

PYRITE OXIDATION IN A MINESPOIL ENVIRONMENT:

A LYSIMETER STUDY¹

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Abstract.-- The oxidation of pyrite (FeS_2) and the effects of its products on a minesoil containing excess neutralization potential was investigated. An anoxic Texas lignite overburden with 0.8% pyrite and 1.6% carbonates (predominantly dolomite) was packed into 0.7 m³ lysimeters and leached monthly with 63.5 mm of deionized rainwater for 12 months. The leachates coming from the lysimeters started at a pH of 8.5 and gradually decreased to a pH of 7.0. The minesoil started at a pH of 8.3 and decreased to pH 6.5 by the end of 12 months. Potential acidity determinations indicate that 50% of the initial pyrite had oxidized; however, the release of acidity was sufficiently slow for the inherent neutralizing materials to consume the acidity and maintain a moderate pH. The sulfuric acid and dolomite interactions led to a significant increase in extractable Ca and Mg with time and the formation of a SO_4 bulge in the lower half of the lysimeters. The relatively slow pyrite oxidation observed in this project is attributed to the low surface areas of the pyrite particles present and the relatively high pH maintained by the dolomite.

INTRODUCTION

The reclamation of mixed overburden minesoil is often hindered by low soil pH due to the oxidation of iron sulfide minerals which are present in many reduced overburden materials. Pyrite (FeS_2) is the most prevalent iron sulfide in Texas lignite overburden (Arora et al., 1980). When left near the surface during reclamation, pyrite oxidizes producing iron oxyhydroxides and sulfuric acid. The production of acidity is usually sufficient to cause reclaimed areas to

become highly acidic. These acidic areas can develop pH values of 2 or less. Identifying and controlling potentially acidic minespoil is essential if reclamation is to be successful.

During the premine characterization of overburden, the pyrite content (potential acidity, PA) and acid neutralizing potential (NP) are quantified using procedures outlined by the U.S. Environmental Protection Agency (1978). This information along with exchangeable acidity (EA) data are used to determine if an overburden contains excess acid forming material. The equation used is:

$$\text{Acid/Base Balance} = \text{NP} - (\text{PA} + \text{EA})$$

A negative acid/base balance indicates that an overburden material will become acidic when left in an oxidizing environment. A positive or zero acid/base balance means that an overburden material is free of pyrite or that acid neutralizing material is present in sufficient quantities to neutralize the potential and exchangeable acidity when it is released in the overburden.

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Stoichiometrically, the theory behind this procedure is valid. However, the procedures used to measure pyrite content and neutralization potential are abiotic and accelerated to make them time efficient. They do not account for differences in reaction rates due to biological influence or chemical equilibria. The rate of pyrite oxidation has been found to increase with increased surface area and the presence of iron and sulfur oxidizing bacteria such as *Thiobacillus ferrooxidans* and decreasing pH (Pugh et al., 1984; Smith and Shumate, 1970). The dissolution of carbonates is decreased by increased particle size, increased partial pressure of CO_2 , and decreased temperature (Thomas and Hafgrove, 1984). These solubility limitations on carbonates cause their acid neutralization capacity to be dependent on the amount of water passing through the soil system (Geidel, 1979).

The objectives of this study were to 1) determine if a pyritic minesoil with a positive acid/base balance would become acidic or produce acid drainage ($\text{pH} < 6.0$) when supplied average rainfall at regular intervals and 2) investigate the fate of the products from pyrite oxidation and acid/base reactions in the minesoil.

METHODS AND MATERIALS

Lysimeters

The lysimeters used in this project were rectangular ($0.75\text{ m} \times 0.75\text{ m} \times 1.2\text{ m}$) and contained 0.675 m^3 of overburden. They were constructed out of exterior grade plywood and waterproofed with fiberglass. The bottom centers of the lysimeters were fitted with a leachate partitioning device, $0.5\text{ m} \times 0.5\text{ m} \times 0.15$, to separate leachate which percolated through the entire lysimeter profile from leachate which may have moved by laminar flow along the sides of the lysimeters.

Overburden Material

The material used in this project was taken from 1.5 m above a coal seam at the Martin Lake mining facility in Panola county, Texas. This facility mines lignite from the Wilcox formation in east Texas (Figure 1). The exact location of overburden material collection was determined by sampling the highwall ahead of the mining operation.

