

Acid Mine Drainage Prevention, Control and Treatment Technology Development for the Stockett/Sand Coulee Area

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EXECUTIVE SUMMARY

The project was initiated to assist the State of Montana to develop a methodology to ameliorate acid mine drainage problems associated with the abandoned mines located in the Stockett/Sand Coulee area near Great Falls, Montana. Extremely acidic water is continuously discharging from abandoned coal mines in the Stockett/Sand Coulee area at an estimated rate of greater than 600 acre-feet per year (about 350 to 400 gallons per minute). Due to its extreme acidity, the water is unusable and is contaminating other water supplies. Most of the local alluvial aquifers have been contaminated, and nearly 5% of the private wells that were tested in the area during the mid-1980's showed some degree of contamination. Significant government money has been spent replacing water supplies due to the magnitude of this problem. In addition, millions of dollars have been spent trying to remediate acid mine drainage occurring in this coal field. To date, the techniques used have focused on the management and containment of mine waters, rather than designing technologies that would prevent the formation of acid mine drainage.

Their efforts have achieved very limited success. Consequently, acidic drainage from abandoned underground coal mines continues to degrade the water resources in the area. The waste of this valuable resource can be brought under control only by developing techniques or integrating a series of techniques that will prevent the formation and control the discharge of the acid water. The discharge of acid mine waters will not naturally decrease in the foreseeable future. Through the implementation of the work described in this proposal, techniques for the prevention and control of the acid mine drainage can be identified and developed.

The project focuses on a thorough documentation of the hydrologic system of the Number 6 Mine site. This site is basically "confined" without major complications associated with interactions with adjacent mines or other operations. Therefore, the hydrologic system can be thoroughly documented. This allows the acid mine drainage prevention and treatment techniques to be designed and tested for a known environment. The results then can be projected to other mines with a high degree of confidence. A number of techniques will be evaluated, including: (1) interception of the recharge water impacting the flow from the mined areas; (2) the use of amendments, such as bactericides, and neutralization chemicals, including fly ash and phosphate; and (3) the use of Maxi-Acid™.

The hydrologic monitoring program has been developed. The monitoring installations have been constructed and are operational. Additional piezometers will be installed during the summer of 1995 and will be incorporated into the program at that time.

Preliminary field work, which includes evaluations of the groundwater acid mine drainage seeps and overburden chemistry, shows that two major aquifers of interest are present at the mine site. A perched aquifer is present at about 70 feet from the surface, and the second is located at about 180 feet and is associated with the coal existing in the area. The water quality of the perched aquifer is very good with a field pH of 7.7 and an EC of 0.7 mS/cm. The water associated with the coal and the underground mine workings is poor, as it represents typical acid mine drainage. The pH values are about 2.0, and the EC levels are about 6 mS/cm. Data collected from three overburden core samples provide a preliminary indication that the overburden materials at the mine site do not significantly contribute to the acid mine drainage problem. The acid-forming materials found in the overburden appear to be associated with the coal and the materials in close proximity to the coal.

Tests conducted to determine if fly ash materials could be used as effective acid neutralization agents are ongoing. Preliminary results using Ag-lime and sludges from pressurized fluidized bed combustion (PFBC) show that such materials will neutralize the acid and slow the kinetics of the acid-forming reactions.

The Maxi-Acid™ process is currently being evaluated as a possible technique that could be applied to the Number 6 Mine acid mine drainage problem. Preliminary data do not provide an indication of whether or not this process will be effective in the amelioration of the acid mine drainage problem.

INTRODUCTION

Site History

Coal mining began in the Stockett/Sand Coulee area during the 1880's and continued until the 1950's. The mines, closed now for many decades, are flooded with water and are generating large quantities of acid mine drainage. Drainage of acidic water in the area exceeds 400 gpm. The earliest known documentation of acid mine drainage in this area was in the 1970's (Walker, 1974), although the acid problem has no doubt existed for much longer. In the early 1980's, the State of Montana's Department of State Lands (DSL) began to investigate possible solutions to the acid mine drainage problem. Westech/Hydrometrics (1982) inventoried the acid mine discharge points. The Montana Bureau of Mining and Geology (MBMG) investigated the characteristics of the acid mine drainage and the relationship between surface water and groundwater (Osborne, et al., 1983). Preliminary site investigations of two mines were reported by Osborne, et al. (1987). In addition, several regional geologic and hydrologic studies were completed (Fisher, 1909; Goers, 1968; Wilke, 1983).

The acid mine drainage from mines in the Stockett/Sand Coulee area has a pH value between 2 and 3. While the total volume of acid drainage is not known, it is estimated to exceed 600 acre-feet per year based on data gathered at several sites during 1983 through 1985. Most of the alluvial aquifers in Sand Coulee and Stockett Creeks have been contaminated. Bedrock aquifers have also been impacted. In a Montana Bureau of Mining and Geology well testing project, nearly 50% of the private wells tested showed some degree of acid mine drainage contamination.

Many attempts at treating the acid mine drainage problem have been made at these sites. Surface materials have been removed, and lime has been applied to the surface areas to increase the alkalinity of groundwater recharge waters, which would then neutralize the acidity of the discharge water. Cropping techniques, such as growing alfalfa in the recharge areas, have also been used to reduce the amount of recharge available to the affected aquifer. Three wetland sites were constructed to provide passive treatment systems for the cleanup of acid waters. However, none of the treatments used at these sites has significantly reduced the amount of acid mine discharge being produced.

Problem and Significance

The emphasis of the project will be on reducing the flow and the acidity of the mine drainage. The challenge at the Stockett/Sand Coulee area, as in other areas of acid mine drainage, is to develop a treatment that will drastically reduce or eliminate the acid formation. Several attempts have been

made to remedy the problem, however, the methods used have focused on treating and managing the acidic discharge, rather than focusing on avoiding the production of acid. Before additional time and money are spent, an appropriate methodology must be identified for the prevention of the formation of acid water.

The appropriate methodology should correct the problem for a long time and not be prohibitively expensive. Both installation costs and maintenance costs are of major concern. Methods must also be designed for specific settings. There is a strong need for new and creative ideas that are goal-oriented and that specifically address the mine setting in this area. Once a realistic technique has been developed, it can be applied to the other mines.

The elimination of acid mine drainage is based on the successful implementation of one or more of the following approaches: (1) INTERCEPTION of recharge to the acid-producing zone; (2) CONTROL of the acid-producing reactions; and (3) TREATMENT of the acidic discharge. Interception and control techniques are the emphasis of this research. The successful implementation of interception and reaction control techniques requires that the specific treatment be designed for specific settings, based on a thorough understanding of the local hydrologic system. A technique or combination of techniques for the Stockett/Sand Coulee area, as in other areas of acid mine drainage, must be developed that will drastically reduce or eliminate the acid drainage. Techniques must be designed that will last for a very long time and are not prohibitively expensive. The emphasis of this project will be on techniques that reduce the amount of flow and that influence the acidity of the mine drainage. The results of the project will be based on groundwater testing (chemical analysis and pump testing) and laboratory testing (column and permeation studies) of the various treatment systems identified in this proposal.

Techniques that will be considered include: (1) weeper wells in both the recharge area and a deeper aquifer (Madison limestone) to allow the very fresh, low-total dissolved solids (TDS), neutral recharge water to "weep" into the deeper aquifer, bypassing the mine voids; (2) horizontal drains to intercept and reduce recharge; (3) injection of bactericide; (4) injection of phosphates; (5) injection of fly ash, including clean coal technology wastes, to neutralize acidity and to prevent subsidence from occurring in the mined areas; (6) injection of lime or caustic to neutralize the acid generated near the reaction zone; (7) injection of vermiculite and zeolites into the mine voids to isolate the acid-producing sulfides from the water; (8) enhanced oxidation of pyritic materials (this technique will remove the acid-forming materials from the site under controlled conditions); and (9) combining several treatments to bring about long-term effects.

