United States
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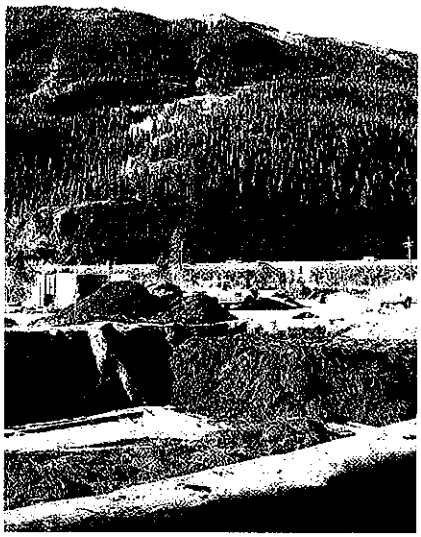
# Anaerobic Compost Constructed Wetlands System (CWS) Technology

## Innovative Technology Evaluation Report



SITE
SUPERFUND INNOVATIVE
TECHNOLOGY EVALUATION

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# Anaerobic Compost Constructed Wetlands System (CWS) Technology

## Innovative Technology Evaluation Report

National Risk Management Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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# Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and ground water; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

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Hugh W. McKinnon, Director
National Risk Management Research Laboratory

# Abstract

As part of the Superfund Innovative Technology Evaluation (SITE) Program, the U.S. Environmental Protection Agency (EPA) evaluated constructed wetlands systems (CWS) for removing high concentrations of zinc from mine drainage at the Burleigh Tunnel in Silver Plume, Colorado.

Exploration geologists have known for many years that metals, most commonly copper, iron, manganese, uranium, and zinc, frequently accumulate in swamps and bogs located in mineralized areas. This understanding forms the basis for the design of CWS—essentially excavated pits filled with organic matter—that have been developed and constructed over the past 15 years to treat drainage from abandoned coal mines in the eastern United States. Mine drainage is routed through the organic material, where metals are removed through a combination of physical, chemical, and biological processes.

In fall 1994, anaerobic compost wetlands in both upflow and downflow configurations were constructed adjacent to and received drainage from the Burleigh Tunnel, which forms part of the Clear Creek/Central City Superfund site. The systems were operated over a 3-year period. The effectiveness of treatment by the CWS was evaluated by comparing the concentration of zinc and other metals from corresponding influent and effluent analyses. By far the dominant toxic metal present in the drainage was zinc. The upflow CWS removed an average of 93 percent of the zinc during the first year of operation, and 49 and 43 percent during the second and third years. The downflow CWS removed an average of 77 percent of zinc during the first year and 70 percent during the second year. (Flow was discontinued to the downflow system in the third year.)

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# Acronyms, Abbreviations, and Symbols

| | |
|---|---|
| °C | Degrees Celsius |
| °F | Degrees Fahrenheit |
| %C | Percent completeness |
| %R | Percent recovery |
| AA | Atomic absorption |
| ARAR | Applicable or relevant and appropriate requirement |
| ASTM | American Society for Testing and Materials |
| AVS | Acid volatile sulfide |
| BOD | Biochemical oxygen demand |
| CDPHE | Colorado Department of Public Health and Environment |
| CDM | Camp, Dresser, & McKee, Inc. |
| CFU | Colony forming units |
| CERCLA | Comprehensive Environmental Response, Compensation, and Liability Act |
| CFR | Code of Federal Regulations |
| CWS | Constructed wetlands system |
| DQO | Data quality objective |
| Eh | Oxidation reduction potential |
| EPA | U.S. Environmental Protection Agency |
| FS | Feasibility study |
| gpm | Gallons per minute |
| $H_2S$ | Hydrogen sulfide |
| HDPE | High-density polyethylene |
| HSWA | Hazardous and Solid Waste Amendments of 1984 |
| ICP | Inductively coupled plasma |
| ITER | Innovative technology evaluation report |
| $LC_{50}$ | Lethal concentration for 50 percent of the test organisms |
| MCAWW | Methods for Chemical Analysis of Water and Wastes |
| MCL | Maximum contaminant level |
| µg | Micrograms |

## Acronyms, Abbreviations, and Symbols (continued)

| | |
|---|---|
| µS | Microsiemens |
| mg/kg | Milligrams per kilogram |
| mg/L | Milligrams per liter |
| MS | Matrix spike |
| NCP | National Oil and Hazardous Substances Pollution Contingency Plan |
| NIST | National Institute of Standards and Technology |
| NPDES | National Pollutant Discharge Elimination System |
| NRMRL | National Risk Management Research Laboratory |
| O&M | Operation and maintenance |
| ORD | Office of Research and Development |
| ORP | Oxidation/reduction potential |
| OSHA | Occupational Safety and Health Administration |
| OSWER | Office of Solid Waste and Emergency Response |
| PPE | Personal protective equipment |
| ppm | Parts per million |
| PRC | PRC Environmental Management, Inc. |
| PVC | Polyvinyl chloride |
| QAPP | Quality assurance project plan |
| QA/QC | Quality assurance/quality control |
| RCRA | Resource Conservation and Recovery Act |
| RI | Remedial investigation |
| RPD | Relative percent difference |
| SARA | Superfund Amendments and Reauthorization Act |
| SITE | Superfund Innovative Technology Evaluation |
| SDWA | Safe Drinking Water Act |
| SOP | Standard operating procedure |
| SRM | Standard reference material |
| SWDA | Solid Waste Disposal Act |
| TCLP | Toxicity characteristic leaching procedure |
| TOC | Total organic carbon |
| TDS | Total dissolved solids |
| TSS | Total suspended solids |
| $yd^3$ | Cubic yards |

## Conversion Factors

| | *To Convert From* | *To* | *Multiply By* |
|---|---|---|---|
| Length | inch | centimeter | 2.54 |
| | foot | meter | 0.305 |
| | mile | kilometer | 1.61 |
| Area: | square foot | square meter | 0.0929 |
| | acre | square meter | 4,047 |
| Volume: | gallon | liter | 3.78 |
| | cubic foot | cubic meter | 0.0283 |
| Mass: | pound | kilogram | 0.454 |
| Energy: | kilowatt-hour | megajoule | 3.60 |
| Power: | kilowatt | horsepower | 1.34 |
| Temperature: | (°Fahrenheit - 32) | °Celsius | 0.556 |

# Acknowledgments

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This project consisted of a demonstration conducted under the SITE program to evaluate the anaerobic compost Constructed Wetland System (CWS) technology developed by the Colorado Department of Public Health and Environment (CDPHE). The technology demonstration was conducted on mineral mine drainage at the Burleigh Tunnel in Silver Plume, Colorado, which is included in the Clear Creek/Central City Superfund site. Passive treatment was selected as the preferred treatment alternative for the Burleigh Tunnel drainage in a 1991 Record of Decision (ROD). This Innovative Technology Evaluation Report (ITER) interprets the data that was collected during the nearly four-year demonstration and discusses the potential applicability of the technology.

The cooperation and participation of the following people are gratefully acknowledged: Mr. Vincent Gallardo, Ms. Ann Vega, and Dr. James Lazorchek of NRMRL; Ms. Holly Fliniau of EPA Region VIII and Mr. Rick Brown of CDPHE.

# Executive Summary

This executive summary of the Constructed Wetlands System (CWS) technology demonstration discusses technology applications, describes system effectiveness, and presents an evaluation of the costs associated with the system and lessons learned during the field demonstration.

## Introduction

The anaerobic compost CWS technology was evaluated under the Superfund Innovative Technology Evaluation (SITE) program. The SITE program was developed by the U.S. Environmental Protection Agency (EPA) in response to the mandate of the Superfund Amendments and Reauthorization Act (SARA) of 1986. The primary purpose of the program is to maximize the use of alternative treatment technologies. To this end, reliable performance and cost data on innovative technologies are developed during demonstrations where the technology is used to treat a specific waste.

After the demonstration, EPA publishes an Innovative Technology Evaluation Report (ITER) designed to aid decision makers in evaluating the technology for further consideration as an appropriate cleanup option. This ITER includes a review of the technology application, an economic analysis of treatment costs, and the results of the demonstration.

For this demonstration, wetlands were designed and constructed to treat mine drainage through a combination of physical, chemical, and biological processes. The mine drainage, containing primarily zinc contamination, flowed into the constructed wetlands where metals were removed by sorption, precipitation, and biological sulfate reduction. The demonstration included the evaluation of two CWS treatment cells (pits) filled with an organic-rich compost (96 percent) and alfalfa hay (4 percent) mixture. Both treatment cells were constructed adjacent to, and received drainage from, the Burleigh Tunnel in Silver Plume, Colorado. The Burleigh Tunnel is part of the Clear Creek/ Central City Superfund site. Passive wetlands treatment was identified by the Colorado Department of Public Health and Environment (CDPHE) as the preferred remedial alternative for the Burleigh Tunnel drainage.

Each treatment cell covered 0.05 acres and differed in flow configuration. One cell was constructed in an upflow configuration, in which water entered from the base of the cell and was forced upward to discharge; the other was constructed in a downflow configuration, in which water entered from the top of the cell and flowed by gravity to discharge. The compost and hay mixture was 4 feet deep in both cells. Flow rates of water into and out of the cells were controlled by a series of v-notch weirs; each cell was designed to treat 7 gallons per minute (gpm).

## Technology Applications Analysis

The primary objectives of the CWS technology demonstration were to (1) measure the reduction of zinc in Burleigh Tunnel drainage resulting from the CWS treatment with respect to cell configuration and seasonal variation (temperature); (2) assess the toxicity of the Burleigh Tunnel drainage; (3) characterize the toxicity reduction resulting from treatment of the drainage by the CWS; and (4) estimate toxicity reductions in the stream (Clear Creek) receiving the Burleigh Tunnel drainage.

CWS treatment effectiveness was evaluated by comparing the concentration of zinc and other metals from corresponding CWS influent and effluent analyses (see Section 3.0). The results indicate the concentration of zinc in the Burleigh Tunnel drainage ranged from 50 to 60 milligrams per liter (mg/L) during the first year of the demonstration. However, in May and June 1995, a great deal of spring snow and rain and a rapid thaw combined to increase the amount of runoff entering the mine network drained by the Burleigh Tunnel. At that time,

flow from the tunnel increased from 45 gpm to more than 300 gpm, and zinc concentrations increased from 55 mg/L (April 12, 1995) to 109 mg/L (August 8, 1995). Over the final 2 years of the demonstration, zinc concentrations in Burleigh Tunnel mine drainage were lower in the winter, dropped again in April or May when flow through the mine workings increased, and rapidly increased in summer, remaining high throughout the fall. During this period, Burleigh Tunnel mine drainage zinc concentrations generally remained between 45 and 84 mg/L, with increases to more than 100 mg/L noted during the late summer and fall. The Burleigh Tunnel drainage is also characterized by moderate pH and alkalinity and low concentrations of metals other than zinc.

### Downflow

In the first year of operation, CDPHE reported the downflow cell developed flow problems on occasion, preventing treatment of the intended amount of water. Remedies, such as fluffing the compost, were tried and were somewhat successful allowing the system to flow at 4 to 6 gpm during the first two years of operation. During the third year, the flow in this cell dropped to less than 1 gpm and flow to this cell was discontinued. The permeability loss is believed to be related to precipitation of metal oxides, hydroxides, and carbonates, settling of fine materials in the cell, and compaction of the substrate material.

In general, the downflow cell was effective in removing zinc during the first year of operation. Zinc removal by this cell ranged from 69 to 96 percent with a mean removal of 77 percent. During the second year of operation, zinc removal ranged from 62 to 79 percent with a mean of 70 percent. During the final 6 months of operation, flow through the downflow cell continued to decline increasing the residence time of the mine drainage in the cell. The increased residence time improved zinc removal. Zinc removal during this period ranged from 67 to 93 percent with a mean of 82 percent.

Aqueous geochemical modeling, observations of cell compost, sulfate-reducing bacteria count results, and acid volatile sulfide data suggest that biological sulfate reduction is not the primary zinc removal mechanism within this cell. Instead, the primary metal removal mechanism is thought to be the precipitation of zinc oxides, hydroxides, and carbonates in aerobic sections of the downflow cell.

### Upflow

During the first 6 months of operation, upflow cell effluent samples contained low (less than 1 mg/L) concentrations of zinc. However, during the later part of 1994 and into 1995, upflow cell effluent zinc concentrations began to increase. The concentrations of zinc ranged from 0.13 mg/L in early 1994 to 60.1 mg/L in May 1997.

In the spring of 1995, heavy spring runoff overwhelmed the CWS system, channeling 20 gpm of aerobic water (nearly three times the design flow) through the upflow cell. This high runoff also apparently mobilized more zinc from the mine workings or mine waters and substantially increased the concentration of zinc in the mine drainage. The large flows created aerobic conditions and the increased zinc loading had a detrimental effect on the upflow cell. These new conditions apparently initiated a change in the cell's microbial ecology. After the high flow event, the upflow cell removed only 50 to 60 percent of the zinc in the mine drainage. Prior to the high flow event, the upflow cell removed greater than 90 percent of the zinc contamination (year 1 mean removal was 93 percent).

The loss of substrate hydraulic conductivity also affected the upflow CWS. During the demonstration, the height of the influent wier was periodically raised to increase the hydraulic pressure to maintain flow through the upflow CWS. The water level was raised approximately 1 foot over the 4-year demonstration. In 1997, this cell developed a visibly obvious preferential pathway in the southeast corner, adjacent to the bermed sidewall. This preferential pathway was eliminated by terminating flow to this section of the wetland through excavating of the wetland substrate to allow installation of a cap on the influent line.

The high initial zinc removal rates in the upflow cell were likely the result of absorption of metals and biological sulfate reduction. The decline in metal removal by the upflow cell after the high flow event is likely related to the decline in sulfate reducing bacteria in this cell. There are several possible reasons for the decline of the sulfate-reducing bacteria including toxicity produced by high zinc concentrations for the bacteria, prolonged exposure to aerobic conditions allowing other wetland bacteria to outcompete the sulfate-reducing bacteria, or the utilization of all the most readily metabolized growth materials by the sulfate reducing bacteria leading to lower activity and eventually lower populations of these bacteria. Ultimately, the primary metal removal mechanism over the last several years of the demonstration was likely chemical precipitation.

## Economic Analysis

An economic analysis was conducted to examine 11 cost categories for the CWS technology. The 11 categories include (1) site preparation; (2) permitting and regulatory requirements; (3) capital equipment and construction; (4) startup; (5) labor; (6) consumables and supplies; (7) utilities; (8) residual and waste shipping and handling; (9) analytical services; (10) maintenance and modifications; and (11) demobilization.

A number of factors affect the estimated costs of treating mine drainage with the CWS technology. These factors generally include flow rate, type and concentration of contaminants, water chemistry, physical site conditions, site location, and treatment goals. In addition, the characteristics of the spent compost produced by a CWS will affect disposal costs since the compost may require treatment for off-site disposal.

Based on the criteria evaluated in the cost analysis, the average estimated cost for a constructed wetland at 50 gallons per minute (gpm) over a 15-year period is $1,744,100 million or $0.0045 per gallon of water treated.

## Treatment Effectiveness

Based on this demonstration, the following conclusions may be drawn about the effectiveness of the anaerobic compost CWS technology.

- The upflow CWS removed an average (arithmetic mean) of 53 mg/L (93 percent) of zinc during the first year of operation.
- Upflow cell zinc removal averaged 41 mg/L (49 percent) during the second year and 30 mg/L (43 percent) during the third year of operation.
- During the first year of operation, the upflow cell effluent was not toxic to Ceriodaphnia dubia or Pimephales promelas.
- The downflow CWS removed an average of 44.2 mg/L (77.4 percent) of zinc during the first year and 58 mg/L (70 percent) during the second year of operation.
- The CWS is relatively easy to construct with readily available materials.

In summary, results from this SITE demonstration and additional tests of the CWS technology suggest that the CWS is capable of reducing the toxicity of contaminated mine drainage by removing metals such as zinc, cadmium, iron, lead, nickel, and silver.

However, the results of this demonstration also clearly show that an anaerobic compost CWS using sulfate reduction may have difficulty in recovering from upset conditions such as the high flow event that occurred during this demonstration.

In addition, application of this technology to mine drainage containing high concentrations of iron may require pretreatment to remove the iron. If not removed, the iron could precipitate in the wetland and could lead to loss of wetland permeability.

## Lessons Learned

The following items highlight lessons learned during the CDPHE constructed wetlands demonstration. The list is partitioned among five categories of considerations (or concerns): theory, design, construction, operation and maintenance, and analytical.

### *Theory*

- An upflow CWS using biological sulfate reduction is capable of reducing the concentration of several metals including zinc, cadmium, nickel, lead, iron, and silver. The extent of metal reduction depends on the concentration of the metal and sulfate in the mine drainage, and the performance of the CWS.
- The primary metal removal process in the downflow CWS did not appear to be biological sulfate reduction. Zinc in the demonstration CWS downflow cell appeared to be primarily removed by chemical precipitation. Generally, zinc removal by the demonstration downflow cell ranged between 70 and 80 percent. However, the accumulation of zinc carbonate in the cell compost may have attributed to a loss of cell permeability during the demonstration.

### *Design*

- A hydraulic residence time of 50 hours (estimated) provided good metal removal in the upflow cell during the first 8 months of the demonstration. However, the decline in metal removal after this initial period and inability to re-establish the sulfate-reducing bacteria in the upflow cell suggest this residence time may be a lower limit for mine drainages containing high metal concentrations.
- Hydraulically, the upflow cell performed well with 4 feet of compost. However, some short circuiting was observed after 3 years of operation.
- The mixture of fresh compost (96 percent) and hay (4 percent) used as a substrate during the demonstration was a superior environment for sulfate-reducing bacteria. However, the compost contains high levels of ammonia that is readily leached during

wetland startup, resulting in elevated levels of ammonia in the discharge. The addition of wood products to the substrate can reduce the amount of ammonia generated. Land treatment has been used at some sites to dispose of wetland startup discharge.

- Each wetland cell should have an easily adjustable influent conveyance with the capability of bypassing 200 to 300 percent of typical peak flows.

### Construction

- Bermed sidewalls lined with high-density polyethylene (HDPE) is a suitable construction technique for cold region applications. However, the use of a geonet on the wetland surface to allow animals and people to walk on the wetland is not recommended. The geonet did not allow additional compost or hay to be added to the wetland. In addition, the use of geofabric to separate the piping networks from the compost is not recommended.

- Effluent collection pipes (polyvinyl chloride [PVC]) should be larger than 1 inch in diameter to prevent clogging from precipitated material. In addition, the effluent collection structure should include cleanouts that allow precipitated material to be periodically removed without driving the precipitate back into the wetland compost.

- Lining a downflow cell with HDPE above the level of the ponded water allows this water to short circuit the wetland compost. Short circuits are most noticeable during the winter when the compost becomes frozen and contracts from the liner, creating a gap between the compost and liner.

### Operation and Maintenance

- Constructed wetlands can require frequent inspections to ensure that proper flows are maintained within the treatment cells. However, properly designed and constructed influent distribution and effluent collection networks may reduce inspection frequency.

- Treatment system downtime with CWS treatment is not high. Effluent piping networks should be cleaned out periodically (once or twice a year was appropriate for the Burleigh Tunnel CWS). The frequency of compost removal and replacement will depend on contaminant loading, metal removal efficiencies, and the desired performance level of the CWS. Compost removal and replacement frequency for the demonstration CWS upflow cell is estimated to be once every 4 to 5 years.

- Straw bales covered with insulated construction blankets (used to cure concrete in cold weather) are an effective insulator for an upflow CWS during winter operation. However, their use requires an upper support structure such as a geonet. An equally effective insulation system could include 6 inches of fresh compost and hay covered by construction blankets, although this system has not been tested.

- Straw bales used for winter insulation must not be allowed to become saturated by water. Their combined weight will compress the wetland compost, making it impermeable.

### Analytical

- Routine (monthly) total metals analysis in conjunction with quarterly dissolved metals analysis were useful in evaluating the performance of the CWS. The mine drainage and effluents were sampled and analyzed every 2 weeks during the first 2 years of the demonstration; however, monthly sampling (conducted over the final year of the demonstration) is adequate to track treatment performance.

- Routine aquatic toxicity testing of the mine drainage and CWS effluent also provides useful water quality information. During the CWS demonstration, these analyses were conducted every 3 to 4 months, but semi-annual analyses could also be used. Demonstration aquatic toxicity testing used two test organisms, fathead minnows (Pimephalus promelas) and water fleas (Ceriodaphnia dubia); however, other test organisms including trout fry could also be used.

- Sulfate-reducing bacteria analyses of wetland compost were conducted monthly during the first 2 years of the CWS demonstration. These analyses, while useful, did not show much variation until the high flow event, and their frequency could easily be reduced to every other month or even a quarterly. Acid volatile sulfide analysis can indicate the accumulation of metal sulfides within the CWS compost; however, the compost sample must be collected from the area of metal filtration. The acid volatile sulfide analysis procedure is not routine for most laboratories, and meaningful results may not be achievable.

- All aqueous field analyses conducted during the CWS demonstration including pH, Eh (effluent), dissolved oxygen (influent), conductivity, and temperature were useful measurements. It should be noted that the platinum element of the Eh probe is prone to poisoning, requiring periodic replacement.

# Section 1
# Introduction

This section provides background information about the SITE program, discusses the purpose of this ITER, and describes the CWS technology. Key contacts for additional information about the SITE program, this technology, and the demonstration site are listed at the end of this section.

## 1.1 Brief Description of the SITE Program and Reports

SARA mandates that EPA select, to the maximum extent practicable, remedial actions at Superfund sites that create permanent solutions (as opposed to land-based disposal) for contamination that affects human health and the environment. In response to this mandate, the SITE program was established by EPA's Office of Solid Waste and Emergency Response (OSWER) and Office of Research and Development (ORD). The SITE program promotes the development, demonstration, and use of new or innovative technologies to clean up Superfund sites across the country.

The SITE program's primary purpose is to maximize the use of alternatives in cleaning up hazardous waste sites by encouraging the development and demonstration of innovative treatment and monitoring technologies. It consists of the Demonstration Program, the Emerging Technology Program, the Monitoring and Measurement Technologies Program, and the Technology Transfer Program. These programs are discussed in more detail below.

The objective of the Demonstration Program is to develop reliable performance and cost data on innovative treatment technologies so that potential users may assess specific technologies. Technologies evaluated either are currently or will soon be available for remediation of Superfund sites. SITE demonstrations are conducted at hazardous waste sites under conditions that closely simulate full-scale remediation, thus assuring the usefulness and reliability of information collected. Data collected are used to assess the performance of the technology, the potential need for pre- and post-treatment processing of wastes, potential operating problems, and approximate costs. The demonstrations also allow evaluation of long-term risks and operating and maintenance (O&M) costs.

The Emerging Technology Program focuses on successfully proven, bench-scale technologies that are in an early stage of development involving pilot-scale or laboratory testing. Successful technologies are encouraged to advance to the Demonstration Program. The constructed wetlands is an example of a successful graduate of the Emerging Technology Program that was evaluated in the Demonstration Program.

Existing technologies that improve field monitoring and site characterization are identified in the Monitoring and Measurement Technologies Program. New technologies that provide faster, more cost-effective contamination and site assessment data are supported by this program. The Monitoring and Measurement Technologies Program also formulates the protocols and standard operating procedures for demonstrating methods and equipment.

The Technology Transfer Program disseminates technical information on innovative technologies in the Demonstration, Emerging Technology, and Monitoring and Measurement Technologies Programs through various activities. These activities increase the awareness and promote the use of innovative technologies for assessment and remediation of Superfund sites. The goal of technology transfer is to promote communication among remedial managers requiring up-to-date technical information.

Technologies are selected for the SITE Demonstration Program through annual requests for proposals. ORD staff review the proposals, including any unsolicited proposals that may be submitted throughout the year, to determine which technologies show the most promise for use at Superfund sites. Technologies chosen must be at

the pilot- or full-scale stage, must be innovative, and must have some advantage over existing technologies. Mobile technologies are of particular interest. Once EPA has accepted a proposal, cooperative agreements between EPA and the technology developer establish responsibilities for conducting the demonstrations and evaluating the technology. The developer is responsible for demonstrating the technology at the selected site and is expected to pay any costs for transportation, operation, and removal of equipment. EPA is responsible for project planning, site preparation, sampling and analysis, quality assurance and quality control (QA/QC), and for preparing reports, disseminating information, and transporting and disposing of untreated and treated waste material. For the CWS evaluation, CDPHE (the lead agency of the Burleigh Tunnel site) identified passive wetlands treatment as the preferred treatment alternative with agreement by EPA and the division of responsibilities was essentially as described.

The results of the CWS technology demonstration are published in two documents: the SITE technology capsule and the present ITER. The SITE technology capsule provides relevant information on the technology, emphasizing key features of the results of the SITE field demonstration. The ITER is discussed in the following section. Both the SITE technology capsule and the ITER are intended for use by remedial managers making a detailed evaluation of the technology for a specific site and waste.

## 1.2 Purpose of the Innovative Technology Evaluation Report

The ITER provides information on the CWS technology and includes a comprehensive description of the demonstration and its results. The ITER is intended for use by EPA remedial project managers, EPA on-scene coordinators, contractors, and other decision makers for implementing specific remedial actions. The ITER is designed to aid decision makers in evaluating specific technologies for further consideration as an option in a particular cleanup operation. This report represents a critical step in the development and commercialization of a treatment technology. To encourage the general use of demonstration technologies, EPA provides information regarding the applicability of each technology to specific sites and wastes. Therefore, the ITER includes information on cost and site-specific characteristics. It also discusses advantages, disadvantages, and limitations of the technology. Each SITE demonstration evaluates the performance of a technology in treating a specific waste. The waste characteristics at other sites may differ from the characteristics of the treated waste. Therefore, successful field demonstration of a technology at one site does not necessarily ensure that it will be applicable at other sites. Data from the field demonstration may require extrapolation for estimating the operating ranges in which the technology will perform satisfactorily. Only limited conclusions can be drawn from a single field demonstration.

## 1.3 Technology Description

The Colorado Department of Public Health and Environment submitted a proposal to the SITE program for demonstrating the anaerobic compost CWS technology. This technology was selected for a SITE demonstration at the Burleigh Tunnel in Silver Plume, Colorado. The demonstration was carried out under a cooperative agreement involving the EPA National Risk Management Research Laboratory (NRMRL), CDPHE, and EPA Region 8.

The Burleigh Tunnel is located approximately 50 miles west of Denver in the Silver Plume - Georgetown mining district (Figure 1), within the Clear Creek/Central City Superfund site. The Silver Plume - Georgetown mining district occupies an area of about 25 square miles surrounding the towns of Silver Plume and Georgetown. The tunnel entrance is at an elevation of 9,152 feet, about 400 feet north of Clear Creek, on the western side of the town of Silver Plume. The area immediately surrounding the tunnel entrance is littered with mill tailings and waste rock dumps. Dilapidated buildings and equipment from previous milling operations are also present. No mining operations are active in the immediate area. The water draining from the Burleigh Tunnel is of near-neutral pH (ranging from 6.9 to 7.9) and has high zinc concentrations (ranging from 44.8 to 109 mg/L). The drainage also contains moderate alkalinity and low levels of metals other than zinc.

A treatability study was conducted at the Burleigh Tunnel between June 18, 1993 and August 12, 1993. The treatability study involved the construction, operation, and sampling of two upflow compost and hay bioreactors that treated mine drainage from the Burleigh Tunnel. The treatability study (PRC 1993) showed that low levels of sulfate in the mine drainage would not limit biological sulfate reduction, thereby permitting the removal of zinc and other metals by the bioreactors or the demonstration scale treatment cells. Construction of the CWS demonstration cells began in August 1993 and was

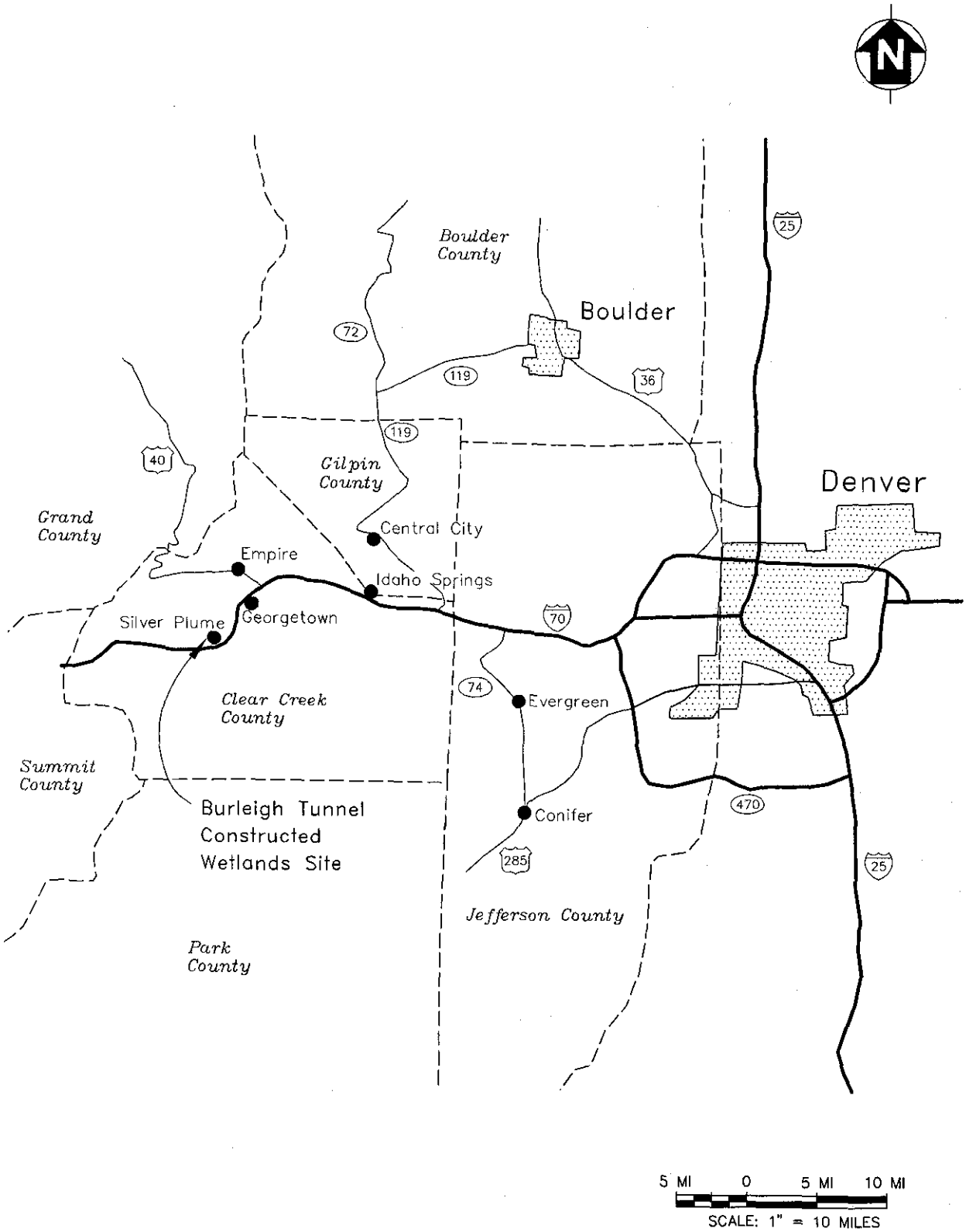


**Figure 1.** Site location.

completed in November 1993. The demonstration began in January 1994 and continued for a 46-month period through November 1997. Evaluation of the CWS technology is based on results of the treatability study and the SITE demonstration at the Burleigh Tunnel site.

### 1.3.1 Treatment Technology

There are generally three types of constructed wetlands: free-water surface systems, subsurface flow systems, and aquatic plant systems (EPA 1988). A free-water system typically consists of shallow basins or channels with slow- flowing water and plant life. A subsurface flow wetland consists of basins or channels filled with permeable substrate material; the water flows through, rather than over, this substrate. An aquatic plant system is essentially a free water surface system with deeper channels containing floating or suspended plants. In general, free-water surface and aquatic plant systems are aerobic wetlands that remove metals primarily by aerobic oxidation of iron followed by precipitation of iron hydroxides, that leads to the precipitation or adsorption of other metals. Aerobic wetlands are most successful in removing iron, arsenic, selenium and, to some extent, manganese from moderately low to neutral pH mine waters (Gusek and others 1994).

Anaerobic compost wetlands are designed to treat mine drainage through a combination of physical, chemical, and biological processes. Mine drainage is directed into constructed wetlands that contain an organic-rich compost substrate. Initially, sorption to the CWS substrate is the primary metal removal mechanism active within the system. Sorption includes adsorption of metals to organic and inorganic wetlands materials and absorption of metals into wetlands microorganisms and plants.

- Adsorption refers to the binding of positively charged ions to mineral surfaces by metal cations in solution. The sorption of inorganic ions is largely determined by complex chemical equilibria involving the charge and size of the element or complex ion, the nature of the sorbing material, and the pH of the aqueous solution. The properties of the surface that influence inorganic sorption include net surface charge and the presence, configuration, and pH dependence of binding sites. The structure of the solid may also affect adsorption reactions.

- Absorption refers to the incorporation of ions or compounds into the cell structure of microorganisms or plants. Metals may also be incorporated into the structure of complex humic substances formed during the degradation of the substrate.

After several months, the sorption capacity of the wetlands is exhausted and metal removal efficiencies by this mechanism decline.

Once the sorption capacity of the CWS substrate is expended, the formation, precipitation, and filtration of metal sulfides become the primary metal removal mechanism in the CWS. The process is believed to be biologically mediated by sulfate-reducing bacteria present in anaerobic zones within the CWS.

The bacteria oxidize organic matter provided by the wetland with the simultaneous reduction of sulfate to hydrogen sulfide. The hydrogen sulfide reacts with dissolved metals to produce metal sulfides. The metal sulfides, with low aqueous solubilities, precipitate and become trapped in the wetlands substrate by filtration. The following reactions illustrate the overall oxidation/ sulfate reduction reactions and subsequent formation of metal sulfides.

$$SO_4^{-2} + 2CH_2O \longrightarrow HS^- + 2HCO_3^- + H^+$$

$$M^{+2} + H_2S \text{ or } HS^- \longrightarrow MS(s) + 2H^+$$

where: M is a metal such as zinc ($Zn^{+2}$), iron ($Fe^{+2}$), nickel ($Ni^{+2}$), and (s) indicates a solid.

In addition, other reactions within the wetlands may contribute to observed metal removal, including mineral precipitation and chelation (binding) to suspended organic material. In general, mine drainage contains low levels of dissolved oxygen that, when exposed to air, will take up oxygen and become aerobic. This process can lead to geochemical disequilibrium where the metal is no longer soluble at this concentration and may initiate metal precipitation. Zinc carbonate (Smithsonite) is an example of a mineral that may precipitate in the demonstration downflow CWS. In addition, the decay of wetland compost and biomass will produce dissolved and suspended organic material in the wetland pore water. These materials can chelate metals in solution. Although chelated metals may not be effectively removed (filtered) by the wetland, they may not be available biochemically to aquatic plants and organisms exposed to the effluent.

### 1.3.2 System Components and Function

Two CWS treatment cells were located adjacent to the Burleigh Tunnel between a compressor building and an old mill. Each cell covered 0.05 acre; the two cells differed in flow configuration. The cell nearest the mine

adit was an upflow system, in which water entered the cell under pressure from the bottom and flowed upward through the substrate material to discharge. The second cell was a downflow system, in which the water entered the cell from the top and flowed by gravity to the bottom for discharge. The demonstration CWS cells were highly engineered systems compared to many of the previously tested constructed wetlands, including the Big 5 wetlands evaluated in the Emerging Technology Program (EPA/540/R-93/523). Figure 2 shows a cross-section schematic of the upflow CWS treatment cell. The downflow cell was identical except the direction of mine drainage flow in the compost is reversed.

Both CWS treatment cells were installed below grade to reduce freezing of the cells during winter. Both had bermed earthen side walls. The base of each cell was made up of a gravel subgrade, a 16-ounce geofabric, a sand layer, a clay liner, and a high density polyethylene liner. The base was separated from the influent or effluent piping by a geonet. A 7-ounce geofabric separated the perforated PVC piping from the compost. The compost was held in place with a combination of 7-ounce geofabric and geogrid in the upflow cell. The perforated effluent piping was also supported by the geogrid in the upflow cell. Up to 6 inches of dry substrate material was located above the perforated piping. The geonet and the perforated piping ensured even distribution of the influent water into the treatment cells and prevented short circuiting of water through the cells. The influent and effluent distribution piping were also staggered horizontally as an additional precaution against short circuiting.

Existing construction near the Burleigh Tunnel entrance required that the upflow cell be 10 percent smaller by volume than the downflow cell. The dimensions of the cells are as follows:

- Upflow cell - 69 feet long, 25.5 feet wide, and 4 feet deep, with an estimated total substrate volume of 198 cubic yards
- Downflow cell - 62 feet long, 33 feet wide, and 4 feet deep, with an estimated total substrate volume at 218 cubic yards

*Note: The dimensions listed are at the top of the cell wall. The volumes listed take into account the sloped walls of the cells.*

The organic-rich compost substrate was composed of a mixture of 95 to 96 percent manure compost and 4 to 5 percent hay. The compost was produced from cattle manure and unidentified paper products. The compost and hay mixture had been identified as the most effective medium in removing zinc from the drainage during the previous bench-scale test (Camp, Dresser and McKee 1993). Wood based substrates have also been used in constructed wetland systems.

The flow to the CWS cells was regulated by a series of concrete v-notch weirs, one for the influent and one for the effluent of each cell. The effluent weir controlled the flow and the hydraulic residence time of the mine drainage through both CWS cells. Each cell was designed for a flow of 7 gpm with a total flow capacity for the two cells of 14 gpm. The remaining flow from the Burleigh Tunnel drainage was diverted to Clear Creek (untreated) via the influent weir. A drainage collection structure was constructed within the Burleigh Tunnel to build sufficient hydraulic head to drive the flow through the two CWS.

### 1.3.3 Key Features of the CWS Technology

Certain features of the CWS technology allow it to be adapted to a variety of settings:

- The hardware components (geosynthetic materials, PVC piping, and flow control units) of the CWS are readily available.
- Compost materials can be composed of readily available materials. However, the actual composition of a substrate material for a site-specific constructed wetland is best determined through pilot studies. Composted manure was used during this study.
- Operation and maintenance costs are low since the systems are generally self-contained, requiring only periodic changes of the compost depending on site-specific conditions.

Other features that should be thoroughly evaluated before constructing a CWS include the following:

- Properties of the drainage to be treated. Some drainages may need some type of pretreatment before entering the CWS. For example, drainage with high iron or aluminum content might prematurely clog the CWS if not pretreated to remove some of the metal.
- Climate conditions must be evaluated to assess the potential for reduced efficiency of the system during different seasons of the year.
- Contingencies if the system does not perform as expected.

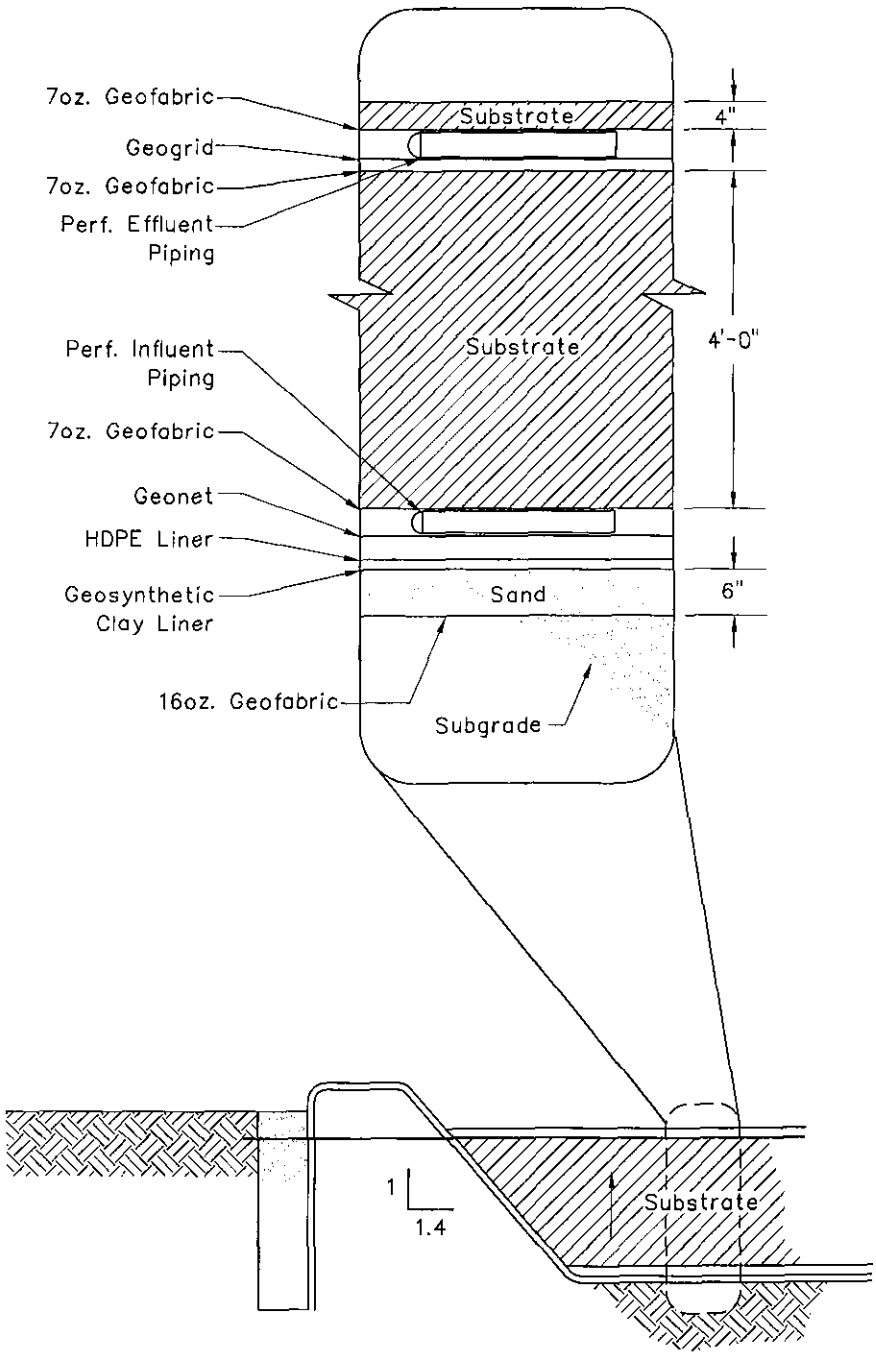


**Figure 2.** Schematic cross-section of an anaerobic CWS upflow cell.

- Proximity to a populated area—odors generally are associated with CWS treatment.
- Land availability near the source of the contaminated water to avoid extended transport. The CWS typically requires more land than a conventional treatment system. Consequently, locations with steep slopes and drainages would make construction more difficult and costly.
- Cost of constructing the system if substrate and other materials are not readily available.
- Possible use of concrete basins to eliminate replacement costs for liners.
- Potential for vandalism of the CWS, which could result in increased costs.
- Seasonal fluctuation of water flow or chemistry and the potential impact to the CWS.
- Production and release of nutrients from substrate and stream standard requirements for discharge of produced nutrients

## 1.4 Key Contacts

Additional information on the CWS technology, the SITE program, and the demonstration site can be obtained from the following sources:

**The CWS Technology**

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**The SITE Program**

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**The Clear Creek/Central City Superfund Site**

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# Section 2
# Technology Applications Analysis

This section of the ITER describes the general applicability of the CWS technology to contaminated waste sites. The analysis is based primarily on the SITE CWS treatability study and demonstration results. A detailed discussion of the treatability study and demonstration results is presented in Section 3.0 of this report. An article containing a constructed wetlands case study is presented in Appendix B.

## 2.1 Applicable Wastes

Constructed wetlands have been demonstrated to be effective in removing organic, metal, and nutrient elements including nitrogen and phosphorus from municipal wastewaters, mine drainage, industrial effluents, and agricultural run-off. The technology is waste-stream specific, requiring characterization of all organic and inorganic constituents.

Because constructed wetlands can treat a wide variety of wastes, they vary considerably in their design. Constructed wetlands can be simple, single-cell systems, such as the two cells evaluated during this demonstration, or complex multicell or multicomponent systems. Complex constructed wetlands may include multiple wetland cells in series, anoxic limestone drains, marshes, ponds, and rock filters. Constructed wetlands tested in the eastern U.S. to remediate slightly acidic coal mine drainage have incorporated an anoxic limestone drain to provide alkalinity, followed by a holding pond, a constructed wetland, a shallow marsh, and finally a rock filter. The holding pond and wetland promote precipitation of iron hydroxides, while the marsh and rock filter remove manganese and suspended solids. Constructed wetlands design criteria are discussed in detail in an article by Gusek and Wildeman (1995).

The results of the CWS demonstration (see Section 3.0) suggest the primary metals removal mechanisms are not identical within the upflow and downflow wetland cells. In the upflow cell, biological sulfate reduction appeared to be the primary zinc removal mechanism. Metals shown to be removed by this process include cadmium, copper, iron, lead, nickel, silver, and zinc (PRC 1995). In addition, biological sulfate reduction may also remove cobalt, mercury, and molybdenum contamination. In the downflow cell, chemical precipitation appeared to be the primary zinc removal mechanism. Because of the numerous geochemical species and complex equilibria involved in wetlands treatment of mine drainage, it is often difficult to predict which metals will precipitate. An equilibrium aqueous geochemical wetlands model (MINTEQ.AK) has been developed to help predict metal removal by constructed wetlands (Klusman 1993).

## 2.2 Factors Affecting Performance

Because CWS designs are so diverse, the number of parameters affecting their operation is also large. In the discussion that follows, the performance factors described pertain to this demonstration CWS (anaerobic compost) or to similar systems treating metal-contaminated mine drainage. These performance factors may or may not be relevant to constructed wetlands designed to treat organic or inorganic (nonmetal) contamination. Several factors influenced the performance of the two demonstration CWS. These factors can be grouped into three categories: (1) mine drainage characteristics, (2) operating parameters, and (3) compost degradation.

### *2.2.1 Mine Drainage Characteristics*

The CWS technology is capable of treating a range of contaminated waters containing heavy metals. However, the effectiveness of a CWS can be reduced as contaminants in high concentrations precipitate and clog the system prematurely. Often, contaminated coal mine drainages in the eastern U.S. contain elevated concentrations of iron or aluminum. When the pH of these drainages is raised during wetland treatment, iron and

aluminum hydroxides can form and precipitate (Hedin and others 1994).

These precipitates can lead to a loss of permeability or a gradual filling of the wetland. Because sulfate-reducing bacteria cannot survive in low pH environments, low pH mine drainage can also affect the ability of the biological sulfate reduction wetland to remove contaminants. The oxidation/reduction potential (ORP) of the mine drainage may also affect the performance of the constructed wetland. However, the extent of the ORP effect is unknown.

### 2.2.2 Operating Parameters

The operating parameters that can be adjusted during the treatment process include the flow rate and hydraulic residence time of water within the wetland. In general, the selection and design for the hydraulic residence time is a function of the rate of metal loading. A hydraulic residence time of 50 to 100 hours was found to work well in the biological sulfate reduction reactors used during the short-term CWS treatability study (Figure 3).

The residence time in the upflow and downflow cells during the demonstration was calculated at between 50 and 60 hours. The calculation was based on the substrate volume of the wetlands, the percent moisture of the substrate (generally, 50 to 65 percent with 50 percent used in the calculation), and a flow rate of 7 gpm.

Maintaining proper hydraulic residence times is one of the most important factors in successful wetlands treatment. In biological-based systems, a short residence time may not allow metals to precipitate and be filtered out by the wetland or may expose the bacteria to inhibitory levels of metal contaminants. Both may result in lower metal removal rates. In chemical precipitation systems, compounds that precipitate slowly may not be removed to the same extent as rapidly precipitating compounds.

Chemical amendments, such as alkalinity or nutrients, are also examples of parameters that can be adjusted during the wetland treatment process. Alkalinity may be added via an anoxic limestone drain or directly to the mine drainage as lime. Nutrients could also be added directly to the mine drainage or applied to the ponded surface water of downflow cells. Neither alkalinity nor nutrients was added to the SITE demonstration CWS.

### 2.2.3 Compost Performance

Compost performance depends on the compost materials used and the characteristics of the mine drainage. When using manure compost, the metals concentrations of the drainage, the nutrient concentrations in the compost, and gradual breakdown and compaction of the compost materials are the most important factors controlling compost effectiveness. Of these factors, substrate breakdown and compaction that leads to a loss of hydraulic conductivity is probably the most important factor. The breakdown of the complex biological polymers to smaller compounds by fermentative bacteria gradually destroys the structural intensity of the compost and leads to compaction. One way to extend substrate lifetime is to include materials that are degraded at a moderate rate. Based on the loss of nutrients and hydraulic conductivity in the upflow CWS, the wetland compost material is expected to last 4 to 5 years before becoming ineffective.

The accumulation of metals within the constructed wetlands may eventually cause the compost material to become a hazardous waste, substantially decreasing the number of compost disposal options and increasing treatment costs.

However, after 4 years of near-continuous operation of the demonstration CWS, neither cell's compost material developed hazardous characteristics based on thresholds defined in 40 Code of Federal Regulations (CFR) Part 261.24. However, the primary contaminant in the Burleigh Mine Drainage, zinc is not a TCLP analysis parameter.

## 2.3 Site Characteristics

Site characteristics are important when considering CWS technology because they can affect system application. All characteristics should be considered before selecting the technology to remediate a specific site. Site-specific factors include support systems, site area and preparation, site access, climate, hydrology, utilities, and the availability of services and supplies.

### 2.3.1 Support Systems

If on-site facilities are not already available, a small storage building equipped with electricity may be desirable near the treatment system. The on-site building could be used for storing operating and sampling equipment (tools, field instrumentation, and health- and safety-related gear) and providing shelter for sampling personnel during inclement weather. The building may also be used for calibrating field equipment for system monitoring.

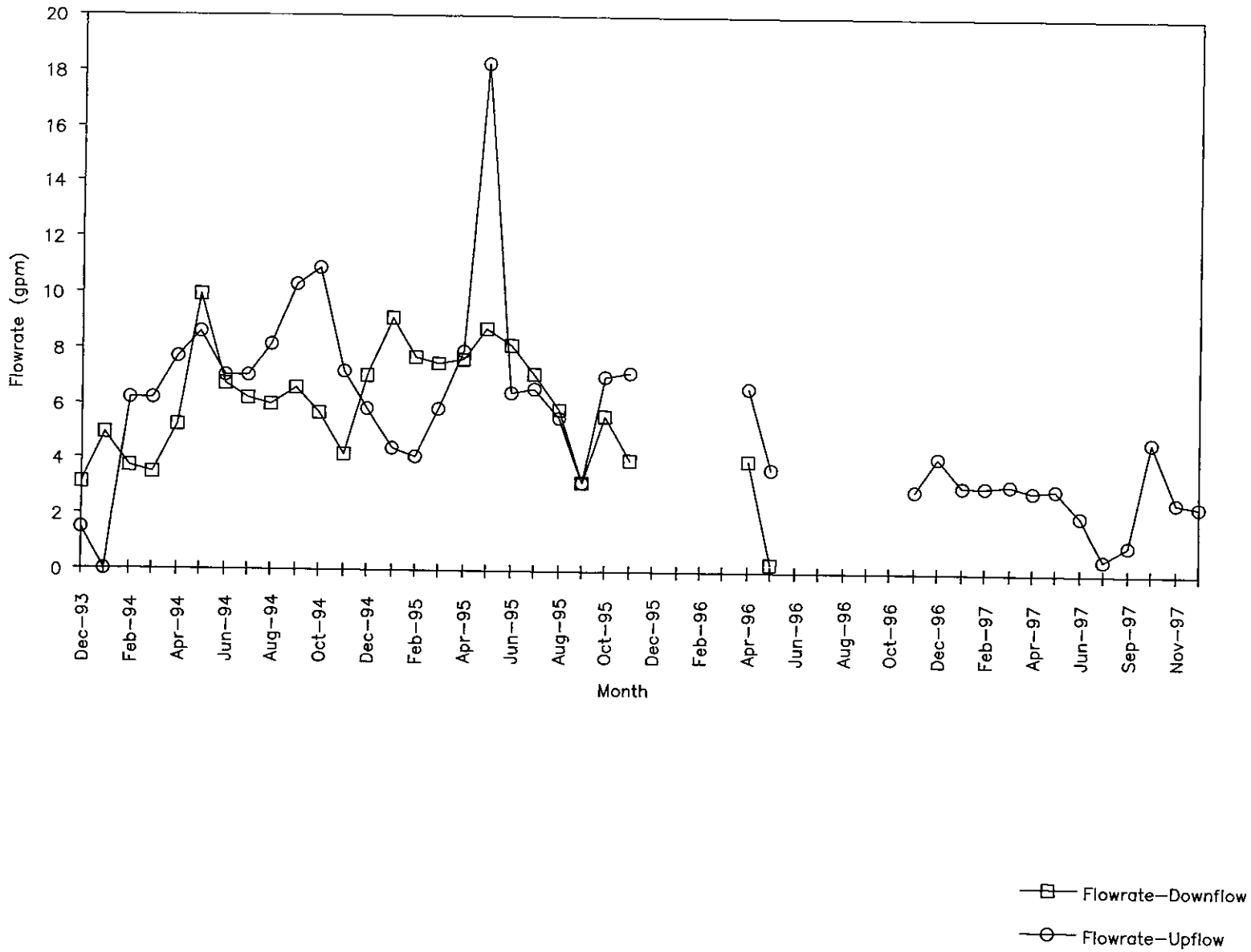


**Figure 3.** Flow rates measured for effluent cells.

### 2.3.2 Site Area, Preparation, and Access

Constructed wetlands typically require a larger level area compared to other treatment options. The results of this investigation suggest that a 50-60 hour hydraulic residence time is near the lower limit required of these systems to provide consistent metal removal. Researchers in this field have suggested that longer residence times ranging from 75 to 150 hours may be required for long-term metal removal (Dr. Ronald Klusman and Dr. Richard Gammons, personal communications) The depth of the compost in the demonstration CWS cells was 4 feet. The maximum depth of compost that can be used while maintaining treatment effectiveness is unknown. Consequently, some sites may require extensive grading and leveling to allow construction of a CWS. Depending on the site, grading and leveling may be cost prohibitive.

Piping or other mechanisms for conveying mine drainage to the wetlands is also necessary. In addition, a relatively constant rate of flow is desired to keep the wetlands active. Thus, site conditions may require a mine drainage collection, storage, and distribution structure.

Furthermore, an upflow constructed wetland may require that the mine drainage distribution network include a dam or pump to maintain sufficient hydraulic head to force the mine drainage through the compost. Also, piping is required to bypass flow around the wetland. This bypass piping or conveyance should be oversized to manage 200 to 300 percent of the predicted maximum mine drainage discharge.

Access roads for heavy equipment (excavation and hauling) are required to install, operate, and maintain a CWS.

