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A study of the chemical behavior of some natural occurring iron disulfide ores

William Louis Shivelbine

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A STUDY OF THE CHEMICAL BEHAVIOR OF SOME
NATURAL OCCURRING IRON DISULFIDE
ORES.

BY

WILLIAM LOUIS SHIVELBINE

THESIS

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INTRODUCTION

A complete investigation of the pyrites deposits of Missouri by Gravel has revealed many large deposits of pyrites available in commercial quantities in the Ozark area. The pyrites has been found occurring in contact with several various types of minerals. In the northcentral Ozark Plateau, pyrites is found associated with hematite-bearing sink structures. In the northwest part of the state, pyrites occurs in coal deposits, which, in the future, may be recovered as a by-product in the production and preparation of coal. Some pyrites, chiefly marcasite, has been found as fracture and cavity fillings in several other districts.

The purpose of this thesis was to study the chemical behavior of pyrites and marcasite ores with principal emphasis being placed on the removal of the sulfur from the iron disulfides.

In common usage in sulfuric acid manufacture before the advent of the large sulfur deposit discoveries in Louisiana, pyrites has been largely replaced by the burning of elemental sulfur because sulfur dioxide concentrations cannot be obtained in sufficient percentages in present pyrites roasting. In order that pyrites mining may become commercially valuable it would be desirable to recover both iron and the sulfur. In the immediate vicinity of the

Ozark pyrites deposits there are no sulfuric acid plants; therefore, the sulfur, if it is to be recovered, must be obtained either in the elemental state or in a combined state that is readily adaptable to shipping.

The present ore reserves of ferrous metals have been estimated to be equivalent to approximately five hundred years' supply at the 1924 rate of consumption. With an increase in the rate of steel produced in the last two decades and primarily the increase during the years of World War II, the five hundred years' estimation may be considerably shortened.

Iron disulfide ores today are practically useless. The large available deposits still remain unmined, and the price of the crude ore is consequently low. Bulk sulfur retails for sixteen dollars per ton, and iron at approximately three dollars per ton at the present market prices.

The goal of this research was to study some of the reactions of marcasite and pyrite so that the chemical knowledge of these ores might be increased.
REVIEW OF THE LITERATURE

As previously stated, pyrites has been found widely occurring in the state of Missouri. Schoolcraft\(^2\) seems to have been the first person to actually record the presence of pyrites in Missouri. In describing the lead mines in 1819, he wrote, "Pyrites are common at the mines, sometimes crystallized in regular cubes of a beautiful brass-yellow colour, and at others, found in tabular masses, or mixed with blende, sulphate of barytes, or calcareous spar. The former variety has generally been mistaken in this region for gold, and many of the stories in circulation of the existence of this metal in the interior of Missouri, have no better foundation. I have disappointed several miners and hunters who brought in specimens, by telling them that it was merely a combination of sulphur and iron".

Most of the pyrites produced in Missouri has been obtained from the bottom of abandoned iron ore deposits in sink structures of the Ozark Plateau.\(^3\) Iron ore mining reached its peak production soon after the Civil War, and it was soon found that most of these iron mines contained pyrites beneath the iron ore. In these days, however, pyrites

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was more to be avoided than sought, for it increased the sulfur content of the ore until it became unfit for iron and steel production.

In 1903, State Geologist, E. R. Buckley saw an increased demand for pyrites in the manufacture of sulfuric acid for the rapidly growing phosphate fertilizer industry. Apparently Buckley's suggestions were considered for in 1904, several carloads of the iron disulfides were shipped from Phelps and Crawford Counties.

Pyrites in Missouri came to the attention of several sulfuric acid plants in the East St. Louis area, and through the next decade pyrites mining increased in strength in Missouri. With the entrance of the United States in World War I in April 1917, the demand for pyrites became much more intense. The imports of Spanish pyrites were discontinued and the need of domestic pyrites became quite critical for the manufacture of sulfuric acid. In 1918, the price of pyrites containing 50 per cent sulfur sold as high as $15 per ton. In Missouri the average price was $9 a ton and production could not meet the demand.

By 1920, however, most of the sulfuric acid companies had discontinued pyrites roasting as a supply for sulfur dioxide and had turned to the use of elemental sulfur. At this time, pyrites mining in Missouri came to an end.

In 1932, pyrites mining was again started in Missouri and continued on a moderately large scale until 1941. Since 1941, pyrites production has ceased entirely although large deposits are still available.

The average value of pyrites has been reported\(^5\) by the U. S. Geological Survey and the U. S. Bureau of Mines in 1940 at $2.53 per ton.

There has been much previous work done on both the concentration of the pyritic ore and on the removal of sulfur from the ore. A condensed review of some of the processes used will therefore be considered at this point.

**Magnetic Concentration** — This treatment not only removes a considerable proportion of the gangue, but it has the additional advantage of eliminating a large proportion of the phosphorus, and in some cases, also the sulfur that is present in the original ore. It is stated that when sulfur is present in the form of pyrites it is more readily removed by magnetic concentration than by calcination. This works very well where the pyrites exists with the gangue in the form of separate particles, such as the Lake Superior ores, and the magnetites of Sweden. It does not, however, work too well on British ores where the pyrites, phosphorus, and silica exist in a very fine state of division in the ore.

WEATHERING - Weathering is not common, but it is carried on to some extent in Sweden where the process has a two-fold object; (1) removal of the shale; (2) removal of the sulfur by slow oxidation. The iron disulfide (pyrites) is oxidized by exposure to atmospheric oxygen and the ferrous sulfate that is formed is dissolved and removed by the rain.

Pyrites ores containing lime should not be weathered since the ferrous sulfate that is formed would in turn react with the lime forming calcium sulfate which is insoluble in the rain.