The first step in solving this problem is to develop a thorough understanding of the hydrogeologic setting and the geochemical reactions that are controlling the formation of the acid

mine drainage. Through this project, the geologic, hydrologic and chemical factors that control the production of the acid mine drainage and the location of these reactions will be identified. Once the hydrogeological mechanisms that generate and control the rate of generation of acid mine drainage are identified, then the potential treatment techniques can be evaluated. Possible treatment techniques will be modeled using a series of laboratory studies and the effects determined. The results of this work will be used to design a field demonstration project for the amelioration of the acid mine drainage problem at the Number 6 Mine.

Anticipated Benefits

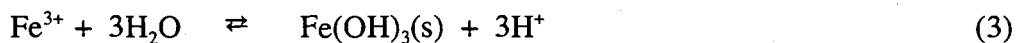
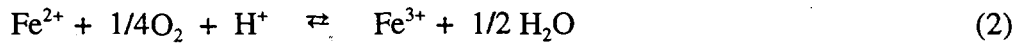
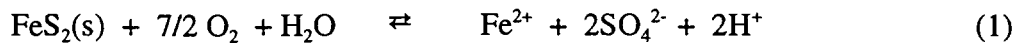
The project directly ensures the quality of the most important public and natural resource in Montana, WATER. Water protection is a statewide as well as a national issue, and water must be protected. Detrimental impacts due to acid mine drainage have been documented in the following areas of Montana: Belt Creek in Cascade County, Sage Creek in Judith Basin County, and North Fork McDonald Creek in Pergus County, as well as in the Stockett/Sand Coulee area. The technology developed from this project pertaining directly to the Number 6 Mine will be applicable to other mines and mining areas and possibly to hard rock mines.

Cleanup and protection of the water resources is a matter of public health, property protection, and resource conservation. Water is also a limiting factor for economic growth. Protection of water resources leads to economic growth. Only through careful development of acid control technology can the water resources in the Stockett/Sand Coulee area be rehabilitated and protected. The project will result in long-term solutions for acid mine drainage. The solutions will be assessed as to maintenance requirements, costs, and longevity. Aquatic habitats will be greatly improved by the eventual implementation of technologies developed from this project. For example, Belt Creek above the acid mine drainage discharge point is a healthy fishery but is devoid of fish below where the acidic discharge water enters the creek. The successful application of treatment systems similar to those developed in this project would result in the rehabilitation of such fisheries. In addition, reductions in acid mine drainage will greatly improve aesthetics and thus the use of the local streams.

BACKGROUND

Acid mine drainage typically has pH values below 2.3, acidity levels near 5000 mg/L, and anionic concentrations (mostly sulfate) exceeding 10,000 mg/L (Caruccio et al., 1981). Iron disulfides in the form of pyrite and marcasite are the predominate contributors to the production of

acid mine drainage. The following reactions occur during the oxidation of the disulfides as described by Stumm and Morgan (1970):



The stoichiometry of equation (1) shows that for every mole of pyrite oxidized to Fe^{2+} , there are two moles of acidity generated as H^+ . Subsequently, the Fe^{2+} is oxidized to Fe^{3+} via reaction (2). This reaction proceeds quite slowly. Stumm and Morgan (1970) observed half-times for Fe^{2+} oxidation on the order of 1000 days. Once the Fe^{3+} is formed, it combines with H_2O to form insoluble $\text{Fe}(\text{OH})_3$ as shown in equation (3). Therefore, the dissolution of each mole of pyrite results in the release of four equivalents of acidity. As the Fe^{3+} concentrations increase with increased acidity, the Fe^{3+} becomes important as an oxidizing agent. Several research efforts have shown that pyrite is rapidly oxidized by Fe^{3+} in the absence of oxygen and at low pH's (Garrels and Thompson, 1960; Smith et al., 1968). This reaction is shown above as (4). Fe^{3+} becomes the only important oxidizing agent when pH's are in the 3 or below range (Singer and Stumm, 1969). These researchers also found that the presence of O_2 did not influence the kinetics of the reaction. Since pyrite can reduce Fe^{3+} to Fe^{2+} faster than Fe^{2+} can be regenerated into Fe^{3+} by O_2 , the pyrite will reduce all the Fe^{3+} and the reaction will stop. Thus, the Fe^{2+} to Fe^{3+} oxidation is considered to be the rate-limiting step in the production of acid. A major catalyst of this reaction is *Thiobacillus ferrooxidans*, which is known to increase the Fe^{2+} oxidation rate by six orders of magnitude (Singer and Stumm, 1970; Nordstrom, 1976). This reaction makes Fe^{3+} readily available for pyrite oxidation.

The amount of acid generated from pyritic materials can be reduced or eliminated by inhibition of the iron-oxidizing bacteria and the reduction in the solubility of Fe^{2+} and Fe^{3+} , with increased pH resulting from the production of alkalinity. In fact, Caruccio (1968) showed that the amount of acidity of mine drainages in western Pennsylvania was a function of (1) the pH of the groundwater, (2) the presence of calcareous materials such as CaCO_3 within the strata, (3) the mode of occurrence of the iron disulfides, and (4) the neutralizing capacity of the groundwater. Similar results were obtained in studies in eastern Kentucky (Caruccio et al., 1976; Caruccio and Geidel, 1978; and Caruccio et al., 1977). From this brief discussion, it is apparent that materials such as CaCO_3 and

CaO that possess neutralization potential can be used with favorable results to reduce acid mine drainage problems. In fact, many studies have shown that limestone materials were effective in neutralizing acid in acid mine drainage applications (Mihok and Chamberlain, 1968; Pearson and McDonnel, 1975; Barton and Vataatham, 1976; Geidel and Caruccio, 1982). In addition, fly ash materials that possess neutralization potential have been used with some success as amendments to surface "soils" to ameliorate acid conditions.

OBJECTIVES

The methods that will successfully prevent acid mine drainage in the Stockett/Sand Coulee area have not been identified. Several attempts have been made to remedy the problem, however, the methods used have focused on treating and managing the acidic discharge, rather than focusing on avoiding the acid production. Before additional time and money are spent, the prevention methodology(s) most likely to correct the acid mine drainage problems must be determined. The overall objective of this project is to carefully and thoroughly evaluate the methods available to control or eliminate the production of acid in the Stockett/Sand Coulee mine area.

The primary focus of this work is to evaluate the methods available and to develop new methods and strategies to address the acid mine drainage problem at the Number 6 Mine site. The project activities include: (1) develop the hydrologic monitoring program; (2) evaluate the chemical nature of the overburden material; (3) determine the acid-forming capacity of the coal and overburden materials; (4) evaluate the acid mine drainage prevention techniques that can be used at the site; and (5) evaluate the use of the Maxi-Acid™ process to deal with the acid mine drainage at the Number 6 Mine.

TECHNICAL APPROACH

Development of the Hydrologic Monitoring Program

A hydrologic mass balance will be developed for the Number 6 Mine area. The mass balance will address vertical and lateral inflow and outflow quantities and flow direction. Monitor wells and flumes will be monitored to gather data that will be used to define these parameters. All existing wells above and adjacent to the mine will be inventoried. Three wells installed as part of an earlier project will be monitored if they are still serviceable. In addition, wells installed in a separate program being implemented by the U.S. Bureau of Mines will also be sampled to supplement the hydrologic information.

Water levels will be measured monthly at each well. Continuous recorders will be installed on three wells located above the mine voids. Water quality samples and field parameter measurements will be collected semiannually at the high and low points on the water level hydrographs. In addition to standard major and minor ion concentrations, laboratory analyses will include sulfide-oxidizing bacteria and sulfate-reducing bacteria, and the ratio of ferrous to ferric ions. Field parameters will include pH, temperature, specific conductivity, Eh, and dissolved oxygen. Tracer tests will also be performed. Tracers will be injected into the overburden and into the mine voids. Different types of tracers, such as sodium bromide and sodium chloride or mixtures of both, will be used at each site to ensure that the results can be related to the correct injection point and time of injection. Shallow seismic surveys will be run to help map the water table.

The data collected from the wells and the shallow seismic surveys will be the basis for defining the recharge rates and direction and rate of groundwater flow. Acid mine drainage prevention techniques will be based on these definitions of the hydrologic systems. For example, the locations and density of recharge interception wells can only be correctly designed with a thorough knowledge of the local system.

