

REMOVAL OF COPPER FROM THE REVERBERATORY SLAG BY  
MEANS OF IRON SULFIDE

by

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## INTRODUCTION

The main loss of copper in its process metallurgy comes from the reverberatory slag carrying as waste approximately 12,000 tons of this metal from the world production each year.

If we consider that the many ores being used recently average one or two percent of copper, the reverberatory slag with its half percent of copper content suggests an important problem of recovery which may have an industrial significance in the future. This has already been tried at the Anaconda Copper Mining Company many years ago by addition of pyrite.

The author has thought that an investigation on removal of copper from the reverberatory slag by means of iron sulfide might be helpful for further work and decided to study this problem which has been treated only once in 1919.

## SUMMARY OF THE WORK

The author has used a slag sample obtained through the courtesy of Anaconda Copper Mining Company, and a synthetic iron sulfide as materials. He fused samples of slag, averaging 100 grams, in graphite crucibles, under different conditions by varying temperatures, time of fusion, and iron sulfide content.

As temperature he used 1100, 1200, and 1300 degrees centigrade, as time of fusion one, three, and five hours, with 0, 5, 10, and 20 percent of iron sulfide additions in slag. These variations gave 36 different fusions; most of these fusions produced a separation of matte at the bottom of the crucible.

The results are summarized as follows: fusions of slag without iron sulfide addition at 1100 degrees centigrade gave no separation; five percent of iron sulfide addition with one and three hours of fusion also gave no separation; but at higher temperatures each fusion gave a matte formation. Increase of iron sulfide content produced an increase in copper recovery reaching 70 percent at higher temperatures for 20 percent iron sulfide addition. Increase of time of fusion favored the increase in copper recovery at 1100 and 1200 degrees centigrade, although it seems to be no effect of time of fusion at 1300 degrees centigrade. The maximum recovery of copper from pure slag fusion is about 40 percent.

## PREVIOUS WORK

The only work done on this subject <sup>which has been published</sup> is by C. G. Maier and G. D. Van Arsdale. But the author thinks that the form in which the copper occurs in the slag is a very important factor in the problem. For this reason he will summarize the previous studies carried out on copper loss in the reverberatory slag.

Thomas Kiddie (1) using dilute sulfuric acid as a solvent determined the copper in the oxidized condition in a number of slags, and concluded that under the conditions investigated, this constituted more than half of the total copper, (1911).

Frank E. Lathe (2) has duplicated the first study and obtained similar results, most of the copper being soluble in sulfuric acid. (1915)

C. G. Maier and G. D. Van Arsdale (3) made a complete and careful microscopic examination of different slags. They also treated finely ground slags with one percent of neutral silver nitrate solution as a means of determining the amount of suspended copper or copper sulfide particles. Oxides and silicates, they considered absent.

Experiments outlined indicate that the copper exists in two physical forms:

1. Dissolved copper sulfide
2. Mechanically suspended particles of sulfide copper varying in composition from matter to  $\text{Cu}_2\text{S} + X \text{ Cu}$ .

The probable cause of the reaction of mechanically suspended

particles, aside from inefficient settling and viscosity, is the attachment of gas bubbles, which probably is due to the action of ferric iron in the slag.

Finally they fused the slag samples at about 1300 degrees centigrade by separate additions of copper bearing pyrite, iron sulfide and a mixture of pyrite and calcium sulfide. From these three experiments the results corresponding to iron sulfide addition are illustrated on figure 1 of page 6.

The original copper content of the slag was 0.31 percent, but the silver nitrate test showed 0.09 percent of copper as suspended sulfide globules, leaving an original dissolved 0.22 percent of copper. The effect of copper bearing pyrite addition was limited to suspended particles. Twenty percent of iron sulfide addition gave about fifty percent of copper recovery, while the recovery increased to 65 percent for the same amount of pyrite and calcium sulfide mixture. There is no data on the kind of crucible used, the time of fusion, and fineness of mixture. (1919)

C. G. Maier and G. D. Van Arsdale (4) found that the effect of magnetite in reverberatory slag was to increase the loss due to sulfide flotation by attached gas particles. (1920)

Frank E. Lathe (5) insisted on the oxide form of copper in reverberatory slag, and discussed the non-accuracy of the silver nitrate method. On the other hand he explained the industrial effort to recover the copper from slags. (1920)

