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# Equilibrium of Copper Matte and Silica-Saturated Iron Silicate Slags at 1300 °C and $P_{SO_2}$ of 0.5 atm



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Experimental study on the phase equilibria between copper matte with silica-saturated iron silicate slags was conducted at 1300 °C and  $P_{SO_2} = 0.5$  atm. The high-temperature isothermal equilibration in silica crucibles under controlled flowing CO-CO<sub>2</sub>-SO<sub>2</sub>-Ar was followed by quenching in an ice-water mixture and direct phase composition analyses by an electron probe X-ray microanalyzer. The equilibrium compositions for matte and slag, as well as the distribution coefficients, were displayed as a function of matte grade. The data set obtained at  $P_{SO_2} = 0.5$  atm and the previous study at  $P_{SO_2} = 0.1$  atm by the authors enabled an investigation on the impacts of  $P_{SO_2}$  as well as Al<sub>2</sub>O<sub>3</sub> and CaO additions on phase equilibria in the multiphase copper matte smelting system. Thermodynamic calculations using MTDATA software were performed to compare the experimental results with modeling. The present results enrich the fundamental thermodynamic information for the matte/slag/tridymite/gas equilibria in the primary copper smelting process at high  $P_{SO_2}$ .

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# I. INTRODUCTION

**COPPER** flash smelting has been the leading technology for primary copper sulfide smelting<sup>[1]</sup> because of its low energy consumption and environmental impact, reduced operational costs, and high on-line availability.<sup>[2,3]</sup> The  $P_{SO_2}$ , generated by the slag and matte formation reactions, in the horizontal settler of the flash smelting furnace (FSF) is equal to the prevailing total pressure.<sup>[4,5]</sup> Since the late 1970s, the smelting capacity of the FSF has been increased by 100 to 200 pct since technical oxygen (> 95 pct O<sub>2</sub>) was adopted into copper smelting,<sup>[2,6]</sup> resulting in increased SO<sub>2</sub> content of the off-gas to > 50 vol pct SO<sub>2</sub>. Therefore, accurate phase equilibria information of the copper matte and slag under a high  $P_{SO_2}$  is essential for the copper smelting process from the standpoint of resource efficiency as well as stable and optimized operation.

The main components of the copper matte-slag equilibrium are described by the Cu-Fe-S-O-SiO<sub>2</sub> system. However, industrial iron silicate-based copper smelting slags contain alumina  $(Al_2O_3)$ , lime (CaO),

and magnesia (MgO),<sup>[7,8]</sup> introduced into the smelting by copper ores, fluxes, and secondary raw materials (such as Waste Electrical and Electronic Equipment, WEEE). Hence, it is essential to extend the studies on matte-slag equilibria from the basic subsystem to the more complicated Cu-Fe-S-O-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO-CaO system under higher SO<sub>2</sub> partial pressures with the aim of providing comprehensive experimental data for copper smelting and industrial practices.

A careful literature review indicated that phase equilibria of copper matte and slag over the past few decades have been studied mainly under the SO<sub>2</sub> partial pressure of 0.1 atm<sup>[9–23]</sup> related to air blowing, while only limited data were reported for the equilibria under higher  $P_{\rm SO_2}$ .<sup>[18–23]</sup> Roghani *et al*.<sup>[19–22]</sup> investigated the phase equilibria of copper matte and different slags with the presence of trace elements at 1250 °C to 1300 °C and  $P_{\rm SO_2}$  of 0.1, 0.5, and 1 atm. They reported that the concentrations of copper, sulfur, and iron in slags were not affected by the prevailing  $P_{\rm SO_2}$ , similar to the observations by Tavera *et al*.<sup>[18]</sup> and Takeda.<sup>[23]</sup> However, the relationship between the matte/slag compositions and the  $P_{\rm SO_2}$  of the system was not fully characterized in those studies. In previous studies at higher  $P_{\rm SO_2}$ ,<sup>[18–23]</sup> the chemical analysis technique was used for measuring the matte and slag compositions, which gave somewhat scattered results due to incomplete separation of matte and slag. In recent publications by Fallah-Mehrjardi *et al*.<sup>[24–27]</sup> for the matte/slag/tridymite equilibria of the Cu-Fe-S-O-SiO<sub>2</sub><sup>[24–26]</sup> and Cu-Fe-S-O-SiO<sub>2</sub>-CaO<sup>[27]</sup> systems at  $P_{\rm SO_2} = 0.25$  atm

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and t = 1200 °C to 1250 °C, the experiments were conducted using a high-temperature equilibration and quenching technique in flowing CO-CO<sub>2</sub>-SO<sub>2</sub>-Ar gas. The equilibrated phase compositions were analyzed directly on the polished sections of the matte and slag phases by EPMA (electron probe X-ray microanalysis)

phases by EPMA (electron probe X-ray microanalysis). Abdeyazdan *et al.*<sup>[28,29]</sup> investigated the effects of MgO and Al<sub>2</sub>O<sub>3</sub> on the matte-slag-tridymite equilibria at 1200 °C to 1300 °C and  $P_{SO_2} = 0.25$  atm. Shishin *et al.*<sup>[30]</sup> equilibrated copper matte and FeO<sub>x</sub>-SiO<sub>2</sub> slags at tridymite saturation under  $P_{SO_2} = 0.1$  to 0.6 atm and t = 1200 °C to 1300 °C. They also studied the impacts of Al<sub>2</sub>O<sub>3</sub>, MgO, and CaO on the phase equilibrium of matte and slag with tridymite saturation at 1200 °C and  $P_{SO_2}$  of 0.25 atm.<sup>[31]</sup> It was found that the dissolution of copper, sulfur, and "FeO" in slag decreased with increasing MgO, Al<sub>2</sub>O<sub>3</sub>, and CaO concentration in slags, whereas the matte composition was not significantly affected by the slag modifiers.<sup>[28,29,31]</sup> Hidayat *et al.*<sup>[32,33]</sup> investigated the matte-slag-spinel

