MATTE/SLAG BEHAVIOUR UNDER HIGH pSO_2 CONDITIONS

by

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TO IRMA AND LUZ ELISA

ABSTRACT

An experimental programme in which Cu-Fe-S mattes, silica saturated Fe-O-SiO_2 slags and controlled pSO_2 atmospheres were equilibrated, has been carried out with the principal objective of examining copper concentrations in the slags under oxidizing (pSO_2 = 0.1 to 1 atmosphere) conditions.

The experiments showed that when slags and mattes are equilibrated, the copper-in-slag concentrations remain low as long as the mattes contain less than 60% Cu, under all temperature and pSO_2 conditions. Copper-in-slag concentrations increase catastrophically under oxidizing conditions when the mattes contain more than 65% Cu. The experiments also showed that whereas FeS has a high solubility for oxygen and is itself soluble in slag under oxidizing conditions, Cu_2S and slag are virtually completely immiscible. Cu-Fe-S mattes behave in an intermediate manner.

In a theoretical part of the work, the conditions under which a pure copper phase will be at equilibrium with Fe-O-SiO_2 slags and Cu-Fe-S mattes have been predicted on the basis of previous experimental a_{FeO} and pO_2 data for slags, and a_{Cu_2S} data for mattes. It is shown that under SiO_2 saturation conditions metallic copper will occur in equilibrium with: (i) 45-50% Cu mattes at iron saturation, with (ii) 79% Cu mattes at magnetite saturation and with (iii) intermediate matte compositions in contact with totally liquid slags.

The overall conclusion of the investigation is that industrial production of mattes containing 60% Cu or below should not cause excessive copper-in-slag losses under any circumstances. Copper losses may become excessive above this matte grade especially under highly oxidizing conditions.

RESUME

Un programme expérimental a été exécuté dans le but d'étudier la concentration du cuivre dans les scories dans des conditions oxydantes (p_{SO_2} = 0.1 α 1 atm). Ce programme de recherche comprenait des expériences d'équilibrage entre des mattes du système Cu-Fe-S, des scories saturées de silice du système Fe-O-SiO_2 et des atmosphères d'une teneur contrôlée en SO_2.

Les expériences ont prouvé qu'en équilibre entre les mattes et les scories, la concentration du cuivre dans les scories n'est pas élevée pour autant que les mattes contiennent moins que 60% Cu, et ce pour toute la gamme de températures et p_{SO_2} étudiées. La teneur des scories en cuivre augmente de façon catastrophique sous des conditions oxydantes quand les mattes contiennent plus que 65% Cu. Les expériences ont aussi prouvé que l'oxygène est très soluble dans les FeS et ce dernier est soluble dans les scories sous des conditions oxydantes, tandis que le Cu_2S et la scorie sont complètement immiscibles. Les mattes du système Cu-Fe-S ont un comportement intermédiaire.

Les conditions sous lesquelles une phase de cuivre pur sera en équilibre avec des scories Fe-O-SiO_2 et les mattes Cu-Fe-S ont été théoriquement calculées sur la base de données expérimentales déjà existantes sur a_{FeO} et p_{O_2} pour des scories et a_{Cu_2S} pour des mattes. Il est démontré que le cuivre métallique, sous conditions de saturation en SiO_2, sera en équilibre avec (i) des mattes contenant

45-50% Cu sous saturation en fer, avec (ii) des mattes contenant 79% Cu sous saturation en magnétite, et avec (iii) des mattes de composition intermédiaire en contact avec des scories complètement liquides.

La conclusion globale de cette étude est que la production industrielle de mattes contenant 60% Cu ou moins, ne devrait, en aucune circonstance, avoir comme résultat des pertes excessives de cuivre dans la scorie. Les pertes en cuivre pourraient devenir excessives quand la teneur en cuivre des mattes dépasse 60%, et surtout sous des conditions oxydantes.

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I. INTRODUCTION

Flash smelting and other autogenous or semi-autogenous processes are gradually being adopted for the smelting of copper, primarily as a consequence of their relatively low overall energy requirements[1]. These processes operate at somewhat higher SO_2 pressures than traditional fuel-fired processes (in which the SO_2 is diluted by hydrocarbon combustion products) and, hence their chemistry of operation is somewhat different than that of the older processes. In addition, flash smelting and the other new processes produce mattes of high copper grade (> 50% Cu) as compared to the 30 to 50% Cu mattes produced by the traditional reverberatory furnace.

This thesis describes an experimental programme in which matte/slag behaviour under conditions similar to those encountered in flash smelting furnaces, i.e.

pSO_2	0.1 to 1 atmosphere
temperature	1423 to 1573 K
matte grade	30 to 79% Cu
slag	SiO_2 saturated

was studied; the object being to determine the nature and compositions of the phases which are likely to predominate in flash furnace (and other novel process) units.

Although the study was primarily scientific in nature, specific attention was paid to the copper contents of the experimental slags and

to the factors which control them. Copper-in-slag concentration is an important economic variable because it determines whether a smelting slag can be discarded directly or whether it requires subsequent copper recovery treatment before discard. Other variables receiving specific attention were oxygen content in matte and sulphur content in slag.

I.1 A BRIEF REVIEW OF COPPER MATTE SMELTING

Matte smelting, as applied to copper, consists essentially of melting and partially oxidizing copper sulphide concentrates (with suitable fluxes) to form:

a) a liquid matte phase containing 30 to 60% copper; and

b) a liquid slag (oxide) phase as devoid as possible of copper.

The matte is more dense ($\rho \simeq 4.6$ tonnes m^{-3}) than the slag ($\rho \simeq 3.5$ tonnes m^{-3})[1] and hence the two phases are readily separated by means of tap-holes at different depths in the furnace.

After separation from slag, matte goes on to be made into crude blister copper. This is performed by oxidizing iron and sulphur from the matte with air (converting) in a separate converting unit, i.e., by the reactions:

$$FeS + 3/2\ O_2 \rightarrow FeO + SO_2$$

(air) (slagged with SiO_2)

$$Cu_2S + O_2 \rightarrow 2Cu + SO_2$$

(blister copper)

The blister copper is subsequently fire- and electrorefined to its final electrical grade form.

Analysis of the mattes and slags of industrial matte smelting operations are summarized in Table I.1.

I.2 SMELTING METHODS

Fig. I.1 summarizes, in flowsheet form, current (1977) industrial matte smelting methods. Far and away the most important smelting units are the fuel-fired reverberatory furnace and the flash furnace. The latter is gradually being adopted as the principal copper smelting method largely as a consequence of its low hydrocarbon fuel requirement[1]. Its major difference from reverberatory furnace smelting is that the thermal requirement of the process is largely provided by combusting the sulphide concentrate in place of hydrocarbon fuel.

In recent years, several novel processes which are also designed to combust the sulphide concentrates for most of their heat requirement have been developed. The most important of these are (i) the Mitsubishi Process, in which concentrates and pure oxygen are blown through lances into a circular hearth furnace; and (ii) the Noranda Process, in which oxygen-enriched air is blown through tuyeres into a matte phase while concentrates are continuously added to the bath. In the latter case the sulphides are melted to form matte by the heat generated in the matte bath. Several installations of each type are currently in production or are being constructed. Fuel requirements of copper matte smelting processes are summarized in Table I.2.

NAME OF SMELTER	TYPE OF FURNACE	TYPE OF CHARGE	Average Concentrates or Calcine Composition %							Matte Composition %			Slag Composition %							Other (%)
			Cu	Fe	S	Al_2O_3	CaO	MgO	SiO_2	Cu	Fe	S	Cu (Total)	SiO_2	Fe	Fe_3O_4	Al_2O_3	CaO	MgO	
Lubumbashi	blast	sinter	27	16	27	1	2	2	5	63	6	20	1.06	29	25		6	5	6	ZnO (14)
Shisakajima	blast	green	31		29					46			0.37	30	29			8		
Mt. Isa	reverberatory	calcine	24	29	32		1	1	5	36	32	24	0.36	36	37		4	8	2	
Inanshia	reverberatory	green	30	20	25	4	1	1	14	47	25	25	0.6	39	29		9	11	3	
Kennecott	reverberatory	green	29	25	31	2			8	41	31	25	0.41	38	37	2	5	6		
Rolidon	electric	calcine and dry concentrates	26		30					34	30	25	0.31	39	32		8	5	3	ZnO (3)
Jinja	electric	green	29	31	25					29	40	25	0.63	36	38		7	4		
INCO	O_2 flash	dry	29	1 Ni	32	33				2.5	47	2 Ni	26	24	0.62	0.13 Ni	36	37	18			
Mitachi	Outokumpu flash	dry	26		25	30				6	49		21	25	*1		34	34				
Toyo	Outokumpu flash	dry	28		23	28					49		25	23	*1		40	33				
Tamano	Outokumpu flash	dry	24		27	26		1		13	47		25	24	0.53		36	37		3		

*Before slag retreatment.

TABLE I.1 Analyses of Mattes and Slags of Industrial Smelting Operations

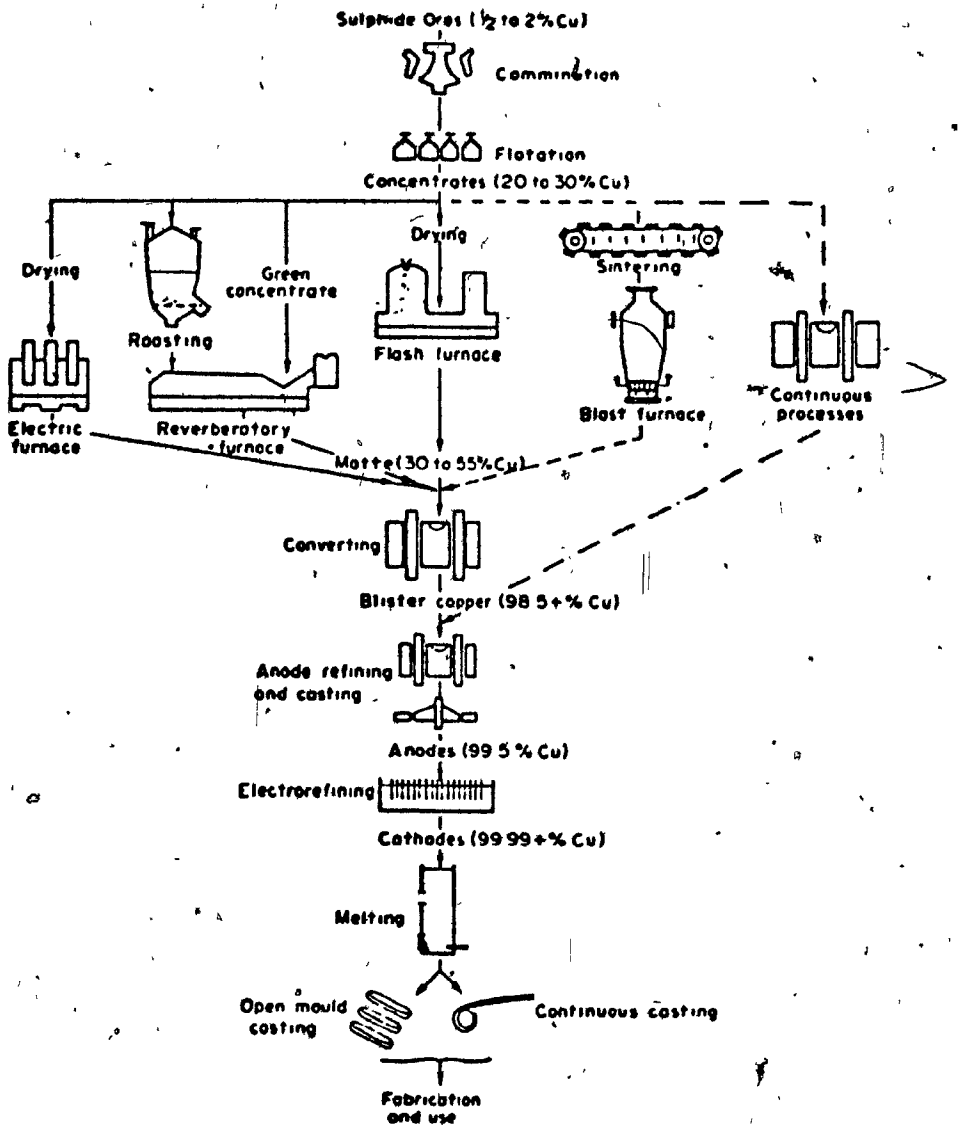


FIG.I.1 Principal processes for extracting copper from sulphide ores. Parallel lines indicate alternative processes (---- Rare; -.-.-. Under Development) Davenport[1].

Smelting Process	Energy Consumption Per Tonne of Charge: Kcal (Including Energy for O_2 Manufacture)	Energy Consumption Per Tonne of Copper: Kcal (Assuming 25% Cu in Charge)
INCO flash	$1x10^5$	$4x10^5$
Electric	$4x10^5$	$16x10^5$
Noranda single step (30% O_2 in tuyeres)	$4x10^5$	$16x10^5$
Outokumpu flash	$5x10^5$	$20x10^5$
Mitsubishi continuous	$6x10^5$	$24x10^5$
Calcine charged reverberatory	$8x10^5$	$32x10^5$
Green charged reverberatory	$13x10^5$	$52x10^5$

TABLE I.2 Energy Requir[illegible] for Smelting in Different Types of Processes[1]

An additional advantage of the processes which combust their sulphide concentrates for much of their thermal requirement is that the effluent gases contain SO_2 at high concentration, i.e., the SO_2 is not heavily diluted by hydrocarbon combustion products. This permits efficient recovery of SO_2 from the effluent gases and relatively straightforward production of by-product sulphuric acid, liquid SO_2 or elemental sulphur. SO_2 concentrations in the gases emanating from matte smelting furnaces are summarized in Table I.3.

I.3 CHEMISTRY OF MATTE SMELTING - ITS INDUSTRIAL IMPORTANCE

The metallurgical engineer of today must concentrate on three fundamental aspects of the copper matte smelting process:

(a) minimization of energy consumption;

(b) minimization of SO_2 (and other) pollution; and

(c) minimization of copper loss.

This thesis is principally concerned with the last of these subjects, i.e., minimization of copper loss in slag.

Matte smelting is carried out under differing oxidizing conditions according to the type of process used. The electric furnace (with its carbon electrodes) operates under the most reducing conditions while flash furnaces and the novel processes (with their small hydrocarbon fuel use) are at the highly oxidizing end of the spectrum. The fuel-burning reverberatory furnace (with its copious quantities of combustion gases) is intermediate in oxidizing potential.

The shift in copper technology towards flash furnace processing has made smelting under highly oxidizing conditions (pSO_2 = 0.1 to 1

	Vol.% SO_2 in Flues		
	Average	Maximum	Minimum
Hearth roaster	5		
Fluid bed roaster	10-15		
Reverberatory furnace	0.5-1.5 The Onahama smelter has by oxygen enrichment, draft control and reduction of air infiltration upgraded the reverberatory off gas to 2.2% SO_2.		
Electric furnace	4-8 Electric furnaces can also be operated under non-oxidizing conditions, in which case the gases contain in the order of 0.4% SO_2.		
Flash furnace			
INCO	80		
Outokumpu	12-15		
Continuous processes			
Mitsubishi		10 (higher with O_2 enrichment)	
Noranda	8		
Worcra	5	8-12 (reaction branch)	1-2 (slag-settling branch)
Converter			
Pierce-Smith	4-5	10	0
Hoboken	8	11	0

TABLE I.3 Concentrations of SO_2 in Gases Produced by Various Smelting and Converting Processes[1]

atmospheres) much more common. The work presented in this thesis recognizes this change in that it is concerned primarily with the matte/slag phases which should exist under flash smelting conditions, i.e.: pSO_2: 0.1 to 1 atmosphere, matte-grades 30 to 79% Cu; and silica-saturated slags. Thus, the investigation is intermediate between early studies under iron saturation conditions (low oxidation potentials) and recent copper metal saturation studies which were directed towards single step copper-making processes.

II. LITERATURE SURVEY

This section discusses the mattes and slags which are encountered in copper smelting and it examines in detail recent metal/slag/gas, matte/slag/gas and metal/matte/slag/gas studies in order to lay the groundwork for the experimental part of this thesis.

II.1 MATTES

Copper smelting mattes may be thought of as homogeneous liquids consisting essentially of Cu, Fe and S and containing a significant amount of dissolved oxygen. Industrial mattes also contain impurities such as Co, Ni, Pb, Zn and precious metals which originate in industrial ores.

Mattes are more dense than slags ($\simeq$ 4.6 tonnes m^{-3} as opposed to $\simeq$ 3.5 tonnes m^{-3}) and, hence, they tend to settle below a slag layer. They have a relatively low viscosity ($\simeq$ 10 centipoise). Their electrical conductivities (300 to 1000 ohm^{-1} cm^{-1}) are much higher than those of molten ionic salts (NaCl, 4 ohm^{-1} cm^{-1}) and slags (0.5 ohm^{-1} cm^{-1}), which indicates that mattes are semiconductors rather than ionic conductors, i.e., they are covalently bonded.

Mattes can be thought, therefore, as being low viscosity, high conductivity liquids in which iron and copper atoms are covalently bonded to sulphur (and oxygen).

Extensive experimental studies of the Cu-Fe-S system have been made and detailed phase diagrams have been prepared. The most complete work is that reported (Figs. II.1.A, II.1.B) by Krivsky and Schuhmann[2]

Fe-Cu-S: 1150°C; Pt= 1 atm.

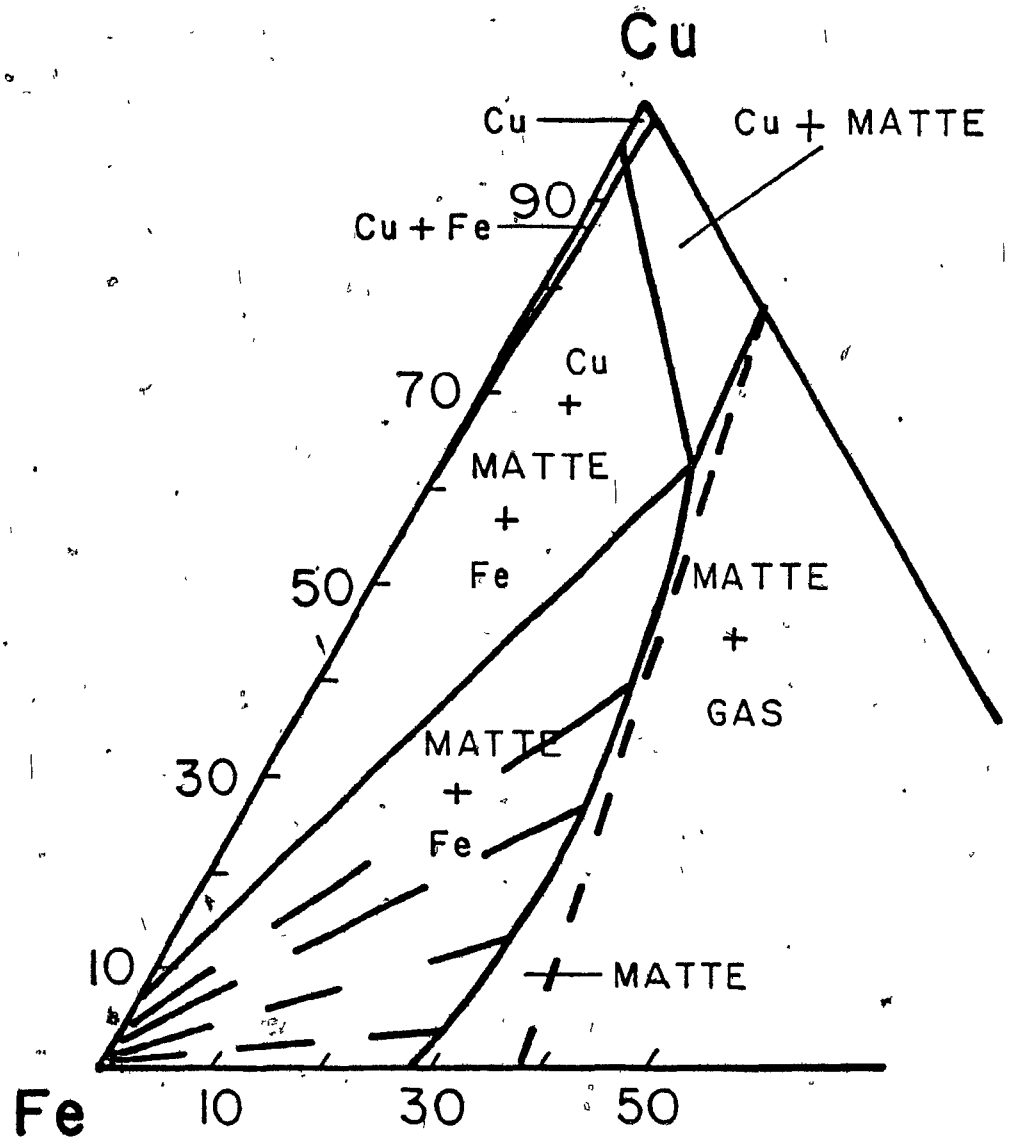


FIG. II.1.A 1423 K isothermal section of the Cu-Fe-S system (Krivsky and Schuhmann[2]).

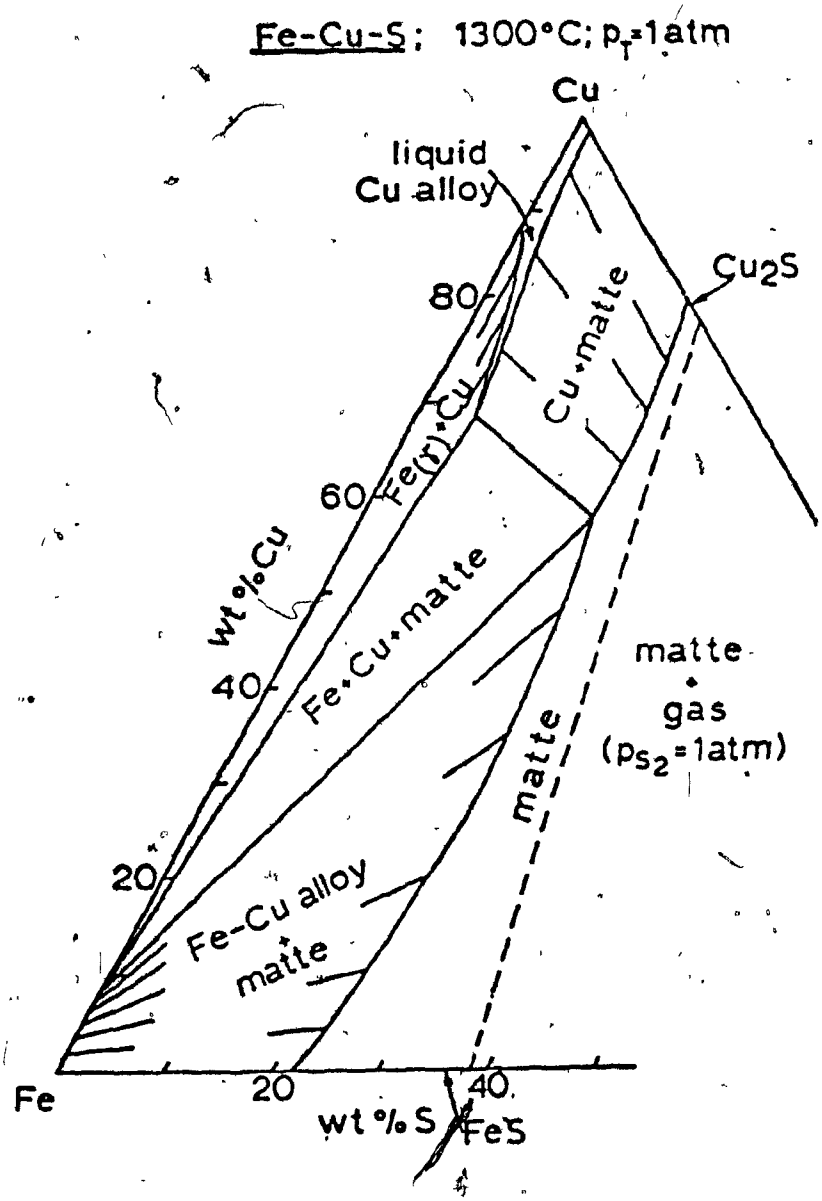


FIG.II.1.B : 1573 K isothermal section of the Cu-Fe-S system (reported by Elliott[3]).

who studied the system in an H_2/H_2S environment, i.e., under oxygen-free conditions. Elliott[3] has combined these data with data on the Cu-Fe-O, Cu-O-S and Fe-O-S diagrams to give an overall picture of matte systems. The liquidus range (1573 K, $\{pO_2 + pS_2 + pSO_2 + pSO_3\} < 1$ atmos.) is illustrated in Fig. II.2.

