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Roasting pyrite for magnetism with minimum sulphur volatilization

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ROASTING PYRITE FOR MAGNETISM WITH MINIMUM SULPHUR
VOLATILIZATION.

by

Dale Irwin Hayes

and

Clark Watson Wright.

—

A

T H E S I S

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

D E G R E E O F

BACHELOR OF SCIENCE IN MINE ENGINEERING

Rolla, Mo.

1912

—

Approved by Osward Copeland
Professor of Metallurgy.

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PROBLEM OF THE WORK.

In Wisconsin and other zinc mining districts the blende is frequently found associated with pyrite and marcasite. In the Wisconsin district, especially, the marcasite content of the mine-run ore is high being frequently equal to and in many cases greater than the sphalerite content. At times the marcasite and sphalerite together constitute as much as 25 or 30% of the mine-run ore.

The characteristic milling treatment of this ore is; first, hand-picking, and then over grizzlies, trom-ells, rougher and cleaner jigs. Owing to the fact that marcasite and sphalerite differ but slightly in specific gravity the jig concentrate obtained is a mixture of the two and varies in composition from all blende to all marcasite.

This product, owing to the high iron content, is not suited for the zinc smelter, and magnetic or electro-static schemes of separation must be resorted to. The magnetic separation as practiced in the district consists of two steps: first, the roast; and second, the subsequent separation. The roaster used is a Mathey and it consists essentially of a fire-box connected with a revolving cylindrical tube mounted with sufficient

slope to cause the ore to pass through it in about one hour. Hot gases enter at the fire-box end and the ore is fed in at the flue-end. During its passage through the roaster the iron mineral is made magnetic. The roast, as practiced, requires very little fuel as the marcasite, on burning to magnetite, produces considerable heat. The roasted product is then sent to a magnetic separator usually of either the Cleveland-Knowles or Ding types and the magnetic material is taken out leaving a practically pure sphalerite which is ready for shipment to the smelter. In the above roast a large portion of the sulphur combined in the marcasite is expelled as the di- and tri-oxides of sulphur.

In this district there is a sale for pyritic material provided the sulphur content be not less than 40 percent. Is there not some method whereby the iron mineral in the concentrate may be made magnetic without expelling so much of the sulphur as to render the iron product unmarketable? To answer this question is our attempt in this work.

The static scheme for separating jack and marcasite is, of course, exceedingly successful and there is a plant in this district using the Huff machine. Our efforts have, however, nothing to do with the static

separation but our attempt is to suggest a method whereby the ordinary roasting plant may be made to deliver the iron to magnetic separators in such a condition that the jack may be well cleaned and yet the iron product contain more than 40 percent sulphur.

MATERIALS USED IN EXPERIMENTS.

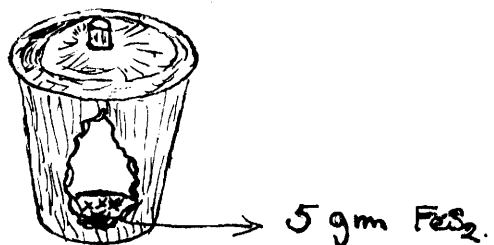
The materials used in our experiments were a clean pyrite, which contained 52.1% sulphur, 46.5% iron, and 1.4% insoluble, and the clean jig-concentrate made in the Wisconsin district which consists essentially of marcasite, blende, and some little gangue.

METHOD OF ATTACKING PROBLEM.

We know of two magnetic compounds to which the iron mineral in the concentrate might be roasted, magnetite (Fe_3O_4) and pyrrhotite, the magnetic sulphide, ($\text{Fe}_n\text{S}_{n+1}$).

We first tried a series of experiments in which pyrite was heated to various determined temperatures in an atmosphere of nitrogen. The purpose of these experiments was to show at what temperatures and what composition the sulphide under treatment became magnetic.