Hidayat *et al.*<sup>[32,33]</sup> investigated the matte-slag-spinel equilibria in the Cu-Fe-O-S-SiO<sub>2</sub> system at  $P_{SO_2}$  of 0.25 atm and t = 1200°C. Chen *et al.*<sup>[34]</sup> investigated the phase equilibria of copper matte and FeO<sub>x</sub>-SiO<sub>2</sub> slag with spinel saturation at 1200 °C to 1250 °C,  $P_{SO_2} = 0.3$ and 0.6 atm, and fixed matte grade of 72 wt pct Cu. Sun *et al.*<sup>[35]</sup> and Chen *et al.*<sup>[34]</sup> studied the effects of CaO on the matte-slag-spinel equilibria and liquidus contours of slags under the same conditions but at different temperatures at 1150 °C to 1250 °C. They reported that the liquidus temperature increased with increasing CaO at constant SiO<sub>2</sub> concentration. In addition, the equilibrium SiO<sub>2</sub> concentration was found to increase significantly with increasing  $P_{SO_2}$ .

icantly with increasing  $P_{SO_2}$ . In our previous works, <sup>[17–15]</sup> matte-slag equilibria at silica saturation have been studied at  $P_{SO_2} = 0.1$  atm and t = 1250 °C to 1300°C with the presence of different trace elements. Therefore, the objective of the present study was to enrich the experimental thermodynamic data for equilibrium phase relations of copper matte and different silica-saturated FeO<sub>x</sub>-SiO<sub>2</sub>, FeO<sub>x</sub>-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and FeO<sub>x</sub>-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO slags at 1300 °C and high  $P_{SO_2}$  of 0.5 atm. The use of silica crucibles ensured the silica saturation of the matte-slag system and provided the possibility to examine the system without extra impurities, such as MgO or Al<sub>2</sub>O<sub>3</sub>, introduced by the substrate. The new experimental data obtained in the present study can be used to update the multi-component and multi-phase databases of related thermodynamic software for copper smelting modeling.

#### **II. EXPERIMENTAL**

The experimental technique used in the present study involved high-temperature isothermal equilibration in controlled CO-CO<sub>2</sub>-Ar-SO<sub>2</sub> atmospheres, quenching, and direct phase composition measurement of the phases using EPMA. The experiments were carried out in a vertical tube furnace (Lenton PTF 14/45/450) equipped with SiC heating elements and a recrystallized alumina work tube. The temperature of the three-zone furnace was regulated by three Eurotherm 3216 PID controllers. The temperature of samples in the furnace was measured by a calibrated S-type Pt/10 pctRh thermocouple (Johnson-Matthey Noble Metals, UK), located next to the silica crucible. Detailed information about the experimental methodology used has been described previously.<sup>[11–15]</sup>

The partial pressure of SO<sub>2</sub> was held constant at 0.5 atm in all experiments. To create the designed O<sub>2</sub> and S<sub>2</sub> partial pressures in the gas mixture for different target matte grades, the gas flow rates were calculated by MTDATA<sup>[36]</sup> software using the SGTE pure substances database.<sup>[37]</sup> The calculated partial pressures and gas flow rates are listed in Table I. All gas flow rates were controlled by DFC26 digital mass flow controllers (Aalborg, USA).

The initial copper matte mixtures were synthesized from high-purity powders of Cu<sub>2</sub>S (99.5 wt pct) and FeS (99.9 wt pct). The silica-saturated iron silicate slags were prepared by mixing Fe<sub>2</sub>O<sub>3</sub> (99.998 wt pct) and SiO<sub>2</sub> (99.995 wt pct) from Alfa Aesar and Al<sub>2</sub>O<sub>3</sub> (99.99 wt pct) and CaO (99.9 wt pct) from Sigma-Aldrich.<sup>[14,15]</sup> All gases used in this study were supplied by AGA-Linde (Finland) with purities > 99.97 vol pct. For each experiment, approximately 0.1 g copper matte mixture with an equal amount of slag mixture was pressed into a pellet before being placed into a silica crucible. The sample pellet was annealed under different gas atmospheres for 4 hour to get uniform matte and slag compositions, as suggested in our previous study.<sup>[14,15]</sup> It should be noted that all experiments were duplicated for increased reliability  $(4 \times 2 \times 3 = 24 \text{ in total})$ . The equilibrated samples were quenched into ice-water mixture so that the phases presented at high temperature and their compositions were attained at room temperature. The quenched samples were cut into half, mounted in epoxy resin (EpoFix, Struers, Denmark), ground by SiC papers, and polished using a metallographic polishing cloth with diamond spray. The polished surfaces were carbon coated using a LEICA EM SCD050 sputtering device (Leica Microsystems, Austria) for electrical conductivity.

