



RETENTION OF COPPER IN COPPER REVERBERATORY SLAGS

By

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Thesis

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I

INTRODUCTION

The amount of copper lost in smelting slags is considerable but thus far no economical method has been devised for preventing this loss.

Two methods of approach are possible, one having for its object the prevention of the copper from entering the slag and the other the recovery of slagged copper.

Before either of the above problems can be solved satisfactorily it is desirable to know the factors controlling the amount of copper in the slag and also the forms in which the copper exists in slags. With this knowledge it may be possible to determine the mechanism by which the contamination took place. Various papers ^{(1-3)*} have already been published on this subject but there is still little agreement among metallurgists.

It is proposed in this research to establish quantitative relations among the amount of copper in the slag, the composition of the slag, the composition of the matte, and the temperature.

* The references are cited at the end.

II,
SUMMARY

Mattes of varying copper content and slags of different compositions were fused in graphite crucibles and were held at a certain temperature for a certain period of time. Mattes were made from FeS and Cu₂S which were prepared synthetically from metallic copper, metallic iron and flowers of sulfur. Slags were also prepared synthetically from chemically pure oxides. After final fusion all the slags were analyzed for copper. Nine out of twenty-seven analyses showed no copper. This absence of copper in some slags indicated that under some conditions the passage of copper into the slag is prevented. Quantitative relations among the amount of copper in the slag, the composition of the slag, the composition of the matte and the temperature were not established because of the complexity of the controlled factors.

III
PREVIOUS WORK

Quite a number of papers have been published on the subject of copper losses in reverberatory furnaces and the forms in which copper occurs in these slags. With the exception of one, all these researches were carried out with commercial slag and consequently the variation in temperature, slag composition and matte composition could not be controlled as desired by the investigators.

In 1912 W. Wanjukoff⁽²⁹⁾ investigated the losses of copper in artificial slags of different degrees of acidity, with the oxides FeO, CaO, MgO, ZnO and Al₂O₃ replacing one another in varying proportions, as well as in contact with matte of all ordinary grades. He gives curves showing the amount of retained copper in the slag as functions of basicity and acidity. He also believes this retained copper is soluble in the slag in the form of sulphides. Some of his photographs show inclusions which put doubt in minds as to the accuracy of some of his results on the relationship between the total copper retained and the true solubility.

IV

OUTLINE OF EXPERIMENTAL WORK

The outline of the experimental work is given below.

- (1) Preparation of the copper sulfide
 - (a) Preparation of the copper sulfide
 - (b) Analysis of the copper sulfide
- (2) Preparation of the iron sulfide
 - (a) Preparation of the iron sulfide
 - (b) Analysis of the iron sulfide
- (3) Preparation of the mattes
 - (a) Preparation of the mattes
 - (b) Analysis of the mattes
- (4) Preparation of the copper-free slags
 - (a) Preparation of the copper-free slags
 - (b) Analysis of the copper-free slags
- (5) Fusion of the mattes and copper-free slags
 - (a) Preparation of graphite crucibles
 - (b) Fusion of the mattes and copper-free slags
 - (c) Analysis of copper-free slags for copper

V

EXPERIMENTAL WORK

Preparation of the Copper Sulfide

The Cu_2S was prepared the same way as described by C. B. Carpenter and C. R. Hayward⁽³⁾. The copper strips were cut into small pieces, placed in a No. 20 graphite crucible in the large gas-filled pot furnace in Room 4-017 of the Fire Metallurgy Laboratory and boiled in sulfur until all the metallic copper disappeared. Figure 1 shows the sketch of the furnace. After cooling, this partly sulfidized material was broken into small pieces, replaced in the crucible with more sulfur and again melted. This procedure was repeated once more. After final melting, the product was broken into small pieces and then ground to 100 mesh. The analysis of this product is shown in Table I.