The selected overburden material was freshly excavated and transported to the lysimeter location. The material was crushed and passed through a 4.9 cm sieve using a wooden maul. The crushed overburden was mixed thoroughly and sub-sampled for a time zero reference material to be characterized. The overburden was then inoculated with material

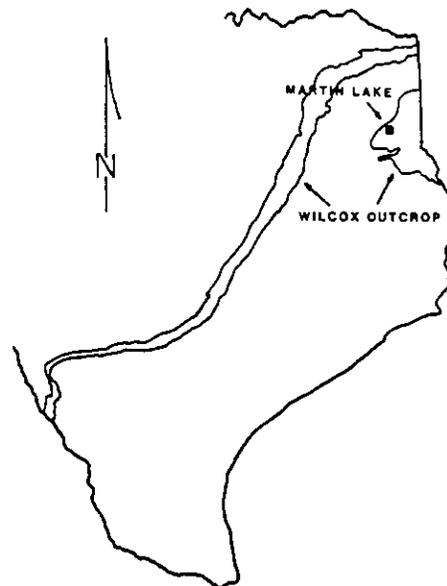


Figure 1. Map of Texas Showing the Wilcox outcrop and the location of the Martin Lake mining facility.

from an acidic minesoil to insure the presence of iron-sulfur oxidizing bacteria and packed into three replicate lysimeters at a bulk density of 1.28 Mg m^{-3} .

Pyrite particles were separated from the time zero reference sample using heavy liquid techniques and tetrabromoethane (specific gravity = 2.8 g cm^{-3}). The pyrite particles were examined with a Joel JSM35-CF scanning electron microscope equipped with a Tracor energy dispersive x-ray analyzer. The microscope was operated at a working distance of 39 mm and with 15 KV of accelerating voltage.

Leaching and Leachate Analysis

After initial hydration to -0.03 MPa , each lysimeter was leached monthly with 32 l of deionized rainwater for 12 months. This is equivalent to 762 mm of rainfall infiltration. The leachate which was produced from the center $0.5\text{ m} \times 0.5\text{ m}$ of the lysimeters using the partitioning device was collected in a nitrogen purged bottle and analyzed for pH, electrical conductivity, SO_4 , Ca, and Mg.

Core Sampling

Core samples were taken at three month intervals during the leaching study, from each lysimeter. The core samples were removed in depth increments: 0-5, 5-10, 10-20, 20-30, 30-40, 40-50, 50-60, 60-70, 70-80, 80-90, and 90-100 cm. Three core samples were taken on

each coring date, from each lysimeter. The three corresponding depth intervals from each lysimeter were composited before analysis. This was done to reduce spatial variability. The holes made by core sampling were backfilled with extra overburden material and marked to prevent subsequent samplings from the same area.

Immediately after compositing, moisture, pH, extractable Ca and Mg with 1N KCl, extractable SO₄ with 0.01M CaH₄(PO₄)₂.H₂O (Tabatabai, 1982), potential acidity (O'Shay, 1982), and neutralization potential (U.S. EPA, 1978) were measured.

RESULTS AND DISCUSSION

Characterization of Overburden

Select chemical and physical properties of the time zero overburden are shown in Table 1. Acid/base balance indicates 11 Cmole Kg⁻¹ excess of neutralization potential. The majority of the neutralization potential is from dolomite. Based on acid/base balance calculations, this material should never become acidic nor produce acid drainage.

Pyrite of a massive morphology were the only iron sulfides identified in the overburden material. A representative pyrite particle is shown in Figure 2. In some areas, as shown by the arrow in Figure 2, the surfaces of the pyrites are coated with a silicate material. These coatings effectively reduce the area available for oxidative attack. Since the oxidation rate of pyrite has been shown to be a function of surface area (Pugh et al., 1981, 1984) these pyrite particles were not expected to be highly reactive.

Leachate

The mean pH of the leachate coming from the lysimeters is shown in Figure 3. After an initial drop from pH 8.5 to 7.5, between the first and second leaching cycles, the leachate gradually decreased to a pH of 6.8. This indicates that the dolomite solubilized at a rate sufficient to neutralize most of the acidity produced by pyrite oxidation. However, the trend shown indicates that pyrite oxidation may be beginning to occur faster than the dolomite can dissolve. The pH may continue to decrease and eventually produce acidic drainage. This trend would be expected due to the difference in acidity and alkalinity production rates and the effect carbonate has on pyrite oxidation kinetics (Caruccio and Geidel, 1981).