In each test, 5 grams of pyrite, all of which had passed a ^{1.35} μ m. screen, was placed in a small graphite crucible which had been lined with clay. The crucible covers were sealed on with the same material. The crucibles were then filled with nitrogen generated by passing air through a solution of pyrogallic acid in caustic potash.



They were next placed in the muffle of an ordinary assay furnace and heated for one hour at temperatures varying from 100° to 900° C., the temperatures used being respectively 100°, 300°, 600°, 700°, 800°, and 900° C. After the roast was completed the crucible was placed in a bell jar of nitrogen to cool.

The pyrite from each test was assayed for sulphur and the amount lifted/^{by}fairly strong magnets ascertained. The results obtained, together with the physical appearance of the roasted material is shown in table No. 1.

Table for Experiment No.1.

| Material | Wt.gm. . | % S. | Physical Condition. |
|-------------------------|----------|------|--|
| Raw Ore | ---- | 52.1 | Ordinary pyrite, clean. |
| 100° C. Ore | 5.0 | 51.0 | No change from raw pyrite. |
| Lifted with weak magnet | .01 | ---- | Very fine stuff only. |
| Lifted with strong mag. | .03 | ---- | Very fine stuff only. |
| Non-magnetic portion | 4.95 | 51.3 | No change from raw pyrite. |
| 300° C. Ore | 5.0 | 51.3 | Brownish color, about the color of pyrrhotite. |
| Lifted with weak magnet | .02 | ---- | Fine stuff. |
| Lifted with strong mag. | .02 | ---- | Fine stuff. |
| Non-magnetic Portion | 4.95 | 51.0 | Brownish color about the color of pyrrhotite. |
| 600° C. Ore | 5.0 | 47.1 | No change from raw ore except a few black specks. When these were broken up raw pyrite was found inside. |
| Lifted with weak magnet | 0.1 | ---- | Some black specks; mostly small |
| Lifted with strong mag. | 1.7 | 47.7 | Most all black specks and some fine stuff. |
| Non-magnetic portion | 3.1 | 51.7 | Some black specks and raw pyrite. |

Table No.1 (con't'd.)

| Material | Wt.gm . | % S. | Physical condition. |
|-------------------------|---------|------|---------------------------------------|
| 700° C. Ore | 5.0 | 38.0 | All dark colored material. |
| Lifted with weak magnet | 5.0 | 38.0 | All dark colored material. |
| Lifted with strong mag. | 5.0 | 38.0 | All dark colored material. |
| Non-magnetic portion | 0 | 0 | Practically no non-magnetic material. |
| 800° C. Ore | 5.0 | 37.5 | All dark colored material. |
| Lifted with weak magnet | 5.0 | 37.5 | All dark colored material. |
| Lifted with strong mag. | 5.0 | 37.5 | All dark colored material. |
| Non-magnetic portion | 0. | 0 | Practically no non-magnetic material. |
| 900° C. Ore | 5.0 | 36.8 | All dark colored material. |
| Lifted with weak magnet | 4.7 | ---- | All dark colored material. |
| Lifted with strong mag. | 4.8 | 36.2 | All dark colored material. |
| Non-magnetic portion | 0 | ---- | Practically no non-magnetic material. |

It seems from the data shown in the above table, first: that the finest material is made magnetic at a comparatively low temperature, second: that the magnetic property seems to be due to a skin of magnetite because

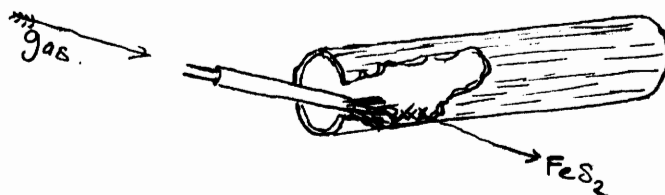
the larger particles, upon being crushed, are found to have a core of apparently unaffected pyrite and a skin of darker material which is probably magnetite, third: that the pyrite roasted at 300° C. looked very much like pyrrhotite but was non-magnetic, fourth: that the best temperature seems to lie between 600 and 700° C.

Experiment No. 2.

