AEROBIC-ANAEROBIC OXIDATION OF PYRITE

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Abstract:

There are two general approaches to control acid mine drainage: treatment of mine effluent, or prevention or abatement of the sulfide oxidation which is responsible for acid mine drainage.

This paper describes one phase of a basic study on the kinetics and mechanism of sulfide (pyrite) oxidation, a study which has provided information necessary to the analysis and evaluation of methods for abatement of acid mine drainage at its source. This study was made to clarify the mechanism by which bacteria catalyze the oxidation of pyrite by using what is assumed to be a chemically analogous system. The regime of bacterial influence are described in terms of conditions at the reaction site. Bacterial-enhanced oxidation rates are compared to rates in a chemical system and the independence of the two mechanisms demonstrated.

Introduction:

Quantitative data on kinetics of pyrite oxidation in a chemical system are available. A general discussion of the thermodynamics and chemistry of pyrite oxidation was given by Clark (4). More quantitative kinetic studies on the effect of oxygen concentration (in vapor or liquid phase), water, and pH on the rate of pyrite oxidation were given by Morth and Smith (11), and Smith, Svanks, and Shumate (16). The latter paper also described work on oxidation of pyrite by ferric ions, here referred to as anaerobic oxidation. Where rate of oxidation is determined by the partial pressure of oxygen, the term aerobic oxidation is used.

Earlier work by Garrels and Thompson (7), who investigated the oxidation of pyrite by ferric sulfate solutions, showed the dependence of ferric/ferrous ratio on anaerobic oxidation rate, and suggested that the rate-controlling mechanism is related to adsorption of ferric and ferrous iron on pyrite surface. They also concluded that the rate of oxidation was chiefly a function of the oxidation-reduction potention (E_h) of solution and independent of the total iron concentration. Over the range of E_h that could be examined by Garrels and Thompson their conclusions are valid; however neither conclusion is basically correct.

A number of publications (2, 3, 6, 12) have taken a geochemical approach to evaluating the effect of E_h, pH, iron concentration, etc. on mine drainage. Unfortunately the geochemists have confused the kinetics of pyrite oxidation by using the E_h - pH stability diagrams to analyze pyritic systems. First, phase equilibrium diagrams give little information regarding kinetics, other than "go, no-go" limitations. But most serious is the implication that the effluent water from a mine or other pyritic system is representative of the water in contact with the reacting site of pyrite. The very fact that the geochemists have great difficulty explaining the source of oxygen or oxidizing agent from analysis of effluent water supports the conclusion (13, 15) that the vast majority of pyrite being oxidized is pyrite exposed to a vapor phase. Only an adsorbed layer or thin film of water acts as the reaction medium. This adsorbed layer of water has very little relation to the effluent stream from a pyritic system such as an underground mine. The designation of aerobic- or anaerobic- controlled regimes is therefore not possible from analysis of effluent water. Relative oxidation rates in natural systems are determined by oxygen partial pressure (aerobic rate) and ferric/ferrous ratio (anaerobic rate) at the site of the reaction.

A recent paper by Barnes and Romberger (3) discusses the effect of bacteria in

pyrite oxidation and confirms earlier statements (16) that the chemical (non-microbial) ferrous ion oxidation rate by dissolved oxygen is negligibly slow. Dugan and Lundgren (5) report the energy supply for Ferrobacillus ferrooxidans to be the oxidation of ferrous to ferric ions. Remarkable increases in pyrite oxidation rate were noted (9, 10) when large quantities of these bacteria were added to the reaction system. The same order of increase was reported (16) for anaerobic oxidation at high ferric/ferrous ratio.

Silverman (14) suggested that bacteria operate through both a "direct" and "indirect" contact mechanism in oxidizing pyrite. Direct oxidation implies the oxidation of pyrite through direct electron transfer between the cell and pyrite on which the cell is adsorbed. Indirect oxidation occurs by oxidation of pyrite by ferric ions, the ferric ions being generated by bacterial oxidation of ferrous ions in solution.

Bailey (1) followed the rate of pyrite oxidation as a function of ferric ion concentration in a biological system and observed no significant change in rate until the bacteria had oxidized the iron in solution to 70 or 80% ferric. This indicates "indirect" oxidation is of primary importance although it does not rule out a significant contribution by direct oxidation. A comparison of anaerobic and bacterial rates as a function of ferric/ferrous ratio in solution will indicate the relative rates of the two mechanisms.

