly enhance the efficiency and lifespan of a downstream constructed wetlands as the basin can be dredged, thus preventing excessive precipitate buildup in the wetlands. Such a pond needs simply to be designed according to existing guidelines with considerations of regulatory requirements, desired capacity, and maintenance. Alternatively, a modified marsh-pond cell with a major portion devoted to deep (3-6 ft) water might be more applicable to acid drainage with low to moderate Fe concentrations.

Longevity of an ALD has been estimated by TVA and TWPC laboratory and field investigations based on the dissolution rate of limestone.^{3,4} These studies include small-scale pilot studies and evaluations of existing ALDs and indicate that ALDs can be expected to last 20-80 years or more if properly designed and constructed.

CASE HISTORIES

Impoundment 4

TVA's Impoundment 4 constructed wetlands (IMP 4) was built in October 1985 to treat acid drainage emanating from a fine coal refuse area at the Fabius Coal Preparation Plant in northeast Alabama.¹ The inflow water quality was characterized by pH = 5.5, total Fe = 65 mg/l, Total Mn = 17 mg/l, acidity = > 200 mg/l, and alkalinity = < 30 mg/l. Flow averaged 34 gal/min. Although significant amounts of Fe and Mn were removed from the acid drainage by the 4-cell, 0.5-acre wetlands (Fe was reduced to less than 10 mg/l), the effluent pH and Mn levels required chemical treatment before final discharge to achieve permit limitations.

In April 1990, an ALD was installed upstream of IMP 4 (Figure 4). The ALD consisted of a trench 10-15 ft wide, 5 ft deep, and 260 ft long excavated into the refuse and seepage area with a swamp-tracked hydraulic excavator. Four-hundred tons of 3/4" - 1 1/2" crushed limestone were backfilled into the open trench. The limestone was covered with two layers of 10-mil plastic over which was placed geofabric and 2 feet of local soil (sandy-silty loam). The surface was slightly crowned, seeded with a mixture including *sericea lespedeza*, mulched, and fertilized.

Figure 5 shows typical pre-ALD and post-ALD water quality for IMP 4 discharge. The ALD has successfully increased alkalinity and enabled the IMP 4 wetlands to meet pH, Fe, Mn, and suspended solids concentrations to compliance levels from the initial operation of the ALD to date; wetlands effluent pH has risen from 3.1 to 6.3, acidity has been reduced from 350 to 40 mg/l, alkalinity has increased from 0 to 100 mg/l, Fe has decreased from 6.0 to 1.0 mg/l, and Mn from 1.6 to 0.2 mg/l.

IMP 4 wetlands influent (i.e., the ALD effluent) had an average pH of 6.3 and concentrations of 85 mg/l Fe and 17 mg/l Mn before the ALD. After the ALD was installed, ALD effluent Fe and Mn concentrations decreased to very low concentrations (Figure 6). This phenomenon probably indicated oxidation and precipitation of Fe and Mn within the ALD. This was verified by a series of excavations into the ALD in May 1991. It was found that the upper portion of the limestone in the unsaturated zone of the ALD was moderately armored with Fe coatings. The stone in the saturated zone showed only traces of Fe precipitates. Two possible reasons for the armoring are hypothesized. First, the DO concentration in the ALD effluent was 1.0-2.0 mg/l with an ORP of less than zero. Although these conditions, in water, may be conducive to keeping iron in the reduced, soluble ferrous form (Fe^{+2}), the atmosphere in the unsaturated zone probably had elevated oxygen levels due to several unsealed monitoring wells in the ALD. Periodic fluctuation of the water levels in this zone may have resulted in increased oxygen availability at the limestone surface for Fe oxidation/hydrolysis, resulting in armoring above the zone of saturation in the ALD.

A second hypothesis assumes that ferric hydrolysis (equation 3) is occurring in the ALD because this reaction is not affected by DO levels. The Fe^{+3} concentration in the acid drainage is probably high enough for ferric

hydrolysis to occur (i.e., $\text{Fe}^{3+}/\text{Fe}^{2+} > .25$). Whether this phenomenon is occurring is under evaluation by TVA¹¹ and the U.S. Bureau of Mines.⁹

The discharge from IMP 4 remained well within compliance levels (i.e., pH = 6-9, Fe < 3.0 mg/l, and Mn < 2.0 mg/l) during this period. It was assumed that, if ferric hydrolysis was occurring in the ALD, the system would plug and eventually fail. However, if the ALD was simply being adversely impacted by oxygen invasion, then a solution to the problem might be to induce saturated conditions throughout the majority of the ALD. In June 1991, the monitoring wells were sealed and an earth dike (Figure 7) was constructed at the discharge point of the ALD to raise the water level in the ALD approximately 3-4 feet. Measurements in the monitoring wells confirmed saturation of the ALD in its upper portion, and Fe levels have increased significantly in the ALD discharge as shown in Figure 6. Saturated conditions in the limestone appear to have ameliorated the precipitation of Fe within the ALD. Further evaluations are ongoing. Based on the above problems, it may be prudent to construct ALDs with high width /length ratio and shallower depths of limestone to ensure saturation.

The total installation cost of the IMP 4 ALD was about \$19,000. This compares to annual costs of about \$20,000 for NaOH and \$10,000 for operation and maintenance associated with conventional treatment of the IMP 4 flow from October 1985 to May 1990.

KIF6 Case History

TVA's Kingston 006 constructed wetlands (KIF 006) was built in October 1987 to treat acid drainage emanating from an ash disposal embankment at the Kingston Fossil Plant in Roane County, Tennessee.¹ Inflow water quality was characterized by pH = 5.5, total Fe = 170 mg/l, total Mn = 4.4 mg/l, alkalinity <40 mg/l, and acidity >400 mg/l with flow averaging 408 gal/min. The 2.3 acre, 3-cell wetlands system consistently removed about 50% of the Fe loading and the pH at the final cell was 2.9. The final cell was pumped to the plant's active ash pond for treatment prior to discharge.

In April 1991, a 10-acre area within the ash disposal area upgradient from KIF 006 was treated with the bactericide ProMac, and reclaimed with lime-amended soil and a grass mixture. This area had been a site where water from the plants bottom ash sluice canal had pooled and presumably contributed significantly to the KIF 006 drainage. In September 1991, an ALD was installed upstream of KIF 006 in an existing seepage collection channel along the toe of the ash embankment. The ALD consisted of a trench approximately 5 ft wide, 5-10 ft deep, and 1400 ft long. The trench was backfilled with 3,600 tons of 3/4" - 1 1/2" crushed limestone which was placed on filter fabric. The stone was covered with geotechnical fabric and 2 - 6 ft of compacted local clay loam. The ash embankment and the ALD cover was sloped approximately 3:1 and seeded with a mixture including sericea lespedeza.

The first cell of the KIF 006 wetlands was converted to an oxidation precipitation pond by dredging to a depth of about 6 - 8 ft. A shallow subsurface rise transversing the midpoint of the cell allows for reareation of the water within the oxidation pond. It is estimated that this cell alone

contains approximately 1,000,000 gallons of acid drainage.

Because of the recent completion of the ALD at KIF 006 (10/1/91), results are not available on any improvement in the water quality. Preliminary results show the pH of the ALD discharge is 6.5, compared to 5.5 for pre-ALD seepage. The total cost of the ALD, the ash pond reclamation with Pro Mac application, and wetlands modifications was approximately \$116,000.

Conclusions

Anoxic limestone drains have been installed at sites in Tennessee, Alabama, West Virginia, and Pennsylvania to increase buffering capacity and alkalinity in acid mine drainage and prevent pH decreases in effluent due to Fe hydrolysis. Results to date are optimistic and in most instances alkalinity has been significantly increased to levels sufficient to buffer the flow from pH decreases. Long-term results must be evaluated to establish the stability of an ALD over the duration of acid drainage at a particular site.

Design, utility, and longevity of an ALD require further examination to develop guidelines and expectations. Particularly, stone gradation and composition, dissolution rates, reaction mechanisms and products, and the nature of ALD-enhanced Mn removal need to be researched. However, the relative simplicity and low cost of the ALD and preliminary studies indicating lifespans of several decades suggest that the system may be an effective means of renovating inefficient, existing aerobic wetlands and an important component of staged wetlands system designs, providing the capability of treating poorer quality waters with less area. To meet effluent compliance limits, TVA advocates the use of ALDs only as a staged portion of aerobic acid drainage wetlands systems, and does not recommend their use as stand alone systems, or as a stage of an anaerobic wetlands system.

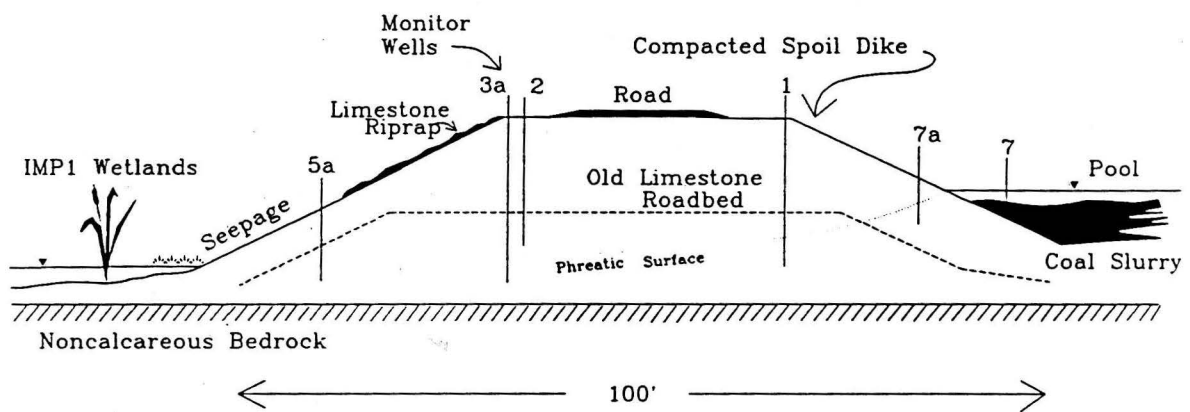
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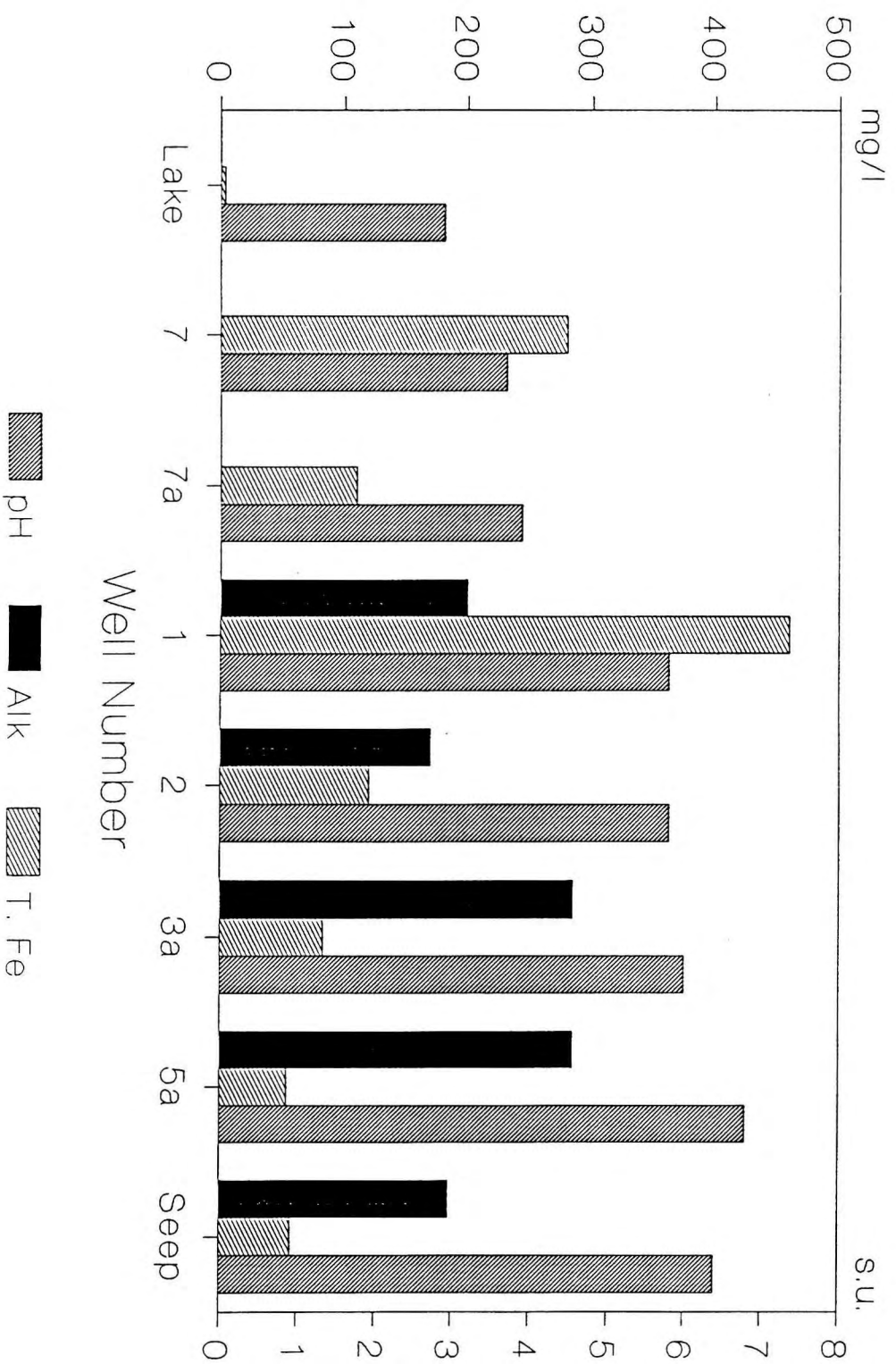
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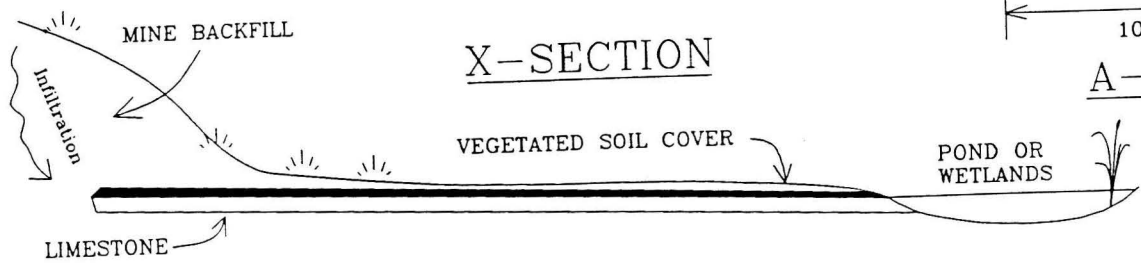
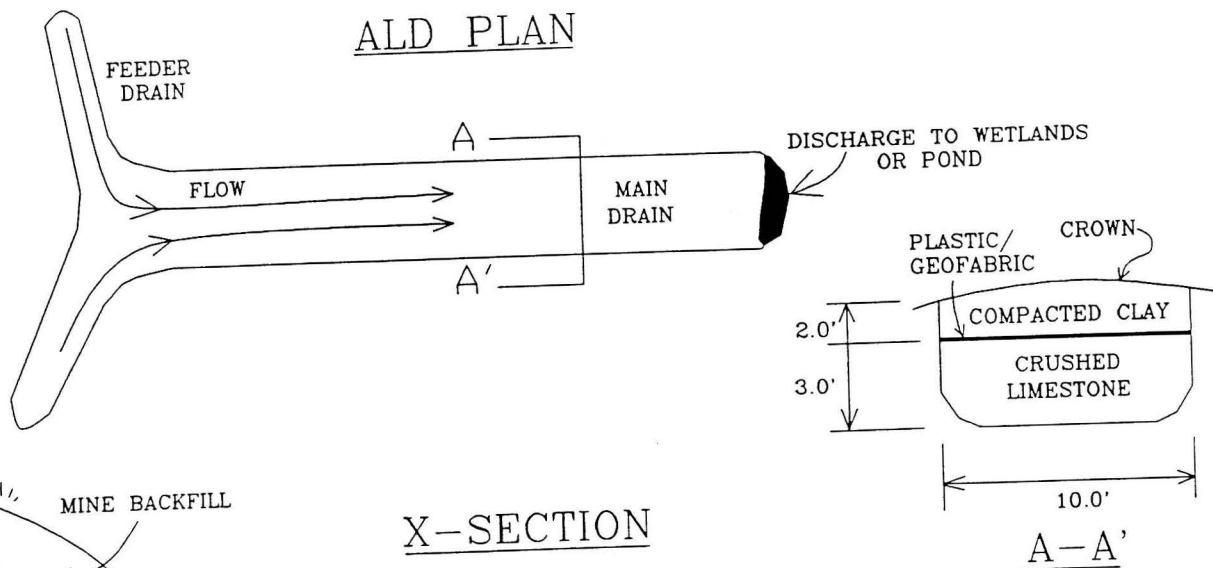
Anoxic Limestone Drains... Brodie et al

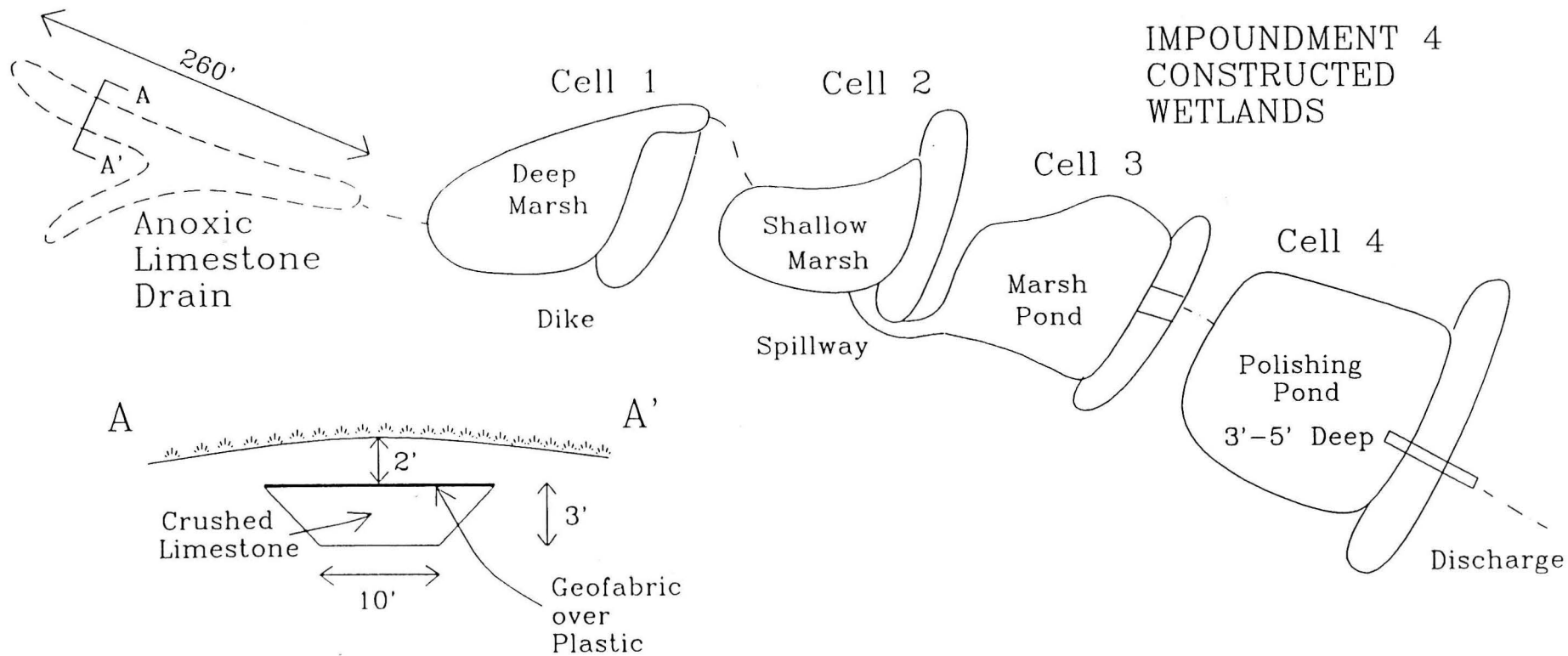
1. Schematic of Slurry Lake 2 Earth Dam "AROAD"
2. Preliminary Data For Monitoring Wells Located in Slurry Lake 2 Dam
3. Generalized Anoxic Limestone Drain Schematic
4. IMP4 Schematic Showing Constructed Wetlands and Anoxic Limestone Drain
5. Average IMP4 Effluent Data Before and After the ALD Installation
6. Fe and Mn Data for IMP4
7. Kingston 006 Constructed Wetlands and Anoxic Drain Schematic

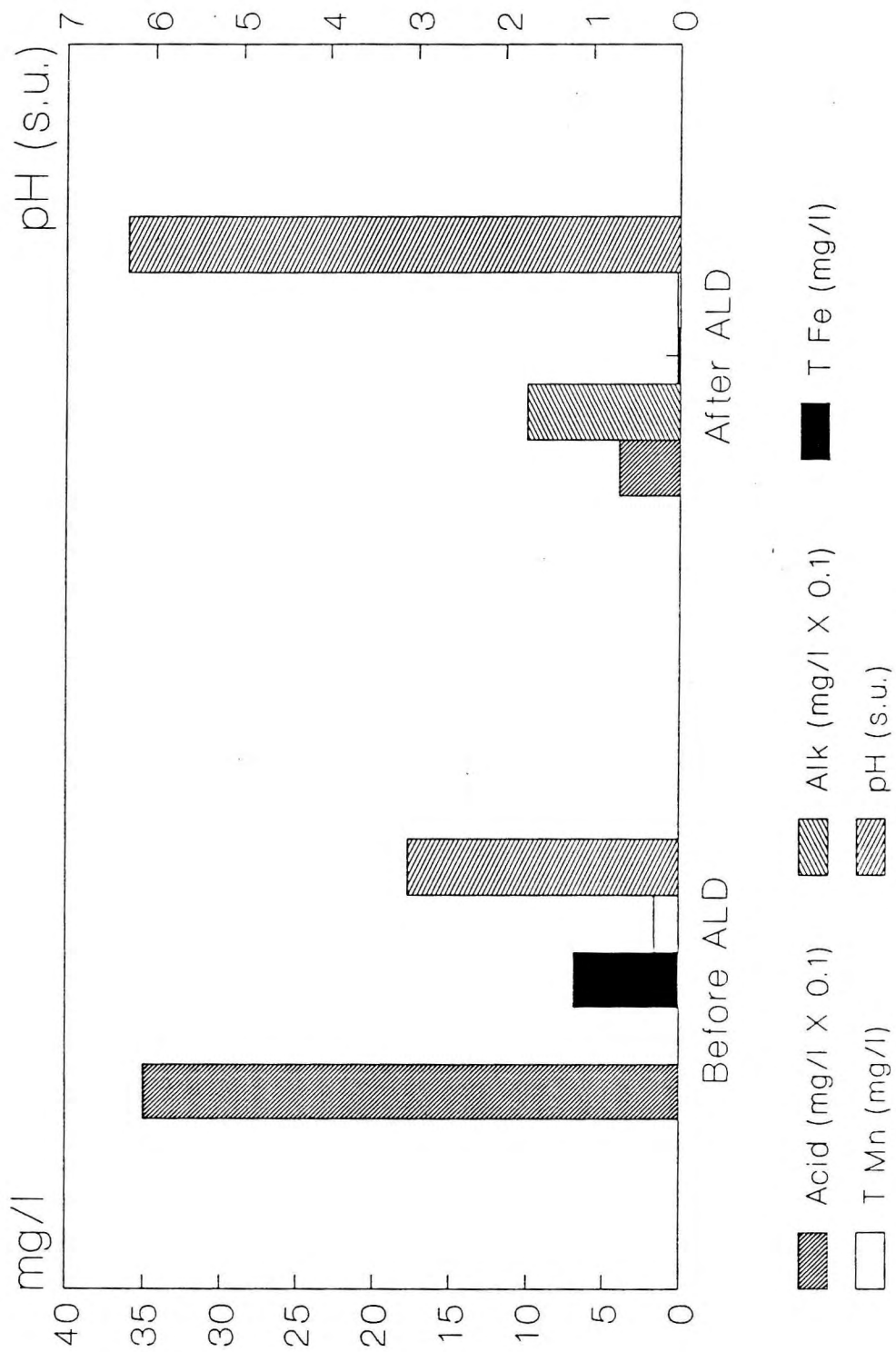


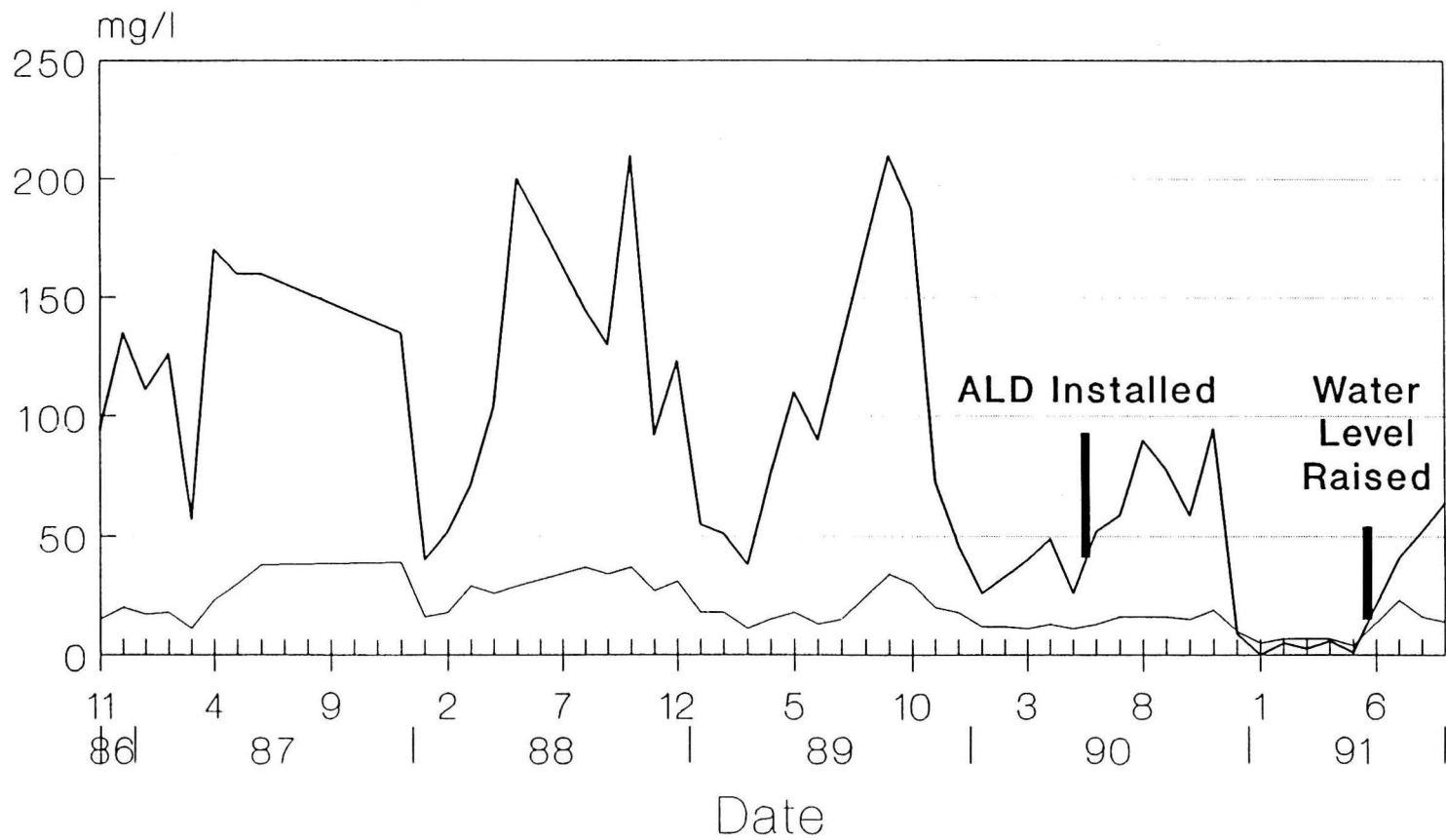


See Figure 1 for well locations.

