MECHANISM OF ACID REMOVAL FROM NEAR SURFACE MINE ENVIRONMENTS

by

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BACKGROUND OF THE STUDY

A. 1982 to 1983 Field Study

In 1982, with the cooperation of the Enoxy Coal Company, Caruccio and Geidel designed a field study to evaluate the effect of the physical characteristics of two rock types on leachate quality (acid loads) (Geidel, et al., 1983). In that study, samples of the acidic sandstone above the Kittanning coal seam and a binder (siliceous, organic rich shale) between the middle and lower Kittanning coal seams of in north-central West Virginia were crushed and sieved to generate five size fractions (less than 1 inch, 1 to 2 inches, 2 to 4 inches, 4 to 6 inches, and greater than 6 inches) of each rock type.

During July and August 1982, these fractions were placed in 8 ft X 4 ft X 2 ft plastic lined wooden tubs located on the Enoxy mine property on a hilltop in an open field. Following each significant rain event, the volume of effluent produced by each tub was recorded and samples were shipped to the University of South Carolina for analysis. Approximately 50 water samples were collected for each size fraction during two time intervals: August 1982 to December 1982 and June 1983 to December 1983.

B. 1987 Laboratory Study

During May 1987, rock samples were collected from the West Virginia field tubs, which had been exposed to the atmosphere since August 1982, and transported to the University of South Carolina. Samples of the 1 to 2 inch size fraction were collected from the entire tub, whereas samples from the 2 to 4 inch size fraction were collected from the surface and middle parts of the tub.

These samples were to be used in a laboratory tub leaching experiment to evaluate the effect of hydrology and selective placement of limestone on the acidity produced within a simulated backfill. Six plastic tubs (1411 X 2411 X 1211) were filled with the 1 to 2 inch size sandstone. Each sample was riffled to obtain a representative subsample for weathering cell experiments, acid-base accounting, and reflected light microscopy. Each week for seven weeks, the sandstones were leached with 500 ml of deionized water. After seven weeks, very little acidity was produced. A plot of the net acid load versus time showed the acid load averaged about 2 mg/kg, and reached a maximum at about 3 mg/kg on day 15 when the rocks were leached following a two week period.

In addition, approximately 500 grams of the 1 to 2 inch sample was tested in six weathering cells kept at 100% humidity. One weathering cell was packed with about 150 grams of crushed 2 to 4 inch size sandstone. Each chamber was leached once a week with 100 ml of deionized water and the leachate analyzed for pH, specific conductance, and acidity. The six weathering cells containing the 1 to 2 inch samples also showed a low net acid load. The average acid load was about 4 mg/kg and the pH ranged from 3.5 to 4.85. However, the plot of net acid load versus time for the crushed 2 to 4 inch sandstone showed a significantly higher acid load.

A subsample of the 1 to 2 inch sandstone was split from each of the six samples and analyzed for total sulfur content and neutralization potential. The total sulfur content of the 1 to 2 inch size fraction ranged from 0% to 0.04%. The neutralization potential (NP) of the sample was also low; ranging from 2.6 to 5.0 tons of CaC03 per 1000 tons of sample.

Polished pellets were examined for pyrite using reflected light microscopy. The 1 to 2 inch size fraction was devoid of pyrite. In contrast, the 2 to 4 inch sandstone slabs contained pyrite, and none of the slabs showed a reaction rim or zonation of oxidation on the outer edge.

The 1987 laboratory study showed the 1 to 2 inch size fraction to be devoid of pyrite and no longer acid producing. In contrast, the 2 to 4 inch sandstone still contained pyrite and generated acidity, but less than that produced in 1983. The 2 to 4 inch and larger size sandstones were hard and durable suggesting the larger size sandstone had not been weathered as intensely as the 1 to 2 inch sandstone.

That an acid producing rock was leached of its pyrite in less than four years under field conditions had never before been documented. The study, then, was redirected to research the factors controlling acid production and the effluent volume.

