SULFIDE TO SULFATE REACTION MECHANISM IN
PYRITIC MATERIALS

A Thesis

Presented in partial fulfillment of the requirements
for the Degree Master of Science

by

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SULFIDE TO SULFATE REACTION MECHANISM
IN PYRITIC MATERIALS

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STATEMENT OF THE PROBLEM

This thesis is devoted to exploratory studies of the reaction of iron disulfide with oxygen to form iron sulfates and sulfuric acid. This reaction, taking place in coal mines and associated refuse piles, is responsible for the acid mine drainage problem. The work included here is a first step to elimination of trial and error approaches to the problem which so far have been unsuccessful. An attempt is made to resolve points of conflict in previous work, and to propose a controlling mechanism for the reaction.
INTRODUCTION

Previous work in the field of acid mine drainage has been of a trial and error nature in an attempt to apply direct measures to solve the problem. Mine seals, flooding, application of inhibitors, and purging with gases have all been tried with various degrees of success. Overall methods such as leaching studies under various conditions on samples from different areas have been tried in order to discover the factors affecting acid production. Work by Sato (24), Rosetti & Cessini (25) and others (4, 6, 16, 17, 21, 25) has been directed toward determination of the actual limiting reaction. However, no actual mechanism has yet been definitely determined. The overall reaction has been shown to be:

$$2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} = \text{FeSO}_4 + \text{H}_2\text{SO}_4$$

However, until the actual kinetics of the process is determined, the trial and error approach to prevent the natural acid formation from pyrites can not be eliminated.

The work described herein is of an exploratory nature as a first step in the attempt to determine the limiting reaction in pyrite oxidation. This is necessary before proceeding to evaluate factors affecting the reaction, and finally, abatement procedures.
This work approached the problem from the analytical, microscopic, kinetic, and electrochemical disciplines.

In the analytical and microscopic approaches, an attempt was made to determine both the chemical composition of the various pyritic materials and their weathering products by wet analysis, and X-Ray and electron diffraction studies. In the kinetic approach, the influence on the rate of oxygen consumption of temperature, agitation, environment, and partial pressure of oxygen was investigated. From these data, it is possible to propose whether the reaction is physically or chemically controlled. In the electrochemical approach, measurements were made of the single potential of sulfide electrodes in oxidizing solutions, in order to determine the initial heterogeneous reaction.
RELATED LITERATURE

The overall problem of acid formation from abandoned mines and refuse piles and its subsequent pollution of water systems is described by Hodge (13) and Hoffert (14). For the better part of the last fifty years, overall attempts have been made to discover the source of this problem and to apply various abatement procedures (15, 4, 8, 19), particularly mine sealing. The source of acid in mine waters was found to be pyritic materials: pyrite and marcasite (2, 4, 7, 8, 16, 26). Various investigators have determined the overall reaction for acid formation as: \[ 2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} = \text{FeSO}_4 + \text{H}_2\text{SO}_4. \] As the acid solution containing ferrous sulfate is diluted when it enters the streams, the ferrous iron is oxidized to the ferric state by dissolved oxygen, and then hydrolyses to form hydrous iron oxides and more sulfuric acid.

Several mechanisms resulting in the above overall reaction have been proposed. Braley (4) allowed several samples of "museum grade" pyrite and marcasite, and "sulfur ball" material of various mesh sizes to oxidize under water for varying lengths of time. The amounts of iron and sulfur formed in the solutions after each oxidation period was determined. The sulfur to iron ratios thus obtained varied between 1 and 2, indicating a loss of sulfur which he attributed to the following reaction:
\[ \text{FeS}_2 + 3\text{O}_2 = \text{FeSO}_4 + \text{SO}_2 \] assuming that some of the \text{SO}_2 formed escaped into the air. All iron found in the solutions was in the ferrous state. More oxidation products were formed from the finer mesh size samples, and more from the crushed "sulfur ball" than from the samples of "museum grade" pyrite and marcasite. No sulfur oxidizing bacteria were found to be present.

Burke and Downs (6) made one of the first investigations of the mechanism of the oxidation reaction. In comparing the reactivities toward water saturated with oxygen, they found "sulfur ball" material to be approximately ten times more reactive than either "museum grade" marcasite or pyrite. Although no actual measurement of porosity of the materials was made, they attributed this greater reactivity to the more porous nature of the "sulfur ball". Their experiments in determining the mechanism of the reaction were conducted by placing cut and polished cubes of this "sulfur ball" material in a reactor in which temperature, partial pressure of oxygen, solution concentration, and agitation of the sample (by rotation) could be varied independently. The rate of reaction was determined by weighing the cube after each run. They found that the speed of revolution of the cube, and the ferrous ion concentration (up to 1 Normal) had no measurable effect on the rate of reaction.
The presence of sulfate ion was found to decrease the reaction rate, completely stopping the reaction at a concentration of 1 normal. Reaction rate was found to increase with temperature, but the increase was not linear. Partial pressure of oxygen over the solution had no effect on the rate until the oxygen was completely excluded from the system.

Another set of experiments was made using dry oxygen. In this system, SO₂ was found in appreciable quantities, although none had been found in the previous system. From these and other data, they concluded that the mechanism started with the heterogeneous reaction: FeS₂ + 3O₂ = FeSO₄ + SO₂ followed by: 2SO₂ + O₂ + 2H₂O = 2H₂SO₄, the second reaction being over twenty times as fast as the first when water was present. It is to be noted however, that the dry oxidation experiments were carried out at 88°C, far above normal mine temperatures.

In a continuation of this work, Mapstone (26) found that by use of peroxides, produced from naphthenic gasoline, ferrous sulfide could also be produced as an intermediate product. On this basis, he proposed the following mechanism:

\[ FeS₂ + O₂ = FeS + SO₂ \]
\[ FeS + O₂ = FeSO₄ \quad (\text{fast}) \]
\[ 2SO₂ + O₂ + 2H₂O = 2H₂SO₄ \]
FeS + H₂SO₄ = FeSO₄ + H₂S
2H₂S + SO₂ = 3S + 2H₂O

He found all intermediates to be present, and postulated the mechanism on that basis.

Li and Paar (16) in an investigation of the role of pyritic materials in the spontaneous combustion of coal piles, oxidized samples of high sulfur coal, pyrite, and marcasite, in a stream of water-saturated oxygen. Runs were made at 25⁰C and 100⁰C. In all runs except one which was a sample of pure pyrite at 100⁰, the products of oxidation remained as solid sulfates. In the exceptional run, some SO₂ was found in the gases after combustion. The rate of oxidation was determined from the amount of sulfates formed after a run of given time. Samples of pure cubic museum grade pyrite, and pure marcasite were oxidized at both temperatures. At 100⁰ the pyrite reacted at a slightly faster rate, while at 25⁰ the reverse was true. The effect of surface area was studied by reacting specific screen fractions of both materials. A flat distribution of particle sizes in any one fraction was assumed, although there was evidence that the distribution in marcasite samples was shifted toward the finer sizes. The rate of oxidation was found to be roughly described by the formula:
R = T/D (K)

R = Reaction Rate
D = Particle Diameter
T = Temperature in Centigrade
K = A constant which varied with the material used

To determine if materials normally found in association with pyrites had any catalytic effect on the oxidation, samples were mixed with coal, clays, and the bacteria "Thiobacillus Thiooxidans". No material had any significant effect other than one sample of Indiana Clay which was presumed to contain an unidentified strain of bacteria. Use of air instead of oxygen roughly halved the reaction rate. Moisture was found essential to the reaction.