The suggestion of Mr. E. J. Carlyle is interesting. He



After Maier and Van Arsdale

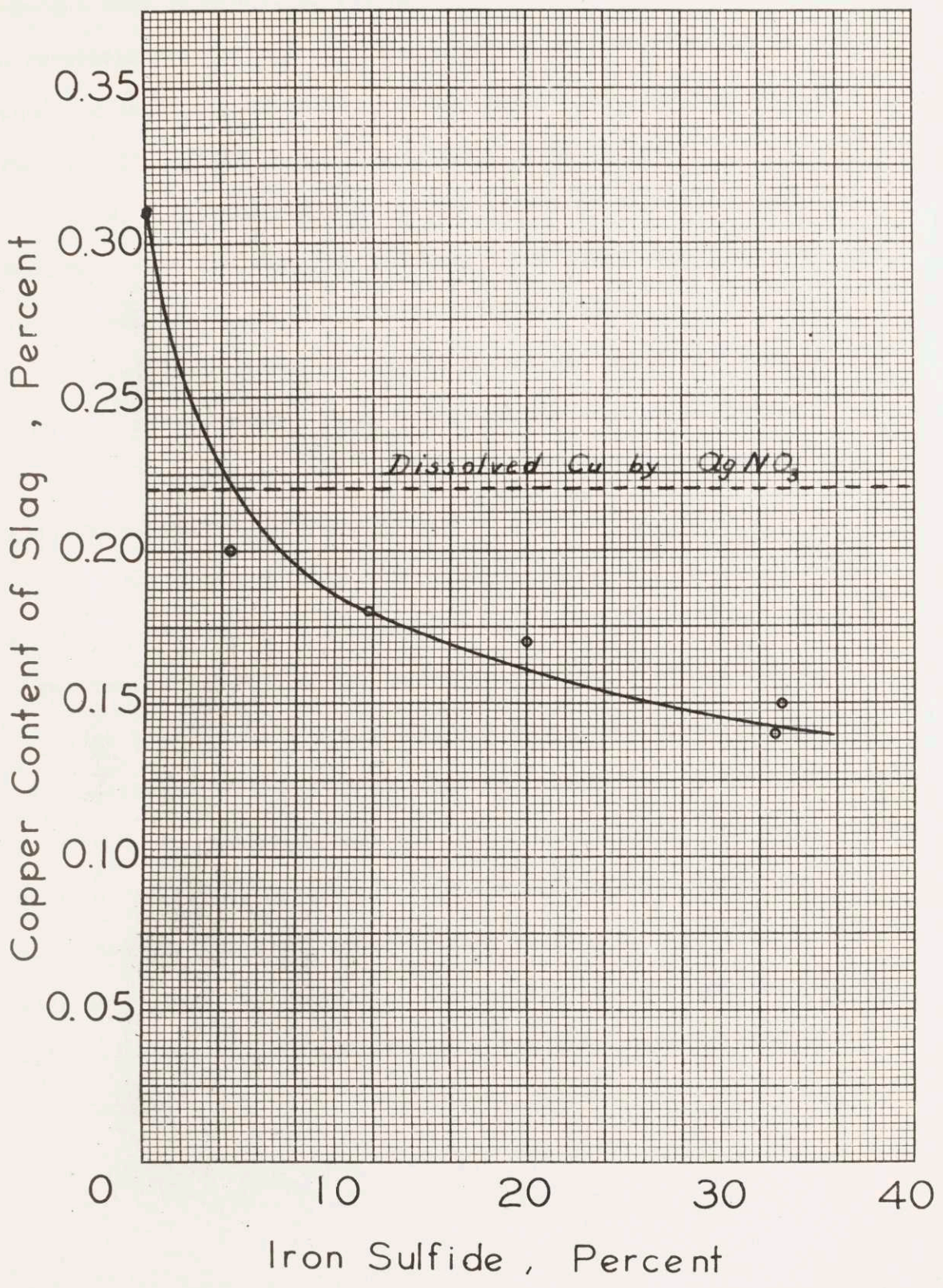


FIG. 1

thought that if a wall of refractory material were built across a reverberatory furnace near the skimming end, high enough to keep back the main body of matte, but low enough to allow the slag to run over it, pyrite could be charged through the roof.

D. M. Gordon (6) studied the effect of magnetite, and concluded that the reducing atmosphere and high temperature tend to decrease the magnetite content of slags. (1926)

Harold H. Block (7) on his investigation of the form of copper in reverberatory slags concluded the absence of copper in the form of oxides, and the presence of true pellet copper with globules of matte. (1928)

In his other study of origins of magnetite in copper slags, (8) he observed that clay crucibles were not satisfactory. They were attacked by both molten sulfides and slag. It was noted, however, that the molten sulfides and slag penetrated the crucible walls, instead of the crucible material dissolving in the melt. (1931)

R. B. Jackman (9 and 10) made a microscopic and X-ray examination of different reverberatory slags and observed larger and fine suspended particles of copper sulfide varying in composition, but similar to bornite, covelite, and possibly to chalcopyrite. He also obtained a concentrate containing 45 percent copper by means of flotation.

## OUTLINE OF WORK

1. Analysis of slag for copper.
2. Grinding of slag and iron sulfide separately through 100 mesh.
3. Preparation of graphite crucibles from graphite electrodes.
4. Preparation and calibration of thermocouple.
5. Preparation and repair of the globar furnace.
6. Fusion of the charges.
7. Separation of matte and slag; weighing them.
8. Dividing the mattes in two; saving one part for further microscopic study; grinding the other part for analysis.
9. Chemical analysis of mattes on copper.
10. Chemical analysis of some slags obtained on copper.

PREPARATION OF MATERIALS AND APPARATUS

The slag was obtained through the courtesy of the Anaconda Copper Mining Company with its chemical analysis as shown in Table 1.

TABLE 1

Composition	Percent
Cu	0.65
S	41.0
SiO <sub>2</sub>	39.2
Al <sub>2</sub> O <sub>3</sub>	6.8
CaO	5.0
Zn	2.8
Pb	0.33

The slag was ground from 10 mesh to 100 mesh in a pulverizer, then sampled, and sent to the chemical analysis in order to check the percentage of copper. Five analyses were made and all averaged 1.15 percent copper in slag.

Iron sulfide was a commercial product, which was made by fusing iron in sulfur, and therefore it was free from copper. This product runs between 75 and 85 percent of ferrous sulfide (FeS) and the rest either excess iron or sulfur. It was in the form of rods five inches long and half an inch in diameter.

