AN INVESTIGATION OF COPPER LOSSES IN COPPER REVERBERATORY SLAGS

By

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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I. INTRODUCTION

The amount of copper lost in smelter slags is considerable but thus far no economical method has been devised for preventing this loss. In general, the copper content of reverberatory slags will range from 0.25 to 0.07 percent; in a few cases it will go above 1.00 percent. The upper limit compares with some of the low grade ores mined in the United States. Copper wasted in slag per ton of copper in matte (or approximately per ton of blister copper) varies from 10 to 100 pounds, the average being 41.85 pounds. Prevention of this loss is a potential source of profit for the smelters especially for those with higher outputs.

At present, because of the war some of the plants are interested in maximum production rather than in maximum yield(*). Thus, in those plants the copper lost in reverberatory slags is much higher. After the war, if copper keeps its position as the first nonferrous metal, the copper in waste-slags may well be another source for the metal.

Two methods of approach are possible for having as their objectives the prevention of the copper from entering the slag and the recovery of slagged copper.

Before either of the above problems can be solved satisfactorily it is desirable to answer many questions such as: How much copper is lost under certain conditions? What are the physical and chemical

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(*) Private communication.

factors influencing this loss? What is the form in which the copper exists in commercial slags? How much of this copper can be saved or recovered? And many other questions as well.

The purpose of this work was to answer these questions by making a complete investigation of copper losses in reverberatory slags and then to suggest methods of prevention of loss and recovery of slagged copper.

The work consists of first an analysis of commercial reverberatory data and then a series of experiments with synthetic and commercial slags.

II. REVIEW OF PREVIOUS WORK

The review of the literature on the subject of copper losses in reverberatory slags cannot be made without including two other subjects which are closely related to copper losses. These are:

(1) Constitution of matte

(2) Presence and function of magnetite in matte and slag

Although there is an abundance of literature on these three subjects, little agreement is found among metallurgists on many points and for many years an intermittent controversy has gone on regarding the presence of magnetite in matte and on forms of copper in slag.

In order to follow the progress of the many researches and theories, the literature is arranged in chronological order, as follows:

KELLER, E.(1)* In a study of the chemical composition of Montana copper mattes, the author points out the remarkable consistency of the sulfur content and the presence of considerable amounts of magnetic oxide in some of the lower grade mattes. He also gives a chemical method to separate magnetic oxide from other matte constituents.

KELLER, H. A.(2) In describing and illustrating slag-pots, the writer mentions the results of a large number of copper-matte analyses which gave a constant tenor of from 21 to 23 percent sulfur and showed the presence of magnetic iron. Further, he quotes from E. Keller(1)

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* The references are cited in the Bibliography.

the following two formulae:

$$(Cu_2S)_x + (Fe_2S)_y$$

$$(Cu_2S)_x + (FeS)_y + (Fe_3O_4)$$

which would correspond to the copper-mattes.

NEILL, J. W.(3) In discussing Mr. H. A. Keller's paper(2), the writer thinks both of the formulae presented therein are wrong; and that "the magnetic quality of the mattes is due to the presence either of metallic iron or of the magnetic iron sulfides Fe_7S_8, Fe_8S_9, etc." He considers the presence of Fe_3O_4 as unlikely because "the conditions of blast-furnace practice are against it" and also because of the lack of magnetism in slags which should contain more Fe_3O_4 than the mattes.

KELLER, E.(4) In answer to Mr. J. W. Neill's criticism(3), he retains his views as to the presence of magnetite in matte. He backs up his argument by theoretical considerations as well as qualitative and quantitative chemical analyses.

KELLER, E.(5) In writing on the subject of "Composition and Character of Mattes", the author says, "Any substance separated from that of the matte itself, is proof of the heterogeneous character of the latter". He reiterates his attempts to separate mattes by washing in a pan. On the rational analysis of copper mattes, he states, "The existence of an iron subsulfide (Fe_2S), or of a monosulfide holding metallic iron in solution, is a question connected only with the lower grades of matte. In mattes of over 55 percent copper, the composition indicates the presence of copper subsulfide (Cu_2S) and of iron monosulfide alone".

LE CHATELIER, H. and ZIEGLER, M.(6) In their research on the harmful influence that small quantities of sulfur exert upon iron, the authors studied the chemical composition, melting points and metallography of iron sulfide of different origins. They detected three distinct constituents in a polished surface: (1) yellow grains of sulfide of iron, (2) white colored metallic iron, and (3) eutectic or "pearlite" between the yellow grains, and frequently around the grains of iron. Cavities in the melted sulfides are due to the evolution of gases and consequent contraction. The excess iron present is due to the fact that ferrous sulfide heated above its melting point, 1200° C, looses sulfur and that the loss in sulfur increases with the temperature. They also show that iron oxide, probably Fe_3O_4, may be present in the sulfide and will form a eutectic with iron sulfide.

HEYWOOD, W. A.(7) From chemical analyses of 2500 slags of the Tennessee Copper Company, the writer concludes that slag losses increase with the grade of matte but with the same grade of matte decrease as the basicity of the slag decreases. Several curves showing the copper losses in slag as a function of copper in matte with varying silica content are shown in Figure 1, which is reproduced from Heywood's article. He also emphasizes the solubility of matte in slag.

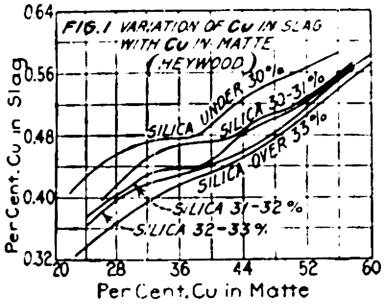

FIGURE 1. Variation of Copper in Slag with Copper in Matte

BOLLES, M. N.(8) In a study of the concentration of gold and silver in iron bottoms, the writer examines the polished sections of several mattes and comes to the following conclusions: "(1) Mattes are not homogeneous, but are composed of distinct mineral entities, and may be likened to igneous rocks in which the mineral constituents fall out upon the lowering of the temperature and ensuing solidifications. (2) The avidity of iron-mattes may be increased by increasing the reducing power and temperature of the furnace, thus obtaining a greater excess of iron in the matte produced. (3) The absorptive power for gold of a matte composed of iron and sulfur is greatly dependent upon the excess of iron contained above that necessary to form FeS."

HEYN, E. and BAUER, O.(9) The authors studied copper and sulfur and gave an equilibrium diagram, which is reproduced in Figure 2, for the system Cu-Cu_2S. Their photomicrographs showed considerable metallic copper which, they think, may have been formed by one of the following reactions:

$$Cu_2S + O_2 = 2\,Cu + SO_2$$

$$Cu_2S + 2Cu_2S = SO_2 + 6Cu$$

and when carbon is present:

$$2Cu + SO_2 + 2C = Cu_2S + 2CO$$

Cavities in the polished surfaces are due to evolutions of gases.

GIBB, A. and PHILP, R. C.(10) In this research work the writers studied the constitution of mattes produced in copper smelting from a chemical and a physical point of view. They examined products of smelting operations as well as the products produced by the subjection

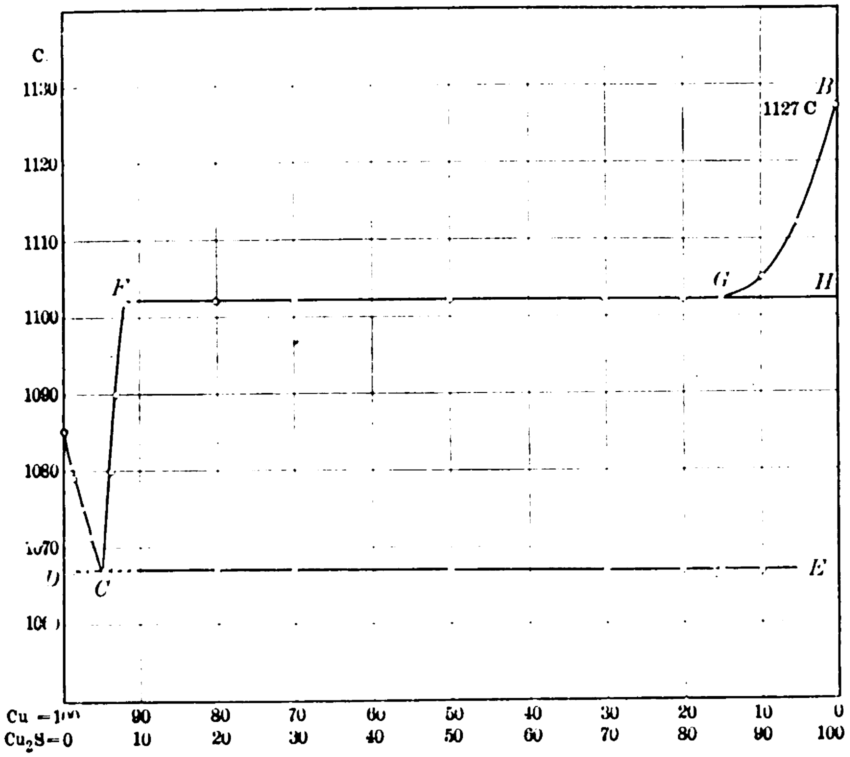

FIGURE 2. The Cu-Cu_2S Equilibrium Diagram

of synthetic mixtures of copper, iron and sulfur, and their compounds to temperature. Neutral solutions of silver nitrate were found satisfactory to determine the chemical combinations. Their conclusions are as follows: Ferrous and cuprous sulfides form the chemical compound $5Cu_2S$, FeS (10 percent FeS and 90 percent Cu_2S). Mattes containing more than 10 percent FeS readily dissolve copper while mattes containing less than 10 percent FeS retain copper in mechanical suspension. The presence of magnetite is considered a doubtful constituent and that it is the result of precipitation by the oxidizing agents rather than an original constituent of the matte.

KELLER, E.(11) In discussing the work of Messrs. A. Gibb and R. C. Philp(10), the author criticizes the chemical procedure for the determination of magnetic oxide of iron. He once more retains his original views as to the presence of magnetite and suggests that magnetic oxide is probably soluble in matte and precipitates out during cooling.

TREITSCHKE, W. and TAMMANN, G.(12) The authors investigated the system FeS-Fe and confirm the results of Le Chatelier and Ziegler. Figure 3 shows their results. They found the melting point of FeS at 1300° C by extropolation.

RONTGEN, P.(13) The writer studied the freezing points and metallography of a series of mixtures made up from Cu_2S and FeS. His results, the equilibrium diagram of the system Cu_2S-FeS given in Figure 4, show a series of seven compounds and one eutectiferous range. The presence of metallic copper may be due to the reaction

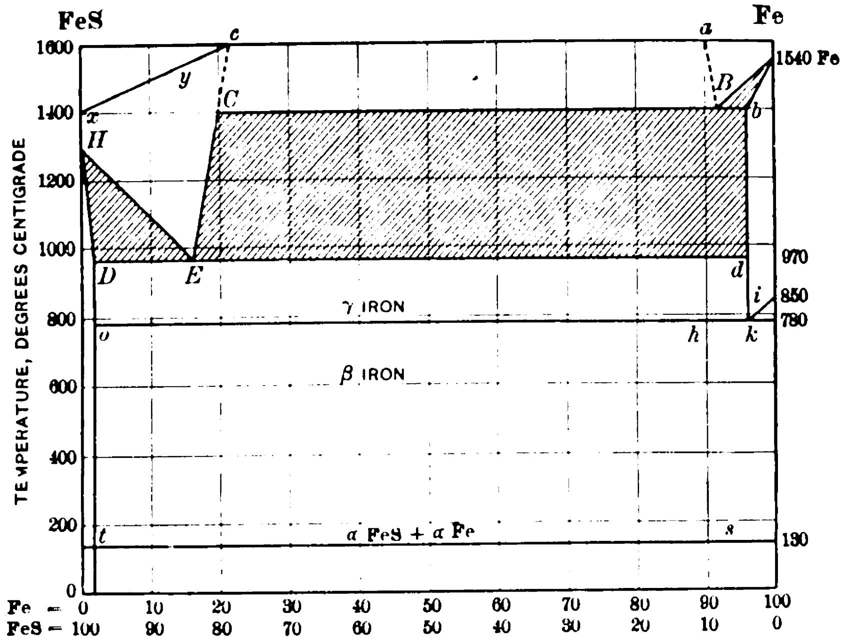

FIGURE 3. Fe-FeS Equilibrium Diagram

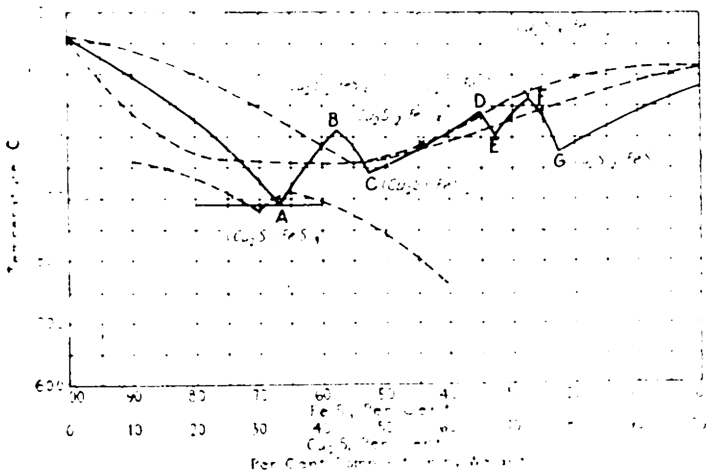

FIGURE 4

(Results of investigations by Rontgen, indicated by full line, and by Baykoff and Troutneff, indicated by broken line)

RINNE, F. and BOEKE, H. E.(14) The authors studied the transformation points of iron sulfide. They found that the transition point of iron sulfide containing 7-8 percent Fe and balance FeS is 137° C. The transition point is lowered as the percentage of free iron decreases.

HOFMAN, H. O. and Associates(15) Professor H. O. Hofman and his associates determined the freezing point curves and examined polished sections of 15 mixtures of Cu_2S and FeS which were prepared by heating metallic iron and copper with stick-sulfur. Their conclusions are quoted below: "(1) Ferrous and cuprous sulfides form no chemical, but a eutectiferous compound. (2) The structure of the eutectic of ferrous and cuprous sulfides becomes merged in that of the pure ferrous sulfide and cannot be distinguished from it. (3) The limited reciprocal solubility of the two sulfides diminishes along the cuprous-sulfide branch of the curve, slowly at first, then more quickly; solubility is complete beyond the alloy, FeS, 20, and Cu_2S, 80 percent."

GIBB, A.(16) In answer to Mr. E. Keller's criticism(11) regarding the presence of magnetite in matte, Mr. Gibb states that the mattes investigated by him and by Mr. Philp were among those "which scarcely show any magnetic property" and came from ores that were free from magnetic oxide of iron. On the chemical procedure for the determination of magnetite, he says, "I consider that when complex mattes are treated with oxidizing solvents, part of the iron, under conditions at present unknown to me, be converted into magnetic iron oxide".

FRIEDRICH, K.(17) On the contribution to the knowledge of metal sulfides, the author makes a thermal study and gives the melting points of Cu_2S, FeS, PbS and Ag_2S. He also states that these sulfides have the property of losing sulfur by volatilization above their melting point.

LARISON, E. L.(18) In many instances magnetite comes from the charge and may go through the furnace unchanged or it is mostly reduced and slagged. Some new magnetite may be formed in the furnace by blast action. Mr. Larison thinks most of the magnetite is unaltered and may report as such in matte. He then discusses the effect of sulfuric acid on mattes containing magnetite.

RIZO-PATRON, A.(19) Mr. Rizo-Patron cites the difficulties encountered in smelting pyritic ores. He was unable to hit a certain exrange of slag composition and to obtain a fluid slag. From his experiences he concludes: "Certain pyritic ores, whose iron sulfide possesses the property of being converted in a great degree into magnetite through action of oxidizing agents, cannot be raw smelted in blast furnaces, for the reason that to succeed in this operation it would be necessary to produce at the same time and in the place (inside the furnace) two opposite actions: (1) oxidizing, to burn the sulfur and oxidize the iron; and (2) reducing, to convert into protoxides the peroxides formed".

SHELBY, C. F.(20) In commenting on Mr. Rizo-Patron's article(19), Mr. Shelby says that the difficulties encountered in smelting pyritic ores are common and are due to the lack of heat in the furnace and also in the settler. This condition may arise by using too little coke, too much air, or running the furnace slowly. The addition of the chemical analysis of mattes to more than 100 percent is due to the presence of magnetite which causes a great deal of trouble during smelting by forming a layer between the matte and slag.

FULTON, C. H. and GOODNER, I. E.(21) The authors studied the constitution of copper-iron and copper-lead-iron mattes by metallographic and chemical means. They conclude that mattes in structure are conglomerates and contain Cu_2S with FeS dissolved in them, FeS with Cu_2S dissolved in them, metallic iron, and metallic copper.

ZIEGLER, M.(22) In this article, Mr. Ziegler studies the alloys of iron with sulfur in connection with harmful effect of sulfur on iron and steel. The work consists of microscopic and chemical investigations. No diagram of the system Fe-S is presented. His results are a generalization of his previous research with Le Chatelier.

BAYKOFF, A. and TROUTNEFF, N.(23) The authors investigated the system Cu_2S - FeS. They found that "the two sulfides were completely soluble in each other in all proportions when just molten and also just solid" with a minima. Their results are shown in Figure 4. In explaining the presence of metallic copper and iron they found that the reaction

$$Cu_2S + Fe \rightleftharpoons FeS + 2Cu$$

is reversible.

BORNEMANN, K. and SCHREYER, F.(24) The authors of this paper also investigated the system Cu_2S - FeS. Their findings closely resemble those of Paul Rontgen(13). They found a series of compounds and solid solutions which are shown in Figure 5.

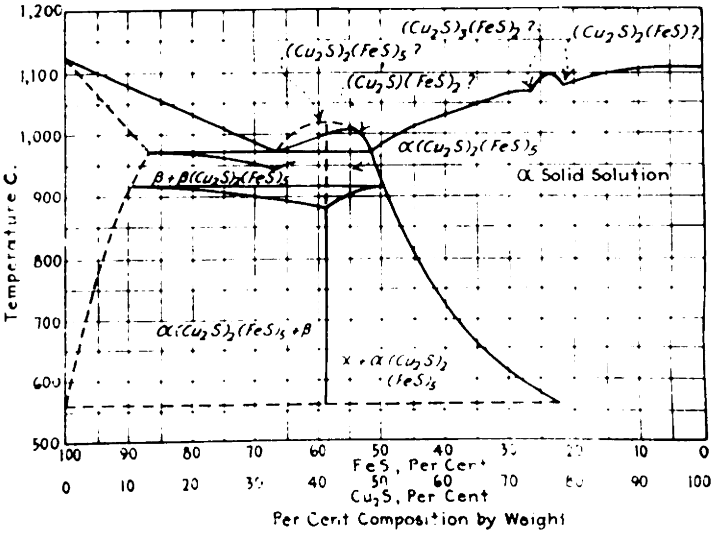

FIGURE 5. Cu_2S - FeS Equilibrium Diagram

WRIGHT, L. T.(25) The ratios of copper, silver and gold in slag to copper, silver and gold in matte do not follow the "law of distribution". Loss of copper is not only due to prills of matte but also due to solubility of copper-bearing compounds. Mr. Wright's reasons for this belief are: "(1) That matte did not separate from slag kept in the molten state even for a long time. (2) That no concentration of the valuable metals was possible by elutriation after fine grinding". Figure 6 shows the variation of copper in slag with copper in matte.

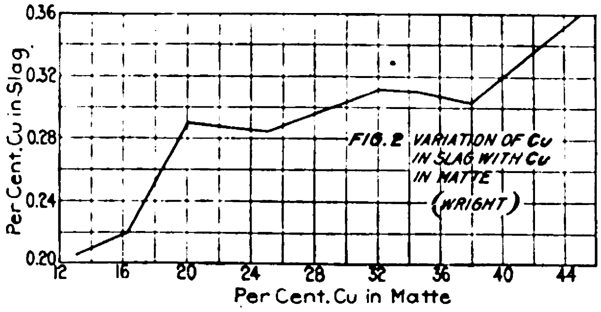

FIGURE 6

Variation of Copper in Slag with Copper in Matte

GRABILL, C. A.(26) The author classified the copper slag losses as follows: (A) Physical or mechanical, which is due to (1) insufficient settling, (2) insufficient difference in specific gravity of matte and slag, and (3) gas flotation. (B) Chemical, which is due to (1) solution of metals or their sulfides and (2) slagging as oxides, ferrites, silicates, etc. A formula is given to determine the copper in slag. It is

$$Cu_s = 0.36 - \left(\frac{0.036}{0.10-Cu_m}\right) + 2.2\ Cu_m^4$$

where Cu_s is the percent copper in slag while Cu_m is the copper in matte expressed decimally.

SUNDT, F. A.(27) From the results of chemical analysis of charge, matte and slag at Chilean smelters, the author finds out that the grade of matte is not the only factor effecting the loss of copper in slag. The amount of copper in the charge also has a pronounced effect. A formula is given to determine the copper lost in slag. It is:

$$x \cdot \frac{Ps}{100} + (90-x)\frac{Pm}{100} = 100\ Pch$$

where x is the weight of slag and Ps, Pm and Pch are percent of copper in slag, matte and charge respectively.

CHANNING, J. P.(28) The author states that, in general, copper lost in slag is in two forms: (1) occluded matte and (2) as oxide or silicate. Matte particles suspended in slag carry the normal amount of copper, gold and silver, and if more copper is found there than would be indicated by the gold content, it is assumed oxidized.

KIDDIE, T.(29) The author says that copper in slag exists both as an oxide and a sulfide. Oxide portion is dissolved in dilute sulfuric acid. When the copper in the slag decreases, the percentage of oxide in the slag decreases also, while the percentage of sulfide increases.

ALLAN, E. T., CRENSHAW, J. L. and JOHNSTON, J.(30) The authors studied the mineral sulfides of iron, such as pyrite, markasite and phyrrotite. The chemical composition, physical properties and crystal formation of mineral sulfides of iron of different origin are presented in detail.

WANJUKOFF, W. H.(31) This writer investigated the losses of copper in artificial slags of different degrees of acidity, with the oxides FeO, CaO, MgO, ZnO and Al_2O_3 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 slag as functions of basicity and acidity. He also believes this retained copper is soluble in the slag in the form of sulfides. His important results are shown in Figures 7, 8, 9 and 10.

JUSCHKEWITSCH, N.(32) In a study entitled, "On the Theory of Copper Matte Smelting Process", the author comes to the following conclusions: (1) FeS - Cu_2S system gives a compound having the formula $(Cu_2S)_2$ FeS; (2) when Cu_2S and Fe are mixed and fused, the reaction $3Cu_2S + Fe = (Cu_2S)_2 FeS + 2Cu$ begins at 400 - 450° C; (3) when Cu and FeS are mixed and fused, the reaction $4Cu + 3FeS = (Cu_2S)_2 FeS + 2Fe$ begins at 400° C; (4) when Cu_2O and FeS are mixed and fused, the reaction $2Cu_2O + 3FeS = (Cu_2S)_2 FeS + 2FeO$ begins at 270 - 280° C. Reactions in 1 to 4 are studied under a dry atmosphere of nitrogen and the rate of reactions increases with temperature. $(Cu_2S)_2$ FeS is considered an equilibrium compound.

LOEBE, R. and BECKER, E.(33) The authors made a further study of the system Fe-FeS. Their findings, in general, agree with those of the previous investigators. They gave 138° and 298° C as the transformation points of FeS. They also stated that transformation points of iron are not influenced by the presence of FeS.

FRIEDRICH, K. and WOHLERT, M.(34) The authors studied the system Cu_2S - Cu. Their results, the equilibrium diagram of the system which is shown in Figure 11, differ from those of Heyn and Baur(9) who made a study of the same system.

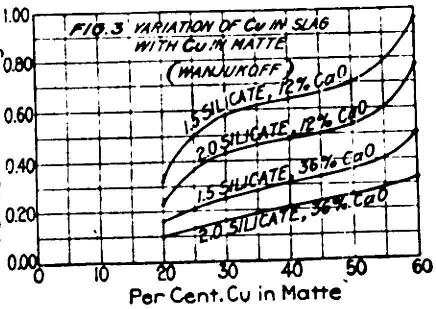

FIGURE 7. Variation of Copper in Slag with Copper in Matte

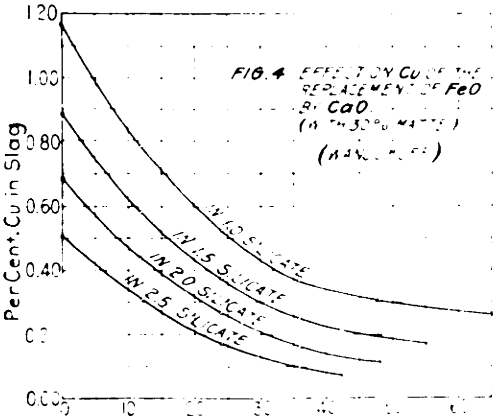

FIGURE 8. Effect on Copper of the Replacement of FeO by CaO

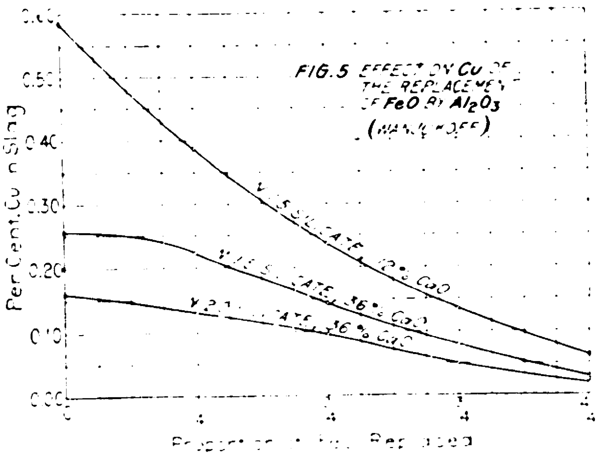

FIGURE 9. Effect on Copper of the Replacement of FeO by Al_2O_3

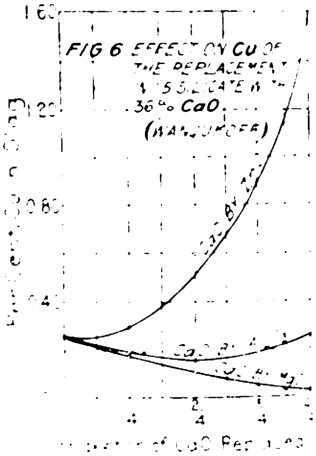

FIGURE 10. Effect on Copper of the Replacement in 1.5 Silicate with 36% CaO

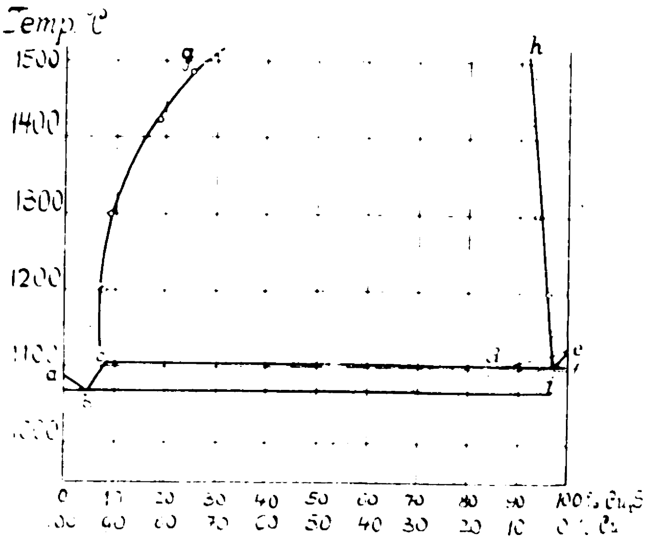

FIGURE 11. Cu_2S–Cu Equilibrium Diagram

BORNEMANN, E. and WAGENMANN(35) In a study of electric conductivity of alloys in a liquid state, the authors include the electrical conductivities of the systems Fe–Cu_2S and FeS–Cu_2S. No attempt is made to construct a diagram from the data.

JAMES, J. W.(36) The author states that the copper content is reduced down to 0.35 - 0.45 percent by treating converter slags running 1.5 - 2.5 per cent copper in a reverberatory furnace. It is believed that this remaining copper is an oxide or silicate.

LATHE, F. E.(37) The author follows Mr. Kiddie's method(29) with slight modifications to dissolve the copper oxide in Granby and Anaconda slags. Then, he concludes by stating, that (1) considerable copper is present as oxide, and (2) copper in slag increases uniformly with the increase of copper in matte and decreases irregularly with increasing silica.

POSNJAK, E., ALLEN, E. T. and MERVIN, H. E.(38) The authors studied the simple sulfides of copper, chalcicite and covellite. Chemical composition, physical properties and crystal formation of synthetic and mineral sulfides of copper of different origin are presented in detail. One of their most important conclusions is that cuprous and cupric sulfide form solid solutions, and when copper sulfides are obtained from Cu and S, the product contains more sulfur than the ratio 2Cu : S.

SCHAD, H. and BORNEMANN, K.(39) In seeking additional data on the Cu_2S - FeS system, the authors confirmed the results of K. Bornemann and F. Schreyer(24) by microscopic work. They found some compounds in the range 50 - 100 percent Cu_2S but they were unable to reproduce them with the exception of $(Cu_2S)_2$ FeS. Another compound containing 41 - 42 percent Cu_2S is $(Cu_2S)_2\ (FeS)_5$.

