THE EFFECT OF OXYGEN ON PYRITE OXIDATION [1]

By

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Abstract. The oxygen dependence of abiotic and biotic pyrite oxidation was examined on three scales: 1) pyrite surfaces to a depth of 20 angstroms, 2) 5 g quantities of pyrite in small columns, and 3) 175 kg quantities of pyritic shale in large columns. Results of these studies indicated that the initial abiotic oxidation of fresh pyrite surfaces was independent of oxygen partial pressures above 10% (0-order reaction) and was proportional to oxygen partial pressures below 10% (first-order reaction). However, the rates of abiotic oxidation measured in small columns were proportional to oxygen partial pressures between atmospheric (21%) and 5%. Small column and large column results indicated that with bacteria present, the rate of pyrite oxidation was independent of oxygen partial pressures down to 1%. Below 1% oxygen, the reaction rate was proportional to oxygen partial pressures (first-order reaction). The oxygen-impermeable and oxygen-consumptive barriers other than water that are economically feasible at present are not capable of maintaining oxygen levels below 1%. Therefore, no reduction in the rate of pyrite oxidation would be would be realized using these techniques unless bacteria were inhibited. The best method for limiting pyrite oxidation was to place pyritic material below a permanent water table. Results of large column experiments indicated that a 96% reduction in pyrite oxidation could be realized by inundating the pyritic material. Results of large column tests corroborated previous work by other researchers that indicated leaching frequency had no effect on pyrite oxidation and total sulfate load.

Additional key words: pyrite oxidation, oxygen dependency.

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Introduction

Early laboratory studies (Braley 1960; Clark 1965; Morth and Smith 1966; Rogowski and Pionke 1984; Nicholson, Gillham and Reardon 1988) showed that the rate of pyrite oxidation was dependent on the partial pressure of oxygen. However, there was no general consensus among researchers: reaction orders of 112, 2/3, 0.81, and I were proposed (Nicholson, Gillham and Reardon 1988; Lowson 1988). Although there was no agreement on reaction order, all studies indicated that the rate of pyrite oxidation could be reduced by limiting oxygen partial pressures. In the field, several strategies including clay capping, plastic liners, and even standard reclamation practices have reduced oxygen partial pressure in spoil and refuse to less than 10 or even 5% (Watzlaf and Erickson 1986; Lusardi and Erickson 1985). However, reducing oxygen partial pressure to these levels did not significantly slow the overall pyrite oxidation rate (Watzlaf and Erickson 1986). A laboratory study (Pugh, Hossner and Dixon 1984) partially explained the discrepancies between field and laboratory results. The study was carried out using framboidal pyrite in an aqueous suspension inoculated with a pure culture of Thiobacillus ferrooxidans. Results of this study indicated that the rate of pyrite oxidation was independent of oxygen partial pressures (0-order) above 8% when bacteria were present. Below 8% oxygen, the pyrite oxidation rate dropped sharply. Based on these results, no reduction in the pyrite oxidation rate would be expected in spoil or refuse piles unless the oxygen partial pressure could be sustained at levels less than 8% or unless bacteria could be inhibited.

Previous studies (Lusardi and Erickson 1985) indicated that the bulk of pyrite oxidation occurred in the unsaturated zone above the water table. Because many published laboratory pyrite oxidation rates (Braley 1960; Clark 1965; Morth and Smith 1966; and Pugh, Hossner, and Dixon 1984) were determined using aqueous pyrite suspensions, these results were not directly applicable to the field. This study was intended to be a comprehensive evaluation of abiotic and biotic pyrite oxidation rates under unsaturated conditions with different oxygen partial pressures. Pyrite oxidation was examined on three different scales: (1) pyrite surfaces to a depth of 20 angstroms; (2) 5 g quantities of pyrite in small columns; and, (3) 175 kg quantities of pyritic shale in large columns. The rationale of this approach was to determine the oxygen dependency of pyrite oxidation in the simplest case (ie. the oxidation of a surface) and observe apparent changes in oxygen dependency with increasing system complexity. Use of this approach could enable an interpolation to field scale.

