PYRITE OXIDATION UNDER UNSATURATED CONDITIONS

PART I: ABIOTIC OXIDATION

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Abstract.--An x-ray photoelectron spectrometer was used to monitor the abiotic oxidation of pyrite under unsaturated conditions. Results of this study indicated that reclamation to inhibit acid production in the unsaturated zone should be directed towards reducing the relative humidity within pyritic zones. Reducing oxygen in the unsaturated zone resulted in reduced acid production only if the oxygen partial pressure was sustained below 10 pct.

INTRODUCTION

Acid drainage from coal and metal sulfide mines is a serious and persistent source of industrial pollution. Over 5,000 miles of streams and rivers in the United States are adversely affected by acid mine drainage (Bureau of Mines, 1985). Treatment of mine effluents to meet discharge water quality standards costs the mining industry $1 million per day.

The oxidation of pyrite is considered the main source of acidity in mine spoils (Grube and others, 1971). Therefore, the proper handling and disposal of pyritic spoil material is critical to any acid drainage abatement plan. Prior to successful implementation of any selective handling and disposal plan, the conditions that influence the rate of pyrite oxidation must be completely understood.

Many investigators have attempted to elucidate the mechanism and kinetics of pyrite oxidation (Nelson and others, 1933; Burke and Downs, 1938; Mapstone, 1954; Braley, 1960; Hanna and others, 1961; Lorenz and Tarpley, 1963; Clark, 1965, Morth and Smith, 1966; Rogowski and Pionke, 1984; Pugh and others, 1984; and Nicholson and others, in press). Other authors (Lowson, 1982; Nordstrom, 1982) have reviewed and reinterpreted published experimental data. To date, no concensus has been reached regarding the identity of intermediates in the reaction mechanism. However, all authors agree that the overall reaction can be described by the following chemical expression:

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \text{---} Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

Authors disagree regarding the rate dependence of pyrite oxidation on oxygen and water availability. Early authors proposed a linear, first-order oxygen dependence indicating that the oxidation rate increases in a linear manner with increasing oxygen availability. Later authors found that the oxygen dependence was non-linear and began adding terms to the kinetic equation that accounted for the isothermal, physical adsorption/desorption of oxygen to/from pyrite surfaces. One recently derived kinetic equation (Nicholson and others, in press) accounts for the near first-order dependency observed for reactions carried out at low oxygen partial pressures or at low pH values. It also accounts for fractional orders of reaction observed at higher oxygen partial pressures or higher pH's. Fractional orders of reaction with values of 0.8, 2/3, and 1/2 have been reported (Lowson, 1982).

Most published kinetic studies were carried out under saturated conditions with submerged pyrite samples. Therefore, no evaluation of the rate dependence on the partial pressure of water could be made. However, one study (Morth and Smith, 1966) indicated that reaction rates increase in a non-linear manner (reaction order greater than 1) as the point of saturation (100 pct relative humidity) is approached. Because the rate of reaction did not level off as the point of saturation was approached (as water is no longer rate-limiting), the authors suggested that water was more important as a reaction medium than as a reactant.

Opinion concerning the optimum placement of known acid-producing material in the backfill is divided (Dyer, 1985). One approach suggests that pyrite oxidation can be reduced to a minimum (minimum water quality degradation) by placing material below a permanent water table. This placement limits oxygen availability to the solubility of oxygen in stagnant or slow-moving ground water and minimizes pyrite oxidation. Based upon the current understanding of pyrite oxidation kinetics, the effectiveness of this method if properly implemented would be hard to dispute.

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A second approach recommends placing acid-producing material "high and dry" in the backfill. This placement, when combined with surface amendments to limit infiltration, will minimize the amount of water contacting the pyritic material. Possible benefits of this placement include a reduction in the amount of water available for reaction and a significant reduction in the contaminant transport. However, the kinetics of pyrite oxidation under unsaturated conditions have only been briefly addressed (Morth and Smith, 1966). A more comprehensive understanding is necessary before the effectiveness of the "high and dry" placement can be predicted.