STAHL, W.(40) In writing on the separation of copper by concentrating matte, the author gives the following reactions:

$$3Cu_2S + Fe = (Cu_2S)_2\,FeS + Cu_2$$

$$(Cu_2S)_2\,FeS + FeS = \underset{\text{chalcopyrite}}{Cu_2Fe_2S_3} + Cu_2$$

$$2(Cu_2S)_2FeS = \underset{\text{bornite}}{(Cu_2S)_3Fe_2S_3} + Cu_2$$

Free copper may react with FeS according to the following reaction:

$$4Cu + 3FeS = (Cu_2S)_2FeS + Fe_2$$

and $$Fe_2 + O_2 + SiO_2 = Fe_2SiO_4$$

These reactions form a closed circuit and the result is a function of the FeS present.

HAWLEY, F. G.(41) The author first recites the troubles caused by magnetic oxide of iron in matte smelting. Then he presents a quantitative chemical method, sufficiently accurate and rapid, for the determination of magnetite in slag and matte.

MAIER, C. G. and VAN ARSDALE, G. D.(42) The losses in copper-smelting slags are studied from the microscopic and chemical point of view. Their experiments indicated that gas flotation and truly dissolved copper are the two important factors causing the loss of copper in slags. Gas flotation is due to the following reaction:

$$FeS + 3Fe_2O_3 = SO_2 + 7FeO$$

Copper sulfide may be in three physical forms: (1) visible globules, (2) invisible globules, and (3) as dissolved. Visible globules are soluble in one percent silver nitrate solution and have a different composition from that of the matte from which they came. About 0.15 to 0.20 percent copper is believed present as dissolved sulfide. The presence of dissolved copper further was supported by experiments where slags fused with saturated and unsaturated pyrite. Figure 12 shows their results on fusion with pyrites. They consider oxides and silicates to be absent.

MAIER, C. G. and VAN ARSDALE, G. D.(43) The authors once more studied a series of representative copper reverberatory and blast furnace slags from chemical and microscopic points of view with special emphasis on the effects of magnetite on slag losses. Magnetite was found to increase the losses due to sulfide flotation by attached

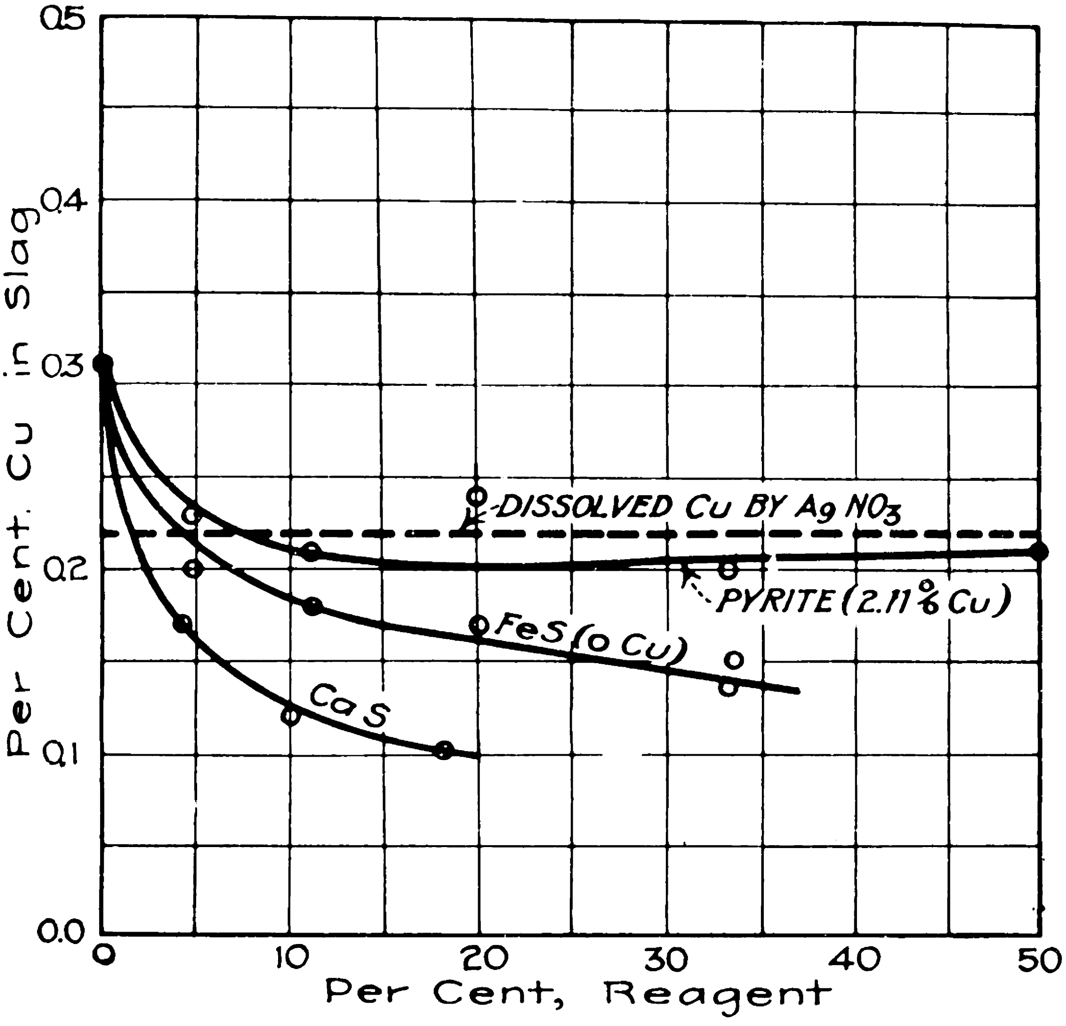

FIGURE 12

Percent Copper Remaining in Slag Against Percent FeS or CaS

gas particles. They reaffirmed their faith in the silver nitrate method for determining suspended sulfide copper, and again assumed that copper oxide or silicates were absent under the ordinary smelting conditions. They also studied the behavior of converter slags in reverberatory furnaces and offered some suggestions for reducing copper slag losses.

LATHE, F. E.(44) A constructive criticism of the previous literature with special emphasis on the paper by Messrs C. G. Maier and G. D. Van Arsdale(42,43) is given by Mr. Lathe. The presence of copper oxide and silicate is maintained on the basis of new experiments. Sulfurous acid, which does not attack copper sulfide,is used with hydrofluric acid to dissolve copper oxide. Undissolved parts of the copper in the slag by these reagents may be present as sulfide. The paper ends with possible improvements in present-day (1920) practice.

MEISSNER, K. L.(45) The author states that the affinity of copper for sulfur is greater than lead, bismuth, antimony, tin and iron but lower than manganese. He calls attention to the reaction:

$$2Cu + FeS = Cu_2S + Fe$$

which is the intersection of lines Cu-FeS and Fe-Cu_2S in the ternary system of Cu-Fe-S.

CARPENTER, C. B. and HAYWARD, C. R.(46) The authors investigated the equilibrium diagram of the system Cu_2S-FeS by the microscopic method and determination of the freezing points. Their results are shown in Figure 13. In explanation of reactions which have an important application to the smelting of copper sulfide ores, they state that, "a loss of sulfur takes place by distillation from molten FeS. The resulting Fe in part dissolves in the remaining FeS and in part dissolves and reacts with Cu_2S, producing Cu and FeS". The latter takes place according to the reaction

$$Fe + Cu_2S = 2Cu + FeS$$

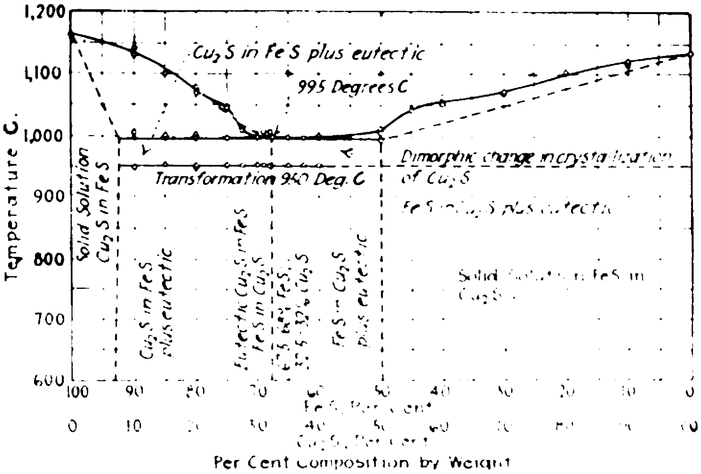

FIGURE 13

Cu_2S-FeS Equilibrium Diagram

EDWARDS, F. H.(47) The Cu_2S-FeS system was investigated by the author by thermal and microscopic means. His results are similar to those of Baykoff and Troutneff(23); that is, Cu_2S and FeS form continuous solid solutions with a minima. The author did not observe any eutectic structure or any definite compound.

GUERTLER, W.(48) In an article entitled, "The Determination of Affinity of Metals to Sulfur by Microscopic Method", the author writes his findings on the following ternary systems: Pb-S-Cu, Bi-Cu-S, Mo-Sb-S, Fe-Ag-S, Fe-Pb-S, Pb-Ag-S, Mn-Cu-S, Pb-Co-S, Cu-Ni-S, Co-Ni-S, Cu-Ag-S, Cu-Fe-S, Cu-Sn-S, Pb-Sb-S, Cu-Sb-S, Ni-Sb-S and Ni-PbS. These systems are very helpful in studying the complex mattes.

TIEDMANN, H.(49) This author made an extensive study to determine the moss copper by microscopic, thermic and conductivity methods.

Some of his conclusions are as follows: (1) Moss copper is maximum at 62 percent copper. This corresponds to the compound $(Cu_2S)_2$ FeS. (2) Moss copper is the result of the decomposition of $(Cu_2S)_2$ FeS into $(Cu_2S)_3$ Fe_2S_3 and Cu. (3) Moss copper is not on the Cu_2S-FeS line of the ternary system Cu-Fe-S but rather closer to the line Cu_2S-Fe_2S_3 on which many Fe, Cu, S minerals fall. (4) Separation of moss copper starts at 548° C and is completed at 180° C.

BOGITCH, M. B.(50) The author studied the copper mattes in the liquid state and constructed the Cu-Fe-FeS-Cu_2S range of the ternary system Cu-Fe-S. Figure 14 shows his results. His interpretation of this figure is as follows:

(1) The triangle ABC covers all the possible industrial mattes. If sulfur is higher than the line Cu_2S-FeS, it volatilizes and burns. If sulfur is lower than the line AC, a precipitation of ferrous bottom, which is poor in sulfur and copper, takes place in obtaining such a matte. The latter forms an acretion corresponding to composition E.

(2) The narrow strip AD corresponds to all possible copper-rich mattes. In this zone the sulfur content does not change a great deal. If, for some reason, the sulfur content is lower than the line AD, a copper-rich bottom precipitates.

(3) The composition (a) may be obtained either by dead roast or by reduction with carbon. Fusion of this material will give "black copper" containing 93-96 percent copper and a "low grade copper or matte" containing 55-60 percent copper.

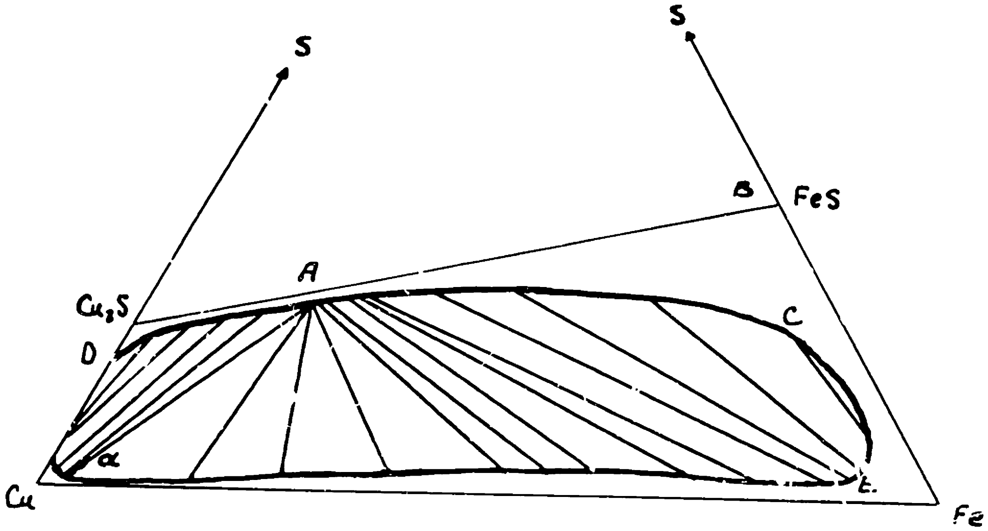

FIGURE 14

Part of Cu-Fe-S System

GORDON, D. M.(51) The presence of magnetite in copper mattes is investigated by magnetic balance analysis and X-ray diffraction methods. The results of the magnetic balance analysis are vague but X-ray proved definitely the presence of magnetite.

GUERTLER, W.(52) In writing on the researches of theoretical nonferrous metallurgy with special attention to copper mattes, the author studies the equilibrium conditions in liquid and solid states of mattes.

REULEAUX, O.(53) This writer, who studied the reactions and equilibrium conditions in the ternary system Cu-Fe-S with reference to copper mattes, first reviews the binary systems Cu-Fe, Cu-S, Fe-S and Cu_2S-FeS. Later, he discusses the range Cu-Fe-FeS-Cu_2S of the ternary system Fe-Cu-S. Figure 15 shows his findings in detail.

GUERTLER, W. and REULEAUX, O.(54) In a concluding article these authors support their previous findings with further microscopic evidence. Their results, in general, agree with those of W. Stahl(40), but they present more adept explanations for some of the phenomena which occur in copper smelting.

FEDOTIEFF(55) The author studies the factors affecting the formation of moss copper in mattes. He starts with the investigation of the system FeS-Cu_2S by microscopic and thermal methods, and notices that above a certain temperature the system is composed of partially eutectic and partially solid solution. Below this temperature, the formation of moss copper takes place. He also states that copper may separate according to the reaction $Cu_2S = Cu + CuS$ in the solid state. The resultant Cu dissolved in solution.

BLOCK, H. H.(56) The form of copper present in reverberatory slags is investigated by X-ray diffraction and microscopic methods. Attempts at magnetic separation were unsuccessful. No copper sulfide is found. Reactions between magnetite and matte or slag are believed one of the important causes of copper loss.

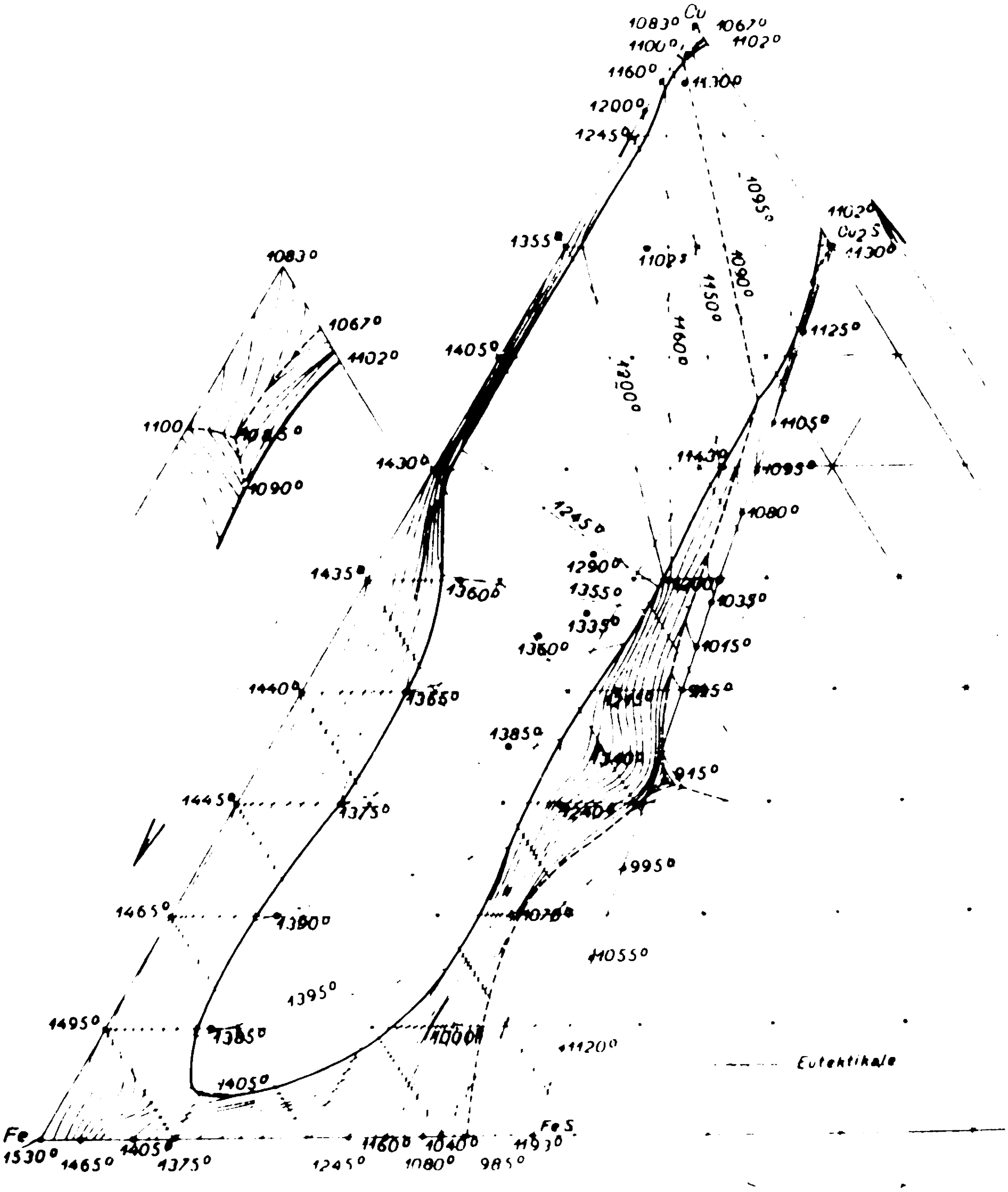

FIGURE 15. Part of the Cu-S-Fe System

WARTMAN, F. S. and OLDRIGHT, G. L.(57) The reactions between pure magnetite and pure iron sulfide are studied under an atmosphere of nitrogen in the temperature range 1000 to 1300° C and may be represented by three equations:

(1) $FeS + 3Fe_3O_4 = 10FeO + SO_2$

(2) $FeS + Fe_3O_4 = 4FeO + S$

(3) $FeS + 4Fe_3O_4 = 13FeO + SO_3$

With the mixtures tried, most of the reduction proceeded according to the first reaction. Increasing the proportion of sulfide increases the rate and also to some extent the importance of the other reactions. Increase of temperature increased the rate of reduction very markedly. Increase of partial pressure over the melt, of the gases formed by the reaction, greatly decreased the rate of reaction.

McLELLAN, R. D.(58) The author made an extensive study of lead and copper furnace slags, including copper reverberatory furnace slags. He used analytical and petrographic (thin sections) methods. He believes sulfur in slags is the reducing agent rather than FeS.

HAWLEY, F. G.(59) A more accurate method of analyzing magnetite in matte is developed.

BLOCK, H. H.(60) The origins of magnetite are studied. Some magnetite is present in the charge, some produced during roasting and some by the action of magnetite crusts with magnetite-free charge. Lime promotes the latter. Magnetite is soluble in both matte and slag.

ROBERTS, L. E. and NUGENT, R. L.(61) Hawley's method for determining magnetite in slag is modified. The results are accurate to 2 percent and agree with the magnetic balance method within 2 percent.

AVETISION, C. K.(62) The author studies the constitution of copper mattes from a chemical point of view. He uses 7 percent KCN solution as the dissolving reagent. His conclusions are as follows: "(1) Only stable compound $(Cu_2S)_2$ FeS, soluble in KCN. (2) Matte with less than 62.7 percent Cu contains excess FeS or FeO; Fe_3O_4, insoluble in KCN. Matte with higher than 62.7 percent Cu contains Cu_2S, soluble in KCN. Mattes with 62.7 percent Cu or more are almost completely soluble. (3) Cooling of matte depending upon the rate with which it proceeds, causes precipitation of Cu, soluble in KCN; at the same time insoluble sulfides are formed, higher in sulfur than FeS, among which is $CuFeS_2$. (4) When matte and sulfides are dissolved in KCN, sulfur dissolves as sulfide and as sulfocyanide."

JACKMAN, ROYAL B. and HAYWARD, CARLE R.(63) New methods of attack are used to find the forms of copper in reverberatory slags. Most of the copper contained in reverberatory slag is in the form of sulfide which may be present as pellets of irregular shape or as dissolved matte. The presence of metallic copper is of minor importance. X-ray examination revealed that the sulfide globules approach the composition of bornite.

HOWAT, D. D.(64) The author investigated the system Cu_2S-FeS by thermal and microscopic means. He carried out all of his thermal determinations in a vacuum. His results, the diagram, show limited solubility of both constituents with the formation of a eutectic. Cu_2S is soluble in FeS up to 20 percent and FeS in Cu_2S up to 40 percent at 970° C. The melting points of FeS and Cu_2S are 1155° and 1120° C respectively. The eutectic composition is 61 percent FeS and 39 percent Cu_2S. The diagram closely resembles that of Hayward and Carpenter(46) with the exception that in Howat's diagram the limits of solubility shift slightly toward the right.

DICE, C. M., OLDRIGHT, G. L. and BRIGHTON, T. B.(65) In connection with drosses in lead smelters, the authors study the mattes produced during lead smelting from the chemical and microscopic points of view. They think that, "the presence of metallic copper in the matte is probably due to the reaction between copper sulfide and iron sulfide to form more copper. Mattes that do not contain iron do not contain metallic copper." They also consider some ternary systems which have important bearings on the operation.

MERVIN, H. E. and LOMBARD, R. H.(66) In order to synthesize the ternary compounds of iron, copper and sulfur, the authors made a systematic study of the ternary system Cu-Fe-S, involving only solid phases and vapor. Figure 16 shows their findings. The following are their notes on this figure:

> "Types of fields. - This composition triangle in weight percent shows the 4 binary and 5 ternary crystalline compounds of Cu, Fe and S. All but two have mineral names. These and their solid solutions or inversion forms are stable with sulfur

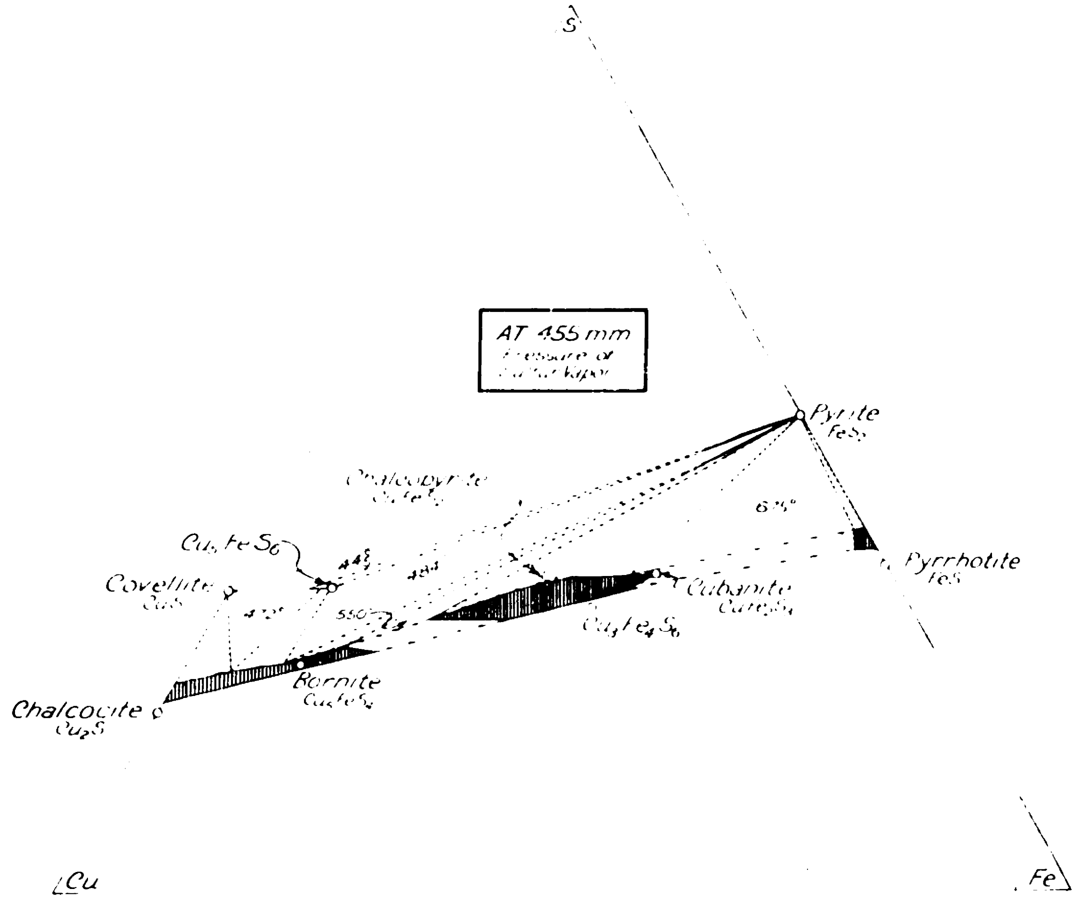

FIGURE 16

Part of Cu-S-Fe System

vapor at a pressure of 455 millimeters, either alone or in the presence of each other without liquid, as shown in Figure (16). A different set of <u>three</u> is stable at each of the five single temperatures indicated within the clear triangular areas. Each of the three has a definite composition represented by a corner of the triangle within which any proportions of the three may be present. Most of the corners are points on the boundaries of solid solutions.

"Where a solid solution, as <u>one</u> phase, covers an area, heavy vertical lining is used. The large central field is the intermediate solid solution, and the others are chalcocite solid solution and pyrrhotite solid solution. The sulfur content decreases with rising temperature, but before enough sulfur is expelled to bring the sulfur content down to the join between Cu_2S and FeS, melting begins. . .

"The other fields (lightly lined, horizontally) lie between solid solutions, or between compounds and solid solutions, and two crystalline phases appear in each field.

"In the upper part of Figure (16) liquid sulfur containing very little CuS and FeS_2 in solution is in equilibrium with covellite and pyrite at 411°; and in the lower part liquids and crystals are present. . ."

GREGG, J. L. and DANILOFF, B. N.$^{(67)}$ The authors present the most probable iron-copper constitution diagram which is shown in Figure 17. They review the early work on the diagram and discuss its present (1939) form. The Cu-Fe binary system is especially important, first, in constructing the ternary system Cu-Fe-S; second, in matte smelting where some metallic copper and metallic iron may be produced; and third, in studying the reaction

$$Fe + Cu_2S = FeS + 2Cu$$

from the equilibrium point of view.

DRUMMOND, P. R.$^{(68)}$ In a study on the constitution of matte, this author first presents a more accurate, although admittedly not perfect, method for the analysis of Fe_3O_4 in mattes. Later, the author states that, "Mattes are not one simple alloy system, but a

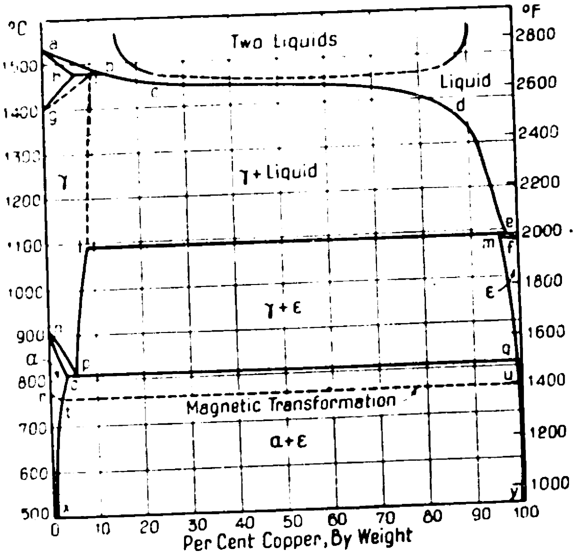

FIGURE 17

Fe-Cu Equilibrium Diagram

complex of sulfides, oxides and possible uncombined metals, depending on the method of fusion and conditions while molten. They might be termed 'the product of their environment'." Possible systems are as follows: (a) $FeS-Cu_2S$, (b) $Fe-FeS-Cu_2S$, (c) $FeS-Cu_2S-Cu$, (d) $FeO-FeS-Cu_2S$, (e) $(FeO-Fe_3O_4)$ - $FeS-Cu_2S$, and (f) $Fe_3O_4-FeS-Cu_2S$. While elaborating on the composition of mattes, he concludes from the previous works that, "$FeO-Fe_3O_4$ are present as a solid solution, which comprise a single component in the eutectic with FeS. Ferrous sulfide, alone, among the matte sulfides, has the power of holding $FeO-Fe_3O_4$ in molten state." He further says, "The author favors, but cannot prove, the theory that the eutectic is FeO-FeS, with Fe_3O_4 dissolve in the FeO." Finally, in tying the constitution of matte to the copper loss, he says, "The eutectic $FeO-Fe_3O_4-FeS$ offers an explanation of the known phenomenon that magnetite floats copper into the slag. Such a eutectic is neither slag nor matte, but partakes of the nature of both. If any of the matte analyses in this paper are compared, it will be seen that in all cases of high magnetite, the silica in the matte is high also. In the matte layer, the eutectic is partly slag, and in the slag layer it is partly matte. When the oxide component of the matte links up with silica to form slag, it drags FeS with it, and the FeS in turn carries copper or nickel in the slag."

