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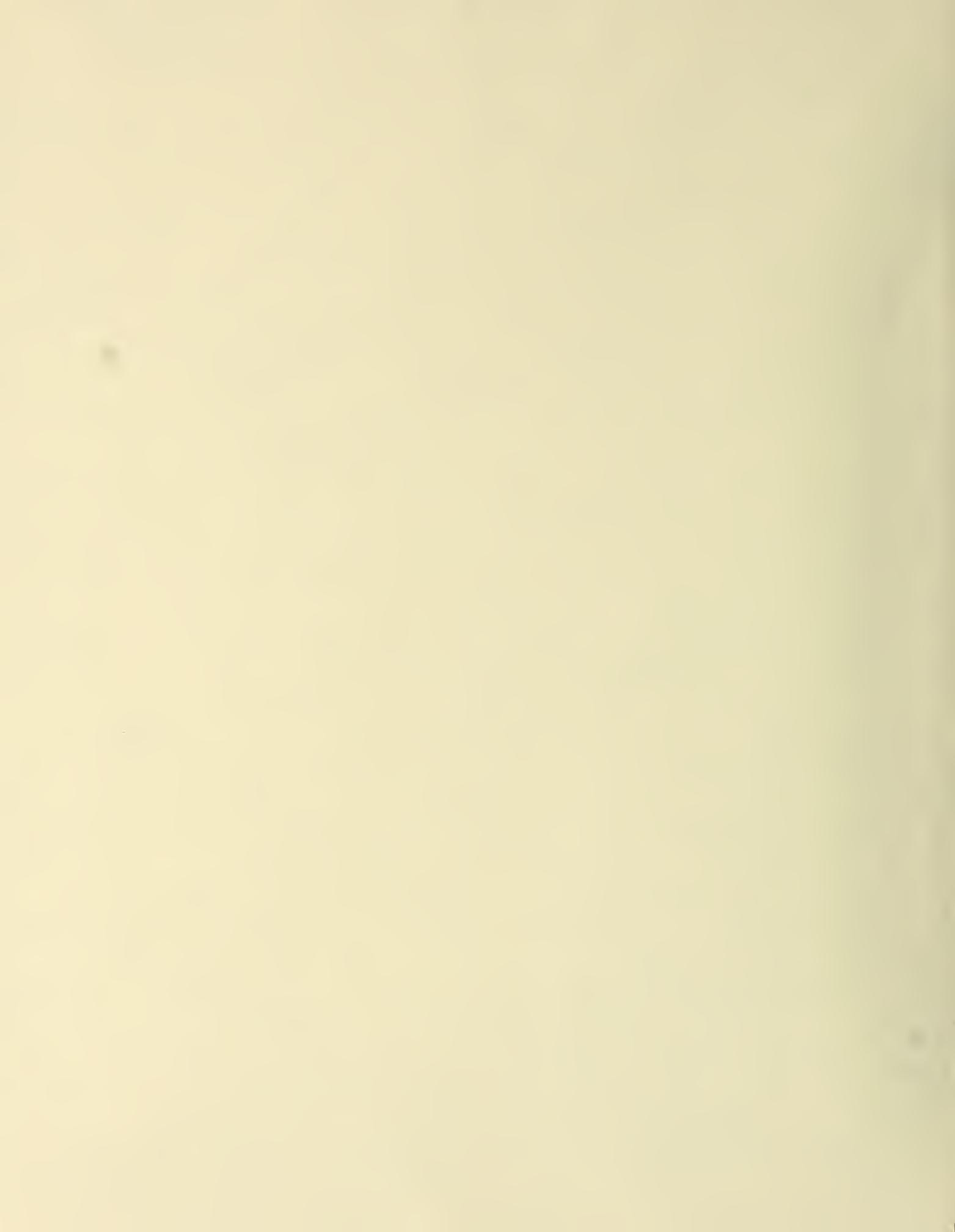
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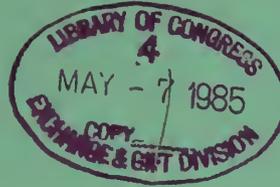




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Control of Acid Mine Drainage

Proceedings of a Technology Transfer Seminar

By Staff, Bureau of Mines



UNITED STATES DEPARTMENT OF THE INTERIOR





*U.S. Bureau of Mines - Information
Circular I.C.*

Information Circular 9027

Control of Acid Mine Drainage

**Proceedings of a Technology Transfer
Seminar**

By Staff, Bureau of Mines



UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
Robert C. Horton, Director

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CONTENTS

| | <u>Page</u> |
|--|-------------|
| Abstract..... | 1 |
| Introduction..... | 2 |
| Prediction of Acid Drainage Potential in Advance of Mining, by Patricia M. Erickson, Richard W. Hammack, and Robert L. P. Kleinmann..... | 3 |
| Hydrologic Aspects of Acid Mine Drainage Control, by Kenneth J. Ladwig..... | 12 |
| Oxygen Content of Unsaturated Coal Mine Waste, by Patricia M. Erickson..... | 19 |
| Control of Acid Mine Drainage by Application of Bactericidal Materials, by Patricia M. Erickson, Robert L. P. Kleinmann, and Steven J. Onysko..... | 25 |
| Alkaline Injection: An Overview of Recent Work, by Kenneth J. Ladwig, Patricia M. Erickson, and Robert L. P. Kleinmann..... | 35 |
| Comparative Tests To Remove Manganese From Acid Mine Drainage, by George R. Watzlaf..... | 41 |
| Treatment of Acid Mine Water by Wetlands, by Robert L. P. Kleinmann..... | 48 |
| In-Line Aeration and Treatment of Acid Mine Drainage: Performance and Preliminary Design Criteria, by Terry Ackman and Robert L. P. Kleinmann..... | 53 |

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

With Factors for Conversion to U.S. Customary Units
and the International System of Units (SI)¹

| Abbreviation or unit | Unit of measure | To convert to-- | Multiply by-- |
|--------------------------|-----------------------------------|--------------------------------|-------------------------|
| acre | acre | hectares | 0.405 |
| cm | centimeter | inches | 0.3937 |
| ft | foot | meters | 0.3048 |
| ft ² | square foot | square centimeter | 929.0 |
| ft ³ | cubic foot | cubic meters | 0.028 |
| ft/s | foot per second | centimeters per second | 30.48 |
| g | gram | ounces | 0.0353 |
| gal | gallon | liters | 3.785 |
| gal/h | gallon per hour | liters per hour | 3.785 |
| gal/min | gallon per minute | liters per minute | 3.785 |
| h | hour | NAP | |
| ha | hectare | acres | 2.471 |
| in | inch | centimeters | 2.54 |
| kg | kilogram | pounds | 2.205 |
| L | liter | cubic inches | 61.025 |
| lb | pound | kilograms | 0.4536 |
| lb/min | pound per minute | kilograms per minute | 0.4536 |
| L/min | liter per minute | gallons per minute | 0.2642 |
| m | meter | feet | 3.28 |
| m ³ | cubic meter | cubic yards | 1.308 |
| m ³ /s | cubic meter per second | gallons per second | 264.2 |
| mile | mile | kilometers | 1.609 |
| mg | milligram | grains | 0.0154 |
| mg/L | milligram per liter | NAP | |
| mg/(L·h) | milligram per liter per hour | NAP | |
| min | minute | NAP | |
| mL | milliliter | cubic inches | 0.061 |
| mm | millimeter | inches | 0.0394 |
| mmho/m | millimho per meter | NAP | |
| μm | micrometer | inches | 3.94 × 10 ⁻⁵ |
| pct | percent | NAP | |
| psi | pound per square inch | grams per square centimeter | 70.307 |
| std ft ³ /min | standard cubic foot per minute | NAP | |
| ton | ton | metric tons | 0.907 |
| yr | year | NAP | |

NAP Not applicable.

¹Owing to the preference of individual authors, U.S. customary and SI units have both been used in this report. Conversion factors are provided for the assistance of the reader.

CONTROL OF ACID MINE DRAINAGE
Proceedings of a Technology Transfer Seminar

By Staff, Bureau of Mines

ABSTRACT

Acid mine drainage can be controlled by water treatment, retardation of the pyrite oxidation reaction system, or enhanced prediction that allows preventive action to be taken. The Bureau of Mines is conducting research in each of these areas; the results of this research are summarized in the eight papers that comprise this volume. Field work to evaluate overburden analysis, alkaline injection, and bactericidal control of acid formation is described, along with two new inexpensive methods to treat acid mine water. These papers were prepared for an acid mine drainage technology transfer meeting held in Pittsburgh, PA, on April 3 and 4, 1985.

INTRODUCTION

Acid drainage from coal mines is one of the most persistent industrial pollution problems in the United States. Over 5,000 miles of streams and rivers are adversely affected, primarily by underground mines that have been abandoned for decades. Meanwhile, at active mining operations and at sites where mining occurred after 1977, discharge water must be treated to meet fairly stringent regulatory limits--at a cost to the industry of over \$1 million per day.

The Bureau of Mines has a special responsibility to facilitate integration of mining and mineral processing with environmental safeguards. This responsibility is twofold: the development of techniques to reduce or eliminate environmental degradation, and the improvement of existing pollution control processes to make them more efficient and more cost effective. Research in acid mine drainage exemplifies the Bureau's concern for these environmental aspects of mining.

This collection of papers summarizes much of the Bureau's recent research on acid mine drainage and will give the reader a sense of where the research is headed, in addition to providing details regarding new technology and recently acquired knowledge. The research papers address four basic objectives:

1. Improved prediction of acid potential.--The Bureau is attempting to address three fundamental problems associated with premine prediction of acid mine water: (1) the lack of field verification for currently available techniques using overburden analysis, (2) difficulties encountered when one attempts to incorporate pyrite reactivity and kinetics into premine prediction, and (3) incorporating the effectiveness of reclamation measures in predicting eventual acid production. Available techniques are being evaluated at sites where the extent of acid production from reclaimed spoil can be monitored. This will enable the Bureau to evaluate their applicability and

the effect of potentially mitigating measures taken by the mining companies. This research should lead to better permitting by State agencies, improved mine planning, and improved reclamation.

2. Improved mine planning.--Improved prediction will allow an awareness of the potential problem, but the effect that mining methods and procedural changes will have on the extent of the problem must still be systematically determined. Fundamental aspects of such factors as hydrology and oxygen diffusion must be understood before modified reclamation plans and new closure methodology can be developed to prevent acid mine drainage in the future.

3. At-source control of acid formation.--Current Bureau research indicates that it is possible to reduce acid loads under certain conditions using long-term inhibition of bacterial catalysis at or near the surface, or chemical treatment to reduce pyrite reactivity. The latter will most likely require the establishment of a near-neutral pH regime or low-Eh environment. Reduced acid loads, although less desirable than total prevention, are now achievable. Water treatment costs and reclamation costs can both be reduced if acid production is decreased.

4. Improved water treatment.--The Bureau has developed two low-cost alternatives to conventional mine water treatment facilities. For low flows of acid water, a low-maintenance system, consisting of a Sphagnum moss wetland to remove iron, followed by limestone neutralization, has been demonstrated to be effective in a pilot-scale test; full-scale tests are in progress. For higher flows, the Bureau has developed a pipeline neutralization and aeration system that can be scaled up or down to meet most treatment needs; the entire system costs only a few thousand dollars and appears to be more efficient than a conventional treatment facility.

PREDICTION OF ACID DRAINAGE POTENTIAL IN ADVANCE OF MINING

By Patricia M. Erickson,¹ Richard W. Hammack,²
and Robert L. P. Kleinmann³

INTRODUCTION

Surface coal mine operators are required by law to identify the potential for acidic drainage prior to opening a new mine (9).⁴ In many cases, particularly in the Appalachian region, the permit application must contain the results of overburden analyses intended to quantify the acidic or alkaline weathering products of the affected strata. These data serve two purposes: to provide the regulatory agency with a means to estimate the hydrologic consequences of the proposed mine, and to allow the proposed operator to plan the mine with regard for probable water treatment requirements. Until the Bureau's current project, there has been no systematic field evaluation of these analytical techniques.

The acid-base account is the most commonly used overburden analysis technique (6). The method is based on measuring the total sulfur content of each lithologic unit and converting that value to an acid potential based on the stoichiometry of complete pyrite oxidation. Similarly, the neutralization potential is determined for each lithology by its ability to neutralize strong acid. The two values, acid and alkaline potential, respectively, are represented as calcium carbonate equivalents for calculation of a net excess or deficiency of neutralizers. A deficiency greater than 5 tons CaCO₃ per 1,000 tons of rock is generally considered a potential source of acid mine drainage (11).

The acid-base account uses rapid and simple analytical techniques; it is, therefore, inexpensive. The results, however, indicate only the total acid and alkaline loads that could be produced if all the pyrite and carbonates reacted. The major flaw in interpreting these data for water quality is that reaction kinetics are ignored. Complete oxidation of pyrite may take decades, even if all the pyrite is reactive; acidity in solution is determined by the rate of oxidation and flushing.

In contrast, calcium carbonate dissolves rapidly to an equilibrium value of approximately 60 mg/L alkalinity at atmospheric CO₂ partial pressure (5). More carbonate mineral dissolves to achieve the same equilibrium concentration if acidity is present; higher concentrations can be dissolved at high carbon dioxide partial pressures (7). Because solution acidity and alkalinity are controlled largely by the kinetics and thermodynamics of many reactions, use of total mass balance data to predict water quality is suspect. The developers of the acid-base account technique did not intend it to predict drainage quality, but rather to identify strata that may produce acid.

Other overburden analytical methods can be classified as simulated weathering techniques. These have in common that the strata, either individually or as a thickness-weighted composite, are subjected to oxidizing conditions to accelerate chemical weathering of the materials. Chemical composition of drainage obtained from periodically leaching the sample is classified as acidic or alkaline and is presumed to qualitatively predict the nature of postmining drainage at the proposed mine.

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⁴Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

Oxidative processes can be accelerated by heat, addition of chemical oxidants, reduced particle size of the solid phase, inoculation with bacteria, and other means; innumerable protocols could be devised for weathering tests. Two methods that have been used for overburden analysis utilize crushed core samples subjected to humidified air streams; the techniques differ in that one utilizes individual weathering tests for each lithology (2) and the other utilizes a composite sample assembled according to the backfilling plan (8).

Weathering tests may provide a realistic estimate of postmining drainage quality if they duplicate the kinetics of relevant reactions under field conditions. These tests require longer periods of time, from several weeks to months, and are more expensive to use than the acid-base account technique. The accuracy of any simulated weathering technique must be verified to determine its predictive capability.

Prediction of acid drainage potential from overburden analyses and other premining data relies on interpretation by

mine operators, consultants, and regulatory personnel. The data merely indicate the maximum acid and alkaline loads (acid-base account) or drainage quality under a given set of conditions (weathering tests). Effects of mining-related factors such as mining method, use of selective handling, and ameliorant applications are not considered in overburden analysis. There is no consensus on a method to combine the lithologic data, mining plans, and reclamation plans into a predictive scheme.

The Bureau is currently conducting contract and in-house research to improve acid drainage prediction. The contract research consists of two phases: (1) field evaluation of three overburden analytical techniques at 30 mine sites and (2) design of an empirical predictive scheme that encompasses overburden data and site-specific factors that could influence actual drainage quality. The in-house research is oriented toward developing an alternative overburden analysis method that takes into account pyrite reactivity. Both projects are discussed in following sections.

CONTRACT RESEARCH PROGRAM--PREMINING PREDICTION OF ACID DRAINAGE POTENTIAL

The Bureau awarded a research contract to Engineers International, Inc., in 1982 to improve the state of premining prediction. Phase 1, nearly complete now, addresses the validity of using available overburden analysis techniques to predict postmining drainage quality. Phase 2 will focus on the development of an empirical predictive scheme encompassing mining-related variables.

FIELD EVALUATION OF OVERBURDEN ANALYSIS

The objective of this phase of the research is to determine the utility of three overburden analysis techniques for predicting drainage quality after mining. To accomplish this goal within a reasonable time, the program plan called for the collection of actual postmining data

and the equivalent of premining overburden data from 30 reclaimed mines. The validity of this phase depends mainly on obtaining overburden samples that represent the overburden in the reclaimed section. At nine sites, cores sampled less than 1 yr ago were available for analysis. At the remaining sites, channel samples from an active highwall adjacent to each reclaimed mine section (used as the postmining water data source) were collected for overburden analysis. This method was chosen for two reasons: (1) The cost was much lower than the cost of drilling cores on adjacent unmined land, and (2) visual observation could be checked against company records to verify continuity of the overburden lithology. Fresh material was exposed on the highwall before sampling.

Site-selection criteria were designed to ensure that the predictive capabilities of the overburden analysis methods would be evaluated. Historical records, provided by State regulatory agencies and the coal companies, were used to eliminate mine sites having significant net acid or alkaline potential. It was felt that any overburden analysis technique can adequately predict an acid or alkaline discharge when the carbonate or pyrite is totally absent, respectively; the target sites were those that are presently difficult to assess.

In some cases, disagreement between overburden analysis results at the time of permitting and actual drainage quality was used to select a site; in other cases, professional judgment had to be used. Sites at which nonstandard practices might be the significant determinant in postmining drainage quality were avoided. These included backfills containing acid drainage treatment sludge, fly ash or preparation plant refuse, and sites treated with ameliorative chemicals other than agricultural limestone and fertilizer.

Samples were subjected to laboratory analyses. Acid-base accounting was used on the samples from all 30 sites; weathering tests published by Caruccio (2) and Sturey (8) were performed on samples from 16 and 5 sites, respectively. Cold alkalinity determinations were also made on Caruccio weathering test samples. Table 1 illustrates other types of information obtained from adjacent areas and available records added to the premining data set.

The most critical postmining data involved the quality of water issuing from the reclaimed mine section. To characterize the drainage, a field monitoring program was instituted at each site to measure the volume and quality of discharges at least eight times during a 1-yr period. Analyses are indicated in table 2. Where possible, data collected by the mine operator were also used.

TABLE 1. - Premining equivalent data collected to supplement overburden sampling and analysis

| <u>Information</u> | <u>Sources</u> |
|--|--|
| Local geology, hydrology, and mining history. | Permit applications, State and Federal agencies. |
| Surface and ground water quality and quantity. | Current project, historical records. |
| Climatic data. | Government records, mining company records. |

TABLE 2. - Analyses performed on premining and postmining water samples

| <u>Field measurements</u> | <u>Laboratory analyses</u> |
|---------------------------|----------------------------|
| SUITE 1 | |
| pH..... | Iron |
| Acidity, alkalinity. | Sulfate |
| Dissolved oxygen.... | |
| Specific conductance | |
| Temperature..... | |
| SUITE 2 | |
| pH..... | Iron |
| Acidity, alkalinity. | Sulfate |
| Dissolved oxygen.... | Calcium |
| Specific conductance | Magnesium |
| Temperature..... | Manganese |
| SUITE 3 | |
| pH..... | Iron |
| Acidity, alkalinity. | Sulfate |
| Dissolved oxygen.... | Calcium |
| Specific conductance | Magnesium |
| Temperature..... | Manganese |
| | Aluminum |

Table 3 summarizes ancillary postmining data, collected primarily for use in phase 2.

Phase 1 data collection is now complete, and statistical analysis is in progress. Table 4 summarizes the ranges of values for acid-base account parameters observed in samples from 30 sites. The most acidic thickness-weighted value for a single overburden column was a

TABLE 3. - Supplementary postmining data

| | |
|-------------|---|
| Mining..... | Maps. Drilling logs. Mining method and equipment. Materials handling. |
| Reclamation | Backfilling plans and maps. Materials handling. Equipment. Chronological records. Topsoil storage. Soil amendments. Vegetation. |

TABLE 4. - Ranges of values of acid-base account parameters for individual lithologies

| <u>Parameter</u> | <u>Range</u> |
|--|--------------|
| pH, paste..... | 3.0 - 7.9 |
| Sulfur, pct: | |
| Total..... | <.05- 8.3 |
| Pyritic..... | <.05- 7.2 |
| Sulfate..... | <.05- .73 |
| Organic..... | <.05- .31 |
| Neutralization potential per 1,000 tons CaCO ₃ | -2.7 -940 |

deficiency of 1,300 tons as calcium carbonate. At the other extreme was a West Virginia site having an excess alkalinity of 1,200 tons as calcium carbonate. Interestingly, one of several toe-of-spoil seeps at the latter site is acidic.

The Caruccio weathering test was performed on overburden samples from 16 sites, having acid-base account results indicating overall neutrality (6 sites), acidity (5 sites), or alkalinity (5 sites). Ranges of cumulative leachate quality for individual lithologies are shown in table 5.

The quality of surface runoff and spoil seepage are the dependent variables for statistical analysis in phase 1. Three sets of primary independent variables were derived from the three overburden analysis methods used in the study. Ancillary data (tables 1 and 3) will be used in this analysis only as needed to

TABLE 5. - Average leachate quality range for Caruccio weathering tests on individual lithologies

| <u>Parameter</u> | <u>Concentration range, mg/L</u> |
|---------------------------------|--------------------------------------|
| Acidity, as CaCO ₃ : | |
| Hot total..... | <1-53,000 |
| Mineral..... | 0-13,000 |
| Alkalinity..... | <1- 380 |
| Sulfate..... | <1-33,000 |

classify sites in the case of bimodal distributions. For example, sites may be classified by degree of vegetative cover, time since mining, or other factors. Significant correlations between dependent and independent variables will be identified by simple linear regression analysis, factor analysis, and multivariate regression analysis. The phase 1 research product will be a set of equations that relate observed drainage quality to overburden analysis data.

EMPIRICAL PREDICTIVE METHOD

Phase 2 of the contract research will focus on the design and testing of a method to predict postmining drainage quality. This phase of the research will make extensive use of the data developed during phase 1. Our working hypothesis is that the mining-related factors play a critical role in the observed drainage quality. Therefore, we expect that the phase 1 results will indicate moderate correlation coefficients between overburden analysis data and postmining drainage quality. The objective of phase 2, then, is to improve the prediction by including the nonnumerical (categorical) factors shown in tables 1 and 3.

The output of the research may come in different forms. For example, there may be a nonlinear equation in which non-numeric factors have been assigned numerical rankings. Alternatively, the predictive method may be based on an n-dimensional decision surface, as in pattern recognition.

IN-HOUSE RESEARCH: PYRITE REACTIVITY ANALYSIS

BACKGROUND

Acid-base accounting methods depend upon sulfur analysis to accurately quantify the potential acidity of overburden materials. Potential acidity is generally considered to be a function of the total sulfur content, although only pyritic sulfur contributes significantly to acid production. Pyritic sulfur must be distinguished from non-acid-producing sulfur forms, in cases where (1) the material is weathered and much of the original pyritic sulfur has been oxidized to sulfate sulfur or (2) the material is carbonaceous and a significant proportion of the total sulfur is bonded to organic molecules.

Pyrite occurs as different forms or morphologies in coal and overburden materials. Many authors have provided petrographic descriptions of various pyrite morphologies; descriptions given by King (3) have been adopted for this study because they are usable and encompass all pyrite morphologies. According to King, pyrite occurs in five basic morphologies: (1) spherical aggregates of euhedral pyrite crystals (framboids), (2) isolated euhedral pyrite crystals, (3) nonspherical aggregates of euhedral pyrite crystals, (4) irregularly shaped massive pyrite, and (5) fracture-filling massive pyrite.

Differences in pyrite reactivity relative to different pyrite morphologies were first noted by Caruccio (1). Caruccio indicated that framboidal pyrite was the most reactive pyrite form and related the percentage of framboidal pyrite to the acid-producing potential of selected samples. Most researchers agree that, in general, the smaller the grain of pyrite, the more reactive the pyrite and the greater the potential acidity.

The importance of reactive pyrite forms in the generation of acid mine drainage was generally dismissed when it was realized that these forms could not account

for all of the acidity observed. However, the oxidation of reactive forms under ambient conditions may establish a chemical environment that favors bacterial catalysis and permits the less reactive pyrite to react. Research into this possible triggering mechanism may identify parameters that are inherently more accurate in predicting potential acidity than total sulfur or pyritic sulfur content alone. Quantification of reactive pyrite forms would not be able to predict total acidity but would allow for more accurate assessment of pyrite oxidation rates, and thus possibly distinguish "go" or "no go" acid generation situations. Initial Bureau research into pyrite reactivity was based on the hypothesis that different pyrite morphologies and grain sizes would thermally decompose and oxidize at different temperatures corresponding to the relative stability of each form; more reactive forms would be expected to react at lower temperatures because of lower activation energies.

Previous studies have used thermogravimetric (TG) and differential thermal analysis techniques (DTA) to investigate the thermal behavior of museum-grade pyrite and marcasite. Warne (10) used DTA thermograms to identify pyrite and marcasite in coal, carbonate, and clay matrices. He found that minimum pyrite concentrations of 0.5 to 1.0 pct could be detected in a coal matrix by DTA despite kaolinite and ankerite interferences. However, DTA thermograms of pyrite and marcasite were so similar that they could not be differentiated. Luganov (4) observed the thermal behavior of pyrite under inert atmospheres. They found that DTA's of pyrite displayed an exothermic effect at 380° C followed by endothermic effects at 480° to 500° C, 550° to 570° C. The exothermic effect at 380° C was attributed to partial oxidation of pyrite by oxygen adsorbed on the surface. Subsequent endothermic effects at 480° to 500° C and 550° to 570° C were thought to represent the reaction of exothermic products with pyrite. DTA's of pyrite

treated with acid and ethanol to dissolve ferric oxides and remove adsorbed oxygen displayed only an endothermic effect at 680° C.

EXPERIMENTAL WORK

A modified evolved-gas analysis technique was used to examine the thermal behavior of sulfur species. This technique employs a resistance furnace for the programmed heating of coal and overburden samples in an oxygen atmosphere. The evolution of sulfur dioxide and sulfur trioxide gases was measured by an infrared detector and recorded simultaneously with the sample temperature on a two-channel recorder. A Leco SC-32 Sulfur Analyzer⁵ was used to ignite samples and monitor the evolution of sulfur oxides.

Initial tests of the evolved-gas analysis technique were made to determine if pyritic and sulfate sulfur could be thermally distinguished. Figure 1 is a thermogram of a sample containing 0.480 g $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and 0.020 g FeS_2 (pyrite). Results of this test indicate that pyritic sulfur and sulfate sulfur can be temporally differentiated or time-resolved at an isothermal furnace temperature of 767° C. Hydrated sulfate salts of calcium, magnesium, manganese, and ferrous

iron were also tested; the sulfate interference in all cases constituted less than 1 pct of the total pyrite response.