This study was specifically designed to examine abiotic pyrite oxidation under unsaturated conditions. Field evidence (Good and others, 1970) suggests that acid production is greatest in the unsaturated zone. An objective of this study was to determine if a significant reduction in the rate of pyrite oxidation will result from the use of special reclamation practices or the selective handling and placement of pyritic material.

EXPERIMENTAL

The pyrite concentrate for this study was prepared from the "sink" fraction from a heavy liquid (bromoform) density separation of a -60 mesh pyritic shale. Combustion furnace results indicated that the concentrate contained about 94 pct pyrite. Immediately prior to experimental weathering, the sample was washed with boiling 4.8 N HCl and then crushed in a methanol slurry. The -200 to +325 mesh fraction was used for the pressing (700 kg/cm^2 pressure) of 13 mm diameter by 0.5 mm cylindrical pellets. Six to ten pellets were placed into each of four 10.2 cm diameter by 12 cm plastic weathering chambers (fig. 1). Prior to each experiment, the chambers were washed with an acidified surfactant (sodium lauryl sulfate) solution and then rinsed with methanol to reduce the likelihood that inadvertent bacterial catalysis could occur.

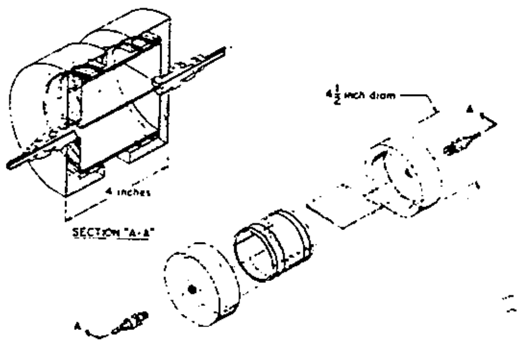

Figure 1.--Schematic of the weathering cells used in this study.

The first experiment consisted of weathering the pyrite pellets under air atmospheres (21 pct O_2) of different humidities. Constant humidities (Handbook of Chemistry and Physics, 1973) were maintained in the chambers by bubbling air through saturated salt solutions (23° C) of potassium nitrite (45 pct relative humidity), sodium nitrite (66 pct relative humidity), ammonium chloride (79.5 pct relative humidity), barium chloride dihydrate (88 pct relative humidity), and lead nitrate (98 pct relative humidity).

Oxygen was the independent variable in the second experiment while the relative humidity was maintained at 98 pct. Atmospheres of 0.5, 5.0, 10.0, or 21.0 pct oxygen with nitrogen balance were maintained in the weathering chambers using compressed gas cylinders containing standard gas mixtures. All gas mixtures were bubbled through a saturated solution of lead nitrate to maintain a constant relative humidity of 98 pct. The flow rate through the weathering chambers (100-200 standard cubic centimeters per minute) was not quantitatively determined because previous studies (Morth and Smith, 1966) have shown that oxidation is independent of flow rate above certain minimum values. Pressure in the chambers was maintained at atmospheric.

At predetermined times, the chambers were opened and one pyrite pellet was removed for analysis. This transfer was carried out in a glove box under a dry, nitrogen atmosphere. The sample was immediately inserted into the preparation chamber of a Leybold Heraeus LHS-10 X-ray photoelectron spectrometer (XPS) and pumped down to a vacuum of 10^{-6} torr. The samples were held at this vacuum until transferred to the 10^{-8} torr vacuum of the analytical chamber and analyzed.

X-ray photoelectron spectroscopy is a surface analysis technique that is sensitive only to a depth of about 25 angstroms (Hercules, 1986), depending upon the material. This depth usually corresponds to the thickness of one or two atomic monolayers and is determined by the depth from which a dislodged electron can escape without energy loss through collisions (inelastic mean free path).