TABLE I
Analysis of Copper Sulfide

Copper	79.51 per cent
Sulfur *	19.54
Insoluble	0.95
Total	100.00

* "by difference"

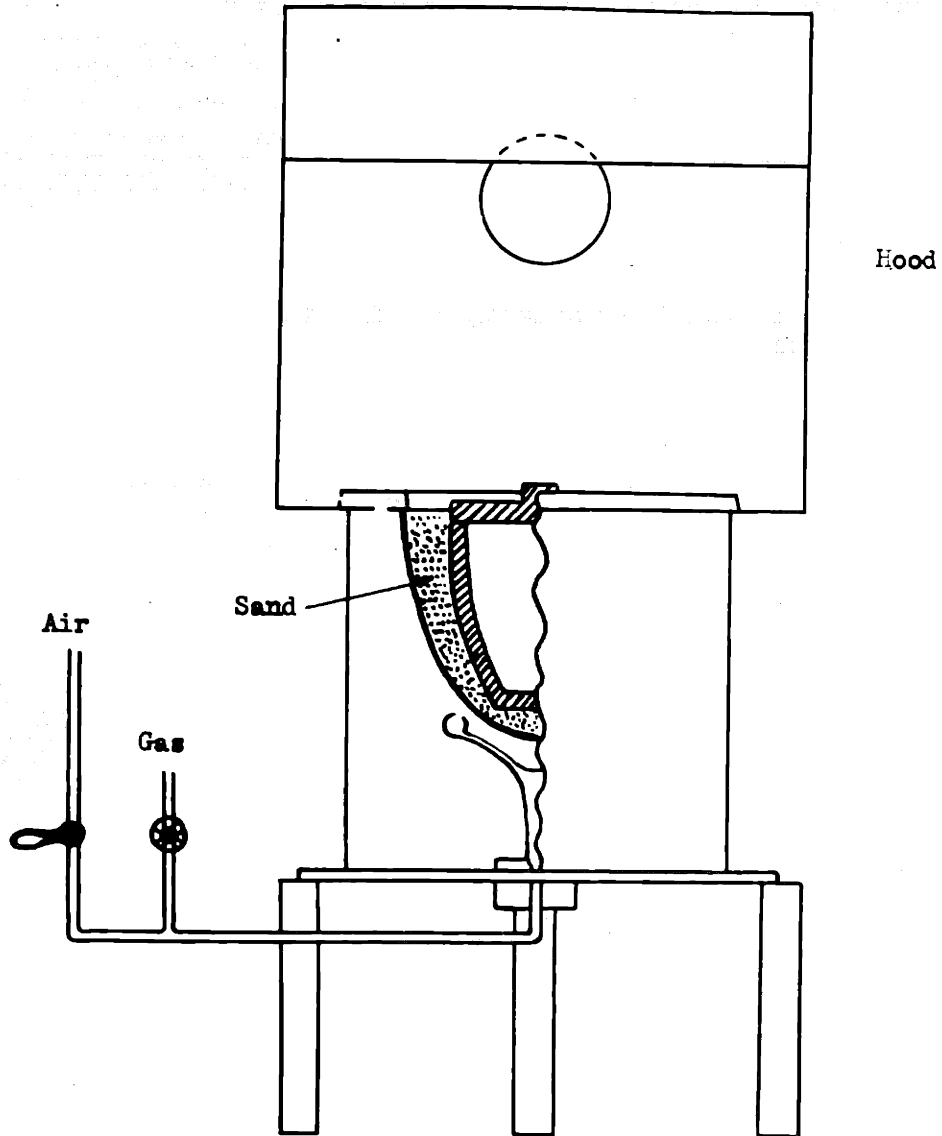


Figure 1 - The Large Pot Furnace

Preparation of the FeS

The FeS was also prepared the same way as described by C. B. Carpenter and C. R. Hayward⁽³⁾ except that in this work iron bars were replaced by iron turnings. The iron turnings were placed in a No. 20 graphite crucible and heated in the large gas-fired pot furnace to a bright redness. Then flowers of sulfur were thrown on it until the iron disappeared. After cooling, this partly sulfidized material was broken into small pieces and replaced in the crucible with more sulfur and again melted. This procedure was repeated once more. After final melting, the product was broken into small pieces and then ground to 100 mesh. The analysis of this product is shown in Table II.

TABLE II

Analysis of Iron Sulfide

Iron	63.00 per cent
Sulfur *	35.95
Insoluble	1.05
Total	100.00

* "by difference"

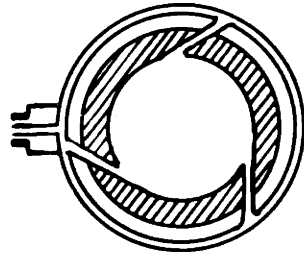
Preparation of the Mattes

Three grades of matte were prepared by mixing proper portions of Cu_2S and FeS which were already ground to 100 mesh in a pulverizer and melted in size I clay crucibles in the small gas-fired pot furnace in Room 4-017 of the Fire Metallurgy Laboratory. Figure 2 shows the small pot furnace. At $1125^{\circ} C$ all the mixture was melted. After melting the mattes were poured into small molds and then ground to 100 mesh. The analyses of the mattes are shown in Table III.