AKSOY, A. M.(69) Retention of copper in slag is studied by fusing three synthetic mattes and three synthetic slags at different temperatures for one hour in graphite crucibles. Nine slags out of twenty-seven did not contain copper. In general, the lower the tempcrature and the lower the grade of matte, the smaller is the amount of copper retained.

KOCATOPCU, S.(70) Anaconda copper reverberatory slag was fused with varying amounts of pyrite for different lengths of time at different temperatures. The writer obtained the highest recovery, 73.2 percent, with 20 percent FeS at 1300° C at the end of one hour. He also recovered as much as 35 percent of copper by fusing the slag alone.

KOZAK, M. A. B.(71) The author studied the solubility of magnetite in copper mattes by fusing the synthetic mattes with magnetite at different temperatures. His conclusions are quoted below: "(1) Iron oxides, especially magnetite, are soluble in mattes to a considerable extent (up to 31.4 percent). (2) The solubility increases with increasing ferrous sulfide content of the matte. (3) Cuprous sulfide did not dissolve any oxide and that the solubility of magnetite in mattes is due to their ferrous sulfide contents alone. In the FeS-Cu_2S system the oxide solubility is believed to be proportional to the FeS content. (4) The ferrous oxide is taken out of the matte by silica. (5) The oxide dissolved in mattes in the presence of silica was mainly magnetite."

III. EXAMINATION OF REVERBERATORY DATA

In the process of making matte in the reverberatory furnace there are several factors which control the amount of copper retained in the slag. To smelter operators, some of the effects of these factors have long been known in a qualitative way. For instance, every smelter operator knows that the higher the grade of matte, the higher is the percentage of copper in the slag. But there has not been any general study that gives some relations which exist between the variables involved in furnace operation.

In the following pages, an attempt is made to examine the commercial reverberatory data and establish some correlations between the variables and the copper loss by using statistical methods of analysis.

A. Reverberatory Data

In order to obtain the commercial reverberatory data a questionnaire (see Appendix I) containing eleven questions was prepared and sent out to twenty-two copper smelters in North and South America. Five smelters did not give the desired information because of the war regulations while two of them did not answer at all. To increase the number of cases in the "sample" some more data were taken from Tables V and VI of Professor C. R. Hayward's "An Outline of Metallurgical Practice".(72)

Tabulation of the Data as Received

Tables I and II show the answers of the smelter superintendents to the questionnaire. A few smelters were not able to answer some of the questions because of the lack of data. Table III shows the additional data.

Calculated Values

The figures, which are reported as received in Tables I, II and III, do not tell how the factors are affecting the copper loss unless some arithmetic operations are carried out on them. For example, the percent of copper does not give the total copper loss unless the volume of slag is known. Again, the differences in specific gravities of matte and slag influence the copper loss rather then the specific gravity of matte or slag alone. Table IV shows all the calculated values. Most of these values are self-explanatory; however, a few of them may deserve more explanation.

The total copper loss in slag depends upon both the copper content of the slag and the amount (volume) of slag produced. This can be formulated as follows:

Total copper loss = percent copper in slag × volume of slag

The volume of slag can be either based on per-unit weight of matte or on per-unit weight of copper in matte. The latter basis is a more logical one since the final product of the smelter unit is copper (blister) and not matte. Table IV gives figures calculated both ways.

Non-ferrous slags are often classified according to their "silicate degree" which is defined as the ratio of the weight of oxygen in the acid oxides in the slag to the weight of oxygen in the basic oxides.

	A-1		A-2		B-1		B-2		C-1		
	S(1)	M(2)	S	M	S	M	S	M	S	M	
Cu	0.70	48.00	0.79	45.87	0.33	36.00	0.43	45.00	0.29	28.00	0
Fe					35.50	35.00	35.50	25.70	34.70	38.50	33
FeO(4)	44.00		45.81		45.65		45.65		44.60		43
Fe_2O_3											36
Fe_3O_4											7
S						25.00	0.70	22.00	0.60	25.00	0
SiO_2	34.00		29.63		38.20		38.00	0.90	37.70	1.30	37
CaO			3.65		6.80		6.90	0.40	3.30	0.30	3
Al_2O_3			4.88		4.40		4.70		6.40		7
MgO							1.80		2.90		3
MnO											
Zn			4.53				0.80		2.50	2.60	
Pb			2.46				0.29	2.00			
Sb & As											
Au(3)			0.001	0.35			0.0007	0.43	0.001	0.195	
Ag(3)			0.540	25.80			0.025	4.90	0.099	8.985	

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(1) Slag composition in percent
(2) Matte composition in percent
(3) In ounces per ton

(4) Where percent Fe is given, it is total Fe as FeO
(5) As Mn

TABLE I

Reverberatory Data

D-1		D-2		D-3		E		F		G		H	
S	M	S	M	S	M	S	M	S	M	S	M	S	M
0.36	33.54	0.34	33.54	0.37	31.72	0.65	43.77	0.33	38.00	0.80	48.98	0.44	26.5
9.60	35.00	41.30	35.00	36.70	36.50		31.50		26.40	40.90	23.90	32.40	35.4
0.90		53.15		47.20		41.00		42.20		52.60		41.65	
				35.00						44.70		41.1	
				11.00	11.00					8.50		0.70	8.3
1.10	26.40	1.10	26.40	0.80	26.90	0.60	25.80	0.70	21.70	1.00	24.50	0.70	24.7
4.70	1.50	34.60	1.50	38.60	0.20	39.20	0.50	39.00		28.70		35.80	0.5
2.70	0.10	2.60	0.10	3.40	0.20	5.00		8.90		0.33		1.90	
7.40	4.00	5.60	4.00	6.30	1.70	6.80		3.35		10.00		5.20	
				0.10				1.15		1.35		4.00	
						2.80		1.60	1.30			4.60	4.6
						0.33	0.89	0.48	4.80			0.70	3.9
0.001	0.29	0.001	0.29	0.0022	0.30		0.194			Trace	0.01	0.005	0.9
0.041	1.57	0.034	1.57	0.068	1.30		24.90			Trace	1.00	0.167	16.1

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E	F		G		H		I		J-1		J-2	
M	**S**	**M**	**S**	**M**	**S**	**M**	**S**	**M**	**S**	**M**	**S**	**M**
43.77	0.33	38.00	0.80	48.98	0.44	26.50	0.52	39.37	0.45	48.52	0.38	58.00
31.50		26.40	40.90	23.90	32.40	35.40	38.80	31.50		22.16		
	42.20		52.60		41.65		49.90		11.00		1.60	
			44.70		41.1		42.6				6.30	
			8.50		0.70	8.30	7.70	10.40				
25.80	0.70	21.70	1.00	24.50	0.70	24.70	1.30	24.40	0.08	24.96		
0.50	39.00		28.70		35.80	0.50	33.00	0.60	50.00		53.65	
	8.90		0.33		1.90		4.10	0.40	11.65		6.65	
	3.35		10.00		5.20		8.50	1.90	13.00		16.77	
	1.15		1.35		4.00				9.84		9.07	
									1.68	2.01(5)	3.32	
	1.60	1.30			4.60	4.60			0.49(6)	1.10(6)		
0.89	0.48	4.80			0.70	3.90						
0.194			Trace	0.01	0.005	0.93	0.0001					
24.90			Trace	1.00	0.167	16.19	0.007					

H		I		J-1		J-2		K		L		M	
S	M	S	M	S	M	S	M	S	M	S	M	S	
0.44	26.50	0.52	39.37	0.45	48.52	0.38	58.00	0.62	46.02	0.38	32.00	0.27	3
32.40	35.40	38.80	31.50		22.16			32.20	25.30		35.00		
41.65		49.90		11.00		1.60		46.50		47.00		39.60	
41.1		42.6				6.30		31.14					
0.70	8.30	7.70	10.40					10.80	5.70				
0.70	24.70	1.30	24.40	0.08	24.96			0.60	24.00	1.60	26.00	0.70	2
35.80	0.50	33.00	0.60	50.00		53.65		32.80	1.10	33.00	0.60	40.20	
1.90		4.10	0.40	11.65		6.65		3.50	0.20	4.00	0.30	8.10	
5.20		8.50	1.90	13.00		16.77		9.60	1.00	8.00	0.60	4.50	
4.00				9.84		9.07						2.00	
				1.68	2.01(5)	3.32							
4.60	4.60			0.49(6)	1.10(6)							2.00	
0.70	3.90											0.70	
0.005	0.93	0.0001						0.0008	0.189	0.004	3.75		
0.167	16.19	0.007						0.026	4.40	0.070	0.225		

	J-2		K		L		M		N		O	
M	S	M	S	M	S	M	S	M	S	M	S	M
8.52	0.38	58.00	0.62	46.02	0.38	32.00	0.27	34.20	0.39	27.62	0.40	16.80
2.16			32.20	25.30		35.00				40.60	37.90	45.70
	1.60		46.50		47.00		39.60		50.70			
	6.30		31.14								41.6	
			10.80	5.70						11.30	7.70(7)	18.50(7)
4.96			0.60	24.00	1.60	26.00	0.70	25.00	1.70	26.50	1.70	23.10
	53.65		32.80	1.10	33.00	0.60	40.20		33.60		32.40	1.00
	6.65		3.50	0.20	4.00	0.30	8.10		3.30		4.80	0.20
	16.77		9.60	1.00	8.00	0.60	4.50		8.20		2.90	0.50
	9.07						2.00					
2.01(5)	3.32											
1.10(6)							2.00				2.10	2.10
							0.70	6.40			0.80	3.20
											0.50	0.80
											0.30	0.50
			0.0008	0.189	0.004	3.75					0.005	0.15
			0.026	4.40	0.070	0.225					0.63	37.40

Plant	Wt. of Slag / Wt. of Matte	Specific Gravity		Thickness in Inches		Fluidity of Slag	Percent Fines Less Than 10μ	Te Du
		Slag	Matte	Slag	Matte			Slag
A-1	1.420	3.64						
A-2	0.973	3.00(1)	5.25(1)	12	20	Thin		2200
B-1	1.220	3.50	4.40					
B-2	0.908	3.45	4.50	12	28	Thin		2130
C-1	2.750	3.10						
C-2	2.910	3.49	4.81	18	24	Stony		2100
D-1								
D-2		3.42						
D-3	0.941	3.43	4.70	14	16	Thin and Thick	18	2341
E	1.090	3.42						
F		3.20(1)	4.60(1)	8	20	Thin		2100
G	0.650	3.06	4.67	7	30	Thin		2150
H	1.987	3.60	4.63	27	9	Creamy	26(3)	2140
I	0.831	3.72	4.62	11	23	Thin	12(4)	2190
J-1	8.470			20	2	Thin and Glassy		1976
J-2	11.000			8	2	Creamy and Glassy		2282
K	1.021	3.43	4.90	7	14	Heavy		2250
L	0.988	3.49	4.70	9	14	Medium and Glassy	12	2000
M	0.626		4.50	10	35	Creamy		2250
N	0.660	3.40(1)	5.10(1)	18	36	Thin	9.5(5)	2200
O	2.000	3.89(2)	4.88(2)	5	9	Thin and Glassy		1954

---

(1) Approximate; (2) Cast samples minus 80 mesh; (3) -13 μ -3 μ (7)
(4) -9 μ ; (5) In roasted feed: 4.6 percent; (6) As metallic copper Cu_2
(14)

TABLE II

Reverberatory Data

Temperature During Tapping			Conver. Slag		Wt. Conv. Slag over Wt. Matte	Form of Copper	Rate of Magnetite Accumulation	Reason for Running Cu Purposely High	Form o Copper Reverb tory S
Slag	Matte	Furnace	% Cu	% Fe_3O_4					
2200	2050	2500	2.5		1.060	(6),(7)	Very Small		(7),(
2130	2060	2350	2.0		0.550	(7),(9)	$\frac{1}{4}$ to $\frac{1}{2}$"/month		(9),(
2100	1990		3.2	22.6	0.965	(10)	Little, None		(11)
2341	1961	2546	2.8	17.7	0.788	(13)	Slow		(13)
2100	1850	2700	2.0		0.700		Very Little		(7),
2150	2110	2820	5.7	23.0	0.700		High	Economy	(8)
2140	1950	2700	2.5	14.3	1.130	(8),(10)	Not noticeable	High Yield	
2190	2095	2435	5.6	27.6	0.675	(13)	Severe		(13)
1976	1852	2282	2.5	4.0	2.500	(10)	High		(11
2282	2012	2462	2.5	4.0		(10)	None	Lack of C	(11
2250		2350	6.8	24.6	0.548	(13)	Slow		(8)
2000	1850	2450	3.0	12.0	0.636	(8),(10)	Negligible		(8)
2250	2010	2620	3.0		0.900	(13)	Varies		(13
2200	2050	2500	2.8	14.6	0.900		Slow		
1954	1873	2199	3.3	28.6	0.800	(8),(6)	Variable		(8) (10

(7) As copper oxides; (8) As matte particles, in suspension; (9) As silicate ($CuSiO_3$); (1
Cu_2S; (11) As Cu_2S dissolved; (12) Mixtures of Cu_2S and FeS, in suspension; (13) As sulf
(14) As metallic copper in solid solution; (15) As Cu_2O dissolved

TABLE III

Reverberatory Data

Plant	Slag Composition in Percent SiO_2	 FeO	 CaO	 MgO	 Al_2O_3	 Cu	% Cu in Matte	(c)	(d)
Anaconda[a]	38.1	41.8	5.2		6.0	0.55	45.38	1.032	0.477
Noranda[a]	39.4	43.4	0.9	1.1	7.5	0.328	22.7	2.125	1.390
Nevada Consolidated[a]	36.9	44.0	5.9		7.3		30.9	1.151	0.859
P. D. Douglas[a]	37.4	44.0	5.7		6.2	0.396	32.13	1.890	0.966
P. D. Clarkdale[a]	35.9	43.8	3.3		6.9	0.299	21.13	3.120	1.142
Magma[a]	38.7	43.6	4.3		5.3		31.0	3.235	
International Nickel[a]	36.5	51.5	1.2	1.3	5.6	0.36	40.0	0.905	0.820
International, Arizona[a]	38.2	47.8	3.9		4.9	0.42	40.94	0.772	0.481
A.S. & R. Plant No. 1[a]	39.3	43.2	6.6	1.1	5.1	0.26	35.1	2.285	1.115
A.S. & R. Plant No. 2[a]	37.6	46.8	6.5		4.9	0.34	32.3	1.090	0.818
A.S. & R. Plant No. 3[a]	38.1	32.7	10.6	1.7	6.1	0.266	37.7	1.574	0.407
A.S. & R. Plant No. 4[a]	37.2	47.2	7.2		5.3	0.36	37.9	1.333	0.546
Roan Antelope[b]	47.3	13.7	11.4	2.9	14.7	1.20	78.73		

(a) From C. R. Hayward(72). (b) From C. R. Wraith(73). (c) Weight of slag/weight of matte.

Al_2O_3, which is one of the constituents of copper slags, may act as either an acid or a base or both. In Table IV two silicate degrees are listed. No. I is based on the assumption that all the Al_2O_3 acts as a basic oxide. In No. II, Al_2O_3 is assumed to form the compound Al_2O_3, 3CaO; $6SiO_2$, and it acts partly as a base and partly as an acid(74).

In Table IV the empty spaces are due to the incompleteness of the questionnaires. This table will also be used in later chapters.

B. Statistical Method of Analysis

The application of statistical methods to the study of blast furnace and open hearth data and other metallurgical problems has been found satisfactory in the past(75-82).

Correlation methods are discussed in any general textbook on statistics. The book which the author followed is Mordecai Ezekiel's "Methods of Correlation Analysis"(83).

The following is a brief resume of the definitions of statistical terms and their significance.

The arithmetical average is well known and it is the quotient of the division of the sum of items into the number of items. The standard deviation measures the scatter from the arithmetical means and is defined as the root-mean-square-deviation. It has certain advantages from the mathematical point of view.

When the relation between the two variables departs slightly or moderately from the linearity, the values of one variable may be es-

Plant No.	Plant Name	Total Cu in Slag per Ton of Matte	Pounds Cu in Slag per Ton Copper in Matte	Silicate Degree		Ratio of FeO to SiO_2	Cu/Ag Ratio i Tons per 100 0	
				I	II		In Matte	I Sl
1	A-1	0.00994	46.4	1.825		1.293		
2	A-2	0.00769	30.7	1.167	1.388	1.546	1.71	1.
3	B-1	0.00402	26.9	1.550	1.437	1.195		
4	B-2	0.00391	19.5	1.348	1.386	1.200	9.18	17.
5	C-1	0.00798	68.9	1.347	1.724	1.182	3.12	2.
6	C-2	0.00865	78.5	1.258	1.676	1.162	3.25	2
7	D-1			1.187	1.649	1.467	21.40	8
8	D-2			1.213	1.528	1.538	21.40	10
9	D-3	0.00348	24.2	1.324	1.670	1.222	24.40	5
10	E	0.00708	36.3	1.520	1.892	1.046		
11	F			1.488	1.803	1.082		
12	G	0.00520	23.8	0.868	1.530	1.832		
13	H	0.00875	73.9	1.373	1.750	1.163	1.63	2
14	I	0.00432	24.4	1.047	1.492	1.512		
15	J-1	0.03810	176.0	1.690	2.270	0.220		
16	J-2	0.04175	161.5	1.819	3.560	0.154		
17	K	0.00632	30.7	1.133	1.763	1.417	10.50	23
18	L	0.00376	26.3	1.145	1.585	1.423	142.00	5
19	M	0.00169	10.9	1.531	1.977	0.985		
20	N	0.00257	20.5	1.111	1.503	1.510		
21	O	0.00800	105.0	1.222	1.462	1.505	0.45	[illegible]

TABLE IV

Reverberatory Data

Ratio of FeO to SiO_2	Cu/Ag Ratio in Tons per 100 Oz. In Matte	Cu/Ag Ratio in Tons per 100 Oz. In Slag	Cu/Au Ratio in Tons per 100 Oz. In Matte	Cu/Au Ratio in Tons per 100 Oz. In Slag	Difference in Specific Gravities of Matte & Slag	Pressure on Hearth in Cm. of Mercury	Total Cu in Converter Slag per Ton of Matte	Total Magnetite i Converter Sl per Ton Matt
1.293								
1.546	1.71	1.46	131.0	790.0	0.97	26.35	0.0265	
1.195					0.90			
1.200	9.13	17.20	105.0	614.0	0.91	31.30	0.0110	
1.182	3.12	2.93	144.0	290.0	0.90			
1.162	3.25	2.86	165.0	228.0	1.32	33.30	0.0309	0.218
1.467	21.40	6.78	115.0	360.0				
1.538	21.40	10.00	115.0	340.0				
1.222	24.40	5.54	105.0	168.0	1.27	23.05	0.0221	0.139
1.046								
1.082					0.80	22.90	0.0140	
1.852					1.61	30.18	0.0399	0.161
1.163	1.63	2.64	28.5	88.0	1.03	25.95	0.0282	0.162
1.512					0.90	27.50	0.0378	0.186
0.220							0.0625	0.100
0.154								
1.417	10.50	23.80	244.0	775.0	1.47	17.30	0.0372	0.135
1.423	142.00	5.43	8.5	95.0	1.21	18.15	0.0191	0.076
0.985							0.0270	
1.510					1.70	45.70	0.0252	0.131
1.505	0.45	6.35	112.0	80.0	0.99	11.76	0.0264	0.229

Table IV, continued

Plant No.	Plant Name	Total Cu in Slag per Ton of Matte	Pounds Cu in Slag per Ton Copper in Matte	Silicate Degree		Ratio of FeO to SiO_2
				I	II	
22	Anaconda	0.00568	27.6	1.491	1.695	1.098
23	Noranda	0.00696	67.4	1.443	2.148	1.178
24	Nev. Consl.			1.320	1.628	1.190
25	P.D.Douglas	0.00748	51.2	1.387	1.622	1.176
26	P.D.Clarkdale	0.00932	97.4	1.378	1.850	1.220
27	Magma			1.532	1.800	1.127
28	Int. Nickel	0.00326	17.9	1.303	1.720	1.410
29	Int. Arizona	0.00324	17.4	1.563	1.677	1.250
30	A.S.R. No. 1	0.00595	37.2	1.463	1.552	1.100
31	A.S.R. No. 2	0.00370	25.2	1.372	1.446	1.243
32	A.S.R. No. 3	0.00419	24.4	1.467	2.108	0.858
33	A.S.R. No. 4	0.00480	27.8	1.315	1.382	1.269
34	Roan Antelope			1.740	2.692	0.290

timated from the values of another, according to the functional relation shown in a set of paired observations. The degree to which two variables are linearly associated can be found by calculating a certain value which is called "coefficient of correlation" and designated by "r". The values of the coefficient of correlation "r" vary from minus one through zero to plus one, the approaches to plus or minus one characterizing good relationships between the two variables. Where the number of observations are small, an adjusted coefficient of correlation is used. Without this adjustment, the observed coefficient of correlation tends to exceed the true correlation. The proportion of samples in which specified departure will occur by chance can be determined by the methods developed by R. A. Fisher(84).

The differences between the estimated values and the actual values are called residual differences or "residuals". The standard deviations of the residuals are termed "standard error of estimate". The latter value serves to indicate the closeness with which new estimated values may be expected to approximate the true but unknown values.

The straight line used to estimate one variable from another is called "regression line" and can be expressed mathematically as follows:

$$Y = a + b X$$

where Y is the dependent variable and X is the independent variable. The choice of independent or dependent variable in a set of paired observations is important and depends upon the particular case being handled. The coefficients a and b may be readily calculated from r, the standard deviations and the averages of the variables involved.

Appendix II-A shows the sample calculations for these statistical quantities. A simple adding machine was used to facilitate the computations.

Such a treatment as outlined above assumes that the observations from all smelters represent random samples with perfect normality. In this case, the application of the tests which tell whether or not the data represent random samples is meaningless because of the small number of samples. But the tests of normality (see Appendix II-B) were applied to each observation and those observations with non-normal characteristics were dropped out. This consequently made the number of observations studied smaller. Although it cannot be proved statistically that the observations represent random samples, the data still can be used. For the object of the examination of the data was to find relations between variables and since no physicochemical reasons exist for expecting differences in these relations between copper smelters, data from all smelters were mixed as it was previously done in similar studies(80,82).

C. Correlations and Their Interpretation

Table V summarizes all the statistical quantities for various sets of X and Y. Figures 18, 19 and 20 show those relationships having a correlation coefficient higher than 0.650.

The number of good correlations is small; however, the remaining correlations still give some idea of how the variables are related.

TABLE V

Statistical Quantities

Variables		Number of Samples	Coefficient of Correlation	Adjusted Coefficient of Correlation	Portion of Samples in Which Specified Departure Will Occur by Chance		C
X	Y		r_{xy}	$\bar{r}_{xy}$		-a-	R
Grade of matte	Total Cu in slag/Cu in matte	23	–0.828	–0.817	0.01	126.7	
Grade of matte	Percent Cu in slag	32	0.788	0.780	0.01	- 0.07	
Fe_3O_4 in Conv. slag	Total Cu in slag/matte	9	0.657	0.595	0.05	0.422	
Cu in Conv. slag	Percent Cu in slag	13	0.517	0.450	0.07	0.46	
Silicate degree I	Percent Cu in slag	29	0.315	0.272	0.07	0.39	
Silicate degree II	Percent Cu in slag	29	0.334	0.285	0.06	0.55	
Percent SiO_2	Percent Cu in slag	31	–0.397	–0.362	0.02	0.90	
Temperature	Percent Cu in slag	15	0.478	0.410	0.03	- 0.15	

TABLE V

Statistical Quantities

ples	Number of Samples	Coefficient of Correlation	Adjusted Coefficient of Correlation	Portion of Samples in Which Specified Departure Will Occur by Chance	Coefficients of Regression Line		Standard Error of Estimate
Y		r_{xy}	$\bar{r}_{xy}$		-a-	-b-	
al Cu in slag/Cu in matte	25	–0.828	–0.817	0.01	126.7	–2.425	15.24
cent Cu in slag	32	0.788	0.780	0.01	– 0.072	0.0137	0.126
al Cu in slag/matte	9	0.657	0.595	0.05	0.422×10^{-4}	0.0329	0.00189
cent Cu in slag	13	0.517	0.450	0.07	0.4643	1.023×10^{-4}	—
cent Cu in slag	29	0.315	0.272	0.07	0.3969	0.0370	—
cent Cu in slag	29	0.334	0.285	0.06	0.5501	0.3012	—
cent Cu in slag	31	–0.397	–0.362	0.02	0.9007	–0.1210	—
cent Cu in slag	15	0.478	0.410	0.03	– 0.1557	2.865×10^{-4}	—

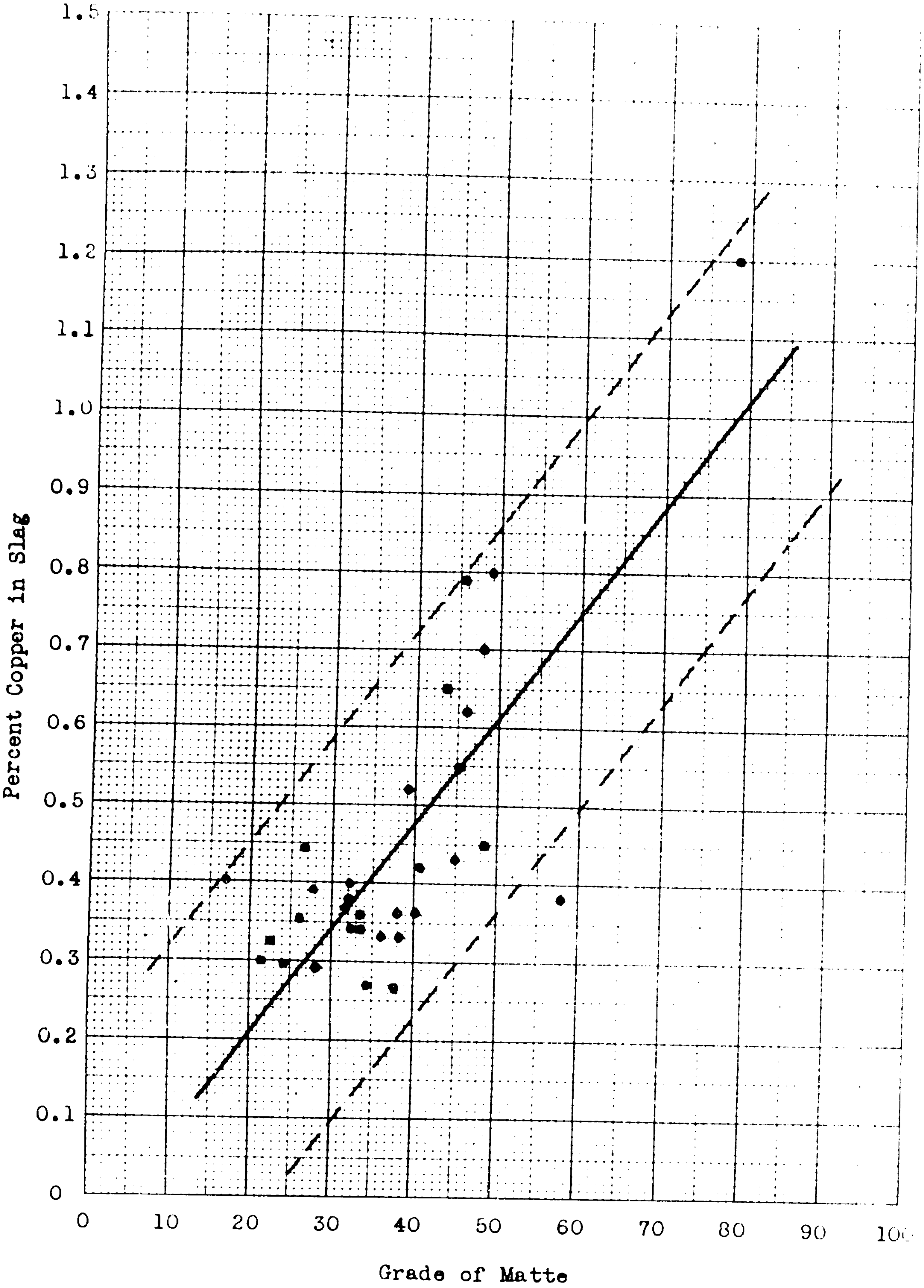

FIGURE 18-Relation between grade of matte and percent copper in slag. Limits of two standard error of estimates are shown.