OBJECTIVES OF THE STUDY

This study was designed to gain an insight to the factors affecting acid production and volume of effluent through an evaluation of the interactive effects of temperature, precipitation, flushing frequency (delta days), time, and size and character of the rock. Only the 1 to 2, 2 to 4, and greater than 6 inch size fractions of the acidic sandstone data were used in the present study, hence the discussion of the 1982 to 1983 field study will focus on these results.

From the 1982 field study, approximately one year of chemical data and physical data (precipitation, temperature, delta days, and time) were used to derive multiple regression descriptive equations and plots. In turn, the regression analyses and plots were used to examine the interactive effects affecting acidity and effluent volumes. Using the 1982 data base, this study was designed to:

1. determine the effect of temperature, time, precipitation (water), and flushing frequency on the volume of effluent produced by each of the size fractions,
2. examine the effect of three different size fractions on the volume of effluent collected,
3. determine the effect of temperature, time, precipitation (water), and flushing frequency on the acidity generated from each of the size fractions, and
4. assess the effect of size on the physical decomposition of the rock and the production of acidic drainage.

METHODOLOGY

A. Data Synthesis

1. Variable Selection

To model the volume of effluent flushed from each tub for a given rain event and the acidity generated from each sandstone tub, the independent variables controlling volume and acidity had to be defined. The following independent variables were deemed important: temperature, precipitation, time, flushing frequency (delta days), size of rocks, weight of rocks, and rock chemistry. Because each size fraction was considered separately, the size and the weight of the sandstone within each tub were excluded as variables for the regression analysis. The sandstone was sampled from the same stratigraphic horizon and determined to be relatively homogeneous. Therefore, rock chemistry could also be excluded as a variable, and variations between tubs could not be attributed to the rock chemistry. The variables used in the regression analyses were temperature, precipitation, delta days, and time.

2. Temperature

Because the temperature affecting acidity is not represented by the temperature at the time of sample collection, the mean **temperature for the time period prior to the sampling event** was used. The mean temperature was calculated by averaging the average low temperatures and average high temperatures for the days between the sampling events.

3. Precipitation

The precipitation, attendant with each sampling event, was measured by a continuous rain gauge installed at the study site. The precipitation had to be of sufficient magnitude to exceed field capacity and induce drainage through the tub/pipe system and into the plastic collection container. As a result, not all precipitation events produced a sample. Occasionally, during prolonged precipitation, samples were collected following a two or three day rain event. In these cases, the precipitation for the period prior to sampling was summed to determine the total precipitation. Often, a single precipitation event was associated with a sample collection.

During November 1983 the rain gauge on the study site malfunctioned, and for this period the NOAA climatological data for West Virginia were used. Precipitation data from four proximate and evenly distributed stations around the Enoxy Coal mine were averaged to determine the precipitation contributing to each sample collected (Fetter, 1980).

4. Flushing Frequency (Delta Days)

a) Volume Regressions

For the volume regressions, the parameter expressing the number of days preceding a sampling event, where a precipitation event did not exceed 0.1 inches, was defined as a delta day. in most cases the delta day was simply the number of days between sampling events. However, when a moderate precipitation event (0.1 inches), occurred between sampling and failed to generate a sample, the delta day was defined as the difference in days between the sampling event and moderate precipitation event.

b) Acidity Regressions

For the acidity regressions the delta day was defined as the number of days between each leaching (sampling) event.

B. Data Entry and Analysis

The data were entered and organized on an electronic spreadsheet using LOTUS 1-2-3 (Lotus, 1986). Using a Hewlett Packard 7475A plotter, plots were generated to determine relationships between variables. The data were then uploaded to the IBM VM/CMS mainframe computer at the University of South Carolina for statistical analysis. The data consisted of six separate data sets: volume data sets for each of the three size fractions and acidity data sets for each of the three size fractions. The data were statistically analyzed using the Statistical Analysis System (SAS) package (SAS, 1985). Six descriptive equations were derived utilizing multiple regression analysis.

C. Volume of Effluent Regression

For each of the three size fractions, independent multiple regression equations were determined. The regression equations are used to describe the effects of **the independent (predictor) variables** on the volume of effluent.