II.2 SLAGS

Copper smelting slags are represented by the Cu-Fe-O-SiO_2 system with CaO and Al_2O_3 as major impurities and other oxides such as MgO and ZnO as minor impurities. Copper smelting slags also contain up to 5% sulphur by virtue of contact with matte and concentrate.

The compositions of smelting furnace slags are adjusted (by adding appropriate amounts of flux) almost to the point of SiO_2-saturation. As will be seen in subsequent discussions, this procedure tends to minimize copper solubility in the slag.

In the high-silica composition range, slags are ionic in structure and they are made up largely of metal cations and silicate polymer anions. They are viscous (500 to 2000 centipoise) and they have a relatively low electrical conductivity (0.2 to 2 $ohm^{-1}\ cm^{-1}$)[1].

It is well established that silicate slags are ionic in nature. It is imperative, therefore, that ionic structure theory be taken into account in any mechanistic analysis of copper and sulphur solubility in slags.

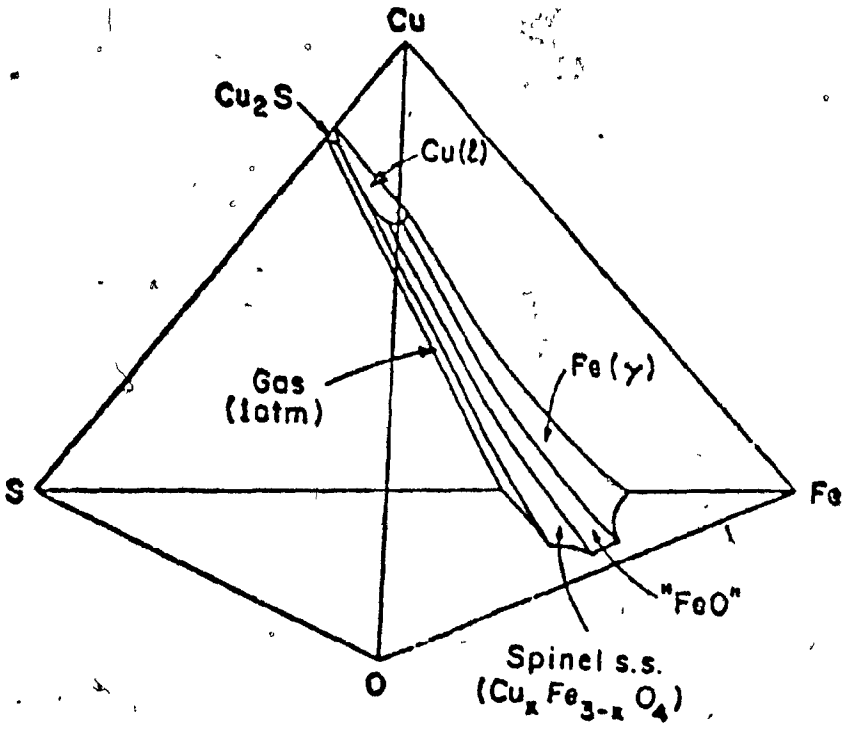


FIG.II.2 Phase volume of the liquid matte phase in the Cu-Fe-O-S tetrahedron (1573 K)[3].

II.3 SMELTING ATMOSPHERES

The gases in smelting furnaces have the following approximate compositions:

Furnace	Gas Composition (Vol %) SO_2	O_2	N_2	CO_2	CO	H_2O	Comments
Reverberatory	0.5 to 1.5	2	85	10	0		Measured 0.3 m above slag surface. Oxygen is due to air leaks.
Electric	0.4 to 5						Leaving furnace. SO_2 concentration depends on type of operation.
INCO flash	90	0	7	0	0	3	No air leakage.
Outokumpu flash	15 to 20	0	60 to 70	5 to 10	0	5 to 10	No air leakage.

This table shows clearly how the switchover to flash furnaces results in a smelting atmosphere which is much more concentrated in SO_2 than the traditional reverberatory and electric furnaces.

II.4 PREVIOUS EXPERIMENTAL WORK ON (METAL AND/OR MATTE)/SLAG/GAS SYSTEMS

Elliott[3] has made an extensive review of existing information on metal/matte/slag/gas systems. His review is best summarized by Figs. II.2 and II.3.A, II.3.B, the last being due primarily to Yazawa and co-workers[4,5,6,7].

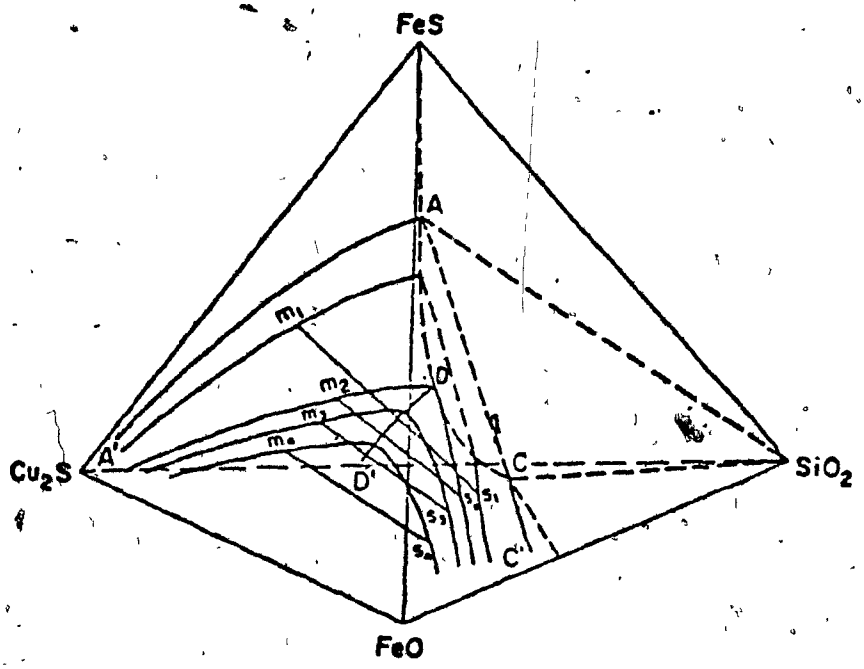


FIG. II.3.A Schematic diagram of the Cu_2S-FeS-FeO-SiO_2 system (1473 K, iron-saturation)[3,7]. 'm_i' and 's_i' describe the mattes and slags which are at equilibrium with each other under SiO_2 saturation conditions.

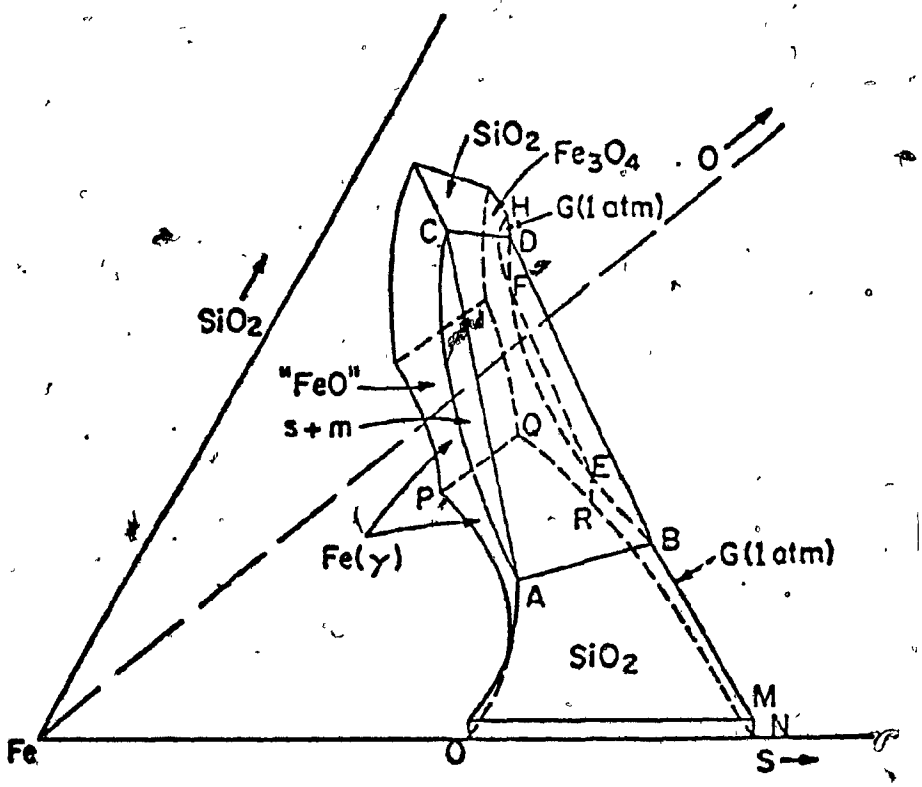


FIG. II.3.B Field of stability of the oxysulfide phase in the composition tetrahedron of the Fe-O-S-SiO_2 system (1573 K, Elliott[3]).

Recent experimental work on copper smelting systems can be divided into three categories of study:

(a)	Cu (metal)/slag/oxygen system:	iron, magnetite and/or silica saturated
(b)	matte/slag/gas (O_2, S_2, SO_2) system:	iron and/or silica saturated
(c)	Cu (metal)/matte/slag/gas (O_2, S_2, SO_2) system:	iron, wustite, magnetite and/or silica saturated

These studies are summarized in Table II.1 and their results are discussed in the following three sub-sections.

System	Experimenter	Temperature Range K	Oxygen Potential Range Atmos.	Comments
$Cu-Fe-O-SiO_2$ System	Ruddle, Taylor and Bates[14]	1573-1673	10^{-12} to 10^{-6}	Silica saturated.
	Toguri and Santander[15]	1573	10^{-10} to 10^{-7}	Fayalite slags, with approximately 6% Al_2O_3.
	Altman and Kellogg[16]	1500-1560	10^{-12} to 10^{-6}	SiO_2 saturated iron silicate slag.
	Bailey et al.[8]	1573	10^{-12} to 10^{-6}	SiO_2 saturated iron silicate slags gave copper solubilities similar to above studies. An industrial slag (38% SiO_2, 16% Fe, 19% CaO, 17% Al_2O_3, 4% K_2O) gave much lower Cu solubilities (II.4).

TABLE II.1 Summary of Recent $Cu-Fe-O-S-SiO_2$ Studies

System	Experimenter	Temperature Range K	Oxygen Potential Range Atmos.	Comments
Cu-Fe-O-S-SiO_2 (no copper phase)	Yazawa and Kameda[10]	1473-1573	Iron saturation	% Cu in slag increases, %S in slag decreases, % O in matte increases with increasing matte grade (Figs. II.9, II.10, II.11).
	Spira and Themelis[12]	1473	Unknown, more oxidizing than Yazawa's work	% Cu in slag and % O in matte higher than Yazawa's (Fig. II.9).
	Bor and Tarassoff[11]	1473	Iron and silica saturation	% O in matte only. Similar results to Yazawa (Fig. II.12).
	Nagamori[9]	1473	Iron and silica saturation	Higher % Cu in slag and lower % S in slag than Yazawa (Figs. II.9, II.10).

TABLE II.1 (cont'd.) Summary of Recent Cu-Fe-O-S-SiO_2 Studies

System	Experimenter	Temperature Range K	Oxygen Potential Range Atmos.	Comments
Cu-Fe-O-S-SiO_2 (copper phase present)	Johansen, Rosenqvist and Torgerson[19]	1400-1700	$pSO_2 = 1$ with or without Fe_3O_4 saturation	Somewhat few experimental results.
	Gevici and Rosenqvist[18]	1523	Fe and/or FeO and/or Fe_3O_4 and/or SiO_2 saturation	Minimum % Cu in slag found at Fe and SiO_2 double saturation (Fig. II.13). Maximum at Fe_3O_4 and SiO_2 double saturation.

TABLE II.1 (cont'd.) Summary of Recent Cu-Fe-O-S-SiO_2 Studies

II.4.A Cu(Metal)/Slag/Oxygen Studies ($Cu-Fe-O-SiO_2$ System)

Although the Cu/slag/oxygen system is not of direct commercial importance, it is a relatively straightforward system to study (under CO/CO_2 atmospheres) and it forms one of the quaternary boundaries of the $Cu-Fe-O-S-SiO_2$ matte/slag quinary system. For these reasons it has received considerable attention as is summarized in Table II.1 and Fig. II.4.

The experimental results are unanimous in showing that the concentration of copper in an oxide (slag) phase coexisting with copper metal increases with:

increasing pO_2,

increasing temperature.

On the basis of these results and other measured and estimated data, Elliott[3] has constructed composition surfaces for the copper-saturated iron-silica oxide phase as is shown in Figs. II.5, II.6 and II.7). In essence, these surfaces indicate for a given temperature, pO_2 and Fe/SiO_2 ratio, the concentration of copper which will be present in an oxide phase in equilibrium with metallic copper. The effect of increasing oxygen potential is clearly shown.

The effects of other slag components (Al_2O_3, CaO, MgO, ZnO) have been reviewed by Bailey[8]. He was unable to draw any definitive conclusions.

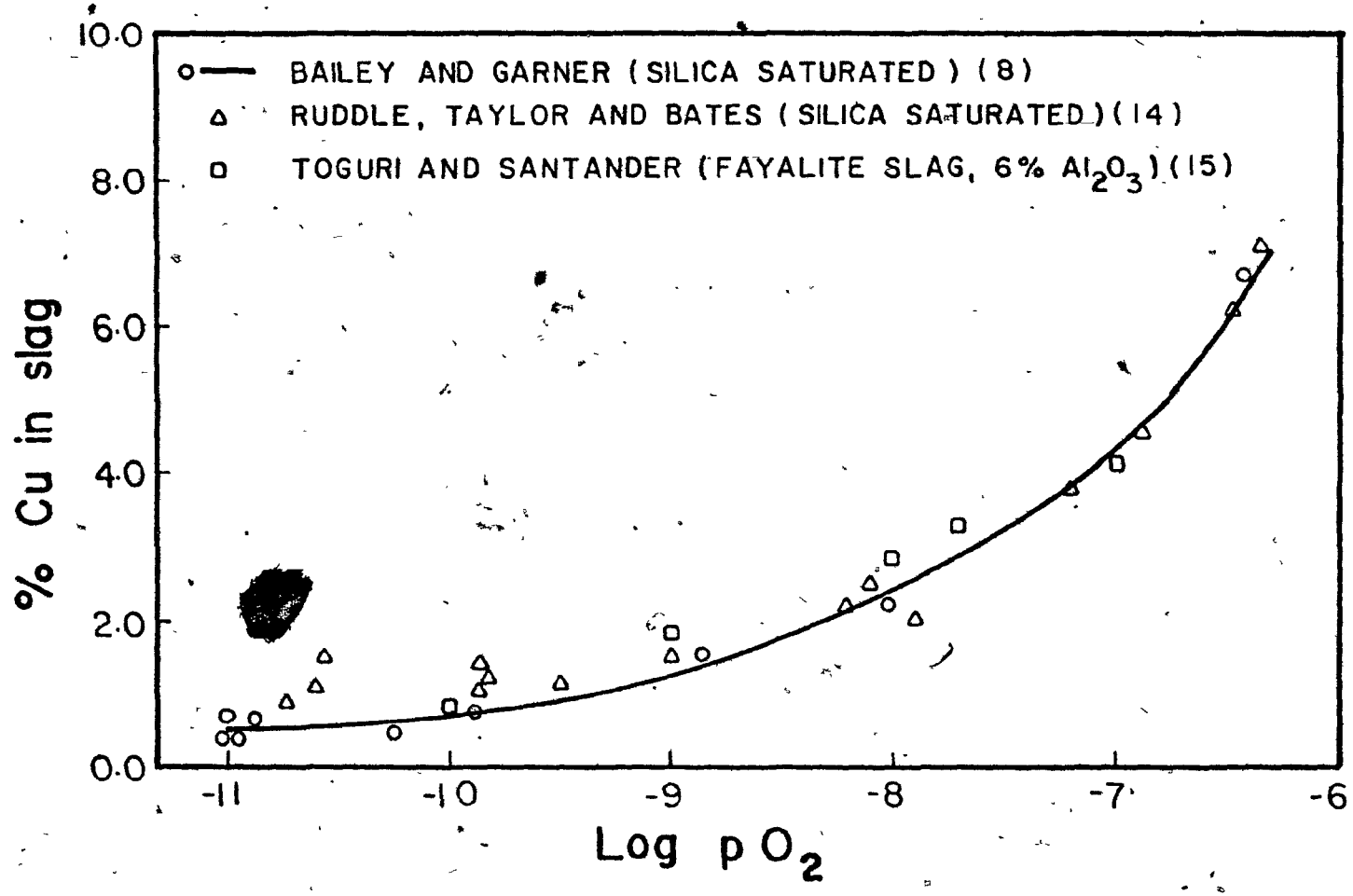


FIG. II.4 Measured copper-in-slag concentrations, Cu-Fe-O-SiO_2 system, under copper and SiO_2 saturation conditions. The increase in copper solubility with increasing pO_2 is notable.

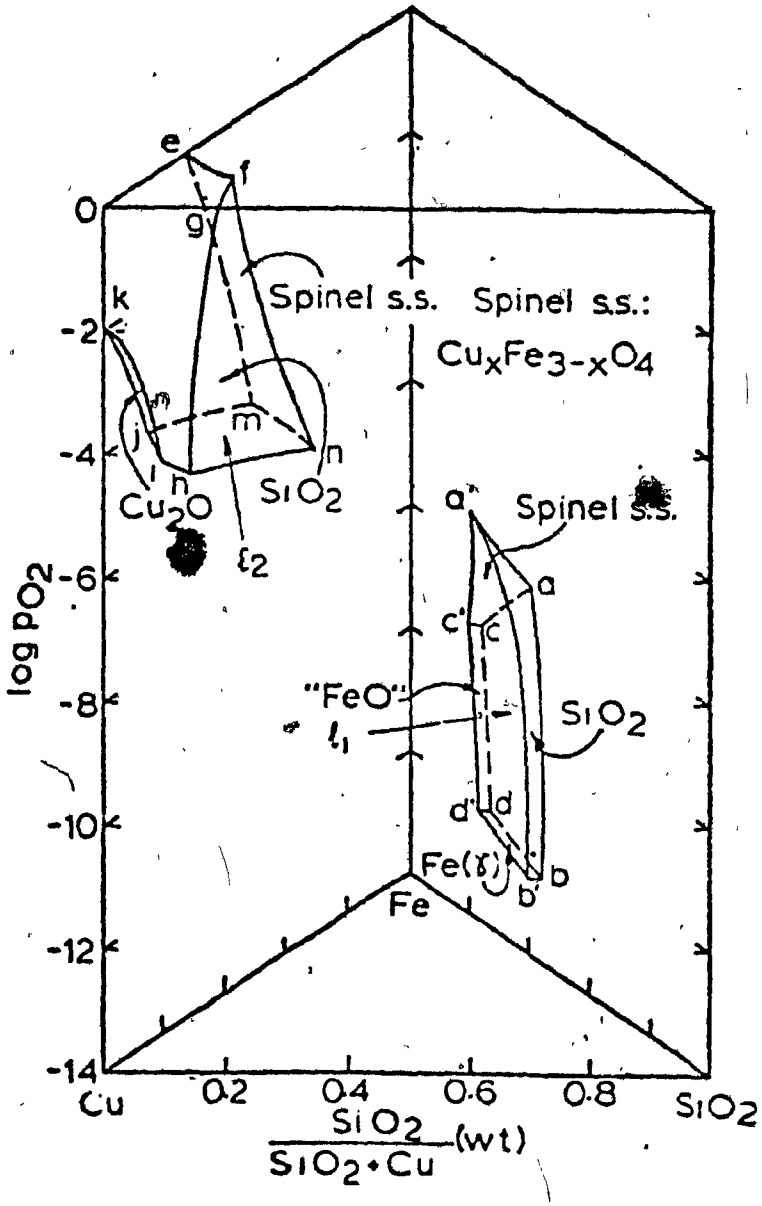


FIG.II.5 Extension of the regions of stability of the liquid ferrous-silicate phase (slag, of ℓ_1) and copper-silicate (ℓ_2) phase into the quaternary volume (1473 K, Elliott[3]).

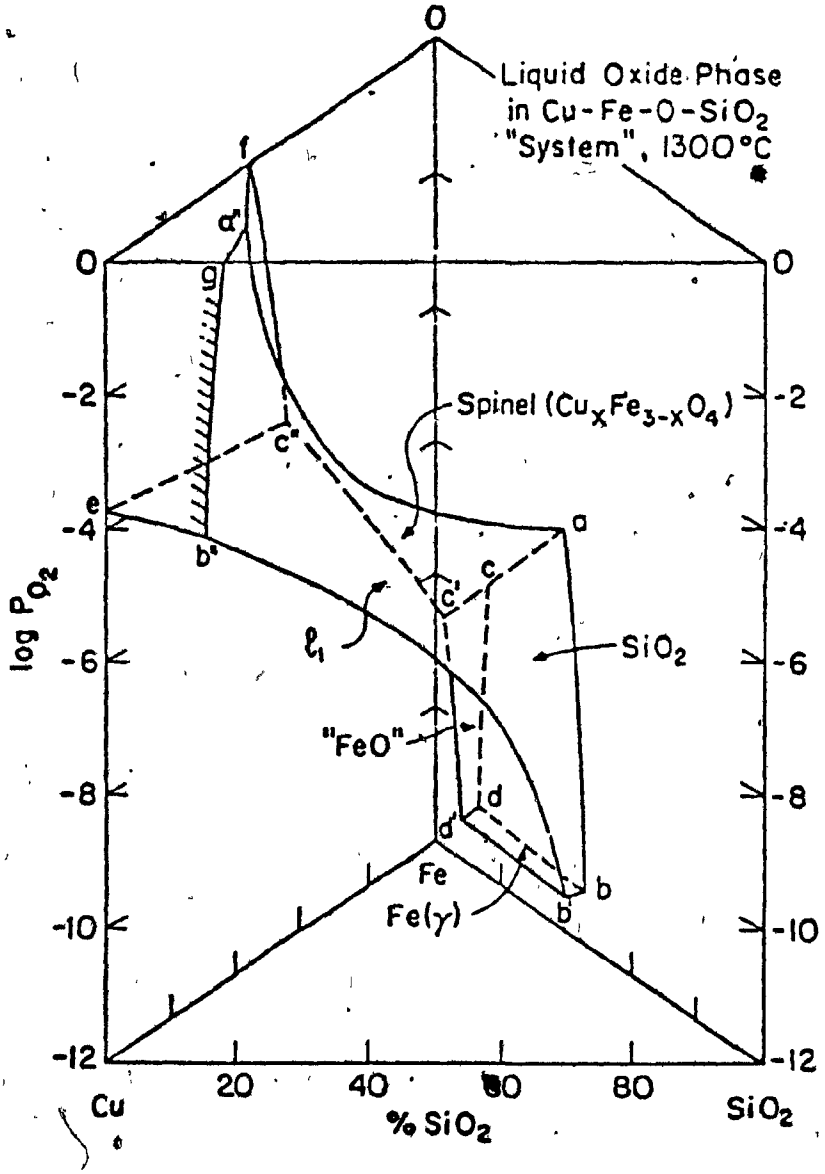


FIG. II.6 Region of stability of the liquid oxy-silicate phase in the Cu-Fe-O-SiO_2 system (1573 K, Elliott[3]).

