OXIDATION OF PYRITE
BY IRON SULFATE SOLUTIONS*

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ABSTRACT. The rate of oxidation of pyrite specimens from three localities was measured in acid iron sulfate solutions. The rate of reduction of ferric ion in these solutions is considered to be a measure of the rate of oxidation of the pyrite. The overall oxidation reaction, in the range 100 percent to 0.1 percent mFe+++ in accord with the classical reaction:

$$\text{FeS}_2 + 8\text{H}_2\text{O} + 14\text{Fe}^{3+} = 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+.$$  

The average rate of reduction from 100 percent mFe+++ to 50 percent mFe+++ is constant for pyrite from a given locality, and differences in the average rates between specimens from different localities could not be related to minor compositional variations of the solutions or of the pyrites. The pH did not affect rate in the tested range, pH 0 to pH 2.

The instantaneous rate of reduction of ferric ion diminishes with decrease in the ferrous-ferrous ratio; it is postulated that instantaneous rate is controlled by differential absorption of ferric and ferrous ions on the pyrite surface, and is proportional to the fraction of pyrite surface occupied by ferric ion.

INTRODUCTION

The oxidation of pyrite in nature is a complex process, involving both organic and inorganic agents. Temple and Koehler (1954) have reviewed the literature, and have made a critical summary of the major factors to be considered.

This paper is restricted to one aspect of the oxidation problem. Because ferric salts are commonly cited (Lindgren, p. 829) as important agents in pyrite oxidation, we studied the action of acid ferric sulfate solutions on pyrite samples from three localities. The solutions were kept acid so that no solids would be produced as oxidation products. The rate of oxidation was determined as a function of pH and ferric sulfate concentration, and the effect of minor amounts of various impurities in solution was assessed.

In essence the experiments consist of permitting clean ground samples of pyrite, sized and weighed so as to ensure a nearly constant surface area, to react with known concentrations of acid ferric sulfate solutions at constant temperature and stirring rate. The concentration of ferric iron was continuously monitored.

EXPERIMENTAL MATERIALS AND PROCEDURE

The three pyrite specimens used in the experiments were obtained from the Harvard Museum collection, and consisted of large crystals from Bingham, Utah; smaller crystals, associated with chlorite, from Chester, Vermont; and fine grained pyrite associated with chalcopyrite, from Rio Tinto, Huelva, Spain. Accessory elements found in the three samples are indicated in table 1.

The pyrite was crushed, and the size fraction between 100 and 200 mesh used for the experiments. Shortly before each experiment the pyrite sample was rinsed with 6N H$_2$SO$_4$, and with distilled water, and was dried with acetone.

Each initial solution of acid ferric sulfate was obtained by preparing an acid ferrous sulfate solution of known strength and oxidizing it quantitatively.

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to ferric by potentiometric titration with cerate or permanganate. The pH was adjusted by addition of H$_2$SO$_4$. Atmospheric oxygen and carbon dioxide were excluded by maintaining a nitrogen atmosphere above the solution.

A weighed sample of pyrite was added to the oxidized solution, and a continuous plot of the potential of the solution and elapsed time was recorded automatically. The solution was stirred by means of a teflon coated magnetic bar placed inside the container. The temperature of the experiments was about 33°C. The small changes in temperature (±2°C) during the experiments are probably responsible for part of the scattering of points in the experimental results. Each experiment was allowed to run for from 24 to 100 hours.

Table 1
Spectrographic analyses of the pyrite specimens
Jun Ito, analyst

<table>
<thead>
<tr>
<th>Element</th>
<th>Bingham, Utah</th>
<th>Spain</th>
<th>Chester, Vt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.0X</td>
<td>0.0X</td>
<td>0.0X</td>
</tr>
<tr>
<td>Zn</td>
<td>0.X</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ni</td>
<td>—</td>
<td>—</td>
<td>0.0X</td>
</tr>
<tr>
<td>Co</td>
<td>—</td>
<td>0.0X</td>
<td>0.0X</td>
</tr>
<tr>
<td>Ag</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>As</td>
<td>vvs</td>
<td>vvs</td>
<td>—</td>
</tr>
<tr>
<td>Ti</td>
<td>—</td>
<td>vvs</td>
<td>0.0X</td>
</tr>
<tr>
<td>Mg</td>
<td>tr.</td>
<td>tr.</td>
<td>tr.</td>
</tr>
<tr>
<td>Mn</td>
<td>tr.</td>
<td>tr.</td>
<td>tr.</td>
</tr>
<tr>
<td>Al</td>
<td>tr.</td>
<td>tr.</td>
<td>tr.</td>
</tr>
<tr>
<td>Si</td>
<td>tr.</td>
<td>tr.</td>
<td>tr.</td>
</tr>
</tbody>
</table>