The micrographs of the polished sections and the preliminary phase compositions were examined using a scanning electron microscope, SEM (Tescan MIRA 3, Brno, Czech Republic) equipped with an UltraDry Silicon Drift Energy Dispersive X-ray Spectrometer, EDS (Thermo Fisher Scientific, Waltham, MA, USA). The elemental concentrations in matte and slag were analyzed with a Cameca SX100 EPMA (Cameca SAS, Genevilliers, France) fitted with five wavelength-dispersive spectrometers (WDS). The EPMA analyses were conducted at an accelerating voltage of 20 kV, beam current of 60 nA, and beam diameter of 100  $\mu$ m for matte and 50 to 100  $\mu$ m for slag. The employed standards and x-ray lines were quartz (Si Ka), almandine (Al K $\alpha$ ), metallic copper (Cu K $\alpha$ ), hematite (Fe K $\alpha$ and O K $\alpha$ ), pentlandite (S K $\alpha$ ), and diopside (Ca K $\alpha$ ). The elemental detection limits of EPMA for matte and slag are presented in Table II. At least eight points were measured in both the matte and slag phase in each



Fig. 1—Typical back-scattered electron micrographs of the matte-slag-silica system at 1300 °C and  $P_{SO_2} = 0.5$  atm; (a) 57.10 wt pct Cu in matte without Al<sub>2</sub>O<sub>3</sub> and CaO in slag; (b) 61.1 wt pct Cu in matte with Al<sub>2</sub>O<sub>3</sub>-containing slag; (c) 64.4 wt pct Cu in matte with (Al<sub>2</sub>O<sub>3</sub> + CaO)-containing slag.



Fig. 2—Copper (a), iron (b), sulfur (c), and oxygen (d) concentrations in the matte at 0.5 atm  $P_{SO_2}$  as a function of oxygen partial pressure or matte grade.

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Fig. 3—Set of graphs describing the slag compositions at 0.5 atm  $P_{SO_2}$ ; (a) copper; (b) sulfur; (c) "FeO"; (d) SiO<sub>2</sub>; (e) Fe/SiO<sub>2</sub> ratio; (f) Al<sub>2</sub>O<sub>3</sub>; (g) CaO.



Fig. 4—An isothermal section of the superimposed phase diagrams of FeO<sub>x</sub>-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (solid lines) and FeO<sub>x</sub>-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-8 wt pct CaO (dotted lines) systems at 1300 °C and  $P_{O_2} = 10^{-7.8}$  atm with the plotted experimental data.<sup>[15]</sup> OX\_LIQ-molten slag; G-gas; TRI-tridymite; SP-spinel; FSP-feldspar; MUL-mullite;  $\Box$ CaO-free slags at 0.1 atm  $P_{SO_2}$ ;  $\odot$ CaO-containing slags at 0.1 atm  $P_{SO_2}$ .

sample for statistical reliability. The raw data were processed by a PAP-ZAF on-line matrix correction program<sup>[38]</sup> before normalizing the results.

#### **III. RESULTS AND DISCUSSION**

The experiments were carried out for a wide target matte grade range of 60 to 75 wt pct Cu at 1300 °C and  $P_{SO_2}$  of 0.5 atm. Typical microstructures of the equi-librated phases obtained at  $P_{O_2} = 10^{-7.56}$  atm for target matte grade of 60 wt pct Cu are shown in Figure 1. The matte-slag equilibrium was found in all samples. A large fraction of recrystallized silica crystals, *i.e.*, tridymite (> 99 wt pct  $SiO_2$ ), was precipitated in the slags, attributed to the silica saturation caused by the silica crucible. The tridymite preferred to form on the slag-crucible interfaces, but some discrete rod-like crystals also existed randomly in the slag. All phases were homogeneous after rapid quenching, except for the matte, where copper-rich veins (90 to 97 wt pct Cu) were found. The copper-rich veins were formed because of the insufficient quenching rate of sulfur-deficient matte. The measured average compositions of matte and liquid slag phases with standard deviations are listed in Table III.

#### A. Matte Composition

The concentrations of copper, iron, sulfur, and oxygen in matte against oxygen partial pressure or matte grade are shown in Figure 2. The data for 0.1 atm  $P_{SO_2}$  are from our previous study.<sup>[15]</sup> As Figure 2(a) shows, the copper concentration in matte increased with increasing oxygen partial pressure, similar to the results at  $P_{SO_2}$  of 0.1 atm<sup>[13,15]</sup> and the observations by other researchers.<sup>[16,21,25–30]</sup> It was noted, in general, that the prevailing  $P_{O_2}$  increased with increasing  $P_{SO_2}$  at a given matte grade, as described in the sulfur-oxygen potential diagram by Yazawa.<sup>[17]</sup> A very similar relationship between the oxygen partial pressure and matte grade at different  $P_{SO_2}$  was also observed by Roghani *et al.*,<sup>[21]</sup> in which copper matte was equilibrated with FeO<sub>x</sub>-SiO<sub>2</sub>-MgO slag at  $P_{SO_2}$  of 0.1 to 1 atm. The  $P_{O_2}$  for different target matte grades in the present study was somewhat lower than the values reported by Roghani et al.,<sup>[21]</sup> in which the partial pressures of  $SO_2$ ,  $S_2$ , and  $O_2$  in the gas phase were controlled by Ar-SO<sub>2</sub>-S<sub>2</sub> gas mixtures.

