AT SOURCE CONTROL OF ACID MINE DRAINAGE: AN UPDATE

by

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INTRODUCTION

The primary objective of the Bureau of Mines Acid Mine Drainage Technical Advisory Committee (AMDTAC) research projects is development of methods for low-cost, at-source control of acid mine drainage (AMD) from reclaimed surface mines. The studies in progress are designed to:

1. Determine the acid-producing characteristics of inactive, reclaimed surface mines;
2. Test the potential effectiveness of bactericidal treatment on inactive/abandoned mined lands.

The first of these studies involves the use of surface geophysical methods for locating sub-surface AMD source areas and flow paths. Definition of the acid-production and transport characteristics of a surface mine is the first step in development of a site-specific, at-source abatement procedure. The principal geophysical method being evaluated is electromagnetic induction (EM). Presented here are the results of three EM studies conducted in Upshur and Randolph counties. Detailed description of the EM technique is given in McNeill (1980) and surface mine applications are given in Ladwig (1982).

The second study concerns refinement of bactericidal control of AMD for use at reclaimed surface mines. The importance of iron-oxidizing bacteria in the formation of acid mine drainage has been established in the laboratory and in the field. A technique to reduce acid production by spraying anionic surfactant solution directly on pyritic material has been developed. These surfactants effectively and economically inhibit bacterial activity when washed into the oxidizing material with infiltrating rainfall. Successful field tests have been conducted at unreclaimed refuse areas (Kleinmann and Erickson, 1983).

At reclaimed surface mines, the hydrology is generally more complicated than at unreclaimed refuse piles. Infiltration is often reduced by revegetation and compaction, and rainfall may not be the predominant source of recharge to the spoil water. Simple surface application of surfactant may not provide adequate transport of the surfactant to the oxidation zone. Use of the anionic surfactant at surface mines requires that first the mechanism of acid-production and transport be described. Presented here are the preliminary results of hydrology and spoil gas studies conducted at a reclaimed surface mine in Upshur County to facilitate surfactant application.

The third study is an investigation of alternative bactericidal agents for use at sites where the soluble surfactants are not useful. Specifically, we are attempting to identify inhibitory compounds that will precipitate in acid producing zones. The precipitate should be sparingly soluble to provide a reservoir of bactericide. Presented here are preliminary laboratory results and a description of pilot scale experiments.

GEOPHYSICAL STUDIES

Background

EM induction is used to measure the ability of a volume of earth material to transmit an electrical current. The ease with which the current is transmitted is a function of the electrical conductivity of the material. High conductivity (low resistivity) indicates good current transmission capabilities. The conductivity of earth material depends on the physical nature of the rock, sediment or soil, and the pore fluid (usually air or water).

The equipment used for this study consists of a transmitter, transmitter coil (wire loop), receiver, receiver coil, and connecting cable. The equipment is entirely portable, requiring only a two-person crew for operation. Readings are taken with the coils at a fixed distance of 10 meters (m), 20 m, or 40 m, depending on the desired depth of penetration. The secondary magnetic field sensed at the receiver is internally converted to terrain conductivity and displayed in millimhos/meter (mmhos/m). The receiver also has an analog display for accurate maintenance of coil separation.

Successive readings taken along a single profile line are generally presented in graphical form to illustrate lateral variations in terrain conductivity. Readings from a series of profile lines are plotted in grid form and contoured to illustrate areal variations in terrain conductivity.

EM surveys were run at three surface mine sites in the Buckhannon area. Two of the sites, Pierce and Hobet, were surveyed in detail and wells were drilled for correlation. At the third site (DLM), a preliminary survey was run for correlation with a concurrent hydrologic study (Caruccio and Geidel , personal communication), but detailed EM work was not done. Some surveying was also done at a fourth surface mine (Island Creek), but the spoil thickness was too great (more than 30 m) to obtain any meaningful results.

Results

Pierce Site

The Pierce site is a 6 hectare (ha) sub-area of a 32 ha surface mine in Upshur County, West Virginia. The site was mined for the Lower and Middle Kittanning seams in the mid-1970's and reclaimed shortly after mining was completed. Reclamation included grading and revegetating, but the site was not returned to approximate original contour (AOC). As a result, present site topography consists of a steep slope at the old highwall, a broad, flat bench over the mined area, and a steep outslope. The mine floor dips gently to the northwest and maximum spoil thickness on the bench area is about 8 m. Following reclamation, a perennial acidic seep with mean annual discharge of 1.1 L/s (18 gal/min) developed at the toe of the outslope.

EM surveying of the site was done to facilitate field application of a bactericidal agent to decrease acid production. This method of abatement requires direct application of the bactericide to the acid-producing zones, so it was of considerable importance to determine the location of any pockets of pyritic material or localized zones of poor water quality.