In our next experiment we roasted some of the concentrate in an atmosphere low in oxygen to see if we could not obtain the same result as when oxygen was absent, and, at the same time, find out if the size of the material roasted had anything to do with the percentage of sulphur retained in the magnetic portion.

We know that, although a candle burns vigorously in air containing 21 percent oxygen by volume, it refuses to burn ^{with intensity} in an atmosphere containing less than about 18 percent oxygen. May it not also be true that a small diminution of the oxygen content of the gases in contact with the ore being washed will prevent the sulphur in the iron material burning? It may also be true that if the roast be conducted for a proper length of time sufficient magnetic sulphide may be formed in each particle to render the material magnetic, and, still, the total amount of sulphur actually expelled be small.

One hundred and seventy grams of the concentrate was roasted about 20 minutes at 630° C. in a piece of tile by playing the flame of a gas jet directly on the concentrate. The end, where the jet was played in, was partly closed to allow just sufficient oxygen in to keep the flame burning well. After the roast the tile was



sealed with clay and the material allowed to cool.

The data obtained is shown in table No.2.

Table for Experiment No.2.

Material roasted 170 grams.

Magnetic portion 73 grams.

Non-magnetic portion 97 grams.

Non-magnetic portion (Zn 43.55%
(Fe 15.32%.

Magnetic portion before sizing test 40.31% S.

Screen analysis of magnetic material.

-10-

| Screen Mesh | Grams | % of whole | % S. |
|----------------|-------|------------|-------|
| On 6 | 6.1 | 8.35 | 40.64 |
| On 10 | 18.5 | 25.34 | 39.98 |
| On 20 | 24.9 | 34.11 | 39.10 |
| On 40 | 15.5 | 21.23 | 40.20 |
| On 60 | 3.2 | 9.38 | 39.97 |
| Under 60 | 4.8 | 6.57 | 42.12 |
| <hr/> | | | |
| Total | 73.0 | 99.98 | 40.31 |

It seems from the foregoing data:-

first:- That the size of the particles has very little to do with the percent of sulphur retained, since the material from all of the screens in a given test carried about the same amount of sulphur.

second:- That a large portion of the iron material can be made magnetic under the conditions used.

third:- That the non-magnetic material was not sufficiently free from iron. The high iron content, however, may be due to three causes:

The roast may have been carried on for too long a time and some of the iron material changed to ferric oxide;

The time of the roast may have been too short and some of the particles did not have time to become magnetic. Again, and this probably accounts for much of the poor cleaning of the jack, the roast may have been uneven due to the fact that our apparatus and the amount of ore used were not well adapted to give each particle the same treatment;

The poor cleaning may have been due to poor magnetic separation but this cause is probably negligible.

Experiment No. 3.

A third experiment was made under about the same conditions as those prevailing in No.2, an iron pipe, however, being used instead of the clay tile to prevent cracking. The results of this experiment are shown in table No. 3.

Table for Experiment No.3.

| Size | Time in Minutes of Roast | Magnetic Part | | Non-magnetic part | |
|--------------------|--------------------------------|---------------|-------|-------------------|-------|
| | | % S. | % Zn. | % Zn. | % Fe. |
| Natural | 5 | 42.1 | 4.37 | 47.35 | 11.11 |
| Natural | 20 | 39.1 | 4.68 | 59.68 | 2.05 |
| Through 16 mesh | 10 | 41.3 | 4.29 | 48.33 | 10.46 |
| Through 16 mesh | 15 | 41.8 | 4.64 | 53.87 | 6.45 |

In this experiment also the jack is insufficiently cleaned. It does seem possible, however, to obtain an iron product with sufficient sulphur to make it marketable.

SUMMATION.

