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A REVIEW OF COPPER CONVERTING

by

D. A. Reeve[1]

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ABSTRACT

The development of copper converting is traced from its beginnings up to the present day. Methods are reviewed for improving converter operations at various plants, both in Canada and abroad. The physical chemistry of (a) the constitution of mattes charged to converters, (b) the converting process itself and (c) converter slags is discussed, and problems caused by magnetite formation and copper losses are mentioned. Emphasis is laid on the new technological developments of air-blast enrichment with oxygen and continuous copper converting. It is concluded that insufficient data are available on the basic chemistry of the converting process.

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ÉTUDE DU CONVERTISSAGE DU CUIVRE

par

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RÉSUMÉ

L'auteur étudie les progrès du convertissage du cuivre depuis ses débuts jusqu'à nos jours. Il passe en revue les méthodes employées pour améliorer les procédés de convertissage dans diverses usines au Canada et à l'étranger. Il étudie la chimie physique de (a) la constitution des mattes servant de charge aux convertisseurs, (b) le procédé de convertissage proprement dit et (c) les scories des convertisseurs, faisant état des problèmes causés par la formation de magnétite et les pertes de cuivre. Il fait ressortir les progrès technologiques réalisés dans l'enrichissement à l'oxygène par courant d'air et dans le convertissage continu du cuivre. Il conclut que les renseignements sur la chimie de base du procédé de convertissage sont insuffisants.

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INTRODUCTION

The greater part of the world's copper is obtained from the smelting of low-grade sulphide ores (assaying about 1.5 percent copper). Before smelting, the ores usually require to be concentrated, generally by flotation, the concentrate obtained often containing about 25 percent copper. The subsequent pyrometallurgical treatment of the concentrate may, in most cases, be divided into three distinct oxidation steps: roasting, smelting in the blast or reverberatory furnace, and converting.

In the roasting operation, some of the sulphur present in the concentrate is removed. Separation of the metal sulphides from the gangue is achieved by smelting with suitable fluxes at about 1250°C. The final copper pyrometallurgical step consists in blowing air through the molten matte, a complex material consisting mainly of FeS, Cu_2S, FeO and Fe_3O_4[1] ,obtained from the smelting operation. The ferrous sulphide is oxidized to ferrous oxide, which is slagged, and the cuprous sulphide is oxidized to copper, the exothermic reactions taking place providing all the heat required.

This final step, known as copper converting, is the subject of this review. Data are collected from other, less recent, reviews and also from other relevant literature which has been published up to the present time. Considerable emphasis is laid on the newer developments of copper converting, namely enrichment of the air blast with oxygen and continuous converting. It is concluded that insufficient information is available on the basic chemical mechanisms of the converting process.

HISTORICAL

The history of copper converting was reviewed recently by Morris[2] at the February 1968 AIME meeting. Prior to 1856, when Bessemer made known his new method for the manufacture of steel, copper sulphide ores were smelted into high-grade matte and shipped to Swansea, Wales, for processing into metallic copper by the "Welsh" process. Several workers tried to adapt the Bessemer process to copper production but were soon discouraged by the fact that the copper chilled as it formed and choked the tuyeres.

In 1880, Manhès and David were the first to apply successfully the Bessemer converter to the copper industry. They overcame the problem of copper blocking the tuyeres, by placing these at the sides of the vessel instead of at the bottom. Peretti[3] pointed out that the bottom-blown converter has its tuyeres in contact with the copper-rich liquid and sulphur would have to be transferred to this phase from the superimposed liquid. This replenishment of sulphur, occurring largely by diffusion, would provide too small a rate of heat liberation to keep the contents of the converter liquid, and thus the tuyeres would become blocked and the process would stop.

For 30 years, up to 1910, converters were lined with a siliceous material which provided the SiO_2 necessary to slag the FeO. The use of these siliceous linings limited to about 35 percent the matte grade that could be treated; this figure, of course, would be considered low by present-day standards. Many metallurgists worked on the problem of using basic-lined converters, but it was not until 1909 that E.A.C. Smith, at Baltimore, realized the importance of maintaining a proper heat balance in the converter and establishing heat control within comparatively narrow limits. This realization led to the Smith patent, No. 943,280, of December 14, 1909, and the

subsequent development of the Pierce-Smith basic refractory-lined copper

converter which is still used today.

CONVERTER PRACTICE

Two types of converter are in use for copper converting:

(a) The upright (Great Falls) converter
(b) The horizontal (Pierce-Smith) converter

The upright converter, developed at the Great Falls (Montana) plant

of the Anaconda Copper Mining Company, is not as common as the Pierce-Smith

type. The converters are lined with magnetite or chrome-magnesite

refractories. More details are to be found in standard metallurgical text-

books[4,5].

In Canada, Noranda Mines Limited at Noranda, Quebec, operates five

Pierce-Smith converters; Gaspé Copper Mines Limited (of the Noranda Mines

Group), at Murdochville, Quebec, one; Hudson Bay Mining and Smelting Company

Limited, at Flin Flon, Manitoba, three; and Falconbridge Nickel Mines Limited,

at Falconbridge, Ontario, four (using copper-nickel mattes).

Important factors which have brought about improvement in converter

operation and production at the Noranda smelter[6] are:

1. Better flux supply which resulted from the use of sized
flux and blended flux of the correct silica content, and
from the weighing of flux feeds.

2. Increased air flow to the converter, together with
metering of the air supply.

3. Mechanical tuyere punchers.

4. Use of radiation pyrometers.

For a 25 percent matte, the desired SiO_2 content of the converter

flux is 67 percent. The temperature rises to 1230°C at the completion of the

slag blow. When this temperature is observed with the pyrometer, the slag

blow is judged to be finished and the converter is ready to be skimmed.

Similar conditions obtain at the Gaspé smelter[7] of the Noranda Mines Group.

One converter can produce 135 tons of copper a day from a 33 percent matte.

At the American Smelting and Refining Company plants[8], copper

converting practice has been standardized to attain a maximum unit blister-

copper production with a minimum of refractory consumption, by careful

location of the tuyeres and by applying magnetite coatings to the hard-burned

magnesite bricks. Seventeen 13 x 30 foot Pierce-Smith converters are operated

by the American Smelting and Refining Company. Tuyeres are located at six-inch

centres four inches below the horizontal centre-line of the shell. They are

1 1/3 inches in diameter but the trend is to increase this to two inches to

increase the air flow. Air is supplied from 13.5 to 15 psig at 2500 cfm,

although some cycles, such as magnetiting, require pressures as low as 8 psig.