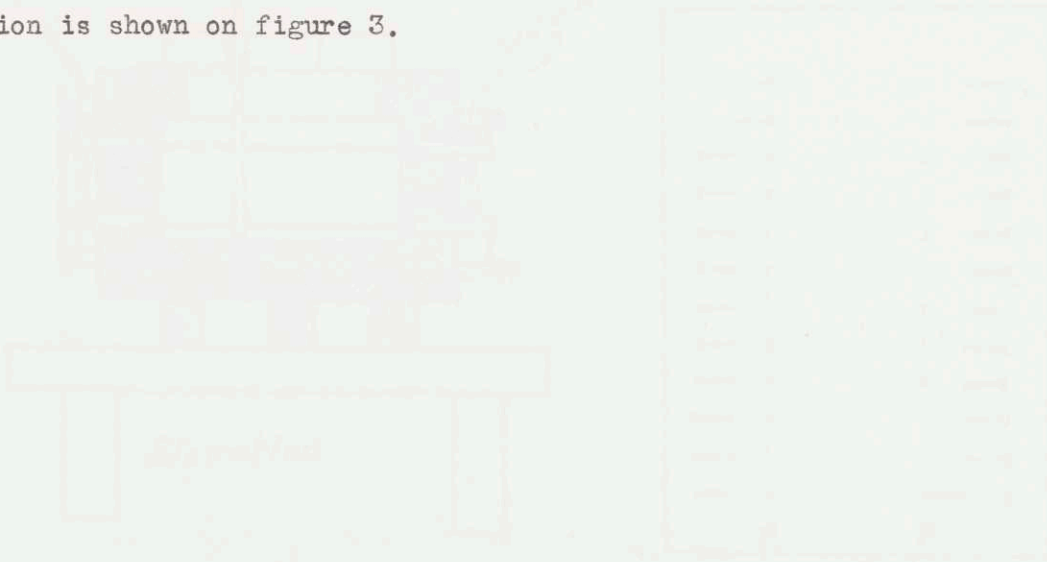
Fusions at 1100 degrees centigrade were carried out in a muffle type gas furnace which was made by the American Gas Furnace Company.

For higher temperatures the globar electric furnace was used. Two silicon carbide resistors of one foot in length were located one on top of another on two opposite side walls of the furnace. The resistor holders were cooled by means of a water cooling system. The top of the furnace is covered with three insulating bricks. The electric circuit is shown on page 11, figure 2.

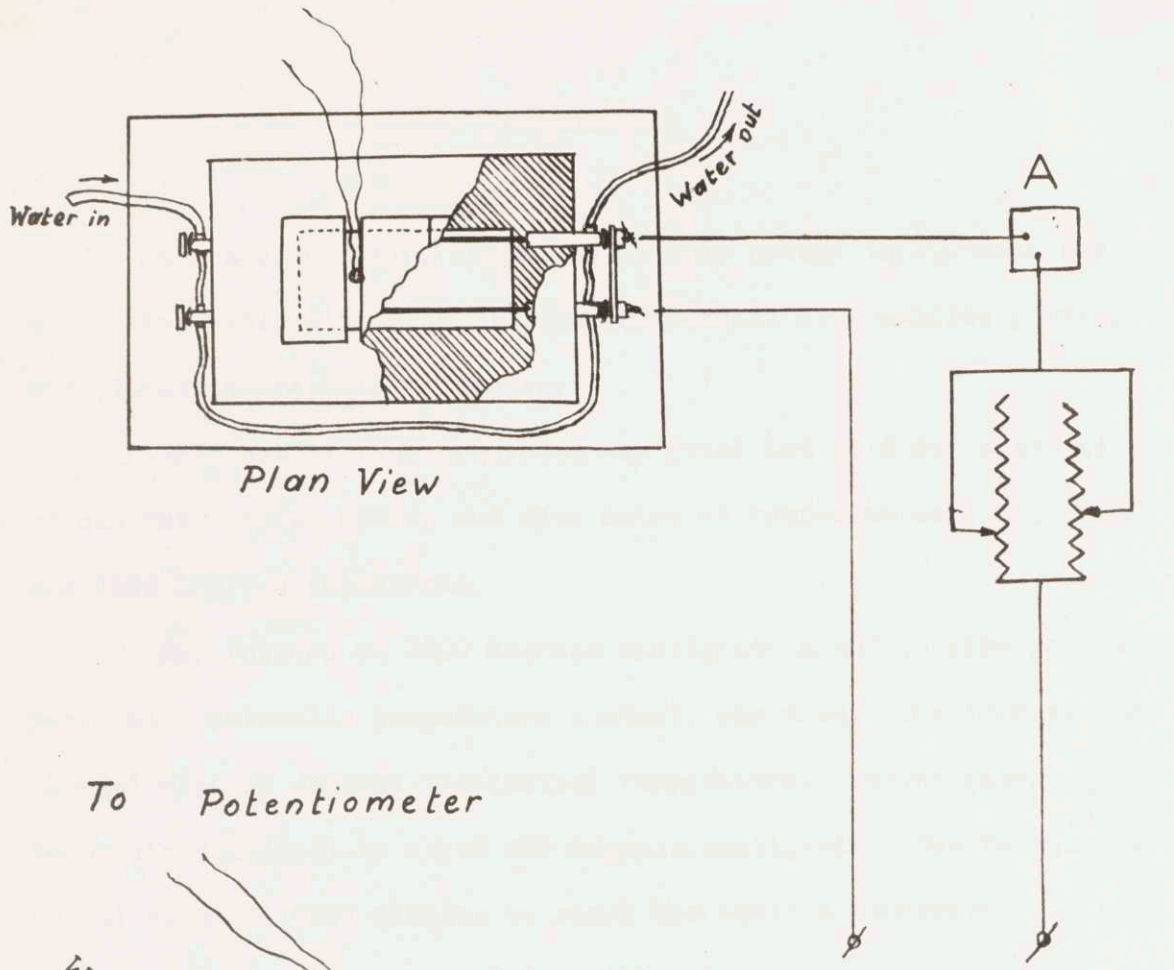
At 1200 degrees centigrade the temperature measurements were carried out with a chromel-alumel thermocouple connected to a potentiometer.

For 1300 degrees centigrade a platinum, platinum-rhodium thermocouple was used.