At silica saturation, the Al<sub>2</sub>O<sub>3</sub> and CaO additions in iron silicate slags led to an increase of the copper concentration in matte at a given  $P_{O_2}$ . For example, under the condition of  $P_{O_2} = 10^{-7.36}$ , the copper



Fig. 5—An isothermal section of the superimposed phase diagrams of FeO<sub>x</sub>-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (solid lines) and FeO<sub>x</sub>-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-8 wt pct CaO (dotted lines) systems at 1300 °C and  $P_{O_2} = 10^{-7.3}$  atm with the plotted experimental data. OX\_LIQ refers to molten slag; G refers to gas; TRI refers to tridymite; SP refers to spinel; FSP refers to feldspar; MUL refers to mullite;  $\triangle$ CaO-free slags of this study at 0.5 atm  $P_{SO_2}$ ;  $\triangle$ CaO-containing slags of this study at 0.5 atm  $P_{SO_2}$ .

			Ga	s riow Ka	tes (mL/m	III)
Target Matte Grade (Wt Pct Cu)	Target $Log_{10}P_{O_2}$ (atm)	Target $Log_{10}P_{S_2}$ (atm)	СО	CO <sub>2</sub>	$SO_2$	Ar
60	- 7.56	- 1.95	25	25	200	160
65	- 7.42	- 2.15	15.5	25	200	140
70	- 7.36	-2.30	12	30	193	148
75	- 7.09	- 2.83	8.5	100	200	90

Table I. Gas Flow Rates Generating  $P_{SO_2} = 0.5$  atm at 1300 °C and the Prevailing  $P_{O_2}$  and  $P_{S_2}$  at Each Target Matte Grade

content in the matte in the Al<sub>2</sub>O<sub>3</sub> and CaO-free system was around 66 wt pct, and it increased to approximately 68 and 70 wt pct in the Al<sub>2</sub>O<sub>3</sub>- and (Al<sub>2</sub>O<sub>3</sub> + CaO)-containing systems, respectively. Alternatively, at the given matte grade, the  $P_{O_2}$  decreased with adding Al<sub>2</sub>O<sub>3</sub> and CaO into slags. Similar observations regarding the effects of Al<sub>2</sub>O<sub>3</sub> and CaO on the matte grade were also found in the literature.<sup>[27,29,31]</sup> The Al<sub>2</sub>O<sub>3</sub> and CaO additions decrease the activity of FeO in slag at silica saturation, thus leading to an increase of copper concentration in the matte, corresponding to reactions [1] and [2] suggested by Yazawa<sup>[17]</sup> and Fallah-Mehrjardi *et al.*,<sup>[26]</sup> respectively.

$$FeS_{(matte)} + 1/2O_{2(slag)} = FeO_{(slag)} + 1/2S_{2(gas)}$$
 [1]

Cas Elan Datas (m.L./min)

$$\operatorname{FeS}_{(matte)} + 3/2O_{2(slag)} = \operatorname{FeO}_{(slag)} + \operatorname{SO}_{2(gas)}$$
 [2]

Figure 2(b) indicates that concentration of iron in the matte decreased from approximately 14 to 2 wt pct with increasing matte grade from 55 to 75 wt pct Cu, independently from  $P_{SO_2}$  and the slag modifiers  $Al_2O_3$  and CaO. The present results for the iron concentration in matte had small deviations from the results by other researchers,<sup>[9,11,13,25,26,31]</sup> but they conform the overall



Fig. 6—The distribution coefficients of copper (a), iron (b), and sulfur (c) between matte and slag as a function of the matte grade.

 Table II.
 Elemental Detection Limits of the EPMA

 Analyses/ppmw (Parts-Per-Million By Weight)

Element	0	Si	Al	S	Ca	Fe	Cu
Matte	1274	251	249	141	110	199	373
Slag	997	205	187	108	88	201	267

decreasing trend with increasing matte grade. These investigations<sup>[9,11,13,25,26,31]</sup> had some differences compared to this study in their experimental conditions employed, such as  $P_{SO_2}$ , slag composition and/or minor elements.

The sulfur concentration in the matte obtained at  $P_{SO_2}$  of 0.5 atm, shown in Figure 2(c), decreased from around 23 to 20 wt pct within the matte grade range investigated. The results for sulfur concentrations in matte in the present study were identical to the observations at  $P_{SO_2} = 0.1$  atm,<sup>[11,15]</sup> suggesting that the sulfur concentration in the matte was not sensitive to

the prevailing  $SO_2$  partial pressure. The results in the literature<sup>[9,13,20,25,26]</sup> are on the higher side of the present results, with similar general decreasing trends.