Matte (60 to 80 tons) is fed to the converter and blowing commences

as soon as the tuyeres are covered. Flux containing between 59 to 72 percent

SiO_2 with small amounts of iron, lime and Al_2O_3 is added immediately after

blowing is commenced. Enough flux is added in about 10 minutes to produce

a slag which will have a silica-to-iron ratio of about 0.54. The slag blow

lasts for about 85 minutes and produces a slag having the following

approximate analysis:

TABLE I

Typical Slag Analysis at the American
Smelting and Refining Company Plants[8]

Copper	-	2.3 percent
SiO_2	-	26.2 percent
Total iron	-	48.0 percent
Lime	-	1.7 percent
Al_2O_3	-	4.5 percent

Magnetite varies between 15
and 22 percent.

Four separate slag blows are required for a 40 to 45 percent copper matte and 160 tons of liquid matte are added for a 60- to 70-ton output of blister copper. The slag blow temperature is 1232°C, although temperatures immediately after flux additions drop to 1150°C or less. The silica-to-iron ratio of 0.54 is maintained throughout the slag blows, but the magnetite content of the slags tends to increase progressively.

White metal (Cu_2S, 85 to 110 tons), with a copper content of about 74 percent, remains after the slag and any unsmelted silica have been skimmed off the bath. The finish blow, which oxidizes the white metal to blister copper, has an operating temperature of 1260°C, slightly higher than the slag blow. Temperature control is achieved by the addition of clean scrap copper from time to time. Blister, containing 98.4 percent copper, is obtained which is charged direct to the casting furnace.

It is common practice to coat converter linings with magnetite to increase refractory life. This is done at the American Smelting and Refining Company by charging the converter with matte so that the tuyeres are submerged only four to six inches, and commencing blowing without the addition of flux. Magnetite begins to form after 1 1/2 to two hours, accompanied by a sharp rise in temperature (1540 to 1650°C); this rise in temperature is controlled by the addition of cold matte. Continuous punching is necessary to prevent blocking of the tuyeres once the magnetite begins to form.

Capacity of the Rhokana Pierce-Smith copper converters[9] was more than doubled by a complete aerodynamic redesign of the air blast system. The tuyeres were submerged to a maximum depth below the surface of the bath to achieve adequate oxygen/sulphur contact time and consequently maximum oxygen efficiency. The pressure drop from the blower to the surface of the liquid in the converter is the sum of the pressure drops across the pipes to

the tuyeres and between the tuyeres and the liquid surface. To operate at maximum blowing depth the second of these must be a maximum and thus the first must be a minimum. This was achieved by making the air blast system more aerodynamic.

Copper converting practice at the Chino Mines Division of the Kennecott Copper Corporation has been described by Nicholson, Lockridge and Beals[10], and that at Rio Tinto by Potts[11]; these will not be detailed here. Lathe and Hodnett[12] have summarized data supplied by 40 copper converter plants in 18 countries. Their summary includes an analysis of the effect of converter slag composition and temperature on the formation and elimination of magnetite and on the life of basic and neutral refractories. Kuznetzov and Beregovskii[13] have published an article, entitled "Technical Progress in Converting Copper Mattes", which is little more than a translation of Lathe and Hodnett's paper with the omission of data from the Bor Copper Mine, Yugoslavia.

THE CONSTITUTION OF MATTES

Because reverberatory mattes are charged directly to the converters, a discussion of the physical chemistry of molten mattes is very relevant to this review.

Ruddle[14] states that "solid mattes are generally held to be either (a) eutectiferous mixtures of the component sulphides Cu_2S and FeS, or (b) mixtures of complex sulphides". The compositions of ordinary copper mattes fall close to the Cu_2S-FeS join in the Cu-Fe-S system. This ternary system has been studied by a number of workers[15-17] but has caused much confusion and proved very difficult to deal with, because of such factors as

similarities between the X-ray patterns of the various copper iron sulphides, the loss of sulphur at elevated temperatures, and ex-solution occurring on quenching melts.

Early workers considered Ruddle's first statement, that solid mattes are eutectiferous mixtures of the component sulphides, to be correct. Carpenter and Hayward[18] and Howat[19] represented the constitution of reverberatory mattes by Cu_2S-FeS phase diagrams showing simple eutectics. These workers experienced difficulty in fixing the exact position of the eutectic, which suggests that the join Cu_2S-FeS is not a true binary. Both of these diagrams were, to some extent, invalidated by the fact that no attempt was made to control or estimate the sulphur pressure over the systems.

The first comprehensive study of the liquidus surface of the Cu-Fe-S ternary system was made by Reuleaux[15], whose diagram is reproduced in Figure 1. Again, the diagram is only approximate, because no attempt was made to control the sulphur pressure over the system. Reuleaux states that the diagram does not apply to equilibrium conditions and a wider miscibility gap would be expected under conditions of very slow cooling. The ternary eutectic at 915°C to the right of the join Cu_2S-FeS explains why Carpenter and Hayward and Howat were unable to fix the exact position of the eutectic in their diagrams. The part of the diagram to the right of the join Cu_2S-FeS is blank, since phases in this area evolve sulphur at elevated temperatures. The main feature, however, of the Cu-Fe-S liquidus projection is the two-liquid area extending from the Cu-S edge nearly to the Fe-S edge.