Standards of museum-grade pyrite were prepared in a silica gel matrix and tested at a furnace temperature of 767° C. Time-resolved, evolved-gas thermograms of pyrite standards are shown in figure 2. A plot of peak area for characteristic pyrite peaks versus the concentration of pyrite standards (fig. 3) yields a linear relationship. This indicates that the Leco SC-32 Sulfur Analyzer may be useful for quantification of pyritic and sulfate sulfur species in samples of low carbon content. The effect of carbonaceous material on pyrite thermograms is shown in figure 4. The large exothermic effect resulting from the combustion of carbonaceous materials effectively masks all pyrite peaks. Interaction of pyrite with the organic matrix and pyrolysis products may result in the shifting of characteristic pyrite peaks.

The relative reactivity of framboidal and isolated euhedral pyrite morphologies was compared by preparing a 3-pct-S

⁵Reference to specific products does not imply endorsement by the Bureau of Mines.

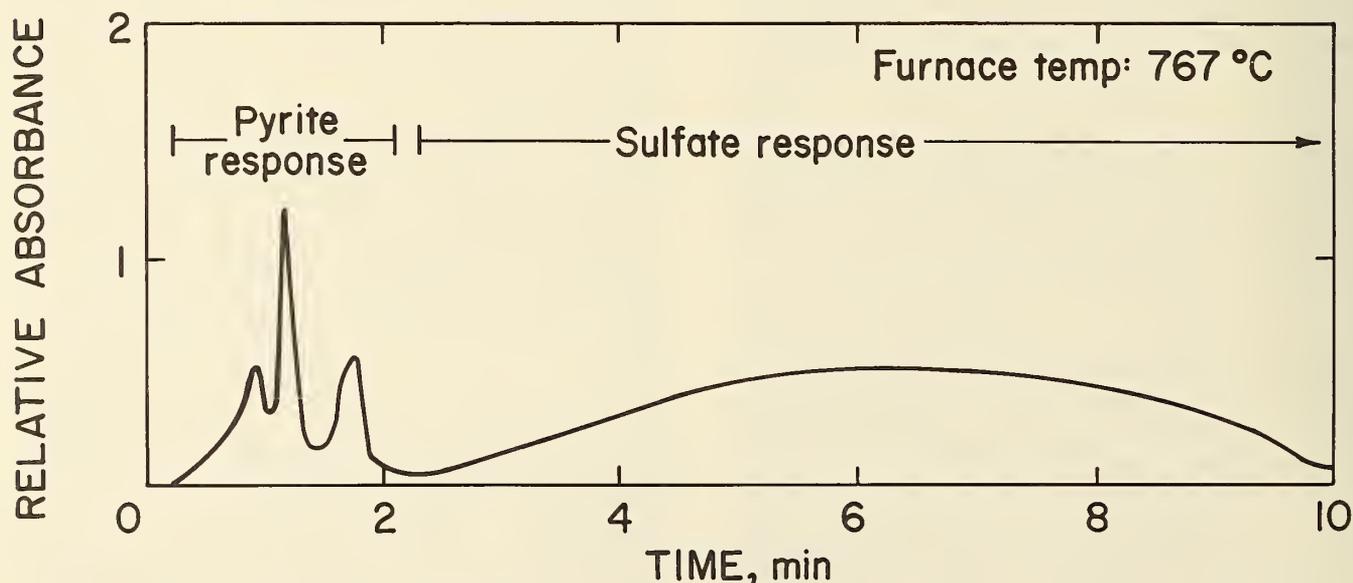


FIGURE 1. - Time-resolved, evolved-gas analysis of a sample containing 0.20 g pyrite and 0.480 g $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$.

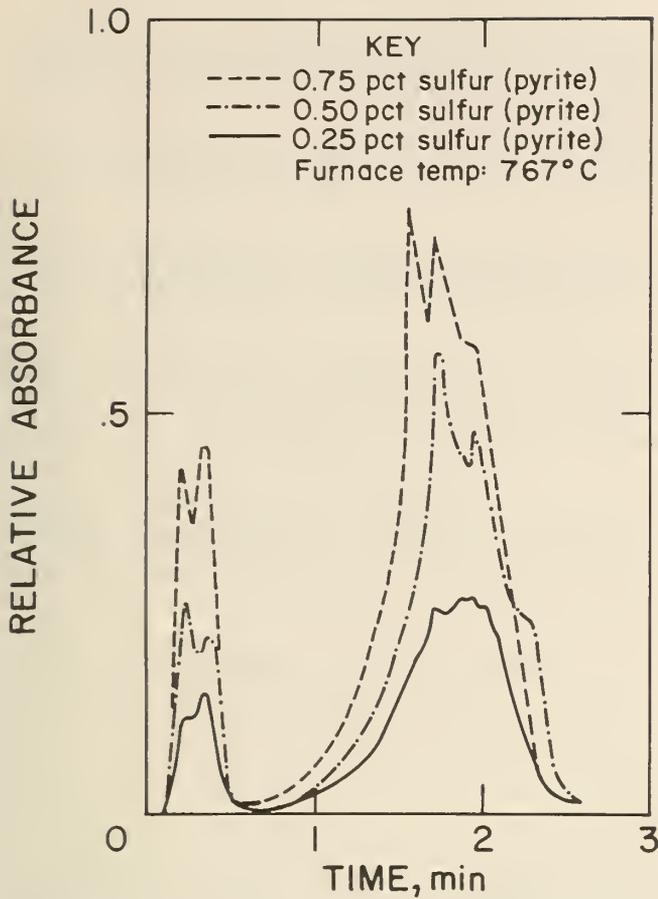


FIGURE 2. - Time-resolved, evolved-gas analysis of pyrite standards.

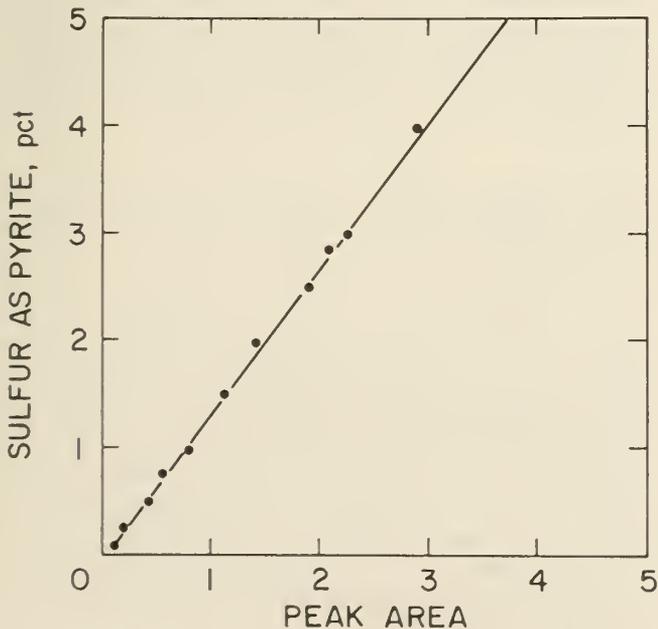


FIGURE 3. - Plot of cumulative pyrite peak area versus sulfur content.

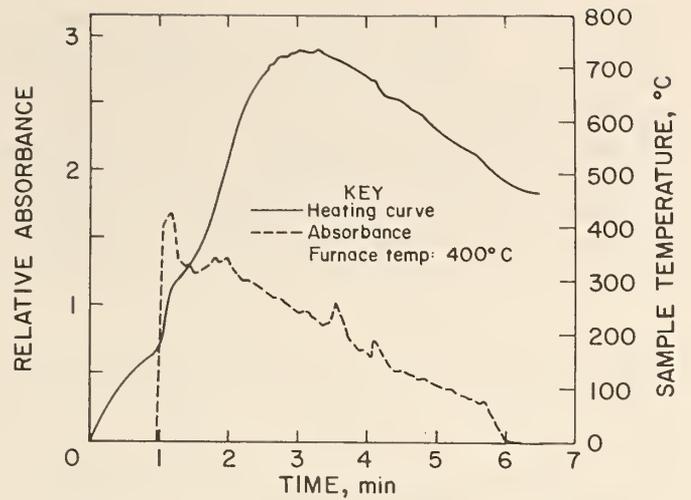


FIGURE 4. - Evolved-gas analysis of carbonaceous sample.

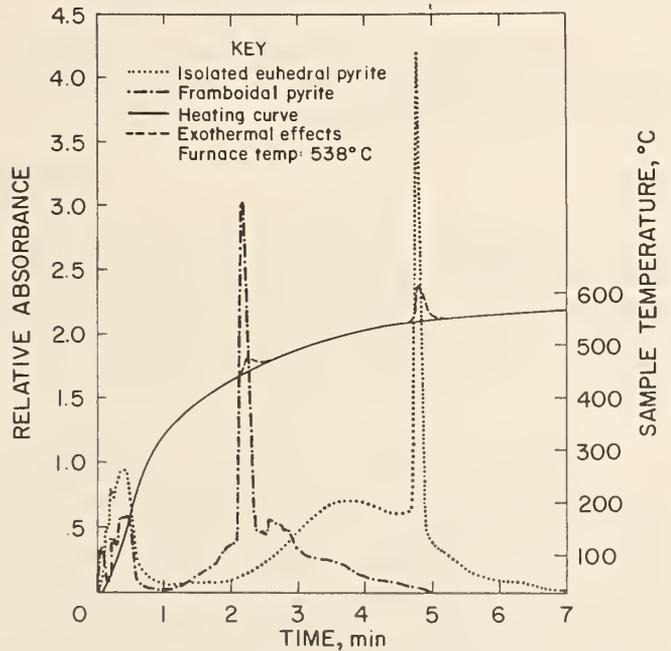


FIGURE 5. - Evolved-gas analysis of isolated euhedral and framboidal pyrite morphologies.

standard of each form in a silica gel matrix (100- to 200-mesh). Framboidal pyrite was supplied by Dr. Alfred Stiller of West Virginia University, who confirmed its purity by Mossbauer spectroscopy. Framboidal and isolated euhedral pyrite standards were run individually at a furnace temperature of 538° C and at purge and lance flows of 4 and 1 L/min, respectively. The superimposition of the two thermograms (fig. 5) illustrates the

difference in thermal reactivity between framboidal pyrite and the more stable isolated euhedral pyrite. At this time, no thermograms have been run on samples containing both framboidal and isolated euhedral pyrite. Therefore, the amount of interaction between pyrite forms, if any, and the characteristics of the resulting thermogram cannot be predicted.

Although Bureau of Mines research into pyrite reactivity is still in preliminary stages, it can be concluded that--

1. Pyritic and sulfate sulfur in non-carbonaceous materials can be differentiated using a Leco SC-32 Sulfur Analyzer.

2. Pyritic sulfur can be quantitatively determined in noncarbonaceous matrices using evolved-gas analysis techniques.

3. Framboidal and isolated euhedral pyrite morphologies differ significantly in thermal reactivity.

4. Carbonaceous materials seriously interfere with the evaluation of sulfur species using evolved-gas analysis.

Future Bureau of Mines research into pyrite reactivity will include--

1. Investigations of the thermal reactivity of other pyrite morphologies.

2. The evaluation of evolved-gas analysis as a quantitative technique for determining pyritic and sulfate sulfur in noncarbonaceous materials.

3. The development of a technique for performing routine evolved-gas analysis of sulfur species in carbonaceous materials.

4. Correlation with contract research.

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HYDROLOGIC ASPECTS OF ACID MINE DRAINAGE CONTROL

By Kenneth J. Ladwig¹

INTRODUCTION

Water is obviously a principal component of the acid mine drainage (AMD) problem, functioning as a reactant in pyrite oxidation, as a reaction medium, and as a transport medium for oxidation products. The role of water as a transport medium is the focus of one segment of the Bureau of Mines AMD program.

Describing the contaminant transport process serves two basic purposes. The first is to develop site-specific characterizations of the hydrology, including defining recharge areas and flow paths, estimating rates and volumes of mine water flow, delineating lateral variations in water quality, and determining contaminant loads at the discharge. The site-specific data are critical to the success of any abatement procedure, regardless of the technical approach chosen. Efficient and cost-effective abatement requires knowledge of sources of spoil water recharge, zones of acid production, and movement of water through the acid-producing zones.

The second purpose is to examine in greater detail the interaction between acid production and hydrologic transport. While field studies are by nature site specific, data obtained from several mines will be used to develop a more generalized conceptual understanding of the transport process. The conceptual model will then serve as the basis for improved reclamation and abatement technology. Of central importance in this phase of the study are (1) the interaction of the mine water with the other components involved in acid generation and (2) the hydrochemical evolution of the mine water.

We investigated the transport process at both underground and surface coal mines, with most of the underground mine work being done in the northern anthracite field of eastern Pennsylvania. The purpose of this work is to describe the hydrogeochemical processes occurring in a flooded mine complex. The initial phase of this work was reported in RI 8837 (4).²

The surface mine work was done principally at reclaimed surface mines in Pennsylvania and West Virginia. Why reclaimed sites? The fact that many reclaimed mines in these States are still producing considerable volumes of AMD attests to the shortfalls of past and current reclamation practices. By monitoring these sites, we can examine what went wrong, determine what steps might be taken to deal with the current problem, and develop methods for avoiding similar problems in the future.

Described in the following sections are results of a case study conducted at a reclaimed surface mine in West Virginia and a summary of the underground mine study in eastern Pennsylvania. The emphasis is on developing a practical monitoring program and then integrating the site hydrology with the AMD abatement plan. While it is unlikely that simple hydrologic modification alone will eliminate the problem, a thorough knowledge of site-specific hydrology is fundamental to the development and execution of a successful abatement plan.

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²Underlined numbers in parentheses refer to items in the list of references at the end of this report.

SURFACE MINE CASE STUDY

SITE DESCRIPTION

A small abandoned mine site in Upshur County, WV, was monitored to evaluate the use of bactericidal treatment to control AMD. The Lower Kittanning seam was mined from the U-shaped, 6-ha site in the late 1970's. Although the site was completely revegetated, including the highwall, the area was not regraded to approximate original contour. Average spoil thickness was about 7 m. Present topography consists of a 12-m slope at the highwall, a relatively flat bench over the mined area, and a 12-m outslope leading to a toe-of-spoil seep (fig. 1).

METHODS

The methods used are standard procedures for surface and ground water monitoring. Relative to perpetual water treatment and AMD abatement costs, the methods are not expensive, nor are they technically complex. As will be illustrated, monitoring can yield valuable information on acid production and movement at a surface mine site. Some type of spoil water monitoring is highly recommended prior to initiating abatement plans.

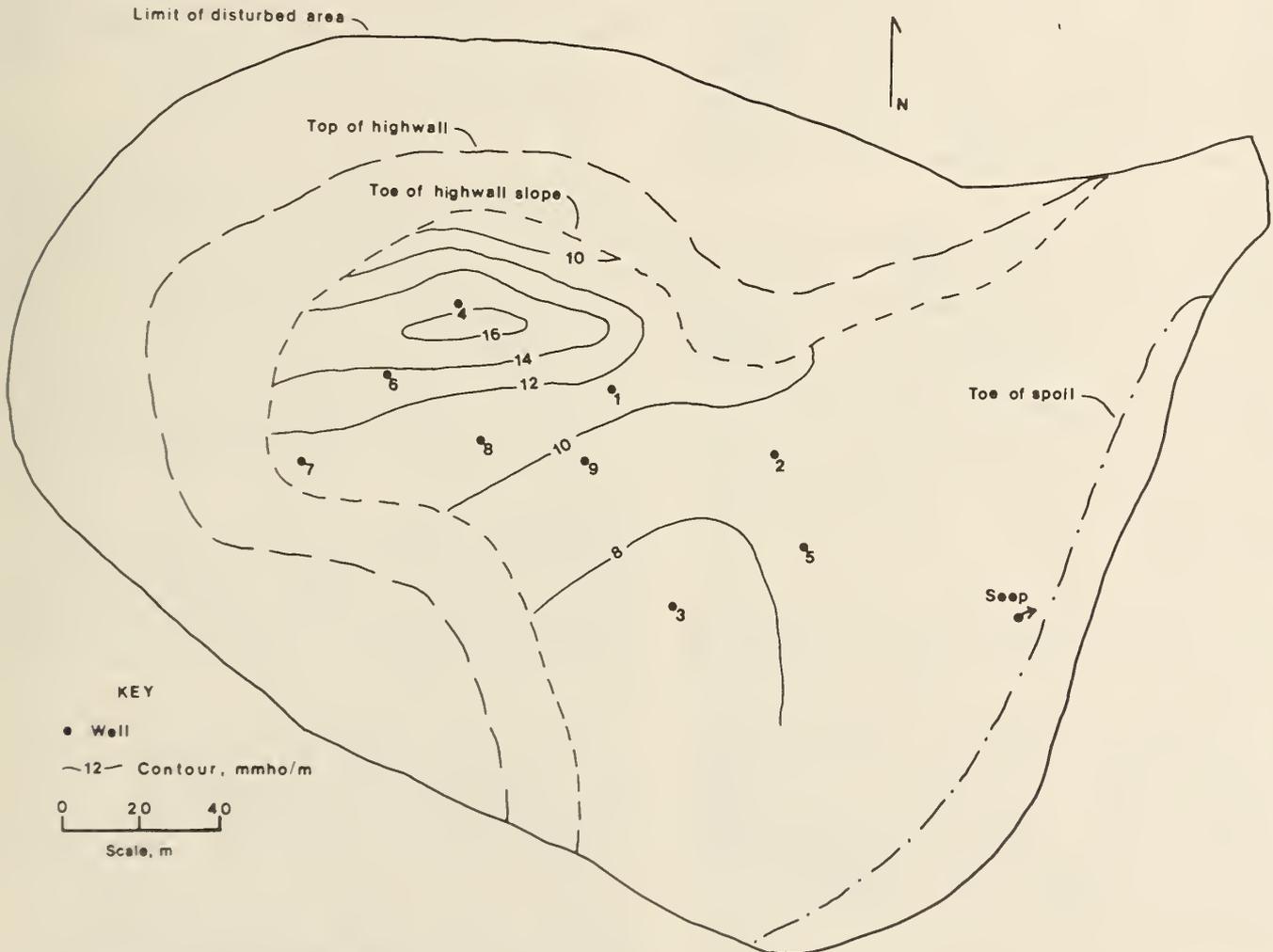


FIGURE 1. - Map of surface mine study site in Upshur County, WV, showing surface features, well locations, and results of an electromagnetic induction survey.

Following initial site reconnaissance to locate all seepage points and describe surface features, a series of electromagnetic induction (EM) surveys were used to describe subsurface features. EM can be used at surface mines to help determine spoil thickness and variations in thickness across a site, and to locate wet zones, mining relicts (highwalls, sidewalls, unmined blocks), mine floor structures, and zones of acid-producing material (3). While they do not eliminate the need for monitoring wells, EM surveys help identify potential trouble areas. Detailed surveying at the Upshur site took just under 2 days to complete.

Monitoring wells were installed to define spoil water flow conditions and spoil water quality. Spoil borings were drilled to the mine underclay, and wells were constructed from 2-in polyvinyl chloride pipe, slotted along the lower 10 ft. The borings were backfilled and the wells were sampled using standard procedures (5).

Spoil samples were collected from several depths during drilling of the monitoring wells. The samples were used to characterize the distribution of materials present on the site and to help reconstruct the backfilling sequence. All samples were visually classified in the field. Selected samples were subjected to laboratory tests, including leaching tests using the method described by Caruccio (2).

Seepage discharge was monitored for flow rate and water quality. Both sampling and flow monitoring were done as near to the point of seepage as possible to minimize mixing with surface runoff. As a compromise between cost, accuracy, and maintenance requirements, flow gaging was done with a simple V-notch weir constructed from plywood and stainless steel (1). The weir was inexpensive and reliable.

RESULTS

The EM surveys revealed an area of high apparent conductivity (greater than 14

mmho/m) on the northwestern part of the site (fig. 1). Progressively lower conductivities were observed in the direction of the seep. Although the cause of the high conductivity was not immediately known, the area enclosed by the 14-mmho/m contour on figure 1 was targeted as a possible trouble spot. A more detailed description of the geophysical survey is given elsewhere (3, site SMI).

Following the geophysical survey, a series of spoil borings were drilled. Spoil samples collected during drilling showed the material in the area of high conductivity (wells 4 and 6) contained significant proportions of a fine-grained, black material. In fact, the entire thickness of spoil at well site 4 was comprised of the black material. Holes drilled outside the high-conductivity zone (wells 1-3, 5, 7-9) contained predominantly weathered sandstone.

The Kittanning coals in the study area are "dirty" seams, and the black material found at well sites 4 and 6 was believed to be coal cleanings or shaly partings. Laboratory tests on the spoil material showed the mean sulfur content of the black material (1.24 pct) was considerably higher than that of the sandstone spoil (0.12 pct). Samples of the underclay were also analyzed and found to have a sulfur content similar to that of the shaly material (1.20 pct). Of 29 spoil samples analyzed, 6 had negative neutralization potential (4 samples from wells 4 and 6, and 2 outslope samples). These data again point to the area inside the 14-mmho/m contour in figure 1 as a primary trouble spot.

Final confirmation was provided by monitor well water samples. The poorest water quality on the site was found in well 4 (fig. 2). Mean sulfate and acidity concentrations at well 4 were about twice as high as the average concentrations for the spoil and seep. Mean iron concentrations at well 4 were more than twice the mean spoil concentration and more than six times the mean seep concentration.

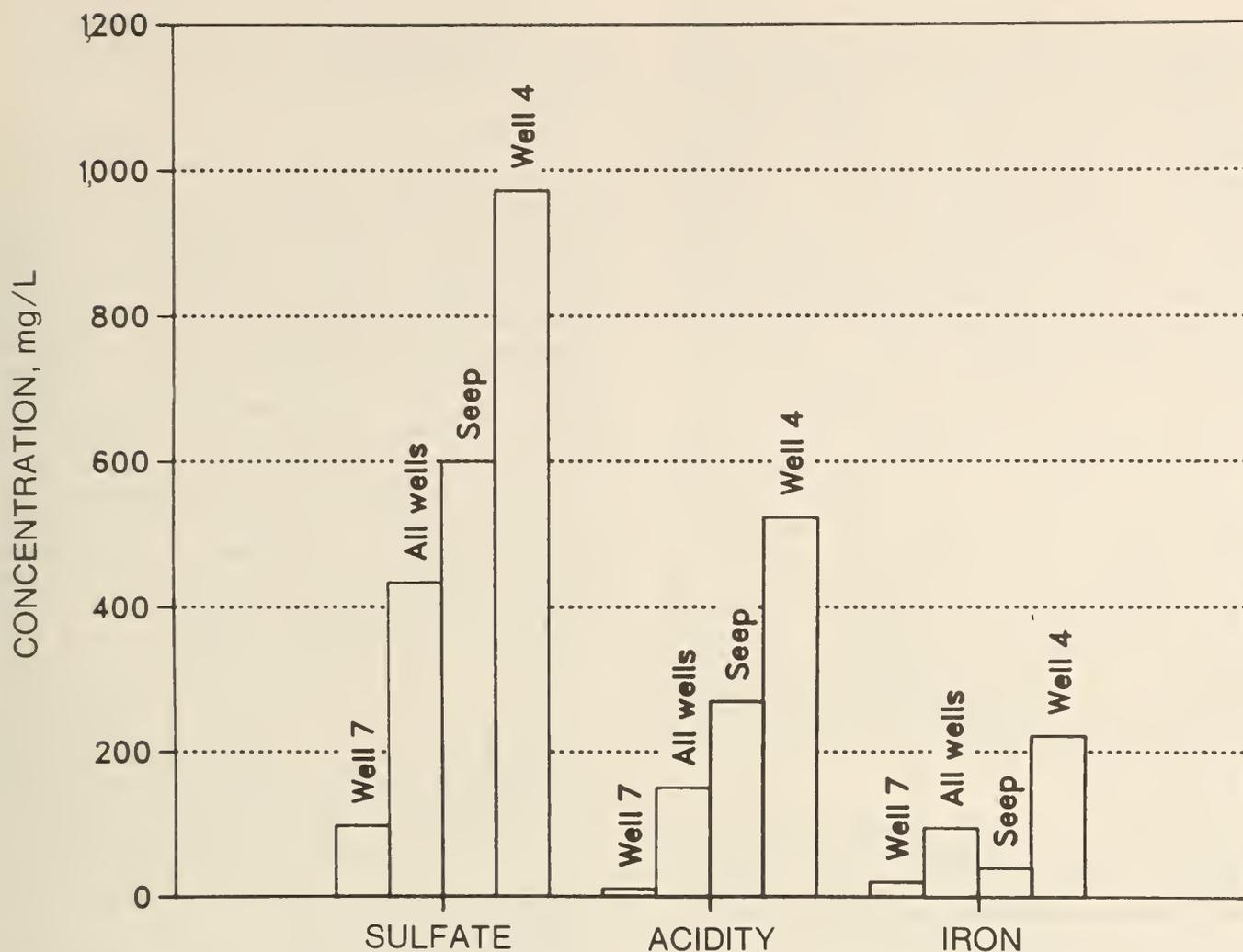


FIGURE 2. - Mean sulfate, acidity, and iron for well 7, well 4, the seep, and averaged for all of the wells drilled into spoil.

Conversely, good-quality water was found on the southern part of the site, particularly near well 7 (fig. 2). The well 7 area receives direct inflow of highwall seepage, as well as infiltration recharge through inert sand soil. As a result, there is much less contamination evident. As this recharge continues to migrate through the spoil, the water leaches some contaminants and mixes with water of poorer quality prior to discharge.

The water quality at the seep lies between that found in the well 4 area and the well 7 area (fig. 2). Flow at the

seep is perennial and anomalously high for such a small site. Total seepage discharge for the 1983 calendar year was 10 million gal, or about 50 pct of the total precipitation for the same period.

Principally two factors contribute to the high volume of discharge. One is the uncontrolled highwall seepage into the spoil on the southern part of the site. The water level in well 7 is the highest on the site at all times of the year, indicating this is a perennial source of recharge. The second factor is the absence of adequate surface water diversions on top of the highwall and on the

mining bench. Surface water from a small recharge area above the site flows onto the highwall and down a channel on the highwall slope. Flows in the channel as high as 15 gal/min have been observed following a rainstorm. All of the channel flow infiltrates directly into the spoil before reaching the bottom of the slope. The mining bench itself is graded back toward the highwall, further stimulating ponding and infiltration at the base of the highwall slope.

DISCUSSION OF RESULTS

The hydrologic study at the Upshur site suggests at least two avenues for site improvement. The first is to attempt to abate acid production at the source. The primary source of acid production at the site appears to be relatively well defined. Abatement procedures targeted directly at the acid-producing area may be the most cost-effective means of obtaining a significant reduction in seep contamination.