### 2.3.3 Climate

The climate at potential constructed wetland sites can be a limiting factor. Extended periods of severe cold, extreme hot and arid conditions, and frequent severe storms or flooding will affect system performance. Extreme cold can freeze portions of the wetland resulting in channeling of the mine drainage through the substrate, thus, reducing the hydraulic residence time. In addition, cold temperatures may reduce microbial activity or populations. Reductions in hydraulic residence time and microbial activity will both lessen the ability of the constructed wetland to remove metals and may require it to be oversized. The large water surface areas and plant life associated with wetlands enhance evaporation and evapotransportation. A constructed wetland in a hot and arid climate may periodically dry up at a site with low water flow rates. If the wetland design does not consider cyclical periods of wet and dry, it may be less effective during the wet periods. Constructing wetlands in areas with frequent flooding or severe storms can lead to hydraulic overloading or washout of substrate materials. The engineering controls required to overcome these climatic or geographic limitations may eliminate the low cost and low maintenance advantages that make constructed wetlands appealing.

### 2.3.4 Utilities

The CWS is a passive treatment technology, so utilities are not required to operate the system. However, in some situations electricity for pumps or on-site analytical instrumentation may be desirable. In remote areas, an on-site storage building should be provided if possible. A telephone connection or cellular phone is required for operating and sampling personnel to contact emergency services if needed and for routine communications.

### 2.3.5 Services and Supplies

The main services required by the CWS are periodic adjustment of system flow rates, cleanout of effluent piping, and the removal and replacement of compost materials. During the CWS demonstration, flow rate adjustments were required every 3 to 6 months, and effluent piping cleanout was conducted once. However, both CWS demonstration cells were operated from a single v-notch weir and the flow diverted to the cells. The frequency of flow adjustment would be lower if each cell had been constructed with its own weir. The time between changeout of wetland compost depends on the chemical constituents of the influent water, the configuration and capacity of the constructed wetland, and the preferred method of disposal. The compost lifetime, estimated from nutrient loss and the development of short circuiting during this demonstration is estimated to be 4 to 5 years.

## 2.4 Availability, Adaptability, and Transportability of Equipment

The components of a simple CWS are generally available locally. The components include standard construction materials for the structure of the wetland cells, liner materials available from several sources, and compost materials, the type of which will depend on the contaminants in the mine drainage. The most suitable compost for a given application can be identified during a treatability study using materials available locally.

## 2.5 Material Handling Requirements

The CWS generates spent compost material. Substrate material will require testing to evaluate disposal options. Depending on the disposal option, dewatering or other pretreatment may be necessary prior to shipment for off-site disposal. Depending on regulatory requirements, the effluent water generated during dewatering may also require additional treatment prior to discharge.

Some CWS compost materials may contain high levels of water-soluble nitrogen or phosphorus compounds. These compounds can be readily leached from the fresh compost during startup of the constructed wetland. Thus, the CWS effluent at startup may require treatment to reduce or remove excess nitrogen or phosphorous. Treatment may include land application, if permitted, or effluent collection for subsequent recycling through the CWS.

## 2.6 Personnel Requirements

Wetlands construction and compost replacement require heavy equipment operators, laborers, and a construction supervisor. After the CWS is installed, personnel requirements include a sampling team and personnel to adjust system flow rates. Sampling personnel should be able to collect water and substrate samples for laboratory analysis and measure field parameters using standard instrumentation.

All personnel should have completed an Occupational Safety and Health Administration (OSHA) initial 40-hour health and safety training course with annual 8-hour refresher courses, if applicable, before constructing, sampling, replacing compost, or removing a constructed wetland at hazardous waste sites. They should also participate in a medical monitoring program as specified under OSHA requirements.

## 2.7 Potential Community Exposures

Fencing and signs should be installed around a CWS to restrict access to the system for both humans and wildlife. The potential routes of exposure include the mine drainage or waste stream, the compost material, and the CWS effluent. The actual exposure risk depends on the constituents of the specific waste being treated and the effectiveness of the treatment.

The CWS may also generate low concentrations of hydrogen sulfide gas, depending on the time of year and the biological activity of the CWS. Odors caused by hydrogen sulfide and volatile fatty acids from the decaying manure may be a nuisance to a local community.

## 2.8 Evaluation of Technology Against RI/FS Criteria

EPA has developed nine evaluation criteria to fulfill the requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), as well as additional technical and policy considerations that have proven important for selecting potential remedial alternatives. These criteria serve as the basis for conducting bench-scale testing during the remedial investigation (RI) at a hazardous waste site, for conducting the detailed analysis during the feasibility study (FS), and for subsequently selecting an appropriate remedial action. Each SITE technology is evaluated against the nine EPA criteria because these technologies may be considered as potential remedial alternatives. The nine evaluation criteria are:

- Overall protection of human health and the environment
- Compliance with applicable or relevant and appropriate requirements (ARAR)
- Long-term effectiveness and permanence
- Reduction of toxicity, mobility, or volume
- Short-term effectiveness
- Implementability
- Cost
- State acceptance
- Community acceptance

Table 1 presents the results of this evaluation for the CWS. The demonstration results indicate the upflow CWS can provide short-term protection of the environment; reduces contaminant mobility, toxicity, and volume; is cost effective; implementable, and is an acceptable remedy to the community and state regulators. However, neither CWS cell tested in this demonstration, provided long-term effectiveness. This in part is the result of low zinc discharge requirements (200 μg/L) at the demonstration site. Other sites may have less strict discharge requirements. In addition, the upset condition resulting from the high flow event also contributed to the lack of long-effectiveness particularly in regards to the upflow cell.

**Table 1.** Evaluation of CWS Treatment Versus RI/FS Criteria

| Criterion | Discussion |
|---|---|
| 1. Overall Protection of Human Health and the Environment | As tested, the CWS provided only short-term effectiveness. In different circumstances, the CWS may provide short- and long-term protection by removing mine drainage contaminants.<br><br>Substrate is a recycled product, not mined or manufactured. |
| 2. Compliance with Applicable or Relevant and Appropriate Requirements (ARAR) | Wetland effluent discharge may require compliance with Clean Water Act regulations.<br><br>Substrate disposal may require compliance with RCRA regulations. |
| 3. Long-Term Effectiveness and Permanence | CWS treatment removes contamination from mine drainage, but may not meet low-level discharge requirements.<br><br>Use of CWS treatment with other technologies may be effective in meeting low-level discharge requirements. |
| 4. Short-term Effectiveness | Presents few short-term risks to workers, community, or wildlife.<br><br>Minimal personal protective equipment required for operators. |
| 5. Reduction of Toxicity, Mobility, or Volume of contaminates through Treatment | CWS treatment reduces contaminant mobility, toxicity, and volume. |
| 6. Implementability | Generally a passive treatment system, but can be active.<br><br>Construction uses standard material and practices common in the industry. |
| 7. Cost | Construction cost of full-scale (50gpm) system is estimated at approximately $290,000.<br><br>O&M of full-scale CWS system is estimated to be $57,000 per year. |
| 8. Community Acceptance | The public usually views the technology as a natural approach to treatment; therefore, the public generally accepts this technology. |
| 9. State Acceptance | CDPHE found the technology shows promise for treating AMD; however, based on constraints at the Burleigh site, including the cold climate and proximity to town, CDPHE recommended not implementing a full-scale, permanent system at the site.<br><br>Colorado Division of Minerals has built several CWSs to treat AMD. |

## 2.9 Potential Regulatory Requirements

This section discusses specific environmental regulations pertinent to operation of a CWS, including the transport, treatment, storage, and disposal of wastes and treatment residuals, and analyzes these regulations in view of the demonstration results. State and local regulatory requirements, which may be more stringent, must also be addressed by remedial managers.

ARARs include the following: (1) CERCLA; (2) the Resource Conservation and Recovery Act (RCRA); (3) the Clean Water Act; and (4) OSHA regulations. These four general ARARs are discussed below; specific ARARs must be identified by remedial managers for each site.

### *2.9.1 Comprehensive Environmental Response, Compensation, and Liability Act*

CERCLA, as amended by SARA, authorizes the federal government to respond to releases or potential releases of any hazardous substance into the environment, as well as to releases of pollutants or contaminants that may present an imminent or significant danger to public health and welfare or the environment.

As part of the requirements of CERCLA, EPA has prepared the National Oil and Hazardous Substances Pollution Contingency Plan (NCP) for hazardous substance response. The NCP, codified at 40 CFR Part 300, delineates methods and criteria used to determine the appropriate extent of removal and cleanup for hazardous waste contamination.

SARA amended CERCLA and directed EPA to:

- Use remedial alternatives that permanently and significantly reduce the volume, toxicity, or mobility of hazardous substances, pollutants, or contaminants.
- Select remedial actions that protect human health and the environment, are cost-effective, and involve permanent solutions and alternative treatment or resource recovery technologies to the maximum extent possible.
- Avoid off-site transport and disposal of untreated hazardous substances or contaminated materials when practicable treatment technologies exist (Section 121[b]).

In general, two types of responses are possible under CERCLA: removals and remedial actions. The CWS technology is likely to be part of a CERCLA remedial action. Remedial actions are governed by CERCLA as amended by SARA. As stated above, these amendments promote remedies that permanently reduce the volume, toxicity, and mobility of hazardous substances, pollutants, or contaminants.

On-site remedial actions must comply with federal and state ARARs. ARARs are identified on a site-by-site basis and may be waived under six conditions: (1) the action is an interim measure, and the ARAR will be met at completion; (2) compliance with the ARAR would pose a greater risk to human health and the environment than noncompliance; (3) it is technically impracticable to meet the ARAR; (4) the standard of performance of an ARAR can be met by an equivalent method; (5) a state ARAR has not been consistently applied elsewhere; and (6) ARAR compliance would not provide a balance between the protection achieved at a particular site and demands on the Superfund for other sites. These waiver options apply only to Superfund actions taken on site, and justification for the waiver must be clearly demonstrated.

### *2.9.2 Resource Conservation and Recovery Act*

RCRA, an amendment to the Solid Waste Disposal Act (SWDA), was enacted in 1976 to address the problem of safe disposal of the enormous volume of municipal and industrial solid waste generated annually. RCRA specifically addressed the identification and management of hazardous wastes. The Hazardous and Solid Waste Amendments of 1984 (HSWA) greatly expanded the scope and requirements of RCRA.

The presence of RCRA-defined hazardous waste determines whether RCRA regulations apply to the CWS technology. RCRA regulations define and regulate hazardous waste transport, treatment, storage, and disposal. Wastes defined as hazardous under RCRA include characteristic and listed wastes. Criteria for identifying characteristic hazardous wastes are included in 40 CFR Part 261 Subpart C. Listed wastes from nonspecific and specific industrial sources, off-specification products, spill cleanups, and other industrial sources are itemized in 40 CFR Part 261, Subpart D.

The CWS demonstration treated mine discharge water from the Burleigh Tunnel, which is included in the Clear Creek/Central City Superfund site. The manure compost was tested regularly to determine whether it would become a hazardous waste during the demonstration. The concern

was that sorption and precipitation of metals could cause the substrate to become a hazardous waste, thus restricting options and increasing cost for material disposal. The substrate did not exhibit the characteristics of hazardous waste after nearly 4 years of operation.

### 2.9.3 Clean Water Act

The objective of the Clean Water Act is to restore and maintain the chemical, physical, and biological integrity of the nation's waters. To achieve this objective, effluent limitations of toxic pollutants from point sources were established. Wastewater discharges are most commonly controlled through effluent standards and discharge permits administered through the National Pollutant Discharge Elimination System (NPDES) by individual states with input from the federal EPA. Under this system, discharge permits are issued with limits on the quantity and quality of effluents. These limits are based on a case-by-case evaluation of potential environmental impacts and on wasteload allocation studies aimed at distributing discharge allowances fairly. Discharge permits are designed as an enforcement tool with the ultimate goal of achieving ambient water quality standards (Metcalf and Eddy 1979).

NPDES permit requirements must be evaluated for each CWS when the effluent water is discharged into a waterway or water body. The requirements and standards that must be met in the effluent for each CWS will be based on the waterway or water body into which the CWS discharges. The effluent limits will be established through the NPDES permitting process by the state in which the CWS is constructed and by EPA.

CDPHE has identified stream standards for Clear Creek at the Burleigh Tunnel discharge. Table 2 provides these standards for both low- and high-flow conditions. The zinc standard for both low- and high-flow conditions is 200 μg/L in the receiving stream (Clear Creek). In order to met this standard, the discharge from Burleigh Tunnel must contain less than 13,650 μg/L zinc under low-flow conditions and 65,700 μg/L under high-flow conditions.

### 2.9.4 Occupational Safety and Health Act

CERCLA remedial actions and RCRA corrective actions must be conducted in accordance with OSHA requirements detailed in 29 CFR Parts 1900 through 1926, especially Part 1910.120, which provides for health and safety of workers at hazardous waste sites. On-site construction at Superfund or RCRA corrective action sites must be conducted in accordance with 29 CFR Part 1926, which provides safety and health regulations for construction sites. State OSHA requirements, which may be significantly stricter than federal standards, must also be met.

Construction and maintenance personnel and sampling teams for the Burleigh Tunnel CWS demonstration all met the OSHA requirements for hazardous waste sites. For most sites, the minimum personal protective equipment (PPE) required would include gloves, hard hats (during construction), steel toed boots, and eye protection. Additional PPE may be required during summer or winter months to protect against extreme temperatures.

## 2.10 Limitations of the Technology

Land required for constructed wetland systems is typically extensive compared to conventional treatment systems. Thus, in areas with high land values, a constructed wetland treatment system may not be appropriate. Land availability relatively close to the source of contaminated water is preferred to avoid extended transport.

The climate at potential constructed wetland sites can also be a limiting factor. Extended periods of severe cold, extreme heat, arid conditions, and frequent severe storms or flooding can result in performance problems. Contaminant levels in treated and discharged water can vary in response to variations of influent volumes and chemistry. This may also be a limiting factor if there is no tolerance in contaminant level discharge requirements.

**Table 2.** Treatment Standards and Influent Concentrations of the CWS SITE Demonstration

| Element | Average Influent Concentration (µg/L) | Colorado Department of Public Health and Environment Chronic Water Quality Standards (Clear Creek) Low Flow (µg/L) | Colorado Department of Public Health and Environment Chronic Water Quality Standards (Clear Creek) High Flow (µg/L) |
|---|---|---|---|
| Aluminum | 20 | – | – |
| Arsenic | 6 | 150 | 150 |
| Cadmium | 89 | 0.84 | 0.49 |
| Copper | <10 | 8.5 | 4.7 |
| Iron | 302 | 1,000 | 1,000 |
| Lead | 16 | 2.25 | 0.84 |
| Magnesium | 46,000 | – | – |
| Manganese | 2,360 | 1,000 | 1,000 |
| Nickel | 47 | 0.1 | 42.09 |
| Potassium | 3,080 | – | – |
| Silver | 0.2 | 0.039 | 0.0117 |
| Sodium | 14,000 | – | – |
| Zinc | 57,000 | 200 | 200 |
| Sulfate | 383,000 | – | – |
| Fluoride | 102 | – | – |
| Chloride | 20,000 | – | – |
| Phosphorus (total) | ND | – | – |
| Orthophosphate | 66 | – | – |
| Nitrate plus Nitrite (as N) | 245 | – | – |
| Nitrite as N | ND | – | – |
| Nitrate as N | 245 | – | – |
| Ammonia | ND | 0.02 | 0.02 |

**Table 2 (continued).** Treatment Standards and Influent Concentrations of the CWS SITE Demonstration

| Element | Average Influent Concentration (µg/L) | Colorado Department of Public Health and Environment Chronic Water Quality Standards (Clear Creek) Low Flow (µg/L) | Colorado Department of Public Heal Environment Chronic Water Quality Sta (Clear Creek) High Flow (µg/L) |
|---|---|---|---|
| TSS | 11,300 | -- | -- |
| TDS | 680,000 | -- | -- |
| Alkalinity (total as $CaCO_3$) | 104,000 | -- | -- |
| Alkalinity (bicarbonate as $CaCO_3$) | 104,000 | -- | -- |
| *Dissolved Oxygen* (mg/L) | 7.9 | -- | -- |
| pH | 7.11 pH units | 6.5-8.5* | 6.5-8.5* |
| Conductivity | 723 µS | -- | -- |
| Temperature | 8.6 °C | -- | -- |

Notes:

* Secondary Maximum Contaminant Level
-- No standards exist

# Section 3
# Treatment Effectivemess

The following sections discuss the treatment effectiveness of the CWS demonstration in Silver Plume, Colorado. The discussion includes a background section, a review of the demonstration, demonstration methodology, site demonstration results, and demonstration conclusions.

## 3.1 Background

The Burleigh Tunnel is located approximately 50 miles west of Denver in the Georgetown-Silver Plume mining district (Figure 1). The Georgetown-Silver Plume mining district occupies an area of about 25 square miles surrounding the towns of Silver Plume and Georgetown. In general, the period of significant silver production in the area commenced in 1872, reached a peak in 1894, and gradually declined after. Mining in the district increased briefly during World Wars I and II, when many old mines were reopened and considerable amounts of lead and zinc were mined from old stopes, dumps, and wastes left from the silver mining boom.

The Burleigh Tunnel drains a group of mines on Sherman and Republican mountains. Many of these mines intercept shallow groundwater migrating through fractures in the rock or surface water collected by stopes. The intercepted waters are transported through the mines and are eventually discharged through the Burleigh Tunnel. The Burleigh Tunnel discharge contains elevated levels of zinc, typically between 45 and 65 mg/L. However, greater than normal precipitation during the spring of 1995 mobilized a large amount of zinc and increased zinc concentrations within the drainage to 109 mg/L. Burleigh Tunnel discharge rates are generally between 40 to 60 gpm and increase to 100 to 140 gpm during spring runoff. The elevated levels of zinc and significant flow rates combine to make the Burleigh Tunnel a major source of zinc to Clear Creek. Because of the large amount of zinc being discharged to Clear Creek and the potential impact of the zinc on the Clear Creek fishery, the drainage from the Burleigh Tunnel was included in the Clear Creek/Central City Superfund site.

The elevation of the Burleigh Tunnel is 9,152 feet, and the climate is typical of mountainous alpine regions in Colorado. Summers are short and cool and winters are long and cold. Strong eastward, down-valley winds are typical during the winter months. Winds are lighter during the summer months and occasionally blow westward, up the valley. Snow accumulation during the winter months in the immediate area of the tunnel is usually not significant due to the open, south-facing exposure of the hillside and high winds. Snow accumulation at higher elevations in more sheltered areas is significant, with some snow fields persisting until late summer. The average annual temperature is approximately 43.5 degrees Fahrenheit (°F), with a mean minimum of 31°F and a mean maximum of 55.9°F. The average annual precipitation is 15.14 inches.

## 3.2 Review of SITE Demonstration

The SITE demonstration was divided into three phases: (1) CWS treatability study; (2) CWS technology demonstration; and (3) site demobilization. These activities are reviewed in the following sections, which also discuss variations from the work plan and the CWS performance during the technology demonstration phase.

### *3.2.1 Treatability Study*

A treatability study was conducted at the Burleigh Tunnel between June 18, 1993, and August 12, 1993. The goal of the treatability study was to show that bacterial sulfate reduction could remove zinc from the low-sulfate mine drainage from the Burleigh Tunnel and to estimate levels of zinc reduction that could be expected by CWS treatment. The treatability study involved the construction, operation, and sampling of two bioreactors. Each bioreactor was

filled with a mixture of composted manure (96 percent) and alfalfa hay (4 percent), the same substrate that was to be used in the CWS demonstration treatment cells. Both reactors used an upflow configuration, in which Burleigh Tunnel drainage entered the bioreactors from the bottom and was forced to flow up through the substrate. The small bioreactor was 4 feet tall and 22 inches in diameter and held approximately 60 gallons of compost and water. The large bioreactor was 8 feet tall and 22 inches in diameter and held approximately 130 gallons of compost and water. The lower 6 inches of each bioreactor was filled with gravel to support inlet piping and minimize channeling. Peristaltic pumps were used to establish a flow rate of 20 to 30 milliliters per minute for the small bioreactor and 50 to 60 milliliters per minute for the large bioreactor. The flow rates for the bioreactors were set to provide an estimated hydraulic residence time of 50 to 100 hours.

The results of the treatability study indicated that after 8 weeks of operation, both bioreactors achieved removal efficiencies of 99 percent for zinc and similar efficiencies for cadmium and manganese. Zinc was the major metal of concern for the Burleigh Tunnel drainage. Sorption of metals in the substrate is believed to be the dominant removal process during the first 1 to 2 weeks of bioreactor operation. After this brief period of sorption, biological sulfate reduction apparently became the primary metal removal process in the bioreactors. Results of sulfate-reducing bacteria counts and sulfate and sulfide analyses indicated that a large population of sulfate-reducing microorganisms was active in the system. The results supported the theory that the bacteria reduce sulfate in the water to hydrogen sulfide ions, which react with dissolved metals to produce insoluble metal sulfides. The results indicated that the Burleigh Tunnel drainage contains a sufficient concentration of sulfate to promote metal removal by microbial sulfate reduction. Compost sample results from both bioreactors indicated that the compost accumulated metals and sulfide but did not become a reactive or hazardous waste after 8 weeks of operation.

### 3.2.2 Technology Demonstration

Site preparation requirements for the CWS demonstration were minimal because of previous mining and treatability study activities. Moreover, the area surrounding the Burleigh Tunnel adit is level and required only minor grading to install the two CWS treatment cells. Construction of the CWS treatment cells and all drainage conveyances was the responsibility of the developer (CDPHE).

The demonstration evaluated two treatment cells that differed only in flow configuration, one upward and the other downward. The demonstration evaluated the ability of each cell to remove zinc and other metals from the Burleigh Tunnel mine drainage without pretreatment. Efforts were made to maintain constant flow rates; however, flow rates did vary. In addition, several events resulted in brief interruptions of flow to the cells. Approximately 12.7 million gallons of water from the Burleigh Tunnel were passively treated by the upflow constructed wetland cell and 11 million gallons by the downflow CWS over the 46-month demonstration. Figure 3 shows the flow rates measured for both wetland cell effluents during the demonstration.

Throughout the demonstration, mine drainage influent and wetlands system effluent samples were collected for analysis of total metals, anions, total suspended solids (TSS), and total organic carbon (TOC). In addition, wetlands substrate samples were collected monthly for sulfate-reducing bacteria analysis and quarterly for analysis of total metals, acid-volatile sulfides (AVS), and toxicity characteristic leaching procedure (TCLP) metals. The substrate samples were analyzed to evaluate the effectiveness of the treatment system in sequestering zinc, to assess the tendency of the substrate to become a hazardous waste, and to estimate the role of sulfate-reducing bacteria within the wetlands substrate.

### 3.2.3 Operational and Sampling Problems and Variations from the Work Plan

The CWS experienced several operational problems during the demonstration. Some of these problems resulted in changes to the schedule and sampling events. Problems encountered and resolutions effected during the demonstration are described below.

- The upflow cell froze in December 1993 and remained frozen until the middle of February 1994. The cell froze because flow to the cells was interrupted when the dike within the Burleigh Tunnel collapsed. The dike was quickly repaired; however, as a result of the cold conditions and the lack of flow to the cells, the upflow cell froze to a depth of 18 inches. A livestock water heater and a steam cleaner were used to thaw the cell so that flow through the cell could be maintained. The freezing of the upflow cell delayed the start of the demonstration by 1 month. In order to prevent the upflow cell from freezing during the winter of 1995, straw bales were placed on top of the cell to provide insulation from the cold.

- The insulation provided by the straw bales maintained the wetland water temperatures consistent with

influent values and the upflow cell effluent piping did not freeze.

- The 1995 spring runoff was exceptionally high, and more flow was channeled to the CWS than the wetlands were designed to handle. More than 20 gpm were flowing through the upflow cell for a 2-week period in early June 1995. CDPHE responded to the flooding by installing a 6-inch bypass pipe to carry overflow from the influent weir around the wetlands Once installed, the bypass allowed flow rates to be returned to 7 gpm for each cell. However, CDPHE had not removed the straw bales insulating the upflow cell before the spring runoff began, and the straw bales became saturated. The weight of the saturated straw compressed the substrate, reducing the flow within the upflow cell to less than 1 gpm. The straw bales were removed from the upflow cell, and flow was restored to the cell within a week.

- In late November 1994, a large block of rock, roughly 10 feet by 10 feet, fell from the hillside and rolled onto a corner of the upflow CWS cell. The rock appeared to have depressed the effluent accumulation network and created a high spot in the piping at the collection point to the effluent weir. The high point in the piping may have resulted in the collection of precipitated metal sulfides in the piping, causing a flow restriction.

- During the summer and fall of 1994 and 1995, the effluent flowrate from the downflow cell could not be maintained at 7 gpm. It was not clear if biological surface growth, chemical precipitation in the cell, or settling and compaction of fine particles in the substrate was responsible for the decreased cell permeability.

- Several substrate sampling techniques were proposed for the demonstration, including polyethylene dipper and sediment core samplers. Both techniques appeared to be equally effective; however, the dippers were determined to be preferable. The dippers were selected because they were inexpensive and could be dedicated to each sampling cell, reducing the number of equipment blank samples required during the demonstration.

### *3.2.4 Site Demobilization*

The demonstration-scale wetland was removed by CDPHE at the end of the demonstration. Wetland removal entailed:

- Removal and disposal of the wetland substrate
  - Filling the wetland cells with site materials
  - Filling or removal of wetland weirs

- The CWS demonstration substrate was not a hazardous material, and potential disposal options included:
  - Disposal at a municipal landfill
  - Disposal in landfill biobeds (compost piles)
  - Mixing with site mining waste rock and soil to provide needed organic matter
  - Reuse in an interim ponded wetland

- The CWS Demonstration substrate was disposed of in a nearby municipal landfill

## 3.3 Demonstration Methodology

The primary objectives of the CWS technology demonstration were to (1) measure the reduction of zinc in Burleigh Tunnel drainage resulting from the CWS treatment with respect to cell configuration and seasonal variation (temperature); (2) assess the toxicity of the Burleigh Tunnel drainage; (3) characterize the toxicity reduction resulting from treatment of the drainage by the CWS; and (4) estimate toxicity reductions in the stream (Clear Creek) receiving the Burleigh Tunnel drainage. In addition, secondary objectives of the demonstration included:

- Estimating the metal removal capacity (lifetime) of the substrate, including the effect of treatment cell flow configuration. The results of influent and effluent metal analyses, CWS flow rate data, and TCLP metal analysis were compared to substrate metal accumulation estimates to evaluate the removal capacities of each CWS treatment cell. The TCLP metals analysis was used because the substrate could become a hazardous waste before its metal removal capabilities were exhausted. Replacing the substrate before it becomes a hazardous waste was determined to be the most cost-effective solution.

- Estimating the extent to which sulfate-reduction processes within the CWS are responsible for the removal of zinc from the drainage. Substrate was analyzed for sulfate-reducing bacteria and acid-volatile sulfides to estimate the extent to which sulfate-reduction processes are removing zinc from the drainage. The approximate number of sulfate-reducing bacteria was correlated to metal removal efficiencies as part of the determination. In addition, the accumulation of AVS in the substrate was compared to metal loading in the treatment cells to determine trends. Furthermore, the AVS analyses included an analysis of zinc to verify that the metal sulfides accumulating in the CWS were zinc sulfides. Previous investigations suggested that AVS analyses were indicative of metal sulfide accumulation attributed to sulfate-reducing bacteria (Reynolds 1991).

- Evaluating the impact of the CWS effluent on Clear Creek. Clear Creek samples were analyzed for total metals, TSS, total dissolved solids (TDS), TOC, nitrate, and phosphate. Results of the stream analyses were compared to CWS effluent analyses to assess the effect of CWS effluent on Clear Creek. Clear Creek samples were collected upstream and downstream of the CWS outfall.

- Estimating the capital and operating costs of the CWS.

Critical parameters are the data required to meet the primary objectives. The primary critical parameters were influent and effluent analyses for zinc (total), and toxicity testing with fathead minnows (Pimephalus promelas) and water fleas (Ceriodaphnia dubia).

Noncritical parameters are data required to address secondary objectives of the demonstration. Secondary objectives provide useful information to potential technology users but are not critical to evaluate the technology. The noncritical parameters of the CWS demonstration included:

- Total metals, nitrate and phosphate analysis of the Burleigh Tunnel drainage and CWS effluents

- Metal loading, metal accumulation, and TCLP metals in CWS substrate samples

- Sulfate-reducing bacteria counts and AVS accumulation in CWS substrate samples

- Clear Creek samples for total metals, TDS, TSS, TOC, biochemical oxygen demand (BOD), and aquatic toxicity

- Construction, operation, maintenance, substrate disposal, and miscellaneous costs

### 3.3.1 Testing Approach

In general, the testing approach of the demonstration incorporated the collection and analysis of wetland influent and effluent samples every 2 weeks for a period of 20 months. Monthly sampling was conducted for the remainder of the nearly 4-year demonstration. The effluent zinc results for each sampling event were compared to influent data and a removal efficiency calculated. An initial 2-week interval was selected because it provided for 3 to 7 pore volumes of water to be passed through the CWS, assuming a hydraulic residence time of between 50 and 100 hours. In addition, the 2-week interval was chosen because several factors, such as precipitation or evaporation, could cause variation in the measured concentration of zinc in wetland effluent samples. By increasing the number of influent and effluent water samples, performance trends display better continuity, the effects of weather are reduced, and calculated removal efficiencies are expected to more closely reflect true values. Also, sampling intervals shorter than 2 weeks were not economically feasible considering the length of the demonstration. The initial 20-month schedule was the maximum time allowable for the demonstration. This time frame is allowed because the CWS is a biological technology and performance depended, in part, on primary substances and nutrients within the substrate. By allowing the system to operate for an extended period, results were expected to show a relationship (positive or negative) between declining nutrient concentrations in the substrate and CWS performance.

The frequency of demonstration toxicity testing was limited to every 3 to 4 months due to budget considerations. Essentially, the sample collection and testing schedule was designed to evaluate toxicity reduction during periods of widely different zinc removal (different seasons) and critical periods for the receiving stream.

### 3.3.2 Sampling, Analysis, and Measurement Procedures

Mine drainage samples were collected from the influent weir, and CWS effluent samples were collected from the effluent weirs. Clear Creek samples were collected above and below the CWS outfall. Influent and effluent samples were analyzed for total recoverable zinc and toxicity (critical analyses), other metals, anions, TDS, TSS, and TOC (effluent only). These samples were collected at the frequency discussed in the previous section.

Two substrate sampling points were located in each cell. Initially, substrate samples were collected monthly for sulfate-reducing bacteria analysis and quarterly for total metals, AVS, and TCLP metals analyses for a period of 20 months. Quarterly and semi-annual sampling was conducted for the remainder of the demonstration. Substrate samples were collected from two locations within each cell, at approximately 1 to 2 feet below the wetland surface.

Mine drainage, wetlands effluent, and substrate were analyzed for critical and noncritical parameters using the methods listed in Table 3.

Field analyses included measurement of pH and conductivity for all aqueous samples, Eh for wetlands effluent samples, and dissolved oxygen for mine drainage

**Table 3.** CWS Demonstration Summary of Standard Analytical Methods and Procedures

| Parameter | Sample Type | Method Number | Method Title | Source |
|---|---|---|---|---|
| Metals | Aqueous and Substrate | 6010A, 6020, 7470 | ICP, ICP/MS, or AA | SW-846[1] |
| Sulfate | Aqueous | 300.0 | Ion chromatography | MCAWW[2] |
| Fluoride | Aqueous | 9056 | Ion chromatography | SW-846 |
| Nitrate/Nitrite | Aqueous | 353.2 and 354.1 | Various | MCAWW[2] |
| Chloride | Aqueous | 300.0 | Ion chromatography | MCAWW[2] |
| Total and Orthophosphate | Aqueous | 365.3 | Various | MCAWW |
| pH | Aqueous | 9040 | Electrometric | MCAWW |
| TSS | Aqueous | 160.2 | Gravimetric | MCAWW |
| TDS | Aqueous | 160.1 | Gravimetric | MCAWW |
| TOC | Aqueous | 9060 | Various | SW-846 |
| Ammonia | Aqueous | 350.1 | Various | MCAWW[2] |
| Alkalinity | Aqueous | 310.1 | Various | MCAWW[2] |
| Sulfide | Aqueous | 376.2 | Various | MCAWW[2] |
| Aquatic Toxicity | Aqueous | EPA SOPs[3] | | EPA[5] |
| Acid Volatile Sulfide (AVS) | Substrate | EPA Method | Acid volatile sulfide | EPA 1991 |
| Sulfate reducing bacteria count | Substrate | None | Anaerobic deep tube | CSM[3] |
| Toxicity leaching procedure | Substrate | 1311 | ICP, ICP-MS or AA | SW-846 |
| Reactive sulfide | Substrate | EPA[4] | Titration | SW-846 |
| Orthophosphate | Substrate | 365.3 | Various | MCAWW |
| Sulfate | Substrate | 300.0 | Various | MCAWW |
| Physical parameters | Substrate | Various[3] | Various[3] | ASTM |
| Residence time | Aqueous | ND | ND | ND |
| pH | Aqueous | SOP[3] 12 | | Tetra Tech[6] |
| Temperature | Aqueous | SOP[3] 11 | | Tetra Tech[6] |
| Dissolved oxygen | Aqueous | SOP[3] 62 | | Tetra Tech[6] |
| Conductivity | Aqueous | SOP[3] 99 | | Tetra Tech[6] |

Notes:

1 Test Methods for Evaluating Solid Wastes, Volumes IA-IC: Laboratory Manual, Physical/Chemical Methods; and Volume II Field Manual. Physical/Chemical Methods, SW-846. 3d Edition. Office of Solid Waste and Emergency Response. U.S. Environmental Protection Agency (EPA). 1986.

2 Methods for Chemical Analysis of Water and Wastes (MCAWW). EPA 600/4-79-020. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. EPA. 1983 and subsequent EPA - 600/4.

3 The analytical methods selected for the analysis of critical and noncritical parameters, and the rationale used in their selection, are discussed in Section 4.2.

4 Interim Guidance for Reactive Sulfide. Section 7.3.4.2, SW-846.

5 Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms. EPA/600/4-90/027F. EPA 1993.

6 These are field measurements made by Tetra Tech.

and Clear Creek samples. All field measurements were made in accordance with standard operating procedures.

## 3.4 Site Demonstration Results

This section presents the results of the CWS demonstration conducted from January 1994 to November 1997. Initially, aqueous chemistry data for the Burleigh Tunnel mine drainage are presented, followed by the demonstration results for the two CWS cells (Sections 3.4.1 through 3.4.3).

Section 3.4.4 presents data for the receiving stream, Clear Creek, and Sections 3.4.5 and 3.4.6 present toxicity results. Tables summarizing analytical results for the Burleigh Tunnel mine drainage are included in Appendix A. An evaluation of demonstration data quality parameters for critical analyses is contained in Section 4.

The data discussed in this section were generally collected using demonstration sampling and analysis techniques. However, influent and effluent data for much of 1996 were collected and analyzed by the CDPHE laboratory (Analytica, in Broomfield, Colorado). In addition, data was not collected by Tetra Tech or CDPHE for 3 months (September through November) in 1996. Tetra Tech discontinued CWS sampling at the end of its initial SITE contract and the resumption of sampling was slowed by contractual delays.

### *3.4.1 Burleigh Mine Drainage Chemistry*

The Burleigh Tunnel drains a network of interconnected mines on Republican Mountain and Sherman Mountain. Unlike many metal mine drainages, the Burleigh Tunnel effluent has near-neutral pH and carbonate alkalinity of approximately 100 mg/L.

The mine drainage contains high levels of zinc that typically range from 45 to 65 mg/L. However, in May and June 1995, a great deal of spring snow and rain and a rapid thaw combined to increase the amount of runoff entering the mine network drained by the Burleigh Tunnel. At that time, flow from the tunnel increased from 45 gpm to more than 300 gpm, and zinc concentrations increased from 55 mg/L (April 12, 1995) to 109 mg/L (August 8, 1995).

Over the final 2 years of the demonstration, zinc concentrations in Burleigh Tunnel mine drainage were lower in the winter, dropped again in April or May when flow through the mine workings increased, and rapidly increased in summer, remaining high throughout the fall. During this period, Burleigh Tunnel mine drainage zinc concentrations generally remained between 45 and 84 mg/L, with increases to more than 100 mg/L noted during the late summer and fall. Zinc concentrations in Burleigh Tunnel mine drainage between September and November 1996 are assumed to be similar to zinc concentrations measured during the same period in 1995. Figure 4 shows zinc concentrations for the Burleigh Tunnel mine drainage measured during the demonstration.

In addition to zinc, cadmium, lead, nickel, and manganese are also demonstration metals of interest. Cadmium, lead, and nickel readily form sulfides and are expected to be removed by the CWS. Manganese does not form a stable sulfide but was shown to be removed in a short-term treatability study conducted prior to the demonstration (PRC 1993). Cadmium, lead, and nickel levels were generally less than 0.1 mg/L in the Burleigh Tunnel mine drainage. After the high flow event in 1995, cadmium levels increased to concentrations ranging from 0.11 to 0.26 mg/L. Lead and nickel levels were generally much lower than cadmium and did not increase to the same extent after the high flow event.

Anion concentrations also increased during the demonstration. Sulfate concentrations in the Burleigh Tunnel drainage ranged from 279 to 652 mg/L and also increased after the high flow event. Carbonate (total alkalinity) concentrations were measured over a relatively narrow range of 82.4 to 125 mg/L. The highest carbonate concentrations were measured during a 1-month period in June and July 1995, corresponding to the period of highest flow from the Burleigh Tunnel. The simultaneous increases in zinc, sulfate, carbonate, and calcium without an increase in pH suggest these mine drainage constituents originate from mineral dissolution. Calcite ($CaCO3$) is commonly found in hydrothermal vein deposits in association with lead-silver-zinc formations (Correns 1969) and is also reported in the Silver Plume mining district. The high concentration of both zinc and carbonate at near neutral pH suggests the Burleigh Tunnel mine drainage is a combination of waters from multiple sources.

### *3.4.2 Downflow CWS*

The downflow cell was operated for approximately 2½ years during the demonstration. Over this period, the system removed 60 to 95 percent of the zinc contamination from the Burleigh Tunnel mine drainage.

Figure 4 shows zinc concentrations in the Burleigh Tunnel mine drainage (influent), and the effluents of both CWS

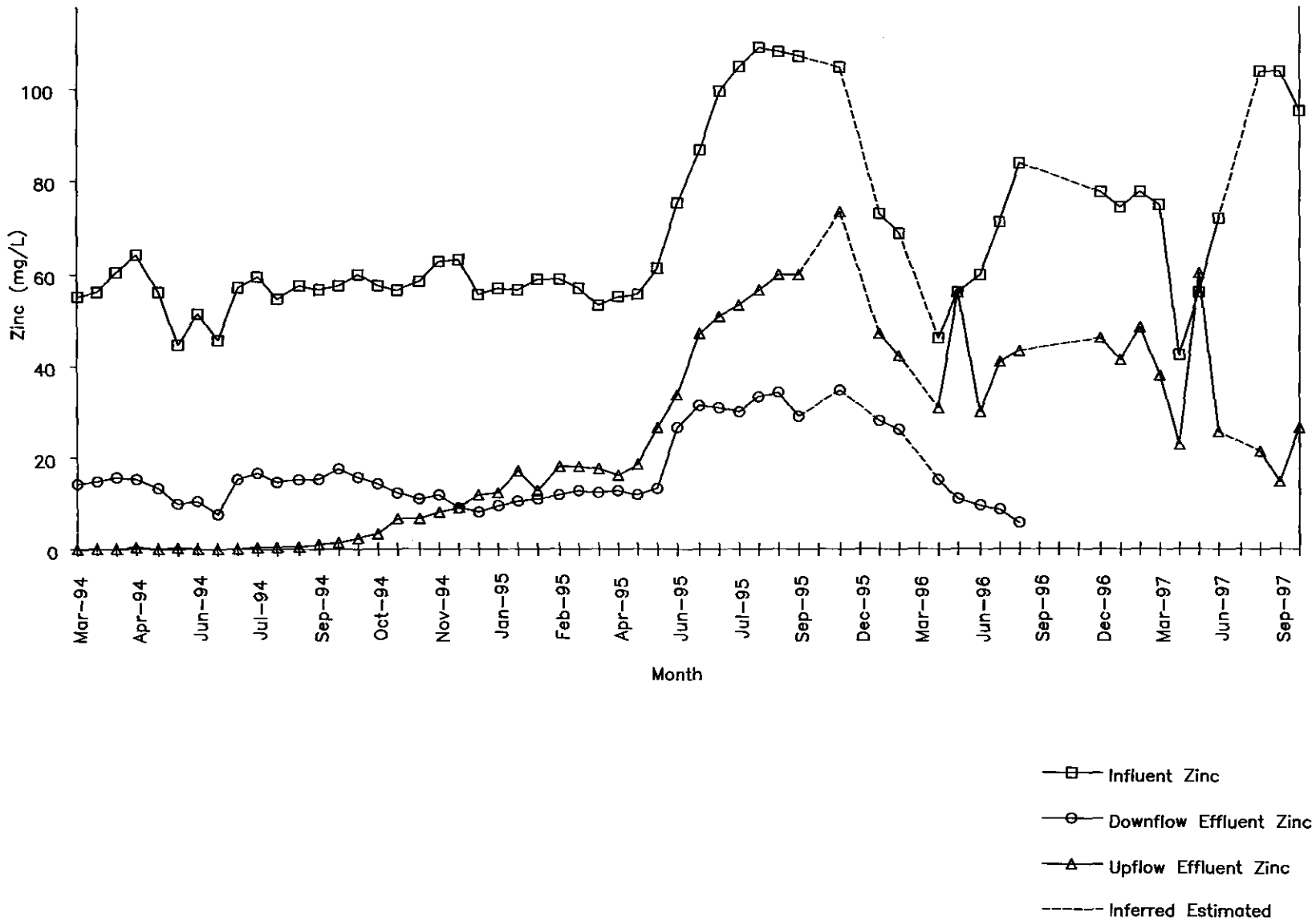


**Figure 4.** CWS zinc concentrations by month.

cells. During the first year of operation, influent zinc concentrations ranged from 45 to 63 mg/L (average of 57.1 mg/L) and the amount of zinc removed by the downflow cell ranged from 35 to 54 mg/L (average of 44.2 mg/L). Zinc removal efficiency during the first year averaged 77.4 percent. During the second year, zinc levels in mine drainage ranged from 53 to 109 mg/L (average of 83 mg/L) and downflow zinc removal ranged from 41 to 78 mg/L (average of 58 mg/L). Zinc removal efficiency during the second year averaged 70 percent. Over the final 6 months this cell operated, influent zinc levels ranged from 46 to 84 mg/L, while downflow CWS zinc removal ranged from 31 to 78 mg/L. In general, greatest zinc removal corresponded to times with the highest influent zinc concentrations, and the lowest zinc removal was observed during periods of lesser zinc in the mine drainage suggesting metal removal was effected by a physical process.

Although present only in low levels in the influent water, cadmium, lead, and nickel were removed to a great extent by the downflow CWS treatment. Influent cadmium concentrations ranged from 0.071 to 0.10 mg/L, while effluent levels ranged from 0.0007 to 0.003 mg/L during the first year. During the second year, cadmium concentrations increased in the influent, ranging from 0.057 to 0.26 mg/L, and downflow effluent levels ranged from 0.0001 to 0.007 mg/L with few detections. Figure 5 shows cadmium concentrations for the influent and both effluents during the first 2 years of the demonstration Substantial cadmium removal continued over the final 6 months by the downflow cell, with the exception of the April 1996 sample.

Samples were not regularly analyzed for lead or nickel during the demonstration. Figure 6 shows lead concentrations for the influent and both effluents during the first 2 years of the demonstration. During the first year, influent lead concentrations ranged from 0.013 to 0.020 mg/L, while downflow effluent concentrations ranged from 0.00065 to 0.0054 mg/L. Throughout the remainder of 1995, influent levels of lead increased slightly while effluent levels remained very low with few detections.

Nickel was also removed by the downflow cell; however, the extent of removal declined when influent nickel concentrations increased after the high flow event. Nickel levels in the influent ranged from 0.033 to 0.68 mg/L, and downflow effluent ranged from 0.0073 to 0.020 mg/L in the first year. Throughout the remainder of 1995, influent nickel levels ranged from 0.045 to 0.093 mg/L, and downflow effluent levels ranged from 0.014 to 0.040 mg/L.

Manganese concentrations in the mine drainage were initially between 1 to 2 mg/L. Manganese removal by the downflow CWS was low during the demonstration. Figure 7 shows manganese concentrations for the influent and both effluents.

The extended residence time of the influent within the downflow cell substrate caused by low flow rates may be one reason the downflow CWS was effective in removing metals from the mine drainage. Both wetland cells were designed to treat 7 gpm; however, the permeability of the downflow cell declined during the first year of operation, and flow through the cell dropped to 4 gpm particularly during the summer months. Although attempts were made to increase its permeability by fluffing the substrate with compressed air, these procedures resulted in only temporary improvements. Flow through the downflow cell improved during winter months when the substrate froze and contracted from the liner allowing the influent to flow down the sides of the interior cell. Flow through the downflow cell averaged 6.5 gpm during the first year; 5.8 gpm in the second year; and 6 gpm over the final 6 months of operation.

Analytical results for the downflow substrate (Table 4) showed a substantial increase in zinc levels over the period of the demonstration. Substrate zinc levels ranged from a low of 59.7 milligrams per kilogram (mg/kg) to a high of 5,630 mg/kg. Substrate samples were generally collected from between 1 to 2 feet below the surface of the CWS. Downflow substrate samples contained little visible evidence of sulfate reduction and low concentrations of AVS. Sulfate-reducing bacteria counts showed much variability (Figure 8).

After the first 6 months of operation, the downflow cell was removing more zinc from the mine drainage compared with the upflow cell. However, the reason for the greater removal was likely the higher residence time of the mine drainage within the downflow wetland. The increasing residence time was a function of mine drainage flow through the cell, that was generally lower in the summer compared to winter. A reduction of flow from 7 to 5 gpm increases residence time by 19 hours nearly a 40 percent increase. The loss of permeability is believed to be related to the loss of permeability in the downflow cell resulting from biological surface growth, chemical precipitation of

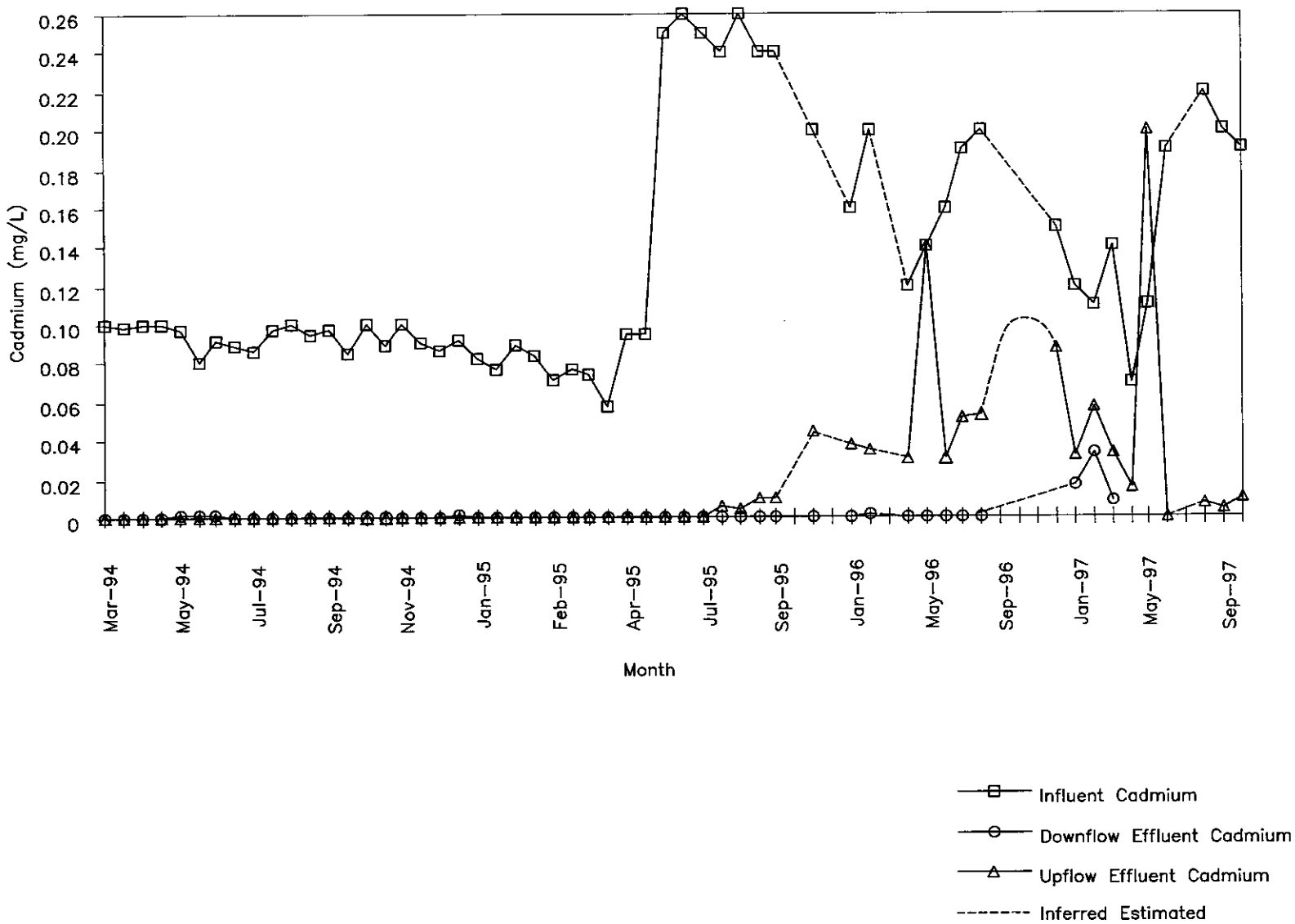


**Figure 5.** CWS cadmium concentrations by month.

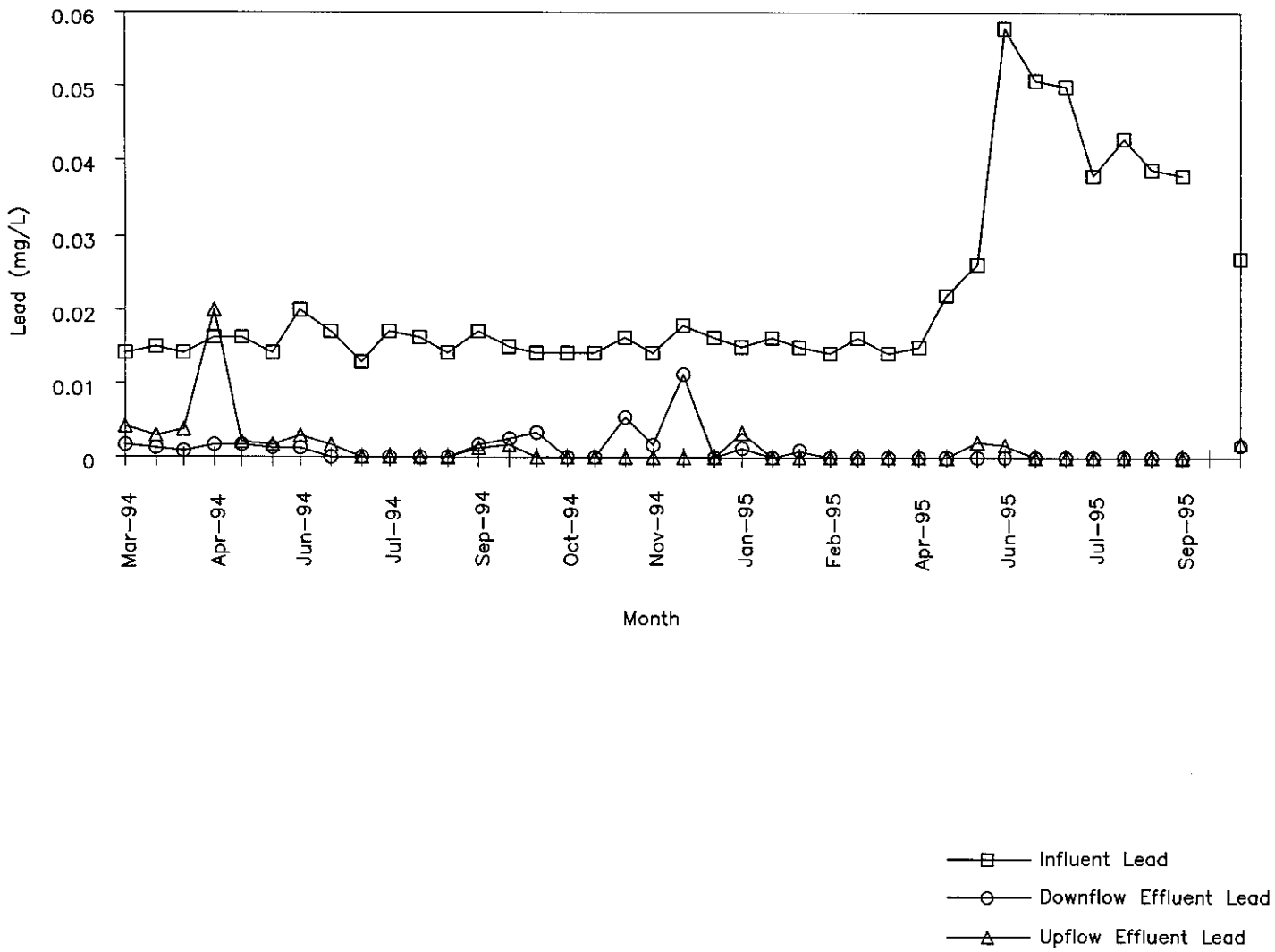


**Figure 6.** CWS lead concentrations by month.

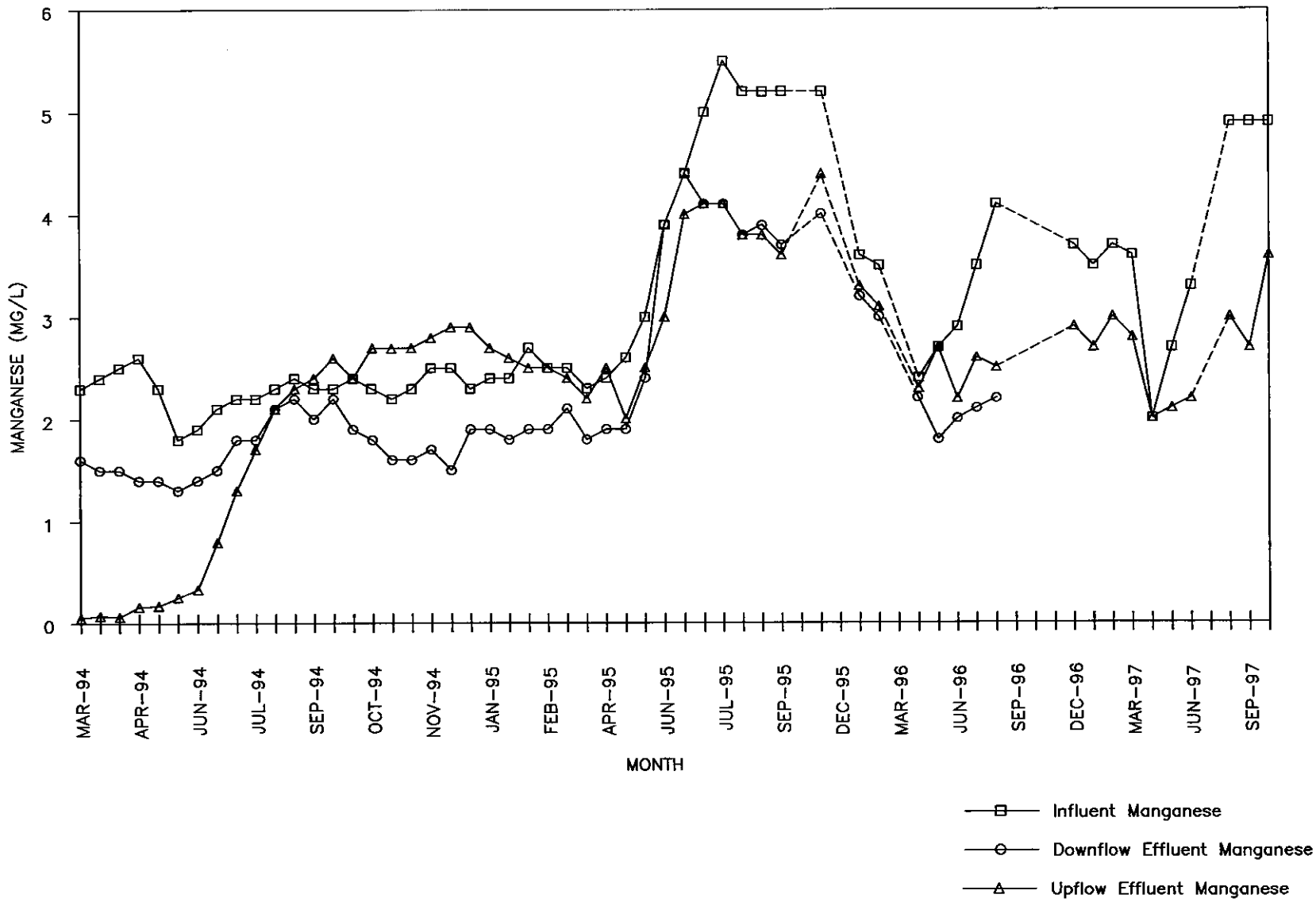


**Figure 7.** CWS manganese removed by month.

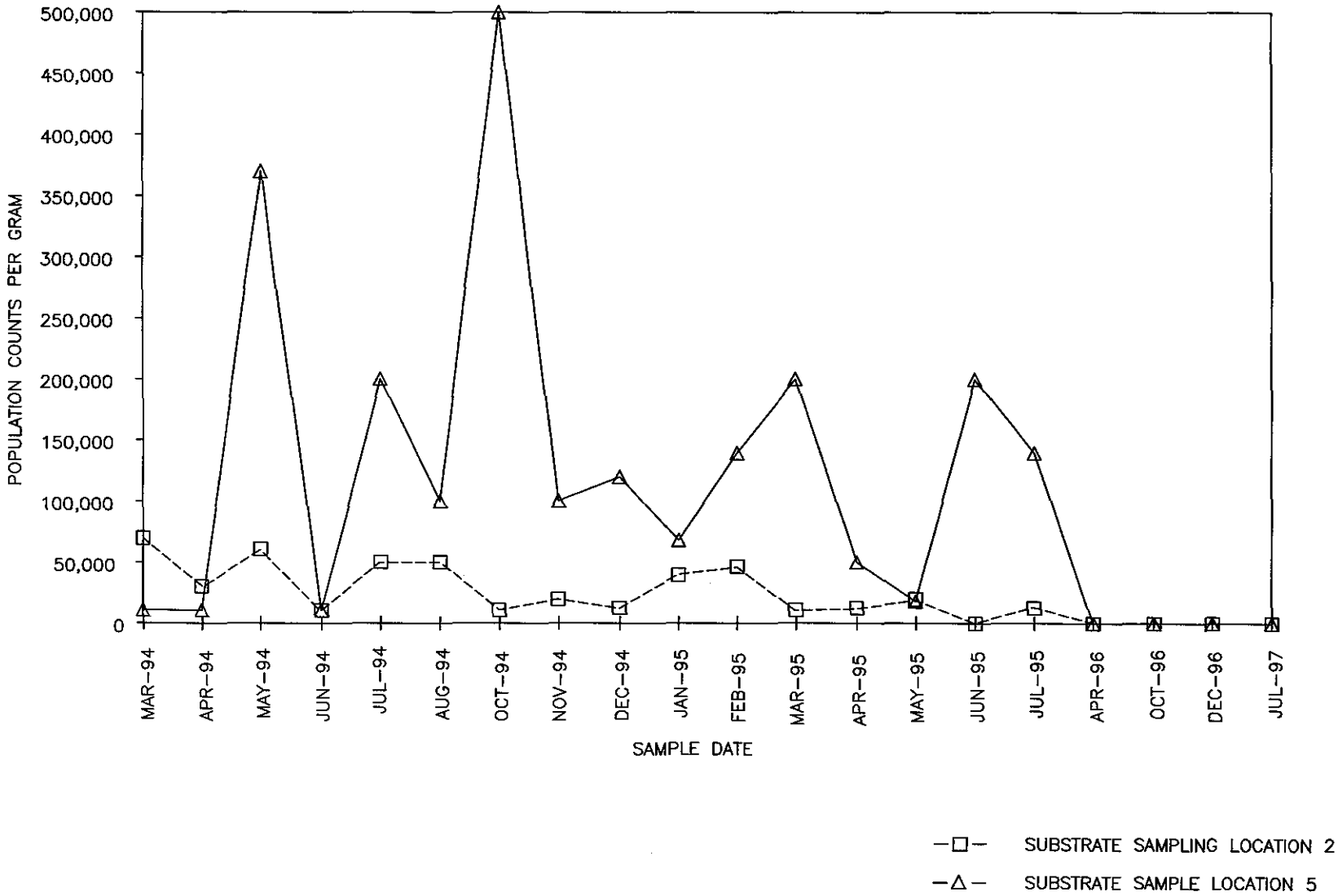


**Figure 8.** Sulfate-reducing bacteria, downflow CWS substrate.

**Table 4.** Average Downflow CWS Substrate Results

| | Cadmium (mg/kg) | Lead (mg/kg) | Nickel (mg/kg) | Zinc (mg/kg) | Acid Volatile Sulfides (mg/kg) | Sulfate-Reducing Bacteria (count) | Ortho-phosphate (mg/kg) |
|---|---|---|---|---|---|---|---|
| 0-6 months | 2.7 | 18 | 3.1 | 1,100 | 180 | $8.5 \times 10^4$ | 34 |
| 6-12 months | 8.0 | 31 | 6.1 | 3,400 | 120 | $1.1 \times 10^5$ | 12 |
| 12-18 months | 23 | 74 | 7.0 | 5,200 | 460 | $3.3 \times 10^5$ | 2.6 |

Notes:

mg/kg Milligram per kilogram
Average Arithmetic Mean
Substrate samples collected from 1-2 feet below wetland surface

zinc compounds, microbial breakdown of the substrate to finer particulates, and the settling of these particles into substrate pore spaces. The increase of flow during winter is believed to result from freezing of the wetland substrate at the edge of the cell causing the substrate to contract from the liner. The contraction allowed ponded water at the surface of the wetland to flow between the frozen substrate and liner to the base of the cell forming a preferential pathway.