McKay and Halpern (17) oxidized aqueous suspensions of pyrite at 100°C to 130°C, and found that the overall rate was proportional to the surface area (external) of the pyrite, and the partial pressure of oxygen, but independant of the composition of the solution. The solution, however, affected the product distribution. At high temperatures and low acidity, sulfuric acid was formed predominantly, while at low temperatures and high acidity, sulfur was formed. The competing reactions were suggested to be:
(1) \( \text{FeS}_2 + 2\text{O}_2 = \text{FeSO}_4 + \text{S} \)

(2) \( 2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} = 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \)

(3) \( \text{FeS}_2 + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + \text{H}_2\text{S} + \text{S} \)

Hydrogen sulfide is then removed by:

(4) \( 2\text{H}_2\text{S} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{S} \)

(5) \( \text{H}_2\text{S} + 2\text{O}_2 = \text{H}_2\text{SO}_4 \)

Ferric sulfate is then formed by:

(6) \( 4\text{FeSO}_4 + \text{O}_2 + 2\text{H}_2\text{SO}_4 = 4\text{Fe(SO}_4)_1.5 + 2\text{H}_2\text{O} \)

The contribution of ferric sulfate to the oxidation was suggested as:

(7) \( \text{FeS}_2 + 8\text{Fe(SO}_4)_1.5 + 4\text{H}_2\text{O} = 9\text{FeSO}_4 + 4\text{H}_2\text{SO}_4 + \text{S} \)

(8) \( \text{FeS}_2 + 14\text{Fe(SO}_4)_1.5 + 8\text{H}_2\text{O} = 15\text{FeSO}_4 + 8\text{H}_2\text{SO}_4 \)

(9) \( \text{H}_2\text{S} + 2\text{Fe(SO}_4)_1.5 = 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{S} \)

(10) \( \text{H}_2\text{S} + 8\text{Fe(SO}_4)_1.5 + 4\text{H}_2\text{O} = 8\text{FeSO}_4 + 5\text{H}_2\text{SO}_4 \)

Sulfur is then oxidized:

(11) \( 2\text{S} + 3\text{O}_2 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 \)

(12) \( \text{S} + 6\text{Fe(SO}_4)_1.5 + 4\text{H}_2\text{O} = 6\text{FeSO}_4 + 4\text{H}_2\text{SO}_4 \)

They observed that the oxidation rate was not directly proportional to the surface area of the particles, and since no change occurred with a change in stirrer speeds, that the mechanism was chemically rather than diffusion controlled. The concentration of sulfuric acid in the solution had no effect on the reaction rate. On the basis of these data, they proposed the reaction to be first order.
in $O_2$ and independant of the solution. Reactions 3, 4, 5, 7, 8, 9, and 10 were found to make little contribution to the system. Reaction 6 determines the ratio of ferrous to ferric iron but has no effect on the rate of oxidation of FeS$_2$. Reactions 1 and 2 may occur as competing reactions, or the sulfur may occur as an intermediate. The suggested mechanism is

$$FeS_2 + O_2 (aq) = FeS_2\cdot O_2 \text{ (rapid chemisorption) followed by:}$$

$$FeS_2\cdot O_2 + O_2 (aq) = (FeS_2\cdot 2O_2)^* = FeSO_4 + S^0$$

Nelson, Snow, and Keyes (21) oxidized suspensions of pyrite at 22°, 50°, 70°, and 90°C. They found the rates of reaction slowed with time and suggested that this was due to an accumulation of ferrous sulfate in the pores of the material, which resulted in less exposed surface for reaction. No ferric iron was found to be present in any of the solutions after oxidation. Both oxygen and air were bubbled through the solution at various rates. This produced no effect on the rate of sulfate formation. The rate of sulfate formation was found to be directly proportional to temperature and (roughly) inversely proportional to particle diameter. Several samples were oxidized in solutions of ferric sulfate. This increased the reaction rate to some extent. Ferric ion was reduced during the course of the run, in some cases being completely reduced to the ferrous state.
Sinnatt and Sumpkin (26) also suggest that the ferric ion will oxidize pyritic material.

Silverman, Rogoff, and Wender (25) investigated the effect of bacteria on the oxidation of pyrite in coals. They found that the strain "Thiobacillus Thiooxidans" had no effect on the reaction rate, but "Ferrobacillus Ferroxidans" accelerated the reaction appreciably. They suggested the following mechanism:

\[ 2\text{Fe}^{3+} + \text{FeS}_2 = 3\text{Fe}^{2+} + 2\text{S}^0 + \frac{1}{2}\text{O}_2 + 2\text{SO}_4^{2-} \]

or F. Ferroxidans

They state that the ferrous ion is stable to oxidation in acid solution without the presence of bacteria. According to Hem (10, 11) and Hem and Cropper (12), however, this is only true when the pH of the solution is below 2.00. At pH values and oxidation potential values normally found in mine waters, the concentration of ferric ion is well below the level needed to produce oxidation at observed rates. In the range of pH and oxidation potential of mine waters, ferrous ion and hydrated ferric oxides are the stable forms of iron, while the sulfate ion is the stable form of sulfur.

Sato (24) measured the single electrode potentials of large crystals of museum grade pyrite in solutions of ferrous and sulfate ion of different pH and ferrous ion concentration. From measured potentials and available free energy data, he postulated
the heterogeneous rate controlling mechanism at the surface of the pyrite to be (at pH values less than 2):

$$\text{FeS}_2 = \text{Fe}^{+2} + 2e + S_2$$

The resulting potential being described by:

$$\text{Eh} = 0.757 + 0.0295 \log (\text{Fe}^{+2})$$

while at pH values greater than 2.0:

$$\text{FeS}_2 + 3\text{H}_2\text{O} = \text{Fe(OH)}_3 + S_2 + 3\text{H}^+ + 3e$$

the potential being described by:

$$\text{Eh} = 0.857 + 0.0591 \text{ pH}$$

It should be noted that the sulfur released is in the form of $S_2$ molecules rather than solid sulfur. These $S_2$ molecules are oxidized immediately to sulfate ions. In other sulfides investigated, he found that the metal atoms moved into solution and formed cations, making a stepwise decrease in the metal to sulfur ratio. The sulfur then oxidizes to the sulfate ion. In the iron disulfides, however, results indicate that the iron and sulfur are released simultaneously as iron atoms and $S_2$, the iron oxidizing then to the cation, and the $S_2$ to sulfate. This mechanism seems plausible due to the nature of the structure
of pyrite and marcasite crystals. No definite mechanism was
postulated for marcasite oxidation due to lack of free energy
data on marcasite.