Analysis of each pyrite pellet consisted of 100 scans of the sulfur 2p region (160-180 eV binding energy, fig. 2) and the iron 2p region (704-728 eV binding energy, fig. 3). The scan data was smoothed and despiked. Corrections were made for errors arising from the use of a non-monochromatic X-ray source. Quantitation of pyritic sulfur was accomplished by integrating the sulfur 2p 1/2 - sulfur 2p 3/2 peak at 162.6 eV binding energy. Quantitation of sulfate sulfur was taken as the integrated value of the sulfur 2p peak at 168.9 eV binding energy. The progress of the oxidation was expressed as percent conversion where:

$$\text{pct. conv.} = \frac{\text{sulfate sulfur}}{\text{total sulfur}} \times 100 \text{ pct} \qquad \text{or}$$

$$= \frac{\text{sulfate sulfur}}{\text{sulfate sulfur + pyritic sulfur}} \times 100 \text{ pct}$$

The 2p splitting in the iron region did not result in resolvable peaks that could be attributed to any particular oxidation state of iron. Therefore, the iron 2p region was used only as a qualitative confirmation of results obtained from the sulfur 2p region.

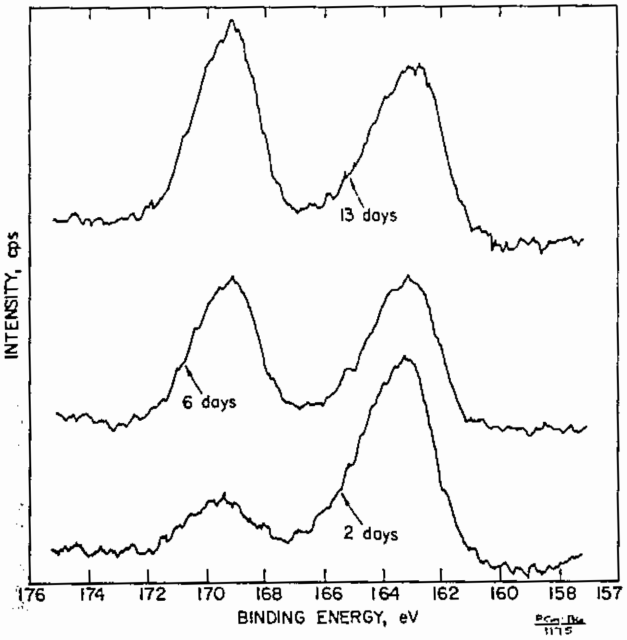

Figure 2.--XPS spectra of the sufur 2p region showing pyritic sulfur (~ 163 eV) and sulfate sulfur (~ 169 eV) after 2, 6, and 10 days of weathering at 98 pct relative humidity and 21 pct oxygen.

STUDY RATIONALE

The use of an X-ray photoelectron spectrometer to monitor pyrite oxidation provides an alternative to methods used in previous kinetic studies. Previous studies have based observed oxidation rates on bulk pyrite content (amount of sulfate produced or oxygen consumed per gram bulk pyrite per hour) although only a small fraction of the bulk pyrite is at the surface and available for reaction. Available pyrite can be calculated from the bulk pyrite content using a surface area estimation or gas absorption techniques but this calculation contains several approximations and can only be regarded as an estimate. In contrast, XPS directly quantitates available pyrite and is relatively independent of differences in surface to volume ratios as it is only sensitive to the upper one or two atomic monolayers.