Loading is the amount of metals retained by the wetland over time. It is a function of the flowrate through the wetland, the concentration of metals in the mine drainage, and the removal efficiency of the treatment. For this discussion, monthly loading of each wetland was calculated from measured flow rates and simultaneously collected samples of the mine drainage and the wetland effluent. Figure 9 shows the monthly zinc loading to the downflow CWS over the demonstration. The graph indicates that loading was initially high (maximum of 60 kg/month) but dropped as the downflow cell flow rate declined in the Fall of 1994. In winter, loading also increased as flow improved. The greatest loading to the downflow CWS occurred during the high flow event in the late spring and early summer of 1995. After the high flow event, loading in this cell declined dramatically and eventually dropped to less than 5 kg/month in May 1996.

The primary metal removal mechanism active in this cell did not appear to be sulfate reduction. Substrate analyses indicate a significant portion of the zinc removal in this CWS occurred in the upper 1 to 2 feet of substrate, where few AVS or sulfate-reducing bacteria were found. Pockets of sulfide-rich substrate were observed in this CWS cell at depths of 3 to 4 feet below the wetland surface, suggesting some sulfate reduction contributes to metal removal in this wetland. Aqueous geochemical modeling of the mine drainage suggests gypsum is oversaturated; however, visual observations of Burleigh Tunnel mine drainage precipitate and historical mine reports suggest the material is a zinc carbonate, probably smithsonite or hydrozincite.

The following can be concluded from the evaluation of the downflow CWS:

- As tested, the downflow CWS did not retain sufficient permeability to be considered a reasonable long-term treatment option.
- Chemical precipitation (suspected to be mineral carbonate accumulations) may have been the primary metal removal process in this CWS treating Burleigh Tunnel mine drainage.
- A 2-foot substrate depth should be adequate, as most metal removal occurred at between 1 to 2 feet below the wetland surface. A thinner substrate should decrease the flow resistence of the downflow CWS and increase the effectiveness of the system.
- A 2-foot downflow CWS may be a good pretreatment for an upflow CWS treating the Burleigh Tunnel mine drainage allowing some physical precipitation of the zinc.

The concentration of orthophosphate in the substrate also decreased after the high flow event in 1995. The high orthophosphate concentration, measured at the beginning of the demonstration, was 114 mg/kg; the low, 1 to 2 mg/kg, was measured in August 1995.

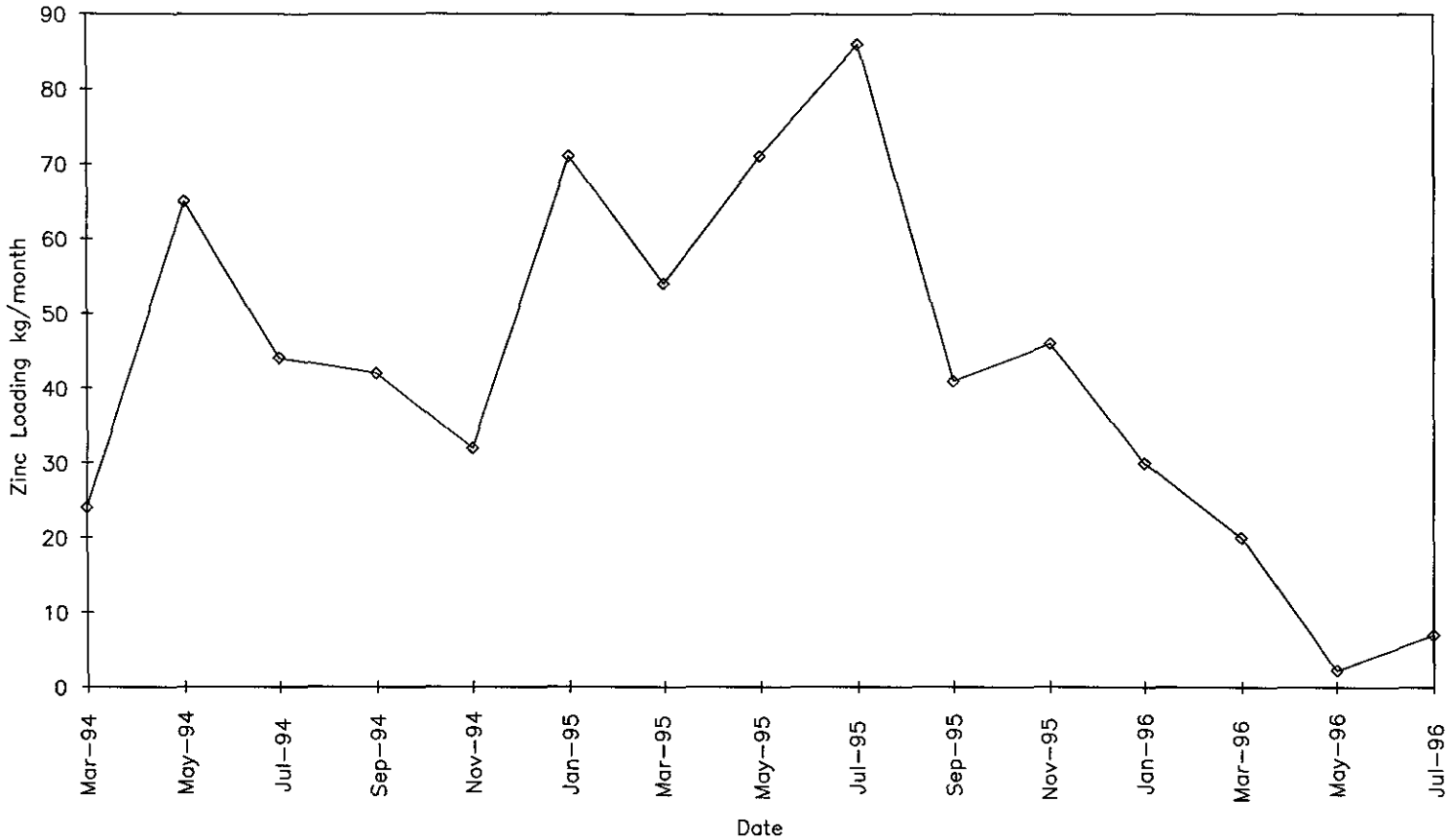


**Figure 9.** Monthly zinc loading, downflow CWS.

### 3.4.3 Upflow CWS

The upflow cell was demonstrated for nearly 4 years and, during this period, removed zinc and other metals initially by adsorption, later by sulfate reduction, and eventually by chemical precipitation (presumed). The adsorption period; appeared to last roughly 4 to 5 months as indicated by manganese removal. After the adsorption phase, sulfate reduction appeared to be the primary metal removal process; however, oxidation/reduction (ORP) measurements suggested the activity of the sulfate-reducing bacteria appeared to drop in late fall and through the winter of 1994. Counts of sulfate-reducing bacteria declined coincidentally with the decline in ORP. The drop may have been caused by lower winter temperatures, or an increase in flow through the cell that occurred in September through October 1994, or may result from the use of all the most easily metabolized materials in the compost substrate by the bacteria. During this period, the concentration of zinc in the upflow effluent increased from 3.2 mg/L (October 12, 1994) to 18 mg/L (March 15, 1995).

By May 1995, zinc levels were approaching levels that are inhibitory to sulfate-reducing bacteria at the observed area loading of 250 square feet per gallon. During May and June of that year, the high flow event exposed the wetland sulfate-reducing bacteria to elevated levels of zinc, and the high influent flow probably created aerobic conditions within the cell. The periodic high zinc concentrations observed in influent waters during the summer and fall of 1996 and 1997 likely prevented the sulfate-reducing bacteria from reestablishing activity to previous levels. The flow was halted to the upflow cell in the summer of 1997 for approximately one month for repairs. At that time, much of the water was removed from the cell, allowing wetland sulfate-reducing bacteria an opportunity to become reestablished.

However, there was no indication that the bacteria became re-established during the final 4 to 5 months of the demonstration. One of the repairs involved plugging a short section of the influent piping in the upflow cell. Visible observation of this influent pipe noted a black coating on the inside of approximately 1/16 inch and accumulations of black precipitate nearly filling the holes in the perforated pipe. Overlying the black material in the piping was a layer of cream colored to yellow material up to 1/8 of an inch thick.

Analytical results for influent and effluent samples from the upflow system showed that zinc was nearly completely removed by this system during the first 8 months of the demonstration (Figure 4). After this period, zinc concentrations in the upflow effluent gradually increased from 1.4 mg/L (September 19, 1994) to 18.5 mg/L in the spring of 1995 corresponding to zinc removal efficiencies of 97.6 and 66.8, respectively. In May and June 1995, high flow from the Burleigh Tunnel increased flow through the upflow cell to 20 gpm and zinc concentrations nearly doubled. Over the next 6 months, as flow decreased from the tunnel, influent zinc concentrations rose to a high of 109 mg/L. From May to November 1995, effluent zinc levels increased from 26.7 to 73.6 mg/L. The amount of zinc removed by the upflow cell averaged 41 mg/L (49.3 percent) during the second year.

During the third year of operation, zinc levels in the influent ranged from 56 to 84 mg/L; however, data were not collected between September and November 1996. Zinc concentrations in the upflow effluent over the third year ranged from 30 to 49 mg/L with an average removal of 30 mg/L (39.6 percent). In the final year of operation, zinc influent concentrations ranged from 42 to 104 mg/L and effluent levels ranged from 15 to 60 mg/L with an average removal efficiency of 65.1 percent. Effluent levels were greater in the May 28, 1997 sample (60 mg/L) compared to the influent sample (56 mg/L). Over the final 6 months, the upflow cell removed greater amounts of zinc as flow through the cell decreased. Flow through the upflow cell at this time ranged from 2 to 5 gpm.

Cadmium removal by the upflow cell followed a pattern similar to zinc removal (Figure 5). Initially, cadmium was removed to nondetect levels; however, cadmium concentrations increased two and a half times after the high flow event. After this period, cadmium removal remained high for 4 months but declined in the latter part of 1995 and remained low through 1996 and 1997.

Lead (Figure 6) and nickel were also removed to lower concentrations by the upflow CWS. Influent lead and nickel concentrations were approximately 0.015 mg/L and 0.043 mg/L, respectively. During the first year, lead was removed to nondetect levels and nickel effluent concentrations ranged from 0.0005 to 0.019 mg/L. Unlike zinc and cadmium, lead and nickel concentrations did not increase significantly after the high flow event; however, the removal of both decreased somewhat until flow values through the cell declined in the final months of the demonstration.

Manganese was initially present in the mine drainage at concentrations ranging from 1 to 3 mg/L. Manganese

was removed by the upflow cell for the first 4 months of operation but was not removed throughout the remainder of the demonstration.

Analytical results for the upflow substrate showed an increase in zinc levels over the period of the demonstration. Table 5 summarizes mean annual results for selected analysis from upflow cell substrate samples collected during the demonstration. Zinc levels ranged from a low of 40 mg/kg to a high of 4,800 mg/kg. The zinc content is expected to be higher in the removal zone of the upflow cell (deeper in the substrate of the cell). In general, upflow substrate samples were collected approximately 2 feet below the wetland surface, above the removal zone. Counts of sulfate-reducing bacteria in the upflow cell were generally very high between April 1994, through July 1995. However, counts were 1 to 2 orders of magnitude lower in upflow cell samples collected in April 1996 through September 1997. The final substrate sample analyzed for sulfate-reducing bacteria contained approximately 250,000 CFU/gram substrate. Figure 10 shows the results of sulfate-reducing bacteria counts conducted on upflow cell substrate samples collected during the demonstration.

The change from strongly reducing to slightly reducing conditions in the fall of 1994 may have made previously removed metal sulfides less stable within the wetland substrate. Substrate observations in the summer of 1997 indicated there were fewer sulfides present compared to substrate samples collected in 1994 and 1995. If half of the zinc removed in the first year of operation were released over the subsequent 2 years, the resulting zinc increase in the effluent would have been 33 mg/L. The higher zinc concentration measured in the May 28, 1997 effluent sample compared to the corresponding influent sample suggests some previously removed zinc was released.

Between March and December 1994, metals loading to the upflow CWS ranged from 53 to 97 kg/month but dropped to 26 kg/month in February 1995. This drop in loading corresponded with the increase of zinc in the effluent, an increase in ORP, and a decrease in flow rate through the cell. Flow through the cell increased in March and April 1995, leading to higher loading. The maximum loading to the upflow CWS (107 kg/month) occurred in May 1995 during the high flow event. Throughout the remainder of the demonstration, loading to this cell declined as the zinc removal efficiency decreased to 40 to 50 percent; eventually, flow through the cell ended in 1997. Figure 11 shows zinc loading to the upflow CWS over the demonstration.

The effect of the high flow event on the performance of the upflow CWS reveals the major shortcoming of passive systems, the inability to adapt to rapidly changing conditions. In this demonstration, the upflow CWS could not adjust to the increased influx of zinc or the change in environmental conditions.

As several constructed wetlands have successfully treated mine drainage with much higher concentrations of zinc, it may be concluded that the bacteria are somehow able to protect themselves from the high metals concentration. If this mechanism is sulfate reduction, the rate of sulfate

**Table 5.** Average Upflow CWS Substrate Results

| | Cadmium (mg/kg) | Lead (mg/kg) | Nickel (mg/kg) | Zinc (mg/kg) | Acid Volatile Sulfides (mg/kg) | Sulfate-Reducing Bacteria (count) | Ortho-phosphate (mg/kg) |
|---|---|---|---|---|---|---|---|
| Year 1 | 0.17 | 9.9 | 1.9 | 40 | 210 | $7.2 \times 10^6$ | 55 |
| Year 2 | 0.18 | 13 | 2.0 | 71 | 460 | $3.2 \times 10^6$ | 54 |
| Year 3 | 5.0 | 40.0 | 4.1 | 1,500 | 1,300 | $2.2 \times 10^5$ | 6.3 |
| Year 4 | 9.6 | NR | 6.2 | 4,800 | 1,000 | $6.2 \times 10^4$ | 6.9 |

Notes:

mg/kg Milligram per kilogram
NR Not Reported
Average = Arithmetic Mean
Substrate samples collected from 1-2 feet below wetland surface

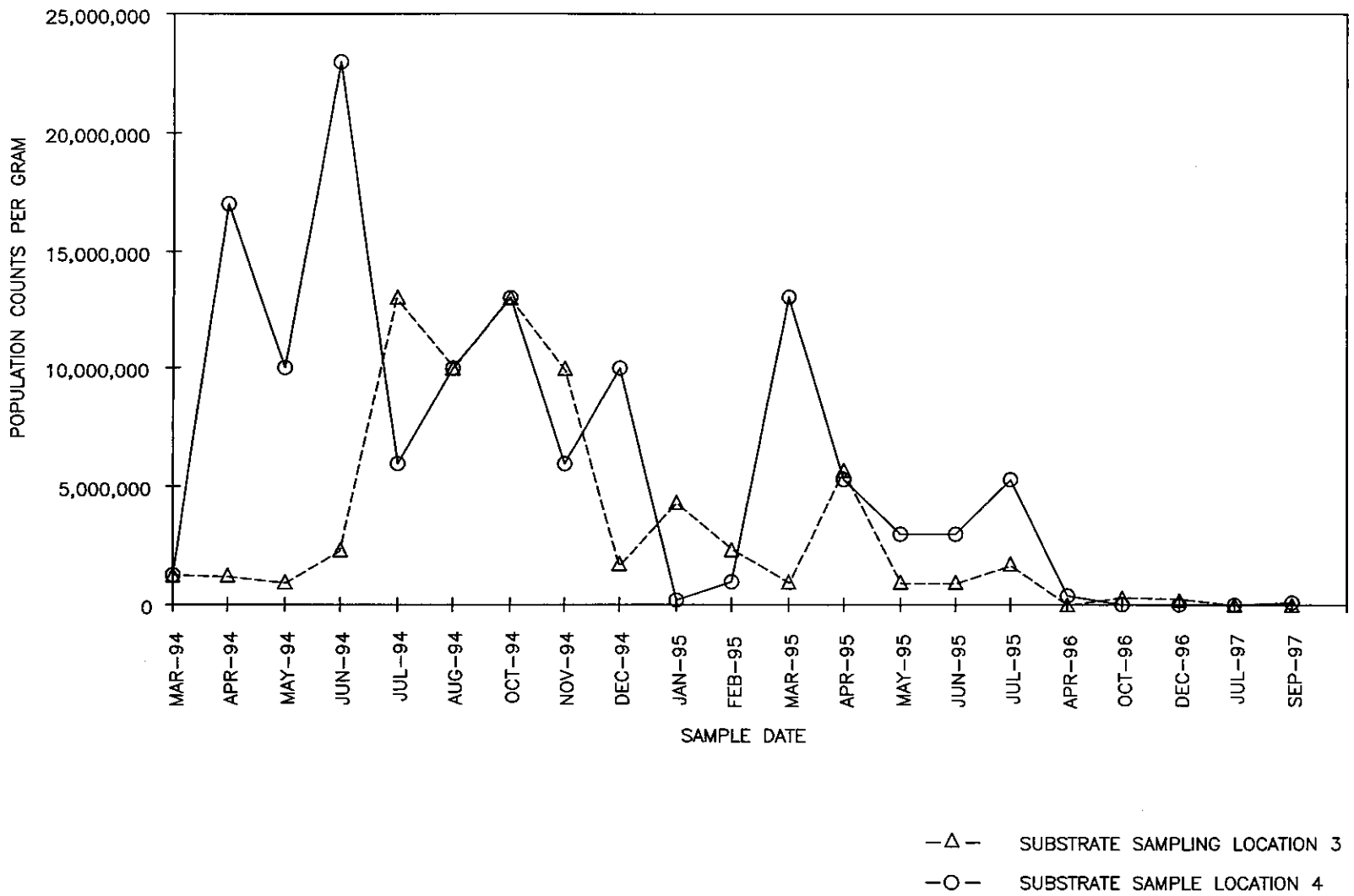


**Figure 10.** Sulfate-reducing bacteria, upflow CWS substrate.

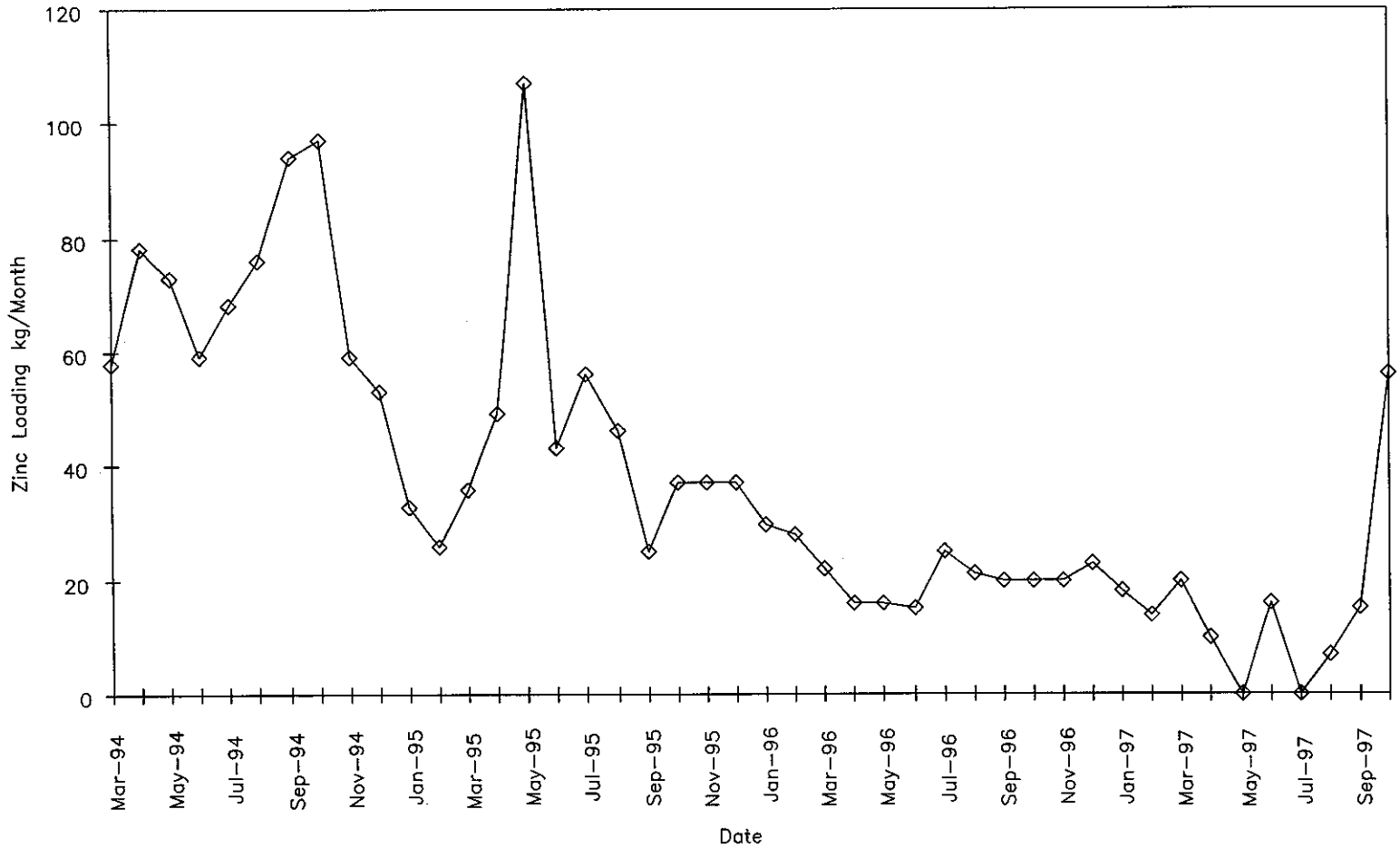


**Figure 11.** Monthly zinc loading, upflow CWS.

reduction must be great enough to reduce zinc concentrations in the substrate to below inhibitory levels. This hypothesis suggests that the effectiveness of an anaerobic compost CWS is a function of the rate of sulfate reduction, residence time of the mine drainage in the wetland substrate, and the concentration of zinc (or other inhibitory metals) in the mine drainage. Low temperature is also a factor that will affect the activity of sulfate-reducing bacteria in the wetland.

The following can be concluded from the evaluation of the upflow cell:

- The upflow CWS is effective in removing many metal contaminants from mine drainage; however, the CWS may have difficulty recovering from rapidly increasing metals loading conditions. Reinnoculation and incubation of sulfate-reducing bacteria may improve recovery of these systems.
- Control of mine drainage flow to the constructed wetland is critical to ensure that residence time and operational conditions are maintained.
- The operational lifetime of an upflow CWS (with a compost substrate depth of 4 feet) is roughly 4 to 5 years.
- The upflow cell had superior hydraulic performance throughout most of the demonstration.
- Winter freezing can be prevented by covering the wetland surface with hay or blankets used in curing concrete.
- Piping cleanouts should allow all piping networks to be easily cleaned.

### 3.4.4 Clear Creek

The untreated Burleigh Tunnel mine drainage and the effluents of both CWS cells discharge to Clear Creek. To assess the impact of treatment on the receiving stream, upstream and downstream samples collected from Clear Creek were also analyzed for total metals and aquatic toxicity. The metals results indicated that although the wetlands may be removing metals from the mine drainage, the demonstration-scale CWS treated only a small portion of the total discharge from the Burleigh Tunnel, not enough to show a measurable decrease in the metals content of the stream. The demonstration-scale CWS treated approximately 30 percent of the total flow from the Burleigh Tunnel, and during high flow treated only about 5 percent of the flow. A full-scale system could show a more significant decrease in the metals content of Clear Creek downstream of the system.

The stream results for upstream versus downstream samples are presented in Tables 6 and 7. The results show that Burleigh Tunnel mine drainage is a significant source of zinc to Clear Creek. However, CDPHE reports there are also additional nonpoint sources of zinc-contaminated water received by the creek.

### 3.4.5 Toxicity Testing Results

Constructed wetland treatment is a complex biogeochemical process involving adsorption, chemical precipitation, and microbial interactions with contaminants. The primary metal removal mechanisms in the CWS are chemical precipitation and microbial sulfate reduction; however, treatment may also complex metal contaminants, making them unavailable to receptor organisms. Thus, aquatic toxicity analyses were conducted by the EPA National Exposure Research Laboratory - Aquatic Toxicity during the demonstration to evaluate the reduction in toxicity resulting from CWS treatment. Two test organisms were used in the toxicity testing: water fleas (Ceriodaphnia dubia) and fathead minnows (Pimephales promelas). A total of eight rounds of aquatic toxicity testing were conducted during the demonstration. Initially, toxicity samples were collected and analyzed every 3 to 4 months until late 1995, when demonstration activities were temporarily suspended. When demonstration monitoring resumed, toxicity testing was conducted every 4 to 6 months. In 1997, a microbial toxicity test was conducted on wetland sulfate-reducing bacteria with Burleigh Tunnel mine drainage. The results of the microbial toxicity test are presented in Section 3.4.6.

Aquatic toxicity testing results correlated well with increasing zinc concentrations observed in the effluents of the treatment cells during the first 2 years of the demonstration. Results of testing conducted during the first 8 months of the demonstration indicate the effluents from both cells were not toxic to either the C. dubia or the P. promelas. The Burleigh Tunnel mine drainage was toxic to both test organisms at low concentration (dilution) throughout the demonstration. Table 8 provides influent and effluent concentrations resulting in the death of 50 percent of the test organisms (LC50) in each round of testing. As zinc concentrations increased in the effluents of both cells through 1995, so did the toxicity to the test organisms.

The first test conducted that year (February 1995) indicated that effluent from the upflow cell had become toxic to C. dubia at a concentration of 8.4 percent. The high runoff event that occurred in the spring of 1995 and

**Table 6.** Clear Creek Upstream

| | Cadmium (mg/L) | Lead (mg/L) | Nickel (mg/L) | Zinc (mg/L) | pH | Conductivity (µS) | Temperature (°C) |
|---|---|---|---|---|---|---|---|
| Average | 0.0022 | 0.0034 | 0.0047 | 0.126 | 7.8 | 155.7 | 5.4 |
| Maximum | 0.0094 | 0.013 | 0.015 | 0.56 | 8.1 | 167.5 | 9.7 |
| Minimum | 0.0 | 0.0 | 0.0 | 0.11 | 7.6 | 144.0 | 0.9 |

Notes:

°C Degrees Celsius
mg/L Milligrams per liter
µS MicroSiemens
ND Not Detected
pH Standard units
Average = Arithmetic Mean

**Table 7.** Clear Creek Downstream

| | Cadmium (mg/L) | Lead (mg/L) | Nickel (mg/L) | Zinc (mg/L) | pH | Conductivity (µS) | Temperature (°C) |
|---|---|---|---|---|---|---|---|
| Average | 0.00075 | 0.0013 | 0.0068 | 0.512 | 7.6 | 132.8 | 4.3 |
| Maximum | 0.0017 | 0.0024 | 0.026 | 0.56 | 8.1 | 173.3 | 9.7 |
| Minimum | ND | ND | ND | 0.14 | 6.5 | 80.0 | -- |

Notes:

°C Degrees Celsius
mg/L Milligrams per liter
µS MicroSiemens
ND Not Detected
pH Standard units
Average = Arithmetic Mean

associated increases in flow through the CWS cells and elevated zinc concentrations resulted in higher zinc levels in the CWS effluents. At that time, the effluent from both cells became toxic to the test organisms. The upflow cell effluent was toxic to C. dubia at a concentration of 0.1 percent and to P. promelas at concentrations ranging from 1.2 to 2.3 percent. The downflow cell effluent was toxic to C. dubia at concentrations ranging from 0.31 to 0.51 percent and to P. promelas at concentrations ranging from 2.6 to 30 percent.

Over the final 2 years of the demonstration, the upflow cell effluent continued to be toxic to C. dubia at concentrations below 1 percent and to P. promelas at a concentration of 14 percent. Toxicity samples were not collected from the downflow cell: operation of this cell was discontinued in September 1996.

Demonstration toxicity testing results indicate that the ability of the wetlands to reduce toxicity to aquatic organisms gradually declined over the first 2 years. In addition, the high flow event in 1995 had a significant impact on zinc and toxicity removal by the upflow cell over the final 2 years of the demonstration.

Water samples for toxicity testing were collected from Clear Creek above and below the CWS discharge three times during the demonstration. As mentioned, the constructed wetlands treated only 30 percent of the mine drainage; thus, the impact of treatment on the receiving stream was minor. One set of samples contained higher toxicity in the upstream sample while samples collected after June 1995 indicated that there was no acute toxicity in the upstream samples but that addition of the mine drainage to the stream resulted in an increase in toxicity.

**Table 8.** CWS Demonstration Toxicity ($LC_{50}$) Results

| Indicator Species | Date Collected | Influent | Upflow Effluent | Downflow Effluent | Clear Creek Upstream | Clear Creek Downstream |
|---|---|---|---|---|---|---|
| Fathead Minnows (*Pimephalus promelas*) | 08/24/94 | 1.1 | No toxicity | NA[2] | No toxicity | No toxicity |
| | 09/19/94 | 0.73 | No toxicity | No toxicity | | |
| | 02/22/95 | 1.6 | No toxicity | No toxicity | | |
| | 06/12/95 | 1.0 | 2.3 | 2.6 | No toxicity | No toxicity |
| | 09/05/95 | 0.62 | 1.2 | 30 | | |
| | 12/10/96 | 0.62 | 1.6 | NA | | |
| | 06/24/97 | 0.69 | 24 | NA | No toxicity | No toxicity |
| | 10/29/97 | 1.4 | 14 | NA | | |
| | 10/29/97[1] | | 11 | | | |
| Water Fleas (*Ceriodaphnia dubia*) | 08/24/94 | 0.46 | No toxicity | NA | No toxicity | No toxicity |
| | 09/19/94 | 0.31 | No toxicity | No toxicity | | |
| | 02/22/95[1] | 1.0 | 8.4 | No toxicity | | |
| | 02/22/95 | | | No toxicity | | |
| | 06/12/95 | 0.10 | 0.43 | 0.51 | No toxicity | No toxicity |
| | 12/10/96 | 0.09 | 0.22 | NA | | |
| | 06/24/97 | 0.43 | 0.41 | NA | No toxicity | No toxicity |
| | 09/05/95 | 0.10 | <0.19 | 0.31 | | |
| | 10/29/97 | 0.15 | 0.13 | NA | | |
| | 10/29/97[1] | | 0.19 | NA | | |

Notes:

[1] Duplicate Sample
[2] NA - Not analyzed

### 3.4.6 Microbial Toxicity Testing

Microbial toxicity testing was undertaken when repairs to the upflow cell indicated that there were few metal sulfides in the wetland substrate compared with observations conducted in previous years. The lack of metal sulfide deposits in the substrate suggested that the sulfate-reducing bacteria were not actively producing sulfide. Thus, Burleigh Tunnel mine drainage was tested at the Colorado School of Mines for toxicity to sulfate-reducing bacteria isolated from the upflow cell.

The tests indicated that the mine drainage is inhibitory to sulfate-reducing bacteria at low concentrations (dilution) corresponding to a zinc concentration of 17.5 mg/L. In addition, zinc sulfate ($ZnSO_4 \cdot 7\ H_2O$) was used to show that the zinc was the toxic constituent (positive control) in the mine drainage. The zinc sulfate was also toxic to the sulfate-reducing bacteria at a similar zinc concentration (18.8 mg/L). The concentration of zinc in the Burleigh Tunnel mine drainage typically exceeds the inhibitory level measured in this study. A similar study conducted using Desulfovibrio desulfricans also found a zinc concentration of 13 mg/L resulted in inhibition to the bacteria. (Paulson and others 1997).

Evidence that sulfate reduction was important to the removal of zinc in the upflow CWS include the large population of sulfate-reducing bacteria observed when zinc removal was also high (first year of demonstration), the accumulation of AVS, primarily zinc sulfide, in the substrate of this cell, and the decline of sulfate-reducing bacteria populations after the high flow event that corresponded with lower zinc removal by the upflow cell.

Visible observations of the upflow cell substrate observed blackening of the substrate during the first year of operation suggesting metal sulfides were accumulating, however, observations of wetland substrate conducted three years later, showed little blackening of the substrate. These results suggest sulfate-reduction was not as an important metal removal mechanism and was occurring to a much lesser extent during the latter portion of the demonstration. These observations also suggest that previously formed metal sulfides are not stable when environmental conditions within the wetland changes.

## 3.5 Attainment of Demonstration Objectives

This section discusses the results of the CWS demonstration in regard to the attainment of primary and secondary demonstration objectives. In addition, metal removal mechanisms, some of the causes for poor performance, and substrate lifetimes are discussed for each cell.

The results of the demonstration were able to achieve many but not all of the primary objectives outlined in Section 3.3. The first primary objective was the measurement of wetland effectiveness with respect to cell flow configuration and seasonal variation. This primary objective was achieved in part. The demonstration zinc results indicate zinc removal is greater with an upflow configured wetland; however, the technology as tested is not capable of meeting low metal discharge requirements for extended periods.

The better zinc removal and flow of the mine drainage through the upflow CWS compared to the downflow CWS indicate the upflow configuration is superior. Unfortunately, it was not possible during this demonstration to determine the effect of season variation on the performance of the upflow CWS. The downflow CWS actually performed better during the winter. The reason for the improved winter performance is discussed in Section 3.4.2.

The second primary objective was to determine the toxicity of the Burleigh Tunnel mine drainage. This primary objective was achieved. The Burleigh Tunnel mine drainage is toxic to both the C. dubia and P. promelas. Measured LC50 values for the P. promelas (fathead minnows) ranged from 0.62 to 1.6 percent (mine drainage) and for the C. dubia (water fleas) ranged from 0.10 to 1.0 percent.

The third primary objective was the characterization of toxicity reduction resulting from CWS treatment. This primary objective was also achieved. The demonstration toxicity results indicate the ability of the wetlands to reduce toxicity to aquatic organisms declined over the first two years of operation. Further, the high flow event had a significant impact on toxicity removal in both wetland cells.

The final primary objective was to estimate the toxicity reduction to the mine drainage receiving stream (Clear Creek). This primary objective was not achieved as none of the demonstration stream samples were toxic to either test organism.

The most significant primary objective not achieved is the inability to determine the seasonal variability of the upflow CWS. During winter, constructed wetlands located in cold climates may be less effective as a result of lower microbial activity. This may require pretreatment of the mine drainage during winter, oversizing the CWS or retaining a portion of the flow until warmer conditions return.

The first secondary objective of the demonstration was to estimate the lifetime of the substrate material. The lifetime of substrate material is estimated to be 4 to 5 years. The estimate is based on the breakdown of the substrate material resulting in settling and compaction of the substrate that leads to flow restrictions. In addition, demonstration substrate data for nutrients indicate elements such as phosphate (orthophosphate) have been depleted in the substrate by this time. If low discharge limits must be met then demonstration results suggest the substrate lifetime is approximately one year (taking into account the demonstration starting time and freezing of the upflow cell during the first year). However, in this situation it would likely be more cost effective to pretreat the mine drainage or amend it with an electron donor such as ethanol to extend the lifetime of the substrate material.

The second, noncritical or secondary objective was to estimate metal removal by sulfate reducing bacterial. This evaluation was expected to be qualitative as the bacteria counts and acid-volatile sulfide analyses are not highly precise and the metal removal may not be uniform throughout the treatment cells. As discussed in Section 3.4.2, the downflow cell data did not indicate the primary metal removal mechanism to be sulfate reduction. Section 3.4.3 discusses the upflow cell results for sulfate-reducing bacteria removal of metals. Data indicated an initial high

rate of removal with a longer term reduction in this mechanism of metals removal.

The third noncritical, secondary objective was to evaluate the impact of the systems effluent on Clear Creek. These data are discussed in Section 3.4.4, and indicate that although the treatment was effective in removing metals from the Burleigh Tunnel drainage, the relatively small portion of the discharge being treated did not produce a measureable decrease in the metals content of Clear Creek.

The fourth and final noncritical objective was to evaluate capital operating costs for the CWS. Section 5.0 of this report provides a detailed economic analysis and successfully provides data useful for estimating costs for application of this technology at other sites.

## 3.6 Design Effectiveness

The following sections discuss the effectiveness of the upflow and downflow CWS tested during the Burleigh Tunnel demonstration. The basic design of each wetland cell is discussed in Section 1.3.2 of this report. This discussion focuses on general design parameters and factors that affected each cell.

The basic design of the CWS demonstration system consisted of a dam inside the Burleigh Tunnel, piping from the dam to the influent weir, the two wetland cells, an effluent weir, and a bypass pipe. The dam collected the mine drainage and provided adequate hydraulic head to drive the mine drainage through the upflow cell. The influent weir partitioned the mine drainage to the CWS cells and channeled the excess water to the bypass piping. From the influent weir, the mine drainage was channeled to a ball valve that separated flow to the CWS cells. Water collected from the cells was piped to the effluent weir and was discharged to Clear Creek. The purpose of the effluent weir was to regulate flow through the wetland cells.

Construction materials associated with this design were generally inexpensive, readily available, and easily transported to remote areas. Installation techniques were also straightforward.

The major drawbacks of this design observed during the demonstration centered on the flow control valves and the inability of the effluent weir to regulate flow through the cells. Because flow through the cells could not be controlled with the effluent weir, flow through the cells was regulated at the influent weir and control valve. Unfortunately, this design meant that any adjustment in flow to one cell affected flow to the other cell. Future systems should use easily controlled flow structures such as weirs to regulate flow to both cells independently.

In addition, the capacity of the initial 4-inch bypass line was insufficient to accommodate the large water volume during spring runoff. Eventually, a 6-inch bypass line was installed. Piping connecting the influent control structure and the cells should be direct and accessible for routine cleanout.

A drawback associated with the use of compost substrates is the high concentration of nitrate in the effluent water during startup. During this demonstration, no attempt was made to remove the nitrate from the water prior to discharge. In a similar wetland evaluation, startup effluents were applied to surface soils. Alternatively, the startup effluent could be stored on site in a pond or tank and fed back into the CWS.

### *3.6.1 Downflow Cell*

The downflow cell consisted of 4 feet of a compost (95 to 96 percent) and hay (4 to 5 percent) substrate. The mine drainage flowed from the top to a PVC piping collection network at the base of the cell. The influent and effluent distribution networks were staggered within the cell to minimize short-circuiting of the mine drainage in the substrate.

The design of the downflow cell is discussed in Section 1.3.2; Figure 2 shows a cross section of the anaerobic CWS in an upflow configuration. The downflow configuration is only a reversal of the influent and effluent flows, not the construction of the cell.

For the most part, the materials used in the construction of the cells–HDPE liner, geonets, and PVC piping were acceptable. However, the geofabric was found to fill with fine material and lose permeability over the 2½-year demonstration. In addition, the cell piping networks did not include cleanouts. Cleanouts should be included in future CWS designs. Finally, the influent piping network did not evenly distribute the mine drainage in this cell. An additional row of perforated piping in this cell would more evenly distribute the mine drainage.

The cell was designed to treat 7 gpm. However, during the demonstration, the downflow cell became less permeable. The permeability loss is believed to be related

to precipitation of metal oxides, hydroxides, and carbonates, settling of fine materials in the cell, and compaction of the substrate material. In winter months, flow through the downflow cell improved; presumably, the contraction of frozen substrate allowed water to flow between the liner and the substrate. However, this short circuiting did not substantially affect metal removal by the cell.

In an attempt to restore flow through the downflow cell, air was injected into the substrate to fluff the material. Although this technique improved flow, the effect was typically short lived. The results of this demonstration indicate that substrates with high concentrations of compost will not retain permeability in a downflow configuration and are not recommended. However, some recent downflow wetlands have used substrate mixtures of 50 percent limestone with sawdust and compost to improve hydraulic characteristics.

### *3.6.2 Upflow Cell*

The design of the upflow CWS is identical to the downflow cell except that the mine drainage is channeled up though the compost substrate. Figure 2 shows a cross section of the demonstration anaerobic compost CWS. The design of the demonstration wetlands is discussed in Section 1.3.2.

In general, the upflow cell retained permeability throughout the demonstration. However, some hydraulic restriction developed during the later half of the demonstration resulting in a preferential flow pathway. In addition, gas buildup produced by fermenative bacteria within the upflow cell may have restricted flow to the effluent lines in the wetland during the last year of the demonstration. Gas was released from the cell by periodically puncturing the upper geofabric with a pitch folk. Replacing the geofabric with a fine mesh geonet could eliminate gas buildup. Also, the decline of sulfate-reducing bacteria and apparent increases in the population of fermentative bacteria likely exacerbated the problem.

The upflow cell was prone to freezing during winter. During startup, the dike within the Burleigh Tunnel gave way, stopping flow to the upflow cell. Flow was restored by thawing the ice around the effluent line with a steam cleaner and water tank heater. The following winter, hay bales were placed over the substrate followed by insulated blankets (identical to insulated blankets used for curing concrete), and the system was operational throughout the winter. However, the straw bales became saturated with water and the combined weight compressed the substrate so that all flow ceased through the cell. Flow through the cell was restored once the hay bales were removed. During year three, the insulated blankets were used alone to insulate the cell and there were no interruptions in flow during this period. In the final year, the ponded water in the upflow cell was allowed to freeze and did so to a depth of approximately 6 inches. There were no interruptions in flow during that winter.

Residence time is an important factor in anaerobic constructed wetlands that use sulfate-reducing bacteria. Decreasing residence times may overload the wetland, exposing the bacteria to inhibitory concentrations of zinc. Based on the size of the wetlands and substrate water volumes (percent moisture results of 50 percent) the calculated residence time for a flow rate of 7 gpm is 48 hours, and 67 hours at a flow rate of 5 gpm. Verification of residence times was one of the more difficult measurements undertaken during the demonstration. Both a chloride tracer (treatability study) and an organic dye test (demonstration) were unsuccessful in measuring residence time. The chloride could not be readily measured as background levels of dissolved salts was somewhat high during the treatability study and the organic dye likely absorbed to the wetland substrate during this demonstration test.

During the final year of the demonstration, flow through the upflow cell began to short circuit in an area adjacent to the southeastern bermed sidewall. An excavation was made into the wetland to the influent line feeding this section of the cell and the line was capped. Dewatering the excavation was somewhat difficult and would have been aided by a sump within the cell. Inspection of the influent line found precipitates coating the piping walls and in the piping perforations. The amount of material in the perforations and the pressure on the piping against the geofabric would have caused a notable restriction in flow. Replacing the geofabric with a fine mesh geonet should alleviate the problem.

# Section 4
# Data Quality Review

This section presents the summarized results of QA procedures established to ensure the validity of the zinc and acute toxicity data collected during the demonstration. Section 4.1 discusses zinc data quality, and Section 4.2 discusses acute toxicity data quality. A comprehensive discussion for both zinc and acute toxicity, along with supporting summary tables, is presented in the Technical Evaluation Report.

## 4.1 Zinc Data Quality Review

This section discusses the results of the QA procedures established to ensure the validity of the zinc data collected during the demonstration. The QA procedures were established prior to the demonstration and were recorded in the quality assurance project plan (QAPP) as part of the demonstration plan. Both field and analytical QA procedures were specified to ensure sample integrity and the generation of data of known quality.

### *4.1.1 Quality Assurance Results for Field Sampling Activities*

The procedures followed during field activities to maintain sample integrity and quality are discussed below. They include specifications for sample collection, labeling, containerization, preservation, holding times, and chain of custody.

**Sample Containerization, Preservation, and Holding Times**

This section describes sample labeling, shipment, chain-of-custody, and laboratory receipt procedures for zinc samples. Conformance with and documentation of these procedures provide a definitive record of sample integrity from origin to analysis.

Each sample container was labeled with a unique sample identification number. The label identified the sampling location, date, time of collection, and analysis to be performed. All chain-of-custody forms included the project number, project name, sampler's name, station number, date, time, sampling location, number of containers, and analytical parameters. Samples were hand-delivered to Quanterra Environmental Services in Arvada, Colorado. Chain-of-custody forms gathered during the demonstration were reviewed for content and completeness and appeared in good order.

All samples analyzed for critical parameters arrived at the laboratory intact. Several of the coolers used for shipping the samples arrived with inside temperatures greater than 4 degrees Celsius as specified in the QAPP. However, the results of associated QA samples suggest that the elevated temperature did not affect sample integrity. All samples were analyzed within their designated holding times (6 months); the majority were analyzed within 1 month of sample collection.

**Equipment and Field Blanks**

Equipment blanks were collected during the demonstration to assess sample contamination resulting from sampling equipment. Throughout the demonstration, dedicated sampling equipment was used for sample collection to reduce sample cross contamination. As a result, few equipment blanks or field blanks were collected during the demonstration. The data quality objective (DQO) for equipment and field blanks was results below reporting limits for all analytes.

Two equipment blanks (WEV090794EB and EB012197) were collected with a polyethelene dipper by pouring deionized water into the dipper and decanting the water into an appropriate sample container. The equipment blank collected in September 1994, contained an estimated zinc concentration of 0.019 mg/L, which is below the 0.020 mg/L reporting limit. The equipment blank collected in January 1997, contained 0.052 mg/L zinc, above the 0.020 mg/L reporting limit.

Field blanks were used to assess whether zinc contamination was introduced during the handling, presentation, or transport of aqueous samples. The field blank was prepared by adding deionized water into an appropriate sample container in place of a real sample.

One field blank was collected during the demonstration (FB060194). Zinc was found in this field blank at a concentration of 0.034 mg/L, slightly above the reporting limit of 0.020 mg/L.

The level of contamination in the equipment and field blanks qualifies data near the reporting limit for accuracy. The source of the contamination is unknown; however, the commercial distilled water is suspected. All of the CWS performance data contained zinc concentrations at least one order of magnitude greater than the reporting limit and in most cases two or three orders of magnitude above the reporting limit. Consequently, the demonstration zinc data are considered acceptable for their intended use.

**Method Blanks**

Method blanks verify that laboratory extraction and sample cleanup and concentration procedures used do not introduce contaminants that compromise the analytical results. Method blanks were prepared and analyzed with each batch of laboratory analysis. The method blank DQO was for results to be below reporting limits for all analytes of interest.

Five out of the 40 batches analyzed during this demonstration contained reportable quantities of zinc in the method blanks. Values ranged from 0.020 mg/L to 0.046 mg/L. All samples corresponding to these five analytical batches were qualified for blank contamination (B). All of the sample results were greater than five times the associated blank contamination; thus, no zinc results were qualified as nondetected due to blank contamination (UB).

### *4.1.2 Quality Assurance Results for Sample Analysis*

Analytical QA includes methods and procedures used to ensure data reliability. This process involves establishing data quality objectives for the project data and developing data quality indicators (quanitative or qualitative measures of precision, accuracy, completeness, representativeness, and comparability) that can be used to determine whether the data meet the project's QA objectives.

The QA objective for the CWS demonstration data were established in the QAPP with specific performance goals for precision, accuracy, representativeness, completeness, and comparability. The following sections evaluate the demonstration data with respect to these performance goals.

**Precision and Accuracy**

Precision is a measure of the reproducibility of measurements under a given set of conditions. Accuracy is the degree of agreement between an analytical measurement and the true value. The overall precision for zinc concentrations was a function of both sampling and laboratory precision. Overall precision was evaluated using data from field duplicates, and laboratory precision was evaluated using data from laboratory duplicates. Relative percent difference (RPD) between duplicate samples was used to evaluate precision using the following formula:

$$RPD = \frac{|(A - B)|}{0.5\ (A + B)} \quad X\ 100$$

where: A = first duplicate concentration
B = second duplicate concentration or

Fifteen field duplicate samples were collected during this demonstration, yielding RPDs ranging from 0 to 3.7 percent. Laboratory duplicate control sampling were analyzed for 51 rounds of sampling activities. All laboratory RPDs were within the established DQO of 20 percent with the exception of one, of 28 percent. Overall, the precision objectives for zinc analyses were achieved.

The accuracy of a measurement is affected by errors introduced through the sampling process and in handling, sample matrix, sample preservation, and analytical techniques. A program of sample spiking at the laboratory and analysis of standard reference materials (SRMs) was also used to evaluate laboratory accuracy.

Accuracy for zinc measurements was estimated as percent recovery (%R) of the true analyte level from SRMs and by evaluation of matrix spike (MS) recoveries. The following formula was used to calculate MS percent recovery:

$$\% R = (S-C)/T \ X\ 100$$

where: S = measured spike concentration
C = sample concentration
T = true or actual concentration of the spike or

MS spiking recoveries were all within the DQO limits with one exception. One MS sample analyzed (collected on July 27, 1994) yielded a recovery of 134 percent, slightly above the DQO. When the data were rechecked by the laboratory, the deviations were not found to bias the results sufficiently to affect data use. The laboratory concluded that the magnitude of the errors was too small relative to the zinc concentrations to have a significant effect on the zinc values.