The distillation of sulfur from pyrites by external heating has been practiced the world over, and as far back as 1863 some 2,440 tons of sulfur were produced in Bohemia by distillation in earthenware tubes. The amount of sulfur recovered was about one-third of that contained in the pyrites treated.

The same process was conducted in China for some hundreds of years by distillation of pyrites in clay crucibles. Less than one-half of the sulfur contained in the pyrites was recovered, and the purity of the product was 97 per cent to 98 per cent. At St. Gobain, France, distillation was conducted in a clay retort placed on the top shelf of an ordinary burner for pyrites smalls.
A shaft furnace is used by Fiderson⁶ for the extraction of sulfur from sulfide ores, by regulating the air supply at the bottom of the furnace in which pyrites or other sulfide ore is roasted along with the reduction of the ore to metal. The sulfide vapor is distilled off and can be suitably collected.

In regard to continuous processes, Hall⁷ in his 1913 and 1915 U. S. patents claims to obtain part of the sulfur by distillation by the application of a direct reducing flame; and in other U. S. patents⁸, a moving mass of pyrites, while being agitated, is heated in the substantial absence of materials capable of combining with it to a temperature at which the loosely combined sulfur atom is expelled. Fresh pyrites is continuously introduced into the heating chamber and the desulfurized ore withdrawn.

In a German⁹ process, the material containing sulfur is heated in the presence of a gas which is inert to sulfur to a temperature at which the molten sulfide decomposes with the separation of elemental sulfur, a low sulfur matte being left as residue.

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6. Fiderson, C. J., English patent 152,827 (from Chem. Abs.)
9. German pat., 313,122 (from Chem. Abs.)
In a Norwegian process\textsuperscript{10}, pyrites is melted in an electric furnace, and it is stated one-half of the sulfur is liberated and one-half may be obtained by electrolysis.

By an English process\textsuperscript{11} it is claimed that practically all of the sulfur from pyrites may be obtained by heating in a retort in a stream of carbon monoxide or nitrogen with addition of small regulated amounts of oxygen, by which the iron is burned to Fe\textsubscript{2}O\textsubscript{3} and the sulfur liberated.

Levy\textsuperscript{12} has treated the pyrites with ferric chloride vapors at a temperature of 500 to 1000 degrees centigrade in an amount just sufficient to convert the iron to FeCl\textsubscript{2}. The sulfur is liberated in vapor form in the elemental state.

Helbig\textsuperscript{13} has patented a method whereby elemental sulfur is obtained by heating iron pyrites with apatite (CaF\textsubscript{2}·3Ca\textsubscript{3}P\textsubscript{2}O\textsubscript{8}), coke, and quartz. On melting down a suitably proportioned charge, one-third of the sulfur present is distilled off solely by the heating, and the remainder of the sulfur is expelled as elemental sulfur by the reactions taking place, the products formed being S, Fe\textsubscript{2}P, CO, and CaSiO\textsubscript{3}. The heating is carried out

\textsuperscript{10} Nor. pat. 176,779, Norsk Hydro Elektrisk Kvallstofaktieselskab

\textsuperscript{11} Frehling, Fleming, and Whitlock – English Pat. 10,295

\textsuperscript{12} Levy, Stanley, I., U. S. 1,946,325, (Feb. 6, 1936)

\textsuperscript{13} Helbig, M., U. S. Pat. 1,315,496, Sept. 9, 1919
preferably in a closed electrically heated furnace with a condenser for recovering the sulfur and various outlets for tapping off the slag and phosphide formed.

On July 2, 1917, the British Sulfur Co. patented a process\textsuperscript{14} in which a portion of the sulfur was distilled off of the ore by direct heating with a reducing flame and the residual sulfur that remained in the ore was removed as sulfur dioxide by roasting. The sulfur dioxide was then converted into hydrogen sulfide by passing it through incandescent fuel, and this hydrogen sulfide subjected to incomplete oxidation. The sulfur was thereby evolved as elemental sulfur and removed.

Hoffman\textsuperscript{15} has developed a process in which the sulfur dioxide formed by roasting pyritic ore is passed through a container in which calcium sulfide and sulfite are heated by open flame gas jets and a gaseous hydrocarbon, such as methane, is supplied to the container to support combustion. Elemental sulfur, carbon dioxide, and water are formed as products.

There are numerous references in the literature to the reduction of \(\text{FeS}_2\) by the use of hydrogen. In the opinion of the author, the most significant and complete

\begin{itemize}
  \item 14. Norwegian Pat. 28,049, July 2, 1917 (from Chem. Abs.)
  \item 15. Hoffman, A. F., U. S., 1,273,370, July 23, 1918
\end{itemize}
work accomplished in this line is the work of Gallo\textsuperscript{16}. In experimental work, Gallo used natural occurring pyrites containing 97.12 per cent FeS\textsubscript{2}. His preliminary experiments have shown that slow heating with hydrogen evolved hydrogen sulfide and formed ferrous sulfide (FeS), while rapid heating evolved a small quantity of elemental sulfur. In systematic experiments, heating was continued up to 600 degrees centigrade and the results recorded graphically. The latter work indicated that reduction took place in three stages,

\begin{align*}
(1) \quad 2\text{FeS}_2 + \text{H}_2 &\rightarrow \text{Fe}_2\text{S}_3 + \text{H}_2\text{S} \\
(2) \quad \text{Fe}_2\text{S}_3 + \text{H}_2 &\rightarrow 2\text{FeS} + \text{H}_2\text{S} \\
(3) \quad \text{FeS} + \text{H}_2 &\rightarrow \text{Fe} + \text{H}_2\text{S}
\end{align*}

and that these three reactions began at 228-30°, 280-5° and 370-5° respectively. Once started, however, a higher temperature and time was necessary to accelerate and complete each of the reactions. To complete the formation of Fe\textsubscript{2}S\textsubscript{3}, equation (1), the temperature should be maintained for some time at 450° centigrade. The third reaction in which the iron is completely reduced, is very slow and required a high temperature. Gallo was the first worker to report the occurrence of

the first and third equations. With a sufficiently high temperature and long enough time (44 hours at 900°C), FeS is completely reduced to Fe. The high temperature and time necessary to reduce FeS means that industrially a desulfurizing basic slag method is to be preferred.
EXAMINATION OF THE ORE SAMPLES