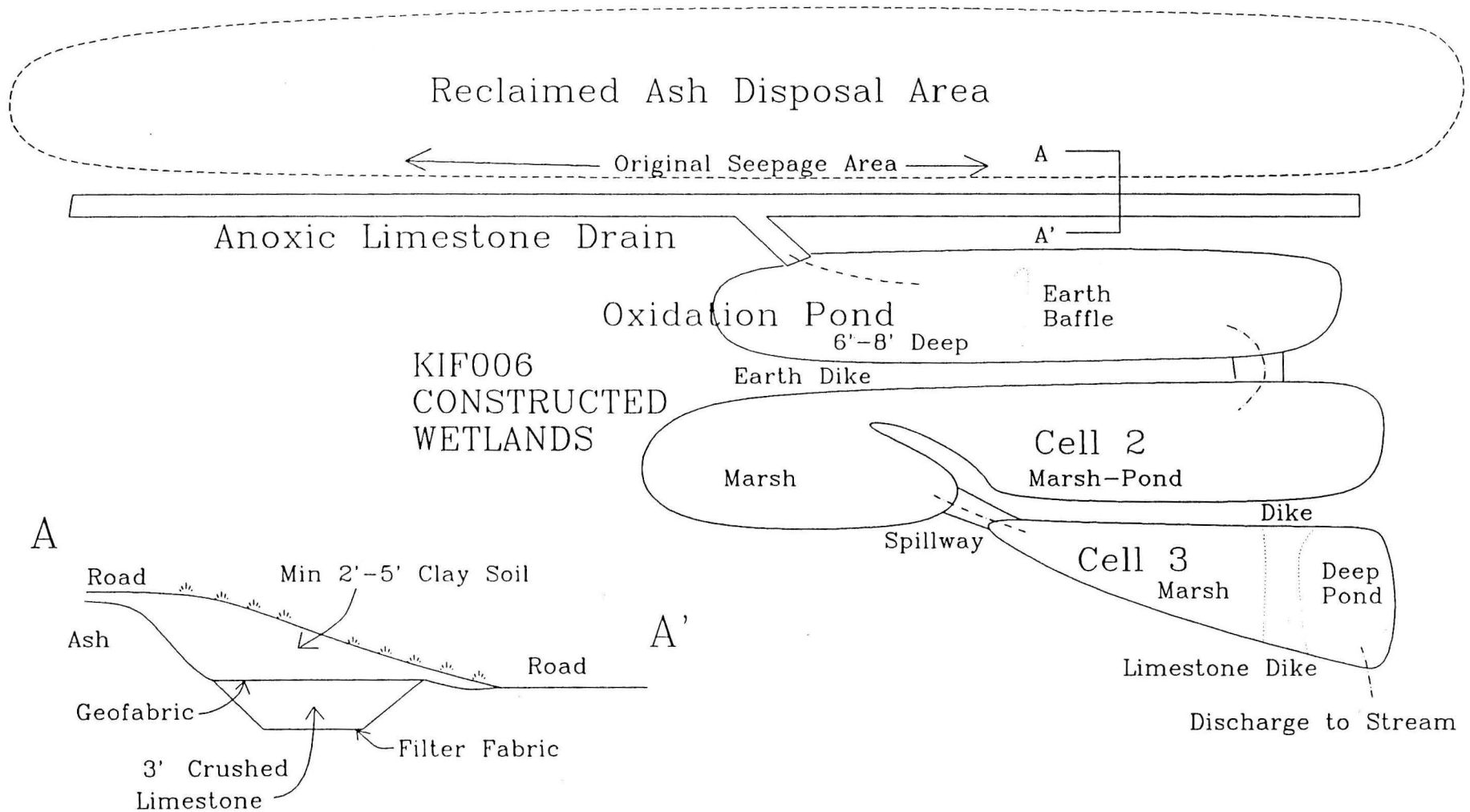








— Total Fe — Total Mn



Wetland Design for Mining Operations

Section IV

THE USE OF BENCH SCALE PERMEAMETERS FOR PRELIMINARY ANALYSIS OF METAL REMOVAL FROM ACID MINE DRAINAGE BY WETLANDS¹

by

Judith L. Bolis, Thomas R. Wildeman, and Ronald R. Cohen²

Abstract. Water drainage from abandoned mines in the Central City-Idaho Springs mining district has impacted the water quality of Colorado front-range water systems. To determine metal removal from mine drainage, permeameters with a high-alkalinity organic substrate were designed to operate in downflow and upflow configurations. Mine drainage from the National and Quartz Hill Tunnels were used in the permeameter testing. Initial flow rates were 10 mL/min and 1 mL/min for the National and Quartz Hill Tunnel drainages, respectively. Both drainages were tested in 3 parallel cells under varying initial conditions. One cell was initially dry, 1 was soaked with water for 1 week to attain anaerobic conditions, and 1 was soaked with water for 1 week and inoculated with established wetland substrate containing sulfate-reducing bacteria. Results indicate an increase of water pH from 5.6 to 7.7 and 2.5 to 7.4 at National and Quartz Hill Tunnels, respectively. Metal removal occurred within all cells for both drainages. The National Tunnel drainage contains metal levels of approximately 42 ppm Fe, 19 ppm Mn, 1 ppm Cu, and 7 ppm Zn. Removal of metals was over 95 %. The Quartz Hill Tunnel drainage contains metal levels of approximately 700 ppm Fe, 80 ppm Mn, 60 ppm Cu, and 140 ppm Zn. Results showed metal removal of over 99 %. Loading rates ranged from 2.1 to 3.8 grams per day per square meter (gdm²) for the National Tunnel and 4.2 to 6.3 gdm² for the Quartz Hill Tunnel. Results indicate that bench scale permeameters can be used to evaluate metal removal from mine drainage and to attain design criteria for larger scale wetlands.

Additional Key Words: acid mine drainage, constructed wetland, wetland design, heavy metals remediation

Introduction

In the design of a wetland treatment system for mine drainage, various stages of experimentation can be performed to determine design criteria (Reynolds

1991). Lab analysis of microorganism activity has been successful for studying wetland treatment at the Big Five Tunnel mine drainage in Idaho Springs (Batal 1989, Machemer 1990, Reynolds 1991, Wildeman & Laudon, 1989). Bench scale permeameters were used to evaluate the hydraulic conductivity of specific substrates at the Big Five wetland and were found to be predictive of pilot scale operations (Lemke 1989). From evaluation of metal removal data, loading rates can be determined which provide design criteria for a treatment system (Hedin 1990, Wildeman 1990, Reynolds, 1991).

To evaluate mine drainages in the Central City-Blackhawk area, a part of the Idaho Springs-Central City Superfund area, bench scale permeameters were designed to evaluate metal removals, change in pH,

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system configuration, initial substrate conditions, and substrate loading rates.

The drainages chosen for analysis flowed from the National Tunnel and the Quartz Hill Tunnel. Both represent 2 completely different types of mine drainage in the Central City district (Wildeman 1974). Characteristics of the National Tunnel drainage are a slightly acidic pH of 5.6 and metal concentrations similar to that of the Big Five tunnel. Preliminary metal concentrations for iron, manganese, copper, and zinc were 42, 19, 0.18, and 7 ppm, respectively. Due to the pH, a significant problem with precipitation of iron hydroxide exists. The Quartz Hill Tunnel drainage represents the extremes of acid mine drainage for the area. The pH ranges from 2.3 to 2.7, while metal concentrations are comparatively high. The preliminary metal concentrations for iron, manganese, copper and zinc were 920, 63, 77, and 91 ppm, respectively.

The objectives were: 1) to evaluate metal removal efficiencies and the change in pH over time, 2) to evaluate an upflow configuration compared to a downflow configuration, 3) to evaluate the system by varying initial substrate conditions, and 4) to determine loading rates.

Materials and Methods

The permeameters for this study were constructed of 32 gallon plastic garbage cans fitted with PVC pipe and designed to operate without valve control in both upflow and downflow configurations. Flowrates were adjusted by raising or lowering the output level. Consideration was made for iron hydroxide clogging, adjustability of flowrates, and limited maintenance. Figure 1 is a diagram of the permeameters in the downflow configuration. Further details of the design and operation of this experiment are described in a report by Bolis and Wildeman (1990).

The permeameters for evaluation of the National Tunnel and Quartz Hill Tunnel mine drainages were setup in the field and in the lab, respectively. At each site, 3 downflow permeameters were setup and designated as Cell A, Cell B, and Cell C. Cell A contained the standard substrate and was considered to be a dry cell. This cell was not soaked or inoculated. Cell B contained the standard substrate and was soaked with city water for 1 week prior to operation. Cell C, which contained the standard substrate, was soaked for one week prior to operation, and was inoculated with substrate containing sulfate reducing bacteria from the

Big Five constructed wetland (Batal 1989).

Previously, mushroom compost had been utilized as substrate at the Big Five constructed wetland (Batal 1989). After titrating the mixture with HCl, it was concluded that it may not provide sufficient buffering capacity for both mine drainages. The permeameter substrate selected was composed of cow manure and planter soil in a 3:1 ratio to provide a soil pH of approximately 8.7.

The permeameters at the National Tunnel were located near the adit with a PVC pipe running mine drainage to the system. A trough system was designed to feed mine drainage into each permeameter with both the trough and permeameters having an overflow system. Water was hauled from the Quartz Hill Tunnel site to the lab in 50 liter carboys. Each cell had an individual reservoir for mine drainage and an overflow system. Each permeameter had at least 1 inch depth of standing water on top of the substrate at all times.

Operation of both sites began in June 1990 and continued through October 1990. Cell A was changed from a downflow configuration to an upflow configuration at the end of 2-months operation at both sites. Fresh inoculated substrate was added to the permeameter and the flow direction was reversed and operated for approximately 2 months. At both sites, it was necessary to make regular checks on the system to adjust the permeameter flowrates, check the mine drainage, and rid the system of any iron hydroxide clogging.

The permeameters were operated at approximately 10 mL/min for National Tunnel and 1 mL/min for Quartz Hill Tunnel. The flowrates of the permeameters were determined by evaluating metal removal rates of the Big Five pilot treatment system in Idaho Springs, CO. The Big Five wetland operates at about 1/8 gpm/100 ft² and has shown to remove metals effectively (Wildeman 1990).

The heavy-metal concentration of the National Tunnel is approximately equal to that of the Big Five Tunnel. Table 1 shows a total of Fe, Mn, Cu, and Zn to be between 80 and 90 ppm for both drainages. Therefore, utilizing an effective flowrate of 1/8 gpm/100 ft², and a surface area of 0.204 m² for the permeameter, a new flowrate was calculated. The flowrate for the National Tunnel was determined to be approximately 10.0 mL/min.

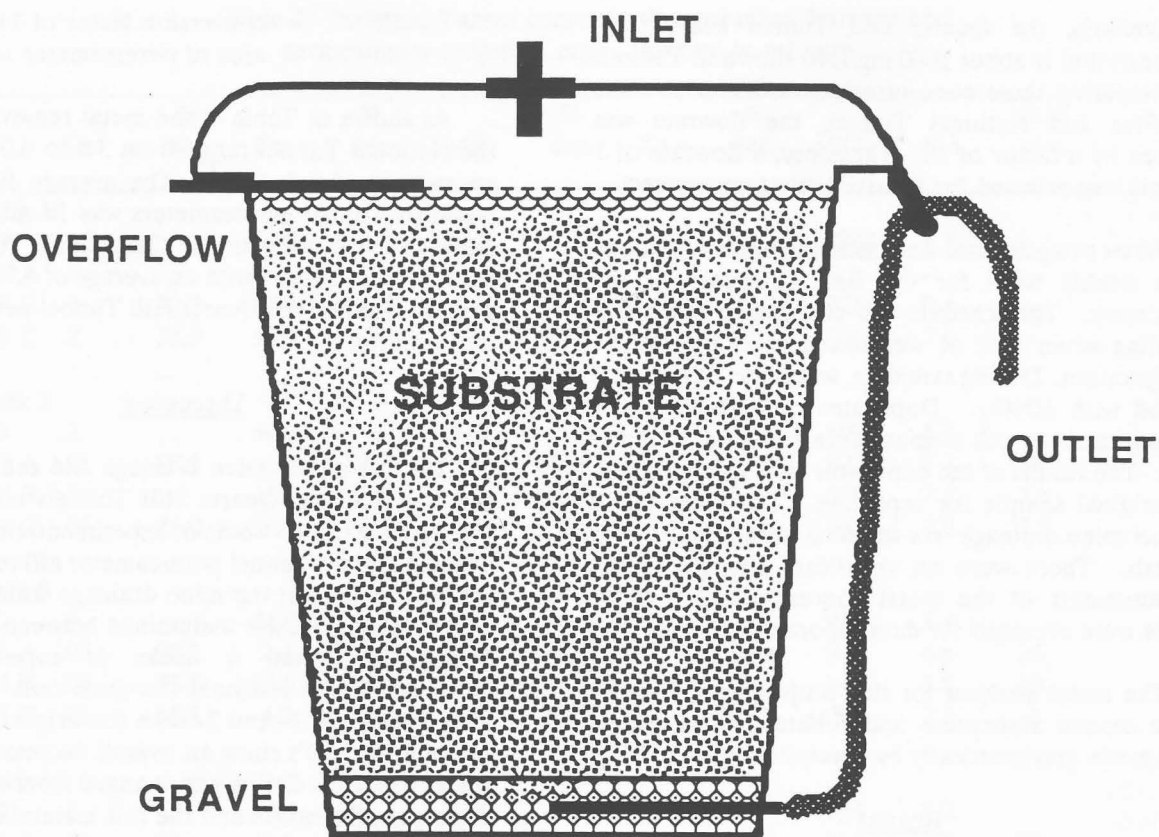


Figure 1. Permeameter in the downflow configuration.

Table 1. Concentrations of Metals in Mine Drainage (ppm)

	Big Five June, 1990	National Tunnel		Quartz Hill Tunnel	
		June, 1973	June, 1990	June, 1973	June, 1990
Eh	700	450	420	450	720
pH	3.0	4.6	5.8	2.6	2.7
Fe	50	50	42	820	920
Mn	32	28	19	80	63
Cu	0.9	1.4	.18	70	77
Zn	10	11	7	130	91

Similarly, the Quartz Hill Tunnel heavy-metal concentration is about 1060 mg/L as shown in Table 1. By comparing these concentrations with those of the Big Five and National Tunnel, the flowrate was reduced by a factor of 10. Therefore, a flowrate of 1 mL/min was selected for Quartz Hill permeameters.

Water sampling and field measurements were done on a weekly basis for the first 10 weeks of the experiment. The schedule was changed to bimonthly sampling when Cell A was changed to the upflow configuration. During sampling, water was filtered and treated with HNO_3 . Duplicates of both the mine drainage and the cell outputs were taken on a regular basis. The results of the duplicates were averaged with the original sample for reporting. The Quartz Hill Tunnel mine drainage was sampled in the field and in the lab. There were no significant changes in the measurements of the metal concentrations. These values were averaged for data reporting.

The metal analyses for this project were done by flame atomic absorption and sulfate determinations were made gravimetrically by precipitation of BaSO_4 .

Results

Tables 2 and 3 show the concentrations of mine drainage influent and permeameter effluent for the National and Quartz Hill Tunnels, respectively. Included in these tables are the percentages of the decrease in the metal concentrations for each permeameter relative to the mine drainage. Also included are the sulfate concentrations, pH's, and the effluent flowrates of each permeameter.

From the metal removal data in Tables 2 and 3, area-adjusted loading rates can be determined (Hedin 1990). Table 4 shows the area-adjusted removal rates for the National Tunnel and Quartz Hill Tunnel mine drainages. Ranges and averages are provided for both iron concentration and total metal concentrations in grams per day per square meter (gdm^2). The following calculation is performed to determine the loading rates (Hedin 1990):

$$\text{Rate} = ([M_{\text{md}}] - [M_{\text{cell}}])(Q)(CF)/A$$

where:

- [M] = concentration of metal
- md = mine drainage
- cell = permeameter cell effluent
- Q = flow rate of mine drainage into permeameter

- CF = conversion factor of 1440 min/day
- A = area of permeameter = 0.204 m^2

As shown in Table 4, the metal removal rates for the National Tunnel range from 3.0 to 6.0 gdm^2 with an average of 4.3 gdm^2 . The average flow for the National Tunnel permeameters was 10 mL/min. The metal removal rates for the Quartz Hill Tunnel range from 5.4 to 8.5 gdm^2 with an average of 6.7 gdm^2 . The average flow for the Quartz Hill Tunnel permeameters was 1 mL/min.

Discussion

The pH of the mine drainage and cell output for the National and Quartz Hill Tunnels are shown in Figure 2 for the 19-weeks of experimentation. The pH of the National Tunnel permeameter effluents parallel the fluctuations of the mine drainage from 5.2 to 5.8. The effluent pH's are maintained between 7.0 and 8.0 during the initial 4 weeks of experimentation. However, as the National flowrates cells were varied after week 6, to 2- and 3-times the original flow of 10 mL/min, the pH's show an overall decrease. Between weeks 9 and 13, Cell A was changed from downflow to upflow configuration and the cell maintained a higher pH for about 4-weeks.

For the Quartz Hill Tunnel, as the mine drainage pH fluctuated from 2.3 to 2.8, the permeameter effluent pH ranged from 6.2 to 8.2. An overall decline in pH occurred during the 19 weeks from around 8.0 to 6.5. In later weeks, the flowrate for Cells B and C, was increased from the established rate of 1 mL/min to 2-3 mL/min. After Cell A was changed from a downflow to upflow configuration in week 13, the effluent pH was approximately the same as Cells B and C.

By comparing the pH fluctuations at both sites, the start-up conditions of dry, soaking with water and inoculation show minor variation. Also, comparing the pH change in the upflow and downflow configurations show few differences.

The comparison of iron concentrations in the mine drainage and permeameter effluent for the National Tunnel and Quartz Hill Tunnel is shown in Figure 3. Cells B and C of National Tunnel had a slower start-up removal rate of about 5 to 7 weeks than Cell A. However, in week 13, as Cell A was changed to an upflow configuration, the removal was similar to Cells B and C in weeks 1-6. Note that the upflow Cell A was inoculated while downflow Cell A was not, perhaps indicating that the inoculum impedes immediate iron

Table 2. National Tunnel concentrations of mine drainage and permeameter output in mg/L, flowrate in mL/min.

	Cu	% dec.	Fe	% dec.	Mn	% dec.	Zn	% dec.	SO ₄ ²⁻	pH	flow rate
Week 1											
MD	.45		50.3		20.5		8.8		938	5.7	
Cell A	--		--		--		--		--	--	
Cell B	.3	33.3	4.7	90.6	1.1	94.6	.6	93.2	3260	7.4	--
Cell C	.2	55.5	13.9	72.4	1.6	92.2	.4	95.5	1200	7.0	--
Week 2											
MD	.2		40.9		20.3		8.2		899	5.2	
Cell A	.05	97.5	.8	98.0	.9	95.6	.05	99.4	871	7.2	38
Cell B	.2	--	18.8	54.0	1.5	92.6	.5	93.9	825	7.3	7.5
Cell C	.05	75.0	5.9	85.6	1.4	93.1	.2	97.6	462	7.0	7.5
Week 3											
MD	.3		44.0		20.3		8.5		935	5.4	
Cell A	.05	98.3	2.1	95.3	11.0	45.8	0.5	94.1	906	6.6	25
Cell B	.08	73.3	14.7	66.6	1.6	92.1	.3	96.5	341	7.5	10
Cell C	.05	98.3	4.3	90.2	1.9	90.6	.2	97.6	86	7.7	2
Week 4											
MD	.2		39.3		20.8		8.5		926	5.9	
Cell A	.05	75	2.6	93.4	12.4	40.4	.05	99.4	871	7.7	30
Cell B	.05	75	11.1	71.8	1.6	92.3	.2	97.6	197	7.7	15
Cell C	.05	75	2.5	93.6	1.3	93.8	.08	99.1	106	7.7	--
Week 5											
MD	.4		42.5		21.6		8.4		947	5.5	
Cell A	.05	87.5	2.4	94.4	14.0	35.2	.08	99.0	687	7.4	22
Cell B	.07	82.5	7.4	82.6	1.3	94.0	.2	97.6	47	7.3	1
Cell C	--		--		--		--		--	--	-
Week 6											
MD	.3		41.4		21.0		8.4		936	5.6	
Cell A	.05	83.3	1.4	96.6	17.0	19.0	.07	99.2	778	6.7	25
Cell B	.05	83.3	3.6	91.3	.7	96.7	.1	98.8	417	7.3	15
Cell C	.05	83.3	.7	98.3	1.9	91.0	.06	99.3	710	6.8	1
Week 7											
MD	.3		41.6		19.0		8.0		936	5.4	
Cell A	.05	83.3	2.2	94.7	14.1	25.8	.06	99.2	738	7.1	15
Cell B	.07	76.7	2.1	95.0	.8	85.8	.1	98.8	272	7.0	9
Cell C	.05	83.3	.6	98.6	1.8	90.5	.04	99.5	804	7.0	5
Week 9											
MD	.2		34.1		20.0		8.4		--	5.5	
Cell A	.05	97.5	2.0	94.1	18.5	7.5	.1	98.8	--	6.7	19
Cell B	.05	97.5	1.3	96.2	8.7	56.5	.05	99.4	--	7.0	38
Cell C	.05	97.5	1.2	96.5	7.9	60.5	.05	99.4	--	6.4	24

Table 2. (continued) National Tunnel concentrations of mine drainage and permeameter output in mg/L, flowrate in mL/min.

Cu	% dec.	Fe	% dec.	Mn	% dec.	Zn	% dec.	SO ₄ ²⁻	pH	flow rate
Week 11										
MD .2		39.9		21.8		8.9		995	5.3	
Cell A --		--		--		--		--	--	
Cell B .07	65	1.5	96.2	17.2	21.1	.1	98.9	941	6.6	130
Cell C .05	75	.1	99.7	13.7	37.2	.01	99.9	873	6.5	35
Week 13										
MD .2		41.9		22.8		9.1		772	5.8	
Cell A .05	75	7.4	82.3	1.5	93.4	.5	94.5	1317	7.5	12
Cell B .07	65	.2	99.5	16.0	29.8	.07	99.2	923	6.7	--
Cell C .05	75	.1	99.8	17.8	21.9	.2	97.8	908	6.7	20
Week 15										
MD .1		42.3		23.1		7.9		860	5.4	
Cell A .08	20	5.5	87	.3	98.7	.3	96.2	664	7.4	7
Cell B .05	50	--	--	--	--	.3	96.2	--	6.3	30
Cell C .05	50	.3	99.3	13.1	43.3	.01	99.9	507	6.4	26
Week 17										
MD .1		54.8		24.8		9.5		1027	5.5	
Cell A .3	--	2.9	94.7	.4	98.4	.1	98.9	752	6.9	9
Cell B .05	50	1.5	97.3	18.6	25	.07	99.3	929	6.3	24
Cell C .05	50	.3	99.5	13.1	47.2	.01	99.9	507	6.4	30
Week 19										
MD .08		49.2		24.4		9.0		1010	5.2	
Cell A .05	62.5	2.9	94.1	2.6	89.3	.4	95.5	1001	6.2	43
Cell B .05	62.5	.05	99.9	3.4	86.1	.05	99.4	--	6.2	42
Cell C .05	62.5	.2	99.6	18.8	23.0	.04	99.6	922	6.5	24

Table 3. Quartz Hill concentrations of mine drainage and permeameter output in mg/L, flowrate in mL/min.