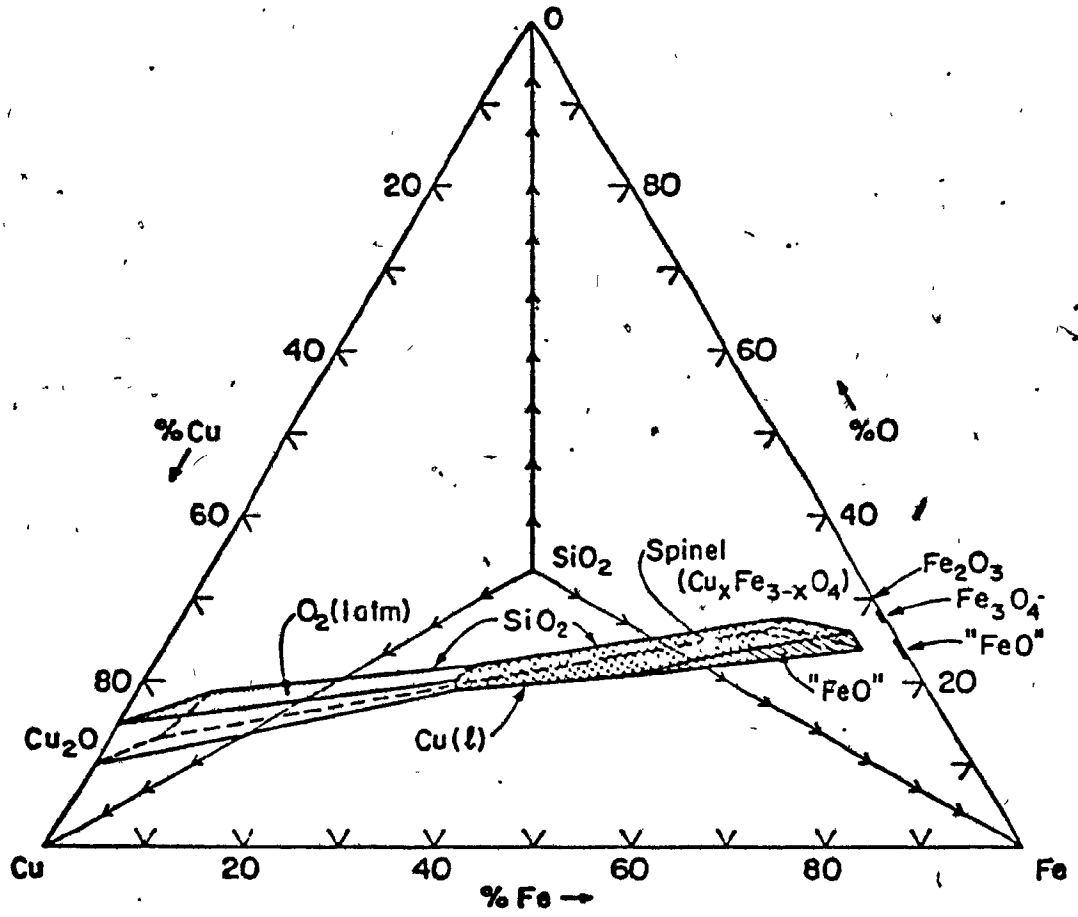


FIG.II.7 Position of the liquid oxide phase in the Cu-Fe-O-SiO_2 composition tetrahedron (1573 K, Elliott[39]).

II.4.B Matte/Slag/Gas (O_2, S_2, SO_2) System

Nagamori[9], Yazawa and Kameda[10], Bor and Tarassoff[11], and Spira and Themelis[12] have carried out significant studies on this system - the first three under iron and silica double saturation conditions and the last without iron saturation (Table II.1). In all cases the experiments were carried out under a neutral atmosphere into which O_2, S_2 and SO_2 could slowly escape. The partial pressures of the gases were not, therefore, truly fixed and the systems cannot be said to have been in true equilibrium. The partial pressures of O_2, S_2 and SO_2 are, however, very low under iron saturation conditions and thus continued flushing of them from the system should not, therefore, appreciably affect the composition of the coexistent condensed phases (Yazawa)[13].

The results of these investigators are presented in Figs. II.8, II.9, II.10, II.11 and II.12 from which it can be concluded (under iron and silica saturation conditions, at least) that with a matte of increasing copper content:

(a) % Cu in the coexistent slag phase increases;

(b) % S in the slag phase decreases; and

(c) % O in the matte decreases.

Spira and Themelis[12] obtained similar results under non-iron saturation conditions.

Elliott[3] has developed a more general view of the matte slag system based largely on the experimental work of Yazawa and co-workers[4,5,6,7] (Figs. II.2, II.4, II.8). The overall matte/slag system is described in terms of a Cu_2S, FeS, FeO, SiO_2 quaternary diagram (Fig. II.3.A) while the copper-free part of the system is described in ternary and quaternary form (Figs. II.3.B, II.8).

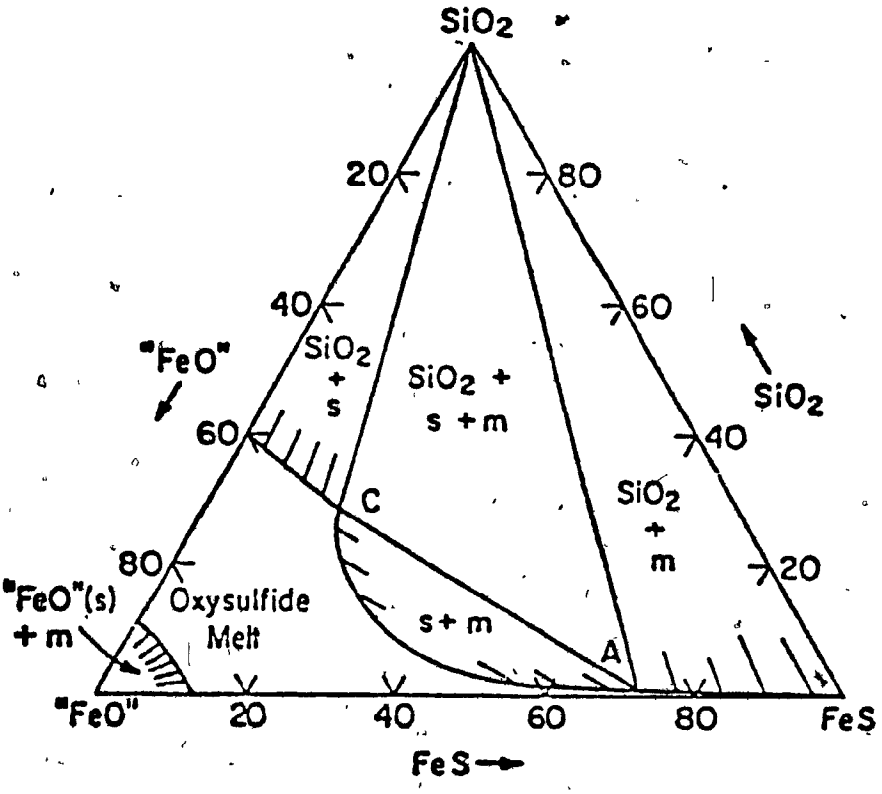


FIG.II.8 The FeO-FeS-SiO_2 system at iron-saturation conditions (1573 K, Elliott[3]).

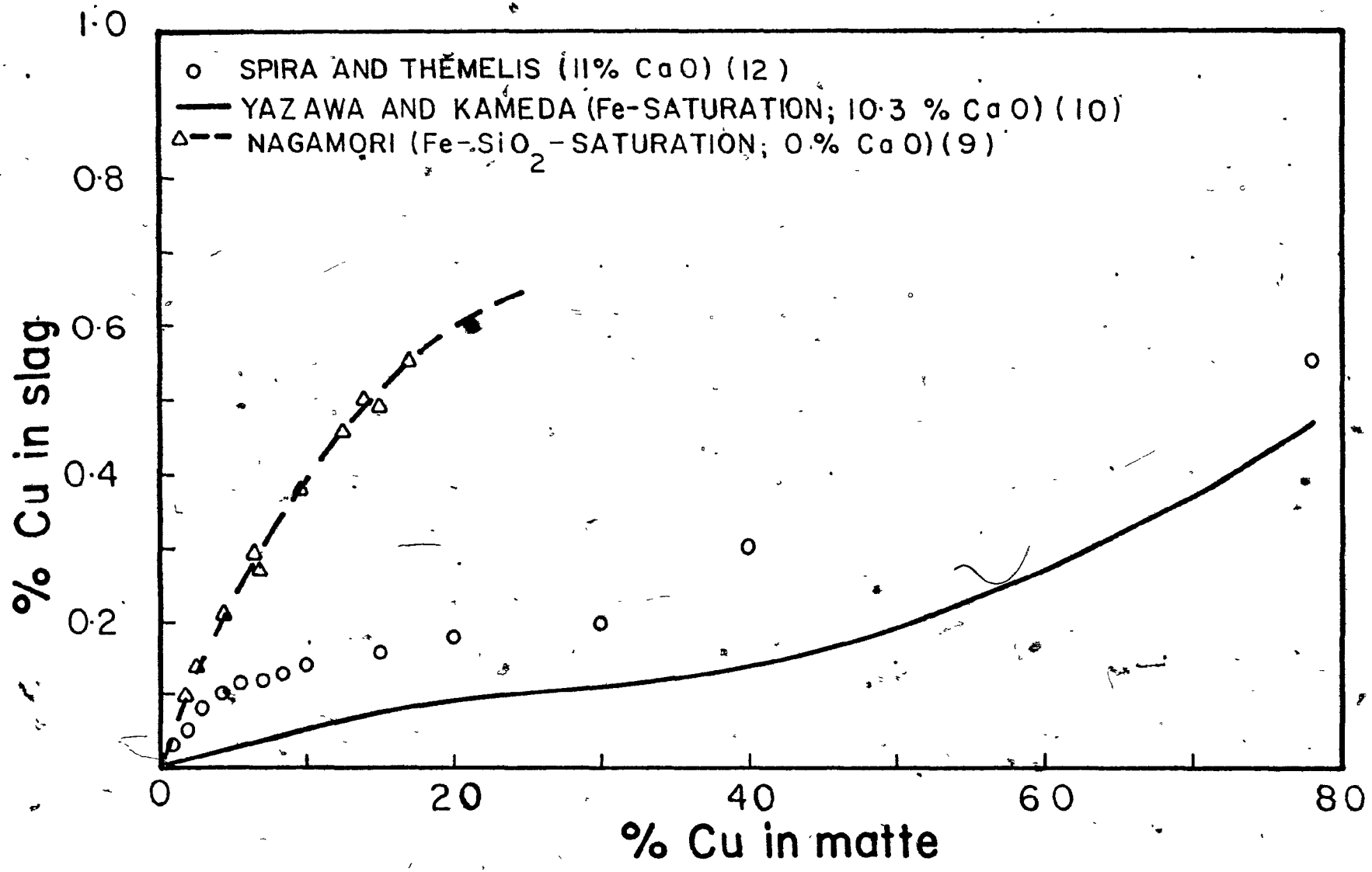


FIG.II.9 Measured copper-in-slag concentrations, Cu-Fe-O-S-SiO_2 system, as a function of matte grade. The experimental conditions are shown in the Figure.

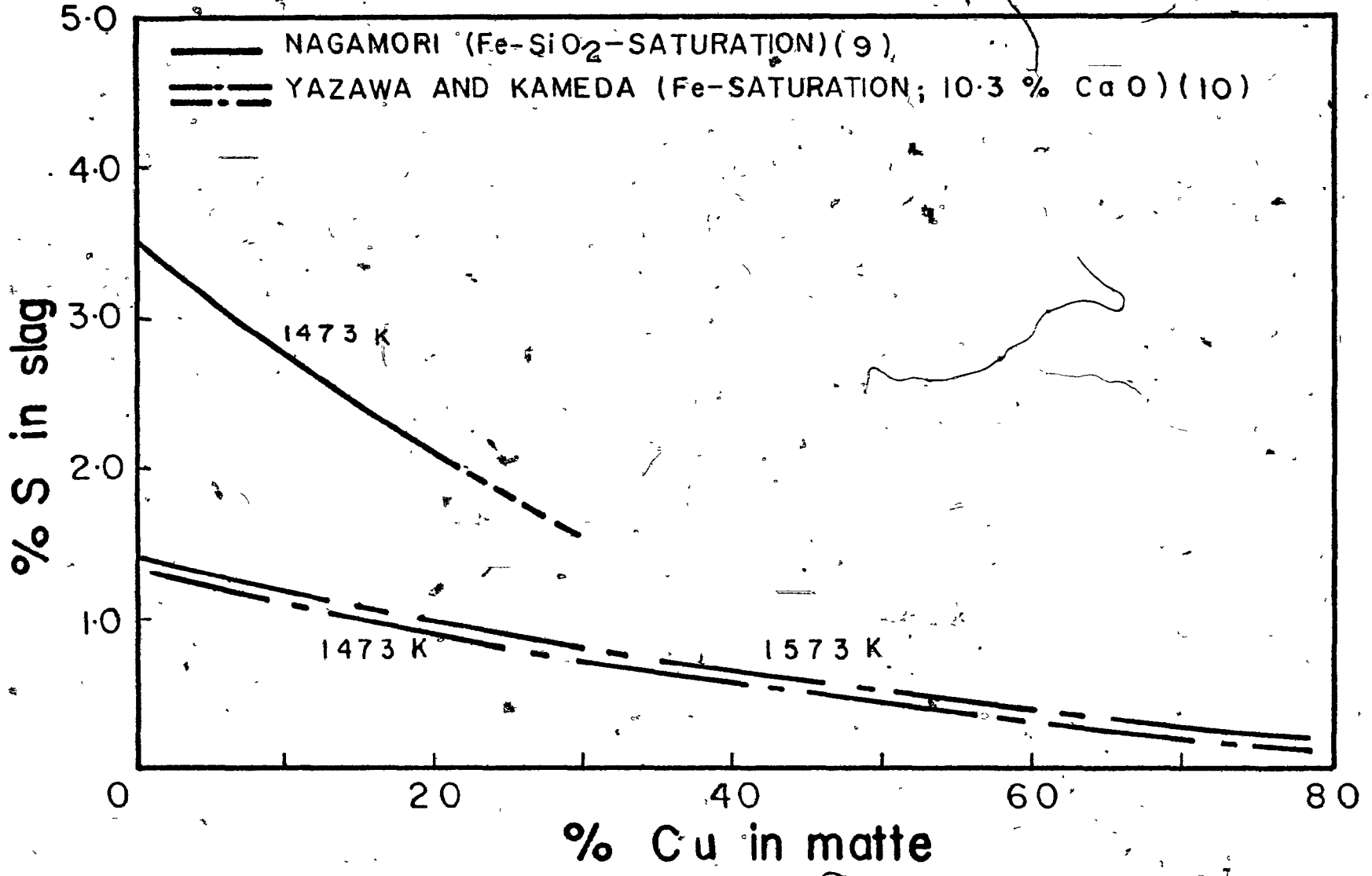


FIG.II.10 Measured sulphur contents of slags, Cu-Fe-O-S-SiO_2 system (iron saturated), as a function of matte grade.

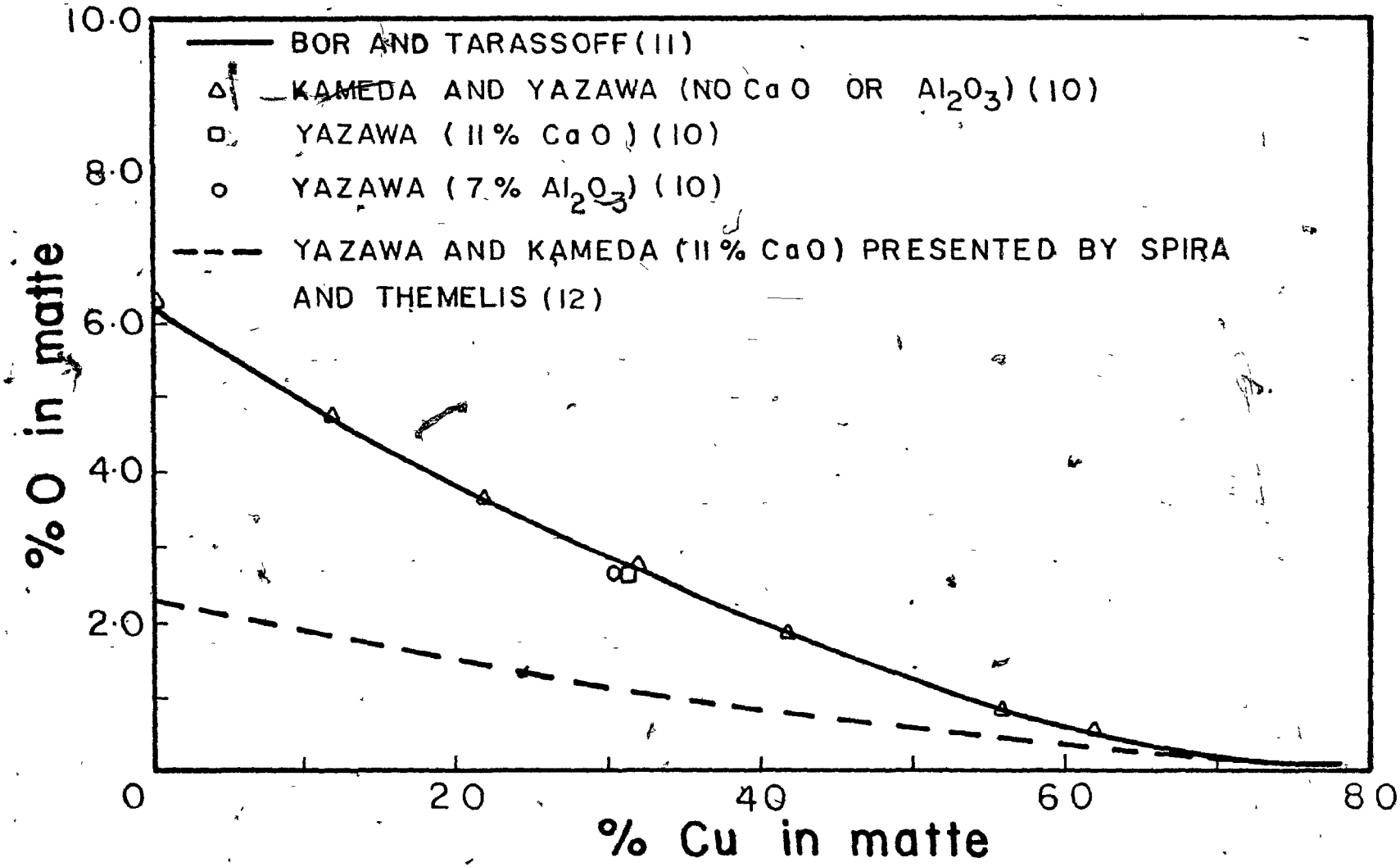


FIG.II.11 Measured oxygen contents of mattes, Cu-Fe-O-S-SiO_2 system (iron saturated), as a function of matte grade. The Bof and Tarassoff[11] data are detailed in Figure II.12.

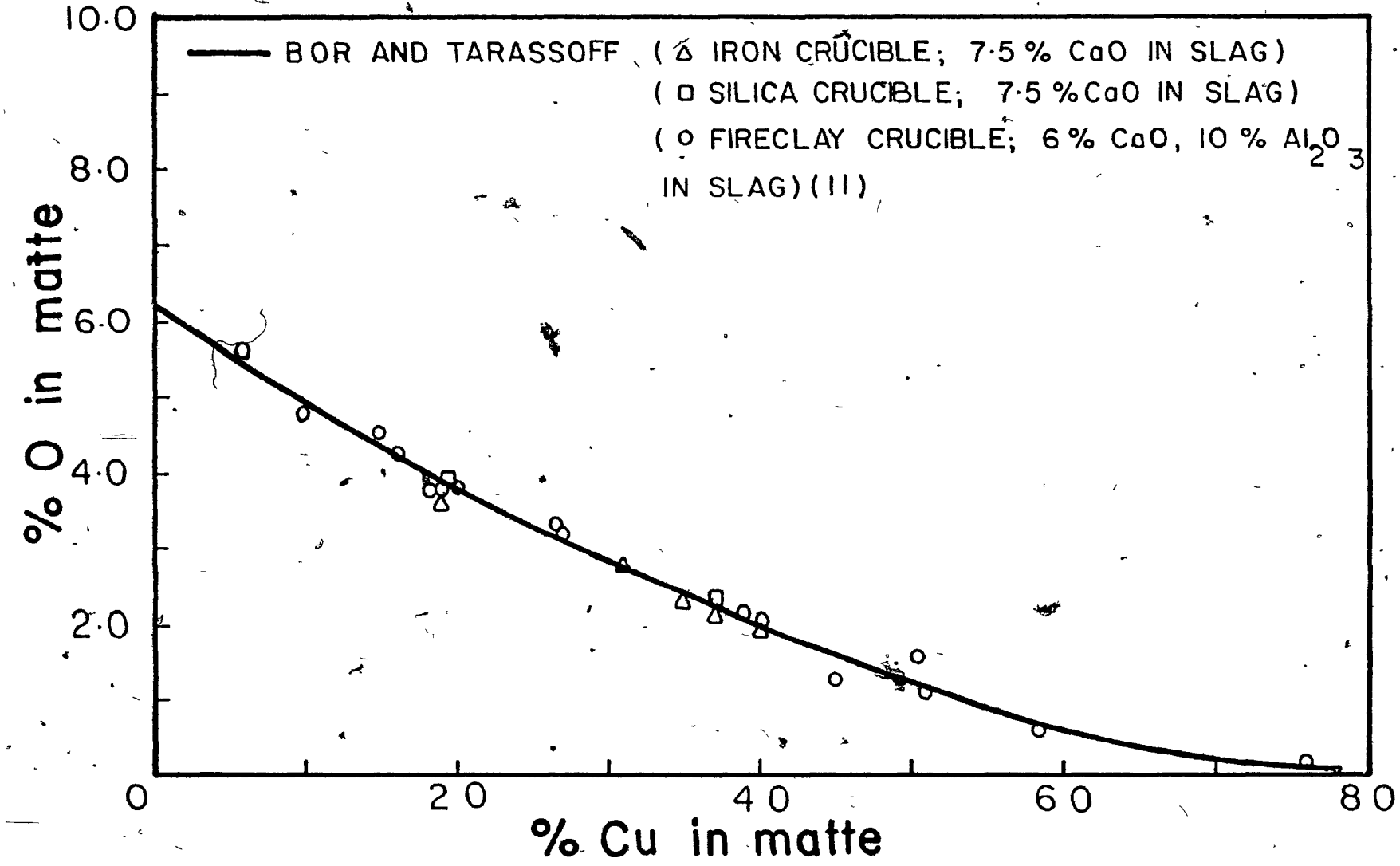


FIG.II.12 Oxygen solubility in mattes under various experimental conditions as measured by Bor and Tarassoff[11] (1473 K).

As would be expected from the discussions above, each representation indicates the presence of large composition regions where matte (oxysulphide) and silicate (slag) phases coexist. The general conclusions from the diagrams are that:

(a) the separation of a sulphide phase from an oxide phase is most efficient when the system is silica saturated; i.e., under these conditions the oxide contains a minimum concentration of sulphur and the sulphide phase contains a minimum concentration of oxygen;

(b) the concentration of copper in the oxide (slag) phase is minimized by silica saturation (under iron saturation conditions, at least, Fig. II.3.A).

Elliott[3] points out that an important missing piece of information is the behaviour of the Cu_2S-FeS-FeO-SiO_2 system under non-iron saturation conditions.

II.4.C Cu (Metal)/Matte/Slag/Gas (O_2, S_2, SO_2) System

In addition to the matte/slag studies described immediately above, several studies of the copper metal/matte/slag system have been made.