Reported results for the SRM indicate that the analytical method measured larger concentrations of zinc than reported in National Institutes of Standards and Testing (NIST) standard reference material 1643c. The higher recoveries were considered to be the result of matrix interferences and the low level of zinc in the SRM. The DQO for accuracy is 75 to 125 percent recovery. SRM recoveries were 123 and 149 percent. Quanterra was immediately notified of the problem, and the laboratory control samples were checked to confirm that all other analytical controls were within acceptable parameters. Tetra Tech determined that some demonstration results with very low levels of zinc may be positively biased. The zinc results affected are from the upflow cell effluent during the first 6 months of operation.

Overall laboratory accuracy for the demonstration data was acceptable.

**Representativeness**

Representativeness expresses the degree to which sample data accurately and precisely represent the characteristics of a population, parameter variations at a sampling point, or an environmental condition they are intended to represent. For the CWS demonstration, the low RPDs associated with field duplicate results suggest the data collected are representative of the CWS system for the environmental and physical conditions at the Burleigh Tunnel site.

**Completeness**

Completeness is a measure of the amount of acceptable data obtained compared to the amount of data needed to achieve a particular level of confidence in the results. Acceptable data are obtained when (1) samples are collected and analyzed in accordance with the QC procedures outlined in the demonstration plan, and (2) criteria that affect data quality are not exceeded. CWS percent project completeness (%C) was calculated using the following equation:

$$\%C = (V/T) \times 100$$

where: %C = percent completeness
V = number of measurements judged acceptable
T = total number of measurements planned

The QA objective for degree of completeness was 90 percent for the critical parameter zinc. All data collected are considered usable for the intended purpose; therefore, the QA objective for completeness was achieved.

**Comparability**

The comparability parameter is designed to identify deviations in the data that may result from inconsistencies in field conditions, sampling methods, or laboratory analysis. During this demonstration, changes in sampling techniques and laboratory analysis were minimized to ensure comparability of results. However, the end of the first SITE contract and delays in restarting the new SITE contract required the use of data collected by CDPHE. The results of a laboratory intercalibration exercise with Quanterra, the CDPHE laboratory (Analytica), and a referee laboratory suggest that the data are comparable.

## 4.2 Acute Toxicity Data Quality Review

This section discusses the results of QA data collected to document the validity of the acute toxicity data. The QA procedures were established prior to the demonstration and recorded in the QAPP as part of the demonstration plan. Both field and analytical QA procedures were specified to ensure sample integrity and the generation of data of known quality.

### *4.2.1 Analytical Quality Assurance*

Analytical QA is the process of ensuring and confirming data reliability. This process includes establishing DQOs for the project data and developing data quality indicators (quantitative or qualitative measures of precision, accuracy, completeness, representativeness, and comparability) that can be used to evaluate whether the data met the project's QA objectives. The QA objectives for acute toxicity testing during the CWS demonstration

were established in the QAPP and are summarized in the following discussions.

**Water Chemistry Results for Environmental Samples and Reference Toxicant Tests**

To ensure that laboratory water quality conditions did not adversely affect the reference toxicant or environmental sample results, water quality parameters were documented throughout all test series. The water chemistry results indicate that the water quality conditions for testing were appropriate for the test organisms during all test dates and that no abnormal water conditions were documented that could influence the survivability results.

**Precision and Accuracy**

Precision and accuracy in toxicity tests are controlled and evaluated through documentation of reference toxicant responses of indicator species against inter- and intra-laboratory historical records; and by carefully controlling and documenting the environmental conditions tested. The following discussion documents the laboratory testing conditions for growth, feeding, and maintenance of indicator species during the tests; and documents the results of indicator species survivability results against laboratory historical records for identical tests.

Acute toxicity and metal concentration in the mine drainage were used to infer a response relationship between the most prevalent toxic component present (zinc) and indicator species survival. Preliminary chemical analysis had identified zinc in various forms as the most predominant metal contaminant.

Zinc sulfate was used as a reference toxicant to simulate the population response of the indicator species to a soluble zinc compound present in the mine drainage matrix. Potassium chloride was used as a laboratory reference test for population viability and toxic response of the indicator species.

Pimephales promelus and Ceriodaphnia dubia were used as the test organism populations in the 48-hour static-renewal acute toxicity tests. Indicator species survival rates (LC50) at the 95 percent confidence level (EPA 1993a) in a static series of potassium chloride and zinc sulfate concentration dilutions were calculated and compared with laboratory historical records. The comparison provided a control on the viability of the test species and the testing methodology.

The quantitative precision and accuracy requirements for acute toxicity for Pimephales promelus and Ceriodaphnia dubia when exposed to zinc sulfate were established by toxicant equivalent concentration values generated from both external and internal laboratory records of earlier tests. The quantitative precision and accuracy objectives for acute toxicity for Pimephales promelus and Ceriodaphnia dubia when exposed to potassium chloride were established by monthly cumulative laboratory toxicant equivalent concentration values.

All reference toxicant results fell within the prescribed ranges, indicating that the response of the indicator species response to test conditions was appropriate for evaluating the toxin present. Therefore, the quantitative results of acute toxicity to the environmental samples are comparable to other tests under identical conditions.

**Sample Duplicates**

The results of sample (field) duplicates is another indicator of overall precision. The sample duplicate was collected on February 27, 1995 from the treated effluent from the downflow cell (samples designated WED and WEDII).

Generally, the analysis of duplicate acute toxicity values for sampling and analytical precision is a numerical comparison of the difference in reported acute toxicity values to the magnitude of the values themselves. However, sample WED for February 27, 1995 was not toxic enough to generate an LC50 value, which is the normal endpoint for acute toxicity analysis. Consequently, the analysis of test sampling and analytical precision presented is a subjective comparison of the sample and duplicate routine chemistry and intermediate toxicity results.

The chemistry for duplicate samples WED and WEDII shows no significant difference, with less than 10 percent variation in all measured parameters. Those variables having the greatest difference – in pH, DO, and temperature – were consistently lower for WEDII than for WED. The values, however, do not strongly indicate a difference in water quality conditions. The initial and final chemistry for both species tests also show slight differences, but no consistent variability in an individual parameter.

Qualitatively, the survival rates for C. dubia of the individual sample dilutions for duplicate samples WED and WEDII both show very slight toxicity, especially noting that both controls had survival rates of 20/20. Quantitatively, the 100 percent WEDII sample yields a survival ratio

# Section 5
# Economic Analysis

This section presents cost estimates for using an anaerobic compost CWS system to treat mine drainage with water chemistry similar to the Burleigh Tunnel. The baseline scenario used for developing this cost estimate was a 50 gpm flowrate, the total flow from the Burleigh Tunnel, and a 15-year system life. The baseline costs were then adjusted for flowrates of 25 gpm and 100 gpm to develop cost estimates for other cases.

Cost estimates presented in this section are based primarily on data compiled during the SITE demonstration at the Burleigh Tunnel (CDPHE 1995). Additional cost data were obtained from standard engineering cost reference manuals (Means 1992). Costs have been assigned to 11 categories applicable to typical cleanup activities at Superfund and RCRA sites (Evans 1990). Costs are presented in year 1995 dollars and are considered estimates, with an accuracy of plus 50 percent and minus 30 percent.

## 5.1 Basis of Economic Analysis

A number of factors affect the costs of treating mine drainage with an anaerobic compost CWS system. These factors generally include flow rate, type and concentration of contaminants, physical site conditions, geographical site location, and treatment goals. The characteristics of spent substrate produced by a CWS system will also affect disposal costs. Spent substrate will require off-site disposal. Mine drainage containing cadmium at 0.05 parts per million (ppm), iron at 50 ppm, nickel at 0.5 ppm, and zinc at 50 ppm was selected for this economic analysis. The following presents additional assumptions and conditions as they apply to each case.

For each case, this analysis assumes that an upflow CWS system will treat contaminated mine drainage continuously, 24 hours per day, 7 days per week. An average metals removal efficiency of 96 percent was assumed for all cases. Based on these assumptions, the CWS system will treat about 26.3 million gallons of water per year of operation at the baseline flowrate of 50 gpm.

- Further assumptions about constructed wetlands treatment for each case include the following:
- A residence time of 75 to 150 hours is recommended for adequate metals removal.
- A porosity of 50 percent is assumed for the substrate material.
- Two baseline wetlands, size of 90 feet by 90 feet by 4 feet (2,300 cubic yards [$yd^3$]), will provide a 78 hour residence time at a flowrate of 50 gpm (wetland size is directly proportional to flowrate). Square wetlands were used for the cost estimation; however, other shapes may be preferable.
- Substrate material will require removal and replacement once every 5 years.
- The spent substrate is not a RCRA hazardous waste: thus, it will be dewatered on site and can be recycled or disposed of at an industrial landfill.
- An aerobic polishing pond to increase displaced oxygen is not required.

This analysis assumes that aquatic-based standards are most appropriate; and the attainment of these standards depends on the affected organisms, receiving waters and volume of mine drainage. Attainment may not be feasible in all cases for the technology as tested during this demonstration.

The following assumptions were also made for each case in this analysis:

- The site is located within 200 miles of the disposal location.
- The site is located within 100 miles of a moderate-sized city.

- The site will allow for gravity flow of the mine drainage through the wetland.
- A staging area is available for dewatering spent substrate.
- Access roads exist at the site.
- Utilities, such as electricity and telephone lines, are available on site.
- The treatment goal for the site will be to reduce zinc contaminant levels by 90 percent.
- Spent substrate will be dewatered and disposed of off site.
- One influent water sample and two effluent water samples will be collected monthly and two composite substrate samples will be collected quarterly to monitor system performance.
- One part-time operator will be required to inspect the system, collect all required samples, and conduct minor maintenance and repairs.

## 5.2 Cost Categories

Cost data associated with the CWS technology have been assigned to one of the following 11 categories: (1) site preparation; (2) permitting and regulatory requirements; (3) capital equipment and construction; (4) startup; (5) labor; (6) consumables and supplies; (7) utilities; (8) residual and waste shipping and handling; (9) analytical services; (10) maintenance and modifications; and (11) demobilization. Costs associated with each category are presented in the sections that follow. Some sections end with a summary of significant costs within the category. Table 9 presents the cost breakdown for the flow variant cases. This table also presents total one-time, fixed costs, and total variable O&M costs; the total project costs; and the costs per gallon of water treated.

### 5.2.1 Site Preparation Costs

Site preparation includes administration, pilot-scale testing, mobilization costs. This analysis assumes a total area of about 65 acres will be needed to accommodate the wetland and staging area, construction equipment, and sampling and maintenance equipment storage areas. A solid gravel (or ground) surface is preferred for any remote treatment project. Pavement is not necessary, but the surface must be able to support construction equipment. This analysis assumes adequate surface areas exist at the site and that only moderate modifications will be required for wetland construction.

Administrative costs, such as legal searches and access rights, are estimated to be an additional $10,000.

Mobilization involves transporting all construction equipment and materials to the site. For this analysis, it is assumed that the site is located within 100 miles of a city where construction equipment is available. The total estimated mobilization cost will be $5,000.

For each case, total site preparation costs are estimated to be $15,000.

### 5.2.2 Permitting and Regulatory Requirements

Permitting and regulatory costs vary depending on whether treatment occurs at a Superfund site and on the disposal method selected for treated effluent and any solid wastes generated. At Superfund sites, remedial actions must be consistent with ARARs, environmental laws, ordinances, and regulations, including federal, state, and local standards and criteria. In general, ARARs must be identified on a site-specific basis. At an active mining site, a NPDES permit will likely be required and may require additional monitoring records and sampling protocols, which can increase permitting and regulatory costs. For this analysis, total permitting and regulatory costs are estimated to be $5,000.

### 5.2.3 Capital Equipment

Capital costs include all wetland construction and construction materials and a site building for housing sampling, monitoring, and maintenance equipment. Construction materials include sand, synthetic liners, geotextile liners, PVC piping, valves, concrete vaults or sumps, weirs, and other miscellaneous materials. Capital costs for the baseline wetland of 50 gpm are presented below. Site preparation and excavation include clearing the site of brush and trees, excavation of the wetland cell, grading the cell, and construction of the earthen berms. The total cost of site preparation and excavation is $19,500 for the 50 gpm system.

Construction of the wetland cell itself involves system design, subgrade preparation and installation of a sand layer, liner, piping distribution and collection systems, and the substrate. Also included is piping to and from the cell as well as system bypass piping, and concrete sumps with weirs at the influent of the wetland to control flow through

**Table 9.** CWS Costs for Different Treatment Flow Rates*

| Cost Categories | System Life 15 Years | | | | | |
|---|---|---|---|---|---|---|
| | 25 gpm | | 50 gpm | | 100 gpm | |
| Fixed Costs | | | | | | |
| Site Preparation | $15,000 | | $15,000 | | $15,000 | |
| Administrative | | $10,000 | | $10,000 | | $10,000 |
| Mobilization | | 5,000 | | 5,000 | | 5,000 |
| Permitting and Regulatory Requirements | $5,000 | | $5,000 | | $5,000 | |
| Capital Equipment | $215,300 | | $345,000 | | $604,500 | |
| System Design | | $50,000 | | $50,000 | | $50,000 |
| Excavation and Site Preparation | | 9,800 | | 19,500 | | 39,000 |
| Wetland Cell Construction | | 120,000 | | 240,000 | | 480,000 |
| Piping and Valves | | 25,500 | | 25,500 | | 25,500 |
| Storage Building | | 10,000 | | 10,000 | | 10,000 |
| Startup | $1,500 | | $1,500 | | $1,500 | |
| Demobilization | $52,250 | | $104,500 | | $209,000 | |
| Excavation and Backfilling | | $10,000 | | $20,000 | | $40,000 |
| Substrate Disposal | | 42,250 | | 84,500 | | 169,000 |
| Total Fixed Costs | $316,000 | | $492,000 | | $844,000 | |
| Variable Costs | | | | | | |
| Labor | $153,000 | | $153,000 | | $153,000 | |
| Operations Staff | | $153,000 | | $153,000 | | $153,000 |
| Consumables and Supplies | $39,000 | | $39,000 | | $39,000 | |
| Personal Protective Equipment | | $39,000 | | $39,000 | | $39,000 |
| Utilities | NA | | NA | | NA | |
| Residual and Waste Shipping and Handling | $120,000 | | $240,000 | | $480,000 | |
| Substrate Disposal | | 40,000 (3) | | 80,000 (3) | | 160,000 (3) |
| Analytical Services | $360,000 | | $360,000 | | $360,000 | |
| Maintenance and Modifications | $247,550 | | $490,100 | | $975,200 | |
| Annual Maintenance | | $5,000 | | $5,000 | | $5,000 |
| Substrate Removal and Replacement | | 80,850 (3) | | 161,700 (3) | | 323,400 (3) |
| Total Variable Costs | $919,550 | | $1,282,100 | | $2,007,200 | |
| Total Costs | $1,235,500 | | $1,774,100 | | $2,851,200 | |
| Total Cost Per Gallon Treated | $0.0063 | | $0.0045 | | $0.0036 | |

*Costs are based on July 1995 dollars, rounded to the nearest $100.
Substrate removal and replacement estimated to be necessary every 5 years.
(3) Number of removals anticipated
NA Not applicable

the system. The total cost for wetland cell construction of a 50 gpm system is $335.000.

A small building is required for storing sampling equipment and providing work space for the system operator. The cost for a simple building with electricity has been estimated at $10,000.

The total capital cost for a 50 gpm wetland system is $345,000.

### 5.2.4 Startup

Startup requirements are minimal for a wetland system. System startup involves introducing flow to the wetland with frequent inspections to verify proper hydraulic operation. Operators are assumed to be trained in health and safety procedures. Therefore, training costs are not incurred as a direct startup cost. The only costs directly related to system startup are labor costs associated with more frequent system inspection. Startup costs are estimated at $1,500.

### 5.2.5 Labor

Labor costs include a part-time technician to sample, operate, and maintain the system. Once the system is functioning, it is assumed to operate continuously at the design flow rate. One technician will monitor the system on a weekly basis. Weekly monitoring will require several hours 2 to 3 times per week to check flowrate and overall system operation. Sampling is assumed to be conducted once a month and will require two technicians for 2 hours. These requirements equate to 175 hours annually for general O&M. An additional 80 hours of labor are included for miscellaneous O&M and review of data. Based on $40 per hour for a technician, the annual cost for general labor O&M is $10,200.

### 5.2.6 Consumables and Supplies

The only consumables and supplies used during wetland operations are disposable PPE. Disposable PPE includes Tyvek coveralls, gloves, and bootcovers. The treatment system operator will wear PPE when required by health and safety plans during system operation. PPE will cost about $25 per day per person on site. Based on the assumed labor required above and an additional 22 days for miscellaneous O&M, PPE will be required 100 days annually, for an annual PPE cost of about $2,500.

### 5.2.7 Utilities

Utilities used by the wetland system are negligible. The wetland system requires no utilities for operation. The only utility required is for electricity for lights in the on-site storage building and for charging monitoring equipment. For this analysis, utility costs are assumed to be zero.

### 5.2.8 Residual Waste Shipping and Handling

The residual waste for the wetland is assumed to be spent substrate. This analysis assumes that substrate will require removal and replacement once every 5 years. It is assumed that spent substrate will be dewatered on site and disposed of at a recycler or landfill. Substrate removal and replacement costs are covered in Section 5.2.11, maintenance and modifications. Loading dewatered substrate into 20 $yd^3$ haul trucks is estimated to cost $14,500. Hauling the substrate to a recycler or landfill is estimated to cost $28,000; disposal of substrate at the landfill costs $42,000. Oversight of substrate removal, hauling and replacement is expected to cost $3,200 (10 8-hour days at $40/hr). Loading of the new substrate is expected to cost $12,000 and the cost of the substrate is $65,200. The total waste shipping and handling cost per substrate replacement is $161,700. Costs for residual waste shipping and handling are based solely on substrate volume. Costs for different sized wetlands are proportional to the 50 gpm baseline system described here.

### 5.2.9 Analytical Services

Analytical costs associated with a wetlands system include laboratory analysis, data reduction and tabulation, QA/QC, and reporting. For each case, this analysis assumes that one influent sample and two effluent samples will be collected once a month and that two substrate samples will be collected quarterly. The substrate samples will be analyzed for total metals. Influent and effluent samples will be analyzed for total metals, ammonia, nitrate, phosphate, BOD, TSS, and TDS. Monthly laboratory analysis will cost about $1,050, and substrate analysis $3,500 per year. Data reduction, tabulation, QA/QC, and reporting are estimated to cost about $660 per month. Total annual analytical services for each case are estimated to cost about $24,000 per year.

### 5.2.10 Maintenance and Modifications

Annual repair and maintenance costs are expected to be minimal and for this analysis are assumed to be $5,000 for each case. No modification costs are assumed to be

incurred. The major maintenance cost will be removal and replacement of the substrate every 5 years. Excavation of substrate material has been estimated to cost $14,500 for the 50 gpm scenario. Replacement of the distribution and collection piping was estimated to cost $14,300. Purchase and transport of new substrate was estimated to cost $65,400. The total estimated cost of substrate removal and replacement is $161,700. The removal and replacement cost will vary proportionally with the wetland size.

### *5.2.11 Demobilization*

Site demobilization costs include excavation of the substrate and concrete vaults and weirs, disposal of substrate, and backfilling the wetland. For the 50 gpm scenario, excavation costs are estimated at $10,000. Substrate disposal costs are $80,000. Backfilling of the wetland is expected to cost $10,000, assuming native material from the original wetland excavation was left on site. The total demobilization cost is estimated to be $104,500. This cost will vary proportionally with wetland size.

# Section 6
# Technology Status

Currently, several hundred constructed and natural wetlands are treating coal mine drainage in the eastern United States. The effectiveness of these systems is discussed in several publications including Hammer 1989, Moshiri 1993, and the proceedings of annual meetings of the American Society for Surface Mining and Reclamation, and several U.S. Bureau of Mines papers (U.S. Bureau of Mines Special Publication SP066-4 and Information Circular IC 9389) (see Appendix B).

In addition, any constructed wetlands designed to treat metal mine drainages have been constructed and tested or are being tested by EPA, various state agencies, and industry. In Colorado, the state Division of Minerals has constructed several wetland systems to treat metal mine drainage. Constructed wetlands treatment is also being considered for the full-scale remedy of the Burleigh Tunnel drainage.

# Section 7
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# Appendix A

## Analytical Results Summary Tables

**Table A-1.** Influent Results

## INFLUENT

| | ANALYTE | ANALYTICAL METHOD | WI030994 03/09/94 mg/L | WI032394 03/23/94 mg/L | WI040694 04/06/94 mg/L | WI042094 04/20/94 mg/L | WI050594 05/05/94 mg/L | WI051994 05/19/94 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | ND | ND | ND | ND | ND | 0.045 |
| | ARSENIC | 6020 | ND | 0.0041 | 0.0068 | 0.020 | 0.060 | 0.052 |
| | CADMIUM | 6020 | 0.10 | 0.099 | 0.10 | 0.10 | 0.098 | 0.081 |
| | CALCIUM | 6010 | 84.8 | 88.0 | 91.7 | 96.9 | 89.9 | 83.2 |
| | IRON | 6010 | 0.31 | 0.33 | 0.33 | 0.34 | 0.32 | 0.21 |
| | LEAD | 6020 | 0.014 | 0.015 | 0.014 | 0.016 | 0.016 | 0.014 |
| | MAGNESIUM | 6010 | 41.8 | 43.1 | 44.2 | 46.5 | 47.1 | 49.1 |
| | MANGANESE | 6010 | 2.3 | 2.4 | 2.5 | 2.6 | 2.3 | 1.8 |
| | NICKEL | 6010 | 0.045 | 0.039 | 0.042 | 0.047 | 0.043 | 0.035 |
| | POTASSIUM | 6010 | 2.6 | 2.9 | 3.0 | 3.1 | 3.6 | 3.2 |
| | SILVER | 6020 | 0.0011 | 0.00012 | 0.000066 | 0.000070 | 0.000098 | 0.00019 |
| | SODIUM | 6010 | 10.3 | 9.3 | 10.9 | 9.1 | 14.0 | 10.5 |
| | ZINC | 6010 | 55.0 | 56.1 | 60.1 | 64.0 | 56.1 | 44.8 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 386 | 374 | 387 | 384 | 317 | 314 |
| | SULFIDE TOTAL | 376.2 | NA | NA | NA | NA | NA | NA |
| | FLUORIDE | 340.2 | 1.0 | 1.2 | 1.1 | 1.1 | 0.98 | 1.0 |
| | CHLORIDE | 300.0 | 19.9 | 21.8 | 22.3 | 21.9 | 19.0 | 15.0 |
| | PHOSPHORUS, TOTAL | 365.3 | ND | ND | ND | ND | ND | ND |
| | ORTHOPHOSPHATE | 365.3 | ND | 0.30 | ND | ND | ND | 0.40 |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | 0.060 | 0.11 | ND | ND |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | ND | ND | 0.060 | 0.11 | ND | ND |
| | AMMONIA | 350.1 | ND | ND | ND | ND | ND | ND |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 16.8 | 8.8 | 20.4 | 15.2 | 7.4 | 8.4 |
| | TDS | 160.1 | 732 | 655 | 640 | 663 | 641 | 622 |
| | TOC | 9060 | 1.1 | NA | NA | ND | NA | NA |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 100 | 107 | 105 | 107 | 104 | 107 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 100 | 107 | 105 | 107 | 104 | 107 |
| | DISSOLVED OXYGEN (mg/L) | -- | 8.1 | 8.3 | 6.8* | | NA | NA |
| | pH | -- | 7.4 | 7.5 | 7.5 | | 7.4 | 7.5 |
| | CONDUCTIVITY (µS) | -- | 730 | 745 | 745 | | 699 | 698 |
| | TEMPERATURE (degrees C) | -- | 6.9 | 7.3 | 7.3 | | 8.9 | 9.4 |

-- = Not applicable

µS = MicroSiemens

mg/L = Milligrams per liter

NA = Not analyzed

ND = Not detected

**Table A-1 (continued).** Influent Results

**INFLUENT**

| | ANALYTE | ANALYTICAL METHOD | WI060194 06/01/94 mg/L | WI062994 06/29/94 mg/L | WI071394 07/13/94 mg/L | WI072894 07/28/94 mg/L | WI081594 08/15/94 mg/L | WI082494 08/24/94 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | ND | 0.068 | ND | ND | ND | ND |
| | ARSENIC | 6020 | ND | ND | ND | ND | ND | ND |
| | CADMIUM | 6020 | 0.092 | 0.089 | 0.086 | 0.098 | 0.10 | 0.0952 |
| | CALCIUM | 6010 | 89.6 | 86.1 | 94.5 | 91.2 | 92.5 | 94.6 |
| | IRON | 6010 | 0.25 | 0.23 | 0.23 | 0.30 | 0.24 | 0.25 |
| | LEAD | 6020 | 0.020 | 0.017 | 0.013 | 0.017 | 0.016 | 0.014 |
| | MAGNESIUM | 6010 | 50.6 | 45.4 | 48.3 | 46.4 | 47.7 | 48.1 |
| | MANGANESE | 6010 | 1.9 | 2.1 | 2.2 | 2.2 | 2.3 | 2.4 |
| | NICKEL | 6010 | 0.033 | 0.045 | 0.044 | 0.043 | 0.042 | 0.046 |
| | POTASSIUM | 6010 | 3.6 | 3.0 | 3.1 | 2.9 | 2.9 | 3.2 |
| | SILVER | 6020 | 0.00019 | ND | 0.00013 | 0.00015 | 0.00017 | ND |
| | SODIUM | 6010 | 13.2 | 12.8 | 13.00 | 12.0 | 14.4 | 15.3 |
| | ZINC | 6010 | 49.1 | 54.2 | 56.8 | 59.1 | 54.7 | 57.5 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 357 | 378 | 377 | 397 | 374 | 403 |
| | SULFIDE TOTAL | 376.2 | NA | NA | NA | NA | NA | NA |
| | FLUORIDE | 340.2 | 1.0 | 1.0 | 0.90 | 1.1 | 1.1 | 1.1 |
| | CHLORIDE | 300.0 | 16.9 | 17.9 | 17.5 | 18.7 | 18.6 | 19.6 |
| | PHOSPHORUS, TOTAL | 365.3 | ND | ND | ND | ND | ND | ND |
| | ORTHOPHOSPHATE | 365.3 | ND | 0.44 | ND | 0.077 | ND | ND |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | ND | 2.0 | 1.7 | 1.9 |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | 2.0 | 1.7 | 1.9 |
| | AMMONIA | 350.1 | ND | ND | ND | ND | ND | ND |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 4.4 | 11.2 | 9.2 | 9.6 | 2.4 | 18.4 |
| | TDS | 160.1 | 657 | 680 | 685 | 707 | 759 | 703 |
| | TOC | 9060 | NA | NA | NA | NA | NA | NA |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 109 | 107 | 109 | 103 | 105 | 102 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 109 | 107 | 109 | 103 | 105 | 102 |
| | DISSOLVED OXYGEN (mg/L) | -- | 8.7 | NA | 8.2 | NA | NA | 7.6 |
| | pH | -- | 7.6 | 7.57 | 7.5 | NA | 7.5 | 7.4 |
| | CONDUCTIVITY (µS) | -- | 775 | 980 | 950 | 927 | 948 | 920 |
| | TEMPERATURE (degrees C) | -- | 9.4 | 9.5 | 9.4 | 9.5 | 9.4 | 9.4 |

** = Degrees Farenheit

-- = Not applicable

µS = microSiemens

mg/L= Milligrams per liter

NA = Not analyzed

ND = Not detected

**Table A-1 (continued).** Influent Results

INFLUENT

| | ANALYTE | ANALYTICAL METHOD | WI090794 09/07/94 mg/L | WI091994 09/19/94 mg/L | WI100494 10/04/94 mg/L | WI101994 10/19/1994 mg/L | WI110294 11/02/94 mg/L | WI112094 11/20/94 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | ND | ND | ND | ND | 0.030 | ND |
| | ARSENIC | 6020 | ND | ND | ND | ND | ND | ND |
| | CADMIUM | 6020 | 0.098 | 0.085 | 0.089 | .10 | 0.10 | 0.091 |
| | CALCIUM | 6010 | 90.2 | 89.7 | 92.6 | 92.4 | 89.2 | 93.5 |
| | IRON | 6010 | 0.29 | 0.29 | 0.31 | 0.25 | 0.28 | 0.32 |
| | LEAD | 6020 | 0.017 | 0.015 | 0.014 | 0.014 | 0.014 | 0.016 |
| | MAGNESIUM | 6010 | 46.5 | 46.6 | 47.3 | 46.7 | 46.2 | 47.3 |
| | MANGANESE | 6010 | 2.3 | 2.3 | 2.3 | 2.4 | 2.2 | 2.3 |
| | NICKEL | 6010 | 0.047 | 0.042 | 0.052 | 0.046 | 0.051 | 0.050 |
| | POTASSIUM | 6010 | 3.9 | 3.1 | 3.0 | 3.0 | 2.9 | 3.1 |
| | SILVER | 6020 | 0.00040* | 0.00041 | 0.00050 | ND | ND | 0.00030 |
| | SODIUM | 6010 | 12.1 | 12.5 | 11.6 | 13 | 14.8 | 14.4 |
| | ZINC | 6010 | 56.4 | 57.6 | 59.7 | 57.6 | 56.5 | 58.2 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 416 | 404 | 400 | 409 | 410 | 407 |
| | SULFIDE TOTAL | 376.2 | NA | NA | NA | NA | NA | NA |
| | FLUORIDE | 340.2 | 1.0 | 1.0 | 1.0 | ND | 1.0 | 1.1 |
| | CHLORIDE | 300.0 | 20.2 | 19.6 | 19.8 | 19.5 | 20.1 | 21.3 |
| | PHOSPHORUS, TOTAL | 365.3 | ND | ND | ND | ND | ND | ND |
| | ORTHOPHOSPHATE | 365.3 | ND | ND | ND | ND | 0.13 | ND |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | ND | ND | ND | ND |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | ND | ND | ND |
| | AMMONIA | 350.1 | ND | ND | ND | ND | ND | ND |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 17.6 | 8.4 | 18.8 | 18.8 | 8.0 | 18.0 |
| | TDS | 160.1 | 711 | 723 | 695 | 695 | 709 | 711 |
| | TOC | 9060 | NA | NA | NA | NA | NA | NA |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 102 | 101 | 112 | 102 | 82.4 | 101 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 102 | 101 | 112 | 102 | 82.4 | 101 |
| | DISSOLVED OXYGEN (mg/L) | -- | 9.5 | 7.8 | NA | NA | NA | NA |
| | pH | -- | 7.41 | 7.4 | 7.4 | 7.1 | 6.9 | 6.9 |
| | CONDUCTIVITY (µS) | -- | 922 | 930 | 935 | 750 | 900 | NA |
| | TEMPERATURE (degrees C) | -- | 9.3 | 9.3 | 9.1 | 8.5 | 8.7 | 8.1 |

-- = Not applicable
µS = MicroSiemens
mg/L = Milligrams per liter

NA = Not detected
ND = Not detected

**Table A-1 (continued).** Influent Results

**INFLUENT**

| | ANALYTE | ANALYTICAL MEIHOD | WI113094 11/30/94 mg/L | WI121494 12/14/94 mg/L | WI010495 01/04/95 mg/L | WI011895 01/18/95 mg/L | WI020195 02/01/95 mg/L | WI021595 02/15/95 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | ND | 0.036 | 0.032 | 0.038 | 0.047 | 0.043 |
| | ARSENIC | 6020 | ND | ND | ND | ND | ND | ND |
| | CADMIUM | 6020 | 0.086 | 0.092 | 0.82 | 0.076 | 0.089 | 0.084 |
| | CALCIUM | 6010 | 95.4 | 98.1 | 87.7 | 90.8 | 90.1 | 100.0 |
| | IRON | 6010 | 0.34 | 0.37 | 0.31 | ND | 0.34 | 0.39 |
| | LEAD | 6020 | 0.014 | 0.018 | 0.016 | 0.015 | 0.016 | 0.015 |
| | MAGNESIUM | 6010 | 47.7 | 48.9 | 46.5 | 45.4 | 44.1 | 49.4 |
| | MANGANESE | 6010 | 2.5 | 2.5 | 2.3 | 2.4 | 2.4 | 2.7 |
| | NICKEL | 6010 | 0.044 | 0.050 | 0.048 | 0.046 | 0.052 | 0.048 |
| | POTASSIUM | 6010 | 2.8 | 3.3 | 2.9 | 3.0 | 2.8 | 3.5 |
| | SILVER | 6020 | 0.00036 | ND | 0.00037 | 0.00021 | ND | ND |
| | SODIUM | 6010 | 14.2 | 19.5 | 15.0 | 15.9 | 14.1 | 20.4 |
| | ZINC | 6010 | 62.8 | 63.0 | 55.5 | 57.1 | 56.6 | 58.9 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 411 | 413 | 395 | 386 | 402 | 390 |
| | SULFIDE TOTAL | 376.2 | NA | NA | NA | NA | NA | NA |
| | FLUORIDE | 340.2 | 1.1 | 1.0 | 1.1 | 1.1 | 1.1 | 1.1 |
| | CHLORIDE | 300.0 | 21.4 | 21.2 | 21.6 | 21.7 | 22.5 | 22.8 |
| | PHOSPHORUS, TOTAL | 365.3 | ND | ND | ND | ND | ND | ND |
| | ORTHOPHOSPHATE | 365.3 | 0.13 | 0.36 | ND | ND | ND | 0.10 |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | ND | ND | 1.7 | ND |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | ND | 1.7 | ND |
| | AMMONIA | 350.1 | ND | ND | ND | ND | ND | ND |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 16.4 | 10.4 | 5.2 | 12.0 | 12.8 | 12.8 |
| | TDS | 160.1 | 711 | 687 | 689 | 693 | 694 | 656 |
| | TOC | 9060 | NA | NA | NA | NA | NA | NA |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 99.6 | 103 | 104 | 106 | 106 | 106 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 99.6 | 103 | 104 | 106 | 106 | 106 |
| | DISSOLVED OXYGEN (mg/L) | -- | NA | 8.0 | 8.5 | 7.3 | 7.6 | NA |
| | pH | -- | 6.9 | 7.54 | 7.5 | 7.5 | 7.9 | 7.0 |
| | CONDUCTIVITY (µS) | -- | 605 | 600 | 610 | 600 | 610 | NA |
| | TEMPERATURE (degrees C) | -- | 7.9 | 8.0 | 6.5 | 9.0 | 7.9 | 8.1 |

* = Dissolved metals
-- = Not applicable
µS = Microsiemens
mg/L = Milligrams per liter

NA = Not analyzed
ND = Not detected

**Table A-1 (continued).** Influent Results

## INFLUENT

| | ANALYTE | ANALYTICAL METHOD | WI022795 02/27/95 mg/L | WI031595 03/15/95 mg/L | WI032995 03/29/95 mg/L | WI041295 04/12/95 mg/L | WI042695 04/26/95 mg/L | WI051095 05/10/95 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | 0.024 | 0.049 | ND | ND | 0.060 | 0.15 |
| | ARSENIC | 6020 | ND | ND | ND | ND | ND | ND |
| | CADMIUM | 6020 | 0.071 | 0.076 | 0.074 | 0.057 | 0.095 | 0.095 |
| | CALCIUM | 6010 | 92.6 | 91.4 | 85.2 | 90.9 | 88.2 | 92.0 |
| | IRON | 6010 | 0.33 | 0.36 | 0.33 | 0.32 | 0.41 | 0.48 |
| | LEAD | 6020 | 0.014 | 0.016 | 0.014 | 0.015 | 0.022 | 0.026 |
| | MAGNESIUM | 6010 | 45.1 | 44.4 | 41.9 | 42.9 | 41.2 | 41.9 |
| | MANGANESE | 6010 | 2.5 | 2.5 | 2.3 | 2.4 | 2.6 | 3.0 |
| | NICKEL | 6010 | 0.068 | 0.045 | 0.045 | 0.048 | 0.071 | 0.054 |
| | POTASSIUM | 6010 | 2.9 | 2.9 | 2.8 | 3.0 | 2.9 | 3.1 |
| | SILVER | 6020 | ND | ND | ND | ND | ND | ND |
| | SODIUM | 6010 | 16.2 | 15.8 | 16.4 | 16.1 | 14.2 | 14.8 |
| | ZINC | 6010 | 58.6 | 57.0 | 53.1 | 55.0 | 55.7 | 61.4 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 384.0 | 384.0 | 368.0 | 376.0 | 370.0 | 374 |
| | SULFIDE TOTAL | 376.2 | NA | NA | NA | NA | NA | NA |
| | FLUORIDE | 340.2 | 1.1 | 1.1 | 1.0 | 1.0 | 1.1 | 1.1 |
| | CHLORIDE | 300.0 | 22.6 | 22.4 | 23.1 | 22.4 | 23.8 | 20.5 |
| | PHOSPHORUS, TOTAL | 365.3 | ND | ND | ND | ND | ND | ND |
| | ORTHOPHOSPHATE | 365.3 | ND | ND | ND | 0.11 | ND | ND |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | ND | ND | 0.14 | ND |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | ND | 0.14 | ND |
| | AMMONIA | 350.1 | ND | ND | ND | ND | ND | ND |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 11.2 | 9.2 | 12.8 | 14.4 | 7.2 | 2.8 |
| | TDS | 160.1 | 692 | 672 | 655 | 656 | 575 | 689 |
| | TOC | 9060 | NA | NA | NA | NA | NA | ND |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 107 | 104 | 107 | 107 | 104 | 103 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 107 | 104 | 107 | 107 | 104 | 103 |
| | DISSOLVED OXYGEN (mg/L) | -- | 7.8 | NA | 7.5 | 8.6 | 7.5 | |
| | pH | -- | 7.4 | 7.5 | 7.7 | 7.5 | NA | |
| | CONDUCTIVITY (µS) | -- | 630 | 620 | 600 | 620 | 600 | |
| | TEMPERATURE (degrees C) | -- | 8.6 | 9.3 | 8.1 | 8.4 | 9.0 | |

* = Dissolved metals
-- = Not applicable
µS = Microsiemens
mg/L = Milligrams per liter

NA = Not analyzed
ND = Not detected

**Table A-1 (continued).** Influent Results

| | | | INFLUENT | | | | | |
|---|---|---|---|---|---|---|---|---|
| | ANALYTE | ANALYTICAL METHOD | WI061295 6/12/1995 mg/L | WI062895 6/28/1995 mg/L | WI071095 7/10/1995 mg/L | WI072695 7/26/1995 mg/L | WI080895 8/8/1995 mg/L | WI082395 8/23/1995 mg/L |
| AQUEOUS | ALUMINUM | 6010 | 0.065 | ND | ND | ND | ND | 0.079 |
| | ARSENIC | 6020 | ND | ND | ND | ND | ND | ND |
| | CADMIUM | 6020 | 0.25 | 0.26 | 0.25 | 0.24 | 0.26 | 0.240 |
| | CALCIUM | 6010 | 94.4 | 111 | 119 | 129 | 123 | 125 |
| | IRON | 6010 | 0.12 | 0.11 | 0.10 | ND | 0.15 | 0.19 |
| | LEAD | 6020 | 0.058 | 0.051 | 0.050 | 0.038 | 0.043 | 0.039 |
| | MAGNESIUM | 6010 | 58.3 | 61.4 | 64.0 | 64.2 | 61.7 | 61.3 |
| | MANGANESE | 6010 | 3.9 | 4.4 | 5.0 | 5.5 | 5.2 | 5.2 |
| | NICKEL | 6010 | 0.061 | 0.073 | 0.081 | 0.084 | 0.093 | 0.086 |
| | POTASSIUM | 6010 | 4.1 | ND | 3.6 | 3.7 | 3.5 | 3.2 |
| | SILVER | 6020 | ND | ND | ND | ND | ND | ND |
| | SODIUM | 6010 | 9.9 | 14.2 | 14.8 | 13.2 | 14.1 | 15.2 |
| | ZINC | 6010 | 75.5 | 86.8 | 99.8 | 105 | 109 | 108 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 499 | 502 | 582 | 596 | 638 | 630 |
| | SULFIDE TOTAL | 376.2 | | | | | | |
| | FLUORIDE | 340.2 | 0.8 | 0.89 | 0.96 | 0.88 | 0.87 | 0.95 |
| | CHLORIDE | 300.0 | 6.9 | | 8.8 | 10.2 | 11.7 | 13.1 |
| | PHOSPHORUS, TOTAL | 365.3 | ND | ND | ND | ND | ND | 0.093 |
| | ORTHOPHOSPHATE | 365.3 | ND | ND | ND | ND | 0.095 | ND |
| | NITRATE PLUS NITRITE AS N | 353.2 | 0.13 | 0.10 | ND | 0.63 | ND | ND |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | 0.13 | ND | ND | 0.63 | ND | ND |
| | AMMONIA | 350.1 | ND | ND | ND | ND | ND | ND |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 20.4 | 20.4 | 24.8 | 22.4 | 18.8 | 32.0 |
| | TDS | 160.1 | 838 | 967 | 1010 | 999 | 10.0 | 1050 |
| | TOC | 9060 | | | | | | |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 120 | 125 | 118 | 107 | 107 | 107 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 120 | 125 | 118 | 107 | 107 | 107 |
| | DISSOLVED OXYGEN (mg/L) | -- | NA | 7.1 | NA | NA | NA | NA |
| | pH | -- | 7.4 | 7.2 | 7.4 | NA | NA | NA |
| | CONDUCTIVITY (µS) | -- | NA | 700 | NA | NA | 750 | NA |
| | TEMPERATURE (degrees C) | -- | 10.2 | 10.3 | 10.3 | NA | 10.4 | NA |

* = Dissolved metals
-- = Not applicable
µS = Microsiemens
mg/L = Milligrams per liter

NA = Not analyzed
ND = Not detected

**Table A-1 (continued).** Influent Results

## INFLUENT

| | ANALYTE | ANALYTICAL METHOD | WI090595 9/5/1995 mg/L | WI110995 11/9/1995 mg/L | CDPHE 1/29/1996 mg/L | CDPHE 2/29/1996 mg/L | CDPHE 4/25/1996 mg/L | CDPHE 5/31/1996 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | ND | ND | NA | NA | NA | NA |
| | ARSENIC | 6020 | ND | ND | NA | NA | NA | NA |
| | CADMIUM | 6020 | 0.24 | 0.20 | 0.160 | 0.200 | 0.12 | 0.14 |
| | CALCIUM | 6010 | 123 | 113 | NA | NA | NA | NA |
| | IRON | 6010 | 0.28 | 0.18 | 0.24 | 0.26 | 0.18 | 0.17 |
| | LEAD | 6020 | 0.038 | 0.027 | NA | NA | NA | NA |
| | MAGNESIUM | 6010 | 60.2 | 56.2 | NA | NA | NA | NA |
| | MANGANESE | 6010 | 5.2 | 5.2 | 3.60 | 3.50 | 2.4 | 2.7 |
| | NICKEL | 6010 | 0.087 | 0.082 | NA | NA | NA | NA |
| | POTASSIUM | 6010 | ND | 3.2 | NA | NA | NA | NA |
| | SILVER | 6020 | ND | ND | NA | NA | NA | NA |
| | SODIUM | 6010 | 12.4 | 15.6 | NA | NA | NA | NA |
| | ZINC | 6010 | 107 | 105 | 73 | 69 | 46 | 56 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 652 | 591 | 490 | 450 | NA | NA |
| | SULFIDE TOTAL | 376.2 | NA | NA | NA | NA | NA | NA |
| | FLUORIDE | 340.2 | 0.88 | 0.97 | NA | NA | NA | NA |
| | CHLORIDE | 300.0 | NA | 17.7 | NA | NA | NA | NA |
| | PHOSPHORUS, TOTAL | 365.3 | 0.067 | 0.060 | NA | NA | NA | NA |
| | ORTHOPHOSPHATE | 365.3 | ND | 0.20 | NA | NA | NA | NA |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | NA | NA | NA | NA |
| | NITRITE AS N | 354.1 | ND | ND | NA | NA | NA | NA |
| | NITRATE AS N | 353.2/354.1 | ND | ND | NA | NA | NA | NA |
| | AMMONIA | 350.1 | ND | ND | NA | NA | NA | NA |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 18.4 | 14.4 | NA | NA | NA | NA |
| | TDS | 160.1 | 1050 | 956 | NA | NA | NA | NA |
| | TOC | 9060 | | | | NA | NA | NA |
| | ALKALINITY, TOTAL: | | | | | | | |
| | AS CaCO3 | 310.1 | 107 | 95.7 | NA | NA | NA | NA |
| | ALKALINITY, BICARB | | | | NA | NA | NA | NA |
| | AS CAC03 | 310.1 | 107 | 95.7 | NA | NA | NA | NA |
| | DISSOLVED OXYGEN (mg/L) | -- | | | NA | NA | NA | NA |
| | pH | -- | | | NA | NA | NA | NA |
| | CONDUCTIVITY (µS) | -- | | | NA | NA | NA | NA |
| | TEMPERATURE (degrees C) | -- | | | NA | NA | NA | NA |

* = Dissolved metals
-- = Not applicable
µS = Microsiemens
mg/L = Milligrams per liter

NA = Not analyzed
ND = Not detected

**Table A-1 (continued).** Influent Results

INFLUENT

| | ANALYTE | ANALYTICAL MEIHOD | CDPHE 6/14/1996 mg/L | CDPHE 7/19/1996 mg/L | CDPHE 8/31/1996 mg/L | WI120996 12/9/1996 mg/L | WI012197 1/21/1997 mg/L | WI022097 2/20/1997 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | NA | NA | NA | ND | ND | ND |
| | ARSENIC | 6020 | NA | NA | NA | NA | NA | NA |
| | CADMIUM | 6020 | 0.16 | 0.19 | 0.20 | 0.15 | 0.12 | 0.11 |
| | CALCIUM | 6010 | NA | NA | NA | 104 | 100.0 | 105 |
| | IRON | 6010 | 0.18 | 0.20 | 0.24 | 0.30 | 0.30 | 0.33 |
| | LEAD | 6020 | NA | NA | NA | NA | NA | NA |
| | MAGNESIUM | 6010 | NA | NA | NA | 52.8 | 51.2 | 52 |
| | MANGANESE | 6010 | 2.9 | 3.5 | 4.1 | 3.7 | 3.5 | 3.7 |
| | NICKEL | 6010 | NA | NA | NA | 0.07 | 0.06 | 0.06 |
| | POTASSIUM | 6010 | NA | NA | NA | 3.1 J | 3.0 J | 3.0 J |
| | SILVER | 6020 | NA | NA | NA | NA | NA | NA |
| | SODIUM | 6010 | NA | NA | NA | 17.4 | 16.4 | 17.0 |
| | ZINC | 6010 | 60 | 71 | 84 | 78 | 74 | 78 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 430 | 490 | 520 | 488 | 491 | 471 |
| | SULFIDE TOTAL | 376.2 | NA | NA | NA | NA | NA | NA |
| | FLUORIDE | 340.2 | NA | NA | NA | NA | NA | NA |
| | CHLORIDE | 300.0 | NA | NA | NA | 17.8 | 18.2 | 18.3 |
| | PHOSPHORUS, TOTAL | 365.3 | NA | NA | NA | NA | NA | NA |
| | ORTHOPHOSPHATE | 365.3 | NA | NA | NA | 0.31 | 0.17 | 0.22 |
| | NITRATE PLUS NITRITE AS N | 353.2 | NA | NA | NA | ND | ND | ND |
| | NITRITE AS N | 354.1 | NA | NA | NA | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | NA | NA | NA | ND | ND | ND |
| | AMMONIA | 350.1 | NA | NA | NA | ND | ND | ND |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | NA | NA | NA | NA | 8.4 | 3.2 |
| | TDS | 160.1 | NA | NA | NA | 849 | 796 | 809 |
| | TOC | 9060 | NA | NA | NA | 0.8J | 1.1 | 1.8 |
| | ALKALINITY, TOTAL: | | | | | | | |
| | AS CaCO3 | 310.1 | NA | NA | NA | 97.6 | 94.9 | 101 |
| | ALKALINITY, BICARB | | NA | NA | NA | | | |
| | AS CAC03 | 310.1 | NA | NA | NA | 97.6 | 94.9 | 101 |
| | DISSOLVED OXYGEN (mg/L) | -- | NA | NA | NA | 7.4 | 8.8 | 8.6 |
| | pH | -- | NA | NA | NA | 7.2 | 5.1 | 7.5 |
| | CONDUCTIVITY (µS) | -- | NA | NA | NA | NA | NA | NA |
| | TEMPERATURE (degrees C) | -- | NA | NA | NA | 10.0 | 8.2 | 3.2 |

* = Dissolved metals
-- = Not applicable
µS = Microsiemens
mg/L= Milligrams per liter

NA = Not analyzed
ND = Not detected

**Table A-1 (continued).** Influent Results

## INFLUENT

| | ANALYTE | ANALYTICAL METHOD | WI032097 3/20/1997 mg/L | WI042297 4/22/1997 mg/L | WI052897 5/28/1997 mg/L | WI062397 6/23/1997 mg/L | WI082897 8/28/1997 mg/L | WI093097 9/30/1997 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | ND | 0.17 | ND | ND | ND | ND |
| | ARSENIC | 6020 | NA | NA | NA | NA | NA | NA |
| | CADMIUM | 6020 | 0.14 | 0.07 | 0.11 | 0.19 | 0.22 | 0.200 |
| | CALCIUM | 6010 | 97.5 | 67.2 | 86.4 | 95.6 | 121 | 119 |
| | IRON | 6010 | 0.34 | 0.34 | 0.24 | 0.26 | 0.3 | 0.33 |
| | LEAD | 6020 | NA | NA | NA | NA | NA | NA |
| | MAGNESIUM | 6010 | 48.8 | 37.3 | 53.8 | 52.3 | 61.9 | 58.4 |
| | MANGANESE | 6010 | 3.6 | 2.0 | 2.7 | 3.3 | 4.9 | 4.9 |
| | NICKEL | 6010 | 0.07 | 0.034 J | 0.042 | 0.030 J | 0.090 | 0.098 |
| | POTASSIUM | 6010 | ND | 2.7 J | 3.3 J | 3.5 J | 4.8 J | 3.4 J |
| | SILVER | 6020 | NA | NA | NA | NA | NA | NA |
| | SODIUM | 6010 | 15.6 | ND | 14.9 | ND | ND | 18.3 |
| | ZINC | 6010 | 75 | 42 | 56 | 72 | 104 | 104 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 476 | 279 | 358 | 428 | 541 | 568 |
| | SULFIDE TOTAL | 376.2 | NA | NA | NA | NA | NA | NA |
| | FLUORIDE | 340.2 | NA | NA | NA | NA | NA | NA |
| | CHLORIDE | 300.0 | 18.7 | 9.3 | 7.2 | 9.2 | 13.8 | 16 |
| | PHOSPHORUS, TOTAL | 365.3 | NA | NA | NA | NA | NA | NA |
| | ORTHOPHOSPHATE | 365.3 | 0.15 | ND | ND | 0.10 | ND | ND |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | 0.14 | ND | 0.14 | ND | 0.19 |
| | NITRITE AS N | 354.1 | 0.0021 J | 0.0046 J | 0.0024 J | 0.0028 J | 0.0037 J | ND |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | ND | ND | ND |
| | AMMONIA | 350.1 | ND | ND | ND | ND | ND | ND |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 7.6 | 1.6 J | 12.4 | 14.4 | | 16.4 |
| | TDS | 160.1 | 751 | 507 | 653 | 765 | 927 | 940 |
| | TOC | 9060 | 0.20 J | 1.30 | 1.4 | 0.98 J | 0.80 J | 0.58 J |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 96.3 | 99.7 | 107 | 121 | | 102 |
| | ALKALINITY, BICARB AS CACO3 | 310.1 | 96.3 | 99.7 | 107 | 121 | | 102 |
| | DISSOLVED OXYGEN (mg/L) | -- | 7.8 | 7.3 | 7.3 | 8 | 8.7 | NA |
| | pH | -- | 6.9 | 7.4 | 7.4 | 7.5 | 6.9 | 6.9 |
| | CONDUCTIVITY (µS) | -- | NA | NA | NA | NA | NA | NA |
| | TEMPERATURE (degrees C) | -- | 8.6 | 9.7 | 10.5 | 9.7 | 9.6 | 9.4 |

* = Dissolved metals
-- = Not applicable
µS = Microsiemens
mg/L = Milligrams per liter

NA = Not analyzed
ND = Not detected

**Table A-1 (continued).** Influent Results

## INFLUENT

| | ANALYTE | ANALYTICAL METHOD | WI102997 10/29/1997 mg/L | WI112597 11/25/1997 mg/L |
|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | ND | ND |
| | ARSENIC | 6020 | NA | NA |
| | CADMIUM | 6020 | 0.19 | 0.22 |
| | CALCIUM | 6010 | 113 | 103 |
| | IRON | 6010 | 0.37 | 0.39 |
| | LEAD | 6020 | NA | NA |
| | MAGNESIUM | 6010 | 58.8 | 50.4 |
| | MANGANESE | 6010 | 4.9 | 4.2 |
| | NICKEL | 6010 | 0.079 | 0.065 |
| | POTASSIUM | 6010 | 3.4 J | ND |
| | SILVER | 6020 | NA | NA |
| | SODIUM | 6010 | 18.3 | 16.5 |
| | ZINC | 6010 | 95 | 86 |
| | ANIONS: | | | |
| | SULFATE | 300.0 | 571 | 548 |
| | SULFIDE TOTAL | 376.2 | NA | NA |
| | FLUORIDE | 340.2 | NA | NA |
| | CHLORIDE | 300.0 | 17.5 | 17.8 |
| | PHOSPHORUS, TOTAL | 365.3 | NA | NA |
| | ORTHOPHOSPHATE | 365.3 | ND | 0.15 |
| | NITRATE PLUS NITRITE AS N | 353.2 | 0.11 | ND |
| | NITRITE AS N | 354.1 | 0.002J | 0.0025J |
| | NITRATE AS N | 353.2/354.1 | NA | NA |
| | AMMONIA | 350.1 | ND | ND |
| | TOTAL SOLIDS: | | | |
| | TSS | 160.2 | 10.4 | 14.8 |
| | TDS | 160.1 | 940 | 869.0 |
| | TOC | 9060 | 0.71J | 1.8 |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 84 | 102 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 84 | 102 |
| | DISSOLVED OXYGEN (mg/L) | -- | 10.3 | 7.5 |
| | pH | -- | 7.2 | 7.2 |
| | CONDUCTIVITY (µS) | -- | NA | NA |
| | TEMPERATURE (degrees C) | -- | 9.2 | 8.9 |

* = Dissolved metals
-- = Not applicable
µS = Microsiemens
mg/L= Milligrams per liter