	Cu	% dec.	Fe	% dec.	Mn	% dec.	Zn	% dec.	SO ₄ ²⁻	pH	flow rate
Week 1											
MD	55.7		672		82.5		136.2		4340	2.7	
Cell A	--		--		--		--		--	--	
Cell B	.3	99.5	7.6	98.9	1.5	98.2	.5	99.6	2410	6.9	.7
Cell C	.2	99.6	15.3	97.7	2.9	96.5	.4	99.7	1300	6.5	--
Week 2											
MD	56.2		666		84.2		141.6		4380	2.6	
Cell A	.4	99.3	8.7	98.7	1.4	98.3	.9	99.4	515	8.6	.9
Cell B	.3	99.5	6.8	99.0	1.7	98.0	.6	99.6	188	7.9	.7
Cell C	.1	99.8	4.8	99.3	1.7	98.0	.2	99.9	109	8.2	.7
Week 3											
MD	56.2		680		84.9		143.2		4300	2.6	
Cell A	.3	99.5	2.6	99.6	1.5	98.2	.6	99.6	280	7.5	1.0
Cell B	.12	99.8	4.5	99.3	1.4	98.4	.3	99.8	520	7.4	1.4
Cell C	.05	99.9	3.8	99.4	1.4	98.4	.1	99.9	237	7.3	1.2
Week 4											
MD	47.5		636		79.4		132.6		4190	2.4	
Cell A	.06	99.9	1.6	99.7	.9	98.9	.3	99.8	450	7.4	1
Cell B	.05	99.9	1.9	99.7	.9	98.9	.2	99.8	773	7.5	1.1
Cell C	.05	99.9	1.0	99.8	1.0	98.7	.2	99.8	412	7.4	.8
Week 5											
MD	54		681		78.2		138.0		4280	2.3	
Cell A	.05	99.9	1.2	99.8	.7	99.1	.2	99.9	640	7.5	.6
Cell B	.05	99.9	1.3	99.8	.7	99.1	.2	99.9	812	7.3	.9
Cell C	.05	99.9	.8	99.9	.8	99.0	.2	99.9	306	7.3	.3
Week 7											
MD	48.4		626		78.2		133.3		4300	2.5	
Cell A	.05	99.9	.9	99.9	1.0	98.8	.2	99.9	1080	7.2	1
Cell B	.05	99.9	1.0	99.8	.6	99.2	.2	99.8	660	7.4	.9
Cell C	.05	99.9	.5	99.9	1.6	98.0	.1	99.9	1180	7.2	.9
Week 9											
MD	55.2		628		78.8		160		3800	2.7	
Cell A	.05	99.9	.46	99.9	1.5	98.1	7.4	95.4	1312	7.1	1.3
Cell B	.05	99.9	.43	99.9	.5	99.4	9.1	94.3	995	7.3	1.4
Cell C	.05	99.9	.3	99.9	3.5	95.5	5.2	96.8	1332	6.9	1.4
Week 11											
MD	69.8		806		70.5		101.5		3992	2.9	
Cell A	--		--		--		--		--	--	--
Cell B	.05	99.9	--		.5	99.3	.2	99.8	1067	8.0	.6
Cell C	.05	99.9	--		1.6	97.7	.3	99.7	556	7.9	.7

Table 3. (continued) Quartz Hill concentrations of mine drainage and permeameter output in mg/L, flowrate in mL/min.

	Cu	% dec.	Fe	% dec.	Mn	% dec.	Zn	% dec.	SO ₄ ²⁻	pH	flow rate
Week 13											
MD	63.5		900.5		82.1		167.9		3829	2.6	
Cell A	.08	99.9	3.0	99.7	.9	98.9	.5	99.7	732	7.5	.4
Cell B	.05	99.9	.3	99.9	1.4	98.3	.2	99.9	1006	7.3	.5
Cell C	.05	99.9	.3	99.9	3.7	95.5	.2	99.9	725	7.2	.6
Week 15											
MD	57.1		692		76.8		159.1		3090	2.5	
Cell A	.4	99.3	3	99.6	.9	98.8	.5	99.7	1777	7.7	.9
Cell B	.05	99.9	.1	99.9	8.5	88.9	.2	99.9	2842	7.0	1.5
Cell C	.05	99.9	.1	99.9	15.7	79.6	.1	99.9	2929	6.8	1.7
Week 17											
MD	54.4		702.9		79.7		177.4		4027	2.5	
Cell A	.04	99.9	1.8	99.7	.6	99.2	.4	99.8	2207	7.7	.7
Cell B	.05	99.9	3.3	99.5	22.0	72.4	.2	99.9	3342	6.6	2.4
Cell C	.24	99.6	--		--		.1	99.9	3089	6.4	2.9
Week 19											
MD	59		633.8		95.9		190		3438	2.3	
Cell A	.26	99.6	1.6	99.7	1.2	98.7	.1	99.9	3430	7.1	1.2
Cell B	.6	98.9	119.2	82.2	58.9	38.6	.1	99.9	3574	6.4	2.1
Cell C	.8	98.6	38.5	93.9	50.5	47.4	.1	99.9	3340	6.4	1.5

removal. However, the inoculated and soaked permeameters are expected to work better. This difference in removal may be due to the National Tunnel permeameters being on-site in the field. During the first 4-weeks, flows were found to be quite variable and the removal may have been affected.

Quartz Hill Tunnel iron-removal data shows nearly 100 % removal of iron from all 3 cells during the experimentation. Variations of the flowrate of 1 mL/min showed no apparent effect on the removal of iron. Again, no significant changes are shown by varying substrate conditions and direction of flow. The consistency of this removal pattern, compared with the removal of iron from the National Tunnel permeameters, may be due to the experiments being run in the laboratory and the flows were monitored daily for the first 4 weeks.

Figure 4 shows a comparison of the removal of manganese for the field experiment at the National Tunnel and the lab experiment for the Quartz Hill Tunnel. As the other figures have illustrated, the fluctuations of metal removal in the field are much greater than the lab experiment. For Cells B and C, the removal of manganese from the National Tunnel water was high in the first 7 weeks of the experiment, while it was poor from Cell A. This may be attributed to the variation in the flowrate of Cell A early in the experiment. After week 7, the decrease in the removal of manganese from Cells B and C may be due to the increased flowrate of the system. Note that in week 13, the upflow configured Cell A shows high removal of manganese. The reason for manganese variability in the National Tunnel permeameters is uncertain. However, Machemer and Wildeman (1991) found that Mn can be removed by adsorption onto the substrate in the early stages of wetland operation. After about 8 weeks, when the substrate sites are saturated, Mn concentration in the effluent increases.

Manganese removal for Quartz Hill Tunnel mine drainage was much more consistent. It averaged over 95 % until week 13 when Cells B and C show an apparent decrease. This is best attributed to the increase in permeameter flowrate, which causes a drop in effluent pH, or to the sorption site being saturated by Mn. The change of Cell A to an upflow configuration shows consistent manganese removal for the remaining 6 weeks. Again, this cell was soaked and inoculated and can be compared with Cell C.

For other heavy metals, the National Tunnel permeameter effluent data indicate nearly 4 weeks is

needed to attain a less-than detection limit for copper as shown in Tables 2 and 3. The copper removal tended to vary with the amount of copper in the mine drainage. Despite fluctuations in the Quartz Hill Tunnel mine drainage, copper removal was near 100% for the entire 19 weeks. Zinc removal from both mine drainages was very effective, as shown in Tables 2 and 3. The data show no apparent differences between the dry, soaked, and inoculated cells, as well as between the upflow and the downflow configurations.

Summary

The conditions of the lab were much more favorable than the field for testing due to weather and maintenance problems. The variation in the soaked and inoculated substrate may only be apparent in the iron and manganese removals of the National Tunnel mine drainage. The dry substrate initiated high iron removal immediately, while the soaked and inoculated substrate initiated manganese removal immediately. Both the upflow and downflow configurations showed equally effective removal of metals and increase in pH.

As shown with both drainages, an increase in the flowrate will cause a decrease in the overall pH of the effluent. Total metal removal of Quartz Hill Tunnel mine drainage was not as sensitive to the flowrate change as the National Tunnel mine drainage. Removal of copper, iron, manganese, and zinc from the mine drainages was nearly 100 % throughout the experiment. The exception was manganese removal, which declined in the last 8 weeks. Declines in manganese removal may be explained by an increase in flowrate, decline in pH, and overloading of the system. The flowrates of 10 mL/min for National Tunnel and 1 mL/min for Quartz Hill Tunnel were sufficient to insure an increase in pH and attain a high metal removal.

Finally, loading rates of the substrate were determined. Metal removal rates for the National Tunnel permeameters range from 3.0 to 6.0 gdm², with an average of 4.3 gdm². The Quartz Hill Tunnel permeameter metal removal rates range from 5.4 to 8.5 gdm², with an average of 6.7 gdm².

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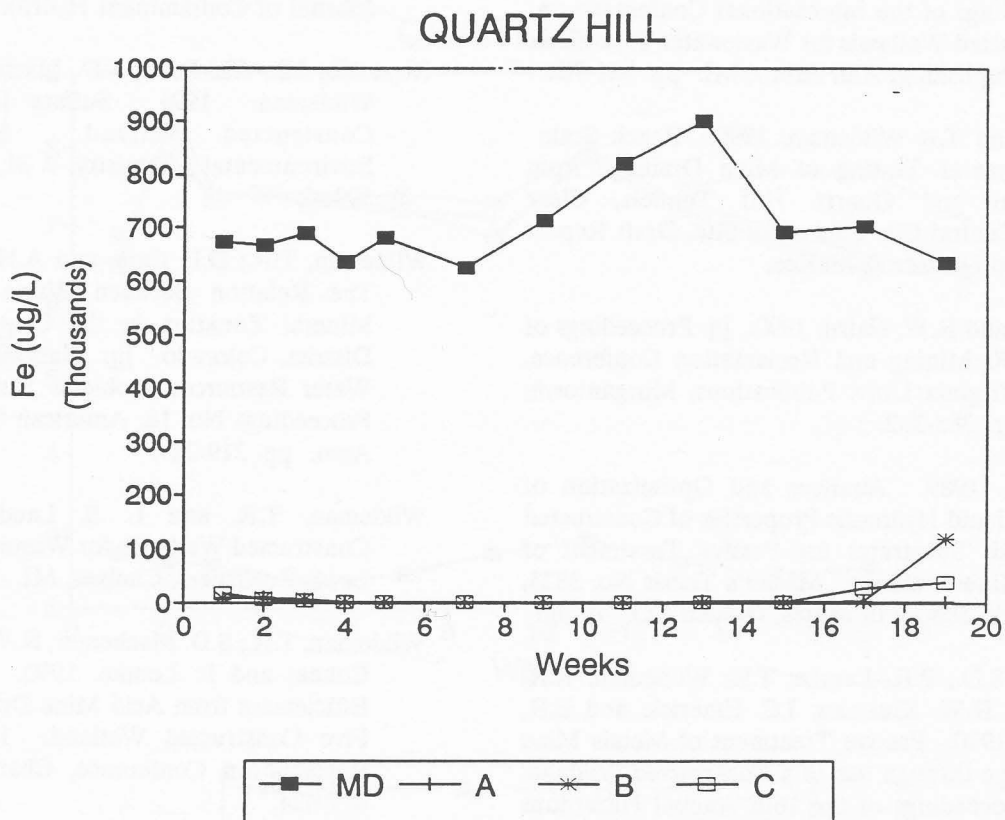
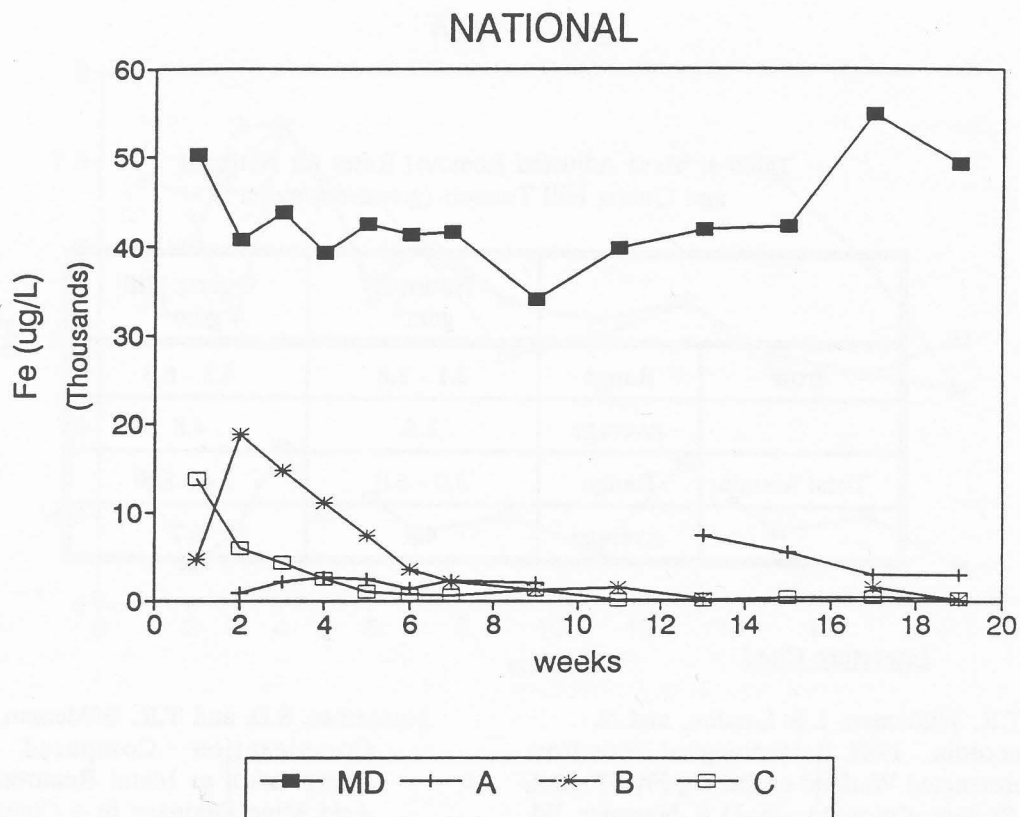


Figure 3. Iron content of mine drainage and permeameter effluents for National Tunnel and Quartz Hill Tunnel.

DETERMINATION OF THE RATE OF SULFIDE PRODUCTION IN A CONSTRUCTED WETLAND RECEIVING ACID MINE DRAINAGE¹

by

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Abstract. The Big Five wetland in Idaho Springs, Colorado was built to treat mine drainage with low pH and high concentrations of heavy metals. Field studies indicated that sulfate reduction and sulfide precipitation are important processes in removing metals from the mine drainage. The approximate summer *in situ* rate of sulfide production by sulfate-reducing bacteria at the wetland was determined to be 1.2 micromoles of sulfide per gram of dry substrate per day by a laboratory serum bottle experiment. Preliminary results indicated that the addition of sodium lactate or an extract of hay significantly increased the rate of sulfide production in the bottles. Sulfate and dissolved metal concentrations decreased, whereas acid volatile sulfide concentration and pH increased with time in the serum bottles. The conditions in the serum bottles were similar to conditions in the wetland output, indicating that the laboratory scale systems could be used to estimate the remediation potential of a constructed wetland for the treatment of mine drainage.

Additional key words: Sulfate-reducing bacteria, heavy metals remediation.

Introduction

Acid mine drainage from abandoned mining operations contributes significantly to water pollution in Colorado streams. Artificial wetlands are currently being considered as possible passive treatment systems for drainage from these sources, utilizing natural biological and geochemical processes to treat the water. The Big Five wetland in Idaho Springs, Colorado was constructed to determine the effectiveness of such a system in treating mine

drainage with low pH and high concentrations of heavy metals and sulfate. The design, construction, and initial operating results of the Big Five wetland treatment system are given in Howard, et al. (1989a and 1989b).

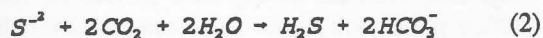
Research projects over the past few years have studied several metal removal processes that could be occurring in the Big Five wetland, including adsorption of metals onto organic materials in the substrate, uptake of metals by the vegetation, and precipitation of metals as sulfides (Machemer et al., 1990, Laudon, 1989). Results of laboratory and field studies indicate that organic adsorption processes are important during the start-up phase of the constructed wetland. However, after several months of operation, organic adsorption sites are filled by the metals and sulfide precipitation becomes the dominant process of metal removal from the incoming mine drainage (Machemer and Wildeman, 1991).

Production of hydrogen sulfide from sulfate by dissimilatory sulfate-reducing bacteria has been shown to be an important process in the sulfur cycle of marine and fresh water environments (Smith and Klug, 1981). Sulfate-reducing bacteria mineralize organic matter in anoxic waters and sediments using sulfate as an electron acceptor according to the

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following reactions:



The products of sulfate reduction (i.e., hydrogen sulfide and bicarbonate ions) are desirable for the treatment of acid mine drainage as the increase in alkalinity will help raise the pH of the water and the hydrogen sulfide can react with the dissolved metals to form sulfide precipitates (Herlihy et al., 1987).

Results of microbiological studies of the Big Five wetland substrate indicate that sulfate-reducing bacteria are present in large numbers, with viable counts ranging from 1900 to 28,000,000 bacteria per gram of dry substrate (Batal, 1989). Analysis of outflow from the wetland shows a decrease in sulfate concentration of approximately 10-20%, significant decreases in concentrations of iron, zinc, and copper (i.e., consistently complete removal of copper and up to 100% removal of iron and zinc depending on flow rate), and an increase in pH as compared to the incoming mine drainage (Machemer and Wildeman, 1991). Significant increases in the sum of acid volatile sulfides (i.e., metal monosulfide precipitates such as FeS and ZnS) plus elemental sulfur over levels measured in the original substrate material have been demonstrated in areas of the Big Five wetland containing mushroom compost. Acid volatile sulfides (AVS) plus elemental sulfur represented 0.15% of the total sulfur in the original compost material. After ten months of operation of the wetland, the compost contained 1.1% of the total sulfur as AVS plus elemental sulfur. However, no significant increases in organic or pyritic forms of sulfur were detected in these areas after the same period of time (Laudon, 1989). All of these results indicate that bacterial sulfate reduction is an important process in the treatment of mine drainage at the Big Five wetland.

The objectives of this study included designing a laboratory scale system to determine an approximate in situ rate of sulfide production by sulfate-reducing bacteria by measuring the change in AVS in the substrate over time and to determine the effects of nutrient amendments on the rate of sulfide production. Another purpose of constructing these laboratory scale wetland substrate systems was to compare values of various parameters such as pH, concentrations of dissolved metals and sulfate, and temperature in the serum bottles to output waters at the Big Five

wetland. From these comparisons, the usefulness of serum bottle systems in initial treatability studies could be evaluated.

Materials and Methods

Collection of Samples and Preparation of Serum Bottles

In June 1990, a 2-liter sample of substrate was collected from an area of the wetland containing mushroom compost. Twelve liters of mine drainage were collected from the adit of the Big Five Tunnel and deoxygenated in the field with nitrogen.

The substrate sample was homogenized on a paint shaker for five minutes. Subsamples of approximately 20 grams were then transferred to 120 ml serum bottles in a glove bag under a nitrogen atmosphere. The bottles were sealed in the glove bag. The following day, 70 ml of deoxygenated mine drainage was added by syringe to each bottle. The bottles were then incubated at 18° C. This temperature was chosen to simulate summer conditions at the wetland.

Determination of Dissolved Metals, Sulfate, and pH in Serum Bottles

Several parameters were determined to be important for comparing conditions in the serum bottles to output waters from the wetland, including pH and concentrations of dissolved metals and sulfate. At approximately five day intervals, an aliquot of the aqueous phase of the serum bottles was removed by syringe. Concentrations of dissolved metals (i.e., zinc, copper, iron, and manganese), sulfate concentration, and the pH of this subsample were determined. Concentrations of dissolved metals were measured by atomic absorption. The sulfate concentration was determined gravimetrically as BaSO₄.

Rate of Sulfide Production

Four bottles were analyzed on the first day after the mine drainage was added for acid volatile sulfides to provide a baseline level of AVS in the substrate sample. AVS was determined with a trapping train similar to the one described by Jorgensen and Fenchel (1974). The bottles were connected to the trapping train and approximately 25 ml of 6M HCl was added by syringe. The H₂S that was produced was flushed from the serum bottles with O₂-free nitrogen and

trapped in the first of two test tubes containing 1N NaOH connected in series. No sulfide was ever detected in the second test tube. Approximately 2 ml of 7.5 M NH_4OH was added to an aliquot of the first trap, and this solution was titrated with 0.01M AgNO_3 to determine the amount of sulfide trapped. The efficiency of the trapping train was determined to be 93% by acidifying a known quantity of ZnS in place of the substrate sample. AVS values determined by titration were corrected accordingly.

Subsequent determinations of AVS were made on triplicate samples at approximately 5-day intervals. The rate of sulfide production was determined by taking the difference in AVS per gram of dry substrate in the subsequent samples from the average AVS per gram of dry substrate in the baseline samples and dividing by the time interval.

Poisoned Controls

Poisoned controls were prepared by adding 11 ml of 5% sodium azide to each of three serum bottles for a final concentration of 0.5%. AVS in these bottles was determined at 15, 35, and 70 day intervals by the method described above.

Nutrient Amendments

Nutrient amendments of either sodium lactate (final concentration of 100 mg/l) or 30 ml of an extract of hay were added to a set of serum bottles. The sodium lactate was chosen because lactate has been found to be a substrate utilized by sulfate-reducing bacteria (Dicker and Smith, 1985). Hay has been used at the Big Five wetland as insulation for the substrate and has appeared to enhance the activity of the sulfate-reducing bacteria. The hay extract was prepared by soaking a sample of hay in distilled water for approximately one week and then removing the supernatant. The AVS produced in these bottles was measured by the method described above approximately two weeks after the addition of the amendments.

Results

Rate of Sulfide Production

Table 1 presents the AVS per gram of dry substrate produced in the serum bottles over 76 days at approximately 5-day intervals. The average rate of sulfide production in the bottles at each time interval is also presented. The initial rate was 1.7 umoles of

sulfide per gram of dry substrate per day for the first 5-day interval. From 5 to 35 days the rate was relatively constant at approximately 1.2 umol/g/day. Beginning with the 40-day time period, the rate of sulfide production began to decrease and this trend continued for the rest of the experiment.

Figure 1 shows the rate of sulfide production in the serum bottles compared to the rate in the poisoned controls. The rate in the controls was minimal compared to the serum bottles, indicating that the production of sulfide in the wetland substrate is predominantly the result of microbial activity.

Effect of Nutrient Amendments

The rates of sulfide production measured in amended bottles were compared to rates measured in unamended serum bottles for corresponding time intervals. These rates in umoles of sulfide per gram of dry substrate per day were as follows:

Sodium lactate	2.4
Hay extract	4.3
No amendment	0.91

The addition of sodium lactate resulted in a rate approximately 2.5 times greater than the rate measured in the unamended bottles. The addition of hay extract resulted in a rate approximately five times greater than in the unamended bottles.

Comparison of Serum Bottles to Mine Drainage and Wetland Output Waters

Table 2 presents a comparison of pH, temperature, concentrations of dissolved metals, and sulfate concentration for serum bottles over a 35-day time period. Mine drainage and output waters from the Big Five wetland treatment system were measured at approximately the same time as the substrate sample was collected.

Table 2 shows that concentrations of dissolved metals in the baseline sample bottles (i.e., measured the day after adding the mine drainage) were lower than the concentrations in the mine drainage. Several processes could have contributed to this immediate removal of some of the metals, including precipitation due to the increase in pH, adsorption onto organic materials enhanced by the agitation of the substrate, and precipitation with residual sulfides in the substrate sample.

Over the course of the experiment, the pH of the serum bottle systems increased, the concentration of

TABLE 1. AVS Production and Rate of Sulfide Production
in Serum Bottles

TIME (days)	B*	5	10	15	20	25	30	35	40	48	55	66	76
AVS ($\mu\text{mol/g}$)	43	52	55	59	68	73	77	84	81	85	89	99	100
RATE ($\mu\text{mol/g/d}$)	**	1.7	1.2	1.1	1.2	1.2	1.1	1.2	0.95	0.86	0.84	0.84	0.74

* Baseline samples

** Not calculated

Note: Values for AVS and rate are the average of three replicates except for values on day 0 (Baseline), which are the average of four replicates and days 10 and 25, which are the average of duplicate samples.

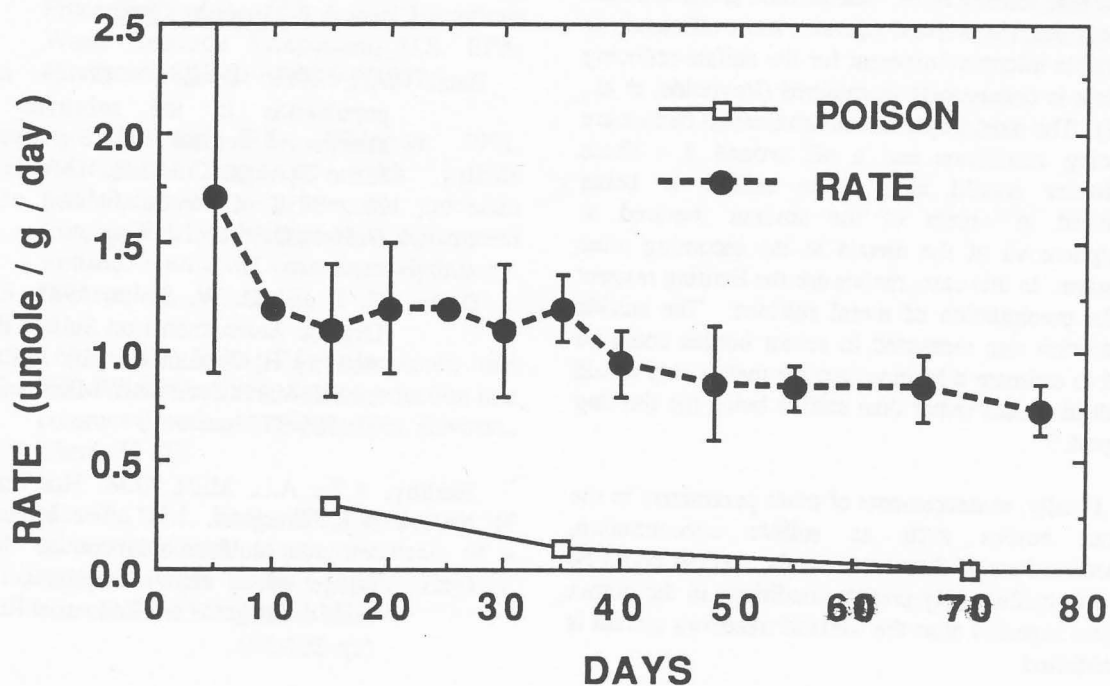


FIGURE 1. Rate of Sulfide Production in Serum Bottles and Poisoned Controls. Error bars represent one standard deviation. Data points without error bars are the average of two samples.

sulfate in the aqueous phase decreased, and the concentrations of dissolved metals decreased. These are the same trends observed when samples of output waters from the Big Five wetland are compared to samples of the incoming mine drainage.

Discussion

Results of these studies indicate the laboratory scale method developed for determining the rate of sulfide production in a wetland substrate could also be used as an inexpensive, initial treatability study of acid mine drainages. A relatively constant rate of sulfide production was measured over a 30-day period. For a treatability study, the serum bottles could be run for just two weeks to obtain a reasonable estimate of the rate of sulfide production in a given system. In addition, the serum bottles could be used to test the effectiveness of different substrates and combinations of nutrient amendments on treating a particular source of mine drainage.