As for the oxygen concentrations in matte obtained at  $P_{SO_2}$  of 0.5 atm in Figure 2(d), decreasing with increasing copper content in matte, were likely independent of the partial pressure of SO<sub>2</sub>. The present results agreed well with the data in previous studies.<sup>[9,11,13,25]</sup> As reported by Fallah-Mehrjardi *et al.*,<sup>[27]</sup> the decreasing trend of oxygen concentration in matte may be related to a stronger ability of iron to form an oxy-sulfide liquid solution at low matte grades. The Al<sub>2</sub>O<sub>3</sub> and CaO additions had no quantifiable effect on the oxygen concentration in the matte, which corresponds to the observations made for iron and sulfur concentrations.<sup>[13,15,27,29,31]</sup>

#### B. Slag Composition

The slag compositions with their standard deviations as error bars against matte grade or silica concentration are shown in Figure 3. The results from the literature<sup>[11,13,16,20,21,25,26,31]</sup> were also plotted in the graphs

			Matte Compo	sition Wt Pct			Liquid Slag Comp	position Wt Pct	
Code	$\mathrm{Log}_{10}P_{\mathrm{O}2}~\mathrm{(atm)}$	0	S	Fe	Cu	"FeO"	$SiO_2$	$Al_2O_3$	CaO
-	- 7.09	$1.10 \pm 0.15$	$19.90 \pm 0.14$	$2.03 \pm 0.02$	$73.73 \pm 0.36$	$60.79 \pm 0.43$	$40.64 \pm 0.30$	N/A	N/A
2	- 7.09	$1.11 \pm 0.07$	$19.90\pm0.15$	$2.40 \pm 0.02$	$73.71 \pm 0.37$	$59.65 \pm 0.21$	$40.27 \pm 0.36$	N/A	N/A
С	- 7.36	$1.47\pm0.07$	$21.06 \pm 0.15$	$7.24 \pm 0.05$	$66.65\pm0.18$	$60.60 \pm 0.46$	$41.10 \pm 0.33$	N/A	N/A
4	- 7.36	$1.50\pm0.08$	$20.99 \pm 0.07$	$6.99 \pm 0.06$	$66.57 \pm 0.12$	$61.91 \pm 0.50$	$38.11 \pm 0.60$	N/A	N/A
5	- 7.42	$1.43\pm0.09$	$22.01 \pm 0.21$	$9.84\pm0.08$	$63.54\pm0.29$	$60.35 \pm 0.36$	$39.09 \pm 0.48$	N/A	N/A
9	- 7.42	$1.66 \pm 0.14$	$21.58 \pm 0.26$	$9.87 \pm 0.12$	$63.39\pm0.34$	$59.36 \pm 0.17$	$39.61 \pm 0.17$	N/A	N/A
7	- 7.56	$1.93 \pm 0.11$	$23.11 \pm 0.20$	$13.74 \pm 0.15$	$57.97 \pm 0.37$	$61.22 \pm 0.41$	$38.17 \pm 0.40$	N/A	N/A
8	- 7.56	$2.72 \pm 0.17$	$23.24\pm0.16$	$14.06 \pm 0.13$	$57.10 \pm 0.47$	$59.91 \pm 0.94$	$36.62 \pm 1.47$	N/A	N/A
6	- 7.09	$0.35\pm0.01$	$20.04\pm0.14$	$1.67\pm0.02$	$74.25 \pm 0.26$	$46.44 \pm 0.27$	$46.93 \pm 0.46$	$7.55 \pm 0.10$	N/A
10	- 7.09	$0.69 \pm 0.09$	$19.99 \pm 0.11$	$1.84\pm0.08$	$73.74 \pm 0.40$	$46.35 \pm 0.18$	$47.44 \pm 0.19$	$7.85 \pm 0.04$	N/A
11	- 7.36	$1.23\pm0.06$	$20.79\pm0.10$	$5.54 \pm 0.04$	$68.60 \pm 0.11$	$47.88 \pm 0.40$	$47.17 \pm 0.49$	$7.36 \pm 0.06$	N/A
12	- 7.36	$1.23\pm0.07$	$21.24 \pm 0.11$	$5.79 \pm 0.04$	$68.17 \pm 0.23$	$47.76 \pm 0.19$	$46.40 \pm 0.20$	$7.10 \pm 0.03$	N/A
13	- 7.42	$1.46 \pm 0.11$	$21.33 \pm 0.04$	$7.47 \pm 0.14$	$65.62\pm0.20$	$47.59 \pm 0.04$	$47.64 \pm 0.14$	$7.83 \pm 0.07$	N/A
14	- 7.42	$1.38\pm0.06$	$21.52\pm0.09$	$7.13 \pm 0.03$	$66.38 \pm 0.14$	$46.30 \pm 0.10$	$47.67 \pm 0.22$	$7.33 \pm 0.07$	N/A
15	- 7.56	$1.50\pm0.06$	$22.67\pm0.15$	$11.37 \pm 0.08$	$61.06 \pm 0.30$	$46.50 \pm 0.16$	$48.15 \pm 0.21$	$8.56\pm0.06$	N/A
16	- 7.56	$1.52\pm0.06$	$22.44\pm0.13$	$10.90\pm0.06$	$61.84\pm0.23$	$45.73 \pm 0.16$	$47.96 \pm 0.14$	$8.18\pm0.07$	N/A
17	- 7.09	$0.82\pm0.08$	$20.28\pm0.17$	$1.22 \pm 0.04$	$74.05\pm0.39$	$30.64\pm0.20$	$56.84 \pm 0.22$	$7.23 \pm 0.06$	$7.62 \pm 0.04$
18	- 7.09	$0.37\pm0.06$	$20.44\pm0.15$	$1.42 \pm 0.01$	$73.88 \pm 0.39$	$30.09\pm0.20$	$57.72 \pm 0.14$	$7.51 \pm 0.10$	$7.77 \pm 0.07$
19	- 7.36	$1.25\pm0.04$	$20.69\pm0.12$	$4.26\pm0.03$	$70.02 \pm 0.37$	$32.27 \pm 0.29$	$55.73 \pm 0.35$	$6.94\pm0.07$	$7.18 \pm 0.03$
20	- 7.36	$0.88\pm0.05$	$20.73 \pm 0.11$	$4.32 \pm 0.03$	$70.19 \pm 0.20$	$33.08 \pm 0.38$	$55.60 \pm 0.24$	$6.75 \pm 0.11$	$7.15 \pm 0.08$
21	- 7.42	$1.41 \pm 0.05$	$21.12 \pm 0.08$	$5.85\pm0.03$	$68.02 \pm 0.13$	$32.03 \pm 0.23$	$56.20 \pm 0.23$	$7.01 \pm 0.14$	$7.32 \pm 0.05$
22	- 7.42	$1.60\pm0.06$	$21.39 \pm 0.11$	$5.81 \pm 0.04$	$67.73 \pm 0.18$	$32.22 \pm 0.87$	$58.10 \pm 0.77$	$7.35 \pm 0.34$	$7.51 \pm 0.13$
23	- 7.56	$1.54\pm0.09$	$22.04\pm0.14$	$8.91 \pm 0.09$	$64.42\pm0.28$	$30.57 \pm 1.50$	$57.59 \pm 0.90$	$7.44\pm0.42$	$7.78 \pm 0.14$
24	- 7.56	$1.14\pm0.06$	$22.10\pm0.30$	$9.02 \pm 0.10$	$63.80\pm0.58$	$31.27 \pm 0.49$	$56.79 \pm 0.33$	$7.41 \pm 0.11$	$7.69 \pm 0.14$
Conce	ntrations lower than the	detection limits of	FPMA are marked as	N/A					