The most complete of these studies is the work of Rosenqvist and co-workers[18,19] whose more significant results are summarized in Figs. II.13, II.14, II.15, II.16). In essence, these investigators prepared mixes of copper metal, iron powder, copper sulphide and 'master' slag (50 to 55% FeO, 12% Fe_2O_3, 37% SiO_2) in proportions calculated to give copper metal and a desired matte and slag composition. These mixes

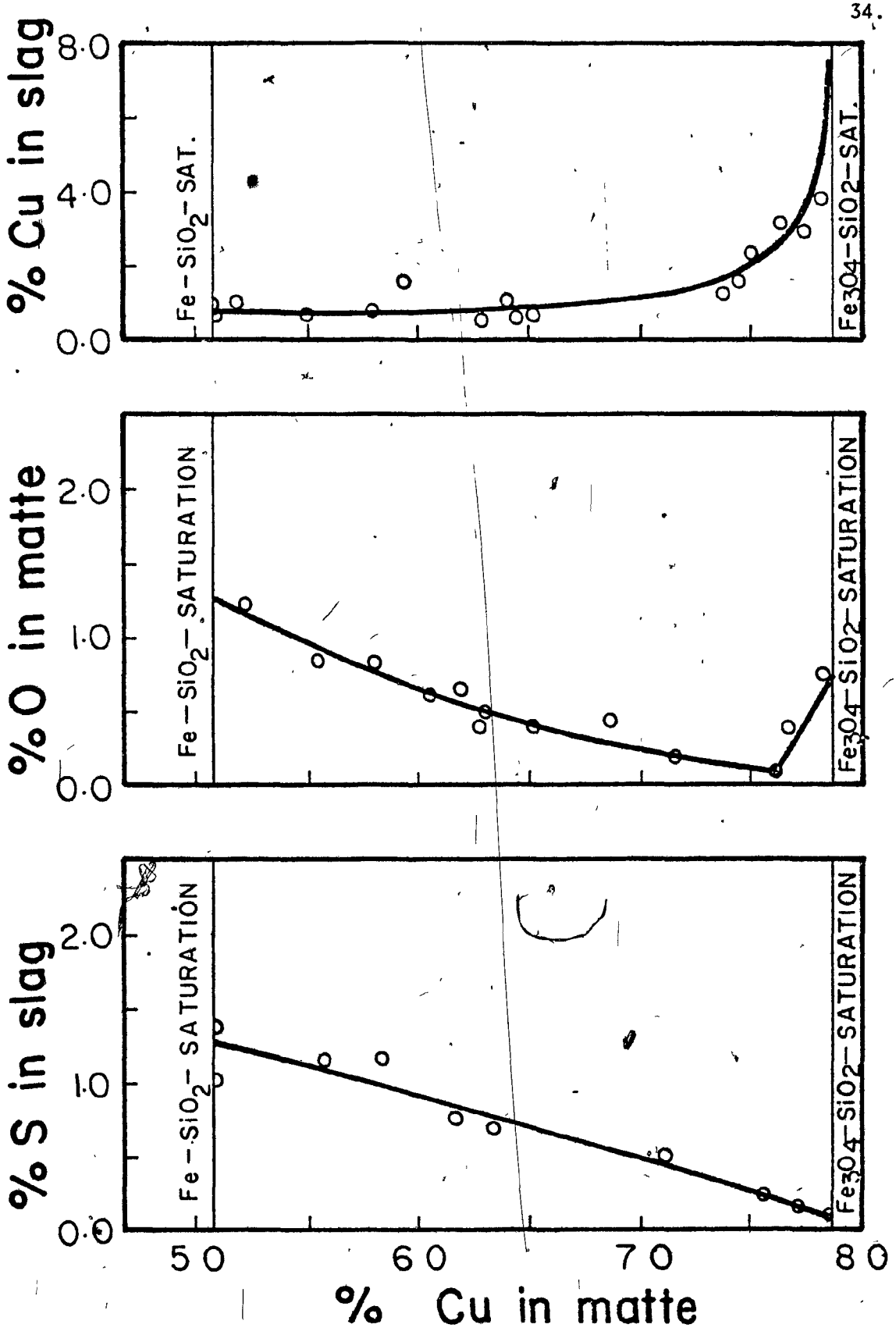


FIG.II.13 Copper-in-slag, sulphur-in-slag and oxygen-in-matte concentrations, Cu-Fe-O-S-SiO_2 system (copper and SiO_2 saturation conditions), as measured by Geveci and Rosenqvist[18] (1523 K).

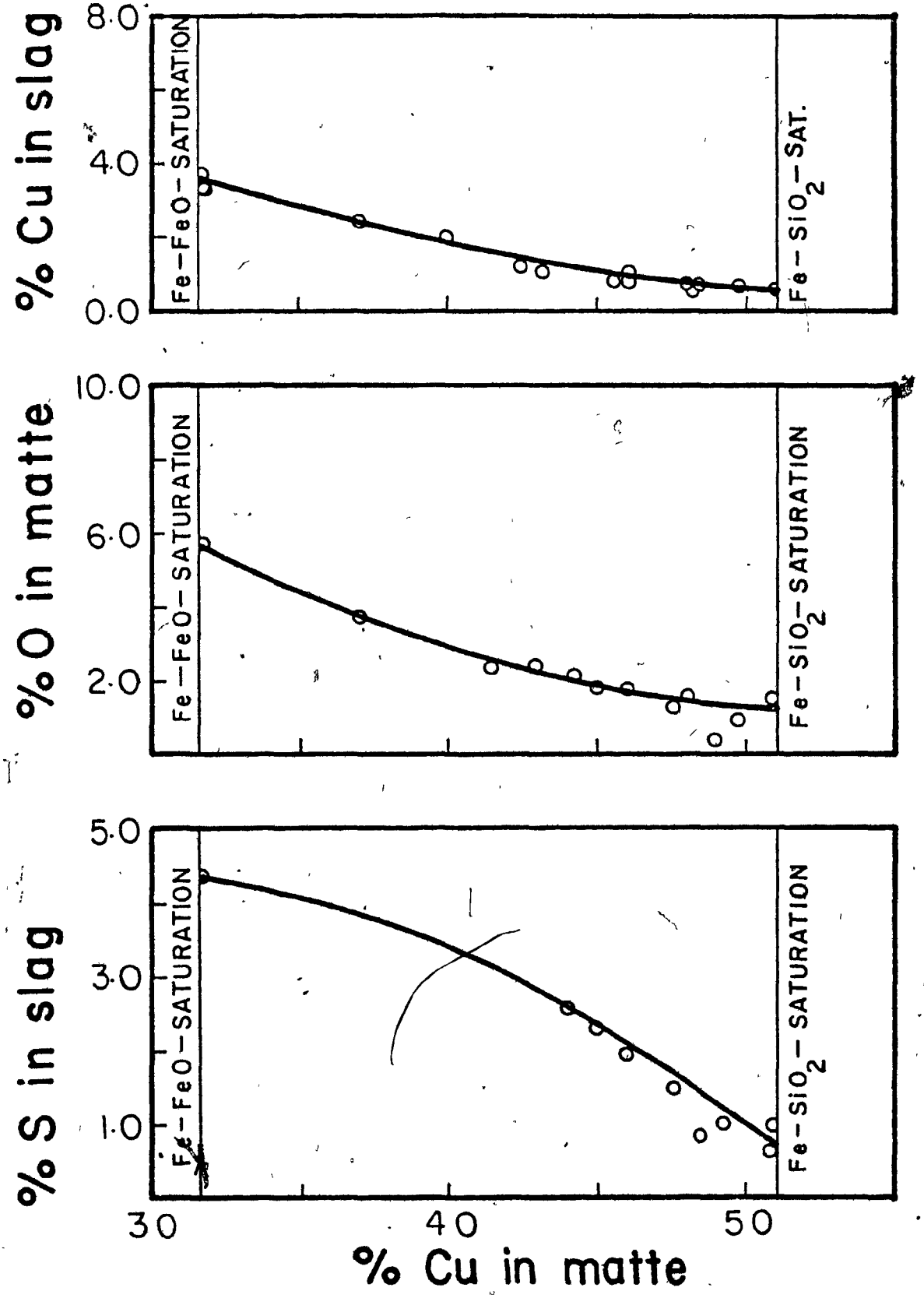


FIG.II.14 Copper-in-slag, sulphur-in-slag and oxygen-in-matte concentrations, Cu-Fe-O-S-SiO_2 system (copper and iron saturation conditions), as measured by Geveci and Rosenqvist[18] (1523 K).

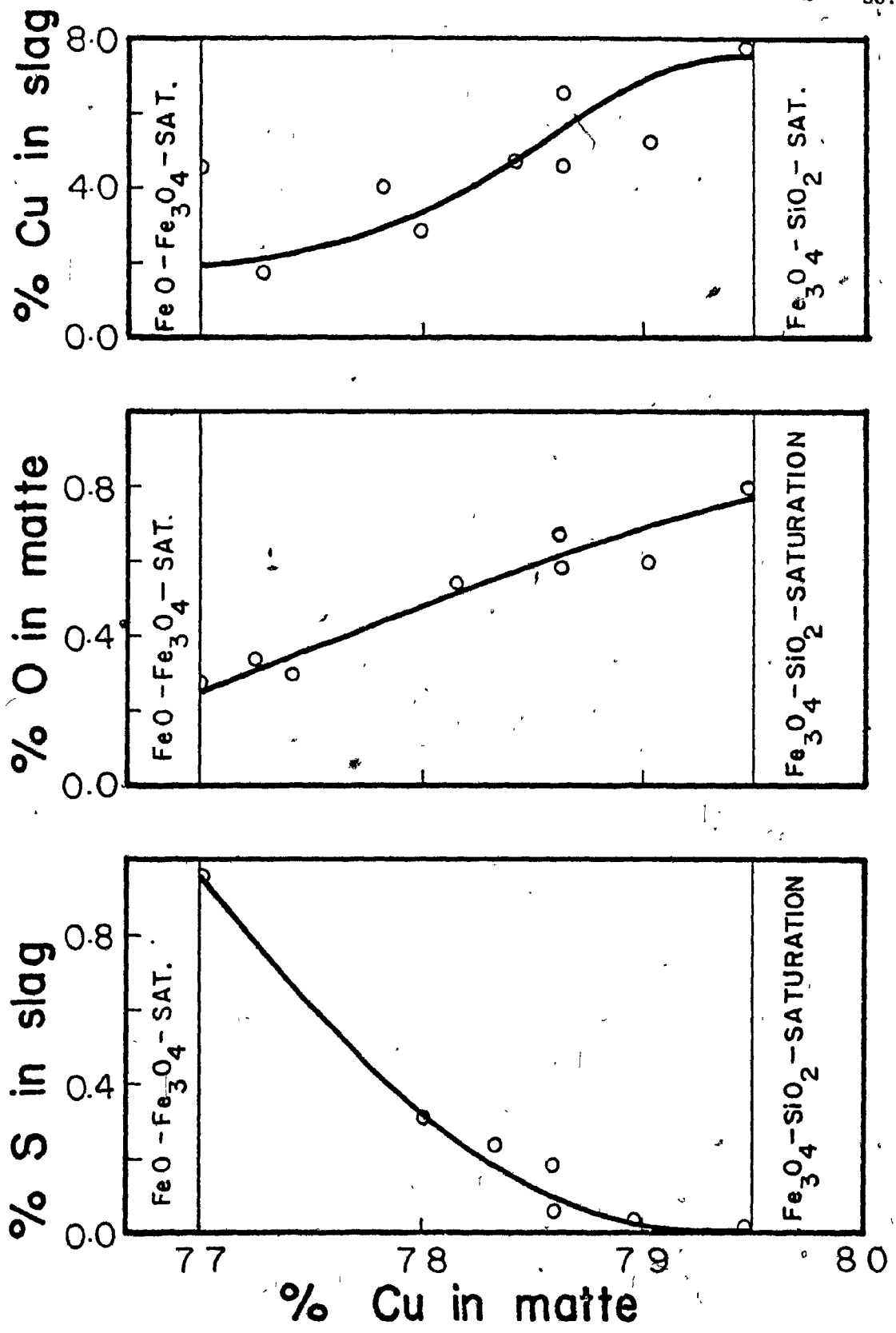


FIG. II.15 Copper-in-slag, sulphur-in-slag and oxygen-in-matte concentrations, Cu-Fe-O-S-SiO_2 system (copper and Fe_3O_4-saturation conditions), as measured by Geveci and Rosenqvist[18] (1523 K).

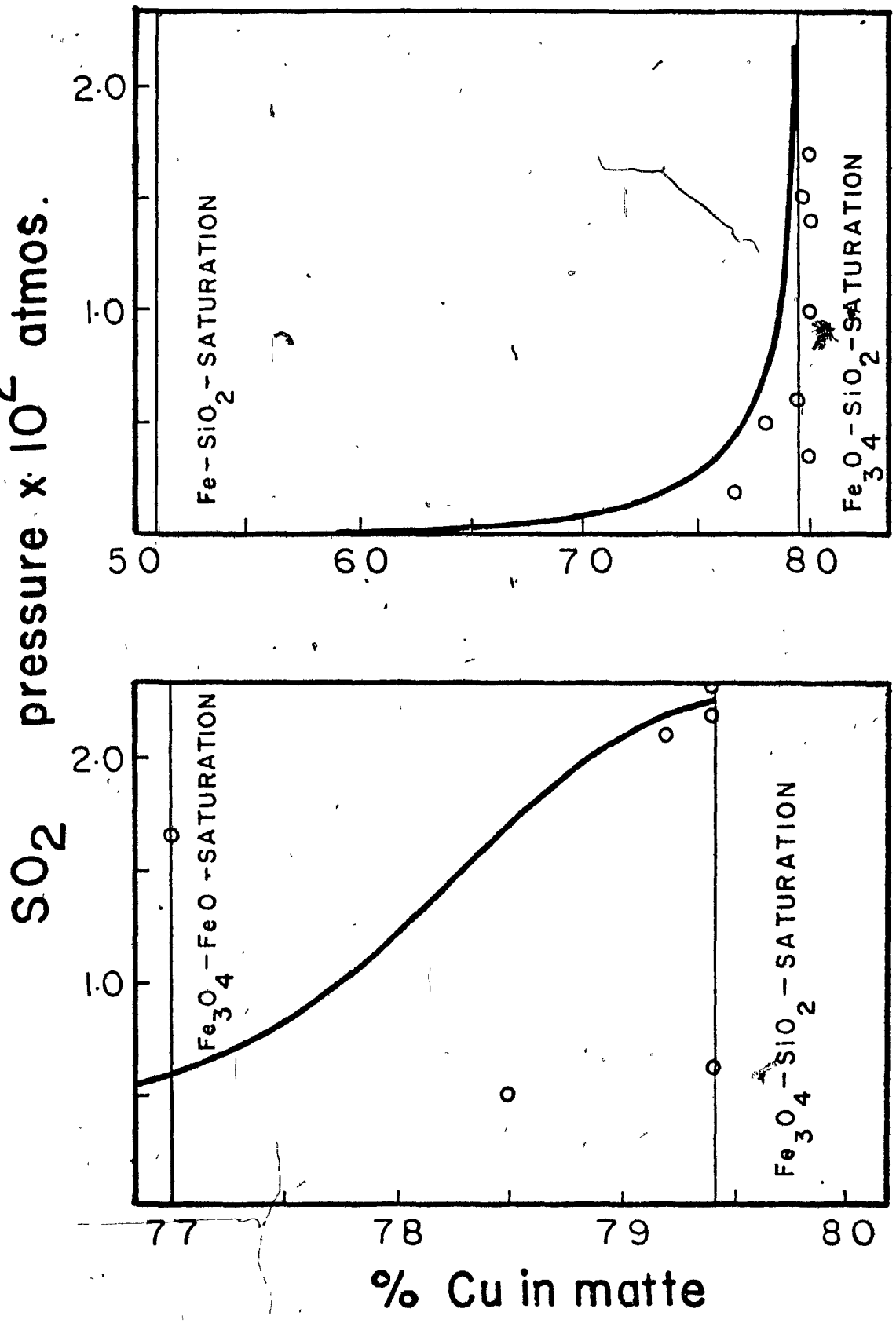


FIG.II.16 SO_2 pressures over the Cu-Fe-O-S-SiO_2 matte/slag system (copper saturation conditions), as measured by Geveci and Rosenqvist[18], 1523 K. Other saturation conditions are indicated in the Figures.

were then melted and held at 1523 K for 5 to 17 hours in a flowing nitrogen atmosphere. The SO_2 content of the effluent nitrogen was also determined for some experiments.

This 4-phase, 5-component (Cu, Fe, O, S, Si) system has, by the phase rule, only two degrees of freedom in addition to temperature. As soon, therefore, as two additional parameters are specified, e.g., (a) the activity or concentration of Cu_2S in the matte; and (b) the activity or concentration of Fe_3O_4 in the slag; the system is fully defined.

Most of Rosenqvist's[18] work was, in fact, carried out in the presence of a fifth separate phase, i.e., in iron, magnetite, or silica crucibles so that after temperature (1523 K) had been specified, only one degree of freedom remained to fully define the system. Matte grade (% Cu in the matte phase) was usually chosen for this final specification.

Based on this discussion and the experimental results of Gevici and Rosenqvist[18], the following observations can be drawn.

SiO_2 Saturation Conditions (Fig. II.13 and II.16)

When the system is altered from iron saturation towards magnetite saturation, the coexistent phases adjust in the following manner:

Matte phase:	% Cu increases
	% Fe decreases
	% O decreases
Slag phase:	% Cu increases
	% S decreases
	Fe^{++}/Fe^{+++} increases (not shown on graphs)
Gas phase:	pSO_2 increases

Iron Saturation Conditions (Figs. II.14, II.16)

Alteration of the system from FeO to SiO_2 saturation affects the phases in the following ways:

Matte phase: % Cu increases
% Fe decreases
% O decreases

Slag phase: % Cu decreases
% S decreases
Fe^{++}/Fe^{+++} decreases (not shown)

Gas phase: pSO_2 decreases (not shown)

Fe_3O_4 Saturation Conditions (Figs. II.15, II.16)

Changing the system from FeO to SiO_2 saturation conditions alters the phases as follows:

Matte phase: % Cu increases
% Fe decreases
% O increases

Slag phase: % Cu increases
% S decreases
Fe^{++}/Fe^{+++} increases (not shown)

Gas phase: pSO_2 increases

Geveci and Rosenqvist[18] conclude that the copper-in-slag content is:

(a) at a minimum (0.5% Cu) under Fe and SiO_2 saturation conditions (50% Cu in matte); and

(b) at a maximum (7.6% Cu) under Fe_3O_4 and SiO_2 saturation conditions (79.5% Cu in matte).

Sulphur in slag is, on the other hand:

(a) at a minimum (0.01% S) at Fe_3O_4 and SiO_2 saturation (79.4% Cu in matte); and

(b) at a maximum (4.4% S) at FeO and Fe saturation (32% Cu in matte);

while oxygen in matte is:

(a) at a minimum (0.05% O) under Fe_3O_4 and SiO_2 saturation conditions (79.5% Cu in matte); and

(b) at a maximum (5.5% O) at Fe and FeO saturation (32% Cu in matte).

II.5 OVERALL STATUS OF Cu-Fe-O-S-SiO_2 STUDIES

The above review indicates that the Cu-Fe-S (matte) ternary system is well known. Likewise, slag structures and properties have been studied extensively.

The Cu-Fe-O-SiO_2 system has been closely examined for oxygen pressures between 10^{-12} and 10^{-6} atmospheres and further experiments in this range would seem to merely repeat previous studies. The system is only partially understood at oxygen pressures between 10^{-6} and 10^{0} atmospheres and further study in this pressure region is well warranted.

Matte/slag studies have been much fewer in number than Cu-O-SiO_2 studies because of their greater experimental complexity. The most complete study is that of Gevici and Rosenqvist[18] for the matte/slag system in the presence of a separate copper phase. There is some scatter

in these results and the experiments are restricted to one temperature so that this work should be repeated and expanded.

Most other matte/slag studies have been carried out under iron saturation conditions, i.e., under conditions which are much more reducing than conditions in flash smelting furnaces. These studies should be extended to more highly oxidizing conditions.

The work in this thesis represents such an attempt to expand matte/slag knowledge away from iron saturation conditions towards industrial smelting (high pSO_2) conditions.

III. EXPERIMENTAL

The experiments of this study consisted essentially of equilibrating Cu_2S-FeS mattes and silica-saturated Fe-O-SiO_2 slags under controlled pressures of SO_2. The principal measured parameters were:

Independent variables	pSO_2 (0.1 to 1.0 atmos).
	Temperature (1423 to 1573 K).
	Initial matte composition.
	Initial slag composition.
	Silica saturation conditions (silica crucible).
Dependent variables (in coexistent phases)	% Cu in slag.
	Fe^{++}/Fe^{+++} ratio in slag.
	% S in slag.
	% O in matte.

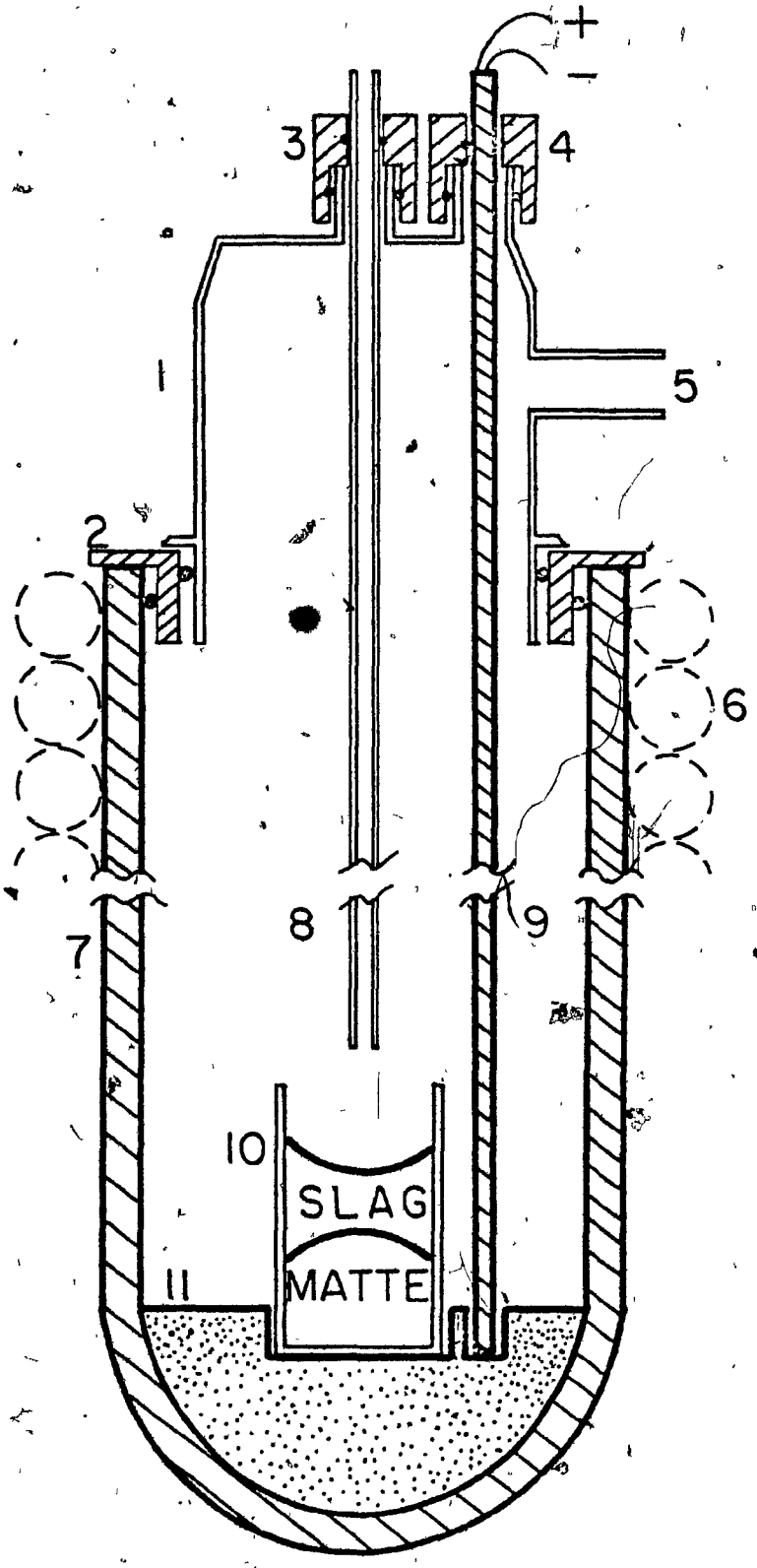
III.1 APPARATUS

The experiments were all carried out in quartz crucibles (23 mm O.D., 20 mm I.D., 35 to 45 mm long, LaSalle Glass Blowing Co., Montreal) placed in a gas tight refractory tube assembly (Fig. III.1), all heated in a 3.7 Kw Kanthal-wound resistance tube furnace (Figs. III.2, III.3).