The sulfide production rate measured in the laboratory could be used to estimate loading rates of metals that could be effectively removed by a constructed wetland. Several methods have been used to estimate loading rates. One method is based on the concept that the wetland operates most efficiently if a suitable microenvironment for the sulfate-reducing bacteria is consistently maintained (Reynolds, et al., 1991). The most important environmental factors are reducing conditions and a pH around 7. These conditions should exist when sulfide is being produced in excess of the amount required to precipitate all of the metals in the incoming mine drainage. In this case, metals are the limiting reagent in the precipitation of metal sulfides. The sulfide production rate measured in serum bottles could be used to estimate a loading rate for metals that would result in metals rather than sulfide being the limiting reagent.

Finally, measurements of other parameters in the serum bottles such as sulfate concentration, concentrations of dissolved metals, and pH could be used to qualitatively predict conditions in the output waters expected after the wetland treatment system is established.

Summary

The summer in situ rate of sulfide production by bacteria in the Big Five wetland substrate was estimated to be 1.2 $\mu\text{mol/g/day}$. The rate of sulfide

production measured in poisoned control bottles was minimal compared to the serum bottles, indicating that the process is predominantly microbiological. Preliminary results indicated that the addition of sodium lactate or an extract of hay significantly increased the rate of sulfide production in the serum bottles. Trends in sulfate concentrations, pH, and concentrations of dissolved metals were similar to conditions measured in output waters from the Big Five wetland, indicating that the serum bottle systems could be used in initial treatability studies for mine drainage.

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TABLE 2. Comparison of pH, Temperature, Sulfate, and Metal Concentrations in Mine Drainage, Wetland Output, and Serum Bottles.

SAMPLE	pH	TEMP. (°C)	SO ₄ ⁻² (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)
Mine Drainage	3.0	15.9	1720	0.573	38.6	30.6	8.58
Wetland Output	6.7	18.1	1460	<0.050	0.640	15.8	0.069
Serum Bottles Baseline*	6.1	18.0	1680	<0.050	10.5	15.5	0.036
Serum Bottles (5 days)*	6.2	18.0	1660	<0.050	7.28	10.8	0.534
Serum Bottles (10 days)**	6.3	18.0	1610	<0.050	4.70	9.78	0.272
Serum Bottles (15 days)**	6.3	18.0	1530	<0.050	8.80	15.3	0.129
Serum Bottles (20 days)**	6.4	18.0	1410	<0.050	8.06	12.0	0.368
Serum Bottles (25 days)**	6.4	18.0	1470	<0.050	6.90	11.3	0.221
Serum Bottles (30 days)**	6.4	18.0	1350	<0.050	4.93	9.72	0.213
Serum Bottles (35 days)**	6.7	18.0	1240	<0.050	4.51	10.6	0.162

* Values for these samples are the average of four replicates.

** Values for these samples are the average of three replicates.

Note: Mine drainage and wetland output values are the average of two samples collected in June, 1990.

HYDRAULIC CONDUCTIVITY OF SUBSTRATES USED FOR PASSIVE ACID MINE DRAINAGE TREATMENT¹

by

Judith L. Bolis, Thomas R. Wildeman and Helen E. Dawson²

Abstract. In anaerobic wetland systems that emphasize flow of acid mine drainage through the substrate, the hydraulic conductivity of the substrate material is an important variable. This paper describes results of hydraulic conductivity measurements obtained from two sets of bench scale experiments conducted in 1990 and 1991 with substrate-filled reactors that were used to treat acid mine drainage in the Clear Creek-Central City Superfund site. In 1990, the reactors were filled with an organic substrate of manure and planter soil and were subjected to three initial substrate conditions: 1) dry, 2) soaked with water for one week, and 3) inoculated and soaked with water for one week. Flow rate measurements indicated that the hydraulic conductivity of the initially dry substrate remained consistent over time, while the hydraulic conductivity of the soaked substrates increased over time. In 1991, a primarily inorganic substrate of limestone and alfalfa was tested in addition to the previously described organic substrate. Initial substrate conditions for both substrate types were 1) dry and inoculated and 2) inoculated and soaked for one week with mine drainage. Results indicate that in both the limestone and manure reactors which started with dry substrate, the hydraulic conductivity fluctuated considerably. The values for the initially dry limestone ranged from 2.1×10^{-3} - 1.3×10^{-2} cm/sec while the initially dry manure ranged from 9.9×10^{-5} - 7.1×10^{-3} cm/sec. The hydraulic conductivity was more consistent in the soaked reactors ranging from 1.3×10^{-3} - 8.8×10^{-3} cm/sec in the soaked limestone and from 3.4×10^{-4} to 6.9×10^{-3} cm/sec in the soaked manure. These results indicate that presoaking the substrate for wetlands treatment of acid mine drainage can assist in providing a more stable hydraulic conductivity and, therefore, a more consistent flow rate.

Key words: hydraulic conductivity, acid mine drainage, bench scale reactor, permeameter

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Introduction

Anaerobic treatment of acid mine drainage has been found to successfully remove metals and raise pH through the bacterial reduction of sulfate to sulfides (Howard et al. 1989). This treatment method requires designing a substrate that will facilitate subsurface flow as well as optimize conditions for bacterial reduction. Typically, the effectiveness of constructed wetlands for treating acid mine drainage or other wastewater depends on the hydraulic conductivity of the substrate. Low hydraulic conductivity, caused by a build up of bacterial growth and sediment fines, may cause

short circuiting of a treatment system (Lemke 1989, Cooper 1989, Watson et al. 1989, Staubitz 1989, Trautman 1989). Specifically, in the treatment of acid mine drainage in constructed wetlands, a decrease in the hydraulic conductivity of a substrate may result in surface flow (Steiner 1989) and, thus, affect the removal efficiency of an anaerobic treatment system that depends on subsurface flow (Machemer et al. 1990). Table 1 lists the hydraulic conductivities reported in the literature for various materials that have been used in the wetlands treatment of acid mine drainage and other wastewater.

Hydraulic conductivities measured in bench scale permeameters have been found to be predictive of the hydraulic conductivities in pilot scale wetlands (Lemke 1989). Lemke measured the hydraulic conductivities of fresh and used organic substrates composed of varying ratios of mushroom compost, peat and wood shavings and determined values ranging from 3.0×10^{-4} cm/sec to 6.7×10^{-7} cm/sec. Bench scale experiments used to simulate the removal of metals from acid mine drainage (Bolis et al. 1991) suggested that hydraulic conductivity is a function of the initial condition of the substrate, i.e., dry versus soaked.

This paper compares the results of hydraulic conductivity measurements obtained in previous bench scale experiments (Bolis et al. 1991) to the results obtained from additional experiments designed to more definitively determine the influence of initial condition and time on hydraulic conductivity. The first set of experiments were conducted in 1990 with acid mine drainage from the Quartz Hill and National Tunnel sites in the Central City/Blackhawk mining district as described by Bolis et al. (1991). The second set of experiments were conducted in 1991 with acid mine drainage from the Big Five Tunnel in Idaho Springs, CO. In the latter experiments, both inorganic and organic substrates were tested in the lab and in the field. The results of the hydraulic conductivity measurements are evaluated with regards to the type of substrate and initial condition of the substrate.

Materials and Methods

1990 Experiments

Substrate hydraulic conductivity was initially evaluated using the National Tunnel and Quartz Hill mine drainage reactors. The reactors were

constructed of 32 gallon plastic garbage cans fitted with PVC pipe and designed to operate without valve control in a downflow configuration (Bolis et al. 1991).

The substrate was a mixture of cow manure and top soil in a 3:1 ratio. Three initial substrate conditions were tested for both drainages. Prior to flowing mine drainage through the system, one reactor was dry, a second reactor was soaked with water for one week, and a third was inoculated and soaked with water for one week. The inoculum was a mixture of substrate from the Big Five wetland that contained sulfate reducing bacteria (Batal 1989).

Experimentation began in June 1990 and continued until November 1990. The reactors were operated in a downflow configuration with a constant head reservoir of water on top of the substrate. Flow rates were maintained at 10 ml/min for the National Tunnel drainage and 1 ml/min for the Quartz Hill drainage by adjusting the height with the effluent pipe. An upflow configuration was also evaluated later in the experimentation on both drainages.

1991 Experiments

The Big Five Tunnel acid mine drainage was used for more extensive evaluation of the hydraulic conductivity of substrates. This drainage is characterized with a pH of approximately 3.0 and metals concentrations of 50 mg/L Fe, 35 mg/L Mn, 10 mg/L Zn, and 1 mg/L Cu (Wildeman and Laudon 1989).

The four reactors used in this study were similar to those used in the previous study. Each reactor had a constant head reservoir of water on top of the substrate. Flow rates were maintained at approximately 10 mL/min adjusted by raising or lowering the effluent level.

Two types of substrate were tested in the reactors: an organic and inorganic substrate. Two of the reactors contained the organic substrate tested in 1990 composed of 75% cow manure and 25% planter soil by volume (Bolis et al. 1991). The pH of this substrate was approximately 8.7. The total amount of substrate used in each reactor was 225 lb, of which 25 lb was inoculum. The inoculum consisted of substrate from currently active cells at the Big Five pilot wetland. One of the reactors was soaked for 1 week with mine drainage prior to operation, the other was left dry.

The second set of reactors contained a primarily inorganic substrate composed of

Table 1. Hydraulic conductivity of substrates used in wetlands treatment of wastewater.

MATERIAL	HYDRAULIC CONDUCTIVITY		USE	REFERENCE
	Reported Values	Equivalent in cm/sec		
Mushroom compost (unused)				
lab downflow	3.50×10^{-3} cm/s	3.50×10^{-3}		
bench-downflow	3.14×10^{-3} cm/s	3.14×10^{-3}		
pilot-downflow	2.96×10^{-4} cm/s	2.96×10^{-4}		
lab-upflow	6.65×10^{-2} cm/s	6.65×10^{-2}		
bench-upflow	1.44×10^{-2} cm/s	1.44×10^{-2}		
pilot-upflow	1.38×10^{-2} cm/s	1.38×10^{-2}	acid mine drainage	Lemke 1989
Old Natural Reed Beds recommended United Kingdom design values	5×10^{-6} m/s	5×10^{-4}		
gravel	3×10^{-3} m/s	3×10^{-1}	general wastewater treatment	Referenced in Cooper and Hobson 1989
pulverized fuel ash	1×10^{-3} m/s	1×10^{-1}		
quarry rejects	8×10^{-5} m/s	8×10^{-3}		
pea gravel	8×10^{-1} m/s	8×10^1		
soil beds (in Europe)	2.6 m/d	3×10^{-3}		
gravel beds (in Europe)	30 m/d	3.4×10^{-2}	general wastewater treatment	Referenced in Watson et al. 1989
suggested range	30 - 864 m/d	$3.4 \times 10^{-2} - 1 \times 10^1$		
reed bed media range:				
clays	1×10^{-7} m/s	1×10^{-5}	reed bed treatment	Referenced in Hobson 1989
coarse gravel	1×10^{-1} m/s	1×10^1		
soil beds	$< 3 \times 10^{-5}$ m/s	3×10^{-3}		
homogeneous mixture (lab test)	80 m/d	9×10^{-2}		
sorted substrate (lab test)	1600 m/d	1.8×10^1	landfill leachate treatment	Staubitz et al. 1989

approximately 77% limestone rock, 14% alfalfa, and 9% inoculum by volume. These reactors contained a total of 260 lb of substrate composed of approximately 198 lb limestone, 37 lb alfalfa, and 25 lb inoculum. The limestone rock ranged in size from 1/8 inch to 1/2 inch. Again, the inoculum was obtained from cells at the Big Five wetland. As with the manure substrate reactors, one of the reactors was soaked with mine drainage for one week prior to operation and the other was left dry.

This experiment began in July 1991 and continued through November 1991. The flow rate through the reactors was maintained at approximately 10 mL/min. The optimum flow rates were determined from evaluation of metal removal rates in bench scale experiments and the Big Five pilot treatment system (Bolis et al. 1991, Wildeman et al. 1990).

For both the 1990 and 1991 sets of experiments, the flow rates were measured and adjusted regularly. The difference in height between the standing water on top of the substrate

and the outlet was measured, as well as the height of the substrate in the reactor in order to assess whether compaction of the substrate occurred during the course of the experiments. Field measurements of pH, Eh, conductivity, and temperature were made on a regular basis. Water sampling and constituent analyses followed procedures established for the Big Five constructed wetland.

1991 Lab Experiments

Hydraulic conductivities of the manure and limestone substrates were also measured in the lab, using both the constant head and a falling head techniques described in Fetter (1988) and EPA Method 9100 (1986). The permeameter used was 45 cm high and 7 cm in diameter. A third substrate, a mixture of manure and hay in a 3:1 ratio was also tested in the lab. This substrate has been utilized by others to evaluate wetlands treatment of acid mine drainage (Euler et al. 1991).

Calculation of Hydraulic Conductivity

Hydraulic conductivity of each reactor substrate was determined from Darcy's Law (Fetter 1988, U.S. EPA 1986). Flow through saturated media is governed by Darcy's Law, as follows:

$$Q = K A \frac{dh}{dl} \quad (1)$$

where Q = volumetric flow rate, (ml/min)
 K = hydraulic conductivity, (cm/sec)
 A = cross sectional area, (cm²)
 $\frac{dh}{dl}$ = hydraulic gradient, (cm/cm)

For a constant head system, hydraulic conductivity can be calculated by rearranging equation (1):

$$K = \frac{Q dl}{A dh} \quad (2)$$

For a falling head system, hydraulic conductivity is calculated as:

$$K = \frac{L}{t} \ln (h_0/h_2) \quad (3)$$

where L = length of system, (cm)
 t = time for water to flow from h_0 to h_2 , (sec)
 h_0 = initial water height, (cm)
 h_2 = final water height, (cm)

Equation (2) was used to calculate the hydraulic conductivity of the bench scale reactors, and both equations (2) and (3) were used to estimate hydraulic conductivity of the lab experiments.

The mean hydraulic conductivities obtained from the reactors and lab experiments were compared using t tests performed at the 0.05 level of significance.

Results

1990 Bench Scale Results

Hydraulic conductivity measurements are plotted versus time for the National and Quartz Hill Tunnels reactor experiments as shown in Figures 1a and 1b. Both figures present the results from three simultaneously operated reactors that were subjected to varying initial

substrate conditions.

Initially, the hydraulic conductivity of the soaked National reactors was less than 5.0×10^{-5} cm/sec for the first 42 days and then increased to stabilize at approximately 5.0×10^{-3} cm/sec by day 126. Overall, the dry National reactor shows minor changes in hydraulic conductivity and the soaked downflow reactors shows an increase in hydraulic conductivity over time. The hydraulic conductivity of the initially dry reactor (measured only in the first 60 days) stabilized quickly, averaging approximately 8.0×10^{-3} cm/sec. Statistical analysis indicated no significant difference in hydraulic conductivity between the soaked reactors.

Hydraulic conductivity measurements for the Quartz Hill reactors are shown in Figure 1b. In the initially dry reactors, the hydraulic conductivity varied from 6.0×10^{-4} cm/sec to 2.0×10^{-3} cm/sec in the first 40 days. Hydraulic conductivity of the soaked reactors was initially lower than that observed in the dry reactor for the first 50 days, ranging from 1.0×10^{-4} cm/sec to 5.0×10^{-4} cm/sec. Statistical analysis showed no significant difference exists between the soaked and inoculated and soaked substrates during this time period. However, the difference between the average hydraulic conductivity in these reactors and the dry reactor is significant. The hydraulic conductivity in the soaked reactors increased to at least 3.0×10^{-3} cm/sec by day 123.

The behavior of the soaked Quartz Hill reactors is similar to that of the soaked reactors of the National Tunnel; hydraulic conductivity in both sets of reactors increased by nearly 1 order of magnitude during the experiment (starting at less than 1.0×10^{-4} cm/sec and increasing to approximately 5.0×10^{-3} cm/sec by day 132).

An upflow soaked and inoculated reactor was started in place of the dry downflow reactor. Hydraulic conductivity measurements began on days 98 and 89 for National and Quartz Hill, respectively. As shown by the National soaked downflow data, hydraulic conductivity increases over time nearly one order of magnitude. The hydraulic conductivity of the soaked and inoculated upflow reactor (days 98 - 126) is higher than the soaked and inoculated downflow reactor (days 14 - 28). Statistical analysis verified no significant difference between the two configurations.

However, for Quartz Hill, under the same initial substrate conditions, the upflow reactor (days 89 - 123) had lower hydraulic conductivity

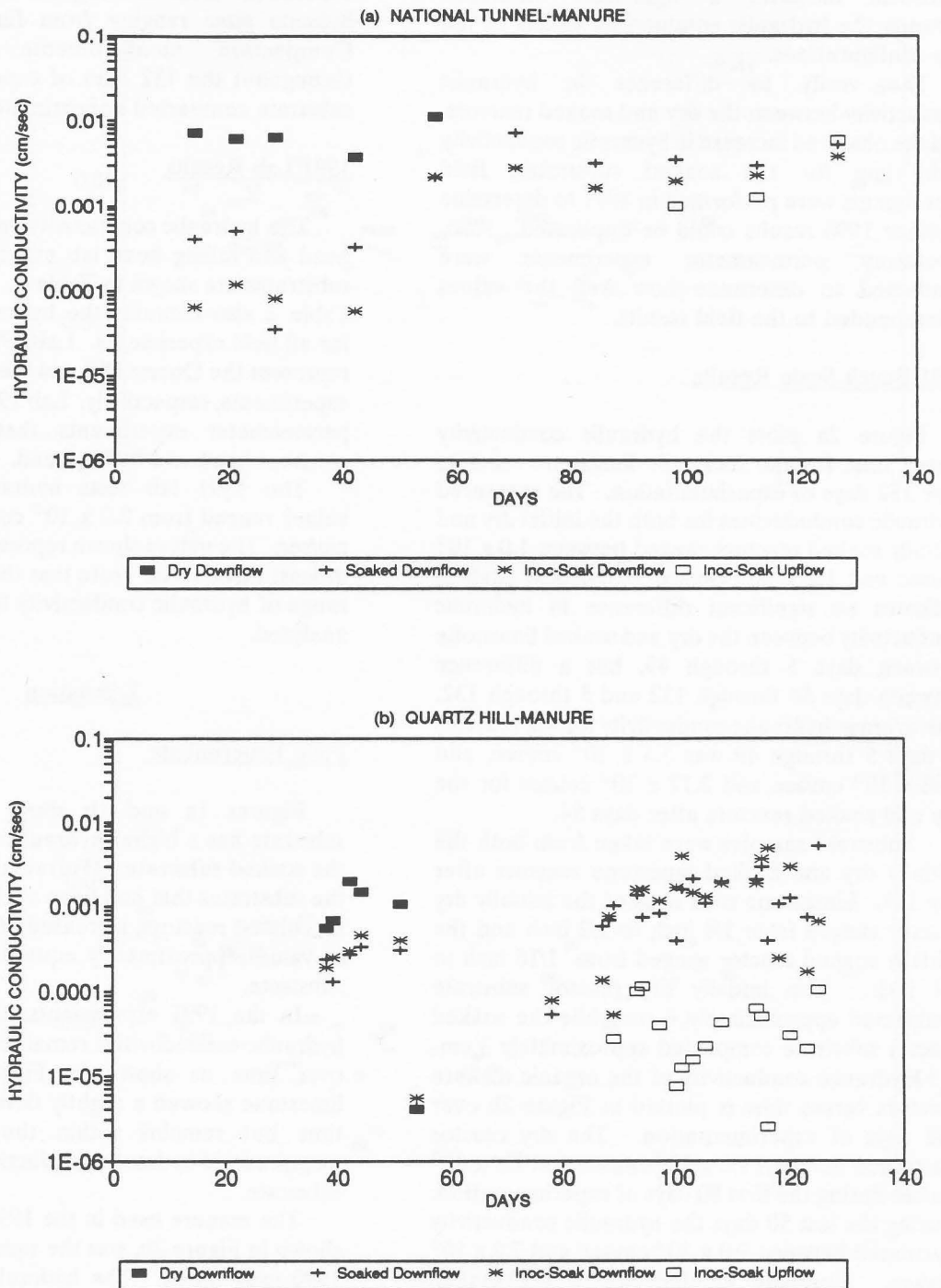


Figure 1. Hydraulic conductivity for the National Tunnel drainage reactors (a) and Quartz Hill drainage reactors (b) with a manure-planter soil substrate operated under three initial substrate conditions in a downflow configuration and one substrate condition in an upflow configuration.

values then the downflow reactor (days 38 - 54). Statistical indicates a significant difference between the hydraulic conductivity values of the two configurations.

~~The~~ ^{the} verify ~~to~~ difference in hydraulic conductivity between the dry and soaked reactors, and the observed increase in hydraulic conductivity with time for the soaked substrates, field experiments were performed in 1991 to determine whether 1990 results could be duplicated. Also, laboratory permeameter experiments were conducted to determine how well the values corresponded to the field results.

1991 Bench Scale Results

Figure 2a plots the hydraulic conductivity versus time for the inorganic limestone reactors over 132 days of experimentation. The measured hydraulic conductivities for both the initial dry and initially soaked reactors ranged between 1.0×10^{-3} cm/sec and 1.2×10^{-2} cm/sec. Statistical analysis indicates no significant difference in hydraulic conductivity between the dry and soaked limestone between days 5 through 49, but a difference between days 54 through 132 and 5 through 132. The average hydraulic conductivity for the reactors in days 5 through 49 was 5.4×10^{-3} cm/sec, and 4.98×10^{-3} cm/sec and 2.17×10^{-3} cm/sec for the dry and soaked reactors after days 54.

Substrate samples were taken from both the initially dry and soaked limestone reactors after day 132. Limestone rock sizes of the initially dry reactor ranged from 1/8 inch to 1/2 inch and the initially soaked reactor ranged from 1/16 inch to 1/4 inch. The initially dry reactor substrate compacted approximately 6 cm while the soaked reactor substrate compacted approximately 3 cm.

Hydraulic conductivity of the organic manure reactors versus time is plotted in Figure 2b over 132 days of experimentation. The dry reactor fluctuated between 1.0×10^{-4} cm/sec and 6.0×10^{-3} cm/sec during the first 80 days of experimentation. During the last 50 days the hydraulic conductivity fluctuated between 9.0×10^{-4} cm/sec and 7.0×10^{-3} cm/sec. Hydraulic conductivity of the soaked manure reactor ranged between 4.0×10^{-4} to 1.0×10^{-3} cm/sec for the first 80 days of experimentation, then increased gradually to 6.9×10^{-3} cm/sec. Statistics verify a difference in hydraulic conductivity between dry and soaked substrate from days 5 through 49 and days 54 through 132, but show no difference overall between days 5 through 132.

Substrate samples taken at the end of the experiment from the organic substrate reactors indicate sizes ranging from fines to 1/8 inch. Compaction measurements indicate that throughout the 132 days of experimentation the substrate compacted approximately 1 cm to 2 cm.

1991 Lab Results

The hydraulic conductivity values for constant head and falling head lab experiments for three substrates are shown in Table 2. For comparison, Table 2 also contains the hydraulic conductivity for all field experiments. Lab 1990 and field 1990 represent the Quartz Hill and the National Tunnel experiments, respectively. Lab 1991 represents the permeameter experiments that included both constant head and falling head.

The 1991 lab tests hydraulic conductivity values ranged from 2.0×10^{-3} cm/sec to 7.3×10^{-2} cm/sec. The values shown represent an average of at least three tests. Note that the table shows the range of hydraulic conductivity for each substrate analyzed.

Discussion

Field Experiments

Figures 1a and 1b show the initially dry substrate has a higher hydraulic conductivity than the soaked substrate. Hydraulic conductivities of the substrates that had been soaked, including the inoculated reactors, increased after about 40 days to values approximately equal to that of the dry substrate.

In the 1991 experiments, the dry limestone hydraulic conductivities remained fairly consistent over time as shown in Figure 2a. Soaked limestone showed a slightly downward trend over time but remains within the same order of magnitude of hydraulic conductivity as the soaked substrate.

The manure used in the 1991 experiments, as shown in Figure 2b, was the same substrate as the 1990 experiment. The hydraulic conductivity of the dry substrate is higher than the soaked substrate but the values for the soaked gradually increase to the same level. This behavior is similar to that observed in 1990.

