

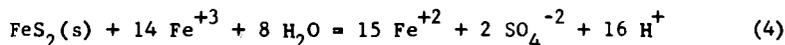
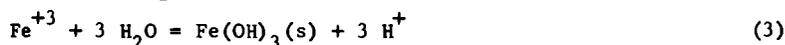
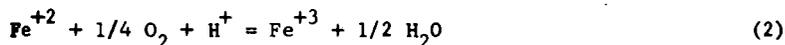
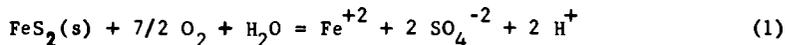
## THE RATE-DETERMINING STEP IN THE PRODUCTION OF ACIDIC MINE WASTES

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Previous studies of the oxidation of iron pyrite and the subsequent release of acidity into mine drainage waters have provided no conclusive results in ascertaining which of the steps in the overall reaction is rate-determining. Although microorganisms have frequently been implicated as the causative agents in the production of acidic mine drainage, the activity of these microorganisms in natural systems has rarely been evaluated. Furthermore, few studies have been conducted in order to assess the catalytic influence of several chemical agents which are indigenous to mine drainage waters and which have been cited in the literature, in various circumstances, as exhibiting catalytic properties in the oxidation of ferrous iron. This paper represents a quantitative evaluation of the individual factors controlling the oxidation of iron pyrite; the relative rates of the various consecutive reactions have been considered in order to elucidate the rate-determining reaction. The laboratory results are complemented by results of a field investigation of iron(II) oxidation in natural mine waters.

The mine-water system can be characterized by the following stoichiometric reactions:



The reactions demonstrate that the dissolution of one mole of iron pyrite leads ultimately to the release of four equivalents of acidity: two equivalents from the oxidation of  $\text{S}_2(-\text{II})$  and two from the oxidation of  $\text{Fe}(\text{II})$  and the ensuing hydrolysis of  $\text{Fe}(\text{III})$ . It should be noted that two oxidants of iron pyrite are readily available: oxygen and iron(III).

OXYGENATION OF FERROUS IRONLABORATORY STUDIES

The rate of oxygenation of ferrous iron over the pH-range of interest in natural waters is shown in Figure 1. These results were obtained in clean laboratory systems and were not subject to the various chemical and biological

complexities imposed by nature. In the acidic pH-region corresponding to conditions encountered in mine drainage waters, the reaction proceeds relatively slowly ( $t_{50} \sim 1000$  days) and is independent of pH. However, the composition of natural mine waters is such that the oxidation reaction may be accelerated. Inorganic ligands, such as sulfate (2), which coordinate with Fe(II) and Fe(III), soluble metal ions, such as copper(II) (3), aluminum, and manganese(II) (1), suspended material with large surface areas and high adsorptive capacities, such as clay particles, materials which accelerate the decomposition of peroxides in the presence of ferrous iron, such as charcoal (4), and microorganisms (5) have all been mentioned in the literature, in various instances, as being capable of catalyzing the oxygenation of ferrous iron. Table 1 presents a summary of the experimental results of a study in which the catalytic properties of the various chemical agents were investigated. The specific results themselves and the experimental procedures employed are described elsewhere (6). It was found that the data obtained in the presence of the various catalysts studied, at constant partial pressure of oxygen, constant pH, and constant concentration of catalyst, could be suitably fitted by a relationship which is first-order in the concentration of ferrous iron:

$$-\frac{d[\text{Fe(II)}]}{dt} = 2.3 k' [\text{Fe(II)}] \quad (5)$$

In addition to the effective catalysts listed in the table, Mn(II), aluminum, amorphous ferric hydroxide, kaolinite, powdered charcoal, and crushed iron pyrite were examined, but no catalytic effects were observed. The studies were conducted in the absence of the microorganisms which are reportedly capable of accelerating the oxygenation reaction. Table 1 shows that the greatest influence on the rate of oxidation of Fe(II) was exerted by the clay particles or their idealized counterparts, alumina and silica, but at areal concentrations much greater than those encountered in most natural mine waters.