The mean Ca, Mg, and SO₄ concentrations in the leachates are shown in Figures 4 and 5. The data show that there was an initial flush

of all three ions with the first leaching cycle. This was due to the presence of soluble salts in the initial overburden material. From the second leaching cycle to the twelfth, there was a steady efflux of Ca (approximately 500 ppm), Mg (approximately 350 ppm), and SO₄ (approximately 3,000 ppm). These data indicate that pyrite oxidized throughout the study releasing acidity and sulfate into the minespoil system. The dolomite neutralized the acidity and resulted in the release of Ca and Mg. With each leaching cycle, these ions were picked up and carried by the wetting front as it moved through the lysimeters. A portion of the ions were washed out of the lysimeters with the leachate.

Table 1. Characteristics of Martin Lake overburden material at time zero.

Texture	silt loam
Sand, %	4.1
Silt	71.8
Clay	24.1
Mineralogy	
Sand	Q,Ch,P,Fe ¹
Silt	Q,Ch,M,Fe
Clay	K,Ch/V,Q
Inorganic carbon ² , %	1.6
Calcite	0.03
Dolomite	1.57
pH; H ₂ O	8.3
Total Sulfur, %	0.8
FeS ₂ content	0.8
Neutralization Potential (NP), Cmole Kg ⁻¹	38.1
Acidity (PA)	27.1
Acid-Base Balance (NP-PA)	11.0
CEC, Cmole Kg ⁻¹	26
Extractable Ions	
SO ₄ , mg Kg ⁻¹	208
Ca	1682
Mg	811

¹K=kaolinite, Ch=chlorite, V=vermiculite, Q=quartz, Ch/V=interstratified, M=mica, P=pyrite, Sm=smectite, Fe=feldspars, Am=amphiboles.

²determined by selective dissolution.

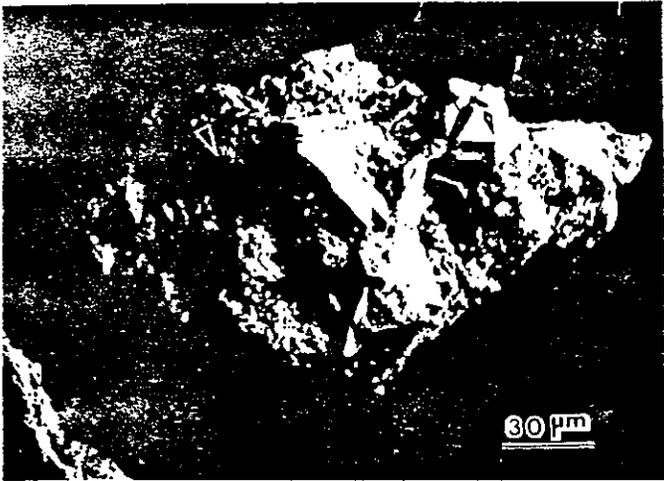


Figure 2. Scanning electron micrograph (500X) of a pyrite particle from the ML material. crystal faces indicative of pyrite are visible. Arrow points to silicate coating.

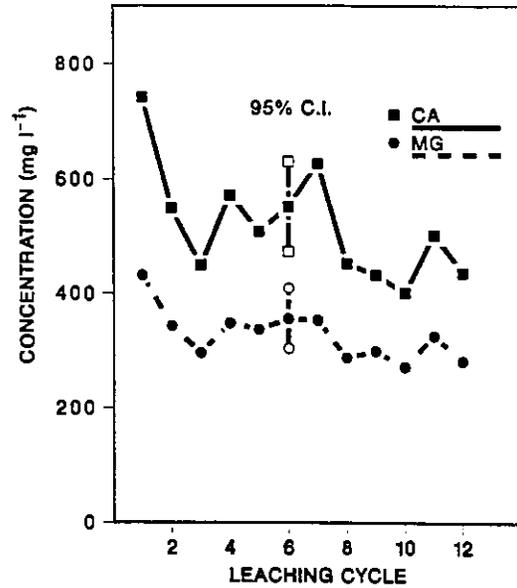


Figure 4. Calcium and magnesium concentration in leachate from lysimeters containing Martin Lake overburden. Each leaching cycle was 30 days. 95% C.I. = 95% confidence interval.

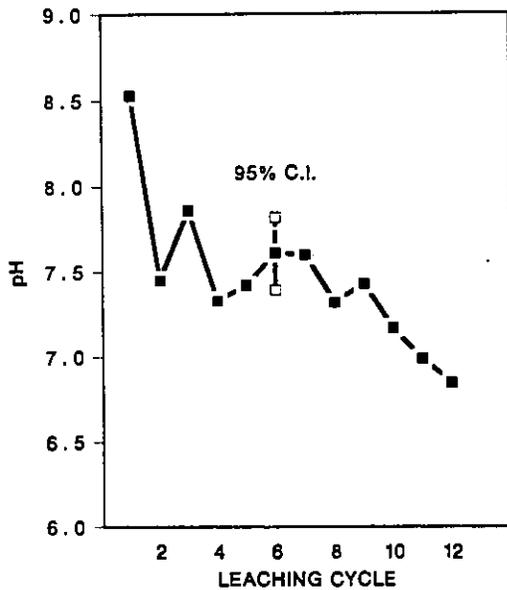


Figure 3. pH of leachate from lysimeters containing Martin Lake overburden. each leaching cycle was 30 days. 95% C.I. = 95% confidence interval.