D. Acid Concentration Regressions

As with the volume regressions, multiple regression models were developed for the acidity concentration for each of the three size fractions. These regression equations were used to describe the effects of temperature, delta days, time, and precipitation on the concentration of acidity produced by the acid producing sandstones. The same procedure and statistical criteria were used for the acid concentration regressions that were used for the volume of effluent regressions.

RESULTS AND DISCUSSION

A. Acidity Variations

1. 1 to 2 Inch Size Fraction of Sandstone

During the summer, 1982, at the start of the field experiment, the 1 to 2 inch sandstone had a pyritic sulfur content of 0.14% (and an NP of 1.3) and began producing significant amounts of acidity in three weeks. Not only is the fall 1982 average acidity higher, but it also covers a larger range than the fall 1983 acidity. The highest acidity and the greatest variability in acidity occurs during the summer of 1983; with values ranging from 114 to 700 mg/l.

Multiple regression analysis provided an understanding of the interrelated effects and contour plots can be used to identify the interrelated effects of time, temperature, and delta days on acid production. Each plot shows the change in the estimated acidity as temperature and delta days simultaneously vary for a given time period. For all three selected times, the highest estimated acidity occurs when the temperature is low and the delta days are high. Moderate to high estimated acidity values occur when the temperature is high and the delta day is low.

The average acidity produced by the 1 to 2 inch size sandstone for fall II was considerably less than that for fall I which indicates that within one year the acid production had decreased. Due to the lack of data from December 1982 to June 1983, it was not possible, using mass balance and stoichiometric relationships, to calculate the time when insignificant acidity was produced. However, assuming a linear decline through time and connecting the two average fall acidity values and then extrapolating the line to the X-axis, the predicted time when minor amount of acidity was generated was approximately 800 days (late fall 1984) to 900 days (early 1985). The acid potential is zero by 1987. Hence, sometime between the fall of 1984 and the spring of 1987 the 1 to 2 inch sandstone was rendered non-acid producing. The short period of time within which the 1 to 2 inch sandstone began generating copious amounts of acidity is due to the small size and large surface area of the rock.

The contour plots indicate that increasing the time between leachings does indeed increase the acidity. The effect of temperature is not as apparent. High temperatures result in estimated acidity values which range from zero to about 500 mg/l depending on the delta days and time. This suggests that relative to the time between leachings, temperature is not very important in estimating the acidity for the 1 to 2 inch size fraction.

2. 2 to 4 Inch Size Fraction of Sandstone

As of 1987, the 2 to 4 inch size fraction of sandstone continued to produce acidity. Initially, in 1982, the pyritic sulfur content was 0.18% (with an NP of 2.3), and the rocks generated large amounts of acidity. As with the 1 to 2 inch sandstone, the 2 to 4 inch sandstone produced significant amounts of acidity in a short time period.

Multiple regression analysis was used to discern the interrelated effect of temperature, delta days, and time on acid production. using the average values for time, temperature, and delta days, the regression equation was solved to determine an average estimated acidity for the 2 to 4 inch size fraction. The effect of time can be determined by solving the regression equation using the minimum and maximum values for time and the average values for temperature and delta days. In a similar manner the effects of temperature and delta days can be determined. The results show that acidity increases with increasing time, temperature, and delta days. Relative to time and delta days, temperature has the smallest effect. Changing the temperature from a minimum to a maximum only increases the estimated acidity about 100 mg/l.

For the 2 to 4 inch size fraction the acid concentration increases with increasing time, temperature, and delta days. Increasing the time has the greatest effect on the acidity, while increasing temperature slightly increases the acidity. The acidity produced in the 1987 study was less than that produced during the 1982 to 1983 field study. This indicates that the 2 to 4 inch sandstone, although not totally leached of its pyrite, is not as acid producing as it was in the past. Because of the surface area to volume ratio, the 2 to 4 inch size, as the 1 to 2 inch size, began generating acidity in a short period of time.

3. Greater Than 6 Inch Size Fraction of Sandstone

In 1982 the sandstone of the largest size fraction had a pyritic sulfur content of 0.23% and an NP of 1. The greater than 6 inch sandstone, unlike the two smaller size fractions, began producing acidity in excess of 100 mg/l after about 80 days (11.5 weeks).