Rossetti and Cessini (23) used potential measurements to
show that different sulfides in contact could produce potentials
and subsequent oxidation in a process similar to that of metal
corrosion.
DISCUSSION OF LITERATURE

Several conclusions may be drawn from the published work in the area of acid formation from pyritic materials. It has been conclusively shown that iron disulfide in one form or another is responsible for the acid formation, and the most generally agreed upon reaction for the overall process is:

\[2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} = \text{FeSO}_4 + \text{H}_2\text{SO}_4\]

Subsequent oxidation of iron to the ferric state has been shown to have no effect on the rate controlling mechanism, especially since in most cases where three valent iron occurs in mine waters, the form found is hydrated ferric oxide.

The crystalline form of iron disulfide found in coal beds and adjacent strata has not yet been conclusively determined. Reports vary, especially in the case of "sulfur balls" which have been reported to be pyrite in one case and marcasite in another. The high reaction rate of this "sulfur ball" material as compared to both museum grade pyrite and marcasite suggested further investigation into its crystalline structure and porous properties. Investigations by Bahr (2) and Grout (7) indicate that certain aspects of the crystallography of pyrite itself influence the reaction rate.

Although the overall reaction has been determined, the
proposed mechanisms and rate controlling reactions vary considerably. Certain intermediate products such as sulfur, \( \text{SO}_2 \), \( \text{H}_2\text{S} \), and \( \text{FeS} \) have been reported in some cases, and not in others. Although the data of Sato indicates a limiting chemical reaction, no conclusive decision can be made on whether the oxidation process is chemically or physically controlled. Although the lack of effects of agitation tends to point to a chemically controlled system, the temperature coefficients of the reaction rates differ considerably from that predicted for a chemical domain as pointed out in Johnstone and Thring (15).

No investigations of the actual surface areas and pore volume distributions of the materials used for oxidation samples have been found. All data so far presented have been on the basis of external surface. Better determination of these properties could be carried out using methods such as nitrogen adsorption (3, 5, 20) or \( \text{CO}_2 \) adsorption (1).

In view of this previous work and the conflicting view of the problem it presents, the following experimental work was carried out.
EXPERIMENTAL WORK

In order to determine the relative reactivities and compositions of pyritic materials obtained from different sources, samples were obtained as shown in Table 1.

TABLE 1

ORIGINAL SAMPLES OF PYRITIC MATERIALS

<table>
<thead>
<tr>
<th>NUMBER</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Museum Grade Pyrite</td>
</tr>
<tr>
<td>2</td>
<td>Museum Grade Marcasite</td>
</tr>
<tr>
<td>3</td>
<td>Coal from O. S. U. Powerhouse</td>
</tr>
<tr>
<td>4</td>
<td>E. E. S. Coal Sample Number 88/464</td>
</tr>
<tr>
<td>5</td>
<td>4 inch diameter sulfur ball from refuse pile</td>
</tr>
<tr>
<td>6</td>
<td>Coal showing pyrite inclusions from Hocking County</td>
</tr>
<tr>
<td>7</td>
<td>Shale showing pyrite inclusions from Hocking County</td>
</tr>
<tr>
<td>8</td>
<td>Sandstone showing pyrite inclusions from Hocking County</td>
</tr>
</tbody>
</table>

All samples were crushed to pass a 1/4 inch mesh screen. They were then separated in a mixture of Bromoform and Carbon Tetra-
chloride having a specific gravity of 2.00. The portion which sank to the bottom was removed, dried, and milled to pass a 60 mesh screen. All particles finer than 150 mesh were saved in reserve. The 60 to 150 mesh portion was placed in a bath of pure bromoform at 30°C and allowed to stand overnight. That portion which floated to the top was discarded, and the heavy portion dried for 1 hour at 110°C and stored in tightly stoppered bottles.

Separate portions of this material were taken for wet analysis for iron and sulfur, X-Ray powder analysis to determine the crystalline form of pyritic material present, and for oxidation studies in the Warburg Respirometer. The results of wet analysis and the X-Ray data on the prepared samples are presented in Table 2.

The determination of total sulfur was made by digesting 0.2 gram samples in concentrated nitric acid and a saturated solution of bromine in carbon tetrachloride. They were then evaporated to dryness, washed with HCl, and evaporated to dryness twice. The residue was dissolved in a dilute HCl solution, and the sulfur precipitated as BaSO₄. The soluble sulfur (sulfate sulfur) in each sample was determined by digestion in 5 normal HCl, followed by filtration and precipitation of the sulfur as BaSO₄. The difference between total
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>FORM (X-RAY)</th>
<th>% TOTAL SULFUR</th>
<th>% SOLUBLE SULFUR</th>
<th>% PYRITIC SULFUR</th>
<th>% FeS₂*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pyrite</td>
<td>47.30</td>
<td>0.05</td>
<td>47.25</td>
<td>88.17</td>
</tr>
<tr>
<td>2</td>
<td>Marcasite</td>
<td>49.72</td>
<td>0.28</td>
<td>49.44</td>
<td>92.92</td>
</tr>
<tr>
<td>3</td>
<td>Pyrite</td>
<td>47.85</td>
<td>0.31</td>
<td>47.54</td>
<td>89.31</td>
</tr>
<tr>
<td>4</td>
<td>Pyrite</td>
<td>43.85</td>
<td>1.06</td>
<td>42.79</td>
<td>82.13</td>
</tr>
<tr>
<td>5</td>
<td>Pyrite</td>
<td>47.92</td>
<td>0.14</td>
<td>47.78</td>
<td>89.59</td>
</tr>
<tr>
<td>6</td>
<td>Pyrite</td>
<td>47.32</td>
<td>0.28</td>
<td>47.04</td>
<td>88.58</td>
</tr>
<tr>
<td>7</td>
<td>Pyrite</td>
<td>45.99</td>
<td>0.22</td>
<td>45.77</td>
<td>86.21</td>
</tr>
</tbody>
</table>

* The percentage of FeS₂ was calculated by taking the difference between total sulfur and soluble sulfur to be pyritic sulfur, and ratioing molecular weights to obtain per cent FeS₂.
sulfur and soluble sulfur was taken to be pyritic sulfur. The percentage of FeS₂ shown in Table 2 was calculated on this basis. The total iron was determined in all samples by titrations chloride titration and was found to be in excess of that required to match the sulfate and pyritic sulfur content.

Since a large quantity of the "sulfur ball" (Sample No. 5) was available for further studies, a complete analysis of the material was made as shown in Table 3.

Oxidation studies were made on all of the samples in the Warburg Respirometer, illustrated in Figure I.