vvs—very, very small
tr.—trace

Fig. 1. Potentiometric titration of ferrous sulfate with potassium permanganate. pH 1.55; total dissolved iron (m²Fe+++ = 1 × 10⁻³m/1; E° = 0.671 volts.
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RESULTS

Figure 1 shows a typical curve for the titration of ferrous sulfate by permanganate, prior to reduction by pyrite. From the equivalence point the formal E° (E°r) is obtained. This potential is related to the molality of ferrous and ferric ions as follows:

\[ Eh = E°_r + 0.059 \log \frac{m_{Fe^{+++}}}{m_{Fe^{++}}} \]  

(1)

The activities of the ions are related by the analogous equation containing E°:

\[ Eh = E° + 0.059 \log \frac{a_{Fe^{+++}}}{a_{Fe^{++}}} \]  

(2)

Because our interest was in the amount of pyrite oxidized, we used equation (1) almost exclusively. The measured oxidation curves of the various ferrous sulfate solutions agree well with curves calculated from E°r and the change in \( m_{Fe^{+++}} \) and \( m_{Fe^{++}} \) expected from addition of increments of oxidizing agent.

Fig. 2. Change in formal E° (E°r) in acid iron sulfate solutions in the range pH 2 to pH 0.

Figure 2 shows the change in E°r with pH in the H₂SO₄—FeSO₄ solutions used. The small change in E°r over the large range of ionic strength from pH=2 to pH=0 (the contribution from FeSO₄ was always negligible) is surprising, inasmuch as E° and E°r are related by

\[ E°_r - E° = 0.059 \log \frac{\gamma_{Fe^{+++}}}{\gamma_{Fe^{++}}} \]

The activity coefficients (γ) of the triply charged ferric ion and the doubly charged ferrous ion would be expected to change differentially with increase in ionic strength, and hence E°r should change strikingly toward lower values at higher ionic strength, that is, lower pH. The ratio of \( \gamma_{Fe^{+++}}/\gamma_{Fe^{++}} \) is, however,
nearly constant, for $E^\circ$ is 0.771 volts, and $E^{\circ'}$ ranges only from 0.660 to 0.689 volts. The gamma ratio averages about 0.02.

Results of the systematic runs on the reduction of ferric ion with two grams of sized pyrite, in which the time required for 50 percent reduction of the ferric iron was determined, are shown in figures 3, 4, 5, and 6. The coordinates used are those found empirically to be most useful for plotting. The potential versus logarithm of time produces a nearly straight line during reduction to 50 percent $m_{Fe^{+++}}$. The differences between would-be duplicate runs

![Figure 3](image_url)

**Fig. 3.** Rate of reduction of ferric iron in solutions having initial concentrations of $4 \times 10^{-5}$ $m_{Fe^{+++}}$ by pyrites from three localities, (1) Rio Tinto, Huelva, Spain; (2) Chester, Vermont; (3) Bingham, Utah. Plus marks indicate time to reduction of 50% ferric iron.

![Figure 4](image_url)

**Fig. 4.** Rate of reduction of ferric iron by pyrite from Bingham, Utah, in solutions having various initial concentrations of ferric. (1), (2) $m_{Fe^{+++}} = 4.08 \times 10^{-6} m/1$; (3), (4) $m_{Fe^{+++}} = 4.16 \times 10^{-5} m/1$; (5) $m_{Fe^{+++}} = 1 \times 10^{-5} m/1$; (6) $m_{Fe^{+++}} = 2.08 \times 10^{-4} m/1$. 