In order to get experimental data on various types of iron disulfide ores, two distinctly different ores were obtained; namely, marcasite and pyrite. Both of these ores had exactly the same empirical formula but differed entirely in their crystalline structure. Both marcasite and pyrite are found occurring as mineral deposits in Missouri, marcasite being the most abundant in the "pyrites-bearing" sink structures. It is common practice to call both marcasite and pyrite ores by the general name "pyrites", and consequently it is very likely that in examining the literature, marcasite will not be mentioned as often as the general term "pyrites".

Marcasite\textsuperscript{17} has the empirical formula \( \text{FeS}_2 \). It is the orthorhombic form of iron disulfide. It is a steely to faintly brassy, brittle, opaque mineral with a greenish-black streak. It usually occurs in small elongated crystals and can readily be distinguished from pyrite by its crystallization. In a moist atmosphere marcasite is oxidized readily to sulfuric acid and iron sulfates. It is much less stable to weathering than is pyrites, and samples of the ore must be kept well stoppered or in extremely dry air. The decomposition seems to be accelerated by the presence of copper,

\textsuperscript{17} Grawe, O. R., Op. Cit., p. 99-100
mere traces being sufficient.

Pyrite is the isometric form of iron disulfide. Except for this difference in crystallization, it is very similar to marcasite and as previously mentioned, has the same chemical formula. Since pyrite is more stable to weathering conditions than is marcasite, it is often erroneously stated to be the most plentiful in the state of Missouri due its existence where all of the marcasite present has already been oxidized and swept away by the rain.

The sample of marcasite ore was secured by Dr. W. T. Schrenk from the Missouri Geological Survey, Rolla, Missouri. The sample of pyrite was obtained from Magnet Cove, near Little Rock, Arkansas. When obtained, it was necessary to determine which ore was marcasite and which was pyrite since both samples were listed as "pyrites". Graye describes a method to differentiate marcasite and pyrite: 18

>A chemical method often used to distinguish marcasite from pyrite is based on the liberation of white or yellowish, finely divided sulfur from powdered marcasite when it is boiled with concentrated nitric acid. Pyrite does not react in this way. Instead of yielding a cloudy solution containing elemental sulfur, pyrite produces a clear amber solution. This test has been open to question,

18. Graye, C. R., Ibid.
but the writer believes failure of the test is due to the use of mixtures of the two minerals rather than the pure minerals."

The chemical method of distinguishing marcasite and pyrite, as described in the preceding paragraph, was applied to both of the ores. It was noticed that the sample, later to be proven as marcasite, gave a small quantity of amber solution indicating pyrites, however, a large yellow sulfur deposit gave promise of primarily marcasite ore. The second ore sample was tested and found to be substantially pyrite with some marcasite present.

In a personal conference with Dr. Grabe, the ore samples were carefully inspected and classified by crystal-line structure methods. The first sample of the ore, the ore from the U. S. Geological Survey, was found to be largely composed of marcasite with scattered crystals of pyrite present. The Arkansas ore, on the other hand, was practically pure pyrite (with perhaps occasional crystals of marcasite present).
The marcasite was obtained in lump size with an average diameter of approximately one-half inch. About five pounds of these lumps were placed in a Dodge Jaw Crusher and crushed into pieces passing through a one-fourth inch standard Tyler screen. These smaller pieces were then slowly fed into a Massco-McCool Pulverizer with plates set for fine pulverization. The powdered ore was screened through a 100 mesh Standard Tyler screen and intimately mixed in a large container. A representative sample of the ore was taken and found to contain 97.05 per cent FeS₂ and 51.91 per cent sulfur. All work involving marcasite in this thesis used this pulverized material. It may be of interest to point out, that during the pulverizing of the ore there was indication of the ore oxidizing inside the pulverizer. The oxidation was accompanied with occasional flashes of fire and the odor of sulfur dioxide.

The sample of pyrite was not crushed in the Jaw crusher due to the fact that it was obtained in a size that would largely pass through a 40 mesh Tyler screen. A five pound sample of the ore was taken and ground in the Massco-McCool pulverizer in the same manner as the marcasite. It was noted that the pyrite showed no indication of oxidizing in the pulverizer even though the feed was at a much greater...
rate than that of the marcasite. The pulverized pyrite was then screened through a 100 mesh Tyler screen, thoroughly mixed, and a representative sample taken for analysis. The pyrite ore was found to contain 95.31 per cent FeS₂ and 50.96 per cent sulfur. This mixed ore was considered to be uniform and was used throughout this thesis as a supply of pyrite samples.
The furnaces used for experimental work in this thesis were of the electrically heated single tube type. The furnaces were 220 volt units and developed maximum temperatures of 1600 to 1800 degrees Fahrenheit. Three different furnaces of varying length were used; five, nine, and thirteen inches respectively.

Iron-constantan thermocouples were used to determine the temperature of the various units. The thermocouples were protected in a porcelain or a fire-clay sheath to prevent decomposition by the sulfur dioxide. It was noticed that iron-constantan thermocouples, if not protected by the fire-clay sheath, would read from 200° F. to 500° F. low after they had been exposed to sulfur dioxide for a short period of time. On examination, it was found that the constantan wire was completely decomposed by the sulfur dioxide and the iron wire was attacked to a somewhat lesser extent. Alundum coatings on the thermocouple were tried but found to be too porous, for the wires were decomposed through the alundum coating.