Furnace temperature was controlled by means of a Pt/Pt-13% Rh thermocouple sensor placed against the bottom of the outer refractory tube and a Lindberg Type 59545 temperature controller (Tech-Met Canada Ltd.,

Fig. III.1 EXPERIMENTAL REACTION SYSTEM SHOWING UPPER AND LOWER PARTS OF THE REACTION TUBE

1. Glass cover.
2. Glass cover brass O-ring adapter.
3. Silica lance brass O-ring adapter.
4. Thermocouple insulator brass O-ring adapter.
5. Gas outlet.
6. Copper water cooling jacket.
7. Reaction tube (600 mm long x 70 mm O.D., 5 mm thickness).
8. Gas lance (silica) (6 mm O.D., 4 mm I.D.).
9. Alumina thermocouple insulator.
10. Quartz reaction crucible (23 mm O.D., 20 mm I.D., 35 to 45 mm long).
11. Alumina holder.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SLAG
MATTE
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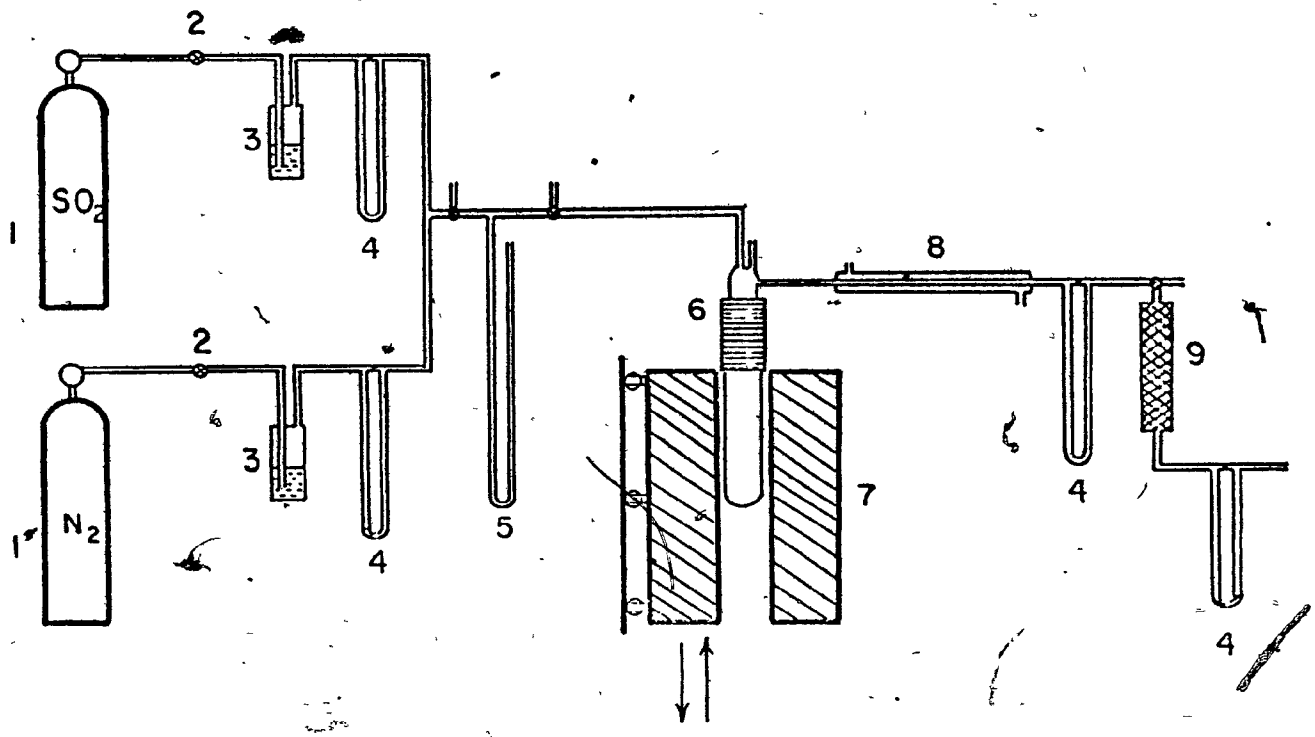

FIG. III.2 Schematic representation of the experimental apparatus:
1) gas tank (SO_2 or N_2); 2) microvalve;
3) H_2SO_4 bubbling flask; 4) capillary flowmeter; 5) H_2SO_4 manometer; 6) reaction tube;
7) vertical tube furnace; 8) heat exchanger;
9) SO_2 absorption tube.

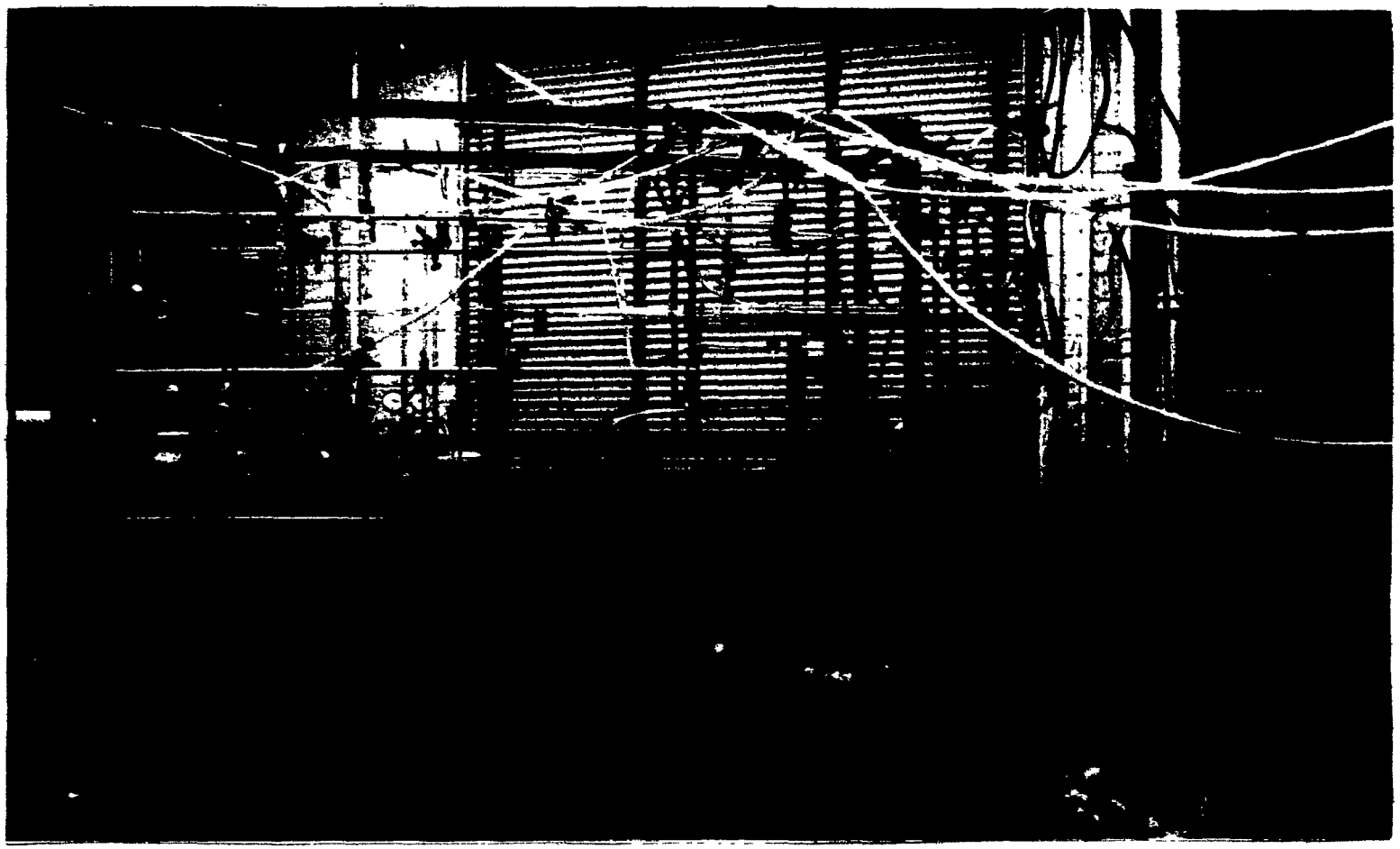

FIG. III.3 Experimental apparatus assembly showing vertical tube furnaces, gas train and temperature controller.

Toronto). The temperature of the reaction crucible was measured with a Pt/Pt-13% Rh thermocouple placed immediately adjacent to the crucible. This temperature was held within ± 1 K during the course of each experiment.

The outer refractory tube (quartz, mullite or alumina, McDanel Industrial Ceramics, Beaver Falls, Pennsylvania) was closed at one end. It was rendered gas-tight at the open end by means of a fitted glass cover, a brass adaptor ring and 'O' rings as shown in Fig. III.1. A second brass plate and 'O' ring assembly at the top of the apparatus permitted entry of a gas lance (for SO_2 and SO_2-N_2 mixtures) and a thermocouple into the system. Watercooling of the top 200 mm of the refractory tube permitted the use of glass, brass and rubber fittings at the top of the apparatus.

Gas Train

The sulphur dioxide pressure of the gas immediately above the reaction crucible was controlled by passing SO_2 or a specified SO_2-N_2 mixture through a quartz lance onto the surface of the crucible contents. The composition of the gas was controlled by fixing the rates of SO_2 and N_2 flow into the lance using microflowmeters (Figs. III.2, III.3). The SO_2 and N_2 were controlled to ± 2% of their concentration as checked by measurements of flows through a water-displacement burette. The total gas flow into reaction crucible (i.e., onto the liquid surfaces) was maintained at 5 cm^3 (NTP) per minute. Gas was removed from the apparatus through a horizontal outlet in the glass cover (Figs. III.1, III.2, III.3).

III.2 MATERIALS

gases:	Sulphur dioxide, pure anhydrous, % 99.98 SO_2 (Welding Products Ltd., Montreal). Nitrogen, ultra high purity, 99.999% N_2 (Canadian Liquid Air, Montreal).
matte components:	Copper sulphide powder (Glidden-Durbee Division of S.C.M., Cleveland). Ferrous sulphide lump (Anachemia Chemicals Limited, Montreal).
slag components:	Silica powder (Anachemia Chemicals Limited, Montreal). Ferric oxide (Fisher Scientific Co. Limited, Montreal).

Master Synthetic Slag

The slag phase in each experiment was formed from powdered master synthetic slag, thereby ensuring a common starting point for all experiments. The master slag was prepared by melting Fe_2O_3 and SiO_2 powder in an induction furnace under argon. The resulting slag was cast and ground to a -150 micrometer powder. Its composition after casting and grinding was 27.9% FeO, 19.9% Fe_2O_3, 52.2% SiO_2 ($Fe/SiO_2 = 0.68$).

III.3 PROCEDURE

Each experiment was begun by charging Cu_2S, FeS, synthetic slag and silica powders to the silica crucible in proportions which would produce the matte and slag compositions desired for that specific experiment. The crucible was then placed in an alumina holder near the bottom

of the refractory tube (Fig. III.1); the system was closed; the lance and thermocouple were fixed in place and a flow of nitrogen was directed through the lance to displace air from the system.

After approximately 1 hour of nitrogen purging the nitrogen flow was switched to the prescribed SO_2-N_2 mixture for the experiment, the tube furnace was raised up over the refractory tube and heating was begun. Heating was carried out very slowly with 7 to 8 hours being allowed for attainment of the experimental temperature. The flow through the silica lance into the reaction crucible was maintained at 5 cm^3 min^{-1} during heating and at 5 ± 0.1 cm^3 min^{-1} once the experimental temperature was reached. This low flowrate ensured that the surface of the slag was blanketed by SO_2 of known partial pressure but that turbulence in the liquids was minimal.

Each experiment was conducted for 20 to 30 hours at temperature to ensure a close approach to equilibrium. This point is discussed in detail in the experimental results section. At the end of the experiment, the furnace power was shut off, with the gas flow being maintained. It is estimated that under these conditions freezing of the liquids was complete in about 10 minutes, i.e., the temperature of the crucible fell to 1073 K in about this time.

After the system had cooled to 500 K, the furnace was dropped below the refractory assembly and the reaction crucible was removed from the apparatus. The crucible was gently broken open and the slag and matte layers were separated for chemical analysis. In general, the layers separated very easily due to a lack of mixing between the phases and to their difference in freezing temperatures.

III.4 CHEMICAL ANALYSIS

The samples were ground (separately) to -150 μm and analysed quantitatively for:

matte	Cu
	total Fe
	O
	SiO_2
slag	Cu
	Fe^{++}
	Fe^{+++}
	S
	SiO_2

Attempts were made to analyse Fe^{++} and Fe^{+++} in matte but copper at high concentration interfered with the analyses and prevented aquisition of any meaningful results.

The following analytical methods were used:

1. Copper: 'long iodide' method duplicated by atomic absorption (after dissolving in HCl and HNO_3).
2. Iron (total): dissolution of sample in HCl and HF, reduction of all iron to Fe^{++} with $SnCl_2$; and back titration of the Fe^{++} against potassium dichromate.
3. Fe^{++} in slag: dissolution of the sample into boiling H_2SO_4 and HF with the crucible (platinum) covered to avoid oxidation of Fe^{++}. The resulting solution was then diluted and titrated with standard potassium dichromate solution (sodium diphenylamine indicator).

4. Fe^{+++} in slag: dissolution into boiling 1:1 HCl followed by hot titration (to clearness) with a standard stannous chloride solution.

5. Sulphur in slag: 'barium sulphate' method (dissolution of sample in HNO_3 and HCl with quantitative precipitation of sulphur as barium sulphate) duplicated by analysis in a LECO Model 762-100 sulphur analyser (LECO Instruments Ltd., Mississauga, Ontario). The latter analysis was made by mixing a small slag sample with pure iron and by treating the mixture like a normal iron or steel sample (combustion to SO_2, infrared SO_2 concentration measurement).

6. Silica in matte and slag: dissolution of sample in boiling HCl and HNO_3 and oxidation with perchloric acid. Following evaporation, the soluble salts were dissolved away from the SiO_2 component and the dried SiO_2 residue was weighed.

7. Oxygen in matte (determined by LECO (Model 775-100) oxygen analysis): In this case a 0.1 gram sample of matte was wrapped in aluminum foil of known oxygen content, and the combination was melted inductively in a stream of hydrogen. The LECO instrument quantified the amount of oxygen by infrared detection of the H_2O formed from exposing the melted sample to the hydrogen stream.

The analyses were normally done in triplicate with a reproducibility generally within ± 2 or 3% of the result.

III.5 RESULTS

The principal experimental results are tabulated in Table III.1 showing pSO_2, temperature and chemical analyses of the coexistent phases.

Matte/Slag Equilibration Time

The experiments were all carried out at temperature for 20 to 25 hours. For comparison, previous investigators have carried out (under somewhat different conditions) their experiments for the following periods of time.

Workers	System	Equilibration Time	Temperature
Gevici and Rosenqvist[18]	Cu-Fe-O-S-SiO_2 (copper phase present)	5 to 17 hrs.	1523 K
Johansen, Rosenqvist and Torgersen[19]	Cu-Fe-O-S-SiO_2 (copper phase present)	28 hrs.	1400 to 1700 K
Nagamori[9]	Cu-Fe-O-S-SiO_2	3 to 5 hrs.	1473 K
Bor and Tarassoff[11]	Cu-Fe-O-S-SiO_2	3 hrs.	1473 K
Toguri and Santander[15]	Cu-Fe-O-SiO_2	48 hrs.	1573 K

It can be seen that the equilibration times of this work are in the same range as those used previously in similar studies. The suitability of these experimental times was tested by carrying out a group of experiments in which pure Cu_2S was equilibrated with master slag for various lengths of time. The parameter examined for invariability with time was Wt% Fe in the matte phase. The results are summarized in Table III.2 from which it is apparent that steady conditions are achieved within 20 to 25 hours of contact.

			MATTE COMPOSITION					SLAG COMPOSITION			
Exp. #	pSO_2 (atms)	T(K)	wt% Cu	wt% Fe	wt% S	wt% SiO_2	wt% O	wt% Cu	Fe^{++}/Fe^{3+++} (weight)	wt% SiO_2	wt% S
1	1.0	1425	76.0	2.3	21.6	0.0	0.04	1.8	5.2	38.0	0.9
2	1.0	1425	68.1	12.7	17.3	0.6	1.3	0.8	4.4	37.6	0.4
3	1.0	1425	67.5	11.5	20.7	0.0	0.3	1.0	5.1	34.7	0.4
4	1.0	1425	55.0	20.0	23.0	0.05	1.0	0.4	5.0	31.6	1.0
5	1.0	1425	50.8	11.6	35.5	1.0	2.0	0.1	6.0	37.5	2.0
6	0.5	1425	76.5	2.2	20.6	0.6	0.1	1.7	6.4	38.5	1.0
7	0.5	1425	70.2	3.0	24.5	2.0	0.3	0.5	5.1	37.7	0.6
8	0.5	1425	61.4	12.3	25.0	0.0	0.5	0.2	6.7	36.3	2.0
9	0.5	1425	49.7	22.0	27.0	0.0	1.3	0.1	7.1	34.0	3.7
10	0.5	1425	42.0	27.5	28.0	0.0	2.7	0.1	4.6	28.1	3.6
11	0.5	1425	41.0	26.8	28.9	0.0	3.3	0.1	4.6	27.4	4.3
12	0.1	1425	79.0	1.0	21.0	0.0	0.0	2.0	5.0	31.0	0.3
13	0.1	1425	69.8	5.0	25.2	0.0	0.0	0.4	5.1	35.6	0.8
14	0.1	1425	65.5	13.6	20.3	1.6	0.2	0.5	5.0	33.6	0.9
15	0.1	1425	51.0	23.0	23.0	0.0	1.2	0.2	7.7	30.9	1.7
16	0.1	1425	49.5	20.0	29.7	0.0	0.0	0.2	7.7	34.7	1.7
17	1.0	1473	71.0	3.1	22.4	3.0	0.5	1.1	5.4	39.7	0.1
18	1.0	1473	70.1	4.5	23.0	1.0	0.6	2.4	5.2	38.5	0.3
19	1.0	1473	66.0	10.0	23.0	0.4	0.6	0.3	5.4	38.2	3.0
20	1.0	1473	65.0	12.0	24.0	0.5	0.5	0.2	4.8	36.7	2.4
21	1.0	1473	62.4	10.8	25.0	1.0	0.8	0.4	5.1	39.0	1.0
22	1.0	1473	60.0	13.4	23.3	0.5	2.0	0.1	5.6	38.4	3.0
23	1.0	1473	55.0	18.0	22.5	1.0	1.0	0.3	6.1	33.0	4.1
24	1.0	1473	42.0	27.0	25.0	0.0	6.0	0.4	4.5	29.2	5.0
25	1.0	1473	36.0	30.3	26.0	0.0	7.7	0.3	7.0	31.3	2.9
26	1.0	1473	29.0	34.0	26.5	0.0	10.5	0.3	5.8	31.4	2.6
27	0.5	1473	76.2	1.0	22.1	0.5	0.2	5.0	5.7	38.5	1.0
28	0.5	1473	74.9	1.6	23.1	0.1	0.5	4.0	4.9	37.7	0.2
29	0.5	1473	69.7	5.5	23.1	1.5	0.2	0.9	5.5	38.0	5.2
30	0.5	1473	59.8	16.4	22.9	0.6	0.6	0.3	5.2	34.9	1.5
31	0.5	1473	49.2	22.2	28.0	0.0	0.6	0.2	5.8	34.3	1.5
32	0.5	1473	42.5	25.0	29.2	0.0	3.3	0.1	6.8	35.1	4.9
33	0.1	1473	79.0	0.5	19.4	0.6	-0.1	2.0	5.7	38.7	0.4
34	0.1	1473	73.7	0.9	22.3	2.9	0.2	2.4	7.2	37.7	0.6
35	0.1	1473	53.0	24.7	22.0	0.0	0.3	0.1	5.8	32.5	2.2
36	0.1	1473	45.5	30.2	22.8	0.1	0.4	0.2	5.8	30.7	2.4
37	1.0	1523	71.5	10.5	18.0	0.0	0.0	2.5	4.5	38.9	0.1
38	1.0	1523	66.4	10.4	20.2	1.1	1.0	0.5	4.3	34.5	0.5
39	1.0	1523	64.9	8.5	24.7	0.2	1.0	0.5	5.2	35.0	0.0
40	1.0	1523	62.0	11.4	25.5	0.1	1.0	0.3	4.9	38.0	2.4
41	1.0	1523	49.7	21.0	25.7	0.1	3.5	0.3	4.7	32.5	5.1
42	1.0	1523	40.0	30.0	23.4	0.0	6.6	0.2	5.0	31.2	4.0
43	1.0	1573	74.0	5.5	20.4	0.0	0.1	2.0	3.0	36.6	0.0
44	1.0	1573	73.2	4.6	22.2	0.0	0.0	1.0	3.7	39.0	0.3
45	1.0	1573	68.8	6.0	23.0	1.2	1.0	0.3	3.0	33.6	5.7
46	1.0	1573	47.5	20.0	27.5	0.0	5.2	0.2	4.8	34.6	7.0
47	1.0	1573	25.7	36.5	30.6	0.0	8.2	0.1	5.4	32.7	7.3

TABLE III.1 Principal Experimental Results under Silica Saturation Conditions

Exp. #	pSO_2 (Atm)	T(K)	Time (hrs.)	% Wt Fe (matte)
1	1.0	1423	10	0.3
2	1.0	1423	20	0.88
3	1.0	1423	25	1.05
4	1.0	1423	35	0.92
5	1.0	1473	10	0.6
6	1.0	1473	15	0.95
7	1.0	1473	20	0.87
8	1.0	1473	30	0.92
9	1.0	1523	10	0.33
10	1.0	1523	15	0.98
11	1.0	1523	20	0.92
12	1.0	1523	25	0.99
13	1.0	1523	30	0.89
14	1.0	1573	10	0.83
15	1.0	1573	15	1.25
16	1.0	1573	20	1.35
17	1.0	1573	25	0.94
18	1.0	1573	30	1.10

TABLE III.2 Experimental Results for Matte/Slag Equilibration Time. Experiments under SiO_2 Saturation Conditions.

IV. DISCUSSION

This section discusses the implications of the experimental results under the headings:

IV.1 Thermodynamic interpretation of results.

IV.2 Behaviour of copper in slag.

IV.3 Behaviour of sulphur in slag.

IV.4 Behaviour of oxygen in matte.

IV.5 Structural representation of results.

IV.6 Prediction of conditions under which a separate copper phase will occur.

IV.7 Industrial implications of the results.

IV.1 THERMODYNAMIC INTERPRETATION OF RESULTS

The principal objective of this thermodynamic interpretation was to determine:

a_{Cu}

a_{Cu_2S}

a_{Cu_2O}

for each experimental equilibration, based on measured values of pSO_2, matte composition and slag composition. Additional parameters calculated along the way were pO_2 and pS_2.

Before describing the calculations, it will be worthwhile to interpret the present and previous matte/slag/gas experiments in terms of the phase rule.

The experimental system described in this thesis consists of 4 phases (SiO_2, two liquids, gas) and 5 components (Cu, Fe, O, S, SiO_2). By the phase rule ($P + F = C + 2$), the system has three degrees of freedom. Thus, once temperature, pSO_2 and matte grade are specified as independent variables, the remainder of the system is fully defined. The experimental approach in this work was essentially, therefore, to fix temperature, pSO_2 and matte grade (% Cu) and to let the slag find its appropriate composition (particularly with regard to its Fe^{++}/Fe^{+++} ratio and sulphur content).