Application of an organic compound is currently being tested at the site to inhibit AMD production. The bacteria-inhibiting compound, potassium benzoate, has been applied at the surface on the northeastern part of the site. (The use of organic compounds such as benzoate to inhibit bacterial catalysis is described elsewhere in these proceedings.) The

effect of the application is being monitored in lysimeters and wells and at the seep.

The second approach is a simple reduction in recharge to the site. For example, subsurface drains to remove clean highwall seepage prior to flow through the spoil and minimal grading to promote runoff rather than infiltration would greatly decrease the total volume of water discharged at the seep. Installation of these controls would reduce mean flow by an estimated 50 to 75 pct and very likely change the character of the seep from perennial to intermittent. Although contaminant concentrations at the seep might increase following flow reduction measures, we expect the reduced volume would more than offset the increased concentration, resulting in a net decrease in contaminant load.

The case study presented here illustrates the use of relatively inexpensive ground water monitoring for targeting AMD abatement measures. Data obtained from such studies are an integral part of the Bureau of Mines research on improving existing abatement technology. As an end product, this work, in conjunction with research on overburden analysis, pyrite reactivity, and spoil air, will be used to develop predictive methods to avoid the pitfalls associated with current mining and reclamation practice.

UNDERGROUND MINES

To study the AMD problem at underground mines, the Bureau initiated a field investigation of the mine water system in the Wyoming Basin of the Northern Anthracite Field. The purpose of the study was to evaluate the effect of mine flooding on AMD formation. Specific project goals included identification of sites where pyrite oxidation may still be occurring and mapping patterns of contaminant flow.

Between 1980 and 1982, nine abandoned mine shafts were monitored for vertical variations in the chemical composition of the mine water system. Each shaft intersected several coal seams. Monitoring

included the collection of shaft water samples, downhole Eh and pH measurement, fluid resistivity logging, spontaneous potential logging, and fluid temperature logging. In addition to the shaft logging, the four major outfalls in the Wyoming Basin were monitored on a weekly basis from October 1982 through September 1983. These data were compared with available historical data for the outfalls.

Water quality at the outfalls in the Wyoming Basin has exhibited marked improvement since inundation of the mine complex. For example, between 1968 and

1980 sulfate concentrations decreased by 49 pct at the Buttonwood Outfall (fig. 3). At all of the outfalls, pH has increased to near neutral and net acidity has decreased.

Weekly monitoring indicated water quality was similar at three of the four outfalls (Buttonwood, South Wilkes Barre, and Askam), despite large differences in respective recharge areas and predicted residence times (table 1). The similarity may reflect a long-term trend toward uniformity coupled with the general improvement in water quality. The Nanticoke Outfall, which exhibits sulfate concentrations 25 to 35 pct higher than the other three outfalls, discharges the "youngest," or most recently formed, mine pool. If a trend toward uniformity does exist, the Nanticoke Outfall water quality may be expected to improve more rapidly than water quality at the other outfalls.

TABLE 1. - Mean pH, sulfate, and flow for the four outfalls in the Wyoming Basin for the period October 1982 through September 1983

| Outfall | pH | Sulfate, mg/L | Flow, gal/min |
|--------------------|-----|---------------|---------------|
| South Wilkes Barre | 5.9 | 1,200 | 25,380 |
| Buttonwood..... | 5.9 | 1,020 | 5,690 |
| Askam..... | 5.9 | 1,130 | 5,650 |
| Nanticoke..... | 6.0 | 1,640 | 2,900 |

No significant seasonal trends in contaminant levels were observed, despite order of magnitude variations in flow. The absence of seasonal trends again implies a uniform source. Thorough mixing of the surface water recharge with the bulk mine pool apparently occurs prior to outfall discharge.

The shaft monitoring revealed marked changes in water quality with depth within the basin. In five of the nine shafts studied, water was layered into two major zones separated by sharp changes in Eh, pH, and water quality parameters. An example of the vertical change in pH and sulfate is shown in figure 4.

The stratification appears to be related to discharge elevations at the time of inundation, as well as to present flow conditions. In each case, the sharp change in water quality occurred just above or below seams with mined barrier pillars. Relative positions of mined barrier pillars, outfall installations, and natural structural features combine to create an environment more favorable to flushing in the shallower parts of the mine system. As a result, the least contaminated water was found in the upper zones of the system, while the poorest quality was observed in flow-restricted, deeper zones.

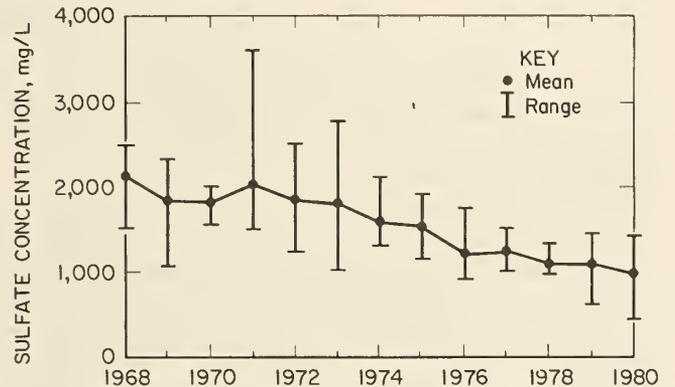


FIGURE 3. - Mean and range of sulfate concentrations at the Buttonwood Outfall.

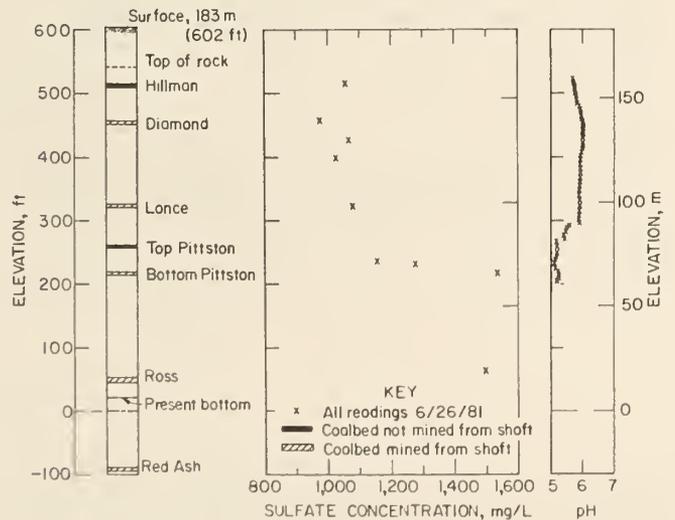


FIGURE 4. - Vertical profile of pH and sulfate in Gaylord shaft, Wyoming Basin.

The improvement in water quality appears to indicate a decrease or cessation of pyrite oxidation, along with neutralization and flushing of preexisting contaminants. The rate of flushing and minimum contamination levels attainable are difficult to quantify. Pyrite oxidation is still occurring at the surface in old refuse piles and strip pits, and these oxidation products are continuously washed into the subsurface flow system. The recharging pollutants are probably confined to small, near-surface flow systems and may tend to control the minimum contamination levels attained at the discharge points.

In addition to the surface contaminants, the reservoir of oxidation products in the flooded mine complex will continue to discharge for many years. Stimulation of flow from the deep zones by the addition of fully penetrating discharge structures may increase the rate of flushing but would aggravate the pollutant load on the surface streams if the discharge is left untreated. The construction of additional outfalls would also lower water levels, increasing the unflooded volume of the mine complex and possibly renewing pyrite oxidation in these areas.

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OXYGEN CONTENT OF UNSATURATED COAL MINE WASTE

By Patricia M. Erickson¹

INTRODUCTION

Acid mine drainage (AMD) results from the oxidation of pyrite in the presence of oxygen, water, and iron-oxidizing bacteria. Any of these three components acting on the pyrite provides a potential control point for reducing AMD formation.

The purpose of this project is to determine the oxygen availability in coal refuse and spoil to improve our understanding of its potential to control acid production.

BACKGROUND

The overall rate of acid production is controlled by the rate-limiting step in the chemical reactions of pyrite. The rate dependence of pyrite oxidation has been investigated in the laboratory. Under a variety of conditions near atmospheric pressure, the pyrite oxidation rate was shown to depend on oxygen partial pressure at values less than 2.0 (11),² 10 (1), or 20 pct (12). The actual rate dependence under field conditions is critical to the design of abatement strategies. If field acid production rates are a function of oxygen availability at all partial pressures, then even a limited reduction in atmospheric diffusion into the pyritic material will reduce the acid load. Alternatively, if oxygen is rate limiting only at low partial pressures, rigorous exclusion of oxygen would be required to affect acid production.

Few reports are available on the oxygen status of coal refuse and spoil. Hons measured pore gas composition as part of a lignite waste revegetation study (8). Jaynes (9-10) monitored oxygen and carbon dioxide within a backfilled surface coal mine and developed an acid production

model. Other models have been presented by Colvin (4) and Brown (1). Further work has been reported on metal mining waste products and solution mining sites (2-3, 7). Oxygen profiles tend to fall into two categories. Compacted materials tend to show decreased partial pressures of oxygen with increasing depth. Oxygen profiles of less compacted materials, such as heap leaching systems and coarse waste disposal sites, appear to be consistent with air convection through exposed faces. Actual field data on acid production rates and pore gas composition are necessary to calibrate available models or formulate new models and to elucidate the probable effects of proposed acid abatement strategies.

To date, Bureau of Mines work has focused on characterizing gas composition profiles in coal mine refuse and spoil. Water quality data are also being collected for investigation of possible correlation between acid production and oxygen availability. Preliminary findings were reported earlier (5). Only the oxygen content of the pore gas is discussed in this paper.

OXYGEN IN COAL REFUSE

Four inactive coal refuse disposal areas, ranging in approximate age from 2

to 12 yr, were included in the study. Soil gas probes (13), installed to depths

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²Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

of 15 to 90 cm, were sampled periodically. Samples were analyzed by gas chromatography for atmospheric gases and low-molecular-weight hydrocarbons.

Table 1 illustrates the range of oxygen concentrations found in pore gas at the four sites. Atmospheric oxygen levels (~21 pct) were generally found only in the uppermost 30 cm of the refuse. Values less than 2 pct were observed at depths as shallow as 15 cm below the surface. Based on the lowest literature values (11), oxygen concentrations were sufficiently low at times to restrict pyrite oxidation.

Long-term monitoring was conducted only at one site (Morgan County, OH). Figure 1 illustrates the average pore gas oxygen

profile generated from 12 sets of gas samples. This profile appears to be consistent with a model of the system based on oxygen diffusion from the atmosphere and oxygen consumption within the refuse by pyrite oxidation. Near-surface pyritic material is undergoing active oxidation, evidenced by runoff acidity in the range of 10,000 to 20,000 mg/L.

Gas composition in the refuse showed a strong seasonal dependence. Figure 2 shows average oxygen profiles for samples taken in the summer and winter seasons. There was very little overlap between the data sets. During the summer, the oxygen profile was sharp and showed the greatest change within the uppermost 15 cm of refuse. Oxygen was found at significant

TABLE 1. - Range of pore gas content in coarse coal refuse

| Depth, cm | Oxygen, moisture-free vol pct | | | |
|-----------|-------------------------------|-----------|-----------------|-------------------|
| | Allegheny County, PA | | Wise County, VA | Morgan County, OH |
| | Site A | Site B | | |
| 15..... | 20.4-20.7 | ND | 20.2-20.8 | 0.3-21.8 |
| 20..... | 18.9-19.9 | 20.0-20.4 | ND | ND |
| 30..... | ND | ND | 9.1-20.7 | .1-20.8 |
| 35..... | 6.5-14.9 | 5.7-17.2 | ND | ND |
| 66..... | ND | .4- 3.5 | ND | ND |
| 90..... | ND | ND | .2- 9.6 | ND |

ND No data.

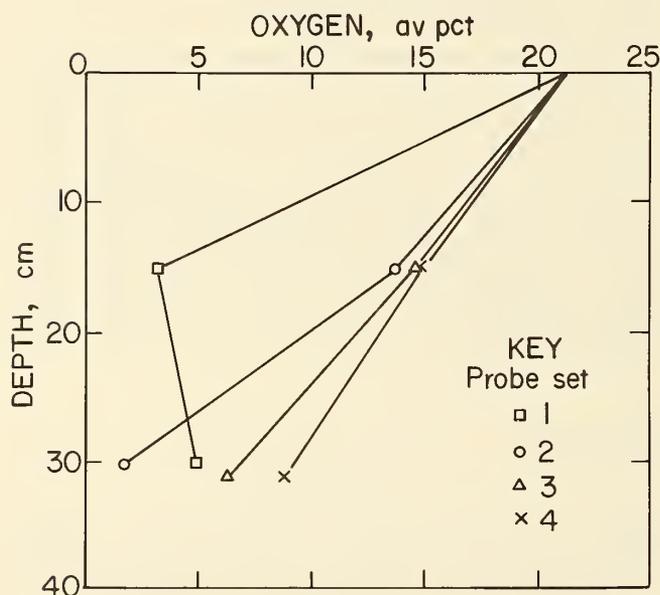


FIGURE 1. - O_2 for four sets of gas probes at the Morgan County, OH, site.

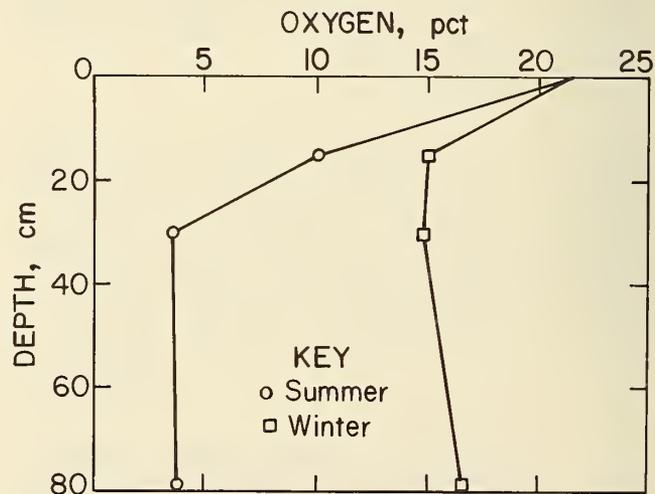


FIGURE 2. - Refuse was more oxygenated at all probe depths in winter (December through February) than in summer (June through August).

concentrations at greater depths in the winter months. One would expect that the oxidation reactions occur at lower rates during the cold season and that the

decreased oxygen consumption explains the higher oxygen content of the pore gas at depths up to 80 cm.

SPOIL OXYGEN CONTENT

We are currently monitoring pore gas composition in spoil at three regraded surface mines. Multiport gas-sampling wells (5) were installed at two or more locations on each site to monitor pore gas composition in the unsaturated zone. The oxygen profiles were distinctly different from those in coal refuse at the Morgan County site and did not show site-to-site consistency. Oxygen concentrations of 5 to 20 pct occurred to depths of several meters and, in some cases, throughout the unsaturated zones.

Figure 3 shows the average oxygen profile obtained from seven gas-sampling wells at an unvegetated site in Clarion County, PA. Overall, the oxygen content of the gas decreased with depth. However, the zones of greatest change in oxygen content differed for individual wells on the 11-acre site (fig. 4). Seasonal trends have not been examined yet.

Figure 5 shows the average oxygen profiles for three wells at a recently revegetated site in Upshur County, WV. This isolated ridge was reclaimed according to state-of-the-art guidelines, including the selective placement of toxic spoil above a nonreactive base pad and below a compacted clay cap (6). Gas-sampling wells were placed parallel to the ridge axis at approximately equal spacing. Sampling ports were located as follows: in the soil, in the top, middle, and bottom of the acidic spoil zone, and in the base pad. Two of the wells showed decreasing oxygen with increasing depth, while the third well showed a peak oxygen content in the middle of the acidic spoil zone (fig. 5). The greatest change in oxygen for a given change in depth occurred in the acidic spoil zone of wells 847 and 846 and between the soil and acidic spoil zones for well 793. The high oxygen values at the 5.9-m depth in

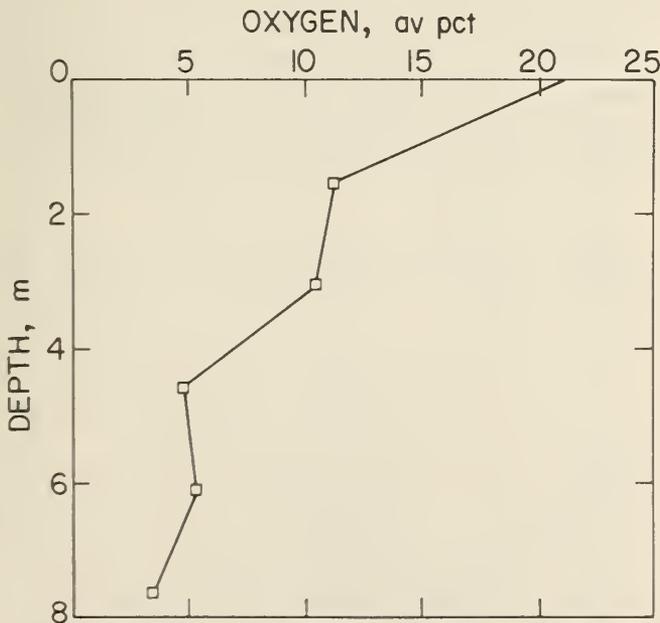


FIGURE 3. - O_2 profile from seven gas-sampling wells at the Clarion County, PA, site.

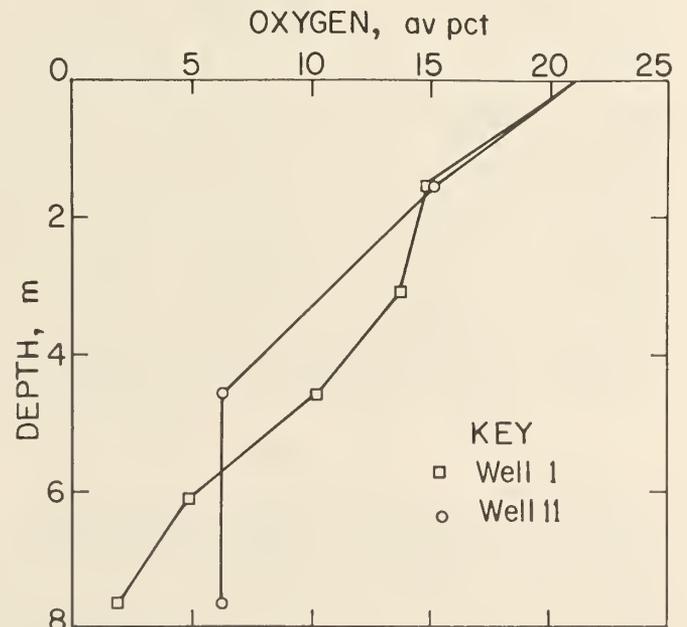


FIGURE 4. - O_2 profiles for two of seven gas-sampling wells at the Clarion County, PA, site. The change in O_2 pct varied for the same depth interval.

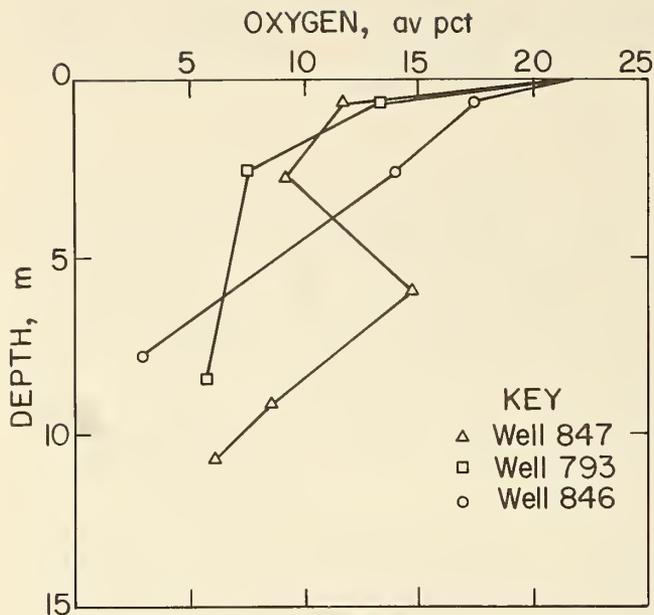


FIGURE 5. - O₂ profiles for three gas-sampling wells at the reclamation study site in Upshur County, WV.

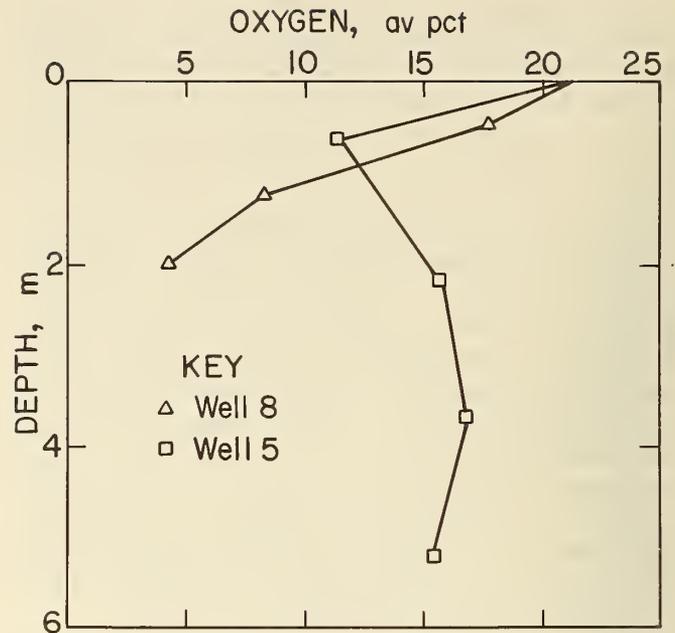


FIGURE 7. - O₂ profiles in revegetated spoil at the abandoned site in Upshur County, WV.

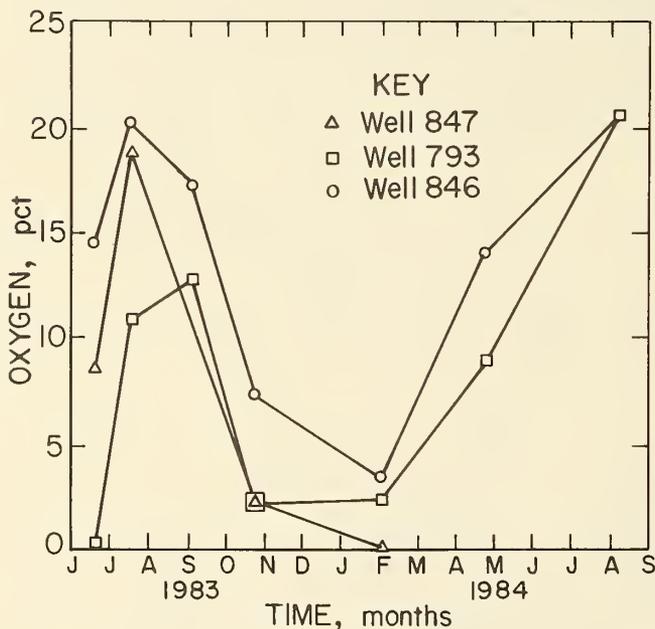


FIGURE 6. - Variation in oxygen content 2 ft below the compacted clay layer at the reclaimed study site in Upshur County, WV.

well 847 may be due to the location of the well on the exposed end of the mined ridge. Well 847 is surrounded by steep slopes on three sides as compared to slopes on two sides for the other wells.

The clay cap was placed over the acidic spoil to minimize rainfall infiltration (6). We also thought it might act as a diffusion barrier. Figure 6 summarizes the preliminary data available from the air well ports located 0.6 m beneath the clay cap. There appeared to be a distinct seasonal increase in oxygen during the spring and summer. The changing oxygen levels indicate that the clay layer is not a good diffusion barrier.

The third site, also located in Upshur County, WV, is an abandoned, revegetated surface mine. A three-port gas well (No. 8) was installed adjacent to buried pyritic material, which has been identified as the major source of acid drainage on the site. A four-port well (No. 5) was placed in the outslope area, which is composed of rocky spoil. Figure 7 shows the average profiles for both wells. Well 8 data indicated a steep decrease in oxygen content within the uppermost 1.8 m of spoil. Well 5 showed a different type of oxygen profile, not consistent with vertical downward diffusion. The location of well 5 on the outslope may account for this observation; diffusion

and/or convection may occur along the outslope face or toe. Similar profiles

have been observed in coarse mining waste rock (7).

DISCUSSION

Pore gas oxygen content in coal refuse generally decreased to only a few percent within 1 m below the surface at four un-vegetated sites. According to most literature reports, a lower limit of 1 or 2 pct oxygen could be used to define the pyrite-oxidizing zone. In that case, the bulk refuse should not be contributing much to the acid load at these sites. However, in the winter months oxygen levels greater than 15 pct were observed at greater depths. In the absence of consumption in the shallow zone, oxygen would be available to oxidize pyrite at greater depths. Cover with a nonpyritic coal refuse would probably not reduce the acid load. Coal mine spoil would probably be an ineffective cover material for the same reason: At the three sites we studied, the spoil pore gas usually contained sufficient oxygen to support pyrite oxidation.

Coal mine spoil oxygen profiles showed great variety among sites and laterally on a single site. In 10 of 12 wells at 3 sites, oxygen usually decreased with depth. These profiles are consistent with oxygen diffusion from the atmosphere downward through the spoil. The notable exceptions were the outslope area at the abandoned site and the exposed end of the ridge at the recently reclaimed site. Profiles from these two areas were similar to profiles observed in coarse waste subject to air convection through exposed slopes (7).

Gas composition monitoring can provide useful information about the location of pyrite oxidation zones. The steep gradient observed in the summer in coal refuse apparently is indicative of a zone of active oxidation. Similar zones in mine spoil, in the absence of a change in diffusion coefficient with depth, may also be indicators of pyrite oxidation. For

example, well 8 at the abandoned West Virginia site showed a steep gradient and is known to be adjacent to a mass of buried pyritic material currently producing acid. Identification of acid source areas will allow application of remedial treatments to selected zones, thereby reducing cost.

The seasonal trends in oxygen profiles are not consistent. We observed peaks in oxygen concentrations during the winter in coal refuse and during the summer in one spoil site. The winter peaks suggest that the refuse is more oxygenated when chemical activity decreases due to lower temperatures. We do not know why peak oxygen levels were observed in the summer at the spoil site.