Contoured results of a rectangular grid of EM profiles obtained using a 10 m intercoil spacing and horizontal dipole are shown in figure 1. The plot is a composite of two surveys run perpendicular to each other. Each survey resulted in collection of 60 data points and required approximately 5 hours field time for a two-person crew. The locations of eight observation wells installed subsequent to the surveying are also shown on figure 1.

Apparent conductivities at the site ranged between 6 and 18 mmhos/m, the highest values occurring in the northwestern (upper left) corner. The highest apparent conductivities (14-18 mmhos/m) appear to be related to a fine grained, carbonaceous material (coal cleanings) buried in the spoil. Drill holes 4 and 6, both located in areas with apparent Conductivities greater than 14 mmhos/m, contained 6 m and 2 m of the cleanings, respectively. Spoil in the six other drill holes contained only a brown, weathered sandstone with particle sizes ranging from clay to small boulders. Samples obtained from the drill holes were analyzed in the laboratory: the cleanings contained a higher percentage of sulfur than the weathered sandstone, with mean values of 1.24 pct and 0.12 pct, respectively. Samples of the underclay were also analyzed and exhibited a mean sulfur content similar to the cleanings, 1.20 pct.

The lowest apparent conductivities on the site were observed in the southeastern (lower right) corner, and are interpreted as the spoil outslope. The outslope is generally composed of very coarse boulders, has a steep hydraulic gradient, and contains little stored spoil water. The coarse material rapidly transmits overflow from the mine floor to the discharge area. Drill holes 2, 3, and 5, all located in areas with apparent conductivities less than 10 mmhos/m, are all believed to be on the outslope. Wells 3 and 5 are dry at all times of the year, while 2 is intermittently dry.

Not surprisingly, the poorest water quality on the site was observed at well 4. Areal variations in water quality were impossible to determine from the raw EM data, due to the more prominent electrical heterogeneity of the spoil material. Similarly, temporal variations in water quality and quantity were not readily evident from a replicate EM survey conducted in spring at high water levels.

Hobet Site

The Hobet site is located on the drainage divide between the Middle Fork and Tygart Rivers. The site has an average spoil thickness greater than 12 m and covers an area of about 20 ha. A perennial acidic seep issues from the toe of spoil with a mean flow of approximately 2.0 L/s (32 gal/min). Results of an EM survey using the 20 m coil spacing and horizontal dipole are shown in figure 2. Three test holes were drilled on the site. All three holes encountered a bouldery sandstone spoil and little or no water to a depth of 12 m. Well 2 did encounter a thin layer of fine-grained black material near the surface.

The results at the Hobet site were not as clearly defined as at Pierce. The low conductivities (less than 4 mmhos/m) on the southern part of the site appear to be related to a coarse sandstone spoil believed to have been brought in from another part of the site. The subtle change in conductivity from 8 to 12 mmhos/m near the seep may be related to flow characteristics and/or changes in spoil material but neither of these was confirmed by drilling. The anomalously high conductivity area (greater than 20 mmhos/m) is believed to result from electrical "noise," possibly a metallic object buried in the spoil.

In short, the EM survey and limited drilling were not sufficient to substantially improve understanding of site hydrology or acid source areas at the Hobet site. The lack of success may be due to the thickness of the spoil (more than twice the thickness of the Pierce spoil), or may simply indicate that no significant shallow electrical features are present on the site. It is important to note that the drill holes encountered very little water in the upper 12 m of spoil . Below 10 - 15m, the resolution of EM surveying at the 20 m coil spacing is greatly diminished.

DLM Mercer Site

The hydrology and spoil characteristics of the DLM Mercer site is described in Caruccio and Geidel (1983). A preliminary EM survey at the site revealed very low conductivities, ranging from about 2-8 mmhos/m. The low values are indicative of a coarse spoil with low intergranular moisture retention. The lack of any anomalously high conductivity zones indicates no localized sources in the survey area. Variations in conductivity at the site are believed to be related to variations in ground water storage. This possibility was supported by a broad correlation between data from test holes dug for the hydrologic study and the observed conductivity distribution. Unfortunately, no detailed surveying was done at this site to tighten the correlation.

Based on the results obtained at these sites and others in WV and PA, a few generalizations can be made regarding the use of EM techniques at reclaimed surface mines:

1. The EM technique is sensitive to at least two important features associated with AMD saturated spoil zones and fine grained, acid producing material. Of these two, it appears to be considerably more sensitive to the latter. Therefore, the technique will be most easily and successfully used at sites where there is a localized acid source, such as refuse or pit cleanings.

2. If no localized source is present, EM variations are much more subtle and somewhat more difficult to interpret. Higher conductivities are generally found in areas with a greater amount of water, but the differences are not always pronounced and can be obscured by background conductivity fluctuations. Interpretation becomes more difficult as the thickness of spoil increases, and particularly as the thickness of unsaturated spoil increases.

