THE EFFECT OF WATER CONCENTRATION ON VAPOR PHASE OXIDATION OF PYRITE

A Thesis

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by

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STATEMENT AND SCOPE OF THE PROBLEM

This experimental work was devoted to the study of the sulfide-to-sulfate reaction mechanism in vapor phase.

Iron sulfide composing "sulfur ball" was oxidized in the range 70 and 95°F. The humidity in the system was varied from 0 to 0.032 lb. water vapor per lb. dry air.

INTRODUCTION

The acid mine drainage problem and importance of preventing it have been emphasized by many scientists. The natural condition under which oxidation occurs and basic aspects of formation of acid are well known. According to Moulton (1) most researchers have adopted five basic procedures to solve the pollution problem:

1. Disrupting acid production by eliminating one of the fundamental components,
2. Reclamation of the acid,
3. Dilution of the acid,
4. Physical treatment of the polluted stream,
5. Biological treatment.

But the fundamental problem was not solved.

Brant and Moulton (2) described the acid production in various coal mining areas. The general over-all reaction and end products has been defined as:

$$2FeS_2 + 7O_2 + 2H_2O = FeSO_4 + H_2SO_4$$

This reaction occurs on the surface of sulfuritic material naturally present in coal mining areas. After the oxidation is initiated and the acid is formed on the surface of sulfur bearing materials, natural water transports the products to the stream system. The acid solution from a mine contains ferrous sulfate. When it leaves the mine and is diluted by other waters, the ferrous iron is oxidized to the ferric state by dissolved oxygen, and forms hydrous iron oxides. For the above over-all reaction several mechanisms have been proposed. However, the actual mechanism has not yet been established.

RELATED LITERATURE

Acid mine drainage that is responsible for water pollution has been studied by many scientists for the past fifty years. Based on basic and applied science, chemical methods to determine mine drainage quality and prevent stream pollution are presented by Cook (5) and Hert (6). Moulton (1) presents a diagram of "Acid Production Cycle," which explains the manner of stream pollution.

It is clear that sulfuric acid is formed when sulfuritic materials are exposed to air in the presence of moisture. The end products and over-all reaction of acid formation is generally given:

$$2FeS_2 + 7O_2 + 2H_2O = FeSO_4 + H_2SO_4$$

One of the first studies, oxidation of pyritic sulfur in coal mines, was made by Burke and Down (7). They used iron disulfide from "sulfur ball," obtained from coal strata, and found out it was ten times as reactive as either synthetic or natural occurring marcasite and pyrite. The apparatus for determinating reaction rate was designed to control the amount of surface exposed, oxygen concentration, concentration of solution, temperature of the system, reduction of liquid film thickness on the surface, and measurement of the amount of oxidation at the end of a certain time period. They observed the effectiveness of the following variables and reported:

1. Hydrogen ion concentration: seemed simply to prevent the inhibition of the reaction caused by the formation of hydroxide films.

2. Oxygen concentration: as the reaction progresses neither the rate at which the oxygen was supplied, nor the concentration, nor the partial pressure of the oxygen had any detactable effect on the rate of reaction until the oxygen was completely excluded from the system.

3. Relative motion of solid and solution: the speed of revolution of the cube in the solution had no effect.

4. Ferrous ion concentration: no detactable effect on the rate of reaction was observed with concentration of ferrous ion as great as 1 N.

5. Sulfate concentration: the substitution of sulfuric acid decreases the reaction rate and at a concentration of 1 normal the reaction rate stopped.

6. Temperature: rate of oxidation was increased with increasing temperature between 0^o - 140^oC but it is not linear.

They proposed a hetrogeneous reaction mechanism which occurs on pyritic surface. The iron sulfide reacts with dissolved oxygen from the solution to give ferrous sulfate and sulfur dioxide, and sulfur dioxide forms sulfuric acid by addition of oxygen and water.

$$FeS_2 + 3O_2 = FeSO_4 + SO_2 \tag{1}$$

$$2SO_2 + O_2 + H_2O = 2H_2SO_4 \tag{2}$$

The first reaction, formation of sulfur dioxide, was assumed to be extremely slow compared to the second reaction. They continued their experiments with dry oxygen and concluded the amount of reaction obtained with pure dry oxygen was considerably less than the amount produced by a saturated solution of air in water at the same condition.

The weathering of pyrite was studied by Mapstone (8). He used a half gram of 72 mesh pyrite with peroxides, produced from naphthalenic gasoline. Essentially it was the continuation of Burke and Downs experiment. Based on these experiments the following scheme was suggested.

1. Oxygen absorbed or chemisorbed on the pyrite surface can be eliminated as sulfur dioxide in the presence of moisture,

$$FeS_2 + O_2 = FeS + SO_2$$

2. The reactive ferrous sulfide can be directly oxidized to sulfate,

$$FeS + 2O_2 = FeSO_4$$

3. The sulfur dioxide is oxidized to sulfuric acid,

$$2SO_2 + O_2 + H_2O = H_2SO_4$$

4. Interaction of ferrous sulfide with the sulfuric acid would liberate hydrogen sulfuide,

$$FeS + H_2SO_4 = FeSO_4 + H_2S$$

5. Interaction of this hydrogen sulfide with sulfur dioxide would give free sulfur,

$$2H_2S + SO_2 = 2S + 2H_2O$$

He found all the intermediates present.