Table III. Measured Compositions of Matte and Liquid Slag Phases at 1300 °C and  $P_{
m SO_2}$  of 0.5 atm

for comparison. Figure 3(a) shows that the copper concentration in FeO<sub>x</sub>-SiO<sub>2</sub> slag at tridymite saturation at 1300 °C and  $P_{SO_2}$  of 0.5 atm stayed almost constant up to the matte grade of 65 wt pct Cu, and then it started to increase with increasing matte grade. Similar observations for copper solubility in slags were also reported in the literature.<sup>[11,13,19–21,23]</sup> However, when Al<sub>2</sub>O<sub>3</sub> and CaO were added in the slag, the copper loss in slags started to increase earlier, at lower matte grades. It also appeared that copper loss in the slag was not sensitive to the partial pressure of SO<sub>2</sub> at a given matte grade, which corresponds to some previous observations.<sup>[18–22,26,39]</sup> However, some researchers<sup>[40,41]</sup> reported that the copper content in the slag increased significantly with increasing  $P_{SO_2}$ .

The copper concentration in the slags generally decreased with the addition of Al<sub>2</sub>O<sub>3</sub> and CaO. The simultaneous addition of Al<sub>2</sub>O<sub>3</sub> and CaO decreased the copper in slag by approximately 0.4 wt pct over the entire matte grade range investigated. This positive impact of  $Al_2O_3$  and CaO on decreasing copper loss in the slags can be also found in other studies.<sup>[13,29,31,42–47]</sup> However, the increasing order of Al<sub>2</sub>O<sub>3</sub> and CaO on lowering the copper loss in slags observed in the present work is contrary to the results by Shimpo et al., [48] in which the phase equilibrium between copper matte and  $FeO_x$ -SiO<sub>2</sub>-based slag was studied at metallic copper and silica double saturation. They reported that the concentration of copper in the CaO-containing slags was higher than that in the Al<sub>2</sub>O<sub>3</sub>-containing slags when the matte grade was < 60 wt pct Cu, after which the CaO-containing slag exhibited a lower copper solubility. It seems that their results are contradictory to other literature. The small additions of basic oxides such as CaO and MgO break up the silica polymers, thus lowering the melting point and viscosity of the slag,<sup>[49,50]</sup> resulting in a decrease of copper losses due to physical entrainment in slags. The chemical losses decreased because of the replacement of copper cations by Al<sup>3+</sup> and Ca<sup>2+</sup>.<sup>[49]</sup> The results for the copper concentration in slags provide potential for improving the recovery of the copper value from slags by controlling the matte grade and adding basic oxides into the smelting system.

Figure 3(b) indicates that the sulfur concentration in all slags decreased with increasing matte grade, similar to the trends described in previous studies.<sup>[13,20,31]</sup> The pure FeO<sub>x</sub>-SiO<sub>2</sub> slags exhibited the highest sulfur solubilities, and it was remarkably reduced by Al<sub>2</sub>O<sub>3</sub> and CaO additions.<sup>[13,27,29,31]</sup> The Al<sub>2</sub>O<sub>3</sub> addition decreased the sulfur concentration by about 50 pct compared to the Al<sub>2</sub>O<sub>3</sub>-free slag at the matte grade of 65 wt pct Cu. The additional CaO in slag led to a further reduction of sulfur content in slag at the given matte grade. The impact of Al<sub>2</sub>O<sub>3</sub> and CaO on decreasing the sulfur content in slag decreased at higher matte grades towards 75 wt pct Cu. Somewhat surprisingly, there seemed to be no strong correlation between the sulfur concentration in the slag and  $P_{SO_2}$ .