In order to provide the basic kinetic information needed to compare oxidation rates in biological systems and analogous chemical systems, the following work was performed.

Experimental Program:

Equipment described by Smith, Svanks, and Shumate (16) was used for the anaerobic and combined aerobic-anaerobic runs. In place of the nitrogen purge line, a metered oxygen supply was added to the titration vessel for aerobic runs. The amount of make-up oxygen required to maintain a constant system pressure (including volume above permanganate burette) was used to determine aerobic oxidation rate.

Stoichiometry of both anaerobic and aerobic oxidation was checked experimentally and found to require 14 moles of ferric ion, and three and one half moles of oxygen to oxidize one mole of pyrite (iron as ferrous). Rates are thereby calculated in terms of micromoles of pyrite oxidized per hour per gram of pyrite, based on oxygen consumed and ferric ions reduced.

Two different types of pyrite were used here: one a 48-70 mesh "sulfur ball" material from the Mc Daniels mine in the Middle Kittanning No. 6 coal in Vinton County, Ohio and the other a "museum grade" sample of the same mesh size. Data on the Sulfur Ball #2 sample of Ref. (16) is also presented.

For some as yet unknown reason, data on the museum grade pyrite could not be consistently reproduced.

Consistent data were obtained on a set of runs, for example, a series of runs at different ferric/ferrous ratios, if operated continuously. But if the reactor were shut down overnight, the rate the following day would often be higher or lower by 25 to 50%. Sulfur ball material was much more predictable, the rate decreased slowly and regularly with reaction time. Over 25% of the original sample was consumed over the series of runs reported. All rates were recalculated to the same base rate; that of Run 23, the Rate vs. Concentration data set shown in Fig. 1. pH of all solutions varied between 0.2 and 0.5. The ferric/ferrous ratio was calculated from the equation: EMF = $0.430 + 0.059 \log (Fe^{+3}/Fe^{+2})$, as determined experimentally for our system.

Two consistent sets of data for the museum grade pyrite are given in Tables 1 and 2. Similar data for McDaniels Sulfur Ball sample are given in Table 3 and graphically in Fig. 2. Results of the combined aerobic-anaerobic oxidation runs are summarized in Table 4.

Treatment of Data:

A simple "dual site" adsorption model gives an equation that correlates experimental data within limits of experimental error.

As one possibility, assume a Fe $(OH)^{++}$ complex is adsorbed on two "reactive sites" of pyrite (dual-site adsorption). Also assume ferrous ions (Fe^{++}) compete for these dual sites. The activated complex formed by ferric ion adsorption is decomposed by electron

transfer from <u>one</u> of the reactive sites to the ferric complex, forming an adsorbed ferrous ion, which is then desorbed.

Using the Hougen-Watson (8) concepts for calculating the rate equation, the following rate equation was derived:

$$r = \frac{k_{3f}\left(\sqrt{K_1} - \frac{\sqrt{K_2}}{K}\sqrt{\frac{Fe^{+2}}{Fe^{+3}}}\right)}{\frac{1}{\sqrt{Fe^{+3}}} + \sqrt{K_1} + \sqrt{K_2}\sqrt{\frac{Fe^{+2}}{Fe^{+3}}}} = \frac{k - k'\sqrt{\frac{Fe^{+2}}{Fe^{+3}}}}{\frac{1}{\sqrt{Fe^{+3}}} + \sqrt{K_1} + \sqrt{K_2}\sqrt{\frac{Fe^{+2}}{Fe^{+3}}}} \qquad (5)$$

where:

k_{3f} = rate constant, electron transfer reaction

K = equilibrium constant, electron transfer reaction

K_1 = adsorption equilibrium constant for ferric ions

K_2 = adsorption equilibrium constant for ferrous ions

Fe^{+2}, Fe^{+3} = concentration of ferrous and ferric ions

At high EMF's, where the square root of the ferrous/ferric ratio (Fe^{+2}/Fe^{+3}) is negligible, this equation may be written:

$$r = \frac{k}{\frac{1}{\sqrt{Fe^{+3}}} + \sqrt{K_1}} \qquad (6) \qquad \text{or} \qquad \frac{1}{r} = \frac{1}{k\sqrt{Fe^{+3}}} + \frac{\sqrt{K_1}}{k} \qquad (7)$$

A plot of $1/r$ vs. $1/\sqrt{Fe^{+3}}$ for anaerobic oxidation at high EMF's should give a straight line with a slope equal to $1/k$ and an intercept equal to $\sqrt{K_1}/k$.