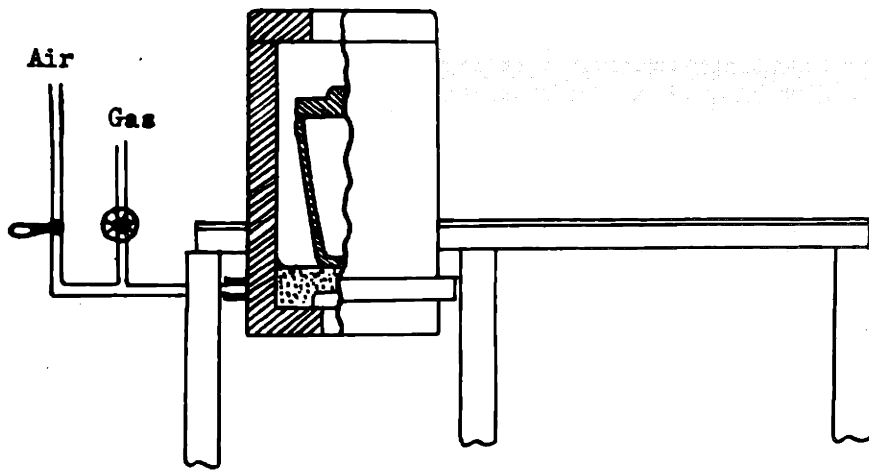
TABLE III

Analysis of Mattes

	Matte I	Matte II	Matte III
	<u>Per Cent</u>	<u>Per Cent</u>	<u>Per Cent</u>
Copper	25.5	37.9	57.9
Iron	44.7	32.5	16.1
Sulfur	24.0	23.0	20.5
Total	94.2	93.4	94.5



Plan View



Elevation

Figure 2 - The Small Pot Furnace

Preparation of the Copper-Free Slags

Five copper-free synthetic slags were prepared by melting the proper mixtures of SiO_2 , FeO , Al_2O_3 , CaO and MgO . All the materials used were chemically pure. Fe_2O_3 was used instead of FeO because of the instability of the latter at low temperatures. Five different 750-gram batches were made from the oxides which were already ground to 100 mesh. To facilitate and assure the melting, the mixtures were shaken in a regular cocktail shaker for half an hour before they were placed in size K clay crucibles. Melting was made in the small gas-fired pot furnace. Four to six hours were required for complete fusion of the charges. After melting the charges were poured into small molds and then ground to 100 mesh. The chemical analyses of these five slags are shown in Table IV.

TABLE IV
Analysis of Copper-Free Slags*

	<u>Slag 1</u> <u>Per Cent</u>	<u>Slag 2</u> <u>Per Cent</u>	<u>Slag 3</u> <u>Per Cent</u>	<u>Slag 4</u> <u>Per Cent</u>	<u>Slag 5</u> <u>Per Cent</u>
SiO_2	36.3	31.0	35.2	32.9	36.5
Al_2O_3	7.9	5.9	6.2	6.0	7.8
CaO	8.2	9.0	13.8	3.9	7.6
MgO	1.0	—	1.0	1.0	1.0
FeO	43.9	49.2	40.6	53.0	46.9
Total	97.8	95.1	96.8	96.8	99.8

* Only Slags 1, 3 and 4 were used for the experiments

Fusion of the Mattes and Copper-Free Slags

Mattes I, II and III and slags 1, 3 and 4 were ground to 100 mesh in a pulverizer. Then each slag was mixed with three different grades of matte giving 9 slag-matte combinations. Each charge consisted of 20 grams matte and 30 grams slag. They were mixed thoroughly on a glazed paper, first with a spatula and then by rolling. After proper mixing the charges were placed in graphite crucibles which were made from graphite electrodes in the machine shop of the Department of Metallurgy. The shape and the dimensions of the crucibles are shown in Figure 3. Finally all nine charges were fused and held one hour at 1100° C in a muffle-type gas furnace with automatic temperature control. The entire procedure was repeated for temperatures 1200 and 1300° C in an electric globalar furnace. Both furnaces are located in Room 8-010 of the Fire Metallurgy Laboratory and their sketches are shown in Figures 4 and 5 respectively. A chromel-alumel thermocouple was used to measure the former temperature while a platinum, platinum-rhodium was used for the latter.