Fig. 5. Rate of reduction of ferric iron by pyrite from Chester, Vermont, in solutions having various initial concentrations of ferric. (1) \( m_{Fe}^{+++} = 4 \times 10^{-4} \text{m/l} \); (2) \( m_{Fe}^{+++} = 1 \times 10^{-4} \text{m/l} \); (3) \( m_{Fe}^{+++} = 1 \times 10^{-3} \text{m/l} \); (4) \( m_{Fe}^{+++} = 1 \times 10^{-2} \text{m/l} \).

Fig. 6. Rate of reduction of ferric iron by pyrite from Rio Tinto, Huelva, Spain, in solutions having various initial concentrations of ferric. (1) \( m_{Fe}^{+++} = 4 \times 10^{-4} \text{m/l} \); (2) \( m_{Fe}^{+++} = 1 \times 10^{-3} \text{m/l} \); (3) \( m_{Fe}^{+++} = 2 \times 10^{-3} \text{m/l} \).

show the magnitude of the error expected in assigning numbers to the times required for half-reduction of a given sample.

Table 2 shows the results of addition of small amounts of impurities to the solutions, in an attempt to assess the possible catalytic action of typical inorganic constituents of natural waters.

Figure 7 shows results of a typical attempt to achieve equilibrium by adding a large amount of fine ground pyrite (−200 mesh) to a dilute iron sulfate solution. The potential drops rapidly, then becomes irregular at the lower potentials, rising and falling with time. No acceptable equilibrium potential was obtained.
The effect of other metal ions in solution on the rate of reduction of Fe\(^{3+}\) by pyrite

Pyrite used: Bingham, Utah, 2gms., -100 +200 mesh.
Original Fe\(^{3+}\) concentration: 4 \times 10^{-4} molal.

<table>
<thead>
<tr>
<th>Time to reduce 50% of Fe(^{3+}) (minutes)</th>
<th>Metal ion</th>
<th>Anion</th>
<th>Concentration (molal)</th>
<th>No. of runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1240-2000 average 1700</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>6</td>
</tr>
<tr>
<td>1100</td>
<td>VO(^{2+})</td>
<td>SO(_4)(^{2-})</td>
<td>8 \times 10^{-4}</td>
<td>3</td>
</tr>
<tr>
<td>1100</td>
<td>VO(^{2+})</td>
<td>SO(_4)(^{2-})</td>
<td>4 \times 10^{-4}</td>
<td>1</td>
</tr>
<tr>
<td>1450</td>
<td>VO(^{2+})</td>
<td>SO(_4)(^{2-})</td>
<td>1.2 \times 10^{-5}</td>
<td>2</td>
</tr>
<tr>
<td>970</td>
<td>Co(^{2+})</td>
<td>NO(_3)(^{-})</td>
<td>2 \times 10^{-4}</td>
<td>3</td>
</tr>
<tr>
<td>2000</td>
<td>Co(^{2+})</td>
<td>NO(_3)(^{-})</td>
<td>3 \times 10^{-5}</td>
<td>1</td>
</tr>
<tr>
<td>2330</td>
<td>Ni(^{2+})</td>
<td>SO(_4)(^{2-})</td>
<td>8 \times 10^{-5}</td>
<td>1</td>
</tr>
<tr>
<td>3250</td>
<td>Cu(^{2+})</td>
<td>SO(_4)(^{2-})</td>
<td>8 \times 10^{-5}</td>
<td>1</td>
</tr>
</tbody>
</table>

In several runs, in each of which more than 90 percent of ferric iron was reduced, the solution was titrated with ceric sulfate. The titrations indicated an increase in dissolved iron of about 7 percent as a result of pyrite oxidation.

DISCUSSION

Variables not affecting pyrite oxidation.—So many variables are involved in a study of oxidation rate that the first step is to eliminate those that show little effect on the process.

A first concern was the possibility that the use of an oxidizing agent to change ferrous iron to ferric iron might influence the ensuing process of reduction of the ferric iron by pyrite. However, runs in which ceric sulfate was used as the oxidant did not differ significantly from those in which potassium
permanganate was used. It was discovered, however, that if an excess of either oxidant was employed, so that the oxidation potential rose temporarily to more than one volt, the behavior of the platinum electrode was affected. It was also discovered, as an interesting sidelight, that the rate of reduction of either ceric sulfate or potassium permanganate by pyrite is very rapid. The typical two gram charge of -100 ± 200 mesh pyrite will decolorize 250 ml of 0.001 N KMnO₄ solution within a few minutes.