Methods and Materials

Materials

The pyrite used in surface and small column studies was hand picked from a sample of the Pittsburgh coalbed collected in Barbour County, WV. The pyritic material was crushed to -60 mesh and subjected to a density separation using tetrabromoethane (2.96 g/cc). The sink portion was washed in boiling 6N HCl to remove sulfate and iron oxides and to kill bacteria. Evolved gas analysis indicated that the pyrite concentrate contained no sulfate sulfur and less than 1% organic sulfur. The material was determined to contain greater than 96% iron disulfide based on total sulfur measurements by combustion furnace.

The material used for large column experiments was a dark gray pyritic shale, superjacent to the Clarion coalbed in Clearfield County Pennsylvania. The shale was crushed to pass 3.8 cm and loaded into four columns containing approximately 175 kg each (Watzlaf and Hammack 1989). The crushed material was analyzed by the combustion furnace method and found to contain 3.5% sulfur.

Surface Weathering Studies

X-ray photoelectron spectroscopy (XPS), a surface analysis technique, was used to examine weathering pyrite surfaces. Because mass transfer or diffusional effects are minimal during the early stages of pyrite surface oxidation, the measured rates better reflect the kinetics of the electron transfer component of pyrite oxidation.

XPS provided quantitative elemental information with a detection limit of approximately 1% of atoms comprising the outermost monolayers. Different formal oxidation states could be distinguished based on chemical shift information (Brundle 1982). Chemical shifts in the sulfur (2p) electron binding energy (Fig. 1) were used in this study to distinguish between pyritic sulfur (reactant) and sulfate sulfur (product). The XPS analysis depth for pyrite was estimated to be about 2.3 nm based on measured inelastic mean free paths for similar semiconductors (Buckley, Woods, and Wouterlood 1987). This depth corresponded to the thickness of 4.24 pyrite unit cells (0.54175 nm/ unit cell).

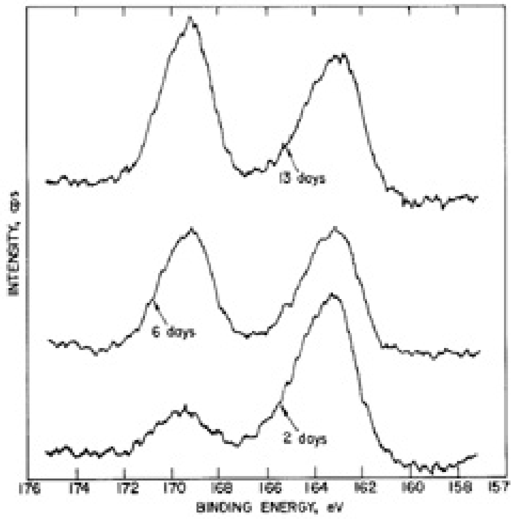
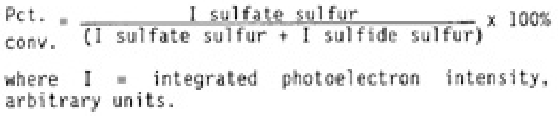


Figure 1. XPS scans of a pyrite surface showing the S (2p) electron region after 2, 6, and 13 days of weathering. Pyritic sulfur and sulfate sulfur peaks occur at 163.5 eV and 169.5 eV, respectively.

The pyrite was weathered at room temperature with a constant humidity of 88% and a oxygen partial pressure of 0.5, 5.0, 10.0, or 21%, balance nitrogen. The conversion of sulfide sulfur to sulfate sulfur was monitored. For each sample, a percent conversion was calculated from the integrated photoelectron intensities for sulfate sulfur (binding energy = 169 eV) and pyritic sulfur (binding energy = 163 eV):



$$\text{Pct. conv.} = \frac{\text{I sulfate sulfur}}{(\text{I sulfate sulfur} + \text{I sulfide sulfur})} \times 100\%$$

where I = integrated photoelectron intensity, arbitrary units.

$$\text{Percent conv.} = \frac{\text{I sulfate sulfur}}{\text{I sulfate sulfur} + \text{I sulfide sulfur}} = \text{x } 100 \text{ pct}$$

where I = integrated photoelectron intensity, arbitrary units.