The instrument for reading the temperature was a Foxboro potentiometer supplied with a copper-resistance cold-junction correction coil. With this correction coil, the temperature could be read directly from the instrument without applying a cold-junction correction. The thermo-
couple and instrument were calibrated at various temperatures with a mercury thermometer and against a Leeds-Northrup potentiometer which had recently been calibrated. The Foxboro instrument and iron-constantan thermocouple were found to be accurate within 2 degrees at 1400°F.
METHOD OF ANALYSIS FOR SULFUR IN THE SAMPLES

There are various means by which sulfur can be determined in ores and ore-residues, but by far the most common is the Parr peroxide fusion method. All analyses in this paper involved the use of this method.

A 1.0 gram sample of the ore, or experimental residue, was carefully weighed and placed in a Parr peroxide bomb (Fig. 1).

**FIG. 1**

A - Top Sealing Cap  
B - Bottom Sealing Cap  
C - Rubber Washer  
D - Asbestos Shield  
E - Peroxide Cup

Fig. 1. Parr Peroxide Bomb
One scoop, 10 to 11 grams, of sodium peroxide was placed in the peroxide bomb with the sample being analyzed and the bomb tightly sealed with screw-caps (A) and (B). In order to protect the rubber gasket (C) from the heat, a heavy piece of asbestos (D) was fitted around the bomb before heating was started. Fusion was then started by heating the cup of the bomb (E) with a Bunsen or Fisher flame until the metal started to turn a dull red. At this point, the entire bomb, with the exception of the asbestos, was plunged into cold water. (This was another protection to keep the rubber gasket from being excessively heated.)

When the bomb has become cool, it was opened and the film of tap water washed away with distilled water and the bomb cap and contents placed in a clean beaker with water added to dissolve the fused product. The beaker was covered with a watch glass at this time for the reaction of the excess Na₂O₂ in water became very violent. After reaction had ceased, the cup was carefully washed free of any adhering particles and removed from the beaker. The solution was partially neutralized with hydrochloric acid to prevent the strongly caustic solution from attacking the filter paper. Care was taken during the addition of HCl to maintain the solution in an alkaline state so that the ferric hydroxide formed would not be dissolved in the acid. The
solution was filtered to remove all of the ferric hydroxide and obtain the sodium sulfate in solution. The filtrate was made slightly acid with HCl, heated to boiling, and rapidly poured into a barium chloride solution to precipitate the insoluble barium sulfate. The barium sulfate was filtered, washed, and ignited in a muffle furnace. The per cent sulfur was calculated by the following formula:

\[
\% \text{ Sulfur} = \frac{\text{Wt. of } \text{BaSO}_4 \times \text{Atomic Wt. of Sulfur}}{\text{Molecular Wt. of } \text{BaSO}_4 \times \text{Wt of Original Sample}} \times 100
\]

It was observed that if the barium chloride solution was added to the filtrate containing the soluble sulfate in the cold, the precipitated barium sulfate had a pronounced tendency to fuse on ignition. It was believed that this phenomenon was the result of some sodium chloride being occluded during the crystallization of the barium sulfate. This occlusion would, of course, lower the melting point of the precipitate and result in a partial fusion with the porcelain. It was found that if the soluble sulfate filtrate was heated to boiling and dumped rapidly into the barium chloride solution, the effect of fusion due to the occluded sodium chloride was reduced to a minimum; consequently, all of the analyses in this thesis have been conducted in that manner.
EXAMINATION OF THE SULFUR LINKAGE

The formula for both pyrite and marcasite has been previously given as FeS₂. The question naturally arises as to how the sulfur is attached. It would seem theoretically feasible that the second sulfur atom would be either (1) merely existing as elemental sulfur in contact with FeS, or (2) loosely combined chemically with the FeS forming a definite compound. The latter theory was the most logical since the percentage composition of pyrite and marcasite was approximately constant; however, an experiment was performed on each possibility in an attempt to gain some knowledge of the structure of the iron disulfides.

In examining the possibility of elemental sulfur in contact with FeS, an attempt was made to dissolve the "free" sulfur with carbon disulfide. A weighed sample of marcasite and a weighed sample of pyrite were agitated for 4 hours in carbon disulfide. The solvent was filtered to remove the particles of iron disulfide, the precipitate washed with CS₂, and the filtrate placed in weighed evaporating dishes. A "blank" consisting of an equal quantity of carbon disulfide in a weighed evaporating dish was prepared also to compare any residual sulfur that might be formed by the evaporation of the carbon disulfide. The solvent was allowed to vaporize from the samples and the "blank", and the evaporating dishes again weighed. When the results were obtained, it was found
that there was no appreciable amount of sulfur dissolved by the carbon disulfide in either the pyrites or the marcasite sample, indicating that the second sulfur atom of FeS$_2$ was chemically combined and not existent as elemental sulfur.

Since the results of the carbon disulfide treatment have indicated that the second sulfur atom of FeS$_2$ was chemically combined, an investigation was made to determine the stability of the chemical combination. This was performed by heating the pyrite ore sample in an inert atmosphere so that any decomposition that occurred would be due entirely to the instability of the ore and not due to oxidation or reduction. The investigation was carried on in the following manner: A Pyrex combustion tube, closed at one end, was filled to a depth of approximately one inch with the pyritic ore. Into the center of this ore was placed an iron-constantan thermocouple adequately protected with a fire-clay sheath, as previously explained.* The thermocouple lead wires were sealed in a rubber stopper which fitted the open end of the pyrex tube. This rubber stopper was also supplied with a fine capillary glass tube tipped with a piece of rubber tubing and a pinch cock. The express purpose of the capillary tube attachment was to serve as an escape for the gases when the pressure was

* Page 17
increased due to the increased temperature. In using a capillary, it was hoped that the excess pressure would be relieved without allowing an appreciable amount of air to enter. The whole system was evacuated by the use of a Cenco-Hyvac pump and the inert gas, helium, was allowed to fill the tube. The operation was repeated three times to insure most of the air removal from the tube.