A flume has been installed at the mine portal and fitted with a continuous water level recorder to allow water flow measurements. Field parameters, including pH, temperature, specific conductivity, Eh, and dissolved oxygen, will be measured monthly at the flume. Water quality samples for laboratory analysis will be collected semiannually at the high and low points on the water level hydrographs. The surface water samples will be analyzed for the same constituents as the well samples. When tracers are injected into the monitor wells, the timing and intensity of the tracers at the surface flow sites will be monitored. Data collected at the surface water sites will be used to define the discharge portion of the hydrologic mass balance. Tritium analysis will be conducted to determine the time of travel and recharge origin for mine waters. This data will also show whether recharge water has a local or regional origin or if the origin of the water changes on a seasonal basis.

Chemical Budget for the Hydrologic System for the Number 6 Mine

The chemical budget for the local hydrologic system will be developed using the data collected at the monitor wells and surface sites and during the drilling operations. In addition, core and/or cutting samples will be visually described in the field at the time of recovery. Samples will be split, with half stored for future work in the event that a need arises. The other half of the samples will be evaluated for chemical characteristics. Samples will be collected at two-foot intervals unless changes in lithology occur. Each material change noted in the lithology will be sampled, if possible.

Each sample will be characterized using a series of parameters that includes: pH, acid-base accounting, pyrite morphology evaluation by scanning electron microscope, particle size distribution, and EC.

Mechanisms that Control Acid Production

A thorough understanding of the acid generation capacity of the material will be developed using several short-term simulated weathering trials. Simulated laboratory weathering experiments will be performed using the modified soxhlet method (Sobek et al. 1982; Sullivan and Sobek 1982; Sullivan et al. 1986a,b). This laboratory weathering method was chosen because the soxhlets establish acid-producing potentials in short time periods. To summarize the method, each soxhlet will receive approximately 100 g of overburden material. The samples will be saturated with distilled, deionized water at a water cycling rate of approximately 0.18 L/h, and a temperature of 20 to 25°C will be maintained. At the end of each 24-hour leaching period, the leachate in the reservoir will be removed and replaced with an equal volume of distilled, deionized water. The influence of CO₂ removal or entrapment on the amount of acid generated will be evaluated. Immediately after the removal of the leachate from the reservoir, pH, total alkalinity, redox potential, and EC will be measured. The leachate solution will be split. One sample will be acidified to pH 2 with HNO₃ and subjected to metals analysis by ICP. The other sample will be subjected to anion analysis by IC. All analytical measurements will be made in accordance with standard operational procedures and a quality control/quality assurance plan.

The acid production and neutralization potential will also be examined using a humidity cell method. The humidity cells (Essington and Wills 1989; Sullivan and Yelton 1988) will be used to simulate the natural weathering of the unprocessed (unground) overburden materials. For this method, a 1-kilogram sample of overburden material will be spread out evenly in the humidity cell (Teflon-coated, 7-cm deep x 33-cm long x 25-cm wide plastic container with a snap-on Teflon-coated plastic lid) with the lid tightly sealed. Dry air will be passed over the sample at a controlled rate for three days. From day 4 to day 7, humidified air is passed over the sample at a controlled rate. On the seventh day, 1 L of distilled, deionized water is added to the sample and allowed to equilibrate for 1 hour. After 1 hour, the aqueous phase will be removed, leachate pH determined, and the solids returned to the humidity cell. This cycle will be continued for no less than 12 weeks to establish acid production trends.

The project focuses on a small study area so that the hydrologic system can be thoroughly documented. This allows the acid mine drainage prevention and treatment techniques to be designed and tested for a known environment. The results then can be projected to other mines with a high degree of confidence.

ACID MINE DRAINAGE PREVENTION TECHNIQUES

The successful control of acid mine drainage and related impacts is based on implementing techniques that intercept the water before it flows through the acid-producing area, controlling the acid-producing reactions, or neutralizing the acid discharge. Combinations of these procedures can be very effective. Based on the thorough documentation of the hydrologic system at the Number 6 Mine, techniques will be evaluated for potential effectiveness. The techniques found to be promising will be tested in laboratory and modeling experiments. Impacts of the implementation of treatment technologies on any water rights will be addressed as part of the design and evaluation of technologies.

Prevention of acid production is preferred over treatment of the acidic drainage. Avoidance of the problem of acid generation is expected to be both easier and much more cost effective. In addition, the release of large quantities of compounds, such as sulfate, after the acid water is treated with a neutralization process dictates additional treatment of the water. Thus, the use of other amendments and/or technologies, such as the sorption/adsorption of elements and compounds by zeolites and vermiculite, may be important.

Interception of the Recharge Water Impacting Flow from the Mined Areas

A method of avoiding the development of acid mine drainage is to intercept the recharge water before it reaches the active acidification zone. The clean water diverted from this zone is then drained by gravity for beneficial use at the ground surface or used to recharge a deeper aquifer. This type of interception plan can be developed successfully if a detailed knowledge of the hydrologic system is acquired. A clear understanding of where the acid-forming reactions are occurring and how much water is moving through the system is required.

Two techniques will be investigated for their possible effectiveness in intercepting recharge water. One will employ the use of horizontal drainage wells and the other will consist of vertical drainage wells. This project will determine the feasibility of using these approaches to dewater the system through modeling and analytical considerations.

Horizontal drainage wells will be designed for installation in the Kootenai sandstone. These wells will be installed parallel to the bedding planes at the base of the aquifer. The perforated zone of the well will be very long, extending several hundred feet. The wells will be designed to intercept as much water moving vertically through the system as possible, allowing the water to drain by

gravity through the wells to a point where it can be put to beneficial use. The design will include locations, arrangement and density of wells, length of completion, angles for drilling and the cost of installation. The quality and quantity of the discharge water from these wells will be estimated, based on the hydrologic description. The best design will be recommended in the final report.

Vertical drainage wells or weeping wells can be designed in such a way that water from an aquifer with a higher head can enter the well and flow out into an aquifer with a lower head. In the Number 6 Mine, it is anticipated that the wells will be completed in the mine roof sandstone and in the deeper Madison limestone. The Madison limestone has a very high buffering capacity, plus a large flow rate. The evaluation of weeping wells will include size, locations, optimal number of wells, quality of discharge water, possible impacts to the receiving aquifer, and the vertical gradient. In the event that weeping wells are eventually installed, the Madison limestone monitor well installed will be in place to monitor any related effects. Data from this monitor well will be used to estimate rates of drainage through the weeping wells, density of the well field, and water quality impacts.

Reduction of the Amount of Acid Generated in the Mine Areas

An attempt to control acid production in the underground mine will be made through control of the chemical reactions that create the acid. Several amendments will be evaluated independently and in combination with other amendments to control the chemical reactions that are producing acid mine drainage. The control techniques that will be evaluated include: (1) injection of bactericide to eliminate the catalytic influence of the *T. ferrooxidans* on the conversion of ferrous iron to ferric iron that enhances the oxidation of the pyritic material; (2) injection of phosphate compounds to precipitate iron phosphate compounds (and other metal compounds); (3) injection of lime or caustic to neutralize the acid generated near the reaction zone, resulting in the precipitation of metal compounds; (4) injection of fly ash, including clean coal technology wastes, to neutralize acidity and to prevent subsidence in the mined areas; (5) injection of vermiculite and zeolites into the mine voids to remove the heavy metal cations from the acid mine drainage waters; (6) injection of organic substrate amendments meant to stimulate sulfate-reducing organisms, which should passively abate acid mine drainage by consuming acid and precipitating secondary FeS as an insoluble precipitate; and (7) combining several treatments looking at long-term effects. The techniques briefly described will be simulated in the laboratory to determine the impact that would be expected in a field demonstration project.

Acid water used in this study for the bench-scale testing will be collected from the mine or will be simulated using the acid mine drainage for a basis. Selected water samples will be used in combination with amendments in a series of column and permeameter studies that will provide

estimations of how the acid-forming reactions would be influenced if the materials were injected into the Number 6 Mine.