#### FIELD STUDIES

In order to compare the experimental results describing the kinetics of ferrous iron oxidation in synthetic mine waters with the rate of the reaction in nature, field investigations were conducted in the bituminous coal region of West Virginia, near Elkins. An underground mine which had been air-sealed by the FWPCA served as a source of mine water having a high concentration of dissolved ferrous iron. Measurements by the FWPCA had indicated that the partial pressure of oxygen inside the mine had been reduced to 7% (7). Samples of the water draining out of the air-sealed mine were collected and

TABLE 1. Chemical Catalysis of the Oxidation of Ferrous Iron

pH	$\log k'' \text{ (day)}^{-1} \text{ (} k'' = -d \log [\text{Fe(II)}]/dt \text{)}$					
	Uncatalyzed Reaction	Catalysis by:				
		$10^{-2} \text{ M SO}_4^{-2}$ at $50^\circ \text{C}$	$10^{-4} \text{ M Cu}^{+2}$	$\text{Al}_2\text{O}_3$ $8000 \text{ m}^2/1$	$\text{SiO}_2$ $3000 \text{ m}^2/1$	Bentonite $10 \text{ gm/l}$
3.0	-3.8	-3.1	-3.4	-	-	-
3.5	-3.6	-	-	-2.5	-	-
3.8	-3.4	-	-	-2.1	-	-
4.0	-3.3	-	-	-1.8	-2.2	-2.2

allowed to stand back in the laboratory exposed to the atmosphere. Aliquots were removed at various intervals and titrated with standardized solutions of permanganate. Figure 2 is an arithmetic plot of the change in  $[\text{Fe(II)}]$  with time; curve A represents a sample which was acidified at the time of collection, in order to serve as a control; curve B corresponds to a sample which was millipore filtered ( $0.8 \mu$  pore diameter) immediately after collection; and curves C and D represent untreated samples. The linearity of curves C and D indicates that the oxidation of  $\text{Fe(II)}$ , in its native solution, is zero-order in  $\text{Fe(II)}$ . The zero-order nature of the oxidation is suggestive of a biological reaction in which the substrate is non-limiting and in which the concentration of microorganisms remains relatively constant, i.e.,

$$-dS/dt = \mu_{\max} B/y = \text{constant} \quad (6)$$

where  $S$  is the concentration of substrate ( $\text{Fe(II)}$ ),  $\mu_{\max}$  is the maximum specific growth rate of the microorganisms,  $y$  is the yield of microorganisms per unit of substrate utilized, and  $B$  is the instantaneous concentration of microorganisms, assumed here to be constant. (8). Curves C and D in Figure 2 satisfy equation 6.

Since the energy released by the oxidation of  $\text{Fe(II)}$  is so small, the oxidation of  $10^{-3} \text{ M Fe(II)}$  would not be expected to significantly change the bacterial concentration if a large number of bacteria were present in the mine water, i.e.,  $B$  should remain constant. If, however, the bacterial concentration were diminished, as by filtration of the mine water,  $B$  would be expected to increase logarithmically as the substrate,  $\text{Fe(II)}$ , is utilized so that

$$-dS/dt = \mu_{\max} B_0 e^{\mu_{\max} t} / y \quad (7)$$

which, after integration, gives

$$S_0 - S = B_0 e^{\mu_{\max} t} / y \quad (8)$$

at  $\mu_{\max} t \gg 1$ , or

$$\log (S_0 - S) = \log \frac{B_0}{y} + \mu_{\max} t/2.3 \quad (9)$$

$S_0$  and  $B_0$  are the initial substrate and bacterial concentrations, respectively. Figure 3 shows the data from curve B of Figure 2 to fit such a microbial relationship. The specific growth rate constant is  $0.076 \text{ hrs.}^{-1}$ , corresponding to a generation time of 9.1 hours. (Silverman and Lundgren observed generation times of about 7.0 hours in their laboratory studies of *Ferrobacillus ferrooxidans* (9).)

To further substantiate biological significance, sterile solutions of ferrous sulfate were inoculated with acid mine drainage. Two sterile controls were maintained: one in which aseptically filtered mine water (220  $\mu$  pore diameter) was used as the inoculum, and another containing sterile ferrous sulfate alone. A decrease in the concentration of ferrous iron was observed, but only for the non-sterile specimen.

Therefore, the oxidation of ferrous iron occurs more rapidly in natural mine water than in any of the synthetic solutions investigated in the laboratory subject to the various chemical catalytic additives. The rapidity of the reaction in nature is apparently the result of microbial catalysis.