The combustion tube was then vertically placed in the five inch electric furnace so that about three inches of the end of the tube containing the ore sample were in the furnace; since the entire tube was 27 inches long, this gave 24 inches of cool tubing on which the ensuing vapors could condense. The furnace was equipped with external variable resistances so that the temperature could be controlled over a period of time.

The furnace and combustion tube were heated rather rapidly from room temperature to 400°F. and the cool portion of the tube was observed for traces of condensed sulfur. There were no traces of sulfur visible at this point, but moisture was found to be collecting near the upper end of the tube. (The original ore had been previously analyzed for moisture content and found to contain 0.49 per cent H₂O). Since there was no sulfur present, the heating was continued, but at a much slower rate than the initial temperature increase. The combustion tube was
carefully observed to detect any traces of condensing sulfur on the side walls. At 650°F. there was a noticeable odor of sulfur dioxide issuing from the capillary tubing, probably due to the sulfur oxidizing in the presence of a small quantity of oxygen. The temperature was held constant at 650° plus or minus 5°F. until it was assured that all of the sulfur reactions taking place at this temperature had gone to completion. On examination, however, it was found that there were no visible signs of elemental sulfur depositing on the sides of the combustion tube. After the partial oxidation reaction had gone to completion, the temperature was again increased gradually at the rate of about 5°F. per minute. From 650° to 940°F. there was no noticeable change in the appearance of the ore nor was there any indication of sulfur being evolved. At 940°, however, there was a slight yellowish-white haze given off and the temperature was held at that point for a two hour period. The haze was in such small quantities and lasted for such a short period of time that it was assumed that the sample did not lose any perceptible amount of sulfur and consequently an analysis was not performed. The heating was again resumed at a rate of approximately 2° per minute. The next noticeable change occurred at 1025°F. at which point some sulfur was volatilized and deposited as elemental sulfur.
on the cool portion of the combustion tube. The temperature was held between 1025° and 1050° for 12 hours to ensure complete volatilization of the available sulfur at that specific temperature. After 12 hours the tube and contents were removed from the furnace and allowed to cool. A sample of the ore was taken at this point by removing the stopper and thermocouple and carefully inserting a glass tube into the cooled residue and withdrawing the sample. Caution was taken not to displace any of the sulfur that had condensed on the tube walls. The sample was analyzed and found to contain 46.3 per cent sulfur.

The tube was again evacuated and filled with inert helium gas as before and the temperature of the system allowed to come to a constant temperature at 1025° Fahrenheit. The resistances were adjusted so that the temperature rise in the residue was again about 1½ to 2° per minute. Between 1025°F. and 1245°F., there was very little sulfur evolved. At 1245°C, however, there was a definite increase in the rate of sulfur evolution. The temperature was held constant at 1245°F. plus or minus 5°F. for 12 hours and a sample taken as before. Analysis was made of the residue and the per cent sulfur was determined to be 36.5 per cent.

Since 1245°F. was nearly the softening point of Pyrex glass, the temperature was not taken above this point at
the time. It was of striking significance, however, to note that the percentage of sulfur in the residue at the two major decomposition temperatures corresponded to the percentage of the two iron-sulfur compounds ferric and ferrous sulfides respectively. The 46.3 per cent sulfur in the residue at 1025°F. compared favorably with FeS_2 (46.2%) while the 36.5 per cent at 1245°F. checked very well the composition of FeS (36.4%).

Since the experiment indicated that FeS was formed by heating FeS_2 at 1245°F. for 12 hours, it appeared that it would be of some interest to determine the period of time it took for this decomposition to go entirely to completion and whether a higher temperature would speed the rate of decomposition. The following procedure was used to obtain the desired data:

A sample of pyrite was placed in the combustion tube to a depth of about one inch and the thermocouple installed as before. The system was evacuated and filled with helium and inserted in the electric furnace at a temperature of 1245°F. Samples were taken at one hour intervals by sampling with a glass tube inserted into the heated ore. Analyses were made on ½ gram samples of the residue and the results tabulated in Table I and Graph I.

The next experiment was performed to determine the effect of increasing the temperature of the furnace on
the rate of decomposition of the pyrite. The procedure for the work duplicated the last run with the exceptions that a quartz tube was used in place of the Pyrex glass tube and the temperature of the furnace was 1550°F Fahrenheit. Samples were made at regular intervals and the results recorded in Table II and Graph I.

Since the maximum temperature obtainable in the furnace used was 1600°F, it was impossible to obtain values for the decomposition rate at higher temperatures. It seems reasonable, however, to assume that the rate would be increased with an increase in temperature until the ore became molten and the remaining sulfur in the FeS was evolved as elemental sulfur and the iron recovered as the molten metal (reference 9, page 7).
### TABLE I

<table>
<thead>
<tr>
<th>% Sulfur in the Residue</th>
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<td>36.49</td>
<td>9</td>
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**Effect of Time on Heating Pyrite at 1245° Fahrenheit**

### TABLE II

<table>
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<th>Time in Hours</th>
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</thead>
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</tr>
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</tr>
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<tr>
<td>36.51</td>
<td>2</td>
</tr>
<tr>
<td>36.50</td>
<td>2½</td>
</tr>
</tbody>
</table>

**Effect of Time on Heating Pyrite at 1550° Fahrenheit**
**GRAPH I**

(Plot of Table I & Table II)

Per Cent Sulfur in Residue Resulting from Heating Pyrite at 1245°F. and 1570°F. for varying periods of Time.