Because sulfate sulfur and sulfide sulfur were the only observed sulfur species, the equation can be rewritten:

$$\text{Percent conv.} = \frac{\text{I sulfate sulfur}}{\text{I total sulfur}} \times 100 \text{ pct}$$

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Immediately prior to weathering, samples for XPS analysis were washed with boiling 4.8 N HC1 to remove sulfate, rinsed with methanol, and dried under vacuum. Cylindrical wafers (13 mm diameter by 0.5 mm) were pressed under 700 kg/cm pressure. Weathering chambers (Fig. 2) were constructed so that wafers could be removed without disturbing the atmosphere within the chamber. 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 bacterial catalysis could occur.

Periodically during the test, one wafer from each oxygen atmosphere was removed and placed in a Leybold-Heraeus LHS-10 photoelectron spectrometer operated at a pressure of $2X10^{-8}$ mbar or lower. X-rays from a magnesium anode (Mg K = 1253.6 eV) and an analyzer pass energy of 100 eV were used for the acquisition of S(2p) data. Binding energy calibrations were carried out by adjusting the measured binding energy for the C(1s) spectrum of adventitious carbon to 284.6 eV and shifting all other measured binding energies correspondingly. Peak areas within the S(2p) region attributable to sulfide sulfur and sulfate sulfur were determined with the Leybold-Heraeus DS-5 data system. The percent conversion was calculated for each wafer and plotted versus weathering time.

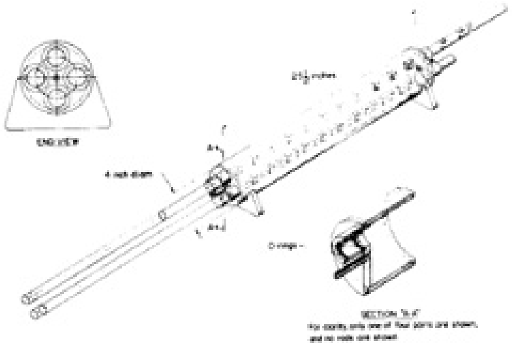


Figure 2. Schematic of chamber used for the XPS-monitored weathering of pyrite wafers. Wafers are placed in rod cut-outs where they can be removed one at a time without disturbing the environment in the chamber.

Small Column Studies

Four 40-cm by 2.54-cm I.D. columns (Fig. 3) were filled with 5 g each of pyrite dispersed in 100 g of 30 - 60 mesh acid-washed silica sand. Glass wool at the base of each column prevented the sample from washing out of the column. The columns were designed to allow pyrite to weather under unsaturated conditions in known oxygen atmospheres. Certified gas mixtures containing 0.005, 0.1, 0.3, 0.5, 1.0, 5.0, 9.6, or 14.5% oxygen, 5.0% carbon dioxide, and balance nitrogen were obtained in compressed gas cylinders. Gas mixtures were bubbled through water to humidify the gas stream, passed through a rotometer, and then introduced into the base of each column (Fig. 3). The gases flowed up through the pyritic material and were exhausted to the atmosphere through a gas trap. A flow rate of 20 ml/min was maintained through each column. Analysis of gases exiting the columns showed that this flow rate was sufficient to maintain constant oxygen content throughout the column. The columns were leached weekly with 200 ml of 16 megohm deionized water (controlled oxygen atmospheres were maintained during leaching periods). A most probable number (MPN) type of bacterial enumeration (American Public Health Association 1985; Cobley and Haddock 1975) was performed on each leachate to determine the presence/absence or number of bacteria.

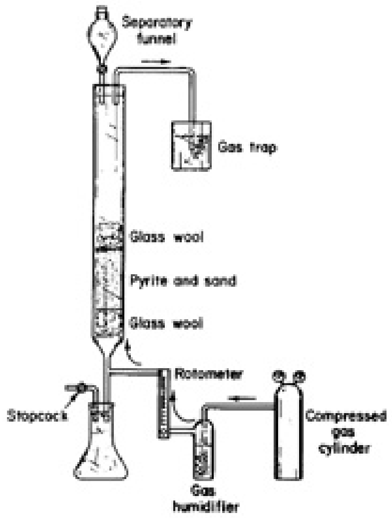


Figure 3. Schematic of set-up used for small column weathering tests.