These data for the three pyrite samples shown in Tables 1, 3, and Table 2 of Ref. (16) are plotted in Fig. 1.

After k and $\sqrt{K_1}$ are calculated from the slope and intercept, k' and $\sqrt{K_2}$ can be determined in the following manner: Assume that reaction rate goes to zero as EMF approaches o. 37* ($\sqrt{Fe^{+2}/Fe^{+3}}$ = 3.0). Then setting the numerator of Equation 5 equal to zero when $\sqrt{Fe^{+2}/Fe^{+3}}$ = 3; $k' = k/3$.

K_2 can be determined from one value of the Rate vs. EMF data where the ferric/ferrous ratio is significant.

The data presented in Ref. (16) for Sulfur Ball #2 may be used to illustrate the calculation of the Rate Equation.

From Fig. 1, slope of line for Sulfur Ball #2 = 0.0061 and Intercept = 0.02, then:
k = 1/0.0061 = 165
k' = 165/3 = 55
($\sqrt{K_1}$)' = Intercept x k = 3.3

(Note: since $\sqrt{Fe^{+2}/Fe^{+3}}$ is <u>not</u> negligible at EMF = 0.650, the intercept value

*From potentiostat measurements of pyrite, these values appear reasonable in systems where the pH is below 1.0.

of 3.3 includes $\sqrt{K_2}$ times $\sqrt{Fe^{+2}/Fe^{+3}}$. By trial and error. $K_1 = 3.3 - 70 \times 0.0137 = 2.3$, when K_2 is calculated from rate at EMF = 0.477. Therefore the rate equation, as calculated using Fig. 1 and one point from Rate vs. EMF data is:

$$r = \frac{165 - 55\sqrt{Fe^{+2}/Fe^{+3}}}{\frac{1}{\sqrt{Fe^{+3}}} + 2.3 + 70\sqrt{Fe^{+2}/Fe^{+3}}} \qquad (8)$$

Table 5 compares calculated and experimental rate for these data.

In like manner, the rate equations for the experimental points given in Fig. 2 can be calculated. The solid lines on Fig. 2 are loci of the calculated rates for different total iron concentrations. Calculated and experimental rates for museum grade pyrite are compared in Table 2.

Interpretation of Data:

The excellent correlation of experimental data by Equation 5 indicates that the form of the adsorption equation, if not the specific mechanism used to derive it, is relevant. It appears that the relative adsorption of ferrous and ferric ions is rate-determining in anaerobic oxidation. A comparison of adsorption equilibrium constants for ferrous and ferric ion is surprising. For sulfur ball pyrite the ratio of K_2/K_1 (ratio of adsorption equilibrium constants for ferrous and ferric ion, respectively) is 900 for Sulfur Ball #2, 2500 for Mc Daniels Sulfur Ball, and 45,000 for Museum Grade pyrite. In other words, the relative adsorption of ferrous ions is much greater than ferric for all types of pyrite. The selective adsorption of ferrous ions is particularly great in museum grade pyrite -- over 20 to 50 times greater than the sulfur ball. It is also interesting to note that the reactivity of the pyrite samples is inversely related to K_2/K_1. The rate curves for the three pyrite samples are compared in Fig. 3

The data show that anaerobic rates are a function of total iron concentration, and are determined by ferrous/ferric ratio, not E_h (EMF). As the E_h of solution is raised to the point where all iron is ferric, the rate becomes constant. Further increase in E_h has negligible effect on rate.

The combined aerobic-anaerobic oxidation runs show the independence of the two reaction modes. The aerobic rate is not influenced by solution E_h or ferric/ferrous ratio, and the anaerobic rate is not changed by the partial pressure of oxygen. This leads to the conclusion that the "reactive sites" for the two oxidation mechanisms are not the same.