The results of the studies on "museum grade" pyrite "museum grade" marcasite, and "sulfur ball" (Samples No. 1, 2, 5) are presented in Figure II. The oxygen consumption curves for all other samples lay between those for No. 2 and No. 5 and were of the same general shape. The samples were run at 20°C, immersed in water, with no agitation. Air was used as the atmosphere in the flask. The curvature of the oxidation curves is due to the procedure used in making the runs. As enough oxygen in the flask was used up to bring the manometer to its limit, the system was adjusted back to atmospheric pressure by admission of air. Since nitrogen is not consumed in the process, there was an accumulation of nitrogen in the system, thus lowering the partial pressure of oxygen. As later results show, the rate of
TABLE 3

ANALYSIS OF SULFUR BALL

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>41.65 %</td>
</tr>
<tr>
<td>Sulfur</td>
<td>46.72 %</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.30 %</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.40 %</td>
</tr>
<tr>
<td>Mn</td>
<td>.005 %</td>
</tr>
<tr>
<td>Ca</td>
<td>.05 %</td>
</tr>
<tr>
<td>Mg</td>
<td>.05 %</td>
</tr>
<tr>
<td>As</td>
<td>trace</td>
</tr>
<tr>
<td>Phosphate</td>
<td>trace</td>
</tr>
<tr>
<td>C</td>
<td>6 %</td>
</tr>
<tr>
<td>H</td>
<td>0.50 %</td>
</tr>
<tr>
<td>TOTAL</td>
<td>98.9 %</td>
</tr>
</tbody>
</table>
SCHEMATIC DRAWING OF WARBURG RESPIROMETER APPARATUS*

FIGURE 5 - c
MANOMETER
SUPPORT
FASTENING OF MANOMETER TO MANOMETER SUPPORT
MANOMETER FLUID RESERVOIR ADJUSTMENT
FLANGE FOR ATTACHING MANOMETER SUPPORT TO SHAKING MECHANISM

FIGURE 5 - d
REACTION FLASK OF ADAPTED 50 ml FLORENCETYPE SHOWING SHELL VIAL INSERT FOR GAS ABSORBENT

FIGURE 5 - e
GLASS BUCKET TYPE GAS ABSORBENT INSERT USED WHEN V_2 IS GREATER THAN 1/6 OF V

FIGURE 5 - u
TERMINOLOGY FOR PARTS OF WARBURG MANOMETERS

FIGURE 5 - e
LOOSE FITTING SHELL VIAL PLACED OVER LEG OPENINGS TO PREVENT ENTRANCE OF DUST

FIGURE II
OXIDATION OF PREPARED SAMPLES OF PYRITIC MATERIAL

[Graph showing three lines labeled #1, #2, and #5 with data points plotted on a grid.]
reaction is dependent on the partial pressure of oxygen in the system. The curves should be linear if the partial pressure is kept constant. In all following runs, using air as the atmosphere, the system was flushed with fresh air each time it was adjusted to atmospheric pressure.

The X-Ray data on the above samples showed all but the sample of "museum grade" marcasite to contain only pyrite within the limits of detection (minimum detectable amount - 5% marcasite). This prompted a further study of the form of pyritic material found in Ohio coal beds. David Stiles of the Department of Mineralogy who was also employed on this project collected the following samples and ran an X-Ray analysis for pyrite and marcasite. The samples and results of the analysis are presented in Table 4.

These data show that with the exception of three samples from separated areas of the number 6 coal bed, the great majority of pyritic material found in coal beds and adjacent strata is pyrite rather than marcasite. This restricts the considerations in experimental work primarily to pyrite. The limit of detection of marcasite by this method leaves open the possibility of small amounts of marcasite (under 5%) being present.

As figure 1 shows, there is a considerable difference between the reaction rates of "museum grade" pyrite, marcasite,
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>LOCATION OR DESCRIPTION</th>
<th>WHERE FOUND</th>
<th>FORM OF FeS₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>Route 75, 1 mile north of junction of Routes 75 and 37</td>
<td>Coal dump</td>
<td>Pyrite</td>
</tr>
<tr>
<td>4A</td>
<td>Sharpsburg area</td>
<td>Dump</td>
<td>Pyrite</td>
</tr>
<tr>
<td>5A</td>
<td>Rheboth area</td>
<td>Coal tipple</td>
<td>Pyrite</td>
</tr>
<tr>
<td>7A</td>
<td>#6 Coal, junction of Routes 37 and 78</td>
<td>Strip mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>8A</td>
<td>#7 Coal, Kimberly</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>9A</td>
<td>Clarian Coal, north of Padro</td>
<td>Dump</td>
<td>Pyrite</td>
</tr>
<tr>
<td>10A</td>
<td>#5 Coal, 3½ miles south of Blackfork</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>11A</td>
<td>Wigluss Coal</td>
<td>Coal bin</td>
<td>Pyrite</td>
</tr>
<tr>
<td>13A</td>
<td>#6 Coal, junction of Routes 37 and 78 &quot;Sulfur ball&quot;</td>
<td>Strip mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>14A</td>
<td>#5 Coal, 3 miles north of Oak Hill</td>
<td>Strip mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>15A</td>
<td>#4 Coal, Radcliff</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>16A</td>
<td>#7 Coal, Carbon Hill</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>17A</td>
<td>#5 Coal, ½ mile east of McArthur</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>18A</td>
<td>#6 Coal, Hanging Rock, Strip Mine</td>
<td>Strip mine</td>
<td>Pyrite &amp; 50% Marcasite</td>
</tr>
<tr>
<td>SAMPLE</td>
<td>LOCATION OR DESCRIPTION</td>
<td>WHERE FOUND</td>
<td>FORM OF FeS2</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------</td>
<td>-------------</td>
<td>---------------</td>
</tr>
<tr>
<td>19A</td>
<td>#4 Coal, Radcliff (Sulfur Ball)</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>20A</td>
<td>#6 Coal 1 mile S of Route 56 on Route 287</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>22A</td>
<td>#6 Coal, Kimberly</td>
<td>Mine</td>
<td>Pyrite &amp; 20% Marcasite</td>
</tr>
<tr>
<td>23A</td>
<td>#6 Coal, ½ mile E of McArthur</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>24A</td>
<td>#4 Coal, 3 miles W of McArthur</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>25A</td>
<td>W of Reinersville</td>
<td>Dump</td>
<td>Pyrite &amp; 10% Marcasite</td>
</tr>
<tr>
<td>26A</td>
<td>#9 Coal, N of Dexter City</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>27A</td>
<td>#5 Coal, 3 miles N of Oak Hill</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>28A</td>
<td>#6 Coal, Carbondale</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>29A</td>
<td>#6 Coal, Route 56, W of Carbondale</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>30A</td>
<td>Pomeroy Coal, N of Pomeroy</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>31A</td>
<td>Upper Coal at Nelsonville Mine</td>
<td>Strip mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>32A</td>
<td>#6 Coal, Buctel</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>33A</td>
<td>Nelsonville</td>
<td>Dump</td>
<td>Pyrite</td>
</tr>
<tr>
<td>34A</td>
<td>#5 Coal, Hanging Rock</td>
<td>Strip mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>35A</td>
<td>Clarian Coal, N of Padro</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td>SAMPLE</td>
<td>LOCATION OR DESCRIPTION</td>
<td>WHERE FOUND</td>
<td>FORM OF FeS₂</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------</td>
<td>-------------</td>
<td>--------------</td>
</tr>
<tr>
<td>36A</td>
<td>#6 Coal, on Route 52 E</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td></td>
<td>of Carbondale</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37A</td>
<td>#5 Coal, junction of</td>
<td>Strip mine</td>
<td>Pyrite</td>
</tr>
<tr>
<td></td>
<td>Routes 78 and 37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38A</td>
<td>Coal Grove</td>
<td>Mine</td>
<td>Pyrite</td>
</tr>
</tbody>
</table>
and pyritic materials which were found in coal beds and adjacent strata, and in sulfur balls. This prompted a microscopic study of the progress of oxidation of surfaces of these materials to detect the presence of possible "active sites" where oxidation begins or proceeds more rapidly.