The rate of oxidation of various mesh sizes of museum grade pyrite, marcasite, and sulfur ball in water were investigated by Braley (9). For the analytical part, pH, acidity, iron, calcium, and sulfate were varied and calculated on the basis of mole per million parts of water. He proposed the following equation.

$$FeS_2 + 3\frac{1}{2} O_2 + H_2O = FeSO_4 + H_2SO_4$$

The ferrous sulfate reacts with water to produce ferrous hydroxide and sulfuric acid.

$$FeSO_4 + 2H_2O = Fe(OH)_2 + H_2SO_4$$

Or it may oxidize to ferric sulfate in the presence of H_2SO_4,

$$2FeSO_4 + H_2SO_4 + \frac{1}{2} O_2 = Fe_2(SO_4)_3 + H_2O$$

$Fe_2(SO_4)_3$ will further react with water to give $Fe(OH)_3$

$$Fe_2(SO_4)_3 + 2H_2O = Fe(OH)_3 + H_2SO_4$$

Le and Parr (10) studied the oxidation of pyrite as a factor in the spontaneous combustion of coal piles. Sample of high sulfur coal, marcasite, and pyrite were reacted with oxygen saturated with water between 25° and 100°C. The rate of oxidation was determined by measuring the increase of sulfate content before and after the oxidation. They concluded:

1. Pyrite will oxidize rapidly and may be a dominating factor in self-heating of coal.
2. The oxidation rate of marcasite and pyrite are the about same but the former breaks down more easily, producing fine particles, thus facilitating oxidation.
3. The rate of oxidation is directly proportional to temperature and inveresly proportional to the diameter of the particle.
4. Dry air or oxygen does not promote the oxidation of pyrites.
5. High textural moisture seems to be accompanied by rapid oxidation of pyrite.

A kinetic study of oxidation of pyrite in aqueous suspension by molecular oxygen, at temperatures between 100° and 130°C, was described by McKay and Halpern (11). They found that the over-all rate of oxidation was proportional to the pyrite surface area, first order in respect to oxygen partial pressure, and independent of the composition of the solution. They found the oxidation of pyrite yields only ferrous sulfate, ferric sulfate, sulfuric acid, and elemental sulfur. Sulfur products of intermediate oxidation state, such as thiosulfate or thionates, were not detected, except hydrogen sulfide only when oxygen was absent. They suggested the following reaction mechanism.

$$FeS_2 + 2O_2 = FeSO_4 + S \tag{1}$$

$$FeS_2 + 7O_2 + H_2O = 2FeSO_4 + H_2SO_4 \tag{2}$$

Sulfuric acid might decompose pyrite without the involvement of oxygen,

$$FeS_2 + H_2SO_4 = FeSO_4 + H_2S + S \quad (3)$$

Thus oxygen can oxidize hydrogen sulfide

$$2H_2S + O_2 = 2H_2O + 2S \quad (4)$$

$$H_2S + 2O_2 = H_2SO_4 \quad (5)$$

Ferric sulfate is formed by oxidation of ferrous sulfate

$$4FeSO_4 + O_2 + 2H_2SO_4 = 4Fe(SO_4)_{1.5} + 2H_2O \quad (6)$$

Then ferric sulfate contributes to the oxidation

$$FeS_2 + 8Fe(SO_4)_{1.5} + 4H_2O = 9FeSO_4 + 4H_2SO_4 + S \quad (7)$$

$$FeS_2 + 14Fe(SO_4)_{1.5} + 8H_2O = 15FeSO_4 + 8H_2SO_4 \quad (8)$$

$$H_2S + 2Fe(SO_4)_{1.5} = 2FeSO_4 + H_2SO_4 + S \quad (9)$$

$$H_2S + 8Fe(SO_4)_{1.5} + 4H_2O = 8FeSO_4 + 5H_2SO_4 \quad (10)$$

The elemental sulfur may be oxidized further to give sulfuric acid

$$2S + 3O_2 + 2H_2O = 2H_2SO_4 \quad (11)$$

$$S + 6Fe(SO_4)_{1.5} + 4H_2O = 6FeSO_4 + 4H_2SO_4 \quad (12)$$

The above possible series of kinetic equations are very complex but investigation showed equations (3) (4) (5) (7) (8) (9) and (10) do not contribute much to the over-all oxidation of pyrite, though they undoubtedly occur. Reaction (6) is fairly slow at 100°C and oxygen partial pressure of 3 atm. They found the reaction is second order with respect to $FeSO_4$ and first order in oxygen as expressed:

$$\frac{d\left[Fe(SO_4)_{1.5}\right]}{dt} = \frac{-d\left[FeSO_4\right]}{dt} = k_1\left[FeSO_4\right]^2 \cdot P_{O_2}$$

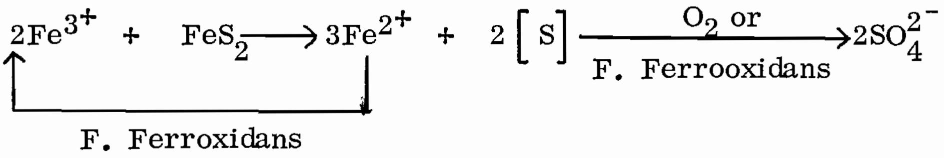
Integration yields

$$\frac{1}{\left[FeSO_4\right]} - \frac{1}{\left[FeSO_4\right]_o} = k \cdot P_{O_2} \cdot t$$

where P_{O_2} represents partial pressure of oxygen, and $FeSO_4$ is the initial $\left[FeSO_4\right]_o$ concentration.

Since P_{O_2} is constant throughout the experiment, the equation is linear. For different pressures of oxygen the experimental data showed a linear increase in rate with partial pressure of oxygen. Based on their experiments, change of stirring rate had no effect on the reaction. The reaction appeared to be a hetrogeneous process on the pyrite surface.