The results reported in this paper suggest that inert cover materials may not be useful as diffusion barriers to reduce pyrite oxidation. Covering the pyritic refuse or spoil with an oxygen-consuming layer is probably a better control strategy. Vegetation, soil containing an active microbial population, and decaying organic matter are candidate cover materials. We are planning to conduct tests this year to evaluate the effects of vegetation and mulch on pore gas profiles in coal refuse. Previously reported revegetation studies have generally neglected measuring oxygen availability; instead, the plant growth and water quality were usually monitored. Measurements of gas diffusion rates are also needed to determine the flux of oxygen through the waste materials.

Future work will also include application of available computer models to fit the field data. The best-fit model will then be used to assess the probable impacts of proposed acid abatement techniques.

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CONTROL OF ACID MINE DRAINAGE BY APPLICATION OF BACTERICIDAL MATERIALS

By Patricia M. Erickson,¹ Robert L. P. Kleinmann,²
and Steven J. Onysko³

INTRODUCTION

The kinetics of acid formation are dependent on the availability of oxygen, the surface area of pyrite exposed, the activity of iron-oxidizing bacteria, and the chemical characteristics of the influent water. The principal iron-oxidizing bacterium involved in accelerating pyrite oxidation is Thiobacillus ferrooxidans (9, 15).⁴ The Bureau of Mines has previously reported the results of

full-scale field tests that showed how anionic surfactants (cleansing detergents) can be used to reduce the activity of T. ferrooxidans (12-13) and thereby abate acid formation. After a brief discussion of the literature, this paper will review the surfactant solution technique and report progress on two alternative procedures.

ACKNOWLEDGMENTS

The controlled release surfactant formulations were provided by BFGoodrich and Granger Technologies, Inc. The

assistance of both companies is gratefully acknowledged.

BACKGROUND INFORMATION

The possible involvement of bacteria in the formation of acid drainage was first reported in 1919 by Parr and Powell, who determined that coal inoculated with an unsterilized ferrous sulfate solution produced drainage with higher concentrations of sulfate than did sterile controls (16). The possibility of reducing acid drainage by bacterial inhibition was first considered in 1953 but was rejected as impractical due to probable rapid repopulation (14). Later laboratory studies demonstrated the vulnerability of T. ferrooxidans in coal and coal refuse to anionic surfactants and consequent acidity reductions of 65 to 80 pct (7).

Full-scale tests at active and inactive coal refuse areas demonstrated that sodium lauryl sulfate (SLS) surfactant application could effectively reduce acid production and thereby lower water treatment costs. Sufficient surfactant was applied by hydroseeder to the coal refuse to saturate the adsorptive capacity of the top 1 ft of refuse, based on a laboratory determination (13). The 1-ft-thick treatment zone was selected for several reasons: (1) Oxidation was assumed to occur largely in a near-surface oxygenated zone (3, 6), (2) desorption and downward migration would result in treatment at greater depth, and (3) it was preferred to undertreat rather than overtreat, to prevent significant surfactant concentrations off the site.

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Water quality improved at the test sites in 1 to 3 months. Acidity, sulfate, and manganese decreased 60 to 90 pct; iron decreased 90 to 95 pct (fig. 1). After about 4 months, contaminant concentrations slowly climbed back to

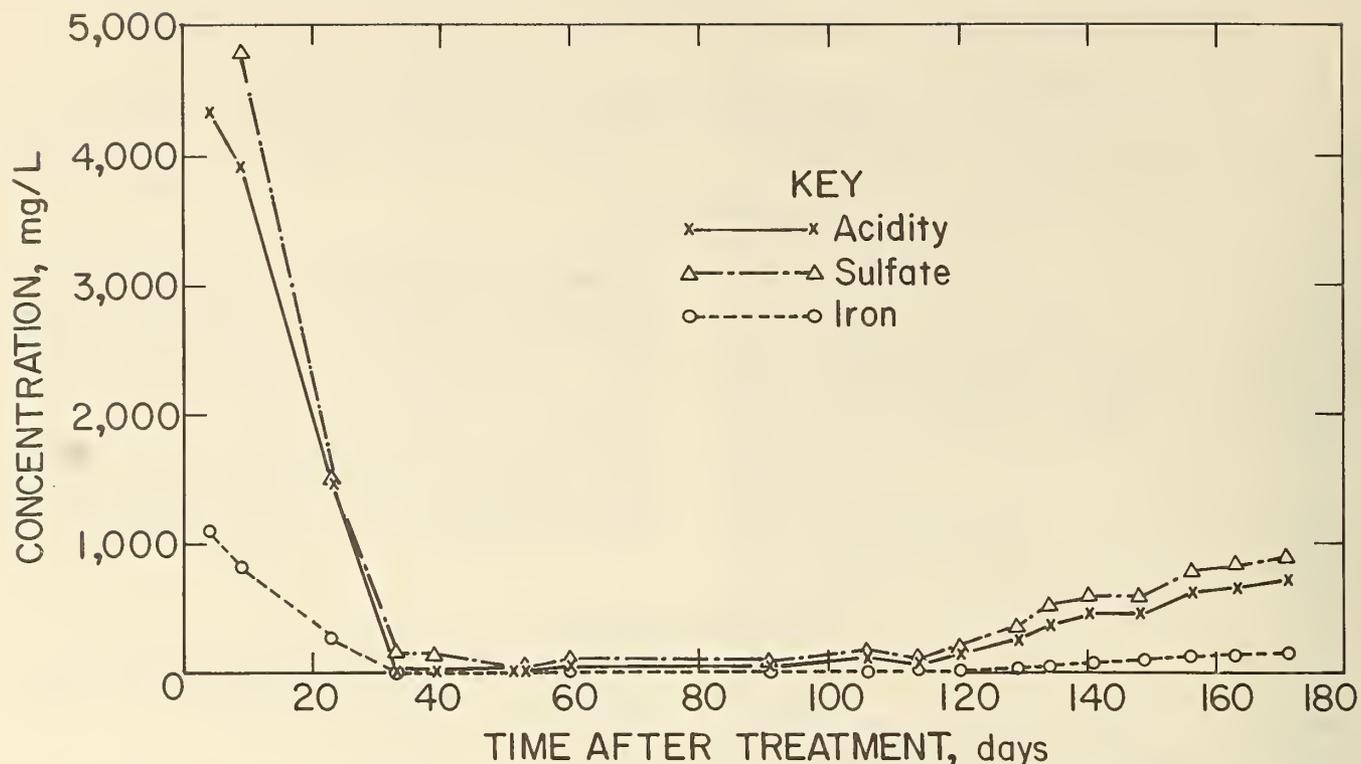


FIGURE 1. - Improvement in drainage quality following surfactant solution application at a site in West Virginia.

previous levels. Effluent surfactant concentrations were negligible.

As a result of these tests, the mining industry has begun to apply surfactants to coal refuse, coal stockpile areas, unreclaimed mine spoil, and waste sulfide rock, with mixed results. One coal company that applied an anionic surfactant two or three times a year to a developing coal refuse pile has had no acid problem over a 5-yr period despite the fact that coal refuse at the plant typically produces acidic drainage within 6 months. At the other extreme are sites where the technique produced no apparent effect or only a short-term improvement in water quality. Some of these failures can be explained simply, such as when the dosage rate or site conditions were obviously inappropriate. At other sites it may never be known why the technique failed to reduce acid production.

A previous report describes in some detail when and how the surfactant should

be applied (13). It is worthwhile to restate the three most significant points:

1. Determine beforehand if the technique is potentially cost effective for the site. Assume a material cost of \$600/acre annually plus the cost of three applications by watering truck or hydro-seeder, a 60-pct decrease in neutralization costs, and a 90-pct decrease in sludge accumulation; if the calculated annual savings are not significantly greater than the assumed costs, the technique is probably not appropriate.

2. The surfactant must reach and adsorb to the pyritic material. If the site is covered with topsoil, a surfactant application will not reach the pyritic material and will therefore accomplish nothing. If an adsorption test indicates that the pyritic material has low adsorptive capacity, the surfactant will wash away rapidly, providing only brief abatement.

3. Owing to slow hydrologic flow-through time or pooled acid water on the old mine floor or in a refuse area, the effect of surfactant treatment may be delayed, masked, or made insignificant. In the case of slow flow-through time (as much as a year at some sites), improvement in water quality at the discharge point cannot occur faster than water flows through the material. If a significant pool of acid water exists, years of continued application of surfactant could be required before an increase in water quality is observed, unless the acid pool is first neutralized or drained.

Application of anionic surfactant solution, although effective in reducing water treatment costs, cannot be regarded as a long-term control measure. Two modifications of the basic approach are being considered by the Bureau of Mines:

1. The surfactant can be rendered less soluble. This has been accomplished using slow-release technology developed for more conventional biocides (2, 10). Controlled release of surfactant over a period of many years may be possible.

2. Other environmentally safe chemicals have been identified that inhibit T. ferrooxidans and that react with acid mine drainage to form slightly soluble precipitates. Thus, these chemicals may form their own slow-release material in the acid-producing environment.

The remainder of this paper will summarize the results of laboratory and pilot-scale experiments and introduce full-scale field tests that are in progress.

SLOW RELEASE OF SURFACTANTS

This approach has been under investigation since surfactants were first considered for field use (7). Early surfactant-rubber formulations reduced acid formation by over 95 pct in a pilot-scale field test but were effective for less than 1 yr (8). Subsequent research has been directed towards extending the release lifetime of the material and field tests of the resultant formulations.

LABORATORY TESTS

Laboratory and pilot-scale tests have been conducted on more than 20 materials manufactured for the tests by BFGoodrich and Granger Technologies. The materials, manufactured prior to 1982, all contained SLS as the active ingredient. The compositions are proprietary, and materials are referred to in this report by alphabetic code.

Laboratory tests were conducted initially to determine which variables most strongly influenced the SLS release rates (11). Every parameter investigated, including nature of matrix, SLS loading,

and surface area, influenced the rate of dissolution.

Figure 2 shows release curves for five formulations for illustrative purpose. The data were obtained by periodically rinsing a 5-g sample with 100 mL deionized water. Leachates were combined to 400 to 500 mL total volumes and analyzed for anionic surfactants by the methylene blue method (1). The percent SLS remaining in the matrix was calculated from the nominal SLS content of the sample and the cumulative mass of SLS extracted. Nominal SLS contents, ranging from 20 to 65 pct of the total sample weight, were normalized to 100 pct for comparison.

All formulations exhibited an initial rapid release of detergent followed by a slower dissolution phase. The first phase was more pronounced in samples having a larger fraction of SLS at or near the pellet surface. For example, samples D and E are cylindrical pellets of the same formulation having diameters of 4.6 and 3.2 mm, respectively. Approximately three times more detergent was dissolved

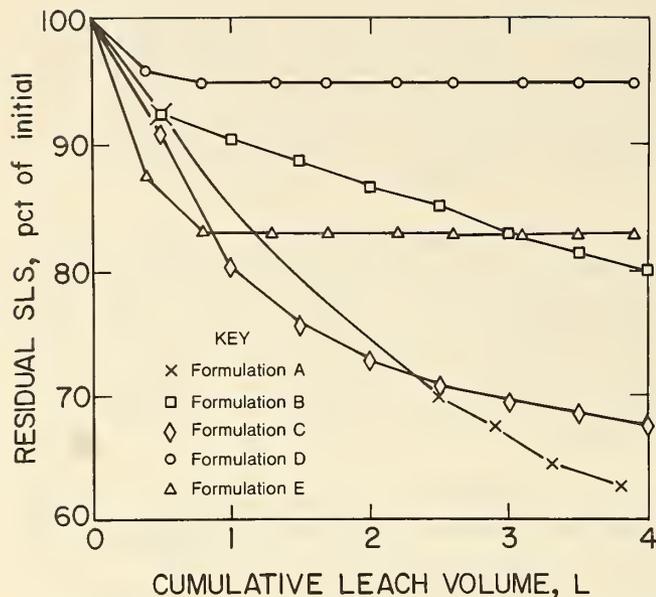


FIGURE 2. - SLS release curves for five controlled-release formulations subjected to intermittent leaching in the laboratory.

from sample E than from sample D in the first liter of leach water (fig. 2).

Under the experimental conditions 4,000 mL is approximately equivalent to 40 in of precipitation. Cumulative extracted SLS at this point ranged from 4 to 38 pct of the total surfactant content of the samples. These values cannot be extrapolated to an expected lifetime, however, because release rates were decreasing over time. In some formulations much of the detergent appeared to be unavailable (curves D and E of figure 2).

While the laboratory results confirmed that surfactant loading, pellet geometry, and matrix type affected SLS release rates, no empirical equations could be developed to predict release curves for new formulations. Outdoor evaluation of potential materials was considered preferable to continued laboratory testing.

PILOT-SCALE TESTS

Pilot-scale testing was conducted outdoors to determine release rates under field conditions. The test area consisted of two small coal refuse piles,

each about 7 ft wide, 12 ft long, and 1.5 ft high at the lengthwise crest. Garden edging was used to divide each slope into six test plots. A rain gage was placed about 15 ft from the refuse piles.

Approximately 250 to 500 g of pellets were spread by hand on each of 21 test plots during February 1983. The coal refuse contained about 5 pct sulfur and produced drainage acidity on the order of 10^4 mg/L prior to the controlled release application. No attempts were made to monitor drainage quality during the experiment.

Periodically, a selected number of pellets were removed at random from each plot and residual SLS content was determined. In one method, the samples were dried to constant weight at room temperature, and SLS release was calculated by weight loss:

$$\text{SLS release} = \text{nominal weight}$$

$$- \text{actual weight}$$

This method is based on the assumption that all weight loss resulted from SLS dissolution. Nominal weights were determined as the mean weight of 10 replicate samples of fresh pellets of the same formulation.

The second method involved aqueous extraction of residual SLS from air-dried samples. The pellets were placed in a minimum of 500 mL deionized water and allowed to equilibrate for several days. The extracts were analyzed for anionic surfactants, and the extracted pellets were air-dried for determination of matrix weight. This method was based on the assumption that all residual SLS could be extracted into deionized water. Values were calculated from actual dry matrix weight and nominal dry matrix weight. A typical release curve is shown in figure 3 for a formulation nominally containing 50 pct SLS by weight. Three calculation methods used to determine residual SLS content usually yielded results that agreed to within 10 pct. This

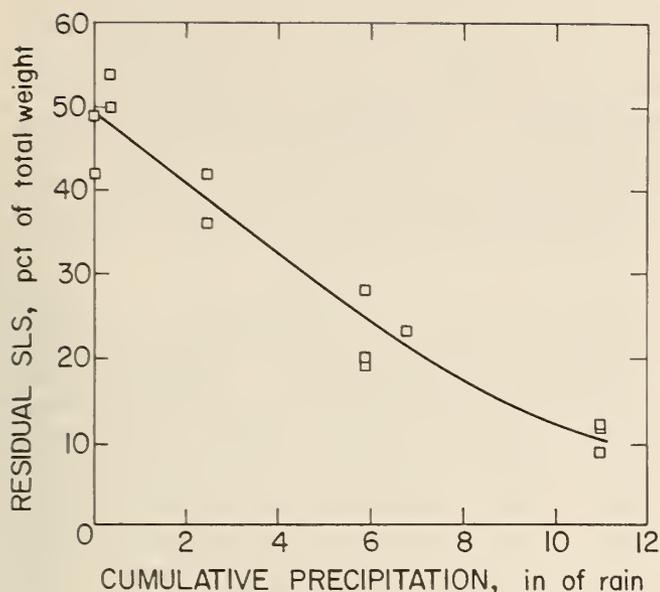


FIGURE 3. - SLS release curve from the outdoor pilot-scale test. Formulation was approximately 50 wt pct SLS. Multiple data points were calculated using weight loss and extraction data.

large variation is due to the indirect measurements mentioned previously. The curves generally followed the same pattern observed in the laboratory study (fig. 2), although SLS release was much more rapid in the field.

Table 1 shows the residual SLS content for all the formulations after 11 in of precipitation. Essentially all the surfactant dissolved from nine of the samples within the 4-month period represented by the tabulated results. Seven of these samples were composed of early matrix formulations. At the other extreme, two samples released essentially none of the surfactant during the pilot-scale test. Several formulations exhibited release rates (residual SLS 65 to 90 pct) that might provide the desired release lifetime of several years.

Negative numbers on table 1 resulted when some of the weight loss assumed to be SLS dissolution was actually loss of matrix. Some of the thinner rubber matrices underwent significant degradation that produced visible shrinkage of the pellets. All samples tested in the

TABLE 1. - Residual SLS after exposure of formulations to 11 in of precipitation on coal refuse test piles

| Plot No | SLS content, pct of initial ¹ | Plot No | SLS content, pct of initial ¹ |
|---------|--|---------|--|
| 1... | -2 | 12... | -15 |
| 2... | 12 | 13... | 18 |
| 3... | 27 | 14... | 20 |
| 4... | -14 | 15... | -7 |
| 5... | 0 | 16... | 98 |
| 6... | -16 | 17... | 65 |
| 7... | -8 | 18... | 20 |
| 8... | -5 | 19... | 47 |
| 9... | 16 | 20... | 125 |
| 10... | -18 | 21... | 83 |
| 11... | 90 | | |

¹Initial SLS content, ranging from 20 to 65 pct, was normalized to 100 pct.

laboratory and in the pilot-scale test exhibited much higher SLS dissolution rates in the latter case. Exposure to ultraviolet light and moist, acidic refuse probably contributed to faster release through degradation of the matrices. Burial of the controlled release pellets beneath a soil cover should retard release rates by reducing degradation and limiting contact with rainfall.

FIELD PROJECTS

The Bureau is participating in one field trial of the controlled release concept (5). The site is a 15-acre isolated ridge in Upshur County, WV, which was mined and reclaimed in three sections. State-of-the-art reclamation techniques, including a clay cap emplaced over the toxic material, were used (19). Surfactant solution and a controlled release surfactant formulation were applied to one section below the clay layer. Since completion of reclamation during spring 1983, seeps and surface runoff have been monitored. To date, the post-mining hydrology has not developed sufficiently to allow characterization of drainage quality from the various sections.

Selection of the controlled release material was based on early laboratory data; we now know that the surfactant is released from the matrix in less than 1 yr when the pellets are applied to the surface of acidic material. Exposed to no sunlight and less water under the clay cap, detergent release should be significantly slowed.

Both Goodrich and Granger are now developing new formulations to optimize surfactant release rates. The former company is currently conducting field tests of 1984 formulations that we have not tested (4). In the oldest test, the controlled release pellets were applied during summer to a portion of a coal refuse site prior to application of seed and soil to the entire site. At the end of the first growing season, there was good vegetation cover on the treated refuse, compared with extensive acid burnout areas on the untreated portion.

ORGANIC ACID INHIBITORS

We began to investigate another alternative for control of T. ferrooxidans when the limitations of the solution surfactant technique became apparent. For materials having low affinity for surfactant and sites having high water flow rates, a less soluble inhibitor was needed. The concept was to identify organic compounds with the following properties:

1. Toxic to T. ferrooxidans but innocuous to other organisms.
2. Sparingly soluble in AMD or neutralized mine drainage.
3. Actively bactericidal once redissolved or in response to acid production.

Preliminary experiments consisted of a survey of 25 organic compounds, which might be inhibitors and which might precipitate as sparingly soluble compounds in AMD. These experiments yielded two candidate compounds: sodium benzoate and potassium sorbate. We found that 0.1-pct solutions of either salt formed organic

precipitates when added to synthetic AMD in the pH range of 4 to 5. The precipitates probably consist of ferric or ferrous salts of the organic acids. Further testing was encouraged by the fact that these organic acids are used as food and beverage preservatives and hence should be environmentally safe.

Laboratory tests of bacterial inhibition have previously been reported (18). In solution cultures of a pure strain of T. ferrooxidans, bacterial activity was monitored as the utilization of ferrous iron in the medium. The bacteria derive energy from oxidation of ferrous iron. Figure 4 illustrates the results in uninhibited bacteria culture, in sterile medium, and in two bacterial cultures containing benzoic acid. We found that 10 mg/L of either benzoic or sorbic acid was sufficient to decrease the rate of ferrous iron oxidation to that of sterile controls.

PILOT-SCALE TESTS

Bactericidal effectiveness of potassium sorbate, sodium benzoate, and SLS was investigated for reducing acid production from fresh and weathered refuse;

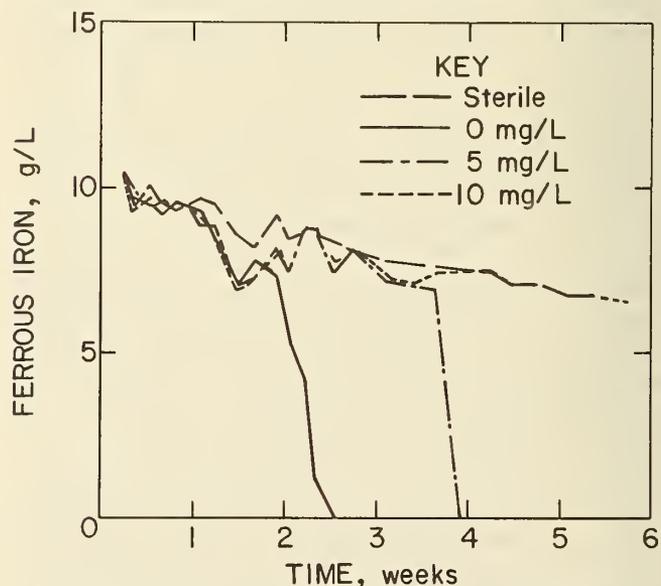


FIGURE 4. - Ferrous iron oxidation by T. ferrooxidans, as a function of added benzoic acid. The sterile culture indicates the rate of abiotic oxidation.

preliminary results have been published previously (17).

Drums filled with 200 kg of fresh coal refuse were leached weekly by saturating the material for 24 h with tap water. The drained leachate was analyzed for pH, acidity, total dissolved iron, and sulfate. In the first week of the experiment, 24 L of inhibitor solution replaced the water in six of the drums. The three inhibitors were each tested at concentrations of 500 and 5,000 mg/L (equivalent to 60 and 600 mg chemical per kilogram of refuse). Ten drums of refuse were "treated" with tap water and used for experimental control.

The low doses of treatment chemicals were marginally effective, delaying acid production 1.5 to 5 weeks after leachate from the control barrels became acidic (fig. 5). High treatment doses of 5,000 mg/L were effective for 8 to 10 weeks (fig. 6). Potassium sorbate yielded the best results in both treatment series.

At low dosage rate, sorbate was least expensive on the basis of cost per week of delayed acidification. However, at the high dosage rate, the duration of the treatments were more similar and the

chemical of choice would probably depend on cost per pound. Approximate bulk prices are \$0.90/lb for sodium benzoate, \$1.67/lb for SLS, and \$3.52/lb for potassium sorbate. Field trials will be required before an accurate cost analysis can be made. The longevity of SLS treatment under field conditions is about twice as great as in the high-dosage pilot-scale test; the experimental conditions of extremely high leaching rates probably underestimate the duration of all three inhibitors.

After 22 weeks of weathering, 9 of the 10 control barrels were treated with the chemical inhibitors to determine their effectiveness in the highly acidic environment of aged refuse. Drainage acidity levels were approximately 8,000 to 14,000 mg/L at the start of this experiment. During the 22-week leaching program, drainage from the untreated barrel retained as a control became 70 pct less contaminated. The easily oxidizable pyrite may have been consumed during the initial 22 weeks of weathering; cumulative sulfate load data indicated approximately 10 pct of the total pyrite had been oxidized before treatments were applied to the aged refuse.

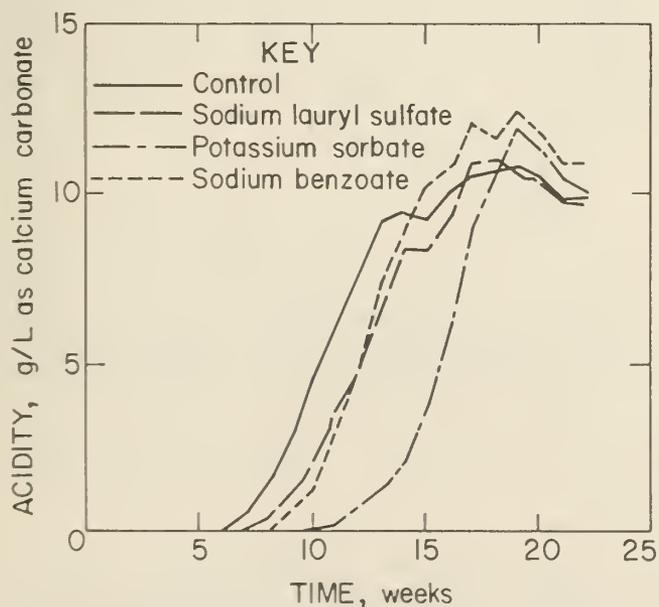


FIGURE 5. - Acidity levels in leachate from coal refuse treated with 500 mg/L of chemical inhibitor.

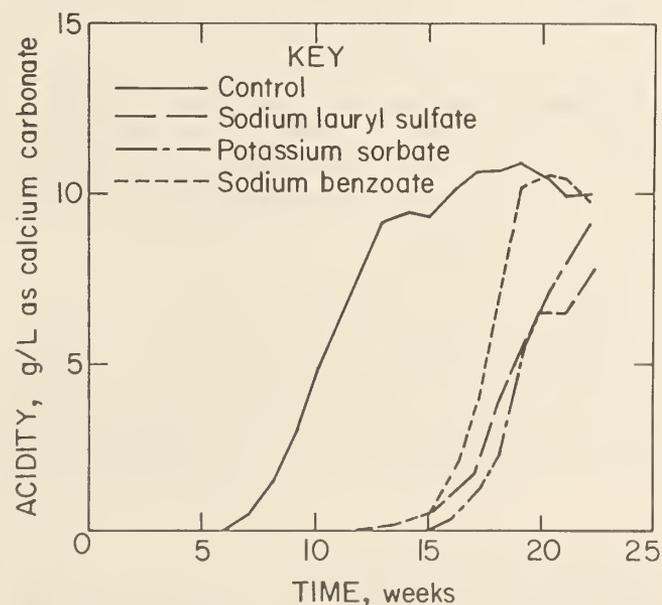


FIGURE 6. - Leachate acidity from fresh coal refuse treated with 5,000 mg/L of chemical inhibitor.