- -- 1570°F.
- -- 1245°F.
REDUCTION OF SULFUR DIOXIDE

Several statements have been made in the literature as to the use of heated carbon as a reducing agent for \( \text{SO}_2 \), the reaction giving elemental sulfur and carbon dioxide as products. An apparatus was set up to study the effects of this type of reduction.

Because of the inconvenience of burning pyrite as a source of sulfur dioxide for experimental work involving sulfur dioxide data alone, a tank of commercial sulfur dioxide was used as a supply. The apparatus was set up according to Fig. II. The quartz combustion tube (A) was fitted with a piece of screen wire about mid-way so that the carbon would be supported in the hot region of the furnace (B). Granulated carbon of approximately one-eighth inch particle size was placed in the tube to a depth of three inches. The furnace was heated to a temperature of 1600°F. and a mixture of 50 per cent air and 50 per cent \( \text{SO}_2 \) was allowed to flow through the heated carbon. The air and sulfur dioxide before entering the furnace were passed through containers (E) (F) of concentrated sulfuric acid to remove any traces of water that might be present.

It was noticed that although there was no elemental sulfur being formed in the water cooled condenser (G), the
Fig. II Sulfur Dioxide Reduction Apparatus

A - Quartz Combustion Tube
B - Electric Tube Furnace
C - Iron-Constantan Thermocouple
D - Gas Mixing Vessel
E - $SO_2$ Drying Vessel
F - Air Drying Vessel
G - Water Cooled Condenser
the gas issuing from the end of the condenser did not have the characteristic odor of sulfur dioxide. On examination, the resulting gas was found to be colorless and possessed a rather pungent odor, not as sharp as SO$_2$, but definitely characteristic. It was found to burn with a blue flame evolving SO$_2$. When passed through water it slowly decomposed with the formation of hydrogen sulfide. These properties were considered and it was decided that the gas being formed was carbonyl sulfide (COS). According to Friend$^{19}$, carbonyl sulfide, or carbon oxy-sulfide, possesses all of these properties with the exception of odor. Friend states that COS may be formed by the direct action of sulfur dioxide on red-hot carbon by the following reaction:

$$4\text{SO}_2 + 9\text{C} \rightarrow 6\text{CO} + 2\text{COS} + \text{CS}_2$$

This reaction would tend to justify the odor given off, for it was not unlike the odor of carbon disulfide.

The reaction may also take place by the following series of equations:

$$2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$$  
$$\text{SO}_2 + \text{C} \rightarrow \text{CO}_2 + \text{S}$$  
$$\text{S} + \text{CO} \rightarrow \text{COS}$$

Hall, in his 1914 patent states that sulfur may be produced by subjecting the ore to the action of a reducing flame of producer gas and to the action of steam in less amounts than is required to form H₂S to any great extent, but in sufficient amount to prevent the formation of material amounts of SO₂ and COS.

Since the author suspected COS to be present in the reduction of SO₂ with heated carbon, it was decided to introduce water vapor into the system in controlled amounts with the following reactions possibly taking place:

\[
\text{COS} + H_2O \rightarrow H_2S + CO_2
\]

\[
2H_2S + SO_2 \rightarrow 2H_2O + 3S
\]

The apparatus in Fig. II was modified slightly to allow water vapor to enter the mixing vessel (D). The sulfuric acid in the drying flask on the air line was replaced with water and the drying vessel on the SO₂ line was completely removed.

The furnace was heated to 1600°F. and the quartz tube again filled with carbon as before. The water in the flask in the air line was heated to gentle boiling and the air and sulfur dioxide rates were approximately equal. A very faint trace of sulfur was observed to be depositing in the condenser but large quantities of carbonyl sulfide were detected issuing from the end.

The experiment was repeated with identical conditions with the exception that more water vapor was entered into the system as a result of stronger boiling in the flask (F). Large quantities of sulfur were observed to be solidifying and carried out of the condenser by the water formed from the condensation of the excess water vapor.

The experiment was repeated at a later date but this time there was very little sulfur deposited. Since there were no instruments for accurately measuring the rates of flow of the various ingredients, it is very possible that the conditions of the previous operation were not duplicated exactly. It was the author's belief that carbonyl sulfide could be eliminated in the reaction of sulfur dioxide with heated carbon by vigorously controlling the conditions of the operation and by adding regulated amounts of water vapor to the system.
EFFECTS OF BURNING PYRITES

Most commercial processes in which pyrites is roasted for the recovery of sulfur dioxide use the Flash Roasting method. In brief, this type of roasting is a process in which the lump pyrite ore is reduced to approximately 60 mesh by grinding in a ball mill. Heated air is passed into the ball mill to dry the ore and carry the dry fines to the combustion chamber where there is a counter-current flow of air meeting the air flow carrying the pyrites. The temperature of the combustion chamber is in excess of 1000°C. The SO₂ leaves the top and the iron oxides fall to the bottom and are removed by doors in the combustion chamber.

Another type of roasting of pyrites is the method in which the ore is ground to approximately 60 mesh and burned in a vertical furnace by passing counter-flow to an oxidizing flame. The SO₂ is carried out with the combustion products and the iron oxides are dropped through the flame and removed at the bottom of the furnace.

Examination was made of the possibility of roasting ground pyrites ore by introducing the ore in the center of a reducing flame in a rotary kiln. A laboratory kiln was constructed for temporary experimental work by mounting a 2½ X 24 inch ceramic combustion tube on four ball bearings. An asbestos belt was led to a hand turned pulley so that the kiln could be rotated at various rates. The burner
used was constructed of Pyrex glass and was designed such that the ore could be introduced in the center of the flame by a jet-effect. Fisher burners were attached so that the combustion tube could be externally heated if necessary. Sketches of the kiln and burner are given in Fig. III.