For the static acid mine drainage tests, each test material will be placed in an individual testing chamber that will be used for both static and dynamic acid mine drainage flow testing. The chambers will be constructed using polyvinyl chloride (PVC) tubing. The acid mine drainage media will be tested for pH, EC, SO_4^{2-} , Al and Fe, at 1, 7, 56, and 90 days. The same chambers used for the static acid mine drainage will be used for the flow system. Simulated acid mine drainage will be pumped from a central storage tank to each chamber. The flow system will be allowed to run for 15 weeks. Also, x-ray diffraction (XRD) will be used to determine the effect of the simulated acid mine drainage on the mineral assemblage of the materials. This information will be compared to samples that were not subjected to the acidic solutions. Evaluations will also be made using scanning electron microscopy/energy dispersive x-ray analysis (SEM/EDX) to assess the mineral development and weathering that may result from exposure to the acid environment.

In addition to the above, the materials will also be evaluated using long-term permeation tests. The materials will be compacted into cylinders that will be placed in permeameters using the simulated acid mine drainage media as the permeation fluid. Water will be used as the permeate for the control tests. Cylinders made from the treatment materials will be allowed to cure for 0, 7, and 28 days prior to placement in the permeameter chambers. The acid permeate will continuously flow through the cylinders. During the permeation, changes in the hydraulic conductivity and elemental constituents of the outflow will be determined. Permeability measurements will be made for a total of 90 days, and chemical evaluations of the permeates will be made at appropriate intervals. Results of the chemical evaluations will be used to assess the geochemistry of the system with the use of the geochemistry model MINTEQA2. These data will provide insight into the interactions between the acid leachate and the waste amendments and the rate of movement or attenuation of the leachate constituents. Adsorption and desorption characteristics of the amendments will also be evaluated relative to the important metal constituents of the simulated acid mine water used in the testing.

Use of Maxi-Acid to Treat Acid Mine Drainage

An effort will be made to use the Maxi-AcidTM process to control the formation of acid from the the acid-forming materials. The site would then be remediated within a few months, after which acid discharges to the environment would cease, rather than allowing the acid to form and discharge from a mine site at a slow rate for an indefinite period. This method of remediation eliminates long-term treatment of acid mine drainage and would be expected to significantly reduce negative impacts to the environment.

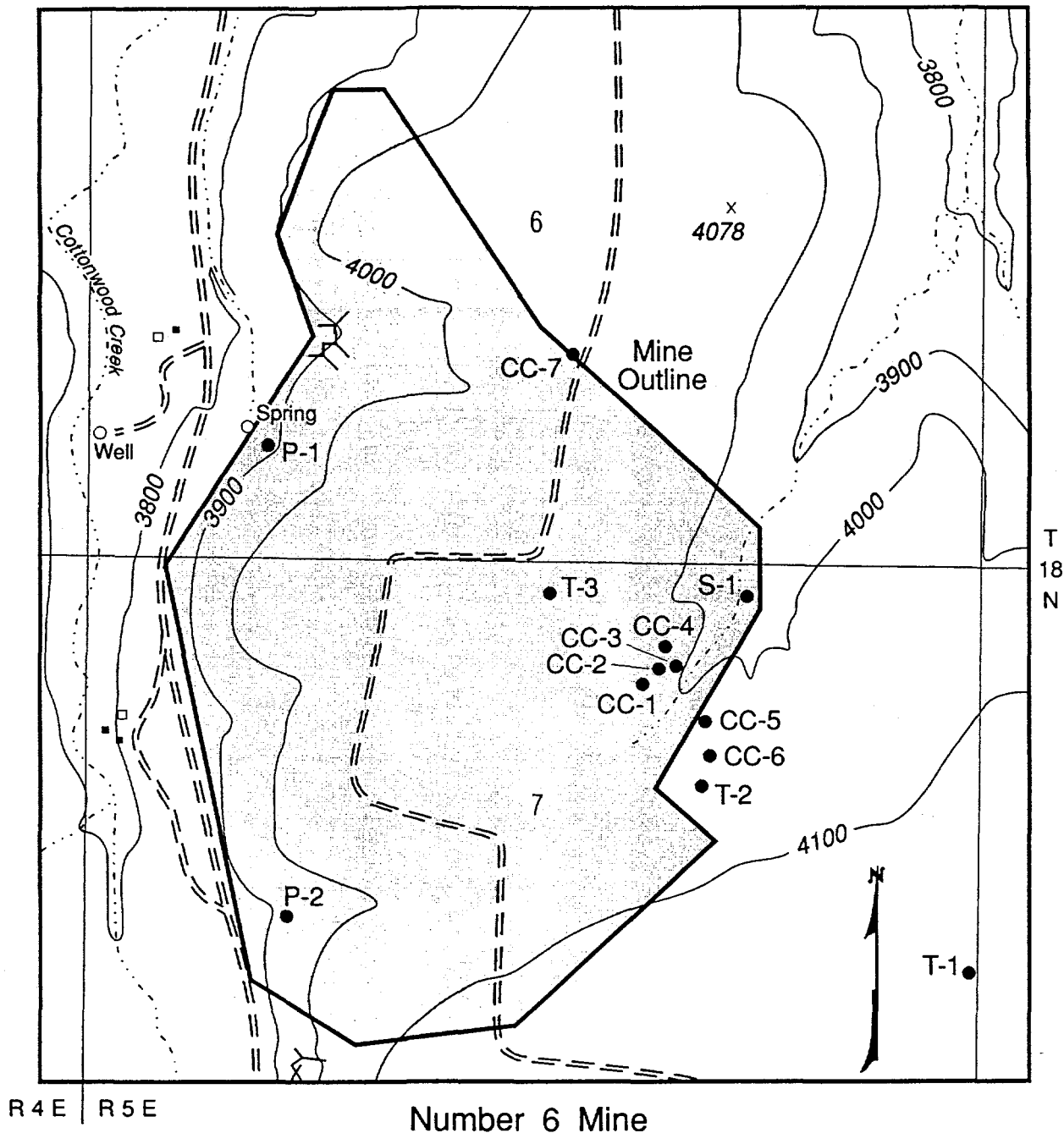
The Maxi-Acid™ process will be examined using simulated weathering columns. The column apparatus will be constructed using a plexiglass column packed with the overburden material that contains the acid-forming material, a reservoir for leachate, and a peristaltic pump for transferring solutions at a constant rate. The materials placed in the columns will be subjected to different environmental conditions that may influence acidity and alkalinity production. Various environmental conditions will be created using amendments and/or conditions, such as the addition of chemical oxidants and acids, injection of gaseous mixtures including oxygen, exposure to wet/dry cycles and saturated versus unsaturated water conditions, and the addition and enhancement of microbial populations (*Thiobacillus ferrooxidans*). Leachates will be sampled and analyzed for pH and elements such as Fe, Al, and Mn. Material samples will be collected to determine the acid-forming potential, using acid/base accounting and humidity weathering.

RESULTS AND DISCUSSION

Development of the Hydrologic Monitoring Program

Much of the work scheduled to be done in the initial period of the project has been started. Groundwater and surface water monitoring programs have been developed, which includes the installation of continuous water level recorders at several piezometer wells, the installation of a Parshall flume with continuous flow measurements at the major acid mine drainage seepage site, monthly level readings on all wells, and monthly flow measurements of surface flows. In addition, water samples are collected on a monthly basis for chemical analysis. The locations of the sampling and the continuous recording sites are shown in Figure 1.

Groundwater monitoring wells and the acid and alkaline seeps (representing surface water located at the site) located at the Number 6 Mine were sampled initially during site visitations. The measurement of water levels and the field analyses of the water samples were collected from these sources (Table 1).



- T Monitor Wells
- C Monitor Wells
- P Acid Discharge
- S Spring Discharge
- Y Mine Portal

Figure 1. Locations of the Water Sampling and the Continuous Water Level Recording Sites

Table 1. Field Data for Site Visits on May 24 through May 26, 1994

Sample collection points and field data collection sites. Refer to Figure 1 for location by number.