3. EM equipment is designed for quick surveying of large areas. More detailed

work can be done to clarify and improve the geophysical interpretation. The Bureau of Mines will be exploring some other geophysical techniques, such as very low frequency (VLF) electro-magnetics and resistivity profiling, to evaluate their applicability at surface mines.

HYDROLOGY AND SOIL GAS STUDIES

Background

The Pierce mine site, described earlier for the geophysical studies, is located on the divide between the Buckhannon and Middle Fork Rivers. The site was mined for the Middle and Lower Kittanning seams in the mid-1970's. Pasture and meadowland reclamation, including revegetation of the reduced highwall, was completed in 1978. Overburden analysis prior to mining identified thin layers of both toxic and non-toxic shale strata above the coal. The reclamation plan called for stockpiling the non-toxic shale for use as topsoil, and mixing the toxic shale with the inert sandstone spoil. The study area is a 6 ha U-shaped portion of the Pierce mine hydrologically isolated from the rest of the site (fig. 3). The study area has a low permeability clay soil with good vegetative cover, but recharge to the spoil from highwall seepage supports a perennial acidic seep at the spoil toe.

The first phase of the study is definition of the hydrology and soil gas composition to determine where the acid is forming and how it is moving through the spoil. Discharge water quality and quantity has been monitored on a biweekly to monthly basis since January, 1983. Seven monitoring wells were installed to determine spoil water flow directions and quality, and two multi-level gas samplers (near wells 5 and 8) were installed to monitor lateral and vertical variations in soil air (fig. 2). An electromagnetic induction survey was also run at the site to further define subsurface conditions.

The second phase of the study will be application of a bactericidal agent, possibly in both liquid and slow-release forms. The method of application depends on the final results of phase 1.

Phase 1 Preliminary Results

Results of the geophysical survey of the site were described in a previous section. The survey, along with spoil boring logs and leaching tests, indicated that acid-producing material is concentrated on the western part of the site near wells 4 and 6.

Discharge monitoring for the period November 1982 to December 1983 revealed a distinct seasonal trend in water quality parameters. In general, concentrations of AMD constituents at the discharge were two-fold higher during low flow months (August- September) than during high flow months (May-June, November-December) indicating some dilution during periods of recharge to the spoil (fig. 4a-c). Despite lower concentrations at high flow, the net effect is a significantly higher discharge load during major recharge events (fig. 4d).

In development of at-source abatement strategies, it is important to note that discharge water quality is a composite of the water quality originating on various parts of the mine site. Analysis of well water samples revealed a wide range in contamination levels across the site (Table 1). The water quality data again point to the area near well 4 as the primary source of acid production. Mean sulfate, iron, and acidity concentrations were two to three times higher in water samples from well 4 than samples from any other well or at the discharge (Table 1).

The spoil water on the Pierce site is recharged by both precipitation and ground water seepage at the highwall . Higher water levels indicate most of the highwall seepage occurs in the area near well 7. Water samples obtained from well 7 were the least contaminated samples analyzed (Table 1).

As oxygen is required for pyrite oxidation, soil gas monitoring is being used to assess spatial and temporal variations in oxygen availability. Preliminary spoil atmosphere analyses from gas samplers (GS) 5 and 8 are shown in Tables 2 and 3.

In samples from GS 8, oxygen concentrations are relatively low, suggesting low atmospheric diffusion or a high rate of oxygen consumption in the near-surf ace spoil. Carbon dioxide values are much higher than the nominal atmospheric concentration of 0.03 pct, possibly deriving from respiration, carbonate mineral dissolution and organic matter oxidation. Significant methane concentrations were found in GS 8. The methane source is unknown; however, water samples from a nearby well showed a significant population of anaerobic bacteria.

The spoil atmosphere at GS 5 is different from the low-oxygen environment of GS 8. Oxygen concentrations ranged from 7.3 to 16.4 pct (Table 3).

Comparing the 2.0-m port in GS 8 with the 2.1-m port in GS 5 shows that the oxygen concentration is at least 2.4 times higher in GS 5. The oxygen concentration does not decrease with depth as it did in three coal refuse sites previously studied. Carbon dioxide concentrations were higher than the atmospheric value. Methane concentrations did not exceed 0.05 pct.

The sum of oxygen and carbon dioxide concentrations is an indication of the extent of net oxygen consumption; that is, respiration does not contribute to the apparent loss of gas. The sum is significantly lower in GS 8 than in GS 5. Oxidation of pyrite by oxygen is a likely reaction resulting in net gas consumption.

The preliminary data indicates that the spoil atmosphere shows significant lateral variability, consistent with spoil water quality changes across the site. A causal relationship has yet to be explored.