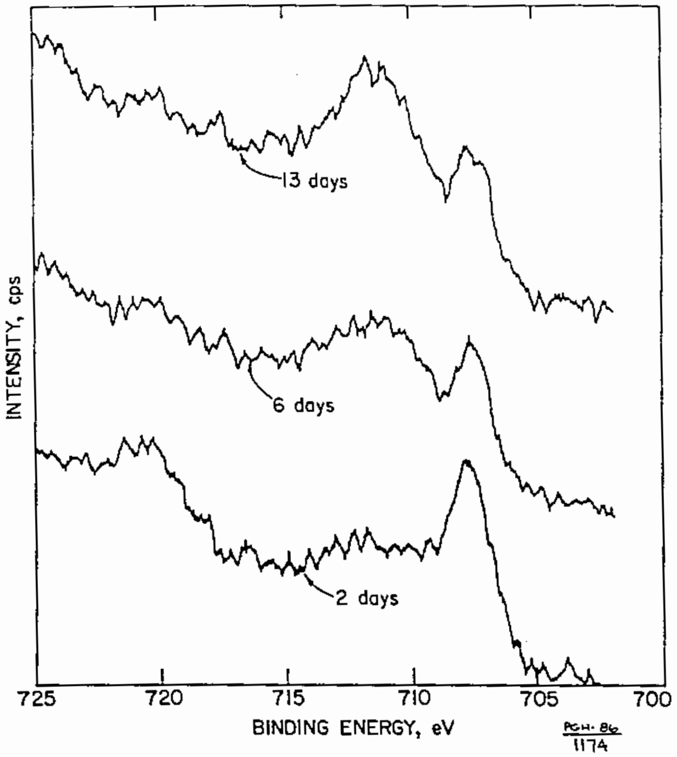

Figure 3.--XPS spectra of the iron 2p region showing pyritic iron (~ 708 eV) and ferric iron (~ 713 eV) after 2, 6, and 9 days of weathering at 98 pct relative humidity and 21 pct oxygen.

A second advantage of XPS is that it directly quantitates sulfate sulfur at the point of formation. Most published studies (Braley, 1960; Clark, 1965; Rogowski and Pionke, 1984; and Nicholson and others, in press) have used sulfate production as a measure of the amount of oxidation that has taken place. In the case of these studies, sulfate cannot be detected until it is dissolved and leached from the sample. This adds the complexity of sulfate solubility and pH-dependent sulfate adsorption considerations. The in-situ sulfate analysis by XPS is simpler and inherently more accurate for kinetic studies. XPS determinations of sulfate sulfur are also preferable to the oxygen consumption methods employed by Morth and Smith (1966). The type of pyrite (sulfur ball) used in many previous studies commonly contains significant amounts of carbonaceous material. Part of the observed oxygen consumption may result from the oxidation of this material and not be attributable to pyrite oxidation. Another source of error would result from the adsorption of oxygen on newly-formed reaction products. However, this error would only be significant in the late stages of pyrite oxidation under unsaturated conditions.

RESULTS AND DISCUSSION

Plots of percent conversion versus time for each atmosphere are shown in figures 4 and 6. Each plot exhibits a linear increase (r > .96, 5 data points) in percent conversion with time from the start of the experiment until 40-50 pct conversion is attained. After 40-50 pct conversion, little or no further oxidation is observed which may be due to:

- o oxidation occurring below the analysis depth (25 angstroms) and/or,
- o mass transfer processes, where the accumulation of reaction products inhibits the diffusion of oxygen or water to pyrite surfaces and/or,
- o the formation of water films in hygroscopic oxidation products that result in the dissolution and movement of soluble salts into the pellet and away from the surface.

The initial linear region was used for the determination of oxidation rates because mass transfer processes appeared to be negligible in this region. The oxidation rate was calculated from the slope of the least squares line that best describes the data in this region. It must be borne in mind that oxidation rates calculated from the initial linear region represent minimum rates because some sulfate may have dissolved in water films and moved into the pellet below the depth of detection. However, this effect has only been observed after 13 days in tests carried out at 98 pct relative humidity. Depth-profiles of samples weathered for 4 days at 21 pct oxygen and 98 pct relative humidity showed no evidence of sulfate movement. With depth (0 to 500 angstroms), the sulfate content decreased as expected with a proportionate increase in pyritic sulfur. It was therefore assumed that the effect of sulfate migration in the early stages of these experiments is negligible and that the oxidation rates measured from the initial linear region are accurate.

Effect of Humidity

The effect of humidity on pyrite oxidation is shown in fig. 4. The percent conversion is plotted versus weathering time for 21 pct oxygen atmospheres with constant relative humidities of 45, 66, 79, 88, and 98 pct. One notable observation from figure 4 is the fact that the plots for 45, 66, 79, and 88 pct relative humidity are very similar and are almost superimposable. However, the plot of data at 98 pct relative humidity displays a distinctly steeper slope.

Figure 5 is a plot of oxidation rate versus relative humidity. The rate is more or less independent of relative humidity between 45 and 88 pct. However, between 88 and 98 pct relative humidity, the oxidation rates almost double. These results generally agree with the findings of Morth and Smith (1966) although their results suggest some dependency on relative humidity below 88 pct.