This approach is not dissimilar to previous work (Themelis[12], Yazawa[10], Bor and Tarassoff[11]) in which temperature, iron-saturation and matte grade were chosen as independent variables and in which slag and gas compositions were allowed to find their appropriate values. The essential difference between these previous iron-saturation experiments and those described here is the fixed, relatively high pSO_2 of the present work.

Geveci and Rosenqvist[18] also proceeded in a somewhat similar manner but with metallic copper as a separate phase. Their system had 5 components, 5 phases (metallic copper, matte, slag, gas and the container material which was Fe, Fe_3O_4 or SiO_2) and hence only two degrees of freedom. Thus, these workers fixed temperature (1523 K) and matte grade: - and allowed the gas and liquid phases to find their appropriate compositions.

The present work can be considered as a further exploration into matte/slag/gas systems under conditions considerably different (particularly with respect to pSO_2) than those of previous studies.

IV.1.A Estimation of pO_2

The first step in the thermodynamic interpretation of the results was to estimate pO_2 from (i) the slag composition of each experiment and (ii) the Fe-O-SiO_2 oxygen pressure data of Muan[20] (Fig. IV.1). The slags in the present work were all very near silica saturation (having been equilibrated for 20+ hours in a quartz crucible) so that the oxygen pressure in each experimental system was determined in accordance with its Fe^{++}/Fe^{+++} ratio along the silica saturation line in Fig. IV.1.

Of course the data of Muan[20] is for copper- and sulphur-free slags so that some error is introduced in this interpretation. However, the total of copper plus sulphur in the slag was usually less than 5% so that the error is likely to be small.

The results of the calculations are presented in Table IV.1.

IV.1.B Calculation of pS_2

Once pO_2 had been estimated for each equilibrium, pS_2 was calculated from it and the appropriate experimental value of pSO_2 by means of the equilibrium expressions:

$$1/2\ S_2 + O_2 \rightleftharpoons SO_2$$

$$\Delta G^o = -361000 + 72.4\ T \text{ (joules)} \qquad \text{IV.1}$$

and

$$\Delta G^o = -RT \ln \frac{pSO_2}{pS_2^{1/2} pO_2} \qquad \text{IV.2}$$

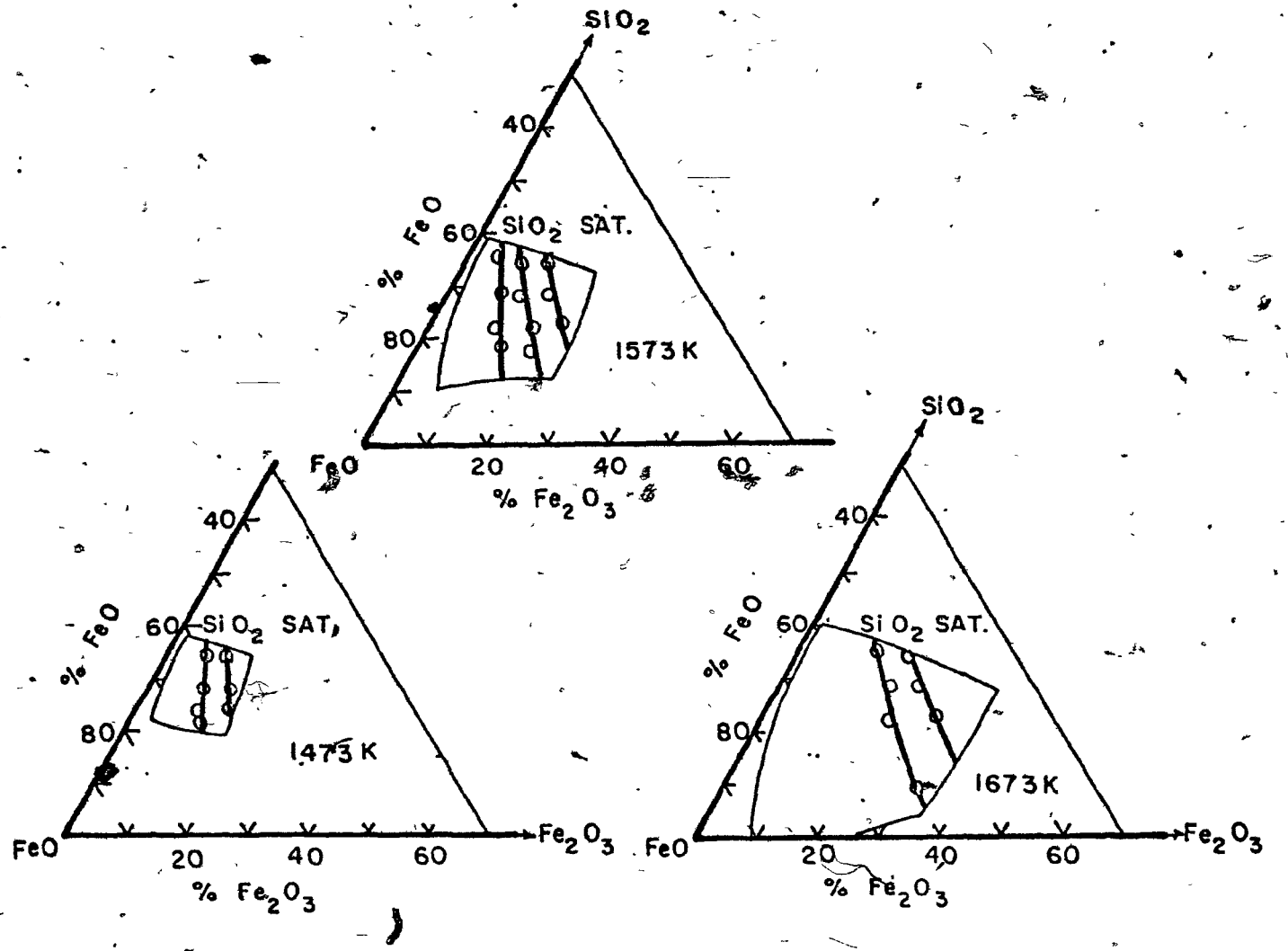

FIG. IV.1 Phase diagrams of the $FeO-Fe_2O_3-SiO_2$ system showing equilibrium oxygen pressures in the melt fields (Muan[20]).

As Table IV.1 shows, sulphur pressures in the experiments varied from 10^{-5} to 10^{-2} atmospheres.

IV.1.C Estimation of a_{Cu_2S}

Activities of Cu_2S in the equilibrated matte phases were estimated from (i) each experimental matte composition and (ii) the Cu_2S-FeS activity data of Bale and Toguri[21] and Krivsky and Schuhmann[2] (Fig. IV.2). Activities determined in this way are reported in Table IV.1 and Fig. IV.3. Bale and Toguri[21] suggest that the Cu_2S-FeS pseudo binary system is well described by Temkin's[22] model so that no temperature adjustments were made in choosing the a_{Cu_2S} values.

This determination suffers from the same problem as the determination of pO_2; i.e., the matte phase contains a small quantity of oxygen (and a trace of SiO_2) in addition to Cu, Fe and S. However, except in a few cases the oxygen and silica components totalled less than 5% so that the error is once again not likely to be large, especially with high matte grades.

IV.1.D Calculation of a_{Cu}

The activity of copper in each experiment was readily calculated from the values of pS_2 and a_{Cu_2S} in sections IV.1.B and IV.1.C using the equilibrium expressions:

$$2Cu_{\ell} + 1/2\ S_{2_g} \rightleftarrows Cu_2S_{\ell}$$

$$\Delta G^{o} = -171000 + 58.6\ T \quad \text{(joules)} \qquad \text{IV.3}$$

This expression is in general agreement with the recent data of Bale and Toguri[21] ± 500 joules per mole of Cu_2S.

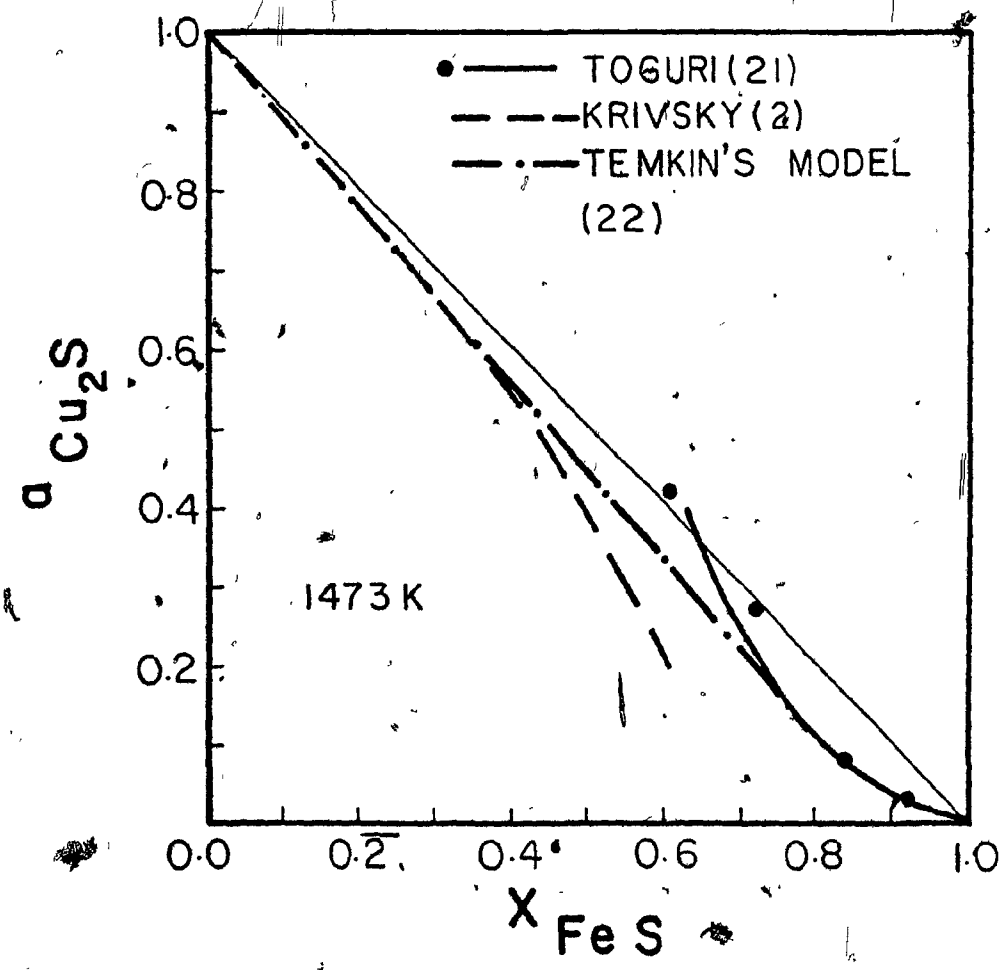

FIG. IV.2 Activity of Cu_2S in Cu-Fe-S mattes as determined by Krivsky[2] and Sawyer et al[21]. Activities predicted by Temkin's cationic ionic lattice model[22] are also shown.

and the equilibrium constant:

$$K_E = \frac{a_{Cu_2S}}{(a_{Cu})^2 (pS_2)^{1/2}} \qquad \text{IV.4}$$

The calculated copper activity values are shown in Table IV.1 and Fig. IV.3.

IV.1.E Calculation of a_{Cu_2O}

As a final step in the thermodynamic interpretation the activity of Cu_2O in each experimental system was calculated from the pO_2 and a_{Cu} values determined in Sections IV.1.A and IV.1.D with the aid of the equilibrium expressions:

$$2Cu_\ell + 1/2\ O_{2\,g} \rightleftarrows Cu_2O_\ell$$

$$\Delta G^o = -144000 + 58.6\ T \quad \text{(joules)} \qquad \text{IV.5}$$

and

$$K_E = \frac{a_{Cu_2O}}{(a_{Cu})^2 (pO_2)^{1/2}} \qquad \text{IV.6}$$

The calculated values are presented in Table IV.1 and Fig. IV.3. They are discussed in Section IV.2.

IV.2 BEHAVIOUR OF COPPER IN MATTE AND SLAG

Perhaps the most important results of this work are presented in Figs. IV.4 and IV.5, both of which plot wt% Cu in slag vs. wt% Cu in matte. Fig. IV.4 presents all the 'raw' data of the investigation while Fig. IV.5 compares the 'best fit' line of the present work with the results of previous investigators. The latter shows clearly that the present

Exp. #	pSO_2(atmos.)	T(K)	% SiO_2	Fe^{++}/Fe^{+++} (weight)	pO_2(atmos.)	pS_2(atmos.)	X_{Cu_2S}	a_{Cu_2S}	a_{Cu}	a_{Cu_2O}
1	1.0	1423	38.0	5.2	5.0×10^{-9}	5.1×10^{-3}	0.94	0.93	0.09	9.3×10^{-5}
2	1.0	1423	37.6	4.4	6.4×10^{-9}	3.5×10^{-3}	0.70	0.72	8.7×10^{-2}	9.5×10^{-5}
3	1.0	1423	34.7	5.1	5.5×10^{-9}	4.2×10^{-3}	0.58	0.52	7.1×10^{-2}	6.0×10^{-5}
4	1.0	1423	31.6	5.9	2.5×10^{-9}	2.0×10^{-2}	0.54	0.49	4.6×10^{-2}	1.7×10^{-5}
5	1.0	1423	37.3	6.0	1.8×10^{-9}	5.6×10^{-2}	0.66	0.62	4.1×10^{-2}	1.0×10^{-5}
6	0.5	1423	38.5	6.4	1.0×10^{-9}	3.2×10^{-2}	0.93	0.92	5.6×10^{-2}	1.6×10^{-5}
7	0.5	1423	37.7	5.3	3.0×10^{-9}	3.5×10^{-3}	0.91	0.90	9.7×10^{-2}	8.4×10^{-5}
8	0.5	1423	34.3	6.7	8.0×10^{-10}	4.9×10^{-2}	0.68	0.65	4.2×10^{-2}	8.3×10^{-6}
9	0.5	1423	34.0	7.1	6.0×10^{-10}	8.8×10^{-2}	0.49	0.41	2.9×10^{-2}	3.4×10^{-6}
10	0.5	1423	28.1	4.6	7.0×10^{-9}	6.5×10^{-4}	0.40	0.25	7.8×10^{-2}	8.3×10^{-5}
11	0.5	1423	27.4	4.6	6.8×10^{-9}	6.9×10^{-4}	0.40	0.24	7.5×10^{-2}	7.6×10^{-5}
12	0.1	1423	31.8	5.0	5.5×10^{-9}	4.2×10^{-5}	0.97	0.97	0.30	1.1×10^{-3}
13	0.1	1423	35.6	5.1	5.3×10^{-9}	4.5×10^{-5}	0.94	0.95	0.29	1.0×10^{-3}
14	0.1	1423	33.0	5.0	5.8×10^{-9}	3.8×10^{-5}	0.70	0.68	0.26	8.4×10^{-4}
15	0.1	1423	30.9	7.7	5.8×10^{-10}	3.8×10^{-3}	0.49	0.40	6.4×10^{-2}	1.6×10^{-5}
16	0.1	1423	34.7	7.7	5.8×10^{-10}	3.8×10^{-3}	0.52	0.44	6.7×10^{-2}	1.7×10^{-5}
17	1.0	1473	39.7	5.4	7.6×10^{-9}	1.6×10^{-2}	0.69	0.68	7.2×10^{-2}	4.8×10^{-5}
18	1.0	1473	39.5	5.2	4.6×10^{-9}	4.5×10^{-2}	0.68	0.65	5.4×10^{-2}	2.2×10^{-5}
19	1.0	1473	30.2	5.4	7.6×10^{-9}	1.6×10^{-2}	0.56	0.48	6.0×10^{-2}	3.4×10^{-5}
20	1.0	1473	36.7	4.8	1.5×10^{-8}	4.3×10^{-3}	0.61	0.56	9.1×10^{-2}	1.0×10^{-4}
21	1.0	1473	39.0	5.1	5.9×10^{-9}	2.7×10^{-2}	0.62	0.58	5.8×10^{-2}	2.8×10^{-5}
22	1.0	1473	38.4	5.6	4.5×10^{-9}	4.8×10^{-2}	0.60	0.55	4.9×10^{-2}	1.7×10^{-5}
23	1.0	1473	33.0	8.1	4.7×10^{-9}	4.4×10^{-2}	0.51	0.42	4.4×10^{-2}	1.4×10^{-5}
24	1.0	1473	29.2	4.5	8.2×10^{-9}	1.4×10^{-2}	0.43	0.30	4.9×10^{-2}	2.3×10^{-5}
25	1.0	1473	31.3	7.9	4.7×10^{-9}	4.4×10^{-2}	0.38	0.22	3.2×10^{-2}	7.5×10^{-6}
26	1.0	1473	31.4	5.8	4.5×10^{-9}	4.8×10^{-2}	0.33	0.12	2.3×10^{-2}	3.8×10^{-6}

.....(cont'd.)

TABLE IV.1 Thermodynamic Quantities Estimated and Calculated from Experimental Data

TABLE IV.1 (cont'd.)

Exp. #	pSO_2(atmos.)	T(K)	% SiO_2	Fe^{++}/Fe^{+++} (weight)	pO_2(atmos.)	pS_2(atmos.)	X_{Cu_2S}	a_{Cu_2S}	a_{Cu}	a_{Cu_2O}
27	0.5	1473	38.5	5.7	5.6×10^{-9}	7.9×10^{-3}	0.97	0.96	0.1	7.9×10^{-5}
28	0.5	1473	37.7	4.9	7.6×10^{-9}	4.2×10^{-3}	0.95	0.95	0.12	1.3×10^{-4}
29	0.5	1473	38.8	5.5	4.9×10^{-9}	1.0×10^{-2}	0.84	0.85	9.0×10^{-2}	6.2×10^{-5}
30	0.5	1473	34.9	5.2	7.4×10^{-9}	4.4×10^{-3}	0.61	0.57	9.0×10^{-2}	7.7×10^{-5}
31	0.5	1473	34.3	5.8	5.6×10^{-9}	7.8×10^{-3}	0.49	0.40	7.0×10^{-2}	3.5×10^{-5}
32	0.5	1473	35.1	6.8	3.9×10^{-9}	1.6×10^{-2}	0.43	0.26	4.0×10^{-2}	1.3×10^{-5}
33	0.1	1473	39.7	5.7	5.6×10^{-9}	3.1×10^{-4}	0.97	0.96	0.24	4.4×10^{-4}
34	0.1	1473	[illegible]	7.2	3.0×10^{-9}	1.1×10^{-3}	0.79	0.78	0.15	1.3×10^{-4}
35	0.1	1473	32.5	8.8	9.3×10^{-10}	1.1×10^{-2}	0.48	0.40	6.0×10^{-2}	1.2×10^{-5}
36	0.1	1473	30.7	5.8	3.0×10^{-9}	1.1×10^{-3}	0.39	0.24	8.0×10^{-2}	4.1×10^{-5}
37	1.0	1523	38.9	4.5	2.9×10^{-8}	8.2×10^{-3}	0.74	0.73	0.11	1.5×10^{-4}
38	1.0	1523	34.3	4.3	6.0×10^{-8}	1.9×10^{-3}	0.67	0.64	0.15	4.1×10^{-4}
39	1.0	1523	35.0	5.2	2.2×10^{-8}	1.4×10^{-2}	0.77	0.76	0.10	1.1×10^{-4}
40	1.0	1523	38.0	4.9	4.1×10^{-8}	4.1×10^{-3}	0.57	0.50	0.11	1.7×10^{-4}
41	1.0	1523	32.3	4.7	7.3×10^{-8}	1.3×10^{-3}	0.51	0.42	0.14	3.9×10^{-4}
42	1.0	1523	31.2	5.0	4.1×10^{-3}	4.1×10^{-3}	0.37	0.19	6.0×10^{-2}	6.8×10^{-5}
43	1.0	1573	36.6	3.8	5.9×10^{-7}	1.2×10^{-4}	0.86	0.85	0.43	7.0×10^{-3}
44	1.0	1573	39.0	3.7	7.4×10^{-7}	7.5×10^{-5}	0.87	0.87	0.48	1.0×10^{-2}
45	1.0	1573	33.8	3.9	6.2×10^{-7}	1.1×10^{-4}	0.83	0.82	0.43	7.4×10^{-3}
46	1.0	1573	34.6	4.8	2.3×10^{-7}	7.8×10^{-4}	0.51	0.44	0.19	9.1×10^{-4}
47	1.0	1573	32.7	5.4	1.1×10^{-7}	3.2×10^{-3}	0.26	0.08	6.0×10^{-2}	5.7×10^{-5}

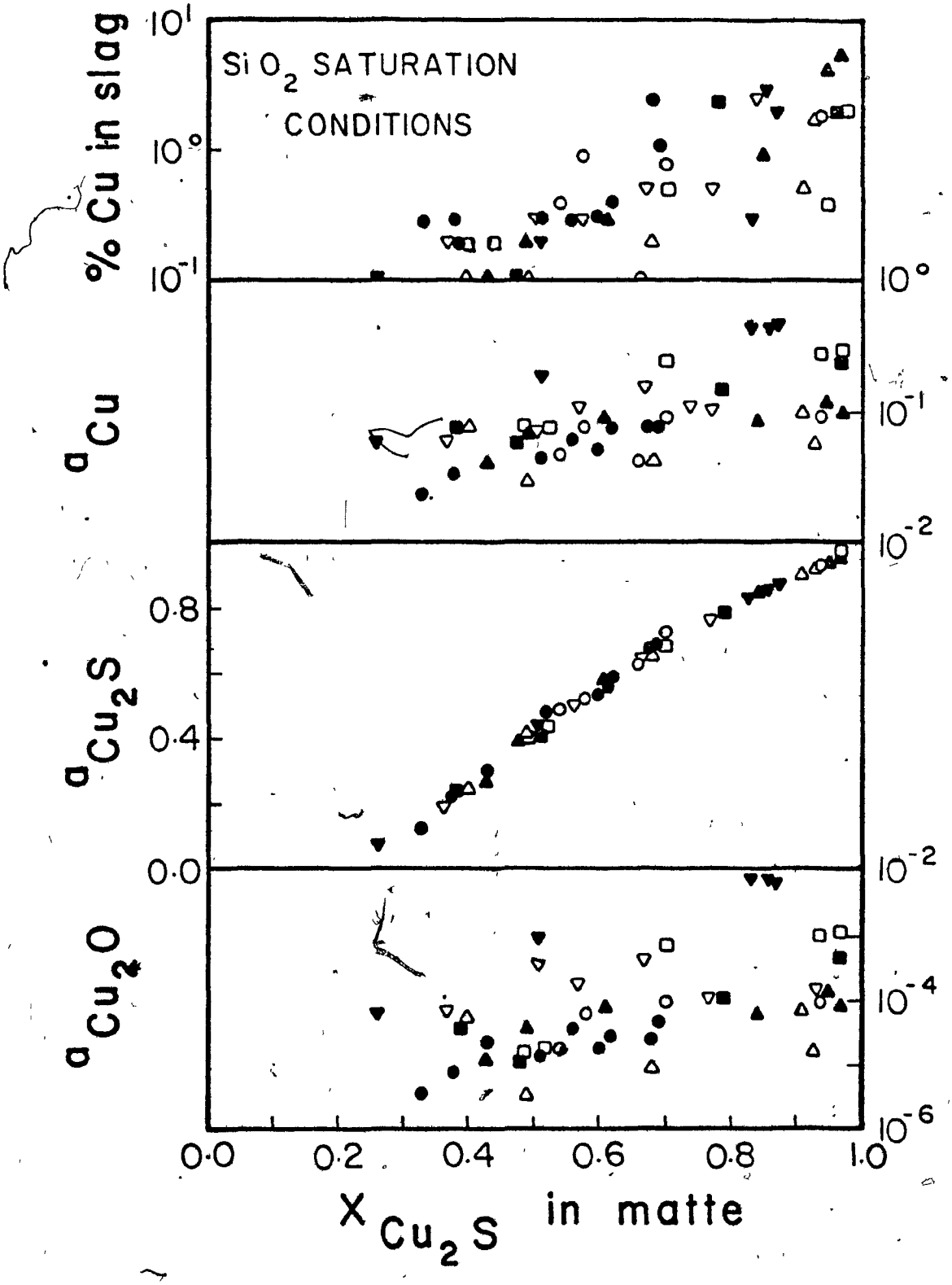

FIG. IV.3 Experimental values of wt% Cu in slag, a_{Cu}, a_{Cu_2S} and a_{Cu_2O} as functions of X_{Cu_2S} in matte, silica saturated system. The upward trend in all variables with increasing matte grade is notable. The experimental conditions were: ○ △ □ 1423 K, pSO_2 = 1.0, 0.5, 0.1 atmos; ● ▲ ■ 1473 K, pSO_2 = 1.0, 0.5, 0.1 atmos; ▽ ▼ pSO_2 = 1.0 atmos, 1523, 1573 K.