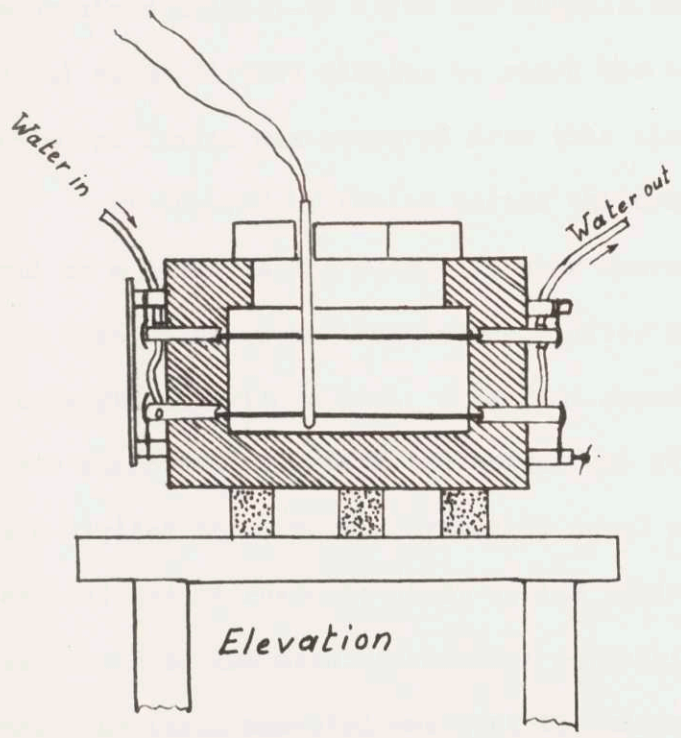
Fire clay crucibles have been tried, but were not satisfactory. Therefore graphite crucibles were made from graphite electrodes two and one-half inches in diameter. The electrodes were cut into pieces of five inches in length. These pieces were bored in the lathe. Their section is shown on figure 3.



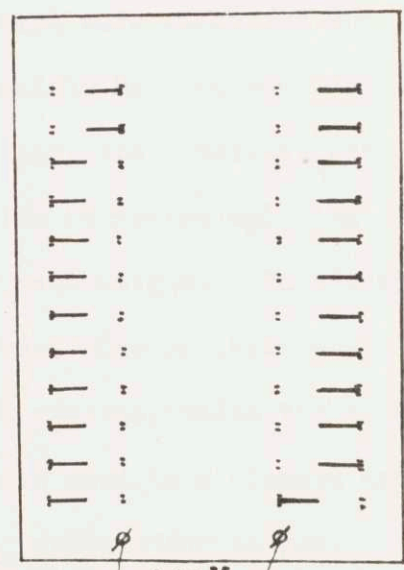
# Globar Furnace



To Potentiometer



Elevation



260V  
Switch Board

Fig. 2

## FUSION

The Anaconda slag which was already ground to 100 mesh was mixed thoroughly with 0, 5, 10, and 20 percent iron sulfide powder, and placed in graphite crucibles.

This set of four crucibles was fused and held for a period of one hour, three hours, and five hours at temperatures 1100, 1200, and 1300 degrees centigrade.

For fusions at 1100 degrees centigrade a muffle type gas furnace, with automatic temperature control, was used. The furnace was charged when it reached the desired temperature. During charging the temperature dropped to about 900 degrees centigrade. The furnace required about fifteen minutes to reach the desired temperature. The period of fusion was measured from this time.

At the end of fusion period the crucibles were taken out and laid on a bench in the room. It took approximately half an hour to cool down to the room temperature. After cooling, the crucibles were cut lengthwise with a saw. A perfect separation of bottom and slag layer was obtained. Both the bottom and slag were weighed. Then they were divided into two approximately equal pieces. One of these was reserved for microscopic study of the polished section, while the other was ground to 100 mesh, first in a porcelain and then in a diamond mortar. The final material was sent to chemical analysis for copper.

For other fusions the same procedure was repeated, except the fusions at 1200 and 1300 degrees centigrade were carried out in an electric globar furnace which a line sketch represents in figure 2.

The set of four crucibles fused at 1200 degrees centigrade for a period of one hour is also shown in figure 3, on page 14.