Duplicate samples of "museum grade" pyrite, "museum grade" marcasite, and "sulfur ball" were mounted in plastic "buttons". These were polished on emery papers and finally on a polishing wheel using 1 micron diamond powder. One of each of the duplicates was then etched for 15 seconds in 50% nitric acid, rinsed with water, then methanol, and dried. All samples were placed in a dessicator kept at 75% humidity and 20°C. Photomicrographs were taken of the specimens immediately after polishing and etching, and at various intervals of time thereafter over a period of five months. The magnification used for all photographs was 500X. The following pages show the progress of oxidation of the initially etched specimens. Those not initially etched proceeded at the same relative rates once started, but a longer induction period was needed before oxidation products began to show.

On the museum grade pyrite specimen, a crack in the surface was used as a point of reference in making the photographs. This proved fortunate, as oxidation began around the area of
the crack and spread from there. The pattern of surface deposit was first a group of spots near the crack, gradually spreading, and forming more rapidly along polishing marks.

On the "sulfur ball" sample, spots began to appear on the surface in the light areas (pyrite). As oxidation proceeded further, the number of spots increased, but the size of the individual spots seemed to remain fairly constant. No overall coating of weathering products appeared in the area of the photograph, but in other areas on the sample surface, an iridescent rust-colored coating was formed.

The marcasite quickly formed an overall coating of weathering products without the spotty appearance found in the other two.

The photographs of the samples of "sulfur ball", in addition to indicating the progress of oxidation, show the structure of the material. The light areas are pyrite and the dark areas appear to be coal. This shows the material to be a loosely packed arrangement of small pieces of pyrite with most of the space between particles filled with coal.

The electron microscope and its associated replica and diffraction techniques were used to determine the structure of "sulfur ball" material and the detection of intermediate products which may lead to a proposed reaction mechanism. In order
MUSEUM GRADE PYRITE - AFTER ETCHING

FIGURE III
MUSEUM GRADE PYRITE - AFTER 1 WEEK

FIGURE IV
MUSEUM GRADE PYRITE - AFTER 1 MONTH

FIGURE V
MUSEUM GRADE PYRITE - AFTER 6 WEEKS

FIGURE VI
MUSEUM GRADE PYRITE - AFTER 2 MONTHS

FIGURE VII
MUSEUM GRADE PYRITE - AFTER 3 MONTHS

FIGURE VIII
MUSEUM GRADE PYRITE - AFTER 5 MONTHS

FIGURE IX
SULFUR BALL - AFTER ETCHING

FIGURE X

36
SULFUR BALL - AFTER 1 WEEK

FIGURE XI
SULFUR BALL - AFTER 1 MONTH

FIGURE XII
SULFUR BALL - AFTER 6 WEEKS

FIGURE XIII
SULFUR BALL - AFTER 2 MONTHS

FIGURE XIV
SULFUR BALL - AFTER 3 MONTHS

FIGURE XV

41
SULFUR BALL - AFTER 5 MONTHS

FIGURE XVI
MUSEUM GRADE MARCASITE - AFTER ETCHING

FIGURE XVII

43
MUSEUM GRADE MARCASITE - AFTER 1 WEEK

FIGURE XVIII
MUSEUM GRADE MARCASITE - AFTER 2 MONTHS

FIGURE XX
MUSEUM GRADE MARCASITE - AFTER 3 MONTHS

FIGURE XXI
to observe the topography of the weathered sulfur ball surface and its adhering products, replicas were made in the following manner: Samples of sulfur ball mounted in plastic left from the series of optical photomicrographs just presented were coated with collodion. The collodion was removed with cellophane tape, placed in an evaporator and coated with carbon. It was then shadowed with a small amount of gadolinium at an angle of 30°, removed from the evaporator, and the tape and collodion dissolved with amyl acetate. The carbon replicas were mounted on copper grids. Figures XXII and XXIII on the next page show two areas on a sample of sulfur ball at a magnification of about 15,000X. The first is a relatively uniform area of pyritic material, and the second a rough area which appears to be small pieces of pyritic material interspersed with another material. The interspersed material appears darker due to the gadolinium shadowing since it is slightly below the level of the pyrite. Due to the relative hardness of pyrite, this material was probably ground slightly deeper in the polishing process. No crystalline forms of either pyritic materials or oxidation products were observed in these micrographs, but rather a number of apparently rounded protrusions on the surface.

Attempts were made to extract some oxidized material from the surface using an extraction replica technique. However,
FIGURE XXII - SULFUR BALL MATERIAL, PYRITE SURFACE - 15,000 X

FIGURE XXIII - SULFUR BALL MATERIAL, MIXED SURFACE - 15,000 X
the oxidation products adhere to the pyrite surface and are not easily removed. The only diffraction patterns so far obtained of extracted material have been of some associated clay minerals which were on the surface of one pyrite sample. The present plan to overcome this difficulty is to mount weathered samples in the microscope for surface diffraction and use this technique for identification of weathering products.

In order to determine significant differences between museum grade pyrite and the sulfur ball material, measurements of the surface area and pore volume distribution of both materials were made. Surface Area was determined using the method of Brunauer, Emmett, and Teller. The pore volume distribution was obtained using nitrogen desorption and the method of calculation presented in Orr and Dallavalle (22). The specific surface of museum grade pyrite in the size range from 60 to 150 mesh to the inch was found to be \(0.12 \pm 0.01\) square meters per gram, and that of the sulfur ball material in the same size range to be \(1.12 \pm 0.02\) square meters per gram.

The pore volume distributions of the two materials are presented in Figure XXIV on the next page, as the change in pore volume per unit change in pore radius in cc./\(\AA^0\) versus the pore radius in \(\AA\). The curves show a much larger total pore volume for the sulfur ball material, and a fairly flat distri-
FIGURE XXIV - PORE VOLUME DISTRIBUTION OF MUSEUM GRADE PYRITE & SULFUR BALL

Change in pore volume in cubic centimeters per gram per unit change in pore radius in Angstroms (x10^5)

0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
Pore radius in Angstroms

SULFUR BALL MATERIAL

MUSEUM GRADE PYRITE
bution of pore volumes, except near the lower limit of detection around 25 Angstrom radius.

The greater surface area and pore volume of the sulfur ball material as predicted from its structure definitely will account to some extent for its greater reactivity, assuming the rate controlling step to be heterogeneous.