Large Column Studies

The large columns were constructed using 1.92-m lengths of 0.29-m diameter cast acrylic (Fig. 4). Three room temperature experiments were conducted with the large columns: (1) comparison of two applied oxygen partial pressures during unsaturated leaching; (2) comparison of four unsaturated leaching frequencies; and (3) comparison of unsaturated leaching with water-saturated leaching. Deionized water was added through the top of the columns for all leaching and flushing tests. For the first test, the tops of the columns were closed to the atmosphere. Certified gas mixtures containing 1.5% and 10.5% oxygen, balance nitrogen were humidified and flowed through the columns at a rate sufficient to maintain a constant oxygen partial pressure throughout the columns (3.1 L/min). For tests two and three, the top of the columns remained open to the atmosphere. During all unsaturated leaching tests, the valve on the final leachate collection system remained open with the end of the tube kept under water to avoid oxygen inflow. During flushing tests, the columns remained saturated with water with a constant water level maintained at 0.15 m above the surface of the shale. Twenty liters of water were added and withdrawn simultaneously to maintain this water level. MPN bacterial enumerations were performed periodically to insure the presence of viable bacterial populations.

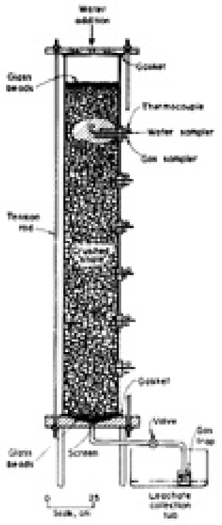


Figure 4. Schematic of set-up used for large column weathering tests.

Analytical

The leachates from both the small column and large column tests were analyzed for sulfate using ion chromatography. Gas chromatography was used to determine oxygen in the effluent gases from the columns.

RESULTS AND DISCUSSION

Surface Studies

The room temperature oxidation of pyrite surfaces was carried out under abiotic conditions at 0.5, 5.0, 10.0, and 21% oxygen and 88% relative humidity. The surface oxidation of pyrite at 21% oxygen is shown in Figure 5. Initial oxidation rates are rapid. The apparent passivation that occurs after 300 hrs of weathering is an artifact of the XPS technique resulting from the mobilization and recrystallization of oxidation products. However, the slope of the least-squares fit line through the initial points is indicative of the oxidation rate. Abiotic surface oxidation rates at 0.5, 5.0, 10.0, and 21% oxygen are shown in Figure 6. Oxidation rates measured by XPS in this study are based on the amount of pyrite at the surface and "available" for reaction and, are significantly faster (20 to 40 times) than rates typically reported. Published oxidation rates are based 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.

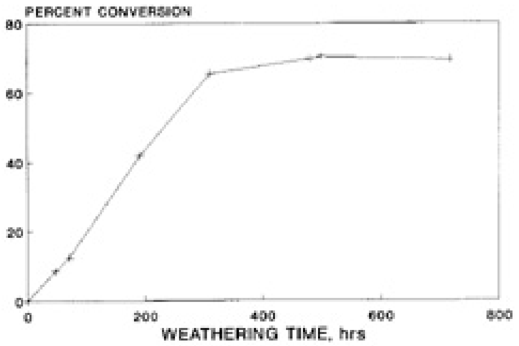


Figure 5. XPS-monitored abiotic weathering of a pyrite surface at 21% oxygen and 88% relative humidity.

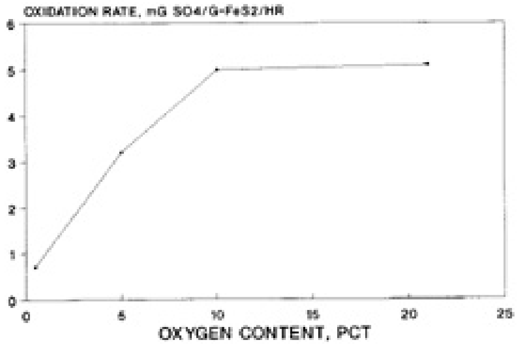


Figure 6. Abiotic surface oxidation rate at different oxygen partial pressures.

In this study, the abiotic surface oxidation rate (Table 1) is found to be independent of oxygen content above 10% (0-th order reaction). Below 10% oxygen, the rates are proportional to the oxygen content (first order reaction).