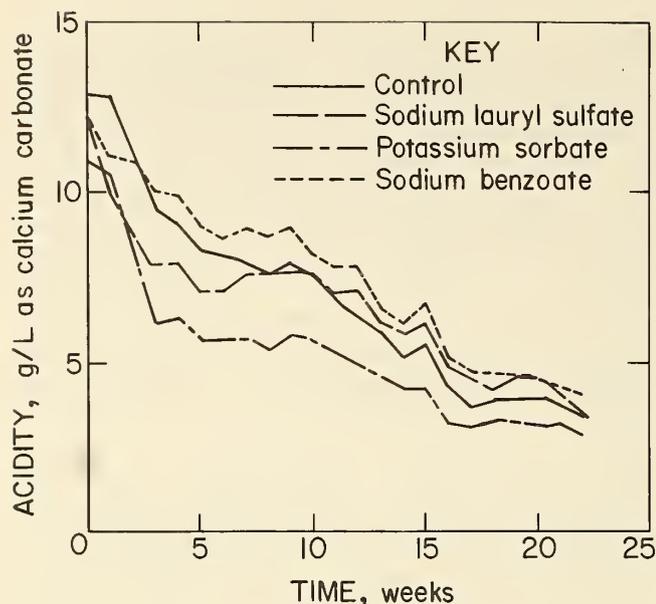


FIGURE 7. - Effect of low doses of treatment chemicals on weathered coal refuse leachate compared with leachate from untreated refuse.

Superimposed on the trend of decreasing contaminant concentrations, additional improvements in drainage quality were observed (figs. 7-8). At the low dosage rate of 500 mg/L, only potassium sorbate produced significantly better drainage than did the control. All three chemicals were effective at the 5,000-mg/L dosage rate. Cumulative acid loads (fig. 9) were 17, 29, and 38 pct lower for sodium benzoate, potassium sorbate, and SLS treatments, respectively, at the end of 22 weeks than in the control drainage. Seven weeks after treatment, when the inhibitors were most effective, cumulative acid loads were 45 to 62 pct lower in the high treatment dose leachates than in the control leachate.

A field test is now in progress at a revegetated mine site in West Virginia. Dry potassium benzoate powder was applied to the surface on 2 acres overlying the major acid-producing zone. Water quality is being monitored in the vadose zone, in

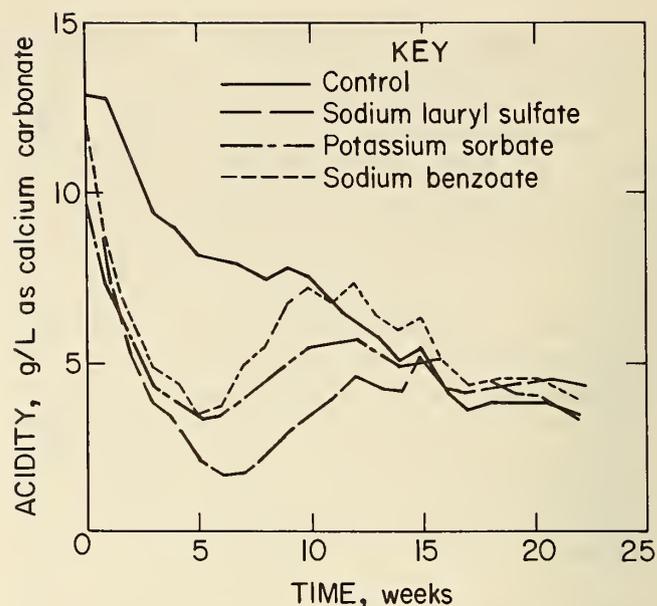


FIGURE 8. - High doses of three treatment chemicals reduced acidity of weathered coal refuse leachate, compared to leachate of untreated coal refuse.

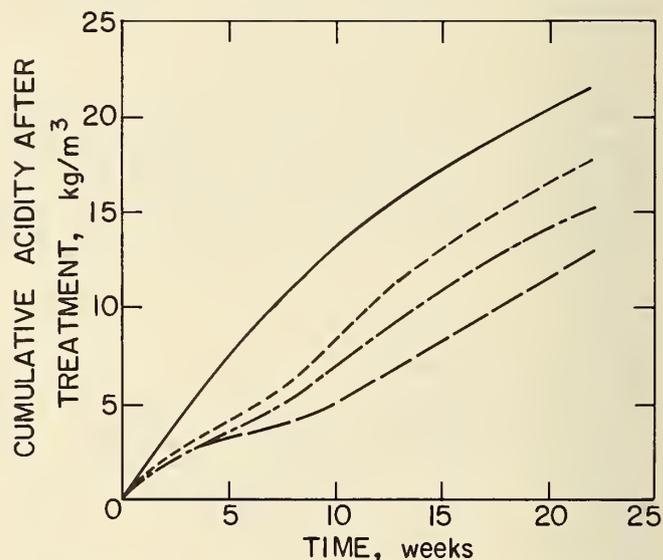


FIGURE 9. - Cumulative acidity produced by weathered coal refuse after application of high doses of inhibitory chemicals. Curve symbols as in figure 8.

the saturated zone, and at the discharge seep.

SUMMARY

Preliminary experiments were conducted on two alternatives to the surfactant solution technique for controlling acid

drainage. Controlled release of surfactants appears to be a feasible means of extending the bactericide lifetime.

Further work, in the form of field tests, is needed to determine the cost effectiveness of this method.

The organic inhibitors, benzoate and sorbate, were of the same general order of effectiveness as surfactant solution in pilot-scale tests. There may be some

cost advantage in using benzoate; a field test of this compound is in progress. Under moderately acidic conditions where adsorption is unlikely, such as in some underground mines, the metal-organic salt precipitate may have further advantages in extending the duration of acid control.

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ALKALINE INJECTION: AN OVERVIEW OF RECENT WORK

By Kenneth J. Ladwig,¹ Patricia M. Erickson,² and Robert L. P. Kleinmann³

INTRODUCTION

Injection of alkaline fluid into surface mine spoil to control acid mine drainage (AMD) is a procedure generating considerable interest in Pennsylvania. At least six different mine companies or contractors have attempted some form of injection in the last 2 yr, and many more are considering its use. This paper gives a brief overview of the current status of alkaline injection and of the Bureau of Mines injection research.

Introduction of alkalinity is the standard method of mitigating acid discharges. Surface alkaline loading prior to flow through the spoil has been used to slow down the acid-production process (1, 5).⁴ More commonly, alkalinity is added to the discharge to neutralize existing acidity with conventional water treatment (4).

The premise of alkaline injection is the in-place neutralization of acid water stored in the spoil. In this respect, alkaline injection is not much different than conventional water treatment. Alkaline materials that have been used for injection are sodium hydroxide, hydrated lime, and sodium carbonate, all of which are commonly used in AMD water treatment. Some of the potential advantages of injection over conventional water treatment follow:

1. Raising the pH of the spoil water may result in the precipitation and filtering of some metals prior to discharge,

decreasing sludge storage and removal requirements.

2. The metal precipitates may coat pyrite surfaces, "armoring" them from further chemical weathering.

3. The alkaline environment within the spoil would be less favorable to continued pyrite oxidation.

4. The high-pH environment would limit metal leaching within spoil.

5. Spoil water that "leaks" through the mine floor discharges to the ground water system untreated. Alkalinity introduced into the spoil water reservoir may offer at least partial treatment of the leakage and decrease overall ground water degradation.

6. Treatment by alkaline injection could be done on an intermittent basis, lowering labor costs.

While the premise of alkaline injection is straightforward, implementation is not. The extent to which any of the above listed advantages are realized is not known. Of the six attempts with which we are familiar, none have yet substantially improved spoil seep water quality. Unfortunately, documentation of these injections was generally incomplete. For this reason, the Bureau initiated a study to evaluate the technical merit of the injection approach.

Described in the following section are two injection programs for which a reasonable amount of documentation was available. At the Fayette site, the Bureau monitored the results of an injection performed by Kaiser Refractories. Much of the data were generously supplied by Bernard Leber of Kaiser Aluminum and Chemical Corp. and Mike Popchak of the

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Kaiser Refractories division. Descriptions and data for the Clearfield site were kindly provided by Jim McNeil of

Al Hamilton Contracting Co. Bureau research on alkaline injection is described in the final section.

EXAMPLES OF ALKALINE INJECTIONS

FAYETTE COUNTY, PA

A lime slurry injection project was conducted at a surface mine in Fayette County in 1983. The 111-ha Fayette site was mined at various times between the mid-1950's and late 1970's. At present, about one-half of the site has been re-vegetated (fig. 1). Spoil thickness ranges from 15 to 30 m.

The site has several toe-of-spoil seepage areas, one of which (seepage area A, figure 1) discharges directly onto the flood plain of a small, perennial stream. Seepage area A has two major seeps, 16 and 18. The proportion of flow from each of these seeps varied throughout the study, but in 1983, flow at seep 18 was generally much higher than at seep 16. Owing to steep topography and space limitations, installation of conventional

treatment facilities and settling ponds between seepage area A and the stream was considered impractical.

In February 1983, Kaiser initiated an injection program in seepage area A. Fifteen injection wells were installed approximately 90 m up gradient from the seepage area (fig. 1). The wells were drilled an average of 18 m to the mine floor. Two-inch-diameter polyvinyl chloride well pipe was placed in each hole and cemented at the surface. The lower 16 m of the pipes were perforated with 0.32-cm holes. Water levels were 3 to 5 m above the mine floor.

Between February and October 1983, 119 tons of hydrated lime were pumped into the wells in slurry form. The slurry concentration ranged from 4 pct lime during the early stages of injection

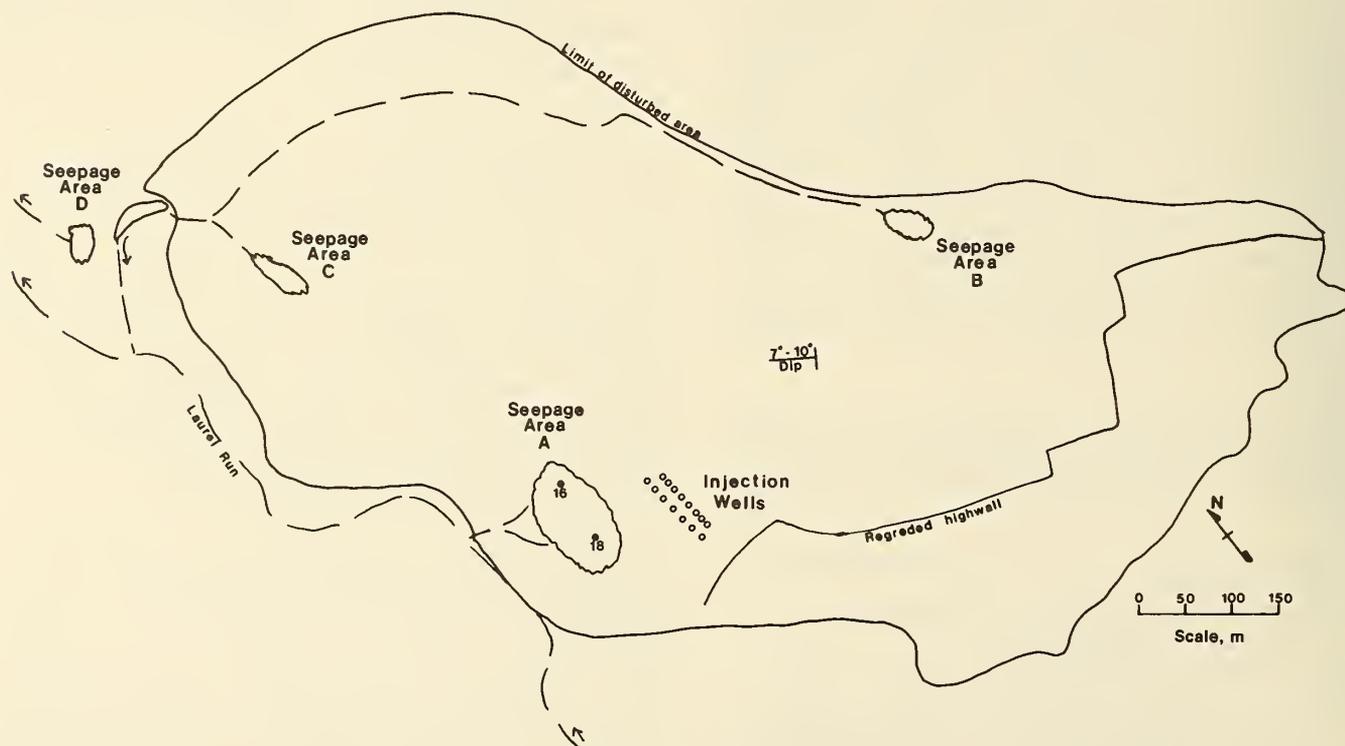


FIGURE 1. - Map of surface mine study site in Fayette County, PA.

to 0.4 pct during the latter stages. Injections were performed weekly at a rate of 7 to 42 tons of lime per week.

The transit time from the injection wells to seepage area A was estimated by analyzing the movement of a sodium tracer in the lime slurry (fig. 2). The first arrival of the injected sodium at seepage area A was about 4 months after the beginning of the injection. Peak concentrations occurred 7 to 9 months after the beginning of the injection. Concentrations began tailing off following the cessation of injection in October. Peak sodium concentrations at the seeps indicated a 1:3 ratio of injected water to spoil water.

Trends in pH and acidity for seeps 16 and 18 are shown in figures 3-6. Although very few pre-injection data were available, there did appear to be a modest improvement at seep 16 beginning about 7 months after the initial injection. The pH at seep 16 increased by 1/4 to 1/2 of a pH unit, while the acidity decreased by 30 to 40 pct. However, no significant changes in water quality were observed at seep 18. As seep 18 comprises a larger percentage of the total flow from seepage area A, the overall impact of the injection was minimal.

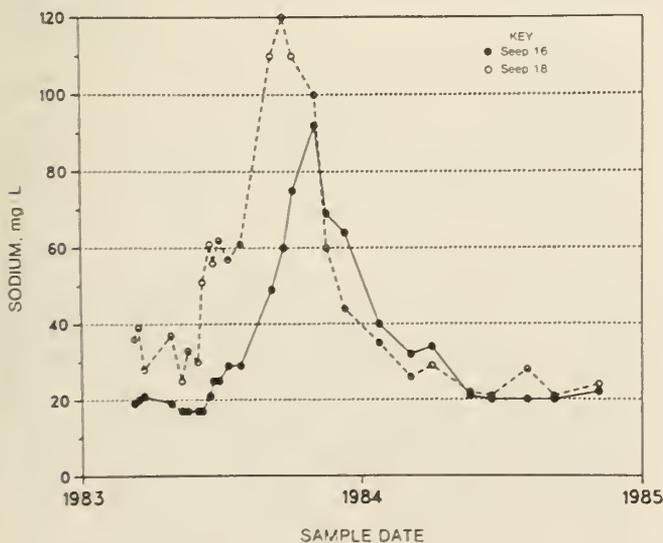


FIGURE 2. - Sodium concentrations at seeps 16 and 17.

Assuming complete reaction, 119 tons of lime is capable of neutralizing 36 million gal of water with an average acidity of 1,000 mg/L. Because the total discharge from seepage area A in 1983 was less than 20 million gal, the high lime dosage should have had a profound impact on seep quality.

The explanation of the poor results may lie in the inefficient mixing of the lime with the spoil water. The solubility of lime in deionized water is 1,600 mg/L at 20° C (1). Saturation with respect to lime would produce a solution of 0.16 pct dissolved lime. Because the lime slurry was mixed at concentrations of 0.4 to 4 pct, 60 to 95 pct of the lime was in suspension rather than solution. At a treatment plant using mixers to induce turbulent flow, much of the suspended lime might eventually contact acidic water and participate in the neutralization reactions. However, the injected fluid was not subjected to continuous turbulent flow and very likely did not mix efficiently with the spoil water. In the absence of turbulence and mixing, suspended lime will settle rapidly. Enhanced solution will occur only along the slurry-spoil water contact surface, considerably slowing the rate of lime consumption. As a conservative estimate, over 50 pct of the 119 tons of lime at the Fayette site may have settled out of suspension shortly after injection.

The lime remaining in solution mixed with the spoil water at a 1:3 dilution rate at the peak injection period, as previously determined from the sodium data. Assuming an initial concentration of 1,600 mg/L dissolved lime in the injection fluid, the maximum lime concentration following 1:3 mixing with the spoil water is 400 mg/L. This amount of lime is capable of neutralizing only 490 mg/L acidity.

These calculations are intended to illustrate in a general sense the controls placed on the system by the solubility of lime and the low velocity of ground water flow. Although these numbers are in

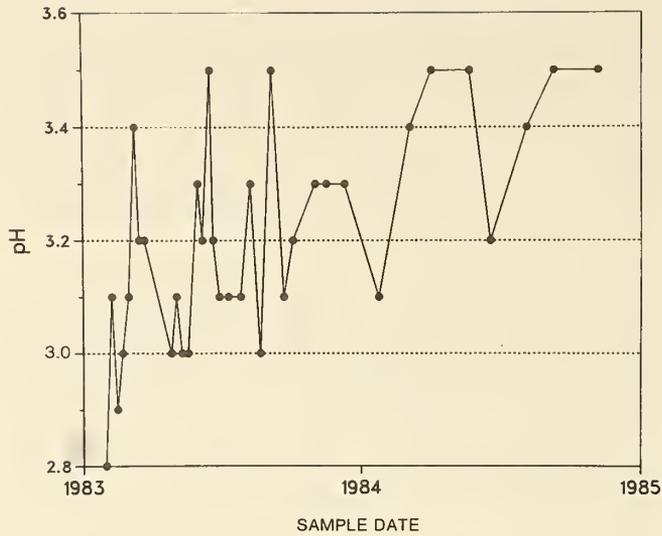


FIGURE 3. - Seep 16 pH. Lime injection began in February 1983.

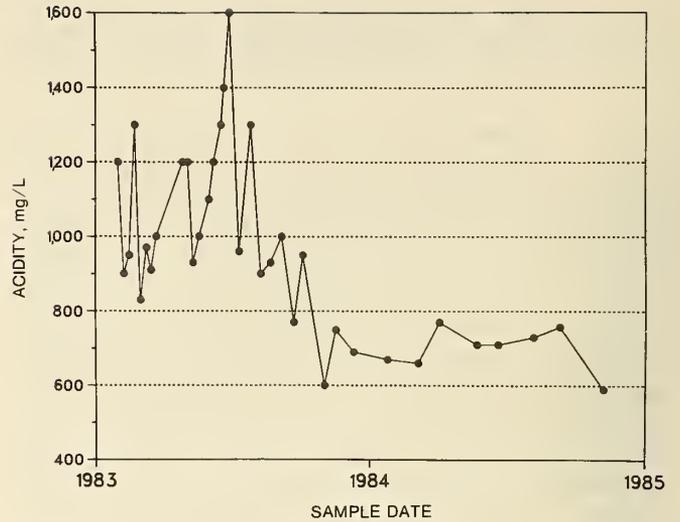


FIGURE 4. - Seep 16 acidity.

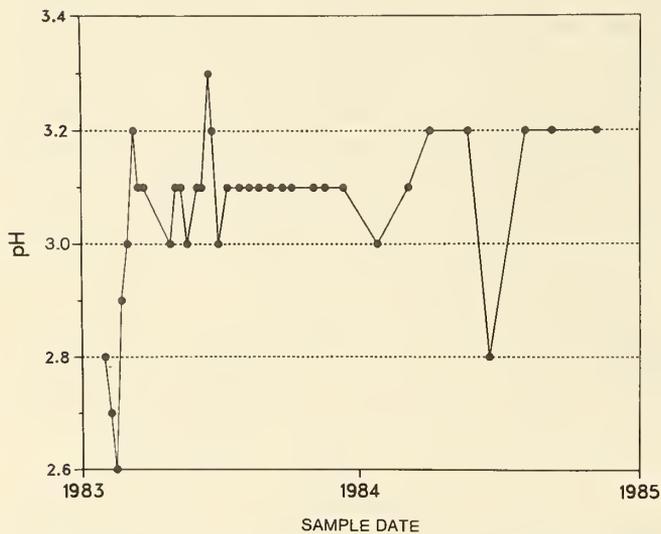


FIGURE 5. - Seep 18 pH. Lime injection began in February 1983.

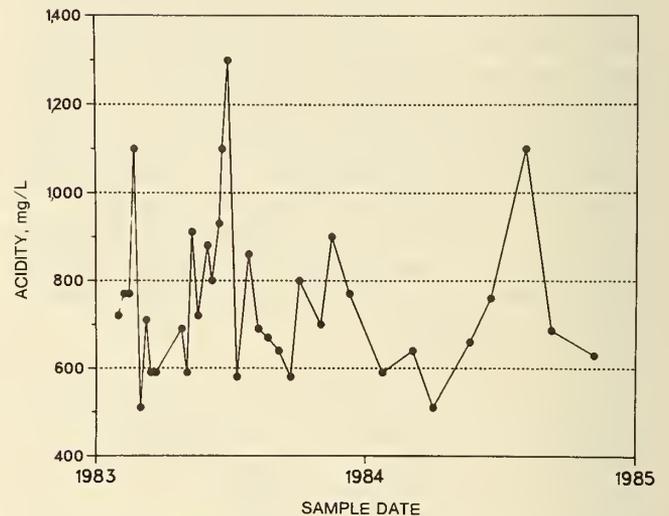


FIGURE 6. - Seep 18 acidity.

reasonable agreement with the data from seep 16, they do not explain why no change was observed at seep 18. Ongoing work at the site is designed to better describe the hydrologic differences between the two seeps.

CLEARFIELD COUNTY, PA

A hydrated lime injection program is also being conducted by a mine company at a site in Clearfield County, PA. The

approach taken at the Clearfield site was similar to that described for the Fayette site. In June 1982, 22 injection wells were drilled an average of 15 m to the mine floor. The wells were located about 75 m upgradient of the toe-of-spoil seep. Approximately 3,000 gal of 4-pct lime slurry are pumped into each well on a monthly basis from April through November. Due to cold temperatures, no injections occur between December and March.

Preliminary data indicate that toe-of-spoil seeps at the Clearfield site have not exhibited appreciable improvement since injection began. However, downstream monitoring does indicate improvement in the receiving stream. In the last 2 yr, there have been reductions in acidity and iron concentrations at the downstream monitoring station.

The lack of improvement at the toe-of-spoil seeps may again be a result of the low solubility of lime, as described for the Fayette site. Why then did the downstream water quality improve?

Owing to other modifications in the watershed contemporaneous with the

injection, it is not possible at this time to attribute the downstream water quality improvement solely to the injection program. If the improvement is related to the injection, it may reflect an improvement in ground water quality below the mine floor. Stored spoil water leaking through the mine floor may contain a high alkaline load following contact with the settled lime. The mine water recharges the underlying ground water system and eventually discharges by diffuse seepage to the receiving stream, resulting in improved water quality downstream from the site. While this is purely conjecture at this time, the downstream water quality improvement certainly merits further study.

BUREAU OF MINES INJECTION PROJECT

The widespread interest in injection technology, along with the limited success to date, prompted a Bureau of Mines study of the injection approach. While alkaline injection is not a cure-all for AMD problems at surface mines, the selective use of injection in combination with other abatement procedures may offer several benefits. Possibly the most valuable potential benefit is the renovation of contaminated ground water below the mine floor, a problem not currently addressed by any other treatment technology.

Critical to the success of alkaline injection is good mixing of the alkaline fluid and the contaminated spoil water. This requires detailed understanding of site hydrology and acid-producing characteristics, including source material, flow paths, flow rates, flow volumes, and spoil-water chemistry. We believe that inadequate mixing, largely due to the low solubility of lime and low flow velocities, was one of the primary shortcomings of the previous injection attempts. Our approach will differ from these attempts in two ways.

First, sodium carbonate solution will replace lime slurry as the alkaline

fluid. Sodium carbonate is about 100 times more soluble than lime (2), allowing mobility of a greater fraction of the alkaline load. The concentration of the sodium carbonate solution will be selected to maximize alkaline loading with minimal density contrasts between the injected fluid and the spoil water.

Second, injection wells will be situated at least 300 m upgradient from the seep to enhance dispersion of the injected fluid. Dispersion in porous media is directly related to distance along the flow path (1). Placing the injection wells on the upgradient end of the site will allow for maximum mechanical dispersion of the alkaline fluid. This will also minimize the possibility of the alkaline fluid migrating directly to the seep as an unreacted plume. Monitoring wells will be sampled to track the progress of the injected fluid in the spoil.

Bureau work to date has consisted of pilot-scale testing of lime and sodium carbonate, and preliminary site evaluation for a full-scale field test. In the pilot-scale tests, sodium carbonate was considerably more mobile than lime. The full-scale field test began in spring of

1985 at the Fayette County site described earlier.

In addition to the field test, we hope to conduct laboratory column studies to simulate and study in detail the reactions between the injected fluid and

spoil water. In particular, we are interested in observing the reaction products--gaseous, aqueous, and solid--and evaluating their effect on the metal ion chemistry and pyrite oxidation system. This work is tentatively scheduled to begin by mid-1985.

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COMPARATIVE TESTS TO REMOVE MANGANESE FROM ACID MINE DRAINAGE

By George R. Watzlaf¹

INTRODUCTION

The Surface Mining Control and Reclamation Act of 1977 mandates that mine drainage discharge water meet quality standards for pH, iron, manganese, and total suspended solids (11).² These standards are shown in table 1. Typical treatment of acid mine drainage involves addition of an alkaline material (such as lime or sodium hydroxide), natural or mechanical aeration, and settling. When mine drainage is neutralized to a pH near 7, the ferrous iron oxidizes and forms an iron sludge, Fe(OH)₃. This treatment satisfies the effluent standards for pH and iron, but may not remove much manganese from the water.

Typical acid mine drainage contains 1 to 8 mg/L manganese, but concentrations of 50 to 100 mg/L are not uncommon (6, 9). At present, most mine operators with manganese problems are using excess alkalinity to raise pH of the mine water to

about 10.0 to precipitate manganese. During the precipitation of manganese, as MnO₂, acid is produced and the pH of the water decreases. Whether or not the pH will fall below 9.0 depends on individual mine water characteristics. If the pH remains above 9.0 the mine operator has two options: apply to State authorities for a variance to discharge high-pH water, or reacidify the high-pH water. An alternative to excess alkalinity is the use of chemical oxidants such as chlorine gas, hypochlorite salts (sodium and calcium), ozone, potassium permanganate, or hydrogen peroxide (2-3, 9). These oxidants can oxidize soluble manganese to insoluble MnO₂ at pH values within the regulatory criteria.

Based on a review of the literature on manganese removal, three chemical treatments were selected for field testing: excess alkalinity, sodium hypochlorite, and potassium permanganate. The selection of these treatment methods was based on ease of use, costs (capital and operating), availability, effectiveness, and likelihood of acceptance by the mining industry.