Second, pH apparently has little effect on oxidation rate in the range 0 to 2. At higher pH values, where Fe(OH)₃ would be expected as an oxidation product, marked effects would undoubtedly occur.

Third, although our experimentation did not systematically explore possible effects, the presence of small concentrations of vanadium, copper, cobalt, or nickel salts (or cerium or manganese as deduced above) had little effect on rate. There is a suggestion of acceleration by vanadium, and retardation by copper, but the effects are probably within our limits of duplication of runs (table 2).

The effects of stirring rate and of anions other than sulfate, either of which might be important, were not investigated.

Oxidation rate as a function of time and ferric iron concentration.—The regular relation between oxidation potential and time, as illustrated by figures 3, 4, 5, and 6, indicates that oxidation of pyrite may be governed by a simple mechanism, except perhaps at low potentials, and the progressive slowing with accompanying lower values points to the concentration of ferric iron as a control.

However, figures 4, 5, and 6 show that the time required for reduction of 50 percent of the ferric iron increases regularly with the original ferric iron concentration (m⁰₉⁺⁺). The average rate of reduction for a given pyrite speci-

![Fig. 8. Average rate of reduction of ferric iron as a function of initial ferric iron concentration, (m⁰₉⁺⁺).](image)
is independent of total iron content of the solution (fig. 8). On the other hand, for a given experiment, the instantaneous rate decreases with time, and consequently with $m_{Fe^{+++}}$. This relation between average and instantaneous rate is explained if it is assumed that the rate is proportional to the ferric—ferrous ratio, or possibly to the fraction of ferric iron present, rather than a function of $m_{Fe^{+++}}$ alone.

The relation between percent ferric iron remaining and time, for any given experiment, is like the relation between the percent of a radioactive element remaining and time. However, unlike radioactive decay, the "half life" of ferric iron is not independent of the original amount present.

Because the amount of ferric iron reduced per unit time is constant at a given ratio of $m_{Fe^{+++}}/m_{Fe^{+++}}$, it appears that the rate-controlling mechanism may be related to adsorption of ferric and ferrous iron on the pyrite surface. If adsorption is rapid, and if the subsequent oxidation reaction is slow, then the reaction rate probably would be proportional to the fraction of the pyrite surface occupied by ferric ions ($Fraction \ Fe^{+++} pyrite = \frac{Fe^{+++} pyrite}{Fe^{+++} pyrite + Fe^{++} pyrite}$).

As a first approximation, the fraction of the pyrite surface occupied by ferric ions might be expected to be roughly proportional to the fraction of ferric ions in the solution. If so,

$$\frac{dm_{Fe^{+++}}}{dt} = k_1 \frac{m_{Fe^{+++}}}{m_{Fe^{+++}}} = k_2 \frac{Fe^{+++} pyrite}{Fe^{++} pyrite + Fe^{+++} pyrite}.$$

As a test of this relation, a number of runs are shown for Rio Tinto pyrite, in which $-\log m_{Fe^{+++}}/m_{Fe^{+++}}$ is plotted against time (fig. 9). All runs give straight line relations. The general equation that describes all the runs is

$$-\log \frac{m_{Fe^{+++}}}{m_{Fe^{+++}}} = \frac{k}{m_{Fe^{+++}}} \text{ time}.$$

Inasmuch as the ferrous and ferric ions have different charges, it might be expected that the adsorption of these ions on a solid surface would not be a simple function of their relations in solution. However, it is possible to obtain essentially the relations observed by using an ion exchange equation, if appropriate empirical constants are applied.

The rate of reduction of ferric ion is, therefore, evidently proportional to the fraction of pyrite surface upon which this ion is adsorbed, and to the total initial surface available. Apparently the fraction of surface occupied by ferric ion depends upon competition between ferric and ferrous ions, and is proportional to the fraction of ferric ion in solution. It seems likely that the fraction of ferric ion in solution, while proportional to that on the pyrite surface, is larger. This accounts for the marked increase in oxidation rate of pyrite at ferric fractions in solution very close to unity—the fraction occupied surface probably increases disproportionately as the ferrous concentration becomes vanishingly low.
Fig. 9. Plot of log fraction ferric remaining $\frac{m_{Fe^{3+}}}{m_{Fe^{2+}}}$ versus time for some runs with Rio Tinto pyrite. (1), (2) $m_{Fe^{2+}} = 4 \times 10^{-2} \text{m/1}$; (3), (4), (5), (6), (7), (8), $m_{Fe^{2+}} = 1 \times 10^{-2} \text{m/1}$; (9), (10) $m_{Fe^{2+}} = 2 \times 10^{-2} \text{m/1}$.