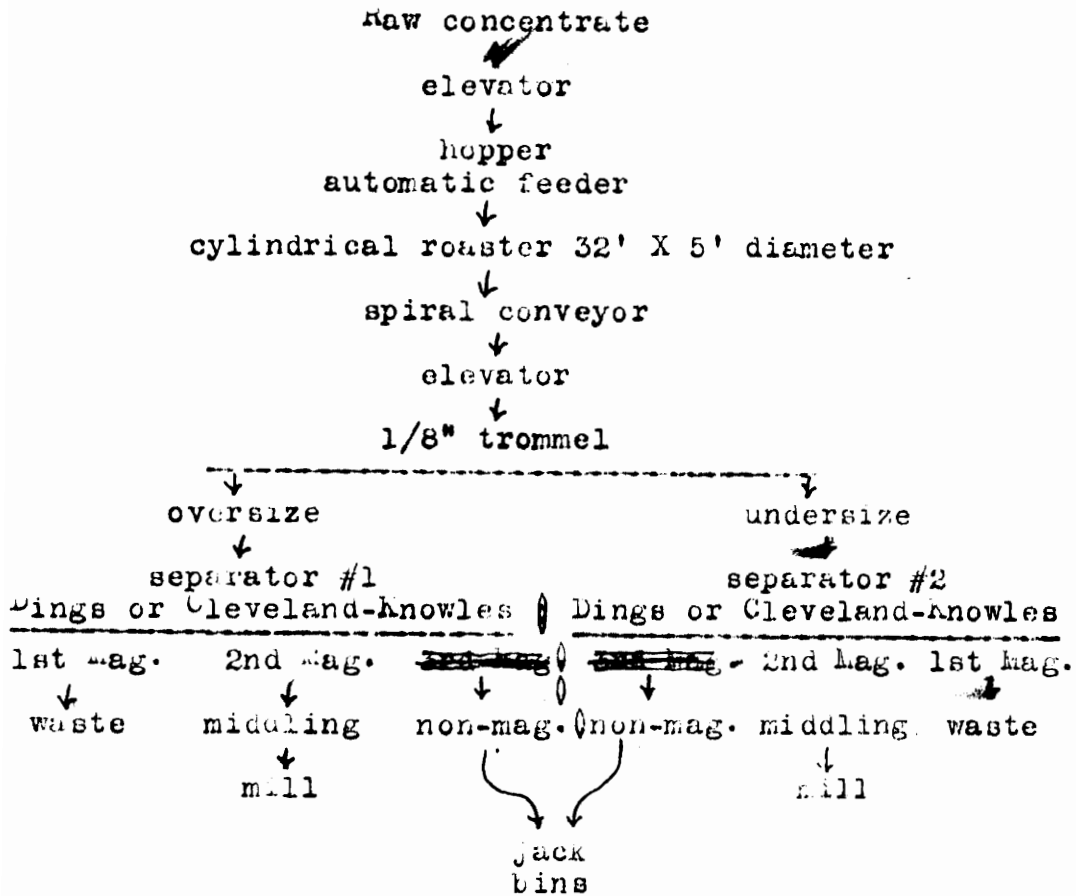
Summing up the above experiments we find that when pyrite is heated at temperatures between 600 and 700° C., in an atmosphere of nitrogen, the resulting product is strongly magnetic and the sulphur loss may be kept so low that the product contains at least 40 per-

cent sulphur. Whether the magnetic properties are due to the magnetic sulphide or to the formation of a skin of magnetite by the small amount of oxygen present we are unable to say.

From experiment No.2 we find that the iron mineral can be made magnetic in an atmosphere low in oxygen and that under these circumstances there may be no larger loss of sulphur than in experiment No. 1 in which oxygen ~~was~~ ^{may} practically ~~be~~ absent. It appears that the sulphur content, when the material is roasted for the length of time given in our experiments, is constant for all sizes up to the maximum tried which was about 0.86m.m.

SUGGESTIONS FOR METHOD OF PROCEDURE IN
PRACTICE IN WISCONSIN.

Flow sheet of the typical present plant:



The furnaces used to prepare the ore for magnetic separation are cylindrical in shape, 5 feet in diameter by 32 feet long. It is built of boiler plate and lined with fire-brick. The shell is fitted with two tires each of which rests upon a set of rollers. Furnaces, of

course, may easily be given any desired inclination thus accelerating or retarding the speed with which the material passes the cylinder.