It is interesting to note that the increase in oxidation rate, over the aerobic rate, is approximately the same for samples heavily inoculated with Ferrobacill us ferrooxidans (9) and samples subject to anaerobic oxidation at high EMF's. This observation, together with those of Silverman (14) and Bailey (1) leads to the conclusion that bacteria such as Ferrobacill us ferrooxidans function to generate a high ferric/ferrous ratio in solution. The rate of oxidation by ferric ions would then be the same in both a biological or chemical system, and determined by the ferric/ferrous ratio and total iron concentration.

These data provide a basis for defining the reaction regime, i. e. aerobic or anaerobic, if data on oxygen concentration and ferric/ferrous at the reaction site are known. Aerobic and anaerobic rates are approximately the same, at oxygen partial pressures of 21%, when EMF = 0.450. This corresponds to a ferric/ferrous ratio of 2.2 or 70% of iron ions in the ferric state. At an EMF of 0.40, where 24% of iron is ferric, the anaerobic rate is one-fifth to one-tenth the aerobic rate in air. Only with microbial-enhance oxidation can ferric/ferrous ratios this high be attained. In other words, if the ferric/ferrous ratio is less than 0.3 (24% ferric), and the partial pressure of oxygen is 15 to 20%, the system is in an aerobic regime - i. e., the oxidation rate is determined by the chemical aerobic mechanism. If oxygen vapor concentration is under 2% and 70% of the iron is in the ferric state, the system is in a anaerobic regime, generated by microbial activity. It must be emphasized that the term "anaerobic" as used here does not mean that the ultimate electron acceptor

is not oxygen. "Anaerobic" implies only that the electron acceptor at the reaction site is a ferric ion. These descriptions are applicable to natural systems where active oxidation sites are exposed to vapor phase. Pyrite immersed in normal ground water is not oxidized.

Summary:

Anaerobic oxidation rate of pyrite is determined by the ferric/ferrous ratio and total iron concentration in solution. The adsorption equilibrium constant for ferrous ions on pyrite is much greater than ferric ions. At least for the three different pyrite samples examined, the reactivity is inversely related to the ratio of the adsorption constants, ferrous-to-ferric.

Aerobic oxidation rate is a function of oxygen concentration at the reaction site. It is not affected by the presence of either ferric or ferrous ions nor the total iron concentration. Since the two rates are also independent, it appears that different "reactive sites" are involved in aerobic and anaerobic oxidation.

The aerobic and anaerobic rates are approximately equal for sulfur ball pyrite when 70% of the iron in solution is in the ferric state and the solution is in equilibrium with air of 21% oxygen. Since such a high ferric/ferrous ratio is only possible in a microbial system in a natural environment, oxidation by ferric ions (anaerobic oxidation) can be significant only in bacteria-catalyzed systems. The oxidation regime can be determined from oxygen and iron concentrations and the ferric/ferrous ratio at the reactive site. Note that the effluent water can not be used to determine these factors since this water is in no way representative of the water in contact with the "reactive sites."

Figure 4 graphically describes the regimes in terms of oxygen concentration and ferric/ferrous ratio at the reaction site. The boundry lines were drawn where the ratio of rates (anaerobic and aerobic) differ by a factor of 5.

Since aerobic and anaerobic oxidation rates are independent and additive, the rate of pyrite oxidation (per unit surface area exposed) can be determined in terms of the equations for anaerobic and aerobic oxidation.

This type of information presented here furnishes the basic data which, combined with a relevant model of a pyritic system e. g. drift mine, gob pile, spoil bank, etc., enables one to evaluate abatement measures or predict acid formation that will develop under various conditions. The kinetics of the total system can be derived only if the basic chemical kinetics are adequately described.