There were several studies made to determine the role of bacteria (12, 13, 14, 15, 16) on pyrite oxidation. One of the works was done by Silverman, Rogoff, and Wender (17) on bacterial action, which was most effective with small particle sizes of pyrite in coal. They found it was Ferrobacillus Ferrooxidans that accelerated the pyrite oxidation. Thiobacillus Thiooxidans did not contribute much to the reaction. They offered the following scheme to explain the beneficial effect of ferric sulphate on the bacterial oxidation of pyrite.



$$2Fe^{3+} + FeS_2 \longrightarrow 3Fe^{2+} + 2\left[S\right] \xrightarrow[\text{F. Ferrooxidans}]{O_2 \text{ or}} 2SO_4^{2-}$$

In the absence of bacteria, ferric ions would soon be reduced to the ferrous state. The extent of pyrite oxidation would be limited by the initial ferric ion concentration, since ferrous ions are stable to air oxidation in acid. However, in the presence of bacteria the supply of ferric ions never becomes limiting.

In an experiment by Nelson, Snow, and Keys (18) the rate of oxidation of pyritic sulfur to soluble sulfate sulfur increased with increasing temperature. The experiments made with ferric sulfate added to the coal-water mixture showed that this compound assists materially in the oxidation of pyritic sulfur in suspended coal. They found the rate of sulfate formation was directly proportional to diameter of particle. Since the rate of oxidation slowed as time passed, they suggested it happened because accumulation of ferrous sulfate in the pores of pyrite covered part of the reactive surfaces. They showed when oxygen was substituted for air, there was not much change in the amount of pyritic sulfur oxidized. There was no ferric iron present in any of the solutions after oxidation. Ferric ion was reduced to the ferrous state during the experimental period.

Leaver and Thurston (19) oxidized ferrous sulphate solutions and solutions of sulphur dioxide by blowing with air. They observed the oxidation rates were very slow. However, the oxidation of mixed solution of ferrous sulphate and sulphur dioxide by air was quite rapid. They expressed the following stages of beginning and final products.

$$(1)\quad 2FeSO_4 + SO_2 + O_2 = Fe_2(SO_4)_3$$

$$(2)\quad H_2O + SO_2 + \frac{1}{2}O_2 = H_2SO_4$$

These two reactions take place simultaneously or in the order given, depending on conditions. During the oxidation process, iron is oxidized first, all the sulphur dioxide being used to make the extra sulfate of the ferric sulphate. The percentage of iron present in the solution does not effect the rate of formation of ferric iron and of sulfuric acid up to at least five grams Fe present per liter of solution.

Oxidation mechanism of sulfide minerals at 25°C was observed by Sato (3). He measured the single electrode potentials of sulfide minerals in solutions of different pH and ferrous ion concentrations. He used large crystals of pyrite for the electrode and adopted free energy value by Kelley (20). In dilute solutions of ionic iron with pH value less than 2.0 the following heterogeneous rate controlling mechanism was postulated.

1. $FeS_2 = Fe^{++} + S_2 + 2e$

the potential was described as,

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

In above equation the sulfur is not in crystalline state, but in diatomic molecular form.

2. $FeS_2 + 3H_2O = Fe(OH)_3 + S_2 + 3H^{+} + 3e,$

and $Eh = 0.875 - 0.0591 \text{ pH}$

The probable oxidation step was described for the Fe-S system:

$$(Fe + S^{--}) \longrightarrow (FeS) \longrightarrow \frac{1}{n}(FeS) \longrightarrow \frac{1}{n}(Fe_{n-x}Sn)$$

$$\longrightarrow Fe^{++} + S$$

Sulfur produced above is not stable in presence of free oxygen. It will be oxidized easily to sulfate ion. Solid sulfur is not produced in the case of disulfide of iron, but instead S_2 molecules appear to be released in the solution simultaneously with ferrous ions. Such S_2 molecules are unstable at room temperature and readily oxidize to sulfur species of higher oxidation state.

Redox potential for ferrous-ferric chemical equilibria was measured by Hem and Cropper (21). They stated the amount of iron, Fe^{+++}, $FeOH^{++}$, $Fe(OH)_2^{+}$, Fe^{++}, and $FeOH^{+}$ state, present in natural water was related to the pH and Eh of the solution. At 20°C they figured:

$$Eh = 0.771 = 0.0592 \log \frac{\left[Fe^{+++}\right]}{\left[Fe^{++}\right]}$$

Later Hem (22) reported on pyrite oxidation that if Eh rises to the level expected in aerated water (about 0.40V), any iron dissolved from pyrite will be redopsited as oxide or hydroxide.

Recently Birle (23) studied the sulfide-to-sulfate reaction mechanism in pyritic material. He used many kinds of pyrite and marcasite samples from various areas, and compared the oxidation rates under different experimental conditions. He found significant differences between museum grade pyrite and sulfur ball material by measuring surface area and pore volume distribution of both materials, and determined the oxidation rate relating them. He explained that the more rapid oxidation of "sulfur ball" material compared to museum grade pyrite was due to the larger surface area and more porous structure of the former. And also based on his experiments, he concluded that oxidation appears to be initiated at certain "active sites," which could be pores, dislocations, areas of stress, or certain crystal faces.

DISCUSSION OF LITERATURE

It is generally agreed that the presence of oxygen and moisture are responsible for the oxidation of sulfuritic material and that the over-all reaction has the following form:

$$2FeS_2 + 7O_2 + 2H_2O = FeSO_4 + H_2SO_4$$

However, the intermediate steps, or reaction mechanism, of this pyrite oxidation is not yet clearly explained. Evidently, like other fluid-solid chemical reactions, oxidation rate is a function of temperature and surface exposed. Actual surface area and pore volume distributions have not been thoroughly investigated. A relation between the oxidation and surface area was reported by Birle, but not others. There are few intermediate products reported. Mapstone (8) reported that he found intermediates such as SO_2, H_2S, and FeS.

It is obvious that most experimental work has been done with a liquid phase present. However, Birle (1) noted that the rate of pyrite oxidation in vapor phase is higher than in the liquid phase as Dr. E. E. Smith (author's adviser) indicated in a progress report (not published) to National Institutes of Health (Project WP 00340).