5/24/94

- Site P-1.1. located at the outflow point closest to the outlet of the mine, east of the historic railroad bed.
pH = 2.75; EC = 5.88 mS/cm; DO = 2.17 mg/L; Eh 398 + 211 = 609 mv; T = 9.8 °C.
- Site P-1.2. located about 30 feet upstream of the rotted-out Parshall flume.
pH = 2.33; EC = 5.57 mS/cm; TDS = 2.79 g/L; DO = 1.72 mg/L; Eh = +613 mv; T = 11.3 to 11.5 °C.
- Site P-1.3. located about 20 feet upstream of the rotted-out Parshall flume where flow is entering the bottom of the stream.
pH = 3.04; Eh = 613 mv; DO = 1.32 mg/L.
- Site P-1.4. located about 5 feet upstream from the Parshall flume. EC = 5.81 mS/cm.
- Site P-1.5. located at the rotted-out Parshall flume.
pH = 3.01; EC = 5.9 mS/cm; DO = 3.13 mg/L; Eh = +420 + C mv; flow ≈ 15 gal./min (based on 15 quarts of water in 14.9 sec and 14.7 sec).
Piezometer (Well) CC-3.
Initial water sample: Depth of water (top) = 157.99 feet; pH = 7.96; EC = 0.95 mS/cm; DO = 5.45 mg/L; Eh = 112.3 + C mv; T = 16.4 °C; water has a light orange color.
After removal of one case volume: pH = 7.25; EC = 0.924 mS/cm; T = 9.7 °C; water has a light orange color.
After two case volumes: pH = 6.75; EC = 1.28 mS/cm; T = 9.6 °C.
After three case volumes: pH = 6.07; EC = 2.07 mS/cm; T = 10.0 °C.
90 gallons were removed in about 30 minutes, resulting in no head difference.
- Spring (Kootenai Formation) S-1.
pH = 7.52; EC = 0.625 mS/cm; Eh = 243 + 214 (C) = 457 mv; T = 7.9 °C and T_{Hg} = 8.5 °C.
- Piezometer (well) CC-2 (deep)
TOC = 161.25 feet to water; TOC to TD = 198 feet. Unable to collect water samples because the casing is crushed. A small sample was collected for field measurements. The data is questionable. pH = 7.72; EC = 0.85 mS/cm; TDS = 0.43 g/L; T = 12.2 °C to 12.9 °C.
- Piezometer (Well) CC-2 (shallow)
TOC = 58.83 feet to water.
Initial water sample: pH = 7.52; EC = 0.68 mS/cm; TDS = 0.42 g/L; T = 11.1 °C.
After two case volumes: pH = 7.55; EC = 0.74 mS/cm; TDS = 0.37 g/L; T = 10.1 °C.
Note: water appears to be heavily influenced by bentonite.
After three case volumes: pH = 7.54; EC = 0.64 mS/cm; TDS = 0.32 g/L; T = 9.6 °C.
- Piezometer (Well) CC-2 (medium depth)
TOC to the water level = 161.64 feet (TOC = top of plastic).
TOC total depth = 173.1 feet; not able to sample the well due to cracked casing.

Table 1. (continued)

5/25/94

Piezometer (well) T-3

TOC to the water level = 64.75 feet; TOC to TD = 80.3 feet

Amount of water bailed until the well was "dry" = 8/3 buckets x 15 quarts/bucket = 40 quarts or 4 gallons.

pH = 7.67; EC = 0.73 mS/cm; T = 13.2 °C.

Note: assumed the well was screened in the Kootenai aquifer.

Piezometer (well) T-2

TOC to the water level = 66.51 feet.

TOC to TD = 99.4 feet (97.6 + 1.8).

Second bucket tested: pH = 7.98; EC = 0.6 mS/cm; T = 10 °C.

fifth bucket tested: the water is very muddy; pH = 7.86; EC = 0.6 mS/cm; T = 9.6 °C.

The well is making about 2 gal/min with 4 feet of working head.

After a 5-minute recovery period: Test 1 - pH = 8.05; EC = 0.61 mS/cm; T = 9.2 °C.

Test 2 - pH = 8.09; EC = 0.61 mS/cm; T = 9.0 °C.

Stock Spring (T18N, R5E, S7) - Knaup

Flow rate = 15 quarts/6.3 s = 35.7 gals/min

Sample collected at the in-flow to the stock tank; high velocity flow; pH = 7.82; EC = 0.65 mS/cm; T (John K.) = 8.1 °C; T (John W.) = 7.6 °C; Eh = 203 + 214 = 417 mv; TDS = 0.33 g/L; DO = 11.8 mg/L; DO = 8.1 mg/L (in the flow area-the drift was thought to be T-related and possibly flow rate).

5/26/94

Piezometer (well) T-1

TOC to the water level = 38.69 feet.

TOC to TD = 53.8 + 1.8 = 55.6 feet.

Sample 1 tested after removing 15 gal of water from the casing - pH = 6.18; EC = 0.79 mS/cm. After a 5-minute recovery pH = 6.32; EC = 0.83 mS/cm; T = 10.5 °C.

Water sample collection; The casing was baled and allowed to recover for 20 minutes.

The water removed from the well was very dirty.

pH = 6.53; EC = 0.81 mS/cm; T(test 1) = 10.0 °C; T(test 2) = 10.4 °C; TDS = 0.4 g/L; Eh = 378 mv.

Piezometer (well) CC-6

TOC (top of steel) to TD = 235 feet

Initial sample removed from the casing becomes orange with time probably due to oxidation occurring in the casing with time.

Initial sample characteristics: pH = 3.4; EC = 5.65 mS/cm; T = 11.4 °C.

After about 5 gal removed from the casing: pH = 3.37; EC = 5.65 mS/cm; T = 10.6 °C;

The sample smells like iron.

After about 8.75 gal removed from the casing: pH = 3.41; EC = 5.46 mS/cm; T = 10.0 °C.

After about 12.5 gal removed from the casing: pH = 3.31; EC = 5.88 mS/cm; T = 9.9 °C

After about 16.25 gal removed from the casing: pH = 3.29; EC = 5.85 mS/cm; T = 10.1 °C; Eh = 218+214 = 432 mv.

No apparent drawdown; the low pH and no apparent oxidation resulting in clear water.

The well appears to be in the mine workings.

Table 1. (continued)

Piezometer (well) CC-5

TOC (top of steel) to TD = 233.8 feet.

No initial sample was tested. The water was clear.

After about 3.75 gal removed from the casing: pH = 3.3; EC = 3.76 mS/cm; T = 11.0 °C.

After about 7.5 gal (about 1 case volume): pH = 3.12; EC = 3.92 mS/cm; T = 10.2 °C.

After about 11.25 gal : pH = 3.12; EC = 4.32 mS/cm; T = 10.5 °C.

After about 15 gal (about 2 case volumes); pH 3.28; EC = 4.13 mS/cm; T = 11.1 °C; Eh = 468 mv.

A small amount of particle was found in this sample.

Piezometer (well) CC-1 (shallow)

TOS (top of steel) to TD = 167.1 feet.

TOS to depth to water = 42.12 feet.

This well was completed in mudstone.

Initial sample: Test results of the first bale - pH = 6.38; EC = 1.29 mS/cm; T = 11.9 °C

After about 13 gal baled: pH = 6.86; EC = 1.46 mS/cm; T = 10.7 °C:

Not sure if the well is producing water; however it appears that water is running down the casing wall.

Seep - south of the historical seep, located about 7BCAC.

Sample collected at the origin: pH = 1.93; EC = 3.4 mS/cm; T = 11.5 °C.

Sample collected about 30 feet downstream of the seep origin: pH = 2.27; EC = 4.44 mS/cm; T = 14 °C.

Sample collected from the site is muddy and black: pH = 2.67; EC = 3.32; T = 12.8 °C;
Eh = 375 mv.