The amount of sulphur present in liquid mattes is less than the stoichiometric requirement to account for all the metals as liquid sulphides, and the compositions of copper mattes generally fall between the Cu_2S-FeS join and the high sulphur boundary of the two-liquid area. Schuhmann[20]
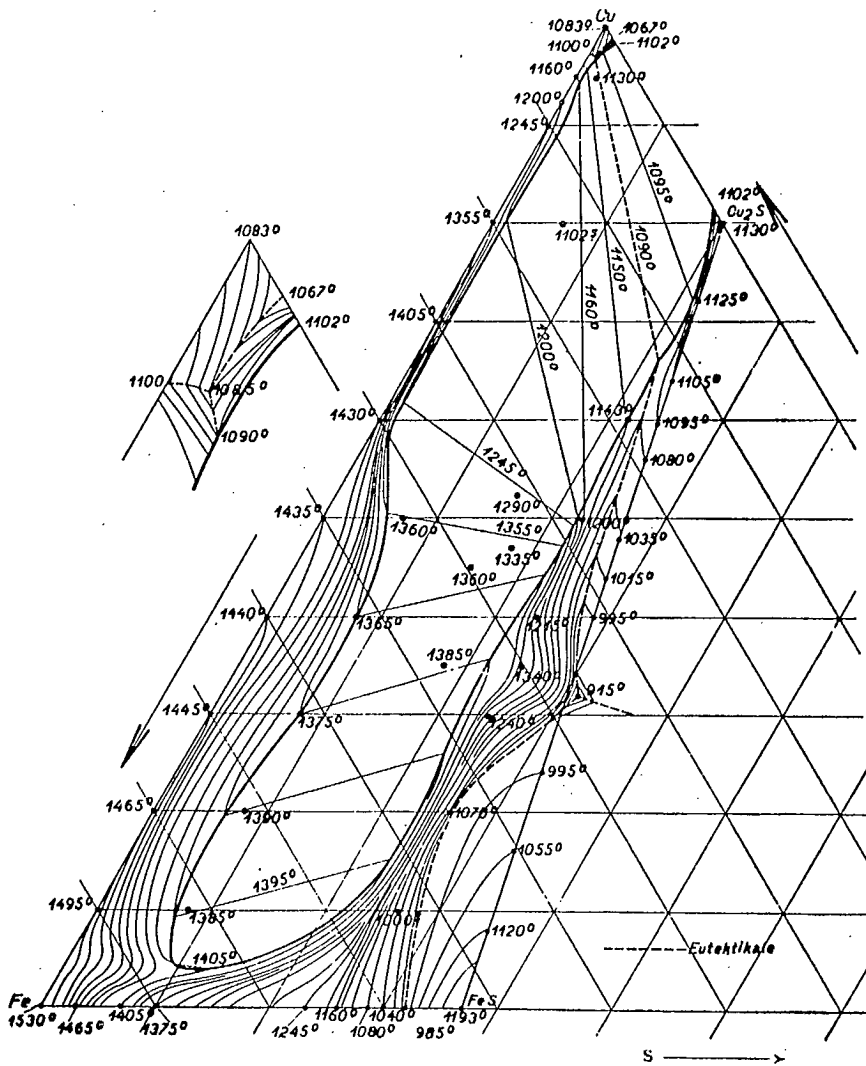
FIGURE 1 - Constitution Diagram of the Cu-Fe-S
System. (After Reuleaux[15])

relates this sulphur deficiency to the fact that as the sulphur content approaches the stoichiometric requirement, the partial pressure of sulphur gas from the melt becomes a considerable fraction of one atmosphere. On cooling, the primary crystal may be iron, copper, or Cu_2S-FeS solid solution, depending in which primary crystallization field the matte composition lies, and the remainder of the matte solidifies as a ternary eutectic.

Merwin and Lombard[16] have studied relations between various solid phases in the Cu-Fe-S system under a sulphur pressure of 455 mm of mercury (0.06 atmosphere), obtained by heating sulphur at 411°C. Their phase diagram showed five ternary crystalline compounds: bornite (Cu_5FeS_4), chalcopyrite ($CuFeS_2$), cubanite ($CuFe_2S_3$), and the previously unreported stoichiometric compositions $Cu_3Fe_4S_6$ and Cu_4FeS_3. Three single-phase solid solution areas are shown in the phase diagram on a band between Cu_2S (solid solution) and FeS (solid solution). The first encloses both chalcocite (Cu_2S) and bornite; the second, referred to as an intermediate phase, falls between chalcopyrite, cubanite and $Cu_3Fe_4S_6$; and the third is the pyrrhotite solid solution.

Schlegel and Schüller[17] have extended Merwin and Lombard's work and produced a liquidus projection for the Cu-Fe-$FeS_{1.08}$-$CuFeS_2$-Cu_2S part of the Cu-Fe-S system. Conventional quenching techniques were used for the low-sulphur side of the Cu_2S-FeS line. Investigations along this line and on the high-sulphur side of it were carried out using evacuated sealed quartz tubes. The diagram obtained was very similar to that of Reuleaux, except that a ternary peritectic at 930°C was introduced close to the ternary eutectic shown in Figure 1. The four primary crystallization fields in this area are now Fe, FeS, the intermediate (chalcopyrite) solid solution, and chalcocite (or bornite) solid solution. The pseudo-binary system

$Cu_2S-FeS_{1.08}$, as given by Schlegel and Schüller, is shown in Figure 2, the temperature of the eutectic E_3 being 940°C.

In a very recent paper, Yund and Kullerud[21], on the basis of lack of experimental data, rejected the two stoichiometric compositions $Cu_3Fe_4S_8$ and Cu_4FeS_3 as proposed by Merwin and Lombard and used by Schlegel and Schüller. Thus, they would consider the composition $CuFeS_{3.08}$ in Figure 2 to be bornite solid solution.

It is interesting to note that a matte consisting solely of Cu_2S and FeS is never attained in practice. Drummond[1] points out that the normal type of commercial matte containing less than 40 percent copper usually contains FeO and Fe_3O_4 as minor constituents. Low-grade mattes made under reducing conditions may contain free iron, and high-grade mattes made under the same conditions may contain free copper.

The thermodynamic properties of mattes will not be discussed here, as they have been reviewed by Ruddle[14] and Schuhmann[20]. However, Krivsky and Schuhmann[22] have shown that Cu_2S-FeS melts are approximately ideal.