Studies report that bacterial growth can block the pore spaces in a wetland system e.g., bacterial growth in a wetland system used to treat landfill leachate decreased the hydraulic conductivity by

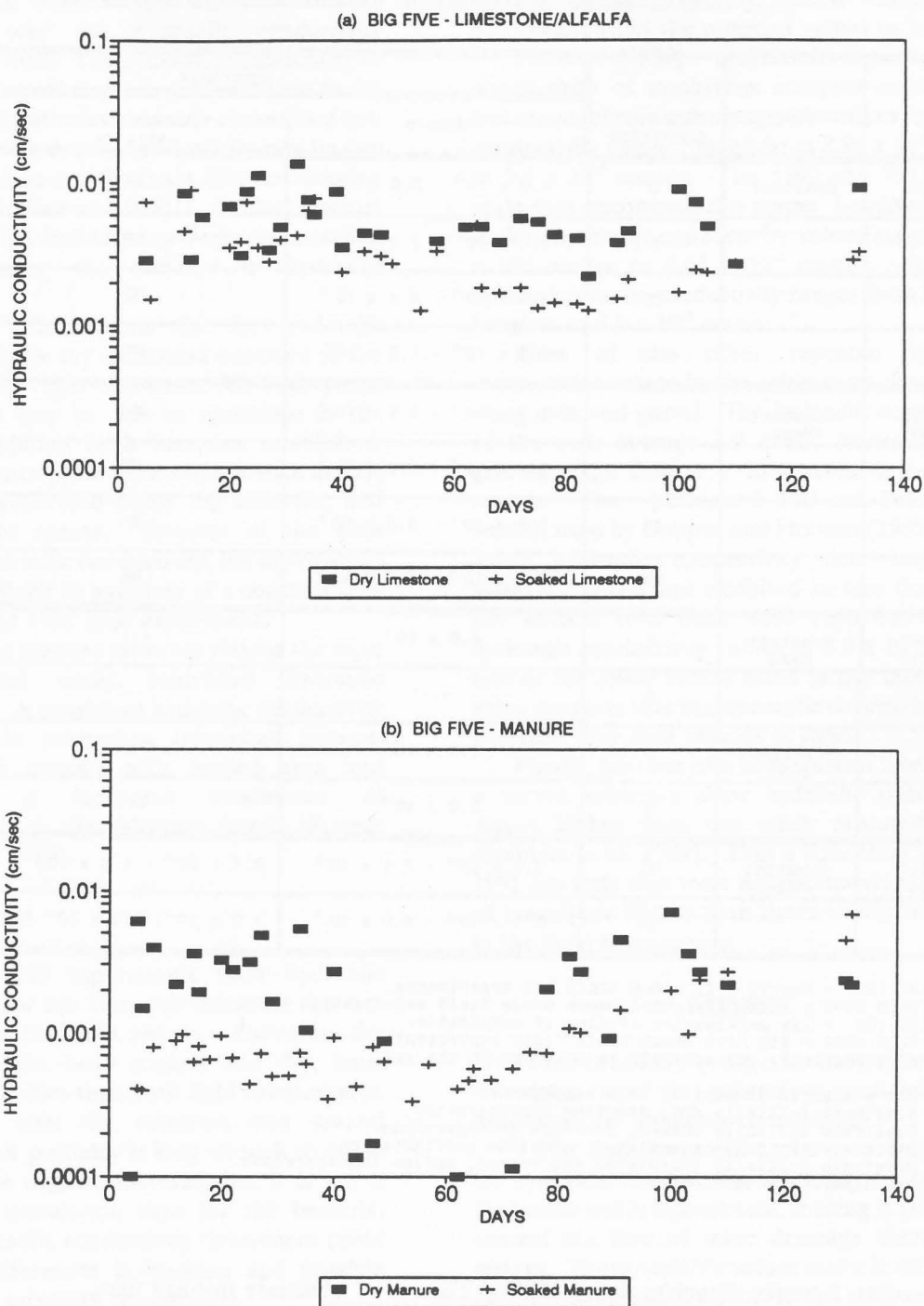


Figure 2. Hydraulic conductivity for the Big Five Tunnel drainage reactors with a limestone-alfalfa substrate (a) and a manure-plantar soil substrate (b) operated under two initial substrate conditions in a downflow configuration.

Table 2. Hydraulic conductivity for various substrates, cm/sec.

TEST	TYPE	SUBSTRATE CONDITION	SUBSTRATE		
			Manure	Limestone -Alfalfa	Manure-Hay
LAB 1990 ^a	Constant Head	D	$4.0 \times 10^{-6} - 2.0 \times 10^{-3}$	NE	NE
		S	$4.4 \times 10^{-6} - 2.9 \times 10^{-3}$	NE	NE
		IS	$5.6 \times 10^{-6} - 4.9 \times 10^{-3}$	NE	NE
		ISU	$2.5 \times 10^{-6} - 1.2 \times 10^{-4}$	NE	NE
FIELD 1990 ^b	Constant Head	D	$3.7 \times 10^{-3} - 1.1 \times 10^{-2}$	NE	NE
		S	$3.5 \times 10^{-5} - 7.2 \times 10^{-3}$	NE	NE
		IS	$5.8 \times 10^{-5} - 3.8 \times 10^{-3}$	NA	NE
		ISU	$9.7 \times 10^{-4} - 5.9 \times 10^{-3}$	NE	NE
LAB 1991 ^c	Constant Head	D	4.0×10^{-2}	---	7.3×10^{-2}
		S	---	--	NE
	Falling Head	D	2.1×10^{-2}	2.0×10^{-3}	2.7×10^{-2}
		S	3.0×10^{-3}	---	NE
FIELD 1991 ^d	Constant Head	DI	$9.9 \times 10^{-5} - 7.1 \times 10^{-3}$	$2.1 \times 10^{-3} - 1.3 \times 10^{-2}$	NE
		IS	$3.4 \times 10^{-4} - 6.9 \times 10^{-3}$	$1.3 \times 10^{-3} - 8.8 \times 10^{-3}$	NE

^a LAB 1990 = Quartz Hill bench scale lab experiments.

^b FIELD 1990 = National Tunnel bench scale field experiments.

^c LAB 1991 = lab permeameter testing of substrates.

^d FIELD 1991 = Big Five bench scale field experiments.

^e No conductivity values could be obtained in the lab.

NE Not evaluated as part of this experiment.

D Substrate initially dry, downflow configuration.

S Substrate initially soaked, downflow configuration.

IS Substrate initially inoculated, downflow configuration.

ISU Substrate initially inoculated and soaked, upflow configuration.

DI Inoculated dry substrate.

50% after 2 weeks (Staubitz et al. 1989). The soaked and inoculated substrate in Figure 1 had anaerobic conditions for 1 week that would allow for a microbial population to become established and thus, lower conductivity. This is also shown in Figure 2b with the soaked manure system. The alfalfa in the limestone substrate also promoted growth of bacteria and may be cause of the minor decrease in hydraulic conductivity of the soaked

substrate through time.

Bacterial activity cannot explain all the observed trends in the hydraulic conductivity. The components of the substrate matrix also affect the hydraulic conductivity, specifically the grain size, pore space and permeability. Another explanation for the trends seen in the manure-soil substrate is that organic material swells when it is soaked and this causes the pore space to decrease. This

would explain why the soaked substrate has a low initial hydraulic conductivity. However, it does not explain why the hydraulic conductivity increases with time. The hydraulic conductivity of the soaked substrate may increase with time as the fines and loosely attached bacteria are worked out. Also, initial low hydraulic conductivity may be due to a buildup of anaerobic slimes that are clogging the substrate (Watson 1989). As the reactors operate, the slime buildup may be slowly removed, therefore causing the increase in hydraulic conductivity.

Significant fluctuations in the hydraulic conductivity of the dry substrates occurred in the first 40 days of experimentation for both years. This variation may be due to variations in the bacterial population as it becomes established. Additionally, entrapped air, and gases such as CO_2 and CH_4 are generated within the substrate, and may clog pore spaces. Because of the wide variation in hydraulic conductivity, the dry reactors were more difficult to maintain at a constant flow in the 1990 and 1991 field experiments.

The soaked manure substrate yielded the most consistent and easily controlled hydraulic conductivities. A consistent hydraulic conductivity is preferred in subsurface treatment systems, particularly in systems with limited area and volume, as it facilitates attachment of microorganisms to the substrate matrix (Steiner and Freeman, 1989).

Lab Experiments

The 1991 lab experiments show hydraulic conductivities for the inorganic substrate that are comparable to the field results. However, the manure substrate, both soaked and dry, have higher conductivities than their field counterparts. For the lab tests the substrate was soaked overnight. This probably is long enough to cause swelling of the organic material, but it is not a long enough inoculation time for the bacteria. Also, the hydraulic conductivity differences could be due to differences in packing and possible sorting of the substrate constituents.

Comparison to Other Conductivity Studies

The hydraulic conductivity values of substrate or materials used in wetlands wastewater treatment systems shown in Table 1 range from 10 cm/sec to 1×10^{-5} cm/sec, depending on the substrates. The reported values of this research

range from 1.0×10^{-4} cm/sec to 3.0×10^{-5} cm/sec for field experiments only. These values are on the lower end of the range of values in Table 1.

Lemke (1989) evaluated the hydraulic conductivity of mushroom compost used in the treatment of mine drainage; downflow hydraulic conductivity values ranged from 2.96×10^{-4} cm/sec to 3.5×10^{-3} cm/sec. The 1990 and 1991 bench scale data encompass this range. Lemke reported upflow hydraulic conductivity values ranging 1.38×10^{-2} cm/sec to 6.65×10^{-2} cm/sec. The 1990 upflow hydraulic conductivity ranges from 2.5×10^{-6} cm/sec to 5.9×10^{-3} cm/sec.

Most of the other reported hydraulic conductivity values in the table were determined using soils and gravel. The hydraulic conductivity of the soils average 3.0×10^{-3} cm/sec and the gravels range from 1×10^1 cm/sec to 3.4×10^{-3} cm/sec. The pulverized fuel ash (burnt coal waste), used by Copper and Hobson (1989), had a lower hydraulic conductivity than any other substrates listed and exhibited surface flow. The old natural reed beds were reported to have hydraulic conductivity values of 5.0×10^{-4} cm/sec, one of the lower values listed in the table. This value suggests that the hydraulic conductivity may decrease over long periods of time.

Finally, lab tests of a homogenous mixture and a sorted substrate show hydraulic conductivity values higher than the other reported values (Staubitz et al. 1989). This is consistent with the 1991 lab tests that were approximately one order of magnitude higher than those values measured in the field experiments.

Summary

Hydraulic conductivity experiments performed on substrates used in subsurface wetlands have generated the following conclusions:

- For both inorganic and organic substrates, the hydraulic conductivity of initially dry substrate fluctuates and is inconsistent, making it difficult to control the flow of mine drainage through the system. These variable values make it difficult to estimate hydraulic conductivity for a dry substrate.
- For primarily organic substrates such as manure-soil, that are soaked prior to applying mine drainage, hydraulic conductivity ranges between 3.3×10^{-4} to 9.8×10^{-4} cm/sec in the first 50 to 90 days and then gradually increase to approximately an order of magnitude greater, ranging from 1.0×10^{-3} to 6.9×10^{-3} cm/sec.
- For primarily inorganic substrates such as

the limestone-alfalfa mixture tested, hydraulic conductivity remains fairly constant over time, averaging approximately 1.23×10^{-3} cm/sec to 8.8×10^{-3} cm/sec.

- Overall, laboratory and field bench scale studies yield hydraulic conductivities ranging from 2×10^{-6} cm/sec to 1.0×10^{-2} cm/sec for the organic manure substrate. Hydraulic conductivities range from 1.3×10^{-3} to 1.3×10^{-2} cm/sec for the inorganic limestone substrate.

- A method for estimating the expected range of hydraulic conductivity for a candidate substrate is to perform a constant and/or falling head permeameter measurements on dry substrates and on substrates that have been soaked for one week. The permeameter should be at least 2 liters in volume so that a representative sample of heterogeneous material can be tested. For a highly organic substrate, hydraulic conductivities obtained in the laboratory may be higher than the values determined in the field.

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THE AEROBIC REMOVAL OF MANGANESE FROM MINE DRAINAGE BY AN ALGAL MIXTURE CONTAINING *CLADOPHORA*¹

by

Laura A. Duggan, Thomas R. Wildeman, and David M. Updegraff²

Abstract. Manganese is a contaminant common to most metal and coal mine drainages. Mn (II) is difficult to remove from solution without chemical treatment due to the high pH required to form insoluble manganese oxides or carbonates. Laboratory studies have indicated that an algal mixture, primarily comprised of *Cladophora* (a green alga), is effective in removing the manganese from solution and substantially raising the pH of the mine drainage through photosynthesis. Two reservoirs were constructed for a bench scale study to examine the effects of algae containing *Cladophora* on mine drainage that had passed through a constructed wetland treatment, but still contained 32 mg/L of manganese. The reservoirs were run statically for two months and then as a flow system for two months. Each reservoir initially contained 97 L of wetland effluent (pH = 5.8), 5 L of pond scum containing *Cladophora*, and one reservoir also contained 12 kg of limestone. The reservoir containing limestone reduced the manganese to concentrations of less than 0.3 mg/L and performed slightly better than the reservoir without limestone, which reduced the manganese to concentrations below 3 mg/L. The *Cladophora* grew extensively and was resistant to high manganese levels often toxic to microbes. Microscopic and phase studies have suggested that the *Cladophora* removed the manganese from solution by forming manganese oxide crusts in the algal mat. These results indicate that an algal mixture containing *Cladophora* may be used as a second stage process to remove manganese and raise the pH of water that has passed through a constructed wetland treatment. In addition, an algal pool appears to be a good candidate for a bench scale aerobic wetland.

Key Words: manganese removal, wetland, algae

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Introduction

The use of microorganisms for the removal of heavy metals from acid mine drainage has become an important alternative to chemical treatment. Constructed wetlands have been proven to substantially increase the pH of the mine drainage and remove many of the heavy metals by precipitating insoluble metal complexes and precipitates (Brodie et al. 1989 and Wildeman and Laudon 1989). Manganese, a common contaminant in most acid mine drainages, is difficult to remove from solution

due to the high pH required to form insoluble manganese oxides, carbonates, or sulfides (Watzlaf and Casson 1990).

The Big Five Wetland in Idaho Springs, Colorado was constructed as a pilot scale anaerobic system emphasizing the microbial reduction of sulfate to sulfide and subsequent precipitation of insoluble metal sulfides (Howard et al. 1989). The pH of the mine drainage was raised from below 3 to above 6 and over 90% of the Fe, Cu, and Zn were removed (Machemer et al. 1990). However, manganese was not removed from the mine drainage due to the inability of manganese to form stable sulfide precipitates under most wetland conditions. Thus, a polishing stage treatment utilizing an alternate microbial process seemed necessary to remove the high levels of manganese.

A laboratory investigation was conducted to study the microbial oxidation of manganese as a possible removal method. Several different types of bacteria and algae were collected from local eutrophic ponds and mine drainage areas and tested with respect to manganese removal from neutralized mine drainage. A sample of pond scum (primarily green and blue-green algae) was found to substantially increase the pH of the mine drainage and remove the manganese from solution to concentrations below the detection limit (< 0.3 mg/L).

Further laboratory studies were conducted with pond scum collected from different local sources. Those samples which were the most effective in removing the manganese and further raising the pH of the mine drainage that had previously passed through the Big Five Wetland, were samples which contained *Cladophora*, a filamentous green alga, along with much lesser amounts of other green and blue-green algae. It appears that the manganese is removed from the water by the precipitation of manganese oxides on the algal cells. The metal precipitation is believed to be at least partially due to the increase in pH and production of oxygen during photosynthesis, as the precipitation of manganese oxides usually requires a pH between 8 and 9 (Stumm and Morgan 1981). Previous laboratory studies also found a large diurnal pH change associated with photosynthesis due to the uptake and release of carbon dioxide (Stumm and Morgan 1981 and Fuller et al. 1988).

Bench scale studies are helpful to test the

effectiveness of the laboratory results and to determine their potential for larger scale studies. Anaerobic bench scale permeameters have been shown to closely model the Big Five Wetland (Bolis et al. 1991). To further examine the manganese removal process and to evaluate the potential of an aerobic pilot scale wetland, two bench scale aerobic reservoirs were constructed. The objectives of this study also included determining a manganese removal rate and testing the resistance of the *Cladophora* to high manganese concentrations and severe weather conditions.

Materials & Methods

The reservoirs were constructed from small plastic swimming pools, approximately 1.1 m in diameter. Each of the two pools initially contained 97 L of effluent from the Big Five Wetland and 5 L of pond scum comprised primarily of *Cladophora* from a local pond. The Big Five effluent contained approximately 32 mg/L of manganese and had a pH of 5.8. The only difference between the two reservoirs was that one reservoir also contained 12 kg of limestone (limestone pieces were approximately 1 cm). This reservoir will be referred to as "reservoir LS", and the reservoir which did not contain limestone will be denoted "reservoir NoLS". The reservoirs were placed outside to have full exposure to the environment.

This experiment was run for approximately four months, from August to December, incorporating a wide range of weather conditions. The reservoirs were static for the first two months of the experiment, with water being added occasionally to account for water loss due to evaporation. The weather was typically warm and sunny during this portion of the experiment. A flow system was installed during the last two months of the experiment to determine approximate loading and removal rates. This was accomplished using a peristaltic pump to monitor flow from a feed tank into the reservoirs, and an outlet tube 7 cm above the bottom of each pool. The diameter of the pools was 1 m at the height of the outlet. The outflows were collected in plastic containers which were connected to the reservoirs by plastic tubing. The weather during this portion of the experiment was typically cold and snowy, and the reservoirs froze several times. The samples were filtered

and acidified after collection and then analyzed for manganese by flame atomic adsorption.

The pH of the waters were measured frequently, as the formation of manganese oxides is highly pH dependent. During the static portion of the experiment, the pH was taken at different areas in each reservoir to account for differences due to the amount of biomass present and because the amount of sunlight received at each location may affect the amount of photosynthesis. The pH values cited below are geometric averages of the several measurements. Each sample collected was a composite sample containing water from different areas within the reservoir. During the portion of the experiment when the pump was monitoring the water flow, the pH's and samples were taken from the water collected in the outflow containers.

Once during the static portion and once during the pump portion of the experiment, a high concentration manganese solution was added to the reservoirs to examine the effectiveness of the algae in removing high manganese concentrations. This 100 mg/L manganese solution was prepared using manganese sulfate and deionized water.

Results

Static Reservoirs

The initial pH of the water in each reservoir was 5.8 and contained 32 mg/L of manganese. During the first week of the experiment, the pH of each reservoir gradually rose with the pH of reservoir LS usually slightly higher than the pH of reservoir NoLS. On the sixth day of the experiment at 7:10 PM, the pH of reservoir NoLS was up to 8.6 and contained 14 mg/L of manganese, and reservoir LS had a pH of 8.8 and contained only 5.4 mg/L of manganese. However, no diurnal pH fluctuation with photosynthesis was observed up to this point. On the tenth day of the experiment, pH cycling and almost complete manganese removal were observed. On this day, the pH rose 0.3 pH units in each pool between 7:00 AM and 3:00 PM, and reservoir NoLS contained 2.5 mg/L manganese and reservoir LS only 0.5 mg/L. After the tenth day much of the water had evaporated from the reservoirs and most of the manganese had been removed. Therefore, on Day 11 at 1:30PM, 20 L of additional mine

drainage effluent from the Big Five Wetland were added (pH = 6.0). This addition lowered the pH to 7.2 and 7.5 for reservoir NoLS and reservoir LS, respectively. However, on Day 12 at 3:15 PM, the pH's were back up to 8.2 and 8.5 of reservoir NoLS and reservoir LS, respectively. For the rest of the static portion of the experiment, Big Five mine drainage effluent was continuously added about twice a week and the reservoir pH's usually recovered within a day or two of the effluent addition.

On Day 20, 40 L of 100 mg/L manganese solution having a pH of 4.9 was added to each reservoir to study the tolerance and removal efficiency of the algae to high manganese concentrations. Before this addition, the water level in the reservoirs was very low (approximately 40 to 50 L). On Day 25 at 9:30 AM, reservoir NoLS had a pH of 7.6 and contained 51 mg/L of manganese, and reservoir LS had a pH of 8.1 and contained 13 mg/L of manganese. By Day 42 at 9:30 AM, reservoir NoLS had a pH of 8.8 and contained 9.7 mg/L of manganese, and reservoir LS had a pH of 9.3 and contained less than 0.3 mg/L of manganese. Thus, both reservoirs appeared to be removing the manganese from a medium pH, high manganese solution.

During the static portion of the experiment, the algal biomass had grown extensively, appeared healthy, and black precipitates could be seen in the algal mat. Therefore, a flow system was designed to simulate a possible pilot scale wetland and determine the efficiency of the reservoirs at different flow rates.

Pump Flow Reservoirs

The pump system was installed in mid-October, on Day 65, with an initial mine drainage effluent flow rate of 3.1 ml/min into each reservoir. The mine drainage effluent had a pH of 6.3 and contained approximately 23 mg/L of manganese. It took several days for the water levels in the pools to reach the outlet. The results are given in Table 1 and outflow manganese concentrations shown in Figure 1. It took a few days longer for the water to reach the outlet in reservoir NoLS, which didn't contain limestone, so the sample on Day 71 was collected from the pool rather than the collection container. No sample was collected for reservoir NoLS on Day 73. On Day 79, the mine drainage effluent in the feed tank was

Table 1. Results of the Pump Flow Experiment

RESERVOIR NoLS				RESERVOIR LS		
DAY #	FLOW (ml/min)	pH	Mn (mg/L)	FLOW (ml/min)	pH	Mn (mg/L)
71	2.1	9.1	3.2	2.5	9.2	1.0
73	3.9	9.3	-----	3.9	8.7	0.7
84	2.1	8.5	32.1	2.4	8.5	14.0
86	-----	8.5	25.3	-----	8.8	1.4
91	3.0	8.1	13.0	1.5	8.2	0.6
94	4.5	8.2	10.1	4.5	8.5	1.2
97	4.0	8.6	4.8	4.5	8.6	2.2
99	-----	8.5	3.2	-----	8.4	1.4
100	-----	8.3	2.3	-----	8.4	0.5
103	3.7	8.5	2.3	3.9	-----	1.0
120	3.1	8.1	3.8	1.8	8.1	0.6
125	3.0	8.2	5.0	3.8	8.2	0.3
127	3.0	8.2	7.2	3.7	8.3	0.7

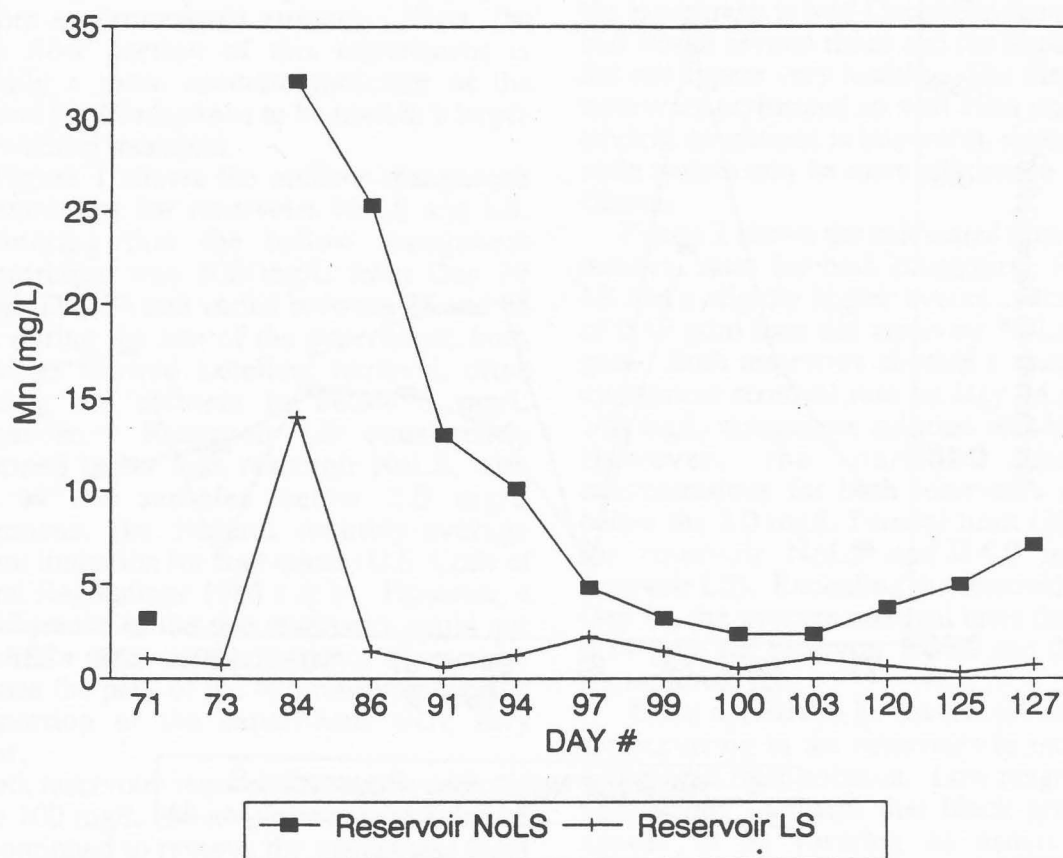


Figure 1. Effluent manganese concentrations for the pump flow experiment.

replaced with the same 100 mg/L manganese solution as was used in the static experiment. This solution was pumped at 5 ml/min until Day 80, when the flow was adjusted to 3 ml/min because the water and algae in the reservoirs were frozen solid except for a small area around the inlet. On Day 84 samples were collected and the remaining 20 L of manganese solution were mixed with 20 L of Big Five mine drainage effluent.

Manganese removal (Table 1) can be used to calculate area adjusted removal rates (Hedin 1990). The units for this rate are grams of manganese removed / day / square meter, which is abbreviated gdm. Figure 2 shows the removal rates which were determined from the following calculation (Hedin 1990):

$$\text{Mn (gdm)} =$$

$$\frac{1.44 * \text{Flow (L/min)} * [\text{Mn in} - \text{Mn out}] \text{ (mg/L)}}{\text{Area (m}^2\text{)}}$$

A value of 29.3 mg/L was used for Mn inflow, which was the average (standard deviation = 3.7 mg/L) manganese concentration of the Big Five Wetland effluent over three of the months this experiment was conducted.

Discussion

The photosynthetic process involves the uptake of carbon dioxide and release of oxygen. A pH greater than 5.5 is required to maintain a supply of carbon dioxide, in the form of bicarbonate, in the water. Since most aerobic wetland treatments involve photosynthesis, this may account for why aerobic wetlands are more effective above pH 5.5 (Brodie et al. 1991). Carbon dioxide is an acid, and therefore its uptake during photosynthesis results in a pH increase. Respiration, the reverse of photosynthesis,

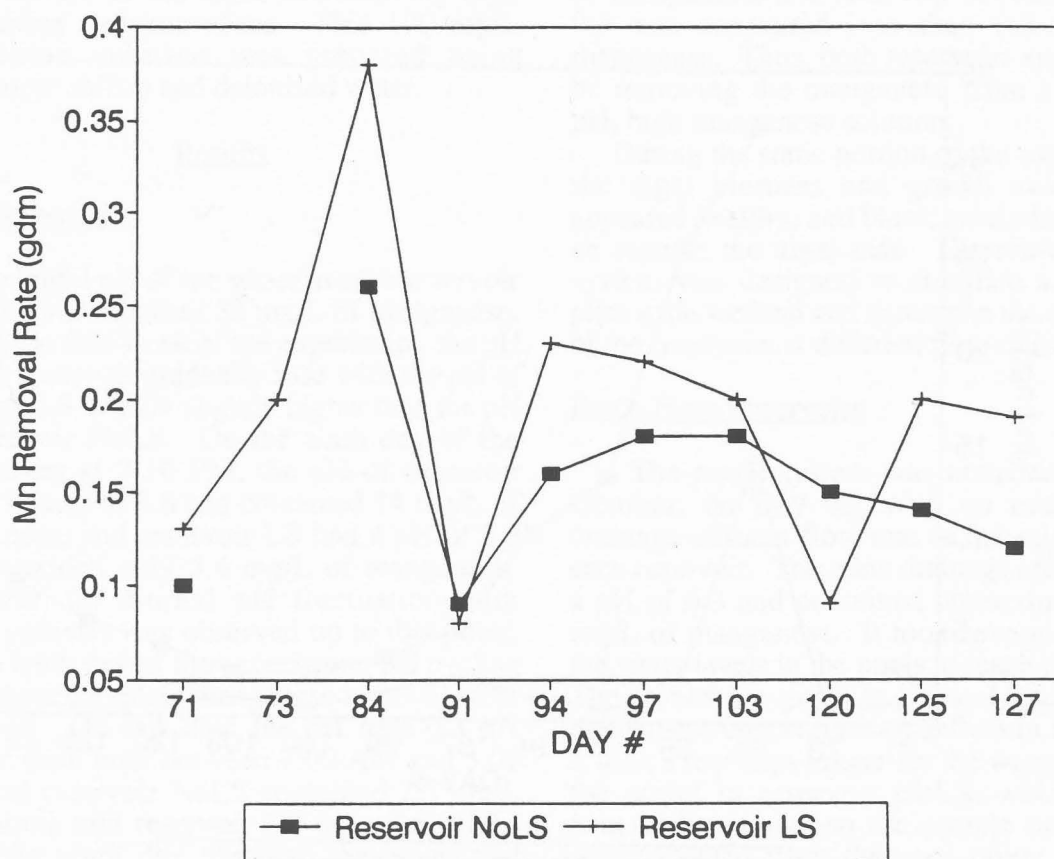


Figure 2. Area adjusted removal rates for the pump flow experiment.

occurs at night and involves the uptake of oxygen and release of carbon dioxide resulting in a lower pH. This uptake and release of carbon dioxide is the cause of the diurnal pH fluctuations observed in the laboratory and reservoir experiments.