The data indicate that two major aquifers of interest are present at the mine site. A perched aquifer is present at a depth of about 70 feet from the surface. The water quality is very good, with a pH of about 7.7 and a relatively low electrical conductivity (EC) of about 0.7 mS/cm. This aquifer, which discharges as a spring at one location on the mining area, currently serves as a primary water source for local cattle operations. The second aquifer of interest is the groundwater associated with the acid mine drainage problem in the area. The groundwater levels are about 180 feet below the surface and extend to a depth of about 200 feet or to the bottom of the coal seam. The quality of this groundwater is poor, as it represents a typical acid mine drainage system. The water from this aquifer surfaces at three known locations at the mine site, with various amounts of flow from about 15 gal/min to very slow seeps (Figure 1). The pH values of the water are typically near 2.0, and EC levels were found to be about 6 mS/cm.

A surface water monitoring location that includes a Parshall flume has been installed at the "high-flow" seep. This site is also equipped with a continuous data logging system. The other seepage flow of acid mine drainage will be monitored and sampled, if possible, on a monthly basis. The completion of the monitoring program, which includes the installation of additional monitoring wells, is scheduled for spring, 1995.

Chemistry of the Overburden Materials

The chemistry of the overburden materials has been evaluated from samples collected during drilling operations undertaken by the U.S. Bureau of Mines at the site (Table 2). Samples were collected from three drill holes that extended from the surface to a depth below the coal. Overburden samples were collected at 5-foot intervals to the depth of the coal. Two of the holes entered old mine workings and one hole was drilled in an area outside the limits of the coal.

The samples were analyzed to indicate zones that may be contributing to the acid load generated at the site. Acid/base potential evaluations were used as a measure of the potential for acid formation. If an excess of neutralization potential is available to neutralize the acid as it forms, the material is not expected to generate acid. This is obviously an oversimplification because of the kinetics of the reactions and the numerous side reactions that occur. However, acid/base potential measurements provide an indication of potential acid generation. The data set shows that most samples have positive acid/base potentials. This means that, in general, the materials are not expected to cause the formation of acid drainage.

Samples collected from drill hole CC-7 contain pyritic materials at depths of 160 feet to 228 feet. However, a large excess of neutralization potential in the same zone should reduce the potential for acid generation. Samples collected from drill holes CC-1 and CC-3 show two zones of pyritic material, which results in negative acid/base potentials. These potentially acid-generating materials are found at depths of 80 feet to 100 feet and from 200 feet to 215 feet in drill hole CC-1, and at 80 to 90 feet and 200 feet to 215 feet in drill hole CC-3. Materials at depths near 200 feet are expected to be very closely associated with the coal. If these materials were exposed to oxidizing conditions, acid would be expected to occur.

The data collected from this testing program provide an indication that the acid mine drainage generated at the Number 6 Mine has little to do with the overburden materials. Since the coal and the materials located in close proximity to the coal contain large amounts of pyritic materials, this material is expected to be the primary source of the acid mine drainage. Additional samples will be collected during the drilling program, which is expected to be completed during the spring of 1995. Information collected at that time, plus the data collected to date, will show which materials are primarily responsible for the acid generated at the Number 6 Mine.

Table 2. Acid/Base Accounting Data for the Overburden at the Number 6 Mine

Sample Site	Depth (feet)	Potential Acidity (t/1000t)	Neutralization Potential (t/1000t)	A/B Potential (t/1000t)	Pyritic Sulfur (t/1000t)	Pyr-ABP (t/1000t)
Site CC-7	0 to 5	0	58.3	58.3		
	5 to 10	0	10.9	10.9		
	10 to 15	0	9.83	9.83		
	15 to 20	0	3.29	3.29		
	20 to 25	0	2.12	2.12		
	25 to 30	0	14.2	14.2		
	30 to 35	0	33.6	33.6		
	35 to 40	0	3.88	3.88		
	40 to 45	0	1.76	1.76		
	45 to 50	0	1.95	1.95		
	50 to 55	0.31	1.43	1.12		
	55 to 60	0.94	2.2	1.26		
	60 to 65	2.5	26.9	24.4		
	65 to 70	1.87	45.3	43.43		
	70 to 75	0.62	72.3	71.68		
	75 to 80	0.62	157	156.38		
	80 to 85	0	166	166		
	85 to 90	0	195	195		
	90 to 95	0.31	135	134.69		
	95 to 100	0.31	139	138.69		
	100 to 105	1.56	411	409.44		
	105 to 110	0	301	301		
	110 to 115	0.31	305	304.69		
	115 to 120	0	240	240		
	120 to 125	0.62	201	200.38		
	125 to 130	0.31	150	149.69		
	130 to 135	0.31	200	199.69		
	135 to 140	0.31	244	243.69		
	140 to 145	0.31	222	221.69		
	145 to 150	0.31	250	249.69		
	150 to 155	0.31	191	190.69		
	155 to 160	1.25	158	156.75		
	160 to 165	11.2	127	115.8	7.19	119.81
165 to 170	10.9	44.4	33.5	5	39.4	
170 to 175	3.44	17.1	13.66	3.75	13.35	
175 to 180	9.68	34	24.32	8.43	25.57	
180 to 185	6.25	52	45.75	3.44	48.56	
185 to 190	11.2	44.6	33.4	9.37	35.23	
190 to 195	17.5	65.5	48	15.3	50.2	
195 to 200	21.9	23	1.1	20	3	
200 to 205	6.25	59.8	53.55	4.69	55.11	
205 to 210	3.12	42.7	39.58	1.56	41.14	
210 to 215	5.31	133	127.69	5	128	
215 to 220	5.62	131	125.38	5.31	125.69	
220 to 225	10.6	65.7	55.1	8.75	56.95	
225 to 228	9.68	36.2	26.52	6.25	29.95	

Table 2. Acid/Base Accounting Data for the Overburden at the Number 6 Mine (continued)

Sample Site	Depth (feet)	Potential Acidity (t/1000t)	Neutralization Potential (t/1000t)	A/B Potential (t/1000t)	Pyritic Sulfur (t/1000t)	Pyr-ABP (t/1000t)
Site CC-1	0 to 5	0	13.1	13.1		
	5 to 10	0	94.3	94.3		
	10 to 15	0	17.7	3.91		
	15 to 20	0	3.91	3.91		
	20 to 25	0	7.23	7.23		
	25 to 30	0	9.85	9.85		
	30 to 35	0	2.03	2.03		
	35 to 40	0	15.5	15.5		
	40 to 45	0	2.81	2.81		
	45 to 50	0	1.53	1.53		
	50 to 55	2.5	10.6	8.1		
	55 to 60	1.87	17.7	15.83		
	60 to 65	0	1.1	1.1		
	65 to 70	0	1	1		
	70 to 75	0	1.15	1.15		
	75 to 80	0	2.36	2.36		
	80 to 85	4.37	1.15	-3.22	3.75	-2.6
	85 to 90	10.6	1.35	-9.25	10.3	-8.95
	90 to 95	30.9	12.4	-18.5	31.2	-18.8
	95 to 100	25	12.7	-12.3	27.2	-14.5
	100 to 105	4.69	13	8.31	3.75	9.25
	105 to 110	3.75	34.4	30.65	5	29.4
	110 to 115	13.1	135	121.9	12.5	122.5
	115 to 120	13.1	421	407.9	16.6	404.4
	120 to 125	0.31	346	345.69		
	125 to 130	0	146	146		
	130 to 135	0.62	204	203.38		
	135 to 140	0	251	251		
	140 to 145	0.31	245	244.69		
	145 to 150	0	246	246		
	150 to 155	0	224	224		
	155 to 160	0	224	224		
	160 to 165	0	242	242		
	165 to 170	0	231	231		
170 to 175	11.6	246	234.4	19.7	226.3	
175 to 180	16.9	204	187.1	23.4	180.6	
180 to 185	26.2	238	211.8	30.3	207.7	
185 to 190	14.7	174	159.3	22.5	151.5	
190 to 195	24.4	119	94.6	25.3	93.7	
195 to 200	21.9	125	103.1	28.1	96.9	
200 to 205	44.4	18	-26.4	11.9	6.1	
205 to 210	47.5	2.21	-45.29	14.4	-12.19	
210 to 215	42.2	7.61	-34.59	12.8	-5.19	

Table 2. Acid/Base Accounting Data for the Overburden at the Number 6 Mine (continued)