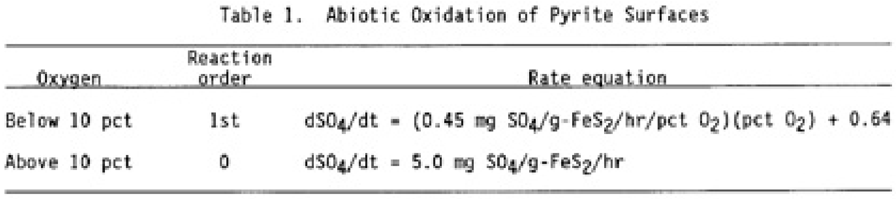


Table 1. Abiotic Oxidation of Pyrite Surfaces

Oxygen	Reaction order	Rate equation
Below 10 pct	1st	$dSO_4/dt = (0.45\ mg\ SO_4/g\text{-}FeS_2/hr/pct\ O_2)(pct\ O_2) + 0.64$
Above 10 pct	0	$dSO_4/dt = 5.0\ mg\ SO_4/g\text{-}FeS_2/hr$

Small Columns

Oxidation without Bacteria. Abiotic oxidation experiments were carried out on HCl-washed pyrite under unsaturated conditions at oxygen contents of 0.5, 5.0, 9.6, and 14.5%. MPN bacterial counts performed on the leachates indicated that the columns were sterile throughout the experiment. Plots of cumulative sulfate in the leachates versus weathering time (Fig. 7) are linear and show that abiotic pyrite oxidation is highly dependent on the oxygen content of the column atmosphere. Oxidation rates were calculated from the slope of the least-squares line fit to cumulative sulfate plots. Abiotic oxidation rates at different oxygen contents are shown in Figure 8 (without bacteria) and Table 2. The abiotic oxidation of pyrite at small-column scale is 1st order above 5% oxygen. Below 5% oxygen, the reaction order appears to fall below 1 which agrees with published results (Nicholson, Gillham, and Reardon 1988). In surface studies, pyrite oxidation was independent of oxygen partial pressures above 10%. However, at small column scale, the reaction is first order in this range. It can be speculated that at surface scale, the diffusional component of pyrite oxidation (the most sensitive to oxygen partial pressure) is minimal.

Oxidation with Bacteria. The room temperature biotic oxidation of pyrite was carried out under unsaturated conditions at oxygen contents of 0.005, 0.1, 0.3, 0.5, 1.0, and 10% (5% oxygen column broke during test). Each column was inoculated with 30 ml of acid drainage from a coal mine in Westmoreland County, PA. MPN's were performed during the experiment to make certain that each column contained viable bacteria.

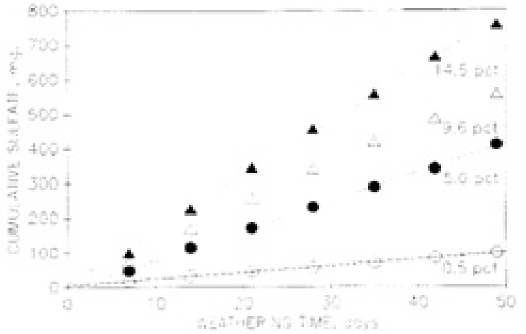


Figure 7. Plots of cumulative sulfate load versus weathering time for the abiotic weathering of pyrite in small columns under different oxygen partial pressures.

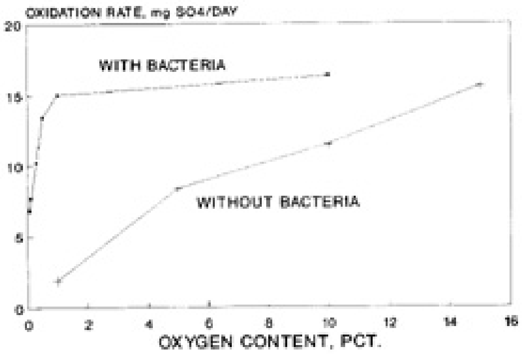


Figure 8. Abiotic rates of pyrite oxidation in small columns maintained at different oxygen partial pressures.