NA = Not analyzed
ND = Not detected

**Table A-2.** Downflow Effluent Results

## DOWNFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | WED030994 03/09/94 mg/L | WED032394 03/23/94 mg/L | WED040694 04/06/94 mg/L | WED042094 04/20/94 mg/L | WED050594 05/05/94 mg/L |
|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | 0.021 | 0.021 | 0.027 | 0.029 | 0.033 |
| | ARSENIC | 6020 | ND | 0.00056 | 0.029 | 0.016 | 0.076 |
| | CADMIUM | 6020 | 0.00034 | 0.00025 | 0.00028 | 0.00053 | 0.00072 |
| | CALCIUM | 6010 | 105.0 | 107.0 | 110.0 | 113.0 | 113.0 |
| | IRON | 6010 | 1.5 | 1.2 | 1.1 | 1.0 | 1.1 |
| | LEAD | 6020 | 0.0015 | 0.0012 | 0.00065 | 0.0015 | 0.0017 |
| | MAGNESIUM | 6010 | 56.7 | 56.9 | 58.6 | 58.3 | 58.9 |
| | MANGANESE | 6010 | 1.6 | 1.5 | 1.5 | 1.4 | 1.4 |
| | NICKEL | 6010 | 0.0073 | 0.0081 | 0.0086 | 0.010 | 0.0090 |
| | POTASSIUM | 6010 | 55.8 | 56.6 | 54.0 | 50.6 | 48.3 |
| | SILVER | 6020 | 0.0015 | 0.00012 | 0.000060 | 0.000089 | 0.0051 |
| | SODIUM | 6010 | 19.0 | 17.1 | 18.1 | 15.3 | 18.6 |
| | ZINC | 6010 | 14.2 | 14.9 | 15.6 | 15.3 | 13.1 |
| | ANIONS: | | | | | | |
| | SULFATE | 300.0 | 350 | 357 | 338 | 337 | 280 |
| | SULFIDE TOTAL | 376.2 | 4.1 | 5.2 | 5.7 | 2.1 | 0.74 |
| | FLUORIDE | 340.2 | 0.82 | 0.93 | 0.88 | 0.90 | 0.87 |
| | CHLORIDE | 300.0 | 15.6 | 28.4 | 27.2 | 28 | 22 |
| | PHOSPHORUS, TOTAL | 365.3 | 9.9 | 10.6 | 11.0 | 10.8 | 10.4 |
| | ORTHOPHOSPHATE | 365.3 | 10.6 | 12.4 | 10.7 | 11.1 | 11.1 |
| | NITRATE PLUS NITRITE AS N | 353.2 | 0.24 | ND | ND | ND | ND |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | 0.24 | ND | ND | ND | ND |
| | AMMONIA | 350.1 | 5.4 | 6.2 | 5.9 | 5.8 | 4.6 |
| | TOTAL SOLIDS: | | | | | | |
| | TSS | 160.2 | 51.0 | 27.0 | 47.0 | 39.2 | 3.8 |
| | TDS | 160.1 | 864 | 781 | 766 | 783 | 753 |
| | TOC | 9060 | 60.4 | 20.6 | 29 | 28.2 | 20.8 |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 193 | 209 | 200 | 213 | 193 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 193 | 209 | 200 | 213 | 193 |
| | ORP (mV) | -- | -77.0 | | -180 | | -184 |
| | pH | -- | 7.3 | | 7.2 | | 7.6 |
| | CONDUCTIVITY (µS) | -- | 845 | | 889 | | 803 |
| | TEMPERATURE (degrees C) | -- | 4.1 | | 5.2 | | 8.8 |

-- = Not applicable
µS = MicroSiemens
mg/L = Milligrams per liter
mV = Millivolts

NA = Not analyzed
ND = Not detected

**Table A-2 (continued).** Downflow Effluent Results

## DOWNFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | WED051994 05/19/94 mg/L | WED060194 06/01/94 mg/L | WED062994 06/29/94 mg/L | WED071394 07/13/94 mg/L | WED072894 07/28/94 mg/L | WED081594 08/15/94 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | 0.024 | 0.030 | 0.017 | 0.012 | 0.017 | 0.016 |
| | ARSENIC | 6020 | 0.066 | 0.0013 | 0.0011 | 0.0010 | 0.0012 | 0.0011 |
| | CADMIUM | 6020 | 0.0011 | 0.00073 | ND | ND | ND | 0.00033 |
| | CALCIUM | 6010 | 107.0 | 112.0 | 106.0 | 118.0 | 116.0 | 114.0 |
| | IRON | 6010 | 1.0 | 1.1 | 1.0 | 1.1 | 1.1 | 1.3 |
| | LEAD | 6020 | 0.0013 | 0.0011 | ND | ND | ND | ND |
| | MAGNESIUM | 6010 | 57.1 | 60.8 | 55.2 | 57.9 | 55.9 | 56.6 |
| | MANGANESE | 6010 | 1.3 | 1.4 | 1.5 | 1.8 | 1.8 | 2.1 |
| | NICKEL | 6010 | 0.0088 | 0.015 | 0.014 | 0.0089 | 0.013 | 0.013 |
| | POTASSIUM | 6010 | 39.5 | 29.2 | 19.8 | 20.8 | 17.8 | 23.0 |
| | SILVER | 6020 | 0.000063 | ND | 0.00010 | 0.00025 | ND | 0.00014 |
| | SODIUM | 6010 | 15.4 | 15.2 | 13.8 | 14.7 | 14.5 | 15.5 |
| | ZINC | 6010 | 9.9 | 10.3 | 12.6 | 15.3 | 16.5 | 14.5 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 270 | 319 | 338 | 337 | 354 | 311 |
| | SULFIDE TOTAL | 376.2 | 3.2 | 2.4 | 2.1 | 1.3 | 6.9 | 1.5 |
| | FLUORIDE | 340.2 | 0.91 | 0.95 | 0.80 | 0.90 | 1.1 | 1.0 |
| | CHLORIDE | 300.0 | 17.4 | 18.4 | 19.6 | 17.8 | 19.8 | 19.2 |
| | PHOSPHORUS, TOTAL | 365.3 | 11.4 | 10.1 | 8.9 | 9.5 | 7.8 | 8.7 |
| | ORTHOPHOSPHATE | 365.3 | 10.6 | 9.2 | 8.6 | 8.6 | 7.5 | 6.7 |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | ND | ND | 2.3 | 1.7 |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | ND | 2.3 | 1.7 |
| | AMMONIA | 350.1 | 4.4 | 3.2 | 2.3 | 3.1 | 2.9 | 3.2 |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | ND | 3.6 | 33.6 | 43 | 45.6 | 43.2 |
| | TDS | 160.1 | 739 | 741 | 709 | 722 | 747 | 759 |
| | TOC | 9060 | 26.3 | 35.6 | 17.8 | 15.9 | 15.4 | 15.6 |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 196 | 208 | 188 | 190 | 188 | 194 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 196 | 208 | 188 | 190 | 188 | 194 |
| | ORP (mV) | -- | -271 | | -253 | -250 | NA | NA |
| | pH | -- | 7.28 | | 7.10 | 7 | NA | 7.06 |
| | CONDUCTIVITY (µS) | -- | 812 | | 1040 | 1010 | 996 | 1006 |
| | TEMPERATURE (degrees C) | -- | 12.2 | | 12.3 | 11.6 | 11.8 | 12.1 |

-- = Not applicable
µS = MicroSiemens
mg/L = Milligrams per liter
mV = Millivolts

NA = Not analyzed
ND = Not detected

**Table A-2 (continued).** Downflow Effluent Results

## DOWNFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | WED082494 08/24/94 mg/L | WED090794 09/07/94 mg/L | WED091994 09/19/94 mg/L | WED100494 10/04/94 mg/L | WED101994 10/19/1994 mg/L | WED110294 11/02/94 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | 0.015 | 0.053 | 0.022 | 0.037 | 0.018 | 0.023 |
| | ARSENIC | 6020 | 0.0011 | ND | 0.0011 | 0.0018 | ND | ND |
| | CADMIUM | 6020 | 0.00030 | ND | ND | 0.00038 | 0.00048 | 0.00041 |
| | CALCIUM | 6010 | 117.0 | 113.0 | 124.0 | 115.0 | 112.0 | 112.0 |
| | IRON | 6010 | 1.7 | 1.8 | 2.0 | 1.8 | 1.7 | 1.8 |
| | LEAD | 6020 | ND | 0.0016 | 0.0023 | 0.0032 | ND | ND |
| | MAGNESIUM | 6010 | 57.5 | 55.8 | 63.9 | 57.6 | 57.7 | 58.0 |
| | MANGANESE | 6010 | 2.2 | 2.0 | 2.2 | 1.9 | 1.8 | 1.6 |
| | NICKEL | 6010 | 0.014 | 0.013 | 0.020 | 0.019 | 0.020 | 0.020 |
| | POTASSIUM | 6010 | 21.7 | 25.0 | 24.9 | 21.6 | 19.5 | 16.8 |
| | SILVER | 6020 | ND | 0.00032* | 0.00034 | 0.0012 | ND | ND |
| | SODIUM | 6010 | 15.6 | 14.5 | 16.4 | 14.4 | 14.5 | 15.5 |
| | ZINC | 6010 | 15.3 | 15.2 | 17.5 | 15.5 | 14.2 | 12.1 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 345 | 349 | 349 | 333 | 353 | 365 |
| | SULFIDE TOTAL | 376.2 | 4.5 | 0.12 | 5.3 | 10.7 | 4.8 | 7.4 |
| | FLUORIDE | 340.2 | 1.0 | 0.94 | 0.96 | 0.88 | 0.85 | 0.87 |
| | CHLORIDE | 300.0 | 21.3 | 22.3 | 21.0 | 21.0 | 20.3 | 20.8 |
| | PHOSPHORUS, TOTAL | 365.3 | 10.4 | 1.6 | 9.1 | 8.8 | 9.0 | 8.2 |
| | ORTHOPHOSPHATE | 365.3 | 7.9 | 8.6 | 13.8 | 8.5 | 8.4 | 8.8 |
| | NITRATE PLUS NITRITE AS N | 353.2 | 1.8 | ND | ND | ND | ND | ND |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | 1.8 | ND | ND | ND | ND | ND |
| | AMMONIA | 350.1 | 3.2 | 2.6 | 2.5 | 2.9 | 2.2 | 1.5 |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 48.8 | 49.6 | 47.2 | 52.0 | 45.6 | 40.0 |
| | TDS | 160.1 | 713 | 741 | 738 | 716 | 698 | 734 |
| | TOC | 9060 | 13.8 | 12.3 | 10.3 | 9.7 | 8.1 | 5.0 |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 191 | 194 | 184 | 200 | 174 | 152 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 191 | 194 | 184 | 200 | 174 | 152 |
| | ORP (mV) | -- | -125 | -163 | -216 | -220 | -331 | -149 |
| | pH | -- | 6.88 | 6.91 | 6.9 | 6.9 | 6.66 | 6.92 |
| | CONDUCTIVITY (µS) | -- | 973 | 997 | 1010 | 960 | 750 | 890 |
| | TEMPERATURE (degrees C) | -- | 13.4 | 12.4 | 10.7 | 9.0 | 6.8 | 4.9 |

-- = Not applicable
µS = MicroSiemens
mg/L = Milligrams per liter
mV = Millivolts

NA = Not analyzed
ND = Not detected

**Table A-2 (continued).** Downflow Effluent Results

## DOWNFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | WED112094 11/20/94 mg/L | WED113094 11/30/94 mg/L | WED121494 12/14/94 mg/L | WED010495 01/04/95 mg/L | WED011895 01/18/95 mg/L | WED020195 02/01/95 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | 0.018 | 0.023 | 0.013 | 0.013 | 0.014 | 0.022 |
| | ARSENIC | 6020 | ND | ND | ND | 0.0039 | 0.0035 | ND |
| | CADMIUM | 6020 | 0.00030 | 0.00030 | 0.00088 | ND | ND | ND |
| | CALCIUM | 6010 | 120.0 | 118.0 | 120.0 | 117.0 | 119.0 | 115.0 |
| | IRON | 6010 | 1.8 | 2.4 | 2.0 | 2.7 | 3.0 | 2.6 |
| | LEAD | 6020 | 0.0054 | 0.0018 | 0.011 | ND | 0.0012 | ND |
| | MAGNESIUM | 6010 | 60.6 | 58.0 | 56.6 | 57.1 | 54.5 | 50.7 |
| | MANGANESE | 6010 | 1.6 | 1.7 | 1.5 | 1.9 | 1.9 | 1.8 |
| | NICKEL | 6010 | 0.019 | 0.019 | 0.017 | 0.013 | 0.014 | 0.018 |
| | POTASSIUM | 6010 | 16.0 | 13.1 | 11.5 | 9.7 | 9.9 | 8.3 |
| | SILVER | 6020 | ND | 0.00022 | ND | ND | ND | ND |
| | SODIUM | 6010 | 14.6 | 14.5 | 15.0 | 14.3 | 14.9 | 15.0 |
| | ZINC | 6010 | 10.9 | 11.7 | 8.8 | 8.3 | 9.7 | 10.5 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 357 | 391 | 391 | 386 | 386 | 380 |
| | SULFIDE TOTAL | 376.2 | 0.11 | 5.8 | 3.1 | 3.3 | 1.6 | 2.3 |
| | FLUORIDE | 340.2 | 0.90 | 1.1 | 0.99 | 1.1 | 1.0 | 1.0 |
| | CHLORIDE | 300.0 | 21.0 | 22.0 | 21.2 | 22.1 | 22.1 | 21.9 |
| | PHOSPHORUS, TOTAL | 365.3 | 6.5 | 7.2 | 7.3 | 6.6 | 6.4 | 6.3 |
| | ORTHOPHOSPHATE | 365.3 | 3.1 | 5.0 | 6.2 | 5.5 | 4.9 | 6.0 |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | ND | ND | ND | ND |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | ND | ND | ND |
| | AMMONIA | 350.1 | 2.2 | 2.0 | 0.41 | 1.6 | 1.5 | 1.3 |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 41.0 | 40.5 | 28.5 | 34.0 | 37.0 | 33.0 |
| | TDS | 160.1 | 750 | 767 | 744 | 729 | 718 | 721 |
| | TOC | 9060 | 6.9 | 20.4 | 5.7 | 4.8 | 5.6 | 4.8 |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 187 | 143 | 152 | 146 | 141 | 129 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 187 | 143 | 152 | 146 | 141 | 129 |
| | ORP (mV) | -- | -170 | -220 | -195 | -20.0 | -6.5 | -7.3 |
| | pH | -- | 7.6 | 7.12 | 7.46 | 7.26 | 7.6 | 7.6 |
| | CONDUCTIVITY (µS) | -- | NA | 600 | 600 | 590 | 590 | 670 |
| | TEMPERATURE (degrees C) | -- | 3.7 | 3.0 | 2.9 | 3.3 | 3.0 | 4.0 |

-- = Not applicable
µS = MicroSiemens
mg/L = Milligrams per liter
mV = Millivolts

NA = Not analyzed
ND = Not detected

**Table A-2 (continued).** Downflow Effluent Results

## DOWNFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | WED021595 02/15/95 mg/L | WED022795 02/27/95 mg/L | WED031595 03/15/95 mg/L | WED032995 03/29/95 mg/L | WED041295 04/12/95 mg/L | WED042695 04/26/95 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | 0.018 | 0.011 | 0.011 | ND | 0.014 | ND* |
| | ARSENIC | 6020 | 0.0011 | 0.0019 | ND | ND | 0.0021 | ND |
| | CADMIUM | 6020 | 0.00033 | ND | ND | ND | ND | ND |
| | CALCIUM | 6010 | 116.0 | 121.0 | 126.0 | 103.0 | 113.0 | 109.0 |
| | IRON | 6010 | 2.4 | 2.1 | 2.2 | 1.8 | 1.8 | 1.7 |
| | LEAD | 6020 | 0.0010 | ND | ND | ND | ND | ND |
| | MAGNESIUM | 6010 | 51.2 | 52.5 | 54.3 | 46.0 | 48.1 | 46.6 |
| | MANGANESE | 6010 | 1.9 | 1.9 | 2.1 | 1.8 | 1.9 | 1.9 |
| | NICKEL | 6010 | 0.016 | 0.015 | 0.018 | 0.019 | 0.014 | 0.014 |
| | POTASSIUM | 6010 | 8.4 | 8.5 | 9.0 | 6.9 | 6.7 | 6.9 |
| | SILVER | 6020 | ND | ND | ND | ND | ND | ND |
| | SODIUM | 6010 | 15.9 | 15.1 | 16.5 | 14.7 | 14.1 | 14.1 |
| | ZINC | 6010 | 10.7 | 11.7 | 13.0 | 12.2 | 12.6 | 11.9 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 359 | 346 | 370 | 341 | 338 | 341 |
| | SULFIDE TOTAL | 376.2 | 1.9 | 1.9 | 3.1 | 3.1 | 0.099 | 1.6 |
| | FLUORIDE | 340.2 | 1.1 | 1.0 | 1.1 | 1.1 | 1.0 | 1.1 |
| | CHLORIDE | 300.0 | 22.1 | 22.7 | 24.4 | 22.5 | 21.8 | 23.8 |
| | PHOSPHORUS, TOTAL | 365.3 | 17.5 | 5.9 | 5.7 | 5.2 | 4.7 | 4.7 |
| | ORTHOPHOSPHATE | 365.3 | 5.1 | 5.8 | 5.7 | 3.8 | 5.4 | 2.4 |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | ND | ND | ND | ND |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | ND | ND | ND |
| | AMMONIA | 350.1 | 1.2 | 1.2 | 1.5 | 1.3 | 1.1 | 1.1 |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 32.4 | 34.0 | 33.0 | 31.0 | 35.0 | 31.2 |
| | TDS | 160.1 | 679 | 723 | 707 | 662 | 655 | 651 |
| | TOC | 9060 | 4.3 | 5.5 | 5.4 | 5.8 | 6.9 | 6.8 |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 140 | 152 | 152 | 141 | 143 | 141 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 140 | 152 | 152 | 141 | 143 | 141 |
| | ORP (mV) | -- | 59.0 | -82.0 | -65.0 | -81.1 | 35.0 | NA |
| | pH | -- | 8.8 | 7.1 | 7.1 | 7.3 | 7.2 | NA |
| | CONDUCTIVITY (µS) | -- | NA | 620 | 680 | 580 | 580 | 600 |
| | TEMPERATURE (degrees C) | -- | 2.8 | 5.6 | 6.8 | 5.6 | 4.8 | 7.0 |

-- = Not applicable
µS = MicroSiemens
mg/L = Milligrams per liter
mV = Millivolts

NA = Not analyzed
ND = Not detected

**Table A-2 (continued).** Downflow Effluent Results

## DOWNFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | WED051095 05/10/95 mg/L | WED061295 6/12/1995 mg/L | WED062895 6/28/1995 mg/L | WED071095 7/10/1995 mg/L | WED072695 7/26/1995 mg/L | WED080895 8/8/1995 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | ND* | ND | ND | ND | ND | 0.015 |
| | ARSENIC | 6020 | ND | ND | ND | ND | ND | ND |
| | CADMIUM | 6020 | ND | ND | ND | ND | ND | ND |
| | CALCIUM | 6010 | 121.0 | 125 | 142 | 144 | 157 | 148 |
| | IRON | 6010 | 2.1 | 4.2 | 3.9 | 3.9 | 2.9 | 2.8 |
| | LEAD | 6020 | ND | ND | ND | ND | ND | ND |
| | MAGNESIUM | 6010 | 47.8 | 52.7 | 61.9 | 68.7 | 71.7 | 68.6 |
| | MANGANESE | 6010 | 2.4 | 3.9 | 4.4 | 4.1 | 4.1 | 3.8 |
| | NICKEL | 6010 | 0.016 | 0.017 | 0.020 | 0.021 | 0.020 | 0.022 |
| | POTASSIUM | 6010 | 6.5 | 6.8 | 7.1 | 8.2 | 7.6 | 6.8 |
| | SILVER | 6020 | ND | ND | ND | ND | ND | ND |
| | SODIUM | 6010 | 14.1 | 8.7 | 10.6 | 12.8 | 12.6 | 12.5 |
| | ZINC | 6010 | 13.3 | 26.5 | 31.2 | 30.8 | 29.7 | 33.1 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 348.0 | 425 | 453 | 525 | 537 | 535 |
| | SULFIDE TOTAL | 376.2 | 0.38 | 0.054 | 6.9 | 5.7 | 0.83 | 10.0 |
| | FLUORIDE | 340.2 | 1.1 | 0.87 | 0.80 | 0.96 | 0.86 | 0.91 |
| | CHLORIDE | 300.0 | 22.6 | 7.0 | 7.2 | 8.6 | 10.1 | 11.1 |
| | PHOSPHORUS, TOTAL | 365.3 | 4.3 | 3.7 | 4.7 | 3.5 | 2.6 | 2.5 |
| | ORTHOPHOSPHATE | 365.3 | 4.1 | 2.2 | 1.5 | 3.7 | 2.0 | 1.6 |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | ND | ND | ND | ND |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | ND | ND | ND |
| | AMMONIA | 350.1 | 0.96 | 0.90 | 0.94 | 1.0 | 0.50 | 0.64 |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 29.2 | 43.0 | 53.6 | 48.0 | 28.0 | 38.8 |
| | TDS | 160.1 | 707 | 763 | 918 | 946 | 959 | 1090 |
| | TOC | 9060 | 4.4 | 6.6 | 11.4 | 5.4 | 7.2 | 4.7 |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 137 | 129 | 195 | 146 | 141 | |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 137 | 129 | 195 | 146 | 141 | |
| | ORP (mV) | | | -80 | -68 | -52 | | 14 |
| | pH | | | 6.8 | 6.6 | 6.7 | | 7.1 |
| | CONDUCTIVITY (µS) | | | NA | 720 | NA | | 850 |
| | TEMPERATURE (degrees C) | | | 11.7 | 12.3 | 13.8 | | 14.1 |

* - Aluminum was re-analyzed 6/2/95 due to blank contamination

-- = Not applicable

µS = MicroSiemens

mg/l = Milligrams per liter

mV = Millivolts

NA = Not analyzed

ND = Not detected

Table A-2 (continued). Downflow Effluent Results

## DOWNFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | WED082395 8/23/1995 mg/L | WED090595 9/5/1995 mg/L | WED110995 11/9/1995 mg/L | CDPHE 1/29/1996 mg/L | CDPHE 2/29/1996 mg/L | CDPHE 4/25/1996 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | ND | 0.016 | ND | *NA* | *NA* | *NA* |
| | ARSENIC | 6020 | ND | ND | ND | *NA* | *NA* | *NA* |
| | CADMIUM | 6020 | ND | ND | 0.00030 | 0.00012 | 0.00072 | 0.15 |
| | CALCIUM | 6010 | 155 | 147 | 149 | *NA* | *NA* | *NA* |
| | IRON | 6010 | 2.7 | 2.2 | 2.4 | NA | 0.28 | 1.7 |
| | LEAD | 6020 | ND | ND | 0.0016 | *NA* | *NA* | *NA* |
| | MAGNESIUM | 6010 | 70.2 | 66.3 | 66.2 | *NA* | *NA* | *NA* |
| | MANGANESE | 6010 | 3.9 | 3.7 | 4.0 | 3.2 | 3.0 | 2.2 |
| | NICKEL | 6010 | 0.026 | 0.028 | 0.04 | *NA* | *NA* | *NA* |
| | POTASSIUM | 6010 | 6.2 | 6.2 | 5.3 | *NA* | *NA* | *NA* |
| | SILVER | 6020 | ND | ND | ND | *NA* | *NA* | *NA* |
| | SODIUM | 6010 | 13.7 | 12.5 | 14.5 | *NA* | *NA* | *NA* |
| | ZINC | 6010 | 34.1 | 29.1 | 34.5 | 28 | 26 | 15 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 539 | 529 | 535 | 440 | 430 | 318 |
| | SULFIDE TOTAL | 376.2 | 11.4 | 5.6 | 3.8 | *NA* | *NA* | *NA* |
| | FLUORIDE | 340.2 | 0.85 | 0.82 | 0.81 | *NA* | *NA* | *NA* |
| | CHLORIDE | 300.0 | 12.2 | 14 | 17.3 | *NA* | *NA* | *NA* |
| | PHOSPHORUS, TOTAL | 365.3 | 3.0 | 2.8 | 2.5 | *NA* | *NA* | *NA* |
| | ORTHOPHOSPHATE | 365.3 | 3.0 | 1.3 | 1.1 | *NA* | *NA* | *NA* |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | ND | *NA* | *NA* | *NA* |
| | NITRITE AS N | 354.1 | 0.0070 | ND | ND | *NA* | *NA* | *NA* |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | *NA* | *NA* | *NA* |
| | AMMONIA | 350.1 | 0.78 | 0.64 | 0.39 | 1.0 | 1.1 | 1.1 |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 50.0 | 45.6 | 12.8 | *NA* | *NA* | *NA* |
| | TDS | 160.1 | 996 | 941 | 957 | *NA* | *NA* | *NA* |
| | TOC | 9060 | 4.2 | 4.9 | 4.2 | *NA* | *NA* | *NA* |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 143 | 179 | 152 | *NA* | *NA* | *NA* |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 143 | 179 | 152 | *NA* | *NA* | *NA* |
| | ORP (mV) | | | | -60 | *NA* | *NA* | *NA* |
| | pH | | | | 6.7 | *NA* | *NA* | *NA* |
| | CONDUCTIVITY (µS) | | | | 750 | *NA* | *NA* | *NA* |
| | TEMPERATURE (degrees C) | | | | 4.7 | NA | NA | NA |

-- = Not applicable
µS = MicroSiemens
mg/L = Milligrams per liter
mV = Millivolts

NA = Not analyzed
ND = Not detected

**Table A-2 (continued).** Downflow Effluent Results

## DOWNFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | CDPHE 5/31/1996 mg/L | CDPHE 6/14/1996 mg/L | CDPHE 7/19/1996 mg/L | CDPHE 8/31/1996 mg/L | WED012197 1/21/1997 mg/l | WED022097 2/20/1997 mg/l |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | *NA* | *NA* | *NA* | NA | 0.098 | ND |
| | ARSENIC | 6020 | *NA* | *NA* | *NA* | NA | NA | NA |
| | CADMIUM | 6020 | 0.00016 | ND | 0.00021 | 0.00013 | 0.016 | 0.034 |
| | CALCIUM | 6010 | *NA* | *NA* | *NA* | NA | 115 | 113 |
| | IRON | 6010 | 0.87 | 0.92 | 1.10 | 1.60 | 0.53 | 0.72 |
| | LEAD | 6020 | *NA* | *NA* | *NA* | NA | 57.3 | 56.9 |
| | MAGNESIUM | 6010 | *NA* | *NA* | *NA* | NA | 3.3 | 5.0 |
| | MANGANESE | 6010 | 1.8 | 2.00 | 2.10 | 2.20 | NA | NA |
| | NICKEL | 6010 | *NA* | *NA* | *NA* | NA | 0.05 | 0.035 |
| | POTASSIUM | 6010 | *NA* | *NA* | *NA* | NA | 0.39 | 3.80 |
| | SILVER | 6020 | *NA* | *NA* | *NA* | NA | NA | NA |
| | SODIUM | 6010 | *NA* | *NA* | *NA* | NA | 16.6 | 16 |
| | ZINC | 6010 | 11 | 9.7 | 8.7 | 5.8 | 55 | 59.7 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 230 | 82 | 340 | 350 | 421 | 322 |
| | SULFIDE TOTAL | 376.2 | *NA* | *NA* | *NA* | NA | 0.13 | ND |
| | FLUORIDE | 340.2 | *NA* | *NA* | *NA* | NA | NA | NA |
| | CHLORIDE | 300.0 | *NA* | *NA* | *NA* | NA | 18.6 | 18.6 |
| | PHOSPHORUS, TOTAL | 365.3 | *NA* | *NA* | *NA* | NA | NA | NA |
| | ORTHOPHOSPHATE | 365.3 | *NA* | *NA* | *NA* | NA | 1.1 | 0.54 |
| | NITRATE PLUS NITRITE AS N | 353.2 | *NA* | *NA* | *NA* | NA | ND | 0.2 |
| | NITRITE AS N | 354.1 | *NA* | *NA* | *NA* | NA | 0.0025 | 0.0055 |
| | NITRATE AS N | 353.2/354.1 | *NA* | *NA* | *NA* | NA | NA | NA |
| | AMMONIA | 350.1 | 0.67 | 1.2 | 0.90 | ND | 0.24 | 0.20 |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | *NA* | *NA* | *NA* | NA | 7.2 | 6.0 |
| | TDS | 160.1 | *NA* | *NA* | *NA* | NA | 787 | 752 |
| | TOC | 9060 | *NA* | *NA* | *NA* | NA | 7.2 | 25.8 |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | *NA* | *NA* | *NA* | NA | 158 | 259 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | *NA* | *NA* | *NA* | NA | 158 | 259 |
| | ORP(mV) | | *NA* | *NA* | *NA* | NA | 110 | 92.0 |
| | pH | | *NA* | *NA* | *NA* | NA | 5.3 | 7.0 |
| | CONDUCTIVITY (uS) | | *NA* | *NA* | *NA* | NA | NA | NA |
| | TEMPERATURE (degrees C) | | *NA* | *NA* | *NA* | *NA* | *1.8* | 1.8 |

-- = Not applicable
µS = MicroSiemens
mg/L = Milligrams per liter
mV = Millivolts

NA = Not analyzed
ND = Not detected

**Table A-3.** Upflow Effluent Results

## UPFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | WEU030994 03/09/94 mg/L | WEU032394 03/23/94 mg/L | WEU040694 04/06/94 mg/L | WEU042094 04/20/94 mg/L | WEU050594 05/05/94 mg/L | WEU051994 05/19/94 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | 0.077 | 0.20 | 0.078 | 0.39 | 0.062 | 0.028 |
| | ARSENIC | 6020 | 0.0062 | 0.0071 | 0.036 | 0.028 | 0.085 | 0.067 |
| | CADMIUM | 6020 | 0.00042 | 0.00049 | 0.00034 | 0.00036 | 0.00024 | 0.00020 |
| | CALCIUM | 6010 | 75.3 | 96.2 | 112.0 | 115.0 | 123.0 | 115.0 |
| | IRON | 6010 | 0.48 | 0.61 | 0.48 | 0.99 | 0.27 | 0.25 |
| | LEAD | 6020 | 0.0042 | 0.0030 | 0.0038 | 0.020 | 0.0022 | 0.0015 |
| | MAGNESIUM | 6010 | 72.7 | 71.4 | 69.3 | 63.1 | 66.0 | 60.1 |
| | MANGANESE | 6010 | 0.051 | 0.072 | 0.065 | 0.16 | 0.17 | 0.25 |
| | NICKEL | 6010 | 0.0054 | 0.0071 | 0.0095 | 0.0086 | 0.0086 | 0.0086 |
| | POTASSIUM | 6010 | 223.0 | 188.0 | 150.0 | 108.0 | 91.2 | 49.4 |
| | SILVER | 6020 | 0.0014 | 0.00015 | 0.000084 | 0.00048 | 0.000071 | 0.000072 |
| | SODIUM | 6010 | 33.9 | 31.2 | 27.3 | 21.8 | 22 | 16.8 |
| | ZINC | 6010 | 0.22 | 0.22 | 0.13 | 0.43 | 0.14 | 0.32 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 354 | 388 | 364 | 343 | 292 | 265 |
| | SULFIDE TOTAL | 376.2 | 0.38 | 7.9 | 9.4 | 1.9 | 0.47 | 2.4 |
| | FLUORIDE | 340.2 | 0.30 | 0.57 | 0.62 | 0.72 | 0.71 | 0.88 |
| | CHLORIDE | 300.0 | 83.2 | 76.0 | 59.7 | 50.0 | 35.5 | 21.8 |
| | PHOSPHORUS, TOTAL | 365.3 | 24.3 | 23.2 | 20.5 | 20.8 | 18.3 | 17.6 |
| | ORTHOPHOSPHATE | 365.3 | 26.8 | 26.7 | 20.9 | 20.6 | 18.6 | 15.9 |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | 0.060 | ND | ND | ND |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | ND | ND | 0.060 | ND | ND | ND |
| | AMMONIA | 350.1 | 23.8 | 19.6 | 15.0 | 12.9 | 10.5 | 6.8 |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 6 | 12.0 | 6.0 | 25.2 | ND | ND |
| | TDS | 160.1 | 1390 | 1200 | 1110 | 1010 | 934 | 804 |
| | TOC | 9060 | 264 | 51.3 | 60.0 | 49.3 | 35.6 | 23.8 |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 367 | 347 | 310 | 308 | 265 | 230 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 367 | 347 | 310 | 308 | 265 | 230 |
| | ORP (mV) | -- | -377 | | -280 | | -269 | -271 |
| | pH | -- | 8 | | 7.85 | | 7.20 | 7.84 |
| | CONDUCTIVITY (µS) | -- | 1410 | | 1222 | | 954 | 893 |
| | TEMPERATURE (degrees C) | -- | 5 | | 6.0 | | 7.8 | 8.8 |

-- = Not applicable
µ/s = MicroSiemens
mg/L = Milligrams per liter
mV = Millivolts

NA = Not analyzed
ND = Not detected

**Table A-3 (continued).** Upflow Effluent Results

## UPFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | WEU060194 06/01/94 mg/L | WEU062994 06/29/94 mg/L | WEU071394 07/13/95 mg/L | WEU072894 07/28/95 mg/L | WEU081594 08/15/94 mg/L | WEU082494 08/24/94 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | 0.045 | 0.021 | ND | 0.38 | 0.015 | 0.023 |
| | ARSENIC | 6020 | ND | ND | ND | ND | ND | ND |
| | CADMIUM | 6020 | ND | ND | ND | ND | ND | ND |
| | CALCIUM | 6010 | 117 | 120 | 132 | 132 | 134 | 132 |
| | IRON | 6010 | 0.26 | 0.47 | 0.79 | 1.4 | 2.7 | 3.3 |
| | LEAD | 6020 | 0.0030 | 0.0017 | ND | ND | ND | ND |
| | MAGNESIUM | 6010 | 61.5 | 61.7 | 61.4 | 58.6 | 58.3 | 57.1 |
| | MANGANESE | 6010 | 0.33 | 0.79 | 1.3 | 1.7 | 2.1 | 2.3 |
| | NICKEL | 6010 | 0.014 | 0.011 | 0.0052 | 0.0075 | 0.0089 | 0.0077 |
| | POTASSIUM | 6010 | 37.3 | 24.2 | 17.3 | 13.7 | 12.8 | 11.3 |
| | SILVER | 6020 | ND | 0.00014 | 0.00015 | ND | 0.00021 | ND |
| | SODIUM | 6010 | 15.7 | 15.6 | 15 | 14.2 | 14.4 | 14.4 |
| | ZINC | 6010 | 0.20 | 0.35 | 0.18 | 0.29 | 0.38 | 0.58 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 330 | 355 | 372 | 356 | 369 | 392 |
| | SULFIDE TOTAL | 376.2 | 5 | 3.2 | 0.59 | 1.5 | 0.69 | 1.0 |
| | FLUORIDE | 340.2 | 0.81 | 0.90 | 0.80 | 1.0 | 0.96 | 1.1 |
| | CHLORIDE | 300.0 | 22.2 | 20.9 | 18.9 | 20.2 | 19.9 | 20.5 |
| | PHOSPHORUS, TOTAL | 365.3 | 27.3 | 12.8 | 13.3 | 10.8 | 10.5 | 9.8 |
| | ORTHOPHOSPHATE | 365.3 | 14.9 | 21.3 | 19.5 | 10.5 | 7.8 | 9.2 |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | ND | 1.9 | 1.7 | 1.8 |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | 0.077 | ND |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | 1.9 | 1.7 | 1.8 |
| | AMMONIA | 350.1 | 5.6 | 3.0 | 3.0 | 2.6 | 1.6 | 1.3 |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | ND | 2.4 | 2.0 | 18.8 | 7.6 | 27.2 |
| | TDS | 160.1 | 808 | 759 | 766 | 816 | 802 | 767 |
| | TOC | 9060 | 28.0 | 11.4 | 9.0 | 9.6 | 8.8 | 6.0 |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 244 | 220 | 211 | 206 | 194 | 183 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 244 | 220 | 211 | 206 | 194 | 183 |
| | ORP (mV) | -- | | -275 | -280 | NA | NA | -344 |
| | pH | -- | | 7.7 | 7.6 | NA | 7.6 | 7.46 |
| | CONDUCTIVITY (µS) | -- | | 1115 | 1090 | 1049 | 1069 | 1037 |
| | TEMPERATURE (degrees C) | -- | | 9.7 | 9.4 | 9.7 | 9.4 | 10.0 |

-- = Not applicable
µ/s = MicroSiemens
mg/L = Milligrams per liter
mV = Millivolts

NA = Not analyzed
ND = Not detected

Table A-3 (continued). Upflow Effluent Results

## UPFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | WEU090794 09/07/94 mg/L | WEU090794E 09/07/94 mg/L | WEU091994 09/19/94 mg/L | WEU100494 10/04/94 mg/L | WB5100494 10/04/94 mg/L | WEU101994 10/19/94 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | 0.052 | ND | 0.023 | 0.017 | 6.1 | 0.015 |
| | ARSENIC | 6020 | ND | ND | ND | 0.0011 | 0.0021 | 0.0011 |
| | CADMIUM | 6020 | ND | ND | ND | ND | 0.024 | ND |
| | CALCIUM | 6010 | 126 | 0.15 | 132 | 127 | 344 | 128 |
| | IRON | 6010 | 4.3 | ND | 5.1 | 5.7 | 92.7 | 5.6 |
| | LEAD | 6020 | 0.0011 | ND | 0.0015 | ND | 0.020 | ND |
| | MAGNESIUM | 6010 | 53.3 | ND | 56.6 | 54.5 | 139.0 | 54.1 |
| | MANGANESE | 6010 | 2.4 | ND | 2.6 | 2.4 | 28.6 | 2.7 |
| | NICKEL | 6010 | 0.0083 | ND | 0.015 | 0.015 | 0.20 | 0.019 |
| | POTASSIUM | 6010 | 10.2 | ND | 9.0 | 11.9 | 7.4 | 7.7 |
| | SILVER | 6020 | 0.00011* | ND* | 0.00046 | 0.00052 | 0.00099 | ND |
| | SODIUM | 6010 | 13.6 | ND | 14.2 | 13.8 | 46.8 | 14.6 |
| | ZINC | 6010 | 0.82 | 0.019 | 1.4 | 2.4 | 9.4 | 3.1 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 395 | ND | 391 | 369 | 1760 | 392 |
| | SULFIDE TOTAL | 376.2 | 0.12 | ND | 0.23 | 5.0 | NS | 1.3 |
| | FLUORIDE | 340.2 | 1.0 | ND | 1.1 | 0.99 | 1.0 | 0.95 |
| | CHLORIDE | 300.0 | 21.1 | ND | 20.4 | 21.4 | 6.0 | 20.2 |
| | PHOSPHORUS, TOTAL | 365.3 | 1.6 | ND | 7.9 | 8.0 | NS | 6.8 |
| | ORTHOPHOSPHATE | 365.3 | 8.8 | ND | 9.8 | 7.1 | ND | 6.8 |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | ND | ND | NS | ND |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | 0.018 |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | ND | NS | ND |
| | AMMONIA | 350.1 | 1.0 | ND | 0.87 | 1.0 | NS | 0.51 |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 27.6 | ND | 28.8 | 37.6 | 49.6 | 40.8 |
| | TDS | 160.1 | 787 | ND | 790 | 750 | 2520 | 734 |
| | TOC | 9060 | 6.4 | ND | 5.8 | 7.4 | NS | 5.3 |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 175 | ND | 164 | 182 | ND | 150 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 175 | ND | 164 | 182 | ND | 150 |
| | ORP (mV) | -- | -315 | | -267 | -260 | NA | -344 |
| | pH | -- | 7.39 | | 7.3 | 7.3 | 5.2 | 6.95 |
| | CONDUCTIVITY (µS) | -- | 1007 | | 990 | 960 | NA | 760 |
| | TEMPERATURE (degrees C) | -- | 9.3 | | 9.2 | 8.7 | 15.0 | 7.7 |

-- = Not applicable
µ/s = MicroSiemens
mg/L = Milligrams per liter
mV = Millivolts

NA = Not analyzed
ND = Not detected

**Table A-3 (continued).** Upflow Effluent Results

## UPFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | WEU101994 10/19/94 mg/L | WEU110294 11/02/94 mg/L | WEU112094 11/20/94 mg/L | WEU113094 11/30/94 mg/l | WEU121494 12/14/94 mg/L | WEU010495 01/04/95 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | 0.025 | 0.025 | 0.012 | 0.013 | 0.015 | 0.020 |
| | ARSENIC | 6020 | ND | 0.0011 | 0.0011 | 0.0014 | 0.0010 | 0.0035 |
| | CADMIUM | 6020 | ND | ND | ND | ND | ND | ND |
| | CALCIUM | 6010 | 130 | 122 | 127 | 123 | 127 | 116 |
| | IRON | 6010 | 5.7 | 7.0 | 6.0 | 7.5 | 6.8 | 6.3 |
| | LEAD | 6020 | ND | ND | ND | ND | ND | ND |
| | MAGNESIUM | 6010 | 54.8 | 52.5 | 53.8 | 51.4 | 52.4 | 53.1 |
| | MANGANESE | 6010 | 2.7 | 2.7 | 2.8 | 2.9 | 2.9 | 2.7 |
| | NICKEL | 6010 | 0.018 | 0.018 | 0.016 | 0.018 | 0.016 | 0.012 |
| | POTASSIUM | 6010 | 7.6 | 11.6 | 9.6 | 7.6 | 7.6 | 15.3 |
| | SILVER | 6020 | ND | ND | 0.00082 | 0.00028 | ND | 0.00033 |
| | SODIUM | 6010 | 15 | 14.2 | 14.7 | 14.5 | 15.6 | 14.5 |
| | ZINC | 6010 | 3.2 | 6.8 | 6.5 | 7.9 | 9.0 | 11.7 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 380 | 371 | 360 | 379 | 375 | 341 |
| | SULFIDE TOTAL | 376.2 | 1.8 | 3.8 | 3.8 | 4.6 | 3.2 | 3.3 |
| | FLUORIDE | 340.2 | 0.97 | 1.1 | 1.0 | 1.2 | 1.1 | 1.1 |
| | CHLORIDE | 300.0 | 20.0 | 23.2 | 23.0 | 22.2 | 22.4 | 25.6 |
| | PHOSPHORUS, TOTAL | 365.3 | 6.9 | 6.2 | 5.5 | 6.9 | 5.3 | 4.8 |
| | ORTHOPHOSPHATE | 365.3 | 6.2 | 5.9 | 2.7 | 2.7 | 4.7 | 3.0 |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | ND | ND | ND | ND |
| | NITRITE AS N | 354.1 | 0.017 | 0.016 | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | ND | ND | ND |
| | AMMONIA | 350.1 | 0.52 | 0.38 | 0.74 | 0.55 | 1.5 | 0.68 |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 36.8 | 52.0 | 49.0 | 47.0 | 44.0 | 51.0 |
| | TDS | 160.1 | 742 | 727 | 745 | 729 | 729 | 707 |
| | TOC | 9060 | 5.6 | 9.4 | 7.3 | 19.1 | 6.4 | 12.5 |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 148 | 141 | 185 | 142 | 157 | 171 |
| | ALKALINITY, BICARB AS CACO3 | 310.1 | 148 | 141 | 185 | 142 | 157 | 171 |
| | ORP (mV) | -- | -344 | -164 | -160 | -216 | -196 | -80 |
| | pH | -- | 6.95 | 7.01 | 7.2 | 6.8 | 7.33 | 7.0 |
| | CONDUCTIVITY (µS) | -- | 760 | 935 | NA | 640 | 670 | 670 |
| | TEMPERATURE (degrees C) | -- | 7.7 | 8.5 | 8.1 | 7.1 | 7.7 | 7.0 |

-- = Not applicable
µs = MicroSiemens
mg/L = Milligrams per liter
mV = Millivolts

NA - Not applicable
ND - Not detected

**Table A-3 (continued).** Upflow Effluent Results

## UPFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | WEU011895 01/18/95 mg/L | WEU020195 02/01/95 mg/L | WEU021595 02/15/95 mg/L | WEU022795 02/27/95 mg/L | WEU031595 03/15/95 mg/L | WEU032995 03/29/95 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | 0.026 | 0.017 | 0.012 | 0.014 | 0.012 | 0.015 |
| | ARSENIC | 6020 | 0.0043 | 0.0015 | 0.0020 | 0.0021 | 0.0012 | 0.0012 |
| | CADMIUM | 6020 | ND | ND | ND | ND | ND | ND |
| | CALCIUM | 6010 | 116 | 119 | 119 | 116 | 116 | 105 |
| | IRON | 6010 | 5.4 | 4.9 | 4.3 | 4.0 | 4.0 | 3.5 |
| | LEAD | 6020 | 0.0034 | ND | ND | ND | ND | ND |
| | MAGNESIUM | 6010 | 49.5 | 49.0 | 49.1 | 48.2 | 48.2 | 44.6 |
| | MANGANESE | 6010 | 2.6 | 2.5 | 2.5 | 2.4 | 2.4 | 2.2 |
| | NICKEL | 6010 | 0.012 | 0.016 | 0.016 | 0.016 | 0.019 | 0.019 |
| | POTASSIUM | 6010 | 10.5 | 9.1 | 9.1 | 8.9 | 7.5 | 5.9 |
| | SILVER | 6020 | ND | ND | ND | ND | ND | ND |
| | SODIUM | 6010 | 15 | 16.7 | 16 | 15.2 | 16.0 | 15.7 |
| | ZINC | 6010 | 12.5 | 16.9 | 12.9 | 17.8 | 18.0 | 17.5 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 347 | 330 | 308 | 340 | 335 | 317 |
| | SULFIDE TOTAL | 376.2 | 3.0 | 6.0 | 3.3 | 4.3 | 2.7 | 4.3 |
| | FLUORIDE | 340.2 | 1.1 | 1.0 | 1.1 | 1.0 | 1.1 | 1.1 |
| | CHLORIDE | 300.0 | 23.0 | 23.4 | 23.4 | 23.6 | 24.3 | 23.0 |
| | PHOSPHORUS, TOTAL | 365.3 | 4.7 | 5.5 | 13.3 | 3.4 | 4.1 | 3.4 |
| | ORTHOPHOSPHATE | 365.3 | 3.0 | 5.0 | 3.7 | 3.0 | 2.6 | 1.8 |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | 1.4 | ND | ND | ND | ND |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | ND | 1.4 | ND | ND | ND | ND |
| | AMMONIA | 350.1 | 0.63 | 0.52 | 0.51 | 0.34 | 0.38 | 0.31 |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 51.0 | 54.0 | 45.2 | 47.0 | 39.0 | 41.0 |
| | TDS | 160.1 | 693 | 692 | 682 | 700 | 671 | 667 |
| | TOC | 9060 | 7.8 | 6.8 | 6.2 | 5.8 | 4.3 | 7.0 |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 168 | 161 | 191 | 150 | 151 | 154 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 168 | 161 | 191 | 150 | 151 | 154 |
| | ORP (mV) | -- | 5 | -11.7 | -44.0 | -65 | -63 | -81.1 |
| | pH | -- | 7.1 | 7.4 | 7.2 | 6.9 | 6.9 | 7.3 |
| | CONDUCTIVITY (µS) | -- | 650 | 610 | NA | 680 | 650 | 580 |
| | TEMPERATURE (degrees C) | -- | 8.3 | 6.1 | 7.6 | 8.4 | 8.8 | 5.6 |

-- = Not applicable
µS = MicroSiemens
mg/L = Milligrams per liter
mV = Millivolts

NA = Not analyzed
ND = Not detected

**Table A-3 (continued).** Upflow Effluent Results

## UPFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | WEU041295 04/12/95 mg/L | WEU042695 04/26/95 mg/L | WEU051095 05/10/95 mg/L | WEU061295 06/12/95 mg/L | WEU062895 6/28/1995 mg/L | WEU071095 7/10/1995 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | 0.013 | ND* | ND* | 0.028 | ND | ND |
| | ARSENIC | 6020 | 0.0028 | ND | ND | ND | ND | ND |
| | CADMIUM | 6020 | ND | 0.00078 | 0.0094 | 0.0084 | 0.0045 | ND |
| | CALCIUM | 6010 | 114 | 106 | 110 | 103 | 121 | 130 |
| | IRON | 6010 | 3.5 | 2.2 | 2.2 | 4.6 | 3.7 | 3.8 |
| | LEAD | 6020 | ND | ND | 0.0019 | 0.0018 | ND | ND |
| | MAGNESIUM | 6010 | 46.5 | 45.3 | 44.5 | 45.2 | 60.2 | 68.2 |
| | MANGANESE | 6010 | 2.5 | 2.0 | 2.5 | 3 | 4.0 | 4.1 |
| | NICKEL | 6010 | 0.013 | 0.015 | 0.022 | 0.019 | 0.026 | 0.026 |
| | POTASSIUM | 6010 | 7.1 | 11.7 | 18.1 | 7.5 | 6.0 | 5.4 |
| | SILVER | 6020 | ND | ND | ND | ND | ND | ND |
| | SODIUM | 6010 | 15.3 | 14.2 | 13.3 | 8.9 | 11.2 | 13.2 |
| | ZINC | 6010 | 15.9 | 18.5 | 26.7 | 33.5 | 47.1 | 50.8 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 326 | 326 | 355 | 326 | 494 | 514 |
| | SULFIDE TOTAL | 376.2 | 0.39 | 2.9 | 1.3 | 0.065 | 1.5 | 1.5 |
| | FLUORIDE | 340.2 | 1.0 | 1.1 | 1.2 | 0.90 | 0.90 | 0.96 |
| | CHLORIDE | 300.0 | 22.5 | 26.0 | 25.9 | 7.6 | 7.0 | 8.3 |
| | PHOSPHORUS, TOTAL | 365.3 | 3.0 | 3.2 | 2.0 | 2.3 | 1.2 | 1.5 |
| | ORTHOPHOSPHATE | 365.3 | 2.7 | 1.6 | 2.4 | 1.5 | 0.34 | 0.48 |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | ND | ND | ND | ND |
| | NITRITE AS N | 354.1 | ND | ND | ND | ND | ND | ND |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | ND | ND | ND |
| | AMMONIA | 350.1 | 0.33 | 0.31 | 0.42 | 0.36 | 0.20 | 0.20 |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 41.9 | 31.2 | 29.0 | 47.3 | 18.8 | 25.6 |
| | TDS | 160.1 | 657 | 607 | 724 | 668 | 885 | 944 |
| | TOC | 9060 | 8.0 | 8.3 | 9.9 | 9.1 | 4.9 | 4.8 |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 152 | 147 | 138 | 181 | 136 | 147 |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 152 | 147 | 138 | 181 | 136 | 147 |
| | ORP (mV) | -- | -7.0 | NA | | -57 | | |
| | pH | -- | 7.1 | NA | | 6.7 | 6.9 | 6.9 |
| | CONDUCTIVITY (µS) | -- | 620 | 620 | | NA | | |
| | TEMPERATURE (degrees C) | -- | 8.5 | 8.0 | | 10.1 | | |

* - Aluminum was re-analyzed 6/2/95 due to blank contamination

-- = Not applicable

NA = Not analyzed

µS = MicroSiemens

ND = Not detected

mg/L = Milligrams per liter

mV = Millivolts

**Table A-3 (continued).** Upflow Effluent Results

## UPFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | WEU072695 7/26/1995 mg/L | WEU080895 8/8/1995 mg/L | WEU082395 8/23/1995 mg/L | WEU090595 9/5/1995 mg/L | WEU110995 11/9/1995 mg/L | CDPHE 1/29/1996 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | ND | ND | ND | ND | ND | *NA* |
| | ARSENIC | 6020 | ND | ND | ND | ND | ND | *NA* |
| | CADMIUM | 6020 | 0.0060 | 0.0046 | 0.0093 | 0.010 | 0.04400 | 0.037 |
| | CALCIUM | 6010 | 144 | 135 | 141 | 137 | 133 | *NA* |
| | IRON | 6010 | 2.5 | 2.5 | 2.1 | 1.8 | 0.93 | 1.6 |
| | LEAD | 6020 | ND | ND | ND | ND | 0.0022 | *NA* |
| | MAGNESIUM | 6010 | 68.6 | 64.4 | 66.1 | 64.3 | 62.1 | *NA* |
| | MANGANESE | 6010 | 4.1 | 3.8 | 3.8 | 3.6 | 4.4 | 3.3 |
| | NICKEL | 6010 | 0.028 | 0.032 | 0.036 | 0.04 | 0.059 | *NA* |
| | POTASSIUM | 6010 | 5.7 | 4.9 | 4.5 | ND | 4.3 | *NA* |
| | SILVER | 6020 | ND | ND | ND | ND | ND | *NA* |
| | SODIUM | 6010 | 12.2 | 13.3 | 14.0 | 12.2 | 15.6 | *NA* |
| | ZINC | 6010 | 53.2 | 56.6 | 59.8 | 59.9 | 73.6 | 47 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 549 | 584 | 561 | 569 | 559 | 460 |
| | SULFIDE TOTAL | 376.2 | 4.3 | 3.5 | 5.2 | 2.8 | 0.84 | *NA* |
| | FLUORIDE | 340.2 | 0.89 | 0.88 | 0.90 | 0.86 | 0.96 | *NA* |
| | CHLORIDE | 300.0 | 10.0 | 11.2 | 12.5 | 13.7 | 17.1 | *NA* |
| | PHOSPHORUS, TOTAL | 365.3 | 1.1 | 1.1 | 1.3 | 1.5 | 0.69 | *NA* |
| | ORTHOPHOSPHATE | 365.3 | 1.0 | 0.9 | 1.2 | 0.43 | 0.80 | *NA* |
| | NITRATE PLUS NITRITE AS N | 353.2 | ND | ND | ND | ND | ND | *NA* |
| | NITRITE AS N | 354.1 | ND | ND | 0.0080 | ND | ND | *NA* |
| | NITRATE AS N | 353.2/354.1 | ND | ND | ND | ND | ND | *NA* |
| | AMMONIA | 350.1 | 0.11 | ND | 0.21 | ND | ND | 0.2 |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | 16.8 | 17.6 | 30.0 | 26 | 5.2 | *NA* |
| | TDS | 160.1 | 961 | 999 | 1010 | 978 | 932 | *NA* |
| | TOC | 9060 | 5.7 | 3.4 | 3.2 | 3.7 | 2.1 | *NA* |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | 135 | 138 | 149 | 160 | 115 | *NA* |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | 135 | 138 | 149 | 160 | 115 | *NA* |
| | ORP (mV) | -- | | | | | | |
| | pH | -- | 6.8 | 7.1 | 7.1 | 6.9 | 7.0 | *NA* |
| | CONDUCTIVITY (µS) | -- | | | | | | *NA* |
| | TEMPERATURE (degrees C) | -- | | | | | | NA |

-- = Not applicable
µS = MicroSiemens
mg/L = Milligrams per liter
mV = Millivolts

NA = Not analyzed
ND = Not detected

**Table A-3 (continued).** Upflow Effluent Results

## UPFLOW EFFLUENT

| | ANALYTE | ANALYTICAL METHOD | CDPHE 2/29/1996 mg/L | CDPHE 4/25/1996 mg/L | CDPHE 5/31/1996 mg/L | CDPHE 6/14/1996 mg/L | CDPHE 7/19/1996 mg/L | CDPHE 8/31/1996 mg/L |
|---|---|---|---|---|---|---|---|---|
| AQUEOUS | ALUMINUM | 6010 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | ARSENIC | 6020 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | CADMIUM | 6020 | 0.035 | 0.030 | 0.140 | 0.031 | 0.051 | 0.053 |
| | CALCIUM | 6010 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | IRON | 6010 | 1.3 | 0.81 | 0.17 | 1.1 | 0.87 | 0.90 |
| | LEAD | 6020 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | MAGNESIUM | 6010 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | MANGANESE | 6010 | 3.1 | 2.3 | 2.7 | 2.2 | 2.6 | 2.5 |
| | NICKEL | 6010 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | POTASSIUM | 6010 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | SILVER | 6020 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | SODIUM | 6010 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | ZINC | 6010 | 42 | 31 | 56 | 30 | 41 | 43.0 |
| | ANIONS: | | | | | | | |
| | SULFATE | 300.0 | 430 | 329 | 420 | 310 | 410 | 45 |
| | SULFIDE TOTAL | 376.2 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | FLUORIDE | 340.2 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | CHLORIDE | 300.0 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | PHOSPHORUS, TOTAL | 365.3 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | ORTHOPHOSPHATE | 365.3 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | NITRATE PLUS NITRITE ASN | 353.2 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | NITRITE ASN | 354.1 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | NITRATE ASN | 353.2/354.1 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | AMMONIA | 350.1 | 0.4 | 0.3 | ND | 0.2 | 0.2 | ND |
| | TOTAL SOLIDS: | | | | | | | |
| | TSS | 160.2 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | TDS | 160.1 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | TOC | 9060 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | ALKALINITY, TOTAL: AS CaCO3 | 310.1 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | ALKALINITY, BICARB AS CAC03 | 310.1 | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | ORP (mV) | -- | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | pH | -- | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | CONDUCTIVITY (µS) | -- | *NA* | *NA* | *NA* | *NA* | *NA* | NA |
| | TEMPERATURE (degrees C) | -- | NA | NA | *NA* | *NA* | *NA* | *NA* |

-- = Not applicable
µS = MicroSiemens
mg/L = Milligrams per liter
mV = Millivolts

NA = Not analyzed
ND = Not detected

Table A-4. Substrate Results - Downflow Cell

## SUBSTRATE - DOWNFLOW CELL

| | ANALYTE | ANALYTICAL METHOD | SD2032394 03/23/94 mg/kg | SD2062994 06/29/94 mg/kg | SD5062994 06/29/94 mg/kg | SD5082594 08/25/94 mg/kg |
|---|---|---|---|---|---|---|
| SEDIMENT | ALUMINUM | 6010 | 1410.0 | 65.6 | 423.0 | 2580.0 |
| | ARSENIC | 6020 | 2.9 | 0.14 | ND | 0.59 |
| | CADMIUM | 6020 | 2.2 | 0.56 | 4.8 | 5.1 |
| | CALCIUM | 6010 | 7040.0 | 406 | 2330.0 | 7650.0 |
| | IRON | 6010 | 2250.0 | 88.7 | 653.0 | 3650.0 |
| | LEAD | 6020 | 7.4 | 3.1 | 53.4 | 16.2 |
| | MAGNESIUM | 6010 | 2140.0 | 145 | 571.0 | 2120.0 |
| | MANGANESE | 6010 | 99.2 | 4.1 | 36.0 | 140.0 |
| | NICKEL | 6010 | 3.9 | ND | 1.9 | 4.9 |
| | POTASSIUM | 6010 | 890.0 | 149.0 | 184.0 | 1360.0 |
| | SILVER | 6020 | 0.061 | 0.024 | 0.79 | 0.16 |
| | SODIUM | 6010 | ND | 76.3 | ND | ND |
| | ZINC | 6010 | 1560.0 | 59.7 | 1000.0 | 2650.0 |
| | ANIONS: | | | | | |
| | SULFATE | 300.0 | 214 | 56.5 | 143.0 | 214 |
| | SULFIDE, REACTIVE | EPA/OSW | 0.40 | 19.1 | 18.6 | 3.2 |
| | SULFIDE, ACID VOLATILE | EPA (Draft) | NA | 226 | 178.0 | ND |
| | FLUORIDE | 340.2 | NA | NA | NA | NA |
| | CHLORIDE | 300.0 | NA | NA | NA | NA |
| | PHOSPHORUS, TOTAL | 365.3 | NA | NA | NA | NA |
| | ORTHOPHOSPHATE | 365.3 | 25.8 | 63.4 | 30.5 | 18.8 |
| | NITRATE PLUS NITRITE AS N | 353.2 | NA | NA | NA | NA |
| | NITRITE AS N | 354.1 | NA | NA | NA | NA |
| | NITRATE AS N | 353.2/354.1 | NA | NA | NA | NA |
| | AMMONIA | 350.1 | NA | NA | NA | NA |
| | WATER (%) | ILMO1.1 | 82 | 62 | 70 | 75 |

NA = Not analyzed
ND = Not detected

**Table A-4 (continued).** Substrate Results - Downflow Cell

## SUBSTRATE - DOWNFLOW CELL

| | ANALYTE | ANALYTICAL METHOD | SD2100494 10/04/94 mg/kg | SD5100494 10/04/94 mg/kg | SD2110294 11/02/94 mg/kg | SD2010495 01/04/95 mg/kg |
|---|---|---|---|---|---|---|
| SEDIMENT | ALUMINUM | 6010 | 2640.0 | 3200.0 | 3200.0 | 2430.0 |
| | ARSENIC | 6020 | 1.5 | 0.97 | 1.3 | 1.5 |
| | CADMIUM | 6020 | 4.6 | 10.5 | 4.3 | 4.3 |
| | CALCIUM | 6010 | 8460.0 | 4890.0 | 11700.0 | 8770.0 |
| | IRON | 6010 | 3410.0 | 4640.0 | 4860.0 | 3460.0 |
| | LEAD | 6020 | 46.4 | 30.8 | 11.3 | 18.2 |
| | MAGNESIUM | 6010 | 2180.0 | 1800.0 | 2910.0 | 2190.0 |
| | MANGANESE | 6010 | 160.0 | 151.0 | 232.0 | 144.0 |
| | NICKEL | 6010 | 3.7 | 6.4 | 7.0 | 4.9 |
| | POTASSIUM | 6010 | 930.0 | 1410.0 | 1140.0 | 729.0 |
| | SILVER | 6020 | 0.17 | 0.29 | 0.069 | 0.28 |
| | SODIUM | 6010 | ND | 108.0 | 92.8 | ND |
| | ZINC | 6010 | 1510.0 | 2850.0 | 3170.0 | 3250.0 |
| | ANIONS: | | | | | |
| | SULFATE | 300.0 | 86.8 | 187.0 | 159.0 | 184.0 |
| | SULFIDE, REACTIVE | EPA/OSW | 103.0 | 79.3 | 1.1 | 15.3 |
| | SULFIDE, ACID VOLATILE | EPA (Draft) | 190.0 | 70.6 | 171.0 | 117.0 |
| | FLUORIDE | 340.2 | NA | NA | NA | NA |
| | CHLORIDE | 300.0 | NA | NA | NA | NA |
| | PHOSPHORUS, TOTAL | 365.3 | NA | NA | NA | NA |
| | ORTHOPHOSPHATE | 365.3 | 39.0 | 3.3 | 12.6 | 6.4 |
| | NITRATE PLUS NITRITE AS N | 353.2 | NA | NA | NA | NA |
| | NITRITE AS N | 354.1 | NA | NA | NA | NA |
| | NITRATE AS N | 353.2/354.1 | NA | NA | NA | NA |
| | AMMONIA | 350.1 | NA | NA | NA | NA |
| | WATER (%) | ILM01.0 | 62 | 70 | NA | 63 |

NA = Not analyzed
ND = Not detected

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# Passive Treatment of Coal Mine Drainage

By Robert S. Hedin, Robert W. Narin,
and Robert L. P. Kleinmann

UNITED STATES DEPARTMENT OF THE INTERIOR

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I

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13. ABSTRACT (Maximum 200 words)

Passive methods of treating mine water utilize chemical and biological processes that decrease metal concentrations and neutralize acidity. Compared to conventional chemical treatment, passive methods generally require more land area, but utilize less costly reagents and require less operational attention and maintenance. Currently, three types of passive technologies exist: aerobic wetlands, wetlands that contain an organic substrate, and anoxic limestone drains. Aerobic wetlands promote mixed oxidation and hydrolysis reactions, and are most effective when the raw mine water is net alkaline. Organic substrate wetlands promote anaerobic bacterial activity that results in the precipitation of metal sulfides and the generation of bicarbonate alkalinity. Anoxic limestone drains generate bicarbonate alkalinity and can be useful for the pretreatment of mine water before it flows into a wetland.