Sample Site	Depth (feet)	Potential Acidity (t/1000t)	Neutralization Potential (t/1000t)	A/B Potential (t/1000t)	Pyritic Sulfur (t/1000t)	Pyr-ABP (t/1000t)
Site CC-3	0 to 5	0	130	130		
	5 to 10	0	43.2	43.2		
	10 to 15	0.31	30.4	30.09		
	15 to 20	0.31	46.4	46.09		
	20 to 25	0	28.7	28.7		
	25 to 30	2.5	15.5	13		
	30 to 35	5.94	17.1	11.16	3.12	13.98
	35 to 40	0	12.8	12.8		
	40 to 45	0.94	33.9	32.96		
	45 to 50	0.31	1.51	1.2		
	50 to 55	0	4.48	4.48		
	55 to 60	0	2.38	2.38		
	60 to 65	0	2.25	2.25		
	65 to 70	0	2.3	2.3		
	70 to 75	0.31	3.02	2.71		
	75 to 80	4.37	5.92	1.55	2.81	3.11
	80 to 85	15.6	5.94	-9.66	13.1	-7.16
	85 to 90	43.1	9.91	-33.19	36.2	-26.29
	90 to 95	61.5	118	56.5	67.2	50.8
	95 to 100	24.1	137	112.9	25.3	111.7
	100 to 105	0	145	145		
	105 to 110	0.62	139	138.38		
	110 to 115	1.25	146	144.75		
	115 to 120	0.94	169	168.06		
	120 to 125	1.56	135	133.44		
	125 to 130	0.62	293	292.38		
	130 to 135	1.87	300	298.13		
	135 to 140	0	242	242		
	140 to 145	0.62	247	246.38		
	145 to 150	5.31	250	244.69	5	245
	150 to 155	0	141	141		
	155 to 160	0.62	144	143.38		
160 to 165	0	237	237			
165 to 170	0.94	238	237.06			
170 to 175	9.06	243	233.94	16.2	226.8	
175 to 180	14.7	234	219.3	24.1	209.9	
180 to 185	20.3	241	220.7	23.7	217.3	
185 to 190	19.7	238	218.3	29.7	208.3	
190 to 195	33.4	144	110.6	40.3	103.7	
195 to 200	40.9	76.7	35.8	45	31.7	
200 to 205	57.5	9.07	-48.43	40.9	-31.83	
205 to 210	54.4	4.13	-50.27	28.4	-24.27	
210 to 215	54.7	1.61	-53.09	19.4	-17.79	

Control of Acid Mine Drainage Through Manipulation of Chemical Reactions

Laboratory testing has been initiated to evaluate the application of amendments to acid-forming materials in an effort to reduce or prevent the formation of acid. Evaluations have been initiated using coal combustion products and Ag-lime as acid neutralization material. The use of CaCO₃, PFBC fly ash sludges, and fly ash materials collected from three power plants located in the vicinity of acid mine drainage problem areas in Montana are under investigation as neutralization materials for a mine spoil material containing high potential acidity levels. The general chemistry of the materials is presented in Table 3.

Table 3. General Chemistry of the Fly Ash Neutralization Materials

Element	Mt.-Rosebud mg/L	Mt.-Coalstrip mg/L	Billings Brick mg/L	Karhula (1:1) mg/L	Tidd mg/L
Ag	<0.01	<0.045	<0.1	<0.01	0.02
Al	<0.045	0.283	0.231	5.51	<0.045
As	<0.1	<0.1	<0.1	<0.1	<0.1
B	0.035	31	27.3	0.953	3.88
Ca	823	405	806	403	398
Cd	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	<0.008	0.045	0.036	<0.008	<0.008
K	29.3	29.9	15.7	28.8	>1000
Mg	0.078	25.4	0.027	1.44	0.565
Mo	0.167	0.388	0.14	1.36	0.139
Na	12.5	172	29.4	196	486
Pb	<0.05	<0.05	<0.05	<0.05	0.107
Se	<0.1	<0.1	<0.1	<0.1	0.141
EC(mS/cm)	3.01	2.61	3.75	3.19	6.98
pH	11.12	8.87	11.97	8.88	8.98
Neut. Potential	292 t/1000t	54.9 t/1000t	226 t/1000t	131 t/1000t	545 t/1000t

Tests using CaCO₃ and PFBC sludges were used to treat a mine spoil material with a pH of about 3 and containing very high levels of potential acidity (-40 tons CaCO₃/1000 tons of material). The tests were conducted in humidity cells over an eight-week period. The data are presented in Figure 2. The CaCO₃ treatment was effective in increasing the pH of the system over the 56-day period without substantial pH reduction. The PFBC material was also effective in increasing the pH of the system. However, this material was slow to react and did not efficiently neutralize acid for about 14 days. This could be explained either by a difference in the kinetics of acid generation and the dissolution of the alkalinity from the PFBC materials or may simply be directly related to or controlled by the dissolution rate of the PFBC materials. Additional humidity cell testing has been initiated using the three fly ash materials generated from power plants located in Montana.