Attempts to achieve equilibrium.—If equilibrium between pyrite and a ferrous-ferric solution could be achieved, it might be possible to deduce the oxidation reaction involved. But as shown in figure 7, which is typical of many similar experiments, no constant ferrous--ferric ratio is obtained. The Eh of the solution becomes unsteady in the vicinity of 0.250-0.300 volts. In part the explanation may be in the experimental conditions, for at an Eh of 0.250, in a solution originally 0.001m in iron, $m_{Fe^{2+}}$ is only about $10^{-7}$. In such a solution, any minor impurities that might oxidize or reduce iron can change the measured potential many millivolts.
If the apparent equilibrium represented by the temporary asymptote in figure 7 is used as an equilibrium Eh, the reaction

$$FeS_2 = Fe^{++} + 2S^0 + 2e$$  \hspace{1cm} (4)

describes the relation well. The observed Eh is about 0.250 volts, the calculated value the same.

The general picture of pyrite oxidation by ferric ion, as we now see it, is that the reaction is described through most of its course by oxidation to Fe$^{++}$ and SO$_4$$^-$.

$$8H_2O + FeS_2 + 14Fe^{+++} \rightarrow 15Fe^{++} + 2SO_4^- + 16H^+$$  \hspace{1cm} (5)

Oxidation to sulfate ion is irreversible. This mechanism is checked by allowing pyrite to be oxidized, and then re-titrating the solution with ceric sulfate. It is found that the iron content of the solution is increased by about the required 7 percent, showing that the sulfur has been carried up to sulfate. Only at very low potentials can reaction (4) hold.

Oxidation of pyrite by ferric ion near equilibrium thus seems to yield molecular sulfur. Any excess of ferric ions will oxidize this sulfur through intermediate species to sulfate ion. There may be a restricted Eh range in which the temporary oxidation product is an intermediate sulfur species, but it appears that under most natural conditions ferrous ion and sulfate ion are produced essentially instantaneously. This corroborates the findings of Temple and Kochler (1954, p. 24).

**SUMMARY AND CONCLUSION**

Oxidation of pyrite specimens by ferric sulfate solutions shows that pyrites from different localities oxidize at markedly different rates, but apparently the mechanism is the same. The rate of oxidation is chiefly a function of the oxidation potential of the solution, and is independent of the total iron content.

The oxidation process, over the range of ferric ion concentration from 100% to less than 0.1 percent m$_{Fe^{+++}}$, apparently is controlled by differential adsorption of ferric and ferrous ions on the pyrite surface. All our data are explained if it is assumed that the rate of oxidation is proportional to the fraction of pyrite surface occupied by ferric ion, and if the occupation of pyrite surface by ferric and ferrous ions is approximately proportional to their concentrations in solution. Thus if pyrite is placed in a solution containing ferric and ferrous ions, rapid adsorption of both species apparently takes place on the pyrite surface. Oxidation to ferrous ions and sulfate ions occurs only at those sites occupied by ferric ions. Because the oxidation process is slow relative to adsorption, the adsorption process controls the rate.

Impurities in solution such as nickel, cobalt, vanadium, manganese, copper, and cerium have little effect on oxidation rate, with just a hint that vanadium accelerates oxidation and copper retards it. The oxidation rate is independent of pH in the range 0 to 2. (No ferric hydroxides are formed.)
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Except under near-equilibrium conditions, pyrite is apparently oxidized by ferric ion to ferrous ion, hydrogen ion, and sulfate ion. The first step of the oxidation process, however, may be to produce molecular sulfur.

Because of the exponential increase in oxidation rate as the ratio of ferric ion to total iron increases, pyrite changes from an essentially inert substance at Eh values in the vicinity of 0.300-0.400 volts, to an active reducing agent at potentials of 0.800 volts and above.

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REFERENCES CITED