THE CONVERTING PROCESS

a. The Slag-Forming Stage

Potts[11] has observed that the temperature range in which it is possible to maintain correct working conditions in basic-lined converters is quite small--approximately 130°C, extending from 1220 to 1350°C. Below 1220°C the matte is too cold to allow formation of a true slag, and above 1350°C wear on the magnetite linings becomes excessive. Potts points out that the matte may be as much as 100° below 1220°C when the matte is charged to the converter, and the necessary increase in heat can only be provided by oxidation of the

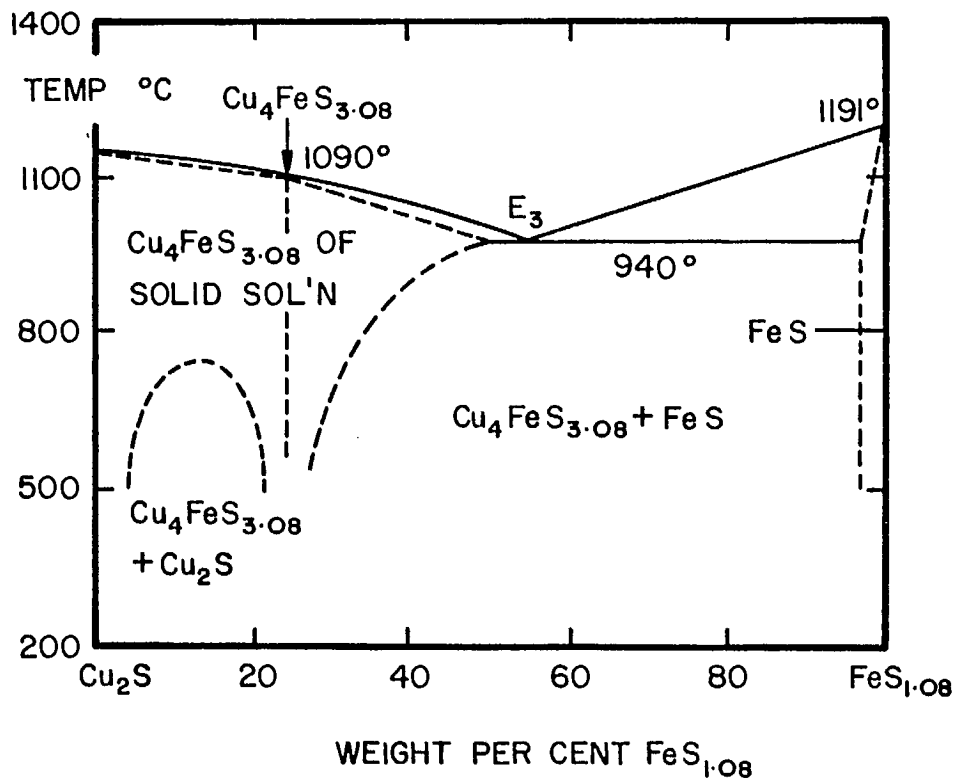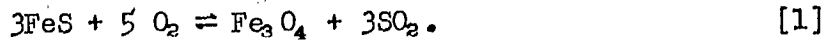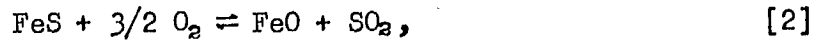FIGURE 2 – The System Cu_2S–$FeS_{1.08}$. (After Schlegel and Schüller[17])

FeS to magnetite:

$$3FeS + 5 O_2 \rightleftharpoons Fe_3O_4 + 3SO_2. \qquad [1]$$
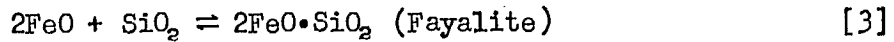
When the necessary temperature has been reached to allow formation of a true

slag, the heat provided by oxidation of FeS to FeO, which is less than provided

by reaction [1], is still sufficient to meet the requirements of the process:

$$FeS + 3/2 O_2 \rightleftharpoons FeO + SO_2, \qquad [2]$$

followed by the slagging reactions:

$$2FeO + SiO_2 \rightleftharpoons 2FeO \cdot SiO_2 \text{ (Fayalite)} \qquad [3]$$

and

$$3FeO + SiO_2 \rightleftharpoons 3FeO \cdot SiO_2. \qquad [4]$$

Reaction [4] seems doubtful as there is no evidence for the existence of

$3FeO \cdot SiO_2$.

Peretti[3] simplifies the process by considering the liquid matte

to consist solely of copper, iron and sulphur and regarding the flux as only

silica. At the start of the operation, air is blown through the liquid matte

on top of which is floating the solid flux. Equation 2 gives the main

reaction, the equilibrium constant, K, for this reaction being given by:

$$K = \frac{a_{FeO} \cdot p_{SO_2}}{a_{FeS} \cdot p_{O_2}^{3/2}}, \qquad [5]$$

where a_{FeO} and a_{FeS} are the activities of FeO and FeS respectively, and

p_{SO_2} and p_{O_2} are the partial pressures of sulphur dioxide and oxygen

respectively. Peretti has calculated the value of K to be 8.5×10^5 at 1500°K,

and thus the SO_2/O_2 ratio must be very large before equilibrium is attained.

The question is asked whether Equation 2 represents the exact

mechanism of the reaction, or is it best described by such reactions as:

$$FeS + 1/2 O_2 \rightleftharpoons FeO + 1/2 S_2, \qquad [6]$$

$$1/2 \; S_2 + O_2 \rightleftharpoons SO_2. \qquad\qquad [7]$$
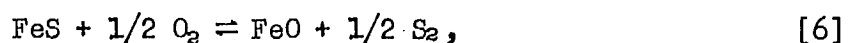
Also, is the reaction caused by oxygen dissolving in the matte followed by a homogeneous reaction in the liquid phase, or is the oxidation of the matte a heterogeneous process occurring at the gas-liquid interface? Peretti doubts the generally accepted belief that oxide is formed as a separate phase and then rises to the matte surface to combine with the silica. He postulates that iron oxide already present in the reverberatory matte reacts with silica at the solid-liquid interface and that the oxide formed on blowing compensates for this reaction either by dissolving in the sulphide liquid if the oxidation is heterogeneous, or by forming in the sulphide liquid if the oxidation is homogeneous.