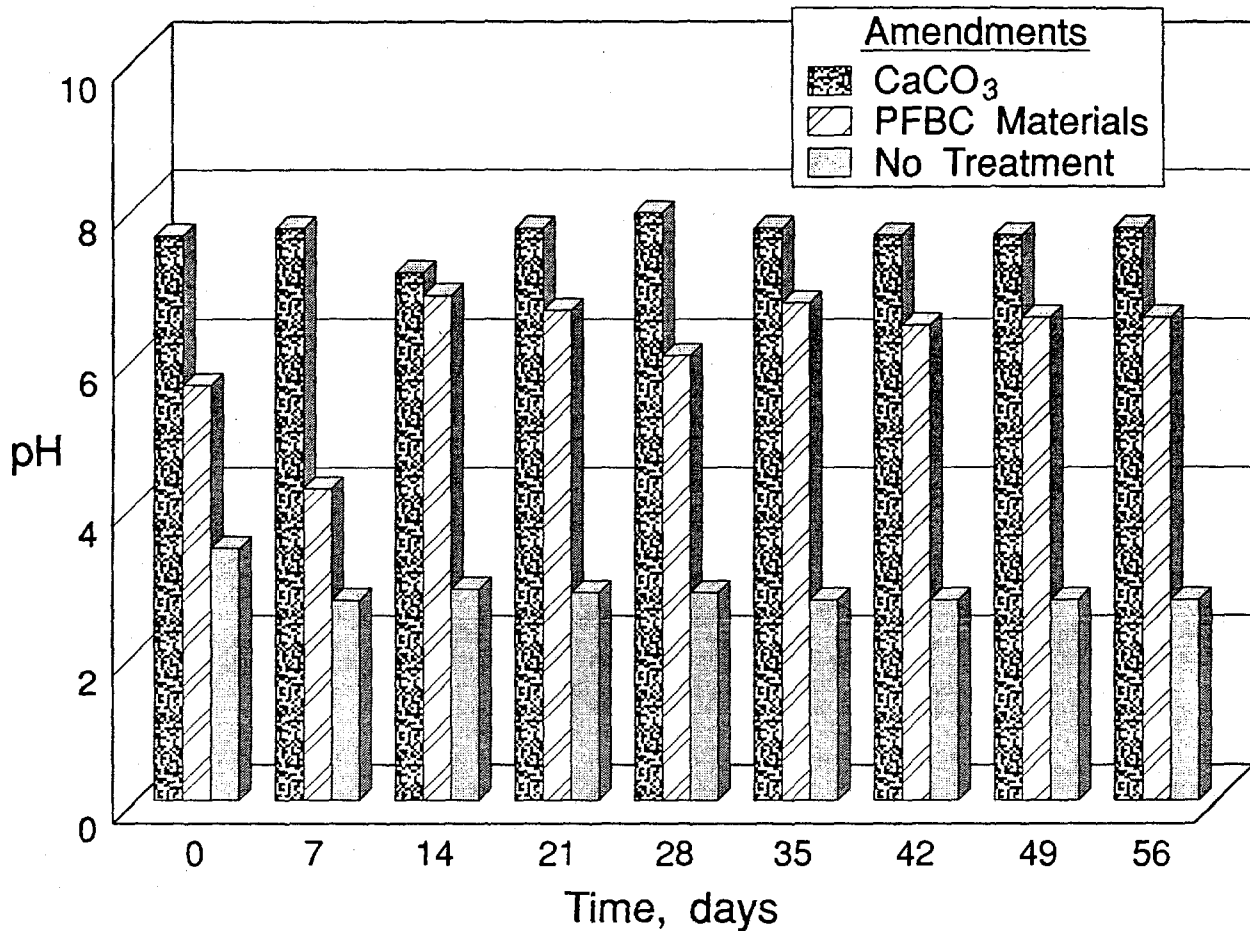


Figure 2. Change in pH of Amended Acid Materials with Time

Control of Acid Mine Drainage Using Maxi-Acid™

The Maxi-Acid™ process is currently being evaluated using a humidity cell technique. The intention of this work is to provide a baseline for our continued effort with Maxi-acid. The humidity cell oxidation process was allowed to proceed for 336 days. The pH and EC data collected during this period are presented in Figures 3 and 4, respectively. The acid-forming materials used in this study had an initial pH of 3.44 and an EC of 3.88 mS/cm. As the humidity cell oxidation progressed, the pH decreased to about 2.75 after 7 days and tended to slowly decrease to about 2.46 after 70 days. From 70 days to 336 days, the pH fluctuated between 2.6 and 3.14 (Figure 3). These data indicate that the acid-forming process is initially accelerated to a level dictated by the mineralogy of the system.

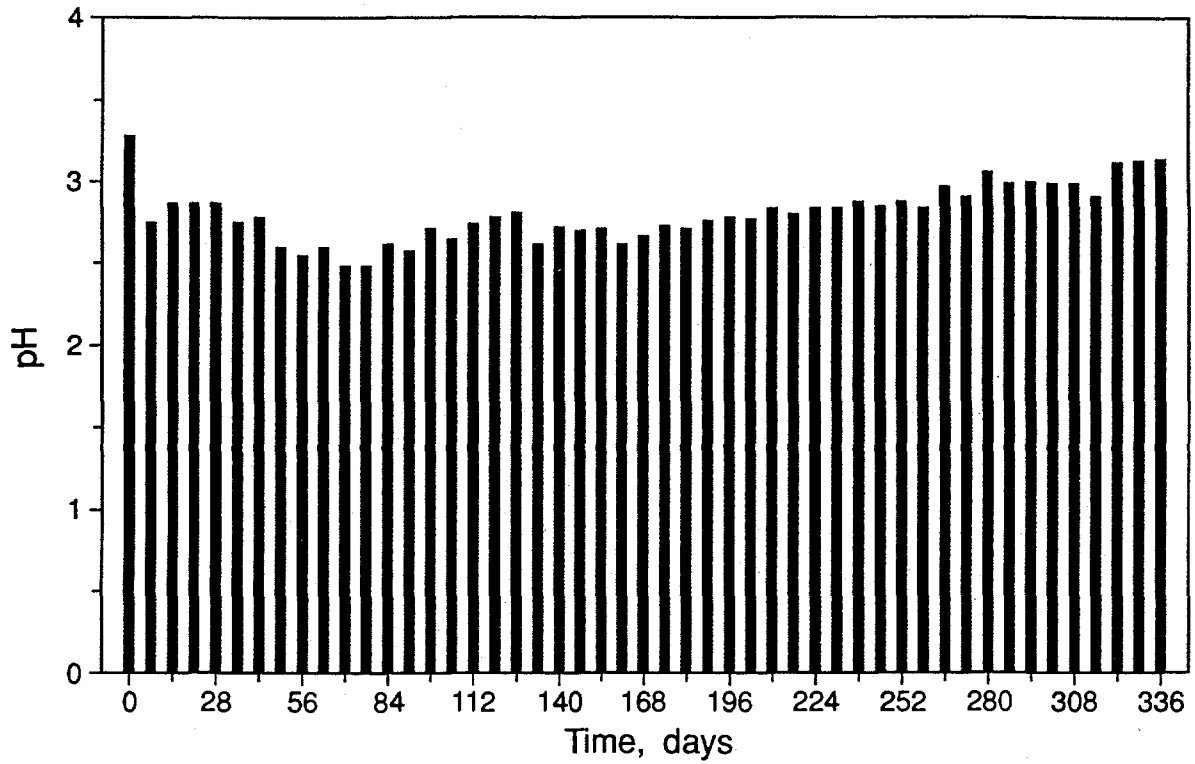


Figure 3. The Influence of Oxidation on the pH of the Acid-Forming Overburden with Time

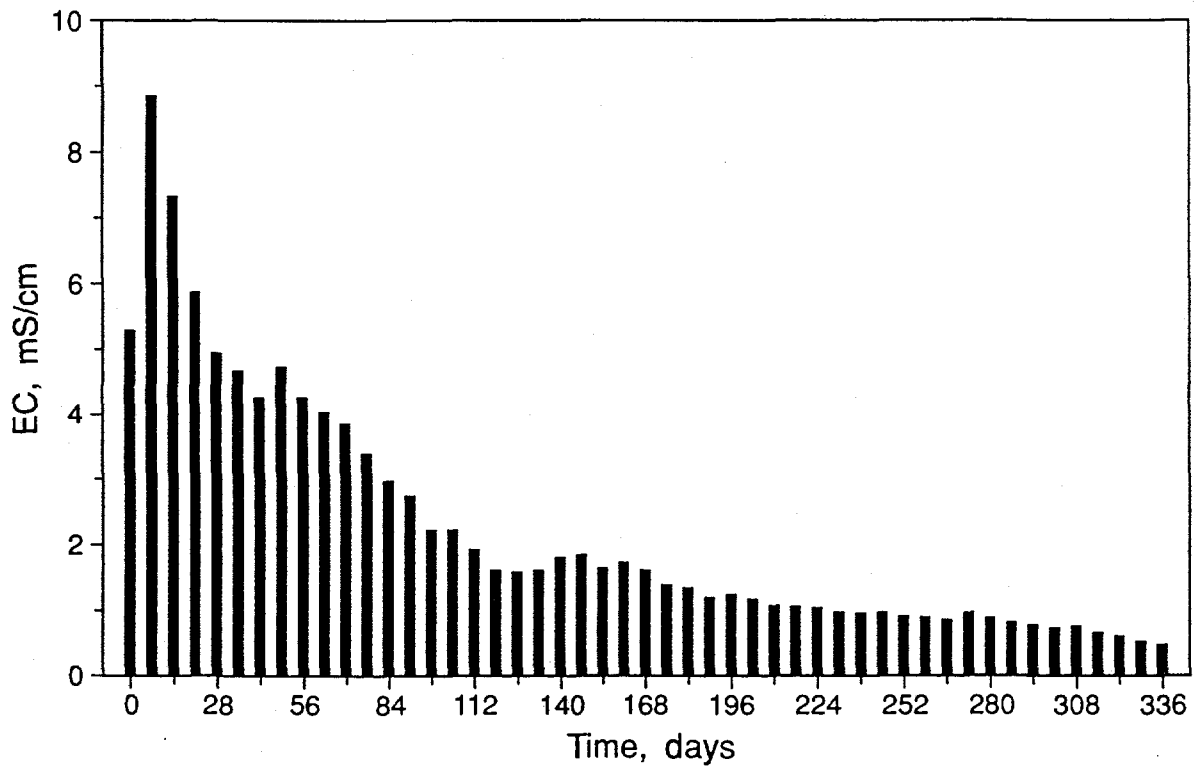


Figure 4. The Effect of Oxidation on the EC of the Acid-Forming Overburden with Time

The EC data shown in Figure 4 provides similar indications. The initial increase in EC from 3.88 to about 9.16 is due to the large amount of reaction products generated by the accelerated acid forming reactions. The EC values decreased from day 7 to day 336 as the oxidation processes continued. This substantial reduction in EC values is due to the use of leaching as part of the weekly operation of the humidity cell, resulting in the removal of reaction products from the system. In addition, the kinetics of the reactions causing the reduction of pyritic materials may be slowing.

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