Iron is present as  $Fe^{2+}$  and  $Fe^{3+}$  in the slags under the conditions of the present study. As the valence state of iron cannot be measured by EPMA, for ease of presentation in the present study, the total iron content in the silica-saturated iron silicate slags was recalculated to "FeO," as shown in Figure 3(c). The "FeO" concentration in the silica-saturated, pure  $FeO_x$ -SiO<sub>2</sub> slag had a slightly decreasing trend with increasing matte grade, as reported by Sukhomlinov et al.<sup>[13]</sup> and Fallah-Mehrjardi *et al.*<sup>[25,26]</sup> With the slag modifiers  $Al_2O_3$  and CaO, the silica-saturated "FeO" concentration in the  $FeO_x$ -SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and  $FeO_x$ -SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO slag stayed almost constant at 46 and 31 wt pct, respectively. The results in the Al<sub>2</sub>O<sub>3</sub> and CaO-containing slags have similar trends as reported by Sukhomlinov et al.<sup>[13]</sup> but the alumina and lime concentrations were different. A comparison of the two data sets obtained at  $P_{SO_2} = 0.1$ and 0.5 atm shows that the "FeO" concentration in slag is independent of the  $P_{SO_2}$ .

The SiO<sub>2</sub> concentrations in slags, shown in Figure 3(d), increased remarkably by approximately 5 wt pct with increasing  $P_{SO_2}$ , similar to the observations by Sun et al.<sup>[35]</sup> The present results for all slags had similar trends with the results obtained at  $P_{SO_2} = 0.1$  atm.<sup>[13,15]</sup> The SiO<sub>2</sub> concentration in the  $FeO_x$ -SiO<sub>2</sub> slag increased slightly from 37 to 40 wt pct over the matte grade range studied, but the results with Al<sub>2</sub>O<sub>3</sub>- and CaO-containing slags showed constant values as a function of matte grade. However, in the study by Roghani et al.<sup>[21]</sup> at  $P_{SO_2} = 0.1$  to 1 atm, the SiO<sub>2</sub> concentration in the FeO<sub>x</sub>-SiO<sub>2</sub>-MgO slag was reported to decrease with increasing matte grade within the matte grade range studied in the present work. They reported that the decrease may be ascribed to the increasing copper solubility in the slag at higher matte grades, and solid silica inclusions floating on top of the slag layer, as well as solid olivine formed as a consequence of using MgO crucibles, may have been a source of error in the silica analyses.<sup>[21]</sup>

The Fe/SiO<sub>2</sub> ratio in slag is a crucial parameter in pyrometallurgical copper smelting, as it is strongly related to the viscosity and liquidus temperature of slag. Figure 3(e) shows that the  $Fe/SiO_2$  ratio in the pure  $FeO_x$ -SiO<sub>2</sub> slag decreased slightly with increasing matte grade, as reported in previous studies,<sup>[13,15,16,25,26]</sup> whereas the results for the  $Al_2O_3$ -containing and CaO-containing slags exhibited no evident changes,<sup>[13,15]</sup> indicating that the addition of Al<sub>2</sub>O<sub>3</sub> and CaO had little effect on the Fe/SiO<sub>2</sub> ratio in the present study. The slight changes in silica and total iron content in slags contributed to the limited effect of matte grade on Fe/  $SiO_2$  ratio in this study. The overall increase of  $SiO_2$ concentration in slag compared with the results at 0.1 atm of  $P_{SO_2}$  lead to the decrease of Fe/SiO<sub>2</sub> ratio in slag at  $P_{SO_2} = 0.5$  atm. A similar decrease of the Fe/SiO<sub>2</sub> ratio in slag by increasing  $P_{SO_2}$  from 0.1 to 0.25 atm at 1200°C was also reported by Fallah-Mehrjardi et al.[16,25]

The experimentally measured Al<sub>2</sub>O<sub>3</sub> and CaO concentrations in the silica-saturated slags were plotted as a function of SiO<sub>2</sub> content and are shown in Figures 3(f) and (g), respectively. Both the Al<sub>2</sub>O<sub>3</sub> and CaO concentrations in the present study increased with increasing SiO<sub>2</sub> concentration in slags for each slag series, as reported in our previous studies at  $P_{SO_2} = 0.1$  atm.<sup>[13,15]</sup> This indicates that the Al<sub>2</sub>O<sub>3</sub> and CaO additions increase the solubility of silica in iron silicate slags,<sup>[51]</sup> although the Al<sub>2</sub>O<sub>3</sub> and CaO concentrations were different between the compared studies. Therefore, when the Al<sub>2</sub>O<sub>3</sub> and CaO concentrations in the silica-saturated FeO<sub>x</sub>-SiO<sub>2</sub>-based slag increased, more SiO<sub>2</sub> should be added at the fixed conditions for attaining fully molten slag and avoiding high content of solids in the smelting slag.