Cumulative sulfate versus weathering time plots for biotic oxidation are shown in Figure 9. Oxidation rates were determined from the slope of the least-squares fit line through the stationary phase. At this time, the effect of sulfate or ferric iron added with the inoculum would be insignificant. The inoculum could, at most, contribute only about 60 mg of sulfate including sulfate from the oxidation of pyrite by ferric iron in the inoculum. Unlike abiotic oxidation, biotic oxidation is not significantly inhibited by reduced oxygen contents (Fig. 8, with bacteria) and Table 3. In fact, the reaction rate is independent of oxygen partial pressures (0-order reaction) above 1%. Below 1% oxygen, the reaction appears to be first order until some point below 0.1%.

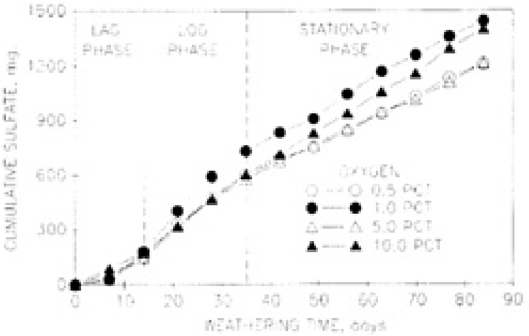


Figure 9. Plots of cumulative sulfate load versus weathering time for the biotic weathering of pyrite in small columns under different oxygen partial pressures.

Table 2. Abiotic Oxidation in Small Columns

Oxygen	Reaction order	Rate equation
Below 5 pct	Fractional	Insufficient data
Above 5 pct	1st	$dSO_4/dt = (0.006 \text{ mg } SO_4/\text{g-}FeS_2/\text{hr/pct } O_2)(\text{pct } O_2) + 4.63$

Table 3. Biotic Oxidation in Small Columns

Oxygen	Reaction order	Rate equation
0.1 - 1 pct	1st	$dSO_4/dt = (0.073 \text{ mg } SO_4/\text{g-}FeS_2/\text{hr/pct } O_2)(\text{pct } O_2) + 7.22$
Above 1 pct	0	$dSO_4/dt = 0.13 \text{ mg } SO_4/\text{g-}FeS_2/\text{hr}$

The oxidation rate at oxygen partial pressures above 1% (0.13 mg SO_4/g-FeS_2/hr) is in good agreement with published rates (Table 4). It is also apparent that the rates of abiotic and biotic pyrite oxidation are not significantly different at oxygen partial pressures above 15% (Fig. 8). The role of bacteria is to sustain high oxidation rates at low oxygen partial pressures.

Large Columns

Small column tests indicated that the rate of biotic pyrite oxidation was independent of oxygen partial pressures (0-th order reaction) above 1%. This indicates that measures taken to reduce oxygen partial pressures would be ineffective at reducing pyrite oxidation unless oxygen could be maintained at levels below 1%. This is not economically possible at present using barriers other than water. In large column tests, no difference in biotic pyrite oxidation rate was found between columns with applied atmospheres of 1.5% and 10.5% oxygen (Fig 10). These results corroborate the results of small column tests and indicate that current oxygen-impermeable or -consumptive barriers (except water) will not be effective at limiting pyrite oxidation without bacterial inhibition.