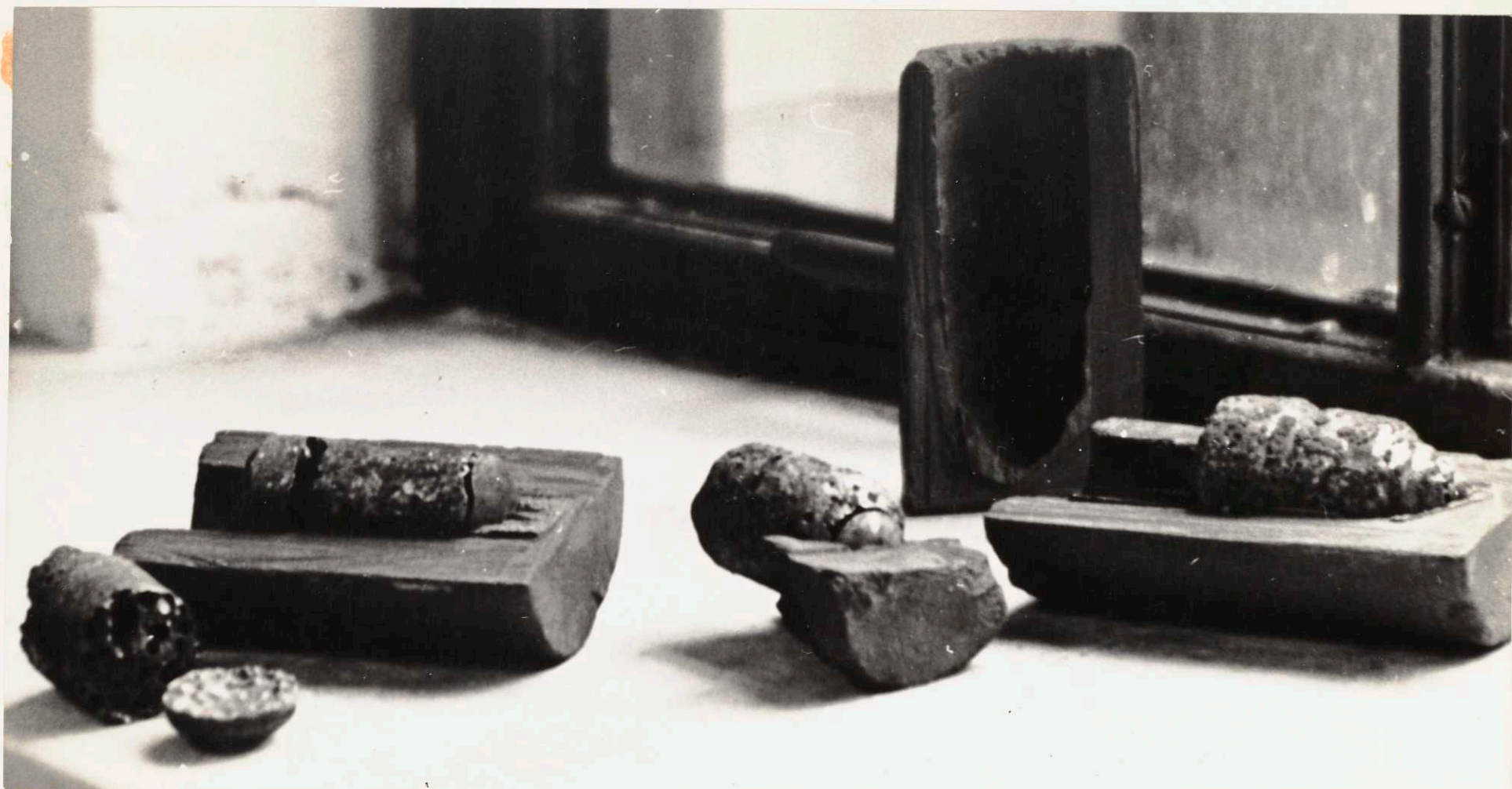


Fig. 3

## ANALYSIS FOR COPPER CONTENT

A weighed sample was decomposed with sulfuric, nitric, and hydrofluoric acids in a platinum dish. Evaporation was carried out to fumes of sulfuric acid. The residue was transferred with water and hydrochloric acid to an erlenmeyer flask and boiled. Ammonia was added, and the excess boiled.

Eight cubic centimeter of glacial acetic acid was added and boiled for two minutes. Then the solution was cooled, diluted to 200 cubic centimeter, and ammonium bifluoride was added until the discoloration due to iron disappeared and the solution became blue or colorless. Three grams of potassium iodide was added, solution was shaken until cuprous iodide precipitated.

The titration was carried out with the standard sodium thiosulfate using starch as indicator.

## DISCUSSION OF RESULTS

For the calculations the copper content of slag is accepted to be 1.15 percent as it is found from analyses carried out in the Institute laboratories.

The results are tabulated on page 17 and illustrated by figures 4, 5, and 6, which show the variation of copper recovery in function of temperature and time of fusion, and iron sulfide addition.

### A. At 1100 degrees centigrade.

No separation of mattelike bottom from pure slag is obtained at this temperature. With five percent iron sulfide addition, the separation is obtained only after five hours of fusion, which shows the effect of fusion period. By increasing time, the washing of matte and copper bearing particles and their settling are favored. Recovery is averaging 45 percent with 20 percent of iron sulfide addition which is the main factor on recovery increase.

### B. At 1200 degrees centigrade.

Separation is obtained from each fusion. The settling time is still an important factor. The highest percentage of copper (38 percent) in matte is obtained at this temperature from the pure slag fusions. Although the weight of the bottom was much smaller than the other separations.

The percentage of copper in matte decreases by addition of iron sulfide. It decreases down to 2.5 percent of copper for 20 percent of

Temperature °C.	Time of Fusion Hours	FeS %	Slag charged Grams	Slag obtained Grams	Cu % in Matte	Weight of Matte Grams	Cu Removed from 100g. of Slag. Gr.	Cu Recovery %
1100	1	0	100					
"	1	5	100					
"	1	10	100		5.145	1.55	0.08	7.0
"	1	20	100		15.94	2.63	0.42	36.2
"	3	0	100					
"	3	5	100	108.				
"	3	10	100	98.6	9.876	2.71	0.265	23.1
"	3	20	100	93.39	26.175	2.13	0.558	48.5
"	5	0	100	98				
"	5	5	100	98.5	3.134	7.32	0.228	19.8
"	5	10	100	98	4.429	4.42	0.416	36.2
"	5	20	100	92.5	26.54	2.2	0.585	51.0
1200	1	0	130	128.5	0.384	35.0	0.097	8.3
"	1	5	75	75.0	2.847	9.9	0.38	33.1
"	1	10	75	74.5	6.903	5.8	0.51	44.3
"	1	20	75	71.	18.599	2.8	0.69	60.0
"	3	0	150	141.5	1.89	31.9	0.40	34.8
"	3	5	75	67.8	3.815	7.5	0.38	33.1
"	3	10	75	70.3	8.68	3.67	0.42	36.2
"	3	20	75	68.5	19.48	2.20	0.57	49.6
"	5	0	150	144	1.13	38.2	0.29	25.2
"	5	5	100	96.5	4.23	16.7	0.70	61.0
"	5	10	100	94.0	6.70	6.59	0.71	61.7
"	5	20	100	92.5	3.378	3.3	0.816	71.
1300	1	0	120	107.0	1.795	20.5	0.325	28.2
"	1	5	75	65.5	6.965	5.8	0.54	47
"	1	10	75	62.5	12.81	3.7	0.63	55.0
"	1	20	75	55.0	24.31	2.6	0.84	73.2
"	3	0	150	129	8.99	4.43	0.27	23.2
"	3	5	75	67.0	5.74	5.76	0.421	37.1
"	3	10	75	66.7	9.17	4.76	0.58	50.3
"	3	20	75	65.0	21.95	2.65	0.747	65.0
"	5	0	150	126.9	10.69	4.6	0.33	28.4
"	5	5	75	63.2	5.55	5.5	0.54	47.0
"	5	10	75	44.6	14.27	3.3	0.615	53.5
"	5	20	75	59.1	24.70	2.3	0.759	66.0