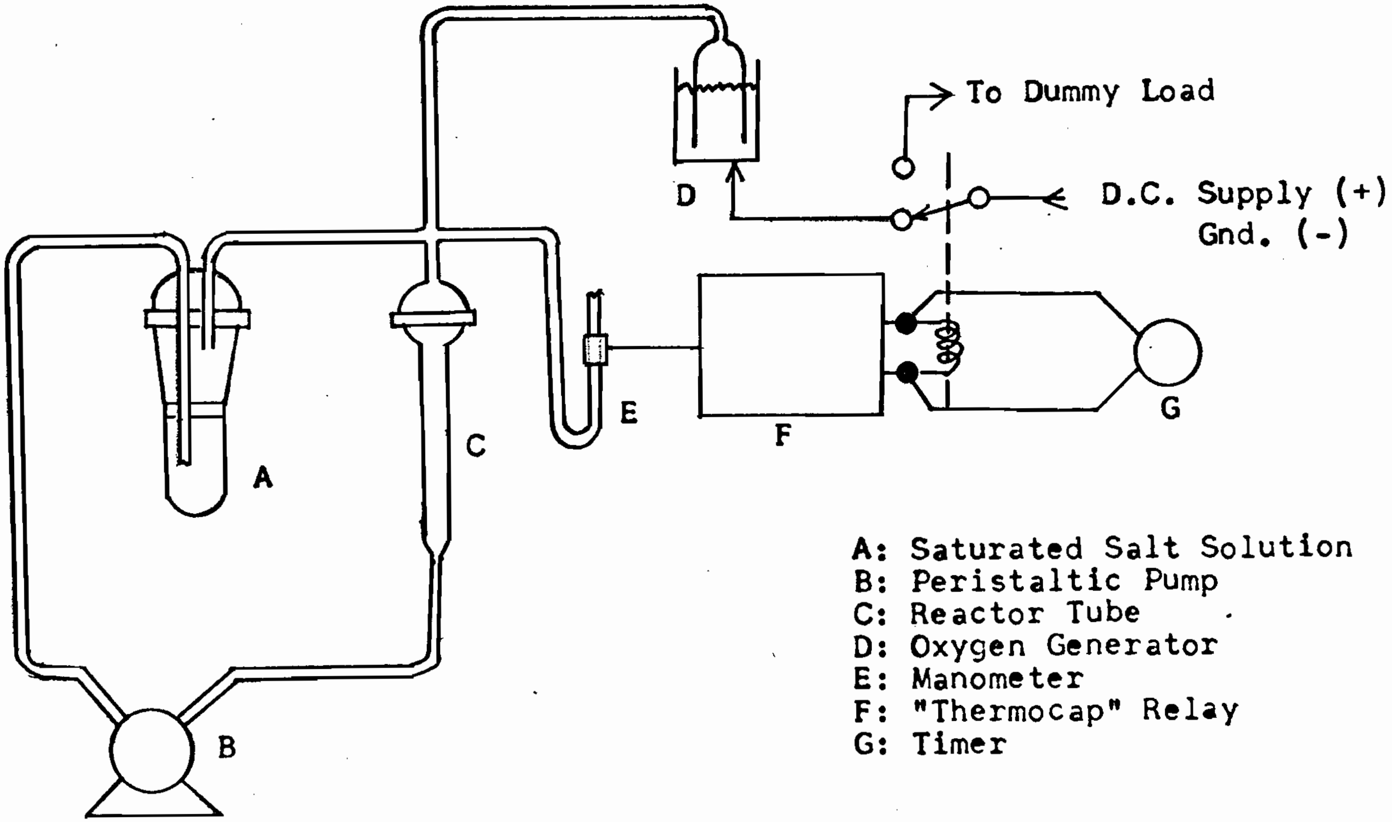
There was no literature concerning vapor phase oxidation of pyrite. It was not even known whether oxidation occurs. It is known that water contributes greatly to the over-all reaction. In view of this, the following experimental works were performed.

EXPERIMENTAL PROGRAM AND EQUIPMENT

Two units of the apparatus described in Figure 1, Page 18, were contained in a constant temperature cabinet. This apparatus was designed to measure the quantity of make-up oxygen required to maintain a constant pressure within the system. Vapor phase was recirculated through the system by a peristaltic pump (B). The humidity of the vapor was maintained by bubbling the recirculating vapor through saturated salt solutions (A). A "Thermo-cap Relay" (F) was used to sense the changing level in the manometer (E), so that when pressure in the system fell below the set-point, an electrolytic cell (D) was energized, supplying oxygen to bring the system pressure back to normal. An electric stop clock (G) was energized along with the electrolytic cell. Knowing the current flow, and total time the electrolytic cell was energized, make-up oxygen supplied could be calculated.

In order to get higher reaction rates, "sulfur ball" pyrite was chosen as a reactant. Samples of "sulfur ball" were obtained by David Stiles, student at The Ohio State University, Department of Mineralogy. He collected various pyrite-containing materials from the Pennsylvanian and Mississippian coal formations of Southeastern Ohio. This "sulfur ball" was treated in the same way as did Birle (23) to obtain over 90% pure pyrite. 70-100 mesh samples were weighed and packed in two reactors the weight of samples were

Figure 1
Vapor Phase Oxidation Apparatus



A: Saturated Salt Solution
B: Peristaltic Pump
C: Reactor Tube
D: Oxygen Generator
E: Manometer
F: "Thermocap" Relay
G: Timer

as follows:

Reactor 1 . . . . 11.78 gram

Reactor 2 . . . . 10.28 gram

The reactor was 13 cm in length and 0.8 cm inside diameter. Before each run, the samples were washed carefully with 250 cc of approximately 15% hydrochloric acid, and rinsed with the same amount of distilled water. The washed samples were dried and stored in a vacuum desiccator.