Rates of metal and acidity removal for passive systems have been developed empirically. Aerobic wetlands remove Fe and Mn from alkaline water at rates of 10-20 $g \cdot m^{-2} \cdot d^{-1}$ and 0.5-1.0 $g \cdot m^{-2} \cdot d^{-1}$, respectively. Wetlands with a composted organic substrate remove acidity from mine water at rates of 3-9 $g \cdot m^{-2} \cdot d^{-1}$. A model for the design and sizing of passive treatment systems is presented in this report.

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## UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

| | | | |
|---|---|---|---|
| cm | centimeter | $L \cdot min^{-1}$ | liter per minute |
| °C | degree Celsius | m | meter |
| ft | foot | $m^2$ | square meter |
| g | gram | $\mu m$ | micrometer |
| $g \cdot cm^{-3}$ | gram per cubic centimeter | meq | milliequivalent |
| $g \cdot d^{-1}$ | gram per day | mg | milligram |
| $g \cdot m^{-2}$ | gram per square meter | $mg \cdot L^{-1}$ | milligram per liter |
| $g \cdot m^{-2} \cdot d^{-1}$ | gram per square meter per day | $mg \cdot L^{-1} \cdot h^{-1}$ | milligram per liter per hour |
| $g \cdot m^{-2} \cdot yr^{-1}$ | gram per square meter per year | mL | milliliter |
| gpm | gallon per minute | min | minute |
| ha | hectare | nmol | nanomole |
| h | hour | $nmol \cdot cm^{-3} \cdot d^{-1}$ | nanomole per cubic centimeter per day |
| kg | kilogram (concentration) | $yd^2$ | square yard |
| $kg \cdot d^{-1}$ | kilogram per day | yr | year |
| $kg \cdot m^{-3}$ | kilogram per cubic meter | | |
| L | liter | | |

# PASSIVE TREATMENT OF COAL MINE DRAINAGE

By Robert S. Hedin,[1] Robert W. Nairn,[2] and Robert L. P. Kleinmann[3]

## ABSTRACT

Passive methods of treating mine water use chemical and biological processes that decrease metal concentrations and neutralize acidity. Compared with conventional chemical treatment, passive methods generally require more land area, but use less costly reagents and require less operational attention and maintenance. Currently, three types of passive technologies exist: aerobic wetlands, organic substrate wetlands, and anoxic limestone drains. Aerobic wetlands promote mixed oxidation and hydrolysis reactions, and are most effective when the raw mine water is net alkaline. Organic substrate wetlands promote anaerobic bacterial activity that results in the precipitation of metal sulfides and the generation of bicarbonate alkalinity. Anoxic limestone drains generate bicarbonate alkalinity and can be useful for the pretreatment of mine water before it flows into a wetland.

Rates of metal and acidity removal for passive systems have been developed empirically by the U.S. Bureau of Mines. Aerobic wetlands remove Fe and Mn from alkaline water at rates of 10-20 and 0.5-1.0 $g \cdot m^{-2} \cdot d^{-1}$, respectively. Wetlands with a composted organic substrate remove acidity from mine water at rates of 3-9 $g \cdot m^{-2} \cdot d^{-1}$. A model for the design and sizing of passive treatment systems is presented in this report.

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# INTRODUCTION

## TREATMENT OF MINE WATER

The mining of coal in the Eastern and Midwestern United States can result in drainage that is contaminated with high concentrations of dissolved iron, manganese, aluminum, and sulfate. At sites mined since May 4, 1984, drainage chemistry must meet strict effluent quality criteria (table 1). To meet these criteria, mining companies commonly treat contaminated drainage using chemical methods. In most treatment systems, metal contaminants are removed through the addition of alkaline chemicals (e.g., sodium hydroxide, calcium hydroxide, calcium oxide, sodium carbonate or ammonia). The chemicals used in these treatment systems can be expensive, especially when required in large quantities. In addition, there are operation and maintenance costs associated with aeration and mixing devices, and additional costs associated with the disposal of metal-laden sludges that accumulate in settling ponds. It is not unusual for the water treatment costs to exceed $10,000 per year at sites that are otherwise successfully reclaimed. Total water treatment costs for the coal mining industry are estimated to exceed $1,000,000 per day (*1*).[4] The high costs of water treatment place a serious financial burden on active mining companies and have contributed to the bankruptcies of many others.

**Table 1.—Federal effluent limitations for coal mine drainage**

| Pollutant or pollutant property | Maximum for any 1 day, $mg \cdot L^{-1}$ | Average of daily values for 30 consecutive days $mg \cdot L^{-1}$ |
|---|---|---|
| Fe total ..... | 6.0 | 3.0 |
| Mn total ..... | 4.0 | 2.0 |

pH between 6.0 and 9.0.

The high costs of chemical systems also limit the water treatment efforts at abandoned sites. Thousands of miles of streams and rivers in Appalachia are currently polluted by the input of mine drainage from sites that were mined and abandoned before enactment of strict effluent regulations (*2-3*). State and Federal reclamation agencies, local conservation organizations, and watershed associations all consider the treatment of contaminated coal mine discharges to be a high priority. Unfortunately, insufficient funds are available for chemical water treatment, except in a few watersheds of special value.

Natural processes commonly ameliorate mine drainage pollution. As contaminated coal mine drainage flows into and through receiving systems (streams, rivers, and lakes), its toxic characteristics decrease naturally as a result of chemical and biological reactions and by dilution with uncontaminated water. The low pH that is common to many mine drainages is raised when the water mixes with less acidic or alkaline water or through direct contact with carbonate rocks. Metal contaminants of coal mine drainage then precipitate as oxides and hydroxides under the aerobic conditions found in most surface waters. Dissolved Fe precipitates as an oxyhydroxide, staining the bottoms of many streams orange and often accumulating to sufficient depths to suffocate benthic organisms. Less commonly, dissolved Mn precipitates as an oxide that stains rocks and detrital material black. Dissolved Al precipitates as a white hydroxide.

During the last decade, the possibility that mine water might be treated passively has developed from an experimental concept to full-scale field implementation at hundreds of sites. Passive technologies take advantage of natural chemical and biological processes that ameliorate contaminated water conditions. Ideally, passive treatment systems require no input of chemicals and little or no operation and maintenance requirements. The costs of passive treatment systems are generally measured in their land use requirements. Passive treatment systems use contaminant removal processes that are slower than that of conventional treatment and thus require longer retention times and larger areas to achieve similar results.

The goal of passive mine drainage treatment systems is to enhance the natural amelioration processes so that they occur within the treatment system, not in the receiving water body. Two factors that determine whether this goal can be accomplished are the kinetics of the contaminant removal processes and the retention time of the mine water in the treatment system. The retention time for a particular minesite is often limited by available land area. However, the kinetics of contaminant removal processes can often be affected by manipulating the environmental conditions that exist within the passive treatment system. Efficient manipulation of contaminant removal processes requires that the nature of the rate-limiting aspects of each removal process be understood.

This U.S. Bureau of Mines (USBM) report describes the chemical and biological processes that underlie the passive technologies currently used in the eastern United States for the treatment of contaminated coal mine drainage. After reviewing the background of passive treatment and the methods used in these studies (Chapter 1), the chemical behavior of mine drainage contaminants is reviewed (Chapter 2). This discussion highlights the difference between alkaline and acidic mine water, and details the processes in passive treatment systems that generate alkalinity. In Chapter 3, contaminant removal is

[4]Italic numbers in parentheses refer to items in the list of references at the end of this report.

evaluated for 13 passive treatment systems through the calculation of contaminant removal rates. These rates, which incorporate the size of the treatment system, the flow rate of the water, and mine drainage chemistry, are the only measures of treatment system performance that can be reliably compared between systems. In Chapter 4, the chemical background provided in Chapter 2 and the observed contaminant removal rates presented in Chapter 3 are combined in a model that gives design and sizing recommendations for future passive treatment systems. Chapter 5 summarizes the results of this study and identifies future research needs.

## BACKGROUND OF PASSIVE TREATMENT

The current interest in passive treatment technologies can be traced to two independent research projects that indicated that natural *Sphagnum* wetlands caused an amelioration of mine drainage pollution without incurring any obvious ecological damage (*4-5*). These observations prompted the idea that wetlands might be constructed for the intentional treatment of coal mine drainage. Research efforts were initiated by West Virginia University, Wright State University, Pennsylvania State University, and the USBM to evaluate the feasibility of the idea. As a result of promising preliminary reports (*6-8*), experimental wetlands were built by mining companies and reclamation groups. Initially, most of these wetlands were constructed to mimic *Sphagnum* moss wetlands. However, *Sphagnum* moss was not readily available, proved difficult to transplant, and tended to accumulate metals to levels that were toxic to the *Sphagnum* after several months of exposure to mine drainage (*9-10*). Instead of abandoning the concept, researchers experimented with different kinds of constructed wetlands. Eventually, a wetland design evolved that proved tolerant to years of exposure to contaminated mine drainage and was effective at lowering concentrations of dissolved metals. Most of these treatment systems consist of a series of small wetlands (<1 ha) that are vegetated with cattails (*Typha latifolia*) (*11-12*). In northern Appalachia, many wetlands contain a compost and limestone substrate in which the cattails root. In southern Appalachia, most wetlands have been constructed without an exogenous organic substrate; emergent plants have been rooted in whatever soil or spoil substrate was available on the site when the treatment system was constructed (*13*).

Recently, treatment technologies have been developed that do not rely at all on the wetland model that the early systems were designed to mimic. Ponds, ditches, and rock-filled basins have been constructed that are not planted with emergent plants, and in some cases, contain no soil or organic substrate (*14*). Pretreatment systems have been developed where acidic water contacts limestone in an anoxic environment before flowing into a settling pond or wetland system (*15*). In these cases, the water is treated with limestone followed by passive aeration; however, the low cost and chemical behavior of limestone make possible the construction of wetland systems that should, theoretically, require no maintenance and last for decades.

A wide diversity of opinions exist on the merits of passive treatment systems for mine drainage. Wieder's analysis of a survey of constructed wetlands conducted by the Office of Surface Mining (OSM) indicated no strong relationships between concentration efficiency and wetland design features, leading him to question the feasibility of the constructed wetland concept (*12*). In a separate study by Wieder and his colleagues, measurements of the Fe content of *Sphagnum* peat exposed to synthetic acid mine drainage were used to calculate that an average wetland system should cease to remove metals after 11 weeks of operation (*16*). These negative reports contrast with many other studies of successful wetlands. Examples include an Ohio wetland that is treating Fe-contaminated mine drainage effectively in its 8th year of operation (*17*) and six Tennessee Valley Authority (TVA) wetlands that have produced compliance water for at least 4 years (*18*). A vast majority of the passive treatment systems constructed in the United States during the last decade achieve performance that is better than Wieder and his colleagues would predict, though not necessarily enough to consistently meet effluent limits. Hundreds of constructed wetlands discharge water that contains lower concentrations of metal contaminants than was contained in the inflow drainage. These improvements in water quality decrease the costs of subsequent water treatment at active sites and decrease deleterious impacts that discharges from abandoned sites have on receiving streams and lakes. In general, the systems that are not 100% effective were improperly designed, were undersized, or both. This report has been prepared so that designers of future systems can avoid these errors.

## ACKNOWLEDGMENTS

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# CHAPTER 1. MATERIALS AND METHODS

## COLLECTION OF WATER SAMPLES

Water samples were collected at passive treatment systems from their influent and effluent points, and, if applicable, between treatment cells within the system. Raw and acidified (2 mL of concentrated HCl) water samples were collected in 250 mL plastic bottles at each sampling point. Measurements of pH and temperature were made in the field with a calibrated Orion SA 270, SA 250 or SA 290 portable pH/ISE meter.[5] Alkalinity was measured in the field using a pH meter and an Orion Total Alkalinity Test Kit. At sites where particulates were visible in water samples, an extra sample was collected that was filtered through a 0.22-$\mu$m membrane filter before acidification. All samples were immediately placed on ice in an insulated cooler and returned to the laboratory within 36 h of collection. Samples were refrigerated at 4° C until analysis.

Substrate pore water samples were collected using a dialysis method similar to that described by Wheeler and Giller (*19*). Lengths of 6,000-8,000 molecular weight dialysis tubing were filled with 250 mL of deionized, deoxygenated water and buried 30-45 cm deep in the organic substrate of the wetland. Three weeks later, the dialysis tubes were retrieved and the contents immediately filtered through a 0.45-$\mu$m membrane filter. Laboratory experiments established that the chemistry of water within the sampling tubes equilibrated with surrounding pore water within 24 h. The 3-week equilibration period was allowed so that chemical anomalies caused by the burial process would dissipate. Portions of the filtered water samples were preserved with NaOH (for dissolved sulfide determinations), HCl (for cation analysis), or were left unpreserved (for alkalinity, acidity, and sulfate analyses).

## ANALYSIS OF WATER SAMPLES

Concentrations of Fe, Mn, Al, Ca, Mg, and Na were determined in the acidified samples using Inductively Coupled Argon Plasma Spectroscopy, ICP (Instrumentation Laboratory Plasma 100 model). The acidified samples were first filtered through a 0.45-$\mu$m membrane filter to prevent clogging of the small diameter tubing in the ICP.

Ferrous iron concentrations were determined on acidified samples by the potassium dichromate method (*20*). Sulfate concentrations were determined by reaction with barium chloride (BaCl) after first passing the raw sample through a cation exchange resin. Thorin was used as the end-point indicator. Dissolved sulfide species were determined using a sulfide-specific electrode.

Acidity was determined by boiling a 50-mL raw sample with 1 mL of 30% $H_2O_2$ (hydrogen peroxide), and then titrating the solution with 0.1 *N* NaOH (sodium hydroxide) to pH 8.3 (*21*). Acidity and alkalinity are reported as $mg \cdot L^{-1}$ $CaCO_3$ equivalents.

## ANALYTICAL QUALITY CONTROL

For each set of samples for a particular site, a duplicate, standard, and spike were analyzed for quality control purposes. The relative standard deviation for the duplicate was always at least 95%. Percent recovery for the standards were within 3% of the original standard. Spike recoveries were within 5% of the expected values.

## FLOW RATE MEASUREMENTS

Mine water flow rates were determined by several methods. Whenever possible, flow was determined with a bucket and stopwatch. In all cases, three to five measurements of the time needed to collect a known volume of water were made at each sampling location, and the average flow rate of these measurements was reported. At two sites where flows were occasionally too high to measure with a bucket (the Latrobe and Piney Wetlands), 0.50 or 0.75 ft H-type flumes were installed and flows were determined from the depth of water in the flume. At the Keystone site, flows were determined by measuring the depth of water in a drainage pipe and then using the Manning formula for measurement of gravity flow in open channels (*22*).

## ANALYSIS OF SURFACE DEPOSITS

The chemical composition of surface deposits collected from several constructed wetlands were determined by the following procedure. The samples were rinsed with deionized water, dried at 100° C, and weighed. The acid-soluble component was extracted by boiling 5 g of dry sample in 20 mL of concentrated HCl for 2 min. The acid extractants were filtered and analyzed for metal content by ICP Spectroscopy and for sulfate content by liquid chromatography. The acid-insoluble material was dried at 100° C and weighed. The acid-soluble component was determined by subtracting the dry weight of the insoluble material from the original dry weight.

[5]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

# CHAPTER 2. CHEMICAL AND BIOLOGICAL PROCESSES IN PASSIVE TREATMENT SYSTEMS

Coal mining can promote pyrite oxidation and result in drainage containing high concentrations of Fe, Mn, and Al, as well as $SO_4$, Ca, Mg, and Na. The solubilities of Fe, Mn, and Al are generally very low ($<1$ mg•L$^{-1}$) in natural waters because of chemical and biological processes that cause their precipitation in surface water environments. The same chemical and biological processes remove Fe, Mn, and Al from contaminated coal mine drainage, but the metal loadings from abandoned minesites are often so high that the deleterious effects of these elements persist long enough to result in the pollution of receiving waters.

Passive treatment systems function by retaining contaminated mine water long enough to decrease contaminant concentrations to acceptable levels. The chemical and biological processes that remove contaminants vary between metals and are affected by the mine water pH and oxidation-reduction potential (Eh). Efficient passive treatment systems create conditions that promote the processes that most rapidly remove target contaminants. Thus, the design of passive treatment systems must be based on a solid understanding of mine drainage chemistry and how different passive technologies affect this chemistry.

This chapter provides the basic chemical and biological background necessary to efficiently design passive treatment systems. The authors begin with a discussion of acidity and alkalinity because many of the decisions about how to treat mine water passively depend on determinations of these parameters. Next, the chemistry of Fe, Mn, and Al in aerobic and anaerobic aquatic environments is described. Throughout the discussion, chemical and biological concepts are illustrated with data collected from passive treatment systems.

## ACIDITY

Acidity is a measurement of the base neutralization capacity of a volume of water. Three types of acidity exist: proton acidity associated with pH (a measure of free $H^+$ ions), organic acidity associated with dissolved organic compounds, and mineral acidity associated with dissolved metals (*23*). Mine waters generally have a very low dissolved organic carbon content, so organic acidity is very low. The acidity of coal mine drainage arises from free protons (low pH) and the mineral acidity from dissolved Fe, Mn, and Al. These metals are considered acidic because they can undergo hydrolysis reactions that produce $H^+$.

$$Fe^{2+} + 1/4O_2 + 3/2H_2O \rightarrow FeOOH + 2H^+ \quad (A)$$

$$Fe^{3+} + 2H_2O \rightarrow FeOOH + 3H^+ \quad (B)$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (C)$$

$$Mn^{2+} + 1/4O_2 + 3/2H_2O \rightarrow MnOOH + 2H^+ \quad (D)$$

These reactions can be used to calculate the total acidity of a mine water sample and to partition the acidity into its various components. The expected acidity of a mine water sample is calculated from its pH and the sum of the milliequivalents of acidic metals. For most coal mine drainages, the calculation is as follows:

$$Acid_{calc} = 50(2Fe^{2+}/56 + 3Fe^{3+}/56 + 3Al/27 + 2Mn/55 + 1000(10^{-pH})) \quad (1)$$

where all metal concentrations are in milligram per liter and 50 is the equivalent weight of $CaCO_3$, and thus transforms milliequivalent per liter of acidity into milligram per liter $CaCO_3$ equivalent. For water samples with pH $<4.5$ (no alkalinity present), equation 1 calculates a mine water acidity that corresponds closely with measurements of acidity made using the standard $H_2O_2$ method (*21*). Using synthetic mine drainages with a wide range of compositions, it was determined that calculated acidities differed from measured values by less than 10% (table 2).

Equation 1 accurately characterizes mineral acidity for samples of actual acid mine drainage as well. At one site where numerous measurements of metal chemistry and total acidity were made, the mean acidity of samples with pH $<4.5$ was 693 mg•L$^{-1}$, while the predicted acidities for these samples averaged 655 mg•L$^{-1}$, a difference of only 6% (figure 1).

Equation 1 can be used to partition total acidity into its individual constituents. When the total acidities of contaminated coal mine drainages are partitioned in this manner, the importance of mineral acidity becomes apparent. A breakdown of the acidic components of three mine drainages is shown in table 3. At each site, the acidity arising from protons (pH) was a minor component of the total acidity. Mine drainage at the Friendship Hill wetland had extremely low pH (2.7), but the acidity of the

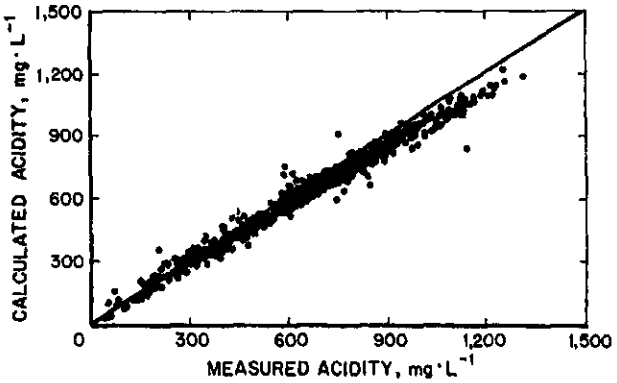


**Figure 1.—Comparison of calculated and measured acidities for water samples collected at Friendship Hill wetland.**

mine water resulted primarily from dissolved ferric iron and Al. The Somerset wetland received water with low pH (3.7), but the acidity of the water resulted largely from dissolved ferrous iron and Mn. At the Cedar Grove system, where the mine water was circumneutral, ferrous iron accounted for 98% of the acidity, while the hydrogen ion accounted for <1% of mine water acidity.

## ALKALINITY

When mine water has pH >4.5, it has acid neutralizing capacity and is said to contain alkalinity. Alkalinity can result from hydroxyl ion ($OH^-$), carbonate, silicate, borate, organic ligands, phosphate, and ammonia (*23*). The principal source of alkalinity in mine water is dissolved carbonate, which can exist in a bicarbonate ($HCO_3^-$) or carbonate form ($CO_3^{2-}$). Both can neutralize proton acidity.

$$H^+ + HCO_3^- \rightarrow H_2O + CO_2 \qquad (E)$$

$$2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2 \qquad (F)$$

In the pH range of most alkaline mine waters (5 to 8), bicarbonate is the principal source of alkalinity.

The presence of bicarbonate alkalinity in mine waters that contain elevated levels of metals is not unusual. Table 4 shows the chemical composition of 12 mine waters in northern Appalachia that contain alkalinity and are also contaminated with ferrous iron and Mn. None are contaminated with dissolved ferric iron or Al because the solubility of these metals is low in mine waters with pH greater than 5.5 (*23-24*).

**Table 2.—Calculated and measured acidities for synthetic acidic mine water**

| Synthetic Mine Water Composition[1] | | | | | Acidity | | |
|---|---|---|---|---|---|---|---|
| pH | $Fe^{2+}$ | $Fe^{3+}$ | Al | Mn | Calculated[2] | Measured[3] | Diff.[4] |
| 3.9 | 98 | 1 | 0 | 0 | 181 | 184 | -2% |
| 3.9 | 0 | 0 | 106 | 0 | 598 | 578 | +3% |
| 3.6 | 0 | 0 | 0 | 97 | 192 | 186 | +3% |
| 3.8 | 13 | 0 | 47 | 42 | 370 | 335 | +9% |

[1]Measured values are the average of three tests. Metal concentrations are $mg \cdot L^{-1}$. Acidities are $mg \cdot L^{-1}$ $CaCO_3$ equivalent.
[2]From reaction 1.
[3]Data determined by the hot $H_2O_2$ acidity method (*21*).
[4](1.00 - meas/cal) × 100.

**Table 3.—Acidic components of mine drainage influent at three passive treatment systems**

| Parameter | Friendship Hill | | | Somerset | | | Cedar Grove | | |
|---|---|---|---|---|---|---|---|---|---|
| | Concentration, $mg \cdot L^{-1}$ | Acid equivalent,[1] $mg \cdot L^{-1}$ | % of total acidity | Concentration, $mg \cdot L^{-1}$ | Acid equivalent,[1] $mg \cdot L^{-1}$ | % of total acidity | Concentration, $mg \cdot L^{-1}$ | Acid equivalent,[1] $mg \cdot L^{-1}$ | % of total acidity |
| $Fe^{2+}$ ..... | 7 | 13 | 1 | 193 | 345 | 69 | 95 | 170 | 98 |
| $Fe^{3+}$ ..... | 153 | 434 | 49 | 9 | 24 | 5 | <1 | <1 | <1 |
| $Al^{3+}$ ..... | 58 | 317 | 36 | 3 | 17 | 3 | <1 | <1 | <1 |
| $Mn^{2+}$ ..... | 9 | 16 | 1 | 59 | 107 | 21 | 2 | 4 | 2 |
| pH ..... | 2.6 | 112 | 13 | 3.7 | 10 | 2 | 6.3 | <1 | <1 |

[1]$CaCO_3$ equivalents calculated from the stoichiometry of reactions A-D.

**Table 4.—Chemical compositions of mine drainages that contain high concentrations of alkalinity**

| Location | pH | Alkalinity, $mg \cdot L^{-1}$ | Al, $mg \cdot L^{-1}$ | $Fe^{2+}$, $mg \cdot L^{-1}$ | $Fe^{3+}$, $mg \cdot L^{-1}$ | Mn, $mg \cdot L^{-1}$ | $SO_4$, $mg \cdot L^{-1}$ | Net alkalinity,[1] $mg \cdot L^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| Ohio: Coshocton | 6.1 | 152 | <1 | 119 | <1 | 2 | 1,325 | -50 |
| Pennsylvania: | | | | | | | | |
| Cross Creek | 6.3 | 300 | <1 | 96 | <1 | 2 | 1,260 | 140 |
| Donegal | 6.6 | 214 | <1 | 39 | <1 | 8 | 830 | 130 |
| Fallston | 6.2 | 120 | <1 | 30 | <1 | 3 | 390 | 66 |
| Keystone | 6.5 | 106 | <1 | 37 | <1 | 1 | 331 | 72 |
| Latrobe | 6.2 | 204 | <1 | 102 | <1 | 6 | 1,200 | 15 |
| New Bethlehem | 6.1 | 163 | <1 | 51 | <1 | 28 | 493 | 51 |
| Possum Hollow | 6.4 | 263 | <1 | 32 | <1 | 1 | 620 | 209 |
| Sligo | 5.5 | 93 | <1 | 43 | <1 | 26 | 1,720 | -31 |
| Somerset | 6.3 | 275 | <1 | 2 | <1 | 6 | 750 | 265 |
| St. Petersburg | 6.1 | 255 | <1 | 29 | <1 | 9 | 250 | 203 |
| Uniontown | 6.3 | 220 | <1 | 70 | <1 | 3 | 950 | 95 |

[1]Alkalinity minus acidity.

Alkalinity and acidity are not mutually exclusive terms. All of the mine waters shown in table 4 contain both acidity and alkalinity. When water contains both mineral acidity and alkalinity, a comparison of the two measurements results in a determination as to whether the water is net alkaline (alkalinity greater than acidity) or net acidic (acidity greater than alkalinity). Net alkaline water contains enough alkalinity to neutralize the mineral acidity represented by dissolved ferrous iron and Mn. As these metals oxidize and hydrolyze, the proton acidity that is produced is rapidly neutralized by bicarbonate. For waters contaminated with $Fe^{2+}$, the net reaction for the oxidation, hydrolysis and neutralization reactions is

$$Fe^{2+} + \tfrac{1}{4}O_2 + 2HCO_3^- \rightarrow FeOOH + \tfrac{1}{2}H_2O + 2CO_2 \quad (G)$$

Reaction G indicates that net alkaline waters contain at least 1.8 $mg \cdot L^{-1}$ alkalinity for each 1.0 $mg \cdot L^{-1}$ of dissolved Fe. Waters that contain a lesser ratio are net acidic, since the oxidation and hydrolysis of the total dissolved iron content results in a net release of protons and a decrease in the pH.

## METAL REMOVAL PROCESSES

Oxidation and hydrolysis reactions already discussed cause concentrations of $Fe^{2+}$, $Fe^{3+}$, Mn, and Al to commonly decrease when mine water flows through an aerobic environment. Whether these reactions occur quickly enough to lower metal concentrations to an acceptable level depends on the availability of oxygen for oxidation reactions, the pH of the water, the activity of microbial catalysts, and the retention time of water in the treatment system. The pH is an especially important parameter because it influences both the solubility of metal hydroxide precipitates and the kinetics of the oxidation and hydrolysis processes. The relationship between pH and metal-removal processes in passive treatment systems is complex because it differs between metals and also between abiotic and biotic processes.

## METAL REMOVAL IN AEROBIC ENVIRONMENTS

### Iron Oxidation and Hydrolysis

The most common contaminant of coal mine drainage is ferrous iron. In oxidizing environments common to most surface waters, ferrous iron is oxidized to ferric iron. Ferrous iron oxidation occurs both abiotically and as a result of bacterial activity. The stoichiometry of the reaction is the same for both oxidation processes.

$$Fe^{2+} + \tfrac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}H_2O \quad (H)$$

The pH of the mine water affects the kinetics of both the abiotic and biotic processes (*25-26*). When oxygen is not limiting, the rate of abiotic Fe oxidation slows 100-fold for every unit decrease in pH. At pH values >8, the abiotic process is fast (rates are measured in seconds), while at pH values <5 the abiotic process is slow (rates are measured in days). In contrast, bacterial oxidation of ferrous iron peaks at pH values between 2 and 3, while less activity occurs at pH values >5 (*27*). The presence of bicarbonate alkalinity buffers mine water at a pH of 6 to 7, a range at which abiotic iron oxidation processes should dominate. Waters containing no alkalinity have a pH <4.5 and the removal of Fe under oxidizing conditions occurs primarily by bacterial oxidation accompanied by hydrolysis and precipitation.

The effect that pH can have on the mechanism of iron oxidation is shown by the data in figure 2. Samples were collected from two mine drainages that were both contaminated with ferrous iron, but had different pH and alkalinity values. The samples were returned to the laboratory and exposed to aerobic conditions. For the circumneutral waters, oxidation of ferrous iron occurred at a

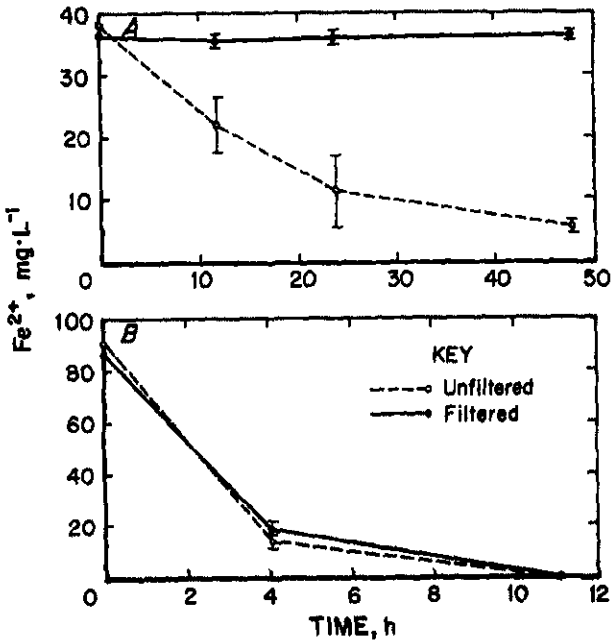


**Figure 2.—Removal of $Fe^{2+}$ from acidic and alkaline mine waters in laboratory experiment. Raw mine drainage was collected from *A*, acidic Latrobe site; *B*, alkaline Cedar Grove site. Splits of each sample were filter-sterilized (0.22-μm filter). The Latrobe samples were shaken throughout experiment; air was bubbled through Cedar Grove samples during experiment.**

rate of 18 mg•L$^{-1}$•h$^{-1}$, while the rate for the raw acidic samples was only 1.4 mg•L$^{-1}$•h$^{-1}$. To evaluate the significance of bacterial processes in iron oxidation, splits of both samples were filter-sterilized (0.22-μm membrane filter) before the experiment was begun. Removal of bacteria had no effect on the oxidation of ferrous iron for the circumneutral water, but completely inhibited ferrous iron oxidation for the acidic water.

As ferrous iron is converted to ferric iron, it is subject to hydrolysis reactions that can precipitate it as a hydroxide (reaction B). The hydrolysis reaction occurs abiotically; catalysis of the reaction by microorganisms has not been demonstrated. The solubility of the ferric hydroxide solid is such that, under equilibrium conditions, negligible dissolved ferric iron (<1 mg•L$^{-1}$) exists unless the pH of the mine water is <2.5. In actuality, the rate of the hydrolysis reaction is also pH dependent, and significant $Fe^{3+}$ can be found in mine water with a pH above 2.5. Singer and Stumm (*25*) suggested a fourth-order relationship with pH, which indicated that ferric iron hydrolysis processes shift from a very rapid rate at pH >3 to a very slow rate at pH <2.5. Figure 3 shows the relationship between pH and concentrations of $Fe^{3+}$ at a site where pH varied by almost 3 units. Ferric iron was not generally indicated unless the pH was <4, and the highest

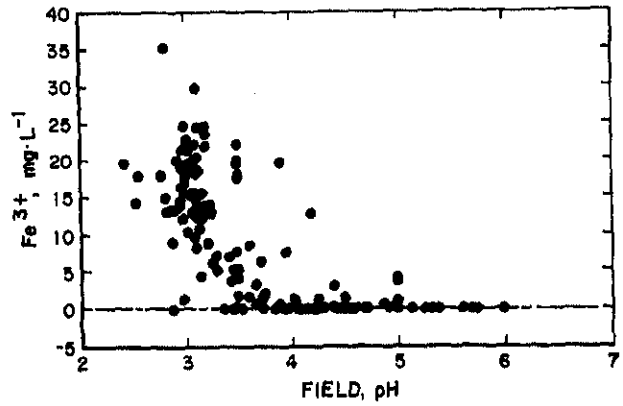


**Figure 3.— Concentrations of $Fe^{3+}$ and field pH for water samples collected from Emlenton wetland.**

concentrations of ferric iron occurred when the pH was <3.

The tendency for dissolved iron to oxidize and hydrolyze in aerobic environments with pH >3 results in the precipitation of ferric hydroxide. Because the net result of the oxidation and hydrolysis process is the production of protons, the process can decrease pH. Thus, natural or constructed wetlands receiving circumneutral net acidic water commonly decrease both Fe concentrations and pH. An example of this phenomenon is shown in figure 4*A*. As water flowed through the constructed wetland, iron concentrations decreased from 95 to 15 mg•L$^{-1}$, and pH decreased from 5.5 to 3.2. Figure 4*B* shows Fe concentrations and pH within a wetland that received mine water with a net alkalinity. Despite the removal of 60 mg•L$^{-1}$ $Fe^{2+}$ and the production of enough protons to theoretically lower the pH to 2.7, the pH did not decrease because bicarbonate alkalinity neutralized the proton acidity.

## Manganese Oxidation and Hydrolysis

Manganese undergoes oxidation and hydrolysis reactions that result in the precipitation of manganese oxyhydroxides. The specific mechanism(s) by which $Mn^{2+}$ precipitates from aerobic mine water in the absence of chemical additions is uncertain. $Mn^{2+}$ may be oxidized to either a +3 or a +4 valance, either one of which rapidly precipitates (reaction D). If MnOOH precipitates, over time it likely oxidizes to the more stable $MnO_2$. In alkaline environments, $Mn^{2+}$ can precipitate as a carbonate, which may also be oxidized by oxygen to $MnO_2$ (*28*).

$$Mn^{2+} + HCO_3^- \rightarrow MnCO_3 + H^+ \qquad (I)$$

$$MnCO_3 + \tfrac{1}{2}O_2 \rightarrow MnO_2 + CO_2 \qquad (J)$$

Regardless of the mechanism by which $Mn^{2+}$ is oxidized to $Mn^{4+}$, the removal of one mole of $Mn^{2+}$ from solution results in the release of two moles of $H^+$ or an equivalent decrease in alkalinity ($HCO_3^-$).

The kinetics of $Mn^{2+}$ oxidation reactions are strongly affected by pH. Abiotic oxidation reactions are very slow at pH <8 (*24*). Microorganisms can catalyze $Mn^{2+}$ oxidation, but their activity is limited to aerobic waters with pH >6 (*29*).

Although the hydrolysis of Mn produces protons, the precipitation of MnOOH does not result in large declines in pH as can happen when FeOOH precipitates. This difference between Mn and Fe chemistry is because of the fact that no natural mechanism exists that rapidly oxidizes $Mn^{2+}$ under acidic conditions. If pH falls below 6, $Mn^{2+}$ oxidation virtually ceases, the proton-producing hydrolysis reaction ceases, and pH stabilizes.

The oxidation and precipitation of $Mn^{2+}$ from solution is accelerated by the presence of $MnO_2$ and FeOOH (*24, 30*). Both solids reportedly act as adsorption surfaces for $Mn^{2+}$ and catalyze the oxidation mechanism. While additions of FeOOH to Mn-containing water might accelerate Mn oxidation, the direct precipitation of FeOOH from mine water containing $Fe^{2+}$ does not generally stimulate Mn-removal processes in passive treatment systems. Figure 5 shows concentrations of Mn and Fe for mine water as it flowed through a constructed wetland that markedly decreased concentrations of both metals. On average, Fe decreased from 150 to <1 mg•L$^{-1}$, while Mn decreased from 42 to 11 mg•L$^{-1}$. Removal of metals occurred sequentially, not simultaneously. Two-thirds of the decrease in iron concentration occurred between the first and second sampling stations. The wetland substrate in this area was covered with precipitated FeOOH and the water was turbid with suspended FeOOH. Despite the presence of large quantities of FeOOH, little change in the concentration of Mn occurred between the first and second sampling station. The slight decrease in Mn that occurred was proportionally similar to the change in Mg, suggesting that dilution was the most likely cause of the decrease in Mn concentrations (the use of Mg to estimate dilution is discussed in detail in chapter 3). Between stations 3 and 5, there was little Fe present in the water and little visual evidence of FeOOH sludge on the wetland substrate. Most of the observed removal of Mn occurred in this Fe-free zone.

The absence of simultaneous precipitation of dissolved Fe and Mn from aerobic alkaline waters likely results from the reduction of oxidized forms of Mn by ferrous iron.

$$MnO_2 + 2Fe^{2+} + 2H_2O \rightarrow 2FeOOH + Mn^{2+} + 2H^+ \quad (K)$$

or

$$MnOOH + Fe^{2+} \rightarrow FeOOH + Mn^{2+} \quad (L)$$

Figure 6 shows the results of a laboratory study that demonstrate the instability of Mn oxides in the presence of ferrous iron. Water samples and Mn-oxides were

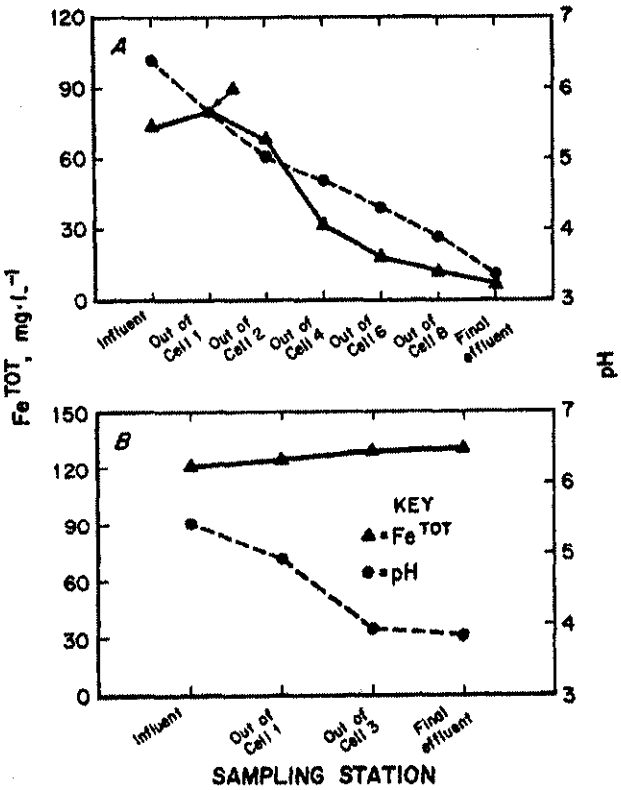


**Figure 4.—Concentrations of $Fe^{tot}$ and field pH at two constructed wetlands. *A*, Emlenton wetland; *B*, Cedar Grove wetland.**

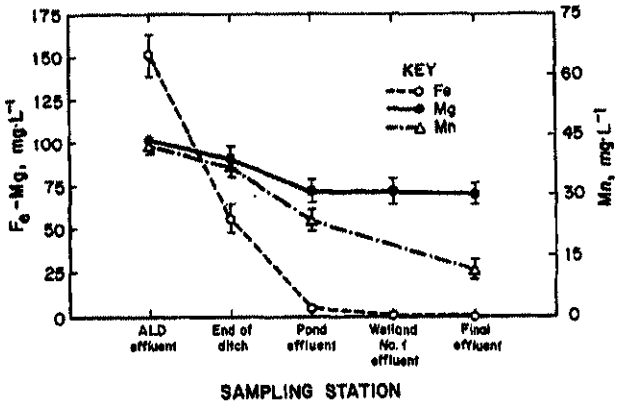


**Figure 5.—Mean concentrations of Fe, Mn, and Mg at the Morrison Wetland. Mine water flows linearly from station 1 to station 5. Verticle bars are one standard error of the mean.**

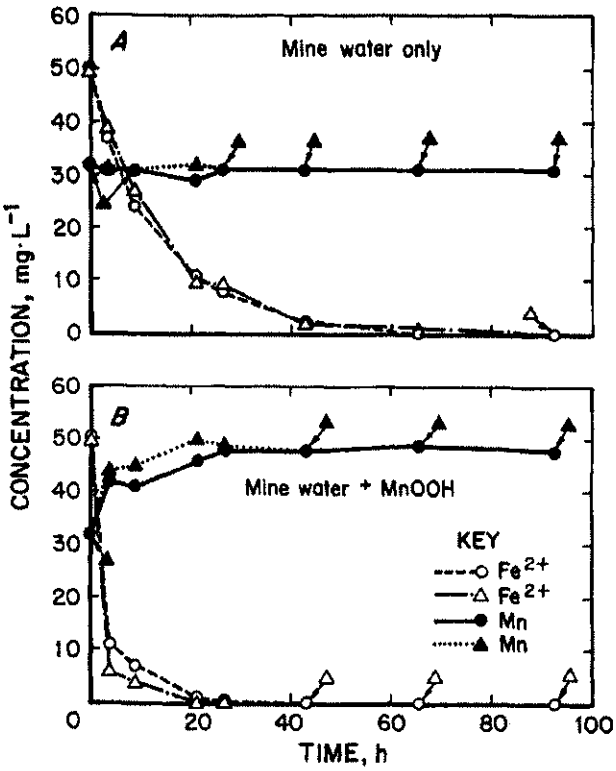


**Figure 6.—Changes in concentrations of $Fe^{2+}$ and $Mn^{2+}$. *A*, absence; *B*, presence of MnOOH. Mine water was collected from influent pipe of Blair wetland. MnOOH was collected from inside of final effluent pipe.**

collected from a wetland that removed Fe and Mn in a sequential manner. The wetland influent was alkaline (pH 6.2, 162 $mg \cdot L^{-1}$ alkalinity) and contaminated with 50 $mg \cdot L^{-1}$ Fe and 32 $mg \cdot L^{-1}$ Mn. Two flasks of mine water received $MnO_2$ additions, while the controls did not receive $MnO_2$. Concentrations of dissolved Fe and Mn were monitored in each flask over a 73-h period. In all flasks, concentrations of Fe decreased to <1 $mg \cdot L^{-1}$. In the control flasks, concentrations of Fe decreased to <3 $mg \cdot L^{-1}$ within 43 h. In flasks that received $MnO_2$, concentrations of Fe decreased to <3 $mg \cdot L^{-1}$ in only 22 h. No change in concentrations of Mn occurred in the control flasks. Concentrations of Mn in the $MnO_2$ flasks increased by 15 $mg \cdot L^{-1}$ during the first 22 h and did not change during the remaining 50 h of the experiment. The association of accelerated precipitation of Fe with solubilization of $Mn^{2+}$ suggests that the $MnO_2$ oxidized $Fe^{2+}$ in a manner analogous to reaction K.

The data presented in figures 5 and 6 demonstrate aspects of Fe and Mn chemistry that are important in passive treatment systems. Iron oxidizes and precipitates from alkaline mine water much more rapidly than does Mn. One reason for the differences in kinetics is that the oxidized Mn solids, which are presumed to result from $Mn^{2+}$ oxidation reactions, are not stable in the presence of $Fe^{2+}$. Concentrations of ferrous iron must decrease to very low levels before $Mn^{2+}$ oxidation processes can result in a stable solid precipitate. In the absence of $Fe^{2+}$, Mn removal is still a very slow process under laboratory conditions. Conditions in a wetland may either accelerate Mn-removal reactions or promote mechanisms that are not simulated in simple laboratory experiments. However, both field and laboratory investigations indicate that, under aerobic conditions, the removal of Mn occurs at a much slower rate than does the removal of Fe (empirical evidence for this concept is presented in chapter 3).

## MINE WATER CHEMISTRY IN ANAEROBIC ENVIRONMENTS

Chemical and microbial processes in anaerobic environments differ from those observed in aerobic environments. Because $O_2$ is absent, $Fe^{2+}$ and $Mn^{2+}$ do not oxidize and oxyhydroxide precipitates do not form. Hydroxides of the reduced Fe and Mn ions, $Fe(OH)_2$ and $Mn(OH)_2$, do not form because of their high solubility under acidic or circumneutral conditions. In passive treatment systems where mine water flows through anaerobic environments, its chemistry is affected by chemical and biological processes that generate bicarbonate and hydrogen sulfide.

### Limestone Dissolution

A major source of bicarbonate in many anaerobic environments is the dissolution of carbonate minerals, such as calcite.

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad (M)$$

Carbonate dissolution can result in higher concentrations of bicarbonate in anaerobic mine water environments than aerobic environments for two reasons. First, the absence of $Fe^{3+}$ in most anaerobic environments limits the formation of FeOOH coatings that armor carbonate surfaces and inhibit further carbonate dissolution in aerobic environments (*31*). Second, the solubilities of carbonate compounds are directly affected by the partial pressure of dissolved $CO_2$ (*23-24, 32*). Anaerobic mine water environments commonly contain high $CO_2$ partial pressures because of the decomposition of organic matter and the neutralization of proton acidity.

The observation that limestone dissolution is enhanced when contact with mine water occurs in an anaerobic environment has resulted in the construction of anaerobic limestone treatment systems. The first demonstration of

this technology was by Turner and McCoy (*15*) who showed that when anoxic acidic mine water was directed through a plastic-covered buried bed of limestone, it was discharged in an alkaline condition. After exposure to the atmosphere metal contaminants precipitated from this alkaline discharge much faster than they did from the original acid discharge.

Since Turner and McCoy described their findings in 1990, dozens of additional limestone treatment systems have been constructed (*33-35*). These passive mine water pretreatment systems have become known as anoxic limestone drains or ALD's. In an ALD, mine water is made to flow through a bed of limestone gravel that has been buried to limit inputs of atmospheric oxygen. The containment caused by the burial also traps $CO_2$ within the treatment system, allowing the development of high $CO_2$ partial pressures (*36*).

Water quality data from an ALD in western Pennsylvania are shown in table 5 and figure 7. This ALD is a rectangular bed of limestone gravel that is 37 m long by 6 m wide by 1 m deep. The limestone bed is covered with filter fabric and 1 m of clay. No organic matter was incorporated into the limestone system. Water samples were collected from the ALD influent and effluent and at four locations within the ALD. The influent mine water contained high concentrations of ferrous iron and Mn and a small amount of alkalinity. As the mine water flowed through the ALD, pH and concentrations of calcium and alkalinity increased while other measured parameters were unchanged. Between the influent and effluent locations, changes in concentrations of alkalinity (137 $mg \cdot L^{-1}$) and Ca (58 $mg \cdot L^{-1}$) were in stoichiometric agreement with those expected from $CaCO_3$ dissolution.

**Table 5.—Chemistry of mine water flowing through the Howe Bridge anoxic limestone drain, January 23, 1992**

| Parameter | In | Well 1 | Well 2 | Well 3 | Well 4 | Eff |
|---|---|---|---|---|---|---|
| pH | 5.9 | 6.1 | 6.4 | 6.5 | 6.5 | 6.3 |
| Alkalinity | 39 | 75 | 141 | 179 | 183 | 176 |
| Ca | 140 | 150 | 183 | 201 | 206 | 198 |
| $Fe^{2+}$ | 249 | 237 | 246 | 246 | 245 | 244 |
| $Fe^{3+}$ | <1 | <1 | <1 | <1 | <1 | <1 |
| Mn | 34 | 33 | 34 | 34 | 34 | 34 |
| Al | <1 | <1 | <1 | <1 | <1 | <1 |
| Mg | 90 | 87 | 91 | 91 | 90 | 90 |
| Na | 11 | 11 | 11 | 11 | 11 | 11 |
| $SO_4$ | 1175 | 1175 | 1200 | 1150 | 1200 | 1200 |
| $CO_2$ | 6.3 | 4.0 | 4.7 | 4.3 | 4.7 | NA |

NA Not available.