As no determination has been made of whether the limiting factor in the oxidation process is physical or chemical, a set of runs was made on the Warburg Respirometer apparatus at the Water Resources Center, varying the environment of the sample. Runs were made at 20, 30, and 40 degrees Centigrade, with the pyritic material immersed in solution or in a controlled humidity environment. Of those samples immersed in solution, some were agitated slowly, some at a faster rate, and some not at all. The solutions used are shown in Table 6 along with their effects on the rate of oxygen absorption. Samples were run with air, and with oxygen as the atmosphere. Those samples run with air were periodically flushed with fresh air to keep the partial pressure of oxygen constant throughout the run. "Sulfur ball" material (Sample No. 5) of size range from 60 to 150 mesh was used for all runs unless otherwise indicated. The results of varying temperature, agitation, and atmosphere are shown in Table 5. Where duplicate or triplicate runs were made, three
TABLE 5  
EFFECTS OF TEMPERATURE, AGITATION, AND ATMOSPHERE ON THE RATE OF  
OXYGEN ABSORPTION OF SULFUR BALL MATERIAL  

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Immersed or 96% Humidity</th>
<th>Agitation</th>
<th>Atmosphere O₂ or Air</th>
<th>Rate of Oxidation *</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>96% H</td>
<td>None</td>
<td>Oxygen</td>
<td>67, 73.7</td>
</tr>
<tr>
<td>30</td>
<td>96% H</td>
<td>None</td>
<td>Oxygen</td>
<td>154</td>
</tr>
<tr>
<td>40</td>
<td>96% H</td>
<td>None</td>
<td>Oxygen</td>
<td>292</td>
</tr>
<tr>
<td>20</td>
<td>Immersed</td>
<td>None</td>
<td>Oxygen</td>
<td>33.0, 33.1</td>
</tr>
<tr>
<td>30</td>
<td>Immersed</td>
<td>None</td>
<td>Oxygen</td>
<td>36.5</td>
</tr>
<tr>
<td>40</td>
<td>Immersed</td>
<td>None</td>
<td>Oxygen</td>
<td>90.0</td>
</tr>
<tr>
<td>20</td>
<td>96% H</td>
<td>None</td>
<td>Air</td>
<td>25.0, 28.7</td>
</tr>
<tr>
<td>30</td>
<td>96% H</td>
<td>None</td>
<td>Air</td>
<td>52, 57.6</td>
</tr>
<tr>
<td>40</td>
<td>96% H</td>
<td>None</td>
<td>Air</td>
<td>86.2</td>
</tr>
<tr>
<td>20</td>
<td>Immersed</td>
<td>None</td>
<td>Air</td>
<td>4.3, 10, 6.8</td>
</tr>
<tr>
<td>30</td>
<td>Immersed</td>
<td>None</td>
<td>Air</td>
<td>12.9</td>
</tr>
<tr>
<td>40</td>
<td>Immersed</td>
<td>None</td>
<td>Air</td>
<td>35.0</td>
</tr>
<tr>
<td>20</td>
<td>Immersed</td>
<td>Fast</td>
<td>Oxygen</td>
<td>33.0, 33.1</td>
</tr>
<tr>
<td>20</td>
<td>Immersed</td>
<td>None</td>
<td>Air</td>
<td>4.3, 10, 6.8</td>
</tr>
<tr>
<td>30</td>
<td>Immersed</td>
<td>None</td>
<td>Oxygen</td>
<td>36.5</td>
</tr>
<tr>
<td>30</td>
<td>Immersed</td>
<td>Slow</td>
<td>Oxygen</td>
<td>130</td>
</tr>
<tr>
<td>30</td>
<td>Immersed</td>
<td>Fast</td>
<td>Oxygen</td>
<td>179</td>
</tr>
<tr>
<td>30</td>
<td>Immersed</td>
<td>None</td>
<td>Air</td>
<td>12.9</td>
</tr>
<tr>
<td>30</td>
<td>Immersed</td>
<td>Slow</td>
<td>Air</td>
<td>34.8</td>
</tr>
<tr>
<td>30</td>
<td>Immersed</td>
<td>Fast</td>
<td>Air</td>
<td>57.4</td>
</tr>
<tr>
<td>40</td>
<td>Immersed</td>
<td>None</td>
<td>Oxygen</td>
<td>90.0</td>
</tr>
<tr>
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<td>Immersed</td>
<td>Fast</td>
<td>Oxygen</td>
<td>219.0</td>
</tr>
<tr>
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<td>Immersed</td>
<td>None</td>
<td>Air</td>
<td>35.0</td>
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<td>Immersed</td>
<td>Fast</td>
<td>Air</td>
<td>71.2, 83.2</td>
</tr>
</tbody>
</table>

*Micrograms of Oxygen per gram of sample per hour
TABLE 6

EFFECT OF SOLUTION COMPOSITION ON THE RATE OF OXIDATION OF
IMMERSED SAMPLES OF SULFUR BALL MATERIAL

All samples are run at 30°C, immersed in the solution, agitated slowly, and kept under an atmosphere of Oxygen.

<table>
<thead>
<tr>
<th>SOLUTION</th>
<th>RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled Water</td>
<td>130</td>
</tr>
<tr>
<td>.001 N Sulfuric Acid</td>
<td>160, 198, 201</td>
</tr>
<tr>
<td>.01 N Sulfuric Acid</td>
<td>152, 224, 228</td>
</tr>
<tr>
<td>.1 N Sulfuric Acid</td>
<td>143, 197, 195</td>
</tr>
<tr>
<td>.001 N Ferric Sulfate, .1N Sulfuric Acid</td>
<td>140, 145, 178</td>
</tr>
<tr>
<td>.01 N Ferric Sulfate, .1N Sulfuric Acid</td>
<td>145, 191, 194</td>
</tr>
<tr>
<td>.1 N Ferric Sulfate, .1N Sulfuric Acid</td>
<td>133, 202, 163</td>
</tr>
<tr>
<td>.01 N Sodium Hydroxide</td>
<td>131</td>
</tr>
<tr>
<td>.02 N Sodium Hydroxide, .01 N Sodium Bicarbonate</td>
<td>131</td>
</tr>
<tr>
<td>.01 N Copper Sulfate</td>
<td>99.2</td>
</tr>
<tr>
<td>.01 N HCl, .01 N Ferric Chloride</td>
<td>111</td>
</tr>
<tr>
<td>.01 N HCl, .1 N Ferric Chloride</td>
<td>117</td>
</tr>
</tbody>
</table>

TABLE 7

COMPARISON OF MUSEUM GRADE PYRITE AND SULFUR BALL MATERIAL

(Same conditions as in Table 6, immersed in water)

<table>
<thead>
<tr>
<th>Material</th>
<th>RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur Ball Material</td>
<td>130</td>
</tr>
<tr>
<td>Museum Grade Pyrite</td>
<td>4.95, 4.00</td>
</tr>
</tbody>
</table>

54
or four figures are shown for the rate. All rates are in micrograms of oxygen absorbed per gram of sample per hour.