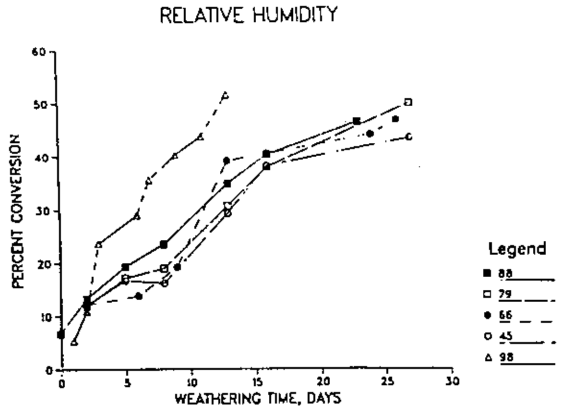

Figure 4.--A plot showing the percent conversion of pyritic sulfur to sulfate sulfur with time at different relative humidity.

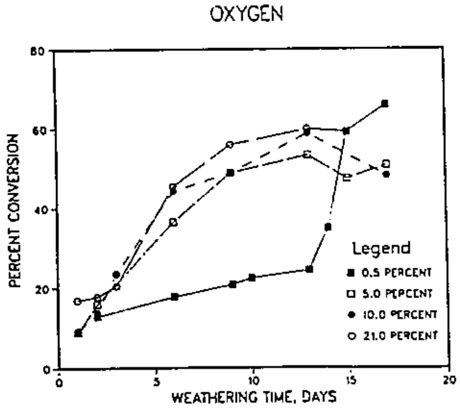

Figure 5.--A plot showing the conversion of pyritic sulfur to sulfate sulfur with time at different oxygen contents.

Effect of Oxygen

Figure 6 is a plot of percent conversion versus time for atmospheres with 98 pct constant relative humidity containing 0.5, 5.0, 10.0, and 21.0 pct oxygen. Curves representing 10 pct and 21 pct oxygen are virtually superimposable until about 45 pct conversion. This indicates that oxygen is not rate-limiting at 10 pct. The oxidation rate in 5.0 pct oxygen is 37 pct lower than the rate in 10 pct and 21 pct oxygen (fig. 7). At 0.5 pct oxygen, the initial rate is 86 pct lower than corresponding rates in air (21 pct oxygen). However, at 24 pct conversion, the rate dramatically increases (fig. 8). Experimental error was originally the suspected cause of this unexpected phenomenon. The chamber was tested for leaks and the experiment was then repeated twice under careful scrutiny with the same results. Although more work is necessary to completely understand this phenomenon, a possible explanation follows. Apparently, at 24 pct conversion, sufficient oxidation products have accumulated on pyrite surfaces to change the oxygen adsorption mechanism. On a fresh pyrite surface, oxygen is physically adsorbed and must compete with other gases for adsorption sites.

Therefore, the rate of oxygen adsorption is a function of the oxygen partial pressure. At least initially, a low oxygen content will result in low rates of oxygen adsorption and reduced oxidation. However, with the accumulation of oxidation products on pyrite surfaces, the mechanism changes to chemisorption which preferentially adsorbs oxygen. The reaction then responds to the much higher oxygen content in the oxygen-enriched oxidation product film, which results in increased oxidation rates. Chemisorption of oxygen into product films is probably active at all oxygen partial pressures but the effect is only apparent in tests carried out in reduced oxygen atmospheres.

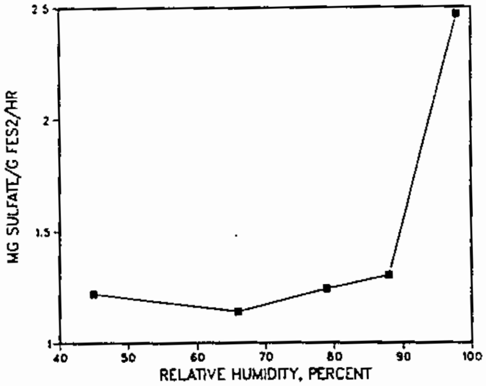

Figure 6.--A plot showing the effect of relative humidity on the rate of pyrite oxidation.