#### OXIDATION OF IRON PYRITE

With the exception of the study by Garrels and Thompson (10), previous investigations of the oxidation of iron pyrite have been concerned almost entirely with oxygen as the oxidant. In most cases, the potentiality of ferric iron as an oxidant of pyrite has been overlooked.

Figure 4 shows the decrease in Fe(III) with time in the presence of various concentrations of iron pyrite, under a nitrogen atmosphere. The concentration of pyrite is large compared to that of Fe(III) so that  $[\text{FeS}_2]$  remains relatively constant during the course of the reaction. The study was conducted below pH 2, where the rate of oxidation of pyrite is independent of pH (10) (11).

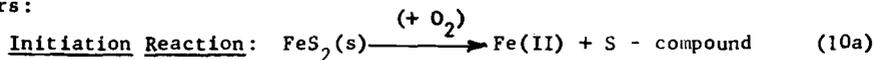
The rapidity of the oxidation of iron pyrite by Fe(III) is readily apparent. For 1 g/l of pyrite, the time required for the reduction of 50% of the ferric iron is approximately 250 minutes, which is considerably less than the half-time for the oxidation of Fe(II) even when accelerated by the chemical catalysts found in natural mine waters.

The rate of reduction of Fe(III) by pyrite in the presence of oxygen is demonstrated in Figure 5, showing that there is virtually no difference between the rate of reduction of Fe(III) by pyrite, or the rate of change of soluble

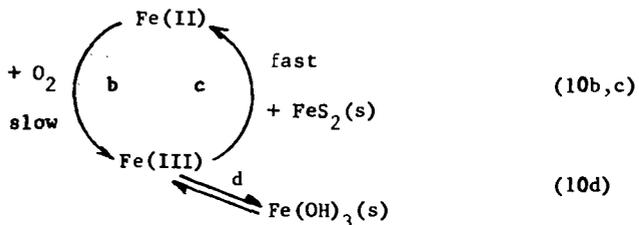
Fe(II), under aerobic and anaerobic conditions. In the presence of 0.20 atm. of oxygen, the oxidant of iron pyrite is ferric iron.

### CONCLUSIONS

In accordance with the experimental results presented, the following model is proposed to describe the oxidation of iron pyrite in natural mine waters:



Propagation Cycle:



The model is similar to and carries with it the same overall consequences as that suggested by Temple and Delchamps (12). The rate-determining step is a reactive step in the specific oxidation of ferrous iron, reaction 10b. As this investigation has demonstrated, the rate of oxidation of Fe(II) under chemical conditions analogous to those found in mine waters is very slow, indeed considerably slower than the oxidation of iron pyrite by Fe(III), reaction 10c.

Reaction 10a serves only as an initiator of the overall reaction: ferrous iron may be released by simple dissociation of the pyrite, or by oxidation of the pyrite by oxygen. Once the sequence has been initiated, a cycle is established in which ferric iron rapidly oxidizes pyrite and is slowly regenerated through the oxygenation of the resultant ferrous iron, reactions 10b and c. Oxygen is involved only indirectly in the regeneration of Fe(III). Precipitated ferric hydroxide deposited in the mine serves as a reservoir for soluble Fe(III); a significant supply of Fe(III) is readily available as an oxidant of pyrite.

The pertinent consequences of the model are as follows:

- 1.) Ferric iron cannot exist for long in contact with pyritic agglomerates.
- 2.) The elimination of oxygen is inconsequential with regard to the specific oxidation of iron pyrite. The exclusion of oxygen, however, does prevent the regeneration of Fe(III).
- 3.) The overall rate of dissolution of pyrite is independent of

its surface structure, since the specific oxidation of pyrite is not the rate-limiting step.

4.) Microorganisms can be influential only by mediating the specific oxidation of ferrous iron, since it, alone, is the rate-determining step.

The solution to the problem of acid mine drainage appears to be dependent upon methods of controlling the oxidation of ferrous iron. Microorganisms, presumably the autotrophic "iron bacteria," markedly enhance the rate of oxidation of ferrous iron, thus accelerating the overall rate of pyrite oxidation. Control measures must be aimed at halting the catalytic oxidation of ferrous iron.