ALTERNATIVE CHEMICALS FOR AMD BACTERIA INHIBITION

Background

Although AMD formation has been shown to be dramatically reduced in anionic surfactant treated coal refuse (Kleinmann and Erickson, 1983), this technology is not appropriate for a number of AMD-producing environments because of poor surfactant sorption to the acid-generating materials and accelerated washout of that compound. Application of inhibitory chemicals that precipitate within the matrix rather than sorb to the surfaces of these acid-generating compounds is one possible method of treatment in such environments. Among the compounds that are known to effectively inhibit acid mine drainage bacteria, sodium benzoate and potassium sorbate have also been shown in this laboratory to exhibit the desired propensity for precipitation on pyritic materials. Upon establishment of the acidic conditions necessary for acceleration of AMD formation by AMD bacteria, these benzoate and sorbate precipitates may be available for bacterial inhibition. The actual species of dissolution and bactericidal action under these conditions could be expected to be benzoic and sorbic acids. These compounds are quite environmentally acceptable in that concentrations of up to 1,000 mg/liter are approved for human consumption by the USDA. Currently, we are studying the effectiveness of benzoate and sorbate for the control of AND formation in laboratory and pilot-scale experiments.

Results

Identification of the potential application of benzoate and sorbate for AMD bacterial control was made in an initial screening of approximately 25 compounds for the propensity to form precipitates in synthetic mine waters. Both benzoate and sorbate readily exhibit this desired effect in these waters. Subsequently, laboratory experiments were conducted to establish if these precipitates might act as bactericides in mine water environments. It was found that the anticipated species of precipitate dissolution, namely, benzoic and sorbic acids, at concentrations of 10 mg/liter or greater can effectively inhibit all biological oxidation of ferrous iron in pure cultures of the AMD bacterial species Thiobacillus ferrooxidans (Onysko, Kleinmann, and Erickson, 1984). That is, benzoic and sorbic acids were shown to be as effective as sterilization or application of 5 mg/liter sodium laurel sulfate (SLS) surfactant to synthetic mine waters (Fig. 5).

Pilot-scale experiments are now in progress to test the practicality of introducing the inhibitory benzoic and sorbic acids into pyritic materials as initial solutions of sodium benzoate and potassium sorbate. Tested concentrations of these compounds include 0.1 and 1.0 percent (i.e., 1,000 and 10,000 mg/liter, respectively) solutions applied to barrels containing 200 kg of air-dried coal refuse. Treated and untreated barrels are being leached once weekly with water and the leachate is analyzed for sulfate, total dissolved iron, acidity and pH. A number of barrels have also been treated with SLS to allow for comparison of the effectiveness of acid generation inhibition documented in any of the 200-Kg coal refuse barrels. In addition, a 20 foot-thick pillar in the Bureau of Mines experimental mine facility has been drilled to provide an underground pilot-scale test. These drill holes will be treated with the new inhibitory agents.

Results, though preliminary, are encouraging. The untreated barrels are now producing acid; the treated barrels are not. The effectiveness of each inhibitor will be determined by relative rates of acid production as a function of time.

SUMMARY

The Bureau of Mines is continuing work on a series of projects at reclaimed surface mines in West Virginia to define acid production and transport, and to develop at-source control methods using bactericidal agents.

Electromagnetic induction surveys were evaluated as a means of identifying acid-source areas and flow paths. The results indicate that high conductivities were related to potentially acid-producing material, such as coal refuse or cleanings, and zones of spoil water storage.

Results of monitoring at the Pierce site illustrate that the hydrology and geochemistry of reclaimed mines can be quite complex and may not be adequately described by point measurements at the discharge. The detailed hydrologic and soil gas monitoring methods being used at the site are providing us with a more complete understanding of the system and a basis to design and evaluate the proposed bactericidal treatment.

Laboratory studies of organic acids as bactericides appear to be promising. Providing a reservoir of the active agent as a sparingly soluble salt at the acid-producing site is a new concept in AMD abatement. A field test will be initiated if pilot tests are successful.

ACKNOWLEDGEMENT

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TABLE 1. Well and seep water quality, Pierce site

	pH	mg/L Acidity	mg/L Iron	mg/L Sulfate
Well 1	6.1	40	110	490
Well 2	4.5	250	25	570
Well 3	Dry	Dry	Dry	Dry
Well 4	3.8	600	260	1100
Well 5	Dry	Dry	Dry	Dry
Well 6	5.1	130	52	330
Well 7	5.8	10	26	110
Well 8	5.7	61	59	230
Seep	3.1	230	36	460

Table 2. Gas composition in GS 8, Pierce site.

Depth, m	Concentration Range, percent of moisture-free volume O_2	CO_2	CH_4
1.2	1.9 - 3.1	1.8 - 4.0	0.65 - 3.4
2.0	0.6 - 3.0	3.1 - 10.9	20.7 - 33.0

Table 3. Gas composition in GS 5, Pierce site.