At three hours fusion the samples were allowed to cool slowly in the furnace, and by cutting them it was observed that there was an intermediary layer between the matte and slag, attached to slag side. The comparatively low percentages obtained in this set is probably due to a slow diffusion both of slag and matte to each other to form this layer. Further microscopic study will clear up this phenomenon.

At each temperature as the weight of matte increases with iron sulfide addition, the corresponding slag weights decrease gradually. There is also a very marked decrease on the total weight of the charge due to sulfur loss and reduction of oxides. Experiments were carried out in reducing atmosphere because of the graphite crucibles; and this prevented any effect of magnetite by reducing it.

The slags were covered by many metallic grains on their contact with the crucibles, while the inside having a homogeneous structure and holes of gas bubbles, (figure 3).

The form of the crucible bottom is important. A flat bottom does not favor a small amount of matte formation, while a conical bottom with a small angle favors separation of any amount of settled matte. 20 percent of iron sulfide addition provided 65 percent of copper recovery at this temperature.

C. At 1300 degrees centigrade.

Increase of temperature from 1200 to 1300 degrees centigrade has no effect on the recovery.

Copper percentages of mattes from pure slags are not high, averaging 5 percent of copper. But their weight is increased conversely

giving approximately the same copper recovery that was obtained at 1200 degrees centigrade. The mattes obtained show magnetic properties; especially those from pure slag fusions have nearly metallic structure and much magnetic property. The color of slags changed from dark brown to yellowish, green-brown. They were also covered with a fine metallic grain formation at their contact with crucibles.

The loss of sulfur was mostly in form of sulfur vapor and not as sulfur dioxide. A continuous formation of sulfur precipitation around the upper part of the silica tube of thermocouple showed it. Reducing atmosphere prevented sulfur dioxide formation.

The maximum recovery obtained is with 20 percent of iron sulfide addition, at 1300 degrees centigrade. This maximum recovery is 73 percent of copper from the slag. This result compared with 50 percent of recovery of C. G. Maier and G. D. Van Arsdale at the same temperature and the same amount of iron sulfide addition is satisfactory.