The furnaces are rotated from a counter shaft through gears set at the ratio of one on the shaft to 50 on the cylinder. The diameter of the furnace at each end is lessened to 2.5 feet by fire-brick walls. The gases on their way to the stack are drawn through a dust chamber. Connections at the ends of the cylinder are made by cast-iron necks projecting into the openings. The bridge wall of the fire box is built so high that the hot gases impinge on the roof of the cylinder and do not strike the hot discharging ore. The furnace makes from one to two revolutions per minute.

The separators used are of the Cleveland-Knowles and Ding types. No attempt will be made here to describe these machines as we are particularly interested in the roasting preliminary to the magnetic separation.

It is apparent that the roaster, run under the conditions described, is not suited to our purpose; that is, making the iron mineral magnetic, but allowing the iron to retain 40 percent sulphur or better. There is too much oxygen allowed to pass into the cylinder or, in other words, the conditions are very favorable for the burning of the sulphur to sulphur dioxide.

There are a number of ways in which the conditions within the cylinder may be made less oxydizing or even carried to the point where the conditions become, actually reducing. This does not mean the oxygen has to be entirely absent or even that the oxygen content must be greatly below 17 or 18 percent since, in order for pyrite to burn, the oxygen under the conditions in the roaster can not be much less than that in ordinary air. One way of regulating the oxygen supply is by maintaining a thick bed of coals, making of the fire box a gas producer. Another method to regulate the oxydizing action is to feed a part of the products of combustion again thru the roaster. This is the Eldred process of combustion and could be made to control not only the oxygen content of the roaster gases but also the temperature.

It seems that by using crude oil as fuel and supplying just enough or even an insufficient supply of air to burn the oil would be a better scheme as it would be more easy to regulate and, at the same time, a reducing atmosphere could be approached if need be. With this scheme the products of combustion would not have to be returned as the front end of the furnace could be almost closed except for the small space required for discharge of ore and for the entrance of the oil burner. Since the

hot ore would burn with a loss of sulphur if discharged into the air, the roasted material could easily be discharged into a closed or cooled hopper. The price of crude oil per heat-unit should not be greatly more ~~expensive~~ ~~expensive~~ than fuel.

As the Mathey furnace is now run the ore takes from one to two hours to pass through it. This consumes entirely too much time for the purpose. We suggest that the speed be increased considerably along with the inclination so that the ore would remain in the furnace from 15 to 20 minutes. Of course, the exact time would have to be determined for each individual ore.

It is evident that the changes to the present plant as suggested would not increase the cost per ton for treatment ~~of~~ an appreciable amount. Should a new plant be built it is suggested that a roaster to handle the tonnage of the present plant would not have to be over one-third as long and from one-half to two-thirds the diameter of the present furnace.

It might be possible to construct a furnace consisting essentially of an enclosed space which could be treated to 700 ° C. or over and through which heated area travelling iron conveyor carrying the ore in a more or less thick bed could be passed. The conveyor, of

course, could not remain for a long time in the hot furnace without being protected by suitable cooling devices. The product from this furnace would, as would the product from any other type of furnace, contain many iron particles still in a non-magnetic condition. This would be particularly true of the scheme suggested because of the fact that that part of the ore resting immediately on the conveyor would necessarily be relatively cold.

A process has recently been invented by Prof. Stewart W. Young of Stanford University whereby the various oxides of sulphur resulting from roasting furnaces may be reduced to elemental sulphur. The process is patented and is called the Thiogen Process. An account of it may be found in the Engineering and Mining Journal May 4th, 1912, (vol. 93, No. 18, p. 873) The reduction in this scheme is accomplished by spraying crude-oil into a hot chamber through which the gaseous products carrying the sulphur oxides are passing. The hydrocarbons formed reduce these oxides to elemental sulphur which is later condensed by a spray of water.