The concentration of oxygen in the vapor phase was measured by gas chromatograph before and after each experiment. In every experiment there was a 2-3% change in oxygen concentration. Every run was started with near 100% oxygen concentration.

The most sensitive part of these experiments was control of humidity in the system. To maintain a constant humidity, saturated salt solutions were adopted (24). Constant humidity solutions were used in which solubility of the salts increased linearly with temperature rise, so that partial pressure of water vapor could be calculated assuming relative humidity was inversely proportional to the amount of solute dissolved in the solution. Partial pressure of water vapor was calculated from relative humidity by the well-known equation:

$$H_R = \frac{100p}{p_s}$$

where, H_R: % relative humidity

p : partial pressure of water vapor

p_s: vapor pressure of water at that temperature

Then, the absolute humidity could be calculated from the partial pressure:

$$H_a = \frac{p}{(P-p)} \quad \frac{(18.02)}{(28.97)}$$

where, H_a: absolute humidity, lb. water vapor per lb. bone dry air

P: total pressure in the system

Table 1 shows the constant humidity solutions and humidity at the temperatures in the system.

Experimental temperatures ranged between 70-95°F at atmospheric pressure. In these experiments, major variables were temperature and humidity. To determine these effects, a reference temperature, (82°F) and relative humidity, (86%) were chosen. At this condition, the rate of reaction was checked regularly. All calculations were made on the basis of this reference condition. A temperature effect was observed when, at the same humidity but different temperatures, rate of oxidation changed. Two sets of points, point 11 and 16, and point 8 and 21, were observed for this purpose. Each set of data was averaged over a steady state period between 25 and 40 hours continuous run which usually started 2 or 3 hours after experimental run began. The steady state was recognized visually by observing oxygen consumption as a function of time.

A correction for change in atmospheric pressure during the course of a run, was made.

TABLE 1

Solute	Temp. °F	Partial Pressure, inch Hg	H_R	H_a
$BaCl_2 \cdot 2H_2O$	70	0.673	91	0.0146
	82	0.947	86	0.0208
	91	1.219	83	0.0270
	95	1.360	82	0.0302
$CaCl_2 \cdot 6H_2O$	70	0.237	32	0.0051
	82	0.331	30	0.0071
$KC_2H_3O_2$	70	0.146	20	0.0031
	82	0.203	18	0.0043
	91	0.255	17	0.0055
$K_2CO_3 \cdot 2H_2O$	70	0.318	43	0.0068
	82	0.474	43	0.0010
	91	0.631	43	0.0137
	95	0.714	43	0.0155
H_2O	70	0.739	100	0.0161
	82	1.102	100	0.0243
	91	1.467	100	0.0327

STATEMENT OF RESULTS

The following tables present operating conditions and results of experimental runs made during the course of this study.

The data of some runs were omitted from these tables due to the failure of pump tubing or decomposition of constant humidity solution.

TABLE 2-a

Operating Conditions for Reactor 1.

Point No.	Run No.	Temp.	Constant Humidity Solutions Used	H_R	H_a
1	1	82	$BaCl_2$	86	0.0208
3	2	82	$BaCl_2$	86	0.0208
8	8	70	$BaCl_2$	91	0.0146
9	11	70	H_2O	100	0.0161
11	12	82	$BaCl_2$	86	0.0208
13	13	82	$KC_2H_3O_2$	43	0.0102
16	15	95	$BaCl_2$	82	0.0302
18	16	82	$BaCl_2$	86	0.0208
20	17	93	K_2CO_3	43	0.0146
22	21	82	Dehydrite	0	0

TABLE 2-b

Operating Conditions for Reactor 2.

Point No.	Run No.	Temp.	Constant Humidity Solutions Used	H_R	H_a
2	1	82	$BaCl_2$	86	0.0208
4	2	82	$BaCl_2$	86	0.0208
5	4	82	H_2O	100	0.0243
6	6	91	$BaCl_2$	83	0.0270
7	7	91	H_2O	100	0.0327
10	11	70	$CaCl_2$	32	0.0051
12	12	82	$BaCl_2$	86	0.0208
14	13	82	$KC_2H_3O_2$	18	0.0043
15	14	91	$KC_2H_3O_2$	17	0.0055
17	15	95	$BaCl_2$	82	0.0302
19	16	82	$BaCl_2$	86	0.0208
21	22	82	$BaCl_2$	86	0.0208

H_R: % relative humidity

H_a : absolute humidity, lbs. water vapor per lb. dry air

TABLE 3

Results of Experimental Runs.

Point No.	No. of Wash	Oxygen Consumption	After Correction for Wash	After Correction for Temp.
1	0	64	77	77
2	0	68	82	82
3	1	63	76	76
4	1	69	84	84
5	3	91	105	105
6	5	99	110	100
7	6	140	153	139
8	7	63	67	75
9	10	76	77	87
10	10	22	23	25
11	11	90	90	90
12	11	78	78	78
13	12	40	40	40
14	12	25	24	24
15	13	36	35	32
16	14	135	129	112
17	14	139	133	115
18	15	93	87	87
19	15	83	78	78
20	16	97	90	80
21	21	92	79	79
22	-	Approx. 0	Approx. 0	Approx. 0

Oxygen Consumption: microgram O_2 consumed per gram of sample per hour.