NOTE.—Water flows linearly from the influent (In) through wells 1, 2, 3, and 4 and out the effluent (Eff). $CO_2$ values are the partial pressure percentages (atmosphere) of gas samples collected from the headspace within the sampling wells. No gas sample could be collected for the effluent because it is an open pipe.

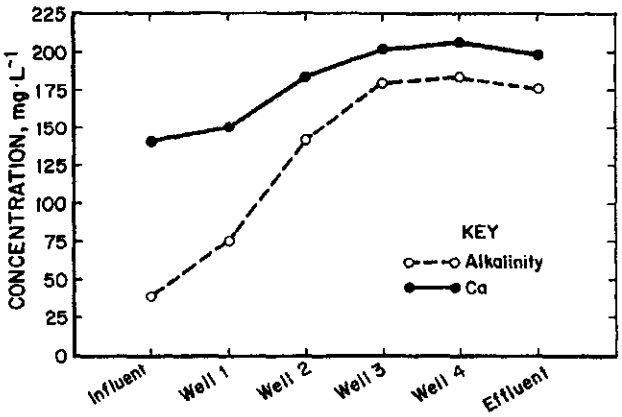


**Figure 7.—Concentrations of Ca, and alkalinity for water as it flows through the Howe Bridge ALD. Water flows linearly from influent to effluent.**

Dissolution of $CaCO_3$ within the ALD was greater than would be expected from an open system in equilibrium with atmospheric concentrations of $CO_2$ (0.035%). An equilibrated open system would only produce alkalinity in the range of 50 to 60 $mg \cdot L^{-1}$, and increase Ca concentrations by 4 to 8 $mg \cdot L^{-1}$. Observations of elevated $CO_2$ gas concentrations within the ALD, and the higher solubility of $CaCO_3$ within the ALD indicate that the ALD acts as a closed system.

Concentrations of alkalinity and Ca changed little between the third well and the ALD effluent. This observation suggests that water within the ALD was already in equilibrium with $CaCO_3$ by the time it reached the third well location. Thus, the amount of alkalinity that can be generated by this ALD is limited to a maximum value that is a function of the $CO_2$ partial pressures within the ALD. Similar observations of solubility-limited alkalinity generation by an ALD have also been made at a second site in western Pennsylvania (*36*).

## Sulfate Reduction

When mine water flows through an anaerobic environment that contains an organic substrate, the water chemistry can be affected by bacterial sulfate reduction. In this process, bacteria oxidize organic compounds using sulfate as the terminal electron sink and release hydrogen sulfide and bicarbonate,

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \qquad (N)$$

where $CH_2O$ is used to represent organic matter. Bacterial sulfate reduction is limited to certain environmental

conditions (*37*). The bacteria require the presence of sulfate, suitable concentrations of low-molecular weight carbon compounds, pH >4, and the absence of oxidizing agents such as $O_2$, $Fe^{3+}$ and $Mn^{4+}$. These conditions are commonly satisfied in treatment systems that receive coal mine drainage and contain organic matter. High concentrations of sulfate (>200 $mg \cdot L^{-1}$) are characteristic of contaminated coal mine drainage. The oxygen demand of organic substrates causes the development of anoxic conditions and an absence of oxidized forms of Fe or Mn. The low-molecular weight compounds that sulfate-reducing bacteria utilize (lactate, acetate) are common end products of microbial fermentation processes in anoxic environments. The pH requirements can be satisfied by alkalinity generated by microbial activity and carbonate dissolution.

Bacterial sulfate reduction directly affects concentrations of dissolved metals by precipitating them as metal sulfide solids.

$$M^{2+} + H_2S + 2HCO_3^- \rightarrow MS + 2H_2O + 2CO_2 \quad (O)$$

For Fe, the formation of pyrite is also possible

$$Fe^{2+} + H_2S + S^0 \rightarrow FeS_2 + 2H^+ \quad (P)$$

The removal of dissolved metals as sulfide compounds depends on pH, the solubility product of the specific metal sulfide, and the concentrations of the reactants. The solubilities of various metal sulfides are shown in table 6. Laboratory studies have verified that metal removal from mine water subjected to inflows of hydrogen sulfide occurs in an order consistent with the solubility products shown in table 6 (*39*). The first metal sulfide that forms is CuS followed by PbS, ZnS, and CdS. FeS is one of the last metal sulfides to form. MnS is the most soluble metal sulfide shown and is expected to form only when the concentrations of all other metals in the table are very low ($\ll$1 $mg \cdot L^{-1}$).

For coal mine drainage, where metal contamination is generally limited to Fe, Mn, and Al, the hydrogen sulfide produced by bacterial sulfate reduction primarily affects dissolved iron concentrations. Aluminum does not form any sulfide compounds in wetland environments and the relatively high solubility of MnS makes its formation unlikely.

**Table 6.—Solubility products of some metal sulfides**

| *Metal sulfide* | *Solubility product*[1] |
|---|---|
| CdS | $1.4 \times 10^{-23}$ |
| CuS | $4.0 \times 10^{-38}$ |
| FeS | $1.0 \times 10^{-19}$ |
| MnS | $5.6 \times 10^{-16}$ |
| NiS | $3.0 \times 10^{-21}$ |
| PbS | $1.0 \times 10^{-29}$ |
| ZnS | $4.5 \times 10^{-24}$ |

[1]See reference 38.

The precipitation of metal sulfides in an organic substrate improves water quality by decreasing the mineral acidity without causing a parallel increase in proton acidity. Proton-releasing aspects of the $H_2S$ dissociation process ($H_2S \rightarrow 2H^- + S^{2-}$) are neutralized by an equal release of bicarbonate during sulfate reduction. An organic substrate in which 100% of the $H_2S$ produced by sulfate reduction precipitated as FeS would have no effect on the mine water pH or alkalinity (although acidity would decrease). In fact, however, the chemistry of pore water in wetlands constructed with an organic substrate characteristically has pH 6 to 8 and is highly alkaline (*40-41*). These alkaline conditions result, in part, from reactions involving hydrogen sulfide that result in the net generation of bicarbonate. Hydrogen sulfide is a very reactive compound that can undergo a variety of reactions in a constructed wetland. In most wetlands (constructed and natural), surface waters are aerobic while the underlying pore waters in contact with organic substrate are anaerobic. When sulfidic pore waters diffuse from the organic substrate into zones that contain dissolved ferric iron, dissolved oxygen, or precipitated Fe and Mn oxides, the hydrogen sulfide can be oxidized (table 7). These reactions affect the mineral acidity and the alkalinity in various manners.

**Table 7.—Sinks for $H_2S$ in constructed wetlands and their net effect on mine water acidity and alkalinity**

| Reaction | Effect | |
|---|---|---|
| | Acidity[1] | Alkalinity[2] |
| $H_2S + 2HCO_3^- \rightarrow H_2S(g) + 2HCO_3^-$ | 0 | +100 |
| $H_2S + 2HCO_3^- + Fe^{2+} \rightarrow FeS + 2H_2O + 2CO_2$ | -100 | 0 |
| $H_2S + 2HCO_3^- + 2Fe^{3+} \rightarrow S^0 + 2Fe^{2+} + 2H_2O + 2CO_2$ | -100 | 0 |
| $H_2S + 2HCO_3^- + 2Fe(OH)_3 \rightarrow S^0 + 2Fe^{2+} + 2H_2O + 4OH^- + 2HCO_3^-$ | +200 | +300 |
| $H_2S + 2HCO_3^- + \frac{1}{2}O_2 \rightarrow S^0 + H_2O + 2HCO_3^-$ | 0 | +100 |
| $H_2S + 2HCO_3^- + FeS + \frac{1}{2}O_2 \rightarrow FeS_2 + H_2O + 2HCO_3^-$ | 0 | +100 |
| $H_2S + 2HCO_3^- + 2O_2 \rightarrow SO_4^{2-} + 2H_2O + 2CO_2$ | 0 | 0 |

[1] Effect based on change in mineral acidity.
[2] Effect based on summed change in bicarbonate and hydroxyl alkalinity.

Table 8 shows the chemistry of surface water and substrate pore water samples collected from a wetland constructed with limestone and spent mushroom compost. Spent mushroom compost consists of a mixture of spoiled hay, horse manure, corn cobs, wood chips, and limestone. At the wetland used in this example, 10 to 15 cm of limestone sand was covered with 20 to 50 cm of compost and planted with cattails. Water flowed through the wetland primarily by surface paths; no efforts were made to force the water through the compost. This design is typical of many compost wetlands constructed in northern Appalachia during the last 10 years. The data shown in table 8 were collected 15 months after the wetland was constructed.

**Table 8.—Surface and pore water chemistry at the Latrobe wetland**

| Parameter | Pore water[1] | | Surface water[2] | |
|---|---|---|---|---|
| | Mean | Std dev | Mean | Std dev |
| Al | 1 | 5 | 35 | 5 |
| Ca | 467 | 188 | 308 | 29 |
| $Fe^{2+}$ | 215 | 183 | 73 | 39 |
| $Fe^{3+}$ | 2 | 9 | 24 | 16 |
| $H_2S$ | 37 | 75 | <1 | 0 |
| Mg | 175 | 48 | 166 | 9 |
| Mn | 24 | 10 | 42 | 2 |
| Na | 11 | 10 | 5 | 1 |
| $SO_4$ | 1,674 | 532 | 1,967 | 115 |
| Acidity[3] | 493 | 340 | 503 | 86 |
| Alkalinity | 885 | 296 | 0 | 0 |
| Net Alkalinity[4] | 392 | NAp | -503 | NAp |
| pH | 6.8 | .8 | 3.1 | .1 |

NAp Not applicable.
Std dev Standard deviation.

[1] A total of 52 water samples were collected on July 25 and August 11, 1988, by the dialysis tube method. Metals were analyzed for every sample. Field pH was measured for 29 samples. Alkalinity was measured for nine samples.

[2] Six samples collected in July and August 1988.

[3] Calculated from pH, $Fe^{2+}$, $Fe^{3+}$, Al, Mn, and $H_2S$ for pore water samples and measured by the $H_2O_2$ method for surface water samples.

[4] Average alkalinity minus average acidity. The nine pore water samples for which alkalinity was measured had a mean net alkalinity of 653 mg/L (std dev = 590).

Surface water at the study site had low pH and high concentrations of Fe, Al, and Mn (table 8). Compared with the surface water, the substrate pore water had higher pH, higher concentrations of alkalinity, ferrous iron, calcium, and hydrogen sulfide, and lower concentrations of sulfate, ferric iron, and aluminum. On average, the pore water had a net alkalinity while the surface water had a net acidity. The alkalinity of the pore water appeared to result from a combination of limestone dissolution and sulfate reduction. The average alkalinity calculated to result from these processes was 703 $mg \cdot L^{-1}$, a value that corresponded reasonably well with the measured difference in acidity, 895 $mg \cdot L^{-1}$.[6]

Compared with surface water, substrate pore water contained elevated concentrations of ferrous iron. High concentrations of $Fe^{2+}$ likely resulted from the dissolution of ferric oxyhydroxides at the redox boundary. FeOOH can be reduced by direct heterotrophic bacterial activity (*42*),

$$CH_2O + 4FeOOH + H_2O \rightarrow 4Fe^{2+} + 8OH^- + CO_2 \quad (Q)$$

and also by $H_2S$ that results from sulfate reduction.

$$H_2S + 2FeOOH \rightarrow 2Fe^{2+} + 4OH^- + S^0 \quad (R)$$

In both cases, the solubilization of ferric hydroxides results in the release of $OH^-$, which acts to raise pH to circumneutral levels and also reacts with dissolved $CO_2$ to form bicarbonate. Reduction of ferric hydroxide has no effect on the net acidity of the mine water because the increase in alkalinity is exactly matched by an increase in mineral acidity. If the Fe-enriched pore water diffuses into an aerobic zone, the ferrous iron content should oxidize, hydrolyze, and reprecipitate as ferric oxyhydroxide.

$$4Fe^{2+} + 8OH^- + O_2 \rightarrow 4FeOOH + 2H_2O \quad (S)$$

Because the pore water has circumneutral pH and is strongly buffered by bicarbonate, the removal of iron by oxidation processes from pore water as it diffuses into aerobic surface waters should occur rapidly. Indeed, during the summer months, when the data in table 8 were collected, comparisons of the wetland influent and effluent indicated that the wetland decreased both concentrations of iron and total acidity on every sampling day (figure 8). The decrease in acidity indicates that alkaline pore water was mixing with surface water and neutralizing acidity. The decrease in concentrations of Fe in the surface water indicates that elevated concentrations of $Fe^{2+}$ observed in the pore water were rapidly removed in surface water environments.

## ALUMINUM REACTIONS IN MINE WATER

Aluminum has only one oxidation state in aquatic systems, +3. Oxidation and reduction processes, which complicate Fe and Mn chemistry, do not directly affect

[6]The difference between surface and pore water concentrations of sulfate averaged 293 $mg \cdot L^{-1}$, which is equivalent to 305 $mg \cdot L^{-1}$ $CaCO_3$ alkalinity (reaction N); the difference in calcium concentrations averaged 159 $mg \cdot L^{-1}$, which is equivalent to 398 $mg \cdot L^{-1}$ $CaCO_3$ alkalinity (reaction M).

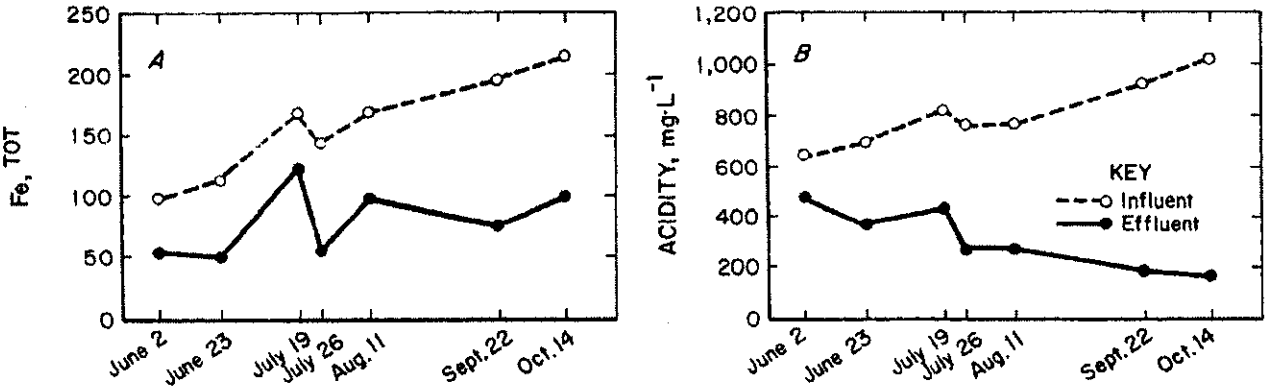


**Figure 8.—Influent and effluent concentrations at the Latrobe wetland during the summer of 1988. *A*, Fe; *B*, acidity.**

concentrations of dissolved Al. Instead, concentrations of Al in mine waters are primarily influenced by the solubility of $Al(OH)_3$ (*23, 43*). At pH levels between 5 and 8, $Al(OH)_3$ is highly insoluble and concentrations of dissolved Al are usually $<1$ mg·L$^{-1}$. At pH values $<4$, $Al(OH)_3$ is highly soluble and concentrations $>2$ mg·L$^{-1}$ are possible.

The passage of mine water through highly oxidized or highly reduced environments has no effect on concentrations of Al unless the pH also changes. In those cases where the pH of mine water decreases (due to iron oxidation and hydrolysis), concentrations of Al can increase because of the dissolution of alumino-silicate clays by the acidic water. When acidic mine water passes through anaerobic environments, the increased pH that can result from carbonate dissolution or microbial activity causes the precipitation of $Al(OH)_3$.

# CHAPTER 3. REMOVAL OF CONTAMINANTS BY PASSIVE TREATMENT SYSTEMS

Chapter 2 described chemical and biological processes that decrease concentrations of mine water contaminants in aquatic environments. The successful utilization of these processes in a mine water treatment system depends, however, on their kinetics. Chemical treatment systems function by creating chemical environments where metal removal processes are very rapid. The rates of chemical and biological processes that underlie passive systems are often slower than their chemical system counterparts and thus require that mine water be retained longer before it can be discharged. Retention time is gained by building large systems such as wetlands. Because the land area available for wetlands on minesites is often limited, the sizing of passive treatment systems is a crucial aspect of their design. Unfortunately, in the past, most passive treatment systems have been sized based on guidelines that ignored water chemistry or on available space, rather than on comparisons of contaminant production by the mine water discharge and expected contaminant removal by the treatment system. Given the absence of quantitative sizing standards, wetlands have been constructed that are both vastly undersized and oversized.

In this chapter, rates of contaminated removal are described for 13 passive treatment systems in western Pennsylvania. The systems were selected to represent the wide diversity of mine water chemical compositions that exist in the eastern United States. The rates that are reported from these sites are the basis of treatment system sizing criteria suggested in chapter 4.

The analytical approach used to quantify the performance of passive treatment systems in this chapter differs from the approach used by other researchers in several respects. First, contaminant removal is evaluated from a rate perspective, not a concentration perspective. Second, changes in contaminant concentrations are partitioned into two components: because of dilution from inputs of freshwater, and because of chemical and biological processes in the wetland. In the evaluations of wetland performance, only the chemical and biological components are considered. Third, treatment systems, or portions of systems, were included in the case studies only if contaminant concentrations were high enough to ensure that contaminant removal rates were not limited by the absence of the contaminant. These unique aspects of the research are discussed in further detail below.

## EVALUATION OF TREATMENT SYSTEM PERFORMANCE

To make reliable evaluations of wetland performance, a measure should be used that allows comparison of contaminant removal between systems that vary in size and the chemical composition and flow rate of mine water they receive. In the past, concentration efficiency (CE%) has been a common measure of performance (*11-12*). Using iron concentration as an example, the calculation is

$$CE\% = \frac{Fe_{in} - Fe_{eff}}{Fe_{in}} \times 100 \qquad (2)$$

where the subscripts "in" and "eff" represent wetland influent and effluent sampling stations and Fe concentrations are in milligram per liter.

Except in carefully controlled environments, CE% is a very poor measure of wetland performance. The efficiency calculation results in the same measure of performance for a system that lowers Fe concentrations from 300 to 100 $mg \cdot L^{-1}$ as one that lowers concentrations from 3 to 1 $mg \cdot L^{-1}$. Neither the flow rate of the drainage nor the size of the treatment system are incorporated into the calculation. As a result, the performances of systems have been compared without accounting for differences in flow rate (which vary from <10 to >1000 $L \cdot min^{-1}$) or for differences in system size (which vary from <0.1 to >10 ha) (*12*).

A more appropriate method for measuring the performance of treatment systems calculates contaminant removal from a loading perspective. The daily load of contaminant received by a wetland is calculated from the product of concentration and flow rate data. For Fe, the calculation is

$$Fe\ (g \cdot d^{-1})_{in} = 1.44 \times flow\ (L \cdot min^{-1}) \times Fe\ (mg \cdot L^{-1})_{in}) \qquad (3)$$

where $g \cdot d^{-1}$ is gram per day and 1.44 is the unit conversion factor needed to convert minutes to days and milligrams to grams.

The contaminant load is apportioned to the down flow treatment system by dividing by a measure of the system's size. In this study, treatment systems are sized based on their surface area (SA) measured in square meter,

$$Fe\ (g \cdot m^{-2} \cdot d^{-1})_{in} = Fe\ (g \cdot d^{-1})_{in} / SA. \qquad (4)$$

The daily mass of Fe removed by the wetland between two sampling stations, $Fe(g \cdot d^{-1})_{rem}$, is calculated by comparing contaminant loadings at the two points,

$$Fe\ (g \cdot d^{-1})_{rem} = (Fe\ g \cdot d^{-1})_{in} - (Fe\ g \cdot d^{-1})_{eff}. \qquad (5)$$

An area-adjusted daily Fe removal rate is then calculated by dividing the load removed by the surface area of the treatment system lying between the sampling points,

$$Fe\ (g \cdot m^{-2} \cdot d^{-1})_{rem} = Fe\ (g \cdot d^{-1})_{rem} / SA. \qquad (6)$$

To illustrate the use of contaminant loading and contaminant removal calculations, consider the hypothetical water quality data presented in table 9.

In systems A and B, changes in Fe concentrations are the same (60 $mg \cdot L^{-1}$), but because system B receives four times more flow and thus higher Fe loading, it actually removes four times more Fe from the water. The concentration efficiencies of the two wetlands are equivalent, but the masses of Fe removed are quite different.

Data are shown for system C for three sampling dates on which flow rates and influent iron concentrations vary. On the first date (C1), the wetland removes all of the Fe that it receives. On the next two dates (C2 and C3), Fe loadings are higher and the wetland effluent contains Fe. From an efficiency standpoint, performance is best on the first date and is worst on the third date. From an Fe-removal perspective, the system is removing the least amount of Fe on the first date. On the second and third dates, the wetland removes similar amounts of iron (2,880 and 3,024 $g \cdot d^{-1}$). Variation in effluent chemistry results, not from changes in wetland's Fe-removal performance, but from variation in influent Fe loading.

**Table 9.—Hypothetical wetland data and performance evaluations**

| System | Wetland size, $m^2$ | Flow rate $L \cdot min^{-1}$ | Fe Concentration In $mg \cdot L^{-1}$ | Fe Concentration Eff $mg \cdot L^{-1}$ | Fe Loading In $Kg \cdot d^{-1}$ | Fe Loading Eff $Kg \cdot d^{-1}$ | Fe removal performance CE % | Fe removal performance Rate $g \cdot m^{-2} \cdot d^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| A | 400 | 10 | 100 | 40 | 1.4 | 0.6 | 60 | 2.2 |
| B | 400 | 40 | 100 | 40 | 5.8 | 2.3 | 60 | 8.6 |
| C1 | 500 | 30 | 40 | <1 | 1.7 | <0.1 | 99 | 3.5 |
| C2 | 500 | 80 | 35 | 10 | 4.0 | 1.2 | 71 | 5.8 |
| C3 | 500 | 150 | 30 | 16 | 6.5 | 3.5 | 47 | 6.0 |
| D | 750 | 50 | 100 | 25 | 7.2 | 1.8 | 75 | 7.2 |

In Influent.
Eff Effluent.
CE Concentration efficiency.

Lastly, consider a comparison of wetland systems of different sizes. System D removes more iron than any wetland considered (5,400 $g \cdot d^{-1}$), but it is also larger. One would expect that, all other factors being equal, the largest wetland would remove the most Fe. When wetland area is incorporated into the measure by calculating area-adjusted Fe removal rates (gram per square meter per day), System B emerges as the most efficient wetland considered.

## DILUTION ADJUSTMENTS

Contaminant concentrations decrease as water flows through treatment systems because chemical and biological processes remove contaminants from solution and because the concentrations are diluted by inputs of freshwater. To recognize and quantify the removal of contaminants by biological and chemical processes in passive treatment systems, it is necessary to remove the effects of dilution. Ideally, studies of treatment systems include the development of detailed hydrologic and chemical budgets so that dilution effects are readily apparent. In practice, the hydrologic information needed to develop these budgets is rarely available, except when systems are built for research purposes. Treatment systems constructed by mining companies and reclamation groups are rarely designed to facilitate flow measurements at all water sampling locations, so estimating dilution from hydrologic information is highly inaccurate or impossible.

An alternative method for distinguishing the effects of dilution from those of chemical and biological processes is through the use of a conservative ion (*44-45*). By definition, the concentration of a conservative ion changes between two sampling points only because of dilution or evaporation. Changes in concentrations of contaminant ions that proportionately exceed those of conservative ions can then be attributed to biological and chemical wetland processes.

In this study, Mg was used as a conservative ion. Magnesium was considered a good indicator of dilution in these systems for both theoretical and empirical reasons. In northern Appalachia, concentrations of Mg in coal mine drainage are often >50 $mg \cdot L^{-1}$, while concentrations in rainfall are <1 $mg \cdot L^{-1}$ and in surface runoff are usually <5 $mg \cdot L^{-1}$. Magnesium is unlikely to precipitate in passive treatment systems because the potential solid precipitates, $MgSO_4$, $MgCO_3$, and $CaMg(CO_3)_2$, do not form at the concentrations and pH conditions found in the systems (*23*). While biological and soil processes exist that may remove Mg in wetlands, their significance is negligible relative to the high Mg loadings that most mine water treatment systems in northern Appalachia receive. The average Mg loading for wetland systems included in this study was ~7,000 g $Mg \cdot m^{-2} \cdot yr^{-1}$. The uptake of dissolved Mg by plants in constructed wetlands can only account for 5 to 10 g $Mg \cdot m^{-2} \cdot yr^{-1}$. This estimate assumes that the net primary productivity of the constructed wetlands is 2,000 $g \cdot m^{-2} \cdot yr^{-1}$ dry weight (*46*) and that the Mg content of this biomass is 0.25% to 0.50% (*47*). The estimate ignores mineralization processes that would decrease the net retention of Mg to lower values. Most constructed wetlands have a clay base that can adsorb Mg by cation exchange processes, but the total removal of Mg by this process is limited to about 100 $g \cdot m^{-2}$. This estimate assumes that the mine water is in contact with a 5-cm-deep clay substrate that has a density of 1.5 $g \cdot cm^{-3}$, a cation exchange capacity of 25 meq per 100 g, and 50% of the available sites are occupied by Mg (*48*). These conservative calculations indicate that less than 2% of the annual Mg loading at the study sites is likely affected by biological and soil processes within the systems.

Empirical data also indicate that Mg is conservative in the wetlands monitored in this study. Table 10 shows influent and effluent concentrations of major noncontaminant ions at eight constructed wetlands. No precipitation had occurred in the study area for 2 weeks previous to collection of the samples, so dilution from rainfall, surface water, or shallow ground water seeps was minimal. Magnesium was the most conservative ion measured. Concentrations of Mg changed by <5% with flow through every wetland, while concentrations of all other ions monitored changed by at least 15% at at least one site.

**Table 10.—Influent and effluent concentrations of Ca, Mg, Na, and sulfate at eight constructed wetlands**

| | Ca | | | Mg | | | Na | | | $SO_4$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | In, $mg \cdot L^{-1}$ | Eff, $mg \cdot L^{-1}$ | Change, % | In, $mg \cdot L^{-1}$ | Eff, $mg \cdot L^{-1}$ | Change, % | In, $mg \cdot L^{-1}$ | Eff, $mg \cdot L^{-1}$ | Change, % | In, $mg \cdot L^{-1}$ | Eff, $mg \cdot L^{-1}$ | Change, % |
| Donegal ..... | 244 | 241 | -1 | 81 | 79 | -2 | 6 | 6 | 0 | 729 | 729 | 0 |
| Emlenton .... | 429 | 433 | +1 | 308 | 306 | -1 | 11 | 10 | -2 | 2,810 | 2,770 | -1 |
| FH ..... | 122 | 189 | +55 | 51 | 51 | 0 | 5 | 7 | +2 | 1,125 | 842 | -25 |
| Gourley ..... | 117 | 120 | +3 | 114 | 117 | +3 | 3 | 4 | +6 | 1,000 | 1,030 | +3 |
| Latrobe ..... | 244 | 256 | +14 | 127 | 125 | -2 | 6 | 11 | +8 | 1,525 | 1,225 | -20 |
| Piney A ..... | 416 | 426 | +2 | 251 | 262 | +4 | 15 | 16 | +4 | 2,190 | 2,120 | -3 |
| Piney B ..... | 355 | 354 | 0 | 217 | 216 | 0 | 27 | 27 | -2 | 2,050 | 2,100 | +2 |
| Somerset .... | 307 | 469 | +53 | 312 | 312 | 0 | 6 | 7 | +15 | 2,740 | 2,300 | -16 |

Eff Effluent.
In Influent.
FH Friendship Hill National Historical Site.

Changes in concentrations of Mg were used to adjust for dilution effects by the following method. For each set of water samples from a constructed wetland, a dilution factor (DF) was calculated from changes in concentrations of Mg between the influent and effluent station:

$$DF = Mg_{eff} / Mg_{in} . \quad (7)$$

Contaminant concentrations were adjusted to account for dilution using the DF. When only an influent flow rate was available, the chemical composition of the effluent water sample was adjusted. For Fe, the adjustment calculation was

$$\Delta Fe_{DA} = Fe_{in} - (Fe_{eff} / DF) \quad (8)$$

where $\Delta Fe_{DA}$ is expressed in milligram per liter. When only an effluent flow rate was available, the chemical composition of the influent water sample was adjusted,

$$\Delta Fe_{DA} = (Fe_{in} \times DF) - Fe_{eff}. \quad (9)$$

Because most of the DF values were <1.00, the adjustment procedures generally resulted in smaller estimates of changes in contaminant concentrations than would have been calculated without the dilution adjustment.

Rates of contaminant removal, expressed as gram per square meter per day, were then calculated from the dilution-adjusted change in concentrations, the flow rate measurement liter per minute, and the SA of the system, in square meter

$$Fe(g \cdot m^{-2} \cdot day^{-1})_{rem} = (\Delta Fe_{DA} \times Flow \times 1.44)/SA. \quad (10)$$

## LOADING LIMITATIONS

A primary purpose of this chapter is to define the contaminant removal capabilities of passive treatment systems. Accurate assessments of these capabilities require that the treatment systems studied contain excessive concentrations of the contaminants. A system that is completely effective (lowers a contaminant to <2 $mg \cdot L^{-1}$) may provide an indication that contaminant removal occurs (if dilution is not the cause of concentration changes), but cannot provide an estimate of the capabilities of the removal processes, as the rate of contaminant removal may be limited simply by the contaminant loading rate. For example, in table 9, the removal rate of Fe for wetland C1 is 3.5 $g \cdot m^{-2} \cdot d^{-1}$. This rate is not an accurate estimate of the capability of the wetland to remove Fe because the loading rate on this day was also only 3.5 $g \cdot m^{-2} \cdot d^{-1}$. The data from C1 are not sufficient to estimate whether the wetland could have removed 10 or 100 $g \cdot m^{-2} \cdot d^{-1}$ of Fe. Only when the wetland is overloaded with Fe (days C2 and C3), can the Fe removal capabilities of the wetland be assessed.

The Morrison passive treatment system demonstrates the necessity of recognizing both dilution and loading-limiting situations in the evaluation of the kinetics of metal removal processes. The Morrison system consists of an anoxic limestone drain followed by a ditch, a settling pond, and two wetland cells. Figure 5, previously presented in chapter 2, shows average concentrations of Fe, Mn, and Mg at the sampling stations. Iron loading and removal rates for the sampling stations are shown in table 11. The treatment system decreased concentrations of Fe from 151 $mg \cdot L^{-1}$ at the system influent station (the ALD discharge) to <1 $mg \cdot L^{-1}$ at the final wetland effluent station. Most of the change in Fe chemistry occurred in the ditch, a portion of the system that only accounted for 4% of the total treatment system SA. Calculations of the rate of Fe removal based on the entire treatment system resulted in a value of 1.3 $g \cdot m^{-2} \cdot d^{-1}$. Because this removal rate is equivalent to the load, it does not represent a reliable approximation of the system's Fe-removal capablity. Only when an Fe removal rate is calculated for the ditch, an area where Fe loading exceeded Fe removal, does an accurate assessment of the Fe removal capabilities result.

**Table 11.—Average concentrations of Fe, Mn, and Mg at the Morrison passive treatment system**

| Station | Cumulative area, $m^2$ | Flow, $L \cdot m^{-1}$ | Concentration, $mg \cdot L^{-1}$ | | | Removal rate[1], $g \cdot m^{-2} \cdot d^{-1}$ | |
|---|---|---|---|---|---|---|---|
| | | | Fe | Mn | Mg | Fe | Mn |
| Influent ..... | 0 | 6.6 | 151 | 42 | 102 | NA | NA |
| Ditch Effluent .... | 43 | NA | 56 | 37 | 91 | 19.2 | 0.17 |
| Pond Effluent .... | 461 | NA | 5 | 24 | 72 | 2.3 | 0.14 |
| Final Effluent .... | 1,076 | NA | <1 | 71 | 71 | 1.3 | 0.13 |

NA Not available.

[1]Removal rate based on cumulative area.

Concentrations of Mn at the Morrison effluent station were generally above discharge limits. Manganese was detectable in every effluent water sample (>.4 mg•L$^{-1}$) and >2 mg•L$^{-1}$ in 75% of the samples. Thus, it was reasonable to evaluate the kinetics of Mn removal based on the SA of the entire treatment system. Concentrations of Mg, however, decreased with flow through the treatment system, suggesting an important dilution component. Effluent water samples contained, on average, 31% lower concentrations of Mg than did the influent samples. On several occassions when the site was sampled in conjunction with a rainstorm, differences between effluent and influent concentrations of Mg were larger than 50%. Measurements of metal removal by the Morrision treatment system that did not attempt to account for dilution would significantly overestimate the actual kinetics of metal removal processes.

Dilution adjustments were possible for every set of water samples collected from a treatment system because concentrations of Mg were determined for every water sample. Problems with loading limitations, however, could not be corrected at every site. At two sites where complete removal of Fe occurred, the Blair and Donegal wetlands, the designs of the systems were not conducive for the establishment of intermediate sampling stations. For these two systems, no Fe removal rates were calculated because complete removal of Fe occurred over an undetermined area of treatment system.

## STUDY SITES

The design characteristics of the 13 passive treatment systems monitored during this study are shown in table 12. At four of the sites, acidic mine water was pretreated with anoxic limestone drains (ALD's) before it flowed into constructed wetlands. The construction materials for the wetlands ranged from mineral substances, such as clay and limestone rocks, to organic substances such as spent mushroom compost, manure, and hay bales. Cattails (*Typha latifolia* and, less commonly, *T. angustifolia*) were the most common emergent plants growing in the systems. Three sites contained few emergent plants. Most of the wetland systems consisted of several cells or ponds connected serially. Two systems, however, each consisted of a single long ditch.

The mean influent flow rates of mine drainage at the study sites ranged from 7 to 8,600 L•min$^{-1}$ (table 12). The highest flow rates occurred where drainage discharged from abandoned and flooded underground mines. The lowest flow rates occurred at surface mining sites. Estimated average retention times ranged from 8 h to more than 30 days.

The average chemistry of the influents to the 16 constructed wetlands are shown in table 13. Data from 15 sampling points are shown. At the REM site, two discharges are treated by distinct ALD-wetland systems that eventually merge into a single flow. The combined flows are referred to as REM-Lower. Mine water at the Howe Bridge system is characterized at two locations. The "upper" analysis describes mine water discharging from an ALD that flows into aerobic settling ponds. The "lower" analysis describes the chemistry of water flowing out of the last settling pond and into a large compost-limestone wetland that is constructed so that mine water flows in a subsurface manner.

**Table 12.—Construction characteristics of the constructed wetlands**

| Site | Constructed year | Design | Substrate | Emergent vegetation | SA, m$^2$ | Water depth, cm | Flow rate,[1] L•min$^{-1}$ | Est. ret. time,[2] days |
|---|---|---|---|---|---|---|---|---|
| Donegal | 1987 | Pond, 8 Cells | LS, SMC | *Typha* | 8,100 | 15 | 501 | 1.7 |
| Cedar | 1989 | 5 Cells | Clay, LS | .. do. | 1,360 | 15 | 156 | 0.9 |
| Keystone | 1989 | Ditch | Topsoil | None | 4,200 | 100 | 8,606 | .3 |
| Blair | 1989 | Ditch | Manure, straw | Mixed | 1,080 | 5 | 11 | 3.4 |
| Shade | 1989 | ALD, 2 Cells | LS | None | 880 | 10 | 10 | 6.4 |
| Piney | 1987 | 1 Cell | HB | Mixed | 2,500 | 50 | 468 | 1.9 |
| Morrison | 1990 | ALD, 3 Cells | Clay, manure | *Typha* | 1,075 | 30 | 7 | 33.9 |
| Emlenton | 1987 | 9 Cells | LS, manure | .. do. | 643 | 50 | 55 | 4.1 |
| Somerset | 1984 | 2 Cells | HB, LS, SMC | .. do. | 1,005 | 15 | 47 | 2.2 |
| Howe | 1991 | ALD, 3 Cells | Clay, LS, SMC | None | 3,000 | 50 | 130 | 8.0 |
| Latrobe | 1987 | 3 Cells | HB, LS, SMC | *Typha* | 2,800 | 15 | 86 | 3.4 |
| REM | 1992 | 2 ALDs, 9 Cells | SMC | .. do. | 4,849 | 30 | 206 | 4.9 |
| FH | 1988 | 6 Cells | LS, SMC | .. do. | 667 | 15 | 15 | 4.6 |

Est. Estimated.
FH Friendship Hill National Historical Site.
HB Haybales.
LS Limestone.
ret. Retention.
SA Surface area of wet area.
SMC Spent mushroom compost.
[1] Average values.
[2] Calculated from the water holding capacity and influent flow rate.

**Table 13.—Average chemical characteristics of influent water at the constructed wetlands (sites are arranged according to the net acidity)**

| Site | Number of samples | pH | Composition, mg•L$^{-1}$ | | | | | | Net Acidity,[1,2] mg•L$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | Alk | Fe | Mn | Al | Mg | $SO_4$ | |
| Donegal | 29 | 7.1 | 202 | 5 | 8 | <1 | 81 | 738 | -182 |
| Cedar | 26 | 6.3 | 336 | 92 | 2 | <1 | 54 | 1,251 | -140 |
| Keystone | 28 | 6.3 | 142 | 37 | <1 | <1 | 14 | 330 | -73 |
| Blair | 12 | 6.2 | 166 | 52 | 30 | <1 | 77 | 645 | -51 |
| Shade | 20 | 6.0 | 31 | <2 | 22 | <1 | 125 | 966 | -17 |
| Piney | 39 | 5.8 | 60 | 1 | 15 | <1 | 225 | 1,845 | -6 |
| Morrison | 34 | 6.3 | 271 | 150 | 42 | <1 | 102 | 1,087 | 75 |
| REM - L | 20 | 6.1 | 128 | 190 | 50 | <1 | 118 | 1,275 | 258 |
| Howe - Lower | 13 | 5.6 | 22 | 185 | 34 | <1 | 91 | 1,128 | 312 |
| Emlenton | 40 | 4.7 | 15 | 89 | 77 | 8 | 249 | 2,317 | 320 |
| Somerset | 43 | 4.4 | 0 | 162 | 50 | 3 | 193 | 1,691 | 373 |
| Howe - Upper | 13 | 6.2 | 160 | 272 | 39 | <1 | 105 | 1,315 | 375 |
| REM-Lower | 9 | 3.5 | 0 | 246 | 92 | 2 | 171 | 1,875 | 496 |
| Latrobe | 43 | 3.5 | 0 | 125 | 32 | 43 | 125 | 1,655 | 617 |
| REM - R | 18 | 5.5 | 57 | 473 | 130 | 3 | 232 | 2,495 | 867 |
| FH | 73 | 2.6 | 0 | 153 | 9 | 58 | 85 | 1,733 | 929 |

Alk Alkalinity.
FH Friendship Hill National Historical Site.
[1]$CaCO_3$ equivalent.
[2]Negative values indicate alkaline conditions.

Ten of the influents to the constructed wetlands had pH >5 and concentrations of alkalinity >25 mg•L$^{-1}$. The alkaline character of five of these discharges resulted from pretreatment of the mine water with ALD's. The high concentrations of alkalinity contained by five discharges not pretreated with ALD's arose from natural geochemical reactions within the mine spoil (Donegal and Blair) or the flooded deep mine (Cedar, Keystone, and Piney). For mine waters that contained appreciable alkalinity, the principal contaminants were Fe and Mn.

Concentrations of alkalinity for six of the influents were high enough to result in a net alkaline conditions (negative net acidity in table 13). A seventh alkaline influent, Morrison, was only slightly net acidic. For these seven influents, enough alkalinity existed in the mine waters to offset the mineral acidity associated with Fe oxidation and hydrolysis.

Nine of the influents were highly acidic. Five of the acidic influents contained alkalinity, but mineral acidity associated with dissolved Fe and Mn caused the solutions to be highly net acidic. These inadequately buffered waters were contaminated with Fe and Mn. Four of the waters contained no appreciable alkalinity (pH <4.5) and high concentrations of acidity. Mine waters with low pH were contaminated with Fe, Mn, and Al.

## EFFECTS OF TREATMENT SYSTEMS ON CONTAMINANT CONCENTRATIONS

The effects of the treatment systems on contaminant concentrations are shown in table 14. Every system decreased concentrations of Fe. At four sites where the original mine discharge contained elevated concentrations of Fe, the final discharges contained <1 mg•L$^{-1}$. Nine of the systems decreased Fe concentrations by more than 50 mg•L$^{-1}$. The largest change in Fe occurred at the Howe Bridge system where concentrations decreased by 197 mg•L$^{-1}$. From a compliance perspective, the most impressive decrease in Fe occurred at the Morrison system where 151 mg•L$^{-1}$ decreased to <1 mg•L$^{-1}$.

Fourteen of the passive systems received mine water contaminated with Mn. Eleven of these systems decreased concentrations of Mn. Changes in Mn were smaller than changes in Fe. The largest change in Mn concentration, 31 mg•L$^{-1}$, occurred at the Morrison site. Only the Donegal treatment system discharged water that consistently met effluent criteria for Mn (<2 mg•L$^{-1}$). Both the Shade and Blair wetland effluents flowed into settling ponds which discharged water in compliance with regulatory criteria. On occassions, the discharges of the Morrison and Piney treatment systems met compliance criteria.

Every wetland system decreased concentrations of acidity. The Morrison system, which received mine water that contained 75 mg•L$^{-1}$ acidity, always discharged net alkaline water. None of the constructed wetlands that received highly acidic water (net acidity >100 mg•L$^{-1}$) regularly discharged water with a net alkalinity. During low-flow periods, the Somerset, Latrobe, and FH systems discharged net alkaline water. The largest change in acidity occurred at the Somerset wetland where concentrations decreased by an average 304 mg•L$^{-1}$.

## DILUTION FACTORS

While contaminant concentrations decreased with flow through every constructed wetland, concentrations of Mg also decreased at many of the sites. Decreases in Mg

indicated that part of the improvement in water quality was because of dilution. Average dilution factors for the treatment systems are shown in table 15. For 9 of the 17 systems, average dilution factors were 0.95 to 1.00 and dilution adjustments were minor. At the remaining eight systems, mean DF values were less than 0.95 and dilution adjustments averaged more than 5%. Water quality data from the Morrison and Somerset constructed wetlands were adjusted, on average, by more than 25%.

Dilution factors varied widely between sampling days. Dilution adjustments were higher for pairs of samples collected in conjuction with precipitation events or thaws. Every system was adjusted by more than 5% on at least one occassion (see minimum dilution factors in table 15). Adjustments of more than 20% occurred on at least one occasion at 13 of the 17 study sites.

Few dilution adjustments were >1.00 (see maximum dilution factors in table 15). Of the 390 dilution factors that were calculated for the entire data set, 13 exceeded 1.05. These high dilution factors could have resulted from evaporation or freezing out of uncontaminated water within the treatment system, from temporal changes in water chemistry, or from sampling errors. Most of the high dilution factors were associated with rainstorm events, suggesting temporal changes in water quality. When dilution factors were >1.00, the calculated rates of contaminant removal were greater than would have been estimated without any dilution adjustment. Because of the limited number of sample pairs with high dilution factors, their presence did not markedly affect the average contaminant removal rates for the constructed wetland study areas.

**Table 14.—Mean water quality for sampling stations at the constructed wetlands**

| Site | Sampling station | n[1] | pH | Fe | Mn | Acidity | Mg |
|---|---|---|---|---|---|---|---|
| Donegal | Pond influent | 6 | 6.4 | 34 | 9 | NAp | 83 |
| | Wetland influent | 29 | 7.1 | 5 | 8 | NAp | 81 |
| | Effluent | 28 | 7.4 | <1 | 2 | NAp | 80 |
| Cedar | Influent | 26 | 6.3 | 92 | 2 | NAp | 54 |
| | Effluent | 27 | 6.4 | 41 | 2 | NAp | 53 |
| Keystone | Influent | 28 | 6.3 | 37 | 1 | NAp | 14 |
| | Effluent | 28 | 6.4 | 32 | 1 | NAp | 14 |
| Blair | Influent | 12 | 6.2 | 52 | 30 | NAp | 77 |
| | Effluent | 8 | 7.0 | <1 | 5 | NAp | 59 |
| Shade | LC influent | 20 | 6.0 | 2 | 23 | NAp | 128 |
| | LC effluent | 20 | 6.8 | <1 | 10 | NAp | 122 |
| Piney | Seep | 21 | 5.4 | 32 | 25 | NAp | 201 |
| | Wetland influent | 39 | 5.8 | 1 | 15 | NAp | 225 |
| | Wetland effluent | 39 | 6.1 | <1 | 11 | NAp | 225 |
| Morrison | Influent | 24 | 6.3 | 151 | 42 | 75 | 102 |
| | Ditch | 24 | 6.4 | 56 | 37 | 64 | 91 |
| | Effluent | 24 | 6.6 | <1 | 11 | -1 | 71 |
| REM-L | Left influent | 20 | 6.1 | 190 | 50 | 258 | 118 |
| | Left effluent | 20 | 3.8 | 84 | 48 | 225 | 112 |
| Emlenton | Influent | 46 | 4.7 | 89 | 77 | 320 | 249 |
| | Effluent | 40 | 3.2 | 15 | 73 | 271 | 234 |
| Somerset | Influent | 43 | 4.4 | 162 | 50 | 373 | 193 |
| | Effluent | 40 | 5.5 | 18 | 33 | 69 | 139 |
| Howe | Influents[2] | 13 | 6.0 | 265 | 37 | 373 | 101 |
| | Upper effluent | 13 | 5.6 | 185 | 34 | 312 | 91 |
| | Lower effluent | 13 | 6.2 | 68 | 33 | 112 | 91 |
| REM-Lower | Influent | 9 | 3.5 | 246 | 92 | 496 | 171 |
| | Effluent | 9 | 2.9 | 115 | 88 | 436 | 166 |
| Latrobe | Influent | 43 | 3.5 | 125 | 32 | 617 | 125 |
| | Cell 3 effluent | 43 | 3.7 | 56 | 29 | 343 | 122 |
| REM-R | Right influent | 18 | 5.5 | 473 | 130 | 867 | 232 |
| | Right effluent | 18 | 3.3 | 338 | 113 | 712 | 201 |
| FH | Influent | 73 | 2.6 | 153 | 10 | 929 | 85 |
| | Effluent | 73 | 2.9 | 137 | 10 | 674 | 85 |

FH Friendship Hill National Historical Site.
LC Limestone cell.
NAp Not applicable.
[1]Number of samples.
[2]The flow-weighted average of two discharges.

**Table 15.—Dilution factors for the constructed wetlands**

| Site | Average | sd | Minimum | Maximum |
|---|---|---|---|---|
| Donegal | 0.99 | 0.05 | 0.76 | 1.04 |
| Cedar | 0.99 | 0.03 | 0.92 | 1.05 |
| Keystone | 0.99 | 0.04 | 0.91 | 1.15 |
| Blair | 0.83 | 0.10 | 0.70 | 1.01 |
| Shade | 0.96 | 0.08 | 0.76 | 1.09 |
| Piney | 1.00 | 0.06 | 0.92 | 1.31 |
| Morrison Ditch | 0.87 | 0.18 | 0.40 | 1.05 |
| Morrison Wetland | 0.69 | 0.25 | 0.27 | 1.12 |
| REM-L | 0.95 | 0.09 | 0.70 | 1.13 |
| Howe Lower | 1.00 | 0.10 | 0.80 | 1.25 |
| Emlenton | 0.94 | 0.09 | 0.68 | 1.04 |
| Somerset | 0.73 | 0.30 | 0.30 | 1.76 |
| Howe Upper | 0.89 | 0.08 | 0.73 | 0.99 |
| REM-Lower | 0.93 | 0.09 | 0.72 | 1.01 |
| Latrobe | 0.95 | 0.08 | 0.75 | 1.14 |
| REM-R | 0.86 | 0.16 | 0.36 | 1.00 |
| FH | 1.00 | 0.12 | 0.58 | 1.34 |

FH Friendship Hill National Historical Site.

## REMOVAL OF METALS FROM ALKALINE MINE WATER

Rates of Fe and Mn removal for the study systems are shown in table 16. Significant removal of Fe occurred at every study site. Fe removal rates were directly correlated with pH and the presence of bicarbonate alkalinity (figure 9). These two water quality parameters are closely related because the buffering effect of bicarbonate alkalinity causes mine waters with >50 mg•L alkalinity to typically have a pH between 6.0 and 6.5. Within the group of sites that received alkaline mine water, there was not a significant relationship between the Fe removal rate and the concentration of alkalinity.

Removal of Fe at the alkaline mine water sites appeared to occur principly through the oxidation of ferrous iron and the precipitation of ferric hydroxide (reaction A, chapter 2). Mine water within the systems was turbid with suspended ferric hydroxides. By the cessation of the studies, each of the alkaline water sites had developed thick accumulations of iron oxyhydroxides. Laboratory experiments, discussed in chapter 2, demonstrated that abiotic ferrous iron oxidation processes are rapid in aerated alkaline mine waters. No evidence was found that microbially-mediated anaerobic Fe removal processes, which require the presence of an organic substrate, contributed significantly to Fe removal at the alkaline sites. Fe removal rates at the REM wetlands, which were constructed with fertile compost substrates, did not differ from rates at sites constructed with mineral substrates (Morrison, Howe-Upper, Keystone).

Rates of Fe removal averaged 23 $g \cdot m^{-2} \cdot d^{-1}$ at the six sites that contained alkaline, Fe-contaminated water. Four of the alkaline systems displayed similar rates despite widely varying flow conditions, water chemistry and system designs. The Keystone system, a deep plantless ditch that lowered Fe concentrations in a very large deep mine discharge by 5 mg $L^{-1}$, removed Fe at a rate of 21 $g \cdot m^{-2} \cdot d^{-1}$. The shallow-water Morrison ditch, which decreased concentrations of Fe in a low-flow seep by almost 100 $mg \cdot L^{-1}$, had an average Fe removal rate of 19 $g \cdot m^{-2} \cdot d^{-1}$. The REM-L and REM-R wetlands, which were constructed almost identically, but received water with contaminant concentrations and flow rates that varied by 200%, displayed Fe removal rates of 20 and 28 $g \cdot m^{-2} \cdot d^{-1}$.

**Table 16.—Fe and Mn removal rates at constructed wetland**

| Site | Fe removal rate | | | | Mn removal rate | | | |
|---|---|---|---|---|---|---|---|---|
| | Mean | Std dev | n | sig?[1] | Mean | Std dev | n | sig? |
| Donegal | NAp | NAp | NAp | NAp | 0.50 | 0.25 | 9 | yes |
| Cedar | 6.3 | 2.2 | 7 | yes | 0.17 | 0.41 | 7 | no |
| Keystone | 20.7 | 5.1 | 15 | yes | NAp | NAp | NAp | NAp |
| Blair | NAp | NAp | NAp | NAp | 0.43 | 0.37 | 6 | yes |
| Shade | NAp | NAp | NAp | NAp | 0.72 | 0.64 | 17 | yes |
| Piney | NAp | NAp | NAp | NAp | 1.07 | 1.34 | 33 | yes |
| Morrison Dit | 19.2 | 10.6 | 24 | yes | 0.17 | 0.41 | 24 | yes |
| Morrison Wet | NAp | NAp | NAp | NAp | 0.20 | 0.18 | 24 | yes |
| REM-L | 28.3 | 5.7 | 20 | yes | -0.05 | 0.13 | 20 | no |
| Howe-Lower | 8.1 | 1.9 | 13 | yes | 0.06 | 0.16 | 13 | no |
| Emlenton | 9.1 | 3.3 | 39 | yes | -0.09 | 0.19 | 39 | no |
| Somerset | 5.0 | 4.9 | 34 | yes | -0.01 | 0.54 | 34 | no |
| Howe-Upper | 42.7 | 8.2 | 13 | yes | -0.43 | 0.49 | 13 | no |
| REM-Lower | 12.0 | 3.4 | 9 | yes | -0.05 | 0.14 | 9 | no |
| Latrobe | 2.1 | 1.0 | 21 | yes | 0.03 | 0.09 | 21 | no |
| REM-R | 20.1 | 4.0 | 18 | yes | 0.10 | 0.33 | 18 | no |
| FH | 0.5 | 0.5 | 73 | yes | 0.00 | 0.02 | 73 | no |

NAp Not applicable.
FH Friendship Hill National Historical Site.
*n* Sample size.
sig? Significant at 0.05 level.
Std dev Standard deviation.
[1]Yes, rate is significantly greater than zero (t-test); no, rate is not significantly greater than zero (t-test).

Two alkaline mine water sites varied considerably from the other sites in their Fe removal capabilities. The Cedar Grove wetland removed Fe at a rate of 6 $g \cdot m^{-2} \cdot d^{-1}$, while the Howe Bridge Upper site removed Fe at a rate of 43 $g \cdot m^{-2} \cdot d^{-1}$. The Cedar Grove system consists of a series of square cells that may have more short-circuiting flow paths than the rectangular-shaped cells of the other systems. The Cedar Grove system also contains less aeration structures than the other systems. Mine water at the site upwells from a flooded underground mine into a pond that dicharges into a three-cell wetland. Limited topographic relief prevented the inclusion of structures that efficiently aerate the water (i.e., waterfalls, steps). The Howe Bridge Upper system, in contrast, very effectively aerates water. Drainage drops out of a 0.3-m-high pipe, flows down a cascading ditch and through a V-notch weir before it enters a large settling pond. Because the rate of abiotic ferrous iron oxidation is directly proportional to the concentration of dissolved oxygen, insufficient oxygen transfer may explain the low rate of Fe removal at the Cedar Site, while exceptionally good oxygen transfer at the Howe Bridge Upper site may explain its high rate of Fe removal.

At sites where the buffering capacity of bicarbonate alkalinity exceeded the mineral acidity associated with iron hydrolysis, precipitation of Fe did not result in decreased pH. This neutralization was evident at the Morrison, Cedar, Keystone, Blair, Piney, and Donegal sites (table 14). At the Howe Bridge and REM wetlands, the mine water was insufficiently buffered and iron hydrolysis eventually exhausted the alkalinity and pH fell to low levels. The effluents of both REM systems had pH <3.5. The Howe Bridge Upper system discharged marginally alkaline water (<25 $mg \cdot L^{-1}$ alkalinity; pH 5.6). Spot checks of the pH of surface water 20 m into the Howe Bridge Lower wetland (which receives the Upper system effluent) always indicated pH values <3.5.

Significant removal of Mn only occurred at five of the constructed wetlands (table 13). Each of these sites received alkaline mine water (figure 10). Each site also either received water with low concentrations of Fe (Piney and Shade) or developed low concentrations of Fe within the treatment system (Blair, Donegal, and Morrison).