## 1 HOUR OF FUSION

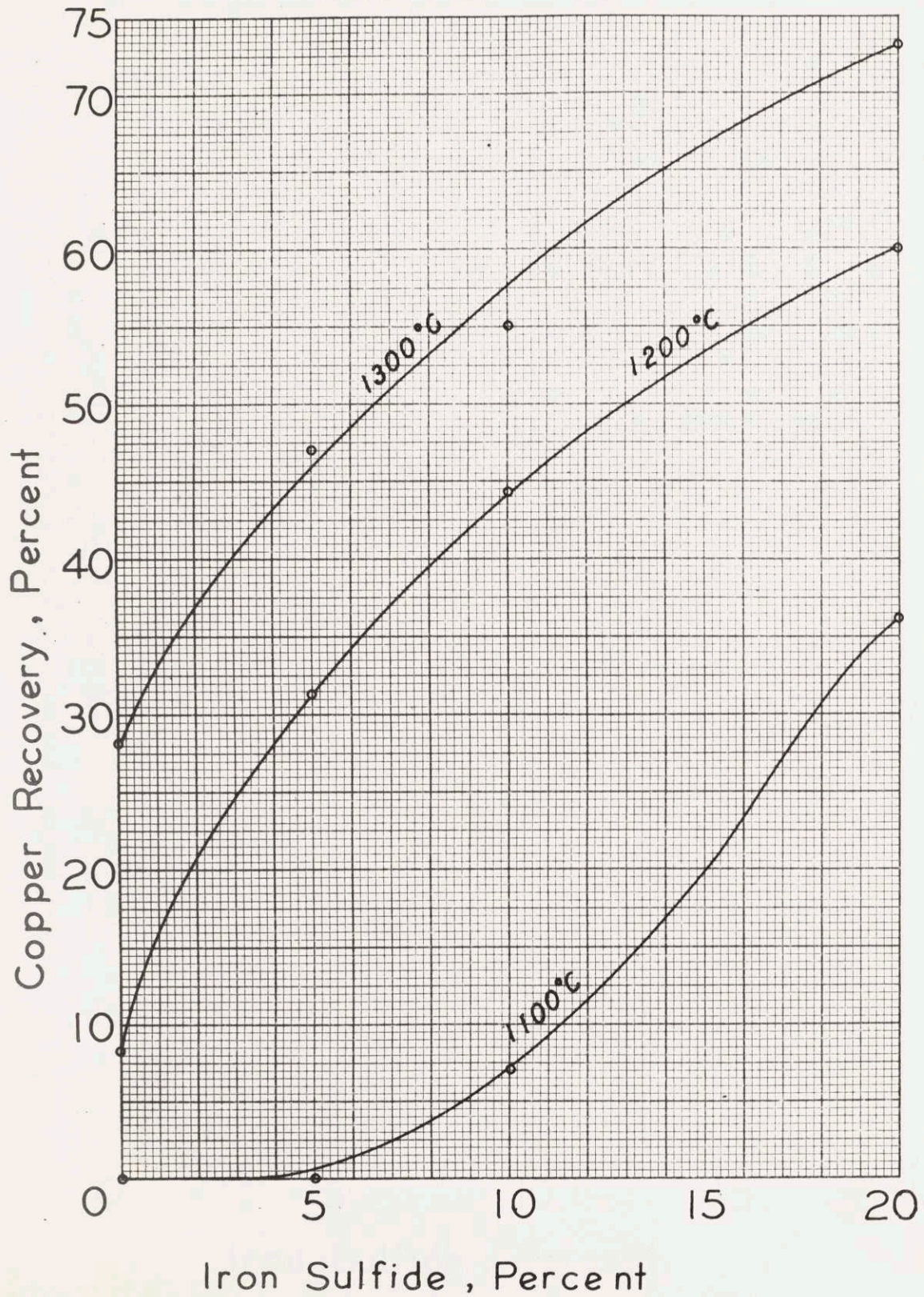


Fig.4

## 3 HOURS OF FUSION

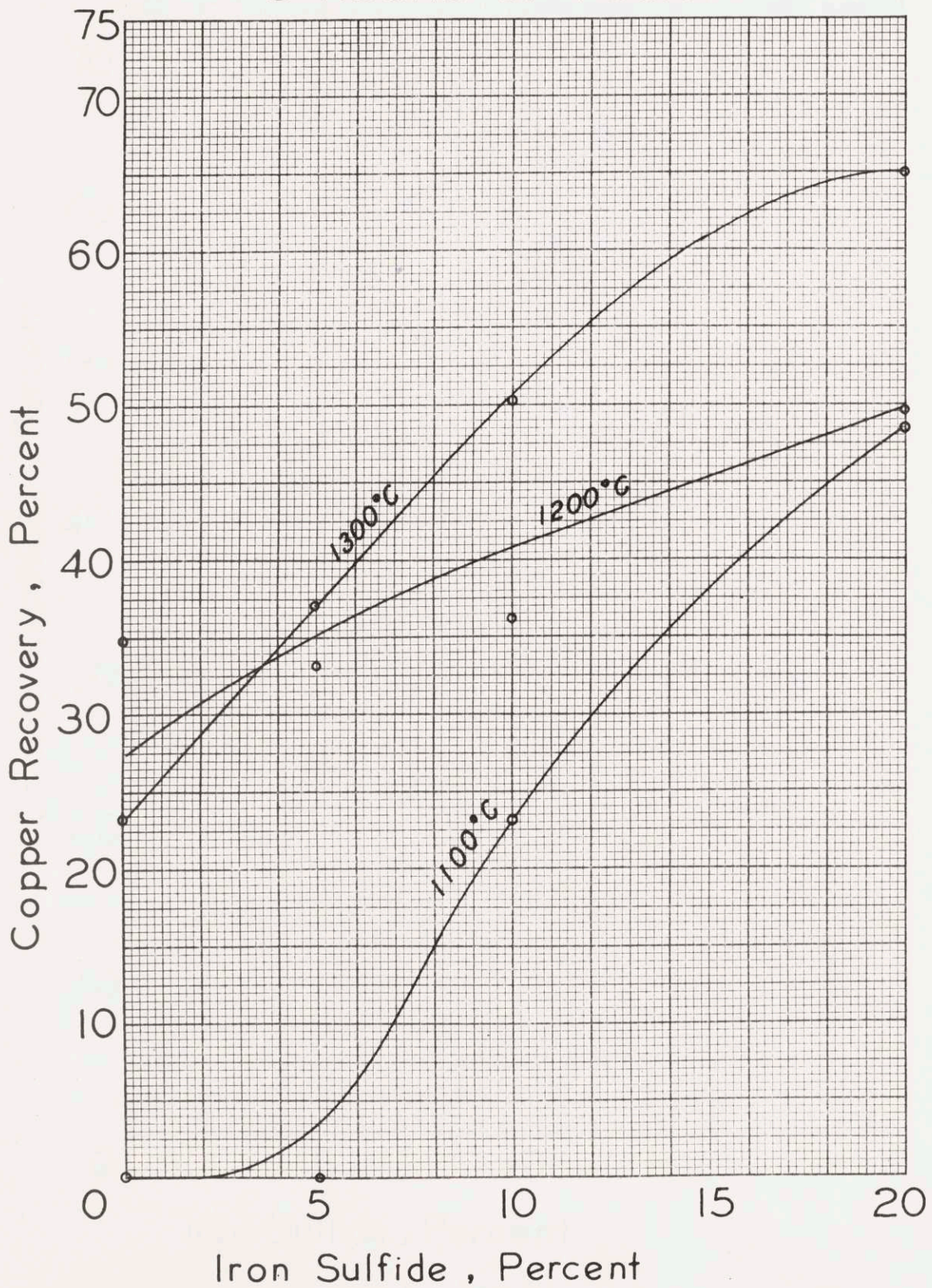


Fig.5



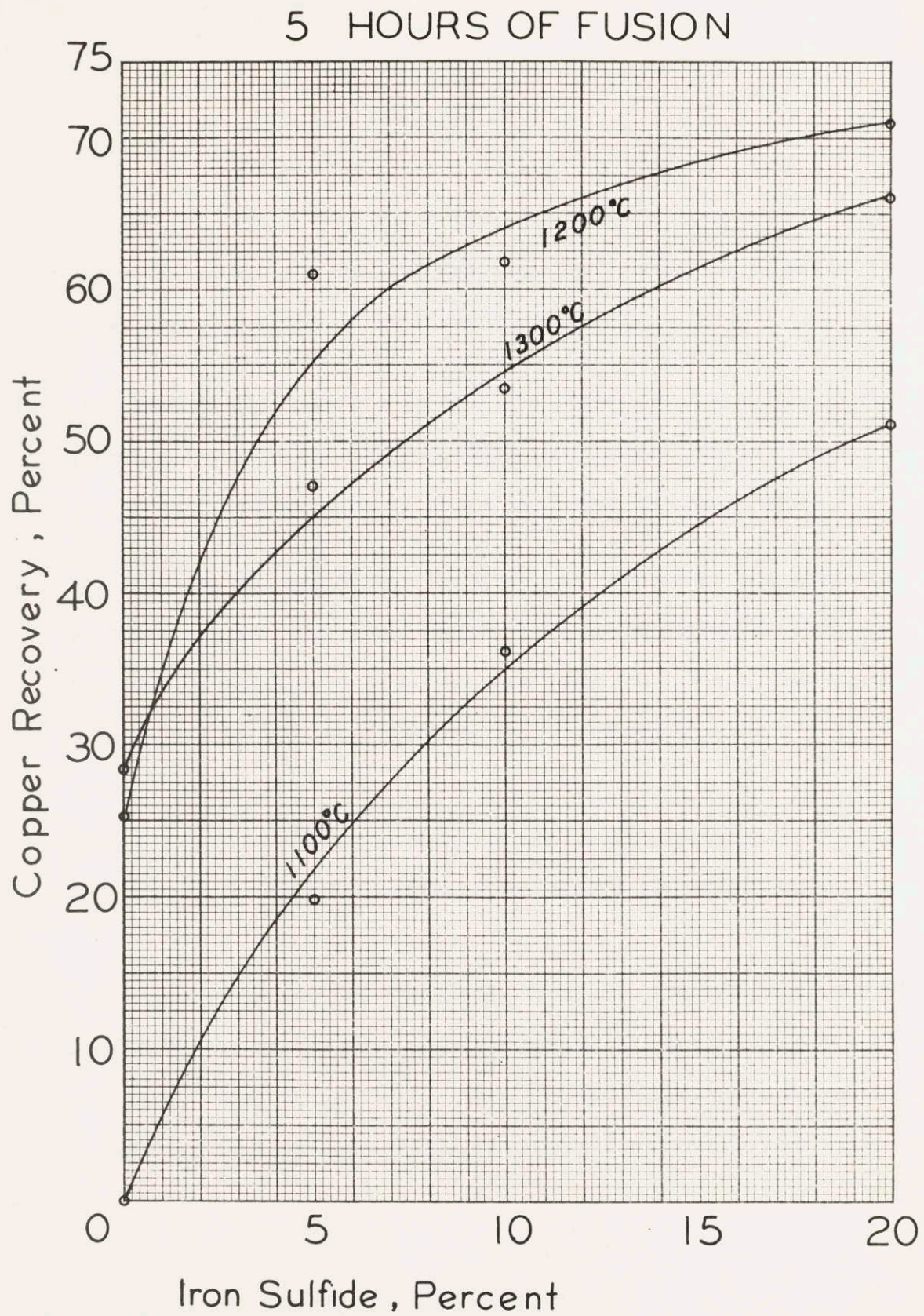


Fig.6

## CONCLUSIONS

1. Removal of copper from the reverberatory slag by means of iron sulfide is possible. The highest recovery reached is 73 percent of copper for 20 percent of iron sulfide addition.
2. Increase of iron sulfide is the main factor on the copper recovery. It washes downward the copper sulfide particles, and generates sulfur for sulfide formation if there is copper in other forms.
3. An increase in temperature provides an increase in the recovery for lower periods of fusion, while for 5 hours of fusion 1200 and 1300 degrees centigrade give the same recovery. For higher depth of settling the time factor may have more importance.
4. The effect of reducing atmosphere was found predominant and very important. It tends to eliminate the effect of magnetite.
5. At higher temperatures the mattes from pure slag fusions were diluted with the excess iron coming from reduction of iron oxide of the silicates. Their magnetic property and metallic aspect suggest the presence of an iron-copper alloy with small quantity of sulfide.

## SUGGESTIONS FOR FURTHER WORK

The results obtained may have a practical importance with the illumination of results by further work.

The microscopic study on polished sections of mattes, slags, and grains covering the slags should be the first investigation.

The effect of the reducing atmosphere merits being studied carefully.