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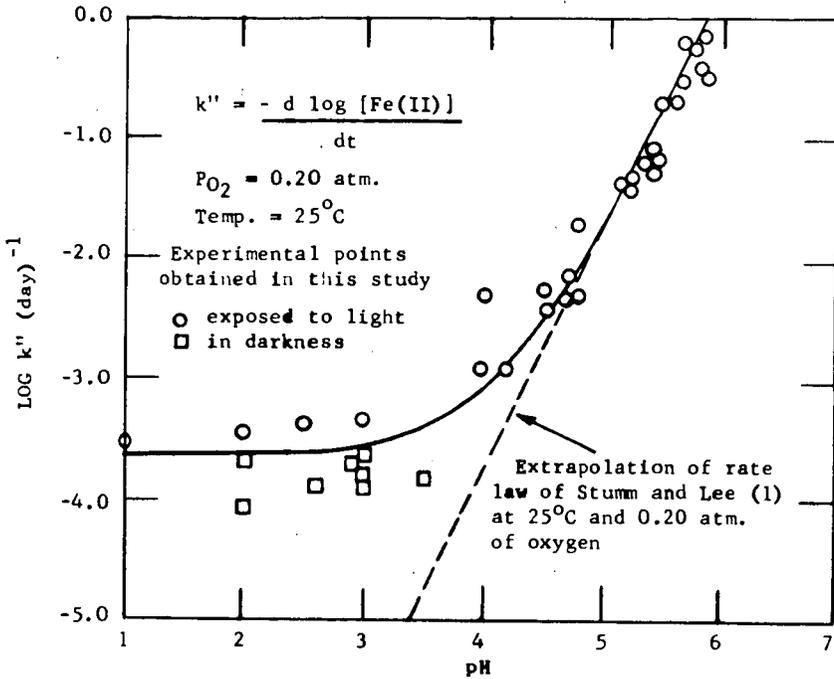


Figure 1. Oxygenation rate of ferrous iron as a function of pH.

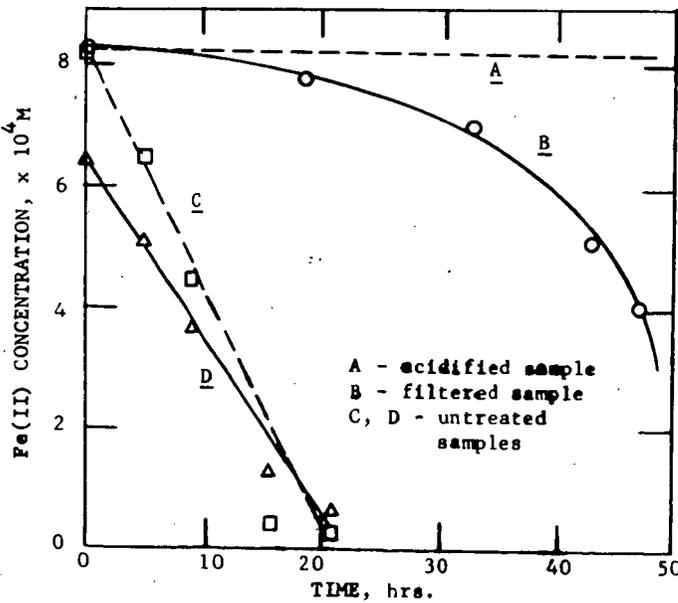


Figure 2. Rate of oxidation of ferrous iron in water collected from air-sealed underground mine.

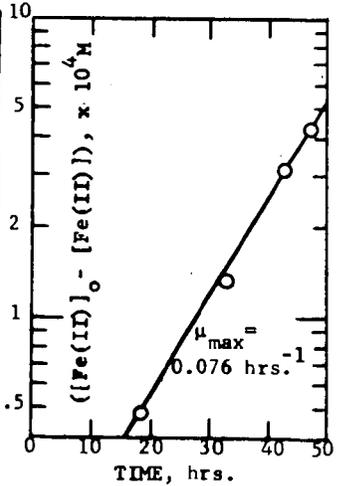


Figure 3. Change in ferrous iron concentration in millipore filtered water.