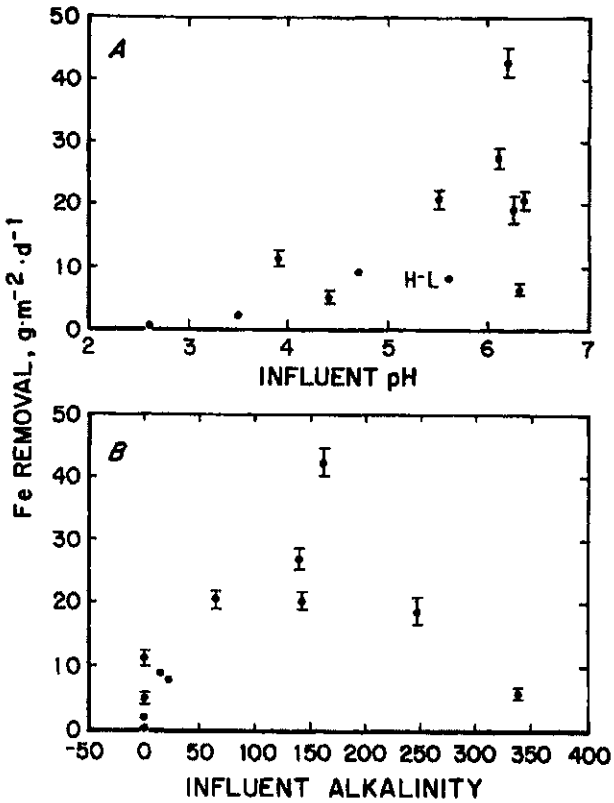


**Figure 9.—Relationship between mean Fe removal rates and *A*, mean influent pH and *B*, mean influent alkalinity concentrations. Vertical bars are one standard error above and below the mean. "H-L" is the Howe-Lower site.**

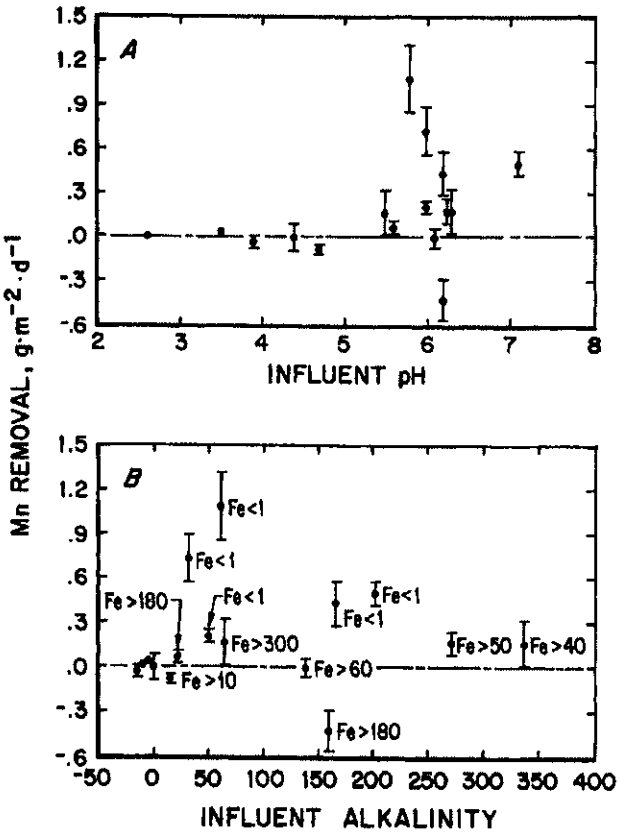


**Figure 10.—Relationship between mean Mn removal rates and *A*, mean influent pH and *B*, mean influent alkalinity concentrations. Vertical bars are one standard error above and below mean. Fe values next to the bars are effluent $Fe^{2+}$ values.**

Alkaline sites that contained high concentrations of Fe throughout the treatment system (Howe-Upper, REM-L, REM-R, and Cedar), did not remove significant amounts of Mn. The Morrison ditch, which contained water with an average 56 $mg \cdot L^{-1}$ Fe, had a significant Mn removal rate. This rate, however, was derived from an average dilution-adjusted decrease in Mn concentrations of only 1.2 $mg \cdot L^{-1}$ or 3% of the influent concentrations. Because of uncertainities with sampling, analysis, and dilution-adjustment procedures that could reasonably bias Mn data by 2-3%, the authors do not currently place much practical confidence in this value.

The five sites that markedly decreased concentrations of Mn had variable designs. The Donegal wetland has a thick organic and limestone substrate and is densely vegetated with cattails. The Blair and Morrison wetlands contain manure substrates and are densely vegetated with emergent vegetation. The Piney wetland was not constructed with an organic substrate and includes deep open water areas and shallow vegetated areas. The Shade treatment system contains limestone rocks, no organic substrate, and few emergent plants. Thus, chemical aspects of the water, not particular design parameters, appear to principally control Mn removal in constructed wetlands.

The removal of Mn from aerobic mine waters appeared to result from oxidation and hydrolysis processes. Black Mn-rich sediments were visually abundant in the Shade, Donegal, and Blair wetlands. As discussed in chapter 2, the specific mechanism by which these oxidized Mn solids form is unclear. The amorphous nature of the solids prevented identification by standard X-ray diffraction methods. However, samples of Mn-rich solids collected from the Shade and Blair wetlands were readily dissolved by alkaline ferrous iron solutions, indicating the presence of oxidized Mn compounds.

$Mn^{2+}$ can reportedly be removed from water by its sorption to charged FeOOH (ferric oxydroxide) particles (*23, 30*). If this process is occurring at the study wetlands, it is not a significant sink for Mn removal. The bottoms of the Morrison ditch, Howe-Upper, Cedar, REM-L, and REM-R wetlands were covered with precipitated FeOOH and the mine water within these wetlands commonly contained 5 to 10 $mg \cdot L^{-1}$ of suspended FeOOH (difference of the Fe content of unfiltered and filtered water samples). After mine water concentrations were adjusted to reflect dilution, no removal of Mn was indicated at four of the sites and very minor removal of Mn occurred at the fifth site (Morrison ditch).

Although the processes that remove Mn and Fe from alkaline mine water appears to be mechanistically similar (both involve oxidation and hydrolysis reactions), the observed kinetics of the metal removal processes are quite different. In the alkaline mine waters studied, Mn removal rates were 20 to 40 times slower than Fe removal.

The presence or absence of emergent plants in the wetlands did not have a significant effect on rates of either Fe or Mn removal at the alkaline mine water sites. In general, bioaccumulation of metals in plant biomass is an insignificant component of Fe and Mn removal in constructed wetlands (*49*). The ability of emergent plants to oxygenate sediments and the water column (*50*) has been proposed as an important indirect plant function in wetlands constructed to treat polluted water (*51*). Either oxygenation of the water column is not a rate limiting aspect of metal oxidation at the constructed wetlands that received alkaline mine water, or physical oxygen transfer processes are more rapid than plant-induced processes.

## REMOVAL OF METALS AND ACIDITY FROM ACID MINE DRAINAGE

Metal removal was slower at constructed wetlands that received acidic mine water than at those that received alkaline mine water. Removal of Mn did not occur at any site that received highly acidic water (figure 10). Removal of Fe occurred at every wetland that received acidic mine water, but the Fe removal rates were less than one-half those determined at alkaline wetlands (figure 9). Because abiotic ferrous iron oxidation processes are extremely slow at pH values $<5$, virtually all the Fe removal observed at the acidic sites must arise from direct or indirect microbial activity. Microbially-mediated Fe removal under acidic conditions is, however slower than abiotic Fe-removal processes under alkaline conditions.

Wetlands that treat acidic mine water must both precipitate metal contaminants and neutralize acidity. At most wetland sites, acidity neutralization was the slower process. At the Emlenton and REM wetlands, Fe removal processes were accompanied on every sampling occasion by an increase in proton acidity which markedly decreased pH (see figure 4*A*, chapter 2). Mine water pH occasionally decreased with flow through the Latrobe and Somerset wetlands. Thus, for the wetlands included in this study, the limiting aspect of acid mine water treatment was the generation of alkalinity or the removal of acidity (which were considered in this report to be equivalent, see chapter 2). The best measure of the effectiveness of the acid water treatment systems was through the calculation of acidity removal rates.

Acidity can be neutralized in wetlands through the alkalinity-producing processes of carbonate dissolution and bacterial sulfate reduction. As was discussed in chapter 2, the presence of an organic substrate where reduced Eh conditions develop promotes both alkalinity-generating processes. In highly reduced environments where dissolved oxygen and ferric iron are not present, carbonate surfaces are not passivated by FeOOH armoring. Decomposition of the organic substrate can result in elevated

partial pressures of $CO_2$ and promote carbonate dissolution. The presence of organic matter also promotes the activity of sulfate-reducing bacteria.

The rates of alkalinity generated from these two processes in the constructed wetlands were determined based on dilution-adjusted changes in the concentrations of dissolved Ca and sulfate, the stoichiometry of the alkalinity-generating reactions, and measured flow rates. The calculations are based on the assumption that Ca concentrations only increase because of carbonate dissolution and that sulfate concentrations only decrease because of bacterial sulfate reduction. One possible error in this approach is that sulfate can co-precipitate with ferric hydroxides in low-pH aerobic environments (*52*). The Fe and sulfate content of surface deposits collected from the constructed wetlands indicate that sulfate is incorporated into the precipitates collected from acidic environments at an average $Fe:SO_4$ ratio of 9.7 (table 17). If all of the Fe removed from mine water is assumed to precipitate as ferric hydroxide with a $Fe:SO_4$ ratio of 9.7:1, then changes in sulfate concentrations attributable to the co-precipitation process amount to only 5 to 30 $mg \cdot L^{-1}$ at the acid mine water sites. Dilution-adjusted changes in sulfate concentrations at the Somerset, Latrobe, Friendship Hill (FH), and Howe-Lower wetlands were commonly 200 to 500 $mg \cdot L^{-1}$.

Rates of acidity removal, sulfate removal and calcium addition for six constructed wetlands that received acidic mine water are shown in table 18. Significant removal of acidity occurred at all sites. The lowest rates of acidity removal occurred at the Emlenton wetland. This site consists of cattails growing in a manure and limestone substrate. No sulfate reduction was indicated (the rate was not significantly >0). Dissolution of the limestone was indicated, but the rate was the lowest observed.

**Table 17.—Fe and $SO_4$ content of ferric oxyhydroxide deposits; sites are arranged by pH**

| Site | pH | Composition, ppm dry weight | | |
|---|---|---|---|---|
| | | Fe | $SO_4$ | $Fe:SO_4$ |
| Emlenton ..... | 3.0 | 471,779 | 64,213 | 7.4 |
| Latrobe ..... | 3.5 | 288,939 | 27,991 | 10.3 |
| Somerset ..... | 3.5 | 461,583 | 48,263 | 9.6 |
| Cedar ..... | 6.4 | 362,300 | 8,946 | 40.5 |
| Keystone ..... | 6.6 | 398,337 | 6,888 | 57.8 |

[1] Field pH measured where substrate sample collected.

The Latrobe, Somerset, FH, Howe-Lower, and REM systems were each constructed with a spent mushroom compost and limestone substrate. Spent mushroom compost is a good substrate for microbial growth and has a high limestone content (10% dry weight). At these five wetlands, sulfate reduction and limestone dissolution both occurred at significant rates (table 18). The summed amount of alkalinity generated by sulfate reduction and limestone dissolution processes (Reactions M and N, chapter 2) correlated strongly with the measured rate of acidity removal at these four sites ($r > 0.90$ at each site). At the FH wetland, 94% of the measured acidity removal could be explained by these two processes (figure 11).

On average, sulfate reduction and limestone dissolution contributed equally to alkalinity generation at these five sites (51% versus 49%, respectively). The average sulfate removal rate calculated for the compost sites, 5.2 g $SO_4^{-2} \cdot m^{-2} \cdot d^{-1}$, is equivalent to a sulfate reduction rate of ~180 $nmol \cdot cm^{-3} \cdot d^{-1}$. This value is consistent with measurements of sulfate reduction made at the constructed wetlands using isotope methods (*41*) as well as measurements of sulfate reduction made for coastal ecosystems (*53*).

**Table 18.—Average rates of acidity removal, sulfate removal, and calcium addition at sites receiving acidic mine water**

| Site | n | Acidity removal rate | | | Sulfate removal rate | | | Calcium addition rate | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | mean | Std dev | sig?[1] | mean | Std dev | sig? | mean | Std dev | sig? |
| Emlenton ..... | 25 | 3.1 | 2.4 | yes | 1.5 | 5.7 | no | 0.8 | 1.21 | yes |
| Somerset ..... | 34 | 9.9 | 8.6 | yes | 5.1 | 5.7 | yes | 1.7 | 1.20 | yes |
| Howe Lower ..... | 13 | 15.4 | 4.1 | yes | 8.9 | 7.2 | yes | 3.9 | 1.40 | yes |
| REM-Lower ..... | 9 | 7.1 | 7.2 | yes | 2.9 | 2.4 | yes | 2.6 | 1.03 | yes |
| Latrobe ..... | 21 | 6.9 | 4.4 | yes | 5.9 | 6.4 | yes | 0.9 | 0.07 | yes |
| FH ..... | 72 | 7.0 | 3.8 | yes | 3.4 | 2.6 | yes | 1.2 | 0.80 | yes |

FH Friendship Hill National Historical Site.
n Sample size.
Std dev Standard deviation.
[1]Yes, rate is significantly greater than zero (t-test); no, rate is not significantly greater than zero (t-test).

The highest rates of acidity removal, sulfate reduction, and limestone dissolution all occurred at the Howe-Lower site. This system differs from the others by its subsurface flow system. Drainage pipes, buried in the limestone that underlies the compost, cause the mine water to flow directly through the substrate. At the Somerset, Latrobe, REM, and FH systems, water flows surficially through the wetlands. Mixing of the acidic surface water and alkaline substrate waters presumably occurs by diffusion processes at the surface-flow sites. By directly contacting contaminated water and alkaline substrate, the Howe-Lower site is extracting alkalinity from the substrate at a significantly higher rate than occurs in surface flow systems. How long the Howe-Upper system can continue to generate alkalinity at the present rates is unknown. Monitoring of the system, currently in its third year of operation, is continuing.

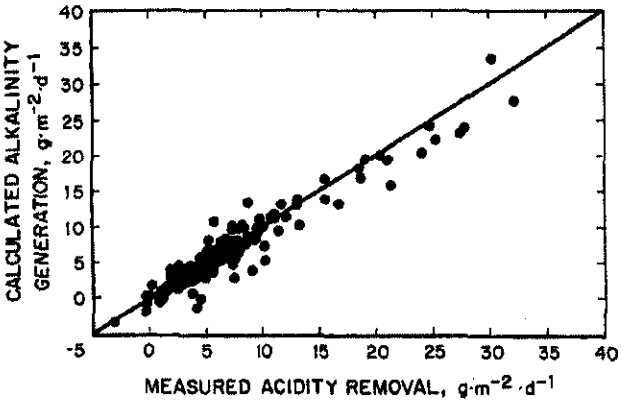


**Figure 11.—Measured rates of alkalinity generation and acidity removal at the Friendship Hill wetland. Units are $g \cdot m^{-2} \cdot d^{-1}$ $CaCO_3$ equivalent.**

## CHAPTER 4. DESIGN AND SIZING OF PASSIVE TREATMENT SYSTEMS

Three principal types of passive technologies currently exist for the treatment of coal mine drainage: aerobic wetland systems, wetlands that contain an organic substrate, and anoxic limestone drains. In aerobic wetland systems, oxidation reactions occur and metals precipitate primarily as oxides and hydroxides. Most aerobic wetlands contain cattails growing in a clay or spoil substrate. However, plantless systems have also been constructed and at least in the case of alkaline influent water, function similarly to those containing plants (chapter 3).

Wetlands that contain an organic substrate are similar to aerobic wetlands in form, but also contain a thick layer of organic substrate. This substrate promotes chemical and microbial processes that generate alkalinity and neutralize acidic components of mine drainage. The term "compost wetland" is often used in this report to describe any constructed wetland that contains an organic substrate in which biological alkalinity-generating processes occur. Typical substrates used in these wetlands include spent mushroom compost, *Sphagnum* peat, haybales, and manure.

The ALD is a buried bed of limestone that is intended to add alkalinity to the mine water (*15, 33-34*). The limestone and mine water are kept anoxic so that dissolution can occur without armoring of limestone by ferric oxyhydroxides. ALD's are only intended to generate alkalinity, and must be followed by an aerobic system in which metals are removed through oxidation and hydrolysis reactions.

Each of the three passive technologies is most appropriate for a particular type of mine water problem. Often, they are most effectively used in combination with each other. In this chapter, a model is presented that is useful in deciding whether a mine water problem is suited to passive treatment, and also, in designing effective passive treatment systems.

Two sets of sizing criteria are provided (table 19). The "abandoned mined land (AML) criteria" are intended for groups that are attempting to cost-effectively decrease contaminant concentrations. In many AML situations, the goal is to improve water quality, not consistently achieve a specific effluent concentration. The AML sizing criteria are based on measurements of contaminant removal by existing constructed wetlands (chapter 3). Most of the removal rates were measured for treatment systems (or parts of treatment systems) that did not consistently lower concentrations of contaminants to compliance with OSM effluent standards. In particular, the Fe sizing factor for alkaline mine water (20 $g \cdot m^{-2} \cdot d^{-1}$) is based on data from six sites, only one of which lowers Fe concentrations to compliance.

**Table 19.—Recommended sizing for passive treatment systems**

| | AML criteria, $g \cdot m^{-2} \cdot d^{-1}$ | | Compliance criteria, $g \cdot m^{-2} \cdot d^{-1}$ | |
|---|---|---|---|---|
| | Alkaline | Acid | Alkaline | Acid |
| Fe ..... | 20 | NAp | 10 | NAp |
| Mn ..... | 1.0 | NAp | 0.5 | NAp |
| Acidity .. | NAp | 7 | NAp | 3.5 |

NAp Not applicable.

It is possible that Fe removal rates are a function of Fe concentration; i.e., as concentrations get lower, the size of

system necessary to remove a unit of Fe contamination (e.g., 1 $g \cdot d^{-1}$) gets larger. To account for this possibility, a more conservative sizing value for systems where the effluent must meet regulatory guidelines was provided (table 1). These are referred to as "compliance criteria." The sizing value for Fe, 10 $g \cdot m^{-2} \cdot d^{-1}$, is in agreement with the findings of Stark (*17*) for a constructed compost wetland in Ohio that receives marginally acidic water. This rate is larger, by a factor of 2, than the Fe removal rate reported by Brodie (*18*) for aerobic systems in southern Appalachia that are regularly in compliance.

The Mn removal rate used for compliance, 0.5 $g \cdot m^{-2} \cdot d^{-1}$, is based on the performance of five treatment systems, three of which consistently lower Mn concentrations to compliance levels. A higher removal value, 1 $g \cdot m^{-2} \cdot d^{-1}$, is suggested for AML sites. Because the toxic effects of Mn at moderate concentrations (<50 $mg \cdot L^{-1}$) are generally not significant, except in very soft water (*54*), and the size of wetland necessary to treat Mn-contaminated water is so large, AML sites with Fe problems should receive a higher priority than those with only Mn problems.

The acidity removal rate presented for compost wetlands is influenced by seasonal variations that cannot currently be corrected with wetland design (*55*). This is not a problem for mildly acidic water, where the wetland can be sized in accordance with winter performance, nor should it be a major problem in warmer climates. In northern Appalachia, however, no compost wetland that consistently transforms highly acidic water (>300 $mg \cdot L^{-1}$ acidity) into alkaline water is known. One of the study sites, which receives water with an average of 600 $mg \cdot L^{-1}$ acidity and does not need to meet a Mn standard, has discharged water that only required chemical treatment during winter months. While considerable cost savings are realized at the site because of the compost wetland, the passive system must be supported by conventional treatment during a portion of the year.

Because long-term metal-removal capabilities of passive treatment systems are currently uncertain, current Federal regulations require that the capability for chemical treatment exist at all bonded sites. This provision is usually met by placing a "polishing pond" after the passive treatment system. The design and sizing model does not currently account for such a polishing pond.

All passive treatment systems constructed at active sites need not be sized according to the compliance criteria provided in table 19. Sizing becomes a question of balancing available space and system construction costs versus influent water quality and chemical treatment costs. Mine water can be treated passively before the water enters a chemical treatment system to reduce water treatment costs or as a potential part-time alternative to full-time chemical treatment. In those cases where both passive and chemical treatment methodologies are utilized, many operators find that they recoup the cost of the passive treatment system in less than a year by using simpler, less expensive chemical treatment systems and/or by decreasing the amount of chemicals used.

A flow chart that summarizes the design and sizing model is shown in figure 12. The model uses mine drainage chemistry to determine system design, and contaminant loadings combined with the expected removal rates in table 19 to define system size. The following text details the use of this flow chart and also discusses aspects of the model that are currently under investigation.

## CHARACTERIZATION OF MINE DRAINAGE DISCHARGES

To design and construct an effluent treatment system, the mine water must be characterized. An accurate measurement of the flow rate of the mine discharge or seep is required. Water samples should be collected at the discharge or seepage point for chemical analysis. Initial water analyses should include pH, alkalinity, Fe, Mn, and hot acidity ($H_2O_2$ method) measurements. If an anoxic limestone drain is being considered, the acidified sample should be analyzed for $Fe^{3+}$ and Al, and a field measurement of dissolved oxygen should be made.

Both the flow rate and chemical composition of a discharge can vary seasonally and in response to storm

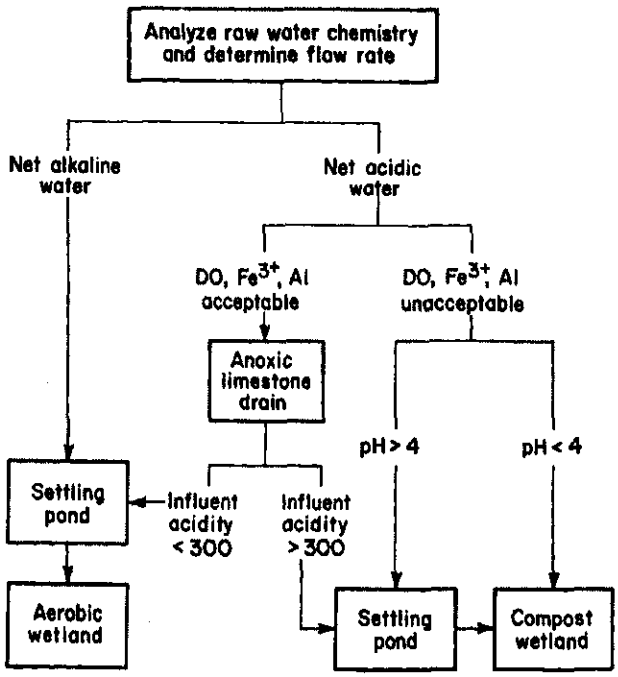


**Figure 12.—Flow chart showing chemical determinations necessary for the design of passive treatment systems.**

events. If the passive treatment system is expected to be operative during all weather conditions, then the discharge flow rates and water quality should be measured in different seasons and under representative weather conditions.

## CALCULATIONS OF CONTAMINANT LOADINGS

The size of the passive treatment system depends on the loading rate of contaminants. Calculate contaminant (Fe, Mn, acidity) loads by multiplying contaminant concentrations by the flow rate. If the concentrations are milligrams per liter and flow rates are liters per minute, the calculation is

$$[\text{Fe,Mn,Acidity}]\ g \cdot d^{-1} = \text{flow} \times [\text{Fe,Mn,Acidity}] \times 1.44 \quad (11)$$

If the concentrations are milligrams per liter and flow rates are gallons per minute, the calculation is

$$[\text{Fe,Mn,Acidity}]\ g \cdot d^{-1} = \text{flow} \times [\text{Fe,Mn,Acidity}] \times 5.45 \quad (12)$$

Calculate loadings for average data and for those days when flows and contaminant concentrations are highest.

## CLASSIFICATION OF DISCHARGES

The design of the passive treatment system depends largely on whether the mine water is acidic or alkaline. One can classify the water by comparing concentrations of acidity and alkalinity.

Net Alkaline Water: alkalinity > acidity
Net Acidic Water: acidity > alkalinity

The successful treatment of mine waters with net acidities of 0 to 100 $mg \cdot L^{-1}$ using aerobic wetlands has been documented in this report and elsewhere (*14, 18*). In these systems, alkalinity either enters the treatment system with diluting water or alkalinity is generated within the system by undetermined processes. Currently, there is no method to predict which of these marginally acidic waters can be treated successfully with an aerobic system only. For waters with a net acidity >0, the incorporation of alkalinity-generating features (either an ALD or a compost wetland) is appropriate.

## PASSIVE TREATMENT OF NET ALKALINE WATER

Net alkaline water contains enough alkalinity to buffer the acidity produced by metal hydrolysis reactions. The metal contaminants (Fe and Mn) will precipitate given enough time. The generation of additional alkalinity is unnecessary so incorporation of limestone or an organic substrate into the passive treatment system is also unnecessary. The goal of the treatment system is to aerate the water and promote metal oxidation processes. In many existing treatment systems where the water is net alkaline, the removal of Fe appears to be limited by dissolved $O_2$ concentrations. Standard features that can aerate the drainage, such as waterfalls or steps, should be followed by quiescent areas. Aeration only provides enough dissolved $O_2$ to oxidize about 50 $mg \cdot L^{-1}$ $Fe^{2+}$. Mine drainage with higher concentrations of $Fe^{2+}$ will require a series of aeration structures and wetland basins. The wetland cells allow time for Fe oxidation and hydrolysis to occur and space in which the Fe floc can settle out of suspension. The entire system can be sized based on the Fe removal rates shown in table 19. For example, a system being designed to improve water quality on an AML site should be sized by the following calculation:

$$\text{Minimum wetland size } (m^2) = \text{Fe loading } (g \cdot d^{-1}) / 20\ (g \cdot m^{-2} \cdot d^{-1}). \quad (13)$$

If Mn removal is desired, size the system based on the Mn removal rates in table 19. Removal of Fe and Mn occurs sequentially in passive systems. If both Fe and Mn removal are necessary, add the two wetland sizes together.

A typical aerobic wetland is constructed by planting cattail rhizomes in soil or alkaline spoil obtained on-site. Some systems have been planted by simply spreading cattail seeds, with good plant growth attained after 2 years. The depth of the water in a typical aerobic system is 10 to 50 cm. Ideally, a cell should not be of uniform depth, but should include shallow and deep marsh areas and a few deep (1 to 2 m) spots. Most readily available aquatic vegetation cannot tolerate water depths greater than 50 cm.

Often, several wetland cells are connected by flow through a V-notch weir, lined railroad tie steps, or down a ditch. Spillways should be designed to pass the maximum probable flow. Spillways should consist of wide cuts in the dike with side slopes no steeper than 2H:1V, lined with nonbiodegradable erosion control fabric, and coarse rip rap if high flows are expected (*18*). Proper spillway design can preclude future maintenance costs because of erosion and/or failed dikes. If pipes are used, small diameter (<30 cm) pipes should be avoided because they can plug with litter and FeOOH deposits. Pipes should be made of polyvinyl chloride (PVC). More details on the construction of aerobic wetland systems can be found in a text by Hammer (*56*).

The geometry of the wetland site as well as flow control and water treatment considerations may dictate the

use of multiple wetland 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 be designed to avoid erosion and/or the mobilization of precipitates.

It is recommended that the freeboard of aerobic wetlands constructed for the removal of Fe be at least 1 m. Observations of sludge accumulation in existing wetlands suggest that a 1-m freeboard should be adequate to contain 20 to 25 years of FeOOH accumulation.

The floor of the wetland cell may be sloped up to about 3% grade. If a level cell floor is used, then the water level and flow are controlled by the downstream dam spillway and/or adjustable riser pipes.

As discussed in chapter 3, some of the aerobic systems that have been constructed to treat alkaline mine water have little emergent plant growth. Metal removal rates in these plantless, aerobic systems appears to be similar to what is observed in aerobic systems containing plants. However, plants may provide values that are not reflected in measurements of contaminant removal rates. For example, plants can facilitate the filtration of particulates, prevent flow channelization and provide wildlife benefits that are valued by regulatory and environmental groups.

## PASSIVE TREATMENT OF NET ACID WATER

Treatment of acidic mine water requires the generation of enough alkalinity to neutralize the excess acidity. Currently, there are two passive methods for generating alkalinity: construction of a compost wetland or pretreatment of acidic drainage by use of an ALD. In some cases, the combination of an ALD and a compost wetland may be necessary to treat the mine water.

ALD's produce alkalinity at a lower cost than do compost wetlands. However, not all water is suitable for pretreatment with ALD's. The primary chemical factors believed to limit the utility of ALD's are the presence of ferric iron ($Fe^{3+}$), aluminum (Al) and dissolved oxygen (DO). When acidic water containing any $Fe^{3+}$ or Al contacts limestone, metal hydroxide particulates (FeOOH or $Al(OH)_3$) will form. No oxygen is necessary. Ferric hydroxide can armor the limestone, limiting its further dissolution. Whether aluminum hydroxides armor limestone has not been determined. The buildup of both precipitates within the ALD can eventually decrease the drain permeability and cause plugging. The presence of dissolved oxygen in mine water will promote the oxidation of ferrous iron to ferric iron within the ALD, and thus potentially cause armoring and plugging. While the short-term performance of ALD's that receive water containing elevated levels of $Fe^{3+}$, Al, or DO can be spectacular (total removal of the metals within the ALD) (*34*), the long-term performance of these ALD's is questionable.

Mine water that contains very low concentrations of DO, $Fe^{3+}$ and Al (all $<1$ mg•L$^{-1}$) is ideally suited for pretreatment with an ALD. As concentrations of these parameters rise above 1 mg•L$^{-1}$, the risk that the ALD will fail prematurely also increases. Recently, two ALD's constructed to treat mine water that contained 20 mg•L$^{-1}$ Al became plugged after 6-8 months of operation.

In some cases, the suitability of mine water for pretreatment with an ALD can be evaluated based on the type of discharge and measurements of field pH. Mine waters that seep from spoils and flooded underground mines and have a field pH $>5$ characteristically have concentrations of DO, $Fe^{3+}$, and Al that are all $<1$ mg•L$^{-1}$. Such sites are generally good candidates for pretreatment with an ALD. Mine waters that discharge from open drift mines or have pH $<5$ must be analyzed for $Fe^{3+}$ and Al. Mine waters with pH $<5$ can contain dissolved Al; mine waters with pH $<3.5$ can contain $Fe^{3+}$. In northern Appalachia, most mine drainages that have pH $<3$ contain high concentrations of $Fe^{3+}$ and Al.

## PRETREATMENT OF ACIDIC WATER WITH ALD

In an ALD, alkalinity is produced when the acidic water contacts the limestone in an anoxic, closed environment. It is important to use limestone with a high $CaCO_3$ content because of its higher reactivity compared with a limestone with a high $MgCO_3$ or $CaMg(CO_3)_2$ content. The limestones used in most successful ALD's have 80% to 95% $CaCO_3$ content. Most effective systems have used number 3 or 4 (baseball-size) limestone. Some systems constructed with limestone fines and small gravel have failed, apparently because of plugging problems. The ALD must be sealed so that inputs of atmospheric oxygen are minimized and the accumulation of $CO_2$ within the ALD is maximized. This is usually accomplished by burying the ALD under several feet of clay. Plastic is commonly placed between the limestone and clay as an additional gas barrier. In some cases, the ALD has been completely wrapped in plastic before burial (*35*). The ALD should be designed so that the limestone is inundated with water at all times. Clay dikes within the ALD or riser pipes at the outflow of the ALD will help ensure inundation.

The dimensions of existing ALD's vary considerably. Most older ALD's were constructed as long narrow drains, approximately 0.6 to 1.0 m wide. A longitudinal section and cross section of such an ALD is shown in figure 13. The ALD shown was constructed in October 1990, and is 1 m wide, 46 m long and contains about 1 m depth of number 4 limestone. The limestone was covered with two layers of 5 mil plastic, which in turn was covered with

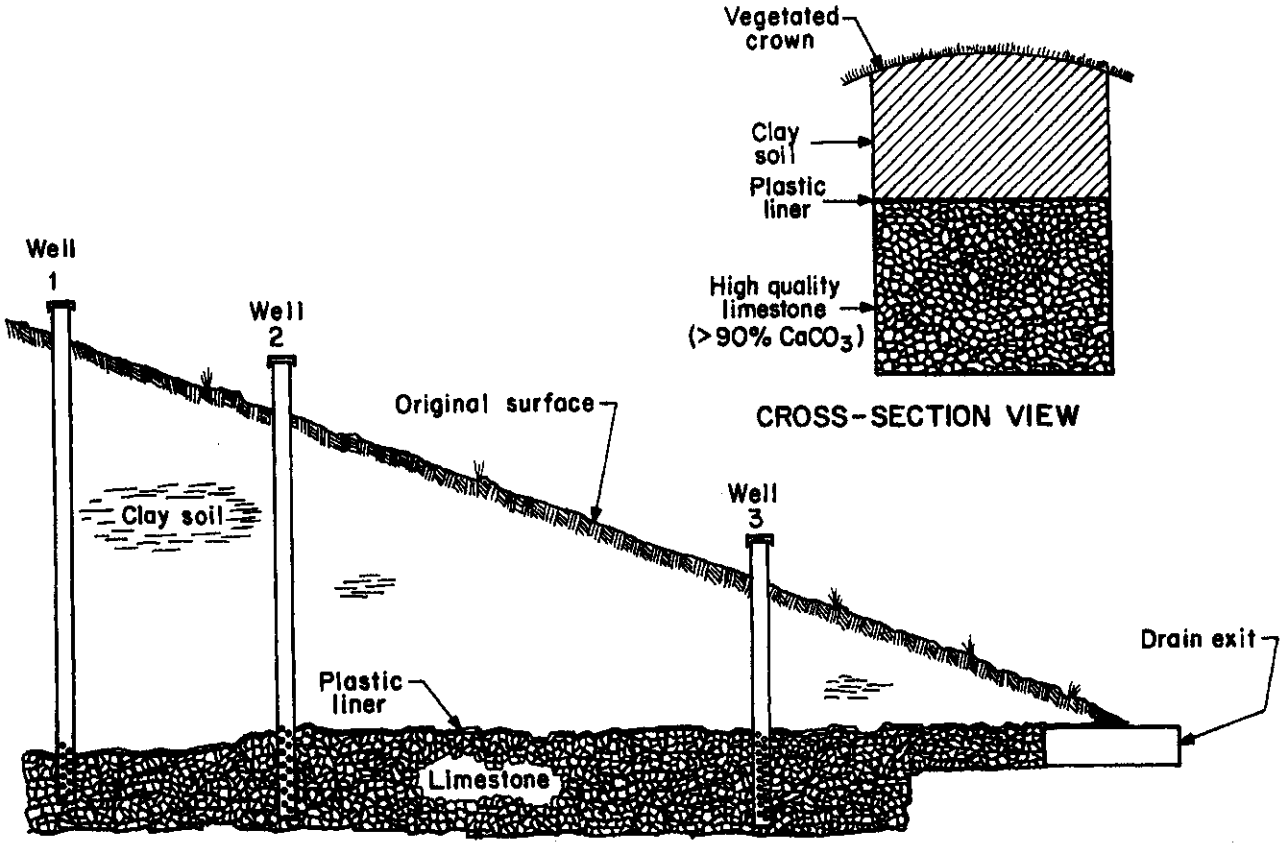


**Figure 13.—Longitudinal-section and cross-section of the Morrison ALD. Wells are for sampling purposes and have no importance to drain's functioning.**

0.3 to 3 m of on-site clay to restore the original surface topography (*34, 36*).

At sites where linear ALD's are not possible, anoxic limestone beds have been constructed that are 10 to 20 m wide. These bed systems have produced alkalinity concentrations similar to those produced by the more conventional drain systems.

The mass of limestone required to neutralize a certain discharge for a specified period can be readily calculated from the mine water flow rate and assumptions about the ALD's alkalinity-generating performance. Recent USBM research indicates that approximately 14 h of contact time between mine water and limestone in an ALD is necessary to achieve a maximum concentration of alkalinity (*57*). To achieve 14 h of contact time within an ALD, ~3,000 kg of limestone rock is required for each liter per minute of mine water flow. An ALD that produces 275 $mg \cdot L^{-1}$ of alkalinity (the maximum sustained concentration thus far observed for an ALD), dissolves ~1,600 kg of limestone a decade per each liter per minute of mine water flow. To construct an ALD that contains sufficient limestone to insure a 14-h retention time throughout a 30-yr period, the limestone bed should contain ~7,800 kg of limestone for each liter per minute of flow. This is equivalent to 30 tons of limestone for each gallon per minute of flow. The calculation assumes that the ALD is constructed with 90% $CaCO_3$ limestone rock that has a porosity of 50%. The calculation also assumes that the original mine water does not contain ferric iron or aluminum. The presence of these ions would result in potential problems with armoring and plugging, as previously discussed.

Because the oldest ALD's are only 3 to 4 yr old, it is difficult to assess how realistic these theoretical calculations are. Questions about the ability of ALD's to maintain unchannelized flow for a prolonged period, whether 100% of the $CaCO_3$ content of the limestone can be expected to dissolve, whether the ALD's will collapse after significant dissolution of the limestone, and whether inputs of DO that are not generally detectable with standard field equipment (0 to 1 $mg \cdot L^{-1}$) might eventually result in armoring of the limestone with ferric hydroxides, have not yet been addressed.

The anoxic limestone drain is <u>one</u> component of a passive treatment system. When the ALD operates ideally, its only effect on mine water chemistry is to raise pH to

circumneutral levels and increase concentrations of calcium and alkalinity. Dissolved $Fe^{2+}$ and Mn should be unaffected by flow through the ALD. The ALD must be followed by a settling basin or wetland system in which metal oxidation, hydrolysis and precipitation can occur. The type of post-ALD treatment system depends on the acidity of the mine water and the amount of alkalinity generated by the ALD. If the ALD generates enough alkalinity to transform the acid mine drainage to a net alkaline condition, then the ALD effluent can then be treated with a settling basin and an aerobic wetland. If possible, the water should be aerated as soon as it exits the ALD and directed into a settling pond. An aerobic wetland should follow the settling pond. The total post-ALD system should be sized according to the criteria provided earlier for net alkaline mine water. At this time, it appears that mine waters with acidities $<150\ mg \cdot L^{-1}$ are readily treated with an ALD and aerobic wetland system.

If the mine water is contaminated with only $Fe^{2+}$ and Mn, and the acidity exceeds $300\ mg \cdot L^{-1}$, it is unlikely that an ALD constructed using current practices will dis-charge net alkaline water. When this partially neutralized water is treated aerobically, the Fe will precipitate rapidly, but the absence of sufficient bufferring can result in a discharge with low pH. Building a second ALD, to recharge the mine water with additional alkalinity after it flows out of the aerobic system, is currently not feasible because of the high DO content of water flowing out of aerobic systems. If the treatment goal is to neutralize all of the acidity passively, then a compost wetland should be built so that additional alkalinity can be generated. Such a treatment system thus contains all three passive technologies. The mine water flows through an ALD, into a settling pond and an aerobic system, and then into a compost wetland.

If the mine water is contaminated with ferric iron ($Fe^{3+}$) or Al, higher concentrations of acidity can be treated with an ALD than when the water is contaminated with only $Fe^{2+}$ and Mn. This enhanced performance results from a decrease in mineral acidity because of the hydrolysis and precipitation of $Fe^{3+}$ and Al within the ALD. These metal-removing reactions decrease the mineral acidity of the water. ALD's constructed to treat mine water contaminated with $Fe^{3+}$ and Al and having acidities greater than $1{,}000\ mg \cdot L^{-1}$ have discharged net alkaline water. The long-term prognosis for these metal-retaining systems has been questioned (*34*). However, even if calculations of system longevity (as described above) are inaccurate for waters contaminated with $Fe^{3+}$ and Al, their treatment with an ALD may turn out to be cost-effective when compared with chemical alternatives (*35*).

When a mine water is contaminated with $Fe^{2+}$ and Mn and has an acidity betweem 150 and $300\ mg \cdot L^{-1}$, the ability of an ALD to discharge net alkaline water will depend on the concentration of alkalinity produced by the limestone system. The amount of alkalinity generated by a properly constructed and sized ALD is dependent on chemical characteristics of the acid mine water. An experimental method has been developed that results in an accurate assessment of the amount of alkalinity that will be generated when a particular mine water contacts a particular limestone (*58*). The method involves the anoxic incubation of the mine water in a container filled with limestone gravel. In experiments at two sites, the concentration of alkalinity that developed in these containers after 48 h correlated well with the concentrations of alkalinity measured in the ALD effluents at both sites.

## TREATING MINE WATER WITH COMPOST WETLAND

When mine water contains DO, $Fe^{3+}$ or Al, or contains concentrations of acidity $>300\ mg \cdot L^{-1}$, construction of a compost wetland is recommended. Compost wetlands generate alkalinity through a combination of bacterial activity and limestone dissolution. The desired sulfate-reducing bacteria require a rich organic substrate in which anoxic conditions will develop. Limestone dissolution also occurs readily within this anoxic environment. A substance commonly used in these wetlands is spent mushroom compost, a substrate that is readily available in western Pennsylvania. However, any well-composted equivalent should serve as a good bacterial substrate. Spent mushroom compost has a high $CaCO_3$ content (about 10% dry weight), but mixing in more limestone may increase the alkalinity generated by $CaCO_3$ dissolution. Compost substrates that do not have a high $CaCO_3$ content should be supplemented with limestone. The compost depth used in most wetlands is 30 to 45 cm. Typically, a metric ton of compost will cover about 3.5 $m^2$ to a depth of 45 cm thick. This is equivalent to one ton per 3.5 $yd^2$. Cattails or other emergent vegetation are planted in the substrate to stabilize it and to provide additional 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 wetland cell.

Compost wetlands in which water flows on the surface of the compost remove acidity (e.g., generate alkalinity) at rates of approximately 2-12 $g \cdot m^{-2} \cdot d^{-1}$. This range in performance is largely a result of seasonal variation: lower rates of acidity removal occur in winter than in summer (*55*). Research in progress indicates that supplementing the compost with limestone and incorporating system designs that cause most of the water to flow through the

compost (as opposed to on the surface) may result in higher rates of limestone dissolution and better winter performance.

Compost wetlands should be sized based on the removal rates in table 19. For an AML site, the calculation is

$$\text{Minimum Wetland Size } (m^2) = \text{Acidity Loading } (g \cdot d^{-1}/7). \quad (14)$$

In many wetland systems, the compost cells are preceded with a single aerobic pond in which Fe oxidation and precipitation occur. This feature is useful where the influent to the wetland is of circumneutral pH (either naturally or because of pretreatment with an ALD), and rapid, significant removal of Fe is expected as soon as the mine water is aerated. Aerobic ponds are not useful when the water entering the wetland system has a pH <4. At such low pH, Fe oxidation and precipitation reactions are quite slow and significant removal of Fe in the aerobic pond would not be expected.

### OPERATION AND MAINTENANCE

Operational problems with passive treatment systems can be attributed to inadequate design, unrealistic expectations, pests, inadequate construction methods, or natural problems. If properly designed and constructed, a passive 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 can plague wetlands with operational problems. Muskrats will burrow into dikes, causing leakage and potentially catastrophic failure problems, and will uproot significant amounts of cattails and other aquatic vegetation. Muskrats can be discouraged by lining dike inslopes with chainlink fence or riprap to prevent burrowing (*13*). Beavers cause water level disruptions because of damming and also seriously damage vegetation. They are very difficult to control once established. Small diameter pipes traversing wide spillways ("three-log structure") and trapping have had limited success in beaver control. Large pipes with 90° elbows on the upstream end have been used as discharge structures in beaver-prone areas (*18*). Otherwise, shallow ponds with dikes with shallow slopes toward wide, riprapped spillways may be the best design for a beaver-infested system.

Mosquitos can be a problem where mine water is alkaline. In southern Appalachia, mosquitofish (*Gambusia affinis*) have been introduced into alkaline-water wetlands. Other insects, such as the armyworm, have devastated monocultural wetlands with their appetite for cattails (*59*). The use of a variety of plants in a system will minimize such problems.

## CHAPTER 5. SUMMARY AND CONCLUSIONS

The treatment of contaminated coal mine drainage requires the precipitation of metal contaminants and the neutralization of acidity. In conventional treatment systems, distinctions between these two treatment objectives are blurred by additions of highly basic chemicals that simultaneously cause the rapid precipitation of metal contaminants and the neutralization of acidity. Passive treatment differs from conventional treatment by its distinction between these two treatment objectives. It is possible to passively precipitate Fe contaminants from mine water, but have little effect on the mine water acidity. Alternatively, it is possible to passively add neutralizing capacity to acidic mine water without decreasing metal concentrations.

Waters that contain high concentrations of bicarbonate alkalinity are most amenable to treatment with constructed wetlands. Bicarbonate acts as a buffer that neutralizes the acidity produced when Fe and Mn precipitate and maintains a pH between 5.5 and 6.5. At this circumneutral pH, Fe and Mn precipitation processes are more rapid than under acidic pH conditions. Given the ability of bicarbonate alkalinity to positively impact both the metal precipitation and neutralization aspects of mine water treatment, it is not surprising that the most noteworthy applications of passive treatment have been at sites where the mine water was net alkaline. The most successful wetlands constructed in western Pennsylvania in the early 1980's treated mine waters that contained alkalinity. All of the early successes of the TVA were, likewise, with waters that were alkaline (*13*). Similarly, the Simco wetland in Ohio, which has discharged compliance water for several years (*17*), receives water containing ~160 $mg \cdot L^{-1}$ alkalinity. In this study, the two treatment systems that met all effluent discharge requirements (Donegal and Blair) both received alkaline, metal-contaminated water.

When mine water is acidic, enough alkalinity must be generated by the passive treatment system to neutralize the acidity. The most common method used to passively generate alkalinity is the construction of a wetland that

contains an organic substrate in which alkalinity-generating microbial processes occur. If the substrate contains limestone, as spent mushroom compost does, then alkalinity will be generated by both calcite dissolution and bacterial sulfate reduction reactions. These alkalinity generating processes are slow relative to processes that remove Fe. Thus, the performance of the constructed wetlands that receive acidic water is usually limited by the rate at which alkalinity is generated within the substrate. While wetlands can significantly improve water quality, and have proven to be effective at moderately acidic sites, no wetland systems that consistently and completely transform highly acidic water to compliance quality are known. Inconsistent or partial treatment indicates undersizing. The authors believe this is because of a lack of awareness of how much larger wetlands constructed to treat acidic water must be than ones constructed to treat alkaline water. The Fe and acidity removal rates measured in this study indicate that the treatment of 5,000 $g \cdot d^{-1}$ of Fe in alkaline water requires ~250 $m^2$ of aerobic wetland. The treatment of the same Fe load in acidic water (where treatment requires both precipitation of the Fe and neutralization of the associated acidity) requires ~1,300 $m^2$ of compost wetland. Thus wetlands constructed to treat acidic water need to be six times larger than ones constructed to treat similarly contaminated alkaline water.

The recent development of limestone pretreatment systems, e.g., the anoxic limestone drain, is a significant advancement in passive treatment technology. When successful, ALD's can lower acidities or actually transform acidic water into alkaline water, and markedly decrease the sizing demands of the wetlands constructed to precipitate the metal contaminants. Because limestone is inexpensive, the cost of an ALD-aerobic wetland passive treatment system is typically much less than the compost wetland alternative. Thus, when the influent water is appropriate, ALD's should be the preferred method for generating alkalinity in passive treatment systems.

Anoxic limestone drains have also been used to increase the performance of existing constructed wetlands. At many poorly performing wetlands that receive acidic water, the wetland was built too small to treat an acidic, metal-contaminated influent, but is large enough for an alkaline, metal-contaminated influent. One of the study sites, the Morrison wetland, was undersized for the highly acidic water that it received. As a result, the wetland effluent required supplemental treatment with chemicals. Since construction of an ALD, and its addition of 275 $mg \cdot L^{-1}$ of bicarbonate alkalinity to the water, the discharge of the wetland has been alkaline, low in dissolved metals, and does not require any supplemental chemical treatment. Similar enhancements in wetland performance through the addition of ALD's have been reported elsewhere in Appalachia (*15, 18*).

## KINETICS OF CONTAMINANT REMOVAL PROCESSES

This report presents an intensive analysis of contaminant removal kinetics in passive treatment systems. The rates presented are generally in agreement with those reported by other investigators. For example, the average Mn-removal rate measured in this study for alkaline, Fe-free waters, 0.5 $g \cdot m^{-2} \cdot d^{-1}$, is consistent with rates reported by the TVA for aerobic wetlands in southern Appalachia (*18*) and by the Pennsylvania Department of Environmental Resources (DER) for constructed wetlands in Pennsylvania (*60*). The average Fe-removal rate reported in this study for alkaline waters, 20 $g \cdot m^{-2} \cdot d^{-1}$, is only slightly greater than has been reported in other studies. The rates of Fe removal for aerobic wetlands in southern Appalachia ranged from 6 to 20 $g \cdot m^{-2} \cdot d^{-1}$ (*18*). Some of the lower rates reported by TVA investigators, however, are from wetland systems that discharge water with <1 $mg \cdot L^{-1}$ Fe and thus are loading limited with respect to Fe. Such sites were intentionally avoided in this study. Stark (*17*), in their studies of a constructed wetland in Ohio, reported Fe removal rates over a range of loading conditions. When the wetland system discharged >15 $mg \cdot L^{-1}$ Fe, and thus was overloaded with Fe, the removal rate averaged 21 $g \cdot m^{-2} \cdot d^{-1}$. When the wetland effluent contained <15 $mg \cdot L^{-1}$ Fe, the removal rate averaged only 11 $g \cdot m^{-2} \cdot d^{-1}$.

## LONG-TERM PERFORMANCE

Passive treatment systems cannot be expected to perform indefinitely. In the long term, wetland systems will fill up with metal precipitates or the conditions that facilitate contaminant removal may be compromised. None of the treatment systems considered in this study demonstrated any downward trends in contaminant removal performance. Therefore, estimates of the long-term performance of passive systems must be made by extrapolating available data. Like the design and sizing of passive treatment systems, estimates of long-term performance vary with the chemistry of the mine water. Systems receiving alkaline water precipitate Fe and Mn contaminants by oxidative processes. The rapid removal of Fe that occurs in alkaline treatment systems means that such systems will inevitably fill up. Stark (*61*) reports that the Fe sludge in a constructed wetland in Ohio is increasing by 3 to 4 cm per year. Similar measurements at Pennsylvania wetlands indicate an increase in sludge depth of 2 to 3 cm per year (*62*). These measurements suggest that dikes that provide 1 m of freeboard should provide sufficient volume for 25 to 50 years of performance.

At some surface mines, water quality tends to improve within a decade after regrading and reclamation are

completed (*63-64*). At these surface minesites, 25 to 50 years of passive treatment may be adequate to mitigate the contaminant problem. At surface mine sites where contaminant production is continual, or at systems constructed to treat drainage from underground mines or coal refuse disposal areas, the system can either be built with greater freeboard or rebuilt when it eventually fills up. Site conditions will determine whether it is more economical to simply bury the wetland system in place and construct a new one, or to excavate and haul away the accumulated solids for proper disposal. Disposal of these excavated sludges is not difficult or unduly expensive because the material is not considered a hazardous waste.

Wetlands that receive acidic water, and function through the alkalinity-generating processes associated with an organic substrate, may decline in performance as the components of the organic substrate that generate alkalinity are exhausted. The compost wetlands described in this report neutralize acidity through the dissolution of limestone and the bacterial reduction of sulfate. Limestone dissolution is limited by the amount of limestone present in the substrate. The limestone content of spent mushroom compost is ~30 $kg \cdot m^{-3}$ (*65*). If a wetland containing a 40 cm depth of compost generates $CaCO_3$-derived alkalinity at a mean rate of 3 $g \cdot m^{-2} \cdot d^{-1}$ (the average rate measured in this study), then the limestone content of the compost will be exhausted in 11 years. The same volume of compost contains ~40 kg of organic carbon. If bacterial sulfate reduction mineralizes 100% of this carbon to bicarbonate at a rate of 5 $g \cdot m^{-2} \cdot d^{-1}$, then the carbon will be exhausted in 91 years. This estimate is increased by the carbon input of the net primary production of the wetland system, but decreased by the fact that some of the carbon is mineralized by reactions other than sulfate reduction. Studies of a salt marsh on Cape Cod, MA, indicated that 75% of the carbon was eventually mineralized by sulfate reduction processes (*66*). Another significant factor that decreases the available carbon is that a portion of the carbon pool is recalcitrant.

A realistic scenario for the long-term performance of a compost wetland is that sulfate reduction is linked, in a dependent manner, to limestone dissolution. Sulfate-reducing bacteria are inactive at pH less than 5 (*37*). Their activity in a wetland receiving lower pH water may depend, in part, on the presence of pH-buffering supplied by limestone dissolution. Thus, limestone dissolution may create alkaline zones in which sulfate reduction can proceed and produce further alkalinity. If this scenario is accurate, then the long-term performance of a compost wetland may be limited by the amount of limestone in the substrate, or according to the above calculations, about 11 years of performance. Under these conditions it would be advisable to increase the chemical buffering capability of the wetland substrate by adding additional limestone during wetland construction. In fact, this procedure is commonly practiced at many constructed compost wetland sites.

The performance of anoxic limestone drains has many aspects that make long-term expectations uncertain. Anoxic limestone drains function through the dissolution, and thus removal, of limestone. Eventually, this chemical reaction will exhaust the limestone. Long-term scenarios about ALD performance fail to consider the hydrologic implications of the gradual structural failure of the systems. In large ALD's, most of the limestone dissolution occurs in the upgradient portion of the limestone bed. It is unknown whether this preferential dissolution will produce partial failure of the integrity of the system or whether the permeability will be adversely affected. Another aspect that affects long-term ALD performance is the fact that ALD's retain ferric iron and aluminum (*34-35*). This retention has raised concerns about the armoring of limestone or the plugging of flow paths long before the limestone is exhausted by dissolution reactions (*34*). No methods are currently available to predict exactly how the retention of these metals affects the performance of ALD's.

## CONTINUALLY EVOLVING PASSIVE TECHNOLOGIES

This document reports the current state of passive mine water treatment technologies. The design and sizing recommendations presented herein represent current methodologies that will subsequently be replaced with more efficient techniques. For example, important experiments are underway in Pennsylvania, Virginia, and West Virginia testing "hybrid" ALD-compost wetland systems. In these experimental systems, organic substrates are used to reduce ferric iron to ferrous iron and strip dissolved oxygen from the water so that the mine water is suitable for flow through an anoxic limestone drain. If these systems prove successful, it may be possible to treat highly acidic water by cycling it between anoxic alkalinity-generating environments and aerobic, metal-removal environments. Experimental systems using this design have recently been constructed in western Pennsylvania (*67*).

While the specific tools of passive treatment are likely to evolve in the coming years, the fundamental mechanisms of passive treatment that have been identified in this report will probably not change markedly. Research has shown that the treatment of contaminated coal mine drainage by constructed wetlands can be explained by well-known chemical and biological processes. Passive treatment, like active treatment with chemicals, requires that the metal contaminants be precipitated and that the acidity associated with these ions be neutralized. By recognizing that these treatment goals need not be accomplished

simultaneously, one can focus on optimization of the individual objectives. As a result, the performance and cost effectiveness of passive treatment systems is rapidly improving. Today, most mine operators who install properly designed passive treatment systems rapidly recoup the cost of their investment through decreased water treatment costs. There is no reason to doubt that this technology will continue to improve and that, over time, passive treatment will be used in applications that are not possible today.

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