Figure 2

O_2 Consumption vs. Absolute Humidity

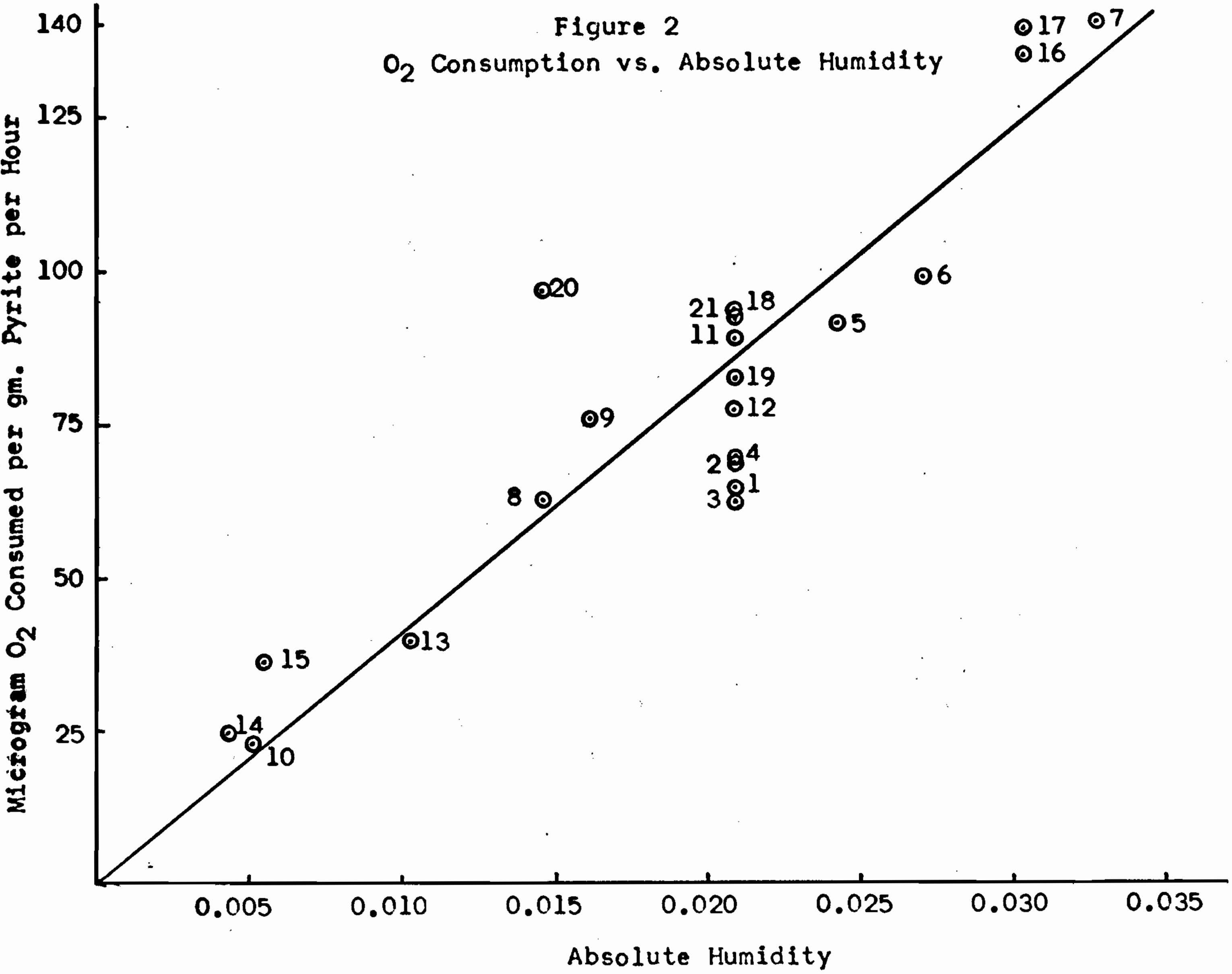


Figure 3

% Change in Rate vs. Number of Wash

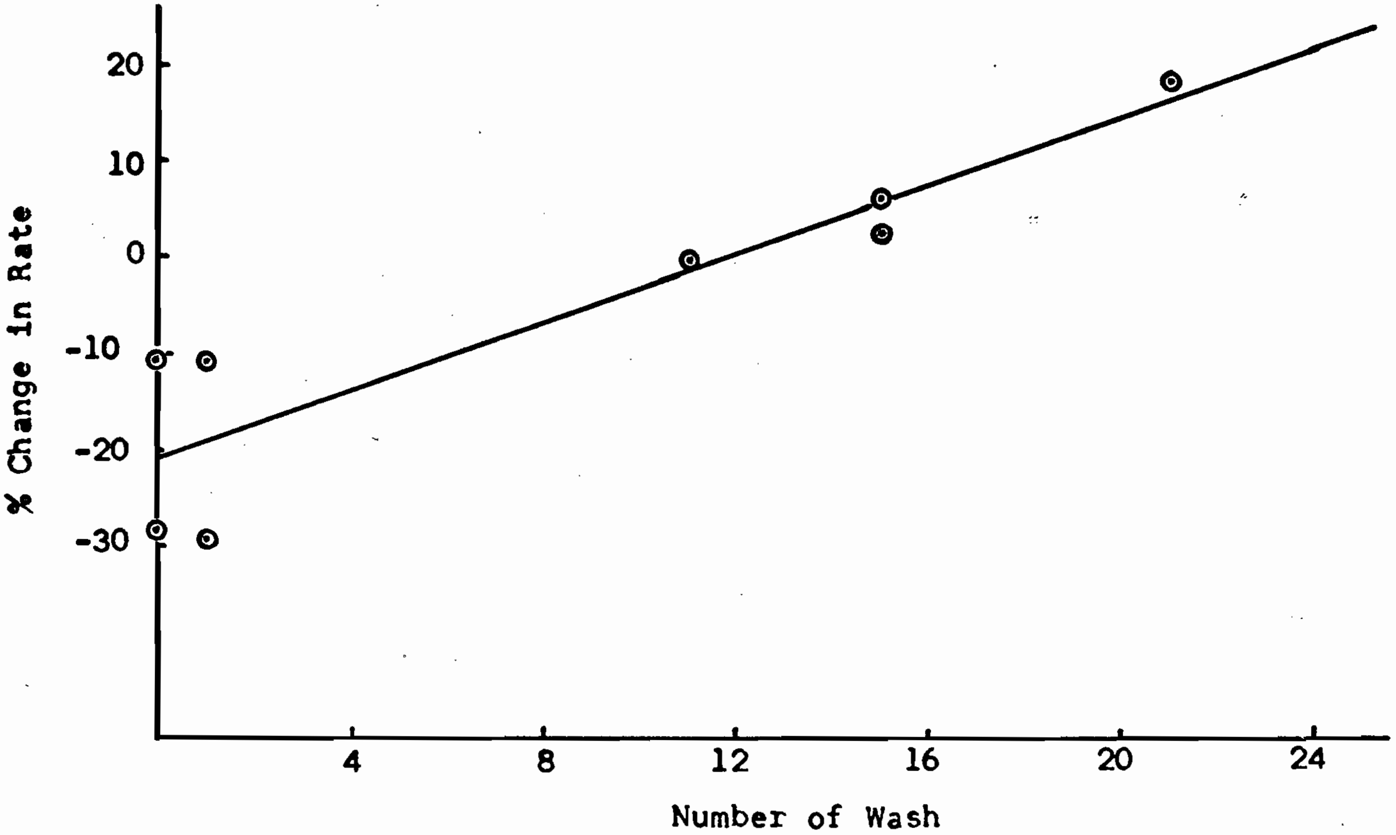
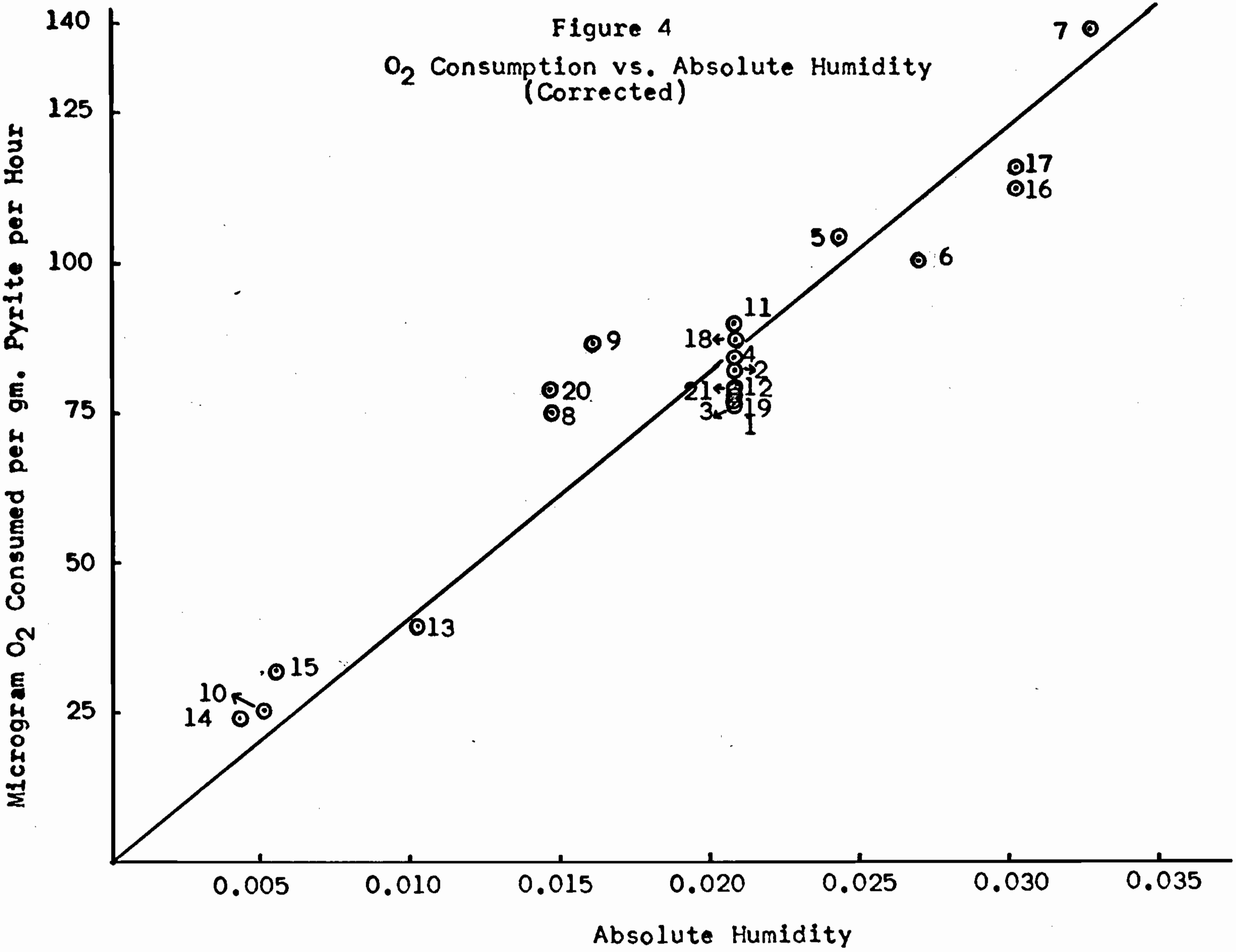


Figure 4

O_2 Consumption vs. Absolute Humidity (Corrected)



DISCUSSION OF RESULTS

From a series of experiments at the reference condition, 82°F and 86% relative humidity, it appeared that the rate of oxidation increased after each run. This increase was linear with respect to number of wash (Figure 3). After each washing an increase in rate of approximately 2% was noted. Nine reference points (point No. 1, 2, 3, 4, 11, 12, 18, 19, and 21) were analyzed using Pearson's least mean square method.