The formation of manganese oxides, specifically MnO_2 , is a desirable manganese removal method due to the extreme insolubility and large sorption capacities of manganese oxides. The reaction appears to be autocatalytic, which greatly increases the manganese removal rate from solution once some MnO_2 or Mn_3O_4 is formed (Stumm and Morgan 1981). The formation of rhodochrosite, MnCO_3 , is also a possible manganese precipitate that could form as it is slightly less soluble than calcite.

The success of the previous laboratory studies and the static portion of this bench scale study indicated that algae containing *Cladophora* is effective in removing manganese from the effluent under warm, sunny, static conditions. However, a large scale wetland treatment system is more dynamic and subject to more environmental stresses. Thus, the pump flow portion of this experiment is probably a more accurate indicator of the potential for *Cladophora* to be used in a larger scale wetland treatment.

Figure 1 shows the outflow manganese concentrations for reservoirs NoLS and LS. Considering that the inflow manganese concentration was 100 mg/L from Day 79 through Day 84 and varied between 28 and 65 mg/L during the rest of the experiment, both reservoirs showed excellent removal, often reducing the effluent to below 5 mg/L manganese. Reservoir LS consistently performed better than reservoir NoLS, with 85% of the samples below 2.0 mg/L manganese, the Federal monthly-average effluent limitation for coal mines (U.S. Code of Federal Regulations 1985 a & b). However, a pH difference in the two reservoirs could not account for the better performance of reservoir LS since the pH's of the two reservoirs during this portion of the experiment were very similar.

Both reservoirs recovered from the addition of the 100 mg/L (58 μM) manganese solution and continued to remove the manganese from the effluent added during the rest of the

experiment. This tolerance to high manganese concentrations is important because manganese concentrations as low as 10-20 μM have been shown to greatly inhibit manganese oxidizing microbes (Nealson et al. 1988). Reservoir LS once again showed more efficient manganese removal than reservoir NoLS. It is also important to note that the reservoirs were almost frozen solid during most of the time the 100 mg/L manganese solution was being added.

The severe weather conditions present during much of the pump flow experiment had a visible effect on the health of the biomass. During the static experiment the thick algal mat was bright green and floated on the surface due to the large number of oxygen gas bubbles produced during photosynthesis. Throughout the pump flow experiment, the algae lost much of its bright green color and most of the algae sank below the water surface. Gas bubbles were still observed during the sunlight hours indicating that photosynthesis was occurring, but to a much lesser extent than during the warmer, sunnier months. At the completion of the experiment in mid-December, the reservoirs had frozen several times and the algal biomass did not appear very healthy. The fact that the reservoirs performed so well even under these adverse conditions is important, though a pilot scale system may be more efficient in a warmer climate.

Figure 2 shows the calculated area adjusted removal rates for both reservoirs. Reservoir LS had a slightly higher average removal rate of 0.19 gdm than did reservoir NoLS of 0.15 gdm. Both reservoirs showed a much higher manganese removal rate on Day 84 when the 100 mg/L manganese solution was being fed. However, the outflow manganese concentrations for both reservoirs were not below the 2.0 mg/L Federal limit (32.1 mg/L for reservoir NoLS and 14.0 mg/L for reservoir LS). Excluding the removal rates for Day 84, the average removal rates decrease to 0.14 gdm for reservoir NoLS and 0.17 gdm for reservoir LS.

There appears to be several processes that are occurring in the reservoirs to remove the manganese from solution. Low magnification microscopy indicates that black precipitates appear to be forming as crusts on the filamentous algae. SEM and XRF analysis suggest that the crusts contain calcium-

manganese oxides which were determined to be amorphous by XRD analysis. The photosynthetic pH increase and production of oxygen would most likely be an important factor in the formation of these manganese oxides. However, it has also been shown that nonliving algae has a high affinity for metal adsorption, indicating a surface adsorption phenomena may be occurring in addition to the formation of oxides (Darnall et al. 1989 and Jeffers et al. 1989). Thus, manganese biosorption by nonliving algae may have been an important manganese removal mechanism during the cold weather when some of the algae may have died. Though further studies need to be performed, it appears that the primary manganese removal processes are adsorption to algal cell walls, auto-oxidation due to photosynthesis, and adsorption to manganese oxides that have formed.

Summary

Both reservoirs were successful in raising the pH and removing the manganese down to below 5 mg/L during most of the experiment. Reservoir LS was more efficient in manganese removal during both the static and flow portions of the experiment, often removing the manganese to concentrations below detection limit. Photosynthesis appears to be an important process contributing to the manganese removal due to its ability to increase pH. Though manganese is required by photosynthetic organisms in the process of oxygen evolution, only trace amounts are usually needed and high manganese concentrations are often toxic to microbes (Nealson et al. 1988). Thus, *Cladophora's* tolerance to high manganese concentrations distinguishes it from many manganese oxidizing microbes. The manganese removal method appears to be the formation of manganese oxide crusts on the filamentous algae. An aerobic wetland treatment utilizing *Cladophora* and limestone would have an estimated manganese removal rate of 0.17 gdm under adverse conditions, and possibly higher under warmer sunnier conditions.

Acknowledgement

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THE USE OF WETLANDS FOR IMPROVING WATER QUALITY TO MEET ESTABLISHED STANDARDS

by: B.A. Filas, P.E.
T.R. Wildeman, Ph.D.
Knight Piésold and Co.

Wetlands and bogs have long been recognized as nature's method of improving water quality. Contaminant reductions can occur through the precipitation of hydroxides, precipitation of sulfides and pH adjustments. Local conditions, oxidation state and water and soil chemistries dictate whether these natural reactions will occur under oxidizing (aerobic) or reducing (anaerobic) conditions.

Man-made or constructed wetlands employ the same principles as do natural wetlands. A thorough knowledge of the water and soil chemistries and the application of basic geochemical principles allows for the design and construction of wetland systems which can often be a cost-effective means of water treatment.

Regulatory Background and Jurisdiction

The term "wetland" has substantial regulatory implications with regard to their use as a water treatment process. Outfalls from water treatment processes are regulated by the U.S. Environmental Protection Agency (EPA) under Section 402 of the Clean Water Act (33 U.S.C. 1344) through the National Pollutant Discharge Elimination System (NPDES) permit program which expressly excludes sludges generated from water treatment processes from NPDES purview. These sludges are included under EPA jurisdiction by the Resource Conservation and Recovery Act (RCRA) (42 U.S.C. 6901). By-products generated from a water treatment process are then regulated depending on character and/or chemical make-up as a solid or hazardous waste.

Section 404 of the Clean Water Act authorizes the Corps of Engineers to require and issue permits for dredge and fill activities in the waters of the United States. The regulatory program included in 33 CFR Parts 320 through 330, does not appear to include a de minimus areal extent for jurisdictional wetlands, nor does it establish dredge or fill volumes below which an operator would be exempt from regulation.

33 CFR Part 323 defines the types of operations requiring a dredge and fill permit from the Corps. 323.3(a) requires a permit for "the discharge of dredged or fill material into the waters of the United States". 323.2(e) defines fill material as "any material used for...changing the elevation of a waterbody".

33 CFR Part 328 defines the key term "waters of the United States" as it applies to the jurisdictional limits of the Corps of Engineers. The term is defined in 328.3 as "all waters,

wetlands adjacent to waters, and tributaries to waters which may be used to support commerce". Such a definition can be interpreted to include virtually all land, water and wetland within the United States.

The scope of wetland-related regulatory programs over the recent past appears to have grown in proportion with the degree of political and public sentiment associated with their impact. The wetland delineation manual jointly issued by the Corps of Engineers, the U.S. Environmental Protection Agency and the U.S. Fish and Wildlife Service, was developed and implemented through the public process in 1989. A revised manual was proposed in the August 1991 Federal Register. While the controversy still persists regarding the proposed 1991 manual, it appears that the three key factors for delineating jurisdictional wetlands will remain: hydrology, hydric soils and the presence or ability to support hydrophytic vegetation.

Man-made wetlands will usually meet all three wetland delineation criteria. The mechanisms by which water treatment is accomplished is through the precipitation or fill of complex metals into the soil substrate. Chemical reactions occurring in the artificial wetland ecosystem result in the deposition of water treatment by-products which may subject an operator to regulation under RCRA Subtitle C (hazardous) or Subtitle D (solid). Effluent discharges to receiving waters would require an NPDES discharge permit.

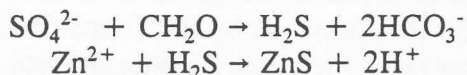
While the regulatory programs and jurisdiction are established and can be interpreted to be jurisdictional over constructed wetlands, their legislative and regulatory intent is not to preclude or inhibit the development of prudent, environmentally and ecologically sound passive treatment systems.

Constructed Wetland Applications to Mining Situations

The use of constructed wetlands to remediate water quality in mining situations is a new technology. Wetland systems have been used in many states for treatment of municipal waste water.⁽¹⁾ Mining situations present a very different application of wetland technologies over municipal wastewater treatment where the focus shifts from biological contaminants to pH adjustment and metals removal.

Passive treatment using constructed wetlands was first introduced on southeastern coal mine drainages in the early 1980's by the Tennessee Valley Authority (TVA).^(1,2) The wetlands were designed to improve pH and remove iron and manganese through aerobic processes. In 1987, the Colorado School of Mines (CSM) project team, of which Knight Piésold and Co. was a member, was commissioned by the U.S. Environmental Protection Agency, through its emerging Technology Program, to evaluate the potential for constructed wetland applications in metal mine drainages.

Development of constructed wetlands for treating metal mine drainages have been studied by the CSM team^(4,7,8,9,10) Noranda⁽⁵⁾ and the U.S. Bureau of Mines⁽⁶⁾. Each of these groups have focused on using sulfate-reducing bacteria in the anaerobic zones of wetlands for ameliorating acidic metal mine drainages. The process can be summarized as follows, where CH₂O is used for organic matter:



The process essentially reverses the reactions that occurred to produce the acid mine drainage. Sulfide rock from the mine reacts with air and water to form acidic drainage under oxidizing conditions. The anaerobic reducing zone in the wetland generates sulfides under reducing conditions as the solution passes through the system. The result is an accumulation of sulfide precipitates within the anaerobic zone which would otherwise be carried in the effluent and subject to water discharge criteria.

The Staged Design Process

Data has shown that contaminant removal is affected by microbial processes in both aerobic and anaerobic zones. Vegetation and the metabolic uptake of contaminants into plant tissues has not been a significant contributor to the reduction in metal concentrations in wetland systems. Rather, utilization of the products of microbial activity has proven more important. The use of the H₂S product from sulfate-reducing bacteria metabolism to remove zinc in the above reaction is an excellent example. However, while anaerobic systems have successfully reduced iron and manganese concentrations in some cases, these metals have not been consistently removed using anaerobic wetlands. TVA's work with aerobic wetlands has successfully and consistently removed iron and manganese to acceptable regulatory levels⁽¹⁰⁾.

The passive system to be used in a given situation must be dictated by the chemistry of the water. Whether a system is anaerobic, aerobic, or both depends upon the local situation. To better determine what might be appropriate, Table 1 lists some characteristic differences between anaerobic and aerobic wetland cells.

TABLE 1**COMPARISON OF AEROBIC AND ANAEROBIC WETLAND CELLS**

AEROBIC	ANAEROBIC
Oxidation process	Reduction process
Surface water flow	Sub-surface water flow
Oxide precipitation	Sulfide precipitation
Less efficient at low pH	Proven efficient to pH of 2.5
Efficient removal of Fe, Mn	Efficient removal of most heavy metals
May freeze in cold climates	All season operation

The design procedure for developing an effective water treatment process using wetlands is no different than the process for developing a conventional water treatment process. It begins with a complete characterization of the water and identifying the treatment goals, followed by designing a process, testing the process in the laboratory and with scale-model prototypes at the site. Simply, the method starts in the laboratory, proceeds to bench-scale experiments, and then goes to pilot-plant testing. An important consideration for development and implementation of any treatment process is that it takes time to carry out. Just as in developing any chemical treatment process, developing a new wetland scheme will probably take at least one year, so planning for passive remediation must consider the lead time required to successfully test, design, construct and commission the system.

Laboratory Proof-of-Principle Tests

The initial phase of a wetland feasibility evaluation occurs in the laboratory. As with any water treatment process design, the chemistry of the water to be treated, the volume and seasonal variations and the target effluent levels must be clearly defined. Candidate substrate materials must be identified that are locally available in sufficient quantities for construction. Once the water is characterized and candidate substrates are identified, the laboratory testing program is conceptualized and developed based on standard geochemical principles. Each of the alternative principles are tested and their performance monitored and evaluated.

Laboratory studies are static rather than flow-through experiments and are typically developed to:

- Test the suitability of the candidate materials for substrates in a constructed wetlands,⁽⁷⁾
- Determine whether removal of a contaminant by microbial processes in a wetland with a known substrate composition is possible.

Over the last two years, Dr. Wildeman has been performing such experiments either for research or consulting on a full-time basis. One proof-of-principle study that involved a solution that simulated the spent effluent from a gold milling operation may be of particular interest to mill operators having underdrainage systems installed in tailing facilities.

The composition of the tailing solution is shown in Table 2. It contains appreciable cyanide in the form of strong and weak complexes. The principles to be proved in this study were:

- Whether the microbes typically present in the anaerobic zone of a wetland would be inhibited by large concentrations of cyanide,
- Whether the microbial processes that typically occur in the anaerobic zone of a wetland would degrade cyanide.

Varying amounts of substrate, milling effluent, and inoculum were added to typical culture bottles. The substrate mixtures contained composted manure and potting soil in various proportions. The bottles were incubated for 50 days and then the solutions in the bottles were analyzed. The analytical results are shown in Table 2 for those samples showing reduction in cyanide concentration.

Cyanide concentrations were reduced with varied efficiencies in all the Table 2 cultures. A decrease in the concentration of sulfate is a good measure of the activity of sulfate-reducing bacteria. In most bottles there was little or no decrease, however, there was an appreciable decrease in the sulfate concentration in bottle number 11 caused by the activity of sulfate-reducing bacteria. In this bottle there is also a great decrease in total cyanide. It appears that in principle, given the proper conditions, cyanide degradation as well as sulfate reduction can occur in the anaerobic zone using this type of wetland substrate.

TABLE 2

**LABORATORY PROOF-OF-PRINCIPLE TESTS ON TAILING SOLUTION
ANALYTICAL RESULTS OF CULTURES SHOWING CYANIDE REDUCTION (Mg/L)**

	Iron	Copper	Sulfate	Total CN	Free CN	pH
Tailing Solution	470	78	298	330	24	9.0
Culture No. 5	85	98	310	57	60	8.9
Culture No. 8	8.2	91	570	56	54	8.1
Culture No. 11	21	10.4	<5	2.3	<5	7.3
Culture No. 12	5.4	6.0	460	2.2	<5	7.3
Culture No. 13	65	142	-	120	72	8.4
Culture No. 17	120	38	360	56	27	8.6
Culture No. 18	160	87	320	2.0	<5	8.4
Culture No. 19	23	58	790	57	42	7.0

The cyanide degradation occurs by a number of processes. In this test, volatilization of cyanide by lowering the solution pH, metabolic use of the cyanide by microbes, and non-metabolic degradation of cyanide to cyanate are all occurring since the inoculum is a consortium of bacteria⁽⁷⁾ and the substrate is complex organic material⁽⁶⁾. The laboratory experiment proved in principle that cyanide degradation, sulfate reduction, and heavy metals removal are all simultaneously possible in the anaerobic zone of a constructed wetland.

Bench-Scale Tests

With completion of the proof-of-principle tests, the mechanism by which water quality improvements occur and the treatment process are both identified. For the cyanide tailing solution example, a consortium of bacteria emphasizing sulfate reduction produced the mechanism for process treatment using anaerobic reactors or wetlands.

Bench-scale tests constitute a low-cost field demonstration of the principles developed in the laboratory. These tests are typically set up in enclosed reactor containers such as plastic garbage cans. The solution inlet and outlet devices are installed at the top and bottom of the can as appropriate and provisions are made for proper solution recovery at the bottom. Substrate materials are then placed into the can prior to solution application.

The primary purpose of kinetic experiments is to determine loading capacities and to optimize flow and drainage through the substrate⁽⁷⁾. A good example of a bench-scale experiment was one recently conducted on a severe mine acid mine drainage near Central City, Colorado⁽⁷⁾. The objective of this experiment was to determine whether recently developed theoretical loading factors for bioreactors using sulfate-reducing bacteria were reasonable. The concentrations of contaminants in the drainage are given in Table 3.

Contaminant concentrations from the outputs of three different bench-scale cells are shown in Table 3. For cell A, the mine drainage was passed through the cell with no delay. For Cell B, the substrate was soaked with city water for one week before mine drainage started passing through the cell. For Cell C, the substrate was inoculated with an active culture of sulfate-reducing bacteria and soaked with city water for one week before mine drainage started passing through the cell. Preparations on Cells B and C were done to insure that there would be a healthy population of sulfate-reducing bacteria before mine drainage flowed through the substrate.

TABLE 3

**BENCH-SCALE TESTS ON ACID DRAINAGE AT QUARTZ HILL
ANALYTICAL RESULTS OF EFFLUENT QUALITY OVER TIME (Mg/L)**

	Mine Drainage	Cell A			Cell B			Cell C		
		24da	43da	71da	24da	43da	71da	24da	43da	71da
Copper	56	0.06	<0.05	NA	<0.05	<0.05	0.21	<0.05	<0.05	0.25
Iron	697	1.6	0.87	NA	1.9	0.96	0.40	1.0	0.46	0.40
Manganese	76.7	0.94	0.97	NA	0.91	0.64	0.48	0.99	1.6	1.6
Sulfate	4270	450	1080	NA	70	660	NA	412	1180	NA
Zinc	123	0.28	0.18	NA	0.17	0.24	0.21	0.16	0.14	0.25
pH	2.5	7.4	7.2	NA	7.5	7.4	8.0	7.4	7.2	7.9

All cells were run in a downflow mode with an application rate of one ml/minute. The high concentrations of iron and low pH provided a severe test of the ability of sulfate-reducing bacteria to remove heavy metals and raise pH. In all cases, copper, zinc, iron and manganese

concentrations were reduced by over 99 percent and pH increased from 2.5 to above 7. These results were consistently maintained over the ten-week test period.

Pilot-Scale Tests

Successful completion of bench-scale tests support a decision to proceed with pilot-scale testing. Bench-scale tests provide relevant results under field climatic and hydrologic conditions. Pilot-scale reactors are constructed in a modular cell which affords expansion and inclusion with the full-scale treatment process. Their design is such that a split of water to be treated is diverted into the reactor at the same application rate as the full-scale system. Data is then collected on the actual performance of the system under actual site conditions.

The constructed wetland at the Big 5 Tunnel near Idaho Springs, Colorado is a good example of a pilot-scale facility which has been operated and the performance monitored for over two years. This system is an anaerobic wetland for treating acid mine drainage with an influent pH below 3. Figure 1 shows effluent concentrations were somewhat erratic during the first six months due to excessive water inflows, but stabilized after that time with a reduction in influent flows.

Removal efficiencies for Cell E at Big 5 over a 27-month period are shown on Figure 2. Removal is determined by dividing the wetland effluent by the influent concentrations. If contaminant removal is complete, the effluent concentration will be low, divided by the high influent concentration resulting in a trend value near zero. Results over the 27-month period suggest consistent and complete removal of copper and zinc, good removal of iron, and inefficient and unreliable removal of manganese and sulfate.

It is important to note here the importance of the laboratory tests to characterize water and substrate. The bench-scale test results at the Quartz Hill Tunnel indicated consistent and substantial reduction in manganese and sulfate, while the Big 5 performance was inefficient at reducing these constituents using the same anaerobic treatment process. The difference here is with the wetland design, substrates and nutrient additives which allow optimization of system performance.

The Limiting Reagent Concept for Loading Anaerobic Reactors

During the development of wetland technology, determining how large a flow of drainage can be handled has been a topic of considerable controversy.^(1,2,10,3) For systems that receive coal mine drainage, loading factors that consider the wetland area over which the drainage flows is the primary method of determining size.^(1,10,3,11) This can be stated as the amount of square feet of wetland per gallon per minute of water to be treated or as the grams of contaminant removed per day per square meter of wetland.⁽¹¹⁾ Loading factors do not seem to adequately explain the

removal of multiple metals even though some metals such as copper and zinc are consistently reduced by greater than 99 percent.⁽¹²⁾

A key factor in sulfate reduction is to create and maintain the optimum microenvironment for sulfate-reducers. The most important environmental conditions are reducing conditions and a pH of around 7. Since the wetland cell is receiving mine drainage of pH below 3 and Eh of above 700 mV, water can easily overwhelm the microenvironment established by the anaerobic bacteria. This leads to the limiting reagent concept for determining how much water can be treated, as an alternative to the use of typical loading factors.

Consider the following precipitation reaction:



At high flows of mine drainage through the substrate, sulfide will be the limiting reagent. The microbial environment will be under stress to produce more sulfide and the pH of the microenvironment will drop, resulting in inconsistent removal of iron. At low flows of mine drainage through the substrate, iron will be the limiting reagent. The excess sulfide will support a reducing environment and with a pH near 7, the microbial population will remain healthy. Under these conditions, removal of the metal contaminants will be consistent and complete. Using this concept, loading factors can then be set such that the heavy metal contaminants are always the limiting reagents. The goal then is to determine how much sulfide a colony of sulfate-reducing bacteria produce per unit volume of substrate per day.

Recent studies suggest that a reasonable figure for sulfide generation is 300 nanomoles sulfide/cubic cm/day.^(7,13) This number, the volume of the wetland cell, and the metals concentrations in the mine drainage are used to set the flow of mine drainage through the wetland cell. This is how the flow of one ml/minute was determined for the bench-scale experiment at Quartz Hill.

Using this concept in a subsurface wetland cell to determine the loading factor can make a significant difference in the performance of the wetland system. Figure 1 data is for an upflow cell at the Big Five site.⁽⁴⁾ The Figure shows removal (as determined by effluent concentration divided by mine drainage concentration) versus time for a period of over two years beginning in September 1989. In the first six months, the flow through the substrate was too high and sulfide was the limiting reagent. The erratic behavior is clearly shown by the confusion of lines. After six months the flow was reduced to make the metals the limiting reagent. This has resulted in year round complete removal of copper and zinc, a nearly complete removal of iron, and a rise in pH from 3 to 6.^(3,5)

Using these concepts of staged design and limiting heavy metals as reagents, a project on remediating an acidic drainage with high heavy metals loading has been successfully carried from the laboratory to the pilot-plant stage for a metal mine drainage in northern California. The project was jointly managed by Knight Piesold and Co. and Camp Dresser and McKee; both firms were involved with the Colorado School of Mines research at the Big Five Site.^(3,5)

Meeting Discharge Standards With Passive Treatment

Water quality discharge criteria have been consistently achieved on coal mine drainages using aerobic wetlands constructed by the Tennessee Valley Authority.⁽¹⁰⁾ TVA's effluent limitations require maximum monthly averages of 3 mg/L of iron, 2 mg/L of manganese and a pH between 6 and 9. When the pH of the drainage is greater than 5 and iron is less than 50 mg/L, effluent quality consistently meets discharge criteria. When pH is below 3 and iron is above 200 mg/L, however, remediation using aerobic constructed wetlands is much more problematic.^(10,3) Further, data collected on coal mine drainages do not consider or document the removal of other metals which may be present.

Both the Quartz Hill Tunnel in Central City and the Big 5 Tunnel in Idaho Springs are located on Clear Creek. The Colorado Department of Health, Water Quality Control Commission has classified Clear Creek for Cold Water Aquatic, recreation and agriculture. The numeric standards are shown on Table 4 (standards effective as of March 1, 1992).

Both the Quartz Hill and Big 5 Tunnels are historic mine drainages which are not subject to NPDES discharge criteria. To assess the performance of bench and pilot-scale systems, the effluent quality is compared with water quality standards. Where biologically-based numeric standards are hardness-based table value standards, the BAT value is used for comparison. BAT values were used for copper and zinc as indicated on Table 4. It is noted that water quality standards are Total Recoverable (TR). Analytical data is reported as Total Metals, so the comparison is conservative.

Figure 3 graphically depicts three of the cyanide solution principle tests in different substrate combinations (Numbers 9, 11 and 13) compared to the original test solution. While it is impossible to correlate discharge criteria to static laboratory tests, the reductions in cyanide and iron concentrations are significant. In the case of the nutrient test, the results are very encouraging for all parameters tested.

Figures 4 and 5 graphically show the quality improvements in the bench-scale test on Cell 3 at Quartz Hill. Water quality standards or BAT values are also identified. Iron, copper and zinc were consistently below the standard; manganese, while it exceeded the standard slightly, showed a substantial reduction in concentration. pH was consistently improved to within the discharge range. Sulfate was reduced by an order of magnitude, but still exceeded stream standards.