Depth, m	Concentration Range, percent of moisture-free volume O_2	CO_2
0.6	7.3 - 14.9	3.4 - 4.9
2.1	10.4 - 15.8	2.2 - 4.5
3.7	11.5 - 16.4	1.8 - 4.3
5.2	12.1 - 16.3	4.3 - 8.8

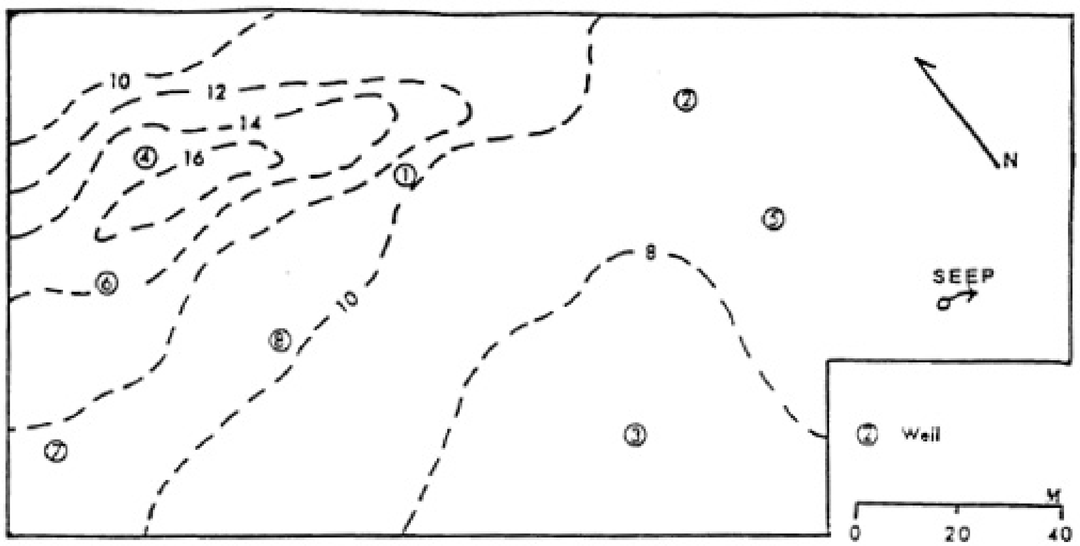


FIGURE 1. APPARENT CONDUCTIVITY DISTRIBUTION AT THE PIERCE SITE.