This increasing rate was apparently due to the oxidation reaction on the surface of pyrite. Probably pits were formed on the surface because acid and water soluble materials such as $Fe(OH)_3$, $FeSO_4$, Fe^{++}, Fe^{+++}, and impurities like Mn, Ca, Mg, in the pyrite were gradually eliminated, which provided more surface area.

To observe the effect of temperature, two sets of data were taken. The first set of points were Points 8 and 20. Temperature difference was 23°F but same absolute humidity: 0.0146 lbs. of water vapor per lb. of dry air. At this condition the rate of oxidation was increased approximately 1% per degree F. The other set, Points 10 and 15, showed 1.7% increase per degree F. The above calculations were made after wash-effect correction. All experimental data were corrected first by wash-effect and then by temperature effect so that they could be brought to reference state, 82°F and middle number of experimental runs. Figure 2 shows the scattering of experimental data and Figure 4 is drawn after corrections were made. This result showed the rate of oxidation reaction is first order with respect to water vapor in the system.

One run was made in which pyrite was previous dried in a 100°C oven and instead of a saturated salt solution, "Dehydrite" was put in the bubbler tube. This experiment showed that essentially no oxidation occurs without moisture.

Comparing metal and pyrite oxidation, the former is reported to have the characteristics of galvanic corrosion as described by Tomashov (25). In galvanic corrosion the presence of water is related to the adsorbed water film which fulfills the function of an electrolyte. The adsorbed water film is directly related to equilibrium moisture which is gained by the material that is exposed and kept in a moist atmosphere at a given temperature. At a constant absolute humidity the percent equilibrium moisture (or adsorbed water) always decreases as the temperature rises.

Referring again to the sets of Points 8 - 20 and 10 - 15; rather than observing a drop in rate as the temperature was increased at constant humidity (decrease in quantity of adsorbed water) the rate actually increased slightly.

This relation is also shown by comparing the oxidation rate at different temperatures and (approximately) the same relative humidity. Referring to Points 16, 17, (95^{o}F and 82% H_R) the nine reference points; 1, 2, 3, 4, 11, 12, 18, 19, 21, (82^{o}F and 86% H_R) the average reaction rate for the first points is 83 and the second 114 microgram oxygen per gram pyrite per hour. The reaction rate increases 38% and the absolute humidity 45% between 82 to 95°F at similar relative humidity. Since the amount of adsorbed water would probably be proportional to relative humidity at these different conditions, this also indicates the independence of reaction rate on amount of adsorbed water.

Commonly for chemically controlled reactions, a rough approximation for the quantitative effect of temperature on the reaction rate is that, for every 10 degree centigrade rise in temperature there is a doubling of the rate of the reaction. This effect of temperature on reaction rate could be deduced by considering the activation energy theory. However, due to a lack of kinetic and thermodynamic data, activation energy can not be calculated. But, there is no doubt that activation energy of "sulfur ball" is very low. The reaction rate in vapor phase increases approximately 20 percent each 10°C increase in temperature.

Considering variation of oxidation rate with respect to a long period of continuous run, there is no evidence that either the diffusion of oxygen or water vapor to the surface of pyrite is rate-controlling. For instance, several runs of a week's duration were made in which the rate of oxidation did not change. This indicates the film resistance can be neglected. In addition, the flow rate of oxygen does not affect the rate of oxidation. Considering the above information, one can not determine if a chemical or physical mechanism is rate-controlling.

The experimental results show the reaction rate is first order with respect to water concentration. These facts can be represented by a straight line passing through the origin:

$$Y = S X$$

where,

Y: rate of oxidation
X: absolute humidity
S: slope of straight line, constant

Here attention is focused on the nature of S. If another type of sample is run, a different value of S is obtained. The arbitary constant S will be a function of, among other things, the surface texture of the pyrite itself. Assume the limiting case where S approaches zero, then no oxidation occurs even if absolute humidity is high.

According to Taylor's proposal (27) that "reactions which are catalyzed by solids actually occur on the surfaces of the solids at points of high chemical activity which are termed "active centers," the activity of a catalytic surface is proportional to the number of active centers per unit area. In connection with Birle's (23) work, the oxidation appeared to be initiated at certain "active sites."

Considering above facts, the following sequence of steps, or mechanism of over-all reaction, is proposed:

$$FeS_2 + H_2O = FeS_2 \cdot H_2O \qquad (1)$$

This reaction would be the initial step of the over-all reaction. Water vapor diffuses to the solid surface where it is adsorbed. This adsorption, which can be assumed to be activated adsorption or chemisorption, forms an active center on the surface.

$$\mathrm{FeS_2 \cdot H_2O \; + \; O_2 \; = \; FeS \cdot H_2O \; + \; SO_2} \qquad (2)$$

Oxygen diffuses to the surface of pyrite. The active center which is formed on the surface is much more reactive than FeS_2 alone.

$$\mathrm{2SO_2 \; + \; O_2 \; \xrightarrow{H_2O} \; 2SO_3} \qquad (3)$$

This reaction is much faster than the second reaction. The contribution of moisture to the reaction can not be neglected. The catalytic combination of sulfur dioxide and oxygen would be stopped when the reaction occurs in dry state (26).

$$\mathrm{SO_3 \; + \; FeS \cdot H_2O \; + \; 2O_2 \; = \; FeSO_4 + H_2SO_4} \qquad (4)$$

The final end-products are obtained.

CONCLUSIONS

1. The vapor-phase oxidation of pyrite is first order in respect to water concentration in the range between 70 and 95°F.
2. The equipment used to study vapor-phase oxidation of pyrite is capable of providing accurate and reproducible reaction rates.
3. Under condition studied, the concentration of water in the vapor-phase, rather than the quantity of adsorbed water, is rate-determining.

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