At the end of a one-hour period the crucibles were taken out and chilled in the air. From 10 to 15 minutes were required to cool down to the room temperature. After cooling, the crucibles were broken one by one to separate the matte bottom from the slag layer. This was accomplished with great ease because there were

no entrapped inclusions, visible to the naked eye, in the slags. Finally they were broken into small pieces by short hammer strokes on a bucking board and then ground to 100 mesh in a diamond mortar and stored away in small bottles for chemical analysis. The 27 slags from the above fusion experiments were analyzed for copper by the titration method*.

* See Appendix I

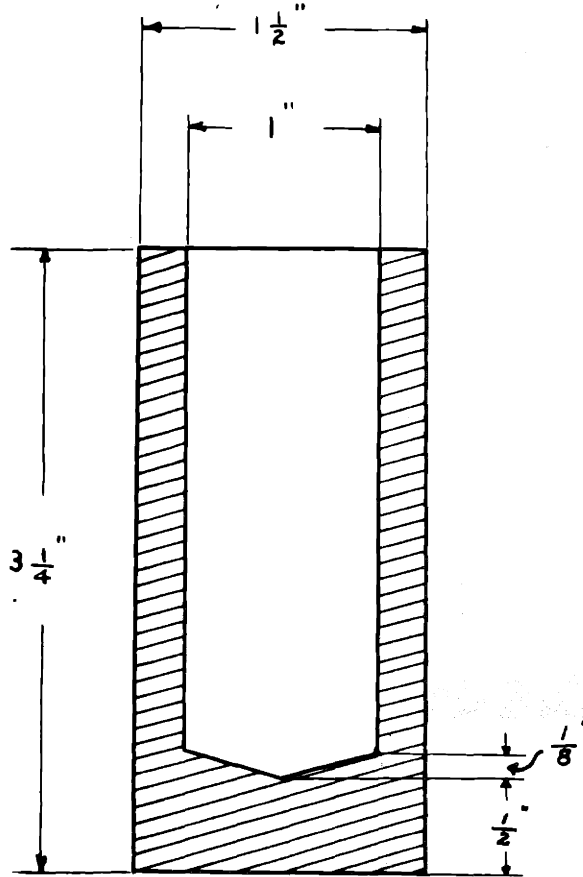


Figure 3 - The Shape and Dimensions of Graphite Crucibles

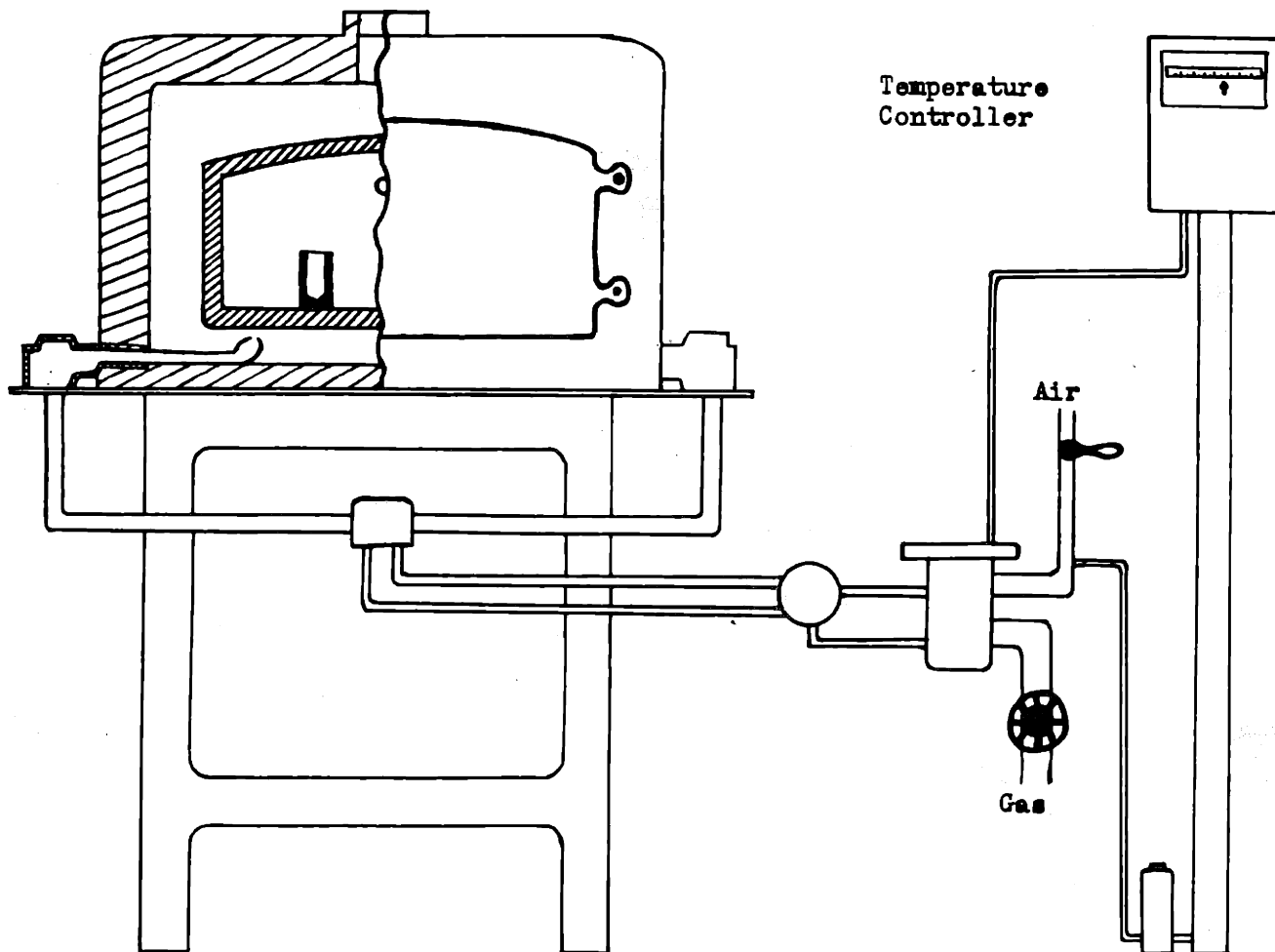


Figure 4 - Muffle Type Gas Furnace With Temperature Controller

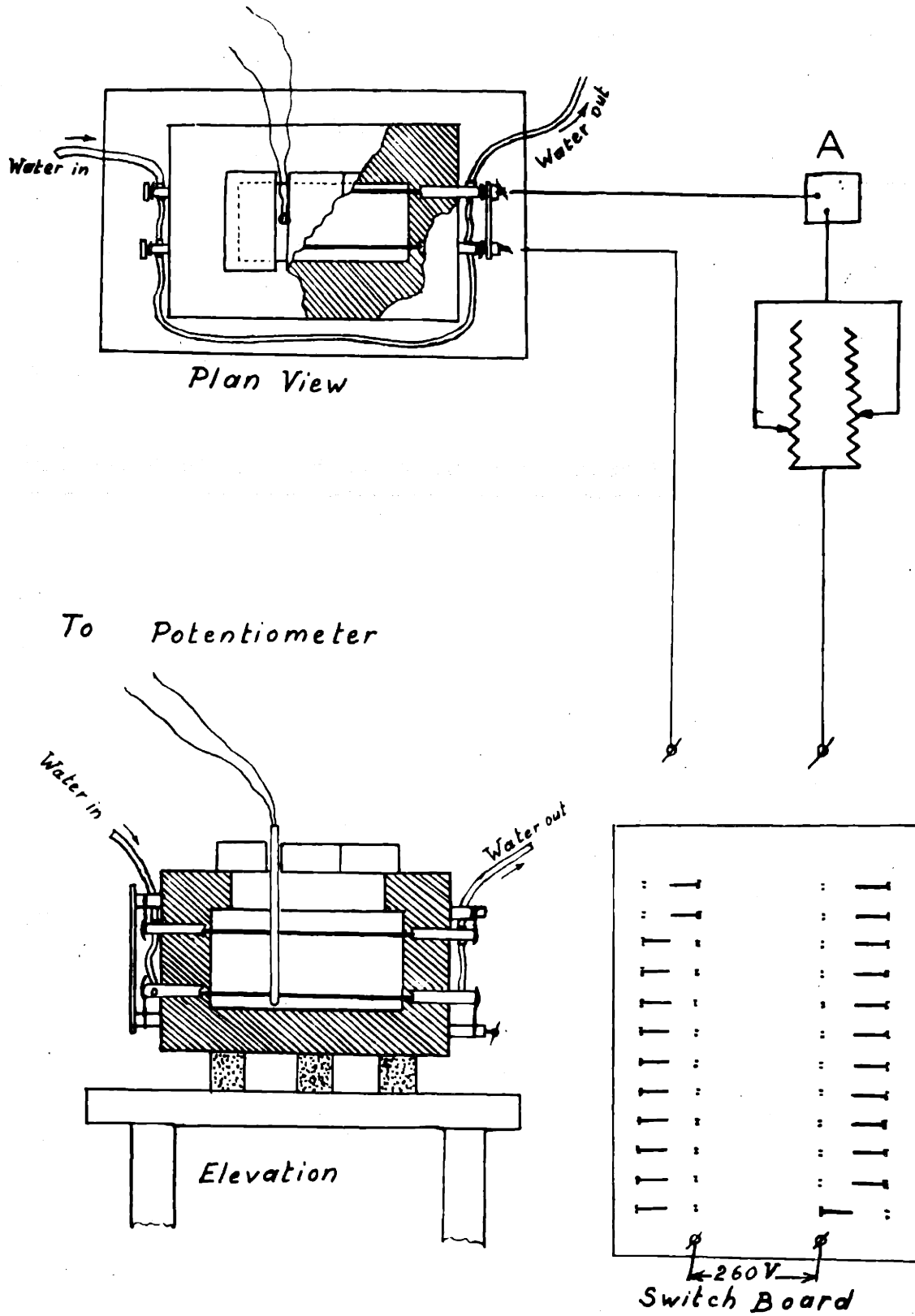