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²Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

TABLE 1. - Effluent limitations

| | Maximum allowable | Average of daily values for 30 consecutive discharge days |
|---------------------------------|-------------------|---|
| Iron, total.....mg/L.. | 7.0 | 3.5 |
| Manganese, total.....mg/L.. | 4.0 | 2.0 |
| Total suspended solids...mg/L.. | 70.0 | 35.0 |
| pH..... | 6.0-9.0 | 6.0-9.0 |

EXTENT OF MANGANESE IN ACID MINE DRAINAGE

Mine drainage discharges that require treatment for removal of manganese are widespread throughout the Eastern U.S. coalfields. A study of mine discharges containing manganese was conducted by Pennsylvania's Department of Environmental Resources for Jefferson, Clearfield, Clinton, Venango, and Clarion Counties. This study found manganese concentrations averaging 75 mg/L and ranging from 20 to 170 mg/L. In southwestern Pennsylvania, mining of the Waynesburg seam can result in manganese concentrations over 200 mg/L. In eastern Kentucky manganese concentrations of 10 to 100 mg/L are common. Mine discharges in southern Illinois typically have 5 to 10 mg/L of manganese, but values in excess of 300 mg/L have been reported (5).

Sodium hypochlorite solution is being used to remove manganese from mine drainage in eastern Kentucky. Two sites were visited used a combination of sodium hypochlorite and sodium hydroxide. At one site, the operator initially used calcium hypochlorite briquettes but had difficulty controlling the quantity of chemical added to the system. At the other treatment facility, a flocculant was

required to achieve adequate settling of the precipitated sludge.

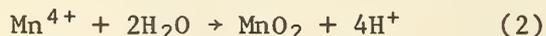
Potassium permanganate has been used to treat mine drainage at a site in Pennsylvania. Granular potassium permanganate was added directly to the sodium hydroxide solution. The operator at this site achieved good results for a few months but had difficulty maintaining the proper dosage. The operator is now using excess alkalinity to remove manganese.

Bureau personnel visited two sites in Pennsylvania that use the excess alkalinity method for removal of manganese. One operator uses sodium hydroxide in liquid form, and the other adds hydrated lime via a flash mixer. At both sites the operators add alkali to raise pH to about 10.0 and discharge at a pH near 9.0.

With adequate control, all three treatment methods can be effective in reducing manganese concentrations below effluent limitations. To directly compare the costs and effectiveness of these methods, they must be used to treat the same mine water.

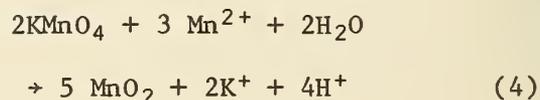
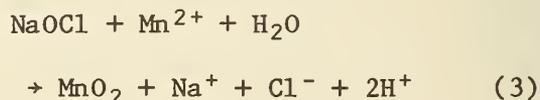
CHEMISTRY OF MANGANESE REMOVAL

The chemistry for removing manganese with pH adjustment is very similar to that of iron removal, but oxidation of Mn^{2+} to Mn^{4+} requires higher pH values than are required for iron oxidation. To remove manganese, the following two reactions are promoted:



The rate of manganese oxidation is pH dependent and extremely slow at pH values less than 8.0. Reduction of manganese concentrations below 2 mg/L can occur at pH 8.4 (8), but most mine drainages require pH values over 9.5 (5, 7-9).

To remove manganese at near-neutral pH, a chemical oxidant must be used. Oxidizing agents commonly used in water treatment include chlorine, sodium hypochlorite, calcium hypochlorite, potassium permanganate, hydrogen peroxide, and ozone. The following reactions show how sodium hypochlorite ($NaOCl$) and potassium permanganate ($KMnO_4$) each oxidize dissolved manganese (Mn^{2+}) and convert it to manganese oxide (MnO_2):



Because these chemicals will oxidize both Fe^{+2} and Mn^{+2} in acid mine drainage, it is reasonable to first oxidize Fe^{2+} , by increasing pH and aerating, before adding an oxidizing agent. This reduces the requirement for the chemical oxidant and lowers costs. Also, some manganese is removed by coprecipitation with iron even at near-neutral pH, by sorption to $\text{Fe}(\text{OH})_3$ (7), further reducing the chemical oxidant requirement.

FIELD TESTS

The purpose of the field tests was to determine the most economic chemical treatment that would successfully reduce manganese concentrations below 2 mg/L. All testing was conducted at the same surface mine site in southwestern Pennsylvania. Based on ease of use, costs (capital and operating), availability, effectiveness, and likelihood of acceptance by the mining industry, sodium hypochlorite, potassium permanganate, and excess alkalinity were chosen for field testing.

The field site is an active surface mine with over half of the site mined and reclaimed. Existing treatment consists of sodium hydroxide (NaOH) addition with two settling ponds connected in series (fig. 1). Raw water contains concentrations of manganese consistently over 100 mg/L. Flow at this site is seasonal and averaged 40 gal/min during the testing period.

Three series of tests were conducted. In all tests, the raw water was first treated with NaOH for pH adjustment and some iron oxidation before adding any other chemicals. Series 1 used chemical dosages based on reaction stoichiometry for complete removal of manganese and iron. Series 2 used varying amounts of each chemical treatment to determine the minimum dosage required to reduce manganese below 2 mg/L. The water in series 2, which was first neutralized with NaOH, still contained high ferrous iron concentrations. Therefore, series 3 tests repeated the procedure of series 2, but used additional aeration to reduce iron levels before further chemical treatment. Reduced iron levels were

Regardless of the method used, controlling the addition of chemical treatment is very important. Many variables influence the removal of iron and manganese, and experimentation with different chemical dosages may be required to achieve optimal results. As the quantity and quality of AMD change, the dosage of the treatment chemical must change to ensure effective manganese removal.

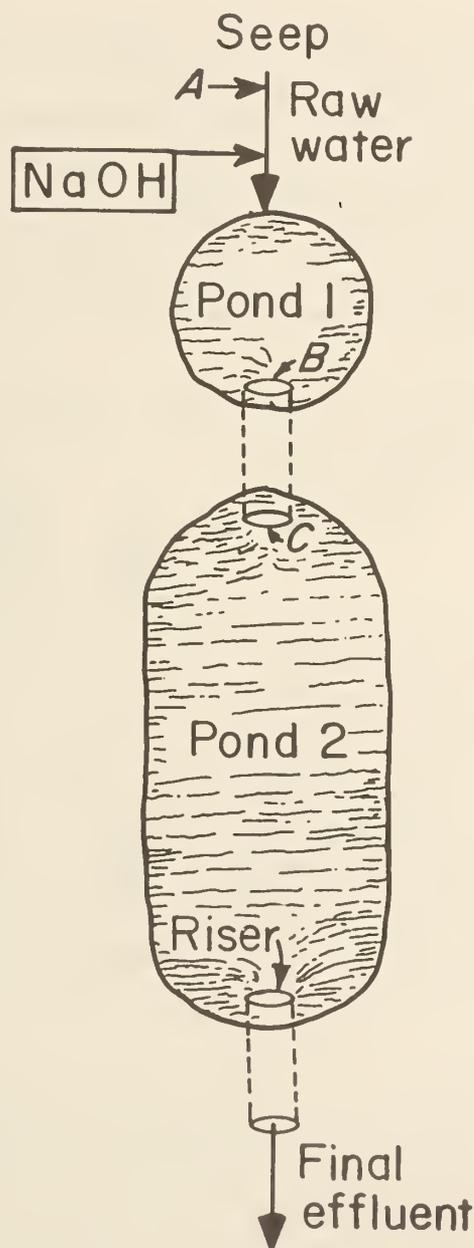


FIGURE 1. - Water treatment system at field site.

expected to lower the chemical requirements for sodium hypochlorite and potassium permanganate.

All costs presented in this study were based on bulk purchases of each chemical, including delivery. The costs for 20-pct sodium hydroxide and 15-pct sodium hypochlorite solutions were \$0.28/gal and \$0.80/gal, respectively. The cost for granular potassium permanganate was \$1.34/lb.

SERIES 1

In these tests, theoretically calculated dosages of the three chemical treatments were used to determine if they would effectively reduce manganese concentrations below 2 mg/L. Raw water was first treated with NaOH to raise pH to 8.8 with some of the precipitated solids settling in pond 1 (fig. 1). The quality of the raw water and water after the initial NaOH treatment and settling is shown in table 2.

TABLE 2. - Water quality for test series 1

| | <u>Raw</u> <u>water</u> | <u>After</u> <u>initial</u> <u>NaOH</u> <u>treatment</u> |
|--|----------------------------|---|
| pH..... | 5.3 | 8.8 |
| Acidity (as CaCO ₃) mg/L.. | 53.0 | - |
| Alkalinity (as CaCO ₃) mg/L.. | - | 82 |
| Fe ⁺²mg/L.. | 230 | 92 |
| Total Fe.....mg/L.. | 230 | 160 |
| Mn.....mg/L.. | 120 | 97 |

Sodium hypochlorite, potassium permanganate, and sodium hydroxide were added as 10-, 3-, and 20-pct solutions, respectively, at point B (fig. 1). Each chemical was gravity-fed from 55-gal drums through plastic tubing. Dosage was regulated with a polyvinyl chloride needle valve. Samples were collected in a 5-gal container at point C (fig. 1). This container was then partially submerged in pond 2 (to maintain pond temperature) and left to settle for 23 h. After the settling period, samples of the supernatant liquid were taken and analyzed.

Series 1 consisted of six tests: two controls, two excess alkalinity, one sodium hypochlorite, and one potassium permanganate. Table 3 shows the results of these tests. Iron was reduced below effluent standards in all six tests. The two controls did not reduce manganese below effluent limitations, but some manganese was removed, probably by sorption to Fe(OH)₃. Also, some manganese oxidation may have occurred since pH in these tests was 8.4 and 8.6. The tests involving additional chemical treatment all reduced manganese concentrations below 2 mg/L.

The cost of each chemical treatment (table 3) indicates that excess alkalinity was the most cost-effective method in this series. However, the dosages of NaOCl and KMnO₄ used in these tests may have been greater than the actual minimum effective dosage. Series 2 tests were performed to determine these minimum chemical requirements.

TABLE 3. - Results of test series 1

| Test | Water quality after 23 h of settling | | | Chemical cost per 1,000 gal of water |
|----------------------------------|---|-------------------|-------------|---|
| | pH | Total Fe, mg/L | Mn, mg/L | |
| Control 1..... | 8.6 | 0.1 | 16 | \$1.06 |
| Control 2..... | 8.4 | 1.2 | 27 | .80 |
| Excess alkalinity 1 (to pH 11.3) | 11.0 | .6 | .6 | 1.55 |
| Excess alkalinity 2 (to pH 10.3) | 9.4 | .6 | 1.1 | 1.31 |
| Sodium hypochlorite..... | 8.1 | .6 | .7 | 2.28 |
| Potassium permanganate..... | 7.0 | .8 | 1.2 | 4.49 |

SERIES 2

This series of tests consisted of trying several dosages of the three treatment chemicals. As in series 1, raw water was first treated with NaOH to raise pH. After the raw water was treated with NaOH, ferrous iron concentrations remained high. This was caused by inadequate aeration and the short detention time of pond 1. The quality of the water used for this series of tests is shown in table 4.

TABLE 4. - Water quality for test series 2 after initial NaOH treatment

| | |
|---|-----|
| pH..... | 9.0 |
| Alkalinity (as CaCO ₃).....mg/L.. | 110 |
| Fe ²⁺mg/L.. | 88 |
| Total Fe.....mg/L.. | 140 |
| Mn.....mg/L.. | 78 |

Twenty-three 400-mL samples were collected at point C (fig. 1). Three samples were used as controls. The remaining 20 were treated as follows: 6 different dosages of NaOCl, 6 different dosages of KMnO₄, and 8 different dosages of NaOH to raise pH between 9.4 and 10.5. These samples were left to settle for 23 h, after which the supernatant liquid was analyzed.

The results of these tests are summarized in figure 2. This graph plots total chemical cost versus the concentration of manganese remaining in solution after 23 h of settling. Included in each chemical cost is the cost for the initial NaOH treatment (\$0.83/1,000 gal).

As in series 1 tests, excess alkalinity proved to be the most cost-effective method. Ferrous iron concentrations of 88 mg/L may have caused an increase in demand for NaOCl and KMnO₄. It was decided to try another series of tests to determine the effects of lower ferrous iron concentrations.

Series 3

In these tests, raw water was collected at the seep (point A of figure 1). NaOH was added to the raw water to raise pH to 7.5. This water was then aerated by

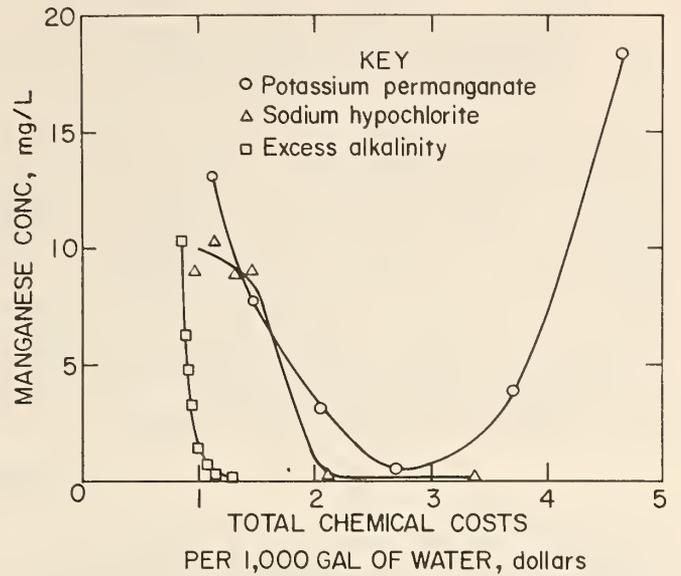


FIGURE 2. - Test series 2: Costs of chemical treatments versus manganese concentrations after 23 h of settling.

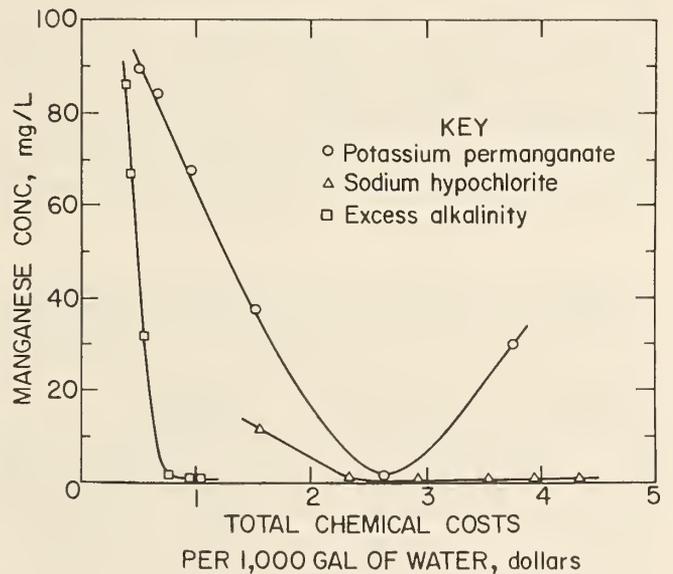


FIGURE 3. - Test series 3: Costs of chemical treatments versus manganese concentrations after 23 h of settling.

pouring it from one bucket to another, causing iron to oxidize and precipitate and pH to decrease. The procedure of neutralization and aeration was repeated until pH stabilized at 7.5. Analysis showed that ferrous iron concentrations were reduced to approximately 1 mg/L (table 5). Treatment chemicals were then added to this water, which was low in ferrous iron.

TABLE 5. - Water quality for test series 3 after initial NaOH treatment and induced aeration

| | |
|---|-----|
| pH..... | 7.5 |
| Alkalinity (as CaCO ₃).....mg/L.. | 21 |
| Acidity (as CaCO ₃).....mg/L.. | 5.0 |
| Fe ⁺²mg/L.. | 0.9 |
| Total Fe.....mg/L.. | 3.7 |
| Mn.....mg/L.. | 95 |

Twenty 400-mL samples were collected and treated as follows: one control, seven NaOCl-treated samples, six

KMnO₄-treated samples, and six excess NaOH samples with pH raised to between 9.2 and 10.5. The samples were left to settle for 23 h. The supernatant liquid was sampled and analyzed.

The results of these tests are shown in figure 3. Again the cost of the initial NaOH (\$0.36/1,000 gal) was added to each cost. As in the first two series of tests, the most cost-effective method was excess alkalinity. The removal of ferrous iron did not reduce the chemical requirements for the NaOCl and KMnO₄.

DISCUSSION AND SUMMARY

Excess alkalinity was the least expensive method to remove manganese from acid mine drainage. Any alkaline material capable of raising pH above 10 can effectively remove manganese. One drawback of the excess alkalinity method is that the final effluent may not meet effluent limitations (pH less than 9.0). The mine operator must get a variance in order to discharge high-pH water. If a variance to discharge high-pH water is not granted, the operator has to either add acid to lower pH or use an oxidizer such as NaOCl or KMnO₄.

Sodium hypochlorite was more expensive than excess alkalinity but less expensive than potassium permanganate. Sodium hypochlorite is commercially sold as a 15-pct-available-chlorine solution. This solution can be easily introduced into the treatment system. A disadvantage of sodium hypochlorite is that it loses potency with age. The 15-pct-available-chlorine is guaranteed 10 pct by time of delivery, and additional storage can lead to further reduction in strength. Another disadvantage is the possibility of residual chlorine in the effluent, which may be regulated by State agencies.

Potassium permanganate was the most expensive of the three chemical treatments. An advantage of potassium permanganate is that it acts as a color indicator for correct dosage. KMnO₄ is sold in nugget or granular form, and if KMnO₄ is to be added as a solution, the diluting and

mixing must be done on site. It is important not to add too much KMnO₄, since an excess will increase manganese concentrations. This effect is shown in figures 2 and 3, where manganese concentrations increase when excess permanganate is added.

In all three treatments, controlling chemical dosage is very important. In addition to wasting money, adding too much chemical can have other deleterious effects. In the case of excess alkalinity, an overdose can result in very high pH values. An overdose of NaOCl can result in residual chlorine. An overdose of KMnO₄ will result in more, not less,

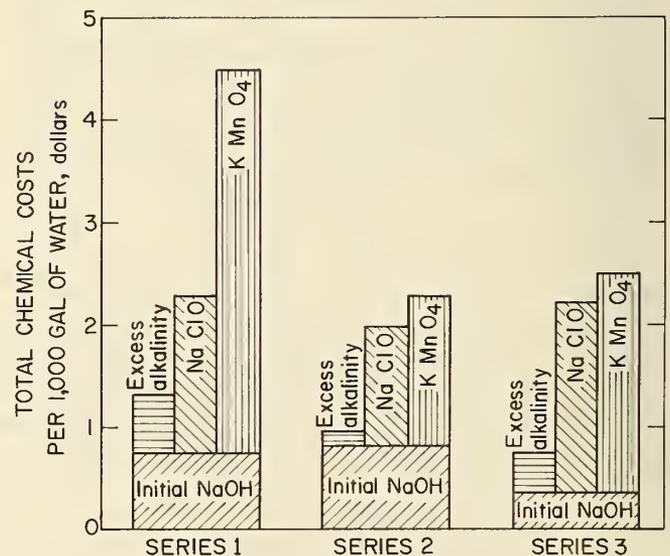


FIGURE 4. - Chemical costs to reduce manganese concentrations below 2 mg/L.

manganese in solution. On the other hand, using too little of any of the three chemicals will result in discharging water that exceeds effluent limitations for manganese.

Cost comparison of the three treatments in each series of tests to reduce manganese concentrations below 2 mg/L is shown in figure 4. Excess alkalinity was the least expensive method of manganese removal, costing an average of \$1 per 1,000 gal of water treated. Although

these chemical costs were less than half of those for both sodium hypochlorite and potassium permanganate, this method is still quite expensive. At this site, the chemical costs of the excess alkalinity method to remove manganese were approximately twice the costs to treat the AMD for neutralization and iron removal. Elsewhere in these proceedings other AMD treatment and abatement methods are presented. The in-line system, in particular, has shown the potential to be an inexpensive method to remove manganese.

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TREATMENT OF ACID MINE WATER BY WETLANDS

By Robert L. P. Kleinmann¹

INTRODUCTION

Wetlands are a potential natural treatment system for small flows of acid mine water. Previous studies of mine water flowing through bogs dominated by Sphagnum moss indicate that such a wetland removes the iron and reduces acidity, without harm to the moss. A group from Wright State University studied a site in the Powelson Wildlife area in Ohio where Sphagnum recurvum was found growing in pH 2.5 water. Iron, magnesium, sulfate, calcium, and manganese all decreased, while pH increased from 2.5 to 4.6 as the water flowed through the bog. A natural outcrop of limestone located at the downstream end provided sufficient neutralization to raise the effluent pH to between 6 and 7 (4).²

A similar study was conducted by a West Virginia University group at Tub Run Bog in northern West Virginia (5). They found that acid drainage flowing into the wetland area rapidly improved in quality. In 20 to 50 m, pH rose from 3.05-3.55 to 5.45-6.05, while only 10 to 20 m of flow through the bog was needed to reduce sulfate concentrations from 210-275 mg/L to 5-15 mg/L and iron from 26-73 mg/L to less than 2 mg/L. Overall, they found that the water quality of the bog effluent was equal or superior to that of nearby streams unaffected by mine drainage.

In laboratory experiments it has been shown that 1 kg (wet weight) of S. recurvum can remove up to 92 pct of the influent 50 mg/L of iron in 16.5 L of pH 3.8 synthetic mine water solution (3) by cation exchange. In a natural wetland, bacterial oxidation and sulfate reduction in the organic-rich bottom waters add to the iron removal capability. It has also been demonstrated in the laboratory that S. recurvum can tolerate acid mine drainage with iron concentrations as high as 500 mg/L for 4 weeks. Although the moss was stressed, iron removal by cation exchange continued. In the field, higher evapotranspiration rates and less ideal conditions result in a long-term threshold of less than 150 mg/L.

Such field observations and laboratory studies suggest that a Sphagnum-dominated biological treatment system is feasible. Since discharge from such a biological treatment system will not meet Federal and State pH limitations (pH 6-9) for mine water discharges, it was decided to incorporate a passive limestone neutralization step down-gradient of the moss to raise the pH to at least 6.0. Normally, limestone in mine water would be rendered useless by Fe(OH)₃ precipitation, but efficient iron removal by the wetland would eliminate this problem.

PILOT-SCALE EVALUATION OF THE BOG-LIMESTONE SYSTEM

The Bureau of Mines decided that a pilot-scale field test was needed to determine if a bog system could be constructed to treat acid mine water. In

September 1981, a contract was initiated with Peer Consultants and Wright State University (subcontractor) to construct a pilot-scale test facility at an actual mine drainage site.

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²Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

A six-section plexiglass tank was constructed and mounted on a steel flat-bed trailer. Live Sphagnum moss was harvested from the previously studied bog in the Powelson Wildlife area and transplanted

into the plexiglass chamber, which was then towed to an acid mine drainage site in the Zaleski State Forest in southeastern Ohio. A sketch of the portable bog system (fig. 1) shows how water flows through the divided chambers sequentially. The first five sections were packed loosely with Sphagnum moss (a mixture of S. recurvum v. brevifolium and S. fimbriatum), while the last section was packed with coarsely crushed limestone. Water samples were collected at the intake, at the end of the Sphagnum moss, and at the outlet. The limestone was also analyzed periodically.

The acid source water for the bog system was an adjacent stream badly contaminated by acid mine drainage. Water was already being pumped from the stream by the U.S. Geological Survey sampling station at the site. A portion of this pumped water was used for our project. Flow rates through the bog during the initial 8 weeks of the test (June-July 1982) ranged from 1.4 to 19.8 gal/h owing to problems with the pumping equipment and inundation of the bog by heavy rainfall. This was subsequently stabilized by increasing the diameter of the inlet tube and inclining the inlet side of the trailer 1.8 in above the outlet side, simulating the natural gradient observed at the bog in the Powelson Wildlife area. A flow rate of approximately 2 gal/h was used during August and September 1982; after September, flow was increased to approximately 18 gal/h, and then to about 25 gal/h during 1983.

Although at times under stress due to inundation, the Sphagnum moss remained

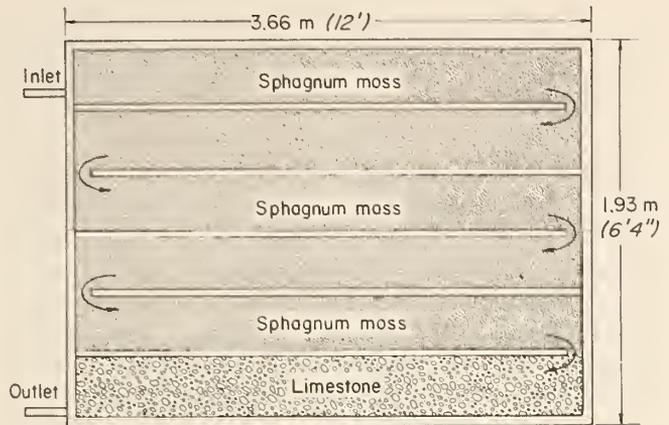


FIGURE 1. - Flow path of acid mine water through the bog-limestone system.

viable throughout the test. Iron was removed from the acid water by the moss so that only minor amounts of visible ferric hydroxide coating occurred on the limestone. Chemical analysis (table 1) confirmed that some coating occurred, but the effect on neutralization was insignificant. Aluminum concentrations, which are not significantly affected by the Sphagnum moss, may prove to be a problem if it turns out that aluminum hydroxide floc armors the limestone.

Dissolved oxygen concentrations indicate that anaerobic conditions did not occur, even at the bottom of the moss mat. Sulfate concentrations were not affected by flow through the bog system, and tests for hydrogen sulfide confirm that little if any sulfate reduction was occurring, presumably owing to the relatively shallow depth (6 in) of the portable bog. Sulfate reduction is an important aspect of acid drainage treatment

TABLE 1. - Results of analysis of limestone samples

| Length of exposure to AMD, weeks | Concentration, mg/L | | | | |
|----------------------------------|---------------------|-----------|----------|---------|-----------|
| | Iron | Manganese | Aluminum | Calcium | Magnesium |
| Unexposed..... | 1,200 | 87.8 | 1,080 | 194,000 | 98,500 |
| 1..... | 1,244 | 76.0 | 722 | 204,000 | 129,000 |
| 3..... | 1,520 | 79.7 | 643 | 207,000 | 128,000 |
| 5..... | 1,538 | 83.2 | 1,050 | 189,700 | 142,650 |
| 13..... | 1,560 | 103 | 1,533 | 200,630 | 108,770 |
| 16..... | 1,751 | 116 | 1,739 | 202,130 | 104,950 |
| 19..... | 1,784 | 120 | 1,526 | 204,100 | 103,248 |
| 23..... | 1,824 | 128 | 4,055 | 201,113 | 101,128 |

by a natural bog (5); its general absence in our pilot-scale test implies that our iron removal rates are probably conservative.