In all cases, increasing temperature increased the reaction rate. However, only in those samples which were not immersed in solution, but kept in an atmosphere at 96% humidity, was a ten degree temperature coefficient of two approached, indicating the possibility of a chemically controlled process. In all cases where the sample was immersed, the coefficient was variable and less than two, indicating a physical regime.

Those samples kept in a 96% humidity environment reacted faster than those immersed in solution, all other factors remaining the same. The degree of agitation of the immersed samples had a large effect on the rate of oxygen consumption. The use of air instead of oxygen as the atmosphere over the sample, decreased the reaction rate by a factor between two and three rather than the predicted value of five for a controlling reaction which is first order in oxygen.

Although the reproducibility of the results on variation of solution composition is not good, it appears that the rate of oxygen consumption is greater in sulfuric acid solution, but decreased by the presence of ferric ion. Qualitative tests on the solutions remaining after oxidation showed only ferrous iron present. The presence of a base appears to have no effect on
the rate, as the rates are the same for water and the two basic runs. Chloride ion appears to slow the reaction somewhat, and copper to a greater extent.

Table 7 shows a twenty to thirty fold increase in the reaction rate of sulfur ball over museum grade pyrite of the same size range.

In all runs, except those with the addition of sulfuric acid, the rate of oxygen consumption remained constant with time. In the runs with sulfuric acid, the rates began to decrease at about 60 to 100 hours, and appeared to become constant again at a lower valve after a 50 to 50 hour interval. Figure XXV on the next page shows this effect using Run No. 21 (0.001 N Sulfuric Acid) as an example and compares it with Run No. 10 (same conditions but with water).
FIGURE XXV
EFFECT OF SULFURIC ACID ON WARBURG OXIDATION CURVE
DISCUSSION OF RESULTS

The results obtained in this experimental work tend to
clear up several of the points of conflict in preceding work.
The X-Ray analyses of samples of pyritic materials from various
Ohio coal beds show all but a very few in different areas of
the #6 coal bed to be essentially pure pyrite. Of the exception-
al samples, all contained no more than 30% marcasite mixed with
pyrite, and all were from the same general locality. This defi-
nitely indicates that the great majority of sulfuri tic material
responsible for acid formation is pyrite rather than marcasite.
Therefore the major amount of experimental work should be done
using pyrite only, since the contribution of marcasite at least
as the starting material, to the overall problem is not sig-
nificant.

The chemical analysis of the sulfur ball (Sample No. 5)
showed no significant amounts of any material which could con-
ceivably catalyze the oxidation reaction. The excess of iron
over that required for pyrite and soluble sulfates is probably
accounted for by the presence of iron and aluminum silicates.
The relatively large amount of carbon found indicates the
presence of organic matter, probably included coal.

The initial Warburg studies showed faster rates of oxida-
dation for "sulfur ball" and material extracted from coal,
shale, and sandstone than for either museum grade pyrite or marcasite. Since all samples were of the same screen fraction, this indicates a considerable difference in the properties of the materials. All samples studied, however, with the exception of the museum grade marcasite itself were found to be pyrite.

The photographs taken of polished and etched surfaces of pyrite, marcasite, and sulfur ball show an immediate difference. Both the pyrite and marcasite show a uniform surface, apparently homogeneous, although with a number of cracks and fissures. The "sulfur ball", however shows random size pieces of pyrite (light material) interspersed with a dark material, probably coal. There is no regularity to the shape of the pyritic material, indicating that no exterior crystal forms are present. The wide distribution of sizes of pyrite particles indicates a microcrystalline conglomerate, rather than well developed crystals as in the case of the "museum grade" materials. There is a possibility of a number of unfilled cavities between the pyrite particles, giving the material a porous structure. This evidence is strengthened by the data on pore volume distribution.

The photographs showing the progress of oxidation indicate a similarity between the samples of pyrite and sulfur ball. The first evidence of weathering is the formation of a pattern of small spots on the surface. On the museum grade pyrite
sample, these first form along the crack and polishing marks, indicating that areas which have been subjected to stress may be more reactive than other areas, possibly due to dislocations or deformation of the lattice near the surface. On the "sulfur ball" sample, weathering again appears as a pattern of spots on the surface of the pyritic material, but this time the pattern is random and does not appear to be related to any other surface features.

Oxidation products appeared on the sulfur ball surface considerably faster than on the museum grade pyrite surface. Oxidation on the marcasite surface appeared as the formation of an overall coating, rather than as spots, but proceeded at a rate considerably more rapid than on the pyrite.

The electron micrographs of replicas of the "sulfur ball" surface again appear to indicate a structure of microcrystalline conglomerate of pyrite interspersed with another material.

The surface area and pore volume distribution data on museum grade pyrite and "sulfur ball" show a very significant difference between the two materials. The surface area of "sulfur ball" is roughly ten times as great as that of pyrite and the total pore volume considerably greater, bearing out the proposed porous structure of this material. As later data shows, the "sulfur ball" was twenty to thirty times more reactive than
the museum grade pyrite under the same conditions. Therefore the greater reactivity of the former can be partially, but not totally attributed to the greater specific surface. No investigation was made of the effect on the reaction, of organic materials, particularly humic acids and humus material found in coals. All indications point to the presence of considerable amounts of coal in "sulfur ball", and a great deal of the pyritic material responsible for acid formation is included in coal and shale. For these reasons, an investigation of the effects of these materials on the rate of reaction of pyrites might be worthwhile.

The second set of runs on the Warburg Respirometer gives a number of indications about the nature of the controlling mechanism. With the exception of the first set of data in Table 5, run with pure oxygen at 96% humidity, the reaction rate increases, but does not double with a ten degree rise in temperature. Only for this one set, does it double. For most simple chemical reactions, a ten degree temperature coefficient of two is obtained.

Agitation had a profound effect on those samples immersed in water or other solutions. The amount of water used was just enough to cover the material. When the samples were agitated, pyritic material was periodically exposed to the atmosphere in the flask.
Finally, the variation in rate of oxygen uptake with partial pressure of oxygen was considerably less than expected. Using air instead of oxygen should decrease the reaction rate by a factor of five. In these experiments, it was decreased by an amount of from two to three.

These three facts tend to indicate that the regime of the controlling mechanism is physical rather than chemical. Two possible limiting mechanisms then may be proposed. The first is diffusion of oxygen to the surface, and the second is diffusion of product away from the surface, making a fresh surface available for reaction.

The reaction was found to proceed at a faster rate in the presence of sulfuric acid, but did not vary significantly over a pH range from 3.0 to 1.0. In this range, iron salts are readily soluble and tend to remain in the ferrous state unless a stronger oxidizing agent than oxygen is added. The lack of reproducibility of results in those runs with ferric sulfate added makes it impossible to evaluate its effect on the reaction. However, qualitative tests on the solutions after oxidation runs showed no ferric iron to be present. This indicates that it probably reacted with the pyrite as previous experimenters have found. The total amount of ferric iron added was not enough to make a significant change in the total oxygen uptake.
Iron tends to oxidize to the ferric state and hydrolyse to form hydrated ferric oxides at pH values greater than 4.0. These could conceivably form a coating on the surface of the pyrite and clog the pores, slowing diffusion and making less surface available for reaction. This may account for the faster rates of reaction at pH values less than 3, and the fact that the presence of base and carbonate did not slow the reaction beyond the point of 130 micrograms of oxygen per gram sample per hour which was the speed in distilled water.