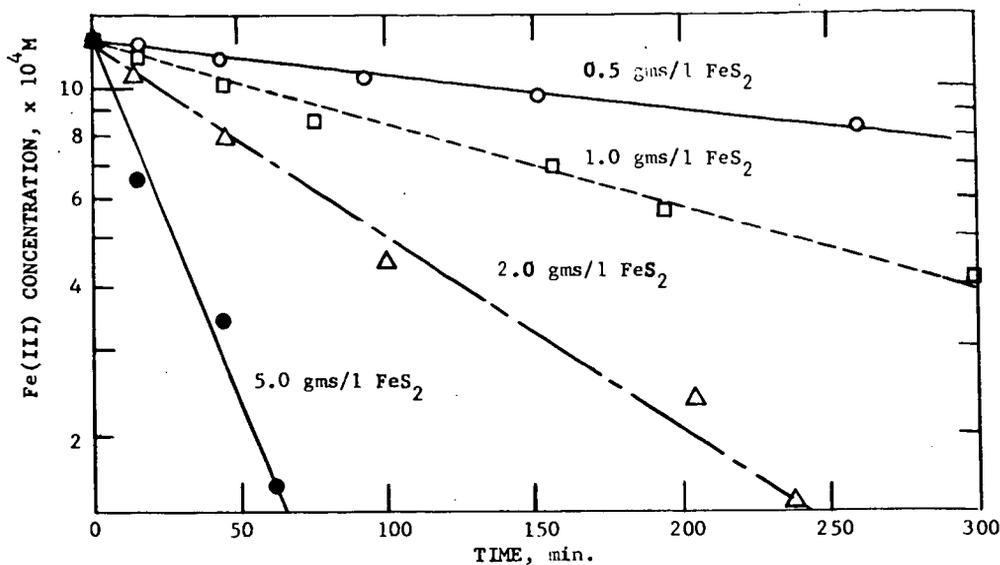


Figure 4. Reduction of ferric iron by iron pyrite in the absence of oxygen.

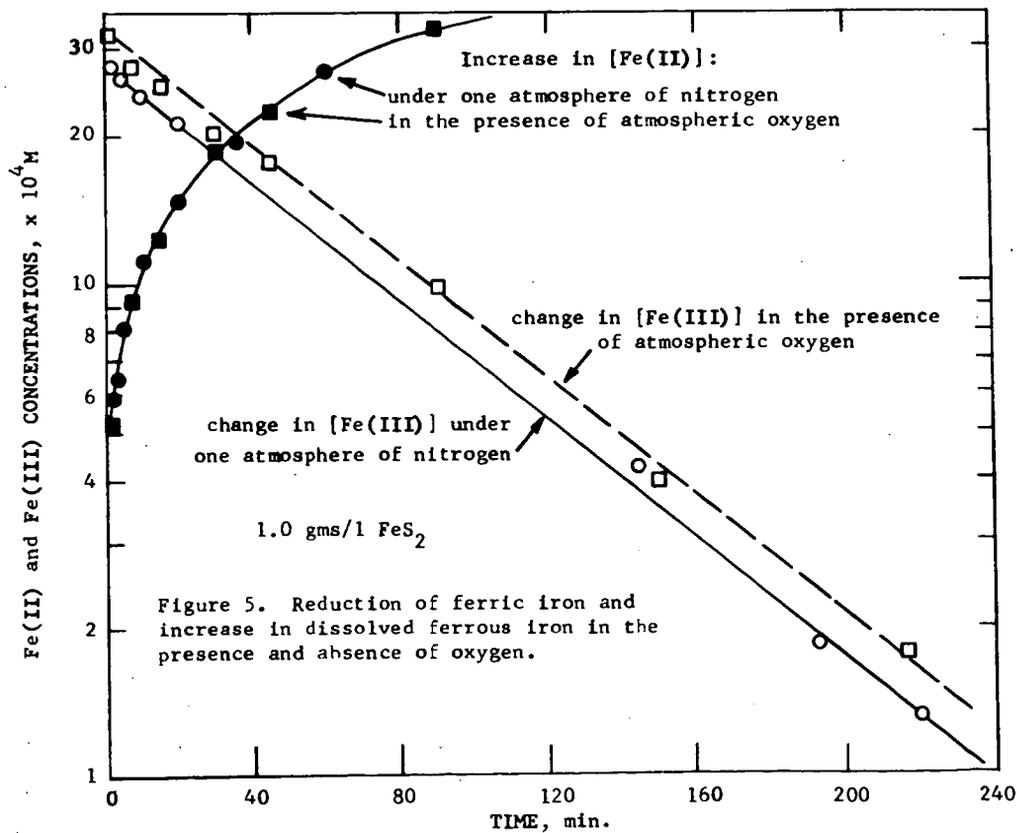


Figure 5. Reduction of ferric iron and increase in dissolved ferrous iron in the presence and absence of oxygen.