Effluent quality from the Big 5 Tunnel pilot scale discharge between October, 1989 to August, 1990 is shown on Figures 6 through 10. The stream standards indicated on Table 4 are also graphically shown in Figures 6 through 10 for comparative purposes.

TABLE 4
WATER QUALITY STANDARDS
CLEAR CREEK

Manganese	1.0 mg/L (TR)
Iron	1.0 mg/L (TR)
Copper	TVS [BAT = 0.5 mg/L (TR)]
Zinc	TVS [BAT = 0.75 mg/L (TR)]
Sulfate	250 mg/L
Cyanide	0.005 mg/L
pH	6.5 to 9.0

Manganese removal was inefficient at the Big 5 facility, averaging only an 11 percent reduction in concentration across the wetland. The average influent manganese concentration during this period was 31.4 mg/l, which did not vary seasonally. Manganese removal efficiencies may be low due to the loading, substrate constituents or retention time in the anaerobic zone. By comparison, manganese was efficiently removed from the Quartz Hill drainage bench scale tests as indicated on Figure 4 under anaerobic conditions. Manganese has also been successfully removed using aerobic processes in other studies.^(10, 14)

An average of 86 percent of iron was removed during the period indicated on Figure 7 at the Big 5 Tunnel. The average influent concentration was 43.7 mg/l, which increased to as high as 60 mg/l during the early spring. Iron concentrations in the wetland effluent rose with the onset of cold weather, and dropped dramatically as temperatures moderated. The peak in influent iron concentrations lagged the peak in effluent concentrations, suggesting that cold weather affected the wetland performance efficiency for removing iron. Cold-weather removal efficiencies were about 60 to 70 percent.

Figures 8 and 9 show wetland effluent zinc and copper concentrations were consistently below water quality standards. Removal efficiencies were nearly 100 percent throughout the monitoring period. Zinc and copper concentrations did not fluctuate seasonally, and averaged 9.1 and 0.56 mg/l respectively over the evaluation period.

Favorable adjustments in pH were consistently realized across the Big 5 pilot scale system. The average influent pH was 3.0 which did not vary seasonally. Effluent pH levels were raised to about 6, which is still below the stream standard for Clear Creek. Additional pH adjustment may be accomplished with reduced loading, increased retention time or substrate additives.

Conclusion

Treating mine discharges using constructed wetlands is a comparatively low-cost alternative to conventional water treatment processes. As with any water treatment process, passive systems are not universally applicable; the water chemistry and treatment reactions by which contaminant concentrations are reduced must be well defined and cautiously tested. Given the proper circumstance, adequate sizing and appropriate design can result in an efficient, passive water treatment process which meets water discharge criteria.

FIGURE 1

**PILOT-SCALE TESTS AT BIG 5 TUNNEL
CELL B - UP 2-YEAR REMOVAL TRENDS**

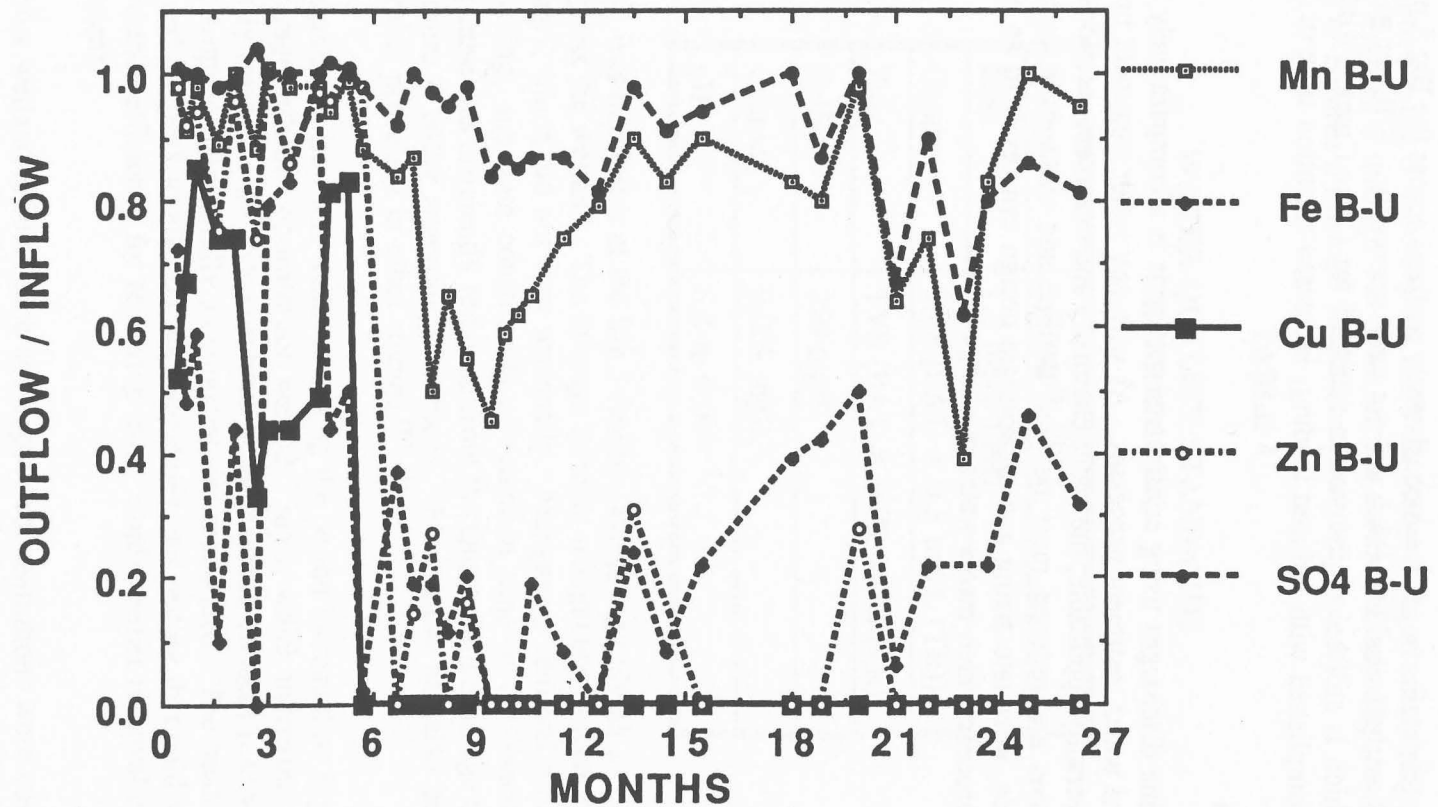


FIGURE 2
PILOT-SCALE TESTS AT BIG 5 TUNNEL
CELL E REMOVAL TRENDS FROM SEPTEMBER, 1989

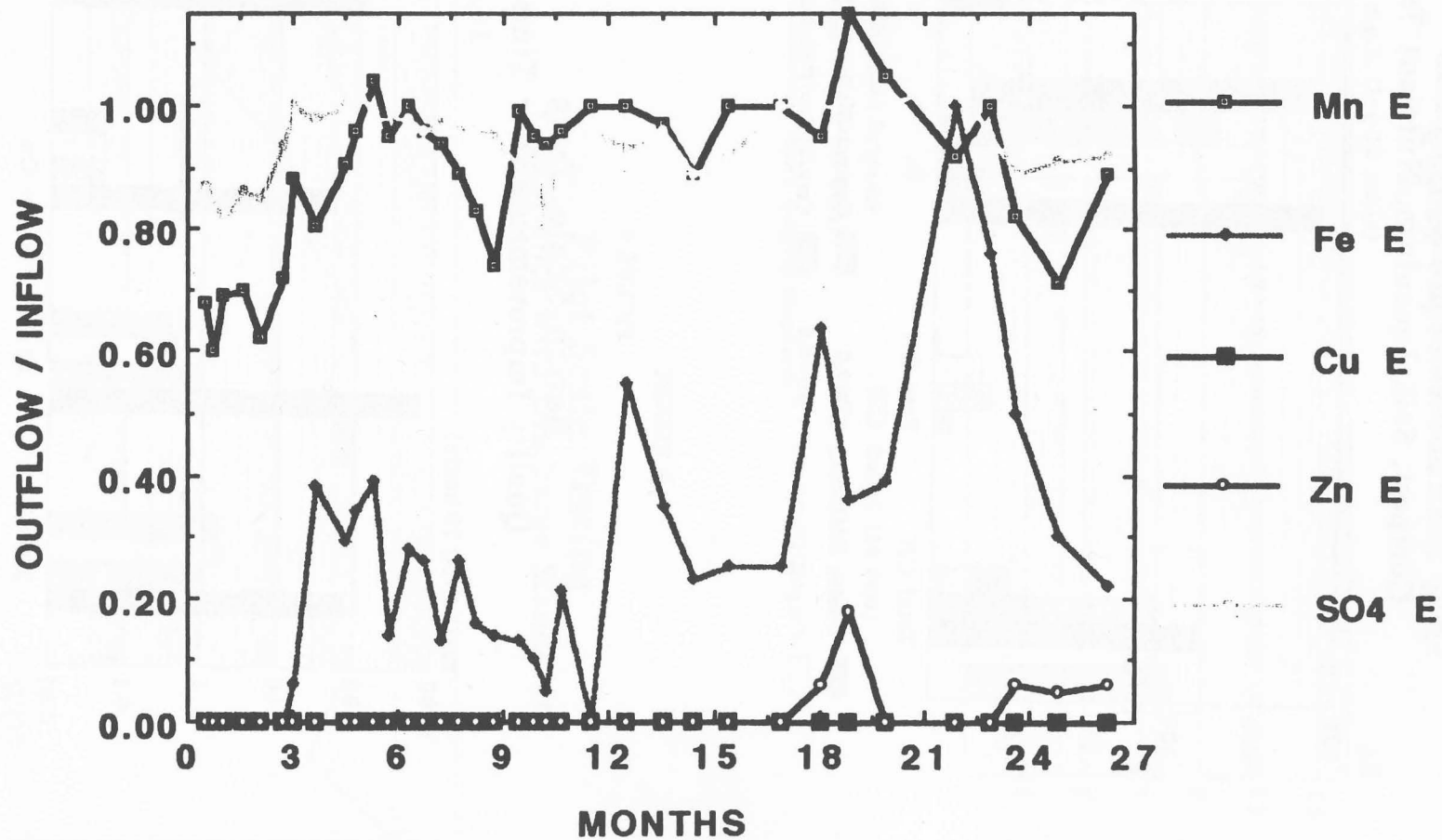


FIGURE 3

Proof-of-Principle Tests Compost, Soil, Inoculum, Nutrient Test

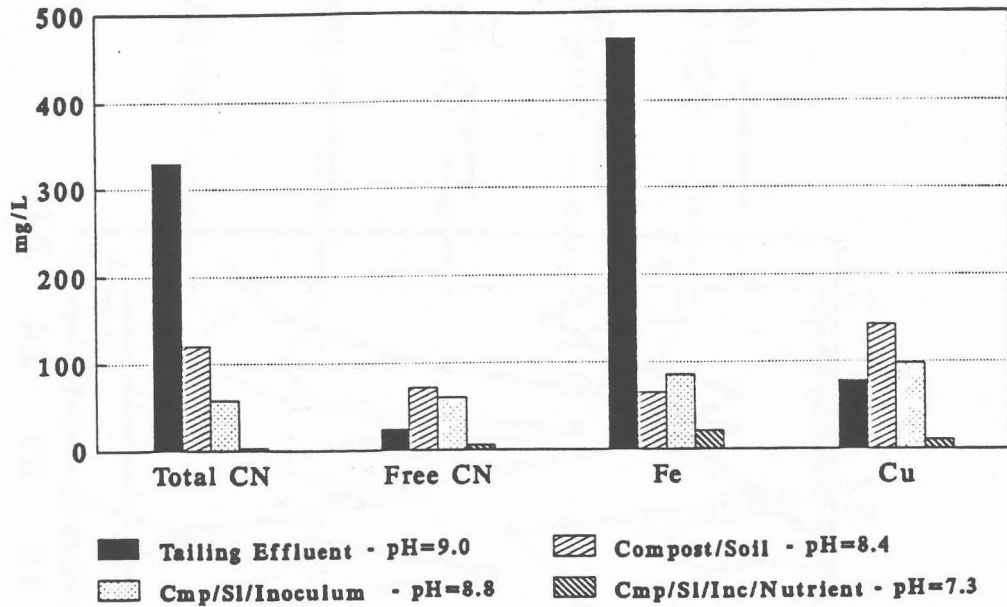


FIGURE 4

Bench-Scale Tests Quality Improvements Over Time

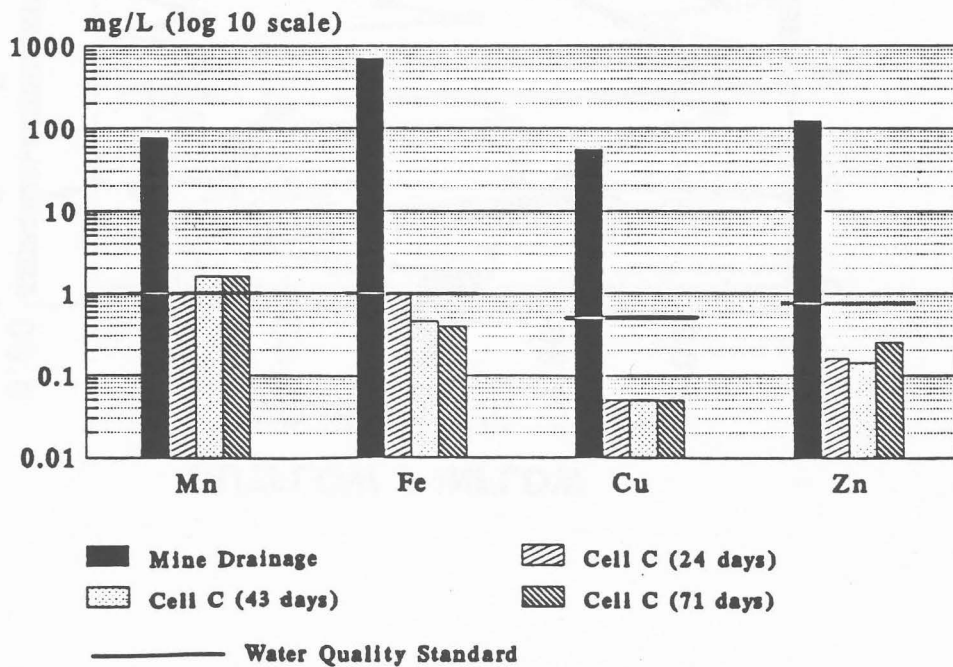


FIGURE 5

Bench-Scale Tests Quality Improvements Over Time

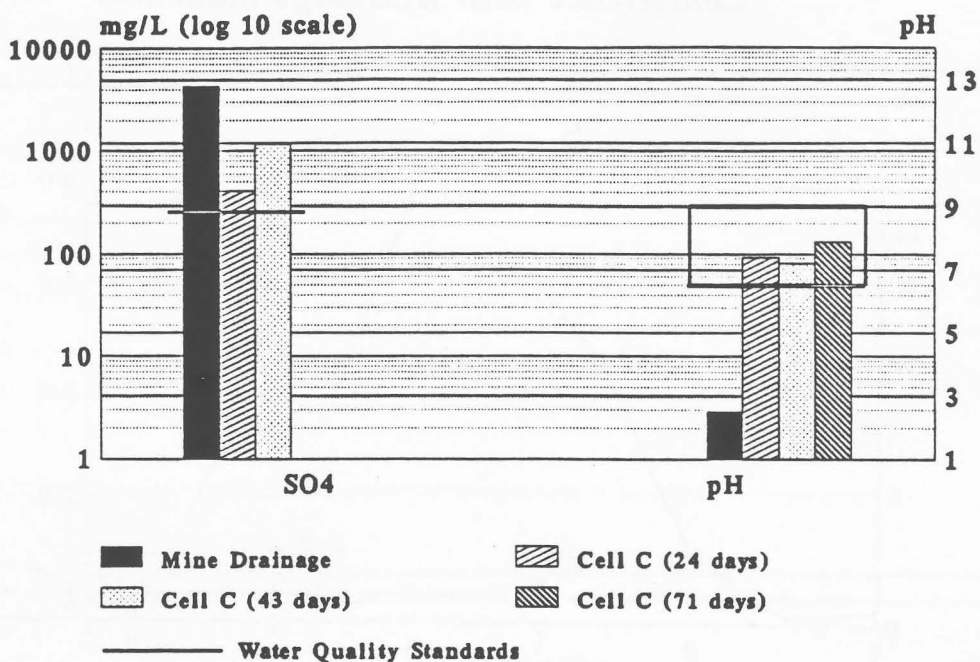


FIGURE 6

Pilot Scale Testing Compliance with Discharge Standards

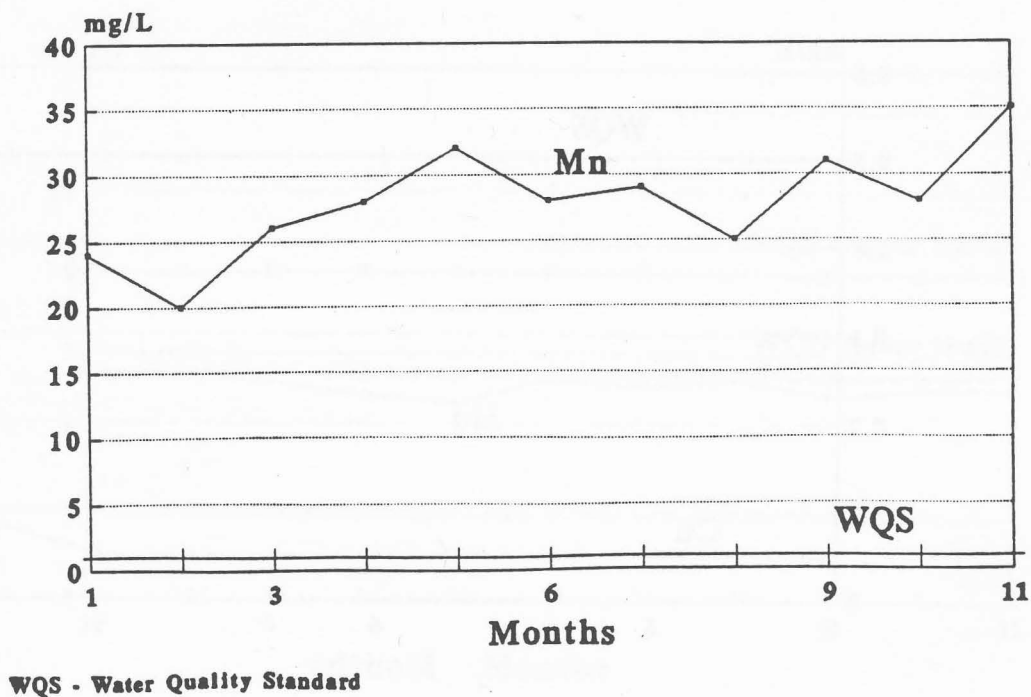


FIGURE 7

Pilot Scale Testing Compliance with Discharge Standards

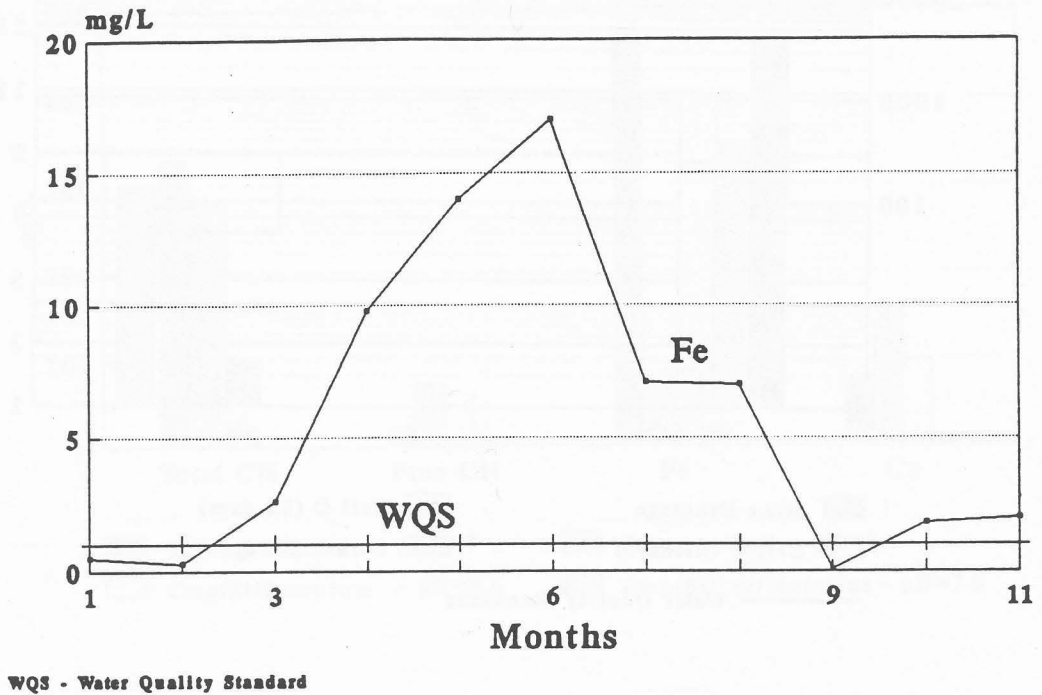


FIGURE 8

Pilot Scale Testing Compliance with Discharge Standards

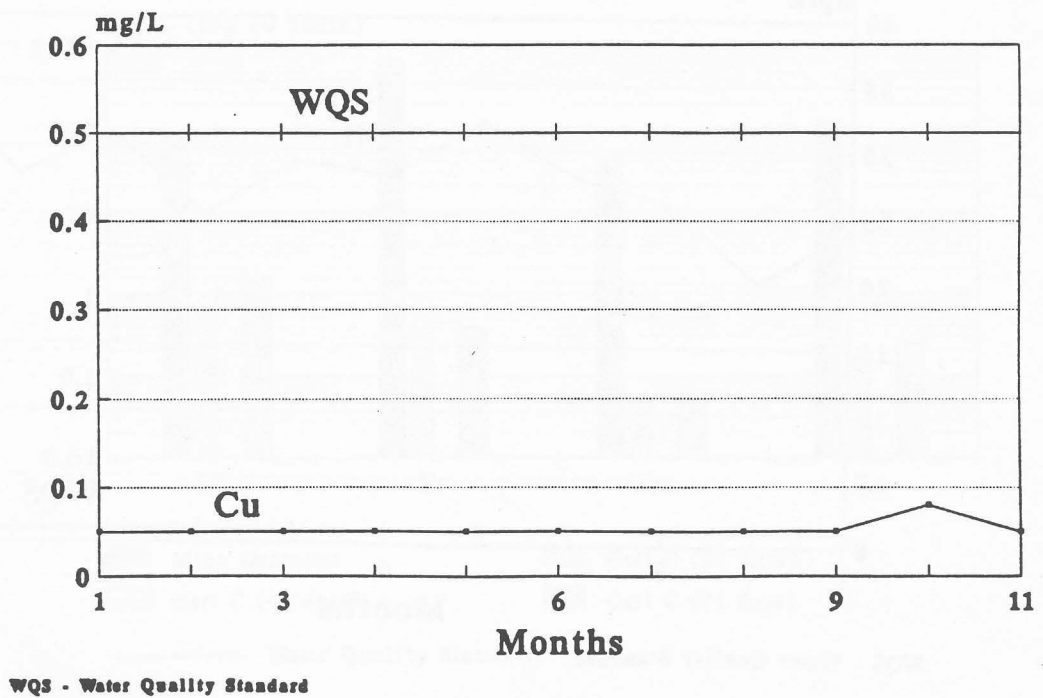


FIGURE 9

Pilot Scale Testing Compliance with Discharge Standards

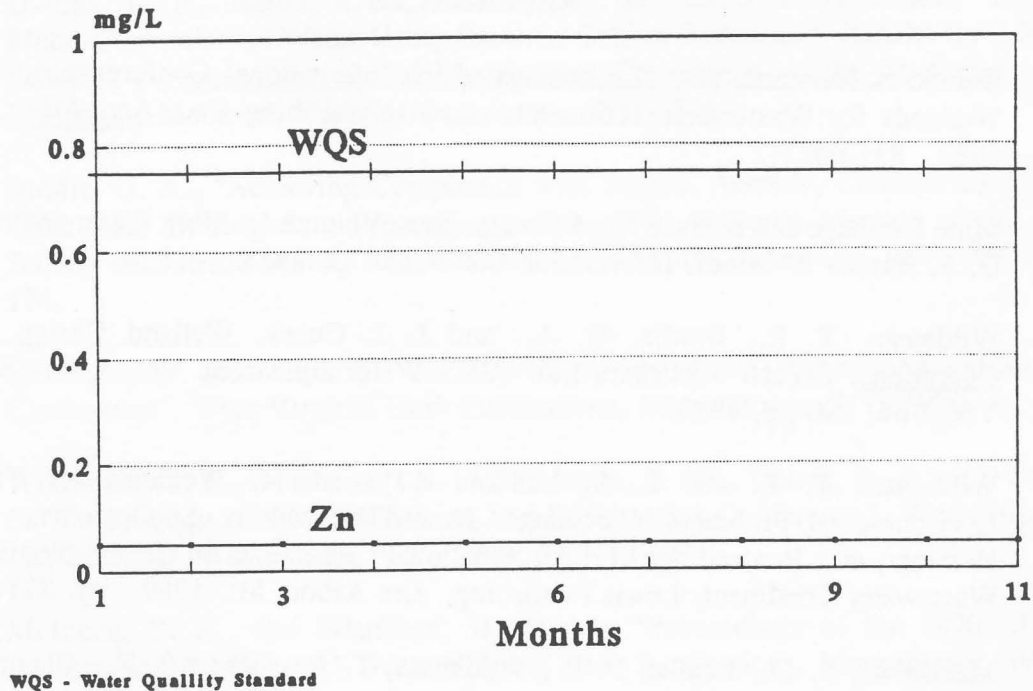
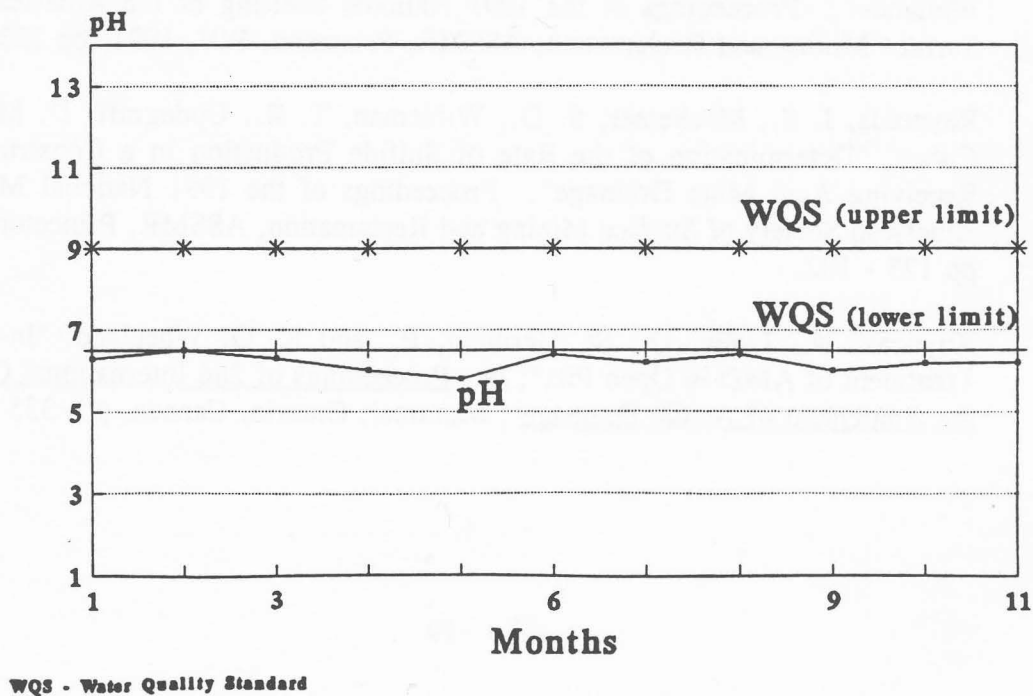


FIGURE 10

Pilot Scale Testing Compliance with Discharge Standards



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**CONSTRUCTED WETLANDS THAT EMPHASIZE SULFATE REDUCTION:
A STAGED DESIGN PROCESS AND OPERATION IN COLD CLIMATES**

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ABSTRACT

At the Big Five wetland, which was built to treat drainage from a metal mine, encouraging results have been attributed to sulfate reduction. Cu and Zn are reduced to below detection limits of 0050 mg/L, Fe is reduced by at least 90 % to below 3 mg/L, and the pH is raised from below 3 to above 6. When it was realized that treatment was primarily through microbial processes within the substrate and that plants were not needed to insure success, the concept of taking a process through design stages has been a development that has accelerated the use of these reactor cells for acid drainage remediation. In staged design, laboratory experiments are initiated to determine what would be reasonable substrate materials for remediation of a particular water. When a reasonable substrate is found, bench scale experiments are initiated as the next stage in the design. In these studies, removal efficiency, permeability, and flow are analyzed to see if a candidate substrate will support sulfate reduction and be hydraulically reasonable. Using this design method, an acid drainage of pH 2.5 was raised to a pH of above 7. The total heavy metals concentration in this drainage was above 900 mg/L and Cu, Zn, Fe, and Mn were all reduced by 99 %.