Figure 2 shows the effect of the Sphagnum moss on ferrous iron concentrations after the flooding problem was corrected. Ferrous iron oxidation averaged 61 pct and peaked at 97 pct. Total iron concentrations, which include suspended $Fe(OH)_3$ floc, were very erratic, with influent concentrations ranging from 15.9 to 640 mg/L within a week's time. These fluctuations reflect resuspension of $Fe(OH)_3$ floc from the stream bottom during storms; our small bog did not have the detention time to filter out this floc well, although presumably a larger bog would. The Sphagnum bed typically removed 50 to 70 pct of the total iron.

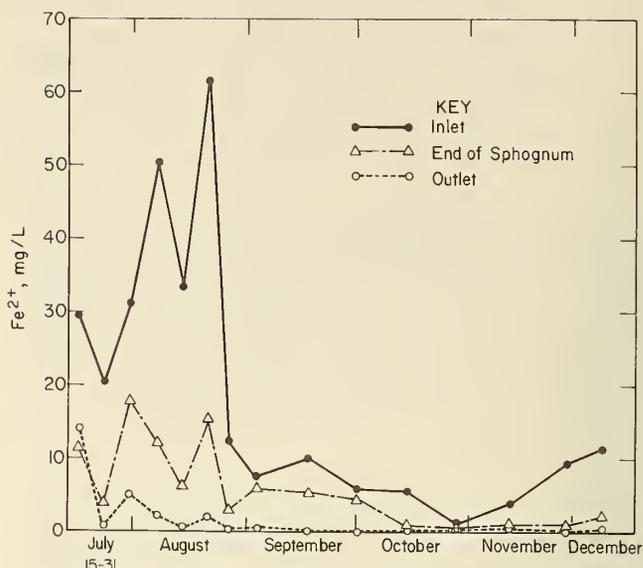


FIGURE 2. - Effect of the Sphagnum moss and limestone on Fe^{2+} concentrations in acid mine water.

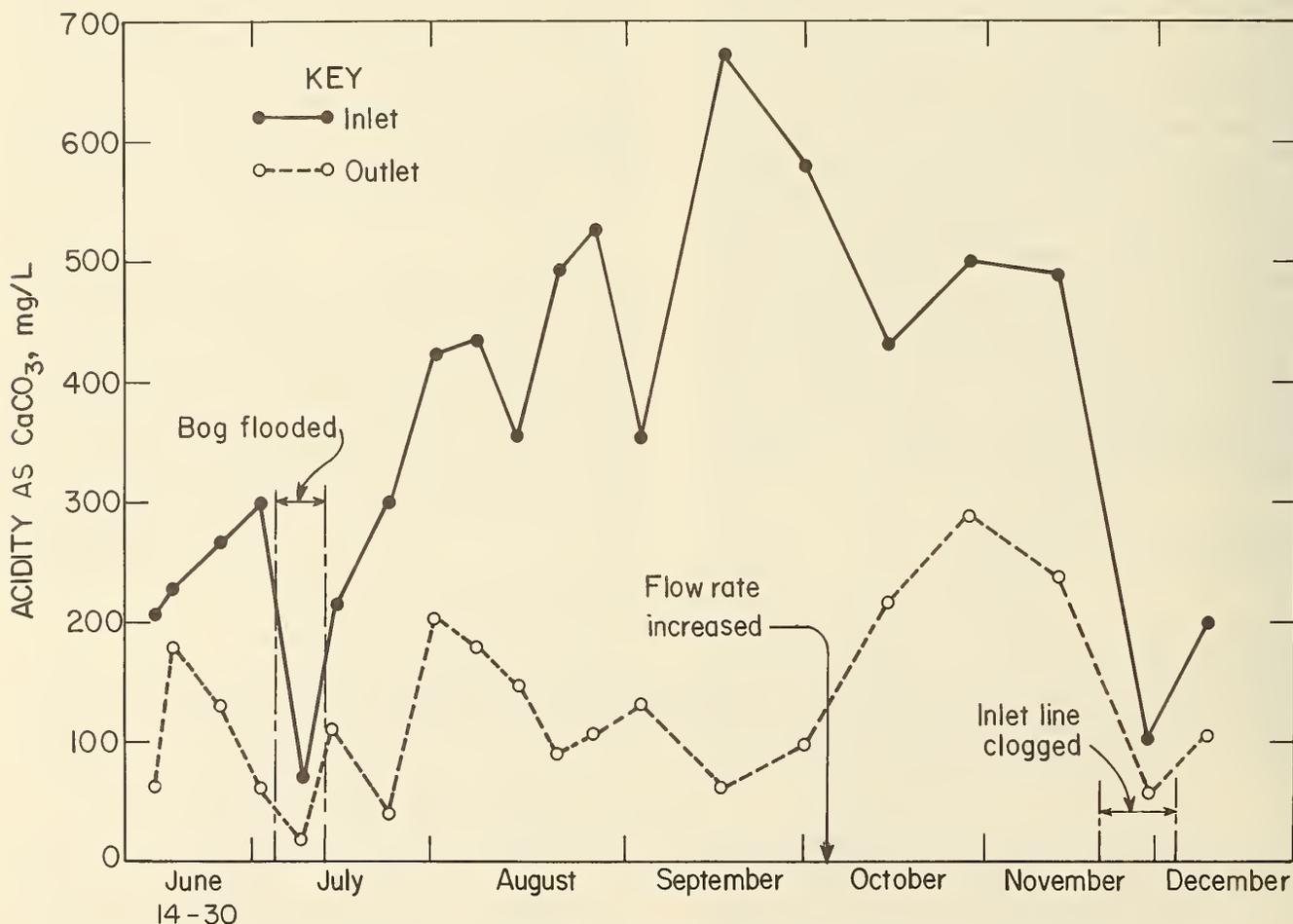


FIGURE 3. - Effect of the bog-limestone system on the titratable acidity of acid mine water.

Acidity was not significantly affected by flow through the Sphagnum mat, but decreased 43 to 90 pct as the water passed through the coarsely crushed limestone (fig. 3). The 90-pct reduction in acidity was observed when the initial acidity of the influent water exceeded 605 mg/L (as CaCO₃); the 43-pct reduction was observed when acidity at the inlet was less than 150 mg/L.

Generally, pH increased as acidity decreased. Adsorption of the H⁺ ion, although known to be significant in a natural bog (3), did not occur enough in our small system to raise the pH as it flowed through the Sphagnum moss. However, as the water flowed through the limestone bed, pH increased an average of 1.4 and as much as 2.5 units.

FULL-SCALE FIELD EVALUATION OF TREATMENT BY WETLANDS

The Bureau of Mines is now involved in field evaluation of the wetland approach at mine sites in Pennsylvania and West Virginia. The wetlands have been constructed by the respective mining companies for water treatment; the Bureau is facilitating monitoring and evaluation of the sites so that others can learn from these efforts. Four wetland areas constructed during 1984 and two volunteer wetland areas on mined lands are currently being monitored; two additional sites are planned for 1985.

At the volunteer wetland areas, C&K Coal Co. is attempting to enhance already established Typha bogs and to divert additional mine water to the wetland areas for treatment. At the better studied of the two areas, flows range from 30 to 40 gal/min, with an influent pH of 5.5 to 5.8. Influent iron concentration averages 20 to 25 mg/L; manganese ranges from 30 to 40 mg/L. The velocity of the water in the wetland ranges from 0.1 to 1.0 ft/s (as measured in less vegetated areas) over a 150-ft width with a total length of about 85 ft. Effluent water has less than 1 mg/L of iron, less than 2 mg/L manganese, and a near-neutral pH. Manganese removal is attributed to bacterial activity (1-2).

A reduction of 88 pct in the ferrous iron concentration in the water was achieved in the moss bed. Initially it was observed that virtually all of the Fe²⁺ reduction occurred as the water passed through the first two chambers containing 24 linear feet (16.5 ft³) of the moss. During the final month of sampling, after the monitoring sites in the portable bog had been changed, this reduction in Fe²⁺ was found to actually occur after the water has passed through only one chamber of 12 linear feet (8.3 ft³) of moss. For the entire bog system, at an average flow of 22 gal/h, levels of Fe²⁺ were reduced by 15 mg/L on average at a rate of 5.5 mg/(L·h) or 1.8 mg/L per cubic foot of moss. The removal rate in the first chamber was of course much higher.

With an understanding of wetlands gained from the pilot-scale test and observation of the volunteer wetland areas, wetland treatment systems have been constructed of Sphagnum alone, and of Sphagnum and Typha together. The vegetation was transplanted from nearby wetlands by personnel of Brehm Laboratory of Wright State University and by Ben Pesavento, of Environment Analytic, who are also responsible for monthly monitoring and sample collection. These initial wetland areas range in size from 750 to 8,500 ft², of which 40 to 60 pct is actual wetted area, and treat flows of 2-8 gal/min. Preliminary results are shown in table 2 for the three wetland areas constructed at least 2 months ago. In addition to cation exchange, oxidation, and removal as iron sulfides, these results may partially reflect dilution of iron and manganese in the bog by ground water.

It appears that wetlands can be constructed in acid mine water discharges and that they will improve drainage quality. They require continuous flow, without a lot of variation; long-term maintenance requirements have yet to be determined. They appear to be most appropriate for relatively small flows (less than 10 gal/min) owing to the large

TABLE 2. - Performance of wetlands 2 months after construction or augmentation, milligrams per liter

| Mine site | Iron | | Manganese | |
|-------------|----------|----------|-----------|----------|
| | Influent | Effluent | Influent | Effluent |
| Mine 1..... | 24 | 0.5 | 43.8 | 16.1 |
| Mine 2..... | 8.7 | 1.2 | 24.5 | 15.5 |
| Mine 3..... | 24 | .6 | 16 | 3.8 |

surface area requirement--we like to allow 200 ft³ of wetted area per gallon per minute of flow. However, only space limits the extension of this system to greater flows. An attempt will be made

to treat acid flows of 50 to 100 gal/min in larger wetland systems, starting with partial treatment in 1985 and, if successful, followed by full-scale tests in 1986.

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IN-LINE AERATION AND TREATMENT OF ACID MINE DRAINAGE: PERFORMANCE
AND PRELIMINARY DESIGN CRITERIA

By Terry Ackman¹ and Robert L. P. Kleinmann²

INTRODUCTION

It is estimated that the U.S. coal mining industry spends over \$1 million per day treating acidic mine water so that it can be legally discharged (4).³ This figure includes the amortized cost of the large water treatment plants (a conventional lime neutralization facility typically costs over \$1 million to construct), treatment chemicals (lime, soda ash, sodium hydroxide, flocculant, etc.), maintenance, electric power, and labor.

Although expensive, conventional acid mine drainage (AMD) treatment is a simple process. The water is neutralized, typically to a pH of 8 to 9, and then aerated to oxidize the iron to the Fe³⁺ state, causing precipitation of Fe(OH)₃ (Yellow-boy) sludge. The water is then separated from the sludge in a series of settling basins or ponds and discharged.

Above a pH of 3.5, the rate of iron oxidation is controlled by dissolved oxygen (DO) and pH. Fully aerated mine water contains about 8 mg/L DO, which is consumed at the rate of 1 mg/L for every 7 mg/L Fe²⁺ oxidized; consequently, the DO initially present can only oxidize 50 to 60 mg/L Fe²⁺ (7). If one assumes, though, that DO is not depleted but instead is maintained at a constant level by continuous aeration, the effect of pH on the rate of iron oxidation can be calculated. Table 1 illustrates the effect of pH on the required aeration time for an initial Fe²⁺ concentration of 100 mg/L. Inspection of the reaction times listed in table 1 reveals why pH is

raised to 7.5 or above at most treatment plants to quickly oxidize the ferrous iron.

TABLE 1. - Time required to oxidize 97 pct of 100 mg/L Fe²⁺ at various constant pH's, and constant oxygen saturation (8 mg/L DO)

| <u>pH</u> | <u>Time, h</u> |
|-----------|------------------------|
| 4.5..... | 3.5 × 10 ⁴ |
| 5..... | 3.5 × 10 ³ |
| 5.5..... | 3.5 × 10 ² |
| 6..... | 3.5 × 10 ¹ |
| 6.5..... | 3.5 |
| 7..... | 3.5 × 10 ⁻¹ |
| 7.5..... | 3.5 × 10 ⁻² |
| 8..... | 3.5 × 10 ⁻³ |
| 8.5..... | 3.5 × 10 ⁻⁴ |

For replenishment of DO in mine water, settling ponds or lagoons are constructed wide and shallow to maximize diffusion of oxygen into the water and thereby increase oxygen transfer from the atmosphere. However, oxygen diffusion is relatively slow (9), so that at many sites supplementary aeration sources are necessary (8). For example, oxygen transfer can be increased by increasing turbulence. This is typically accomplished by incorporating a series of open-channel drops in the flow path of the water. Mechanical aerators can also be used to continuously introduce bubbles of air into the water. This continuous replenishment of DO is effective in maintaining a rapid reaction rate, but it also has disadvantages: a separate aeration tank or basin is required; there are high initial capital costs; and there are operating costs associated with power consumption and maintenance, especially where gypsum precipitation is a problem.

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³Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

This report describes a Bureau of Mines-designed treatment system that has been tested at mine sites in Pennsylvania and West Virginia. The in-line aeration and treatment system (ILS) functions in existing AMD pipelines, using energy provided by existing mine water discharge

pumps. It appears to be a low-cost alternative to conventional treatment plants and, in fact, appears to accelerate iron oxidation rates. The system has no moving parts and thus has the advantages of low maintenance and operating costs.

UNIT DESCRIPTION

The ILS consists of two off-the-shelf components: a jet pump (3) and a static mixer. Both components can be described as aeration and mixing devices. Jet pumps are simply nozzles that entrain air by Venturi action (fig. 1). The jet pump used is made of polyvinyl chloride (PVC). Water enters under pressure and is converted by the jet pump into a high-velocity stream. This stream then passes through a suction chamber, which is open to the atmosphere. If the system is being used for neutralization as well as

aeration, the suction chamber also serves as the injection point for the neutralizing material. Multiple jet pump units may be placed in parallel as long as water pressures of at least 20 psi are maintained.

After passing through the jet pump, the flow enters the static mixer (fig. 2). The static mixer consists of 1-ft sections of pipe made of copolymer polypropylene resins, laminated together end to end with fiberglass. Inside each

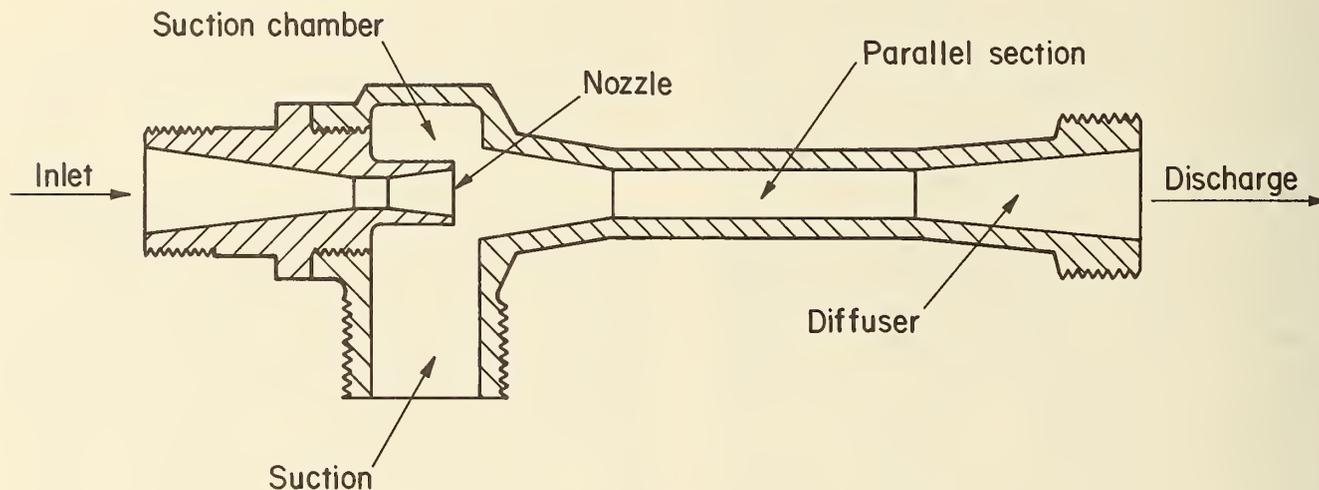


FIGURE 1. - Jet pump diagram.

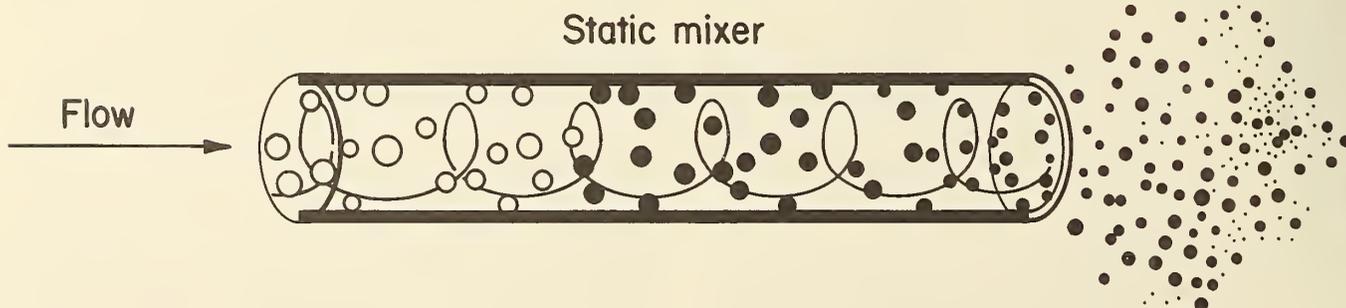


FIGURE 2. - Diagram of the static mixer. Air bubbles are reduced in size by the turbulence, significantly increasing interfacial contact.

section is a 1-ft helix that forces the water to follow a spiral path. Static mixers are used routinely in sewage and industrial waste water treatment plants as vertical airlift aeration and mixing units, but that design was modified somewhat for this horizontal application:

each helical unit was rotationally offset 90° from its neighbor, thereby interrupting the corkscrew every foot and enhancing the mixing action. Eight 1-ft sections were used, which provided the contact time of a normal 32-ft pipe because of the induced spiral flow.

PERFORMANCE CHARACTERISTICS

AERATION OF NEAR-NEUTRAL MINE WATERS

The ILS was first tested as an aeration unit at a mine site in Greene County, PA. Influent Fe^{2+} levels were erratic but often exceeded 100 mg/L at near-neutral pH. As an alternative to mechanical aeration, the ILS was installed at the end of the discharge pipe from the underground mine.

Monitoring the discharge from the site began on the fourth day after installation of the ILS. Ferrous iron concentrations dropped from 10 to 20 mg/L before installation of the ILS to 0.2 to 0.9 mg/L. Total iron concentrations fell from over 20 mg/L to less than 2 mg/L.

Subsequent aeration tests were conducted with more acidic water. Iron oxidation continued to be impressive despite an influent pH of 4.6 to 5.6. Figure 3 is a graph of average Fe^{2+} values for all samples of pH 5.5 ± 0.2 . Although very little iron oxidation occurred in the ILS, the discharge from the first pond (24-h detention time) averaged only 6 mg/L Fe^{2+} . This represents not only much greater iron oxidation than without the ILS at this pH, but also a much faster rate than expected in oxygen-saturated water (table 1). A more detailed analysis of this topic may be found in RI 8868 (2).

SIMULTANEOUS NEUTRALIZATION AND AERATION

The suction port of the jet pumps can be used for addition of neutralizing chemicals without significantly interfering with air intake. Field tests were

conducted at actual mine sites using sodium hydroxide (NaOH), quick lime (CaO), or hydrated lime ($\text{Ca}(\text{OH})_2$), with the latter two added as slurries. The effluent pH was easily adjusted in each case, and the violent mixing action of the ILS minimized excessive lime use.

Tables 2-4 allow the comparison of actual NaOH or lime consumption with theoretical "best case" neutralization. The theoretical values are derived assuming optimal efficiency (90 pct for CaO, 95 pct for $\text{Ca}(\text{OH})_2$, and 99 pct for NaOH) and a pH endpoint of 8.3 (5); our experience indicates that conventional treatment plants use 25 pct more lime than these calculated values.

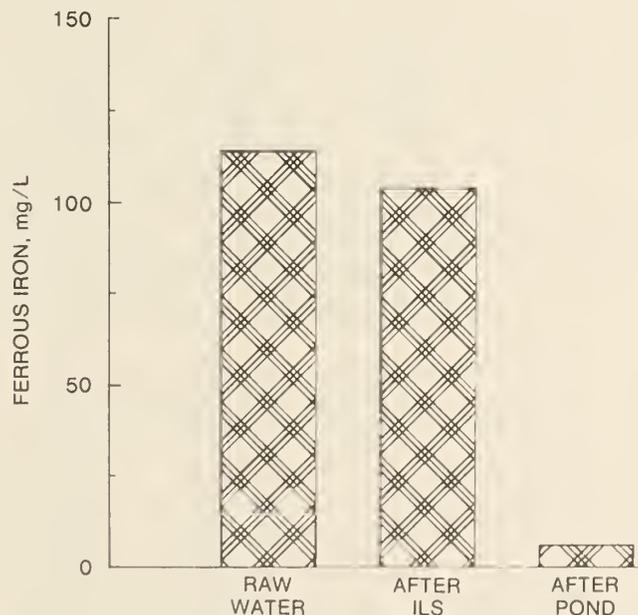


FIGURE 3. - Effect of the ILS as an aeration system on average Fe^{2+} concentration at pH 5.5 ± 0.2 at the Greene County, PA, site. Pond has a 24-h detention time.

TABLE 2. - NaOH use at site 2--Braxton County, WV

| Test run | Raw pH | Net acidity of raw water, mg/L | Flow, gal/min | Na in raw water, mg/L | Na in treated water, mg/L | Treated pH | Theoretical NaOH use, lb/min | Actual NaOH use, lb/min |
|------------------|--------|--------------------------------|---------------|-----------------------|---------------------------|------------|------------------------------|-------------------------|
| SINGLE TREATMENT | | | | | | | | |
| 1... | 3.2 | 3,784 | 521 | 22 | 1,243 | 5.1 | 13.4 | 5.3 |
| 2... | 3.3 | 3,951 | 469 | 22 | 1,216 | 5.3 | 12.6 | 4.7 |
| 3... | 3.2 | 3,784 | 543 | 23 | 1,000 | 5.2 | 14.0 | 4.4 |
| 4... | 3.2 | 4,022 | 533 | 23 | 1,176 | 5.0 | 14.6 | 5.1 |
| 5... | 2.7 | 3,689 | 385 | 27 | 1,634 | 6.6 | 9.7 | 5.2 |
| 6... | 2.6 | 3,689 | 533 | 23 | 1,094 | 4.9 | 13.4 | 4.8 |
| 7... | 2.5 | 3,713 | 530 | 23 | 1,209 | 4.9 | 12.9 | 5.2 |
| 8... | 2.8 | 3,677 | 261 | 35 | 1,779 | 6.8 | 6.5 | 3.8 |
| 9... | 2.9 | 3,641 | 345 | 35 | 3,558 | 12.8 | 8.5 | 10.1 |
| DOUBLE TREATMENT | | | | | | | | |
| 10.. | 4.8 | 75 | 543 | 1,860 | 1,865 | 8.4 | 0.3 | 0.03 |
| 11.. | 4.6 | 89 | 475 | 1,831 | 2,193 | 11.3 | .3 | 1.4 |
| 12.. | 4.6 | 87 | 340 | 1,865 | 2,021 | 9.9 | .2 | .4 |
| 13.. | 4.6 | 95 | 523 | 1,728 | 2,175 | 10.7 | .4 | 1.9 |
| 14.. | 4.6 | 71 | 475 | 1,514 | 2,153 | 10.6 | .2 | 2.5 |
| 15.. | 4.3 | 68 | 337 | 1,888 | 1,872 | 8.6 | .1 | .04 |

TABLE 3. - Lime use at site 3--Armstrong Country, PA

| Sam-ple | Raw pH | Net acidity of raw water, mg/L | Flow, gal/min | Ca in raw water, mg/L | Ca in treated water, mg/L | Treated pH | Theoretical lime use, lb/min | Actual lime use, lb/min |
|---------|--------|--------------------------------|---------------|-----------------------|---------------------------|------------|------------------------------|-------------------------|
| 1... | 2.7 | 830 | 363 | 284 | 1,078 | 11.7 | 1.7 | 4.4 |
| 2... | 3.0 | 753 | 363 | 271 | 268 | 3.1 | 1.5 | .0 |
| 3... | 3.0 | 830 | 363 | 277 | 618 | 7.3 | 1.7 | 1.9 |
| 4... | 3.0 | 791 | 363 | 279 | 671 | 8.8 | 1.6 | 2.2 |
| 5... | 2.9 | 830 | 363 | 287 | 608 | 5.7 | 1.7 | 1.8 |
| 6... | N/A | 791 | 363 | 280 | 692 | 8.8 | 1.6 | 2.3 |
| 7... | 2.9 | 830 | 363 | 286 | 617 | 6.9 | 1.7 | 1.8 |

TABLE 4. - Lime use at site 4--Westmoreland County, PA

| Sam-ple | Raw pH | Net acidity of raw water, mg/L | Flow, gal/min | Ca in raw water, mg/L | Ca in treated water, mg/L | Treated pH | Theoretical lime use, lb/min | Actual lime use, lb/min |
|---------------------|--------|--------------------------------|---------------|-----------------------|---------------------------|------------|------------------------------|----------------------------|
| 1..... | 5.6 | 973 | 469 | 445 | 1,015 | 8.4 | 2.6 | 4.1 |
| 2..... | 5.7 | 877 | 457 | 454 | 1,020 | 7.7 | 2.3 | 4.0 |
| 3..... | 5.4 | 1,010 | 457 | 424 | 1,057 | 7.0 | 2.6 | 4.5 |
| 4..... | 5.4 | 1,040 | 469 | 419 | 1,164 | 6.9 | 2.8 | 5.4 |
| 5..... | 5.6 | 942 | 542 | 451 | 749.8 | 6.6 | 2.9 | 2.5 |
| 6..... | 5.5 | 1,012 | 485 | 425 | 901 | 7.0 | 2.8 | 3.5 |
| 7..... | 5.5 | 1,062 | 485 | 421 | 909 | 6.9 | 2.9 | 3.3 |
| 8 ¹ | 5.4 | 986 | 485 | 420 | 1,018 | 7.1 | 2.7 | 4.5 |
| 9..... | 5.4 | 1,018 | 485 | 405 | 948 | 7.0 | 2.8 | 4.1 |
| Plant ² | 4.8 | 1,280 | 1,450 | 421 | 1,081 | 8.2 | 10.5 | ³ 14.7 419.1 |

¹Fe and Mn in filtered samples were within effluent standards.