ACKNOWLEDGEMENT

TABLE 1

Museum Grade Pyrite
Rate vs. Conc. at EMF = 0.700

Total Iron (gm./liter)	r	$\dfrac{1}{\sqrt{Fe^{+3}}}$	$\dfrac{1}{r}$
0.125	0.83	21.1	1.21
0.250	1.25	14.9	0.80
0.500	1.5	10.5	0.63
1.00	2.2	7.45	0.45
2.00	3.1	5.3	0.34
4.00	4.0	3.73	0.25
8.00	4.9	2.64	0.20
10.00	5.2	2.35	0.195

*Fe^{+3} in moles/liter

TABLE 2

Museum Grade Pyrite
Rate vs. EMF; Iron Conc. = gm/liter

EMF.	$\dfrac{Fe^{+3}}{Fe^{+2}}$	$r_{exp.}$	$r_{calc.}$ *
0.700	37,700	5.2	5.2
0.650	5,300	3.8	2.8
0.600	760	1.36	1.35
0.550	108	0.54	0.59
0.500	15.4	0.23	0.23
0.477	7.3	0.15	0.14

$$*r_{calc.} = \frac{20 - 6.7\sqrt{Fe^{+2}/Fe^{+3}}}{\sqrt{\dfrac{1}{Fe^{+3}}} + 1.4 + 300\sqrt{Fe^{+2}/Fe^{+3}}}$$

Note: "r" (Rate) in units of microgram-mole FeS_2 oxidized per hour per gram of sample.

TABLE 3

Rate vs. Iron Concentration
EMF. Setting = 0.650; pH = 0.5
Mc Daniels Sulfur Ball

Run 23		Run 50	
r	Fe Conc. (gm/liter)	r	Fe Conc. (gm/liter)
19.3	5.0	19.1	4.3
18.7	3.85	14.2	2.26
14.3	2.15	11.3	1.26
10.9	1.10	9.1	0.675
8.5	0.59	4.8	0.193
6.5	0.31	11.7	1.28
5.3	0.183	8.2	0.54
		6.2	0.29

TABLE 4

Combined Aerobic and Anaerobic Oxidation

Run No.	EMF	Iron Conc. (gm/liter)	Rate by 100% O_2	Rate by Fe^{+3} Ions	
31	-	-	3.6	-	(aerobic only)
33	500	1.00	3.6	4.5	
34	-	-	3.5	-	(aerobic only)
35	500	1.00	3.4	4.4	
38	500	0.40	3.5	3.5	
41	550	0.20	3.4	5.1	
45	550	0.20	3.5	5.0	

TABLE 5

Rate vs. EMF, Sulfur Ball #2, Ref. 16
Iron Concentration = 1 gm./liter, pH = 0.2

EMF	$r_{exp.}$	$r_{calc.}$*
0.65	14	14
0.60	12.5	12.3
0.55	11	9.2
0.50	6.1	5.4
0.477	3.6	3.6
0.460	2.1	2.7
0.430	0.56	1.3

$$* \ r = \frac{165 - 55\sqrt{Fe^{+2}/Fe^{+3}}}{\frac{1}{\sqrt{Fe^{+3}}} + 2.3 + 70\sqrt{Fe^{+2}/Fe^{+3}}}$$
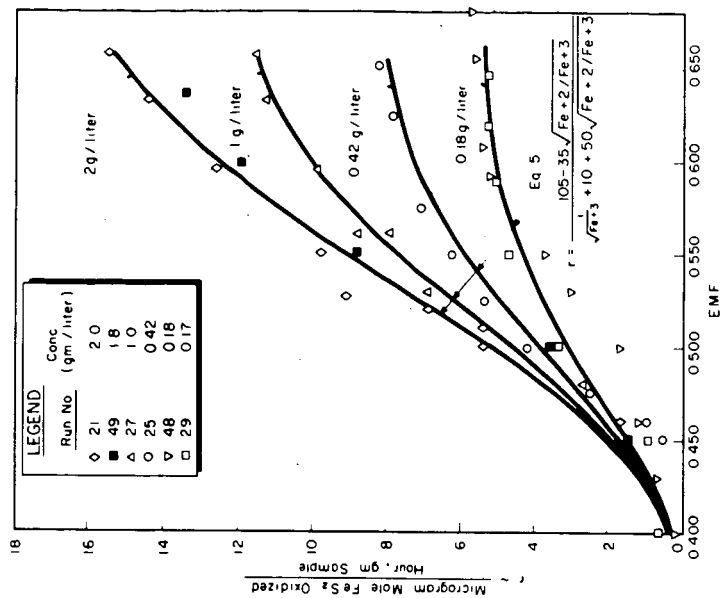
FIG. 2
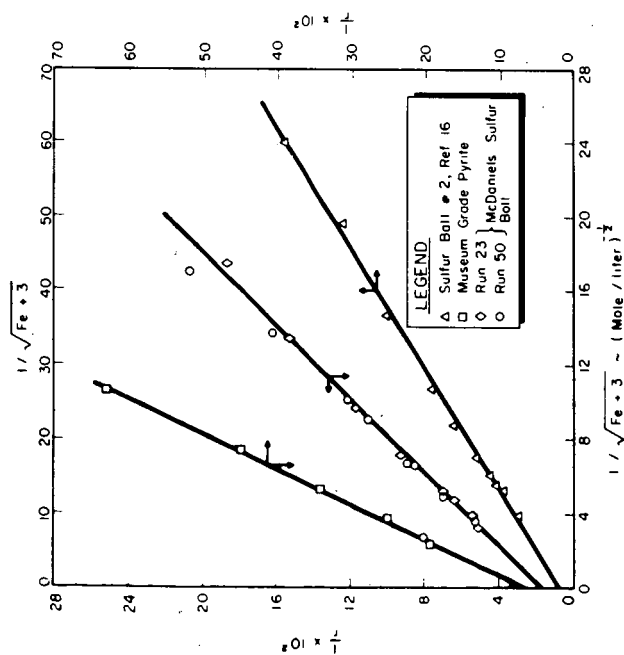## Rate vs. EMF for McDaniels Sulfur Ball