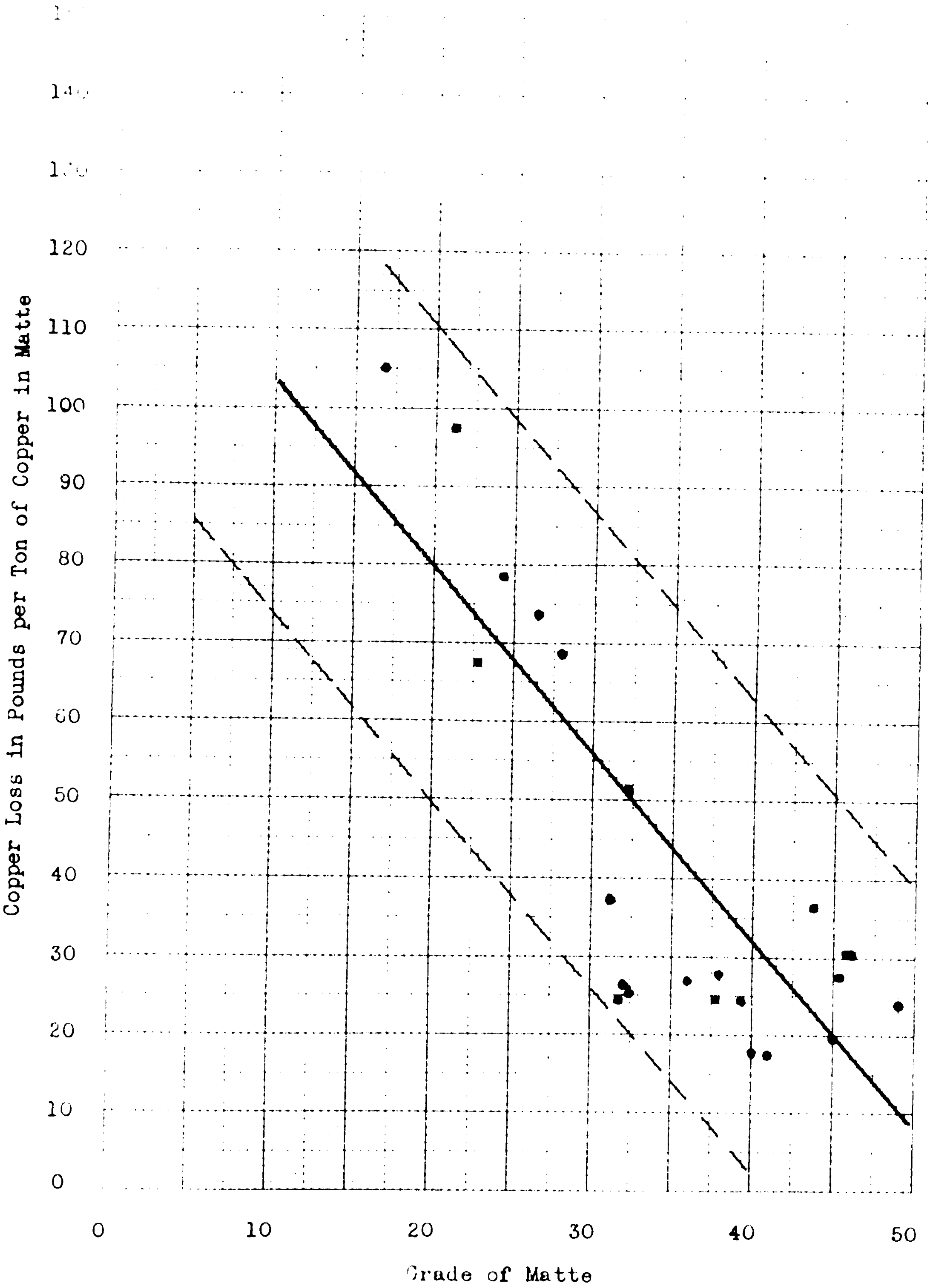

FIGURE 10 - Relation between grade of matte and copper loss in pounds per ton of copper in matte. Limits of two standard error of estimates are shown.

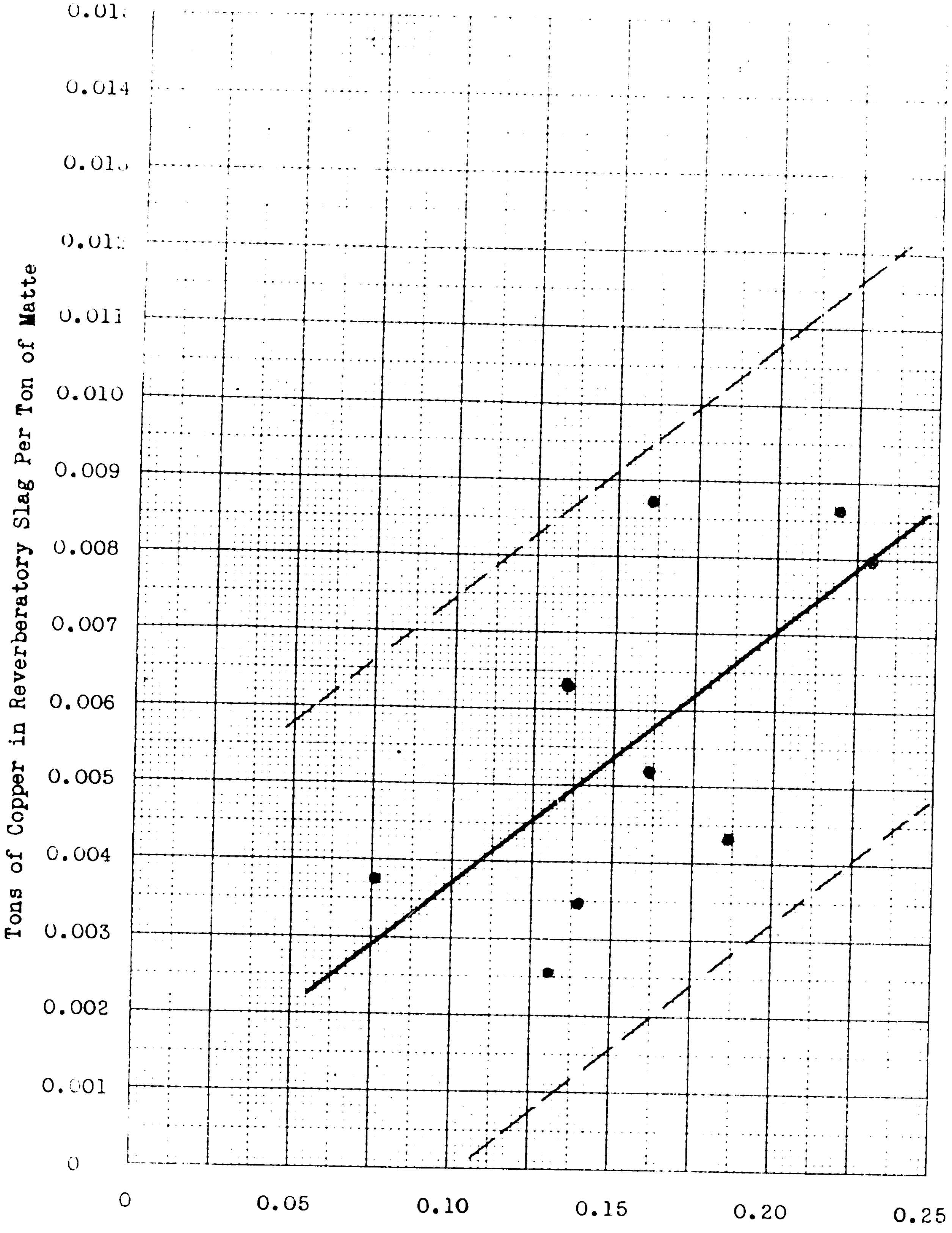

FIGURE 20 - Relation between magnetite content of converter slag and copper loss. Limits of two standard error of estimate are shown.

The grade of matte seems to be the most important factor affecting the slag loss. The higher the grade of matte, the lower the copper loss in slag per ton of copper in matte.

The silicate degree is of value for the comparison of the slags, and is based on the assumption that equivalent amounts of one base may be substituted for another without changing the properties of slag. Of course, this assumption is not true but still the silicate degree is a useful criterion. From the positive slope (b) of silicate degree I and II, it may be concluded that the higher the silicate degree the higher the percent of copper in slag. This explains the mechanical entrapment of copper in slag; because, in general, the more acid slags have a greater viscosity and, consequently, prevent the settling of copper-bearing particles (see Chapter V).

The percent of SiO_2 seems to affect the copper loss in the opposite way from that of the silicate degree, and the effect is more pronounced.

The higher the temperature, the higher is the percent of copper in slag. This contradicts the above statement when the mechanical entrapment is considered, because the temperature is expected to lower the viscosity and, consequently, allows more copper-bearing particles to settle. Then the increase of copper content with increasing temperature may be attributed to the solubility of some copper-bearing compound (see Chapter VII), or to the stirring of the bath caused by some chemical reactions (see Chapter VI), whose rate increases with temperature.

Both the copper and the magnetite (the effect of the latter being markedly stronger) in converter slag increase the copper loss. This is true because the higher the magnetite content of converter slag, the greater the chance for magnetite to react with ferrous-sulfide in the furnace with the evolution of sulfurous gases (see Chapter VI), which bring up matte particles into the slag layer.

IV. FORMS OF COPPER IN REVERBERATORY SLAGS

After studying some of the factors controlling the amount of copper in slag in the previous chapter, the next logical step in minimizing this loss is to investigate the forms in which the copper exists in commercial slags. As it has already been pointed out in Chapter II, there is little agreement among metallurgists on this subject. This diversity of opinions is clearly shown in Table II, last column, which summarizes the answers of smelter superintendents to the question in the questionnaire, "Have you any idea about the form of copper in reverberatory slag?"

The probable forms in which copper may exist in slags are as follows:

(1) Matte particles in suspension
(2) Matte as dissolved
(3) Cu_2S in suspension
(4) Cu_2S as dissolved
(5) Intermediate between (1) and (3)
(6) Intermediate between (2) and (4)
(7) Metallic copper in suspension
(8) Metallic copper as dissolved
(9) Copper oxides in suspension
(10) Copper oxides as dissolved
(11) Copper silicates, ferrites and aluminates

Before the investigation of the existence of these forms of copper in five commercial slags which were obtained from widely scattered smelters, some experiments were performed with synthetic mattes and slags to facilitate the study by eliminating the effects of certain constituents of mattes.

A. Preparation of Materials

Ferrous Sulfide

The ferrous sulfide was prepared the same way as described by Hayward and Carpenter(46), except that in this work iron bars were substituted for iron turnings. The iron turnings were placed in a No. 20 graphite crucible and heated in a 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 and then the product was ground to 100 mesh. It analyzed 63.00 percent Fe, 35.95 percent S, and 1.05 percent insoluble. The theoretical composition of FeS is 63.51 percent Fe and 36.49 percent S. During final melting, the temperature should be as low as possible because otherwise some distillation of sulfur from FeS may take place.

Cuprous Sulfide

The cuprous sulfide was also prepared in the same way as that described by Hayward and Carpenter(46). The copper strips taken from a dynamo were cut into small pieces and put in a No. 20 graphite crucible containing boiling sulfur. After all the metallic copper had disappeared, the crucible was cooled and a bluish-gray material was obtained. This partly sulfidized material was broken into small pieces, replaced in the crucible with more sulfur and melted in the gas-fired pot furnace. This procedure was repeated once more (without the addition of sulfur) in order to eliminate the excess sulfur by evaporation. The product was ground to 100 mesh and analyzed 79.51 percent Cu, 19.84 percent S and 0.65 percent insoluble. The theoretical composition of Cu_2S is 79.86 percent Cu and 20.14 percent S.

Synthetic Mattes

Three grades of matte were prepared by mixing the proper amounts of Cu_2S and FeS, which were already ground to 100 mesh in a pulverizer. The iron contamination from the pulverizer is usually small. Then the mixtures were melted down in size I clay crucibles in a small gas-fired pot furnace. At 1125° C all the mixtures melted. When cooled, they were ground to 100 mesh and analyzed as shown in Table VI.

TABLE VI

Composition of Mattes in Percent

Cu	25.5	37.9	57.9
Fe	44.7	32.5	16.1
S	24.0	23.0	20.5

Copper-free Synthetic Slags

Two 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. Two 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 two slags are shown in Table VII.

TABLE VII

Composition of Slags in Percent

	Slag 1	Slag 2
SiO_2	31.0	36.5
Al_2O_3	5.9	7.8
CaO	9.0	7.6
MgO	-	1.0
FeO	49.2	46.9
Total	95.1	99.8

Iron in the slags reported as FeO. This is not true, because some portion of the iron is in the ferric state. Bowen and Schairer(85) state that "the reduction of most of the iron to the ferrous state is a matter of experience in the use of the gas furnace and is attended with variable success." Slag 1, of which the composition totals 95.1 percent, contains considerable iron in the ferric state - Fe_3O_4 or Fe_2O_3.

Synthetic Slags

Mattes I, II and III and slags 1 and 2 were ground to 100 mesh in a pulverizer. Then each slag was mixed with three different grades of matte giving six slag-matte combinations. Each charge consisted of 30 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 at M. I. T. The shape and dimensions of the crucibles are shown in Figure 21. All six charges were fused and held one hour at 1200° C. in an electric globar furnace. A chromel-alumel thermocouple was used to measure the temperature. 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 the crucibles to room temperature. After cooling, the crucibles were broken one by one to separate the matte bottom from the slag layer.

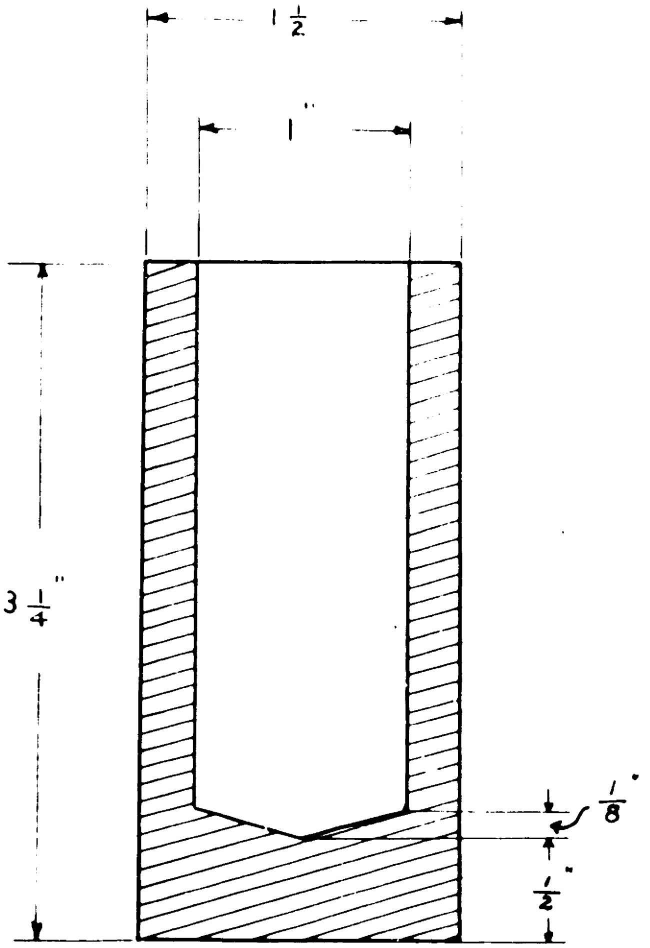

Fig. 21 - The Shape and Dimensions of Graphite Crucibles

Commercial Mattes and Slags

Samples of commercial mattes were obtained from Plants A and D, while commercial slags were obtained from Plants A, B, C, D and E.

B. Microscopic Work

Several sections of FeS, Cu_2S, synthetic mattes and slags and commercial mattes and slags were polished by the modified Harvard process (see Appendix 3). Then the polished sections were examined under the microscope at varying magnifications in the Mineral Dressing Laboratory of the Department of Metallurgy at M. I. T., for their physical characteristics. Later, etch reactions as outlined by M. N. Short(86) were carried out in the Economic Geology Laboratory of the Department of Geology at M. I. T. Table VIII shows the possible constituents of slags and mattes with their physical characteristics as well as their behavior towards different etching reagents. The results of the microscopic work are as follows.

Ferrous Sulfide

Figure 22 shows the microstructure of FeS. It consists of a yellow-brown matrix with occasional traces of iron (very light areas). The black spaces are cavities which are caused by the evolution of gases, possibly S_2 or SO_2, and consequent contraction.

Cuprous Sulfide

Figure 23 shows the microstructure of Cu_2S. It consists of uniform, bluish-gray grains embedded in bakelite.

TABLES VIII and IX

Physical and Chemical Properties of Some Copper-Iron-Sulfur Minerals

Compound	Formula	Composition in Percent				Color	Hardness	Isotropic or Anisotropic
		Cu	Fe	S	O			
Chalcocite	Cu_2S	79.86	-	20.14	-	Gray, bluish gray	Soft	Anis.*
Covelite	CuS	66.48	-	33.52	-	Light blue to dark blue (Indigo blue)	Soft	Anis.
Pyrrhotite	FeS	-	63.53	36.47	-	Light yellow	Hard	Anis.
Pyrite	FeS_2	-	46.55	53.45	-	Yellowish white Brass yellow	Very hard	Is.
Chalcopyrite	$CuFeS_2$	34.64	30.42	34.94	-	Bright yellow Pinkish cream	Medium	Anis.*
Cubanite	$CuFe_2S_3$	23.42	41.14	35.44	-	Bright yellow Pale brownish	Medium	Anis.
(New Compound)	$Cu_3Fe_4S_6$	31.45	36.83	31.72	-	Bright yellow	Medium	
Bornite	Cu_5FeS_4	63.32	11.13	25.55	-	Grayish yellow-orange	Soft	Is.**
(New Compound)	Cu_5FeS_6	56.15	9.81	33.98	-	Bronze, grayish orange	Soft	
Metallic Copper	Cu	100.00	-	-	-	Coppery pink	Soft	Is.
Metallic Iron	Fe	-	100.00	-	-			

SVIII and IX

f Some Copper-Iron-Sulfur Minerals

cent Q	Color	Hardness	Isotropic or Anisotropic	Reflectivity	Etching Reagent HNO_3 Eff.	HNO_3	HCl	KCN	$FeCl_3$	KOH	Hg_2Cl
–	Gray, bluish gray	Soft	Anis.*	29	x	x	s	x	x	–	s
–	Light blue to dark blue (Indigo blue)	Soft	Anis.	18 – 26	–	s	–	x	–	–	–
–	Light yellow	Hard	Anis.	37	–	s	x	–	–	x	–
–	Yellowish white Brass yellow	Very hard	Is.	54	s	x	–	–	–	–	–
–	Bright yellow Pinkish cream	Medium	Anis.*	42	–	s	–	–	–	–	–
–	Bright yellow Pale brownish	Medium	Anis.	41	–	s	–	–	–	–	–
–	Bright yellow	Medium									
–	Grayish yellow-orange	Soft	Is.**	18	x	x	–	x	x	–	–
–	Bronze, grayish orange	Soft									
–	Coppery pink	Soft	Is.	85	x	x	s	x	x	x	x
–											

				Etching Reagent							
Color	Hardness	Isotropic or Anisotropic	Reflectivity	HNO_3 Eff.	HNO_3	HCl	KCN	$FeCl_3$	KOH	Hg_2Cl	Aqua Regia
ed internal reflection luish gray	Soft	Anis.	29	x	x	x	x	x	–	–	
ray	Medium	Anis.	22.2	–	s	x	–	–	–	–	
ray	Medium	Anis.	23.1	–	–	x	–	–	–	–	
ray	Soft or hard	Is.	21	–	–	x	–	–	–	–	x

66)

---

* Sometimes iotropic
** Sometimes aisotropic

s = slightly
– = negative
x = positive

TABLE VIII (continued)
TABLE IX

		Composition in Percent							
Compound	Formula	Cu	Fe	S	O	Color	Hardness	Isotropic or Anisotropic	Re
Cuprite	Cu_2O	88.85	–	–	11.15	Red internal reflection Bluish gray	Soft	Anis.	
Tenorite	CuO	79.80	–	–	20.20	Gray	Medium	Anis.	
Delafossite	$Cu_2O \cdot Fe_2O_3$	41.85	36.92	–	21.23	Gray	Medium	Anis.	
Magnetite	Fe_3O_4	–	72.35	–	27.65	Gray	Soft or hard	Is.	

Prepared from M. N. Short(86) and H. E. Mervin and R. H. Lombard(66)

* Sometimes isotr
** Sometimes aniso

Synthetic Mattes

Figures 24, 25, 26, 27, 28 and 29 show the microstructures of synthetic Mattes I, II and III.

(a) Matte I (25.5 per cent Cu). It consists mostly of yellow-brown areas with some pearlite-like structure (eutectic). Magnetite is also present.

(b) Matte II (37.9 percent Cu). It resembles that of Matte I; in addition, it contains metallic copper in the capillary form as well as inside the grains.

(c) Matte III (57.9 percent Cu). It consists of mottled* sulfide (solid solution), grayish in color. More metallic copper but little magnetite is present.

Commercial Mattes

Figures 34, 35, 36 and 37 show the microstructures of commercial Mattes A and D.

(a) Matte A (48.00 percent Cu). The structure resembles that of the synthetic Matte II. In this case, more magnetite and more metallic copper are present. Black spaces are cavities.

(b) Matte D (33.54 percent Cu). The entire sample is made up from mottled yellow-brown areas. Very little metallic copper but considerable magnetite is present.

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* Mottling is a general term for more or less indefinite and fine-grained color differences which develop during cooling(66).

Copper-free Synthetic Slags

Figures 30 and 31 show the microstructure of copper-free synthetic slags. Light-colored grains gave positive test for magnetite. Dendritic magnetite is also present. The body of the slag is dark-colored and varies in structure from one slag to another.

Synthetic Slags

Figures 32 and 33 show the microstructure of synthetic slags. The structures are very similar to those of copper-free slags except that in this case they contain round, sulfide particles.

Commercial Slags

The microstructure of commercial slags is shown in Figures 38 to 61. Examination of these samples under the microscope showed the following:

(a) Matte particles having the same composition as the original matte. Figures 40 for Slag A and Figures 50, 51, 53, 54, 55 for Slag D show the matte particles (compare these with the structures of Matte A and D).

(b) Sulfide particles, mostly round, scattered haphazardly throughout the body of the slag. They vary a great deal in size and color (mottled). Chalcocite was found in all the slags. Some of the sulfide particles in Slag D gave a positive test for bornite. Figures 38, 39, 40 to 49, 52, 53 and 56 to 61 show these sulfide particles.

(c) Metallic copper. It was noted in a few polished sections, Figures 56, 57 and 59, in close association with sulfides.

(d) Magnetite. Almost all the specimens contained magnetite. They associate very closely with sulfides.

(e) Round Holes. Especially where the close association exists between magnetite and sulfide particles, round empty holes are very frequent.

As it is seen from the above, copper exists in forms (1), (3), (5) and (7) as itemized on page 52 . Other forms were not found by the examination of the polished sections.

The close association of magnetite with sulfide particles is due to the reactions between magnetite and ferrous sulfide (see Chapter VI) with evolution of sulfurous gases. Round holes may be due to entrapped gas bubbles or to the disappearance of FeS while the reactions are progressing. Of course, the final composition of the sulfide particles seen under the microscope will depend on the extent to which FeS - Fe_3O_4 reactions take place. Figure 52 is a good illustration of this phenomena. (Note the magnetite around the hole at right in Figure 52.)

The presence of metallic copper may be due to the bessemerizing, as suggested by Figure 59, of the Cu_2S giving Cu and S (see Chapter VI). It may also be the direct result of the entrapped matte particles, in the slag, containing moss or capillary copper after the FeS - Fe_3O_4 reaction is completed.

It was impossible to carry out the etch reactions for small particles. But at high magnifications they were similar to the large particles. The use of the electron microscope for the identification of small particles was considered but the microscopes in the Departments of Physics and Biology at M. I. T. were not available at this time.

C. Thin Sections

Several thin sections of commercial slags C and D were prepared and examined under the ordinary microscope. Figures 62 to 69 show the pictures of different sections. Magnetite was identified readily; the dark areas of Figures 62, 63, 66 and 67. The white areas are holes. The remaining part of the structure was made up from a transparent yellowish crystalline mass, Figures 64, 65, 68 and 69, imbedded in dark matrix.

Note

The pictures on the following pages were taken in the Mineral Dressing Laboratory of the Department of Metallurgy, M. I. T., with a leica camera. Super XX-35 millimeter Eastman-Kodak films were used. All the pictures were photographically enlarged to the cut-size from the negatives.