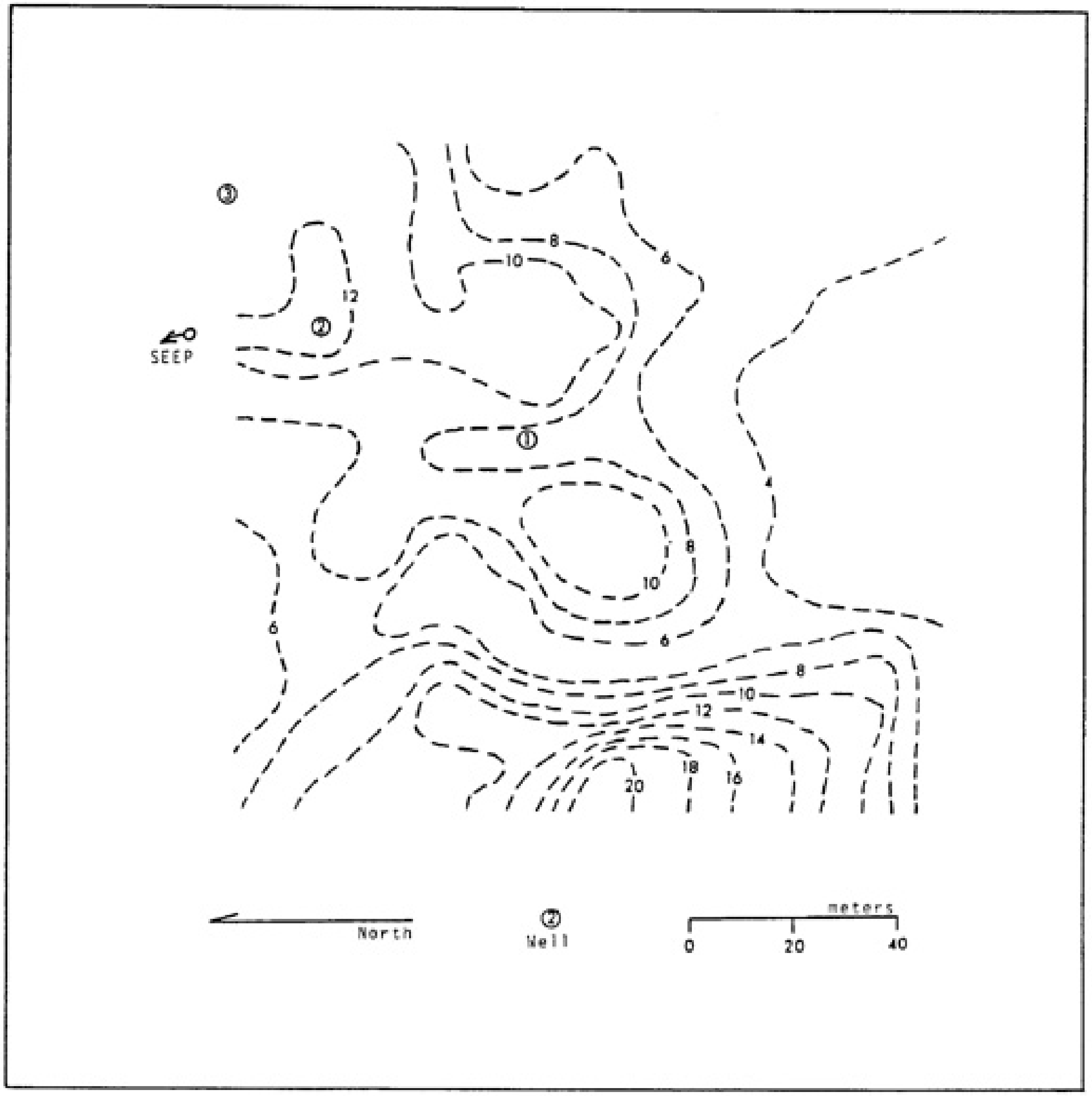


FIGURE 2. APPARENT CONDUCTIVITY DISTRIBUTION AT THE HOBET SITE.

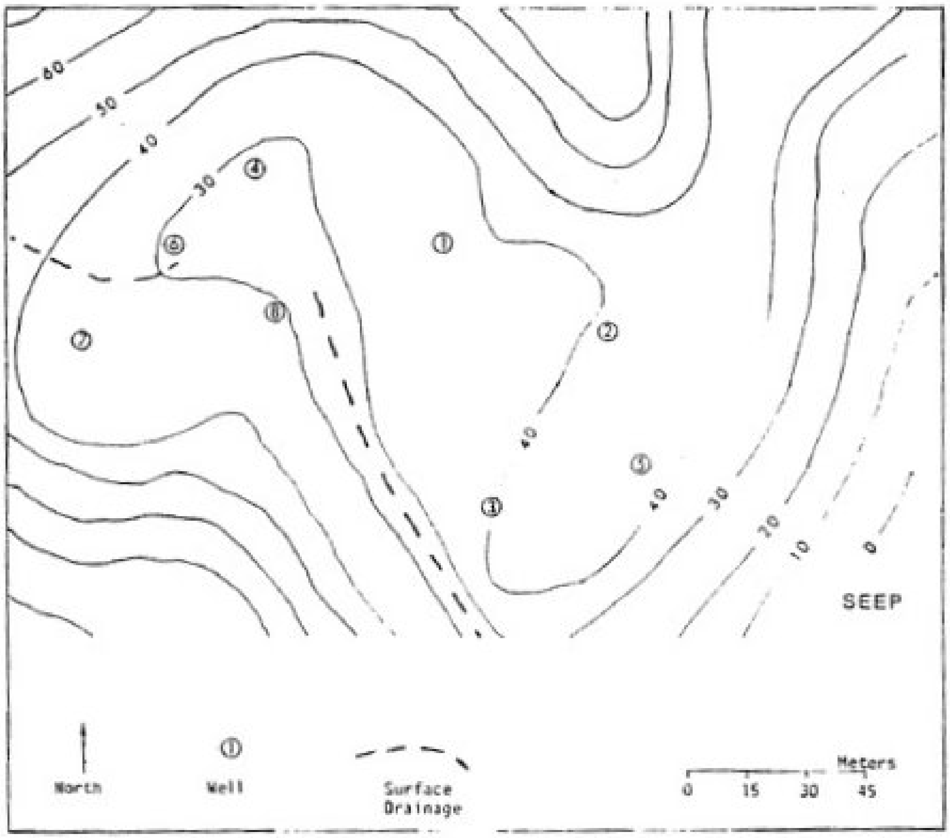


FIGURE 3. TOPOGRAPHIC MAP OF THE PIERCE SITE, SHOWING WELL AND SEEP LOCATION.