Determining how well these anaerobic cells operate in the winter is done at the pilot plant site in Idaho Springs, CO. It's been found that over the last four winters, those cells that emphasize anaerobic removal within the substrate have operated continuously and effectively the year round. Winter operation is added by the fact that the water temperature of the acid drainage is always between 14 and 16 ° C, and the cell can be readily insulated from the cold. Activity of the sulfate reducing bacteria may decrease during the winter, however it appears that organic complexation of metals helps to maintain low concentrations of metals in the effluent.

INTRODUCTION

For contaminant removal, use of a constructed wetland allows one to maximize one or two processes over the many that occur in a natural wetland. Consequently, over the last decade, constructed wetlands have received considerable attention (Hammer, 1989). The Big Five Pilot Wetland in Idaho Springs, CO, was built to demonstrate the removal of heavy metals from a metals mine drainage (Wildeman and Laudon, 1989, Howard et al., 1989). The original design and construction was completed in the summer and fall of 1987 (Howard et al., 1989), and consisted of three cells 18.6 m² in size. From the beginning, Cell A, which contained a mushroom compost substrate performed better than Cells B and C which contained a substrate consisting of equal parts of peat, aged manure, and decomposed wood. Selected values for the mine

TABLE 1. CONCENTRATIONS (mg/l) OF METALS, PERCENT REDUCTION OF METALS, pH, AND FLOW RATES (GALLON/MINUTE) IN THE BIG FIVE MINE DRAINAGE AND WETLAND CELL OUTPUT WATERS.*

Water Sample	Mn	% red.	Fe	% red.	Zn	% red.	Cu	% red.	pH	flow rate
=====										
INITIAL OPERATION										
December 11, 1987										
Mine Drainage	34		32		10.6		1.02		2.8	
Cell A	27	21	18	45	7.8	27	0.44	57	4.6	1.0
Cell B	33	1	24	26	9.8	12	0.89	12	3.1	1.0
Cell C	34	0	22	32	9.6	9	0.91	10	3.3	1.0
August 19, 1988										
Mine Drainage	26		37		8.1		0.91		2.9	
Cell A	25	4	20	56	<0.1	100	0.17	81	5.5	0.51
Cell B	26	0	15	59	6.1	24	0.55	40	3.2	0.24
Cell C	25	4	11	70	5.8	28	0.38	58	3.5	0.34
CELL A MODIFICATION										
February 21, 1989										
Mine Drainage	27		32		9.3		0.56		3.0	
Cell A	22	19	12	63	4.5	52	<.05	100	5.1	0.28
Cell B	27	0	28	13	6.1	34	0.82	0	3.4	0.31
Cell C	25	7	31	3	7.2	23	0.26	53	3.5	0.32
May 6, 1989										
Mine Drainage	30		42		10.4		0.76		3.0	
Cell A	33	-10	28	33	7.8	25	<.05	100	3.5	0.92
Cell B	27	10	10	76	6.2	40	0.36	53	3.0	0.83
Cell C	29	3	9	79	6.4	38	0.46	39	3.2	0.81
August 1, 1989										
Mine Drainage	32		43		9.4		0.75		2.9	
Cell A	31	3	39	9	5.2	45	<.05	100	4.1	0.30
Cell B	26	19	24	44	6.6	30	0.46	39	3.1	0.48
Cell C	32	0	18	58	4.8	48	0.09	88	3.7	0.43
CELL B MODIFICATION										
October 3, 1989										
Mine Drainage	35		46		9.9		0.66		3.2	
Cell B-Up	34	3	39	15	9.3	6	0.59	11	3.5	0.29
Cell B-Down	23	34	8	83	0.8	92	<.05	100	6.5	0.16
Cell E	24	31	<1	100	<0.1	100	<.05	100	6.3	0.062
November 5, 1989										
Mine Drainage	32		38		8.7		0.61		2.9	
Cell B-Up	31	3	17	55	8.4	3	0.48	21	3.6	0.22
Cell B-Down	20	38	<1	100	6.0	31	<.05	100	5.9	0.24
Cell E	20	38	<1	100	<.1	100	<.05	100	6.5	0.11
January 13, 1990										
Mine Drainage	31		33		9.0		0.59		2.9	
Cell B-Up	30	3	33	0	8.9	1	0.49	17	3.2	0.21
Cell B-Down	27	13	12	64	8.1	10	0.44	25	3.2	0.20
Cell E	28	10	10	70	<.1	100	<.05	100	6.0	0.10

*The area of Cells A, B, and C is 200 ft²; the area of Cells B-Up, B-Down, and E is 100 ft².

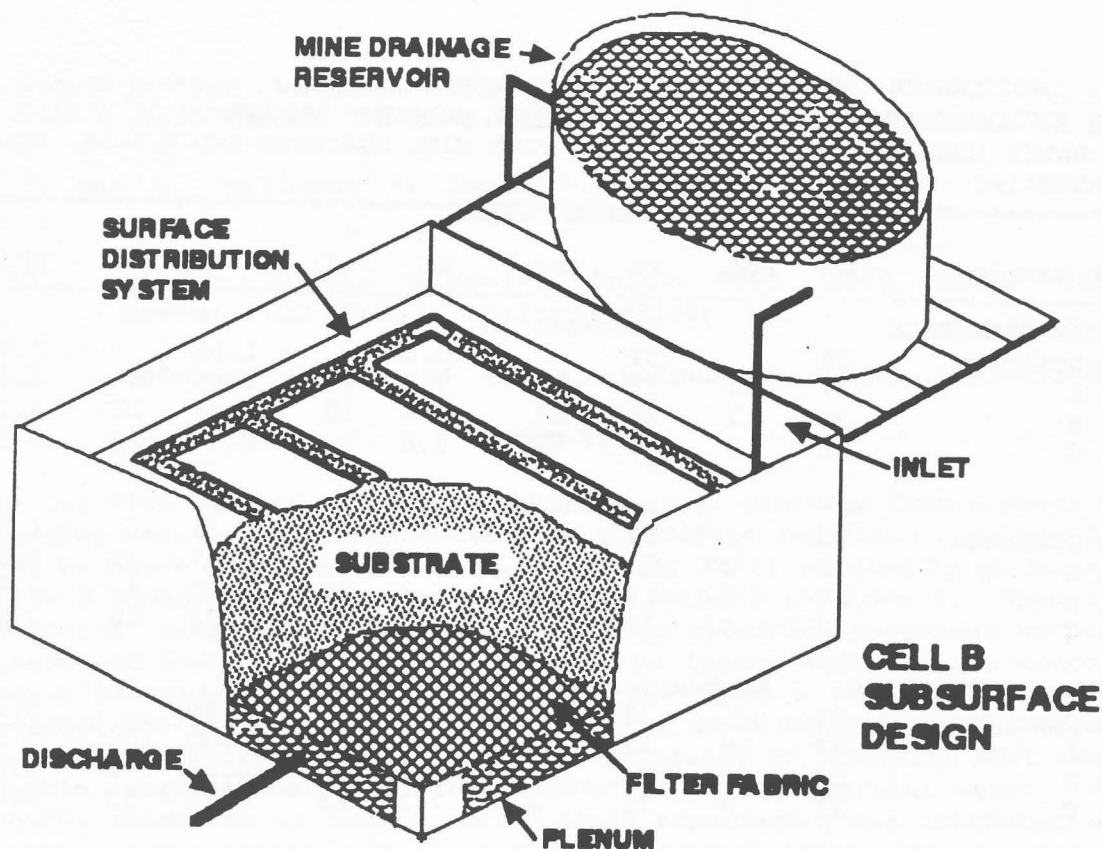


Figure 1. A cut-a-way view of the modification done to Cell B. Two identical subcells were constructed: the figure shows a downflow configuration.

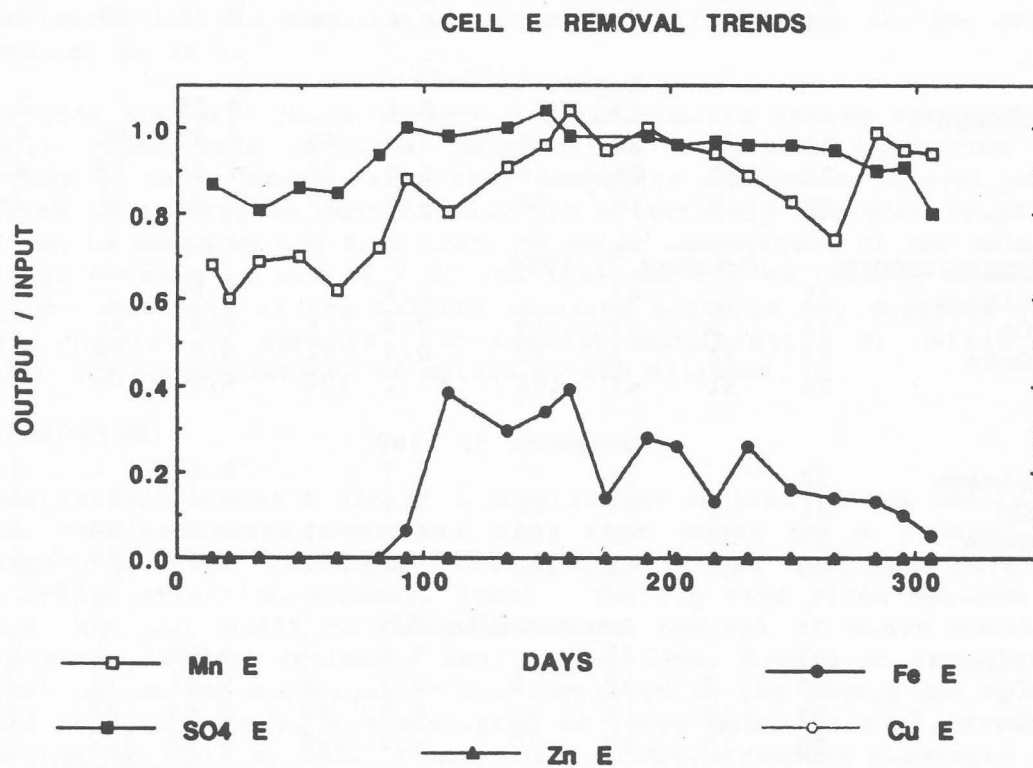


Figure 2. Cell E removal data for 12 months since September 1, 1989.

drainage input and the cell outputs are shown in Table 1. The results of various studies lead to the conclusion that sulfate reduction followed by sulfide precipitation is the primary heavy metal removal process (Machemer and Wildeman, 1991).

In August, 1989, Cell B was remodeled to incorporate a number of design features that should improve contact with the substrate. The original cell was divided into two identical cells that can be operated in either the upflow or downflow configuration. It is comparable to a trickling-flow filter process. Values on removal of Mn, Fe, Cu, and Zn and increases in pH for Cell B-Upflow and Cell B-Downflow are given in Table 1. Just as for the original Cell A design, removal has been impressive from initiation of flow.

When Cell B was remodeled, Cell E was constructed using the original substrate from Cell B. It was designed to operate as a downflow, subsurface wetland. Construction was completely accomplished with materials found locally. From the initiation of flow on September 1, 1989, removal of Cu, Zn, and Fe has been 100 %, and Mn removal averages 25 %. Removal results are given in Table 1, and are shown for a full 12 months in Figure 2. Again, laboratory experiments have confirmed that sulfate reduction with subsequent precipitation of metal sulfides is the predominant removal process in Cell E (Machemer and Wildeman, 1991)).

Once it was determined that sulfate reduction and subsequent precipitation of sulfides was the primary removal process, project objectives concentrated on how to employ knowledge of the biochemistry of sulfate reduction in the wetland design process. This is currently being done through the use of two ideas particularly suited to wetlands that employ anaerobic removal processes such as sulfate reduction: The limiting reagent concept, and staged design of wetlands.

THE LIMITING REAGENT CONCEPT

In the design of wetlands for wastewater treatment, there is a strong emphasis on determining the loading factor which gives an indication of how large a wetland should be to remove the contaminants of concern (Hedin and Nairn, 1990). This can be stated as the amount of square feet of wetland per gallon per minute of water to be treated or as the grams of contaminant removed per day per square meter of wetland (Hedin and Nairn, 1990). In our experiences, at the Big Five site typical measures of loading factor do not seem to explain the removal of metals even though heavy metals such as Cu and Zn are reduced by greater than 99 % (Wildeman, et al., 1990). We have discovered that a key factor in sulfate reduction is to insure that the optimum microenvironment for sulfate-reducers must be maintained. The most important environmental conditions are reducing conditions and a pH of around 7. Since the wetland cell is receiving mine drainage of pH below 3 and Eh of above 700 mV, the water can easily overwhelm the microenvironment established by the anaerobic bacteria. This leads to the limiting reagent concept for determining how much water can be treated, as an alternative to the use of typical loading factors.

Consider the following precipitation reaction:



At high flows of mine drainage through the substrate, sulfide will be the limiting reagent, the microbial environment will be under stress to produce more sulfide, the pH of the microenvironment will drop, and removal will be inconsistent. At low flows of mine drainage through the substrate, iron will be the limiting reagent, the excess sulfide will insure a reducing environment and a pH near 7, the microbial population will remain healthy, and removal of the metal contaminants will be consistent and complete. Using this idea, loading factors should be set to insure that the heavy metal contaminants are always the limiting reagents. The question then is how much sulfide can a colony of sulfate-reducing bacteria produce per cubic cm of substrate per day?

Recent studies suggest that a reasonable figure for sulfide generation is 300 nanomole sulfide / cubic cm / day (Reynolds, et al., 1991, McIntire and Edenborn, 1990). This number, the volume of the wetland cell, and the metals concentrations in the mine drainage are used to set the flow of mine drainage through the wetland cell. Using this concept in a subsurface wetland cell to determine the loading factor has resulted in year round complete removal of Cu and Zn, a nearly complete removal of Fe, and a rise in pH from 3 to 6 (Machemer, et al., 1990, Machemer and Wildeman, 1991).

STAGED DESIGN OF WETLANDS

Upon determining that precipitation of metals by sulfide generated from sulfate-reducing bacteria is the important process, it was realized that establishing and maintaining the proper environment in the substrate is the key to success for removal. This means that processes operating on the surface of the wetland are not that important. In particular, plants are not necessary in a wetland emphasizing subsurface processes. If this is the case, then a large pilot cell, such as was built at the Big Five site, is not necessary to determine if a wetland that emphasizes anaerobic processes for removal will work. Consequently, study of wetland processes and design of optimum systems can proceed from laboratory experiments to bench scale studies to design and construction of actual cells. We call this "staged design of wetland systems".

In current laboratory studies, culture bottle experiments are used for fundamental studies on how to establish simple tests to determine the production of sulfide by bacteria, and of what substrate will provide the best initial conditions for growth of sulfate-reducing bacteria. (Reynolds, et al., 1991) In these experiments, the production of sulfide at 18 °C has been 1200 nanomole/gm of dry substrate/day. Currently, the culture bottle experiments are being repeated using S-35 to establish that all the sulfide is produced by microbial processes.

Other laboratory studies have concentrated on the practical aspects of wetland design. One industrial concern was interested in whether cyanide concentrations typical of milling-waste effluents would kill sulfate-reducing bacteria. Culture bottle tests showed that sulfate reduction was retarded until the concentration of total cyanide was below 10 mg/L. Another industrial concern wanted to determine whether Cu concentrations above 100 mg/L would kill or retard sulfate-reducing bacteria. Culture bottle tests conducted over the course of one month showed that sulfate reduction was still vigorous at heavy metal concentrations above 100 mg/L.

Table 2. Constituent concentrations in mg/L in the Quartz Hill Tunnel mine drainage and in effluents from the bench scale tests.

Sample	Days Operated	Mn <-----	Fe Concentration in mg/L	Cu	Zn	SO ₄ ----->	pH
Mine Drainage	24	80.	630	48	133	4240	2.4
Cell A	24	0.94	1.6	0.06	0.27	450	7.4
Cell B	24	0.91	1.9	<0.05	0.17	770	7.5
Cell C	24	0.99	1.0	<0.05	0.16	412	7.4
Mine Drainage	43	80.	640	50	135	4300	2.5
Cell A	43	0.97	0.87	<0.05	0.18	1080	7.2
Cell B	43	0.64	0.96	<0.05	0.24	660	7.4
Cell C	43	1.6	0.46	<0.05	0.14	1180	7.2
Mine Drainage	71	70.	820	70.	101	NA	2.6
Cell B	71	0.48	0.40	<0.05	0.21	NA	8.0
Cell C	71	1.6	0.40	<0.05	0.25	NA	7.9

For bench scale studies, plastic garbage cans are used to conduct experiments to provide answers necessary to the design of a subsurface cell. (Bolis et al., 1991) Typical design parameters include determining the optimum loading factor, substrate, cell configuration, and the permeability of the substrate. In a bench scale study just recently completed, garbage cans filled with substrate were used to determine whether using the sulfide generation figure of 300 nanomole sulfide/cubic cm of substrate/day could be used to set the conditions for treating severely contaminated effluent that flows from the Quartz Hill Tunnel in Central City, CO. Contaminant concentrations for this drainage are shown in Table 2. Using the limiting reagent concept described above and the amount of substrate contained in the garbage can, flow could not exceed one milliliter/minute to insure that sulfide would always be in excess. Contaminant concentrations from the outputs of three different bench scale cells are shown in Table 2. For cell A the mine drainage was passed through the cell with no delay. For cell B the substrate was soaked with city water for one week before mine drainage started passing through the cell. For Cell C, the substrate was inoculated with an active culture of sulfate-reducing bacteria and soaked with city water for one week before mine drainage started passing through the cell. Preparations on cells B and C were done to insure that there would be a healthy population of sulfate-reducing bacteria before mine drainage flowed through the substrate. All cells were run in a downflow mode of the mine drainage through the substrate. In all three cells removal of Cu, Zn, Fe, as well as Mn is greater than 99 %. The increase in pH is from about 2.5 to above 7. These results were consistently maintained for over ten weeks of operation.

The substrate used was a mix of 3/4 cow manure and 1/4 planting soil. The results from cells B and C show that the cow manure has an indigenous population of sulfate-reducing bacteria that are quite active. Inoculation with an active culture of bacteria is not necessary in this case. Also, since the results from cell A are comparable to those of cells B and C, the

population of sulfate reducers can withstand immediate exposure to severe mine drainage and still produce sufficient quantities of sulfide. The key to good initial activity is to endure that the flow of mine drainage is low enough that its low pH does not disturb the micro-environment established by the bacteria.

Another feature of the results shown in Table 2 is that Mn is removed in all three cells. Typically, Mn is the most difficult contaminant in mine drainage to remove (Machemer and Wildeman, 1991, Machemer, et al., 1990, Hedin and Nairn, 1990, Wildeman, et al., 1990, McIntire and Edenborn, 1990). It is usually presumed that removal of Mn has to be achieved by raising the pH to above 7, and then introducing the effluent into an aerobic wetland cell so that Mn will be oxidized to MnO_2 . Removal in an anaerobic cell must be as Mn(II). Analysis of possible species at a pH above 7, suggest that removal could be as MnS or $MnCO_3$. In this case, it is hypothesized that $MnCO_3$ is the precipitate because it is more insoluble than the sulfide. In either case, a key to Mn removal in an anaerobic cell appears to be the ability to raise the pH of the effluent above 7. If raising the pH to above 7 can be consistently achieved, then all the contaminants in mine drainage can be removed in one anaerobic cell.

OPERATIONS DURING THE WINTER

The last four winters have allowed observations on how well wetland cells operate during the winter. Not all of the cells have kept operating during the winter. Two key factors allow winter operation: The mine drainage water is about 12 to 15 °C the year round, and portions of the site are in winter sun throughout the day. Below, the winter success of each cell is described.

Cell A has operated continuously through all four winters. This is the case even when the flow was cut back from 4 L/min to 1 L/min. Three reasons can be given for the winter success of Cell A:

1. It is continuously in the sun.
2. More of the water flows through the substrate rather than across the surface.
3. The inlet is small and insulated so the energy within the water is not lost.

When the flow into Cell C was cut back to 1 L/min, it has frozen over the last two winters. This cell is more shaded during the winter. Also the dense growth of *Typha* in Cell C inhibits solar radiation from reaching the substrate-water interface. In addition, Cell C still has the original rock box inlet. This inlet allows much of the water energy to be lost.

Cell D was built in the summer of 1989 and in both winters it has frozen. This is primarily a surface flow cell and the depth of the substrate is only 0.5 meter. Also it is not well insulated.

Cell E has worked well over the last two winters. It is shallow, but is a subsurface flow cell. The important feature that keeps Cell E operating during the winter is that much of the water that enters the cell flows across the surface and over the spillway. This excess water insulates the substrate.

The modified B Cells have operated over the winter primarily because the surface of the cells was insulated with hay and plastic. In fact, the temperature of the outlet only dropped 4 to 5 °C during January and February. On Cell B-Upflow the new outlet installed in the spring of 1990 was not insulated. It froze in December, 1990 and the cell had to be turned off for the winter. Cell B-Downflow did have an insulated outlet, and it has continued operations throughout both winters.

Guidelines for Winter Operation

From these observations, a number of guidelines can be established for insuring the operation of wetland systems in cold winter climates.

- o Use the thermal energy within the mine drainage water to best advantage. Insure that delivery systems are insulated. Keep inlet structures small and insulated.
- o Place wetland cells so they receive winter sun. If this cannot be completely achieved, at least insure that outlets are in winter sun.
- o Insulate the top of the cell with excess mine water as in Cell E or with hay and plastic as in the B Cells.
- o Insulate the outlet and allow a method for the effluent to flow away from places where it could cause freezing problems. This is especially important if it is planned to sample water during the winter.
- o If possible, design subsurface flow systems such as Cells B and E. The thermal energy within the substrate will aid operation, whereas in a surface flow system the waters are exposed to the elements.

CONCLUSIONS

Using constructed wetlands for wastewater treatment is still a developing technology. However, the results from the Big Five Pilot Wetland that was funded by the Emerging Technology Program (ETP) of the U. S. EPA shows promising removal of heavy metals and increase of pH for acid mine drainage. Conclusions from the project include:

1. Toxic metals such as Cu and Zn can be removed and the pH of mine drainage can be increased on a long term basis.
2. The major removal process is sulfate reduction and subsequent precipitation of the metals as sulfides. Exchange of metals onto organic matter can be important during the initial period of operation.
3. A downflow, trickling filter style of configuration achieves the best contact of the water with the substrate.
4. Removal efficiency depends strongly on loading factors. For bacterial-sulfate reduction, a volume-instead of a surface-loading capacity works better. Using the limiting reagent concept also gives good removal results.
5. Permeability of the substrate is a critical design variable for successful operation. Using laboratory and bench-scale tests, a good indication of the soil permeability in a constructed wetland can be determined.
6. Solutions to problems such as plugging of plumbing by ferric hydroxides and freezing of discharge lines during winter have to be designed and constructed into the passive nature of wetlands to achieve long term operation.
7. Since the removal process is primarily bacterial, a staged design process works well. Laboratory experiments gives good indications of

the removal capacities of substrate materials; bench-scale tests give flow versus removal values; and pilot scale experiments can be sized so that systems are the size of a typical wetland module. completion of the project consists of constructing more modules.

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