The experimentally measured slag compositions (tridymite-slag phase boundaries) at 0.1 and 0.5 atm  $P_{SO_2}$  were plotted onto the superimposed phase diagrams of FeO<sub>x</sub>-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and FeO<sub>x</sub>-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO systems, shown in Figures 4 and 5, respectively. The phase diagrams were calculated by MTDATA thermo-dynamic software using the MTOX database.<sup>[36]</sup> The prevailing  $P_{O_2}$  for Figures 4 and 5 is  $10^{-7.8}$  and  $10^{-7.3}$ atm, respectively, which are the presenting middle points of the oxygen partial pressure ranges investigated at each  $P_{SO_2}$ . Our previous experimental results achieved at 1300 °C and 0.1 atm  $P_{SO_2}^{[15]}$  fit well with the calculated phase boundaries in Figure 4, whereas the present experimental data at 0.5 atm  $P_{SO_2}$  are on the higher side of the predicted lines, shifting the tridymite-slag phase boundary towards the  $SiO_2$  corner, as shown in Figure 5. The increased  $SiO_2$ concentration with increasing  $P_{SO_2}$ , as shown in Figure 3(d), is the main reason for the difference between the experimental results at 0.5 atm  $P_{SO_2}$  and the predicted computational lines. It should be noted that modeling was executed for 'pure'  $FeO_x$ -SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (-CaO) systems by varying  $P_{O_2}$ , whereas the experiments in the present study included additional elements, such as S, Cu, and other minor elements. This is one of the main reasons for the deviations between the experimental and computational results. Moreover, it is evident that the  $P_{SO_2}$  had a great impact on the slag composition, and the experimental results were not possible to replicate with MTDATA by varying only  $P_{O_2}$ . Although deviations existed, the calculated phase diagrams give guidance for exploring the primary phases and phase assemblages of slags.

# C. Distributions of Copper, Iron, and Sulfur Between Matte and Slag

The deportment of valuable and impurity elements into the matte phase can be described by the elemental matte-slag distribution coefficients. The distribution coefficients of copper, iron, and sulfur between matte and slag were calculated using the following Eq. [3]:

$$L^{m/s}(Me) = [wt pct Me]_{inmatte} / (wt pct Me)_{inslag}$$
 [3]

where [wt pct Me] and (wt pct Me) refer to the experimentally measured elemental concentrations in matte and slag, respectively. The distribution coefficients of elements investigated are displayed in Figure 6 as a function of matte grade.

The distribution coefficients for copper between matte and  $FeO_x$ -SiO<sub>2</sub> slag had no significant changes over the entire matte grade range studied, fluctuating around 60. The values for Al<sub>2</sub>O<sub>3</sub>- and CaO-containing slag were higher and decreased along with increasing matte grade,<sup>[13,15]</sup> indicating that lower matte grade and additions of Al<sub>2</sub>O<sub>3</sub> and CaO were favored regarding the deportment of copper into the matte phase. The copper distribution coefficients seemed not to be affected by the  $P_{SO_2}$ , similarly to the distribution coefficients of iron and sulfur. The distribution coefficient values for iron were < 1, suggesting that iron was highly distributed into the slag and its deportment into slag was improved by increasing the matte grade. Contrary to the results of copper and iron, the distribution coefficients of sulfur had an increasing trend with increasing matte grade.<sup>[13]</sup> The distribution coefficient of sulfur between matte and pure  $FeO_x$ -SiO<sub>2</sub> slag was around 25 at the matte grade of 65 wt pct Cu, and its value increased to approximately 60 and 150 by  $Al_2O_3$  and  $(Al_2O_3 + CaO)$ additions, respectively.

#### **IV. CONCLUSIONS**

The present study provides new fundamental information for the experimental phase equilibria of copper mattes and different silica-saturated  $\text{FeO}_x\text{-SiO}_2$ ,  $\text{FeO}_x\text{-}$  $\text{SiO}_2\text{-}\text{Al}_2\text{O}_3$ , and  $\text{FeO}_x\text{-}\text{SiO}_2\text{-}\text{Al}_2\text{O}_3\text{-}\text{CaO}$  slags under the conditions of 1300 °C and 0.5 atm  $P_{\text{SO}_2}$ . The current observations involved high-temperature equilibration in silica crucibles under controlled CO-CO<sub>2</sub>-SO<sub>2</sub>-Ar flowing gas atmosphere, quenching of the equilibrated samples, and direct phase analyses by EPMA. The present results will not only deepen our understanding on the equilibration of matte/slag/tridymite system but can also provide new insight and guidance for the industrial operation practices.

A comparison of the data obtained at 0.1 and 0.5 atm  $P_{SO_2}$  indicates that concentrations of iron and sulfur in the matte were independent of  $P_{SO_2}$  and additions of Al<sub>2</sub>O<sub>3</sub> and CaO at a given matte grade. However, by increasing the  $P_{SO_2}$ , a higher  $P_{O_2}$  is needed to obtain a given matte grade. Copper loss in the slag increased with increasing matte grade but did not vary with  $P_{SO_2}$ . Al<sub>2</sub>O<sub>3</sub> and CaO additions into iron silicate slags can effectively decrease copper losses in the slag. Sulfur concentration in the slag decreased with increasing matte grade and with Al<sub>2</sub>O<sub>3</sub> and CaO additions, but it was not sensitive to  $P_{SO_2}$ . The equilibrium SiO<sub>2</sub> concentration in silicat-saturated iron silicate slags generally

increased by 5 to 7 wt pct with increasing  $P_{SO_2}$ , and the corresponding Fe/SiO<sub>2</sub> ratio of the slags was lower at higher  $P_{SO_2}$ , *i.e.*, 0.5 atm. The increase of Al<sub>2</sub>O<sub>3</sub> and CaO concentrations in silica-saturated iron silicate slags also led to an increase of SiO<sub>2</sub> solubility in the slags.<sup>[51]</sup>

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# **CONFLICT OF INTEREST**

The authors declare that they have no competing interest.

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