During the slag-forming stage the Cu_2S is oxidized to Cu_2O, the equations most commonly used to describe this being:

$$Cu_2S + 3/2 \; O_2 \rightleftharpoons Cu_2O + SO_2, \qquad\qquad [8]$$

$$Cu_2O + FeS \rightleftharpoons Cu_2S + FeO. \qquad\qquad [9]$$
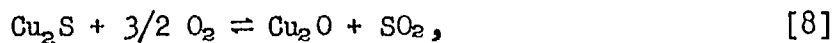
Again, Peretti has calculated that the equilibrium constant at 1500°K for reaction [8] is very large (3×10^3), so that a large SO_2/O_2 ratio is necessary for equilibrium. The copper losses in converter slags usually are very small (<5 percent), and Peretti concluded that "either (a) the copper is oxidized at an appreciable rate and is then returned to the matte by reaction with the iron, or (b) the rate of copper oxidation in the presence of iron is very small". These alternatives would require different reaction mechanisms but would produce the same end result.

b. The Blister-Forming Stage

This stage is usually represented by the reaction:

$$Cu_2S + O_2 \rightleftharpoons 2Cu + SO_2, \qquad\qquad [10]$$

although some authors (e.g. Potts[11]) believe the copper reduction takes place in two steps:

$$Cu_2S + 3/2\ O_2 \rightleftharpoons Cu_2O + SO_2, \qquad\qquad [11]$$

$$2Cu_2O + Cu_2S \rightleftharpoons 6Cu + SO_2. \qquad\qquad [12]$$
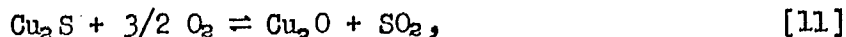
The question arises again as to whether the oxidation mechanism is heterogeneous or homogeneous, and if, in fact, these equations adequately express the reaction mechanism.

CONVERTER SLAGS

Converter slags are composed largely of silica and ferrous oxide, with small quantities of alumina, magnesia and lime. Yazawa and Kameda[23-25] have reported partial liquidus diagrams for the systems Cu_2S-FeS-FeO, FeS-FeO-SiO_2 and Cu_2S-FeS-FeO-SiO_2. These have been reviewed by Toguri, Themelis and Jennings[26]. Some data on the quinary system Cu_2S-FeS-FeO-Fe_2O_3-SiO_2 were obtained by Korakas[27]. From these data it can be seen that the Fe_2O_3 content of the slag increases as the matte becomes enriched in copper. As the silica content of the slag increases, the less Fe_2O_3 it will contain for a given Fe/Cu ratio in the matte; but there is always sufficient Fe_2O_3 for magnetite to be precipitated during the final stages of converting.

Other phase diagrams for SiO_2 and FeO, together with Al_2O_3, MgO and CaO, are to be found in "Phase Diagrams for Ceramists"[28]. These diagrams indicate that additions of Al_2O_3 and CaO reduce the freezing points of SiO_2-FeO slags, whereas additions of MgO increase the freezing points.

The thermodynamic properties of steelmaking slags have been investigated by many workers, notably Chipman. Much of this work is applicable to copper slags, but will not be discussed here as it forms an

extensive subject within itself.

The relatively high electrical conductivities of liquid slags have led many writers, notably Chipman and Chang[29], to think that liquid slags are very largely dissociated into ions. When solid, the slags contain one or more compounds (e.g. fayalite) and the ionic structures of these compounds are believed to persist in the liquid state, the long-range order being lost but the short-range order remaining, so that each negative ion is loosely co-ordinated by positive ions. Ruddle[14] points out that the ionic theory of slags has not been applied to copper converting, and postulates that iron is present in these slags as Fe^{2+} and Fe^{3+}, together with SiO_4^{4-}, SiO_3^{2-} and a small quantity of O^{2-} ions. Calcium and magnesium will exist as Ca^{2+} and Mg^{2+} respectively, while aluminum may be present as Al^{3+} or AlO_3^- ions.

MAGNETITE FORMATION

Large quantities of magnetite, formed mainly during the slagging period, affect the efficiency and operation of the converting process. Magnetite accretions cause blocking of the tuyeres, necessitating continuous punching, and increase copper losses in the slag. Excess magnetite in the converter slag causes problems in the reverberatory furnace when recycled.

On the other hand, magnetite formation is utilized in blowing a magnetite lining on the converter walls to increase refractory life (see previous section, Converter Practice, on page 5). Also, Korakas[27] notes that magnetite may act as a thermal regulator, since the oxidation of FeS to Fe_3O_4 is the most exothermic reaction taking place.

Ruddle[14] and Lathe and Hodnett[12] have summarized existing data on this subject, and practical aspects relating to industrial converters have

been examined by Gronningsater and Drummond[30], Potts[11], Mossman[31], and

Barker, Jacobi and Wadia[32]. Laboratory tests on the behaviour of magnetite

during copper converting have been carried out by Ellwood and Henderson[33]

and Korakas[27].

Magnetite occurs in copper converters due to its presence in the

matte charged to the converters and due to the oxidation of FeS in the charge

in the absence of sufficient SiO_2 to slag the FeO as it is produced and thus

prevent its further oxidation. Schuhmann[20] has estimated that the partial

pressures of oxygen and sulphur change from 5.2×10^{-8} atm and 10^{-2} atm,

respectively, at the beginning of the conversion to 3.4×10^{-6} atm and

2.7×10^{-6} atm, respectively, at the end of the process (this assumes a

sulphur dioxide partial pressure of 1 atm), so that the equilibrium

$$6FeO + O_2 \rightleftharpoons 2Fe_3O_4 \qquad [13]$$

shown in Equation 13 would be expected to shift towards the right.

The sulphur dioxide resulting from the reduction of magnetite by

FeS according to Equation 14 is quickly removed

$$3Fe_3O_4 + FeS \rightleftharpoons 10 FeO + SO_2 \qquad [14]$$
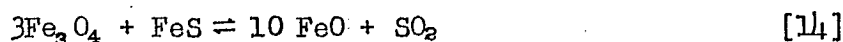
during the converting process, so that this reaction cannot attain equilibrium

and should proceed at relatively low temperatures. It is even thermodynamically

possible for this reaction to go backwards if insufficient silica is present

so that the activity of FeO is very high and, indeed, Mossman[31] has reported

that this does occur at the Hurley Copper Smelter.