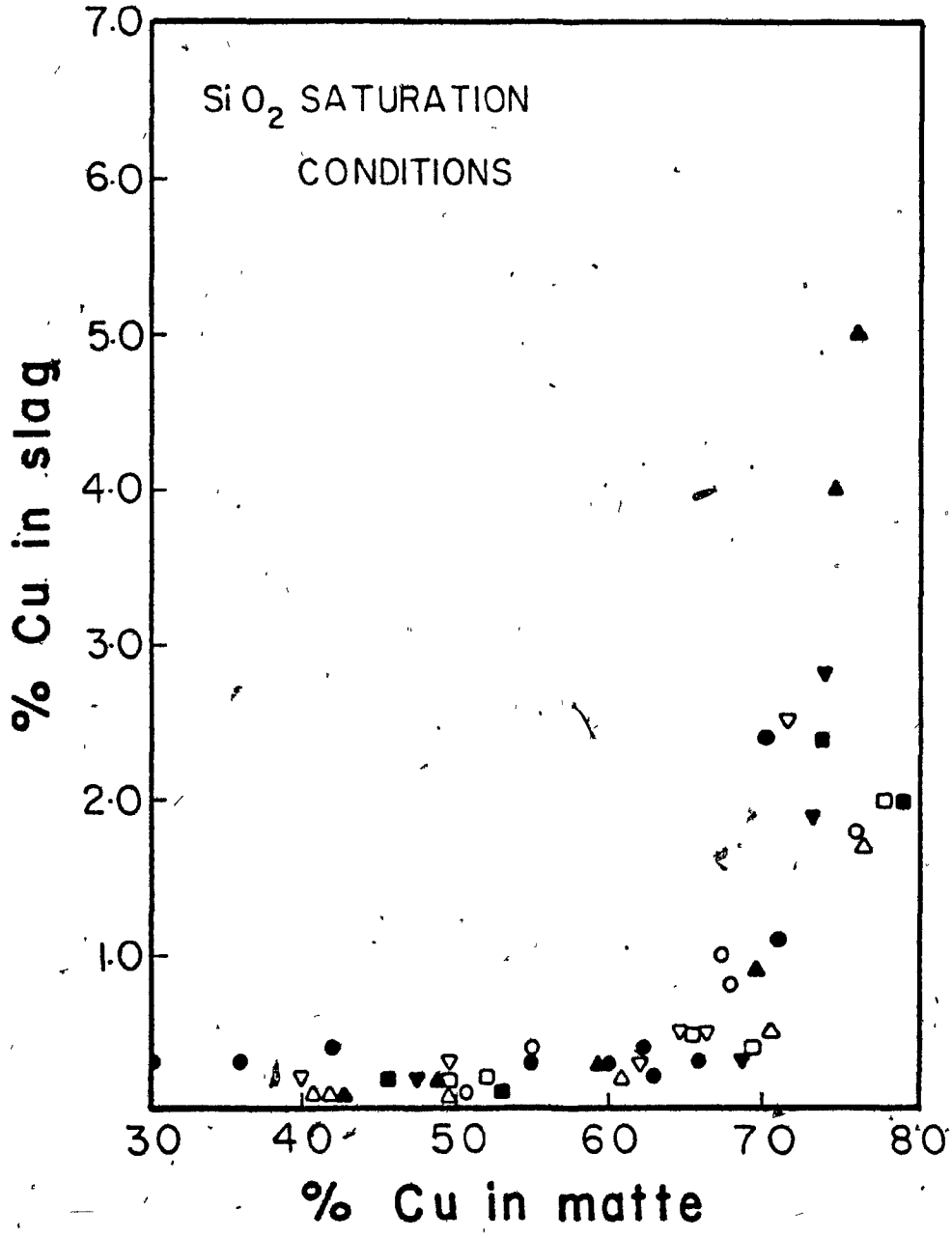

FIG. IV.4 Experimental copper-in-slag results, silica-saturated system. The experimental conditions were: ○ △ □ 1423 K, pSO_2 = 1.0, 0.5, 0.1 atmos; ● ▲ ■ 1473 K, pSO_2 = 1.0, 0.5, 0.1 atmos; ▽ ▼ pSO_2 = 1.0 atmos, 1523, 1573 K.

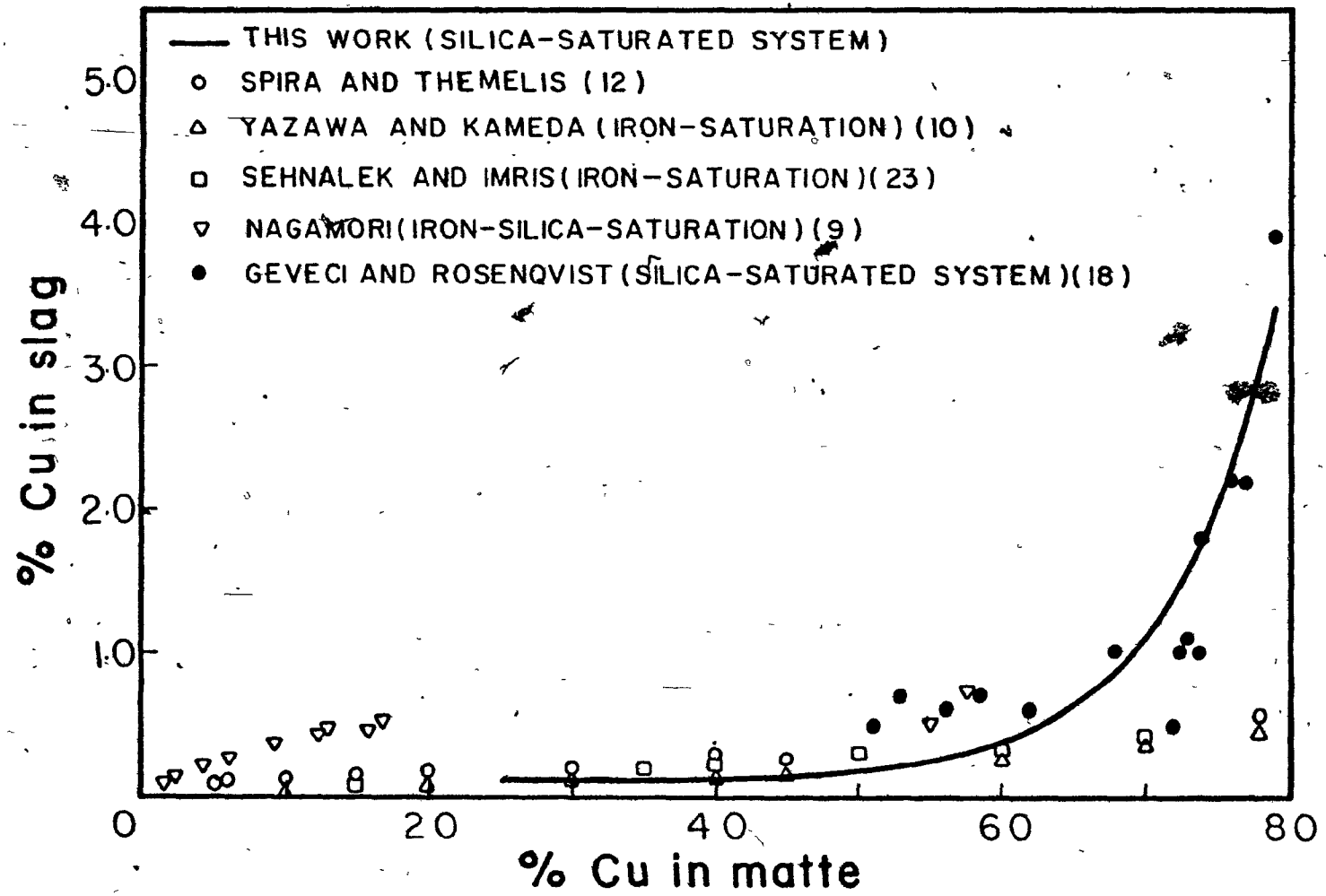

FIG. IV.5 Experimental Cu-in-slag results of the present work compared with those of previous investigators.

results are in good agreement with those of previous workers.*

A notable feature of the present work and that of Geveci and Rosenqvist[18] is the sharp rise in copper-in-slag content at matte grades above about 60% Cu. Moreover it can be seen that under the highly reducing conditions of iron saturation (Fig. IV.5) such a sharp increase does not apparently occur. These two observations suggest that whereas copper-in-slag concentration is not appreciably affected by oxidizing potential (as represented by iron saturation conditions and high pSO_2 conditions as extremes) at matte grades below 60% copper, the effect becomes very noticeable for mattes above this grade.

IV.2.A Thermodynamic Interpretation of Copper-in-Slag Concentrations

Fig. IV.3 shows weight% Cu in slag and the activities of Cu, Cu_2S and Cu_2O calculated in Section IV.1 all plotted as a function of mole fraction of Cu_2S in the matte. All three activities increase with matte grade so it comes as no surprise that copper-in-slag concentrations should also increase with increasing matte grade. Interpretation of these data is continued in Section IV.5.

IV.2.B Effect of pSO_2 on Copper Behaviour

At matte grades below 60% Cu it appears (Fig. IV.4) that pSO_2 has no appreciable effect on copper-in-slag concentrations so that as long as matte grades are kept below that value there should be no overwhelming copper loss problem with high pSO_2 processes such as the INCO flash furnace.

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* *The experimental results of Nagamori[9] (Fig. IV.5) show somewhat larger Cu-in-slag concentrations than previous workers. There is no apparent reason for this as he took great care to ensure that there was no physical entrainment of matte in his slags.*

Above matte grades of 60% Cu, the experimental results become confused, probably because a small error in the determination of % Cu in matte tends to appreciably distort the picture.

It is clear, however, that under the oxidizing conditions encountered in smelting processes (i.e., non-iron saturation conditions), production of mattes containing more than 60% copper will always lead to large copper-in-slag losses.

IV.3 BEHAVIOUR OF SULPHUR IN SLAG

Fig. IV.6 shows the experimental values of wt% sulphur in slag and the 'best fit' line as a function of matte grade. The experimental values of previous workers are also shown.

The clearest point established by these results is that the solubility of pure Cu_2S in silica-saturated Fe-O-SiO_2 slags is very limited, the solubility of pure FeS is quite high (equivalent to 6[32] or 7[10]% S) and that the solubility of Cu_2S-FeS mattes in slag is intermediate between these extremes. Somewhat surprisingly, there does not seem to be a discernable correlation between % S in slag and temperature or pSO_2.

Fig. IV.6 shows that for mattes containing less than about 60% Cu, the sulphur-in-slag contents measured here are slightly higher than those of recent investigators. However, there is considerable disagreement between these workers themselves so that a clear-cut picture of sulphur solubility at low matte grades awaits further experimentation. On the basis of this work, it is suggested that LECO analysis (Section III.4) for sulphur is a rapid and accurate analytical technique for this purpose.

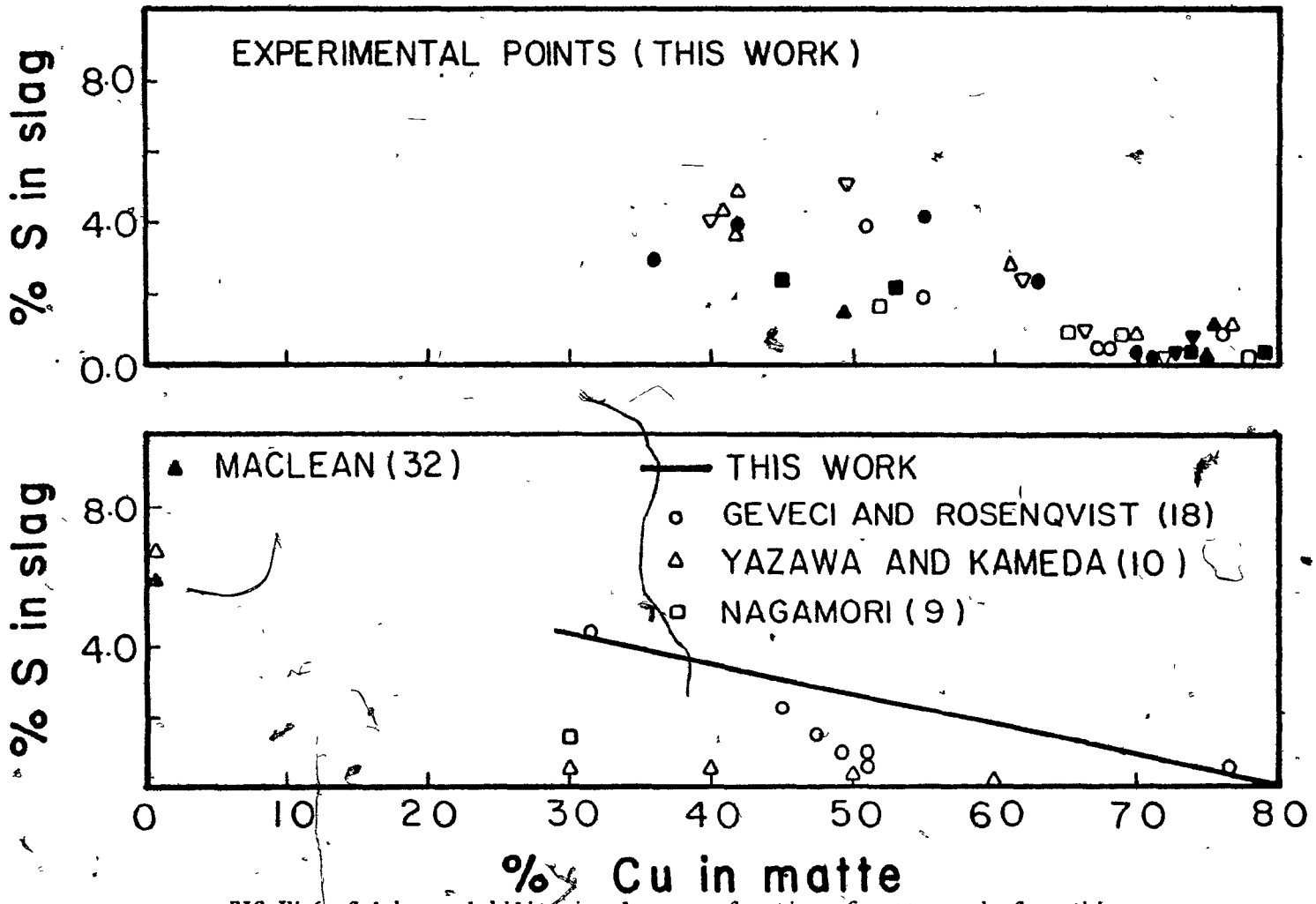

FIG. IV.6 Sulphur solubility in slag as a function of matte grade from this and previous work, silica saturation conditions. The negligible solubility of Cu_2S and the appreciable solubility of FeS in silica saturated slags are notable. The experimental conditions were: ○△□ 1423 K, pSO_2 = 1.0, 0.5, 0.1 atmos; ●▲■ 1473 K, pSO_2 = 1.0, 0.5, 0.1 atmos; ▽▼ pSO_2 = 1.0 atmos, 1523, 1573 K.

A possible explanation for the rather high sulphur-in-slag concentrations of the present work (% Cu in matte $< 60\%$), is that the slag was not truly saturated with SiO_2. However, as Yazawa[13] has shown, this effect is very small unless the % SiO_2 in slag falls below 30% SiO_2.

As a general conclusion about sulphur solubility, then, the principal controlling factor is matte grade with all other factors being secondary. The sulphur-in-slag solubility of Cu_2S is negligible but the solubility increases with decreasing matte grade.

IV.4 BEHAVIOUR OF OXYGEN IN MATTE

The measured concentrations of oxygen in the equilibrated mattes of the present investigation are presented in Fig. IV.7 which also compares the 'best fit' line with the data of previous workers.

As with sulphur in slag, the most noticeable feature of the results is the remarkable difference between the behaviour of Cu_2S and FeS. There is virtually no oxygen solubility in Cu_2S but considerable (up to 10% (Spira and Themelis[12]) in FeS, with intermediate values for Cu-Fe-S mattes. Matte composition appears to overwhelm all other effects (i.e., temperature and pSO_2).

Like sulphur solubility in slag (Section IV.3), the present experimental oxygen solubilities are, for matte grades below 60% Cu, somewhat higher than those of previous workers. These two sets of results are therefore internally consistent at least. Yazawa[13] notes that a lack of SiO_2 saturation will increase oxygen-in-matte solubility but this effect is quite small for SiO_2 contents above 30%.

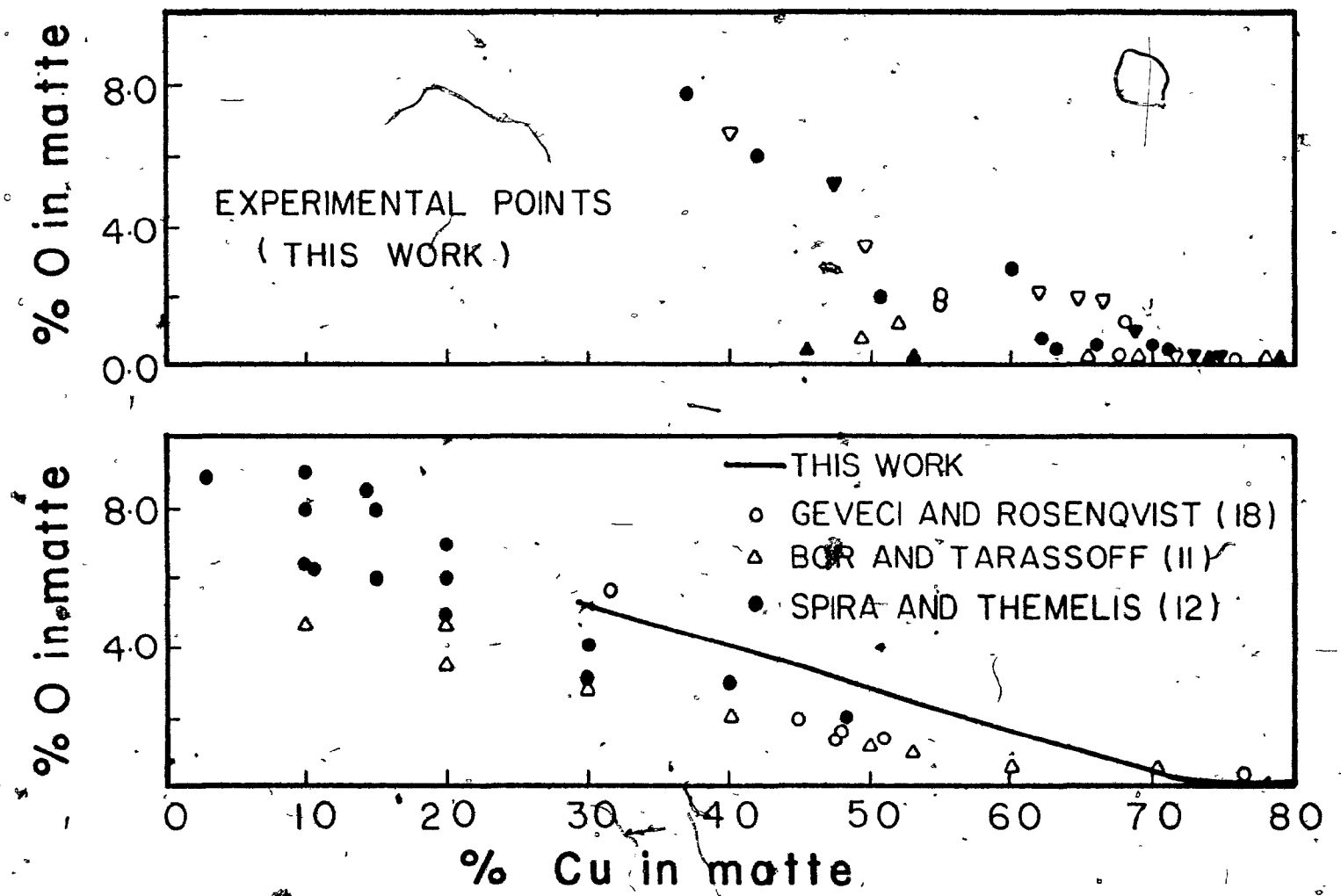

FIG. IV.7 Oxygen solubility in slag as a function of matte grade from this and previous work, silica saturation conditions. The negligible solubility of oxygen in Cu_2S and the appreciable solubility in FeS are notable. The experimental conditions were: ○△□1423 K, pSO_2 = 1.0, 0.5, 0.1 atmos; ●▲■1473 K, pSO_2 = 1.0, 0.5, 0.1 atmos; ▽▼ pSO_2 = 1.0 atmos, 1523, 1573 K.

IV.4.1 SiO_2 in Matte

As can be seen from the experimental data (Table III.1), there seems to be a small SiO_2 solubility in the equilibrated mattes (< 3%).

Bor and Tarassoff[11], in discussing SiO_2 solubility in matte, suggest that under iron and SiO_2 saturation conditions the solubility of SiO_2 in mattes (10 to 40% Cu) is less than 1%, decreasing with increasing matte grade. This trend towards low SiO_2 solubilities in high grade mattes is confirmed by the present experimental results (Table III.1). Some of the higher values of the present work may, in fact, be due to inclusion of traces of quartz crucible in the analytical sample.

IV.5 STRUCTURAL REPRESENTATION OF RESULTS

Nagamori[9], Toguri[15] and Yazawa[13] have recently published thorough discussions as to how copper-in-slag behaviour might best be explained in structural terms. Much of the discussion has centred around the distinction between 'oxide' and 'sulphide' copper in the slags. However, this concept of separate categories of copper-in-slag does not fit well with the basic concept of slags as solutions of anions and cations.

There are, nevertheless, some basic observations which require explanation.

(a) Why does the copper-in-slag concentration increase catastrophically for matte grades above 60 or 65% Cu?

(b) Why is FeS more soluble in slags than Cu_2S?

(c) Why is oxygen much more soluble in FeS than Cu_2S?

These points are discussed in the next two subsections.

IV.5.A Catastrophic Copper-in-Slag Loss for 60+ % Cu Mattes

For sulphur-free systems, Toguri[15,16] and Altman[17] suggest that wt% Cu-in-slag is related to Cu_2O activity by the relationships:

1500 K	wt% Cu = $34(a_{Cu_2O})^{1/2}$	Altman
1523 K	wt% Cu = $28(a_{Cu_2O})^{1/2}$	Toguri

The Toguri value is probably somewhat low because his slags also contained some alumina dissolved from the experimental crucibles.

Since the sulphur content of the present experimental slags was less than one per cent for matte grades above 65% Cu, it would seem that these relationships could be applied to the present results over this experimental range.

There is, of course, considerable scatter in the present a_{Cu_2O} results (Fig. IV.3) which makes precise interpretation difficult but if a_{Cu_2O} is said to be enveloped within $10^{-2.5}$ and 10^{-4} at $X_{Cu_2S} = 0.9$ (75% Cu) it can be seen that Altman predicts copper-in-slags of between 0.3 and 2% which is reasonably close to the present experimental values (Fig. IV.4). The lower values of wt% Cu in slag reported by Yazawa[10] and Sehnalek[23] for iron saturation conditions (Fig. IV.5) are due, of course, to the low values of oxygen partial pressure and a_{Cu_2O} under such conditions.