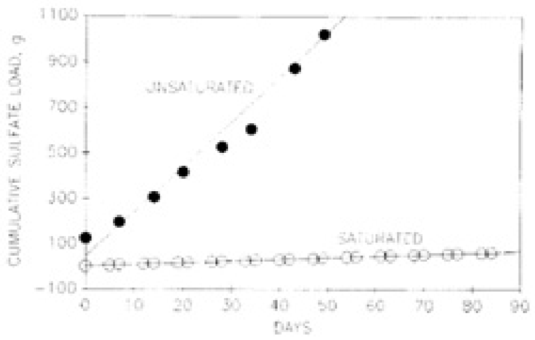
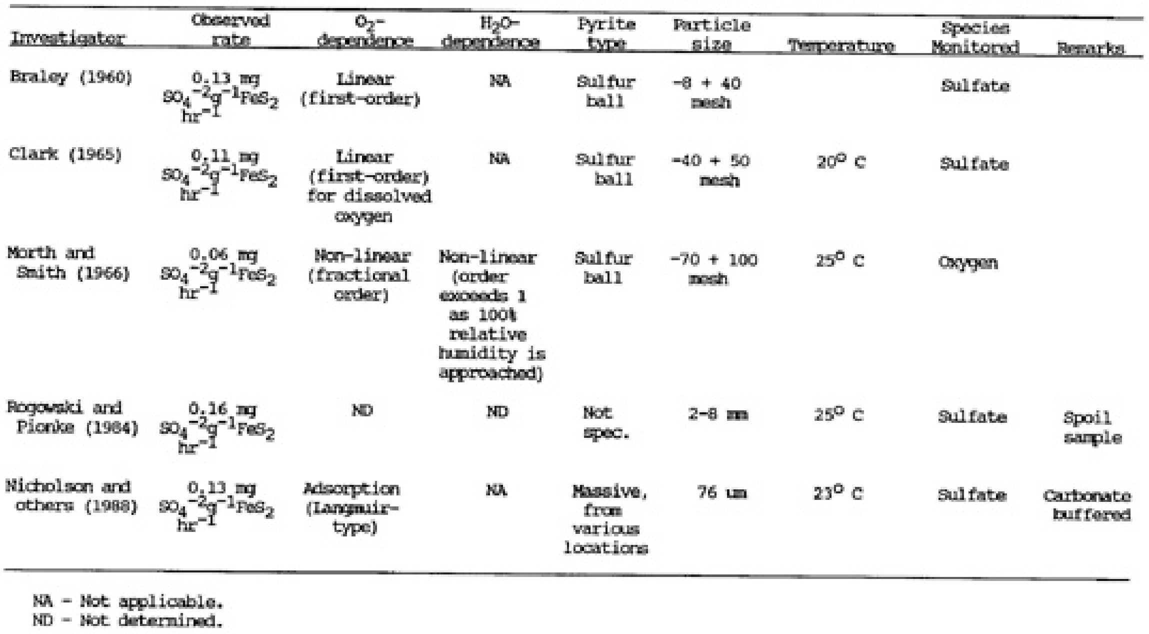


Figure 10. Plots of cumulative sulfate load versus weathering time for saturated and unsaturated pyritic shale in large columns.

Table 4. 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	Remarks
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}	ND	ND	Not spec.	2-8 mm	25° C	Sulfate	Spoil sample
Nicholson and others (1988)	0.13 mg $SO_4^{-2}g^{-1}FeS_2$ hr^{-1}	Adsorption (Langmuir-type)	NA	Massive, from various locations	76 um	23° C	Sulfate	Carbonate buffered

NA - Not applicable.
ND - Not determined.

The effect of leaching frequency is shown in Figure 11. Columns 1-4 were leached as follows: column #1, 1L every day; column #2, 7L every 7 days; column #3, 14L every 14 days; and column #4, 21L every 21 days. The results of this experiment indicated that the build up of weathered products did not retard pyrite oxidation by surface passivation. An alternative explanation is that the solubilization of sulfate minerals under these conditions may be slower than pyrite oxidation. Therefore, leaching frequency tests may only be indicative of the rate of oxidation product solubilization rather than pyrite oxidation.

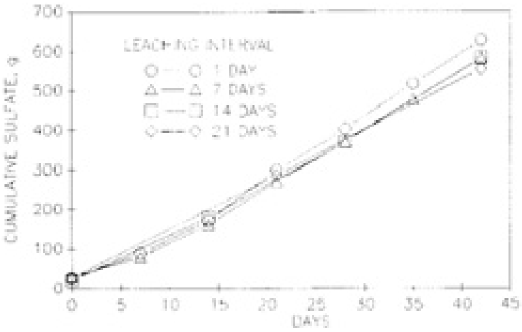


Figure 11. Plots of cumulative sulfate load versus weathering time at different leaching frequencies.