Wartman and Oldright[34] have studied reaction [14] by measuring

the amount of sulphur dioxide expelled when ferrous sulphide is heated with

magnetite for 2 hours in a current of purified nitrogen, and have concluded

that the reaction rate increases greatly with temperature and an insignificant

amount of magnetite is reduced below 1200°C. Ruddle[14] points out, however,

that the rate at which FeS is first oxidized to FeO and then to Fe_3O_4 is probably more or less constant, being controlled largely by the amount of air being blown through the converter. The concentration of FeS will be very low at the end of the slag-forming period, so that not much Fe_3O_4 will be reduced at this stage. Ruddle also notes that magnetite formation in the converter depends on the rates of reactions [13] and [14] and the rate of the slagging reaction [3]:

$$2FeO + SiO_2 \rightleftharpoons 2FeO \cdot SiO_2.$$
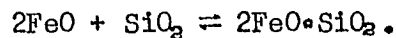
In his analysis of converter practice at Rio Tinto, Potts[11] recommends that the initial temperature of the reverberatory matte charged to the converter must be at least 1250°C to avoid formation of magnetite at the beginning of the blow. It is desirable to add flux after the blow has started, to avoid cooling the bath. Plenty of siliceous flux is necessary to minimize magnetite formation; Gronningsater and Drummond[30] recommend that the slag should contain at least 28 percent silica.

Korakas[27] has shown that the magnetite content of converter slags increases very rapidly when matte composition approaches that of copper sulphide. Ellwood and Henderson[33] report that much of the magnetite in the slag can be reduced by the addition of various reducing agents in conjunction with the silica additions. The largest reductions were obtained by adding iron (83.6 percent reduction) and FeS (71.2 percent reduction).

Toguri, Themelis and Jennings[26] comment that a knowledge of phase relations in the system $Cu_2S-FeS-Fe_2O_3$ would be of interest to the formation of magnetite in copper converters.

COPPER LOSSES

Until a few years ago, opinions were divided as to the extent to which copper present in both reverberatory and converter slags was in true solution or merely entrained as metal or matte. The results of Ruddle, Taylor and Bates[35] indicate that a large amount of the copper in molten slags is present in the oxidized form in true solution. This is partly precipitated as metal on cooling, and the solubility depends on the degree of oxidation of the slag as reflected by its ferric oxide content. They found that, for slags in equilibrium with copper, the solubility as oxide rose from just under one percent at saturation with iron to seven to nine percent in the most highly oxidized slags.

Investigations on the solubility of copper in iron silicate slags have also been carried out at Birmingham University (U.K.) as a Ph.D. project[36], but this work has not yet been made available.

THE USE OF OXYGEN IN COPPER CONVERTING

The development of the basic oxygen furnace in steelmaking has aroused interest both in the use of oxygen-enriched air fed to the tuyeres in copper converting and in the use of an oxygen lance.

a. Oxygen Enrichment at the Tuyeres

As long ago as 1904, Borchers[37] reported that better results were obtained for the converting of copper mattes when air enriched to 25 to 28 percent oxygen was used. He ascribed this improvement to the high temperatures generated during the blow and to the intensity of the reactions. Using a

laboratory-scale converter, Tonakanov[38] in 1934 showed that air enrichment with 21 to 38 percent oxygen increased the converting rate, the process temperature, the tuyere life, and the sulphur dioxide in the exhaust gases. This oxygen enrichment resulted in a satisfactory copper product with no increase in the impurity levels, a normal and highly fluid slag, and no adverse effects on lining life.

There has been a considerable amount of controversy in the Russian literature regarding the benefits of using oxygen-enriched air blasts. M. V. Iolko[39] maintained that oxygen enrichment intensifies the converting process, but Shalygin and Meyerovich[40] disagreed with him and concluded that oxygen enrichment is not as valuable as it may seem. In a later note[41], Iolko supported his original statement and attacked Shalygin and Meyerovich for criticizing his paper. A number of other publications[42-45] have also appeared in the Russian Journal of Non-Ferrous Metals in recent years, but the writer feels that these do not merit individual discussion here.

The production of blister copper from copper concentrates was studied by Tsuramoto[46] in Japan, at the Saganoseki Smelter, using a commercial-size converter supplied with bottled oxygen. It was concluded that, by using oxygen-enriched air, copper concentrates could be smelted direct to blister copper, and this process has now been adopted at the Hitachi Smelter. Arentzen[47] has reported the results of a test program, at the Anaconda Company Smelter, using an air blast enriched with 25.5 to 44.2 percent oxygen. Foaming was found to occur during the white-metal blow, and a microscopic examination of the froth material indicated that copper oxide was reacting with copper sulphide to form metallic copper and sulphur dioxide.

b.   Oxygen Top Blowing of Copper Mattes

Kurzinski[48] points out that top blowing increases production rates

as compared to standard converter practice, because greater overall thermal efficiency is realized since the sensible heat lost in the nitrogen during air blowing would be eliminated. Top blowing should increase refractory life, since the reaction zone is located immediately opposite the oxygen jet. With conventional bottom blowing converters, the reaction zone is directly in front of the tuyeres and immediately adjacent to the refractory lining of the vessel.

Nelmes, Charles and Cowan[49] found that the introduction of oxygen into a copper converter was more satisfactory when a lance was used rather than tuyere injection, because of a series of burn-outs of the tuyere panels caused by excessive temperatures. A refractory-coated, water-cooled, copper lance was found to be the most satisfactory means of introducing oxygen. Nelmes and his co-workers found that the extremely rapid oxidation of the iron raised the temperature in the converter very quickly indeed, thus tending to prevent the formation of magnetite.

Shalygin and Diomidovskii[50] investigated the top-blowing of copper mattes in an experimental converter having a bath depth of 400 to 450 mm. The lance was located 250 to 450 mm above the bath and a high blast pressure was employed. At small time intervals during the blow, quartz flux was added so that a slag containing no less than 25 percent SiO_2 was obtained. Ramachandran, Krishnan and Mallikarjunan[51] are the only authors to report a bench-scale investigation of copper matte top-blowing. They took 100-g samples of mixtures of Cu_2S and FeS in graphite crucibles and heated them until molten, stirring with a graphite rod. Oxygen, at various flowrates, was blown into the furnace with a quartz tube (0.5-mm diameter) whose tip was situated 10 cm from the surface of the molten matte. It was concluded that the yield of copper depended on the oxygen injection pressure and the

blow time.