The slag used in these experiments was running very high on copper. If a study on slags containing low copper percentage, such as 0.3 or 0.4 percent, gives the same recovery as obtained here the importance of the results will be higher from practical point of view.

- (1) Thomas Kiddie, "Notes on Metal Losses in Copper Slags," Journal of the Canadian Mining Institute, 1911, Vol. 14, p.487.
- (2) Frank E. Lathe, "Metal Losses in Copper Slags," Engineering and Mining Journal, 1915, Vol. 100, pp.215, 263, and 305.
- (3) C. G. Maier and G. D. Van Arsdale, "Copper Smeltery Slag from Microscopic and Chemical Point of View," Engineering and Mining Journal, 1919, Vol. 107, p.812
- (4) C. G. Maier, and G. D. Van Arsdale, "Effect of Magnetite on Slag Losses," Chemical and Metallurgical Engineering Journal, 1920, Vol. 22, pp.1101, 1157.
- (5) Frank E. Lathe, "Copper Losses in Slags," Engineering and Mining Journal, 1920, Vol. 110.
- (6) D. M. Gordon, An Investigation of the Presence of Magnetite in Copper Mattes and Slags, Thesis at M.I.T. (1926)
- (7) H. H. Block, An Investigation of the Form of Copper Present in Reverberatory Slags, Thesis at M.I.T. (1928)
- (8) H. H. Block, Origin of Magnetite in Copper Reverberatory Slag, Thesis at M.I.T. (1931)
- (9) R. B. Jackman, The Forms in Which Copper Occurs in Reverberatory Slag, Thesis at M.I.T. (1932)
- (10) Carle R. Hayward and R. B. Jackman, "Forms of Copper Found in Reverberatory Slags," Transactions of the A.I.M.E., 1933, Vol. 106, p.111.