An average estimated acidity is determined by solving the regression equation using the average values for time and temperature. The effect of time can be determined by solving the regression equation with the minimum and maximum values for time (1 and 460 days) and the average value for temperature. The effect of temperature can then be determined by solving the equation with the minimum and maximum values for temperature (35 and 75 F) and the average value for time. For the greater than 6 inch size, the acidity increases with time but decreases with increasing temperature.

The contour plot of temperature versus time again shows that the acidity is highest when the temperature is low and the time high (420 days). The lowest acidity occurs when the temperature is high and the time low (60 days).

For the greater than six inch sandstone, time is the most important variable in determining acidity, and acidity increases exponentially with time. The delayed production of acidity for the largest size fraction is a function of the large rock size, whereby only the pyrite proximate to the outer surface is initially oxidized.

B. Volume Variations

1. Precipitation

The volume of effluent collected from each of the field tubs during the 1982 to 1983 field study is largely controlled by the amount of precipitation and is independent of the size fraction. Likewise, for all three size fractions precipitation is the single most important independent variable for estimating volume.

2. Temperature

The effect that temperature has on the volume of effluent is similar for the 1 to 2 and 2 to 4 inch size fractions but different for the greater than 6 inch size fraction. Intuitively, one would expect that the higher the temperature the more the rocks would dry out and as a result there will be a decrease in the leachate volume. This holds for the 1 to 2 and 2 to 4 inch sandstone, but is inconsistent for the greater than 6 inch size, the higher the temperature, the greater the volume of leachate as estimated using the regression equation. The difference in the estimated volume of leachate when the temperature is varied from a maximum to a minimum, is small which suggests that the volume of effluent is only marginally affected by large changes in temperature.

3. Delta Days

The effect of delta days on the volume of leachate is similar to the effect of temperature and is evident when the regression equations are solved using average values for precipitation and temperature but a minimum (1 day) and maximum (16 days) value for delta days. Intuitively, one would expect that the longer the time period between precipitation events the more the rocks would dry out and the less the volume of leachate produced. The above is true for all three size fractions; the greater the delta day the less the leachate volume. The effect of delta days, however, is more prominent in the 1 to 2 and 2 to 4 inch size fractions than in the greater than 6 inch size whereby the range in volume of leachate differs by 9.0 L, 10.6 L, and 2.2 L, respectively (when the delta days are varied from a minimum to a maximum value).

The effect of temperature and delta days is evident when temperature and delta days are varied simultaneously for a given precipitation. For a constant precipitation (0.5 inches), a low temperature and low delta day generate a high estimated volume, and a high temperature and high delta day generate a low estimated leachate volume for the I to 2 and 2 to 4 inch size fraction. The contour plot of temperature versus delta days at a constant precipitation for the greater than 6 inch sandstone shows that the volume of leachate is essentially independent of temperature and depends primarily on delta days.

4. Discussion

Leachate will emanate from the tub/pipe system and into the collection barrels only if the moisture content of the samples within the tubs exceeds field capacity. The variables which affect the field capacity of the tubs are precipitation, temperature, and delta days. As a result, a small precipitation event occurring when the rocks are dry does not generate leachate.

For all three size fractions, precipitation most affects the estimated volume of leachate. The effects of temperature and delta days on the estimated leachate volume are much more subtle.

The 1 to 2 inch and 2 to 4 inch size fractions behave similarly. Coupling the variables, temperature and delta days, creates a single variable that describes the season of the year. Low temperatures and low delta days are common in the fall and spring. whereas high temperatures and high delta days are common during the summer. Greater leachate volumes are more common during the fall and spring than during the summer.

In the greater than 6 inch sandstone tub, the porosity is much larger than the porosity of the other two sizes which allows air to circulate throughout the entire sample in the tub. The effect of temperature and delta days on the volume of leachate for the greater than 6 inch sandstone, compared to the other two sizes, differs because of the larger porosity associated with the 6 inch sandstone. The estimated volume of effluent for the largest size fraction is independent of temperature and decreases with increasing delta days.