At the recent Conference of Metallurgists of the Canadian Institute of Mining and Metallurgy (in Vancouver, August 1968), Jackson[52] reported an investigation at Falconbridge into the use of oxygen-enriched air for the smelting of semi-dried Ni-Cu concentrate in the converter. It was found that this smelting was only possible in limited amounts and that for autogenous smelting an oxygen enrichment level of 80 percent would be required. Operation at this oxygen concentration was not considered to be attractive, because of probable technical difficulties and high oxygen consumption per ton of concentrate smelted.

CONTINUOUS CONVERTING OF COPPER MATTES

Most of the important developments in copper converting occurred during the 25 years following Bessemer's announcement of his new process. Since that time, efforts to produce copper more economically have been concentrated mainly on increasing the capacity of the production equipment and increasing the amount of automation (pp. 3-6). These efforts, however, do not avoid the basic flaw in the process, that it is a batch operation. The most recent trend in copper metallurgy is toward the development of methods for the continuous converting of copper mattes.

Sehnalek, Holeczy and Schmiedl[53] have analyzed the thermodynamics of converter reactions and have shown that the concentration of FeS in the matte must be reduced to a few thousandths of one percent before the formation of blister copper is possible. This reduction can be achieved locally by oxygen lancing, even when iron-bearing matte is fed continuously into the converter. They point out that the three layers formed in a converter, namely

slag, white metal and blister copper, make possible the continuous converting
of mattes. A reverberatory type of furnace was used, similar to that used at
the Leningrad Mining Institute by Diomidovskii et al.[54]. Air was introduced
at 6 atm pressure through three lances in the roof of the converter. The
blister obtained assayed about 98 percent copper and the slag about one
percent.

Recently, Worner[55] has described the WORCRA process for the
treatment of powdered copper concentrates. Smelting is "zonalized", with
each zone seeking its equilibrium in a steady state. A U-shape furnace is
used, with concentrate and flux being introduced to a mildly oxidizing
atmosphere in the middle of the furnace. The melt flows to one end, passing
under air lances as it reaches the converting zone where blister copper is
tapped off continuously. Slag moves towards the other end of the furnace,
passing through a reducing zone; it is tapped off continuously and its
entrained matte settles for tapping at intervals.

Figure 3 is an idealized diagram showing the progressive changes
which occur in the slowly flowing matte stream as it is sequentially lanced
to white metal and finally to metallic copper. Near the copper taphole end
the slag is highly oxidized, but as it moves back counter-current to the
matte stream its magnetite and copper contents are progressively decreased.

Continuous copper converting has the following advantages over
common converting practice: avoiding long shut-down times, minimizing heat
losses, providing raw materials continually and without loss, reducing copper
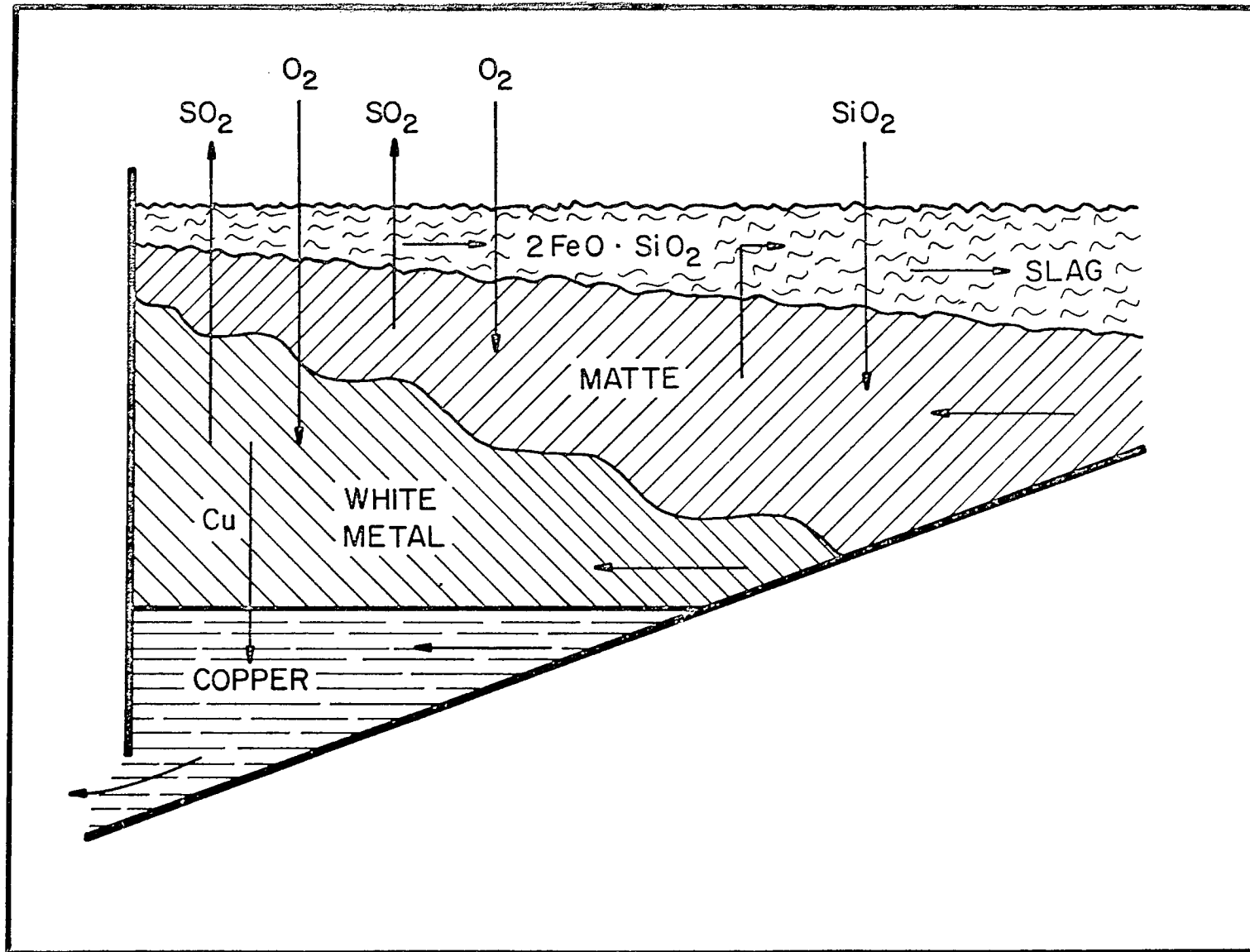losses, and increasing copper recovery.