Figure 5 - Globar Electric Furnace

VI
RESULTS

The results of the chemical analysis of the fused slags for copper are given in Table V.

TABLE V
Per Cent of Copper in Fused Slags

<u>Combination</u>		<u>Temperature in ° C</u>		
<u>Matte</u>	<u>Slag</u>	<u>1100</u>	<u>1200</u>	<u>1300</u>
I	1	None*	0.13	None
	3	3.10	None	6.30
	4	1.30	0.10	0.54
II	1	None	None	4.60
	3	None	None	0.50
	4	0.06	None	1.30
III	1	1.70	0.52	0.27
	3	0.44	4.80	—
	4	None	8.80	0.72

* In this work all "Nones" refer to less than 0.01 per cent copper

VII
DISCUSSION AND CONCLUSION

In Table III the analyses of mattes were given in terms of copper, iron and sulfur. Actually these elements of matte are in the form of Cu_2S , FeS and excess iron which may be FeO , Fe_3O_4 or metallic iron. Table VI shows the analysis of matte on this basis. In constructing this table it is assumed that all the copper is united with sulfur and the remaining sulfur is united with the equivalent iron.

TABLE VI
Analysis of Matte

	<u>Matte I</u> <u>Per Cent</u>	<u>Matte II</u> <u>Per Cent</u>	<u>Matte III</u> <u>Per Cent</u>
Cu_2S	31.9	47.4	72.4
FeS	48.2	37.0	16.5
Fe (excess)	14.1	9.0	5.6
Total	94.2	93.4	94.5

In Tables III and VI the matte analyses do not add up to 100 per cent. This is not an unusual case especially with commercial mattes ⁽⁵⁾. About one per cent of the unaccounted portion is the insolubles which came from the FeS and Cu₂S. The rest may be some impurities which might have come from the clay crucible during the preparation of the mattes. Microscopic examination of the polished sections* of the mattes showed no metallic iron but the presence of both crystalline and noncrystalline magnetite. Upon this fact the assumption that all the excess iron is in the form of magnetite is justifiable. On this basis Table VII gives the per cent magnetite in the mattes.