This process might be applied to a roaster such as described above and the sulphur obtained combined with the magnetic iron material thereby increasing the sulphur content.

Much of the sulphur escaping, under the conditions in the roaster which we have suggested, is undoubtedly elemental. Simple cooling of the gases below the boiling point of sulphur (444° C.) would probably not result in great condensation because in gases very dilute in sulphur as are these roasted gases the vapor tension of sulphur would probably allow it to support its partial pressure to low temperatures.

From the results of our experiments, the conditions of which could be obtained in practice, it seems that the present plants in the Wisconsin district could, at little expense, be made to deliver an iron product sufficiently magnetic and yet containing enough sulphur to be marketable.

BIBLIOGRAPHY.

J. C. Clark, at the Missouri School of Mines and Metallurgy, in 1911, did some work in connection with pyrite smelting which is of interest in our problem. Mr. Clark investigated the behavior of pyrite when subjected to heat at different temperatures in an atmosphere of nitrogen. There is considerable literature dealing with the action of pyrite under the conditions named, especially under the conditions obtained in the blast furnace. From Mr. Clark's work it appears that pyrite begins to change its composition even as low as 200 or 300 degrees centigrade. A pyrite containing when raw 52 percent sulphur after being heated to 200 degrees centigrade assayed 51 percent and, after being heated to 300 degrees centigrade, contained only 49.8 percent sulphur. This same pyrite, when heated in an atmosphere of nitrogen to 400 degrees centigrade, still carried 49.2 percent sulphur, but, when heated to 500 degrees centigrade, had remaining in it only 40 percent sulphur. When, in this series of experiments carried on by Mr. Clark, the temperature was gradually increased to 800 degrees the sulphur content fell only to 38.7 percent. After being subjected to a temperature of 1600 degrees

centigrade the material retained 35.5 percent sulphur. In each of the experiments the pyrite was heated for one hour at the temperature mentioned. From the work of Mr. Clark it appears that there is a sudden drop in the sulphur content when the material is carried from 400 to 500 degrees centigrade and that the material does not go lower in sulphur content than that of pyrrhotite (38 or 39 percent) until temperatures considerably higher than 900 degrees centigrade are reached.

If there is a sudden break in the sulphur content under the conditions suggested in our experiments for the roasting, as is shown in the experiments of Mr. Clark, it is a very important point to consider.

C. G. Gunther: Electro-magnetic Ore Separation.

Pyrite and marcasite are neither attracted by the most intense magnetic fields; therefore, to separate either of these minerals from blende, a preliminary roast is necessary. There are two methods of rendering the iron magnetic: a slight roast, forming the magnetic sulphide or a more complete roast, forming the magnetic oxide of iron. These two compounds are strongly magnetic and are attracted by fields of low intensity.

The roast must be uniform as the efficiency of

the separator will depend largely on the character of the material presented to it. Any separator will make a clean product when fed a properly roasted material but the best separator will not efficiently clean poorly roasted material.

Pyrite and marcasite begin to change over to the magnetic sulphide at 370° C. and, to obtain the best results, the roast of a marcasite blende ore must be carried on between this temperature and the ignition point of sphalerite which is about 600° C. This temperature may, however, be slightly exceeded (620°) without harmful results.

Ores should be sized before being roasted due to the fact that the small particles are more easily oxidized and may be over-roasted while the larger particles are not sufficiently converted to magnetic compounds.

Care should be used in cooling ore to prevent decrepitation and it should be fed to the separator immediately without any crushing. If ore is crushed it should be re-roasted.

Richards: Ore Dressing, Vol.2, p.813, article 597
Roasting for Magnetism.

Pyrite is weakly magnetic but may, upon being

roasted under oxidizing conditions, be converted into the magnetic sulphide (Fe_7S_8) by driving off some sulphur as sulphur dioxide. There is a tendency for the iron to oxidize, however, thereby making the process to obtain magnetic sulphide hard to regulate unless some carbonaceous matter is added toward the end of the roast to act as a reducing agent or protector of the sulphide from the action of oxygen.

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