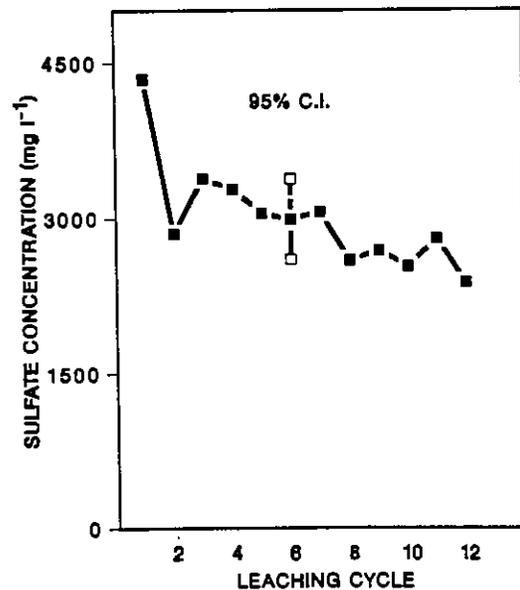


Figure 5. Sulfate concentration in leachate from lysimeters containing Martin Lake overburden. Each leaching cycle was 30 days. 95% C.I. = 95% confidence interval.

Core Samples

The mean pH of the core material removed from the lysimeters on the four sampling dates is shown in Figure 6. After starting with a pH of 8.3 at time zero the minesoil pH progressively decreased to a pH between 6.5 and 7.0 with no significant difference with depth.

The mean extractable SO_4 , Ca, and Mg data for the four core sampling dates are shown in Figures 7 through 9. The continual release of these ions, as is shown in the leachate data, is confirmed with this data. The sulfate produced by pyrite oxidation was translocated with the leachate and portions of it were retained within the lower half of the lysimeter. Following 181 days of monitoring, sulfate accumulated at a depth of 50 to 70 cm forming a large sulfate bulge. The retention was most probably due to the precipitation of the sulfate as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Portions of the Ca and Mg released from the dissolution of dolomite were retained by the cation exchange capacity of the minesoil and not translocated with the leachate. This caused a significant increase in extractable Ca and Mg with each successive sampling date. The accumulation of sulfate as gypsum was not confirmed by the extractable Ca data in Figure 8. This discrepancy may be due to the different extractants used in the determinations or the sulfate may be precipitating as a different salt. This is a question which needs further investigation. The amount and type of sulfate salt precipitating in the pore spaces of a developing minesoil will have a significant impact on its future hydraulic conductivity.

The initial pyrite in the overburden and that remaining in the core material at each coring date was measured using a modified H_2O_2 procedure (O'Shay, 1983). The goal was to determine the rate at which the pyrite oxidized. However, the heterogenous distribution of the pyrite in the lysimeters introduced variability in the data which would not allow inferences about the pyrite oxidation rate to be made. When all of the data are averaged, 50% of the initial pyrite was oxidized during the 12 month study. This extrapolates to an average calculated oxidation rate of $11.1 \text{ mg pyrite Kg spoil}^{-1} \text{ day}^{-1}$.

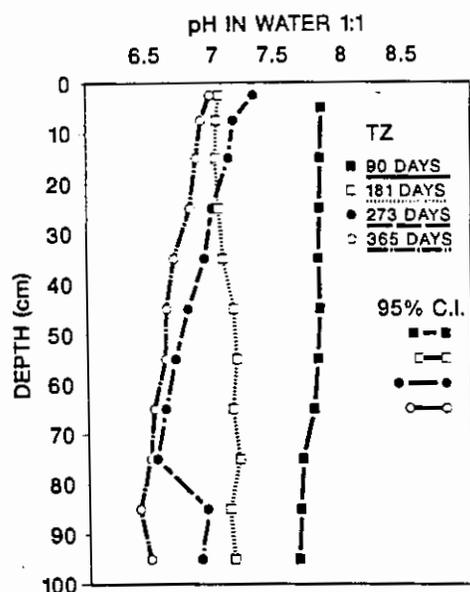


Figure 6. Water pH of Martin Lake core material taken from lysimeters plotted as a function of depth and sampling date. TZ = time zero value, 95% C.I. = 95% confidence interval