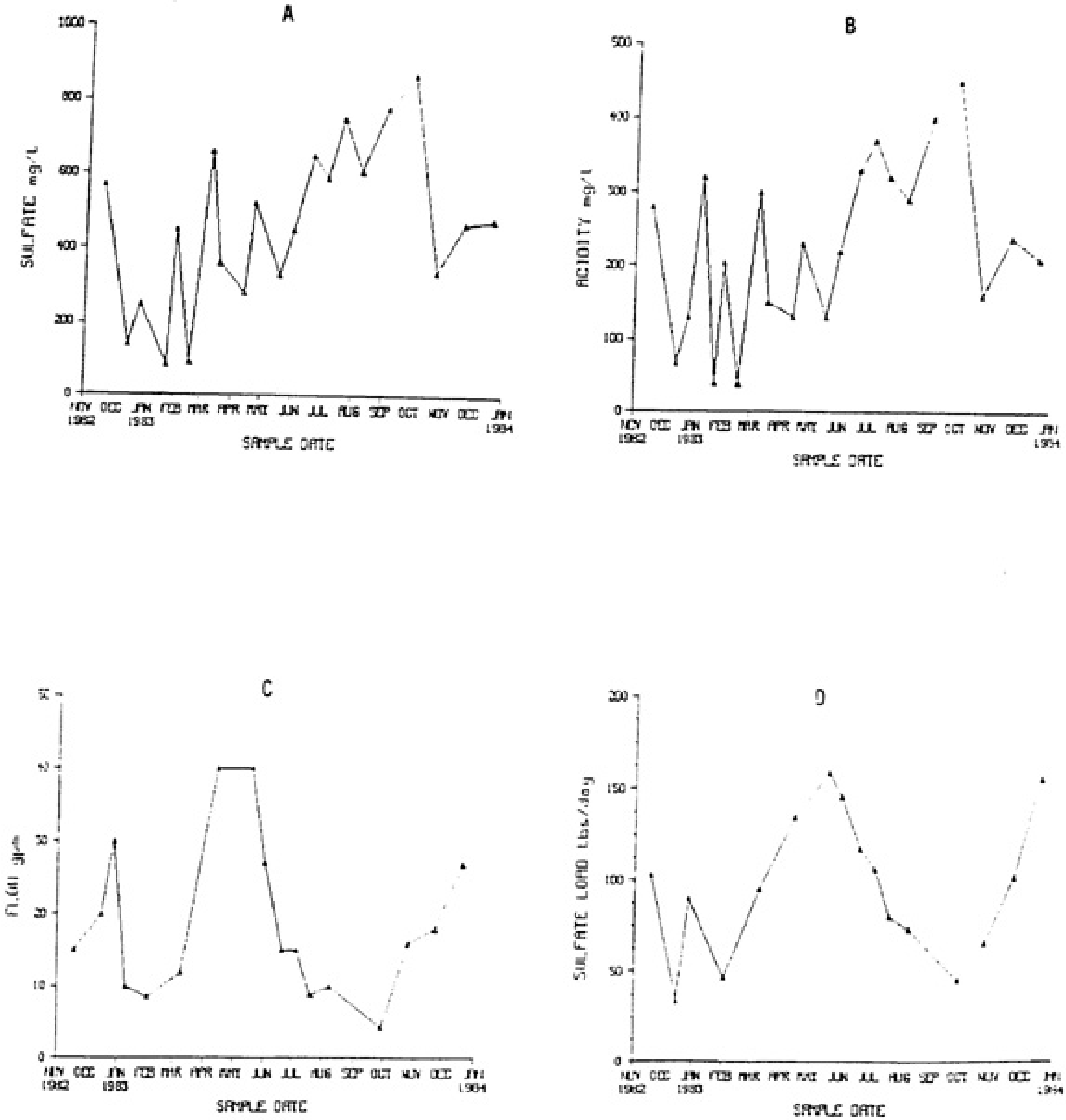
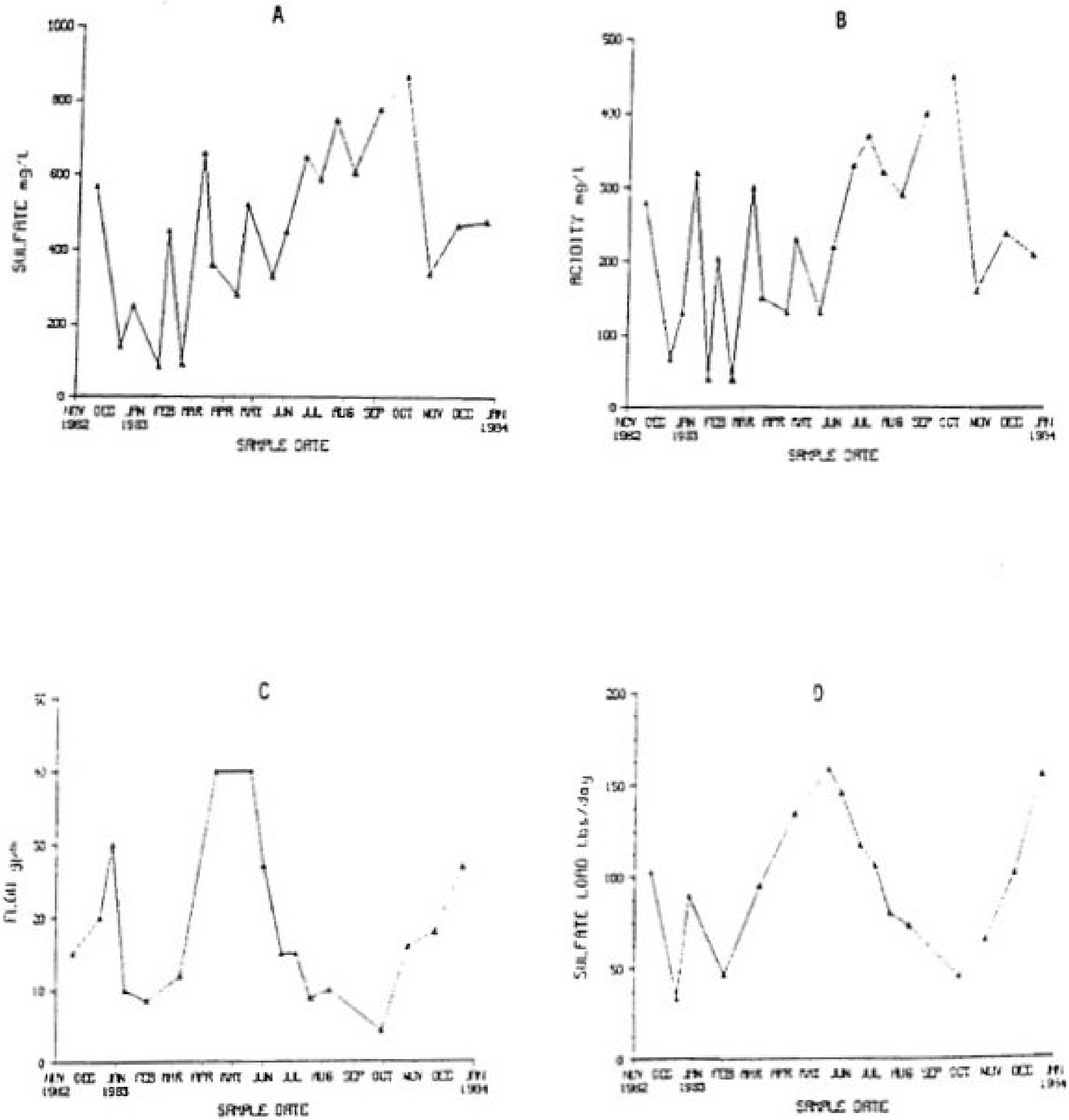