SUMMARY

In 1982 to 1983, Caruccio and Geidel conducted a field study to evaluate the effect of the physical characteristics that sandstone and binder samples have on leachate quality. Four years later, as part of this study, some of the rocks which had been used in the 1982 to 1983 field study were leached under laboratory conditions. The tests showed the sandstone samples of the 1 to 2 inch size fraction to be devoid of pyrite and no longer acid producing. Prior to this, the total leaching of pyrite from a sample under field conditions within a short time period had never been observed. For this study, multiple regression analysis was used to examine the interactive effects between the temperature, time, delta days, and precipitation on the production of acidity and effluent volumes.

Analyses of the 1982 field data showed that from 1982 to early 1985, in two and one half years, the acid potential of the 1 to 2 inch sandstone declined from about 400 mg/1 to essentially zero. While the acid production of the 2 to 4 inch sandstone increased throughout the duration of the 1982 to 1983 field study, in 1987 the 2 to 4 inch rocks had a paucity of pyrite and less acid production potential. In contrast, the acid production of the greater than 6 inch sandstone increased exponentially with time during the 1982 to 1983 field study. The exponential expression may be related to a character of size which delays the production of acid and the release of acidity.

The 1 to 2 and 2 to 4 inch sandstone size fractions generated copious amounts of acidity within a short time period. In contrast, the greater than 6 inch sandstone took about 80 days to generate acidity in excess of 100 mg/l. This difference was attributed to variations in size which affects the surface area to volume ratio.

The plots of acidity versus temperature show a positive correlation for all sizes. The highest acidity for the I to 2 and 2 to 4 inch sandstones occur during summer 1 (1983) when the temperatures are highest. In general, the acidity produced increases with increasing temperature. Furthermore, the acidity produced increases with increasing delta days for the 1 to 2 and 2 to 4 inch size fractions.

The volume of effluent is largely controlled by the amount of precipitation. The effects of temperature and delta days on the volume of effluent are more subtle. With increasing temperature, the volume of effluent decreases for the 1 to 2 and 2 to 4 inch fractions but increases for the greater than 6 inch size. While with increasing delta days, the volume of effluent decreases for all three size fractions.

CONCLUSIONS AND APPLICATIONS

1. The rate of pyrite oxidation is a function of the rock type and size, and permeability of the rock. Consequently, the smaller rocks with a larger surface area to volume ratio allow water and oxygen to more readily penetrate the entire rock thickness, oxidize the pyrite, and leach the accumulated oxidation products from the system.
2. The acid concentration for any of the sizes is not related to the amount of precipitation.
3. For the greater than 6 inch sandstone, time is the most important variable when estimating the acid concentration. The effect of temperature is minimal, and the effect of delta days is weak.
4. The amount of acidity produced is not a function of a single variable but a result of the interactions between time, temperature, delta days, and rock size.

5. The larger the delta day, the greater the moisture deficiency of the rocks which extends soil moisture requirements and causes less volume of effluent with the subsequent precipitation event. For the 1 to 2 and 2 to 4 inch size fractions, a critical delta day exists beyond which the volume of effluent becomes independent of delta days.
6. For the 1 to 2 and 2 to 4 inch sizes, when temperature and delta days are coupled and varied simultaneously, the volume of effluent is low when the temperature and delta days are high, and the volume of effluent is high when the temperature and delta days are low. Coupling the variables temperature and delta days creates a new variable which describes the season of the year.
7. The large porosity within the greater than 6 inch size tub suppresses the effect that temperature and delta days have on the leachate volume. The leachate volume is independent of temperature for the greater than 6 inch sandstone.
8. The rapid depletion of the pyrite in the 1 to 2 and 2 to 4 inch sizes in a short time period supports the notion that acid producing material near the ground surface will oxidize readily and render the interflow component of the seep low in acidity.
9. Within a backfill, the storage of acidity and the subsequent flushing of periodical slugs of acid is a function of the frequency of significant precipitation events (delta days).
10. When field testing a rock pile for potential acid production, the size of the rock being tested, climate (temperature and frequency of precipitation events), and duration of experiment will affect the results obtained. In addition, decreasing the porosity by decreasing the size or degree of sorting will affect the moisture content of the rock pile. The retained moisture in turn will allow acid production to continue uninhibited.

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