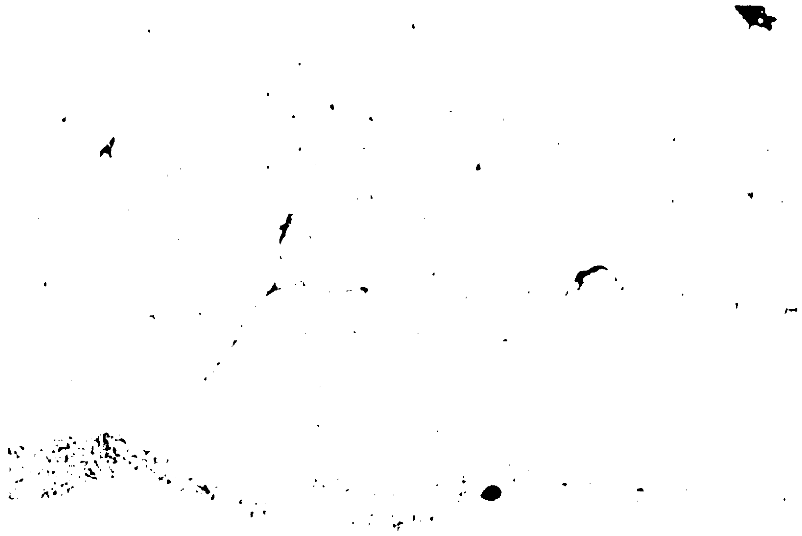


FIGURE 22. Ferrous Sulfide. 100 X

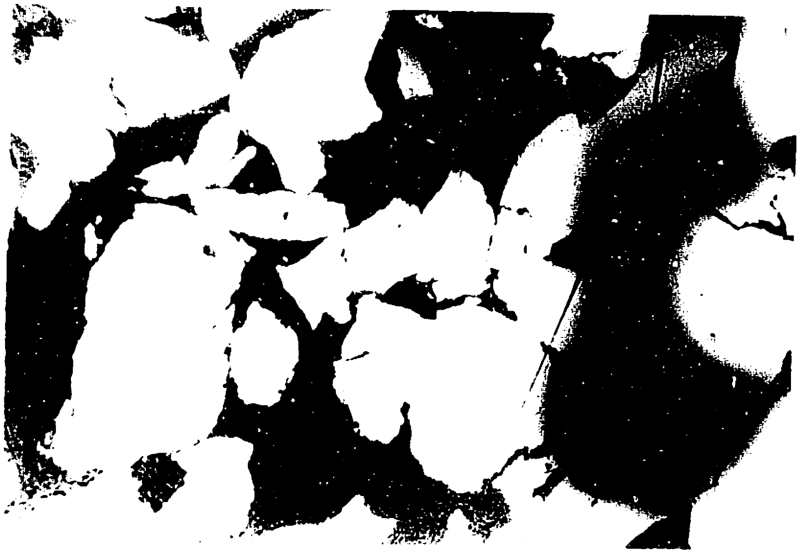


FIGURE 23. Cuprous Sulfide. 100 X

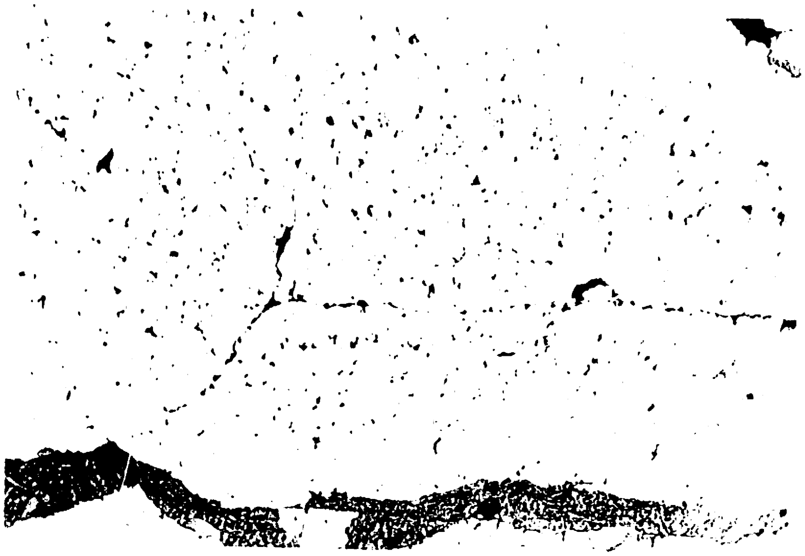


FIGURE 22. Ferrous Sulfide. 100 X

FIGURE 23. Cuprous Sulfide. 100 X

FIGURE 24. Matte I. 100 X

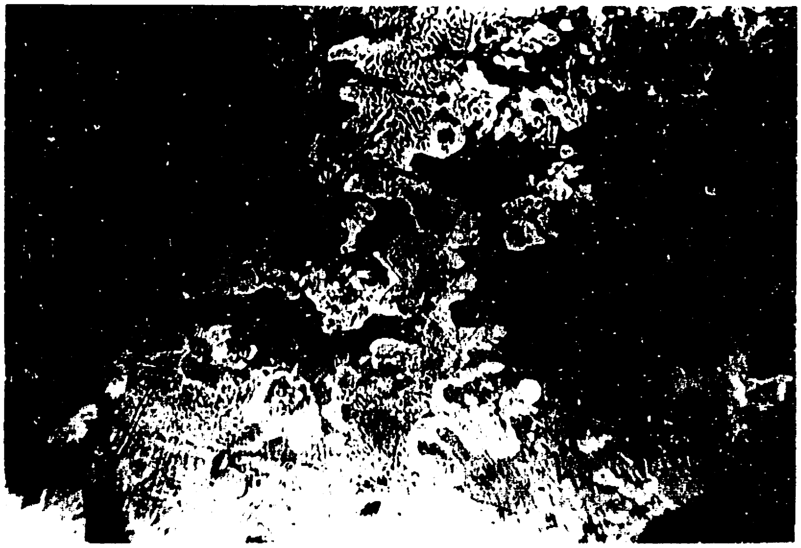


FIGURE 25. Matte I. 500 X

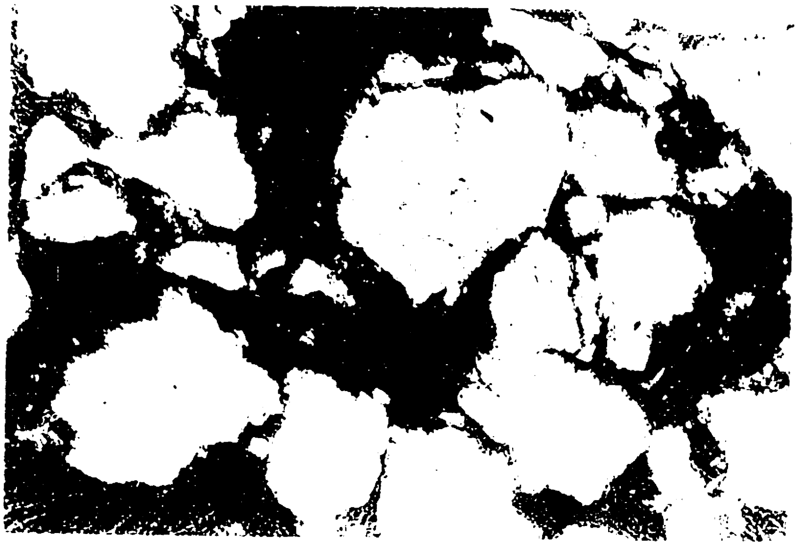


FIGURE 24. Matte I. 100 X

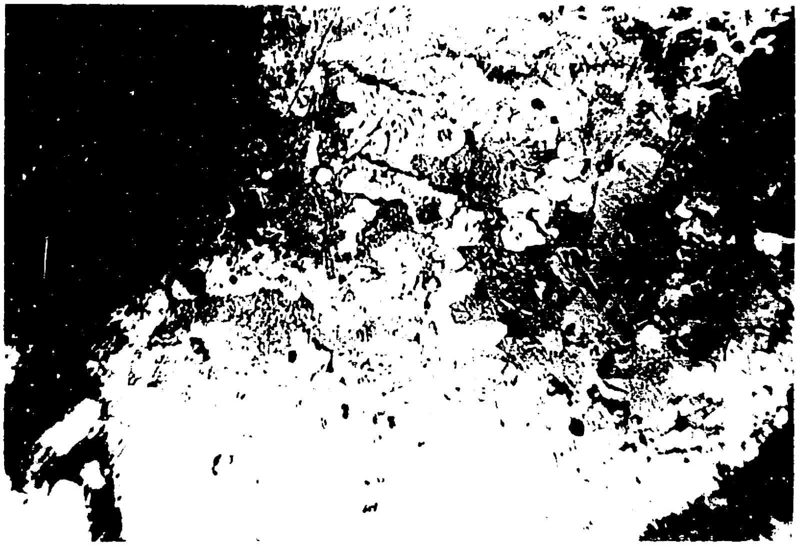


FIGURE 25. Matte I. 500 X

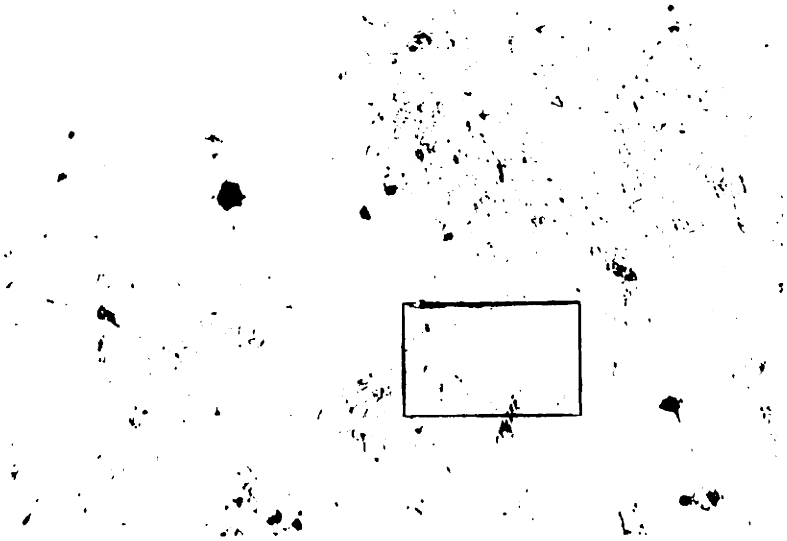


FIGURE 26. Matte II. 100 X

FIGURE 27. Matte II. 500 X

FIGURE 26. Matte II. 100 X

FIGURE 27. Matte II. 500 X

FIGURE 28. Matte III. 100 X

FIGURE 29. Matte III. 500 X

FIGURE 28. Matte III. 100 X

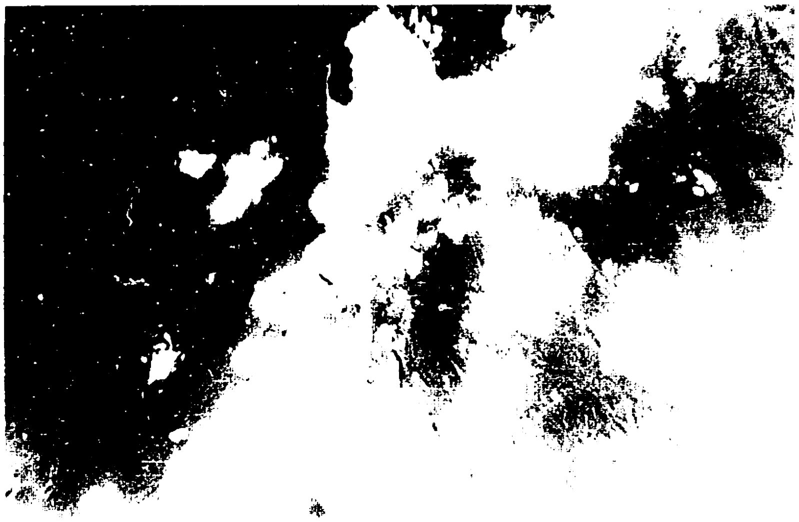


FIGURE 29. Matte III. 500 X

FIGURE 30. Synthetic Slag. 100 X. (Copper-free)

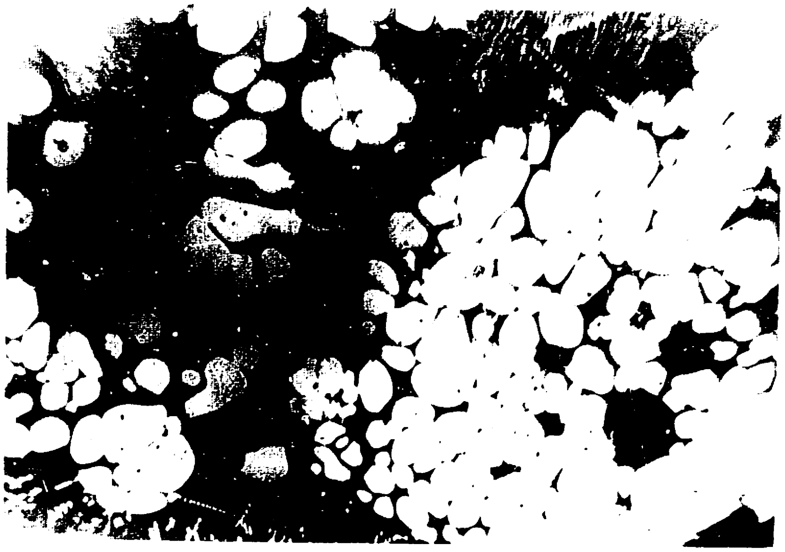


FIGURE 31. Synthetic Slag. 500 X. (Copper-free)

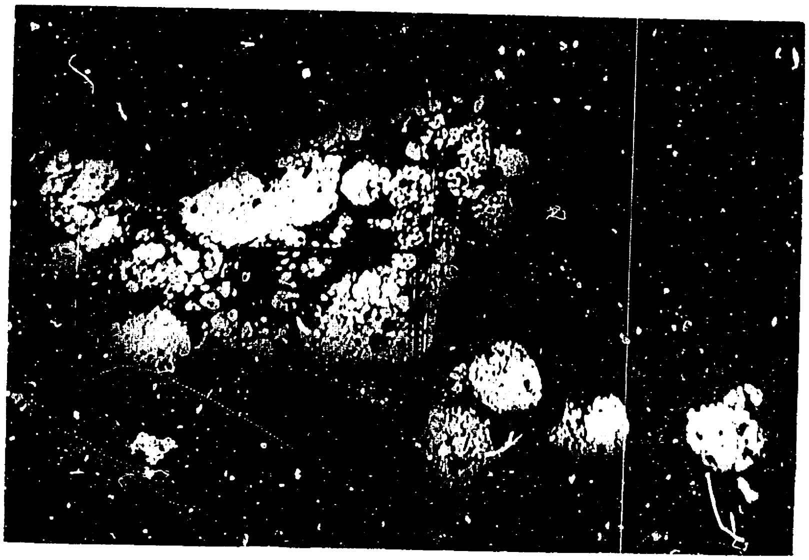


FIGURE 30. Synthetic Slag. 100 X. (Copper-free)

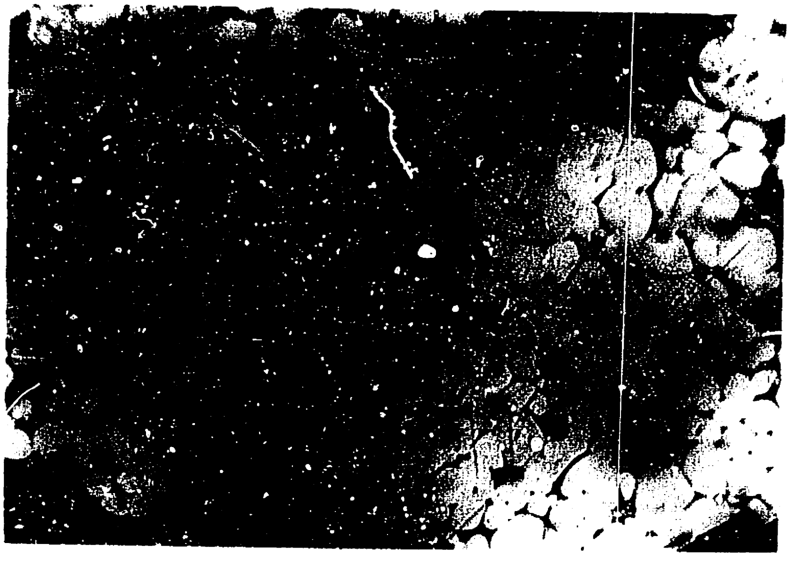


FIGURE 31. Synthetic Slag. 500 X. (Copper-free)