IV.5.B Relative Solubilities of and in Cu_2S and FeS

In examining the reasons for:

(a) the negligible solubility of Cu_2S in slag and the considerable solubility of FeS in slag;

(b) the negligible solubility of oxygen in Cu_2S and the considerable solubility of oxygen in FeS;

the properties of these two sulphides (and FeO) can be tabulated:

Property	Cu_2S	FeS	FeO
Melting point K[1]	1130	1190	1377
Density at 1523 K (tonnes m^{-3})[24,25]	5.8	3.8	5.7 (solid)
Specific electrical conductance at 1523 K (Ω^{-1} cm^{-1})[24,26]	100	1500	200 (at melting point)

The free energies of formation of these three compounds and Cu_2O are:

$$2Cu_\ell + 1/2\ S_{2_g} \rightarrow Cu_2S_\ell \qquad \Delta G^o_{1523\ K} = -84000 \text{ joules}$$

$$Fe_s + 1/2\ S_{2_g} \rightarrow FeS_\ell \qquad \Delta G^o_{1523\ K} = -73000 \text{ joules}$$

$$2Cu_\ell + 1/2\ O_2 \rightarrow Cu_2O \qquad \Delta G^o_{1523\ K} = -54000 \text{ joules}$$

$$Fe_s + 1/2\ O_2 \rightarrow FeO_\ell \qquad \Delta G^o_{1523\ K} = -163000 \text{ joules}$$

It can be seen from the above data that liquid Cu_2S differs from FeS only with respect to its much greater density* and its much smaller electrical conductivity. It appears to behave like a semi-conducter[26] (small positive temperature effect on conductivity) whereas the electrical behaviour of FeS resembles electronic conduction.

These observations suggest that Cu_2S is more strongly covalently bonded than FeS and that as a consequence it resists being dissolved and broken up by the ionic structure of slags. Of course, this explanation must be regarded as speculative and further structural experimentation is required to fully explain these phenomena.

IV.6 PREDICTION OF CONDITIONS UNDER WHICH A SEPARATE COPPER PHASE WILL OCCUR

The recent extensive studies into single-step coppermaking make it of great interest to predict the conditions under which a pure copper phase ($a_{Cu} \simeq 1$) will occur.

There are (Section IV.1) only two degrees of freedom in this system so that once temperature and one other parameter are specified the system is completely defined. The calculations of this thesis (summarized again, below) can be used to make these predictions.

The basic assumptions in the calculation are:

(a) that the oxygen pressure and a_{FeO} of the system can be calculated from the slag composition (Fe^{++}/Fe^{+++} ratio along the SiO_2 saturation line) as if Cu and S have no

---

* *Interestingly Cu_2S, like water, expands on freezing because its liquid density at the freezing point (5.9 tonnes m^{-3}) exceeds its solid density (5.6 to 5.8 tonnes m^{-3}).*

effect, i.e., that the data of Muan[20], Darken and Gurry[27,28], Schuhmann and Ensio[29], Michal and Schuhmann[30] and Darken[31] apply to the system;

(b) that the activities of Cu_2S and FeS in matte are closely represented by the Temkin[22] cationic lattice model as noted by Bale et al[21].

The usual method of calculation was to specify the temperature of the system and the Fe^{++}/Fe^{+++} ratio of the silica saturated slag, which of course fully defines the remainder of the system. The limiting values of the Fe^{++}/Fe^{+++} ratio for the slag were at iron saturation and magnetite saturation which mark the limits of the liquid slag field.

The predictions were made by the following sequence of calculations:

(a) Having specified temperature, the Fe^{++}/Fe^{+++} ratio along the SiO_2 saturation line was specified.

(b) pO_2 and a_{FeO} equivalent to the prescribed slag composition and temperature were determined from the data of Muan[20], Darken and Gurry[27,28], Schuhmann and Ensio[29], Michal and Schuhmann[30] and Darken[31] (as replotted in Fig. IV.8).

(c) a_{Cu_2O} was calculated from the pO_2 in (b) and $a_{Cu} = 1$ (copper saturated system) using equations IV.5 and IV.6.

(d) The activity of Fe in the system was calculated from a_{FeO} and pO_2 according to the equations:

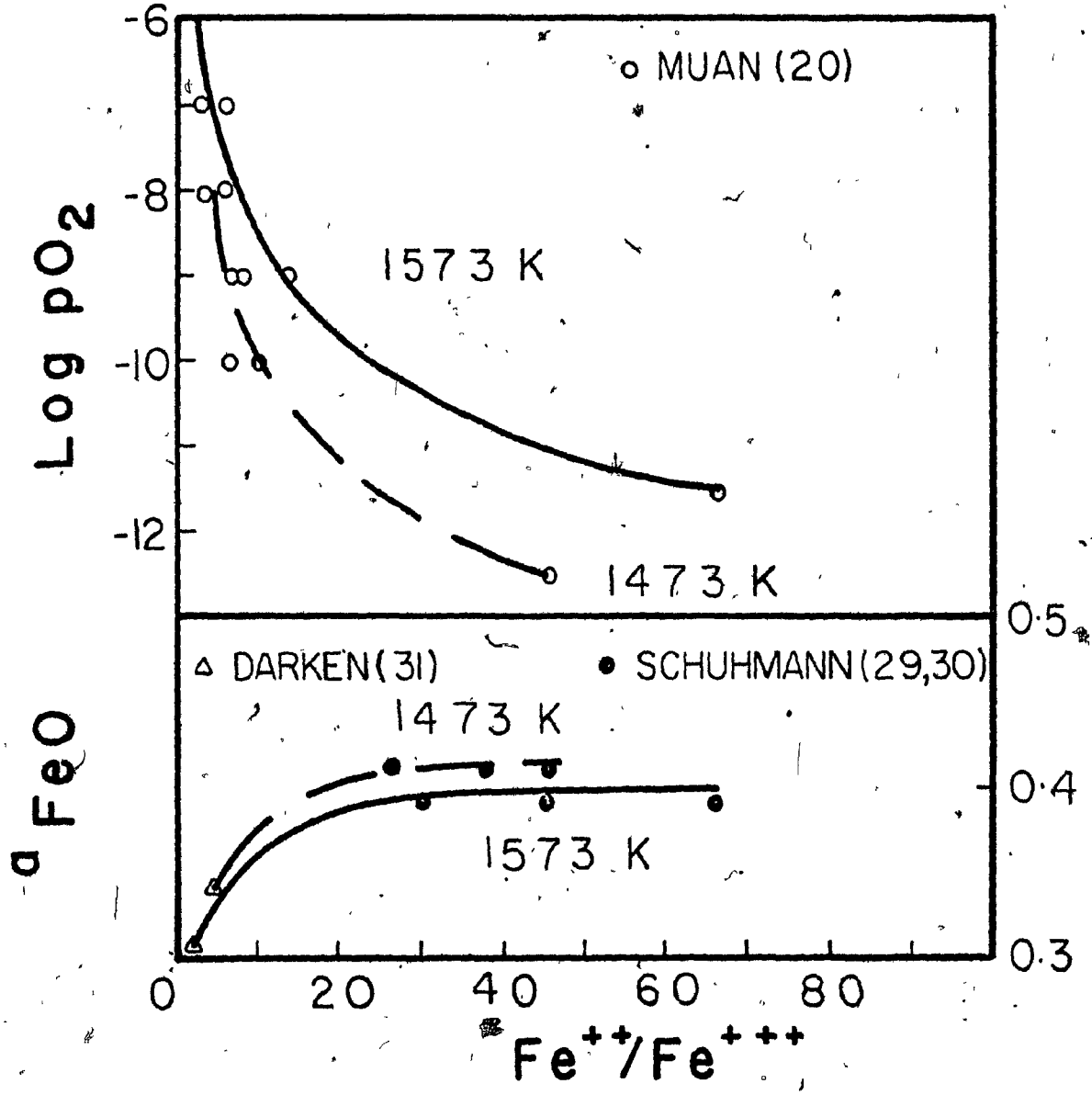

FIG. IV.8 Estimated oxygen pressure values and activity values of FeO for given Fe^{++}/Fe^{+++} ratio in slag from available data[20,29,30,31]. The a_{FeO} lines are also based on $a_{Fe_3O_4}$ and pO_2 data[20,27,28].

$$Fe_S + 1/2\ O_2 \rightleftarrows FeO_\ell$$

$$\Delta G^o = -233000 + 46.0\ T \quad \text{joules} \qquad \text{IV.7}$$

$$K_E = \frac{a_{FeO}}{a_{Fe_s}(pO_2)^{1/2}} \qquad \text{IV.8}$$

(e) The ratio a_{Cu_2S}/a_{FeS} of the system was calculated from a_{Cu}, a_{Cu_2O}, a_{Fe} and a_{FeO} using the equations:

$$2Cu_2O + Cu_2S \rightleftarrows 6Cu + SO_2$$

$$\Delta G^o = 97000 - 103.0\ T \quad \text{joules} \qquad \text{IV.9}$$

$$K^I_E = \frac{(a_{Cu})^6\ pSO_2}{(a_{Cu_2O})^2\ a_{Cu_2S}} \qquad \text{IV.10}$$

and

$$2FeO + FeS \rightleftarrows 3Fe + SO_2$$

$$\Delta G^o = 220000 - 46.4\ T \quad \text{joules} \qquad \text{IV.11}$$

$$K^{II}_E = \frac{(a_{Fe})^3\ pSO_2}{(a_{FeO})^2\ a_{FeS}} \qquad \text{IV.12}$$

which combine to give

$$\frac{K_E^{II}}{K_E^{I}} = \frac{a_{Cu_2S}}{a_{FeS}} \times \frac{(a_{Fe})^3}{(a_{FeO})^2} \times \frac{(a_{Cu_2O})^2}{(a_{Cu})^6}$$

or

$$\frac{a_{Cu_2S}}{a_{FeS}} = \frac{K_E^{II}}{K_E^{I}} \times \frac{(a_{FeO})^2}{(a_{Fe})^3} \times \frac{(a_{Cu})^6}{(a_{Cu_2O})^2}$$

(f) The composition of the matte which is equivalent to this a_{Cu_2S}/a_{FeS} ratio was calculated using the Temkin cationic matte model (assuming the system to be oxygen-free) proposed by Bale et al[21], i.e.;

$$a_{Cu_2S} = \left(\frac{n_{Cu}}{n_{Cu} + n_{Fe}}\right)^2 \cdot \frac{n_S}{n_S} = \left(\frac{2X_{Cu_2S}}{2X_{Cu_2S} + X_{FeS}}\right)^2 \cdot 1 \qquad \text{IV.13}$$

$$a_{FeS} = \frac{n_{Fe}}{n_{Cu} + n_{Fe}} \cdot \frac{n_S}{n_S} = \left(\frac{X_{FeS}}{2X_{Cu_2S} + X_{FeS}}\right) \cdot 1 \qquad \text{IV.14}$$

and the mole fraction summation;

$$X_{Cu_2S} + X_{FeS} = 1 \qquad \text{IV.15}$$

which lead to

$$X_{Cu_2S} = \left(\frac{a_{Cu_2S}/a_{FeS}}{4 + a_{Cu_2S}/a_{FeS}}\right)^{1/2} \qquad \text{IV.16}$$

(g) The activity of Cu_2S was calculated from X_{Cu_2S} in (f) using Equations IV.13 and IV.15.

(h) pSO_2 was calculated from a_{Cu}, a_{Cu_2S} and a_{Cu_2O} by Equations IV.9 and IV.10.

The results of the calculations are summarized in Fig. IV.9 which shows the matte composition range over which it is possible to produce metallic copper (SiO_2 saturation, liquid Fe-O-SiO_2 slag). The limit at the low matte grade end is iron saturation of the system ($a_{Fe} = 1$) while the upper limit is magnetite saturation ($a_{Fe_3O_4} = 1$). The following points can be noted.

(a) Copper can be at equilibrium with matte/slag/silica/gas in the range of matte grades of

44% to 79% Cu	1573 K
48% to 79% Cu	1473 K

(b) The equilibrium pSO_2 is very low at iron saturation conditions (10^{-6} or 10^{-7} atmos.) but it approaches 1 atmosphere at magnetite saturation.

It is of interest to compare these predictions with the measurements of Geveci and Rosenqvist[18] who found, under SiO_2 saturation conditions (1523 K), that:

(a) Cu can be at equilibrium with matte/slag/silica/gas for matte grades between 50 and 79.4% copper;

(b) the equilibrium pSO_2 is very low under iron saturation conditions and increases to 0.02 atmospheres at 79% Cu in matte (the latter in comparison with predictions of 10^{-2} atmospheres (1473 K) and 4×10^{-1} atmospheres (1573 K)).

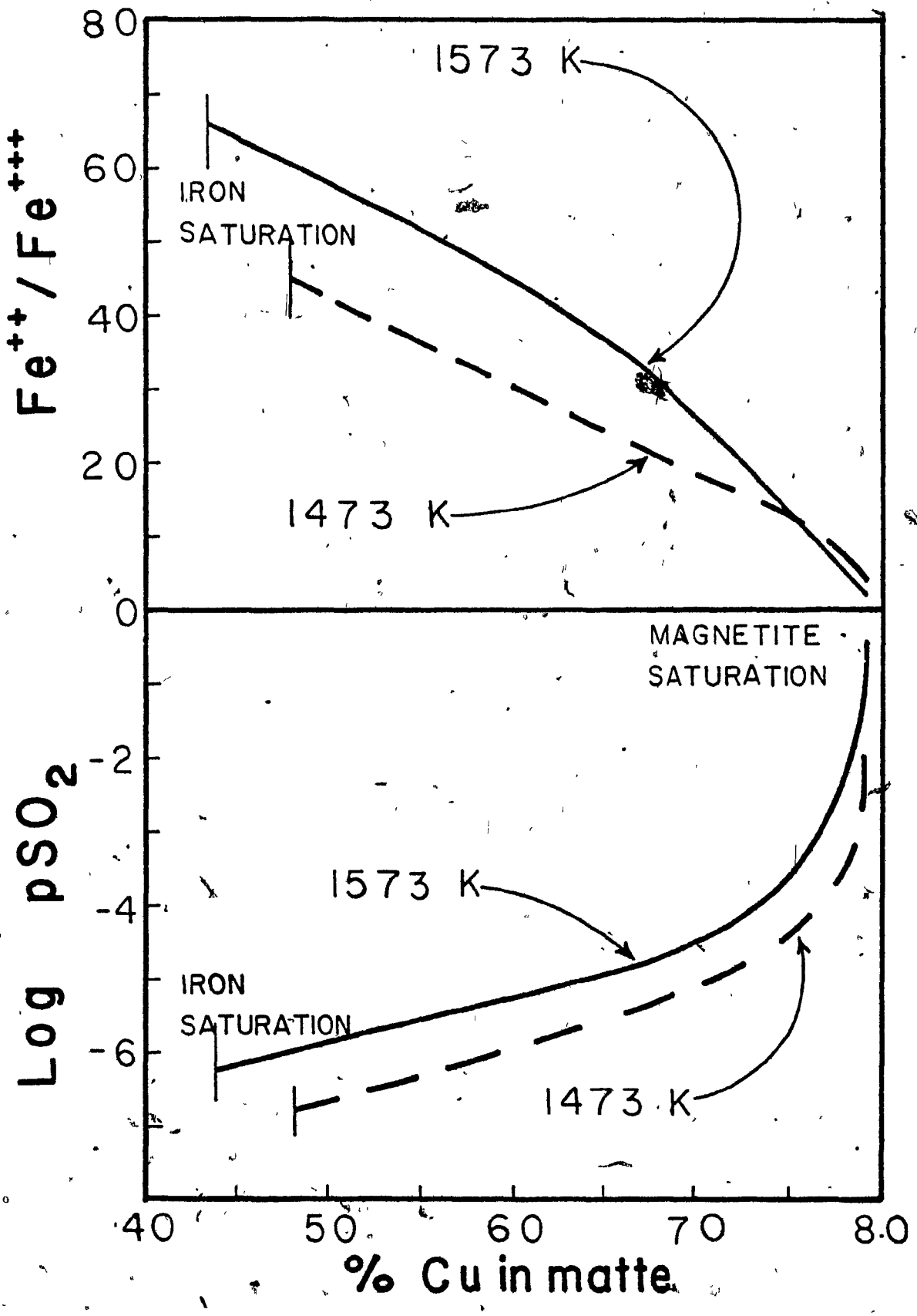

FIG. IV.9 Conditions under which metallic copper ($a_{Cu} = 1$) can be at equilibrium with matte and slag as calculated in Section IV.6.

The predictions are, therefore, very close to the experimental data reported by Géveci and Rosenqvist[18].

The precise composition of the matte which is in equilibrium with Cu, Fe_3O_4 and SiO_2 is predicted to be:

79.6% Cu (1473 K)

79.8% Cu (1573 K)

Geveci and Rosenqvist[18] report 79.4% Cu under these conditions and Rosenqvist[19] 79.5% Cu and Sehnalek (reported by Rosenqvist[19]) 78.9% Cu so that these predictions also seem to be reasonably accurate.

It appears, therefore, that Cu_2S-FeS activities, pO_2 and a_{FeO} slag data, and metal/matte/slag/gas experiments are well tied-in together.

IV.7 INDUSTRIAL IMPLICATIONS OF THE RESULTS

The results of this work show that matte smelting presents very few operating problems as long as the grade of the matte product is kept below 60% Cu. Under these conditions copper losses in slag are at a tolerable level (Fig. IV.4) and they are not appreciably influenced by temperature or SO_2 pressure.

From what can be gathered from industrial processes, it appears that production of mattes containing more than about 60% Cu also leads to difficult problems with impurities in the matte phase as well as high Cu-in-slag concentrations. This problem was not studied in this work but it is important to note that such problems exist.

With regard to producing copper directly from concentrate it is now clear that it is possible to produce copper directly from relatively low grade mattes. Conditions which promote such metal production are:

(a) low oxidizing potentials as represented by relatively high Fe^{++}/Fe^{+++} ratios in slags;

(b) low SO_2 pressures above the system.

Of course, it is not possible to obtain these conditions while oxygen or air are being passed through matte to remove sulphur from the system. However, they might be achieved by alternately passing (i) air or oxygen then (ii) reducing gas (CO or H_2) through the system. Copper would be produced during the reducing gas stage from low grade mattes thereby minimizing the copper-in-slag loss problem. How other impurities might behave during such a process is not known.

V. FUTURE WORK

On the basis of this investigation it is suggested that:

1. The present study should be extended to lower matte grades in order to complete the overall picture of the matte/slag/SO_2 system.
2. The study should be extended to include the CaO-Fe_3O_4 slags currently used by the Mitsubishi process[33].
3. Theoretical and experimental investigations of the Cu-Fe-O-S-SiO_2 system under copper saturation and controlled pSO_2 conditions should be undertaken in order to confirm the calculations of Section IV.6.
4. An investigation into the distribution of minor elements (e.g. As, Bi, Sb) between slag and matte (or slag, matte and metal) under controlled pSO_2 conditions should be undertaken.

These studies will further improve our knowledge of copper smelting systems.

VI. CONCLUSIONS

1. An experimental programme in which matte, slag and SO_2 (0.1 to 1.0 atmospheres) were equilibrated (1423-1573 K) has been carried out with the principal objective of examining copper-in-slag concentrations under oxidizing conditions.
2. The experiments were carried out under SiO_2 saturation conditions so that the system consisted of 5 components (Cu, Fe, O, S, Si) and 4 phases (quartz container, matte, slag, gas), hence 3 degrees of freedom. Specification of pSO_2, temperature and a particular matte grade fully defined the system.
3. The experiments showed that when slags and mattes are equilibrated, the copper-in-slag concentrations remain low as long as the mattes contain less than 60% Cu, under all temperature and pSO_2 conditions. Copper-in-slag concentrations increase dramatically under oxidizing conditions when the mattes contain more than 65% Cu.
4. Cu_2S is virtually insoluble in iron-silicate slags under all conditions. FeS has considerable solubility (up to 7% S) and Cu_2S-FeS mattes exhibit intermediate behaviour. It is suggested that the strong covalent nature of Cu_2S prevents it from dissociating in ionic slags.
5. Oxygen is virtually insoluble in Cu_2S but dissolves up to 10% in FeS, with mattes exhibiting intermediate behaviour. Oxygen will apparently not 'fit' into the covalent Cu_2S structure.

6. Conditions under which a pure copper phase will be at equilibrium with Fe-O-SiO_2 slags and Cu-Fe-S mattes have been predicted on the basis of previous experimental a_{FeO} and pO_2 data for slags, and a_{Cu_2S} data for mattes. It is shown that under SiO_2 saturation conditions metallic copper will occur in equilibrium with: (i) 45-50% Cu mattes at iron saturation, with (ii) 79% Cu mattes at magnetite saturation and with (iii) intermediate matte compositions within the liquid slag field. These predictions confirm the experimental results of Geveci and Rosenqvist.

7. The experimental copper-in-slag results show that industrial production of mattes containing 60% Cu or below should not cause excessive copper-in-slag losses. Copper losses may become excessive above this matte grade especially under highly oxidizing conditions.

APPENDIX I.1 Details of Experiments

Exp.#	Wt. Cu_2S gr.	Wt. FeS gr.	Wt. SiO_2 gr.	Wt. Slag gr.	Total Weight
1	5.5496	3.3297	0.925	5.67	15.4743
2	6.4746	0.9249	-	4.7308	12.1306
3	5.5496	1.8499	0.4	4.7308	12.5306
4	5.0000	5.0000	1.33	6.3934	17.7234
5	4.5000	5.7857	1.34	6.5761	18.2018
6	6.4746	0.9249	-	4.7308	12.1303
7	5.5496	1.8499	0.4	4.7308	12.5303
8	5.5496	3.3297	0.925	5.6700	15.4743
9	5.0000	5.3000	1.335	6.4000	18.0350
10	5.0000	5.0000	1.33	6.3934	17.7234
11	4.5000	5.7857	1.34	6.5761	18.2018
12	5.5496	1.8499	0.4	4.7308	12.5303
13	5.5496	3.3297	0.925	5.6700	15.4743
14	6.4746	0.9249	-	4.7308	12.1303
15	5.0000	5.0000	1.33	6.3934	17.7234
16	4.5000	5.7857	1.34	6.5761	18.2018
17	6.4746	-	-	4.1395	10.6141
18	6.0000	0.4746	-	4.1395	10.6141
19	5.5496	3.3297	0.9250	5.6700	15.4743
20	5.5496	1.8499	-	4.7308	12.1303
21	6.4746	0.9249	-	4.7308	12.1303
22	6.0120	1.3875	-	4.7308	12.1303
23	5.5496	2.5225	0.8731	5.2100	14.1552
24	5.5496	4.3164	1.0275	6.3000	17.1935
25	5.0000	5.0000	1.33	6.3934	17.7234
26	4.5000	5.7857	1.34	6.5761	18.2018
27	6.4746	0.9249	-	4.7308	12.1303
28	6.4746	-	-	4.1395	10.6141
29	5.5496	1.8499	0.4	4.7308	12.5303
30	5.5496	3.3297	0.925	5.6700	15.4743
31	5.0000	5.0000	1.33	6.3934	17.7234
32	4.5000	5.7857	1.34	6.5761	18.2018
33	6.4746	-	-	4.1395	10.6141
34	6.4746	0.9249	-	4.7308	12.1303
35	5.0000	5.0000	1.33	6.3934	17.7234
36	4.5000	5.7857	1.34	6.5761	18.2018
37	6.4746	0.9249	-	4.7308	12.1303
38	5.5496	3.3297	0.925	5.6700	15.4743
39	5.5496	1.8499	0.4	4.7308	12.5303
40	5.0000	5.0000	1.33	6.3934	17.7234
41	4.5000	5.7857	1.34	6.5761	18.2018
42	4.0000	6.2857	1.35	6.5761	18.2118
43	5.5496	1.8499	0.4	4.7308	12.5303
44	6.4706	0.9249	-	4.7308	12.1303
45	5.5496	3.3297	0.925	5.6700	15.4743
46	4.5000	5.7857	1.34	6.5761	18.2018
47	5.0000	5.0000	1.33	6.3934	17.7234

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