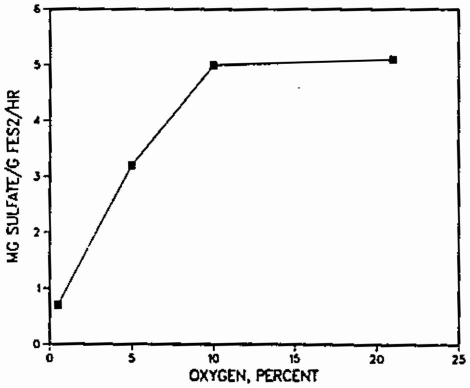

Figure 7.--A plot showing the effect of oxygen content on the rate of pyrite oxidation.

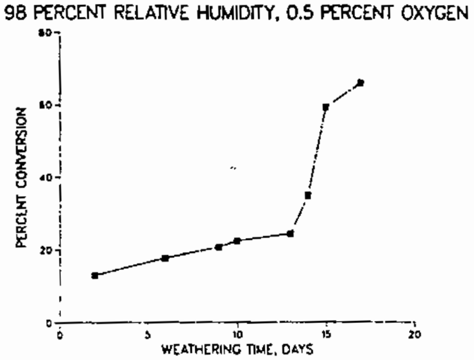

Figure 8.--A plot of percent conversion versus weathering time for 0.5 pct oxygen and 98 percent relative humidity. Note the unexpected increase after 14 days.

CONCLUSIONS

The preliminary examination of the role of water films that form in hygroscopic reaction products may have provided the most unexpected result of this study. Water films that develop on weathering pyrite surfaces may have the capability of creating microenvironments that contain more oxygen and water than the surrounding atmosphere. These films can sustain pyrite oxidation rates in excess of what would be expected based on the oxygen partial pressure in the surrounding atmosphere.

In humid environments, frequent infiltration of rainfall will wash away oxidation products before the mass transfer of reactants or products is significantly inhibited. Therefore, in these environments, only the initial oxidation rates (initial linear region) will be important. Conclusions based upon initial oxidation rates that have immediate practical application include:

(1) reclamation to achieve a 10 pct oxygen content in pyritic mine spoils will result in little or no reduction in the rate of acid production;

(2)reclamation to achieve a 5 pct oxygen content will provide a 36 pct reduction in rate of acid production; and

(3)maintaining known acid-producing material at relative humidities less than 88 pct will reduce the rate of pyrite oxidation by 50 pct.

The fact that these conclusions are based on abiotic pyrite oxidation should be borne in mind. This study was designed to examine the pyrite oxidation that precedes and establishes the conditions necessary (pH < 4.5) for bacterial catalysis. Conclusions from this study may or may not be relevant to bacteria mediated pyrite oxidation.

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Table 1.--Pyrite oxidation rates, oxygen dependence, and water dependence reported by other authors

Investigator	Observed rate	O_2-dependence	H_2O-dependence	Pyrite type	Particle size	Temperature	Species Monitored
Braley (1960)	0.13 mg $SO_4^{-2}g^{-1}FeS_2$ hr^{-1}	Linear (first-order)	NA	Sulfur ball	-8 + 40 mesh		Sulfate
Clark (1965)	0.11 mg $SO_4^{-2}g^{-1}FeS_2$ hr^{-1}	Linear (first-order) for dissolved oxygen	NA	Sulfur ball	-40 + 50 mesh	20° C	Sulfate
Morth and Smith (1966)	0.06 mg $SO_4^{-2}g^{-1}FeS_2$ hr^{-1}	Non-linear (fractional order)	Non-linear (order exceeds 1 as 100% relative humidity is approached)	Sulfur ball	-70 + 100 mesh	25° C	Oxygen
Rogowski and Pionke (1984)	0.16 mg $SO_4^{-2}g^{-1}FeS_2$ hr^{-1}	Not determined	Not determined	Not spec.	2-8 mm	25° C	Sulfate
Nicholson & others (in press)	0.13 mg $SO_4^{-2}g^{-1}FeS_2$ hr^{-1}	Adsorption (Langmuir-type)	NA	Massive, from various locations	76um	23° C	Sulfate

NA - Not applicable