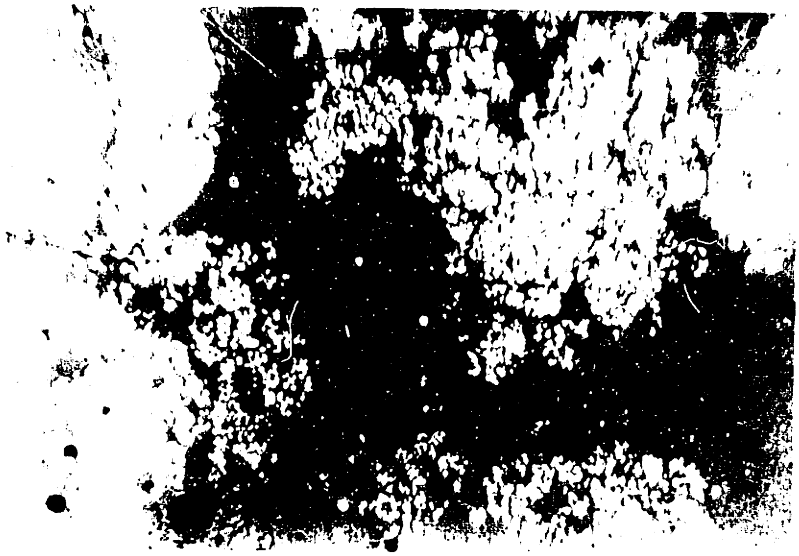


FIGURE 32. Synthetic Slag. 100 X

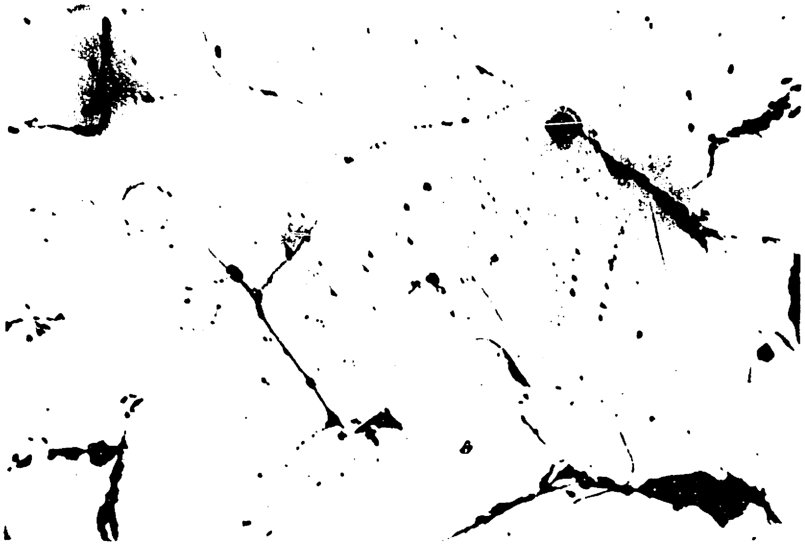


FIGURE 33. Synthetic Slag. 500 X

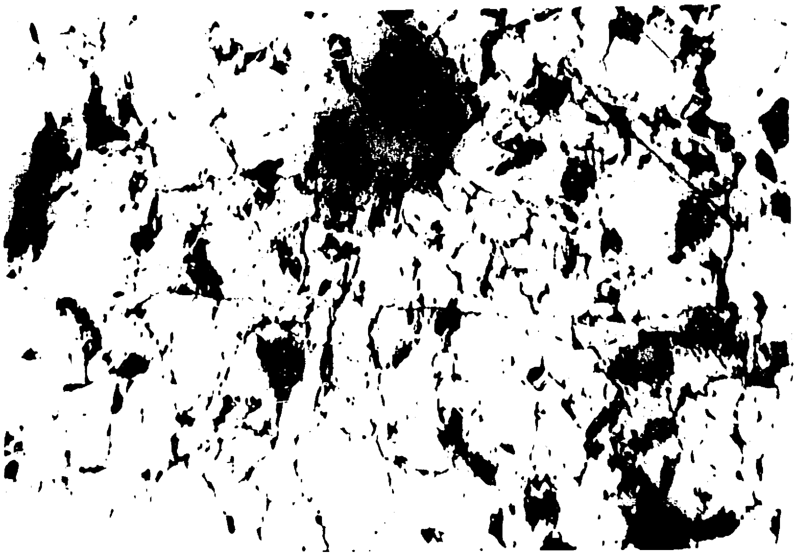


FIGURE 34. Matte A. 100 X

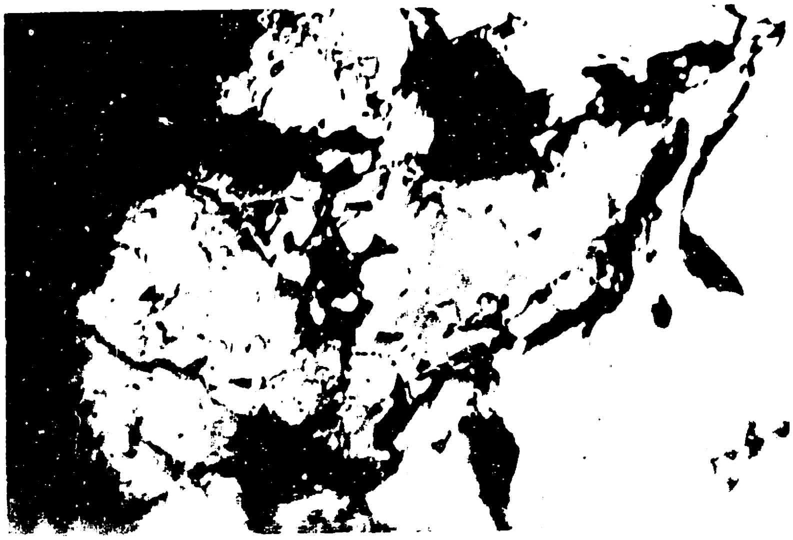


FIGURE 35. Matte A. 500 X

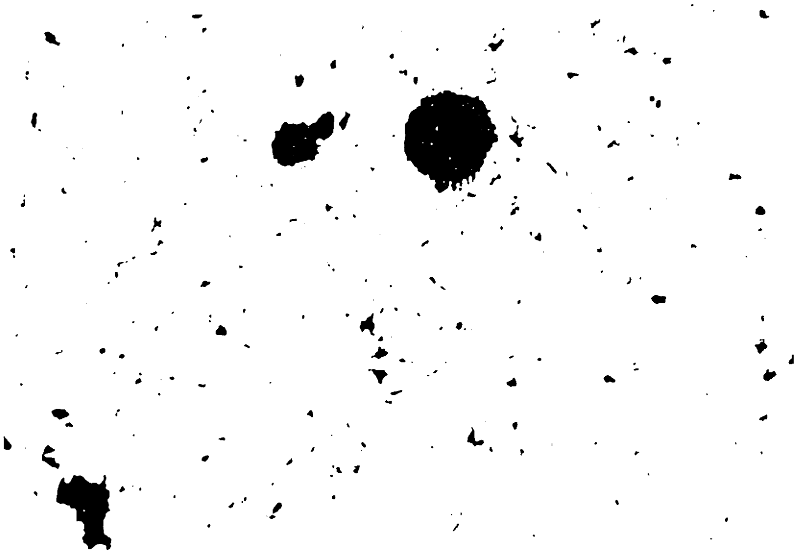


FIGURE 36. Matte D. 100 X

FIGURE 37. Matte D. 500 X

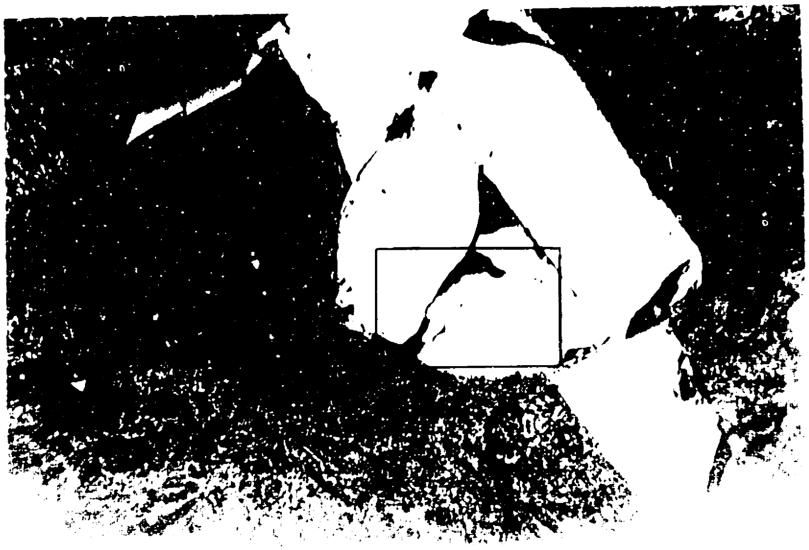


FIGURE 38. Slag A. 100 X

FIGURE 39. Slag A. 500 X

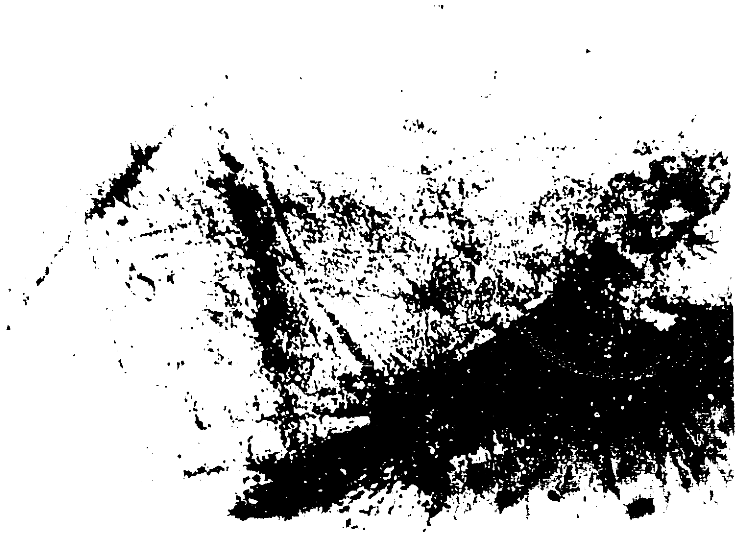


FIGURE 40. Slag A. 100 X

FIGURE 41. Slag A. 500 X

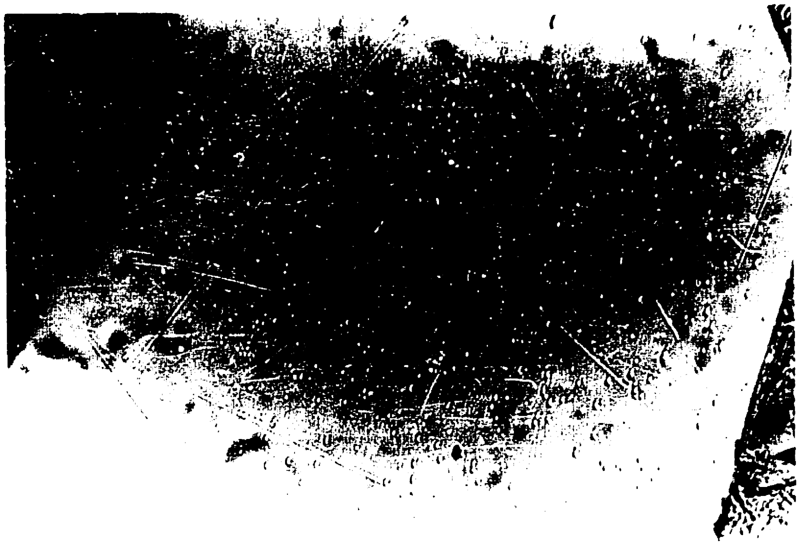


FIGURE 42. Slag B. 100 X

FIGURE 43. Slag B. 500 X

FIGURE 44. Slag B. 100 X

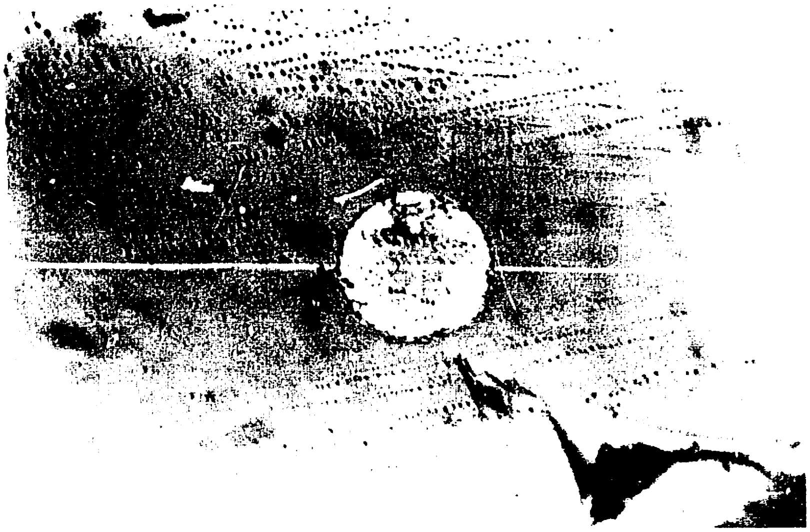


FIGURE 45. Slag B. 500 X

FIGURE 46. Slag C. 100 X

FIGURE 47. Slag C. 500 X

FIGURE 48. Slag C. 100 X

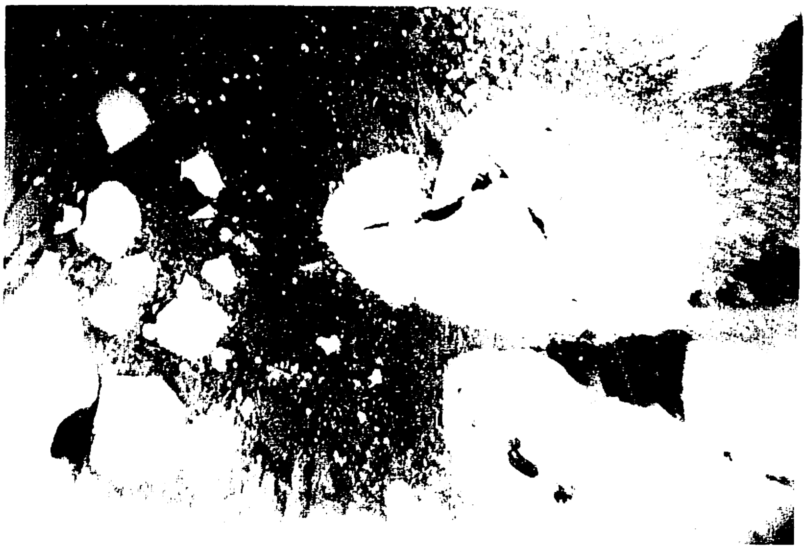


FIGURE 49. Slag C. 500 X

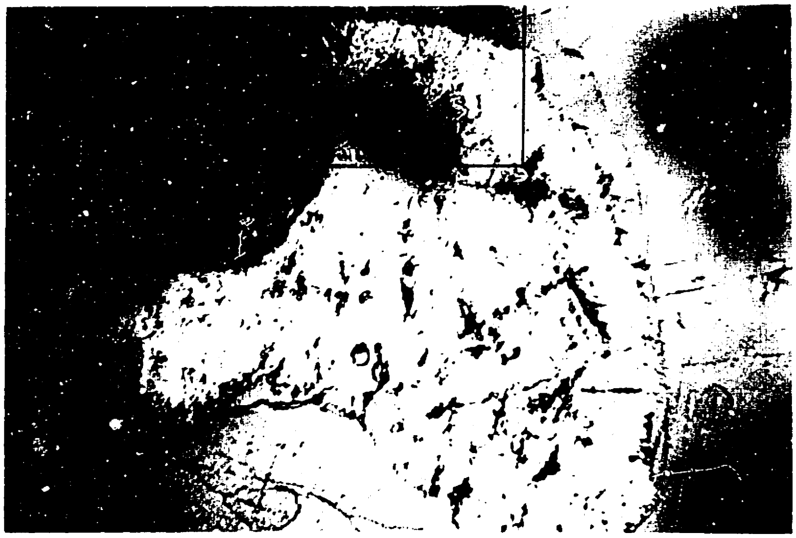


FIGURE 50. Slag D. 50 X

FIGURE 51. Slag D. 100 X

FIGURE 52. Slag D. 100 X

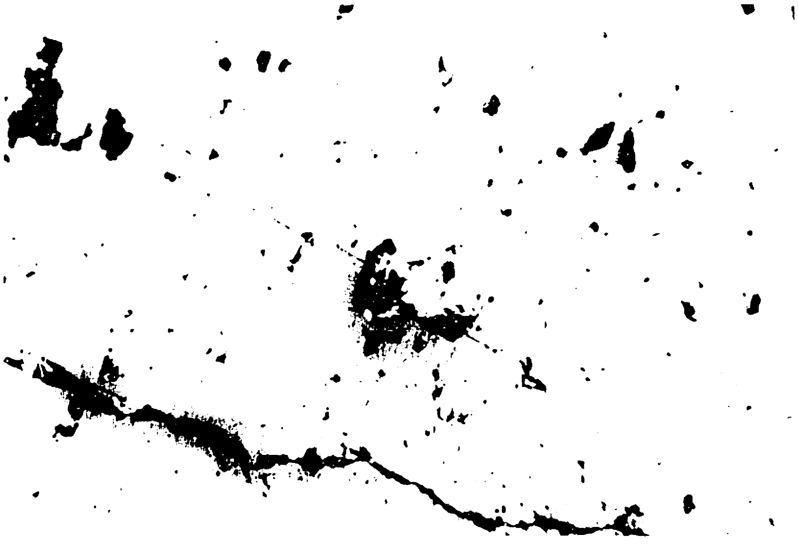


FIGURE 53. Slag D. 100 X

FIGURE 54. Slag D. 100 X

FIGURE 55. Slag D. 500 X

FIGURE 56. Slag D. 100 X

FIGURE 57. Slag D. 500 X

FIGURE 58. Slag D. 100 X

FIGURE 59. Slag D. 100 X

FIGURE 60. Slag E. 100 X

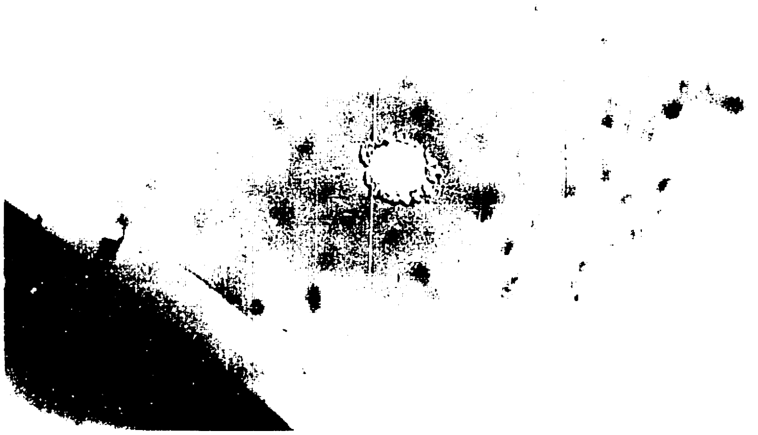


FIGURE 61. Slag E. 500 X

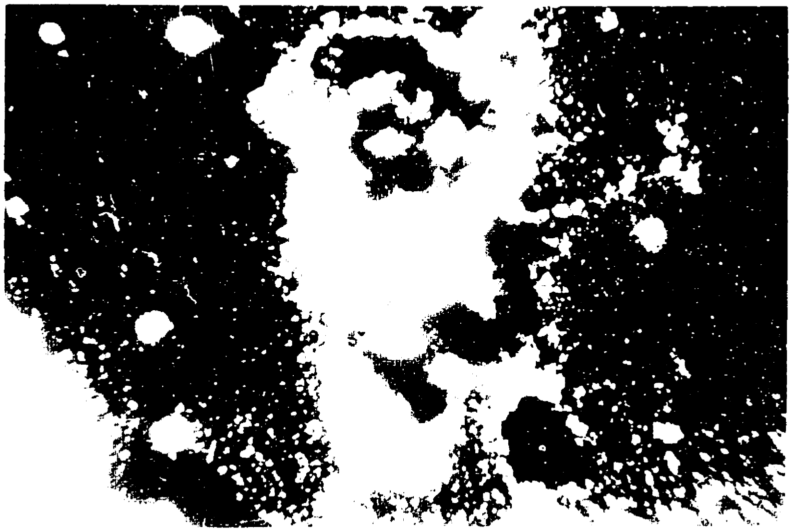


FIGURE 62. Slag C. 100 X

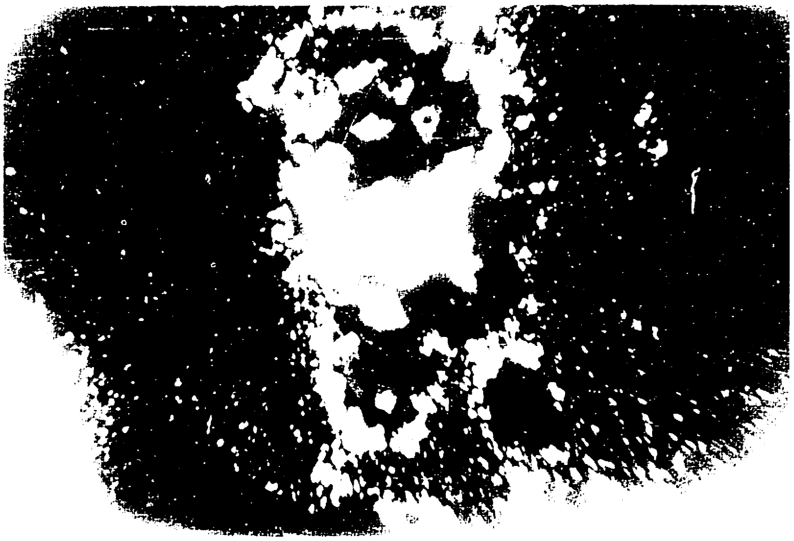


FIGURE 63. Slag C. 100 X

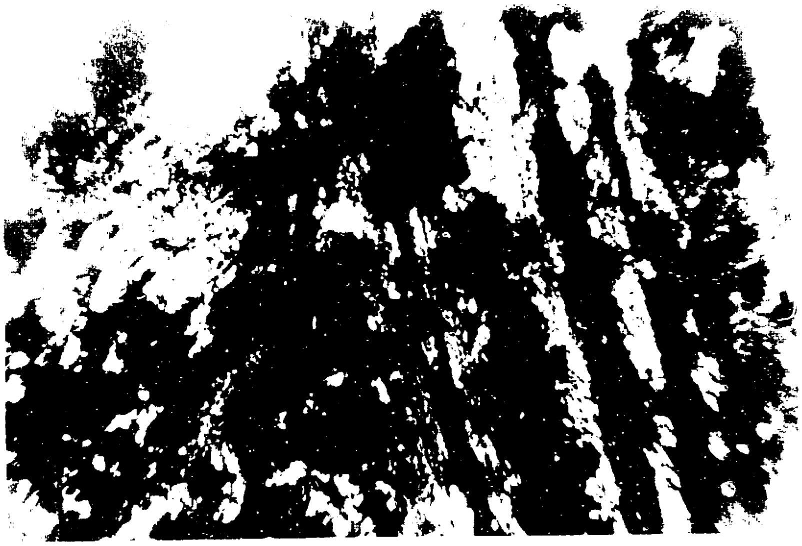


FIGURE 64. Slag D. 100 X

FIGURE 65. Slag D. 100 X

FIGURE 66. Slag C. 100 X

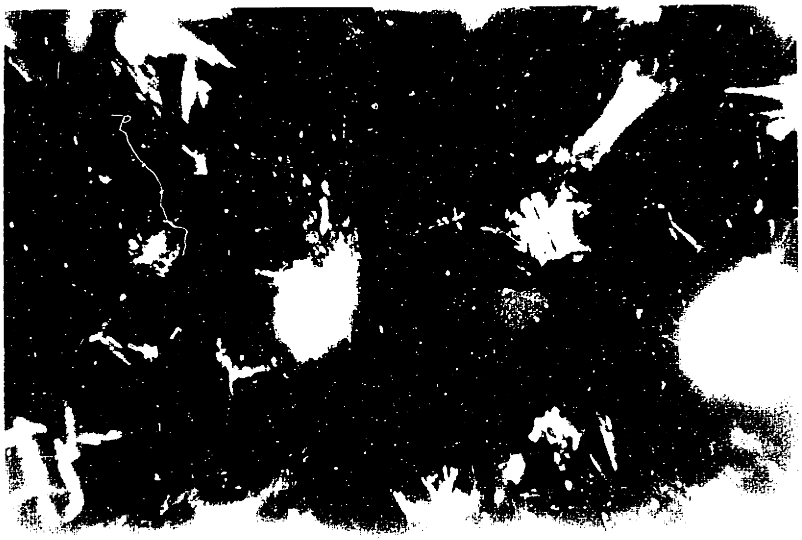


FIGURE 67. Slag C. 100 X

FIGURE 68. Slag C. 100 X

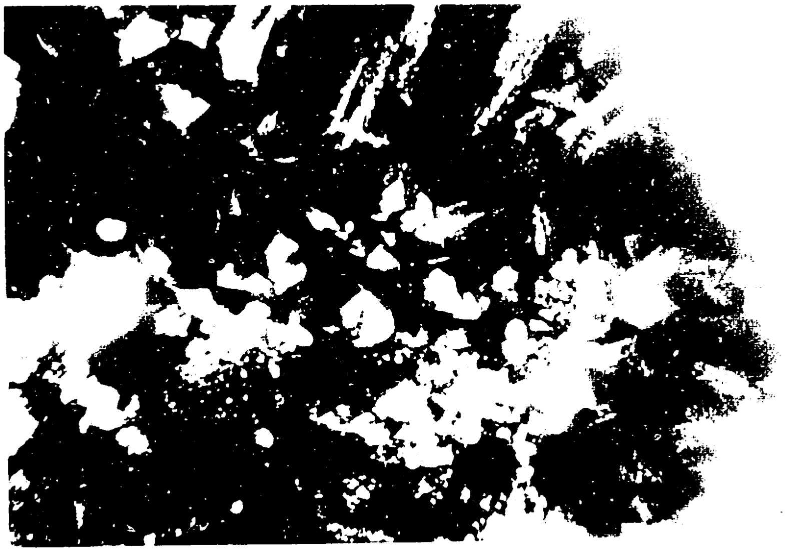


FIGURE 69. Slag C. 100 X

V. PHYSICAL FACTORS INFLUENCING COPPER LOSS

Examination of polished sections of different slags revealed the presence of small sulfide grains varying in composition from the original matte to $Cu_2S + xCu$. The presence of these grains is probably due to insufficient settling and currents which are caused by temperature differences as well as by the evolution of gases in the molten matte or slag. Copper lost this way is called physical or mechanical loss. The factors controlling the loss are as follows.

A. Velocity of the Sinking Particles

The velocity with which these sulfide grains sink and consequently join the matte before the slag is tapped is one of the factors of fundamental importance. The mean sinking velocity is given by Stokes' formula which is applicable to particles from 0.2 micron to 1000 micron.

$$V_m = \frac{2}{9}\,\frac{g\,(\Delta_m - \Delta_s)\,r^2}{\mu} \qquad (1)$$

where μ is the viscosity of slag, r is the radius of grain, Δ_m is the density of matte, Δ_s is the density of slag, g is the acceleration of gravity and V_m is the mean velocity of the particle.

Viscosity

As is seen from Stokes' formula, the sinking velocity is inversely proportional to the viscosity of the slag.

As far as the writer knows, there are no published data on the viscosity of reverberatory slags*. However, a simple and less expensive method for measuring viscosity is developed here. In principle the method is similar to those of Saybolt (or Redwood and Engler); that is, the time required to empty a certain volume of a liquid through a capillary is a measure of viscosity. With the exception of Petroskas' spoon viscosimeter(87), the writer found no reference to the use of this principle for slags. Viscosity of slags depends on (1) composition and (2) temperature. The viscosity generally decreases with increasing temperature. With the apparatus, which will be described shortly, the viscosity of five commercial slags were measured at different temperatures. The results are given in Tables X and XI.

---

* K. Endell, R. Fehling and R. Kley(88) gave 70 poises as the absolute viscosity of a copper slag having the following chemical composition:

SiO_2	47.34 percent
Al_2O_3	18.80
Fe_2O_3	3.02
CaO	18.63
MgO	7.57
Alk.	4.57

As it is seen from this composition, the slag measured for the viscosity is far off from the average composition of reverberatory slags.

TABLE X

Viscosities of Slags

Slag	Time of Flow* (in seconds)	Temperature (in °C)	Viscosity (in poises)
A-1	11.0	1470	3.65
B-1	11.9	1400	4.02
C-1	17.3	1400	6.06
D-1	15.5	1480	5.81
E	13.9	1420	4.98

---

* For 55 c.c. of slag

TABLE XI

Viscosities of Slags

Slag	Time of Flow* (in seconds)	Temperature (in °C)	Viscosity (in poises)
A-1	15.0	1300	5.91
B-1	14.4	1300	5.37
C-1	20.0	1300	7.25
D-1	18.7	1300	7.42
E	19.9	1300	7.95

---

* for 50 c.c. of slag

(a) Apparatus and method. Several graphite crucibles, having the dimensions as in Figure 70, were made from graphite electrodes in the Machine Shop of the Department of Metallurgy. A 0.185-inch hole (No. 13 drill) was drilled through the bottom of each crucible and the holes were closed with a tapered 1/2-inch graphite rod. Then the crucible was filled with the slag to be measured for viscosity and placed in a globar electric furnace, Figure 71, having a hole at the center of its bottom. After 15 or 20 minutes the graphite rod was pulled out and the time of flow was measured with a chronometer. The temperature of the slag was recorded at the time of pull by using a platinum-platinum rhodium thermocouple.

(b) Calibration. A graphite crucible with the standard hole at the bottom was later calibrated with pine and linseed oils whose viscosities were determined accurately with a modified MacMicholson viscosimeter in the Ceramics Laboratories of the Department of Metallurgy. The calculations are shown in Appendix 4.

(c) Limitations of the method. No. 1 (3-inch outside diameter) commercial graphite crucibles were used but found unsatisfactory because the binding materials of the crucible seemed to react slightly on the slag. On the other hand, crucibles made from graphite electrodes were not wetted by the slag. This decreased any error due to surface tension in the measurements. Although a smaller sized hole at the bottom of the crucible is desirable for accurate measurement of viscosity, it causes trouble when the slag flows out. The 0.185-inch hole was found satisfactory and practical in this case. Under

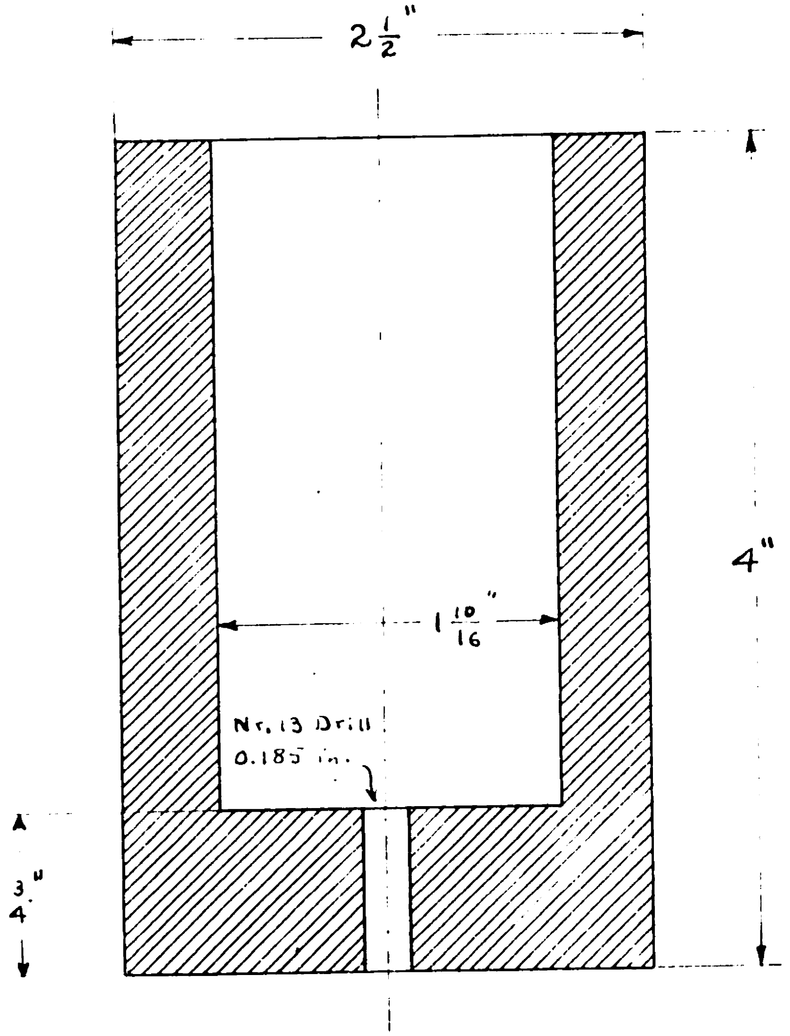
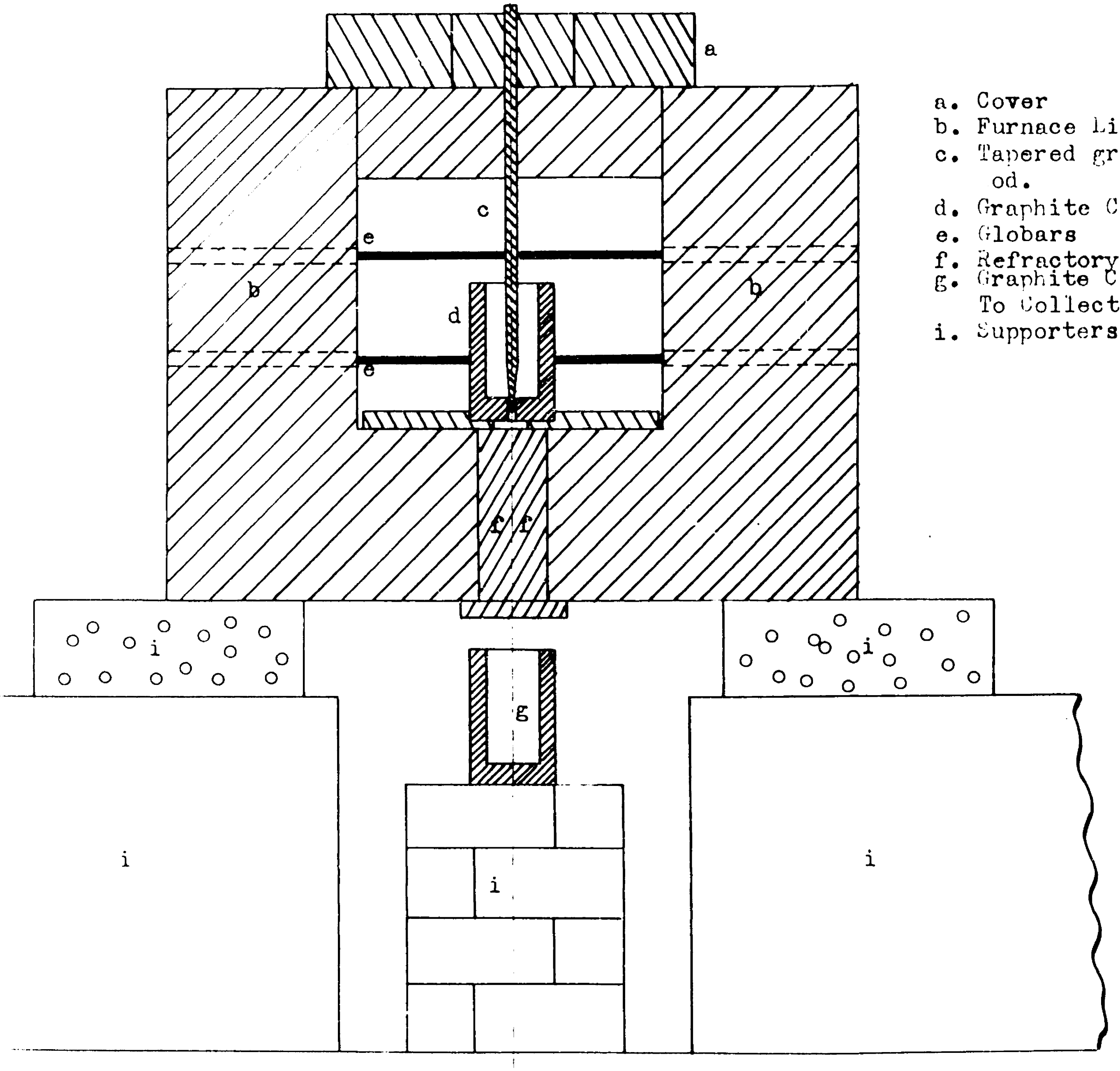


Fig. 70
The Shape and Dimensions of Graphite Crucibles
for Viscosity Measurements



a. Cover
b. Furnace Lining
c. Tapered graphite
 od.
d. Graphite Crucible
e. Globars
f. Refractory Plug
g. Graphite Crucible
 To Collect Slag
i. Supporters

Fig. 71
Globar Electric Furnace Which is used for Viscocity Tests

the above conditions results of viscosity measurement were reproducible within 12 percent. Viscosities obtained in this way are probably not the absolute viscosities but relative ones. However, under the circumstances, it is considered satisfactory since the object was to find the viscosity range of the reverberatory slags rather than the absolute viscosity of a particular slag.

Radius of Grain

From formula (1) the sinking velocity is proportional to the square of the radius of particles. Thus, large particles will sink with a high velocity while small ones will have a very slight sinking velocity. Consequently all factors affecting coagulation will also help settling of small particles. These factors are as follows.

(a) Surface tension. The greater the surface tension of sulfide grains, the faster their coagulation under fixed conditions. No data are available on this at present.

(b) Viscosity of grains. The lower the viscosity of the sulfide grains, the greater their coagulation. No data are available on the viscosity of sulfides of copper and iron. Also the variation in composition of the sulfides complicates the problem. In general, sulfides have a lower viscosity than silicates.

(c) Melting points of grains. As a rule, melting point and viscosity proceed simultaneously. Sulfide compounds having a high melting point will be found in a very finely dispersed state. On the other hand, sulfide globules having a low melting point will coagulate easily. Certain compounds may be added to slag, such as pyrite (see Chapter VIII) to lower the melting point and consequently ease the coagulation. Melting points of several copper-iron sulfide compounds are given in Table XII.

(d) Temperature. The effect of temperature on the viscosity of the slag has already been mentioned. Of course, the same thing applies to the sulfides. The effect of temperature on the viscosity of the sulfides is more pronounced than on the viscosity of the silicates; that is, for the same temperature difference the change in the viscosity of sulfides is greater.

(e) Gases. The evolution of gases from the magnetite-ferrous sulfide reaction (see Chapter VI) and from other sources causes more intimate contact between dispersed sulfide particles. This in return facilitates the coagulation of the grains. Any stirring of the bath should be followed by a period of rest so that the coagulated particles will have time to sink. The formation of gases may also have flotative action on the sulfides either in the slag layer or the matte layer.

The amount of fines in the flotation concentrates is considerable. Table XIII shows the screen analysis of the flotation concentrates, which are used for raw smelting, at Plant (I). Another source of fines in the furnace is the dust that settles on the surface of the slag.

Density of Matte and Slag

According to Stokes' formula, the sinking velocity is directly proportional to the difference in density between the sulfide particles and the slag. The densities of commercial mattes and slags are given in Table II, columns 3 and 4. Table XIV shows differences in density between some sulfide compounds and slag.

TABLE XII

Melting Points of Some Copper-Iron-Sulfur Minerals

Name	Formula	Melting Point (in °C)
Copper	Cu	1083
Iron	Fe	1535
Pyrrhotite	FeS	1163
Pyrite	FeS_2	1171
Chalcocite	Cu_2S	1128
Covellite	CuS	103*
Chalcopyrite	$CuFeS_2$	
Cubanite	$CuFe_2S_3$	
Bornite	Cu_5FeS_4	
Cuprite	Cu_2O	1235
Tenorite	CuO	1026**
Magnetite	Fe_3O_4	1538**
Mattes:	$XCu_2S + YFeS$	
10% Cu_2S		1135
20% Cu_2S		1075
30-50% Cu_2S		1000
60% Cu_2S		1060
70% Cu_2S		1075
80% Cu_2S		1095
90% Cu_2S		1020

---

* Transition point
** Decomposes

TABLE XIII

Size Distribution of Flotation Concentrates

	Size Mesh	Size Micron	Percent Weight Material	Accumulative Percent Weight
On	100	147	0.74	0.74
On	150	104	2.10	2.84
On	200	74	5.28	8.12
On	270	52	30.74	38.86
On	400	37	14.13	52.99
Thru	400	37	47.01	100.00
		Infrazier Products		
On	400	37	2.12	55.11
On	570	26	12.92	68.03
On	800	18.5	8.28	76.31
On	1120	13	5.90	82.21
On	1600	9	5.89	88.10
Thru	1600	9	11.90	100.00

TABLE XIV

The Differences in Specific Gravities Of Some Minerals and Reverberatory Slags

Compound	Δ_m	$\Delta_m - \Delta_s$*
Chalcocite	5.6	2.1
Covellite	4.6	1.1
Pyrrhotite	4.6	1.1
Pyrite	4.06	0.56
Chalcopyrite	4.2	0.70
Cubanite		
Bornite	5.15	1.65
Copper	8.92	5.42
Iron	7.86	4.36
Magnetite	5.07	1.57
Commercial mattes	4.40-5.25	0.9-1.75

---

* Average value of Δ_s is about 3.5 (see Table 2, Column 2)

Acceleration

Again, according to Stokes' formula, the sinking velocity is directly proportional to the acceleration of gravity. Although it varies in different parts of the world, its effect may be neglected. Acceleration may be increased by applying an external force, such as centrifugal force. This latter principle may be used to recover the copper in slag. However, the application of an external force while the slag is in the furnace seems quite impracticable.

Mean Sinking Velocity

Mean sinking velocity is equal to the distance travelled by the particles, or the thickness of the slag layer, divided by time.

(a) Thickness of the slag layer. The average thickness of the slag layer at different plants is given in Table II, columns 5 and 6.

(b) Time. The longer the time, the greater the amount of sunken particles. "In modern reverberatory practice, the relation between the rate of charging and weight of material in the furnace is such that an average particle of charge will go through the furnace in from 9 to 15 hours, and would pass beyond the smelting zone within an hour or so."(57)

B. Currents in the Slag Layer

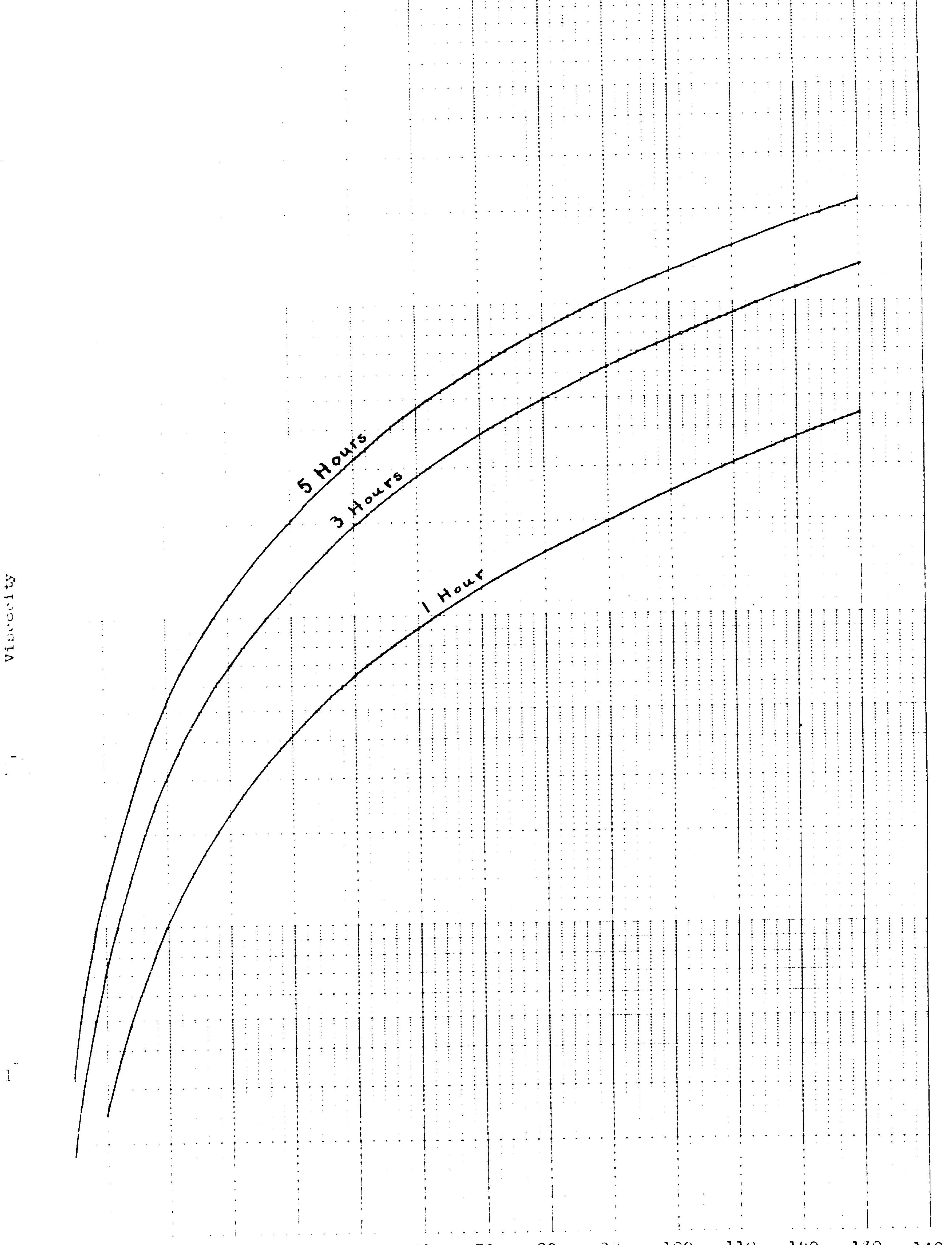
The temperature of the slag on the surface of the bath and at the slag-matte interface is quite different. In general, the former is 100° - 200° C higher than the latter. Also, the temperature of the slag varies along the length of the reverberatory furnace, the firing end being 100° - 400° C higher. These variations in temperature and evolution of gases, which have already been mentioned, cause certain currents influencing coagulation of the particles in the slag layer. In fact, the presence of these currents makes impossible the application of the formula for the rate of coagulation caused only by the Brownian movement.

C. Shape of the Particles

In Stokes' formula, the shape of the particles is assumed to be spherical. Of course, any deviation from this assumption will influence the sinking velocity. For instance, elongated particles offer more frictional resistance.