The flame was adjusted so that there was enough air entering to keep the temperature of the flame at a high point, but insufficient to the amount of creating oxidizing conditions. The kiln was allowed to heat up to the maximum temperature attainable before the ore was allowed to enter with the flame. When the pyrite was introduced, however, it was found that due to the necessarily high rate of gas flow and the smallness of the combustion tube, the ore was carried out of the combustion tube before complete reaction was attainable.

Several variations of the process were tried; including rotating the kiln at various angles varying from horizontal to completely vertical, externally heating the kiln by the use of Fisher burners, and controlling the amount of air to the flame so that its properties were varied from reducing to oxidizing conditions. Even with all of the various conditions, however, the best decomposition of the ore that could be attained in this particular equipment was a small percentage of the ore
FIG. III

Rotary Kiln and Burner

A -- Ceramic Combustion Tube
B -- Pulley Drive
C -- Ball Bearing
D -- Ash Trap
E -- Jet-Feed Burner
F -- Ore Inlet
G -- Air Inlet
H -- Gas Inlet
oxidized to the red oxide of iron, $\text{Fe}_2\text{O}_3$. The literature is surprisingly devoid of information on this type of roasting, and it is believed by the author that continued research work in the future could yield a process similar to this that would be not only practical but very economical. The use of larger equipment that would allow the ore to remain in longer contact with the flame would yield invaluable data.

The remaining portion of this thesis was devoted to the collection of critical data for various burning conditions of the ore with the hope that the work will be carried on in the future.

The first experiment to be performed on the burning characteristics of pyrite and marcasite ore was the examination of the burning rates with dry air at various temperatures. The equipment was set up as illustrated in Fig. IV. The equipment was constructed such that a constant volume of air was passed over a known weight of ore in a prescribed length of time. The per cent residual sulfur in the treated mass was then determined by analysis.

When the furnace was heated, the quartz tube extending through it was explored by means of the thermocouple, and it was found that there was a zone near the center of the furnace about 4 inches long in which the temperature was nearly constant. A porcelain boat was loaded with 3.000
FIG. IV

Burning Characteristics Apparatus

A -- Iron-Constantan Thermocouple
B -- Boat containing Ore
C -- Electric Tube Furnace
D -- Quartz Combustion Tube
E -- Asbestos Plug
F -- Air Inlet
G -- Thermocouple Lead Wires
H -- Concentrated Sulfuric Acid
I -- Sodium Hydroxide
J -- Furnace Lead Wires
grams of the ore and inserted into the center of the constant temperature zone. Into the end of the tube near the sulfuric acid wash bottle was inserted the thermocouple, protected by the fire-clay sheath, the end of which just touched the sample boat. The combustion products passed through a flask containing sodium hydroxide to absorb $\text{SO}_2$, $\text{SO}_3$, and sulfur. For all of the experiments 12 liters of air were passed over the 3,000 grams of pyrites. The time required for reaction was two hours, plus or minus 10 minutes due to inaccuracy of the air rate control.

This 12 liters of air was calculated to be a 2 liter excess based on the following equation which would use the maximum amount of oxygen for reaction:

$$4\text{FeS}_2 + 15\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_3$$

Since it was quite apparent that the equation did not entirely fit the reaction, there was unquestionably a greater excess of oxygen than the calculated minimum excess of two liters. The sample was carefully stirred after 6 liters of air had been passed through. At the end of the run, the sample and boat were cooled in a sealed test-tube, which prevented further oxidation from taking place while the ore was cooling.

The first experiment was performed on pyrite ore passing through a 100 mesh screen. The 12 liters of air
passing over the boat had first been dried by bubbling through a flask containing concentrated sulfuric acid. The temperature was varied for each run and ranged from $1120^\circ F$ to $1700^\circ F$. The results of this experiment are tabulated in Table III and plotted on Graph II.

The second experiment was performed on marcasite ore which had passed through a 100 mesh screen. Dry air was again used, and the temperature range was $600^\circ F$ to $1150^\circ F$. The results were tabulated in Table IV and plotted on Graph III.

During one of the latter runs, a small quantity of water erroneously entered the combustion tube with the air and the per cent residual sulfur on analysis was found to be less than should have been present if the air had been dried. This created the idea that perhaps air that was saturated with water would effect the desulfurization of the ore to a greater extent than would dry air. It is a known fact that at incipient red-heat, steam will decompose ferrous sulfide with the formation of a black mass containing $Fe_3O_4$, and the evolution of $H_2S$ and $H_2$:

$$3FeS + 4H_2O \rightarrow Fe_3O_4 + 3H_2S + H_2$$

Also at higher temperatures, sulfur dioxide and sulfur are products of the reaction.

The experiments performed on the pyrite and marcasite ores were repeated with water saturated air replacing the dry air. In order to maintain saturated air, the flask, which previously contained sulfuric acid as a drying medium, was filled with water and the air was bubbled through it before entering the furnace. The water was brought to a very gently boil and the rate of effusion was kept as nearly constant as possible so that the results of the various runs would be comparable. Twelve liters of air per two hours measured at room temperature were again used in the following experiments.

The results of decomposing pyrite with water saturated air at temperature ranges from 650°F. to 1650°F. were plotted in Table V and Graph IV.

Water saturated air reacting with marcasite at temperatures from 500°F. to 1200°F. The data were tabulated in Table VI and Graph V.
Effect of Treating Pyrite Ore with Dry Air at Various Temperatures

Per Cent Sulfur in Residue

Temperature in °F.
<table>
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<th>Temperature in °F.</th>
<th>% Sulfur in Residue</th>
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<td>1700</td>
<td>0.12</td>
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Effect of Treating Pyrite Ore with Dry Air at Various Temperatures
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<thead>
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<th>Temperature in °F.</th>
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**Effect of Treating Marcasite Ore With Dry Air at Various Temperatures**
GRAPH III
(Plot of Table IV)

Effect of Treating Marcarite Ore with Dry Air at Various Temperatures

Temperature in °F.