FIG. 1
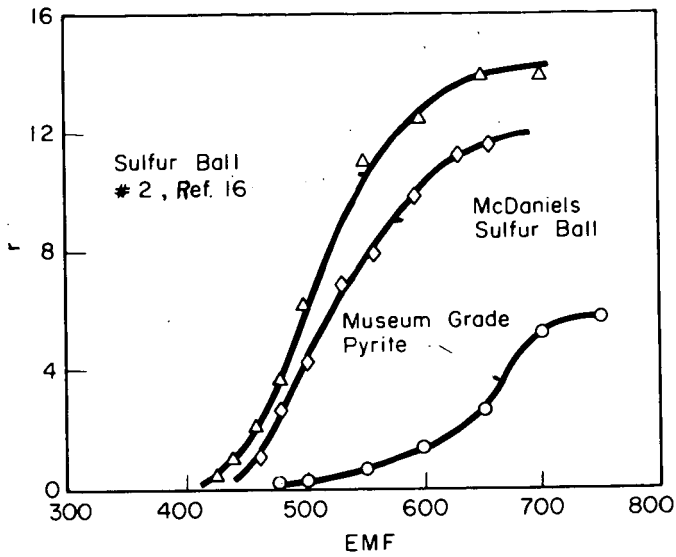## Reciprocal Rate vs. Reciprocal Ferric Conc.
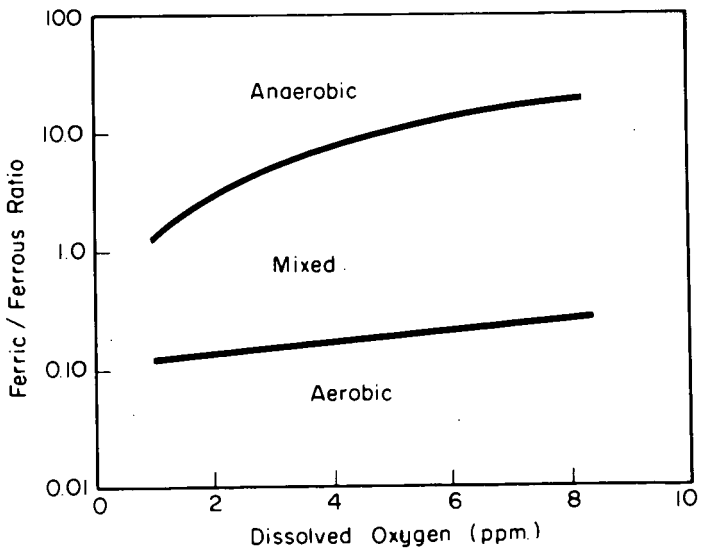
FIG. 3
Rate vs. EMF for Three Pyrite Samples

FIG. 4
Reaction Regime for High Iron, Low pH Systems

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