D. Settling Curves

Figure 72 shows the relation between particle size and viscosity for different times of settling. These curves were plotted by assuming (1) the average thickness of the slag layer is 12 inches, (2) the difference in density of sulfide particle and slag is one and (3) g is equal to 980 centimeters per second per second. The examination of Figure 72 will show that particles having a size less than 50 microns will not settle even in 5 hours under average conditions existing in the reverberatory furnace.


Viscosity
5 Hours
3 Hours
1 Hour
80
90
100
110
120
130
140

VI. CHEMICAL CONSIDERATIONS

There are several chemical reactions which take place in the reverberatory furnace which effect the copper loss both qualitatively (form of copper in slag) and quantitatively. In general, there are two types of reactions: (1) Formation of matte and slag by metathesis and (2) formation of SO_2 and the consequent elimination of part of the sulfur on the charge. It is the second type of reactions which will be discussed here.

A. Reaction between Magnetite and Ferrous Sulfide

The presence of magnetite in copper reverberatory furnaces is a frequently mentioned cause of high copper losses in slag. The sources of this oxide of iron are:

(a) Concentrates, though a relatively unimportant one
(b) Roaster calcines
(c) Converter slag
(d) Furnace reactions

These high copper losses occur in several ways:

(a) Magnetite favors the formation and retention of copper ferrite in the slags
(b) Crystals of solid magnetite make the slag less fluid and entrap the globules of matte

(c) These crystals prevent the separation of matte from slag by creating a false bottom at the slag-matte interface

(d) Several reactions between magnetite and some of the constituents of slag and matte evolve gasses which agitate the bath violently and prevent the separation of matte from slag

(e) Magnetite crystallizes on the bottom of the furnace to such a level that the operation of the furnace is disrcontinued

From what has been said above, it seems logical to conclude that any magnetite present in the furnace should be reduced and slagged. This section will deal with the reduction of magnetite by ferrous sulfide under the conditions which exist in the furnace, from a thermodynamic point of view.

Wartman and Oldright(57) studied the reactions between pure magnetite and pure ferrous sulfide. The products of these reactions were FeO, SO_2, S_2 and SO_3*. In their conclusion, they represented the reactions between magnetite and ferrous sulfide by the following chemical equations:

$$FeS + 3Fe_3O_4 = 10FeO + SO_2 \quad (a)$$

$$FeS + Fe_3O_4 = 4FeO + \tfrac{1}{2}S_2 \quad (b)$$

$$FeS + 4Fe_3O_4 = 13FeO + SO_3 \quad (c)$$

---

* The writer also confirmed the evolution of SO_2 and S_2 from fusion of mattes which contained a considerable amount of magnetite.

Data

The following equations are taken from K. K. Kelley(89)

$$2FeS\ (l) + SO_2\ (g) = 2FeO\ (l) + 3/2\ S_2\ (g) \qquad (1)$$

$$\Delta F^0 = 38{,}340 - 0.51\ T \log T + 0.04 \times 10^{-3} T^2 - 1.022 \times 10^5 T^{-1} - 11.27\ T$$

$$3FeS\ (l) + 2SO_2\ (g) = Fe_3O_4\ (s) + 5/2\ S_2\ (g) \qquad (2)$$

$$\Delta F^0 = 7{,}530 + 23.61\ T \log T - 9.10 \times 10^{-3} T^2 + 2.852 \times 10^5 T^{-1} - 52.58\ T$$

$$S_2\ (g) + 2O_2\ (g) = 2SO_2\ (g) \qquad (3)$$

$$\Delta F^0 = -\ 172{,}630 + 3.43T \log T - 0.712 \times 10^{-3} T^2 + 0.168 \times 10^5 T^{-1} + 24.30\ T$$

$$2SO_2\ (g) + O_2\ (g) = 2SO_3\ (g) \qquad (4)$$

$$\Delta F^0 = -\ 43{,}200 + 4.61\ T \log T + 26.88\ T$$

Equilibrium Constants of Reactions (a), (b) and (c)

The standard free energy equations of reactions (a), (b) and (c) are found in the following manner:

Reaction (a) - Reaction (1) and reaction (2) is multiplied by 5 , and -3 , respectively, and then are added.

$$\left.\begin{array}{l} 2FeS\ (l) + SO_2\ (g) = 2FeO\ (l) + 3/2\ S_2\ (g) \\ \Delta F^\circ = 38{,}340 - 0.51\ T \log T + 0.04 \times 10^{-3}\ T^2 - 1.022 \times 10^5 T^{-1} - 11.27T \end{array}\right) \times 5$$

$$\left.\begin{array}{l} 3FeS\ (l) + 2SO_2\ (g) = Fe_3O_4\ (s) + 5/2\ S_2\ (g) \\ \Delta F^\circ = 7{,}530 + 23.61T \log T - 9.10 \times 10^{-3} T^2 + 2.852 \times 10^5 T^{-1} - 52.58T \end{array}\right) \times -3$$

Sum $FeS\ (l) + 3Fe_3O_4\ (s) = 10FeO\ (l) + SO_2\ (g)$

$$\Delta F^\circ = 169{,}110 - 73.38T \log T + 27.5 \times 10^{-3} T^2 - 13.666 \times 10^5 T^{-1} + 101.39T$$

Reaction (b) - Reaction (a) and reaction (2) are multiplied by 2/5 , and 1/5 , respectively, and then are added.

$$\left.\begin{array}{l} FeS\ (l) + 3Fe_3O_4\ (s) = 10FeO\ (l) + SO_2\ (g) \\ \Delta F^\circ = 169{,}110 - 73.38T \log T + 27.5 \times 10^{-3}T^2 - 13.666 \times 10^5T^{-1} + 101.39T \end{array}\right) \times 2/5$$

$$\left.\begin{array}{l} 5FeS\ (l) + 2SO_2\ (g) = Fe_3O_4\ (s) + 5/2\ S_2\ (g) \\ \Delta F^\circ = 7{,}530 + 23.61T \log T - 9.10 \times 10^{-3}T^2 + 2.852 \times 10^5T^{-1} - 52.58T \end{array}\right\} \times 1/5$$

Sum $FeS\ (l) + Fe_3O_4\ (s) = 5FeO\ (l) + \frac{1}{2}S_2\ (g)$

$$\Delta F^\circ = 69{,}150 - 24.63T \log T + 9.18 \times 10^{-3}T^2 - 4.896 \times 10^5T^{-1} + 30.04T$$

Reaction (c) - Reactions (1), (2), (3) and (4) are multiplied by 13/2 , –4 , –1/4 , and 1/2 respectively, and then are added.

$$\left.\begin{array}{l} 2FeS\ (l) + SO_2\ (g) = 2FeO\ (l) + 3/2\ S_2\ (g) \\ \Delta F^\circ = 38{,}340 - 0.51T \log T + 0.04 \times 10^{-3}T^2 - 1.022 \times 10^5T^{-1} - 11.27T \end{array}\right) \times 13/2$$

$$\left.\begin{array}{l} 5FeS\ (l) + 2SO_2\ (g) = Fe_3O_4\ (s) + 5/2\ S_2\ (g) \\ \Delta F^\circ = 7{,}530 + 23.61T \log T - 9.10 \times 10^{-3}T^2 + 2.852 \times 10^5T^{-1} - 52.58T \end{array}\right) \times -4$$

$$\left.\begin{array}{l} S_2\ (g) + 2O_2\ (g) = 2SO_2\ (g) \\ \Delta F^\circ = -172{,}630 + 3.43T \log T - 0.712 \times 10^{-3}T^2 + 0.168 \times 10^5T^{-1} + 24.30T \end{array}\right) \times -\frac{1}{4}$$

$$\left.\begin{array}{l} 2SO_2\ (g) + O_2 = 2SO_3\ (g) \\ \Delta F^\circ = -43{,}700 + 4.61T \log T + 26.88T \end{array}\right) \times \frac{1}{2}$$

Sum $4Fe_3O_4\ (s) + FeS\ (l) = SO_3\ (g) + 13FeO\ (l)$

$$\Delta F^\circ = 240{,}647 - 96.307T \log T + 36.838 \times 10^{-3}T^2 - 18.093 \times 10^5T^{-1} + 146.694T$$

The standard free energies of reactions (a), (b) and (c) at 1100°, 1200°, 1300°, 1400° and 1500° C are calculated and listed in Table XV.

TABLE XV

ΔF° of Reactions (a), (b) and (c)

Temperature °C	Reaction (a)	Reaction (b)	Reaction (c)
1100	43,059	21,237	95,276
1200	34,756	18,045	85,982
1300	26,787	14,956	77,111
1400	19,162	11,981	68,701
1500	11,886	9,125	60,777

From Table XV and the equation

$$\Delta F^\circ = -\,R\ T\ \ln K = -\,4.575\ T\ \log K$$

the equilibrium constants of reactions (a), (b) and (c) are calculated and tabulated in Table XVI.

TABLE XVI

K of Reactions (a), (b) and (c)

Temperature °C	Reaction (a)	Reaction (b)	Reaction (c)
1100	1.395×10^{-7}	4.158×10^{-4}	6.780×10^{-16}
1200	6.960×10^{-6}	2.100×10^{-3}	1.703×10^{-13}
1300	1.894×10^{-4}	8.305×10^{-3}	1.924×10^{-11}
1400	3.135×10^{-3}	2.720×10^{-2}	1.057×10^{-9}
1500	3.425×10^{-2}	7.500×10^{-2}	3.212×10^{-8}

The Equilibrium Pressures of SO_2, S_2 and SO_3

The equilibrium constants of reactions (a), (b) and (c) are:

$$K_{(a)} = (\alpha_{FeO})^{10} \cdot p_{SO_2}/(\alpha_{Fe_3O_4})^{3} \cdot (\alpha_{FeS})$$

$$K_{(b)} = (\alpha_{FeO})^{4} \cdot p_{S_2}^{\frac{1}{2}} / (\alpha_{Fe_3O_4}) \cdot (\alpha_{FeS})$$

$$K_{(c)} = (\alpha_{FeO})^{13} \cdot p_{SO_3}/(\alpha_{FeO})^{4} \cdot (\alpha_{FeS})$$

where α refers to activity.

In order to facilitate the calculations of the equilibrium pressure, the following assumptions were made.

(a) The activity of magnetite is taken as unity.

(b) The activity of FeS is proportional to its molal concentration in matte. In copper reverberatory practice the molal concentration of FeS varies somewhere between 0.35 and 0.90.

(c) The activity of FeO is estimated to be between 0.20 and 0.40. It is indeed true that for a given slag composition the activity of FeO cannot be obtained without experiments. However, in the absence of experimental data it may be assumed somewhat smaller than its molal concentration.

Employing $\alpha_{FeS} = 0.35$ and $\alpha_{FeO} = 0.40$, the equilibrium pressures of SO_2, S_2 and SO_3 are calculated and listed in Table XVII.

Table XVIII shows the results of similar calculations employing $\alpha_{FeS} = 0.9$ and $\alpha_{FeO} = 0.20$.

The last columns in Tables XVII and XVIII represent the total of equilibrium pressures of the evolved gases. The pressure of SO_3 is omitted from these summations since it is very small in comparison with others. Table XIX shows the percent of S_2 in total at equilibrium.

TABLE XVII

Equilibrium Pressures of SO_2, S_2 and SO_3

When $\alpha_{FeS} = 0.35$ and $\alpha_{FeO} = 0.40$

Temp. °C	p_{SO_2}	p_{S_2}	p_{SO_3}	$p_{SO_2 + S_2}$
1100	4.739×10^{-4}	3.231×10^{-5}	3.599×10^{-11}	5.062×10^{-4}
1200	2.364×10^{-2}	8.242×10^{-4}	9.040×10^{-9}	2.446×10^{-2}
1300	6.434×10^{-1}	1.288×10^{-2}	1.021×10^{-6}	6.563×10^{-1}
1400	1.065×10	1.382×10^{-1}	5.611×10^{-5}	1.079×10
1500	1.163×10^{2}	1.051	1.705×10^{-3}	1.176×10^{2}

TABLE XVIII

Equilibrium Pressures of SO_2, S_2 and SO_3

When $\alpha_{FeS} = 0.9$ and $\alpha_{FeO} = 0.20$

Temp. °C	p_{SO_2}	p_{S_2}	p_{SO_3}	$p_{SO_2 + S_2}$
1100	1.226	5.470×10^{-2}	7.451×10^{-7}	1.281
1200	6.117×10	1.395	1.872×10^{-4}	6.257×10
1300	1.665×10^{3}	2.182×10	2.114×10^{-2}	1.687×10^{3}
1400	2.755×10^{4}	2.341×10^{2}	1.162	2.778×10^{4}
1500	3.010×10^{5}	1.780×10^{3}	3.530×10	3.028×10^{5}

TABLE XIX

$(p_{S_2}/p_{SO_2 + S_2}) \times 100$

Temperature °C	$\alpha_{FeO} = 0.40$ $\alpha_{FeS} = 0.35$	$\alpha_{FeO} = 0.20$ $\alpha_{FeS} = 0.90$
1100	6.38	4.27
1200	3.47	2.23
1300	1.96	1.29
1400	1.28	0.84
1500	0.89	0.59

No data showing the percentages of SO_2, S_2 and SO_3 in reverberatory furnace gases were available to compare the equilibrium pressures with actual values*.

Discussion

Magnetite will be reduced on the surface of the bath because the temperature is high enough and the combustion products will carry away the gaseous products of reactions (a), (b) and (c). At the bottom of the furnace the situation is different. In order that the reactions may proceed towards the right, the total pressure of the evolved gases must be equal to the atmospheric pressure plus the head produced by

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* Even tho percentages of some of these gases are known they still cannot be used directly because they may be the products of some other reactions in the furnace.

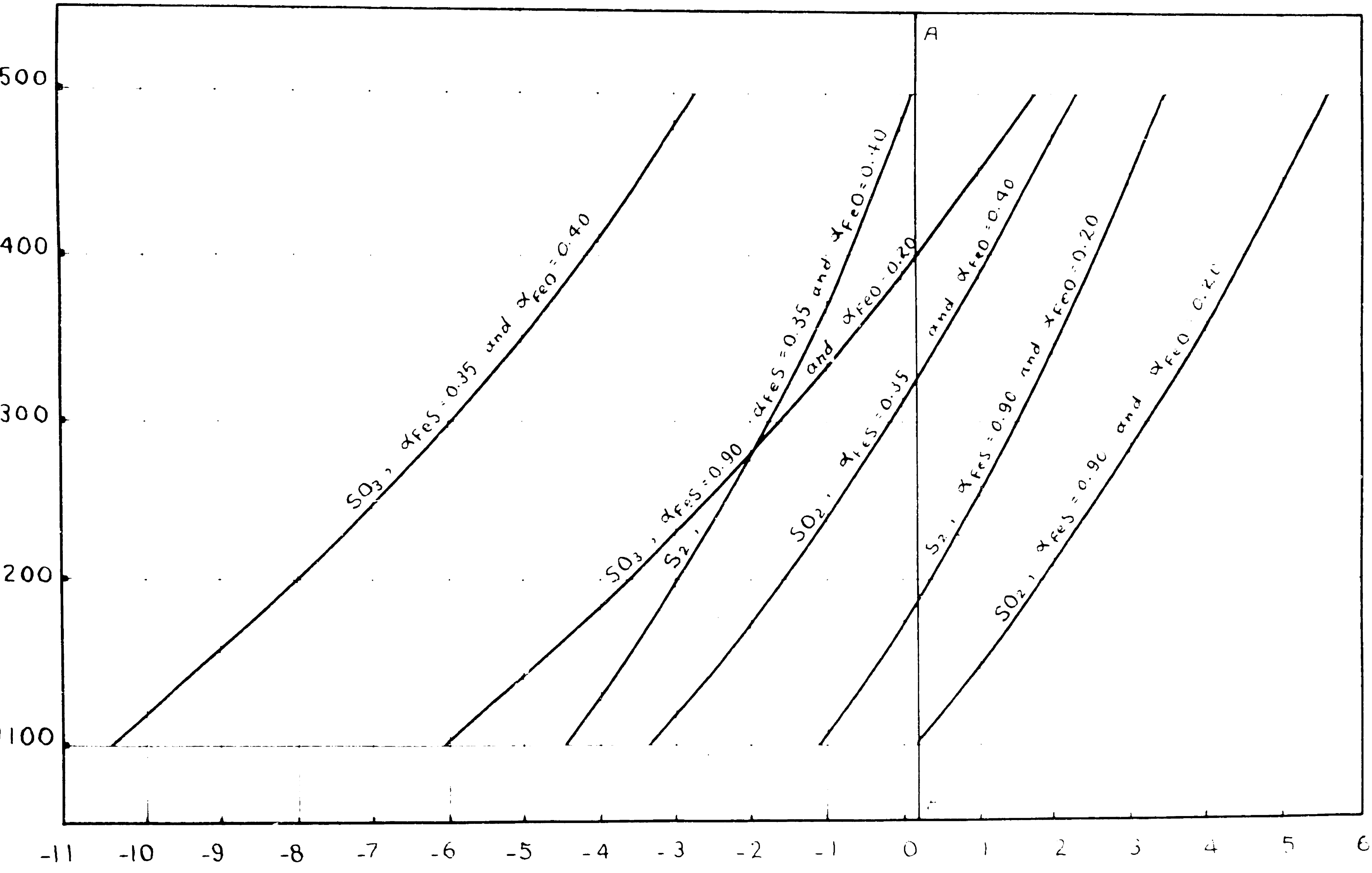
the overlaying layers of slag and matte. Under average conditions this pressure is about 100 centimeters of mercury (see Table 4,Col.13) and is represented by the vertical line AB in Figure 73 in which equilibrium pressures are plotted against temperature. Any value of the pressures falling to the right of the line AB indicates that magnetite at the bottom of the furnace will be reduced by ferrous sulfide. The intersections of pressure curves with the line AB give the minimum temperatures for the reduction at the bottom of the furnace. In Table XX these temperatures are listed under the given condition.

TABLE XX

Minimum Temperatures for the Evolution of SO_2, S_2 and SO_3 at the Bottom of the Furnace (in °C)

	$\alpha_{FeO} = 0.40$ $\alpha_{FeS} = 0.35$	$\alpha_{FeO} = 0.20$ $\alpha_{FeS} = 0.90$
SO_2	1325	1104
S_2	—	1197
SO_3	—	1400

During the operation of the reverberatory furnace the temperature of the bottom is hardly over 1200° C and not less than 1000° C. In this temperature range, to show the effect of α_{FeO} and α_{FeS}, Figure 74 is given. In constructing this figure it is assumed that the pressure of SO_2 is equal to 100 centimeters of mercury (or 1.317 atmospheres),


A
500
400
300
200
100
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
1
2
3
4
5
6
SO_3, α_{FeS} = 0.35 and α_{FeO} = 0.40
SO_3, α_{FeS} = 0.90 and α_{FeO} = 0.20
S_2, α_{FeS} = 0.35 and α_{FeO} = 0.40
SO_2, α_{FeS} = 0.35 and α_{FeO} = 0.40
S_2, α_{FeS} = 0.90 and α_{FeO} = 0.20
SO_2, α_{FeS} = 0.90 and α_{FeO} = 0.20

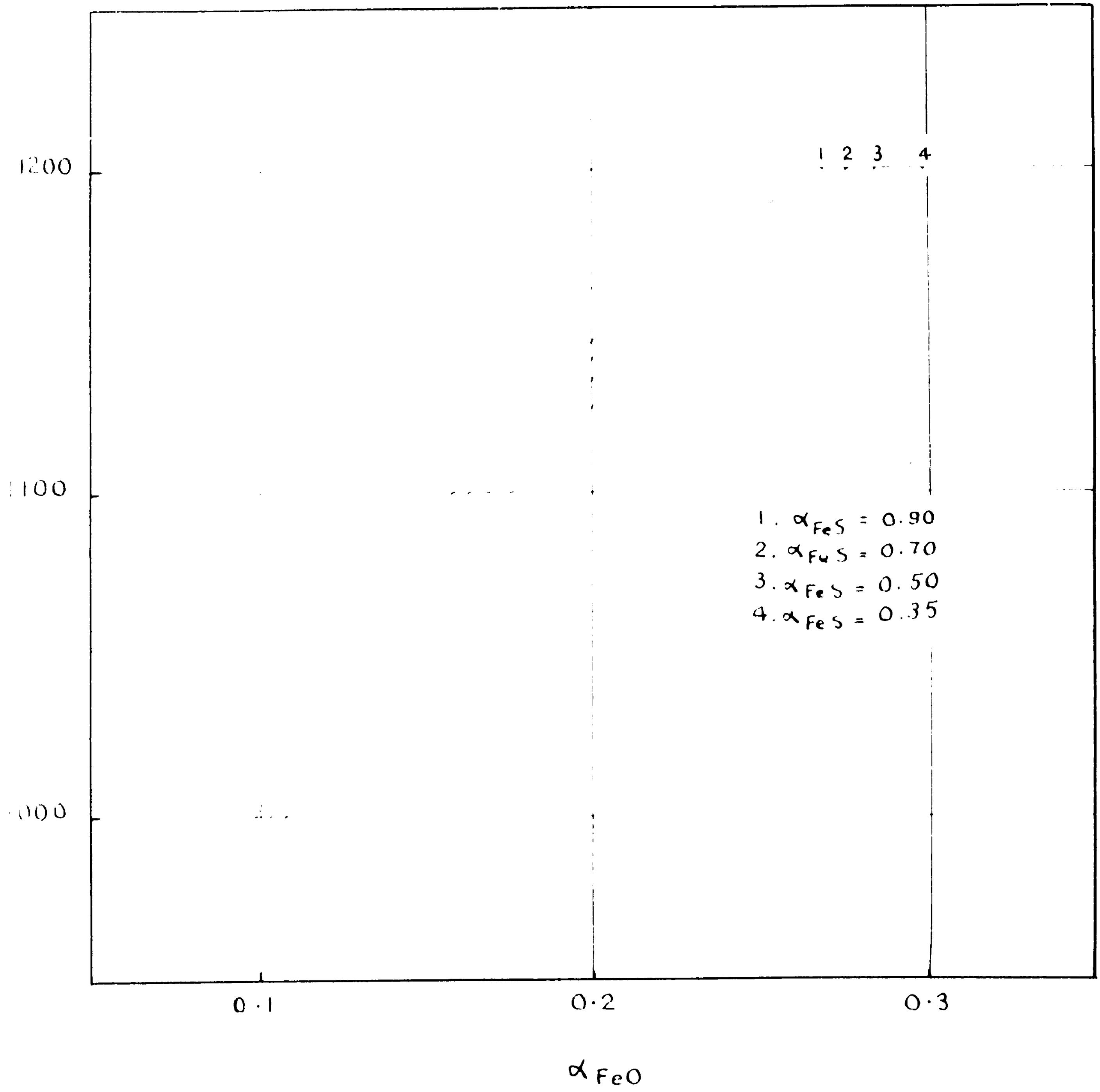


Fig. 74
Activity of FeO Against Temperature

i.e., the reaction (a) just meets the requirement in order to proceed to the right. Similar curves can be constructed for S_2 and $SO_2 + S_2$ but reference to Table XIX will show that the pressure of S_2 contributes very little to the total.

Figure 74 when supported by experimental facts has a practical value. For a given activity of FeO in the slag and a known matte composition the minimum temperature at which the reduction of magnetite by ferrous sulfide takes place can be obtained easily. Also for a given temperature and matte composition the activity of slag can be estimated.

In the foregoing sections nothing has been said about the rates of the reactions. Rate of reaction is a matter which can only be determined experimentally, but in this case some evidences indicate that the reactions reach equilibrium since it takes an average particle from 9 to 15 hours to pass through the furnace in modern reverberatory practice.

There are two other factors which should be mentioned here; namely, agitation of the bath and viscosity of the bath. When the bath is agitated by some means, the pressure requirement for the evolution of SO_2, S_2 and SO_3 at the bottom of the furnace will be eliminated and the case will be similar to that of the reduction of magnetite on the surface of the bath.

A viscous bath will retard the contact of magnetite with ferrous sulfide but the reduction will take place readily since the gaseous products of reactions are closer to the top. On the other hand, a fluid bath will accelerate the contact of magnetite with ferrous sulfide but may also cause the accumulation of magnetite on the bottom if the reaction rate is not great enough to take care of all of the magnetite. The optimum viscosity is a matter which can be determined by diffusion, discussion of which will be eliminated here.

It is true that the activity of FeO and FeS changes with temperature and composition, but in the calculations these changes are ignored under the given conditions.

The following conclusions may be drawn:

(1) Reaction (a) is the most important one in the reduction of magnetite.

(2) Magnetite is reduced by ferrous sulfide on the surface of the bath.

(3) The reduction of magnetite at the bottom of the furnace depends on:

    (a) Temperature; the higher the temperature the greater the reduction

    (b) Activity of FeO; the lower the activity of FeO the greater the reduction

    (c) Activity of FeS; the higher the activity of FeS the greater the reduction.

To remedy the accumulation of magnetite on the bottom of the furnace one or more of the following suggestions should be tried:

(1) Raise the temperature of the matte, probably by heating the bottom of the furnace by some means

(2) Agitate the bath

(3) Lower the activity of slag

To decrease the copper losses in slag due to the reduction of magnetite enough time should be allowed for settling after the complete elimination of magnetite.

B. Cu_2S, FeS , Metallic Iron and Metallic Copper

Both Cu_2S and FeS are not stable at high temperatures and they lose their sulfur with liberation of metallic copper and metallic iron, respectively. The thermodynamic properties of Cu_2S and FeS are given by K. K. Kelley(89).

$$2Cu_2S\ (l) = 4Cu\ (l) + S_2 \qquad (1)$$

$$\Delta F^\circ = 66{,}420 + 23.60T \log T - 0.44 \times 10^{-3}T^2 - 90.62T$$

and

$$2FeS\ (l) = 2Fe\ (l) + S_2 \qquad (2)$$

$$\Delta F^\circ = 80{,}280 + 18.28T \log T - 0.44 \times 10^{-3}T^2 - 86.30T$$

On the surface of the bath some metallic iron and metallic copper will be produced because the temperature is high enough and the products of combustion will carry away the sulfurous gases of reaction (1) and (2). In the matte layer, the liberation of metallic copper and metallic iron depends upon the pressure of sulfur vapor which must be equal to, or exceed, the atmospheric pressure plus the hydrostatic head produced by the overlaying matte and slag. Also, metallic copper, metallic iron, Cu_2S and FeS must maintain equilibrium according to the following reaction:

$$FeS\ (l) + 2Cu\ (l) = Cu_2S\ (l) + Fe\ (l) \qquad (3)$$

which is reported by several investigators(10,13,23,40,45, 46).

The standard free energy equation of reaction (3) may be obtained by subtracting the standard free energy equation of reaction (1) from that of reaction (2) and dividing the resulting equation by two. When this is done the following equation is obtained:

$$\Delta F^\circ = 6{,}930 - 2.66T \log T + 2.16T$$

From this equation the equilibrium constant of reaction (3) may be calculated by the well known formula:

$$\Delta F^\circ = - R\,T \ln K$$

where

$$K = \frac{\alpha_{Cu_2S} \cdot \alpha_{Fe}}{\alpha_{FeS} \cdot \alpha_{Cu^2}}$$

or in this case

$$K = \frac{(Cu_2S) \cdot (Fe)}{(FeS) \cdot (Cu)_2}$$

In order to find the metallic contents of the bath, the temperature and the concentrations of Cu_2S and FeS of the bath must be known.

Metallic copper (which sometimes called moss copper or capillary copper) is found in mattes, especially in those with higher Cu_2S content; metallic copper may be found in slag when the matte is entrapped mechanically. The presence of small amounts of metallic iron in both matte and slag is seldom. This may be seen from the equilibrium ratio since the concentration of metallic copper (a number less than one) appears as squared and consequently it is considerably higher than the concentration of metallic iron. For example, at 1200° C (K = 2.194) and $(Cu_2S)/(FeS) = 0.55$ (40 percent copper matte), the (Cu) is 1.62 percent when the (Fe) is 0.10 percent.

C. Ferrous Sulfide and Copper Oxide

Copper oxide may be present in the charge and also in the converter slag in small quantities. During smelting, it reacts with FeS producing FeO, which reports in the slag, and Cu_2S, which goes to the matte, according to the following reaction(89)

$$Cu_2O\ (l) + FeS\ (l) = FeO\ (l) + Cu_2S\ (l)$$

$$\Delta F^\circ = -\ 21{,}870 - 2.40T$$

The concentration of Cu_2O may be computed from the equilibrium constant

$$K = \frac{\alpha_{FeO} \cdot \alpha_{Cu_2S}}{\alpha_{Cu_2O} \cdot \alpha_{FeS}} \quad \text{or} \quad \frac{(FeO) \cdot (Cu_2S)}{(Cu_2S) \cdot (FeS)}$$

and from this

$$(Cu_2O) = \frac{(FeO)}{K} \times \frac{(Cu_2S)}{(FeS)}$$

The limits of all the factors which control the Cu_2O concentration are known: (FeO) varies from 0.20 to 0.40 (see Section A), $(Cu_2S)/(FeS)$ ratio varies from 0.137 to 2.23 and finally K from 1.013×10^4 at 1100° C to 2.100×10^3 at 1500° C. With the aid of these figures, the highest Cu_2O concentration is calculated and it is 4.25×10^{-4}. In other words, Cu_2O is present in very small concentrations which may be negligible if the above reaction assumes equilibrium.