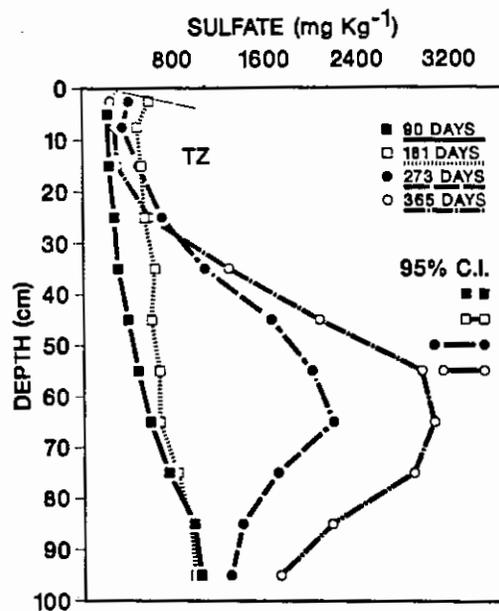


Figure 7. Extractable sulfate in Martin Lake core material taken from lysimeters plotted as a function of depth and sampling date. TZ = time zero value, 95% C.I. = 95% confidence interval

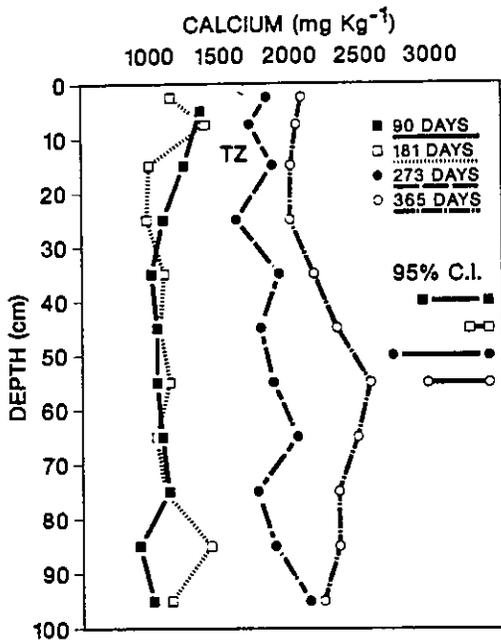


Figure 8. Extractable calcium in Martin Lake core material taken from lysimeters plotted as a function of depth and sampling date. TZ = time zero value, 95% C.I. = 95% confidence interval

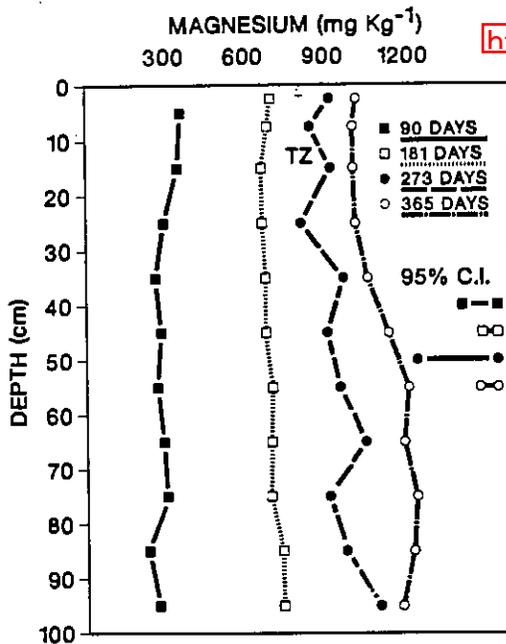


Figure 9. Extractable magnesium in Martin Lake core material taken from lysimeters plotted as a function of depth and sampling date. TZ = time zero value, 95% C.I. = 95% confidence interval

CONCLUSIONS

Pyrite, in the minesoil studied, oxidized sufficiently slow for the excess neutralization potential to neutralize the acidity produced and prevent the formation of acidic minesoil and acid drainage. Oxidation of the pyrite was probably slowed due to the low surface areas of the pyrite particles exposed for oxidative attack. Also the microbial oxidation of pyrite was inhibited by the relatively high pH maintained by the dolomite.

Calcium, magnesium and sulfate salts produced in the oxidation of pyrite and the dissolution of dolomite were translocated through the lysimeters with leach waters. This resulted in an increase in extractable calcium and magnesium throughout the lysimeters and the accumulation of sulfate in the lower half of the lysimeters. Sulfate accumulation was probably due to the precipitation of gypsum.

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