Another difference in the reaction occurs in the presence of sulfuric acid. After a period of about 100 hours of reaction, the rate begins to slowly decrease, and after another 30 to 50 hours becomes fairly constant at a somewhat lower rate. It may be postulated from this that iron salts may be slightly less soluble in sulfuric acid due to the common ion effect and tend to crystallize in the pores, partially clogging them, and making less surface available for reaction. This is in agreement with work by Nelson, Snow, and Keyes (21).

Both cupric ion and HCl decreased the reaction rate, but until further investigation with different concentrations of these materials is made, no evaluation of this fact can be made.

The data obtained in this project and that of other workers indicate a possible sequence in the weathering process of the
following type:

1. Diffusion of oxygen to the surface and into cracks and pores through an adsorbed or condensed film of water.
2. Adsorption of oxygen on the surface of the pyrite.
3. At this point, the initial chemical reaction takes place.

This is a heterogeneous reaction between pyrite and adsorbed oxygen and has been stated in the following ways by previous workers:

\[
\begin{align*}
\text{a} & \quad \text{FeS}_2 + 3\text{O}_2 = \text{FeSO}_4 + \text{S}_2 \quad (4,6) \\
\text{b} & \quad \text{FeS}_2 + 2\text{O}_2 = \text{FeS} + \text{SO}_2 \quad (26) \\
\text{c} & \quad \text{FeS}_2 + 2\text{O}_2 = \text{FeSO}_4 + \text{S} \quad (16) \\
\text{d} & \quad \text{FeS}_2 \cdot \text{O}_2 + \text{O}_2 (\text{aq}) = (\text{FeS}_2 \cdot 2\text{O}_2)^* + \text{FeSO}_4 + \text{S}^0 \quad (17) \\
\text{e} & \quad 2\text{Fe}^{+3} + \text{FeS}_2 = 3\text{Fe}^{+2} + 2\text{S}^0 \quad (25,26)
\end{align*}
\]

With the exception of "b" and "e" above, all reactions appear to be complex and could be composed of two or more steps of differing rates. Reaction "b" was discounted by Sato (24) who derived from his measurements of single electrode potentials that the iron is first to react, going into solution as Fe\(^{+2}\), and S\(_2\) molecules being released as follows:

\[
\text{FeS}_2 = \text{Fe}^{+2} + \text{S}_2 + 2\text{e} \quad (21)
\]

At the moment, the reactions proposed by Sato seem the simplest
and most plausible. Attempts were made by the author to duplicate some of this work and extend it, but until equipment and techniques are perfected, no evaluation can be made of these measurements.

This mechanism, and the fact that both the data of the author and of previous workers indicates that a reaction similar to "e" takes place, indicate that as long as the solution containing products remains in contact with the pyrite, only ferrous iron salts will be formed.

4. $S_2$ molecules are very unstable and would be quickly oxidized to sulfate ion at the pH and oxidation potentials normally encountered in mines, this accounting for the absence of sulfur as an intermediate.

$$S_2 + 3O_2 = 2SO_3 = (\text{in solution}) 2SO_4^{2-}$$

5. After reaction, the products diffuse out of the pores and away from the surface into the bulk of the solution. This may be complicated by iron hydroxide formation at the surface under unusually basic conditions, or the formation of iron sulfate salts on the surface and in pores under the right concentrations of sulfate ion and ferrous ion.

6. As the bulk solution leaves the reaction site, and eventually the mine, it becomes diluted with fresh water, thus lowering the acidity, and aerating the solution. Both of these con-
citions cause hydrolysis to hydrated ferric oxides and sulfuric acid which are commonly found in streams in areas of heavy acid formation.

Present results indicate that either steps 1 or 6 may be controlling, and could very well be interrelated. If the controlling mechanism is definitely shown to be physical, then the method of determining the initial chemical reaction will have to be independant of these diffusion limitations. At present, accurate electrode potential measurements seem to be the best method for confirming this hypothesis.
WORK IN PROGRESS

As this project will be continuing it might be well to note the work presently in progress and which will be completed in the near future before proceeding to make recommendations.

The Warburg studies are being continued. Runs will be made with the addition of various bacteria known to have definite effects on iron and sulfur oxidation. Single crystals of pyrite with definite faces exposed are presently being run, in order to determine whether or not a given crystal face is more reactive than another. Samples of museum grade pyrite and marcasite and of sulfur ball of different mesh sizes are being run to determine accurately the effect of surface area. In addition, a set of runs at 100°C is being made.

Electron microscope work is being continued with emphasis on surface diffraction techniques. For this purpose, samples of various types of pyritic material are being weathered under accelerated conditions, in order to form a relatively thick coating of products. With this technique, it may be possible to detect the presence of small amounts of intermediate materials.

Potential measurements based on the techniques of Sato (24) are being made, but as yet no significant data has been obtained. When the experimental difficulties are eliminated, different
faces of single pyrite crystals will be used as electrodes, and the free energies of reaction determined for the various faces. In addition a more intensive investigation of the effects of solution composition on the reaction will be made. From these data, the initial surface reaction may be derived, even though the controlling mechanism may be physical.
CONCLUSIONS

1. The great majority of sulfuric material found near coal seams and responsible for acid mine drainage is pyrite rather than marcasite.

2. "Sulfur ball" and extracted pyritic materials from coal and surrounding strata appear to be a microcrystalline conglomerate of pyrite in small pieces cemented together with another material, probably coal.

3. The more rapid oxidation of "sulfur ball" material and pyrites from coal beds as compared to museum grade pyrite is due partially to the larger surface area and more porous structure of the former.

4. From observation of micrographs of oxidized material, oxidation appears to be initiated at certain "active" sites, which could be pores, dislocations, areas of stress, or certain crystal faces.

5. The oxidation of pyritic material submerged in solution appears to be a physically rather than chemically controlled process. Diffusion of oxygen to the reaction site and diffusion of products away from the surface may be limiting factors.
RECOMMENDATIONS

1. Determine further the effects of varying partial pressure of oxygen on the rate of oxidation.

2. Definitely isolate the various strains of iron and sulfur oxidizing bacteria and then determine which strains accelerate the oxidation of pyrite. This could lead to the mechanism of the chemical reaction as well as to possible methods of inhibition.

3. Determine what effects if any the various organic materials found in coal have on the rate of oxidation, especially humic acid and humus material.

4. Continue surface diffraction studies on samples weathered under various conditions to determine the type of intermediates produced.

5. Use the "electron probe" where possible to examine the surface of pyritic materials before and during oxidation to detect and determine the nature of "active sites", and initial oxidation products.
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