VII. SOLUBILITY OF COPPER SULFIDE IN SLAG

The solubility of matte and of copper sulfide alone, about 0.15 - 0.20 percent in slag, is claimed by several investigators, but thus far no positive proof of this has been presented. The points supporting the belief in solubility were: (1) that the matte did not separate from the slag kept in the molten state even for a long time, (2) that no concentration of the valuable metals was possible by elutration after fine grinding and (3) that, in general, the percent of copper increases with increasing temperature.

It is not proper to speak of the solubility of matte in slag. For matte is a variable complex material containing at least two constituents, one of which is attacked by magnetite.

Whether or not the copper sulfide is soluble in slag is important when the mechanism of slag loss is considered. It is not known for certain whether the FeS carries the copper, as Cu_2S, into the slag, or whether Cu_2S by itself is retained in the slag.

The way to tell whether or not Cu_2S is dissolved in slag is to melt Cu_2S and copper-free synthetic slags together under various conditions (temperature, time, composition of slag), and examine the slag after the fusion.

A. Preparation of Materials

The preparation of cuprous sulfide and two copper-free synthetic slags was described in Chapter IV.

B. Experiments

Preliminary Experiments

One of the serious problems in this work was the choice of the crucible which could be used for the melting of Cu_2S and slag without reacting with either one of them. To investigate the behavior of different kinds of crucibles, several charges made up from 50 grams of Cu_2S and 50 grams of copper-free slag were fused in graphite, magnesia, clay, magnesia-lined clay and alumina-lined clay crucibles at 1100° - 1300° C. With the exception of the graphite crucible, all the other crucibles reacted with the slag and did not give a good separation of the slag from the Cu_2S bottom, and also absorbed considerable amounts of Cu_2S.

The Cu_2S bottom and the slag separated perfectly in graphite crucibles and there was no loss of weight in the charge but very small amounts of metallic iron globules were found in the slag. The presence of metallic iron was due to the reduction of FeO, or Fe_3O_4, in the slag by the graphite. The reduction of this small amount of iron was not found objectionable and it was decided to use graphite crucibles for the other experiments.

Experiments with Graphite Crucibles

Three series of experiments, which are tabulated in Table XXI, were carried out by fusing the charges made up from 50 grams of Cu_2S and 50 grams of copper-free slag No. 2 containing no magnetite, at 1200° and 1300° C for one and two hours. At the end of each fusion,

TABLE XXI

Results of Fusions with Graphite Crucibles

Series	Time in Hours	Temperature in Degrees C	Percent Copper	Remarks
A	1	1200	0.87	Both Cu_2S and slag are less 100 mesh, intimately mixed.
	2	1200	0.52	
	1	1300	0.52	
	2	1300	—	
B	1	1200	0.65	Slag is less than 100 mesh, and Cu_2S is 1/8 inch in size, intimately mixed.
	2	1200	0.32	
	1	1300	0.40	
	2	1300	0.22	
C	1	1200	0.48	Both Cu_2S and slag are 1/8 inch in size, not mixed intimately.
	2	1200	0.23	
	1	1300	0.12	
	2	1300	0.08	

crucibles were taken out from the furnace and chilled in the air. The Cu_2S bottom separated from the slag. A suitable piece of slag was set aside for the microscopic examination and the remaining part ground to 100 mesh. Finally, it was analyzed for copper.

The chemical analysis of copper in slag in small quantities with high silicon, iron and aluminum is quite troublesome. Sometimes the results on the same samples did not check. Then it was decided to send out some of the samples to be analyzed by other methods - sulfocyanide and spectroscopic estimate - in order to check the results. The procedure for the method used at M. I. T. is given in Appendix V. In Table XXI the correct figures are reported.

The microscopic examination showed that all the samples had a few small round, bluish-gray globules scattered haphazardly throughout the body of the slag. Figure 75 shows a typical structure.

From Table XXI it may be concluded that the higher the temperature and the longer the time, the smaller the amount of copper retained in the slag. This is contrary to the belief that the Cu_2S is soluble in slag. For with increasing temperature, solubility is expected to increase and not to decrease, which is the case here. Also, on the other hand, the influence of time and temperature and the microscopic examination indicate the mechanical suspension of Cu_2S. However, this is not a conclusive proof of insolubility of Cu_2S in slag, because there is always the possibility that part of the Cu_2S retained in the slag as soluble and part of it as mechanical suspension.

FIGURE 75. Slag from the Cu_2S and Copper-free Fusions (Original Magnification 100 X).

Experiments with Platinum Crucibles

With the above idea in mind, separation of the Cu_2S particles was tried by keeping the slag in a molten state for longer periods of time. For this purpose platinum crucibles were used rather than graphite ones to eliminate the stirring caused by CO which may come from the reduction of the FeO of the slag by the carbon. Three chilled synthetic slags containing varying amounts of copper and no magnetite were placed in platinum crucibles and fused at 1200° C for different periods of time. At the end of the fusions, crucibles were taken out and chilled in the air. The upper part of the slag was separated and analyzed for copper by the sulfo-cyanide method. Table XXII shows the original and final copper contents of the slag as well as the length of fusion time.

The results (last column of Table XXII) indicate that any Cu_2S retained in the slag is in mechanical suspension. The latter statement applies when Cu_2S is present alone in the slag. In commercial slags where FeS is also present, the Cu_2S is carried in the slag by FeS. For it is known that oxides of iron dissolve in FeS and consequently when the oxide component of this oxide-sulfide system links up with the silica of the slag, it drags FeS with it, and since FeS and Cu_2S are mutually soluble, the FeS also carries Cu_2S into the slag. This Cu_2S is not soluble in the body of the slag, but is in solution with FeS.

TABLE XXII

Results of Fusions with Platinum Crucibles

Original Copper Content	Time of Fusion in Hours	Final Copper Content
0.19	12	0.04
0.20	24	0.02
0.20	24	0.04
0.14	48	0.00
0.14	48	0.00

VIII. RECOVERY OF COPPER

In order to have some idea as to how much of the slagged copper can be recovered, several experiments, which will be presented here, were carried out.

A. Addition of FeS and CaS

When ferrous sulfide, or pyrite, is added to the molten copper slag, a bottom which contains part of the copper of the slag is obtained. The amount of copper in this bottom (low grade matte) depends on (1) amount of ferrous-sulfide, or pyrite, added, (2) temperature and (3) amount and form of copper in the slag. The passage of copper from the slag to the ferrous sulfide is believed to be due to the distribution effect between the slag and the sulfide phases, but it may also be due to the floculating effect of the added reagent, which allows the settlement of the particles by coagulation. The addition of calcium sulfide with ferrous sulfide, or pyrite, increases the amount of copper which reports in the bottom.

The recovery of slagged copper in this way has been investigated by the Anaconda Mining Company many years ago, but their results were not published. In this connection, the suggestion offered by E. J. Carlyle(44) is interesting. Mr. Carlyle thinks that "if a wall of refractory material were built across a reverberatory furnace near the skimming end, high enough to keep the main body of matte, but low enough to allow the slag to run over it, pyrite could be charged through the roof".

The experiments carried out here were aimed to study the factors effecting the recovery.

Materials Used

The commercial slag A-1 containing 0.70 percent copper, synthetic ferrous sulfide, whose preparation is described in a previous chapter, and chemically pure calcium sulfide were the materials used for the purpose.

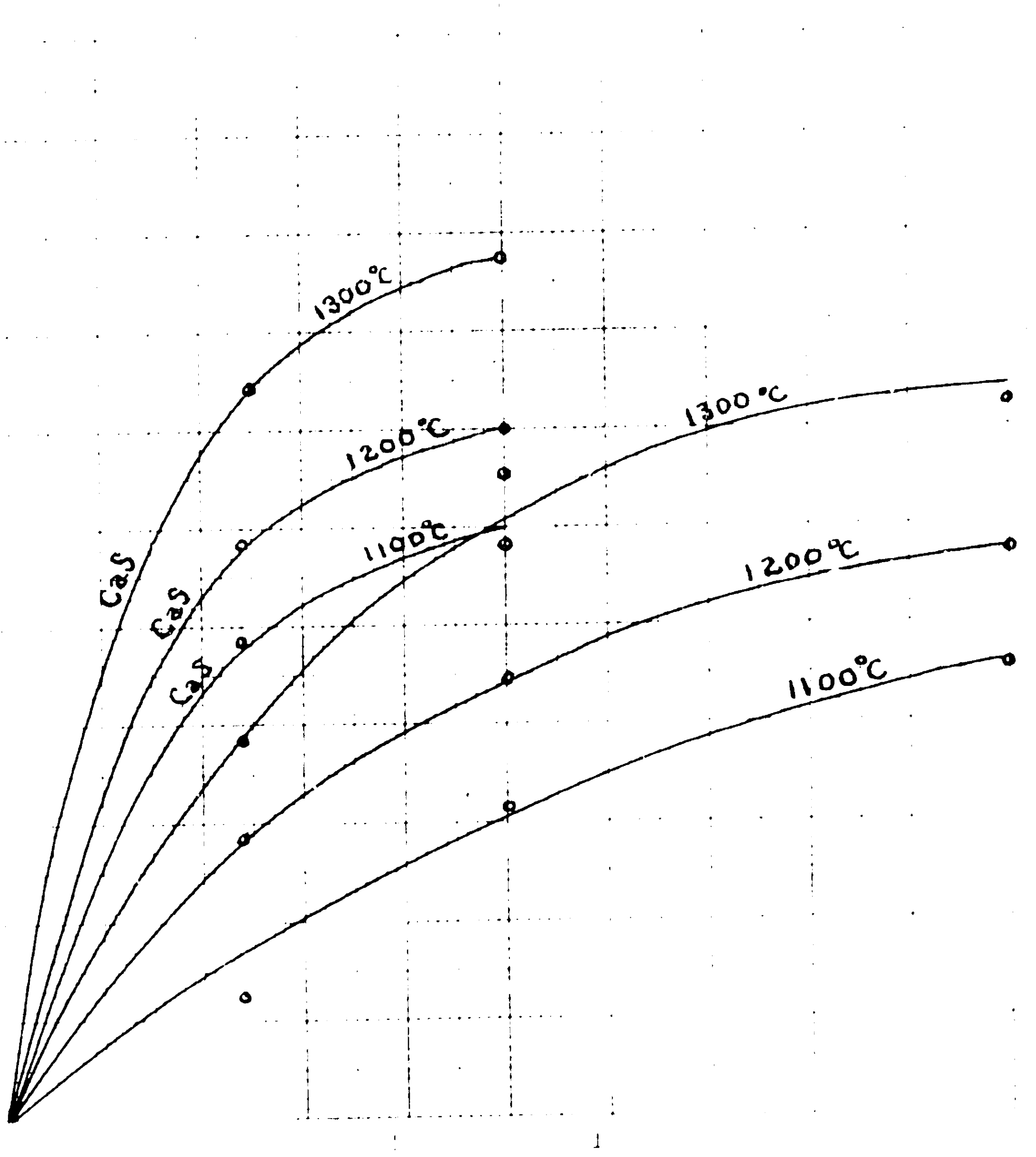
Fusions

Fifty-gram portions of slag A-1 were mixed with varying amounts of FeS and CaS and placed in graphite crucibles (Figure 21). They were fused at 1100°, 1200° and 1300° C for 1 hour in an electric globar furnace. At the end of the fusion, crucibles were taken out and chilled in air. After cooling, the crucibles were broken and a perfect separation of matte bottom from the slag was obtained. The mattes were ground to 100 mesh and analyzed for copper. The results are given in Table XXIII. Figure 76 shows several curves giving percentage recoveries at different temperatures with varying amounts of FeS and CaS. The highest recovery, 87.2 percent, was obtained at 1300° C with 12.5 percent FeS and 12.5 percent CaS. The highest concentration of copper, 14.5 percent, was obtained at 1300° C with 6 percent FeS and 6 percent CaS although with a lower recovery, 74.4 percent.

TABLE XXIII

Results of Fusions

Percent FeS	Percent CaS	Temperatures in ° C	Weight of Bottom in Grams	Percent Cu in Bottom	Percent Recovery
6	-	1100	1.3	3.50	12.8
6	-	1200	1.8	5.55	28.6
6	-	1300	2.0	6.75	38.6
12.5	-	1100	3.0	3.66	31.4
12.5	-	1200	2.9	5.35	44.2
12.5	-	1300	3.1	7.42	65.7
25	-	1100	3.9	4.10	45.7
25	-	1200	4.3	4.65	57.1
25	-	1300	4.4	5.80	72.9
6	6	1100	2.3	7.40	48.6
6	6	1200	3.0	6.83	58.6
6	6	1300	1.8	14.50	74.4
12.5	12.5	1100	5.7	3.60	58.6
12.5	12.5	1200	4.8	5.10	70.0
12.5	12.5	1300	5.1	5.98	87.2



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B. Flotation of Slag

It is a well known fact that sulfides of copper are readily separated from the gangue material by flotation. Since the microscopic examination revealed the presence of a considerable amount of sulfides in slag in mechanical suspension, several experiments were performed to recover the copper in slag by flotation. The commercial slag A-1 containing 0.70 percent copper was treated as follows: 500 grams of this slag were ground in a pebble mill with 200 grams of water. The discharge of the mill was placed in the cell of a Fagergren laboratory flotation machine. After the addition of proper reagents into the cell, the slag was floated. Table XXIV gives the time of grinding, the amounts of the reagents used and the assays of the concentrates. The percent recoveries are calculated and reported. A concentrate containing 7.2 percent copper with 43.2 percent recovery and another one containing 4.8 percent copper with 59.3 percent recovery were obtained. These concentrates may be further concentrated.

C. Magnetic Separation

The isodynamic magnetic separator in the Mineral Dressing Laboratory of the Department of Metallurgy was used to separate the copper-bearing particles from the rest of the commercial slags. Although the separator divided the slag into several portions, no concentrate containing more than one percent copper was obtained.

TABLE XXIV

Flotation of Slag

Sample No.	Weight of Concentrates	% Cu in Concentrates	Total Cu in Concentrates	Percent Recovery	Time of Grinding	$CuSO_4$ (5 % sol.) in cc.	K-Amyl Xanthate*	H_2SO_4 in cc.	Pine Oil
1.	29.3	3.9	1.142	32.6	1	1	0.5	-	2 drops
2. First Conc.	21.0	7.2	1.510	43.2	1	-	0.1	-	1 drop
2. Second Conc.	5.2	1.9	0.099	2.8	1	-	0.4	-	1 drop
2. Total				46.0					
3.	43.2	4.8	2.075	59.3	2	5	0.5	1	1 drop

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* One percent solution

IX. CONCLUSIONS

The following conclusions are made:

(1) From the examination of the reverberatory data it was shown that: (a) the copper content of the slag is increased with grade of matte, silicate degree, copper content of converter slag and temperature and is decreased with percent silica;

(b) the magnetite content of converter slag increases total copper lost per ton of matte; and

(c) the grade of matte decreases total copper lost per ton of copper in the matte.

(2) The form in which copper exists in the slag is mostly as sulfide varying in composition from the original composition of matte to Cu_2S and free copper. The final composition of these sulfides depends upon the extent of the reaction between magnetite and ferrous sulfide.

(3) Viscosity of copper reverberatory slags ranges from 3 to 8 poises around 1300° C. Copper-bearing particles 50 microns in size will not settle even in 5 hours in slags having the above viscosity. Imperfect settling is the most important cause of copper losses.

(4) Magnetite is a very troublesome compound and it should be reduced in the furnace by ferrous sulfide. This can be assured completely by

(a) raising the temperature of matte - maximum 1325° C.;

(b) lowering the activity of FeO in the slag; and

(c) stirring the bath.

(5) Cuprous sulfide is not directly soluble in the body of the slag but it is in solution in ferrous sulfide which dissolves the oxides of iron in the slag.

(6) The presence of copper oxide in slag is very unlikely because

(a) no oxide of copper was detected under the microscope, and

(b) any oxide of copper present in the furnace will react with ferrous sulfide and produce cuprous sulfide and iron oxide.

(7) Most of the copper lost in slag can be recovered by the addition of ferrous sulfide and calcium sulfide or by flotation; the recovery being 87.2 percent in the former and 59.3 percent in the latter case,

X. SUGGESTIONS FOR FURTHER WORK

The following suggestions are made for further work on the copper losses in reverberatory slags.

(1) More data on the reverberatory practice will make the results of statistical analysis more reliable and also will allow the subclassification of the data and consequently bring out more corrections some of which may have been observed in this work.

(2) The use of the electron microscope in identifying the small particles of copper-bearing material in the polished sections has great potentialities for the future.

(3) Viscosity is one of the most important properties of slag, and thus far no method or apparatus has been standardized for measuring it at the copper smelters. Some method, probably similar to the one described in Chapter V, can be developed to be used at the plant.

(4) In addition to the chemical reactions in Chapter VI, there are some others, especially when the matte contains Pb, Zn and Ni, which may be studied.

(5) As is already pointed out in Chapter V, sinking velocity is directly proportional to the acceleration of the earth. The sinking velocity may be increased as much as one thousand fold by applying a centrifugal force. Using this principle, the reverberatory slag, while it is still hot, can be poured into a revolving furnace which separates out the copper-bearing particles in a short time.

(6) The recovery of slagged copper by flotation may be economical on a plant scale because (a) when the slag coming out from the furnace is granulated in water, it can later be ground much more readily, and (b) large scale operation may bring down the cost. Further studies in flotation are required before the copper is recovered this way.

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APPENDIX I

QUESTIONNAIRE

[illegible] plant ______________________ Date ______________

1. Analysis of slag and matte (fill in the following table).

	Percent	
	Slag	Matte
Cu		
Fe		
FeO		
Fe_2O_3		
Fe_3O_4		
S		
SiO_2		
CaO		
Al_2O_3		
MgO		
Zn		
Pb		
Au*		
Ag*		

* In oz.per ton

2. The weight of slag per unit weight of matte, i.e.,

$$\frac{\text{weight of slag}}{\text{weight of matte}} = \text{\_\_\_\_\_\_\_\_\_\_} =$$

3. Specific gravity of (a) slag ____________

(b) matte ____________

4. Average thickness of (a) slag layer ________ inches

(b) matte layer ________ inches.

5. Fluidity of slag (check one)

Thin ___ heavy ___ Stony ___

thick ___ creamy ___ Glassy ___

6. Please give, if possible, the percentage of fines less than ten microns in the concentrates: ____________

____

7. Temperature of (a) slag when tapped ________ °F

(b) matte when tapped ________ °F

(c) furnace during tapping ________ °F

8. Converter slag charged to reverberatory,

(a) percent copper ______________

(b) percent magnetite ______________

(c) weight of converter slag charged to reverberabory per unit weight of matte ____

(d) Form of copper in converter slag ____

9. Rate of magnetite accumulation in the reverberatory ______________________________

10. Do you purposely run the copper high in slag for any specific reason? If so please state reason, if possible ____

____

____

11. Have you any idea about the form of copper in reverberatory slags? ______

____

____

APPENDIX II

A. Calculation of Statistical Quantities

In order to show the calculations of all the statistical quantities, the correlation between the grade of matte (X) and copper loss in pounds per ton of copper in matte (Y) is taken as an example. The values of X and Y are shown in Table (I). This table also gives the squares of X and Y, the product XY and the sums of each column.

The arithmetic mean of X and Y are calculated readily as follows:

$$M_x = \Sigma X/n = (805.54)/(23) = 35.023$$

$$M_y = \Sigma Y/n = (962.6)/(23) = 41.85$$

The standard deviation is designated generally by the Greek letter σ and computed as follows:

$$\sigma_x = \sqrt{(\Sigma X^2)/(n) - M_x^2} = \sqrt{(29994.18)/(23) - (35.023)^2} = 8.795$$

$$\sigma_y = \sqrt{(\Sigma Y^2)/(n) - M_y^2} = \sqrt{(55564.30)/(23) - (41.85)^2} = 25.770$$

Another value which is sometimes called "product moment" is calculated in the following manner:

$$\Sigma(xy) = \Sigma(XY) - n\,M_x\,M_y = 29400.272 - (23)(35.023)(41.85) = - 4312.868$$

Now, the coefficient of correlation, r_{xy}, may be computed as follows:

$$\Sigma\, r_{xy} = \Sigma(xy)/(n)(\sigma_x)(\sigma_y) = 4312.868/(23)(8.795)(25.770) = - 0.828$$

TABLE (I)

Plant No. from Table IV	X	Y	X^2	Y^2	XY
2	45.87	30.7	2106.06	942.49	1408.209
3	36.00	26.9	1296.00	723.61	968.400
4	45.00	19.5	2025.00	380.25	877.500
5	28.00	68.9	784.00	4747.21	1926.200
6	24.23	78.5	586.99	6162.25	1902.050
9	31.72	24.2	1006.49	585.64	767.624
10	43.77	36.3	1915.81	1317.69	1588.851
12	48.98	23.8	2399.04	566.44	1165.724
13	26.50	73.9	702.25	5461.21	1958.350
14	39.37	24.4	1549.98	595.36	960.628
17	46.02	30.7	2117.84	942.49	1412.814
18	32.00	26.3	1024.00	691.69	841.600
21	16.80	105.0	282.24	11025.00	1764.000
22	45.38	27.6	2059.34	761.76	1252.488
23	22.70	67.4	515.29	4542.76	1529.980
25	32.13	51.2	1032.37	2621.44	1645.056
26	21.13	97.4	446.48	9486.76	2058.062
28	40.00	17.9	1600.00	320.41	716.000
29	40.94	17.4	1676.80	302.76	712.356
30	31.10	37.2	967.21	1383.84	1156.920
31	32.30	25.2	1043.29	635.04	813.960
32	37.70	24.4	1421.29	595.36	919.880
33	37.90	27.8	1436.41	772.84	1053.620
Total	805.54	962.6	29994.18	55564.30	29400.272

Once r_{xy} has been computed, the value adjusted for the number of cases can then be obtained by the following equation:

$$\bar{r}^2_{xy} \text{ (adjusted } r_{xy}) = 1 - (1 - r^2_{xy})\cdot(n - 1)/(n - 2) =$$
$$1 - (1 - 0.828^2)\cdot(23 - 1)/(23 - 2)$$
$$\bar{r}_{xy} = 0.817$$

From $\bar{r}_{xy}$, the standard error of estimate computed by the use of equation

$$\bar{S}_{yx} = \sqrt{\frac{Y^2 - n\,(M_y)^2}{n - 1} \times (1 - \bar{r}^2_{xy})}$$
$$= \sqrt{\frac{55564.30 - 23\,(41.85)^2}{23 - 1} \times (1 - 0.817^2)} = 15.24$$

Finally, the coefficients of the regression line are computed as follows:

$$b_{yx} = \Sigma\,(xy)/(n)(\sigma^2_x) = -\,4312.868/(23)(8.795^2) = -\,2.425$$
$$a = M_y - b\cdot M_x = 41.85 - (-2.425)(35.023) = 126.7$$

Then, the regression equation is

$$Y = 126.7 - 2.425\,X$$

The portion of the samples in which specified departure will occur by chance is found first by computing t from Fisher's formula

$$t = r\sqrt{n - 2}\,/\sqrt{1 - r^2}$$

which is developed for a small number of samples; then the probability of the occurrence of the correlation purely by chance is obtained from the table or the diagram by looking up t and n.

B. Normality Test

In order to tell whether or not an observation is normal, first the ratio of average deviation to standard deviation is computed. This ratio is designated by a and is expressed as follows:

$$a = \frac{\text{Average deviation}}{\text{Standard deviation}} = \frac{\dfrac{\sum^{n} |d - \bar{d}|}{n}}{\left[\dfrac{\sum^{n} (d - \bar{d})^2}{n}\right]^{\frac{1}{2}}}$$

Applying this formula to the observations X and Y in the previous pages

$$a_X = 0.857$$

$$a_Y = 0.822$$

Now, from the Normality Tables (the one the author used is Table III in "Industrial Statistics" by H. A. Freeman(90)), the 1 percent levels of a with a sample size 23 are 0.896 and 0.699. The values a_X and a_Y are within this range and therefore the observations under consideration are normal.

APPENDIX III

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.

APPENDIX IV

	Density at 25° C (in gm. per c.c.)	Viscosity at 25° C* (in c. poises)	Time of flow** (in seconds)
Pine Oil	0.905	15.5	6.6
Linseed Oil	0.905	64.4	9.3

---

* Determined by modified MacMicholson Viscosimeter

** For 50 cubic centimeters of liquid

The formula for calibration is as follows:

$$\frac{\mu}{\rho} = At - B/t$$

where μ equals viscosity, ρ equals density, t equals time and A and B are constants.

For pine oil:

$$\frac{0.155}{0.905} = A\ (6.6) - B/6.6 \qquad (1)$$

For linseed oil:

$$\frac{0.644}{0.905} = A\ (9.3) - B/9.3 \qquad (2)$$

By solving (1) and (2)

$$A = 0.128$$

$$B = 4.46$$

Then,

$$\mu/\rho = 0.128t - 4.46/t$$

Or,

$$\mu = \rho\,(0.128t - 4.46/t)$$

APPENDIX V

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

Decompose 1 to 2 grams of the sample with sulfuric acid, nitric acid and hydrofloric 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 glainel 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.

BIOGRAPHICAL NOTE

Alaettin Mustafa Aksoy was born in Istanbul, Turkey, in 1916. He attended elementary school and lycee in Izmir, Turkey. Later he studied architecture for two years at the Istanbul School of Engineering. Then he won a competitive examination and was awarded a scholarship to study metallurgical engineering at the Massachusetts Institute of Technology. This scholarship was granted by the Maden Tetkik ve Arama Enstitusu (The Institute of Mining Study and Research), Ankara, Turkey. In June 1940 he received the degree of Bachelor of Science from the Department of Metallurgy at the Massachusetts Institute of Technology, and in June 1942 was awarded the degree of Master of Science in Metallurgy from the same Institution.

In August 1942 he was appointed Instructor in Metallurgy at the Department of Mining and Metallurgical Engineering of Lafayette College, Easton, Pennsylvania, for the academic year 1942 - 43. In the spring of 1943 he returned to the Massachusetts Institute of Technology to complete his work for the degree of Doctor of Science.

In September 1943 he presented to the Faculty a thesis entitled "An Investigation of Copper Losses in Copper Reverberatory Slags".

ABSTRACT

The reverberatory data obtained through the courtesy of several copper smelters were examined by using statistical methods of analysis. Several factors effecting the copper loss were related. There were:

(1) The copper content of the slag is increased by the grade of matte, silicate degree, copper content of the converter, slag and temperature, and is decreased by the percent of silica;

(2) The total copper lost per ton of matte is increased by the magnetite content of the converter slag; and

(3) The total copper lost per ton of copper in matte is decreased by the grade of matte.

The forms in which copper exists in slag were investigated by examining the polished and thin sections of commercial and synthetic slags under the microscope. Commercial slags were obtained from five widely scattered copper smelters. The synthetic slags were made from synthetic mattes and synthetic copper-free slags. The proper portions of Cu_2S and FeS, both of which were prepared from their respective elements, were fused together to obtain the synthetic mattes. The synthetic slags were prepared from chemically pure oxides. The sections were polished by the modified Hammond process. The examination of the polished sections of the slags showed:

(1) Matte particles having the same composition as the original matte;

(2) Sulfide particles, mostly round, scattered haphazardly throughout the body of the slag, which varied a great deal in size and color;

(3) Metallic copper noted in a few samples;

(4) Magnetite in almost all the specimens; and

(5) Round holes.

The close association of the sulfide particles with the magnetite and the presence of round holes are due to the reaction between the magnetite and ferrous sulfide.

Insufficient settling and currents which are caused by temperature differences as well as by the evolution of gases in the molten slag and matte are the most important causes of the copper losses. Stokes' law was applied to the study of settling in matte and slag layers using plant and experimental data. A simple and less expensive method was developed to measure the viscosity of the slags. The time required to empty a constant volume of slag through a capillary hole of a specially machined graphite crucible was taken as a measure of the viscosity. By this method the viscosity of the fine commercial slags were found to be 3 to 8 poises around 1300° C. Several settling curves were plotted. These showed that even in 5 hours particles less than 50 microns in size will not settle.

Reactions between Fe_3O_4 and FeS, FeS and Cu, Cu_2S and Fe, and Cu_2O and FeS were studied from a thermodynamic point of view. Any magnetite present in the furnace should be reduced and this can be assured by raising the temperature of the furnace, stirring the bath, and by lowering the activity of FeO of the slag. It was found that concentrations of metallic iron are considerably smaller than those of metallic copper and the equilibrium concentration of Cu_2O is so small that its presence in the slag may be neglected.

Although the solubility of Cu_2S, 0.15 - 0.20 percent, in the body of the slag is claimed by several investigators, the experiments, which consisted of fusions of Cu_2S and synthetic copper-free slags in graphite and platinum crucibles and the consequent examination of the slag for copper, showed that Cu_2S is not soluble in the slag in the absence of FeS. Cu_2S is retained in the slag because it is in solution in the FeS which dissolves the oxides of iron of the slag.

Slagged copper was recovered from the commercial slags by the addition of FeS and CuS, and recovery curves were plotted. The highest recovery, 87.2 percent, was obtained at 1300° C with 12.5 percent FeS and 12.5 CuS; the highest concentration of copper, 14.5 percent, was obtained at 1300° C with 6 percent FeS and 6 percent CuS although with a lower recovery, 74.4 percent. Flotation methods were also used to recover the slagged copper. By this method 59.3 percent of the original copper in the slag was recovered.