Per Cent Sulfur in Residue
<table>
<thead>
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<th>Temperature in °F.</th>
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Effect of Treating Pyrite Ore with Water Saturated Air at Various Temperatures
GRAPH IV
(Plot of Table V)

Effect of Treating Pyrite Ore with Water
Saturated Air at Various Temperatures

Per Cent Sulfur in Residue

Temperature in °F.
### TABLE VI

<table>
<thead>
<tr>
<th>Temperature in °F.</th>
<th>% Sulfur in Residue</th>
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<tr>
<td>1200</td>
<td>9.17</td>
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</tbody>
</table>

Effect of Treating Marcasite Ore with Water Saturated Air at Various Temperatures
GRAPH V
(Plot of Table VI)

Effect of Treating Marcasite Ore with Water Saturated Air at Various Temperatures

Temperature in °F.

Per Cent Sulfur in Residue
Comparison of
The Effects of Burning Pyrite Ore in
Dry Air and Water Saturated Air.

A --- Dry Air
B --- Water Saturated Air
GRAPH VII
(Composite of Graphs IV & VI)

Comparison of
The Effects of Burning Marcasite Ore
with Dry Air and Water Saturated Air

A --- Dry Air
B --- Water Saturated Air

Per Cent Sulfur in Residue
Examination of the graphs presented a striking variety of manners in which iron disulfides were decomposed. Pyrite ore oxidized with dry air (Graph II) indicated that from approximately 34 per cent sulfur (nearly the percentage sulfur in FeS) down to less than 0.12 per cent, the progressive decomposition varied smoothly with the increased temperature. The last portions of sulfur were more difficult to remove, and consequently a higher temperature was required to oxidize the ore completely. At 1700° F. the decomposition was almost complete for the range examined.

Pyrite ore treated with water saturated air, however, (Graph IV) has been found to start desulfurization at a lower temperature than that required for the identical ore with dry air. There was a definite break in the curve around 34 per cent indicating that the ore containing sulfur in amounts greater than that contained in FeS was easier to oxidize, again confirming the theory that the second sulfur atom in FeS₂ was loosely combined. The remaining portion of the curve indicated that the amount of desulfurization varied directly with the increase in temperature. The curve was not quite as steep, however, as the dry air curve from 0 to 34 per cent.

By plotting the data from the dry air treatment of marcasite ore, one obtained a smooth curve as shown in Graph III. The rate of desulfurization was almost a straight
line until the percentage of sulfur in the residue was below 10 per cent. At quantities lower than 10 per cent sulfur, the desulfurization still varied directly with temperature but at a much slower rate as was indicated by the slopes of the lines.

The curve of Graph V, illustrating the desulfurization of marcasite ore when treated with water saturated air at various temperatures, was rather indefinite. The points examined were quite incoherent with any definite line except for the fact that the percentage of sulfur generally decreased with increased temperature. The deviation was possibly accounted for by the fact that the rate of steam ebullition into the furnace could not be too accurately controlled.

Graphs VI and VII were drawn to compare the degree of desulfurization of the ore by using the two types of treatments, viz., dry air treatment and water saturated air treatment.

Examination of Graph VI which compares the two methods of oxidizing pyrite, showed that the corresponding curves cross. Analyzing this fact, it was realized that for temperatures below 1215°F., water saturated air was more efficient for the desulfurization of pyrite than was dry air. Above 1215°, however, dry air affected the desulfurization to a greater extent than did the presence of moisture.
Similarly, in the examination of marcasite (Graph VII), the presence of moisture facilitated greater oxidation at temperatures below 620°F., while dry air was more efficient at higher temperatures. It was also of striking significance in the marcasite comparison, that the difference in the amounts of desulfurization due to moisture presence was much greater than the effect created by similar treatments of pyrite ore.
SUMMARY

1. Marcasite was found to be less stable to oxidation than pyrite ores. This was found true not only in instances of grinding where marcasite ignites explosively due to the heat of friction, but also in cases where the ore is burned in moist or dry air at elevated temperatures.

2. The second sulfur atom of the molecule FeS$_2$ was much more loosely combined than the first sulfur atom, or the sulfur in FeS; but, it apparently existed in a true chemical combination since there was no weight loss when the ore was treated with carbon disulfide.

3. When pyrite was heated in an inert atmosphere, so that oxidation does not take place, decomposition took place in two major steps. The first noticeable desulfurization took place at 1025°F. where the percentage of residual sulfur was approximately that contained in Fe$_2$S$_3$. The second major decomposition was affected at 1245°F. where the percentage of sulfur was equivalent to that of FeS.

4. The effect of increasing the temperature to reduce the time of desulfurization was examined. It was found that at 1245°F., a definite quantity of pyrite ore decomposed in an inert gas, helium, in 8 hours. At 1550°F., however, desulfurization on the same quantity of ore was accomplished in a matter of only 2 hours.

5. It was found that carbonyl sulfide (COS) was formed when sulfur dioxide was passed over incandescent carbon.
Data are not complete on this work but it is believed that the formation of COS could be eliminated by the use of proper amounts of water vapor added to the sulfur dioxide while it is reacting with incandescent carbon. The possible reactions that occur are given.

6. The rate of desulfurization has been found to increase with an increase in temperature. In general, it may be stated that higher temperatures are believed to be required to remove the last portions of sulfur than the first portions. This statement applies both to pyrite and to marcasite ores; however, marcasite was found to be easier to decompose than pyrite, as has been previously mentioned.

7. At lower temperatures, air saturated with water vapor was found more effective as an oxidizing agent than dry air. At higher temperatures, dry air was the most efficient. Graphs are plotted to illustrate these statements.
## INDEX

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<th>Analysis,</th>
<th>Page</th>
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