Results of this study indicate that attempts to limit pyrite oxidation under unsaturated conditions would be difficult and undoubtedly expensive. However, water is an effective oxygen barrier. Figure 12 compares the rates of release of sulfate under unsaturated and water-saturated conditions. For unsaturated leaching, sulfate was released at a rate of 18.2 g/day compared to 0.7 g/day when the shale remained inundated and flushed biweekly with 20 L of oxygen- saturated water (D.O. = 8 mg/L). Stoichiometrically, the amount of oxygen added through flushes with oxygen-saturated water can account for 0.2 g/day of sulfate from the oxidation of pyrite. The remaining 0.5 g/day of sulfate released could be due to additional pyrite oxidation from ferric iron resident in the columns or dissolved oxygen transferred from the atmosphere. It is also possible that some of the sulfate is from the continued solubilization of previously formed sulfate compounds. Additional tests using oxygen-depleted water for the 20-L flushes resulted in a sulfate release rate of 0.5 g/day.

The importance of maintaining complete water inundation was illustrated during these tests. A leak developed between tests that dropped the level of the water to 0.5 m below the surface of the shale. It is not known how long this upper 0.5 m of shale was exposed, but it was for no more than 32 days. During and for a short period after resaturation, the sulfate release rate into solution was a minimum of 6.9 g/day, ten times the rate during saturation. After resaturation, the sulfate release rate dropped to pre-leak levels.

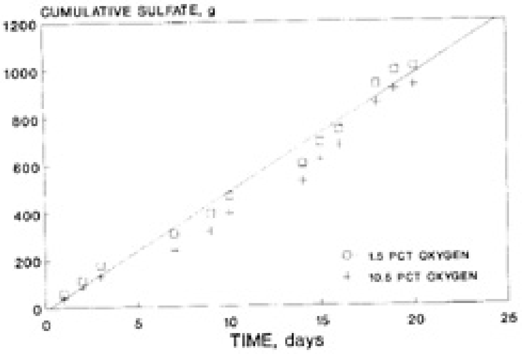


Figure 12. Plots of the cumulative sulfate load versus weathering time for large columns maintained at oxygen partial pressures of 1.5% and 10.5%.

Implications for Spoil Handling

When material is first exposed by mining, fresh pyrite surfaces occur along fractures in the newly broken rock. The pH of the material is near-neutral, which limits ferric ion solubility and the catalytic effect of bacteria on pyrite oxidation. In this scenario, the abiotic surface oxidation rates determined by XPS are applicable. These rates are rapid because the reaction is not diffusion-limited at this point. The oxygen partial pressure would have to be maintained below 10% to affect pyrite oxidation rates in fresh material. Although these conditions may only exist for a few days, the initial abiotic oxidation is important because it establishes the low-pH. ferrous iron-rich environment necessary for the growth of iron-oxidizing bacteria.

Once bacterially-mediated pyrite oxidation is established, the oxygen partial pressure would have to be maintained below 1% to realize any reduction in oxidation rate. Reducing oxygen partial pressures to this level with solid covers is not practical. However, if bacteria are inhibited, any reduction in oxygen partial pressure from atmospheric (21%) will result in a proportional decrease in pyrite oxidation rate.

The most effective strategy for limiting pyrite oxidation is to place pyritic material below a permanent water table. Results of this study indicate that pyrite oxidation rates can be reduced by at least 96% with inundation. However, it is important that pyritic spoil be immediately flooded. Any storage above the water table will result in rapid pyrite oxidation even at low levels of oxygen unless bacteria are inhibited. The oxidation products that form during storage will be solubilized when the material is flooded, resulting in an slug of degraded water. However, once the stored oxidation products are removed, water quality will improve. Any field trial of inundation must allow for differentiation between sulfate derived from product solubilization and sulfate from on-going pyrite oxidation. It is also desirable that groundwater flow through the impoundment be slow and from an oxygen-depleted source, if possible. Oxidation rates determined for oxygen-saturated aqueous pyrite suspensions (Nicholson, Gillham, and Reardon 1988) are equivalent to the rates determined in this study for unsaturated conditions. This indicates that flooding will not reduce pyrite oxidation if the pyrite is contacted by a high flow of oxygen-saturated water. However, these conditions are unlikely to exist in an inundated backfill.

Results of this study indicate that under unsaturated conditions, pyrite oxidation rates can only be reduced by bacterial inhibition in conjunction with an oxygen-consumptive or oxygen-impermeable barrier. Inundating pyritic material will reduce oxidation rates by at least 96% and is the most effective means of controlling pyrite oxidation.

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