²Normal plant operation.

³Measured by chemical analysis.

⁴Physically measured dry feed.

Table 2 represents a two-stage process, using NaOH to treat mine water with high acidity and high iron. Samples 1 through 9 represent a single treatment pass through the ILS from pond 1 to pond 2 (initially empty before the test). Samples 10 through 15 represent water pumped from pond 2 through the ILS to pond 3 36 h after the first treatment. Effluent water from the two-stage treatment met effluent standards. Actual NaOH usage was calculated from the difference in sodium concentrations in unfiltered, acidified samples of treated and raw water. Theoretical NaOH requirement was calculated by Lovell's equations (5). NaOH use was approximately half of that theoretically required. However, iron was precipitated as both $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$ in the first step of the treatment. As explained later, $\text{Fe}(\text{OH})_2$ will eventually oxidize, adding acidity to the pond water.

Table 3 summarizes the results of a field test using $\text{Ca}(\text{OH})_2$. This operation did not allow a quantitative comparison with actual consumption of lime by the conventional water treatment plant, but the plant operator felt that lime usage was reduced enough to design an ILS to replace the existing system. Except at high pH (sample 1), the ILS values met discharge criteria and approached the theoretical optimal values for lime consumption. As discussed later, both iron and manganese were reduced to effluent levels at a discharge pH as low as 6.9, indicating that greater potential cost savings can be obtained.

Table 4 presents the results of a field test using CaO slurry to neutralize water being pumped from an underground mine pool. Owing to the high levels of dissolved iron (over 500 mg/L), the ILS unit could not oxidize all of the iron in a single pass; as at the NaOH site (table 2), some of the iron precipitated as $\text{Fe}(\text{OH})_2$. Water sample 8, which met discharge standards after filtration, can be used for comparing actual costs with those for operation of the conventional treatment plant (table 4, bottom row). Since flow through the ILS is one-third

that of normal plant operation, the observed lime use of 4.5 lb/min at pH 7.1 must be scaled up to 13.5 lb/min. This is within 1 pct of the amount of lime consumed in neutralizing acidity during operation of the conventional treatment plant (as calculated from chemical analysis) but is 30 pct more efficient than actual lime use, as measured during normal plant operation. Analysis of the sludge during operation of the conventional treatment plant confirms that a lot of unreacted lime is being wasted, especially in the aeration basin, owing to insufficient mixing action.

IRON OXIDATION

During field testing of the ILS, it became apparent that iron oxidation was proceeding much faster than anticipated. At low pH (4.6 to 5.5), iron oxidation was accelerated by a factor of 10 to 400; at near-neutral pH (6.9 to 7.5), iron oxidation was accelerated by as much as 1,000 (2). Figure 3 illustrates iron oxidation at the Greene County, PA, test site; 98.7 pct of the 190 mg/L Fe^{2+} in the influent water was oxidized in the 4-s transit time in the ILS. Most of this oxidation apparently occurred in the jet pump section of the ILS since water samples collected between the jet pump and the static mixer had an average pH of 6.7 and an Fe^{2+} concentration of only 4.8 mg/L. To obtain such rapid iron oxidation in a conventional water treatment system, the pH would have to be raised to at least 8.5.

However, the iron oxidation capacity of the existing ILS design is limited. As influent Fe^{2+} concentrations approach 300 mg/L, the efficiency of the system decreases. Tables 5 and 6 document field trials with average influent Fe^{2+} concentrations of 965 and 527 mg/L, respectively. The amount of Fe^{2+} oxidized during transit through the ILS ranged between 283 and 479 mg/L using NaOH (table 5) and between 163 and 345 mg/L using CaO (table 6). The amount of Fe^{2+} oxidized was calculated as the difference between Fe^{2+} concentrations in acidified, unfiltered samples of raw and treated water. The

TABLE 5. - Oxidation site 2--Braxton County, WV

| | Single treatment | | | | | Double treatment | | | | | | | | | |
|--|------------------|-------|-------|-------|-------|------------------|-------|-------|-------|--------|--------|--------|--------|--------|--------|
| | Run 1 | Run 2 | Run 3 | Run 4 | Run 5 | Run 6 | Run 7 | Run 8 | Run 9 | Run 10 | Run 11 | Run 12 | Run 13 | Run 14 | Run 15 |
| Fe ²⁺ oxidized ¹mg/L.. | 342 | 369 | 342 | 283 | 479 | 366 | 451 | 380 | 425 | 12 | 0 | 20 | 19 | 0 | 19 |
| Fe ²⁺ oxidized.....pct.. | 37 | 40 | 37 | 31 | 48 | 37 | 45 | 38 | 42 | 34 | 0 | 84 | 83 | 0 | 91 |
| Fe ²⁺ removed ²mg/L.. | 615 | 769 | 612 | 581 | 1,000 | 723 | 824 | 1,000 | 1,000 | 34 | 3.8 | 24 | 23 | 3.8 | 21 |
| Fe ²⁺ removed.....pct.. | 66 | 83 | 66 | 64 | 100 | 73 | 82 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Mn removed (unfiltered).....mg/L.. | 1 | 2 | 0.4 | -1.2 | 0 | -1.2 | 0.3 | -0.6 | 4.3 | 15.4 | 3.1 | 0.6 | 2.7 | 2.2 | 1.9 |
| Mn removed (unfiltered).....pct.. | 2 | 3 | 1 | -2 | 0 | -2 | 0.5 | -1 | 6 | 58 | 23 | 5 | 20 | 18 | 15 |
| Mn removed (filtered).....mg/L.. | -2 | 1 | -4 | 2 | 67 | 2 | 10 | 67 | 72 | 26 | 14 | 13 | 13 | 12 | 12 |
| Mn removed (filtered).....pct.. | -3 | 2 | -7 | 2.5 | 94 | 3 | 14 | 95 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| O ₂ consumed.....std ft ³ /min.. | 2.4 | 2.3 | 2.4 | 2.0 | 2.4 | 2.6 | 3.2 | 1.3 | 1.9 | 0.1 | 0 | 0.1 | 0.1 | 0 | 0.1 |
| O ₂ consumed.....lb/min.. | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.3 | 0.1 | 0.2 | 0.01 | 0 | 0.01 | 0.01 | 0 | 0.01 |
| Effluent pH..... | 5.1 | 5.3 | 5.2 | 5.0 | 6.6 | 4.9 | 4.9 | 6.8 | 12.8 | 8.4 | 11.3 | 9.9 | 10.7 | 10.6 | 8.6 |
| Initial Fe ²⁺ concentration mg/L.. | 930 | 930 | 930 | 903 | 1,000 | 1,000 | 1,000 | 1,000 | 1,000 | 34 | 4 | 24 | 23 | 4 | 21 |

¹Fe²⁺ oxidized as Fe(OH)₃.

²Fe²⁺ removed as Fe(OH)₃ and Fe(OH)₂; samples were retained 11 days to simulate settling before analysis.

TABLE 6. - Oxidation site 4--Westmoreland County, PA

| | Run 2 | Run 3 | Run 4 | Run 5 | Run 6 | Run 7 | Run 8 | Run 9 | Run 10 |
|--|--|-------|-------|-------|-------|-------|-------|-------|--------|
| | Fe ²⁺ oxidized ¹mg/L.. | 243 | 228 | 193 | 163 | 208 | 236 | 345 | 254 |
| Fe ²⁺ oxidized.....pct.. | 44 | 47 | 36 | 31 | 40 | 43 | 62 | 46 | 39 |
| Fe ²⁺ removed ²mg/L.. | 542 | 480 | 489 | 475 | 377 | 494 | 512 | 551 | 522 |
| Fe ²⁺ removed.....pct.. | 98.4 | 99 | 92 | 89 | 72 | 89 | 92 | 100 | 92 |
| Mn removed (unfiltered).....mg/L.. | 1.0 | 0.6 | 0.2 | 1.3 | 0.2 | -0.1 | 2.2 | 0.4 | 0.7 |
| Mn removed (unfiltered).....pct.. | 7 | 4 | 1 | 9 | 1 | -0.6 | 15 | 3 | 5 |
| Mn removed (filtered).....mg/L.. | 12.9 | 12.3 | 10.9 | 9.7 | 2.2 | 9.2 | 10.1 | 12.8 | 11.1 |
| Mn removed (filtered).....pct.. | 87 | 90 | 78 | 66 | 15 | 62 | 68 | 87 | 75 |
| O ₂ consumed.....std ft ³ /min.. | 1.5 | 1.4 | 1.2 | 1.0 | 1.5 | 1.4 | 2.1 | 1.5 | 1.3 |
| O ₂ consumed.....lb/min.. | 0.14 | 0.12 | 0.11 | 0.09 | 0.13 | 0.13 | 0.19 | 0.14 | 0.12 |
| Effluent pH..... | 8.4 | 7.7 | 7.0 | 6.9 | 6.6 | 7.0 | 6.9 | 7.1 | 7.0 |
| Initial Fe ²⁺ concentration.....mg/L.. | 551 | 486 | 532 | 532 | 524 | 553 | 554 | 552 | 565 |

¹Fe²⁺ oxidized as Fe(OH)₃.

²Fe²⁺ removed as Fe(OH)₃ and Fe(OH)₂.

amount of Fe^{2+} removed was calculated in the same way from unacidified, filtered treated water. Filtering was assumed to approximate settling of iron hydroxides.

At these high levels of influent Fe^{2+} , additional quantities of Fe^{2+} were removed as $\text{Fe}(\text{OH})_2$, which produces a green sludge in the ILS effluent at a pH as low as 4.9. $\text{Fe}(\text{OH})_2$ is unstable below a pH of about 7; its formation in the ILS suggests that a transient pH of at least 8 (6) exists at the point of alkaline injection and that the dissolution of oxygen cannot match the chemical oxygen demand represented by the Fe^{2+} at that pH. The formation of $\text{Fe}(\text{OH})_2$ has both advantages and disadvantages: the precipitation of both sludge forms reduces dissolved iron concentrations, allowing discharge of the effluent water, but the $\text{Fe}(\text{OH})_2$ sludge will gradually oxidize to $\text{Fe}(\text{OH})_3$, lowering the pH of the sludge and, through diffusion, the effluent water. The difference on tables 5-7 between iron oxidized and iron removed reflects formation and precipitation of $\text{Fe}(\text{OH})_2$.

The apparent high transient pH in the jet pump may partially explain the extremely high rate of iron oxidation in the ILS. Table 1 indicates that a 1-s pH of 8.5 to 9.0 would be sufficient if DO is continuously replenished; an instantaneous pH over 10 would reduce the

required reaction time to milliseconds in whatever fraction of the fluid is at a high pH. It is not known whether the apparent limitation on iron oxidation is due to limited air intake and the rate of oxygen dissolution (from the bubbles into the water), or to limited catalysis by some other mechanism.

Apparent oxidation of dissolved iron in the pond, after ILS treatment, continues to be rapid for several days (1). This apparent effect is caused by fine-ground suspended $\text{Fe}(\text{OH})_2$ or $\text{Fe}(\text{OH})_3$ particles that are analyzed as dissolved iron in unfiltered samples. These particles slowly settle in the pond, mimicking oxidation and hydrolysis; filtration with a $0.45 \mu\text{m}$ filter confirms this explanation.

REMOVAL OF MANGANESE

Manganese, when present in mine water at concentrations greater than 4 mg/L, can significantly add to the costs of water treatment. In a conventional treatment plant, the pH must be raised to above 10 (typically 10.5) for rapid oxidation and removal of manganese; this adds greatly to the costs of neutralization, produces an effluent that is unacceptably alkaline, and can cause redissolution of iron. Three of the four field sites where the ILS was tested had manganese problems. Manganese averaged 68 mg/L at the West Virginia site (table 5),

TABLE 7. - Oxidation site 3--Armstrong County, PA

| | Run 1 ¹ | Run 2 | Run 3 | Run 4 | Run 5 | Run 6 | Run 7 |
|--|--------------------|-------|-------|-------|-------|-------|-------|
| Fe^{2+} oxidized ²mg/L.. | 6 | 75 | 67 | 74 | 77 | 76 | 78 |
| Fe^{2+} oxidized.....pct.. | 7 | 98 | 94 | 98 | 97 | 99 | 99 |
| Fe^{2+} removed ³mg/L.. | 0.3 | 75 | 70 | 74 | 78 | 77 | 78 |
| Fe^{2+} removed.....pct.. | 0.4 | 99 | 99 | 99 | 98 | 99 | 99 |
| Mn removed (unfiltered).....mg/L.. | 0.2 | 2.1 | 0.1 | 0.4 | -0.3 | -0.6 | -0.4 |
| Mn removed (unfiltered).....pct.. | 2 | 21 | 1 | 4 | -3 | -7 | -4 |
| Mn removed (filtered).....mg/L.. | -0.2 | 9 | 9 | 9 | 2 | 9 | 6 |
| Mn removed (filtered).....pct.. | 2 | 95 | 91 | 90 | 24 | 99 | 69 |
| O_2 consumed.....std ft ³ /min.. | 0.02 | 0.4 | 0.3 | 0.3 | 0.4 | 0.4 | 0.4 |
| O_2 consumed.....lb/min.. | 0.002 | 0.03 | 0.02 | 0.03 | 0.03 | 0.03 | 0.03 |
| Effluent pH..... | 3.1 | 11.7 | 7.3 | 8.8 | 5.7 | 8.8 | 6.9 |
| Initial Fe^{2+} concentration....mg/L.. | 80.5 | 75.9 | 71.3 | 74.7 | 79.5 | 77.3 | 79.5 |

¹Untreated sample, run through ILS without neutralization.

² Fe^{2+} oxidized as $\text{Fe}(\text{OH})_3$.

³ Fe^{2+} removed as $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$.

14 mg/L at the Westmoreland County, PA, site (table 6), and about 10 mg/L at the Armstrong County, PA, site (table 7). At all three sites, manganese was reduced to within effluent limits after passage through the ILS.

At the West Virginia site, the first treatment step raised the pH to 4.9 to 6.8 and had little apparent effect on manganese concentrations in unfiltered samples. However, 6 h after discharge to the pond, and despite the low pH, manganese concentrations had fallen to 13.5 mg/L, an 80-pct reduction. Sealed water samples kept in the laboratory showed similar declines in manganese concentrations, with no detectable dissolved manganese present after 11 days of storage.

At the Westmoreland County site, water treated to a pH of 7.1 or greater met effluent standards for manganese after filtration. Filtered samples that had been treated to a pH of 6.9 to 7.0 approached manganese effluent standards

(3.1-5.6); it was not possible to collect samples after settling.

At the Armstrong County site, a similar pattern was observed. Fe^{2+} was reduced to below effluent standards at a pH of 5.7 and up, but manganese exceeded effluent limits under pH 7.3. ILS test runs at pH 7.3 or above met effluent standards.

It appears that manganese was precipitating as very small particles during neutralization and aeration in the ILS. Filtration removed most of these particles; settling removed all of them. It is possible that the transient pH in the jet pump was high enough to allow for rapid formation of MnO_2 . Alternatively, it is possible that the manganese is being removed from solution as a coprecipitate on particles of iron hydroxide as they form and swirl in the ILS. It has previously been shown that adsorption of manganese by $Fe(OH)_3$ increases rapidly above pH 8, rising from 0.15 to over 0.6 mol Mn^{2+} per mol Fe^{3+} at pH 8.6 (7).

PRELIMINARY DESIGN SPECIFICATIONS

Three parameters should be considered in the design of the ILS: available water pressure, flow, and influent Fe^{2+} concentration. Table 8 partially summarizes flow capacity of the existing ILS design at various water pressures. In general, adding jet pumps (in parallel) increases capacity. The ILS that was designed and tested by the Bureau had valves on two of the three jet pumps. This allowed for variable flow rates and is a potentially useful feature on sites where surface runoff during storm events determines treatment requirements.

Additional helixors influence flow capacity and may increase oxygen transfer.

Increased water pressure increases flow capacity. If flows are above 500 gal/min, larger capacity jet pumps can be substituted or additional jet pumps can be placed in parallel.

If Fe^{2+} levels are above 300 mg/L, a two-stage treatment process may be necessary. This can actually be quite efficient, as shown in tables 2 and 5, and does not necessarily require a second ILS unit. For example, a surface mine can, by installing valves in multiple suction and discharge lines, pump the once-treated water from the first-stage settling pond through the same ILS to another settling pond. Similarly, an

TABLE 8. - Flow rates for the ILS, gallons per minute

| Test design | 20 psi | 30 psi | 40 psi | 50 psi | 64 psi |
|---|--------|--------|--------|--------|--------|
| 3 jet pumps in parallel with 1 helixor.. | NA | 411 | 469 | 521 | NA |
| 3 jet pumps in parallel with 2 helixors in series..... | 329 | 317 | 457 | 542 | NA |
| 2 jet pumps in parallel with 2 helixors in series..... | NA | 261 | 310 | 344 | 363 |

NA Not available.

underground mine that is intermittently discharging through an ILS unit into a settling pond can pump from the pond through the same ILS to a second settling pond while the underground pump is off. However, if there is continuous flow, then two ILS units and a second pump are necessary. Our tests of the two-step process indicate that a 50-pct reduction in neutralization costs is possible with such a system (table 2).

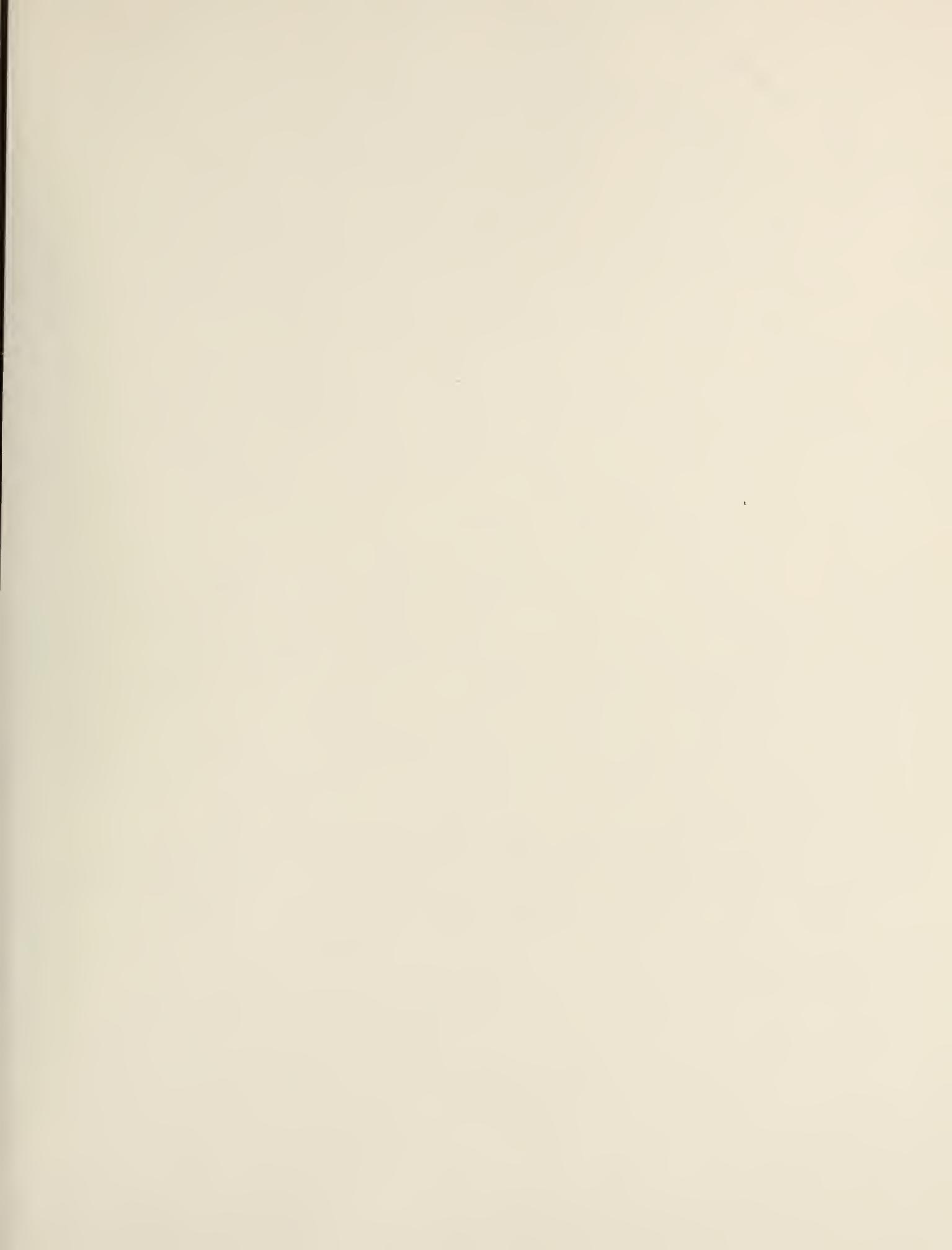
Actual oxygen consumption rates, as calculated from the amount of iron oxidized during passage through the ILS, are shown on tables 5-7. Air transfer tables provided by the jet pump manufacturer do not appear to correlate with observed oxygen consumption. For example, in our ILS design, sample 2 (table 5) consumed 2.3 std ft³/min O₂ operating at 40 psi, with three jet pumps in parallel and with 10 psi back pressure; the manufacturer's tables predict 1.5 std ft³/min per jet or 4.5 std ft³/min of air intake for the three-jet pump system. Sample 1, operating at 50 psi, consumed 2.4 std ft³/min O₂; the same tables predict 0 std ft³/min of air intake under these operating conditions. Actual air flow measurements are needed so that oxygen transfer can be quantified.

Another aspect of system design is cost. The 3-in PVC jet pumps and static mixers cost about \$900 and \$2,500 each, respectively. Associated PVC plumbing costs about \$500. For our tests we purchased a hydraulic pump with a diesel power unit capable of providing pressures up to 50 psi with three jet pumps, but any heavy-duty pump should serve. The total cost is, of course, much less than for construction of a conventional emplaced treatment system. Operating costs should also be low owing to the efficient mixing action, efficient iron oxidation, and lack of moving parts.

There are other advantages. The system is small, and if desired, portable. It requires no electrical power, although it does add slightly to the load on the mine water discharge pump (approximately 10 pct). The basic design is simple and easily modified to cover a wide range of flow and pressure conditions and can operate continuously or intermittently. It can also be dismantled easily for use elsewhere if water treatment is no longer required. Finally, although settling ponds are required, they do not serve as aeration basins and therefore do not require as large an area as would be the case for a conventional treatment plant.

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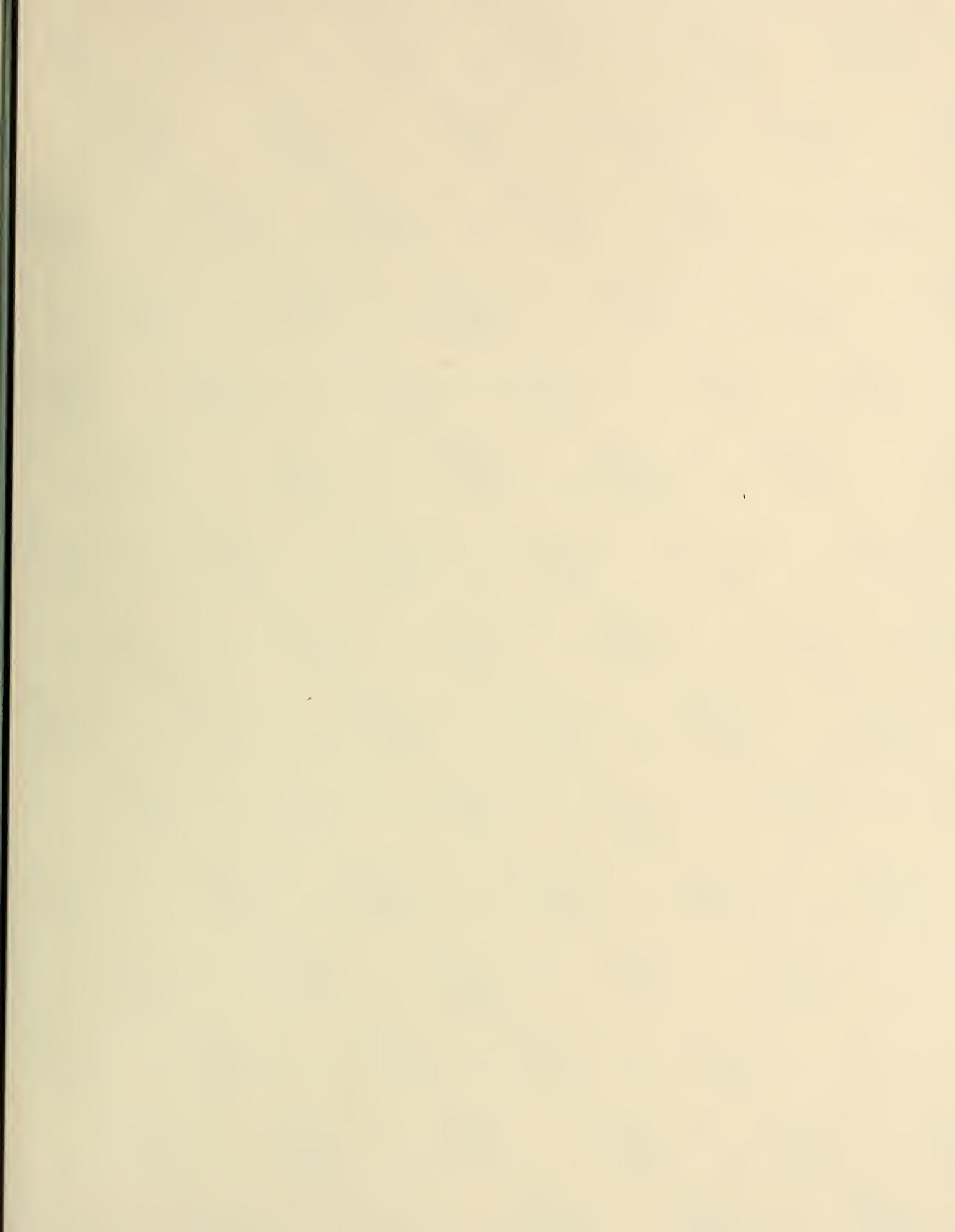
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