FIGURE 4. SEASONAL TRENDS IN DISCHARGE SULFATE CONCENTRATION (a), ACIDITY (b), FLOW (c), AND SULFATE LOAD (d) AT THE PIERCE SITE.



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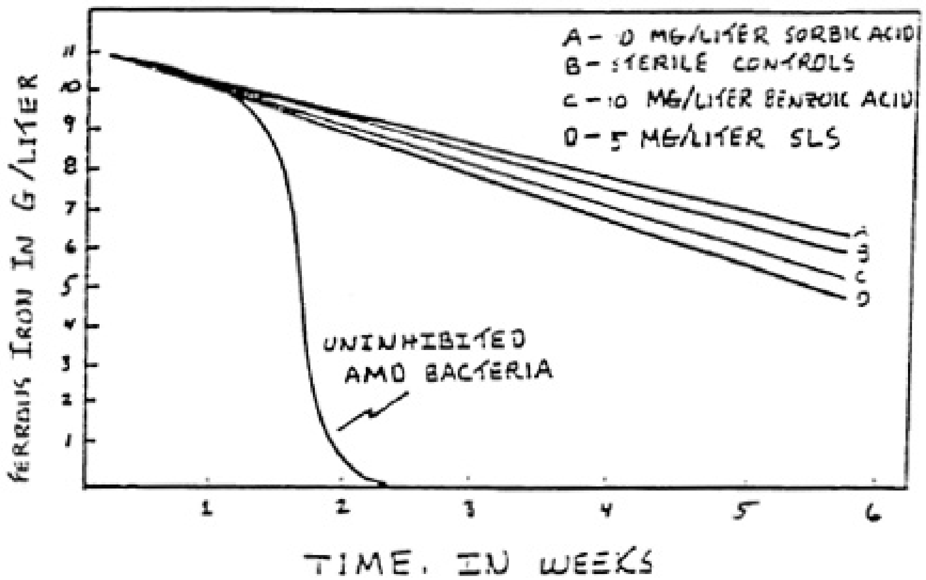

FIGURE 5. FERROUS IRON DISAPPEARANCE DATA AS A MEASURE OF ACID MINE DRAINAGE ACTIVITY IN STERILE MINE WATER CONTROLS, UNINHIBITED AMD BACTERIA CULTURES, AND AMD BACTERIA CULTURES SUPPLEMENTED WITH THE INDICATED CONCENTRATIONS OF BACTERICIDAL COMPOUNDS.