FIGURE 3 - Idealized diagram showing changes in composition within the
converter section of the WORCRA copper smelting furnace. (After Worner[55])

DISCUSSION AND CONCLUSIONS

Early workers attributed the selective oxidation of FeS in the presence of Cu_2S to the high affinity of copper for sulphur. Kelley[56], however, showed that, thermodynamically, copper has little more affinity for sulphur than has iron but iron has a much greater affinity for oxygen. Since Kelley's work, investigations into the chemistry of copper converting have been concerned mainly with thermodynamics. Schuhmann[20] has surveyed the thermodynamics of copper smelting, Peretti[3] has analyzed the converting of copper matte from a thermodynamic standpoint, and Korakas[27] has applied thermodynamic data to magnetite formation.

Thermodynamics describes systems in which no reactions are taking place, i.e., which are at equilibrium. The results of investigations conducted under equilibrium conditions may possibly be of doubtful value when studying the dynamic converting process. Korakas[27], however, claims that the converter seems to work in conditions approaching those of equilibrium because of agreement between experimental and calculated thermodynamic results. Quarm[57] disagrees with this statement and holds that the very high reaction rates expected at furnace temperatures are, in general, no criterion that equilibrium conditions may be expected to obtain in smelting processes. The fact that reactions are occurring is, in itself, direct evidence of lack of equilibrium.

Schuhmann[20] makes a distinction between equilibrium conditions and actual process conditions, this being characteristic of the application of thermodynamics to chemical processes in general. Equilibrium data describe only limiting conditions within which processes must operate, and do not constitute a basis for choosing between different reaction mechanisms. It

is to be inferred from Schuhmann's statements, and also from Peretti's
remarks about reaction mechanisms in both the slag-forming and blister-
forming stages of copper converting (pp. 12 and 13), that proof is lacking of the
mechanisms of the reactions taking place. It must be expected that few further
major advances in the metallurgy of copper converting can take place until
research efforts are focussed on the reactions actually occurring and their
relative velocities.

Converter chemistry is discussed by Quarm[57] in the hope that it
will suggest ways of approaching these problems. He notes that the oxygen
efficiency during the blowing of white metal is in the neighbourhood of
100 percent and, since gas-liquid contact time is very short, reactions
occurring must be rapid. A mechanism based on the direct oxidation of liquid
sulphide by air is not possible, because cuprous oxide must react with ferrous
sulphide before it reacts with cuprous sulphide to maintain the selectivity
of the oxidation. This is unlikely because the reaction of cuprous oxide
with cuprous sulphide is so fast that it is almost explosive.

The oxidation of ferrous sulphide by magnetite according to
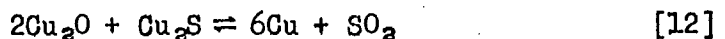reaction 14 is slow, according to the results of Wartman and Oldright[34]:

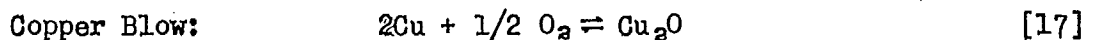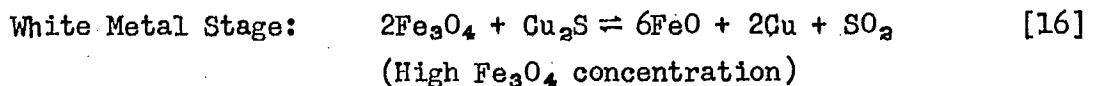$$3Fe_3O_4 + FeS \rightleftharpoons 10\ FeO + SO_2 \qquad [14]$$
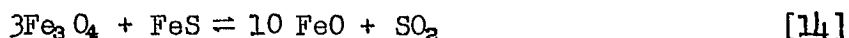
This is to be expected, as magnetite is solid at the temperatures used by
Wartman and Oldright and the velocity of this type of reaction is governed by
the speed at which reactants can migrate to the phase boundary. From Wartman
and Oldright's later experiments[58] with cuprous sulphide and magnetite, it
can be seen that magnetite would be expected to oxidize ferrous sulphide, as
opposed to cuprous sulphide, under converter conditions.

These facts, together with the fact that if magnetite were reduced
by FeS the concentration of magnetite would remain low until the iron in the

matte had been so depleted that the oxygen was being supplied faster than it could be used, are used to propose a new reaction mechanism for the chemistry of copper converting. (It is interesting to note that Mossman[31] found the pattern of magnetite concentration mentioned above to exist at the Hurley Smelter, New Mexico.)

As the concentration of magnetite in the matte rises after the FeS has been removed, the cuprous sulphide will begin to be oxidized to copper. This molten copper will absorb oxygen from the air and retain it in solution, which is, according to Quarm, the most reactive form of oxygen for the oxidation of cuprous sulphide, leading to the initiation of an oxidation cycle resulting in the production of blister copper.

The following reaction mechanism is postulated on the basis of these arguments, although Quarm does point out that it would be difficult to obtain experimental proof of the true function of magnetite in the first stage of the process:
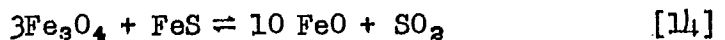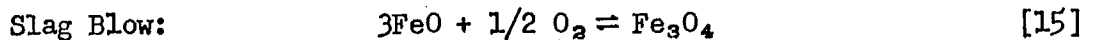
Slag Blow:	$3FeO + 1/2\ O_2 \rightleftharpoons Fe_3O_4$	[15]
	$3Fe_3O_4 + FeS \rightleftharpoons 10\ FeO + SO_2$	[14]
White Metal Stage:	$2Fe_3O_4 + Cu_2S \rightleftharpoons 6FeO + 2Cu + SO_2$	[16]
	(High Fe_3O_4 concentration)	
Copper Blow:	$2Cu + 1/2\ O_2 \rightleftharpoons Cu_2O$	[17]
	$2Cu_2O + Cu_2S \rightleftharpoons 6Cu + SO_2$	[12]

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