TABLE VII

Per Cent Magnetite in Mattes

	<u>Matte I</u>	<u>Matte II</u>	<u>Matte III</u>
Magnetite	19.5	12.4	7.7

In Table IV the slag analyses do not also add up to 100 per cent. This is mostly due to the experimental error in the chemical analyses. Microscopic examination of the copper-free slags also revealed the presence of small amounts of magnetite.

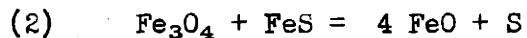
* See Appendix II

It is very difficult to establish quantitative relations from the results shown in Table V without further experiments. Nine out of 27 analyses showed no copper. This may be interpreted as the copper in some unknown form and under some unknown condition does not pass into the slag. To enlighten this point, horizontal and vertical sections of each slag were prepared. Microscopic examination of these sections showed that all 27 slags had tiny small yellow particles of which the largest had a diameter of about 0.004 millimeters. The number of particles was less in those slags which showed no copper by chemical analysis. Identification, counting of these particles and photographing the sections was abandoned for the reason which is given in the next section.

The formation of these particles may be due to either one of the following reasons:

- (1) Imperfect settling
- (2) Some chemical reactions evolving gases

The author is of the opinion that reason (2) plays a far more important role than reason (1). Vigorous evolution of sulfur dioxide and deposition of sulfur on the cooler parts of the furnace during the fusions are evidences, although not conclusive, to support this opinion. Also several authorities^(19,25,27,30) on the subject agree that there are some reactions between magnetite and iron sulfide both of which are the constituents of the matte. Wartman and Oldright⁽³⁰⁾ give the following reactions:



Reaction (1) is the most important one. These reactions were not studied under the equilibrium conditions of copper reverberatory furnaces. Therefore it is impossible to relate quantitatively the amount of copper in the slag with the amount of magnetite.

It is impossible to draw any definite conclusion from this work because of the complexity of the factors involved. However, the absence of copper in 9 out of 27 slags strongly indicates that there are some conditions, although unknown at present, which prevent the passage of copper from the synthetic mattes into the synthetic slags.

VIII

SUGGESTIONS FOR FURTHER WORK

This work constitutes a preliminary study of the copper losses in reverberatory slags. For further work the author strongly suggests treating the controlling factors separately. The following suggestions* it is hoped will help any research in this direction.

- (1) After each fusion, slag and matte should be examined microscopically because this may eliminate the necessity for a series of experiments.
- (2) The effect of the crucible should be studied.
- (3) Instead of mixing matte and slag for fusion, a series of experiments should be carried out by mixing Cu_2S and slag. The absence of FeS in this mixture will eliminate any evolution of gases and also will give the solubility of Cu_2S , if any, in slag.
- (4) Identification of copper-bearing constituents in the slags by means of various methods.
- (5) A theoretical thermodynamic study of the possible reactions between magnetite and iron sulfide.
- (6) Assurance of perfect settling by means of lengthening the time of fusion or carrying out the experiments in a centrifugal furnace.

* The study of some of these has already been undertaken by the author.

- (7) Solubility of magnetite in matte.
- (8) Application of the results to the commercial slags. For this, studies of the commercial slags should be done side by side with the synthetic ones.

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APPENDIX I

The method of chemical analyses for copper in fused slags is outlined below.

Decompose 1 to 2 grams of sample with sulfuric acid, nitric acid and hydrofluoric acid in a platinum dish. Evaporate to fumes of sulfuric acid. Transfer with water and hydrochloric acid to an erlenmeyer flask and boil. Add ammonia and boil out excess. Add 8 cubic centimeters glacial acetic acid and boil for 2 minutes. Cool, dilute to 200 cubic centimeters. Add ammonium bifluoride until the discoloration due to iron disappears and the solution is blue or colorless. Add 3 grams potassium iodide, shake until copper iodide precipitates, titrate with standard sodium thiosulfate using starch as indicator.

APPENDIX II

The sections of matte and slag were polished as outlined below.

- (1) A flat surface is obtained by grinding the specimen on a glass plate with No. 600 carborundum.
- (2) The specimen is mounted in bakelite by means of a hydraulic press.
- (3) If the surface is porous or crumbly, it is impregnated with bakelite solution.
- (4) The specimen is ground on the cast iron lap of the Graton-Vanderwilt polishing machine using M 305 abrasive.
- (5) Step (4) is repeated with F-1232 abrasive.
- (6) Finally the specimen is polished on the lead lap with MgO.